CHAPTER 5

Quantum Mechanics – II

❖ Schrodinger Wave Equation for a Particle in a Three Dimensional Box

In the first chapter of this book, we derived and discussed the Schrodinger wave equation for a particle in the one-dimensional box. In this chapter, we will extend that procedure to the particle in a three-dimensional box. In order to do so, consider a particle trapped in a 3-dimensional box of length, breadth, and height as *a*, *b* and *c*, respectively. This means that this particle can travel in any direction i.e. along *x-, y- and z*-axis. The potential inside the box is 0, while outside to the box it is infinite.

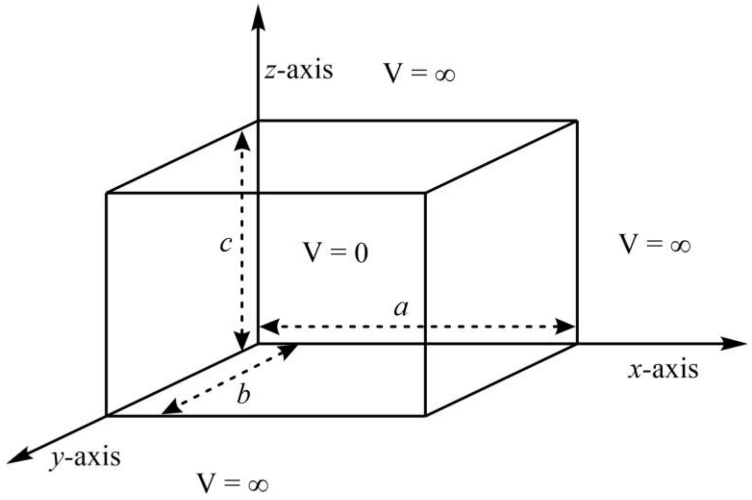


Figure 1. The particle in a three-dimensional box.

So far we have considered a quantum mechanical system of a particle trapped in a three-dimensional box. 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 particle in a three-dimensional box. 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 obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\widehat{H}\psi = E\psi \tag{1}$$

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

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

or

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi = E\psi \tag{3}$$

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi - E\psi = 0 \tag{4}$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \tag{5}$$

The above-mentioned second order differential equation is the Schrodinger wave equation for a particle moving along three dimensions. Since the conditions outside and inside the box are different, the equation (5) must be solved separately for both cases.

1. The solution of Schrodinger wave equation for outside the box: After putting the value of potential outside the box in equation (5) i.e. V = ∞, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-\infty)\psi = 0 \tag{6}$$

Since E is negligible in comparison to the ∞, the above equation becomes

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\infty\psi = 0 \tag{7}$$

$$\infty\psi = \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2} \tag{8}$$

$$\psi = \frac{1}{\infty}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) = 0 \tag{9}$$

The physical significance of the equation (9) is that the particle cannot go outside the box, and is always reflected back when it strikes the boundaries. In other words, as the function describing the existence of particles is zero outside the box, the particle cannot exist outside the box.

2. The solution of Schrodinger wave equation for inside the box: After putting the value of potential inside the box in equation (5) i.e. V = 0, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-0)\psi=0 \tag{10}$$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \tag{11}$$

The above equation has three variables and is difficult to solve directly. Therefore, it is better to separate variable, we already know the steps to solve a one-variable equation. To do so, consider that the wave function ψ is the multiplication of three individual functions as

$$\psi(x,y,z)=\psi(x)\times\psi(y)\times\psi(z)=XYZ \tag{12}$$

Using the above expression in equation (11), we get

$$\frac{\partial^2 XYZ}{\partial x^2}+\frac{\partial^2 XYZ}{\partial y^2}+\frac{\partial^2 XYZ}{\partial z^2}+\frac{8\pi^2 mE}{h^2}XYZ=0 \tag{13}$$

From the rules of partial derivative, the equation (13) takes the form

$$YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}XYZ=0 \tag{14}$$

Now divide the above equation by XYZ on both side i.e.

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}=0 \tag{15}$$

Assuming

$$k^2=\frac{8\pi^2 mE}{h^2} \tag{16}$$

The equation (15) becomes

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+k^2=0 \tag{17}$$

Also fragmenting the constant k^2 along three *x*-, *y*- and *z*-axis i.e. $k^2=k_x^2+k_y^2+k_z^2$, the equation (17) can

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+k_x^2+k_y^2+k_z^2=0 \tag{18}$$

The above equation can be written as the sum of three equations with only one variable in each i.e.

$$\frac{\partial^2 X}{\partial x^2} + k_x^2 X = 0 \tag{19}$$

$$\frac{\partial^2 Y}{\partial y^2} + k_y^2 Y = 0 \tag{20}$$

$$\frac{\partial^2 Z}{\partial z^2} + k_z^2 Z = 0 \tag{21}$$

The equations (19-21) are simple one-dimensional differential equations whose solutions can be obtained just like in the one-dimensional box. The solution of equation (19) will give the *x*-dependent wave function as well the energy distribution along *x*-axis i.e.

$$\psi_{n_x}(x) = X = \sqrt{\frac{2}{a}}\, Sin\frac{n_x \pi x}{a} \quad and \quad E_{n_x} = \frac{n_x^2 h^2}{8ma^2} \tag{22}$$

Similarly, the solution of equation (20) will be

$$\psi_{n_y}(y) = Y = \sqrt{\frac{2}{b}}\, Sin\frac{n_y \pi y}{b} \quad and \quad E_{n_y} = \frac{n_y^2 h^2}{8mb^2} \tag{23}$$

Just like the above two, the solution of equation (21) will be

$$\psi_{n_z}(z) = Z = \sqrt{\frac{2}{c}}\, Sin\frac{n_z \pi z}{c} \quad and \quad E_{n_z} = \frac{n_z^2 h^2}{8mc^2} \tag{24}$$

After putting the expressions of individual wave functions from equation (22-24) in equation (12), the total wave function can be obtained i.e.

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{abc}}\, Sin\frac{n_x \pi x}{a}\, Sin\frac{n_y \pi y}{b}\, Sin\frac{n_z \pi z}{c} \tag{25}$$

Since $k^2 = k_x^2 + k_y^2 + k_z^2$, the total energy must be the sum of individual energies i.e.

$$E_{n_x n_y n_z} = \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\frac{h^2}{8m} \tag{26}$$

Where n_x, n_y, n_y are the discrete variable whose permitted values from boundary conditions can be 0, 1, 2, 3, 4….∞. Nevertheless, it is worthy to note that even though the *n* = 0 is permitted by the boundary conditions, we still don't use it in equation (25); which is obviously because it makes the whole function zero.

❖ The Concept of Degeneracy Among Energy Levels for a Particle in Three Dimensional Box

The solution of Schrodinger wave equation for a particle of mass '*m*' trapped in three dimensional of sides *a*, *b* and *c* with zero potential inside and infinite potential outside provide the total wave function ψ as

$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{abc}}\, Sin\frac{n_x \pi x}{a}\, Sin\frac{n_y \pi y}{b}\, Sin\frac{n_z \pi z}{c} \tag{27}$$

Where n_x, n_y, n_y are the discrete variable whose permitted values from boundary conditions can be 1, 2, 3, 4….∞. The variable *x*, *y* and *z* represent the position of the particle along the corresponding axis. Besides, the expression for total energy is

$$E_{n_x n_y n_z} = \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\frac{h^2}{8m} \tag{28}$$

For a cubical box, all the sides become equal (*a* = *b* = *c*). Using this condition in equation (27), the total wave function representing different quantum mechanical states take the following form.

$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{a^3}}\, Sin\frac{n_x \pi x}{a}\, Sin\frac{n_y \pi y}{a}\, Sin\frac{n_z \pi z}{a} \tag{29}$$

Similarly, the energy expression also changes to

$$E_{n_x n_y n_z} = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8ma^2} \tag{30}$$

Now, in order to define various quantum mechanical states, we need to put valid set quantum numbers. The expression for first quantum mechanical and corresponding energy can be obtained by putting $n_x = n_y = n_z = 1$ in equations (29–30) i.e.

$$\psi_{111} = \sqrt{\frac{8}{a^3}}\, Sin\frac{\pi x}{a}\, Sin\frac{\pi y}{a}\, Sin\frac{\pi z}{a} \quad \text{and} \quad E_{111} = \frac{3h^2}{8ma^2} \tag{31}$$

Similarly, the next state with energy can be obtained by putting $n_x = n_y = 1$ and $n_z = 2$ in equations (29–30) i.e.

$$\psi_{112} = \sqrt{\frac{8}{a^3}}\, Sin\frac{\pi x}{a}\, Sin\frac{\pi y}{a}\, Sin\frac{2\pi z}{a} \quad \text{and} \quad E_{112} = \frac{6h^2}{8ma^2} \tag{32}$$

If $n_x = n_z = 1$ and $n_y = 2$; the wavefunction and energy become

$$\psi_{121} = \sqrt{\frac{8}{a^3}}\, Sin\frac{\pi x}{a}\, Sin\frac{2\pi y}{a}\, Sin\frac{\pi z}{a} \quad \text{and} \quad E_{121} = \frac{6h^2}{8ma^2} \tag{33}$$

If $n_y = n_z = 1$ and $n_x = 2$, the state with energy becomes

$$\psi_{211} = \sqrt{\frac{8}{a^3}}\, Sin\frac{2\pi x}{a}\, Sin\frac{\pi y}{a}\, Sin\frac{\pi z}{a} \quad \text{and} \quad E_{211} = \frac{6h^2}{8ma^2} \tag{34}$$

It can be clearly seen that three quantum mechanical states ψ_{112}, ψ_{121} and ψ_{211} possess the same amount of energy (i.e. $6h^2/8ma^2$); and therefore, are said to be degenerate. In other words, there are three different ways of existence of the particle inside the box so that the particle possesses $6h^2/8ma^2$ energy as total.

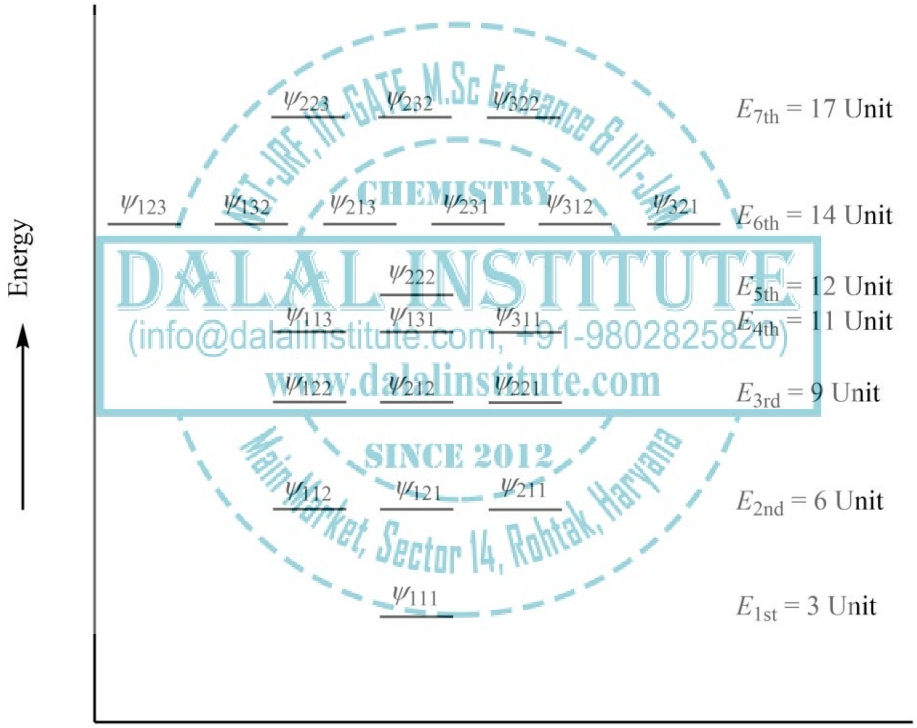


Figure 2. The energy level diagram representing different quantum mechanical states (in the units of $h^2/8ma^2$) for a particle trapped in a cubical box.

Hence, the degeneracy of the ground state is one i.e. there is only one way for the particle to exist in the box to create zero-point energy ($3h^2/8ma^2$). On the other hand, the degeneracy of first excited stated is 3 as ψ_{112}, ψ_{121} and ψ_{211}, all have 6 units of energy. Moreover, after careful examination of energy diagram, it can be concluded that degeneracy is 1 if $n_x = n_y = n_z$, 3 if $n_x = n_y$ or $n_y = n_z$ or $n_x = n_z$, and 6 if $n_x \neq n_y \neq n_z$.

❖ Schrodinger Wave Equation for a Linear Harmonic Oscillator & Its Solution by Polynomial Method

A diatomic molecule is the quantum-mechanical analog of the classical version of the harmonic oscillator. It represents the vibrational motion and is one of the few quantum-mechanical systems for which an exact solution is available. In this section, we will discuss the classical and quantum mechanical oscillator and their comparative study.

➢ *The Classical Treatment of Simple Harmonic Oscillator*

In order to understand the vibrational states of a simple diatomic molecule, we must understand the classical oscillator first. In order to do so, consider a spring of length *r* in which a displacement '*x*' is incorporated by expending or compressing it.

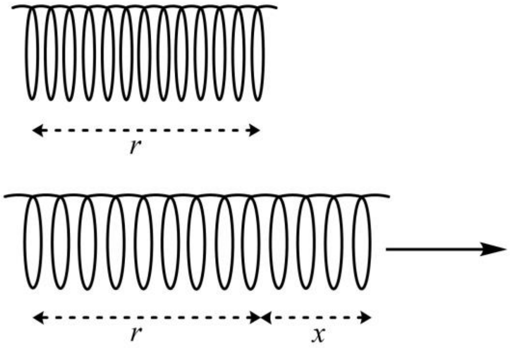


Figure 2. The pictorial representation of the displacement-inducing in a typical spiral.

For a moment, imagine that the spiral is extended by a displacement of '*x*'; then the restoring force (*F*) developed in the spiral can be obtained using Hook's law as

$$F = -kx \tag{35}$$

Where *k* is the constant of proportionality. The minus sign is because the restoring force and the displacement both are vector quantity but in the opposite direction. In other words, if we expend the spiral, the spiral will try to compress itself and vice-versa. From equation (35), it seems that the restoring force depends only upon displacement induced only, however, it is found that stronger spirals have larger restoring force than the weaker ones for the same magnitude of displacement, indicating a lager force constant. Therefore, the physical significance of the force constant lies in the fact that it can be used to comment on the strength of oscillator.

Since the potential energy in this expended state is simply the amount of work done in the process of incorporating the displacement '*x*', we need calculate the same for further analysis. The restoring force is proportional to the displacement, and therefore, is a variable quantity; suggesting that we need to carry out the integration force curve vs displacement. Suppose that the total displacement "*x*" is fragmented in very small “*dx*” segments. The amount of work done in inducing ‘*dx*’ displacement will be ‘*dw*’ and can be given by the following relation

$$dw = F.dx \tag{36}$$

The total work from zero displacement to ‘*x*’ displacement will be

$$W = \int_0^x F.dx \tag{37}$$

$$= \int_0^x -kx.dx \tag{38}$$

$$= -k\left[\frac{x^2}{2}\right]_0^x \tag{39}$$

$$W = -\frac{1}{2}kx^2 \tag{40}$$

Since there is no electrostatic attraction, the potential energy (*V*) of the system at displacement will simply be

$$V = \frac{1}{2}kx^2 \tag{41}$$

The above equation represents a parabolic behavior and shows that the potential energy varies continuously with the displacement. Larger the displacement, higher will be the potential energy.

