<u>**C11T**</u>

Quantum Mechanics and Applications # Credits 04

Syllabus Chapter: 3. Quantum theory of hydrogen-like atoms

3.1 Angular momentum operators:

In classical mechanics the angular momentum of a particle having position $\vec{r}$ and linear momentum $\vec{p}$ is given by:

$\vec{L} = \vec{r} \times \vec{p}$ ……… (3.1)

[Note that $\vec{L}$ is described with respect to a point, from which the position vector is measured, i.e. with respect to the origin. Thus $\vec{L}$ depends on the choice of origin.]

In quantum mechanics, position and momentum are represented by operators $\hat{\vec{r}}$ and $\hat{\vec{p}}$, given by:

$\hat{\vec{r}} = \vec{r}$ and $\hat{\vec{p}} = -i\hbar\vec{\nabla}$.

And therefore the angular momentum operator $\hat{\vec{L}}$ is given by:

$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = \vec{r} \times -i\hbar\vec{\nabla} = -i\hbar\, \vec{r} \times \vec{\nabla}$.

However, quantum mechanical particles have another type of angular momentum called spin angular momentum $(\vec{S})$ which has no classical analogy with the classical angular momentum. The operator, representing the spin angular momentum, is called spin angular momentum operator $(\hat{\vec{S}})$. [We shall discuss about the spin angular momentum in a little detail later.] To differentiate from spin angular momentum, in quantum mechanics $\vec{L}$ is called **orbital angular momentum** and $\hat{\vec{L}}$ is called **orbital angular momentum operator**.

In quantum mechanics, the most frequently used operators related to orbital angular momentum, are $\hat{L}^2$ and $\hat{L}_z$ representing respectively the square and Z-component of orbital angular momentum.

Components of orbital angular momentum operator

$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}}$

$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y,\ \ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z,\ \ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$

$\hat{\vec{L}} = -i\hbar\, \vec{r} \times \vec{\nabla}$.

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right);\quad \hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right);\quad \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \text{……} (3.2)$$

Commutation relation among $\hat{L}_x, \hat{L}_y, \hat{L}_z$

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z]$$

Now $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$ and $\hat{x} = x$ and so on.

Therefore, only pairs among $\hat{x}, \hat{y}, \hat{z}, \hat{p}_x, \hat{p}_y, \hat{p}_z$, which do not commute, are $\hat{x}$ and $\hat{p}_x$, $\hat{y}$ and $\hat{p}_y$, $\hat{z}$ and $\hat{p}_z$.

Also $[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$.

Therefore: $[\hat{L}_x, \hat{L}_y] = [y\hat{p}_z, z\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z]$

$= [y\hat{p}_z, \hat{p}_x z] + [\hat{p}_y z, x\hat{p}_z] \qquad = y\hat{p}_x[\hat{p}_z, z] + \hat{p}_y x[z, \hat{p}_z] \qquad = y\hat{p}_x(-i\hbar) + \hat{p}_y x(i\hbar)$

$= i\hbar(x\hat{p}_y - y\hat{p}_x)$

i.e. $[\hat{L}_x, \hat{L}_y] = i\hbar\,\hat{L}_z$. Similarly $[\hat{L}_y, \hat{L}_z] = i\hbar\,\hat{L}_x$; and $[\hat{L}_z, L_x] = i\hbar\,\hat{L}_y$ ……… (3.3)

Spin Angular Momentum ($\vec{S}$)

Like every small particle, electron also has **spin angular momentum ($\vec{S}$)** which is different from orbital angular momentum. Spin angular momentum of an electron is its **intrinsic** angular momentum. Orbital angular momentum can change due to transition of the electron from one quantum state to another, but **spin angular momentum of an electron never changes**. **Electron spin is a quantum mechanical phenomenon** and is different from the classical spin of a body which is the sum of the orbital motions of its constituent particles about the spin axis. Corresponding to its spin motion, electron has **spin magnetic moment** also. Existence of electron spin was first suggested by and its theoretical basis was first given by **Goudsmit & Uhlenbeck in 1925** to explain anomalous Zeeman effect. They also explained the result of Stern-Gerlach Experiment (1922) with the concept of electron spin. The concept of electron spin has been developed by Pauli (1927) and further, with the development of relativistic quantum mechanics, by Paul Dirac (1928).

To understand that spin is not a classical concept, you may do the following problem:

Problem 4.25 If the electron were a classical solid sphere, with radius

$$r_c = \frac{e^2}{4\pi\epsilon_0 mc^2}$$

(the so-called **classical electron radius**, obtained by assuming the electron's mass is attributable to energy stored in its electric field, via the Einstein formula $E = mc^2$), and its angular momentum is $(1/2)\hbar$, then how fast (in m/s) would a point on the "equator" be moving? Does this model make sense? (Actually, the radius of the electron is known experimentally to be much less than r_c, but this only makes matters worse.)

Griffiths, Introduction to Quantum Mechanics, 2nd Edition, Page-172, Problem: 4.25.

3.1.1 General theory of angular momentum

Spin angular momentum has no expression similar to that of orbital angular momentum as expressed by equation (3.1). But both spin and orbital angular momentum operators satisfy the common relations given below. Representing both spin and orbital angular momentum operators by $\hat{\vec{J}}$ and their components by $\hat{J}_x, \hat{J}_y, \hat{J}_z$ these relations can be written as:

$$\hat{\vec{J}} = \hat{J}_x\hat{\imath} + \hat{J}_y\hat{\jmath} + \hat{J}_z\hat{k} \;\; [\text{where } \hat{\imath}, \hat{\jmath}, \hat{k} \text{ are unit vectors along X, Y \& Z axes}] \ldots\ldots\ldots (3.4A)$$

$$\hat{J}^2 = \hat{J}_x{}^2 + \hat{J}_y{}^2 + \hat{J}_z{}^2 \ldots\ldots\ldots (3.4B)$$

$$[\hat{J}_x, \hat{J}_y] = i\hbar\,\hat{J}_z, \;\; [\hat{J}_y, \hat{J}_z] = i\hbar\,\hat{J}_x, \;\; [\hat{J}_z, \hat{J}_x] = i\hbar\,\hat{J}_y \ldots\ldots\ldots (3.4C)$$

Based on these relations the theory of angular momentum was developed.

Commutation relation among $\hat{J}^2$ and $\hat{J}_x, \hat{J}_y, \hat{J}_z$:

$$[\hat{J}^2, \hat{J}_x]$$

$$= [\hat{J}_x{}^2 + \hat{J}_y{}^2 + \hat{J}_z{}^2, \hat{J}_x]$$

$$= [\hat{J}_x{}^2, \hat{J}_x] + [\hat{J}_y{}^2, \hat{J}_x] + [\hat{J}_z{}^2, \hat{J}_x]$$

$$= [\hat{J}_x\hat{J}_x, \hat{J}_x] + [\hat{J}_y\hat{J}_y, \hat{J}_x] + [\hat{J}_z\hat{J}_z, \hat{J}_x]$$

$$= \hat{J}_x[\hat{J}_x, \hat{J}_x] + [\hat{J}_x, \hat{J}_x]\hat{J}_x + \hat{J}_y[\hat{J}_y, \hat{J}_x] + [\hat{J}_y, \hat{J}_x]\hat{J}_y + \hat{J}_z[\hat{J}_z, \hat{J}_x] + [\hat{J}_z, \hat{J}_x]\hat{J}_z$$

$$= \hat{J}_y(-i\hbar\,\hat{J}_z) + (-i\hbar\,\hat{J}_z)\hat{J}_y + \hat{J}_z(i\hbar\,\hat{J}_y) + (i\hbar\,\hat{J}_y)\hat{J}_z$$

$$= 0$$

Thus $[\hat{J}^2, \hat{J}_x] = 0$. Similarly, $[\hat{J}^2, \hat{J}_y] = 0$ and $[\hat{J}^2, \hat{J}_z] = 0$. …….. (3.5)

i.e. $\hat{J}^2$commute with the components of $\hat{\vec{J}}$.

Or, compactly: $[\hat{J}^2, \hat{\vec{J}}] = 0$……… (3.5A)

$\hat{J}^2$and any component of $\hat{\vec{J}}$, say $\hat{J}_z$, can have simultaneous eigen function, say f. If $\lambda\hbar^2$ and $\mu\hbar$ are eigenvalues of $\hat{J}^2$ and $\hat{J}_z$ for their simultaneous eigen function f, then we should have:

$$\hat{J}^2 f = \lambda\hbar^2 f \;\; \ldots\ldots\ldots (3.6A) \;\; \text{and} \;\; \hat{J}_z f = \mu\hbar f \ldots\ldots\ldots (3.6B).$$

3.1.1.1 'Ladder operators'

$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ are called ladder operators for reason to be clear in the following discussions. Note that $\hat{J}_\pm{}^\dagger = \hat{J}_\mp$.

 # Commutation relation of $\hat{J}^2$ with ladder operators

$\left[\hat{J}^2, \hat{J}_\pm\right] = \left[\hat{J}^2, \hat{J}_x\right] \pm i\left[\hat{J}^2, \hat{J}_y\right] = 0,$ since $\hat{J}^2$ commutes with $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$. ……… (3.7)

 # Commutation relation of $\hat{J}_z$ with ladder operators

$\left[\hat{J}_z, \hat{J}_\pm\right] = \left[\hat{J}_z, \hat{J}_x\right] \pm i\left[\hat{J}_z, \hat{J}_y\right] = i\hbar\, \hat{J}_y \pm \hbar\, \hat{J}_x = \pm\hbar\left(\hat{J}_x \pm i\hat{J}_y\right) = \pm\hbar\hat{J}_\pm$ …….. (3.8A)

$\left[\hat{J}_x, \hat{J}_\pm\right] = \left[\hat{J}_x, \hat{J}_x\right] \pm i\left[\hat{J}_x, \hat{J}_y\right] = \mp\hbar\hat{J}_z$ ……… (3.8B)

$\left[\hat{J}_y, \hat{J}_\pm\right] = \left[\hat{J}_y, \hat{J}_x\right] \pm i\left[\hat{J}_y, \hat{J}_y\right] = -i\hbar\hat{J}_z$ ……… (3.8C)

 # Let $\hat{J}^2$and $\hat{J}_z$ have the simultaneous f. Show that $\hat{J}_\pm f$ will also be the simultaneous eigen function of $\hat{J}^2$and $\hat{J}_z$.

$\hat{J}^2\left(\hat{J}_\pm f\right) = \hat{J}_\pm \hat{J}^2 f = \hat{J}_\pm \lambda\hbar^2 f = \lambda\hbar^2\left(\hat{J}_\pm f\right)$ [since $\hat{J}^2$commute with $\hat{J}_\pm$]

i.e. $\hat{J}_\pm f$ is the eigen function of $\hat{J}^2$.

$\hat{J}_z\left(\hat{J}_\pm f\right) = \left[\hat{J}_z, \hat{J}_\pm\right] f + \hat{J}_\pm \hat{J}_z f = \pm\hbar\hat{J}_\pm f + \hat{J}_\pm \mu\hbar f = \pm\hbar\hat{J}_\pm f + \mu\hbar\hat{J}_\pm f = (\mu\hbar \pm \hbar)\left(\hat{J}_\pm f\right)$

Thus $\hat{J}_\pm f$ is the eigen function of $\hat{J}_z$.

Therefore $J_\pm f$ is the simultaneous eigen function of $\hat{J}^2$and $\hat{J}_z$.

 # Home Task: If $\hat{J}_z f = \mu\hbar f$, and $\hat{J}^2 f = \lambda\hbar^2 f$, then show that:

$\hat{J}_z\left(\hat{J}_\pm f\right) = (\mu\hbar \pm \hbar)\left(\hat{J}_\pm f\right),$

$\hat{J}_z\left({\hat{J}_\pm}^2 f\right) = (\mu\hbar \pm 2\hbar)\left({\hat{J}_\pm}^2 f\right),$

$\hat{J}_z\left({\hat{J}_\pm}^3 f\right) = (\mu\hbar \pm 3\hbar)\left({\hat{J}_\pm}^3 f\right) \ldots$

and $\hat{J}^2\left(\hat{J}_\pm f\right) = \lambda\hbar^2\left(\hat{J}_\pm f\right),$ $\hat{J}^2\left({\hat{J}_\pm}^2 f\right) = \lambda\hbar^2\left({\hat{J}_\pm}^2 f\right),$ $\hat{J}^2\left({\hat{J}_\pm}^3 f\right) = \lambda\hbar^2\left({\hat{J}_\pm}^3 f\right) \ldots\ldots\ldots$

 # Ladder operators:

We have:

$\hat{J}_z f = \mu\hbar f$

$\hat{J}_z\left(\hat{J}_+ f\right) = (\mu\hbar + \hbar)\left(\hat{J}_+ f\right)$ & $\hat{J}_z\left(\hat{J}_- f\right) = (\mu\hbar - \hbar)\left(\hat{J}_- f\right)$

$\hat{J}_z\left({\hat{J}_+}^2 f\right) = (\mu\hbar + 2\hbar)\left({\hat{J}_+}^2 f\right)$ & $\hat{J}_z\left({\hat{J}_-}^2 f\right) = (\mu\hbar - 2\hbar)\left({\hat{J}_+}^2 f\right)$

$\hat{J}_z\left({\hat{J}_+}^3 f\right) = (\mu\hbar + 3\hbar)\left({\hat{J}_+}^3 f\right)$ & $\hat{J}_z\left({\hat{J}_-}^3 f\right) = (\mu\hbar - 3\hbar)\left({\hat{J}_-}^3 f\right)$

……. …… …… …… ……

$\hat{J}_z\left({\hat{J}_+}^n f\right) = (\mu\hbar + n\hbar)\left({\hat{J}_+}^n f\right)$ & $\hat{J}_z\left({\hat{J}_-}^n f\right) = (\mu\hbar - n\hbar)\left({\hat{J}_-}^n f\right)$

Thus by each operation of $\hat{J}_+$ on f, we obtain a function for which the eigen value of $\hat{J}_z$ is raised by $\hbar$. Similarly by each operation of $\hat{J}_-$ on f, we obtain a function for which the eigen value of $\hat{J}_z$ is lowered by $\hbar$. Therefore $\hat{J}_+$ is called raising operator and $\hat{J}_-$ is called lowering operator. Or in general $\hat{J}_\pm$ are called ladder operators.

However it should be noted that, by operating on any eigen function f, $\hat{J}_\pm$ cannot raise or lower the eigen value of $\hat{J}^2$.

