6.2.1.3 The F-equation

The Equation (6.23) is similar to that for particle in a ring, the solutions of which are

$$\left.\begin{aligned} F &= \frac{1}{\sqrt{\pi}} \sin M\varphi \\ F' &= \frac{1}{\sqrt{\pi}} \cos M\varphi \end{aligned}\right] \quad \text{...(6.10)}$$

and

$$F'' = \frac{1}{\sqrt{2\pi}} e^{\pm iM\varphi} \quad \text{...(6.12)}$$

where M is a quantum number which has values $0, \pm 1, \pm 2 \dots$. It differs only in that the eigenvalue here does not contain energy term, E.

6.2.1.4 The P-equation—Legendre and Associated Legendre Functions

The Equation (6.24) is known as Legendre differential equation. It is tedious and lengthy to work out its solution. Such equations are solved using polynomial method. Rather than describing the solutions in a rigorous manner, we shall discuss some of the significant properties of the solutions.

It should be obvious that for each value of $|M|$ there will be a corresponding Legendre equation and a new set of solutions. (The symbol $||$ indicates that only the magnitude and not the sign of M is to be used).

Well-behaved solutions are obtained only for some discrete values of β. This is not so obvious but we may examine a few cases.

Consider, first, the case of $|M| = 0$. The Legendre equation is

$$\frac{d^2 P}{d\theta^2} + \frac{\cos\theta}{\sin\theta} \cdot \frac{dP}{d\theta} + \beta \cdot P = 0 \quad \text{...(6.26)}$$

The solutions to this equation exist as polynomials in cos θ, called "Legendre polynomials", given as

$$P_l(x) = \frac{1}{2^l \cdot l\,!} \cdot \frac{d^l}{dx^l}(x^2 - 1)^l, \quad \text{...(6.27)}$$

where $x = \cos\theta$ and l is an integer including 0.

Some of these polynomials along with the characteristic values of β are listed below in Table 6.1.

Table 6.1 Polynomial Solutions of Equation (6.26)

P i.e., $f(\cos\theta)$	$\frac{dP}{d\theta}$	$\frac{d^2P}{d\theta^2}$	L.H.S. of Equation (6.26)	β
$P_0 = 1$	0	0	β	0
$P_1 = \cos\theta$	$-\sin\theta$	$-\cos\theta$	$-2\cos\theta + \beta\cos\theta$	2
$P_2 = 3\cos^2\theta - 1$	$-6\cos\theta\sin\theta$	$-6(\cos^2\theta - \sin^2\theta)$	$-6(3\cos^2\theta - 1) + \beta(3\cos^2\theta - 1)$	6
$P_3 = 5/3\cos^3\theta - \cos\theta$	$-5\cos^2\theta\sin\theta + \sin\theta$	$-5(\cos^3\theta - 2\cos\theta\sin^2\theta) + \cos\theta$	$-12(5/3\cos^3\theta - \cos\theta) + \beta(5/3\cos^3\theta - \cos\theta)$	12

The indices of the functions P correspond to the highest power of cos θ in the polynomial. It can be seen that

$$\beta = l\,(l+1) \qquad \text{...(6.28)}$$

where $l = 0, 1, 2, 3$

For $|M| \neq 0$, the solutions have the form,

$$P_l^{|M|}(x) = (1-x^2)^{|M|/2} \cdot \frac{d^{|M|}}{dx^{|M|}} \cdot P_l(x) \qquad \text{...(6.29)}$$

with $P_l(x)$ defined as earlier. The polynomials (6.29) are called "associated Legendre polynomials".

[We may work out the functions for a few values of $|M|$ and l;

$$|M| = 0,\; l = 0,\; P_0^0(x) = 1 = P_0(x) = 1$$

$$l = 1,\; P_1^0(x) = P_1(x) = \frac{1}{2}(2x) = x = \cos\theta$$

$$l = 2,\; P_2^0(x) = P_2(x) = \frac{1}{8} \cdot \frac{d^2}{dx^2}(x^2-1)^2 = \frac{1}{2}(3x^2-1)$$

$$= \frac{1}{2}(3\cos^2\theta - 1)$$

$$|M| = 1,\; l = 1,\; P_1^1(x) = (1-x^2)^{1/2} \cdot \frac{d}{dx}\{P_1(x)\}$$

$$= (1-x^2)^{1/2} \cdot \frac{d}{dx}\left[\frac{1}{2} \cdot \frac{d}{dx}(x^2-1)\right]$$

$$= (1-x^2)^{1/2} = \sin\theta$$

$$l = 2,\; P_2^1(x) = (1-x^2)^{1/2} \cdot \frac{d}{dx}\{P_2(x)\}$$

$$= (1-x^2)^{1/2} \cdot \frac{d}{dx} \cdot \left[\frac{1}{8} \cdot \frac{d^2}{dx^2}(x^2-1)^2\right]$$

$$= (1-x^2)^{1/2} \cdot \frac{d}{dx}\left[\frac{1}{2}(3x^2-1)\right]$$

$$= (1-x^2)^{1/2} \cdot 3x = 3\sin\theta \cdot \cos\theta$$

and so on.