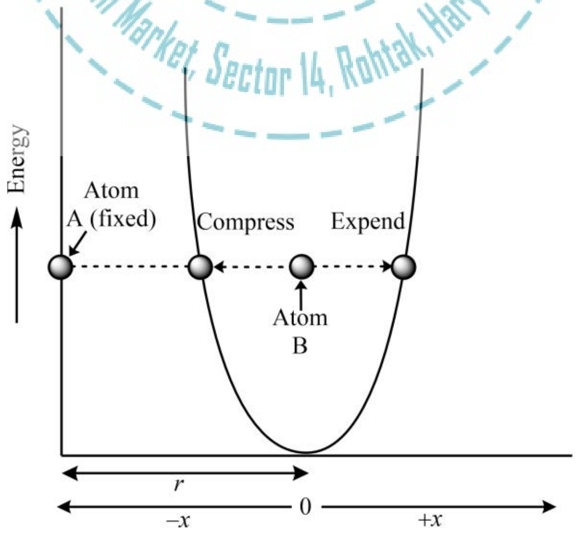


Figure 3. The variation of potential energy as a function of displacement in a classical oscillator.

If ‘m’ is the reduced mass of the diatomic molecule, the equilibrium vibrational frequency ‘v’ of the oscillator can be given as

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{42}$$

Where m is the reduced mass defined by the ratio of the product to the sum of individual masses i.e. $m = m_1 m_2/(m_1 + m_2)$. It is obvious that the energy levels of a simple harmonic oscillator in classical mechanics are continuous (including zero), and have a limit over the expansion and compression for each value. Furthermore, the classical oscillator is bound to spend most of its time in the extreme state (fully compressed and fully expended) and the least time in the equilibrium position.

- ***The Quantum Mechanical Treatment of Simple Harmonic Oscillator***

In order to find out the quantum mechanical behavior of a simple harmonic oscillator, assume that all the vibrational states can be described by a mathematical expression ψ. Since we don’t know the exact nature of ψ, we need to follow the postulates of quantum mechanics. Therefore, after applying the Hamiltonian operator over this symbolic wave function, we have

$$H\psi = E\psi \tag{43}$$

$$\left(\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V\right)\psi = E\psi \tag{44}$$

or

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} + V\psi - E\psi = 0 \tag{45}$$

Rearranging, we have

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{46}$$

After putting the value of potential energy form equation (41) in equation (46), we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \tag{47}$$

Now put the value of k form equation (42) in equation (47) i.e.

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - 2\pi^2 v^2 m x^2)\psi = 0 \tag{48}$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\left(\frac{8\pi^2 mE}{h^2}-\frac{16\pi^4 m^2\nu^2 x^2}{h^2}\right)\psi=0 \tag{49}$$

After defining constants

$$\alpha=\frac{8\pi^2 mE}{h^2}\quad and\quad \beta=\frac{4\pi^2 m\nu}{h} \tag{50}$$

The equation (49) takes the form

$$\frac{\partial^2\psi}{\partial x^2}+(\alpha-\beta^2x^2)\psi=0 \tag{51}$$

or

$$\frac{\partial^2\psi}{\partial x^2}+(\alpha-\beta\beta x^2)\psi=0 \tag{52}$$

Now define a new variable $y=\sqrt{\beta}x$, then we have the derivative as

$$\frac{dy}{dx}=\sqrt{\beta} \tag{53}$$

Squaring both side of the equation (53), and then rearranging

$$\frac{d^2y}{dx^2}=\beta\quad or\quad dx^2=d^2y/\beta \tag{54}$$

Now put the value of dx^2 and βx^2 in equation (52), we get

$$\beta\frac{\partial^2\psi}{\partial y^2}+(\alpha-\beta y^2)\psi=0 \tag{55}$$

Dividing the above equation by β, we get

$$\frac{\partial^2\psi}{\partial y^2}+\left(\frac{\alpha}{\beta}-y^2\right)\psi=0 \tag{56}$$

The equation (56) can be solved asymptotically i.e. at very large values of y. Thus, when $y\gg\alpha/\beta$, the equation (56) becomes

$$\frac{\partial^2\psi}{\partial y^2}-y^2\psi=0 \tag{57}$$

The two possible solutions of the above equation are

$$\psi=e^{\pm y^2/2} \tag{58}$$

Nevertheless, only one of them is acceptable because for $\psi = e^{+y^2/2}$, the wavefunction becomes infinite as y tends to approach ∞. Therefore, the only single-valued, continuous and finite solution we left with is

$$\psi = e^{-y^2/2} \tag{59}$$

Since the acceptable solution given above is valid only at very large values of *y*, it is quite reasonable to think that the exact solution may also contain some pre-exponential part to attain validity at all values of *y*. Therefore, after incorporating some *y*-dependent unknown function '*F*(*y*)' in equation (59), we get

$$\psi = F(y)\, e^{-y^2/2} \tag{60}$$

In order to find the value of *F*(*y*), differentiate the equation (60) first i.e.

$$\frac{d\psi}{dy} = -ye^{-y^2/2}.F + \frac{dF}{dy}e^{-y^2/2} \tag{61}$$

Differentiating again, we get

$$\frac{d^2\psi}{dy^2} = \left[-y.(-y)e^{-\frac{y^2}{2}}.F(y) + \left(-1.e^{-y^2/2}.F(y)\right) + \left(-y.e^{-y^2/2}\frac{dF}{dy}\right)\right] + \left[-y.e^{-y^2/2}\frac{dF}{dy} + e^{-y^2/2}\frac{d^2F}{dy^2}\right] \tag{62}$$

or

$$\frac{d^2\psi}{dy^2} = y^2e^{-y^2/2}.F(y) - e^{-y^2/2}.F(y) - 2y.e^{-y^2/2}\frac{dF}{dy} + e^{-y^2/2}\frac{d^2F}{dy^2} \tag{63}$$

or

$$\frac{d^2\psi}{dy^2} = \left[\frac{d^2F}{dy^2} - 2y.\frac{dF}{dy} + (y^2 - 1)\,F\right]\, e^{-y^2/2} \tag{64}$$

Now, after using equation (60) and equation (64) in equation (56), we get

$$\left[\frac{d^2F}{dy^2} - 2y.\frac{dF}{dy} + (y^2 - 1)\,F\right]\, e^{-y^2/2} + \left(\frac{\alpha}{\beta} - y^2\right)F(y)\, e^{-y^2/2} = 0 \tag{65}$$

or

$$\left[\frac{d^2F}{dy^2} - 2y.\frac{dF}{dy} + \left(\frac{\alpha}{\beta} - 1\right)\,F(y)\right]\, e^{-y^2/2} = 0 \tag{66}$$

Now because of the quantity $e^{-y^2/2}$ will be zero only at $y = \pm\infty$, the sum of the terms present in the bracket must be zero at normal *y*-values i.e.

$$\frac{d^2F}{dy^2} - 2y.\frac{dF}{dy} + \left(\frac{\alpha}{\beta} - 1\right) F(y) \ = 0 \tag{67}$$

The above differential equation is a “Hermit differential equation” and can be solved to find the expression for the “unknown” function $F(y)$. The solution of equation (67) can be obtained by the polynomial method by expressing the function $F(y)$ as a power series in terms of variable ‘y’.

$$F = a_0 + a_1y + a_2y^2 + a_3y^3 + a_4y^4 \dots \dots \dots \dots \tag{68}$$

Differentiating the above equation, we get

$$\frac{dF}{dy} = a_1 + 2a_2y + 3a_3y^2 + 4a_4y^3 \dots \dots \dots \dots \tag{69}$$

Differentiating again, we get

$$\frac{d^2F}{dy^2} = 2a_2 + 6a_3y + 12a_4y^2 \dots \dots \dots \dots \tag{70}$$

Using equation (68-70) in equation (67), we get

$$\begin{aligned}[2a_2 + 6a_3y + 12a_4y^2 \dots] - 2y[a_1 + 2a_2y + 3a_3y^2 + 4a_4y^3 \dots] \\ + \left(\frac{\alpha}{\beta} - 1\right)[a_0 + a_1y + a_2y^2 + a_3y^3 + a_4y^4 \dots] = 0\end{aligned} \tag{71}$$

or

$$\begin{aligned}[2a_2 + 6a_3y + 12a_4y^2 \dots] - [2a_1y + 4a_2y^2 + 6a_3y^3 + 8a_4y^4 \dots] \\ + \left[\left(\frac{\alpha}{\beta} - 1\right)a_0 + \left(\frac{\alpha}{\beta} - 1\right)a_1y + \left(\frac{\alpha}{\beta} - 1\right)a_2y^2 + \cdots\right] = 0\end{aligned} \tag{72}$$

After further rearranging

$$\begin{aligned}\left[2a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_0\right] + \left[6a_3y - 2a_1y + \left(\frac{\alpha}{\beta} - 1\right)a_1y\right] \\ + \left[12a_4y^2 - 4a_2y^2 + \left(\frac{\alpha}{\beta} - 1\right)a_2y^2\right] + \cdots = 0\end{aligned} \tag{73}$$

or

$$\begin{aligned}\left[2a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_0\right] + \left[6a_3 - 2a_1 + \left(\frac{\alpha}{\beta} - 1\right)a_1\right]y \\ + \left[12a_4 - 4a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_2\right]y^2 + \cdots = 0\end{aligned} \tag{74}$$

The above equation is valid only when coefficients of the individual power of y are zero i.e.

For y^0

$$2a_2 + \left(\frac{\alpha}{\beta} - 1\right) a_0 = 0 \tag{75}$$

For y^1

$$6a_3 + \left(\frac{\alpha}{\beta} - 1 - 2\right) a_1 = 0 \tag{76}$$

For y^2

$$12a_4 + \left(\frac{\alpha}{\beta} - 1 - 4\right) a_2 = 0 \tag{77}$$

Similarly, for y^k

$$(k+1)(k+2)a_{k+2} + \left(\frac{\alpha}{\beta} - 1 - 2k\right) a_k = 0 \tag{78}$$

The above equation can be rearranged for the coefficient a_{k+2} i.e.

$$a_{k+2} = -\frac{\left(\frac{\alpha}{\beta} - 1 - 2k\right) a_k}{(k+1)(k+2)} \tag{79}$$

Where k is an integer. The expression given above is popularly known as the recursion formula, and allows one to determine the coefficient a_{k+2} of the term y^{k+2} in terms of a_k-coefficient of the y^k term. In simple words, we can calculate a_2, a_4, a_6 etc. in terms of a_0 if we set $a_1 = 0$; likewise, the coefficients a_3, a_5, a_7 etc. can be obtained in terms of a_1 if we set $a_0 = 0$.

However, the power series will still be made up of the infinite number of terms, making function $F(y)$ infinite at $y = \infty$. Therefore, we must restrict the number of terms so that the function remains acceptable. This can be made possible if, at a certain value of $k = n$, the numerator in equation (79) becomes zero i.e.

$$\frac{\alpha}{\beta} - 1 - 2k = \frac{\alpha}{\beta} - 1 - 2n = 0 \tag{80}$$

or

$$\frac{\alpha}{\beta} = 2n + 1 \tag{81}$$

Where $n = 0, 1, 2, 3$ .... etc. The series that is obtained so contains a finite number of terms and is called as "Hermit polynomial" i.e. $H_n(y)$. All these Hermit polynomials are generating-function defined and are given below.

$$H_n(y) = (-1)^n . e^{y^2} . \frac{d^n}{dy^n} . e^{-y^2} \tag{82}$$

For instance, some of the Hermit polynomials for *n* = 0, 1 and 2 are calculated as given below.

For *n* = 0, the equation (82) becomes

$$H_0(y) = (-1)^0 . e^{y^2} . \frac{d^0}{dy^0} . e^{-y^2} \tag{83}$$

$$H_0(y) = 1. e^{y^2} . 1. e^{-y^2} = e^{y^2-y^2} = e^0 \tag{84}$$

$$H_0(y) = 1 \tag{85}$$

For *n* = 1, the equation (82) becomes

$$H_1(y) = (-1)^1 . e^{y^2} . \frac{d}{dy} . e^{-y^2} \tag{86}$$

$$H_1(y) = (-1). e^{y^2} . (-2y). e^{-y^2} \tag{87}$$

$$H_1(y) = (-1). (-2y). e^{y^2-y^2} = 2y. e^0 \tag{88}$$

$$H_1(y) = 2y \tag{89}$$

For *n* = 2, the equation (82) becomes

$$H_2(y) = (-1)^2 . e^{y^2} . \frac{d^2}{dy^2} . e^{-y^2} \tag{90}$$

$$H_2(y) = (+1). e^{y^2} . \frac{d}{dy} . -2y. e^{-y^2} \tag{91}$$

$$H_2(y) = e^{y^2}\left[(-2y)e^{-y^2}(-2y) + (-2)e^{-y^2}\right] \tag{92}$$

$$H_2(y) = e^{y^2}\left[(4y^2 - 2)e^{-y^2}\right] \tag{93}$$

$$H_2(y) = (4y^2 - 2)e^{y^2-y^2} = (4y^2 - 2)e^0 \tag{94}$$

$$H_2(y) = 4y^2 - 2 \tag{95}$$

The total wavefunction: After knowing the unknown part *F*(*y*), the complete eigenfunction for a simple harmonic oscillator in the quantum mechanical world can be written as

$$\psi_n(y) = N_n H_n(y)\, e^{-y^2/2} \tag{96}$$

Where N_n is the normalization constant for *n*th state while the symbol $H_n(y)$ represents the Hermit polynomial of nth order in terms of *y*-variable. Once the wavefunctions are obtained in terms of *y*, they can easily be converted into *x*-dependent function by simply putting $y = \sqrt{\beta}x$.

Table 1. Eigenfunctions representing various quantum mechanical states of a simple harmonic oscillator.

