Central Force

Many physical problems have spherical symmetry and the potential depends only on $r$.

$$V(r) = f(r)$$

Such problems are conveniently solved using spherical coordinates $(r, \theta, \phi)$. In spherical coordinates

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

The time-independent Schrödinger equation reads

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

Since the potential depends on $r$ only, we look for solutions that are separable into a function of $r$ and a function of $\theta$ and $\phi$. Assume that

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$
Substitute $\psi = RY$ into the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \left[ \frac{Y}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) \right] + \frac{R}{r^2 \sin^2 \theta} \left( \frac{\partial^2 Y}{\partial \phi^2} \right) + VRY = ERY$$

Dividing by $RY$ and multiplying by $-2mr^2/\hbar^2$:

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

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0$$

The terms in the first curly bracket depends only on $r$, whereas the remainder depends only on $\theta$ and $\phi$. Each must be a constant. Let the constant be $l(l + 1)$,

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

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = -l(l + 1)$$
The Angular Equation

Consider the angular equation first. Multiply the last equation on the previous page by $Y \sin^2 \theta$, it becomes

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

Try separation of variables again,

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$$

Substitute into the first equation and dividing by $\Theta \Phi$, we find

$$\left\{ \frac{1}{\Theta} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l + 1) \sin^2 \theta \right\} + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = 0$$

The first term is a function only of $\theta$, and the second is a function only of $\phi$, so each must be a constant. Let the constant be $m^2$,

$$\frac{1}{\Theta} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l + 1) \sin^2 \theta = m^2$$

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m^2$$
The \( \phi \) Equation

The solution of the \( \phi \) equation

\[
\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi
\]

is simply

\[
\Phi(\phi) = e^{im\phi}
\]

- The solution \( e^{-im\phi} \) is included by allowing \( \phi \) to take negative values.
- The normalization factor will be absorbed into \( \Theta \).
- It is required that

\[
\Phi(\phi + 2\pi) = \Phi(\phi)
\]

Thus, \( m \) must be an integer

\[
m = 0, \pm 1, \pm 2, \cdots
\]
The $\theta$ Equation

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + [l(l + 1) \sin^2 \theta - m^2] \Theta = 0$$

This equation is discussed in mathematical method. The solution is

$$\Theta(\theta) = AP_l^m(\cos \theta)$$

$P_l^m$ is the associated Legendre function,

$$P_l^m(x) = (1 - x^2)^{|m|/2} \left( \frac{d}{dx} \right)^{|m|} P_l(x)$$

$P_l(x)$ is the $l$th Legendre polynomial. It is defined by the Rodrigues formula:

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l.$$
Properties of $P_l(x)$ & $P^m_l(x)$

- In order for $P^m_l(\cos \theta)$ to be finite in $[0, \pi]$, $l$ must be an integer;

$$l = 0, 1, 2, \cdots$$

- If $|m| > l$, then $P^m_l = 0$, therefore

$$m = -l, -l + 1, \cdots, -1, 0, 1, \cdots, l - 1, l$$

- The “other solution” of the second order differential equation is physically unacceptable because it diverges at $\theta = 0$ and/or $\theta = \pi$.

- Note that $P_l(x)$ is a polynomial of degree $l$ in $x$, and is even or odd according to the parity of $l$. But $P^m_l(x)$ is not necessarily a polynomial.

- On the other hand, $x$ always appears in the form of $\cos \theta$ in problems of our interest. We thus only need $P^m_l(\cos \theta)$. Since $\sqrt{1 - \cos^2 \theta} = \sin \theta$, $P^m_l(\cos \theta)$ is always a polynomial in $\cos \theta$, and in case $m$ is odd, multiplied by $\sin \theta$. 
$P_i(x)$ and $P_i^m(x)$

Some Legendre polynomials and associated Legendre functions of $\cos \theta$ are listed below.

\[
P_0(x) = 1 \\

\begin{align*}
P_1(x) &= x \\
P_1^1 &= \sin \theta \\
P_1^0 &= \cos \theta \\
P_2(x) &= \frac{1}{2} (3x^2 - 1) \\
P_2^2 &= 3 \sin^2 \theta \\
P_2^1 &= 3 \sin \theta \cos \theta \\
P_2^0 &= \frac{1}{2} (3 \cos^2 \theta - 1) \\
P_3(x) &= \frac{1}{2} (5x^3 - 3x) \\
P_3^3 &= 15 \sin \theta (1 - \cos^2 \theta) \\
P_3^2 &= 15 \sin^2 \theta \cos \theta \\
P_3^1 &= \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1) \\
P_3^0 &= \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)
\end{align*}
\]
Wave Function and Normalization

Wave function

\[ \psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \]

where

\[ Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \]
\[ \Theta(\theta) = AP_l^m(\cos \theta) \]
\[ \Phi(\phi) = e^{im\phi} \]

Normalization of the wave function

\[
\int |\psi|^2 d^3r = \int |R(r)Y(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi
\]
\[
= \int |R|^2 r^2 dr \int |Y|^2 \sin \theta d\theta d\phi = 1
\]

\( R \) and \( Y \) can be normalized individually

\[
\int_0^\infty |R|^2 r^2 dr = 1
\]
\[
\int_0^{2\pi} d\phi \int_0^\pi |Y|^2 \sin \theta d\theta = 1
\]
Spherical Harmonics

The normalized angular wave functions are called spherical harmonics:

\[ Y_{l}^{m}(\theta, \phi) = \epsilon \sqrt{\frac{(2l + 1)(l - |m|)!}{4\pi}} \frac{e^{im\phi}}{l + |m|!} \frac{l + |m|!}{l + |m|!} P_{l}^{m}(\cos \theta), \]

where \( \epsilon = (-1)^{m} \) for \( m \geq 0 \) and \( \epsilon = 1 \) for \( m \leq 0 \).

The spherical harmonics of different \( l \)s or \( m \)s are orthogonal.

\[ \int_{0}^{2\pi} \int_{0}^{\pi} [Y_{l}^{m}(\theta, \phi)]^{*} [Y_{l'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{ll'}\delta_{mm'}. \]

Some spherical harmonics

\[ Y_{0}^{0} = \sqrt{\frac{1}{4\pi}} \]

\[ Y_{1}^{0} = \sqrt{\frac{3}{4\pi}} \cos \theta \]
\[ Y_{1}^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \]
\[ Y_{2}^{0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \]
\[ Y_{2}^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} \]
\[ Y_{2}^{\pm 2} = \mp \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm i2\phi} \]
\[ Y_{3}^{0} = \sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta) \]
\[ Y_{3}^{\pm 1} = \pm \sqrt{\frac{21}{64\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi} \]
\[ Y_{3}^{\pm 2} = \mp \sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta e^{\pm i2\phi} \]
\[ Y_{3}^{\pm 3} = \mp \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm i3\phi} \]