❖ Schrodinger Wave Equation for Hydrogen Atom: Separation of Variable in Polar Spherical Coordinates and Its Solution

In the first section of this chapter, we derived and discussed the Schrodinger wave equation for a particle in a three-dimensional box. In this section, we will apply the procedure to an electron that exits around the nucleus. In order to do so, consider an electron at a distance *r* from the center of the nucleus, and this electron can travel in any direction i.e. along *x-, y- and z*-axis. The potential energy of such an electron-nucleus system will be $-Ze^2/r$; where Ze and e are charges on nucleus and electron respectively.

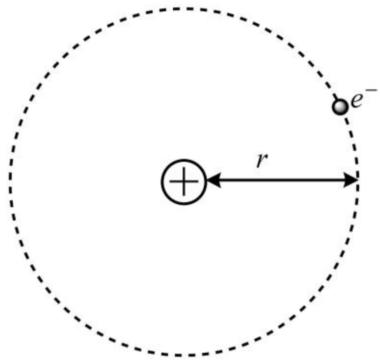

Figure 12. An electron around nucleus at *r* distance.

So far we have considered a quantum mechanical system of an electron around the nucleus. Now suppose that we need to find various physical properties associated with different states of this system. Had it been a classical system, we would use simple formulas from classical mechanics to determine the value of different physical properties. However, being a quantum mechanical system, we cannot use those expressions because they would give irrational results. Therefore, we need to use the postulates of quantum mechanics to evaluate various physical properties.

Let ψ be the function that describes all the states of the electron around the nucleus. At this point we have no information about the exact mathematical expression of ψ; nevertheless, we know that there is one operator that does not need the absolute expression of wave function but uses the symbolic form only, the Hamiltonian operator. The operation of Hamiltonian operator over this symbolic form can be rearranged to give to construct the Schrodinger wave equation; and we all know that the wave function as well the energy, both are the obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\hat{H}\psi = E\psi \tag{246}$$

After putting the value of three-dimensional Hamiltonian in equation (1), we get

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right]\psi = E\psi \tag{247}$$

or

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi=E\psi \tag{248}$$

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi-E\psi=0 \tag{249}$$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \tag{250}$$

After putting the value of potential energy of the electron-nucleus system in equation (250), we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi=0 \tag{251}$$

The above-mentioned second order differential equation is the Schrodinger wave equation for an electron around the nucleus. However, since it is neither completely in cartesian nor completely in polar coordinates (contains x, y, z as well as r variable), the solution is very much difficult. Therefore, recall the transformation of cartesian coordinates to polar coordinates in three dimensions as given below.

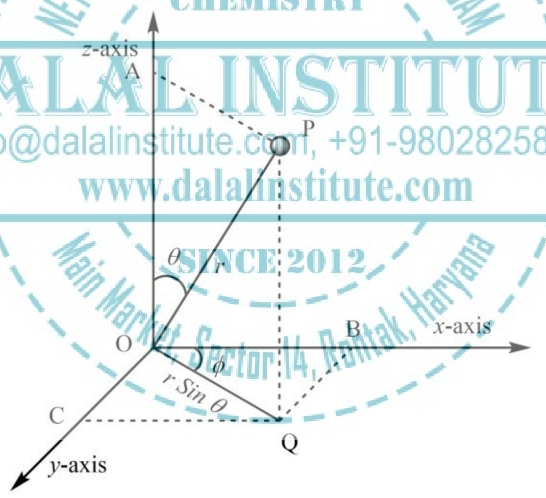

Figure 13. Correlation between cartesian and polar coordinates in three dimensions.

In tringle AOP, the side OA is simply the z-coordinate and can be obtained as

$$\frac{OA}{OP}=Cos\,\theta \quad\Rightarrow\quad OA=OP\,Cos\,\theta \quad\Rightarrow\quad z=r\,Cos\,\theta \tag{252}$$

Similarly, in AOP

$$\frac{AP}{OP}=Sin\,\theta \quad\Rightarrow\quad AP=OP\,Sin\,\theta \quad\Rightarrow\quad OQ=r\,Sin\,\theta \tag{253}$$

In tringle BOQ, the side OB is simply the x-coordinate and can be obtained as

$$\frac{OB}{OQ} = Cos\ \phi \quad \Rightarrow \quad OB = OQ\ Cos\ \phi \quad \Rightarrow \quad x = r\ Sin\ \theta\ Cos\ \phi \tag{254}$$

Since the side BQ equal to OC, BQ also represents the y-coordinate and can be obtained as

$$\frac{BQ}{OQ} = Sin\ \phi \quad \Rightarrow \quad BQ = OQ\ Sin\ \phi \quad \Rightarrow \quad y = r\ Sin\ \theta\ Sin\ \phi \tag{255}$$

Now using equation (252-254), the equation (251) can be transformed to polar coordinates as given below.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\ Sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \tag{256}$$

or

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \tag{257}$$

Which is the Schrodinger wave equation for hydrogen and hydrogen-like species in polar coordinates.

➢ ***Separation of Variables***

The wave function representing quantum mechanical states, in this case, is actually a function of three variable r, θ and ϕ. Now, we know that it is easier to solve three differential equations with one variable in each rather a single differential equation with three variables. Therefore, in order to separate variables, consider that the wave function ψ is the multiplication of three individual functions as

$$\psi(r,\theta,\phi) = \psi(r) \times \psi(\theta) \times \psi(\phi) = R.\Theta.\Phi \tag{258}$$

After putting the value of equation (258) in equation (257) and then multiplying throughout by r^2, we get

$$\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\Phi R}{Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{R\Theta}{Sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} + \frac{8\pi^2\mu r^2}{h^2}\left(E + \frac{Ze^2}{r}\right)\Theta\Phi R = 0 \tag{259}$$

Furthermore, divide equation (259) throughout $\Theta\Phi R$ i.e.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta}\frac{1}{Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{Sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} + \frac{8\pi^2\mu r^2}{h^2}\left(E + \frac{Ze^2}{r}\right) = 0 \tag{260}$$

or

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2\mu r^2}{h^2}\left(E + \frac{Ze^2}{r}\right) = -\frac{1}{\Theta}\frac{1}{Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{1}{\Phi}\frac{1}{Sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} \tag{261}$$