α/*β*	*n*	*H_n*(*y*)	*ψ_n*(*y*)	*ψ_n*(*x*)
1	0	1	$N_0 . e^{-y^2/2}$	$N_0 . e^{-\beta x^2/2}$
3	1	$2y$	$N_1 . 2y . e^{-y^2/2}$	$N_1(2\sqrt{\beta}x)e^{-\beta x^2/2}$
5	2	$4y^2 - 2$	$N_2(4y^2 - 2)e^{-y^2/2}$	$N_2(4\beta x^2 - 2)e^{-\beta x^2/2}$
7	3	$8y^3 - 12y$	$N_3(8y^3 - 12y)e^{-y^2/2}$	$N_3(8\beta^{3/2}x^3 - 12\sqrt{\beta}x)e^{-\beta x^2/2}$

The normalization constant can be obtained by recalling the fact that every wave function must describe the corresponding state completely. This means that square of wave function under consideration over the whole configurational space must be equal to unity i.e.

$$\int_{-\infty}^{+\infty} \psi_n^2\, dx = \int_{-\infty}^{+\infty} \left[N_n H_n(x)\, e^{-\frac{\beta x^2}{2}}\right]^2 = 1 \tag{97}$$

$$\frac{N_n^2}{\sqrt{\beta}}\, 2^n\, n!\, \sqrt{\pi} = 1 \tag{98}$$

$$N_n^2 = \frac{\sqrt{\beta}}{2^n\, n!\, \sqrt{\pi}} \tag{99}$$

$$N_n = \left(\frac{\sqrt{\beta}}{2^n\, n!\, \sqrt{\pi}}\right)^{1/2} \tag{100}$$

It can be clearly seen from the above equation that the normalization consents are different for different states. For instance, some of the normalization constants are given below.

$$N_0 = \left(\frac{\sqrt{\beta}}{2^0\, 0!\, \sqrt{\pi}}\right)^{1/2} = \left(\frac{\beta}{\pi}\right)^{1/4} \tag{101}$$

$$N_1 = \left(\frac{\sqrt{\beta}}{2^1\, 1!\, \sqrt{\pi}}\right)^{1/2} = \frac{1}{\sqrt{2}}\left(\frac{\beta}{\pi}\right)^{1/4} \tag{102}$$

$$N_2 = \left(\frac{\sqrt{\beta}}{2^2\, 2!\, \sqrt{\pi}}\right)^{1/2} = \frac{1}{2\sqrt{2}}\left(\frac{\beta}{\pi}\right)^{1/4} \tag{103}$$

The eigenvalues of energy: Since we have already proved that the total wavefunction for a simple harmonic oscillator is acceptable only when the following condition of equation (81) is satisfied i.e.

$$\frac{\alpha}{\beta} = 2n + 1 \tag{104}$$

Furthermore, we also know that

$$\alpha = \frac{8\pi^2 mE}{h^2} \quad and \quad \beta = \frac{4\pi^2 m\nu}{h} \tag{105}$$

After using the value of α and β, the equation (104) take the form

$$\frac{8\pi^2 mE}{h^2} \times \frac{h}{4\pi^2 m\nu} = 2n + 1 \tag{106}$$

or

$$E = (2n + 1)\frac{4\pi^2 m\nu}{h} \times \frac{h^2}{8\pi^2 m} \tag{107}$$

or

$$E_n = (2n + 1)\frac{h\nu}{2} \tag{108}$$

or

$$E_n = \left(n + \frac{1}{2}\right)h\nu \tag{109}$$

Where n is a discrete variable (vibrational quantum number) with values 0, 1, 2, 3…∞. The symbol E_n represents the vibrational energies of different vibrational states.

- ***The Classical and Quantum-Mechanical Interpretation of Vibrational States***

In order to have a relative interpretation of vibrational states in the classical and quantum-mechanical framework, recall the classical expression for potential energy curve of simple harmonic oscillator i.e.

$$V = \frac{1}{2}kx^2 \tag{110}$$

Where k is the force constant and x is the displacement induced. Also, the general expressions for all the vibrational states and corresponding energies are

$$\psi_n(x) = N_n H_n(x)\, e^{-\beta x^2} \quad and \quad E_n = \left(n + \frac{1}{2}\right)h\nu \tag{111}$$

Where N_n and $H_n(x)$ are the normalization constant and Hermit polynomial for nth state.

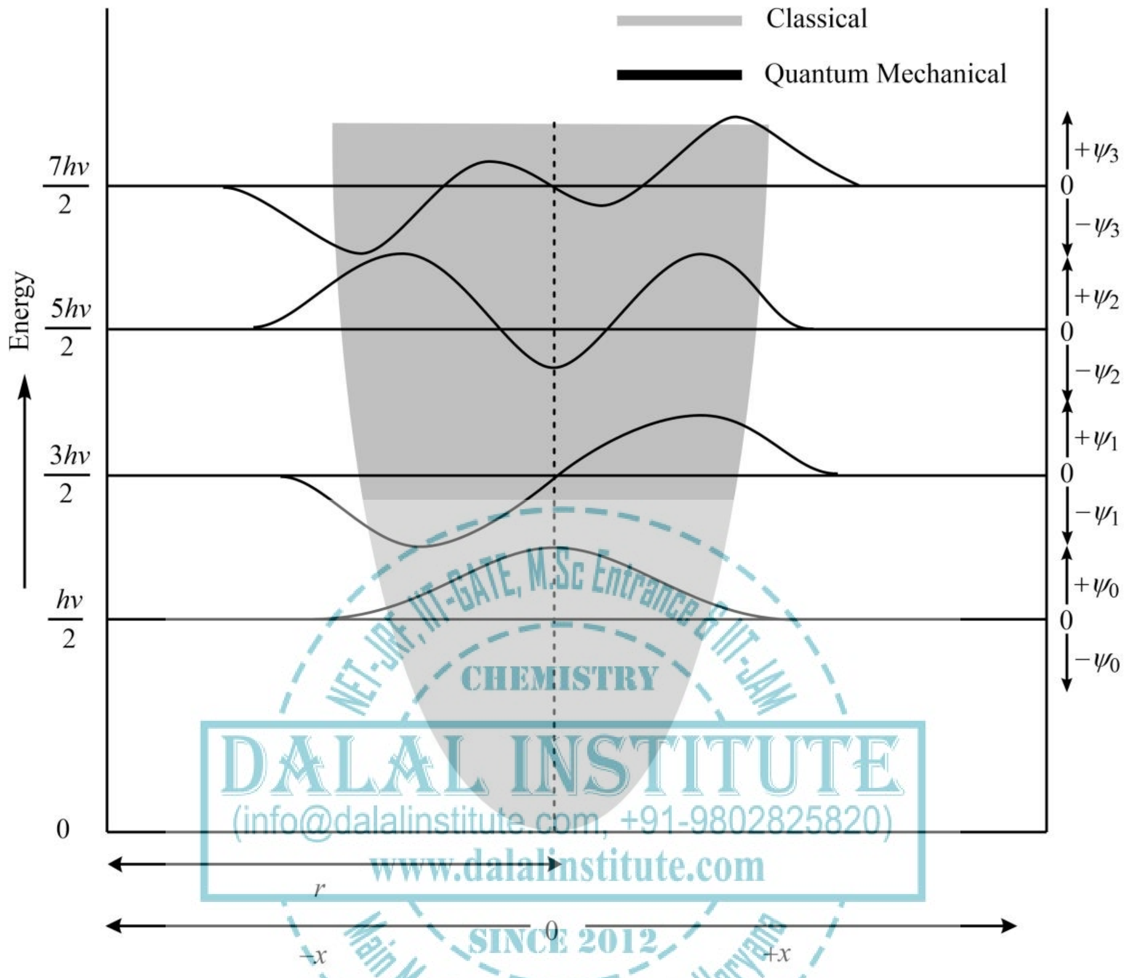


Figure 4. The depiction of various vibrational states of a simple harmonic oscillator in the classical and quantum mechanical framework.

After looking at the figure given above, the following points can be made about the differences and similarities in the classical and quantum mechanical oscillators.

i) It can be clearly seen that the energy levels of a classical oscillator are continuous including zero while the energy levels the quantum-mechanical analog is discontinuous with zero-point energy of $hv/2$. In other words, the classical oscillator can have zero vibrational energy but the vibrational motion cannot be ceased completely in case of the quantum mechanical version of the simple harmonic oscillator.

ii) There is always a limit over the compression as well as over the expansion in the classical oscillator to have a certain amount of energy. On the other hand, since the function becomes zero only at infinite displacement, there is no limit over the compression and expansion in the quantum oscillator theoretically.

iii) The classical oscillator spends more time in the extreme states i.e. fully compressed and fully expended, and spends the least time with equilibrium bond length. As far as the ground vibrational state of the quantum mechanical oscillator is concerned, it spends most time with equilibrium (because the function is maximum for r_{equ} or $x = 0$), and probability to spend time in compressed and expended mode decreases as the magnitude of compression and expansion increases.

iv) If we plot the square of wavefunction vs displacement incorporated, it can be clearly seen that the most probable bond lengths shift towards the compressed and expanded states as the quantum number increases which is in accordance with the Bohr's correspondence principle.

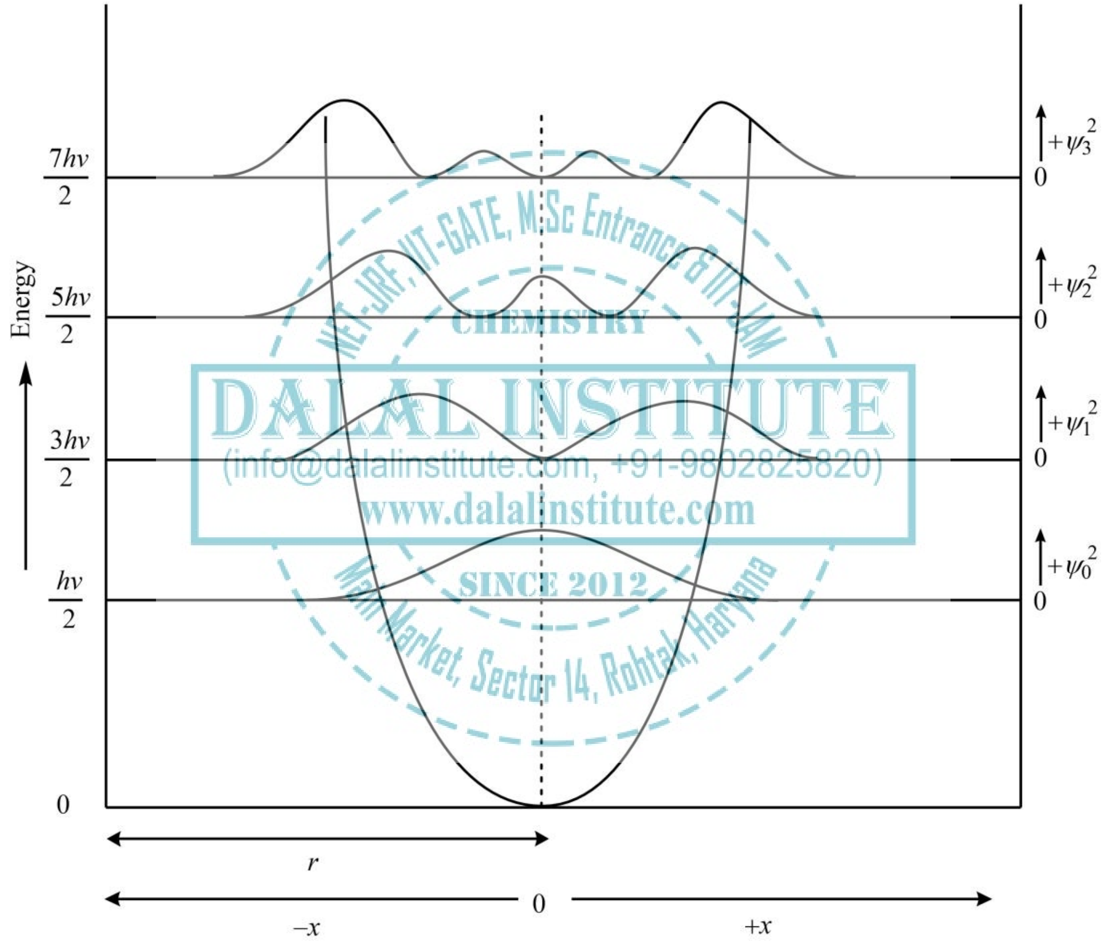


Figure 5. The variation of probability as a function of bond length or displacement in different vibrational states of a simple harmonic oscillator.

Furthermore, it also worthy to note that all ψ_{even} states are symmetric while all ψ_{odd} wavefunctions are asymmetric in nature with n nodes.

❖ Zero Point Energy of a Particle Possessing Harmonic Motion and Its Consequence

In order to understand the minimum or the zero-point energy of a simple harmonic oscillator, recall the general wavefunction representing all the vibrational states of a simple harmonic oscillator i.e.

$$\psi_n(y) = N_n H_n(y)\, e^{-y^2/2} \tag{112}$$

Where y is a displacement-based variable with a value equal to $\sqrt{\beta}x$. The constant β depends upon the reduced mass of the oscillator (m) and equilibrium vibrational frequency (v) as

$$\beta = \frac{4\pi^2 mv}{h} \tag{113}$$

The symbol N_n and $H_n(y)$ are the normalization constant and Hermit polynomial for nth state i.e.

$$N_n = \left(\frac{\sqrt{\beta}}{2^n\, n!\, \sqrt{\pi}}\right)^{1/2} \quad and \quad H_n(y) = (-1)^n . e^{y^2} . \frac{d^n}{dy^n} . e^{-y^2} \tag{114}$$

Also, the general expression for the energies is given below.

$$E_n = \left(n + \frac{1}{2}\right) hv \tag{115}$$

Now, for the ground vibrational state ($n = 0$), N_0 and $H_0(y)$ can be obtained from equation (114) i.e.

$$N_0 = \left(\frac{\beta}{\pi}\right)^{1/4} \quad and \quad H_0(y) = 1 \tag{116}$$

After using the values of y, N_0 and $H_0(y)$ in equation (112), the ground state function becomes

$$\psi_0(x) = \left(\frac{\beta}{\pi}\right)^{1/4} .1. e^{-\beta x^2/2} \tag{117}$$

Hence, the ground state wave function does not collapse at $n = 0$, which means that corresponding energy can also be obtained by putting $n = 0$ in equation (115) i.e.

$$E_0 = \left(0 + \frac{1}{2}\right) hv \tag{118}$$

or

$$E_0 = \frac{1}{2} hv \tag{119}$$

The above equation gives the minimum energy which is always possessed by a simple harmonic oscillator.

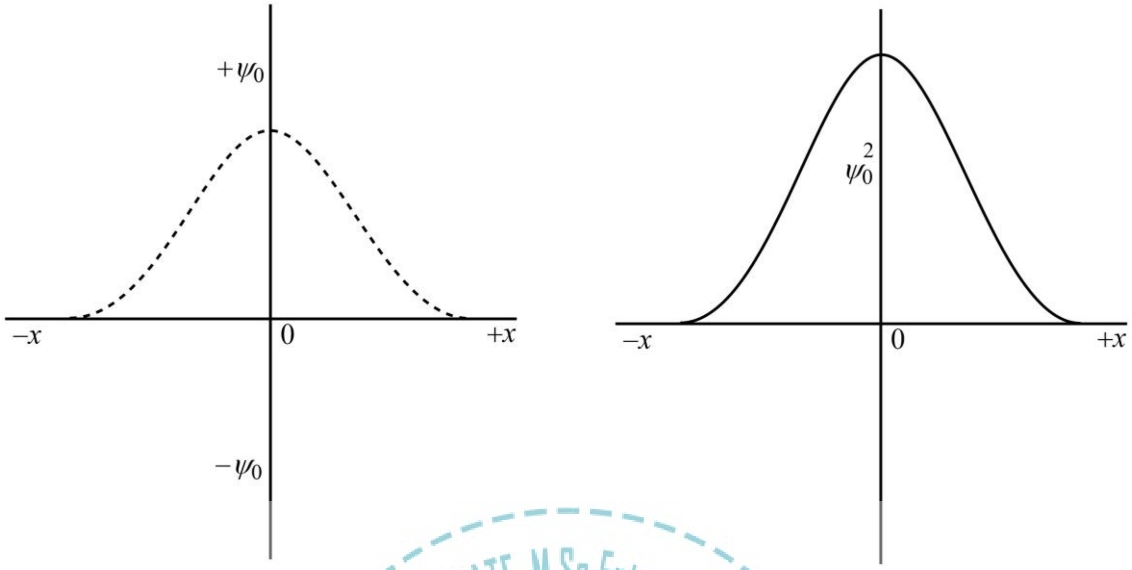


Figure 6. The variation of ground vibrational wavefunction and probability as a function of bond length or displacement in a simple harmonic oscillator.