 # Show that: $\hat{J}^2 = \hat{J}_\pm\hat{J}_\mp + \hat{J}_z^{\ 2} \mp \hbar\hat{J}_z$

Proof: $\hat{J}_\pm\hat{J}_\mp = (\hat{J}_x \pm i\hat{J}_y)(\hat{J}_x \mp i\hat{J}_y) = \hat{J}_x^{\ 2} + \hat{J}_y^{\ 2} \mp i(\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x)$

$= \hat{J}^2 - \hat{J}_z^{\ 2} \mp i[\hat{J}_x, \hat{J}_y] = \hat{J}^2 - \hat{J}_z^{\ 2} \mp i(i\hbar)$

Therefore, $\hat{J}_\pm\hat{J}_\mp = \hat{J}^2 - \hat{J}_z^{\ 2} \pm \hbar\hat{J}_z$

$\Rightarrow \hat{J}^2 = \hat{J}_\pm\hat{J}_\mp + \hat{J}_z^{\ 2} \mp \hbar\hat{J}_z$

 # Limit on the number of operation of the eigen function by raising or lowering operator

We have, if $\hat{J}_z f = \mu\hbar f$, and $\hat{J}^2 f = \lambda\hbar^2 f$, then:

$\hat{J}_z(\hat{J}_+ f) = \hbar(\mu + 1)(\hat{J}_+ f)$ & $\hat{J}_z(\hat{J}_- f) = \hbar(\mu - 1)(\hat{J}_- f)$

$\hat{J}_z\left(\hat{J}_+^{\ 2} f\right) = \hbar(\mu + 2)\left(\hat{J}_+^{\ 2} f\right)$ & $\hat{J}_z\left(\hat{J}_-^{\ 2} f\right) = \hbar(\mu - 2)\left(\hat{J}_+^{\ 2} f\right)$

$\hat{J}_z\left(\hat{J}_+^{\ 3} f\right) = \hbar(\mu + 3)\left(\hat{J}_+^{\ 3} f\right)$ & $\hat{J}_z\left(\hat{J}_-^{\ 3} f\right) = \hbar(\mu - 3)\left(\hat{J}_-^{\ 3} f\right)$

…….

$\hat{J}_z(\hat{J}_+^{\ n} f) = \hbar(\mu + n)(\hat{J}_+^{\ n} f)$ & $\hat{J}_z(\hat{J}_-^{\ n} f) = \hbar(\mu - n)(\hat{J}_-^{\ n} f)$

And

$\hat{J}^2(\hat{J}_\pm f) = \lambda\hbar^2(\hat{J}_\pm f)$, $\hat{J}^2\left(\hat{J}_\pm^{\ 2} f\right) = \lambda\hbar^2\left(\hat{J}_\pm^{\ 2} f\right)$, $\hat{J}^2\left(\hat{J}_\pm^{\ 3} f\right) = \lambda\hbar^2\left(\hat{J}_\pm^{\ 3} f\right)$,

…

$\hat{J}^2(\hat{J}_\pm^{\ n} f) = \lambda\hbar^2(\hat{J}_\pm^{\ n} f)$

Thus for the eigen functions obtained by multiple operations of $\hat{J}_\pm$ on f, the eigen value of $\hat{J}_z$ changes in each step by $\pm\hbar$ but the eigen value of $\hat{J}^2$ remains constant.

Now, we have, $\langle J^2\rangle = \langle J_x^{\ 2}\rangle + \langle J_y^{\ 2}\rangle + \langle J_z^{\ 2}\rangle$

Also the expectation value of the square of an observable is always positive. i.e.

$\langle {J_x}^2 \rangle \geq 0$ & $\langle {J_y}^2 \rangle \geq 0$

Therefore $\langle J^2 \rangle \geq \langle {J_z}^2 \rangle$ and hence the eigen value of $\hat{J}^2$ is greater than the eigen value of ${\hat{J}_z}^2$.

Now each operation by $\hat{J}_+$ on the eigen function raises the eigen value of $\hat{J}_z$ by $\hbar$, but the eigen value of $\hat{J}^2$ remains the same i.e. $\lambda\hbar$. This operation cannot continue infinitely and there must be some upper limit of the number of this operation, since eigen value of ${\hat{J}_z}^2$ must not exceed that of $\hat{J}^2$. If f_u be the eigen function obtained by maximum number of allowed operation by $\hat{J}_+$ then further operation by $\hat{J}_+$ will produce null result.

Thus $\hat{J}_+ f_u = 0$.

On the other hand, by each operation of the eigen function by the lowering operator, the eigen value of $\hat{J}_z$ decreases by $\hbar$. After n times of operation by the lowering operator, we obtain an eigen function, for which the eigen value of $\hat{J}_z$ is $\hbar(\mu - n)$. With the increase of n, initially the magnitude of $\hbar(\mu - n)$ decreases and as n exceeds μ, $\hbar(\mu - n)$ becomes negative and its magnitude starts to increase. Consequently, the eigen value of ${\hat{J}_z}^2$, i.e. $\hbar^2(\mu - n)^2$ will increase and may exceed $\lambda\hbar^2$, which is unacceptable. Thus there must be some upper limit of the number of allowed operation of the lowering operator on f.

Thus, if f_l be the eigen function obtained by maximum number of allowed operation of $\hat{J}_-$ on f, then $\hat{J}_- f_l = 0$.

 # Allowed eigen values of $\boldsymbol{J_z}$ and $\boldsymbol{J^2}$:

From 5. We can write

$$\hat{J}^2 f = \left(\hat{J}_-\hat{J}_+ + {\hat{J}_z}^2 + \hbar\hat{J}_z\right) f = \hat{J}_-\hat{J}_+ f + {\hat{J}_z}^2 f + \hbar\hat{J}_z f = \hat{J}_-\hat{J}_+ f + \mu^2\hbar^2 f + \mu\hbar^2 f \text{ .....(i)}$$

and

$$\hat{J}^2 f = \left(\hat{J}_+\hat{J}_- + {\hat{J}_z}^2 - \hbar\hat{J}_z\right) f = \hat{J}_+\hat{J}_- f + {\hat{J}_z}^2 f - \hbar\hat{J}_z f = \hat{J}_+\hat{J}_- f + \mu^2\hbar^2 f - \mu\hbar^2 f \text{........(ii)}$$

Let $\hbar j$ and $\hbar j'$ be the eigen values of $\hat{J}_z$ for eigen functions f_u and f_l respectively. i.e. these are the highest and lowest eigen values of $\hat{J}_z$.

Then using (i):

$$\hat{J}^2 f_u = \hat{J}_-\hat{J}_+ f_u + {\hat{J}_z}^2 f_u + \hbar\hat{J}_z f_u = 0 + \hbar^2 j^2 f_u + \hbar^2 j f_u = \hbar^2 j(j+1) f_u.$$

And using (ii):

$\hat{J}^2 f_l = \hat{J}_+\hat{J}_- f_l + \hat{J}_z{}^2 f_l - \hbar \hat{J}_z f_l = 0 + \hbar^2 j'^2 f_l - \hbar^2 j' f_l = \hbar^2 j'(j'-1) f_l.$

Since $\hat{J}^2$ have same eigen value λ for raised or lowered eigen function, therefore:

$\lambda = \hbar^2 j(j+1) = \hbar^2 j'(j'-1)$

$\Rightarrow j' = -j \; or \; j' = j+1.$

But $j' = j+1$ gives eigen value of $\hat{J}_z$ for f_l to be $(j+1)\hbar$ which is greater than the eigen value of $\hat{J}_z$ for f_u i.e. greater than $j\hbar$. This is impossible.

Therefore $j' \neq j+1$ and we must have $j' = -j$ only.

Thus the highest and the lowest eigen values of $\hat{J}_z$ are $j\hbar$ and $-j\hbar$.

And since the eigen values of $\hat{J}_z$ are raised or lowered by $\hbar$ in each step of operation of the eigen function by $\hat{J}_+$ or $\hat{J}_-$, the eigen values of $\hat{J}_z$ will be:

$-j\hbar, \; -(j-1)\hbar, \; \ldots\ldots\ldots, (j-1)\hbar, \; j\hbar.$

Or in general, eigen values of $\hat{J}_z$ are given by:

$J_z = m\hbar$, where $m = -j \; to + j$ in integer steps.

Also eigen values of $\hat{J}^2$ are given by: $\lambda\hbar^2 = j(j+1)\hbar^2.$

Restrictions on the values of j.

Since m changes from $-j$ to $+j$ in integer steps, so we must have:

$j = -j + N$, [where N is an integer]

$\Longrightarrow 2j = N, \quad \Longrightarrow j = N/2$

Thus j is an integer (for N = even) or half integer (for N = odd). Thus:

$j = 0, \quad 1/2, \quad 1, \quad 3/2, \quad 2, \quad 5/2, \quad 3, \quad 7/2, \ldots\ldots etc.$

For each value of j,

$m = -j, \; -j+1, \ldots\ldots \; \ldots\ldots \; j-1, \; j$, total $2j+1$ number of values

Example: if $j = 3$, then $m = -3, -2, -1, 0, 1, 2, 3$

i.e. if j is integer, then $m = 0, \pm 1, \; \ldots\ldots \pm j$.

And if $j = \frac{5}{2}$, then $m = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$

i.e. if j is half integer, then $m = \pm\frac{1}{2}, \pm\frac{3}{2} \ldots\ldots \pm j$

3.1.1.2 **Eigen functions suffixed by j and m:**

Now the eigen functions should be suffixed by j and m as f_{jm}. They can also be represented by the ket $|jm\rangle$.

Thus $J^2 f_{jm} = J^2|jm\rangle = j(j+1)\hbar^2|jm\rangle = j(j+1)\hbar^2 f_{jm}$,

And $J_z f_{jm} = J_z|jm\rangle = m\hbar|jm\rangle = m\hbar f_{jm}$,

with $j = 0, 1/2, 1, 3/2, 2, 5/2, 3, 7/2, \dots \dots etc.$ and $m = -j, -j+1, \dots, \dots j-1, j$.

j and m are called angular momentum quantum number and magnetic quantum number.

Note that all the above relations for components $\hat{\vec{J}}$ can be proved and are applicable for components of $\hat{\vec{L}}$ (orbital angular momentum) and $\hat{\vec{S}}$ (spin angular momentum). And all the relations for $\hat{J}^2$ can be proved and are applicable for $\hat{L}^2$ and $\hat{S}^2$ also.

***However there is some extra restriction on the orbital angular momentum quantum number and orbital magnetic quantum number as we shall see later.**

3.1.2 Orbital Angular Momentum:

3.1.2.1 Expressions of L_x, L_y, L_z in spherical polar coordinates:

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}}$$

$$= \vec{r} \times -i\hbar\vec{\nabla}$$

$$= -i\hbar r\hat{r} \times \left(\hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\varphi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

$$= -i\hbar\left(r\hat{r} \times \hat{r}\frac{\partial}{\partial r} + r\hat{r} \times \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + r\hat{r} \times \hat{\varphi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

$$= -i\hbar\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

Using the expressions:

$\hat{\theta} = \cos\theta\cos\varphi\,\hat{\imath} + \cos\theta\sin\varphi\,\hat{\jmath} - \sin\theta\,\hat{k}$ and $\hat{\varphi} = -\sin\varphi\,\hat{\imath} + \cos\varphi\,\hat{\jmath}$

We get:

$$\hat{\vec{L}} = -i\hbar\left((-\sin\varphi\,\hat{\imath} + \cos\varphi\,\hat{\jmath})\frac{\partial}{\partial\theta} - \left(\cos\theta\cos\varphi\,\hat{\imath} + \cos\theta\sin\varphi\,\hat{\jmath} - \sin\theta\,\hat{k}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

Thus:

$$\left.\begin{aligned}
\hat{\boldsymbol{L}}_{\boldsymbol{x}} &= -\boldsymbol{i}\hbar\left(-\sin\boldsymbol{\varphi}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\theta}} - \cot\boldsymbol{\theta}\cos\boldsymbol{\varphi}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\varphi}}\right) \\
\hat{\boldsymbol{L}}_{\boldsymbol{y}} &= -\boldsymbol{i}\hbar\left(\cos\boldsymbol{\varphi}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\theta}} - \cot\boldsymbol{\theta}\sin\boldsymbol{\varphi}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\varphi}}\right) \\
\hat{\boldsymbol{L}}_{\boldsymbol{z}} &= -\boldsymbol{i}\hbar\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\varphi}}
\end{aligned}\right\} \ldots\ldots\ldots (3.9)$$

3.1.2.2 Prove the relation: $\hat{\boldsymbol{L}}_{\pm} = \pm\boldsymbol{e}^{\pm\boldsymbol{i\varphi}}\hbar\left(\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\theta}} \pm \boldsymbol{i}\cot\boldsymbol{\theta}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\varphi}}\right)$.

Ans.: We have

$$\hat{L}_x = -i\hbar\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

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

Then

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y = -i\hbar\left((-\sin\varphi + i\cos\varphi)\frac{\partial}{\partial\theta} - \cot\theta\,(\cos\varphi + i\sin\varphi)\frac{\partial}{\partial\varphi}\right)$$

$$= -i\hbar\left(ie^{i\varphi}\frac{\partial}{\partial\theta} - \cot\theta\, e^{i\varphi}\frac{\partial}{\partial\varphi}\right) = e^{i\varphi}\hbar\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y = -i\hbar\left((-\sin\varphi - i\cos\varphi)\frac{\partial}{\partial\theta} - \cot\theta\,(\cos\varphi - i\sin\varphi)\frac{\partial}{\partial\varphi}\right)$$

$$= -i\hbar\left(-ie^{-i}\ \frac{\partial}{\partial\theta} - \cot\theta\, e^{-i\varphi}\frac{\partial}{\partial\varphi}\right) = -e^{-i\varphi}\hbar\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

Hence:

$$\hat{L}_\pm = \pm e^{\pm i\varphi}\hbar\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right) \ldots\ldots\ldots (2)$$

3.1.2.3 Prove the relation: $\hat{L}_+\hat{L}_- = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right)$

Ans.: We have

$$\hat{L}_+ = e^{i\varphi}\hbar\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right) \quad \textit{and} \quad \hat{L}_- = -e^{-i\varphi}\hbar\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

Therefore, $\hat{L}_+\hat{L}_-\psi = -\hbar^2 e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)e^{-i\varphi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\varphi}\right)\psi$

$$= -\hbar^2 e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\left(e^{-i\varphi}\frac{\partial\psi}{\partial\theta} - i\cot\theta\, e^{-i\varphi}\frac{\partial\psi}{\partial\varphi}\right)$$

$$= -\hbar^2 e^{i\varphi}\left[\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\left(e^{-i}\ \ \frac{\partial\psi}{\partial\theta}\right) - \left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\left(i\cot\theta\, e^{-i}\ \ \frac{\partial\psi}{\partial\varphi}\right)\right]$$

$$= -\hbar^2 e^{i\varphi}\left[\frac{\partial}{\partial\theta}\left(e^{-i\varphi}\frac{\partial\psi}{\partial\theta}\right) + i\cot\theta\frac{\partial}{\partial\varphi}\left(e^{-i}\ \ \frac{\partial\psi}{\partial\theta}\right)\right.$$
$$\left. - \frac{\partial}{\partial\theta}\left(i\cot\theta\, e^{-i\varphi}\frac{\partial\psi}{\partial\varphi}\right) - i\cot\theta\frac{\partial}{\partial\varphi}\left(i\cot\theta\, e^{-i}\ \ \frac{\partial\psi}{\partial\varphi}\right)\right]$$

$$= -\hbar^2 e^{i\varphi}\left[e^{-i}\ \ \frac{\partial^2\psi}{\partial\theta^2} + i\cot\theta\left(-ie^{-i\varphi}\right)\frac{\partial\psi}{\partial\theta} + i\cot\theta\, e^{-i\varphi}\frac{\partial^2\psi}{\partial\varphi\partial\theta}\right.$$
$$\left. -i(-\operatorname{cosec}^2\theta)e^{-i\varphi}\frac{\partial\psi}{\partial\varphi} - i\cot\theta\, e^{-i\varphi}\frac{\partial^2\psi}{\partial\theta\partial\varphi} - i^2\cot^2\theta\left(-ie^{-i\varphi}\frac{\partial\psi}{\partial\varphi} + e^{-i}\ \ \frac{\partial^2\psi}{\partial\varphi^2}\right)\right]$$

$$= -\hbar^2 e^{i\varphi}\left[e^{-i}\ \ \frac{\partial^2\psi}{\partial\theta^2} + \cot\theta\, e^{-i\varphi}\frac{\partial\psi}{\partial\theta} + \boldsymbol{i\cot\theta\, e^{-i\varphi}\frac{\partial^2\psi}{\partial\varphi\partial\theta}}\right.$$
$$\left. \boldsymbol{+i\operatorname{cosec}^2\theta\, e^{-i\varphi}\frac{\partial\psi}{\partial\varphi} - i\cot\theta\, e^{-i\varphi}\frac{\partial^2\psi}{\partial\theta\partial\varphi} - i\cot^2\theta\, e^{-i\varphi}\frac{\partial\psi}{\partial\varphi}} + \cot^2\theta\, e^{-i\varphi}\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

$$= -\hbar^2\left[\frac{\partial^2\psi}{\partial\theta^2} + \cot\theta\frac{\partial\psi}{\partial\theta} + i(\operatorname{cosec}^2\theta - \cot^2\theta)\frac{\partial\psi}{\partial\varphi} + \cot^2\theta\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

$$\hat{L}_+\hat{L}_-\psi = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right]\psi$$

$$\hat{L}_+\hat{L}_- = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right]$$