The above equation holds true if we put both sides equal to a constant β i.e.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=\beta \tag{262}$$

and

$$\frac{1}{\Theta}\frac{1}{Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{Sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=-\beta \tag{263}$$

The equation (262) contains only r variable, and therefore, is called as the "radial equation". However, the equation (263) still contains two variable, and thus, needs further separation. To do so, first multiply equation (263) throughout by $Sin^2\theta$ i.e.

$$\frac{Sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-\beta\, Sin^2\theta \tag{264}$$

or

$$\frac{Sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\, Sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \tag{265}$$

The above equation also holds true if we put both sides equal to a constant m^2 i.e.

$$\frac{Sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\, Sin^2\theta=m^2 \tag{266}$$

and

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2 \tag{267}$$

The equation (266) contains only θ variable, and therefore, is called as "theta equation". Likewise, the equation (267) contains only ϕ variable, and therefore, is called as "phi equation".

➢ ***Solutions of R(r), Θ(θ) and Φ(ϕ) Equations***

The single variable equations obtained after separation of variables can be solved separately to yield r, θ and ϕ-dependent functions which then are multiplied give total wave function.

1. The solution of Φ(ϕ) equation: Recall and rearrange the differential equation obtained after separation of variables having ϕ dependence i.e.

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2 \qquad\Rightarrow\qquad \frac{\partial\Phi}{\partial\phi}+m^2\Phi=0 \tag{268}$$

The general solution of such an equation is

$$\Phi(\phi)=Ne^{im\phi} \tag{269}$$

Where N represents the normalization constant. The wavefunction given above will be acceptable only if m has integer value i.e. $0, \pm 1, \pm 2,$ etc. This can be understood in terms of single-valued, continuous and finite nature of quantum states.

i) The boundary condition for function Φ: If we replace the angle "ϕ" with "$\phi + 2\pi$", the position of point under consideration should remain the same i.e.

$$\Phi(\phi + 2\pi) = \Phi(\phi) \tag{270}$$

Therefore

$$Ne^{im(\phi+2\pi)} = Ne^{im\phi} \tag{271}$$

$$e^{im(\phi+2\pi)} = e^{im\phi} \tag{272}$$

$$e^{im\phi}.e^{im2\pi} = e^{im\phi} \tag{273}$$

$$e^{im2\pi} = e^{im\phi}e^{-im\phi} \tag{274}$$

$$e^{im2\pi} = e^{im\phi-im\phi} = e^{0} \tag{275}$$

$$e^{im2\pi} = 1 \tag{276}$$

Since we know from the Euler's expansion $e^{ix} = Cos\ x + i\ Sin\ x$, the equation (276) takes the form

$$e^{im2\pi} = Cos\ 2\pi m + i\ Sin\ 2\pi m \tag{277}$$

After putting the value of equation (277) in equation (276), we get

$$Cos\ 2\pi m + i\ Sin\ 2\pi m = 1 \tag{278}$$

The relation holds true only when we use $m = 0, \pm 1, \pm 2, \pm 3, \pm 4,$ etc.

ii) The normalization constant for function Φ: In order to determine the normalization constant for the Φ function, we must put the squared-integral over whole configuration space as unity i.e.

$$\int_0^{2\pi} \Phi^*\Phi\, d\phi = 1 \tag{279}$$

$$N^2\int_0^{2\pi} e^{im\phi}.e^{-im\phi}\, d\phi = 1 \tag{280}$$

$$N^2\int_0^{2\pi} e^{im\phi-im\phi}\, d\phi = N^2\int_0^{2\pi} e^{0}\, d\phi = 1 \tag{281}$$

$$N^2[\phi]_0^{2\pi} = N^2[2\pi] = 1 \tag{282}$$

or

$$N = \sqrt{\frac{1}{2\pi}} \tag{283}$$

After using the value of normalization constant in equation (269), we get

$$\Phi_m(\phi) = \sqrt{\frac{1}{2\pi}} e^{im\phi} \tag{284}$$

Which is the complete solution of ϕ-equation.

Table 1. Complex and real forms of some normalized Φ-functions.

$\lvert m \rvert$	Complex form	Real form
0	$\Phi_0(\phi) = \sqrt{\frac{1}{2\pi}}$	$\Phi_0(\phi) = \sqrt{\frac{1}{2\pi}}$
1	$\Phi_{+1}(\phi) = \sqrt{\frac{1}{2\pi}} e^{i\phi}$	$\Phi_{+1}(\phi) = \sqrt{\frac{1}{\pi}} Cos\ \phi$
	$\Phi_{-1}(\phi) = \sqrt{\frac{1}{2\pi}} e^{-i\phi}$	$\Phi_{-1}(\phi) = \sqrt{\frac{1}{\pi}} Sin\ \phi$
2	$\Phi_{+2}(\phi) = \sqrt{\frac{1}{2\pi}} e^{i2\phi}$	$\Phi_{+2}(\phi) = \sqrt{\frac{1}{\pi}} Cos\ (2\phi)$
	$\Phi_{-2}(\phi) = \sqrt{\frac{1}{2\pi}} e^{-i2\phi}$	$\Phi_{-2}(\phi) = \sqrt{\frac{1}{\pi}} Sin\ (2\phi)$
3	$\Phi_{+3}(\phi) = \sqrt{\frac{1}{2\pi}} e^{i3\phi}$	$\Phi_{+3}(\phi) = \sqrt{\frac{1}{\pi}} Cos\ (3\phi)$
	$\Phi_{-3}(\phi) = \sqrt{\frac{1}{2\pi}} e^{-i3\phi}$	$\Phi_{-3}(\phi) = \sqrt{\frac{1}{\pi}} Sin\ (3\phi)$

2. The solution of Θ(θ) equation: Recall and rearrange the differential equation obtained after separation of variables having θ-dependence i.e.