It is well-known that the classical oscillator spends more time in the extreme states i.e. fully compressed and fully expended, and spends the least time with equilibrium bond length. However, as far as the ground vibrational state of the quantum mechanical oscillator is concerned, it spends the most time with equilibrium (because the function is maximum for r_{equ} or $x = 0$), and probability to spend time in compressed and expended mode decreases as the magnitude of compression and expansion increases. Moreover, there is always a limit over the compression as well as over the expansion in the classical oscillator to have a certain amount of energy; however, since the function becomes zero only at infinite displacement, there is no limit over the compression and expansion in the quantum oscillator theoretically.

It is also worthy to note that the energy given by the equation (119) is in joules. However, in many textbooks or papers, it is also reported in terms of wavenumbers. To do so, we need first put the value of frequency as $\nu = c/\lambda$ and then $1/\lambda = \bar{\nu}$ in the equation (119) i.e.

$$E_0 = \frac{1}{2}h\frac{c}{\lambda} = \frac{1}{2}hc\bar{\nu} \tag{119}$$

Where c is the velocity of light. Now, to convert the zero-point energy in wavenumbers, divide equation (119) by hc i.e.

$$\bar{\nu}_0 = \frac{1}{2}\frac{hc\bar{\nu}}{hc} = \frac{\bar{\nu}}{2} \tag{120}$$

❖ Schrodinger Wave Equation for Three Dimensional Rigid Rotator

In order to study the rotational behavior of a diatomic molecule, consider a system two masses m_1 and m_2 joined by a rigid rod of length "*r*". Now assume that this dumbbell type geometry rotates about an axis that is perpendicular to *r* and passes through the center of mass.

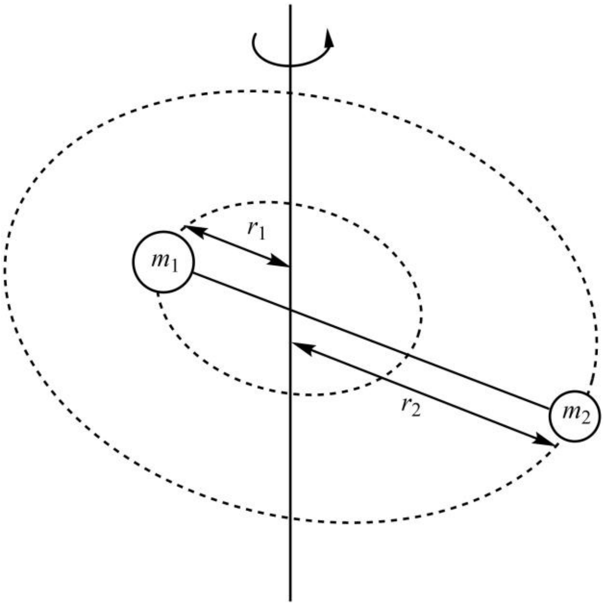


Figure 7. The pictorial representation of the diatomic rigid rotator in classical mechanics.

If v_1 and v_2 are the velocities of the mass m_1 and m_2 revolving about the axis of rotation, the total kinetic energy (*T*) of the rotator can be given by the following relation.

$$T = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 \tag{121}$$

Since we know that linear velocity v is simply equal to the angular velocity ω multiplied by the radius of rotation *r* i.e. $v = \omega r$, the equation (121) takes the form

$$T = \frac{1}{2}m_1(r_1\omega)^2 + \frac{1}{2}m_2(r_2\omega)^2 \tag{122}$$

$$T = \frac{1}{2}(m_1r_1^2 + m_2r_2^2)\omega^2 \tag{123}$$

$$T = \frac{1}{2}I\omega^2 \tag{123}$$

Where *I* is the moment of inertia with definition $I = \sum m_ir_i^2$. Furthermore, we know from mass-center that

$$m_1 r_1 = m_2 r_2 \tag{124}$$

Now since $r = r_1 + r_2$, we rearrange equation (124) to give

$$r_1 = \frac{m_2}{m_1 + m_2} r \qquad and \qquad r_2 = \frac{m_1}{m_1 + m_2} r \tag{125}$$

In the two-mass system $I = m_1 r_1^2 + m_2 r_2^2$, so have

$$I = m_1 \left(\frac{m_2}{m_1 + m_2} r\right)^2 + m_2 \left(\frac{m_1}{m_1 + m_2} r\right)^2 \tag{126}$$

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r^2 \tag{127}$$

$$I = \mu r^2 \tag{128}$$

Where $\mu = m_1 m_2 / m_1 + m_2$ is the reduced mass of the rigid diatomic system. Since we that the kinetic energy and linear moment of a particle of mass m moving with velocity v are

$$T = \frac{1}{2} m v^2 \qquad and \qquad p = mv \tag{129}$$

The counterparts in the angular motion can be written as

$$T = \frac{1}{2} I \omega^2 \qquad and \qquad L = I\omega \tag{130}$$

Multiplying and dividing the rotational kinetic energy by I, we have

$$T = \frac{I^2 \omega^2}{2I} = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{131}$$

It is clear from the above equation that the kinetic energy of a classical rotator can have any value because the value-domain of angular velocity is continuous. Moreover, as no external force is working on the rotator, the potential can be set to zero. In other words, the Hamiltonian for diatomic rigid rotator can be given as

$$\hat{H} = \hat{T} + \hat{V} \tag{132}$$

$$\hat{H} = \frac{\hat{L}^2}{2I} + 0 \tag{133}$$

The expression for the operator $\hat{L}^2$ in polar coordinates is

$$L^2 = -\frac{h^2}{4\pi^2} \left[\frac{1}{Sin\,\theta} \frac{\partial}{\partial\theta} \left(Sin\,\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta} \frac{\partial}{\partial\phi}\right] \tag{134}$$

Using equation (134) in equation (133), the Hamiltonian operator takes the form

$$\hat{H} = -\frac{h^2}{8\pi^2 I}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial}{\partial\phi}\right] + 0 \tag{135}$$

Now, let ψ be the function that describes all the rotational states of the diatomic rigid rotator. The operation of Hamiltonian operator over ψ 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

$$\hat{H}\psi = E\psi \tag{136}$$

After putting the expression of the Hamiltonian operator from equation (135) in equation (136), we get

$$-\frac{h^2}{8\pi^2 I}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial}{\partial\phi}\right]\psi = E\psi \tag{137}$$

or

$$-\frac{h^2}{8\pi^2 I}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi}\right] = E\psi \tag{138}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi} = -\frac{8\pi^2 IE\psi}{h^2} \tag{139}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi} + \frac{8\pi^2 IE\psi}{h^2} = 0 \tag{140}$$

The above differential equation contains two variable ϕ and θ, and therefore, is difficult to solve. Thus, we need to use the same mathematical technique we used to study particle in a 3-dimensional box i.e. the separation of variables. To do so, consider the total wavefunction as the product of two independent, one θ-dependent and other as a ϕ-dependent function only i.e.

$$\psi(\theta,\phi) = \psi(\theta) \times \psi(\phi) = \Theta \times \Phi \tag{141}$$

After putting the value of equation (141) in equation (140), we get

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta\Phi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\Theta\Phi}{\partial\phi} + \frac{8\pi^2 IE\Theta\Phi}{h^2} = 0 \tag{142}$$

Since the first and second terms contain the partial derivatives w.r.t. θ and ϕ, respectively; function Φ and Θ must be kept constant correspondingly, i.e.,

$$\Phi\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\frac{1}{Sin^2\,\theta}\frac{\partial\Phi}{\partial\phi}+\frac{8\pi^2 IE\Theta\Phi}{h^2}=0 \tag{143}$$

Dividing the above equation by $\Theta\Phi$, the equation (143) takes the form

$$\frac{1}{\Theta}\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{Sin^2\,\theta}\frac{\partial\Phi}{\partial\phi}+\frac{8\pi^2 IE}{h^2}=0 \tag{144}$$

After multiplying equation (144) by $Sin^2\theta$, we get

$$\frac{Sin\,\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial\Phi}{\partial\phi}+\frac{8\pi^2 IE}{h^2}Sin^2\theta=0 \tag{145}$$

Rearranging

$$\frac{Sin\,\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 IE}{h^2}Sin^2\theta=-\frac{1}{\Phi}\frac{\partial\Phi}{\partial\phi} \tag{146}$$

At this point, we can set both sides equal to constant m^2 i.e.

$$\frac{Sin\,\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 IE}{h^2}Sin^2\theta=m^2=-\frac{1}{\Phi}\frac{\partial\Phi}{\partial\phi} \tag{147}$$

The equation (147) can be fragmented into two equations, each containing a single variable i.e.

$$\frac{\partial\Phi}{\partial\phi}+m^2\Phi=0 \tag{148}$$

And

$$Sin\,\theta\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\frac{8\pi^2 IE}{h^2}Sin^2\theta-m^2\Theta=0 \tag{149}$$

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

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\frac{8\pi^2 IE}{h^2}-\frac{m^2\Theta}{Sin^2\theta}=0 \tag{150}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\frac{8\pi^2 IE}{h^2}-\frac{m^2}{Sin^2\theta}\right)\Theta=0 \tag{151}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{Sin^2\theta}\right)\Theta=0 \tag{152}$$

Where the constant β is defined as

$$\beta = \frac{8\pi^2 IE}{h^2} \tag{153}$$

The solution of Φ equation: Recall the differential equation obtained after separation of variables having ϕ dependence i.e.

$$\frac{\partial \Phi}{\partial \phi} + m^2 \Phi = 0 \tag{154}$$

The general solution of such an equation is

$$\Phi(\phi) = N e^{im\phi} \tag{155}$$

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 the point under consideration should remain the same i.e.

$$\Phi(\phi + 2\pi) = \Phi(\phi) \tag{156}$$

Therefore

$$N e^{im(\phi+2\pi)} = N e^{im\phi} \tag{157}$$

or

$$e^{im(\phi+2\pi)} = e^{im\phi} \tag{158}$$

$$e^{im\phi} . e^{im2\pi} = e^{im\phi} \tag{159}$$

$$e^{im2\pi} = e^{im\phi} e^{-im\phi} \tag{160}$$

$$e^{im2\pi} = e^{im\phi - im\phi} = e^0 \tag{161}$$

$$e^{im2\pi} = 1 \tag{162}$$

Since we know from the Euler's expansion $e^{ix} = Cos\ x + i\ Sin\ x$, the equation (162) takes the form

$$e^{im2\pi} = Cos\ 2\pi m + i\ Sin\ 2\pi m \tag{163}$$

After putting the value of equation (163) in equation (162), we get

$$Cos\ 2\pi m + i\ Sin\ 2\pi m = 1 \tag{164}$$

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.

$$\int_0^{2\pi} \Phi^*\Phi \, d\phi = 1 \tag{165}$$

or

$$N^2 \int_0^{2\pi} e^{im\phi}.e^{-im\phi} \, d\phi = 1 \tag{166}$$

$$N^2 \int_0^{2\pi} e^{im\phi-im\phi} \, d\phi = N^2 \int_0^{2\pi} e^0 \, d\phi = 1 \tag{167}$$

$$N^2[\phi]_0^{2\pi} = N^2[2\pi] = 1 \tag{168}$$

$$N = \sqrt{\frac{1}{2\pi}} \tag{169}$$

After using the value of normalization constant in equation (155), we get

$$\Phi(\phi) = \sqrt{\frac{1}{2\pi}} e^{\pm im\phi} \tag{170}$$

Solution of Θ equation: Recall the differential equation obtained after separation of variables having θ dependence i.e.

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{Sin^2\theta}\right)\Theta = 0 \tag{171}$$

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

$$Sin^2\theta + Cos^2\theta = 1 \tag{172}$$

$$Sin^2\theta = 1 - Cos^2\theta \tag{173}$$

$$Sin\,\theta = \sqrt{1 - Cos^2\theta} \tag{174}$$

$$Sin\,\theta = \sqrt{1 - x^2} \tag{175}$$

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

$$\frac{\partial x}{\partial \theta} = -Sin\, \theta \tag{176}$$

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

$$\frac{\partial \Theta}{\partial \theta} = \frac{\partial \Theta}{\partial x} . \frac{\partial x}{\partial \theta} \tag{177}$$

After putting the values of $\partial x/\partial \theta$ from equation (176) in equation (177), we get

$$\frac{\partial \Theta}{\partial \theta} = -Sin\, \theta \frac{\partial \Theta}{\partial x} \tag{178}$$

After removing Θ from both sides

$$\frac{\partial}{\partial \theta} = -Sin\, \theta \frac{\partial}{\partial x} \tag{179}$$

Multiplying both sides of equation (178) by $Sin\, \theta$, we have

$$Sin\, \theta \frac{\partial \Theta}{\partial \theta} = -Sin^2\, \theta \frac{\partial \Theta}{\partial x} \tag{180}$$

$$Sin\, \theta \frac{\partial \Theta}{\partial \theta} = -(1 - x^2) \frac{\partial \Theta}{\partial x} \tag{181}$$

Now, after putting the values of equation (179) and (181) in equation (171), we get

$$\frac{1}{Sin\, \theta}\left(-Sin\, \theta \frac{\partial}{\partial x}\right)\left[-(1 - x^2)\frac{\partial \Theta}{\partial x}\right] + \left(\beta - \frac{m^2}{1 - x^2}\right)\Theta = 0 \tag{182}$$

or

$$\frac{\partial}{\partial x}\left[(1 - x^2)\frac{\partial \Theta}{\partial x}\right] + \left(\beta - \frac{m^2}{1 - x^2}\right)\Theta = 0 \tag{183}$$

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.

$$\Theta(\theta) = (1 - x^2)^{\frac{m}{2}} . X(x) \tag{184}$$

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

$$\frac{\partial \Theta}{\partial x} = -mx(1 - x^2)^{\frac{m}{2} - 1} . X + (1 - x^2)^{\frac{m}{2}} . \frac{dX}{dx} \tag{185}$$

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

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial\Theta}{\partial x}\right]=\frac{\partial}{\partial x}\left[-mx(1-x^2)^{\frac{m}{2}}.X+(1-x^2)^{\frac{m}{2}+1}.\frac{dX}{dx}\right] \tag{186}$$

$$\begin{aligned}=\left[-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{\frac{m}{2}-1}\right]X-\left[2x(m+1)(1-x^2)^{\frac{m}{2}}\right]X'\\+\left[(1-x^2)^{\frac{m}{2}+1}\right]X''\end{aligned} \tag{187}$$

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 (184) and equation (187) in equation (183), we get

$$\begin{aligned}\left[-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{\frac{m}{2}-1}\right]X-\left[2x(m+1)(1-x^2)^{\frac{m}{2}}\right]X'\\+\left[(1-x^2)^{\frac{m}{2}+1}\right]X''+\left(\beta-\frac{m^2}{1-x^2}\right)(1-x^2)^{\frac{m}{2}}.X=0\end{aligned} \tag{188}$$