3.1.2.4 Express the operator $\hat{L}^2$ in spherical polar coordinates.

Ans.: We have

$$\hat{L}^2 = \hat{L}_\pm\hat{L}_\mp + \hat{L}_z{}^2 \mp \hbar\hat{L}_z$$

$$\left[\mathit{Substituting}\ \hat{J} = \hat{L}\ \mathit{in\ the\ relation}\ \hat{J}^2 = \hat{J}_\pm\hat{J}_\mp + \hat{J}_z{}^2 \mp \hbar\hat{J}_z\right]$$

Taking the 1st relation $\hat{L}^2 = \hat{L}_+\hat{L}_- + \hat{L}_z{}^2 - \hbar\hat{L}_z$

And substituting expressions of $\hat{L}_+\hat{L}_-$ and $\hat{L}_z{}^2$ we get:

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right) - \hbar^2\frac{\partial^2}{\partial\varphi^2} + i\hbar^2\frac{\partial}{\partial\varphi}$$

$$= -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \cot^2\theta \frac{\partial^2}{\partial \varphi^2} + i \frac{\partial}{\partial \varphi} + \frac{\partial^2}{\partial \varphi^2} - i \frac{\partial}{\partial \varphi} \right)$$

$$= -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + cosec^2\theta \frac{\partial^2}{\partial \varphi^2} \right)$$

Or, $$\boldsymbol{\hat{L}^2 = -\hbar^2 \left(\frac{1}{sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right)} \ldots \ldots \ldots (3.10)$$

Remember: $$\boldsymbol{\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}} \ldots \ldots \ldots (\mathbf{3.9})$$

3.2 Hydrogen Atom:

Hydrogen atom is a two body problem consisting of the nucleus and the electron revolving about their common centre of mass. The problem can be converted to a one body problem in which the nucleus can be considered fixed and the electron moving around the nucleus will have the effective mass $\mu = \frac{m_e M_N}{m_e + M_N}$, m_e and M_N being the mass of the electron and the nucleus respectively.

3.2.1 Motion in Spherically Symmetric Potential:

Potential of the electron in hydrogen atom is: $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$ …………………(3.11)

Nature of the potential is spherically symmetric (central potential) and this suggests that spherical polar coordinates will be suitable for the treatment of hydrogen atom problem.

The potential is time independent. Therefore it is possible to write time independent Schrodinger equation for hydrogen atom:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r,\theta,\varphi) + V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

In spherical polar coordinates

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

Therefore the Schrodinger equation becomes:

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

Or, $$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) + \frac{2\mu r^2}{\hbar^2}[E - V(r)]\psi(r,\theta,\varphi) = 0$$

... (3.12)

3.2.2 Separation of variables:

To solve the differential eqn. we use method of separation of variables by assuming:

$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$.

Then Schrodinger eqn. becomes, after some rearrangements:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}[E - V(r)] = -\frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\varphi)}{\partial\theta}\right) - \frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\varphi)}{\partial\varphi^2}$$

Since two sides of the equation are functions of different variables, they are independent of each other. Therefore both of them are equal to a constant, say, λ. Thus the above equation gives two equations, one angular and other radial:

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\varphi)}{\partial\theta}\right)+\frac{\partial^2 Y(\theta,\varphi)}{\partial\varphi^2}+\lambda\sin^2\theta\, Y(\theta,\varphi)=0 \quad \ldots\ldots\ldots (3.13)\ [\textbf{Angular eqn.}]$$

And $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\left[\frac{2\mu}{\hbar^2}[E-V(r)]-\frac{\lambda}{r^2}\right]R(r)=0 \ldots\ldots\ldots (3.14)\ [\textbf{Radial or } \boldsymbol{r} \textbf{ eqn.}]$$

Note: The angular part i.e. equation (3.13) can be written as

$$-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\varphi)}{\partial\theta}\right)-\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\varphi)}{\partial\varphi^2}=\lambda Y(\theta,\varphi) \ldots\ldots\ldots (3.13A)$$

But the angular momentum operator L^2 is given by:

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

Therefore Eqn. (3.13A) can be written as:

$$\hat{L}^2 Y(\theta,\varphi)=-\hbar^2\left(\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)Y(\theta,\varphi)=\lambda\hbar^2 Y(\theta,\varphi) \ \ldots (3.13B)$$

Therefore Eqn. (B) is the eigen value equation of the operator $\hat{L}^2$ and $\lambda\hbar^2$ is the eigen value of $\hat{L}^2$. We will see shortly more interesting things related to this.

To solve eqn. (3.13) again we apply the method of separation of variables by assuming:

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

Then this eqn. becomes, after rearrangements:

$$\frac{sin\,\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(sin\,\theta\frac{d\Theta(\theta)}{d\theta}\right)+\lambda\, sin^2\theta=-\frac{1}{\Phi(\varphi)}\frac{d^2\Phi(\varphi)}{d\varphi^2}.$$

As before, the two sides of the equation are functions of different variables. So they are independent of each other and so are equal to a constant, say, m^2. Thus the above equation gives two equations:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\lambda\sin^2\theta=m^2$$

Or, $$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta)=0 \quad \dots\dots\dots (3.15)\ [\boldsymbol{\theta}\ \textbf{eqn}.]$$

And $$\frac{d^2\Phi(\varphi)}{d\varphi^2}+m^2\Phi(\varphi)=0 \dots\dots\dots (3.16)\ [\boldsymbol{\varphi}\ \textbf{eqn}.]$$

To solve the $\boldsymbol{\theta}$ eqn. and the $\boldsymbol{\varphi}$ eqn. we don't need the expression or functional form of the potential $\boldsymbol{V(r)}$. It will be required to solve the radial equation.

3.2.2.1 Solution of the $\boldsymbol{\varphi}$ eqn.:

Equation (3.16) has solutions:

$\Phi(\varphi)=Be^{\pm im\varphi}\ for\ m\neq 0 \quad and, \qquad \Phi(\varphi)=C+D\varphi \quad for\ m=0.$

Φ and it's derivative must be continuous within $0\leq\varphi\leq 2\pi$. Also for Φ to be single valued, one must have $\Phi(\varphi+2\pi)=\Phi(\varphi)$.

Therefore:

$(i) \qquad Be^{\pm im(\varphi+2\pi)}=Be^{\pm im\varphi} \ \Rightarrow e^{\pm 2\pi im}=1 \quad \Rightarrow\ m=0,\pm1,\pm2,\pm3.$

$(ii) \qquad D=0.$

Then, for all possible values of m, the normalised solutions can be written as:

$\Phi(\varphi)=N_\varphi e^{im\varphi}$, with $m=0,\pm1,\pm2,\pm3\dots\dots\dots$

Where N_φ is the normalisation constant which can be obtained from the normalisation condition:

$$\int_0^{2\pi}\Phi^*\Phi d\varphi=\int_0^{2\pi}N_\varphi{}^* e^{-im\varphi}N_\varphi e^{im\varphi}d\varphi=1\Rightarrow \left|N_\varphi\right|^2=\ 2\pi$$

$\Rightarrow N_\varphi=\frac{1}{\sqrt{2\pi}}$, assuming N_φ to be real.

Thus the discrete solutions of eqn. (3.16) are given by:

$$\boldsymbol{\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi},\ \textbf{with}\ m=0,\pm1,\pm2,\pm3\dots\dots\dots;\ \dots\dots\dots(3.17)}\ .$$

Note: The φ eqn i.e. equation (3.16) can be modified as:

$$\frac{d^2\Phi(\varphi)}{d\varphi^2} + m^2\Phi(\varphi) = 0 \ \Rightarrow \quad -\hbar^2\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2} = m^2\hbar^2\Phi(\varphi)$$

$$\left[\text{Since } \Phi(\varphi) \text{ is single variable function, therefore } \frac{d}{d\varphi} \text{ can be replaced by } \frac{\partial}{\partial\varphi}\right]$$

$$\Rightarrow \left(-i\hbar\frac{\partial}{\partial\varphi}\right)^2 \Phi(\varphi) = (m\hbar)^2\Phi(\varphi) \ \ldots\ldots\ldots (3.16\text{A})$$

But the Z component of angular momentum operator, i.e. L_z is given by:

$$L_z = -i\hbar\frac{\partial}{\partial\varphi} \ldots\ldots\ldots (3.9)$$

Therefore Eqn. (3.16A) can be written as:

$$L_z{}^2\Phi(\varphi) = (m\hbar)^2\Phi(\varphi) \ \ldots\ldots (3.16\text{B})$$

Therefore Eqn. (3.16B) is the eigen value equation of the operator $L_z{}^2$ for eigen function $\Phi(\varphi)$ and $(m\hbar)^2$ is the eigen value of $L_z{}^2$.

Also:

$$L_z\Phi_m(\varphi) = -i\hbar\frac{\partial}{\partial\varphi}\left(\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right) = m\hbar\left(\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right) = m\hbar\Phi_m(\varphi) \quad \text{[using (3.17)]}$$

Thus we see that the eigen values of the Z component of orbital angular momentum operator are $m\hbar$, where m is zero or integer (positive or negative) but cannot have any half integer value. **m is called orbital magnetic quantum number**.

Extra restriction on orbital angular momentum quantum number and orbital magnetic quantum number:

In general angular momentum quantum number j can be zero, positive integer and netative half integer.

Magnetic quantum number m can be zero, positive and negative integer if j is an integer and positive and negative half integer if j is a half integer:

$m = 0, \pm 1, \ \ldots\ldots \pm j$ if j is integer.

$m = \pm\frac{1}{2}, \pm\frac{3}{2} \ldots\ldots \pm j$ if j is half integer.

But, as we have seen above, the orbital magnetic quantum number can be zero and positive and negative integer only:

$m = 0, \pm 1, \pm 2, \dots .$

If l is orbital angular momentum quantum number then from the general theory of angular momentum we can say that the limiting values of magnetic orbital quantum number m are related to l as:

$m = 0, \pm 1, \dots \pm l.$

Since m cannot be a half integer, therefore l also cannot be a half integer. Thus though in general the angular momentum quantum number j can be a positive integer or a positive half integer, the orbital angular momentum quantum number l can only be a positive integer.

3.2.2.1 Solution of the θ eqn.:

In Eqn. (3.15), let $\cos\theta = w$ and $\Theta(\theta) = P(w)$. [Since $0 \le \theta \le \pi$, so $-1 \le w (= \cos\theta) \le +1$]

Then $\quad \dfrac{d}{d\theta} = \dfrac{d}{dw}\dfrac{dw}{d\theta} = -\sin\theta \dfrac{d}{dw} = -\sqrt{1-w^2}\dfrac{d}{dw};$ $\quad$ and eqn. (3.15) becomes:

$$-(1-w^2)\frac{d}{dw}\left(-(1-w^2)\frac{dP(w)}{dw}\right) + \lambda(1-w^2)P(w) - m^2P(w) = 0$$

Or, $\frac{d}{dw}\left((1-w^2)\frac{dP(w)}{dw}\right) + \left(\lambda - \frac{m^2}{1-w^2}\right)P(w) = 0 \; \dots\dots\dots\dots (3.18)$

The 2nd order differential equation (3.18) has two linearly independent solutions, each of which is an infinite series (Frobenius method) with recurrence relation:

$$a_{\nu+2} = \frac{\nu(\nu+1) - \lambda}{(\nu+1)(\nu+2)} a_\nu \; \dots\dots\dots (3.19)$$

$$\lim_{\nu \to \infty} \frac{a_{\nu+2}}{a_\nu} w^2 = \lim_{\nu \to \infty} \frac{\nu(\nu+1) - \lambda}{(\nu+1)(\nu+2)} w^2 = w^2 \; \dots\dots\dots (3.19A)$$

Thus the infinite series converge for $w^2 < 1$, but they become indeterminate at $|w| = 1$ or $w = \pm 1$ (Note: $w = \pm 1$, for $\theta = 0$ & π).

To be physically meaningful solutions the series should be finite everywhere not only between $-1 < w < +1$ but also $w = \pm 1$.

Now, for $\lambda = l(l+1)$, where $l = 0, 1, 2, 3, \dots\dots\dots$, any one of the two series terminates for $\nu = l$ and becomes a polynomial in w, which remains finite at $w = \pm 1$ and this finite series or polynomial is acceptable as a physically meaningful solution for all values of θ, including 0 and π.

Thus eqn. (3.18) has physically meaningful solutions if:

$\boldsymbol{\lambda = l(l+1)}$, where $\boldsymbol{l = 0, 1, 2, 3, \dots \dots \dots}$ i.e. 0 or any positive integer …….. (3.20)

Then eqn. (3.17) becomes:

$$\frac{d}{dw}\left((1-w^2)\frac{dP(w)}{dw}\right)+\left(l(l+1)-\frac{m^2}{1-w^2}\right)P(w)=0 \quad \dots \dots \dots \dots (3.21)$$

Which is the well-known 'associated Legendre differential eqn.' with solutions:

$$P(w) = P_l^m(w) = P_l^m(\cos\theta)$$

$P_l^m(w)$ or $P_l^m(\cos\theta)$ are called associated Legendre functions and can be given by the Rodrigues's formula:

$$P_l^m(w) = (1-w^2)^{\frac{|m|}{2}}\left(\frac{d}{dw}\right)^{|m|}[P_l(w)] \dots \dots \dots \dots \dots \dots (3.22)$$

There are different conventions of defining $P_l^m(w)$ and eqn. (8) is one of them*. In the convention followed here, we see that: $P_l^{-m}(w) = P_l^m(w)$.