$$\frac{Sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\ Sin^2\theta=m^2 \tag{285}$$

or

$$Sin\ \theta\frac{\partial}{\partial\theta}\left(Sin\ \theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\beta Sin^2\theta-m^2\Theta=0 \tag{286}$$

Now dividing the above equation by $Sin^2\theta$, we get

$$\frac{1}{Sin\ \theta}\frac{\partial}{\partial\theta}\left(Sin\ \theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\beta-\frac{m^2\Theta}{Sin^2\theta}=0 \tag{287}$$

or

$$\frac{1}{Sin\ \theta}\frac{\partial}{\partial\theta}\left(Sin\ \theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{Sin^2\theta}\right)\Theta=0 \tag{288}$$

After defining a new variable $x = Cos\ \theta$, we have

$$Sin^2\theta+Cos^2\theta=1 \tag{289}$$

$$Sin^2\theta=1-Cos^2\theta \tag{290}$$

$$Sin\ \theta=\sqrt{1-Cos^2\theta} \tag{291}$$

$$Sin\ \theta=\sqrt{1-x^2} \tag{292}$$

Also, since we assumed $x = Cos\ \theta$, the first derivative w.r.t. θ will be

$$\frac{\partial x}{\partial\theta}=-Sin\ \theta \tag{293}$$

The derivative of Θ function w.r.t. θ can be rewritten as

$$\frac{\partial\Theta}{\partial\theta}=\frac{\partial\Theta}{\partial x}.\frac{\partial x}{\partial\theta} \tag{294}$$

After putting the values of $\partial x/\partial\theta$ from equation (293) in equation (294), we get

$$\frac{\partial\Theta}{\partial\theta}=-Sin\ \theta\frac{\partial\Theta}{\partial x} \tag{295}$$

After removing Θ from both sides

$$\frac{\partial}{\partial\theta} = -Sin\,\theta\frac{\partial}{\partial x} \tag{296}$$

Multiplying both sides of equation (295) by $Sin\,\theta$, we have

$$Sin\,\theta\frac{\partial\Theta}{\partial\theta} = -Sin^2\,\theta\frac{\partial\Theta}{\partial x} \tag{297}$$

$$Sin\,\theta\frac{\partial\Theta}{\partial\theta} = -(1-x^2)\frac{\partial\Theta}{\partial x} \tag{298}$$

Now, after putting the values of equation (296) and (298) in equation (288), we get

$$\frac{1}{Sin\,\theta}\left(-Sin\,\theta\frac{\partial}{\partial x}\right)\left[-(1-x^2)\frac{\partial\Theta}{\partial x}\right] + \left(\beta - \frac{m^2}{1-x^2}\right)\Theta = 0 \tag{299}$$

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial\Theta}{\partial x}\right] + \left(\beta - \frac{m^2}{1-x^2}\right)\Theta = 0 \tag{300}$$

The equation given above is a Legendre's polynomial and has physical significance only in the range of $x = +1$ to -1. Therefore, consider that one more form of Θ function so that this condition is satisfied i.e.

$$\Theta(\theta) = (1-x^2)^{\frac{m}{2}}.X(x) \tag{301}$$

Where X is a function depending upon variable x. The differentiation of the above equation w.r.t. x yields

$$\frac{\partial\Theta}{\partial x} = -mx(1-x^2)^{\frac{m}{2}-1}.X + (1-x^2)^{\frac{m}{2}}.\frac{dX}{dx} \tag{302}$$

After multiplying the above equation by $1-x^2$ and $\partial/\partial x$, we get

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial\Theta}{\partial x}\right] = \frac{\partial}{\partial x}\left[-mx(1-x^2)^{\frac{m}{2}}.X + (1-x^2)^{\frac{m}{2}+1}.\frac{dX}{dx}\right] \tag{303}$$

$$= \left[-m(1-x^2)^{m/2} + m^2x^2(1-x^2)^{\frac{m}{2}-1}\right]X - \left[2x(m+1)(1-x^2)^{\frac{m}{2}}\right]X' + \left[(1-x^2)^{\frac{m}{2}+1}\right]X'' \tag{304}$$

Where $\partial/\partial x$ and $\partial^2/\partial x^2$ are represented by the symbol X' and X'', respectively. Now, after using the value of equation (301) and equation (304) in equation (300), we get

$$\left[-m(1-x^2)^{m/2} + m^2x^2(1-x^2)^{\frac{m}{2}-1}\right]X - \left[2x(m+1)(1-x^2)^{\frac{m}{2}}\right]X' + \left[(1-x^2)^{\frac{m}{2}+1}\right]X'' + \left(\beta - \frac{m^2}{1-x^2}\right)(1-x^2)^{\frac{m}{2}}.X = 0 \tag{305}$$

Dividing the above expression by $(1-x^2)^{m/2}$, we have

$$(1-x^2)X'' - 2(m+1)xX' + [\beta - m(m+1)]X = 0 \tag{306}$$

or

$$(1-x^2)X'' - 2\alpha xX' + \lambda X = 0 \tag{307}$$

Where $\alpha = m+1$ and $\lambda = \beta - m(m+1)$. Now assume that the function X can be expressed as a power series expansion as given below.

$$X = a_0 + a_1x + a_2x^2 + a_3x^3 \dots\dots\dots\dots \tag{308}$$

$$X' = a_1 + 2a_2x + 3a_3x^2 \dots\dots\dots\dots \tag{309}$$

$$X'' = 2a_2 + 6a_3x + 12a_4x^2 \dots\dots\dots\dots \tag{310}$$

Putting values of equation (308-310) in equation (307), we get

$$(1-x^2)(2a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3) - 2\alpha x(a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3) + \lambda(a_0 + a_1x + a_2x^2 + a_3x^3) = 0 \tag{311}$$

or

$$(2a_2 + \lambda a_0) + [6a_3 + (\lambda - 2\alpha)a_1]x + [12a_4 + (\lambda - 2\alpha - 2)a_2]x^2 \dots\dots\dots = 0 \tag{312}$$