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

$$(1-x^2)X''-2(m+1)xX'+[\beta-m(m+1)]X=0 \tag{189}$$

or

$$(1-x^2)X''-2\alpha xX'+\lambda X=0 \tag{190}$$

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.

$$X=a_0+a_1x+a_2x^2+a_3x^3\dots\dots\dots\dots \tag{191}$$

$$X'=a_1+2a_2x+3a_3x^2\dots\dots\dots\dots \tag{192}$$

$$X''=2a_2+6a_3x+12a_4x^2\dots\dots\dots\dots \tag{193}$$

Putting values of equation (191-193) in equation (190), we get

$$\begin{aligned}(1-x^2)(2a_2+6a_3x+12a_4x^2+20a_5x^3)\ -2\alpha x(a_1+2a_2x+3a_3x^2+4a_4x^3)\\+\lambda(a_0+a_1x+a_2x^2+a_3x^3)=0\end{aligned} \tag{194}$$

or

$$(2a_2+\lambda a_0)+[6a_3+(\lambda-2\alpha)a_1]x+[12a_4+(\lambda-2\alpha-2)a_2]x^2\dots\dots\dots=0 \tag{195}$$

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.

$$(n+1)(n+2)a_{n+2}+[\lambda-2n\alpha-n(n-1)]a_n=0 \tag{196}$$

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

$$a_{n+2} = \frac{2n\alpha + n(n-1) - \lambda}{(n+1)(n+2)} a_n \tag{197}$$

After putting values of α and λ in equation (197), we get

$$\frac{a_{n+2}}{a_n} = \frac{(n+m)(n+m+1) - \beta}{(n+1)(n+2)} \tag{198}$$

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.

$$(n+m)(n+m+1) - \beta = 0 \tag{199}$$

$$\beta = (n+m)(n+m+1) \tag{200}$$

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.

$$\beta = l(l+1) \tag{201}$$

Where $l = 0, 1, 2, 3$ etc. After putting the value of *β* from equation (201) in equation (183), we get

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial \Theta}{\partial x}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]\Theta = 0 \tag{202}$$

The general solution of equation (202) is

$$\Theta = NP_l^m(x) = NP_l^m(Cos\,\theta) \tag{203}$$

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

$$P_l^m(x) = (1-x^2)^{m/2}\frac{d^m P_l(x)}{dx^m} \tag{204}$$

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

$$P_l(x) = \frac{1}{2^l\, l!}\frac{d^l (x^2-1)^l}{dx^l} \tag{205}$$

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.

$$\int_{-1}^{+1} P_k^m(x)\, P_l^m(x) = 0 \qquad if\ k \neq l \tag{206}$$

$$\int_{-1}^{+1} P_k^m(x)\, P_l^m(x) = \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} \qquad if\ k = l \tag{207}$$

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

$$\int_{-1}^{+1} \Theta_{m,l}\, \Theta_{m,l}^{*}(d\theta) = 1 \tag{208}$$

$$N^2 \int_{-1}^{+1} P_k^m(x)\, P_l^m(x)\, dx = 1 \tag{209}$$

After solving the integral, we get

$$N^2 . \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} = 1 \tag{210}$$

$$N = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \tag{211}$$

Using the value of normalization constant in equation (203), we get

$$\Theta(\theta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\, \theta) \tag{212}$$

The complete eigenfunction of rigid rotator: The total eigenfunction for the rigid rotator now can be obtained by simply multiplying the solution of ϕ-dependent and θ-dependent differential equations i.e. equation (170) and equation (203).

$$\psi_{l,m}(\theta,\phi) = \Theta_{l,m}(\theta)\Phi_m(\phi) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\, \theta). \sqrt{\frac{1}{2\pi}} e^{\pm im\phi} \tag{213}$$

$$\psi_{l,m}(\theta,\phi) = \sqrt{\frac{1}{2\pi}} \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\, \theta). e^{\pm im\phi} \tag{214}$$

❖ Energy of Rigid Rotator

The energy of a rigid rotator can be understood only after considering its classical and quantum mechanical aspects. In the previous section of this chapter, we discussed the classical and quantum mechanical nature of the rigid rotator. consider a system two masses m_1 and m_2 joined by a rigid rod of length "*r*". Now assume that this dumbbell type geometry rotates about an axis that is perpendicular to *r* and passes through the center of mass.

➢ *The energy of Classical Rigid Rotator*

If v_1 and v_2 are the velocities of the mass m_1 and m_2 revolving about the axis of rotation, the total kinetic energy (*T*) of the rotator can be given by the following relation.

$$T = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 \tag{215}$$

Since we know that linear velocity v is simply equal to the angular velocity ω multiplied by the radius of rotation *r* i.e. $v = \omega r$, the equation (215) takes the form

$$T = \frac{1}{2}m_1(r_1\omega)^2 + \frac{1}{2}m_2(r_2\omega)^2 \tag{216}$$

$$T = \frac{1}{2}(m_1r_1^2 + m_2r_2^2)\omega^2 \tag{217}$$

$$T = \frac{1}{2}I\omega^2 \tag{218}$$

Where *I* is the moment of inertia equal with definition $I = \sum m_i r_i^2$. Furthermore, the value of I can also be written as

$$I = \left(\frac{m_1m_2}{m_1 + m_2}\right)r^2 \tag{219}$$

$$I = \mu r^2 \tag{220}$$

Where $\mu = m_1m_2/m_1 + m_2$ is the reduced mass of the rigid diatomic system. After multiplying and dividing the rotational kinetic energy by *I* i.e. equation (218), we have

$$T = \frac{I^2\omega^2}{2I} = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{221}$$

Where *L* is the angular momentum of the rotator. It is clear from the above equation that the kinetic energy of a classical rotator can have any value because the value-domain of angular velocity is continuous. Moreover, as now the external force is working on the rotator, the potential can be set to zero. Therefore, we can conclude that the total energy of a classical diatomic rigid rotator is given by equation (221).

- ***The energy of Quantum Mechanical Rigid Rotator***

In order to understand the energy of a quantum mechanical rigid rotator, recall the Schrodinger wave equation for the same first i.e.

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi}+\frac{8\pi^2IE\psi}{h^2}=0 \tag{222}$$

Where ψ is the mathematical expression defining various quantum mechanical states depending upon two variables θ and ϕ. During the course of the solution of the above equation, a constant β is defined for simplicity as given below.

$$\beta=\frac{8\pi^2IE}{h^2} \tag{223}$$

However, the boundary conditions that keep the function single-valued, continuous and finite; also proved that the constant β must satisfy the following condition also.

$$\beta=l(l+1) \tag{224}$$

Where $l=0,1,2,3,4$ etc. After equating the value of β from equation (223) and equation (224), we get

$$\frac{8\pi^2IE}{h^2}=l(l+1) \tag{225}$$

$$E_l=\frac{h^2}{8\pi^2I}\,l(l+1) \tag{226}$$

Hence, unlike the classical counterpart, the energy levels of quantum mechanical rigid rotators are discontinuous.

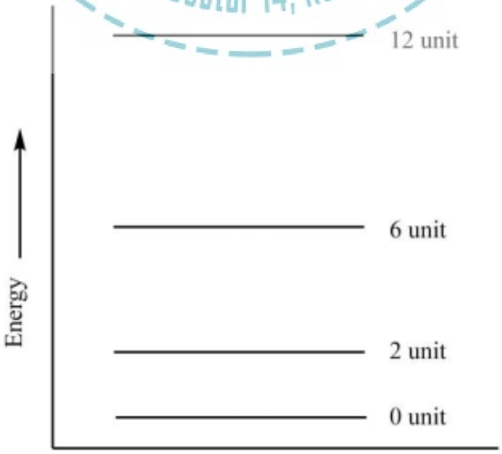


Figure 8. The energy level diagram of the diatomic rigid rotator in units of $h^2/8\pi^2I$.

❖ Space Quantization

The solution of the Schrodinger wave equation for the diatomic rigid rotator provided the mathematical descriptions of all the rotational states along with their corresponding energies. The general form of total eigenfunction for the rigid rotator is given below.

$$\psi_{l,m}(\theta,\phi) = \sqrt{\frac{1}{2\pi}}\sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}.P_l^m(Cos\,\theta).e^{\pm im\phi} \tag{227}$$

Where ψ is the mathematical expression defining various quantum mechanical states depending upon two variables θ and ϕ. Furthermore, the most important property of a rigid rotator after energy is the angular momentum which can be obtained using the last postulate of quantum mechanics i.e.

$$< L >= \oint \psi_{l,m}(\theta,\phi)\,\hat{L}\,\psi_{l,m}(\theta,\phi) \tag{228}$$

$$L_l = \sqrt{l(l+1)}\frac{h}{2\pi} \tag{229}$$

Alternatively, we know that the energies of various rotational states of rigid rotators are given by the following relation.

$$E = \frac{h^2}{8\pi^2 I}\,l(l+1) \tag{230}$$

Where $l = 0, 1, 2, 3, 4$ etc. Also, we know that the angular momentum and energy are related classically as

$$E = \frac{1}{2}\,I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{231}$$

or

$$L = \sqrt{2EI} \tag{232}$$

After using the value of energy from equation (230) into equation (232), we get

$$L_l = \sqrt{2I.\frac{h^2}{8\pi^2 I}\,l(l+1)} \tag{233}$$

or

$$L_l = \sqrt{\frac{h^2}{4\pi^2}\,l(l+1)} \tag{234}$$

or

$$L_l = \sqrt{l(l+1)}\frac{h}{2\pi} \tag{235}$$

Which is exactly the same as given by equation (229). Since $l = 0, 1, 2, 3, 4$ etc., the quantum mechanically allowed values of angular momentum (in the units of $h/2\pi$) are given below.

$$L_0 = \sqrt{0(0+1)}\text{ unit} = 0\text{ unit} \tag{236}$$

$$L_1 = \sqrt{1(1+1)}\text{ unit} = \sqrt{2}\text{ unit} \tag{237}$$

$$L_2 = \sqrt{2(2+1)}\text{ unit} = \sqrt{6}\text{ unit} \tag{238}$$

$$L_3 = \sqrt{3(3+1)}\text{ unit} = \sqrt{12}\text{ unit} \tag{239}$$

However, there is boundary condition in quantum mechanics that says that only integral effects are allowed reference direction if the angular momentum is generated by integral quantum number and half-integral effects are allowed in reference direction if the momentum is generated by half-integral quantum number.

This can be understood by taking the example of a diatomic molecule rotating in the first excited rotational state i.e. $l = 1$. The angular momentum of such a molecule will be $\sqrt{2}$ or 1.414 units. However, since this angular momentum is obtained using an integral quantum number ($l = 1$), only integral effects (i.e. $+1, 0, -1$) are allowed in reference direction. Now if *z*-axis is the reference direction, the effect of any vector $\vec{A}$ in the reference direction is calculated by multiplying its magnitude with the cosine of the angle it makes with reference direction.

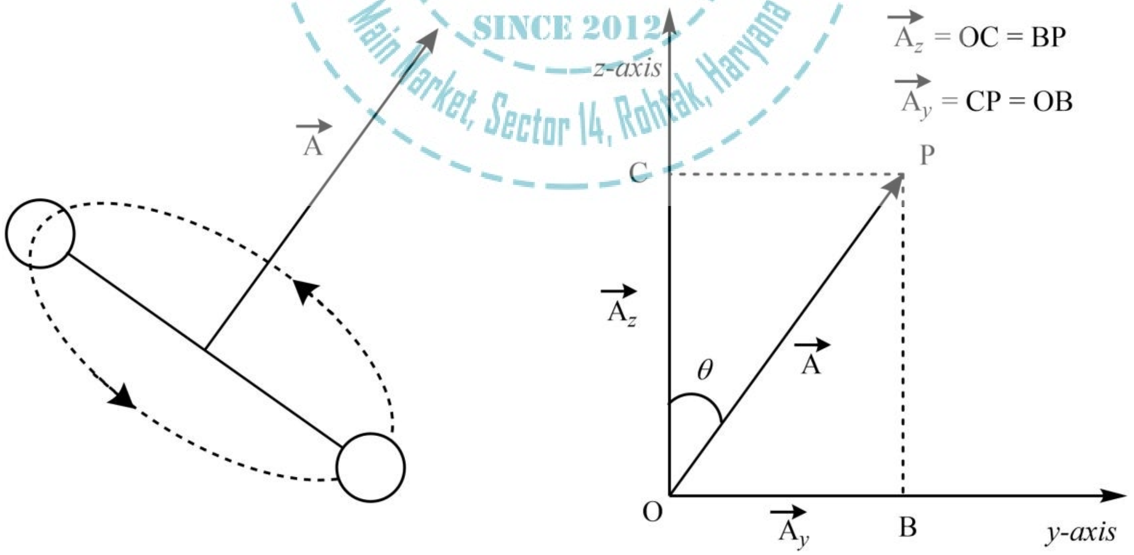


Figure 9. The angular momentum of the diatomic rigid rotator (left) and its rectangular resolution.

In tringle OPC, the side OC represents the effect of the angular momentum vector $\vec{A}$ along z-axis, can be calculated as given below.

$$\frac{OC}{OP} = Cos\ \theta \tag{240}$$

$$OC = OP. Cos\ \theta \tag{241}$$

$$\vec{A}_z = A\ Cos\ \theta \tag{242}$$

Hence, a diatomic molecule in its first rotational state cannot rotate in xy-plane since it will generate $\sqrt{2}$ or 1.414 units of angular momentum along the z-axis (from right-hand thumb rule). In other words, the $\sqrt{2}$ units of angular momentum cannot orient itself along z-axis because this makes $\theta = 0°$ and since $Cos\ 0 = 1$, $\vec{A}_z = A$ i.e. angular momentum effect along the z-axis is also 1.414 unit which is not allowed quantum mechanically. The effects of angular momentum allowed in the z-direction are $+1, 0, -1$; for which angles required are determined as follows.

$$+1 = \sqrt{2}\ Cos\ \theta \quad \Rightarrow \quad \theta = Cos^{-1}\frac{1}{\sqrt{2}} = 45° \tag{243}$$

$$0 = \sqrt{2}\ Cos\ \theta \quad \Rightarrow \quad \theta = Cos^{-1}\frac{0}{\sqrt{2}} = 90° \tag{244}$$

$$-1 = \sqrt{2}\ Cos\ \theta \quad \Rightarrow \quad \theta = Cos^{-1}\frac{-1}{\sqrt{2}} = 135° \tag{245}$$

Hence, we can say that in order to be allowed, the 1.414 units of angular momentum must orient itself only at 45°, 90° and 135° in space from reference direction (z-axis in this case).

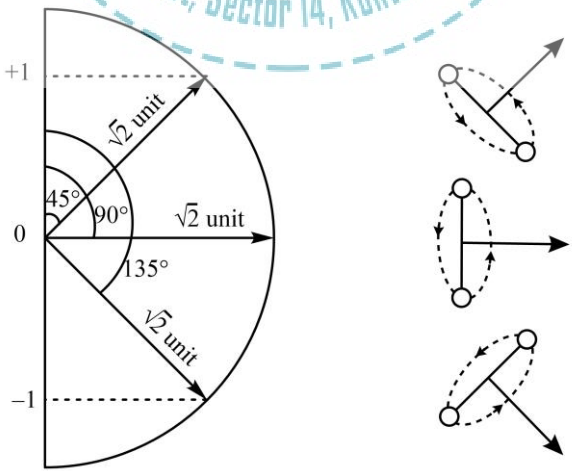


Figure 10. The space quantization of angular momentum of rigid rotator in $l = 1$ rotational state.