Putting cos θ for x, we may write the associated Legendre functions that are solution of Equation (6.24) as

$$P_l^{|M|}(\cos\theta) = (1-\cos^2\theta)^{|M|/2}\cdot\frac{d^{|M|}}{d(\cos\theta)^{|M|}}\{P_l(\cos\theta)\} \quad \text{...(6.30)}$$

$$= (\sin\theta)^{|M|}\cdot\frac{d^{|M|}}{d(\cos\theta)^{|M|}}\left[\frac{1}{2^l\cdot l!}\cdot\frac{d^l}{d(\cos\theta)^l}\cdot(\cos^2\theta-1)^l\right] \quad \text{...(6.31)}$$

The normalisation factor is given as

$$N = \left[\frac{(2l+1)}{2}\cdot\frac{(l-|M|)!}{(l+|M|)!}\right]^{1/2} \quad \text{...(6.32)}$$

It is now easy to tabulate some of the associated Legendre functions $P_l^{|M|}(\cos\theta)$. The functions and their normalisation factors for various values of $|M|$ and l are given in Table 6.2.

Table 6.2 Some Associated Legendre Functions

$\|M\|$	l	$P_l^M(\cos\theta)$	N
0	0	1	$1/\sqrt{2}$
	1	$\cos\theta$	$\sqrt{3/2}$
	2	$1/2\,(3\cos^2\theta-1)$	$\sqrt{5/2}$
	3	$3/2\,(5/3\cos^3\theta-\cos\theta)$	$\sqrt{7/2}$
1	1	$\sin\theta$	$\sqrt{3/4}$
	2	$3\sin\theta\cos\theta$	$\sqrt{5/12}$
	3	$3/2\sin\theta\,(5\cos^2\theta-1)$	$\sqrt{7/24}$
2	2	$3\sin^2\theta$	$\sqrt{5/48}$
	3	$15\sin^2\theta\cos\theta$	$\sqrt{7/240}$

The associated Legendre functions $P_l^M(\cos\theta)$ are characterised by two parameters l and M. The value of M is restricted to 0, ±1, ±2, ±3, ... while that of l can be 0, 1, 2, 3, ... The nature of the functions imposes a restriction on the uppermost value of M that $M \le l$, that is, states with $|M| > l$ cannot exist. It will be clear with the following example. Consider a state with $l = 1$ and $M = +2$. The corresponding associated Legendre polynomial derived from Equations [(6.29), (6.30)] will vanish as shown on next page.

$$P_1^2(x) = (1-x^2)\frac{d^2}{dx^2}\left[\frac{1}{2}\frac{d}{dx}(x^2-1)\right]$$

$$= (1-x^2)\cdot\frac{1}{2}\frac{d^2}{dx^2}(2x) = 0$$

This means that for a given value of l, M can be chosen from the set.

$$M = -l,\ (-l+1), \ldots 0, \ldots (l-1), +l$$

We shall see later that l and M are identified with the quantum numbers of energy and angular momentum,

[*Exercise:* For $|M| = 1$, verify that the values of l for the first two $P(\theta)$ functions are 1 and 2.

For $|M| = 1$, the first Legendre function is

$$P_1^1(\theta) = \sin\theta \times 1$$

Writing P for $\quad P_1^1(\theta),\ \dfrac{dP}{d\theta} = \cos\theta;\ \dfrac{d^2P}{d\theta^2} = -\sin\theta.$

The Legendre equation becomes

$$-\sin\theta + \frac{\cos\theta}{\sin\theta}\cdot\cos\theta - \frac{\sin\theta}{\sin^2\theta} + \beta\sin\theta = 0$$

or

$$\frac{\cos^2\theta - \sin^2\theta}{\sin\theta} - \frac{1}{\sin\theta} + \beta\sin\theta = 0$$

or

$$-2\sin\theta + \beta\sin\theta = 0,\ \text{or}\ \beta = 2,\ \therefore l = 1$$

The second Legendre function is $P_2^1(\theta)$ or simply $P = \sin\theta\ \cos\theta$

A similar procedure will lead to

$$\beta = l(l+1) = 6,\ \text{or}\ l = 2].$$

6.2.1.5 Orthonormality of the $P(\theta)$ Functions

The normalisation factor for each $P(\theta)$ function can be obtained directly from Equation (6.32). However, it is instructive to normalise $P(\theta)$ functions in some simple cases by using the relation,

$$\int_0^\pi \{P(\theta)\}^2\, d\tau = \int_0^\pi \{P(\theta)\}^2 \sin\theta\, d\theta = 1$$