The above equation is satisfied only if each term on the left-hand side is individually equal to zero i.e. coefficients of each power of x are vanish. The general expression for the coefficients must follow the condition given below.+

$$(n+1)(n+2)a_{n+2} + [\lambda - 2n\alpha - n(n-1)]a_n = 0 \tag{313}$$

Where $n = 0, 1, 2, 3$ etc. Summarizing the result, we can write

$$a_{n+2} = \frac{2n\alpha + n(n-1) - \lambda}{(n+1)(n+2)} a_n \tag{314}$$

After putting values of α and λ in equation (314), we get

$$\frac{a_{n+2}}{a_n} = \frac{(n+m)(n+m+1) - \beta}{(n+1)(n+2)} \tag{315}$$

Which is the Recursion formula for the coefficients of the power of x. Now, in order to obtain a valid wavefunction, the power series must contain a finite number of terms which is possible only if numerator becomes zero i.e.

$$(n+m)(n+m+1) - \beta = 0 \tag{316}$$

$$\beta = (n+m)(n+m+1) \tag{317}$$

Since we know that *m* as well *n* both are the whole numbers, their sum must also be a whole number. Therefore, the sum of *n* and *m* can be replaced by another whole number symbolized by *l* i.e.

$$\beta = l(l+1) \tag{318}$$

Where $l = 0, 1, 2, 3$ etc. After putting the value of β from equation (318) in equation (300), we get

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial \Theta}{\partial x}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]\Theta = 0 \tag{319}$$

The general solution of equation (319) is

$$\Theta = NP_l^m(x) = NP_l^m(Cos\,\theta) \tag{320}$$

Where N is the normalization constant and $P_l^m(x)$ is the associated "Legendre function" which is defined as given below.

$$P_l^m(x) = (1-x^2)^{m/2}\frac{d^m P_l(x)}{dx^m} \tag{321}$$

Where $P_l(x)$ is the Legendre polynomial given by

$$P_l(x) = \frac{1}{2^l\, l!}\frac{d^l(x^2-1)^l}{dx^l} \tag{322}$$

In order to proceed further, we must discuss the concept of orthogonality and the normalization of the "Legendre's function".

i) Orthogonality of associated Legendre's function: The orthogonality of the associated Legendre's polynomial follows the conditions given below.

$$\int_{-1}^{+1} P_k^m(x)\, P_l^m(x) = 0 \qquad if\ k \neq l \tag{323}$$

$$\int_{-1}^{+1} P_k^m(x)\, P_l^m(x) = \frac{2}{(2l+1)}\frac{(l+m)!}{(l-m)!} \qquad if\ k = l \tag{324}$$

ii) Normalization of associated Legendre's function: The normalization of the associated Legendre's polynomial follows the conditions given below.

$$\int_{-1}^{+1} \Theta_{m,l}\, \Theta_{m,l}^*(d\theta) = 1 \tag{325}$$

$$N^2 \int_{-1}^{+1} P_k^m(x)\, P_l^m(x)\, dx = 1 \tag{326}$$

$$N^2 . \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} = 1 \tag{327}$$

$$N = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \tag{328}$$

Using the value of normalization constant in equation (320), we get

$$\Theta_{l,m}(\theta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\,\theta) \tag{329}$$

Which is the complete solution of Θ-equation.

Table 2. Some normalized Θ-functions and corresponding spherical harmonics.

Θ-functions	Spherical harmonics
$\Theta_{0,0} = \frac{1}{\sqrt{2}}$	$Y_{0,0} = \frac{1}{\sqrt{2}} . \sqrt{\frac{1}{2\pi}}$
$\Theta_{1,0} = \sqrt{\frac{3}{2}}\, Cos\,\theta$	$Y_{1,0} = \sqrt{\frac{3}{2}}\, Cos\,\theta . \frac{1}{\sqrt{2\pi}}$
$\Theta_{1,\pm 1} = \sqrt{\frac{3}{4}}\, Sin\,\theta$	$Y_{1,\pm 1} = \sqrt{\frac{3}{4}}\, Sin\,\theta . \sqrt{\frac{1}{2\pi}} e^{\pm i\phi}$
$\Theta_{2,0} = \sqrt{\frac{5}{8}}\,(3Cos^2\,\theta - 1)$	$Y_{2,0} = \sqrt{\frac{5}{8}}\,(3Cos^2\,\theta - 1) . \frac{1}{\sqrt{2\pi}}$
$\Theta_{2,\pm 1} = \sqrt{\frac{15}{4}}\, Sin\,\theta\, Cos\,\theta$	$Y_{2,\pm 1} = \sqrt{\frac{15}{4}}\, Sin\,\theta\, Cos\,\theta . \sqrt{\frac{1}{2\pi}} e^{\pm i\phi}$
$\Theta_{2,\pm 2} = \sqrt{\frac{15}{16}}\, Sin^2\,\theta$	$Y_{2,\pm 2} = \sqrt{\frac{15}{16}}\, Sin^2\,\theta . \sqrt{\frac{1}{2\pi}} e^{\pm i2\phi}$

3. The solution of R(*r*) equation: Recall and rearrange the differential equation obtained after separation of variables having *r*-dependence i.e.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=\beta \tag{330}$$

After putting $\hbar = h/2\pi$ and rearranging, we get

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\beta \tag{331}$$

After multiplying by R on both sides and then dividing by r^2 throughout, we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}(E-V)R=\frac{\beta R}{r^2} \tag{332}$$

Now, as we know from the solution of Θ-equation that $\beta = l(l+1)$, the above equation takes the form

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}(E-V)R=\frac{l(l+1)R}{r^2} \tag{333}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}(E-V)R-\frac{l(l+1)R}{r^2}=0 \tag{334}$$

or

$$\frac{1}{r^2}\left[r^2\frac{\partial^2 R}{\partial r^2}+2r\frac{\partial R}{\partial r}\right]+\left[\frac{2\mu}{\hbar^2}(E-V)-\frac{l(l+1)}{r^2}\right]R=0 \tag{335}$$

$$\left[\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}\right]+\left[\frac{2\mu}{\hbar^2}(E-V)-\frac{l(l+1)}{r^2}\right]R=0 \tag{336}$$