Since the orientation of angular momentum can orient itself in any direction from the *z*-axis as far as the effective angular momentum +1 unit along *z*-direction; therefore, we should use a cone around the same at 45°. The same is true for 0 and −1 effects with 90° and 135°, respectively.

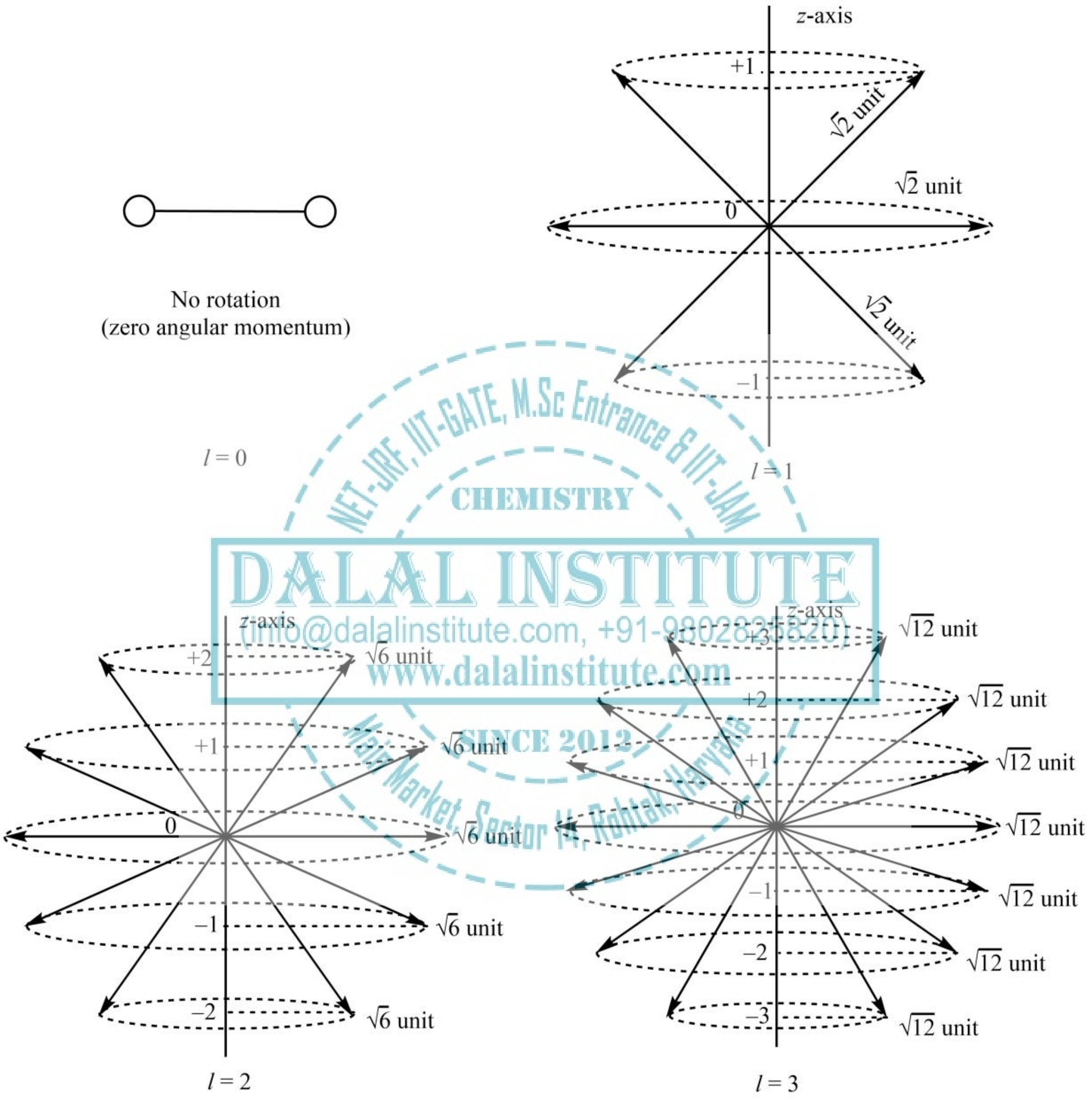


Figure 11. The space quantization of angular momentum of the rigid rotator in $l = 0, 1, 2$ and 3 states.

It is also worthy to mention that the concept of space quantization is equally applicable to the angular momentums of all other systems also like orbital or spin angular momentum of electrons or nuclei.

❖ 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.

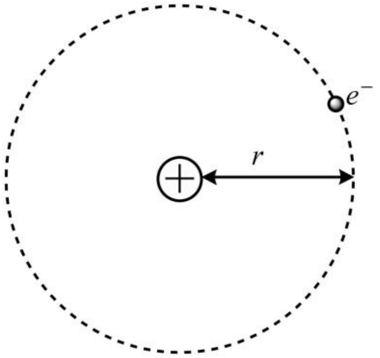


Figure 12. An electron around nucleus at *r* distance.

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

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

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.

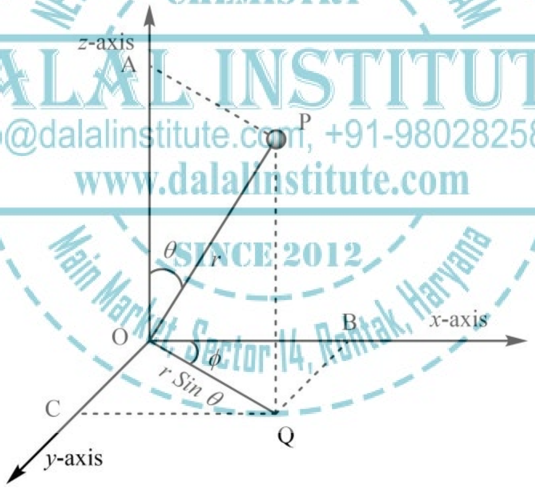


Figure 13. Correlation between cartesian and polar coordinates in three dimensions.

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.

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

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

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

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

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

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

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

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

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
$\Theta_{0,0} = \frac{1}{\sqrt{2}}$	$Y_{0,0} = \frac{1}{\sqrt{2}} . \sqrt{\frac{1}{2\pi}}$
$\Theta_{1,0} = \sqrt{\frac{3}{2}}\, Cos\, \theta$	$Y_{1,0} = \sqrt{\frac{3}{2}}\, Cos\, \theta . \frac{1}{\sqrt{2\pi}}$
$\Theta_{1,\pm1} = \sqrt{\frac{3}{4}}\, Sin\, \theta$	$Y_{1,\pm1} = \sqrt{\frac{3}{4}}\, Sin\, \theta . \sqrt{\frac{1}{2\pi}} e^{\pm i\phi}$
$\Theta_{2,0} = \sqrt{\frac{5}{8}}\, (3Cos^2\, \theta - 1)$	$Y_{2,0} = \sqrt{\frac{5}{8}}\, (3Cos^2\, \theta - 1) . \frac{1}{\sqrt{2\pi}}$
$\Theta_{2,\pm1} = \sqrt{\frac{15}{4}}\, Sin\, \theta\, Cos\, \theta$	$Y_{2,\pm1} = \sqrt{\frac{15}{4}}\, Sin\, \theta\, Cos\, \theta . \sqrt{\frac{1}{2\pi}} e^{\pm i\phi}$
$\Theta_{2,\pm2} = \sqrt{\frac{15}{16}}\, Sin^2\, \theta$	$Y_{2,\pm2} = \sqrt{\frac{15}{16}}\, Sin^2\, \theta . \sqrt{\frac{1}{2\pi}} e^{\pm i2\phi}$

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	$R_{3,2}=\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^{3/2}-\left(\frac{Zr}{a_0}\right)^2\;e^{-Zr/3a_0}$

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.

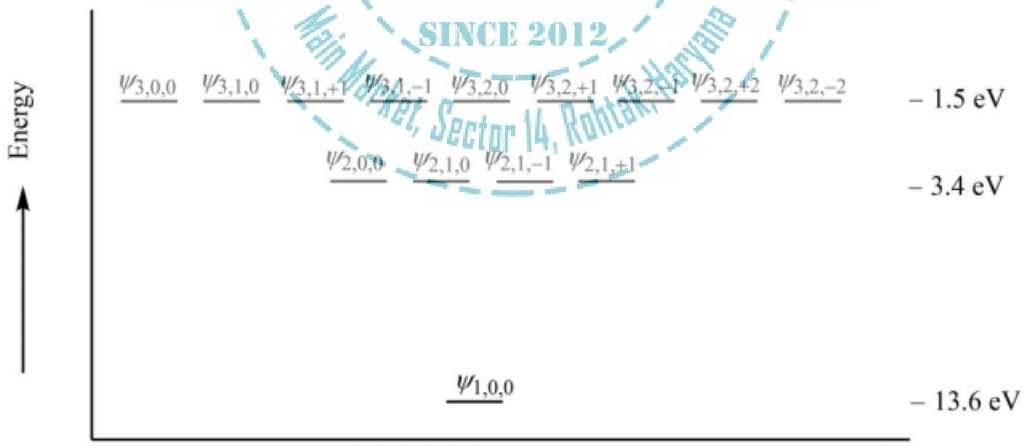


Figure 14. The energy level for various quantum mechanical states of the hydrogen atom.

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.

❖ Principal, Azimuthal and Magnetic Quantum Numbers and the Magnitude of Their Values

The Schrodinger wave equation for hydrogen and hydrogen-like species in the polar coordinates can be written as:

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{Sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi=0 \tag{406}$$

After separating the variables present in the equation given above, the solution of the differential equation was found to be

$$\psi_{n,l,m}(r,\theta,\phi)=R_{n,l}.\Theta_{l,m}.\Phi_m \tag{407}$$

$$=\sqrt{\left(\frac{2Z}{na_0}\right)^3\left[\frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}.\exp\left(-\frac{Zr}{na_0}\right).\left(\frac{2Zr}{na_0}\right)^l.\sum_{k=0}^{k=n-l-1}\frac{(-1)^{k+1}[(n+l)!]^2\left(\frac{2Zr}{na_0}\right)^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{408}$$

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

It is obvious that the solution of equation (406) contains three discrete (n, l, m) and three continuous (r, θ, ϕ) variables. In order to be a well-behaved function, there are some conditions over the values of discrete variables that must be followed i.e. boundary conditions. Therefore, we can conclude that principal (n), azimuthal (l) and magnetic (m) quantum numbers are obtained as a solution of the Schrodinger wave equation for hydrogen atom; and these quantum numbers are used to define various quantum mechanical states. In this section, we will discuss the properties and significance of all these three quantum numbers one by one.

➢ *Principal Quantum Number*

The principal quantum number is denoted by the symbol n; and can have value 1, 2, 3, 4, 5…..∞. The label "principal" is allotted because valid values of l and m can be defined only after defining an acceptable value of n. Some of the most important significances of the principal quantum number are given below.

1. The energy of an electron in hydrogen-like systems: The principal quantum number gives the energy of the electron in all hydrogen and hydrogen-like species by the following relation.

$$E_n=-\frac{\mu Z^2e^4}{2\,n^2\,\hbar^2} \tag{409}$$

Where μ is the reduced mass of the system while e represents the electronic charge. The symbol Z represents the nuclear charge of the one-electron system. Now since main shells are nothing but the classification of different quantum mechanical states of electron on the basis of energy only, we can also say that n tells about the main shells in the modern wave mechanical model of the atom.

2. Degeneracy in hydrogen-like systems: Since the total number of wave functions that can be written for a given value of *n* are n^2, we can say that the degeneracy of any energy level is also n^2. In other words, we can say that because the energy depends only upon the value of *n*, all wave functions with the same value of *n* must possess the same energy. For instance, if we $n = 2$, a total of four wave-functions can be written i.e. $\psi_{2,0,0}, \psi_{2,1,0}, \psi_{2,1,+1}$ and $\psi_{2,1,-1}$. Owing to the same value of *n*, all of these states are bound to have the same energy, and thus, are degenerate.

3. The maximum number of electrons per unit cell: Since two electrons can have the same set of principal, orbital and magnetic quantum numbers via opposite spins, the maximum number of electrons per unit cell will be $2n^2$ i.e. the double of the degeneracy. For instance, if we $n = 2$, the maximum number of electrons that can be filled in the second main shell is $2 \times 2^2 = 8$. Similarly, if we $n = 3$, the maximum number of electrons that can be filled in the third main shell is $2 \times 3^2 = 18$.

4. Spectra of elemental hydrogen: In order to understand this concept, recall the energy expression for the hydrogen atom i.e.

$$E_n = -\frac{m\,e^4}{2\,n^2\,\hbar^2} = -\frac{4\pi^2 m\,e^4}{2\,n^2 h^2} \tag{410}$$

In the SI system, the above equation needs to be corrected for permittivity factor ($4\pi\varepsilon_o$) i.e.

$$E_n = -\frac{4\pi^2 m\,e^4}{2\,n^2 h^2 (4\pi\varepsilon_o)^2} Joules = -\frac{4\pi^2 m\,e^4}{32\,\pi^2 n^2 h^2 \varepsilon_o^2} Joules \tag{411}$$

or

$$E_n = -\frac{m\,e^4}{8\,n^2 h^2 \varepsilon_o^2} Joules \tag{412}$$

Converting Joules into cm^{-1} (dividing by *hc*) the above equation takes the form

$$\bar{\nu}_n = -\frac{m\,e^4}{8\,n^2 h^3 c\,\varepsilon_o^2} cm^{-1} = -\frac{R}{n^2} cm^{-1} \tag{413}$$

Now the selection rules for electronic transitions are

$$\Delta n = anything \qquad and \qquad \Delta l = \pm 1 \tag{414}$$

This means that electron can move from *s* to *p*-orbital only; and all *s*–*s*, *p*–*p*, *d*–*d* and *f*–*f* transitions are Laporte forbidden. Now assume that electron shows a transition from an initial quantum mechanical state (n_1) to the final quantum mechanical state (n_2). The energy of absorption can be formulated as:

$$\Delta\bar{\nu} = \bar{\nu}_{n_2} - \bar{\nu}_{n_1} = \left(-\frac{R}{n_2^2}\right) - \left(-\frac{R}{n_1^2}\right) cm^{-1} \tag{415}$$

or

$$\Delta\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^{-1} \tag{416}$$

The above equation can also be used to determine the wavenumber of the emission spectral line of the hydrogen atom. All the possibilities and corresponding series are given below.