If $m = 0$ then eqn. (3.21) becomes Legendre differential equation with solutions:

$$P_l(w) = \frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^l (w^2-1)^l \dots \dots \dots \dots \dots (3.23)$$

In $(w^2-1)^l$ maximum power of w is $2l$. So it is clear from eqn. (3.23), that in $P_l(w)$, maximum power of w is l. Therefore $P_l(w)$ can be differentiable $\leq l$ times for non-zero result. Thus, as seen from eqn. (3.22), to get non-zero $P_l^m(w)$ we must restrict m as:

$\boldsymbol{|m| \leq l}$ or, $\boldsymbol{m = -l, -l+1, \dots -1, 0, 1, \dots l-1, l}$ ……… (3.24)

Note 1: With $\lambda = l(l+1)$ eqn. (3.13A) becomes:

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

… (3.13C)

Therefore eigen value of L^2 is $l(l+1)\hbar^2$. Thus the orbital angular momentum L has the values:

Note 2: $L_z = m\hbar$ and $m = -l, -l+1, \dots -1, 0, 1, \dots l-1, l$. Thus m has $2l+1$ number of values. Extreme of m are restricted by l. Therefore m is often written as m_l.

Table-3.1

$P_l(w)$ and $P_l^m(w)$ for few small values of l and m

l	$P_l(w) = \frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^l (w^2-1)^l$	m	$P_l^m(w) = (1-w^2)^{\frac{\lvert m\rvert}{2}}\left(\frac{d}{dw}\right)^{\lvert m\rvert}[P_l(w)]$
0	$P_0 = \frac{1}{2^0\, 0!}\left(\frac{d}{dw}\right)^0 (w^2-1)^0 = \mathbf{1}$	**0**	$P_0^0 = (1-w^2)^0\left(\frac{d}{dw}\right)^0 [P_0(w)] = \mathbf{1}$
1	P_1 $= \frac{1}{2^1\, 1!}\left(\frac{d}{dw}\right)^1 (w^2-1)^1$ $= \frac{1}{2}\cdot 2w$ $= w$ $= \mathbf{\cos\theta}$	**0**	$P_1^0 = (1-w^2)^0\left(\frac{d}{dw}\right)^0 [P_1(w)]$ $= P_1(w)$ $= w = \mathbf{\cos\theta}$
		± 1	$P_1^{\pm 1} = (1-w^2)^{\frac{\lvert\pm1\rvert}{2}}\left(\frac{d}{dw}\right)^{\lvert\pm1\rvert}[P_1(w)]$ $= \sqrt{(1-w^2)}\frac{d}{dw}w$ $= \sqrt{(1-w^2)} = \mathbf{\sin\theta}$
2	P_2 $= \frac{1}{2^2\, 2!}\left(\frac{d}{dw}\right)^2 (w^4-2w^2+1)$ $= \frac{1}{2}(3w^2-1)$ $= \mathbf{\frac{1}{2}(3cos^2\theta-1)}$	**0**	$P_2^0 = (1-w^2)^0\left(\frac{d}{dw}\right)^0 [P_2(w)] = [P_2(w)]$ $= \frac{1}{2}(3w^2-1) = \mathbf{\frac{1}{2}(3cos^2\theta-1)}$
		± 1	$P_2^{\pm 1} = (1-w^2)^{\frac{\lvert\pm1\rvert}{2}}\left(\frac{d}{dw}\right)^{\lvert\pm1\rvert}\left[\frac{1}{2}(3w^2-1)\right]$ $= \sqrt{(1-w^2)}\frac{d}{dw}\left[\frac{1}{2}(3w^2-1)\right]$ $= 3w\sqrt{(1-w^2)} = 3\,\mathbf{\cos\theta\sin\theta}$
		± 2	$P_2^{\pm 2} = (1-w^2)^{\frac{\lvert\pm2\rvert}{2}}\left(\frac{d}{dw}\right)^{\lvert\pm2\rvert}\left[\frac{1}{2}(3w^2-1)\right]$ $= \mathbf{3}(1-w^2)$ $= 3\mathbf{sin^2\theta}$

Thus the normalised solutions of the θ-eqn. is:

$$\Theta(\theta) = \Theta_{lm}(\theta) = N_{lm}P_l^m(w) = N_{lm}P_l^m(\cos\theta)$$

where N_{lm} is the normalisation constant which can be obtained from the normalisation condition:

$$\int_{w=1}^{-1} |N_{lm}P_l^m(w)|^2 dw = 1$$

Since $\displaystyle\int_{w=1}^{-1} P_k^m(w)P_l^m(w)dw = \frac{2}{(2l+1)} \cdot \frac{(l+|m|)!}{(l-|m|)!}\delta_{kl}$

we have $\displaystyle |N_{lm}|^2 = \frac{1}{\int_{w=1}^{-1}\left|P_l^m(w)\right|^2 dw} = \frac{(2l+1)}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}$ ……………… (3.25)

$\displaystyle \Rightarrow N_{lm} = \pm e^{i\delta}\sqrt{\frac{(2l+1)}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}}$, Where $e^{i\delta}$ is an arbitrary complex phase factor.

Verify: $\displaystyle \left|\pm e^{i\delta}\sqrt{\frac{(2l+1)}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}}\right|^2 = \frac{(2l+1)}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}$.

However N_{lm} is taken as $N_{lm} = \epsilon\sqrt{\frac{(2l+1)}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}}$ [where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$], to make $\Theta_{lm}(\theta)$ and $Y_{lm}(\theta, \varphi)$ same as in other conventions of defining P_l^m. Note that ϵ is always equal to 1 or -1.

Thus the solutions of the θ equation and the angular eqn. are given by:

$$\Theta_{lm}(\theta) = \epsilon\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^m(\cos\theta) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.26)$$

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

$$\left.\begin{aligned} &Y_{lm}(\theta,\varphi) = \epsilon\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\varphi} \\ &with\ \epsilon = (-1)^m \text{ for } m \geq 0\ \ \&\ \ \epsilon = 1 \text{ for } m \leq 0 \end{aligned}\right\} \ldots\ldots\ldots \quad (3.27)$$

Table-3.2

$P_l^m(w)$ and $Y_{lm}(\theta,\varphi)$ for few small values of l and m

l	m	$P_l^m(w)$ (From Table 3.1)	$Y_{lm}(\theta,\varphi)=\epsilon\left[\frac{2l+1}{4\pi}\frac{(l-\lvert m\rvert)!}{(l+\lvert m\rvert)!}\right]^{\frac{1}{2}}P_l^m(\cos\theta)e^{im\varphi}$ $with\ \epsilon=(-1)^m$ for $m\geq 0$ & $\epsilon=1$ for $m\leq 0$
0	0	$P_0^0(\cos\theta)=1$	$\boldsymbol{Y_{00}(\theta,\varphi)}=\left[\frac{0+1}{4\pi}\frac{(l-0)!}{(l+0)!}\right]^{1/2}P_1^0e^0=\boldsymbol{\frac{1}{\sqrt{4\pi}}}$
1	0	$P_1^0(\cos\theta)=\cos\theta$	$\boldsymbol{Y_{10}(\theta,\varphi)}=\left[\frac{2+1}{4\pi}\frac{(l-0)!}{(l+0)!}\right]^{1/2}P_1^0e^0=\sqrt{\frac{3}{4\pi}}\cos\theta$
	±1	$P_1^{\pm1}(\cos\theta)=\sin\theta$	$\boldsymbol{Y_{1\pm1}(\theta,\varphi)}=\mp\left[\frac{2+1}{4\pi}\frac{(l-1)!}{(l+1)!}\right]^{1/2}P_1^{\pm1}e^{\pm i\varphi}$ $=\mp\sqrt{\boldsymbol{\frac{3}{8\pi}}}\ \boldsymbol{\sin\theta\, e^{\pm i\varphi}}$
2	0	$P_2^0(\cos\theta)$ $=\frac{1}{2}(3cos^2\theta-1)$	$\boldsymbol{Y_{20}(\theta,\varphi)}=\left[\frac{2\times2+1}{4\pi}\frac{(2-0)!}{(2+0)!}\right]^{\frac{1}{2}}P_2^0e^{i0\varphi}$ $=\sqrt{\boldsymbol{\frac{5}{16\pi}}}\boldsymbol{(3cos^2\theta-1)}$
	±1	$P_2^{\pm1}(\cos\theta)=3\cos\theta\sin\theta$	$\boldsymbol{Y_{2\pm1}(\theta,\varphi)}=\mp\left[\frac{2\times2+1}{4\pi}\frac{(2-1)!}{(2+1)!}\right]^{\frac{1}{2}}P_2^{\pm1}e^{\pm i\varphi}$ $=\mp\sqrt{\boldsymbol{\frac{15}{8\pi}}}\boldsymbol{\cos\theta\sin\theta\, e^{\pm i\varphi}}$
	±2	$P_2^{\pm2}(\cos\theta)=3sin^2\theta$	$\boldsymbol{Y_{2\pm2}(\theta,\varphi)}=\left[\frac{2\times2+1}{4\pi}\frac{(2-2)!}{(2+2)!}\right]^{\frac{1}{2}}P_2^{\pm2}e^{\pm2i\varphi}$ $=\sqrt{\boldsymbol{\frac{15}{32\pi}}}\boldsymbol{sin^2\theta e^{\pm2i\varphi}}$

Prove: $\boldsymbol{Y_{l,-m}(\theta,\varphi) = (-1)^m [Y_{lm}(\theta,\varphi)]^*}$

Proof: Let $m = m_0$, where m_0 is $+ve$.

Then $\quad Y_{lm}(\theta,\varphi) = Y_{lm_0}(\theta,\varphi) = (-1)^{m_0}\left[\frac{2l+1}{4\pi}\frac{(l-|m_0|)!}{(l+|m_0|)!}\right]^{1/2} P_l^{m_0}(\cos\theta)e^{im_0\varphi}$

$$= (-1)^{m_0}\left[\frac{2l+1}{4\pi}\frac{(l-m_0)!}{(l+m_0)!}\right]^{1/2} P_l^{m_0}(\cos\theta)e^{im_0\varphi}$$

$$[Y_{lm}(\theta,\varphi)]^* = \left[Y_{lm_0}(\theta,\varphi)\right]^* = (-1)^{m_0}\left[\frac{2l+1}{4\pi}\frac{(l-m_0)!}{(l+m_0)!}\right]^{1/2} P_l^{m_0}(\cos\theta)e^{-im_0\varphi}$$

And $\quad Y_{l,-m}(\theta,\varphi) = Y_{l,-m_0}(\theta,\varphi) = \left[\frac{2l+1}{4\pi}\frac{(l-|-m_0|)!}{(l+|-m_0|)!}\right]^{1/2} P_l^{-m_0}(\cos\theta)e^{-im_0\varphi}$

$$= \left[\frac{2l+1}{4\pi}\frac{(l-m_0)!}{(l+m_0)!}\right]^{1/2} P_l^{m_0}(\cos\theta)e^{-im_0\varphi}$$

$$= \frac{\left[Y_{lm_0}(\theta,\varphi)\right]^*}{(-1)^{m_0}}$$

$$= \frac{[Y_{lm}(\theta,\varphi)]^*}{(-1)^{m}}$$

$$= (-1)^m[Y_{lm}(\theta,\varphi)]^*$$

Hence the proof.

End of Notes on Angular part.

*Special Page

Doing the following mathematics is optional, must avoid it if you have not enough time to waste

One convention of defining $P_l^m(w)$ has been discussed in the preceding section. Another convention of defining $P_l^m(w)$ is:

$$P_l^m(w) = (1-w^2)^{\frac{m}{2}}\left(\frac{d}{dw}\right)^m [P_l(w)]$$

And $P_l^{-m}(w) = (1-w^2)^{\frac{-m}{2}}\left(\frac{d}{dw}\right)^{-m} [P_l(w)] = (-1)^m \frac{(\boldsymbol{l}-\boldsymbol{m})!}{(\boldsymbol{l}+\boldsymbol{m})!} P_l^m(w)$

With $0 \le m\ (integer) \le l$.

Prove: $\boldsymbol{P_l^{-m}(w) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(w)}$

Ans.:

Libniz's formula: $\left(\frac{d}{dx}\right)^n [A(x)B(x)] = \sum_{s=0}^{n} \frac{n!}{(n-s)!\,s!}\left(\frac{d}{dx}\right)^{n-s} A(x)\left(\frac{d}{dx}\right)^s B(x).$

Therefore $\left(\frac{d}{dw}\right)^{l+m} (w^2-1)^l = \left(\frac{d}{dw}\right)^{l+m} [(w+1)^l (w-1)^l]$

$$= \sum_{s=0}^{l+m} \frac{(l+m)!}{(l+m-s)!\,s!}\left(\frac{d}{dx}\right)^{l+m-s} (w+1)^l \left(\frac{d}{dx}\right)^s (w-1)^l$$

$$= \sum_{s=m}^{l} \frac{(l+m)!}{(l+m-s)!\,s!}\left(\frac{d}{dx}\right)^{l+m-s} (w+1)^l \left(\frac{d}{dx}\right)^s (w-1)^l$$

$$= \sum_{s=m}^{l} \frac{(l+m)!}{(l+m-s)!\,s!}\frac{l!}{(s-m)!}(w+1)^{s-m}\frac{l!}{(l-s)!}(w-1)^{l-s}$$

$$= \sum_{s=m}^{l} \frac{(l+m)!}{(l+m-s)!\,s!}\frac{l!}{(s-m)!}\frac{l!}{(l-s)!}(w+1)^{s-m}(w-1)^{l-s}$$

$$= (l!)^2(l+m)! \sum_{s=m}^{l} \frac{1}{(l+m-s)!\,s!\,(s-m)!\,(l-s)!}(w+1)^{s-m}(w-1)^{l-s}$$

$$= (l!)^2(l+m)!\left(\frac{(w+1)^0(w-1)^{l-m}}{l!\,m!\,0!\,(l-m)!} + \frac{(w+1)^1(w-1)^{l-m-1}}{(l-1)!\,(m+1)!\,1!\,(l-m-1)!} + \cdots \right.$$

$$\left. \dots + \frac{(w+1)^{l-m-1}(w-1)^1}{(m+1)!\,(l-1)!\,(l-m-1)!\,1!} + \frac{(w+1)^{l-m}(w-1)^0}{m!\,l!\,(l-m)!\,0!}\right)$$

Again: $\left(\frac{d}{dw}\right)^{l-m}(w^2-1)^l = \left(\frac{d}{dw}\right)^{l-m}[(w+1)^l(w-1)^l]$

$$= \sum_{s=0}^{l-m}\frac{(l-m)!}{(l-m-s)!\,s!}\left(\frac{d}{dx}\right)^{l-m-s}(w+1)^l\left(\frac{d}{dx}\right)^{s}(w-1)^l$$

$$= \sum_{s=0}^{l-m}\frac{(l-m)!}{(l-m-s)!\,s!}\frac{l!}{(s+m)!}(w+1)^{s+m}\frac{l!}{(l-s)!}(w-1)^{l-s}$$

$$= \sum_{s=0}^{l-m}\frac{(l-m)!}{(l-m-s)!\,s!}\frac{l!}{(s+m)!}\frac{l!}{(l-s)!}(w+1)^{s+m}(w-1)^{l-s}$$

$$= (l-m)!\,(l!)^2\sum_{s=0}^{l-m}\frac{1}{(l-m-s)!\,s!\,(s+m)!\,(l-s)!}(w+1)^{s+m}(w-1)^{l-s}$$

$$= (l-m)!\,(l!)^2\left(\frac{(w+1)^m(w-1)^l}{(l-m)!\,0!\,m!\,l!} + \frac{(w+1)^{1+m}(w-1)^{l-1}}{(l-m-1)!\,1!\,(m+1)!\,(l-1)!} + \cdots \right.$$

$$\left. \dots + \frac{(w+1)^{l-1}(w-1)^{m+1}}{1!\,(l-m-1)!\,(l-1)!\,(m+1)!} + \frac{(w+1)^l(w-1)^m}{0!\,(l-m)!\,l!\,m!}\right)$$

$$= (l-m)!\,(l!)^2(w+1)^m(w-1)^m\left(\frac{(w+1)^0(w-1)^{l-m}}{(l-m)!\,0!\,m!\,l!} + \frac{(w+1)^1(w-1)^{l-m-1}}{(l-m-1)!\,1!\,(m+1)!\,(l-1)!} \right.$$

$$\left. \dots + \frac{(w+1)^{l-m-1}(w-1)^1}{1!\,(l-m-1)!\,(l-1)!\,(m+1)!} + \frac{(w+1)^{l-m}(w-1)^0}{0!\,(l-m)!\,l!\,m!}\right)$$