Putting the value of potential energy for atomic hydrogen or hydrogen-like species again in the above equation, we get

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[\frac{2\mu E}{\hbar^2}+\frac{2\mu Ze^2}{\hbar^2 r}-\frac{l(l+1)}{r^2}\right]R=0 \tag{337}$$

As we know from the classical mechanics that elliptical orbits represent bound states have energies less than zero whereas hyperbolic orbits represent unbound states have energies greater than zero. Now assume that electron around the nucleus is bound somehow i.e.

$$-\frac{2\mu E}{\hbar^2}=\alpha^2 \quad and \quad \frac{\mu Ze^2}{\hbar^2\alpha}=\lambda \tag{338}$$

Using equation (338) in equation (337), we get

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[-\alpha^2 + \frac{2\alpha\lambda}{r} - \frac{l(l+1)}{r^2}\right]R = 0 \tag{339}$$

At this stage, we need to define a new variable $\rho = 2\alpha r$, so that

$$\frac{\partial \rho}{\partial r} = 2\alpha \tag{340}$$

Which follows

$$\frac{\partial R}{\partial r} = \frac{\partial R}{\partial \rho}.\frac{\partial \rho}{\partial r} = 2\alpha\frac{\partial R}{\partial \rho} \tag{341}$$

Also

$$\frac{\partial^2 R}{\partial r^2} = \frac{\partial}{\partial r}\left[\frac{\partial R}{\partial r}\right] = \frac{\partial}{\partial r}\left[2\alpha\frac{\partial R}{\partial \rho}\right] = \frac{\partial}{\partial r}\frac{\partial \rho}{\partial \rho}\left[2\alpha\frac{\partial R}{\partial \rho}\right] = \frac{\partial \rho}{\partial r}\frac{\partial}{\partial \rho}\left[2\alpha\frac{\partial R}{\partial \rho}\right] \tag{341}$$

$$\frac{\partial^2 R}{\partial r^2} = 2\alpha\frac{\partial}{\partial \rho}\left[2\alpha\frac{\partial R}{\partial \rho}\right] = 4\alpha^2\frac{\partial^2 R}{\partial \rho^2} \tag{342}$$

After using the values of $\partial R/\partial r$ and $\partial^2 R/\partial r^2$ from equation (341) and equation (342) in equation (339), we get the following.

$$4\alpha^2\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{r}2\alpha\frac{\partial R}{\partial \rho} + \left[-\alpha^2 + \frac{2\alpha\lambda}{r} - \frac{l(l+1)}{r^2}\right]R = 0 \tag{343}$$

Now divide the above equation by $4\alpha^2$ i.e.

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{1}{\alpha r}\frac{\partial R}{\partial \rho} + \left[-\frac{1}{4} + \frac{\lambda}{2\alpha r} - \frac{l(l+1)}{4\alpha^2 r^2}\right]R = 0 \tag{344}$$

Using $\rho = 2\alpha r$, we get

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0 \tag{345}$$

When $\rho \to \infty$, the above equation takes the form

$$\frac{\partial^2 R}{\partial \rho^2} - \frac{1}{4}R = 0 \tag{346}$$

The general solutions of the differential equation given above are

$$R(\rho) = e^{+\rho/2} \qquad and \qquad R(\rho) = e^{-\rho/2} \tag{347}$$

The function $R(\rho) = e^{+\rho/2}$ becomes ∞ when $\rho = \infty$, and hence, is not acceptable. Therefore, we are left with

$$R(\rho) = e^{-\rho/2} \tag{348}$$

Since the acceptable solution given above is valid only at very large values of ρ, it is quite reasonable to think that the exact solution may also contain some pre-exponential part to attain validity at all values of ρ. Therefore, after incorporating some ρ-dependent unknown function '$F(\rho)$' in equation (348), we get

$$R(\rho) = F(\rho)\, e^{-\rho/2} \tag{349}$$

Differentiating above equation with w.r.t ρ at first and second order and then putting the values of $R(\rho)$, $\partial R/\partial\rho$ and $\partial^2 R/\partial\rho^2$ in equation (345), we get

$$\frac{\partial^2 F}{\partial \rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{\partial F}{\partial \rho} + \left[-\frac{1}{\rho} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]F = 0 \tag{350}$$

For simplification, put $\partial^2 R/\partial\rho^2 = F''$ and $\partial R/\partial\rho = F'$ i.e.

$$F'' + \left(\frac{2}{\rho} - 1\right)F' + \left[-\frac{1}{\rho} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]F = 0 \tag{351}$$

Hence, the problem has been reduced to the determination of the solution of F which can be assumed as

$$F(\rho) = \rho^s G(\rho) \tag{352}$$

Where $G(\rho)$ represents a power series expansion of ρ i.e.

$$G(\rho) = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 \ldots \tag{353}$$

Or we can say that

$$G(\rho) = \sum_{k=0}^{k=\infty} a_k \rho^k \tag{354}$$

It is also worthy to mention that $a_0 \neq 0$. Now differentiating equation (352) w.r.t. ρ, we get

$$F'(\rho) = s\rho^{s-1}G + \rho^s G' \tag{355}$$

The double derivative of the same will be

$$F''(\rho) = s(s-1)\rho^{s-2}G + 2s\rho^{s-1}G' + \rho^s G'' \tag{356}$$

After putting the values of $F(\rho)$, $F'(\rho)$ and $F''(\rho)$ from equation (352, 355, 356) into equation (351), we get

$$s(s-1)\rho^{s-2}G + 2s\rho^{s-1}G' + \rho^s G'' + \left(\frac{2}{\rho} - 1\right)[s\rho^{s-1}G + \rho^s G'] + \left[-\frac{1}{\rho} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]\rho^s G = 0 \tag{357}$$