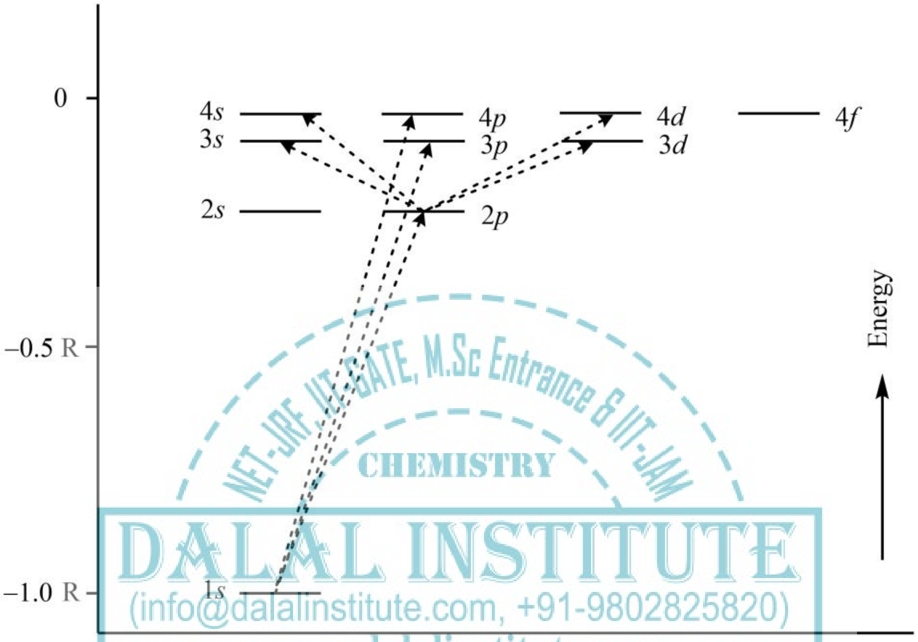


Figure 15. Energy level diagram of the hydrogen atom in the units of Rydberg constant.

At this stage, we must consider all the possibilities that may arise from the transitioning of the electron from different quantum mechanical states. These transitions are grouped in various series labeled as Lyman, Balmer, Paschen, Brackett and Pfund series.

Table 5. Different spectral series in the hydrogen atom.

Series name	Lower state (n_1)	Higher state (n_2)	Region
Lyman	1	2, 3, 4, 5, …. ∞	UV
Balmer	2	3, 4, 5, 6, …. ∞	Visible
Paschen	3	4, 5, 6, 7, …. ∞	Near IR
Brackett	4	5, 6, 7, 8, …. ∞	Mid IR
Pfund	5	6, 7, 8, 9, …. ∞	Far IR

➢ *Azimuthal Quantum Number*

The azimuthal quantum number is denoted by the symbol *l*; and can have value *n*–1, *n*–2, *n*–3…..0. The label azimuthal quantum number is also called as “angular momentum quantum number” because the values of *l* also govern the orbital angular momentum of the electron in a particular quantum mechanical state. Some of the most important significances of the principal quantum number are given below.

1. Orbital angular momentum of the electron: The azimuthal quantum number gives the angular momentum of the electron in all hydrogen and hydrogen-like species by the following relation.

$$< L >= \oint \psi_{n,l,m}(r,\theta,\phi)\,\hat{L}\,\psi_{n,l,m}(r,\theta,\phi) \tag{417}$$

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi} \tag{418}$$

After looking at the equation (418), it is obvious that it’s only the ‘*l*’ quantum number that controls the magnitude of the orbital angular momentum quantum number. Furthermore, owing to the quantized nature of ‘*l*’ quantum number, the angular momentum of an electron in an atom is also quantized. For instance, if we use *l* = 0, 1, 2, 3 in equation (418), we will get 0, $\sqrt{2}$, $\sqrt{6}$ and $\sqrt{12}$ units of angular momentum, respectively.

2. Subshells in the main shell: The azimuthal quantum number can also be used to classify different quantum mechanical states on the basis of orbital angular momentum. In other words, subshells are nothing but the classification degenerate quantum mechanical states on the basis of angular momentum.

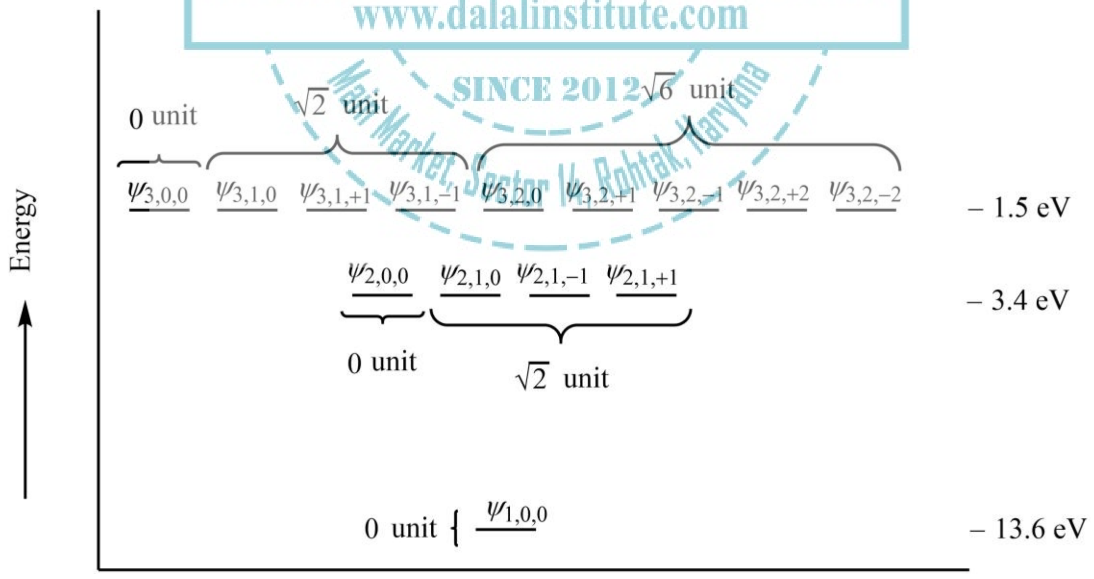


Figure 16. Energy level diagram of the hydrogen atom with further classification.

3. Shape and number of angular nodes in atomic orbital: The angular momentum quantum number, *l*, also controls the number of angular nodes that pass through the nucleus. An angular node (planar or conical) is observed when the angular part of the wave function passes through zero and changes sign.

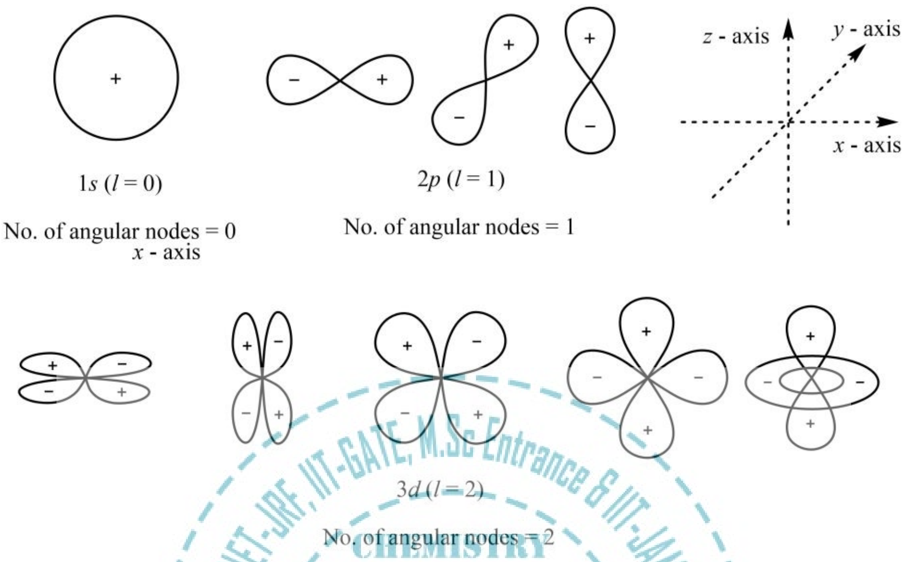


Figure 17. Different orbitals and the corresponding angular nodes.

4. The energy of different subshells in multi-electron atoms: In hydrogen and H-like atoms (i.e. one-electron systems), the energy levels depend only upon the principal quantum number. However, these energy levels also split according to the magnitude of *l* as well. Quantum states of higher *l* are placed above than the states with lower *l*. For instance, the energy of 2*s* orbital is lower than 2*p*, 3*d* exists at higher position than 3*p*.

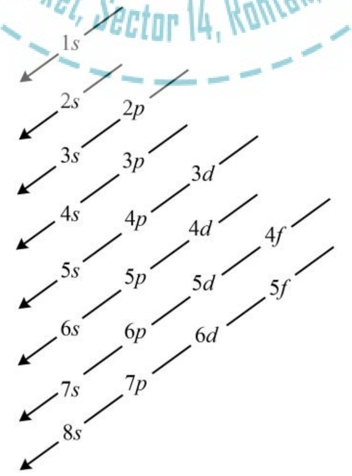


Figure 18. The energy pattern of different subshells in multi-electron atoms.

- ***Magnetic Quantum Number***

The magnetic quantum number is denoted by the symbol m, and can have values $+l$ to $-l$ in unit steps. In other words, the quantum number m is nothing but the allowed effects of orbital angular momentum in the z-direction. The label "magnetic quantum number" arises because m affects the energy of the electron in an externally applied magnetic field. In the absence of such a field, all spherical harmonics corresponding to the different arbitrary values of m will be equivalent. Some of the most important significances of the principal quantum number are given below.

1. The orientation of orbital angular momentum: The azimuthal quantum number gives the angular momentum of the electron in all hydrogen and hydrogen-like species by the following relation:

$$L_l = \sqrt{l(l+1)}\frac{h}{2\pi} \tag{419}$$

Since $l = 0, 1, 2, 3, 4 \ldots\ldots (n-1)$ etc., the quantum mechanically allowed values of orbital angular momentum (in the units of $h/2\pi$) are given below.

$$L_0 = \sqrt{0(0+1)}\text{ unit} = 0\text{ unit} \tag{420}$$

$$L_1 = \sqrt{1(1+1)}\text{ unit} = \sqrt{2}\text{ unit} \tag{421}$$

$$L_2 = \sqrt{2(2+1)}\text{ unit} = \sqrt{6}\text{ unit} \tag{422}$$

$$L_3 = \sqrt{3(3+1)}\text{ unit} = \sqrt{12}\text{ unit} \tag{423}$$

However, there is boundary condition in quantum mechanics that says that only integral effects are allowed reference direction if the angular momentum is generated by integral quantum number and half-integral effects are allowed in reference direction if the momentum is generated by half-integral quantum number.

Since, $L_z = L\ Cos\ \theta$, $\sqrt{2}$ units of orbital angular momentum cannot orient itself along z-axis because this makes $\theta = 0°$, and since $Cos\ 0 = 1$, $\vec{L}_z = L$ i.e. orbital angular momentum effect along the z-axis is also 1.414 unit which is not allowed quantum mechanically. The effects of angular momentum allowed in the z-direction are $+1, 0, -1$; for which angles required are determined as follows.

$$+1 = \sqrt{2}\ Cos\ \theta \quad\Rightarrow\quad \theta = Cos^{-1}\frac{1}{\sqrt{2}} = 45° \tag{424}$$

$$0 = \sqrt{2}\ Cos\ \theta \quad\Rightarrow\quad \theta = Cos^{-1}\frac{0}{\sqrt{2}} = 90° \tag{425}$$

$$-1 = \sqrt{2}\ Cos\ \theta \quad\Rightarrow\quad \theta = Cos^{-1}\frac{-1}{\sqrt{2}} = 135° \tag{426}$$

Hence, we can say that in order to be allowed, the 1.414 units of orbital angular momentum must orient itself only at 45°, 90° and 135° in space from reference direction (*z*-axis in this case). Since the orientation of angular momentum can orient itself in any direction from the *z*-axis as far as the effective orbital angular momentum +1 unit along *z*-direction; therefore, we should use a cone around the same at 45°. The same is true for 0 and −1 effects with 90° and 135°, respectively.

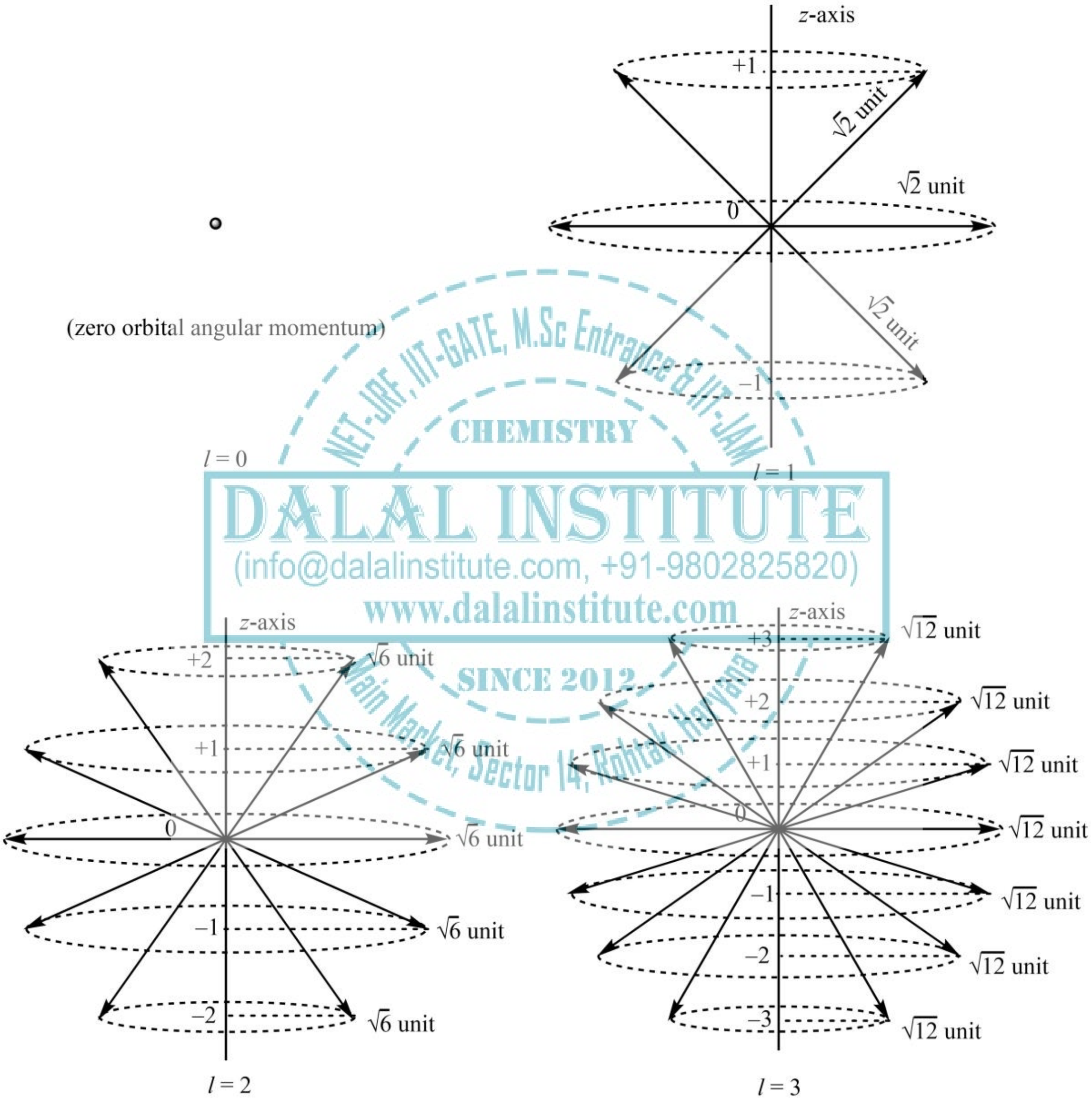


Figure 19. The space quantization of orbital angular momentum of an electron for $l = 0, 1, 2$ and 3 states.