The factor $\sin\theta$ comes from the volume element $d\tau$ in polar coordinates.* Thus, for the function $P_0^0(\theta)\ (l = 0,\ M = 0)$

$$\int_0^\pi \{P_0^0(\theta)\}^2 \sin\theta\ d\theta = \int_0^\pi (N\cdot 1)^2 \sin\theta\, d\theta = 1$$

or $$N^2 [-\cos\theta]_0^\pi = N^2 \cdot 2 = 1$$

or $$N = \frac{1}{\sqrt{2}}$$

[*Exercise:* Find the normalisation factor for the function $P_2^1(\theta)$

[Hint : $\int_0^\pi (N \sin\theta \cos\theta)^2 \sin\theta \, d\theta = 1$

or $$N^2 \int_0^\pi \sin^3\theta \cos^2\theta \, d\theta = 1$$

or $$N^2 \int_0^\pi \sin\theta (\cos^2\theta - \cos^4\theta) \, d\theta = 1$$

or $$N^2 \left[-\frac{\cos^3\theta}{3} + \frac{\cos^5\theta}{5} \right]_0^\pi = 1$$

or $$N^2 \cdot \frac{4}{15} = 1,$$

or $$N = \sqrt{15/4}\ ]$$

$P(\theta)$ functions belonging to the same value of M and different values of l must be orthogonal. This should be obvious if we see the Legendre equation as an eigenvalue equation

$$\left[\frac{d^2}{d\theta^2} + \frac{\cos\theta}{\sin\theta} \cdot \frac{d}{d\theta} - \frac{M^2}{\sin^2\theta} \right] P = -\beta P$$

Thus, for example,

$$\int_0^\pi P_0^0(\theta) \cdot P_2^0(\theta) \, d\tau = \int_0^\pi \left(\frac{1}{2}\right)^{1/2} \left(\frac{5}{8}\right)^{1/2} (3\cos^2\theta - 1) \sin\theta \, d\theta$$

$$= \left(\frac{5}{16}\right)^{1/2} \left[-\frac{3\cos^3\theta}{3} + \cos\theta \right]_0^\pi = 0$$

However, $P(\theta)$ functions for different values of M will not necessarily be orthogonal because they will not be eigenfunctions of the same operator on account of the term $M^2/\sin^2\theta$ in the operator.

6.2.2 The Complete Wave Function (Spherical Harmonics)

The complete wave function of the particle on a sphere (or a rigid rotator) may now be written as

$$\psi_{l,M}(\theta, \varphi) = P_{l,M}(\theta) \cdot F_M(\varphi) = NP_l^{|M|}(\cos\theta) \cdot \frac{1}{\sqrt{2\pi}} e^{iM\varphi} \quad ...(6.33)$$

where N is normalisation factor given by Equation (6.32) of the associated Legendre function $P_l^{|M|}$ (cos θ) given by Equation (6.31). This function is characterised by two quantum numbers l and M. Expressed as trigonometric functions (real form) they represent harmonic waves on the surface of a sphere and are called "spherical harmonics". Spherical harmonics for a few sets of l and M values are listed below.

Table 6.3 Spherical Harmonics

l	M	$\psi_{l,M}(\theta, \varphi)$
0	0	$\psi_{0,0} = \frac{1}{2\sqrt{\pi}}$
1	0	$\psi_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
1	+1	$\psi_{1,+1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\varphi}$
1	−1	$\psi_{1,-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{-i\varphi}$
2	0	$\psi_{2,0} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
2	+1	$\psi_{2,+1} = -\left(\frac{15}{16\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{i\varphi}$
2	−1	$\psi_{2,-1} = \left(\frac{15}{16\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{-i\varphi}$
2	+2	$\psi_{2,+2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{2i\varphi}$
2	−2	$\psi_{2,-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{-2i\varphi}$

6.2.2.1 Spherical Harmonics in Real Form

The spherical harmonics listed above have the disadvantage that most of them are complex and no real picture can be drawn of them. They can be transformed into real form which are more convenient to work with by using the following theorem

$$e^{i\varphi} + e^{-i\varphi} = 2\cos\varphi$$
$$e^{i\varphi} - e^{-i\varphi} = 2i\sin\varphi$$

Then the degenerate functions, for example $\psi_{1,+1}$ and $\psi_{1,-1}$, can be combined to give real functions without altering the eigenvalue

$$\frac{1}{\sqrt{2}}(\psi_{1,+1} + \psi_{1,-1}), \text{ or } \psi_{1+'} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\varphi \qquad ...(6.34)$$

$$\frac{1}{i\sqrt{2}}(\psi_{1,+1} - \psi_{1,-1}), \text{ or } \psi_{1-}, = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \sin\varphi \qquad \text{...(6.35)}$$

The factor $\frac{1}{\sqrt{2}}$ is necessary to keep the functions normalised; ψ_{1+} and ψ_{1-} refer to the + and − combinations respectively.

But a new feature emerges out of these combinations, the significance of the quantum number M is lost. In ψ_{1+} and ψ_{1-}, for example, the quantum number l is 1 but the value of M is undetermined.