Therefore $\dfrac{\left(\frac{d}{dw}\right)^{l-m}(w^2-1)^l}{\left(\frac{d}{dw}\right)^{l+m}(w^2-1)^l} = \dfrac{(l-m)!\,(l!)^2(w+1)^m(w-1)^m}{(l!)^2(l+m)!} = \dfrac{(l-m)!}{(l+m)!}(w^2-1)^m$

$$\Rightarrow\Rightarrow \left(\frac{d}{dw}\right)^{l-m}(w^2-1)^l = \frac{(l-m)!}{(l+m)!}(w^2-1)^m\left(\frac{d}{dw}\right)^{l+m}(w^2-1)^l$$

Now, $P_l^{-m}(w) = (1-w^2)^{\frac{-m}{2}}\left(\frac{d}{dw}\right)^{-m}[P_l(w)]$

$$= (1-w^2)^{\frac{-m}{2}}\left(\frac{d}{dw}\right)^{-m}\left[\frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^{l}(w^2-1)^l\right] \quad = (1-w^2)^{\frac{-m}{2}}\frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^{l-m}(w^2-1)^l$$

$$= (1-w^2)^{\frac{-m}{2}}\frac{(l-m)!}{(l+m)!}(w^2-1)^m\frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^{l+m}(w^2-1)^l$$

$$= (1-w^2)^{\frac{-m}{2}}\frac{(l-m)!}{(l+m)!}(-1)^m(1-w^2)^m\frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^{l+m}(w^2-1)^l$$

$$= (-1)^m\frac{(l-m)!}{(l+m)!}(1-w^2)^{\frac{m}{2}}\left(\frac{d}{dw}\right)^{m}\left[\frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^{l}(w^2-1)^l\right]$$

$$= (-1)^m\frac{(l-m)!}{(l+m)!}(1-w^2)^{\frac{m}{2}}\left(\frac{d}{dw}\right)^{m}[P_l(w)]$$

$$= (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(w).$$

In this convention N_{lm} is equal to $N_{lm} = \sqrt{\frac{(2l+1)}{2}\cdot\frac{(l-m)!}{(l+m)!}}$

And $Y_{lm}(\theta,\varphi) = \sqrt{\frac{(2l+1)}{4\pi}\cdot\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\varphi}$

Note that

$$\boldsymbol{Y_{l,-m}(\theta,\varphi)} = \sqrt{\frac{(2l+1)}{4\pi}\cdot\frac{(l+m)!}{(l-m)!}}P_l^{-m}(\cos\theta)e^{-im\varphi}$$

$$= \sqrt{\frac{(2l+1)}{4\pi}\cdot\frac{(l+m)!}{(l-m)!}}(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta)e^{-im\varphi}$$

$$= (-1)^m\sqrt{\frac{(2l+1)}{4\pi}\cdot\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{-im\varphi} = \boldsymbol{(-1)^m[Y_{lm}(\theta,\varphi)]^*}$$

This result is same as that obtained by our other convention. **Thus use of $\boldsymbol{\epsilon}$ [$= (-1)^m$ for $m \geq 0$ and $= 1$ for $m < 0$] in the other convention is justified.**

3.2.3 Solution of Radial Equation:

With $\lambda = l(l+1)$, where $l = 0,1,2$ ... the radial equation (3.14) becomes:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\left[\frac{2\mu}{\hbar^2}[E-V(r)]-\frac{l(l+1)}{r^2}\right]R(r)=0 \quad \dots\dots\dots\dots\dots (3.27)$$

With $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$, this equation becomes:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\epsilon_0 r}\right)-\frac{l(l+1)}{r^2}\right]R=0$$

Or, $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu E}{\hbar^2}+\frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0 r}-\frac{l(l+1)}{r^2}\right]R=0 \quad \dots\dots\dots\dots\dots (3.28)$$

To make the equation simpler, we put:

(i) $\boldsymbol{\alpha} = \sqrt{\frac{\mathbf{-8\mu E}}{\hbar^2}}$ ...... (3.28A) and (ii) $\boldsymbol{\rho} = \boldsymbol{\alpha r} = \sqrt{\frac{\mathbf{-8\mu E}}{\hbar^2}}\boldsymbol{r} = \sqrt{\frac{\mathbf{8\mu|E|}}{\hbar^2}}\boldsymbol{r}$ ...... (**3.28B**)

[Note that, since the energy of the electron of a Hydrogen atom is negative, therefore $\frac{-8\mu E}{\hbar^2} = \frac{8\mu|E|}{\hbar^2}$ is positive. Hence $\boldsymbol{\alpha} = \sqrt{\frac{\mathbf{-8\mu E}}{\hbar^2}}$ is not imaginary.]

$$Then \ \frac{d}{dr}=\frac{d\rho}{dr}\frac{d}{d\rho}=\alpha\frac{d}{d\rho}.$$

And from eqn. (3.28):

$$\frac{\alpha^2}{\rho^2}\alpha\frac{d}{d\rho}\left(\frac{\rho^2}{\alpha^2}\alpha\frac{dR}{d\rho}\right)+\left[\frac{2\mu E}{\hbar^2}+\frac{2\mu}{\hbar^2}\frac{Z\alpha e^2}{4\pi\epsilon_0\rho}-\frac{\alpha^2 l(l+1)}{\rho^2}\right]R=0;$$

$$\Rightarrow \frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\frac{1}{\alpha^2}\left[-\frac{1}{4}\alpha^2+\frac{2\mu}{\hbar^2}\frac{Z\alpha e^2}{4\pi\epsilon_0\rho}-\frac{\alpha^2 l(l+1)}{\rho^2}\right]R=0;$$

$$\Rightarrow \frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\left[-\frac{1}{4}+\frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2\alpha\rho}-\frac{l(l+1)}{\rho^2}\right]R=0 \quad \dots\dots\dots\dots\dots\dots (3.29)$$

Now we put:

$$\lambda=\frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2\alpha}=\frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2}\sqrt{\frac{\hbar^2}{8\mu|E|}}=\frac{Ze^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{\mu}{2|E|}}=\frac{Ze^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{\mu}{-2E}} \quad \dots\dots\dots\dots (3.29A)$$

Then eqn. (3.29) becomes:

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]R=0 \quad \dots\dots\dots\dots\dots \quad (3.30)$$

At $\rho \longrightarrow \infty$, the above equation reduces to:

$$\frac{d^2R}{d\rho^2}-\frac{1}{4}R=0$$

having solutions: $R = Ae^{\pm\frac{1}{2}\rho}$, where A is any constant.

Therefore as the solution of eqn. (3.30) we can assume a trial solution of the form:

$$R = F(\rho)e^{\pm\frac{1}{2}\rho},$$

where $F(\rho)$ is a function in ρ and is to be determined to obtain the solution for R.

However we reject the solution $R = F(\rho)\boldsymbol{e^{+\frac{1}{2}\rho}}$ because R must remain finite at $\rho \longrightarrow \infty$ but $\boldsymbol{e^{+\frac{1}{2}\rho}}$ blows up at $\rho \longrightarrow \infty$ and proceed with:

$$R = F(\rho)e^{-\frac{1}{2}\rho} \quad \dots\dots\dots\dots \quad (3.30A)$$

$$Then\ \frac{dR}{d\rho}=\frac{dF}{d\rho}e^{-\frac{1}{2}\rho}-\frac{1}{2}Fe^{-\frac{1}{2}\rho}=\left(F'-\frac{1}{2}F\right)e^{-\frac{1}{2}\rho}$$

$$and\ \frac{d^2R}{d\rho^2}=\frac{d^2F}{d\rho^2}e^{-\frac{1}{2}\rho}-\frac{1}{2}\frac{dF}{d\rho}e^{-\frac{1}{2}\rho}-\frac{1}{2}\frac{dF}{d\rho}e^{-\frac{1}{2}\rho}+\frac{1}{2}\cdot\frac{1}{2}Fe^{-\frac{1}{2}\rho}=\left(\frac{d^2F}{d\rho^2}-\frac{dF}{d\rho}+\frac{1}{4}F\right)e^{-\frac{1}{2}\rho}$$

$$=e^{-\frac{1}{2}\rho}\left(F''-F'+\frac{1}{4}F\right)$$

And eqn. (3.30) reduces to:

$$\left(F''-F'+\frac{1}{4}F\right)e^{-\frac{1}{2}\rho}+\frac{2}{\rho}\left(F'-\frac{1}{2}F\right)e^{-\frac{1}{2}\rho}+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]Fe^{-\frac{1}{2}\rho}=0$$

$$\Rightarrow F''-F'+\frac{1}{4}F+\frac{2}{\rho}F'-\frac{1}{\rho}F+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]F=0$$

$$\Rightarrow F''+\left(\frac{2}{\rho}-1\right)F'+\left[\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right]F=0$$

$$\Rightarrow \rho^2F''+(2\rho-\rho^2)F'+[(\lambda-1)\rho-l(l+1)]F=0 \quad \dots\dots\dots\dots\dots\dots\dots \quad (3.31)$$

This 2nd order differential equation can be solved by Frobenius series method assuming:

$$F(\rho) = \sum_{\nu=0}^{\infty} a_\nu \rho^{\nu+s}, \qquad \text{with } a_0 \neq 0, \quad \dots\dots \dots\dots\dots\dots (3.31A)$$

Then $F'(\rho) = \sum_{\nu=0}^{\infty} a_\nu(\nu+s)\rho^{\nu+s-1}$ *and* $F''(\rho) = \sum_{\nu=0}^{\infty} a_\nu(\nu+s)(\nu+s-1)\rho^{\nu+s-2}$

Then eqn. (13) becomes:

$$\rho^2 \sum_\nu a_\nu(\nu+s)(\nu+s-1)\rho^{\nu+s-2} + 2\rho \sum_\nu a_\nu(\nu+s)\rho^{\nu+s-1} - \rho^2 \sum_\nu a_\nu(\nu+s)\rho^{\nu+s-1}$$
$$+(\lambda-1)\rho \sum_\nu a_\nu \rho^{\nu+s} - l(l+1)\sum_\nu a_\nu \rho^{\nu+s} = 0$$

Or, $$\sum_\nu a_\nu(\nu+s)(\nu+s-1)\rho^{\nu+s} + 2\sum_\nu a_\nu(\nu+s)\rho^{\nu+s} - \sum_\nu a_\nu(\nu+s)\rho^{\nu+s+1}$$
$$+(\lambda-1)\sum_\nu a_\nu \rho^{\nu+s+1} - l(l+1)\sum_\nu a_\nu \rho^{\nu+s} = 0$$

Or, $$\sum_\nu a_\nu[(\nu+s)(\nu+s-1) + 2(\nu+s) - l(l+1)]\rho^{\nu+s}$$
$$-\sum_\nu a_\nu[(\nu+s) - (\lambda-1)]\rho^{\nu+s+1} = 0$$

Or, $$\sum_\nu a_\nu(\nu+s+1-\lambda)\rho^{\nu+s+1} - \sum_\nu a_\nu[(\nu+s)(\nu+s+1) - l(l+1)]\rho^{\nu+s} = 0$$
$$\dots\dots\dots (3.32)$$

Eqn. (3.32) should be valid for all values of ρ. Therefore the coefficients of each power of ρ must vanish separately. Equating the coefficient of ρ^s to zero we get (remember $\nu = 0,1,2,....$ [eqn. (3.31A)]; i.e. ν can not be negative):

$$a_0[s(s+1) - l(l+1)] = 0.$$

Since $a_0 \neq 0$ [see eqn. (14)], so we must have:

$$s^2 - l^2 + s - l = 0 \;\Rightarrow\; (s-l)(s+l+1) = 0 \;\Rightarrow\; s = l \text{ or } -(l+1).$$

Now, for $s = -(l+1)$, the 1st term in the expression of $F(\rho)$ i.e. $a_0\rho^{-(l+1)} \to \infty$ at $\rho \to \infty$, even for $l = 0$.

Therefore only acceptable value of s is $s = l$.

Then Eqn. (3.31A) becomes:

$$F(\rho) = \sum_{\nu=0}^{\infty} a_\nu \rho^{\nu+s} = \sum_{\nu=0}^{\infty} a_\nu \rho^{\nu+l} = \rho^l \sum_{\nu=0}^{\infty} a_\nu \rho^\nu \text{ with } a_0 \neq 0, \dots\dots\dots\dots (3.31B)$$

And Eqn. (3.32) becomes:

$$\sum_\nu a_\nu(\nu + l + 1 - \lambda)\rho^{\nu+l+1} - \sum_\nu a_\nu[(\nu + l)(\nu + l + 1) - l(l + 1)]\rho^{\nu+l} = 0$$

$$\sum_\nu a_\nu(\nu + l + 1 - \lambda)\rho^{\nu+l+1} - \sum_\nu a_\nu(\nu^2 + 2\nu l + \nu)\rho^{\nu+l} = 0$$

$$\sum_\nu a_\nu(\nu + l + 1 - \lambda)\rho^{\nu+l+1} - \sum_\nu a_\nu \nu(\nu + 2l + 1)\rho^{\nu+l} = 0$$

Equating the coefficient of $\rho^{\nu+l+1}$ to zero we get the following recursion relation:

$$a_{\nu+1} = \frac{\nu + l + 1 - \lambda}{(\nu + 1)(\nu + 2l + 2)} a_\nu \quad \dots\dots\dots\dots (3.33)$$

Now for large values of ν,

$$\frac{a_{\nu+1}}{a_\nu} = \frac{\nu + l + 1 - \lambda}{(\nu + 1)(\nu + 2l + 2)} = \frac{1}{\nu}.$$

Again in the expression of e^ρ, i.e.

$$e^\rho = \sum_{\nu=0}^{\infty} \frac{\rho^\nu}{\nu!} = \sum_{\nu=0}^{\infty} A_\nu \rho^\nu \; (say),$$

$$\frac{A_{\nu+1}}{A_\nu} = \frac{\nu!}{(\nu + 1)!} \longrightarrow \frac{1}{\nu} \text{ for large values of } \nu.$$

Thus for large values of ν, $F(\rho) = \rho^l \sum_{\nu=0}^{\infty} a_\nu \rho^\nu$ behaves like $\rho^l e^\rho$. And $R = F(\rho)e^{-\rho/2}$ [eqn. (3.30A)] behaves like $\rho^l e^{\rho/2}$, which tends to infinity for $\rho \to \infty$ and thus is not acceptable. Therefore the series $\sum_{\nu=0}^{\infty} a_\nu \rho^\nu$ should terminate at some value of ν. This can be done by restricting λ to be equal to some integer n i.e. imposing the condition:

$$\boldsymbol{\lambda = n} \quad \dots\dots\dots (\mathbf{3.34})$$

such that $a_{\nu+1} = \dfrac{\nu + l + 1 - \lambda}{(\nu + 1)(\nu + 2l + 2)} a_\nu = \dfrac{\nu + l + 1 - n}{(\nu + 1)(\nu + 2l + 2)} a_\nu$ vanishes for

$$\boldsymbol{\nu = n - l - 1} \quad \dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{3.34A})$$

Again if $a_{\nu+1}$ vanishes, then all higher coefficients $a_{\nu+2}, a_{\nu+3}, \dots\dots\dots$ will also vanish and the series will terminate. The non-vanishing coefficient of highest order term will be $a_\nu = a_{n-l-1}$.