Multiplying throughout by $4\rho^2$, we get

$$4\rho^2 s(s-1)\rho^{s-2}G + 4\rho^2.2s\rho^{s-1}G' + 4\rho^2.\rho^s G'' + (8\rho - 4\rho^2)[s\rho^{s-1}G + \rho^s G'] + [-4\rho + 4\rho\lambda - 4l(l+1)]\rho^s G = 0 \tag{358}$$

or

$$4s(s-1)\rho^s G + 8s\rho^{s+1}G' + 4\rho^{s+2}G'' + 8s\rho^s G - 4s\rho^{s+1}G + 8\rho^{s+1}G' - 4\rho^{s+2}G' - 4\rho^{s+1}G + 4\lambda\rho^{s+1}G - 4l(l+1)\rho^s G = 0 \tag{359}$$

or

$$4s(s-1)\rho^s G + 8s\rho^s G - 4s\rho^{s+1}G - 4\rho^{s+1}G + 4\lambda\rho^{s+1}G - 4l(l+1)\rho^s G + 8s\rho^{s+1}G' + 8\rho^{s+1}G' - 4\rho^{s+2}G' + 4\rho^{s+2}G'' = 0 \tag{360}$$

or

$$[4s(s-1)\rho^s + 8s\rho^s - 4s\rho^{s+1} - 4\rho^{s+1} + 4\lambda\rho^{s+1} - 4l(l+1)\rho^s]G + [8s\rho^{s+1} + 8\rho^{s+1} - 4\rho^{s+2}]G' + 4\rho^{s+2}G'' = 0 \tag{361}$$

Dividing throughout by ρ^s, we get

$$[4s(s-1) + 8s - 4s\rho - 4\rho + 4\lambda\rho - 4l(l+1)]G + [8s\rho + 8\rho - 4\rho^2]G' + 4\rho^2 G'' = 0 \tag{362}$$

If $\rho = 0$, the function $G(\rho) = a_0$ and the above equation takes the form

$$[4s(s-1) + 8s - 4l(l+1)]a_0 = 0 \tag{363}$$

Since $a_0 \neq 0$, the quantity that must be equal to zero to satisfy the above result is

$$4s(s-1) + 8s - 4l(l+1) = 0 \tag{364}$$

$$s(s-1) + 2s - l(l+1) = 0 \tag{365}$$

$$s(s+1) - l(l+1) = 0 \tag{366}$$

$$s(s+1) = l(l+1)$$

Which implies that

$$s = l \qquad or \qquad s = -(l+1) \tag{367}$$

Now, if we put $s = -(l+1)$ the first term in the function $F(\rho)$ becomes $a_0/0^{l+1}$ at $\rho = 0$ which infinite, and hence is not an acceptable solution. Thus, the only we are left with is $s = l$; after using the same in equation (362), we get

$$[4l(l-1)+8l-4l\rho-4\rho+4\lambda\rho-4l(l+1)]G+[8l\rho+8\rho-4\rho^2]G'+4\rho^2G''=0 \tag{368}$$

$$[-4l\rho-4\rho+4\lambda\rho]G+[8l\rho+8\rho-4\rho^2]G'+4\rho^2G''=0 \tag{369}$$

Dividing the above equation by 4ρ, we get

$$[-l-1+\lambda]G+[2l+2-\rho]G'+\rho G''=0 \tag{370}$$

Now differentiating equation (353) at first and second order, we get

$$G'(\rho)=a_1 1\rho^{1-1}+a_2 2\rho^{2-1}+a_3 3\rho^{3-1}\ldots=\sum_{k=0}^{k=\infty}a_k.k.\rho^{k-1} \tag{371}$$

Similarly

$$G''(\rho)=a_2.2.(2-1)\rho^{2-2}+a_3.3.(3-1)\rho^{3-2}\ldots=\sum_{k=0}^{k=\infty}a_k.k.(k-1).\rho^{k-2} \tag{372}$$

After using the values equation (354, 371, 372) into equation (370), we get

$$[-l-1+\lambda]\sum_{k=0}^{k=\infty}a_k\rho^k+[2l+2-\rho]\sum_{k=0}^{k=\infty}a_k.k.\rho^{k-1}+\rho\sum_{k=0}^{k=\infty}a_k.k.(k-1).\rho^{k-2}=0 \tag{373}$$

The above equation holds true only if the coefficients of individual powers of ρ become zero. So, simplifying equation (373) for two summation terms (a_k and a_{k+1}), we have

$$[-l-1+\lambda][a_k\rho^k+a_{k+1}\rho^{k+1}]+[2l+2-\rho][a_k.k.\rho^{k-1}+a_{k+1}.(k+1).\rho^k]+\rho[a_k.k.(k-1).\rho^{k-2}+a_{k+1}.(k+1).k.\rho^{k-1}]=0 \tag{374}$$

$$-la_k\rho^k-a_k\rho^k+\lambda a_k\rho^k-la_{k+1}\rho^{k+1}-a_{k+1}\rho^{k+1}+\lambda a_{k+1}\rho^{k+1}+2la_k.k.\rho^{k-1}+2a_k.k.\rho^{k-1}-\rho a_k.k.\rho^{k-1}+2la_{k+1}.(k+1).\rho^k+2a_{k+1}.(k+1).\rho^k-\rho a_{k+1}.(k+1).\rho^k+\rho.a_k.k.(k-1).\rho^{k-2}+\rho.a_{k+1}.(k+1).k.\rho^{k-1}=0 \tag{375}$$

Now putting a coefficient of ρ^k equal to zero, we get

$$-la_k\rho^k-a_k\rho^k+\lambda a_k\rho^k-a_k.k.\rho^k+2la_{k+1}.(k+1).\rho^k+2a_{k+1}.(k+1).\rho^k+a_{k+1}.(k+1).k.\rho^k=0 \tag{376}$$

$$-la_k-a_k+\lambda a_k-a_kk+2la_{k+1}(k+1)+2a_{k+1}(k+1)+a_{k+1}(k+1)k=0 \tag{377}$$

or

$$[-l-1+\lambda-k]a_k+[2l(k+1)+2(k+1)+(k+1)k]a_{k+1}=0 \tag{378}$$

$$[2l(k+1)+2(k+1)+(k+1)k]a_{k+1}=-[-l-1+\lambda-k]a_k \tag{379}$$

or

$$a_{k+1}=\frac{l+1-\lambda+k}{2l(k+1)+2(k+1)+(k+1)k}a_k \tag{380}$$

or

$$a_{k+1}=\frac{l+1-\lambda+k}{(k+1)(2l+k+2)}a_k \tag{381}$$

The equation (384) is the recursion formula where k is an integer. This expression allows one to determine the coefficient a_{k+1} in terms of a_k which is arbitrary.