Thus the series $\sum_{\nu=0}^{\infty} a_\nu \rho^\nu$ converts to a polynomial

$$L(\rho) = \sum_{\nu=0}^{\boldsymbol{n-l-1}} a_\nu \rho^\nu$$

and then $F(\rho) = \rho^l \sum_{\nu=0}^{\boldsymbol{n-l-1}} a_\nu \rho^\nu = \rho^l L(\rho)$. ………….(3.35)

Note that if the integer $n \leq 0$, then, $\nu = \lambda - l - 1 = n - l - 1$ becomes – ve, which contradicts the assumption $\nu = 0,1,2 \dots\dots$(see eqn. (3.31A)).

Therefore $\boldsymbol{n}$ will have only positive integral values:

$\boldsymbol{n = 1, 2, 3} \dots\dots$

3.2.3.1 Before proceeding further in solving the radial equation, let us explore the following interesting results:

(i) Energy eigen values:

From eqns. (3.29A) & (3.34) we have:

$$\lambda = \frac{Ze^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{\mu}{-2E}} = n$$

$$\boldsymbol{E_n = -\frac{\mu Z^2 e^4}{32\pi^2\hbar^2{\epsilon_0}^2 n^2} = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n^2}}, \quad \textbf{with } \boldsymbol{n = 1, 2} \dots\dots\dots (3.36)$$

Where $a_0 = \frac{4\pi\hbar^2\epsilon_0}{\mu e^2}$ is the well known expression of first Bohr radius.

$$\alpha_n = \sqrt{\frac{-8\mu E_n}{\hbar^2}} = \sqrt{\frac{8\mu}{\hbar^2}\frac{\mu Z^2 e^4}{32\pi^2\hbar^2{\epsilon_0}^2}\frac{1}{n^2}} = \frac{\mu Z e^2}{2\pi\hbar^2\epsilon_0 n} = \frac{2Z}{a_0 n} \dots\dots\dots\dots (3.37)$$

For $Z = 1$, eqn. (3.36) gives Bohr energies of Hydrogen atom.

(ii) Principal quantum number: The integer n is called principal quantum number and gives the discrete energy levels of Hydrogen atom, which are the same as given by Bohr theory of Hydrogen atom.

(iii) Relation between orbital angular momentum quantum number and principal quantum number ($\boldsymbol{l \leq n-1}$):

We have

(a) $l = 0,1,2, \dots \dots;$

(b) $\nu = n - l - 1$, i.e. $l = n - \nu - 1$; and

(c) $\nu = 0,1,2 \dots$ i.e. $\nu_{min} = 0$.

Then, for a given n:

$$l_{max} = n - \nu_{min} - 1 = n - 1$$

Thus $\boldsymbol{l}$ can have integral values between $\boldsymbol{0}$ and $\boldsymbol{n-1}$. Therefore $\boldsymbol{l}$ has $\boldsymbol{n}$ number of values.

3.2.3.1 Radial Wave Functions:

With $\lambda = n$, from equation (3.31A):

$$F(\rho) = \rho^l \sum_{\nu=0}^{n-l-1} a_\nu \rho^\nu = \rho^l L(\rho), \qquad n = 1,2,3 \dots \dots \dots \dots \dots (3.31B)$$

$$F'(\rho) = l\rho^{l-1}L(\rho) + \rho^l L'(\rho)$$

$$F''(\rho) = l(l-1)\rho^{l-2}L(\rho) + l\rho^{l-1}L'(\rho) + l\rho^{l-1}L'(\rho) + \rho^l L''(\rho)$$

$$= l(l-1)\rho^{l-2}L(\rho) + 2l\rho^{l-1}L'(\rho) + \rho^l L''(\rho)$$

The equation

$$\boldsymbol{\rho^2 F'' + (2\rho - \rho^2)F' + [(\lambda - 1)\rho - l(l+1)]F = 0} \dots \dots \dots \dots \dots \dots (\mathbf{3.38})$$

reduces to:

$$\rho^2[l(l-1)\rho^{l-2}L(\rho) + 2l\rho^{l-1}L'(\rho) + \rho^l L''(\rho)] + (2\rho - \rho^2)[l\rho^{l-1}L(\rho) + \rho^l L'(\rho)]$$
$$+[(n-1)\rho - l(l+1)]\rho^l L(\rho) = 0$$

Or, $l(l-1)\rho^l L(\rho) + 2l\rho^{l+1}L'(\rho) + \rho^{l+2}L''(\rho) + 2l\rho^l L(\rho) + 2\rho^{l+1}L'(\rho)$
$$-l\rho^{l+1}L(\rho) - \rho^{l+2}L'(\rho) + (n-1)\rho^{l+1}L(\rho) - l(l+1)\rho^l L(\rho) = 0$$

Or, $\rho^{l+1}\{\rho L''(\rho) + (2l + 2 - \rho)L'(\rho) + (n - l - 1)L(\rho)\} = 0$

Since this Eqn. is true for all values of ρ, so the bracketed term must vanish:

$$\rho L''(\rho) + (2l + 2 - \rho)L'(\rho) + (n - l - 1)L(\rho) = 0$$

$$\rho \frac{d^2 L(\rho)}{d\rho^2} + (2l + 2 - \rho)\frac{dL(\rho)}{d\rho} + (n - l - 1)L(\rho) = 0 \;\dots\dots\dots\dots\dots\dots (3.39)$$

Solving Eqn. (3.29) is not simple. Let us compare Eqn. (18) with **associated Laguerre differential equation**:

$$x\frac{d^2 L_q^p(x)}{dx^2} + (p + 1 - x)\frac{dL_q^p(x)}{dx} + (q - p)L_q^p(x) = 0 \;\dots\dots\dots\dots\dots\dots\dots.(3.39A)^*$$

where $L_q^p(\rho)$ are the associated Laguerre polynomials. We see that Eqns. (3.39) & (3.39A) become identical for $p = 2l + 1$ and $q = n + l$.

Therefore the solutions of equation (3.39) are given by associated Laguerre polynomials $L_{n+l}^{2l+1}(\rho)$. Equation (3.31B) becomes:

$$F_{nl}(\rho) = \rho^l \sum_{\nu=0}^{n-l-1} a_\nu \rho^\nu = \rho^l L(\rho) = \rho^l L_{n+l}^{2l+1}(\rho) \;\dots\dots\dots\dots\dots\dots (3.40)$$

Associated Laguerre Polynomials:

Associated Laguerre polynomials $L_q^p(x)$ are given by (see Zettili) Rodrigues formula as:

$$L_q^p(x) = \left(\frac{d}{dx}\right)^p L_q(x) \;\dots\dots\dots\dots\dots\dots (3.41)$$

Where $L_q(x)$ are Laguerre polynomials given by:

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q (x^q e^{-x}) \;\dots\dots\dots\dots\dots\dots (3.42)$$

Laguerre polynomials $L_q(x)$ satisfy Laguerre differential equation:

$$x\frac{d^2 L_q(x)}{dx^2} + (1 - x)\frac{dL_q(x)}{dx} + qL_q(x) = 0 \;\dots\dots\dots\dots\dots\dots\dots.(3.39B)$$

Therefore from eqn. (3.30A) $[R = F(\rho)e^{-\rho/2}]$, eqn. (3.40) $[F_{nl}(\rho) = \rho^l L_{n+l}^{2l+1}(\rho)]$ and eqn. (3.28B) $[\rho = \alpha r]$ we can write:

$$R = F(\rho)e^{-\rho/2} = \rho^l L_{n+l}^{2l+1}(\rho)e^{-\rho/2} = \rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho)$$

$$R_{nl} = N_{nl}\,(\alpha_n r)^l\, e^{-\alpha_n r/2} L_{n+l}^{2l+1}(\alpha_n r)$$

where N_{nl} is normalisation constant.

N_{nl} can be evaluated from the normalisation relation:

$$\int_0^\infty {R_{nl}}^2 r^2 dr = 1$$

Or, $${N_{nl}}^2 \frac{1}{{\alpha_n}^3} \int_0^\infty e^{-\rho}\rho^{2l} L_{n+l}^{2l+1}(\rho)\rho^2 d\rho = 1$$

Or, $${N_{nl}}^2 \left(\frac{a_0 n}{2Z}\right)^3 \int_0^\infty e^{-\rho}\rho^{2l} L_{n+l}^{2l+1}(\rho)\rho^2 d\rho = 1$$

Orthogonal relation of associated Laguerre polynomials is given by:

$$\int_0^\infty e^{-\rho}\rho^{2l} L_{n+l}^{2l+1}(\rho)\rho^2 d\rho = \frac{2n[(n+1)!]^3}{(n+l+1)!}$$

Therefore:

$$N_{nl} = \pm\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}{\alpha_n}^3} = \pm\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2Z}{a_0 n}\right)^3} = \pm 2\left(\frac{Z}{a_0 n}\right)^{\frac{3}{2}}\sqrt{\frac{(n-l-1)!}{n[(n+l)!]^3}}$$

We chose negative value of N_{nl} to make the first wave function of hydrogen atom positive.

$$N_{nl} = -2\left(\frac{Z}{a_0 n}\right)^{\frac{3}{2}}\sqrt{\frac{(n-l-1)!}{n[(n+l)!]^3}} \quad \ldots\ldots\ldots (3.43)$$

Then the radial wave functions are given by:

$$R_{nl}(r) = -2\left(\frac{Z}{a_0 n}\right)^{\frac{3}{2}}\sqrt{\frac{(n-l-1)!}{n[(n+l)!]^3}}\, e^{-\alpha_n r/2}(\alpha_n r)^l L_{n+l}^{2l+1}(\alpha_n r)$$

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2Z}{a_0 n}\right)^3}\, e^{-\frac{Zr}{a_0 n}}\left(\frac{2Zr}{a_0 n}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{a_0 n}\right) \quad \ldots\ldots\ldots (3.44)$$

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2}{a_0 n}\right)^3}\, e^{-\frac{r}{a_0 n}}\left(\frac{2r}{a_0 n}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{a_0 n}\right) \quad [\text{For Hydrogen atom } Z = 1]$$

$$\ldots (3.45)$$

Thus the final solution for the hydrogen atom wave function is given by:

$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$ ……… (3.46)

With

$$R_{nl}(r) = -2\left(\frac{1}{na_0}\right)^{\frac{3}{2}}\sqrt{\frac{(n-l-1)!}{n[(n+l)!]^3}}\left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$Y_{lm}(\theta,\varphi) = \epsilon\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\varphi}$$

$With\ n = 1,2,\dots\dots;\ \ l = 0,1,2,\dots\dots(n-1);\ \ m = 0,\pm1,\dots\dots\pm l.$

$And\ \epsilon = (-1)^m$ for $m \geq 0$ & $\epsilon = 1$ for $m \leq 0$

$$a_0 = \frac{4\pi\hbar^2\epsilon_0}{\mu e^2}$$

P_l^m = associated Legendre polynomials and L_{n+l}^{2l+1} = associated Laguerre polynomials.

*Note that there are another convention of writing the associated Laguerre differential equation. In this convention this equation is given by [See Boas and Arfken]:

$$x\frac{d^2L_n^k(x)}{dx^2} + (k+1-x)\frac{dL_n^k(x)}{dx} + nL_n^k(x) = 0 \quad \dots\dots\dots\dots\dots\dots\dots (A)$$

In this convention associated Laguerre polynomials $L_n^k(x)$ are given by (see Arfken) Rodrigues formula as:

$$\boldsymbol{L_n^k(x) = (-1)^k\left(\frac{d}{dx}\right)^k L_{n+k}(x) = \frac{e^{-x}x^k}{n!}\left(\frac{d}{dx}\right)^n\left(e^{-x}x^{n+k}\right)} \quad \dots\dots\dots\dots\dots\dots (\mathbf{B})$$

Where $L_m(x)$ are Laguerre polynomials and in this convention are given by:

$$\boldsymbol{L_m(x) = \frac{e^x}{m!}\left(\frac{d}{dx}\right)^m\left(x^m e^{-x}\right)} \quad \dots\dots\dots\dots\dots\dots (\mathbf{C})$$

Laguerre polynomials $L_m(x)$ satisfy Laguerre differential equation:

$$x\frac{d^2L_m(x)}{dx^2} + (1-x)\frac{dL_m(x)}{dx} + mL_m(x) = 0 \quad \dots\dots\dots\dots\dots\dots\dots. (D)$$

First few radial wave functions:

Let we want to find the expressions of first few radial wave functions namely $R_{nl} = R_{10},\ R_{20}$ and R_{21}. Then required values of n & l are 1,0; 2,0 and 2,1. Therefore the values of p and q will be:

$n = 1, l = 0 \Rightarrow \qquad p = 2l + 1 = 1, \qquad q = n + l = 1$

$n = 2, l = 0 \Rightarrow \qquad p = 2l + 1 = 1, \qquad q = n + l = 2$

$n = 2, l = 1 \Rightarrow \qquad p = 2l + 1 = 3, \qquad q = n + l = 3$

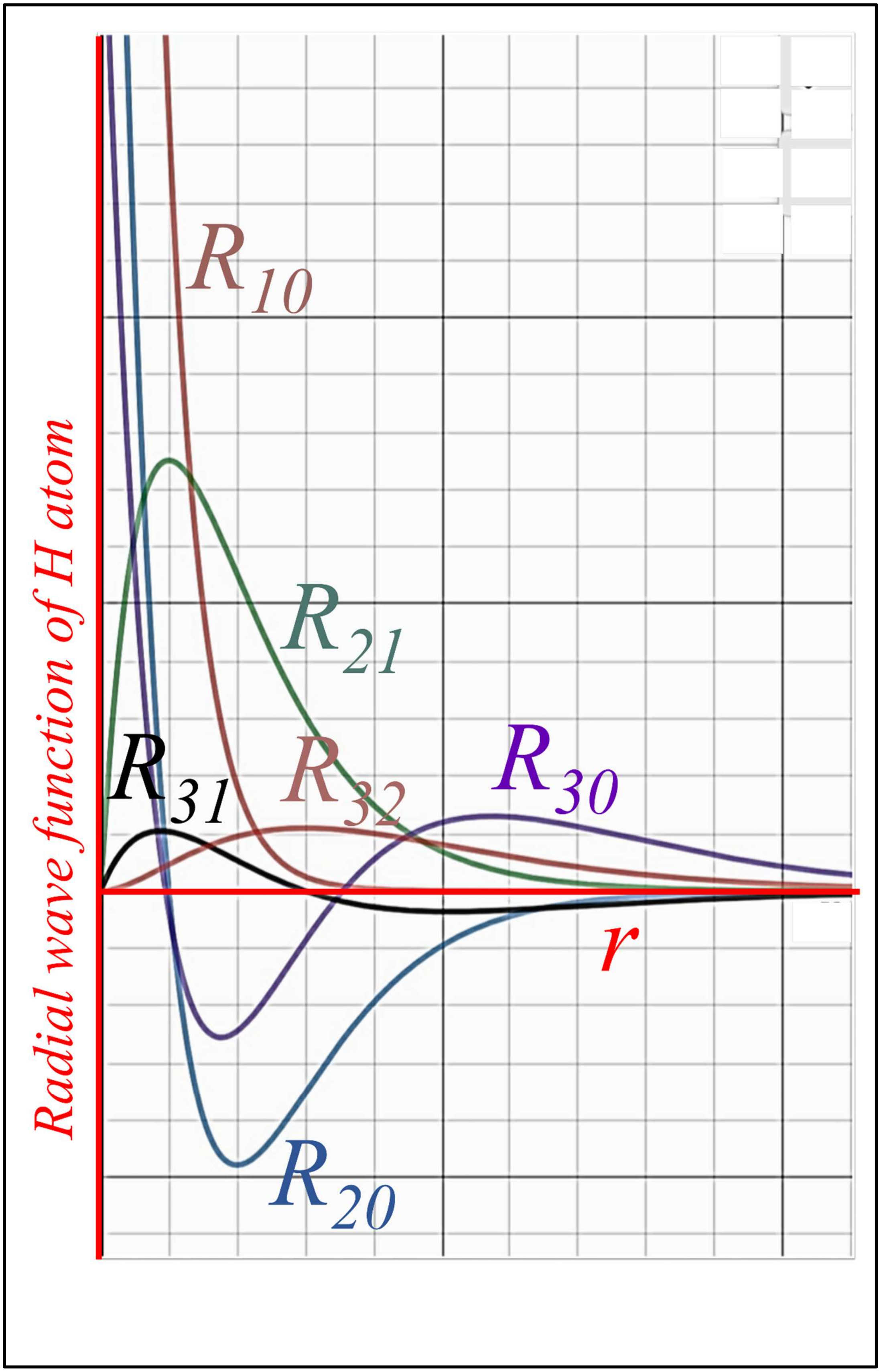
Then the required associated Laguerre polynomials required in Hydrogen Atom problem are $L_q^p(x) = L_1^1(x), L_2^1(x)$ and $L_3^3(x)$ and the required Laguerre polynomials $L_q(x) = L_1(x), L_2(x)$ and $L_3(x)$.

Table-3.3

$\boldsymbol{L_1(x), L_2(x), L_3(x);\ L_1^1(x), L_2^1(x), L_3^3(x)}$	
$L_q(x) = e^x \left(\frac{d}{dx}\right)^q (x^q e^{-x})$	$L_q^p(x) = \left(\frac{d}{dx}\right)^p L_q(x)$
$n = 1, l = 0;\ p = 2l + 1 = 1, q = n + l = 1$	
$\boldsymbol{L_1(x)} = e^x \left(\frac{d}{dx}\right)^1 (x^1 e^{-x}) = e^x(1 - x)e^{-x}$ $\boldsymbol{L_1(x) = 1 - x}$	$\boldsymbol{L_1^1(x)} = \left(\frac{d}{dx}\right)^1 L_1(x) = \frac{d}{dx}(1 - x)$ $\boldsymbol{L_1^1(x) = -1}$
$n = 2, l = 0; p = 1, q = 2$	
$\boldsymbol{L_2(x)} = e^x \left(\frac{d}{dx}\right)^2 (x^2 e^{-x}) \ = e^x \frac{d}{dx}[(2x - x^2)e^{-x}]$ $= e^x[(2 - 2x)e^{-x} - (2x - x^2)e^{-x}]$ $= 2 - 2x - 2x + x^2$ $\boldsymbol{L_2(x) = 2 - 4x + x^2}$	$\boldsymbol{L_2^1(x)} = \left(\frac{d}{dx}\right)^1 L_2(x)$ $= \frac{d}{dx}(2 - 4x + x^2)$ $\boldsymbol{L_2^1(x) = -4 + 2x}$
$n = 2, l = 1; p = 2l + 1 = 3, q = n + l = 3$	
$\boldsymbol{L_3(x)} = e^x \left(\frac{d}{dx}\right)^3 (x^3 e^{-x}) = e^x \left(\frac{d}{dx}\right)^2 [(3x^2 - x^3)e^{-x}]$ $= e^x \frac{d}{dx}[(6x - 3x^2)e^{-x} - (3x^2 - x^3)e^{-x}]$ $= e^x \frac{d}{dx}[(6x - 6x^2 + x^3)e^{-x}]$ $= e^x[(6 - 12x + 3x^2)e^{-x} - (6x - 6x^2 + x^3)e^{-x}]$ $\Rightarrow \boldsymbol{L_3(x) = 6 - 18x + 9x^2 - x^3}$	$\boldsymbol{L_3^3(x)} = \left(\frac{d}{dx}\right)^3 L_3(x)$ $= \left(\frac{d}{dx}\right)^3 (6 - 18x + 9x^2 - x^3)$ $\boldsymbol{= -6}$ $\Rightarrow \boldsymbol{L_3^3(x) = -6}$

Table-3.4

$\boldsymbol{R_{10}},\ \boldsymbol{R_{20}}$ **and** $\boldsymbol{R_{21}}$	
$L_q^p(x) = \left(\frac{d}{dx}\right)^p L_q(x)$	$R_{nl} = -2\left(\frac{1}{na_0}\right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{n[(n+l)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$
$\boldsymbol{n = 1, l = 0;\ p = 2l + 1 = 1, q = n + l = 1}$	
$\boldsymbol{L_1^1(x) = -1}$	$\boldsymbol{R_{nl} = R_{10}} = -2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} \sqrt{\frac{(1-0-1)!}{1 \times [(1+0)!]^3}} \left(\frac{2r}{a_0}\right)^0 e^{-\frac{r}{a_0}} L_1^1\left(\frac{2r}{a_0}\right)$ $= -2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} (-1)$ $\boldsymbol{R_{10}} = 2\left(\frac{\boldsymbol{1}}{\boldsymbol{a_0}}\right)^{\boldsymbol{3/2}} \boldsymbol{exp}\left(-\frac{\boldsymbol{r}}{\boldsymbol{a_0}}\right)$
$\boldsymbol{n = 2, l = 0; p = 2l + 1 = 1, q = n + l = 2}$	
$\boldsymbol{L_2^1(x) = -4 + 2x}$	$\boldsymbol{R_{nl} = R_{20}}$ $= -2\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \sqrt{\frac{(2-0-1)!}{2 \times [(2+0)!]^3}} \left(\frac{2r}{2a_0}\right)^0 e^{-\frac{r}{2a_0}} L_2^1\left(\frac{2r}{2a_0}\right)$ $= -2\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \sqrt{\frac{1}{2^4}}\ e^{-\frac{r}{2a_0}} L_2^1\left(\frac{r}{a_0}\right) = -2\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \frac{1}{4} e^{-\frac{r}{2a_0}} \left(-4 + \frac{2r}{a_0}\right)$ $\boldsymbol{R_{20} = 2\left(\frac{1}{2a_0}\right)^{3/2} \left(1 - \frac{r}{2a_0}\right) exp\left(-\frac{r}{2a_0}\right)}$
$\boldsymbol{n = 2, l = 1; p = 2l + 1 = 3, q = n + l = 3}$	
$\boldsymbol{L_3^3(x) = -6}$	$\boldsymbol{R_{nl} = R_{21}}$ $= -2\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \sqrt{\frac{(2-1-1)!}{2[(2+1)!]^3}} \left(\frac{2r}{2a_0}\right)^1 e^{-\frac{r}{2a_0}} L_3^3\left(\frac{2r}{2a_0}\right)$ $= -2\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \frac{1}{\sqrt{2 \times 6^3}} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \times (-6)$ $\boldsymbol{R_{21} = \frac{2}{\sqrt{3}} \left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{r}{2a_0}\right) exp\left(-\frac{r}{2a_0}\right)}$
Similarly we can show: $\boldsymbol{R_{30} = 2\left(\frac{1}{3a_0}\right)^{3/2} \left[1 - 2\frac{r}{3a_0} + \frac{2}{3}\left(\frac{r}{3a_0}\right)^2\right] e^{-\frac{r}{3a_0}}}$; $\boldsymbol{R_{31} = \frac{8}{3\sqrt{2}} \left(\frac{1}{3a_0}\right)^{3/2} \left(1 - \frac{1}{2}\frac{r}{3a_0}\right) \left(\frac{r}{3a_0}\right) e^{-\frac{r}{3a_0}}}$; $\boldsymbol{R_{32} = \frac{4}{3\sqrt{10}} \left(\frac{1}{3a_0}\right)^{3/2} \left(\frac{r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}}$ ………	



https://www.desmos.com/calculator/uwv75iytfu

Fig. 3.1 Plot of first few radial wave functions of hydrogen atom

The time independent part of hydrogen atom wave function i.e. the solution of the time independent Schrodinger equation for hydrogen atom is given by:

$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$ ... ... (3.46)

With symbols having usual meaning.

The probability of finding the electron in a volume element

$d\tau = dr\, rd\theta\, r\sin\theta\;\, d\varphi = r^2 dr \sin\theta\, d\theta d\varphi$

is given by:

$\rho d\tau = |\psi_{nlm}|^2 d\tau = |R_{nl}(r)|^2 |Y_{lm}(\theta,\varphi)|^2 r^2 dr \sin\theta\, d\theta d\varphi$

$= |R_{nl}(r)|^2 r^2 dr |Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi$

The probability of finding the electron in a spherical shell between radii r and $r + dr$ is given by:

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |R_{nl}(r)|^2 |Y_{lm}(\theta,\varphi)|^2 r^2 dr \sin\theta\, d\theta d\varphi$$

$$= |R_{nl}(r)|^2 r^2 dr \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi$$

$$= |R_{nl}(r)|^2 r^2 dr \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi$$

But $Y_{lm}(\theta,\varphi)$ are normalised in the limit $\theta = 0$ to π and $\varphi = 0$ to 2π. Therefore

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi = 1$$

Thus:

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |R_{nl}(r)|^2 |Y_{lm}(\theta,\varphi)|^2 r^2 dr \sin\theta\, d\theta d\varphi = |R_{nl}(r)|^2 r^2 dr \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi$$

$= |R_{nl}(r)|^2 r^2 dr$

$= D_{nl}(r) dr$

Where $D_{nl}(r) = |R_{nl}(r)|^2 r^2$ ……… (3.47) is called the radial probability density.

Expressions of radial probability densities $D_{nl}(r)$ for small values of n *and* l

To see the plots of D_{nl} browse https://www.desmos.com/calculator/hd85wvs3me

For D_{10}, D_{20}, D_{30} browse https://www.desmos.com/calculator/z5j8sa5krc

For D_{21}, D_{31} browse https://www.desmos.com/calculator/nans2odf1e

For D_{32} browse https://www.desmos.com/calculator/ee3daxe6ht

Table-3.5

n,l	R_{nl}	$D_{nl}(r)=\|R_{nl}(r)\|^2r^2$ For $a_0=1$
1,0	$R_{10}=2\left(\frac{1}{a_0}\right)^{3/2}e^{-\frac{r}{a_0}}$	$D_{10}(r)=\|R_{10}(r)\|^2r^2=4\left(\frac{1}{a_0}\right)^3r^2e^{-\frac{2r}{a_0}}$ $=4r^2exp(-2r)$
2,0	$R_{20}=2\left(\frac{1}{2a_0}\right)^{3/2}\left(1-\frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}$	$D_{20}(r)=\|R_{20}(r)\|^2r^2$ $=\frac{1}{2}\left(1-\frac{r}{2}\right)^2r^2exp(-r)$
2,1	$R_{21}=\frac{2}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}$	$D_{21}(r)=\|R_{21}(r)\|^2r^2$ $=\frac{4}{3}\left(\frac{1}{2a_0}\right)^3\left(\frac{r}{2a_0}\right)^2r^2e^{-\frac{r}{a_0}}=\frac{1}{24}r^4exp(-r)$
3,0	R_{30} $=2\left(\frac{1}{3a_0}\right)^{\frac{3}{2}}\left[1-2\frac{r}{3a_0}+\frac{2}{3}\left(\frac{r}{3a_0}\right)^2\right]e^{-\frac{r}{3a_0}}$	$D_{30}(r)=\|R_{30}(r)\|^2r^2$ $=\frac{4}{27}\left(1-\frac{2r}{3}+\frac{2r^2}{27}\right)^2r^2\exp\left(-\frac{2r}{3}\right)$
3,1	R_{31} $=\frac{8}{3\sqrt{2}}\left(\frac{1}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{1}{2}\frac{r}{3a_0}\right)\left(\frac{r}{3a_0}\right)e^{-\frac{r}{3a_0}}$	$D_{31}(r)=\|R_{31}(r)\|^2r^2$ $=\frac{32}{2187}\left(1-\frac{r}{6}\right)^2r^4\exp\left(-\frac{2r}{3}\right)$
3,2	$R_{32}=\frac{4}{3\sqrt{10}}\left(\frac{1}{3a_0}\right)^{3/2}\left(\frac{r}{3a_0}\right)^2e^{-\frac{r}{3a_0}}$	$D_{32}(r)=\|R_{32}(r)\|^2r^2=\frac{8}{45}\left(\frac{1}{3a_0}\right)^3\left(\frac{r}{3a_0}\right)^4r^2e^{-\frac{2r}{3a_0}}$ $=\left(\frac{8}{98415}\right)r^6\exp\left(-\frac{2r}{3}\right)$