Now, since the series $G(\rho)$ consists of the infinite number of terms, the function $F(\rho)$ becomes infinite at a very large value of k i.e. infinite. Consequently, the function $R(\rho)$ will also become infinite if the number of terms is not limited to a finite value. Therefore, we must break off the series to a finite number of terms which is possible only if the numerator becomes zero i.e.

$$l+1-\lambda+k=0 \tag{382}$$

Define a new quantum number "n" at this stage as

$$\lambda=l+1+k=n \tag{383}$$

Since l and k are integers, n can be 1, 2, 3, 4 …. and so on. Moreover, as $n\geq l+1$, the largest value that l can have is $n-1$. Hence, the value of l has a domain ranging from 0 to $n-1$. Putting $\lambda=n$ in equation (370)

$$[-l-1+n]G+[2l+2-\rho]G'+\rho G''=0 \tag{384}$$

Defining $2l+1=p$ and $n+l=q$, we get

$$[q-p]G+[p+1-\rho]G'+\rho G''=0 \tag{385}$$

The solution of the equation given above is the "associated Laguerre polynomial" multiplied by a constant factor i.e.

$$G(p)=CL_q^p(\rho)=CL_{n+l}^{2l+1}(\rho) \tag{385}$$

The constant C can be set as normalization constant and "associated Laguerre polynomial" is

$$L_{n+l}^{2l+1}(\rho)=\sum_{k=0}^{k=n-l-1}\frac{(-1)^{k+1}[(n+l)!]^2\rho^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{385}$$

After using the value of $F(\rho)$ from equation (352) in equation (349), we get radial wavefunction as

$$R(\rho) = \rho^s G(\rho)\, e^{-\rho/2} \tag{386}$$

Since $s = l$ and also using $G(p)$ from equation (385), the above equation takes the form

$$R_{n,l}(\rho) = C\, e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \tag{387}$$

Now, after using the value of $L_{n+l}^{2l+1}(\rho)$ from equation (385) in equation (387), we get

$$R_{n,l}(\rho) = C\, e^{-\rho/2} \rho^l \sum_{k=0}^{k=n-l-1} \frac{(-1)^{k+1}[(n+l)!]^2 \rho^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{388}$$

i) The normalization constant for function R(r): In order to determine the normalization constant for the *R* function, we must put the squared-integral over whole configuration space as unity i.e.

$$\int_0^\infty R_{n,l}^2(r).r^2.dr = 1 \tag{389}$$

The factor r^2 is introduced to convert the length *dr* into a volume around the center of the nucleus. At this point, recall the value of ρ again but in terms of equation (338, 383) i.e.

$$\rho = 2\alpha r = \frac{2\mu Z e^2 r}{\hbar^2 \lambda} = \frac{2\mu Z e^2 r}{\hbar^2 n} = \frac{2Zr}{n}.\frac{\mu e^2}{\hbar^2} \tag{390}$$

Since $a_0 = \hbar^2/\mu e^2$ i.e. the "Bohr radius", the equation (390) takes the form

$$\rho = \frac{2Zr}{n}.\frac{1}{a_0} \tag{391}$$

So that

$$r = \frac{na_0}{2Z}\rho \tag{392}$$

Also

$$dr = \frac{na_0}{2Z}d\rho \tag{393}$$

After using the values of $R_{n,l}(\rho)$, *r* and *dr* from equation (388, 392, 393) in equation (389), we get

$$C^2 \int_0^\infty e^\rho.\rho^{2l}.\left[L_{n+l}^{2l+1}(\rho)\right]^2.\left[\frac{na_0}{2Z}\rho\right]^2.\left[\frac{na_0}{2Z}\right]d\rho = 1 \tag{394}$$

or

$$C^2\left(\frac{na_0}{2Z}\right)^3\left[\frac{2n\{(n+l)!\}^3}{(n-l-1)!}\right]=1 \tag{395}$$

or

$$C=\sqrt{\left(\frac{2Z}{na_0}\right)^3\left[\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]} \tag{395}$$

After using the value of normalization constant from above equation into equation (388), we get

$$R_{n,l}(\rho)=\sqrt{\left(\frac{2Z}{na_0}\right)^3\left[\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}\;e^{-\rho/2}\rho^l\sum_{k=0}^{k=n-l-1}\frac{(-1)^{k+1}[(n+l)!]^2\rho^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{396}$$

$$=\sqrt{\left(\frac{2Z}{na_0}\right)^3\left[\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}.\exp\left(-\frac{Zr}{na_0}\right).\left(\frac{2Zr}{na_0}\right)^l.\sum_{k=0}^{k=n-l-1}\frac{(-1)^{k+1}[(n+l)!]^2\left(\frac{2Zr}{na_0}\right)^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{397}$$

Which is the complete solution of R-equation.

Table 3. Some of the initial radial wave functions in terms of distance from the center of the nucleus for the hydrogen atom and other hydrogen-like species.

n	l	Radial wave function ($R_{n,l}$)
1	0	$R_{1,0}=2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$
2	0	$R_{2,0}=\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	$R_{2,1}=\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$R_{3,0}=\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}-2\left(\frac{Zr}{a_0}\right)^2\right)e^{-Zr/3a_0}$
3	1	$R_{3,1}=\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6\left(\frac{Zr}{a_0}\right)-\left(\frac{Zr}{a_0}\right)^2\right)e^{-Zr/3a_0}$
3	2	$R_{3,2}=\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^{3/2}-\left(\frac{Zr}{a_0}\right)^2e^{-Zr/3a_0}$

The total wavefunction: After solving the ϕ-, θ- and r-dependent equations, we have $\Phi_m(\phi)$, $\Theta_{l,m}(\theta)$ and $R_{n,l}(r)$ functions. Now, recall the total wave function that depends upon all the three variable i.e.

$$\psi_{n,l,m}(r,\theta,\phi) = \psi_{n,l}(r) \times \psi_{l,m}(\theta) \times \psi_m(\phi) \tag{398}$$

After putting the values of $\Phi_m(\phi)$, $\Theta_{l,m}(\theta)$ and $R_{n,l}(r)$ from equation (397) in equation (398), we get

$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}.\Theta_{l,m}.\Phi_m \tag{399}$$

$$= \sqrt{\left(\frac{2Z}{na_0}\right)^3 \left[\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}.\exp\left(-\frac{Zr}{na_0}\right).\left(\frac{2Zr}{na_0}\right)^l.\sum_{k=0}^{k=n-l-1}\frac{(-1)^{k+1}[(n+l)!]^2\left(\frac{2Zr}{na_0}\right)^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{400}$$

$$\times\sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}.P_l^m(Cos\,\theta)\times\sqrt{\frac{1}{2\pi}}e^{im\phi}$$

Which is the complete expression for all the quantum mechanical states of a single electron around the nucleus.

Table 4. Some of the initial total wave functions for the hydrogen atom and other hydrogen-like species.

n	l	m	Total wave function ($\psi_{n,l,m}$)
1	0	0	$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{2,0,0} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	0	$\psi_{2,1,0} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}\, r\, Cos\theta$
2	1	±1	$\psi_{2,1,\pm1} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}\, Sin\theta\, e^{-i\phi}$
3	0	0	$\psi_{3,0,0} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}-2\left(\frac{Zr}{a_0}\right)^2\right)e^{-Zr/3a_0}.\frac{1}{\sqrt{4\pi}}$
3	1	0	$\psi_{3,1,0} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6\left(\frac{Zr}{a_0}\right)-\left(\frac{Zr}{a_0}\right)^2\right)e^{-Zr/3a_0}.\sqrt{\frac{3}{2}}\,Cos\,\theta.\frac{1}{\sqrt{2\pi}}$
3	1	±1	$\psi_{3,1,\pm1} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6\left(\frac{Zr}{a_0}\right)-\left(\frac{Zr}{a_0}\right)^2\right)e^{-Zr/3a_0}.\sqrt{\frac{3}{2}}\,Sin\,\theta.\sqrt{\frac{1}{2\pi}}e^{\pm i\phi}$

The eigenvalues of energy: Since the series $G(\rho)$ consists of infinite number of terms, the function $F(\rho)$ becomes infinite at a very large value of k i.e. infinite. Consequently, the function $R(\rho)$ will also become infinite if the number of terms are not limited to a finite value. Therefore, we must break off the series to a finite number of terms which is possible only if the numerator in equation (381) becomes zero i.e.

$$l+1-\lambda+k=0 \tag{401}$$

or

$$\lambda=l+1+k=n \tag{402}$$

Where n is the principal quantum number and can have values 1, 2, 3. 4 …. because *l* and *k* are integers always. Now recall the value of λ from equation (338) and then squaring both sides, we get

$$\lambda^2=\frac{\mu^2 Z^2 e^4}{\hbar^4 \alpha^2} \tag{403}$$

Also putting the value of α^2 from equation (338) in equation (403), we get

$$\lambda^2=\frac{\mu^2 Z^2 e^4}{\hbar^4 \alpha^2}=-\frac{\mu^2 Z^2 e^4}{\hbar^4}\cdot\frac{\hbar^2}{2\mu E}=-\frac{\mu Z^2 e^4}{2\,E\,\hbar^2} \tag{404}$$

$$E_n=-\frac{\mu Z^2 e^4}{2\,\lambda^2\,\hbar^2}=-\frac{\mu Z^2 e^4}{2\,n^2\,\hbar^2} \tag{405}$$

Which is the same as given by the pre-wave-mechanical quantum theory.

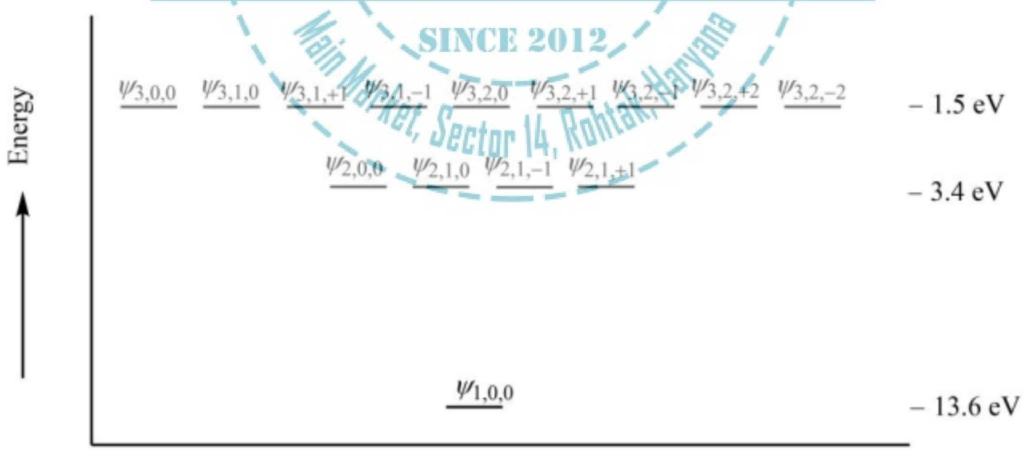

Figure 14. The energy level for various quantum mechanical states of the hydrogen atom.

It is also worthy to note that the total number of wave functions that can be written for a given value of n are n^2, and therefore, we can say that the degeneracy of any energy level is also n^2.

International Edition

A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL

First Edition

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ISBN: 978-81-938720-1-7
9 788193 872017 >
MRP: Rs 800.00

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