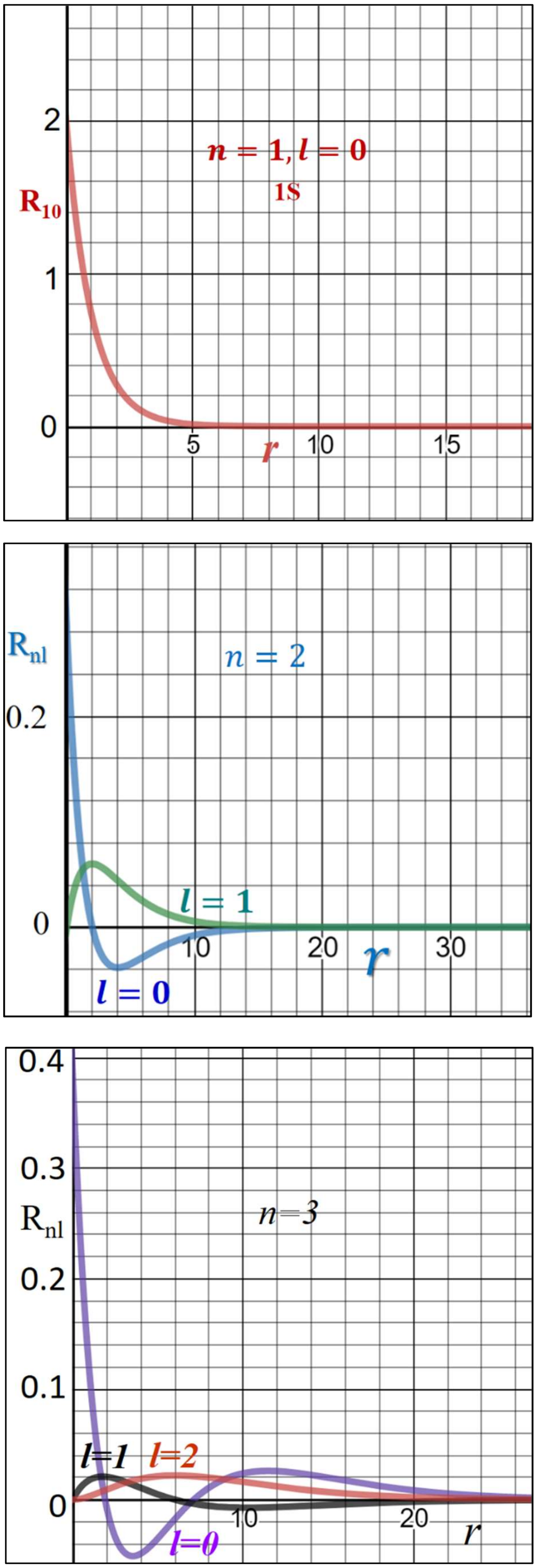


Fig. 3.2A First few radial wave functions of Hydrogen atom With $a_0 = 1$

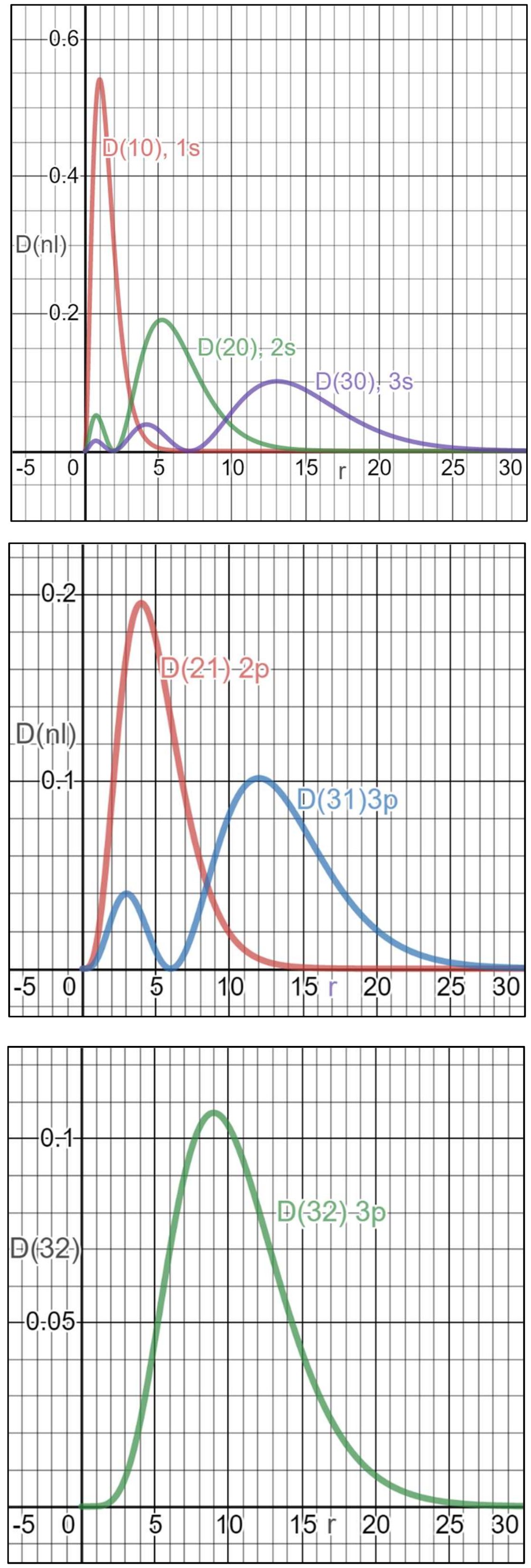


Fig. 3.2B Radial probability densities of Hydrogen atom for small n & l. With $a_0 = 1$

Problems

P.3.1 Prove that the radial probability density for the hydrogen atom on 1s state is maximum at $\boldsymbol{r = the\ Bohr\ radius}$. [S. N. Ghoshal, 2nd Ed. Chapter VII, Page-286].

Ans. Radial probability density of $1s$ state ($n = 1, l = 0$):

$$D_{nl} = D_{10} = |R_{10}|^2 r^2 = \left|2\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}\right|^2 r^2 = 4\left(\frac{1}{a_0}\right)^3 r^2 e^{-\frac{2r}{a_0}}$$

For D_{10} to be maximum:

$$\frac{d(D_{10})}{dr} = 0$$

$$\Rightarrow \frac{d(D_{10})}{dr} = 4\left(\frac{1}{a_0}\right)^3\left(2re^{-\frac{2r}{a_0}} - \frac{2r^2}{a_0}e^{-\frac{2r}{a_0}}\right) = 4\left(\frac{1}{a_0}\right)^3\left(1 - \frac{r}{a_0}\right)2re^{-\frac{2r}{a_0}} = 0$$

$\Rightarrow r = a_0$.

Hence the proof.

P.3.2 Calculate $\boldsymbol{< r >}$, for the hydrogen atom on 1s state. [S. N. Ghoshal, 2nd Ed. Chapter VII, Page-286].

$$< \boldsymbol{r} > = \int \psi_{nlm}{}^*(r, \theta, \varphi) r \psi_{nlm}(r, \theta, \varphi)\, d\tau$$

$$= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} [R_{nl}(r)]^* \ [Y_{lm}(\theta,\varphi)]^* \ rR_{nl}(r)Y_{lm}(\theta,\varphi)r^2 dr \sin\theta\, d\theta d\varphi$$

$$= \int_{r=0}^{\infty} |R_{nl}(r)|^2 r^3 dr \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi$$

$$= \int_{r=0}^{\infty} |R_{nl}(r)|^2 r^3 dr$$

$$= \int_{r=0}^{\infty} D_{nl}\, r\, dr$$

[Since $Y_{lm}(\theta,\varphi)$ are normalised within $\theta = 0$ to π and $\varphi = 0$ to 2π, therefore $\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}|Y_{lm}(\theta,\varphi)|^2 \sin\theta\, d\theta d\varphi = 1$]

In $1s$ state $(n = 1, l = 0)$ of Hydrogen atom,

$$< \boldsymbol{r} > = \int_{\boldsymbol{r=0}}^{\infty} D_{nl}\, r\, dr = 4\left(\frac{1}{a_0}\right)^3 \int_0^{\infty} r^3 e^{-\frac{2r}{a_0}} dr$$

$$= 4\left(\frac{1}{a_0}\right)^3 \left(\frac{a_0}{2}\right)^4 \int_0^{\infty} \left(\frac{2r}{a_0}\right)^3 e^{-\frac{2r}{a_0}} d\left(\frac{2r}{a_0}\right)$$

$$= \frac{a_0}{4}\int_0^{\infty} x^3 e^{-x} dx$$

$$= \frac{a_0}{4} 3!$$

$$= \frac{3}{2}a_0$$

P.3.2 Calculate the expectation values of potential energy and kinetic energy for the hydrogen atom on 1s state is maximum. [S. N. Ghoshal, 2nd Ed. Chapter VII, Page-286-287].

Ans.: Expectation values of potential energy:

$$< \boldsymbol{V} > = \int \psi_{nlm}{}^{*}(r,\theta,\varphi) V(r) \psi_{nlm}(r,\theta,\varphi)\, d\tau$$

$$= -\frac{e^2}{4\pi\epsilon_0}\int \psi_{nlm}{}^{*}(r,\theta,\varphi)\frac{1}{r}\psi_{nlm}(r,\theta,\varphi)\, d\tau$$

$$= -\frac{e^2}{4\pi\epsilon_0}\int_{\boldsymbol{r=0}}^{\infty} |R_{nl}(r)|^2 r^2 \frac{1}{r} dr$$

$$= -\frac{e^2}{4\pi\epsilon_0}\int_{\boldsymbol{r=0}}^{\infty} D_{nl}\, \frac{1}{r}\, dr$$

In $1s$ state $(n = 1, l = 0)$ of hydrogen atom,

$$< \boldsymbol{V} > = -\frac{e^2}{4\pi\epsilon_0} 4\left(\frac{1}{a_0}\right)^3 \int_0^{\infty} r e^{-\frac{2r}{a_0}} dr$$

$$= -\frac{e^2}{4\pi\epsilon_0} 4\left(\frac{1}{a_0}\right)^3 \left(\frac{a_0}{2}\right)^2 \int_0^{\infty} \left(\frac{2r}{a_0}\right) e^{-\frac{2r}{a_0}} d\left(\frac{2r}{a_0}\right)$$

$$= -\frac{e^2}{4\pi\epsilon_0 a_0}\int_0^{\infty} xe^{-x}dx$$

$$= -\frac{e^2}{4\pi\epsilon_0 a_0}.$$

Expectation values of kinetic energy:

$$< T > = \int \psi_{nlm}^*(r,\theta,\varphi)\hat{T}\psi_{nlm}(r,\theta,\varphi)\, d\tau$$

$$= -\frac{\hbar^2}{2\mu}\int \psi_{nlm}^*(r,\theta,\varphi)[\nabla^2\psi_{nlm}(r,\theta,\varphi)]\, d\tau$$

In $1s$ state ($n = 1, l = 0$) of hydrogen atom,

$$< T > = -\frac{\hbar^2}{2\mu}\int \psi_{100}^*(r,\theta,\varphi)[\nabla^2\psi_{100}(r,\theta,\varphi)]\, d\tau$$

$$= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} \psi_{100}^*(r,\theta,\varphi)\ \ [\nabla^2\psi_{100}(r,\theta,\varphi)]\, r^2dr\sin\theta\, d\theta d\varphi$$

$$\psi_{100}(r,\theta,\varphi) = R_{10}(r)Y_{00}(\theta,\varphi) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}\frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}$$

$$< T > = -\frac{\hbar^2}{2\mu}\frac{1}{\pi}\frac{1}{{a_0}^3}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} e^{-\frac{r}{a_0}}\left[\nabla^2 e^{-\frac{r}{a_0}}\right] r^2dr\sin\theta\, d\theta d\varphi$$

$$= -\frac{\hbar^2}{2\mu}\frac{1}{\pi}\frac{1}{{a_0}^3}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} e^{-\frac{r}{a_0}}\left[\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)e^{-\frac{r}{a_0}}\right] r^2dr\sin\theta\, d\theta d\varphi$$

$$= -\frac{\hbar^2}{2\mu}\frac{1}{\pi}\frac{1}{{a_0}^3}\int_{r=0}^{\infty} e^{-\frac{r}{a_0}}\left[\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)e^{-\frac{r}{a_0}}\right] r^2dr\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\sin\theta\, d\theta d\varphi$$

$$= -\frac{\hbar^2}{2\mu}\frac{1}{\pi}\frac{1}{{a_0}^3}\int_{r=0}^{\infty} e^{-\frac{r}{a_0}}\left[\left(\frac{1}{{a_0}^2}-\frac{2}{r}\frac{1}{a_0}\right)e^{-\frac{r}{a_0}}\right] r^2dr\ 4\pi$$

$$= -\frac{\hbar^2}{2\mu}\frac{4}{{a_0}^3}\int_{r=0}^{\infty} e^{-\frac{2r}{a_0}}\left(\frac{r^2}{{a_0}^2}-\frac{2r}{a_0}\right) dr$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{4}{{a_0}^5}\left(\frac{a_0}{2}\right)^3 \int_{r=0}^{\infty} \left(\frac{2r}{a_0}\right)^2 e^{-\frac{2r}{a_0}}\ d\left(\frac{2r}{a_0}\right) - \frac{8}{{a_0}^4}\left(\frac{a_0}{2}\right)^2 \int_{r=0}^{\infty} \left(\frac{2r}{a_0}\right) e^{-\frac{2r}{a_0}}\ d\left(\frac{2r}{a_0}\right)\right]$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{2{a_0}^2} \int_{x=0}^{\infty} x^2 e^{-x}\ dx - \frac{2}{{a_0}^2} \int_{x=0}^{\infty} x e^{-x}\ dx\right]$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{2{a_0}^2} 2! - \frac{2}{{a_0}^2}\right]$$

$$= \frac{\hbar^2}{2\mu {a_0}^2}$$

$$= \frac{\hbar^2}{2\mu}\left(\frac{\mu e^2}{4\pi\hbar^2\epsilon_0}\right)^2$$

$$= \frac{\mu e^4}{32\pi^2\hbar^2{\epsilon_0}^2}.$$

Special Page

Significance of the term $\frac{l(l+1)}{r^2}$:

Let us rewrite the above equation as: $\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+[E-V(r)]R(r)-\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}R(r)=0$

Or, $\quad ER(r)=-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}R(r)+V(r)R(r)$

Or, $\quad ER(r)=\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V(r)\right]R(r)$

Now $\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}=\frac{l(l+1)\hbar^2}{2mr^2}=\frac{L^2}{2mr^2}$, where $L=\sqrt{l(l+1)}\,\hbar$ is the quantum mechanical expression of orbital angular momentum of the electron in which l are called orbital angular momentum quantum number.

Therefore $\quad ER(r)=\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{L^2}{2mr^2}+V(r)\right]R(r)$

Or, $\hat{E}\equiv H\equiv-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{L^2}{2mr^2}+V(r)$ ……………….. (A)

Now, $-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$ is the radial part of $\frac{\left(-i\hbar\vec{\nabla}\right)^2}{2m}=\frac{\vec{p}^{\,2}}{2m}=T=K.E.\,of\ the\ particle.$

Thus $-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$ is the kinetic energy of the electron for its motion in radial coordinate r.

Hydrogen atom problem is a central force problem since the electron moves under the central Coulomb potential of the nucleus.

Thus $-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$ is the kinetic energy of the particle due to radial motion of the particle.

Now remember the central force problem of classical mechanics. The total energy of the particle moving under central force is given by:

$E=\frac{1}{2}m\left(\dot{r}^2+r^2\dot{\theta}^2\right)+V(r)=\frac{1}{2}m\dot{r}^2+\frac{1}{2}mr^2\left(\frac{L}{mr^2}\right)^2+V(r)$

[Remember, in central force problem of classical mechanics, $\dot{\theta}=\frac{L}{mr^2}$]

Or, $E=\frac{1}{2}m\dot{r}^2+\frac{L^2}{2mr^2}+V(r)=\frac{1}{2}m\dot{r}^2+\left[\frac{L^2}{2mr^2}+V(r)\right]$ …………….(B)

In writing the energy equation in the style (like Eqn. (B)) $\frac{L^2}{2mr^2}$ is termed as 'potential' energy arising out due to the angular momentum of the particle. This is also called the centrifugal potential since the centrifugal force on the particle moving under central force can be derived from it.

Comparing (A) and (B) we can say that the term $\frac{l(l+1)}{r^2}$ in the radial equation of hydrogen atom problem is related to the orbital angular momentum of the electron.