It is also worthy to mention that all the orientations of orbital angular momentum are degenerate in the absence of any externally applied magnetic field.

2. The energy of different orientations: The probability of different orientations of orbital angular momentum, and also the corresponding magnetic fields, are same. However, after applying the magnetic field along the *z*-direction, the situation will not be the same.

The orientation with a maximum negative value of orbital angular momentum along the z-axis will have magnetic dipole aligned along the applied magnetic field, and thus, will be most stable. Conversely, the orientations with the maximum positive value of orbital angular momentum along the z-axis will have magnetic dipole aligned opposite to the applied magnetic field, and thus, will be least stable. Likewise, the orientations with angular momentum component in between will also have intermediary energies in this case.

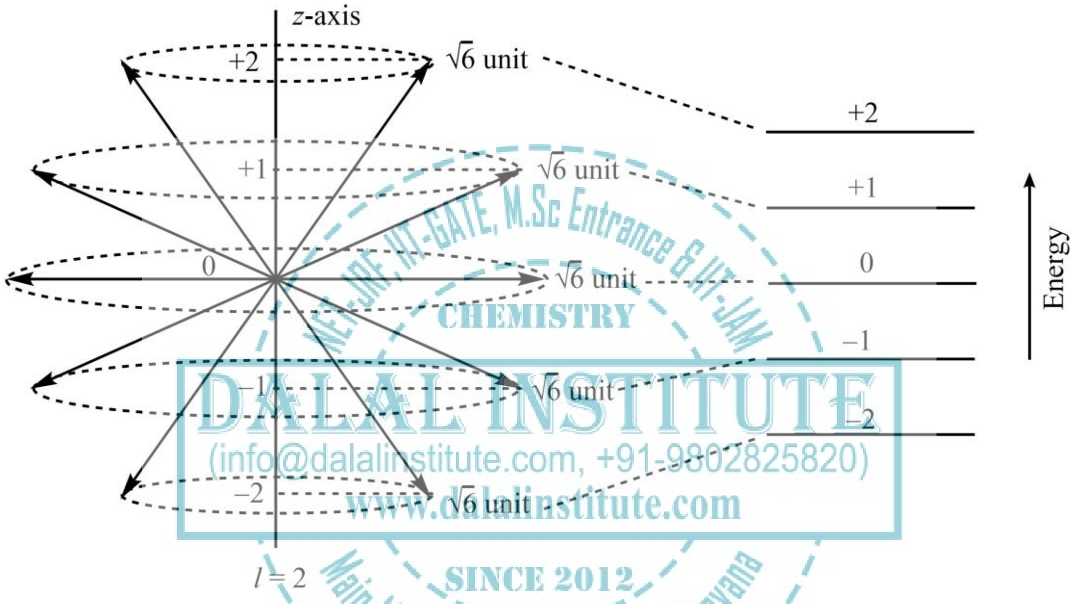


Figure 20. Different orientations of the orbital angular momentum of an electron in a *d*-subshell and corresponding energies in the applied magnetic field.

To understand this, consider the typical case of *d*-subshell. The orbital angular momentum for the corresponding electron can be obtained using equation (419) i.e.

$$L = \sqrt{2(2+1)}\frac{h}{2\pi} \tag{427}$$

$$L = \sqrt{6}\frac{h}{2\pi} \tag{428}$$

The allowed effects of orbital angular momentum in the *z*-direction are $+2, +1, 0, -1, -2$ in the units of $h/2\pi$. Therefore, each spectral line arising from the transition to the *d*-subshell will split in a quintet in the presence of the externally applied magnetic field.

❖ Probability Distribution Function

The probability distribution function is the behavior of ψ^2 at various points around the nucleus as a function of distance r from the nucleus. The plots of such functions are also called as the probability distribution curves. Nevertheless, since it is only the radial part ($R_{n,l}$) that varies with the distance from the nucleus, the graphs of ψ^2 must behave in the same manner. To understand this more precisely, consider the plot of the first two quantum mechanical states of an electron in a hydrogen atom.

➢ *Probability Distribution of $\psi_{1,0,0}$ State (1s Orbital)*

In order to understand the probability distribution function of the electron in the ground state of the hydrogen atom, recall the mathematical expression for the same i.e.

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \tag{429}$$

Squaring both sides, we get

$$\psi_{1,0,0}^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0} \tag{430}$$

It is obvious from the equation (429, 430) that the pre-exponential part is simply a constant and variation depends only upon the exponential part.

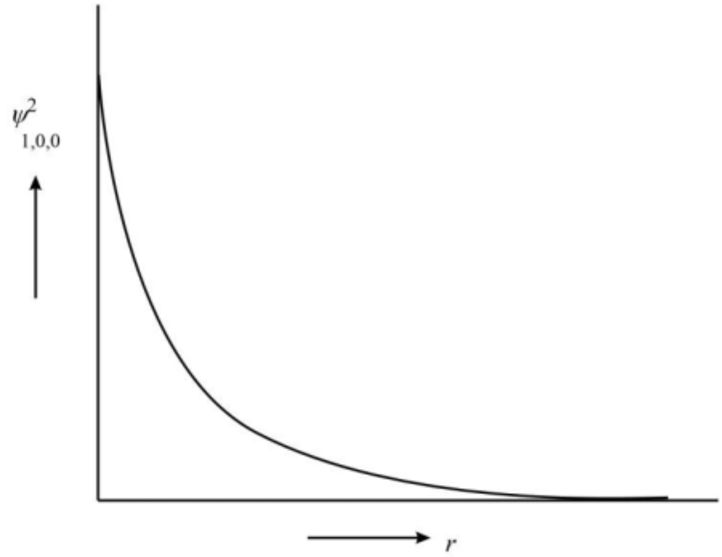


Figure 21. The variation of electron density vs distance from the center of the nucleus in 1*s* orbital.

Hence, it can be concluded that the density of the electron wave is highest at the center of the nucleus and decreases as the distance from the center of the nucleus increases, and becomes zero only at infinite.

➢ *Probability Distribution of $\psi_{2,0,0}$ State (2s Orbital)*

In order to understand the probability distribution function of an electron in the 2*s* state of the hydrogen atom, recall the mathematical expression for the same i.e.

$$\psi_{2,0,0}=\frac{1}{4\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0} \tag{431}$$

Squaring both sides, we get

$$\psi_{2,0,0}^{2}=\frac{1}{16\pi a_0^{3}}\left(2-\frac{r}{a_0}\right)^{2}e^{-r/a_0} \tag{432}$$

It is obvious from the equation (431, 432) that the pre-exponential part is simply a constant and variation depends only upon the exponential part.

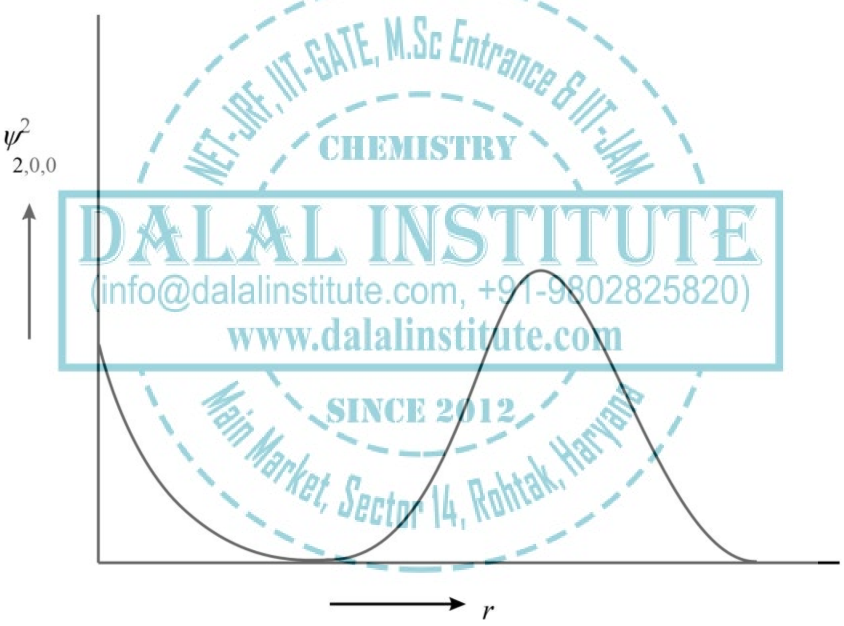


Figure 22. The variation of electron density vs distance from the center of the nucleus in 2*s* orbital.

Hence, it can be concluded that the density of electron wave is non zero at the center of the nucleus and decreases as the distance from the center of the nucleus increases, and becomes zero at $r = 2a_0$. Now since the wave function changes sign after $2a_0$, the density of electron wave after that increases first and then decreases exponentially and finally becomes zero at infinite distance. Now it's quite confusing because we have been told that the electron cannot reside within the nucleus and the probability of finding the electron inside the nucleus is almost zero, meaning that there must be something else that also governs the probability.

❖ Radial Distribution Function

The radial distribution function is the behavior of $R_{n,l}^2 . 4\pi r^2 dr$ as a function of distance *r* from the center of the nucleus. These plots solve the problem posed by the simple "probability distribution curves" which suggested that the probability of finding the electron must be highest at the center of the nucleus in the ground electronic state. In the radial distribution plots, we assume that the probability of finding the particle at a distance *r* from the nucleus depends not only upon the density of electron wave but also varies with the magnitude of the volume of the spherical shell of *dr* thickness at the same distance. This is quite rational because the *r* can be in any direction around the nucleus.

Consider that the space around the nucleus is divided into an infinite number of concentric shells of thickness *dr*. Now though the electron density will show a decrease with increasing *r*, the volume of the concentric shells will increase. More volume at distance *r* means more the chances of finding the electron at same. The two effects will try to counter each other, and therefore, the resultant probability at distance *r* must be the multiplication of the two effects i.e.

$$Radial\ probability = \psi_{n,l,m}^2 \times dV_{shell} \tag{433}$$

Nevertheless, since it is only the radial part ($R_{n,l}$) that varies with the distance from the nucleus, the above expression for simplicity can be reduced to

$$Radial\ probability = R_{n,l}^2 \times dV_{shell} \tag{434}$$

Now as we have already derived the mathematical expression of radial wavefunction hydrogen atom already in this previously, the only thing we need is the mathematical expression of the volume element also.

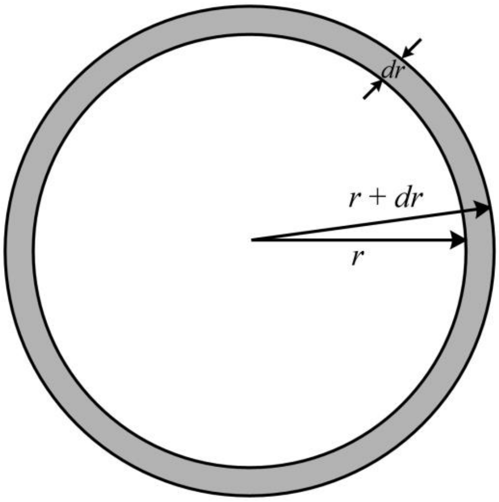


Figure 23. The depiction of a concentric shell of thickness *dr* around the nucleus of a hydrogen atom at a distance *r*.

The volume of the shaded portion (spherical shell of thickness *dr*) can be obtained subtracting the volume of the inner sphere from the outer sphere i.e.

$$dV = \frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3 \tag{435}$$

$$= \frac{4}{3}\pi(r^3 + dr^3 + 3r^2dr + 3r\,dr^2) - \frac{4}{3}\pi r^3 \tag{436}$$

$$= \frac{4}{3}\pi r^3 + \frac{4}{3}\pi dr^3 + 4\pi r^2dr + 4\pi r\,dr^2 - \frac{4}{3}\pi r^3 \tag{437}$$

$$dV = \frac{4}{3}\pi dr^3 + 4\pi r^2dr + 4\pi r\,dr^2 \tag{438}$$

Since *dr* is very small, the terms involving square and cube of *dr* can be neglected for simplicity. All this leaves us with only one term i.e. $dV = 4\pi r^2dr$. After using the value of *dV* in equation (434), we get

$$Radial\ probability = R_{n,l}^2 \times 4\pi r^2dr \tag{439}$$

To understand this more precisely, consider the plot for the ground quantum mechanical state of an electron in a hydrogen atom i.e. 1*s* orbital.

- ***Radial Probability Distribution Curve for Ground State of Hydrogen Atom***

The valid values of *n*, *l* and *m* that can be put in the general form of the hydrogenic wavefunction to obtain ground state are 1, 0 and 0, respectively. Therefore, we can start by writing the mathematical expression for the same i.e.

$$R_{1,0} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \tag{440}$$

The probability distribution function can be obtained by squaring equation (440) i.e.

$$R_{1,0}^2 = \frac{4}{a_0^3}e^{-2r/a_0} \tag{441}$$

After multiplying the "probability distribution function" with "volume element", the expression for the "radial distribution function" can be formulated. Mathematically, we can say that

$$P(r) = \frac{4}{a_0^3}e^{-2r/a_0} \times 4\pi r^2dr \tag{442}$$

It is obvious from the equation (442) that probability will become zero if we put *r* = 0 ($4\pi r^2dr = 0$). Now, if we increase the *r*, the radial probability will first increase due to increasing volume element, attaining maxima; and then it will start declining due to the dominance of $R_{1,0}^2$ part. In other words, the density of electron-wave decreases exponentially but the volume of the concentric shell increases continuously.

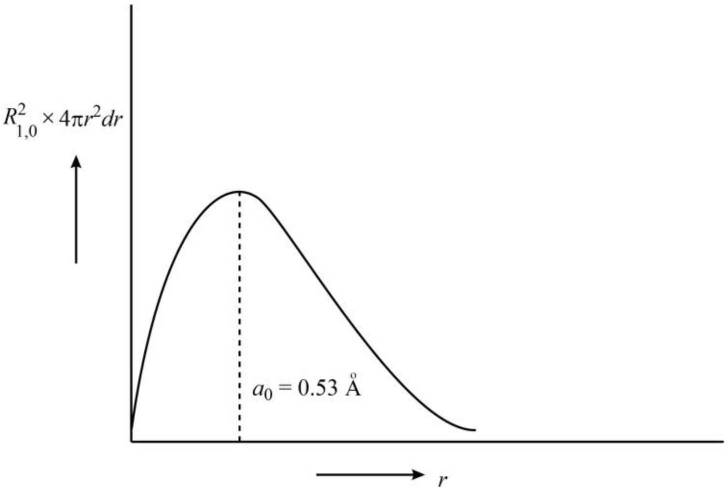


Figure 24. The variation of radial probability as a function of r (1*s* orbital).

In order to find the radius of maximum probability, we need to put dP/dr equal to zero. It has been found that the radius of maximum probability will come out to be 0.53×10^{-10} m, which is exactly equal to the radius of the first Bohr orbit (a_0).

- ***Radial Probability Distribution Curves for Other Hydrogenic Wavefunctions***

The other valid sets of n, l can be put in the general form of radial part of the wavefunction, to obtain $R_{n,l}^2$, and hence the corresponding "radial distribution functions".

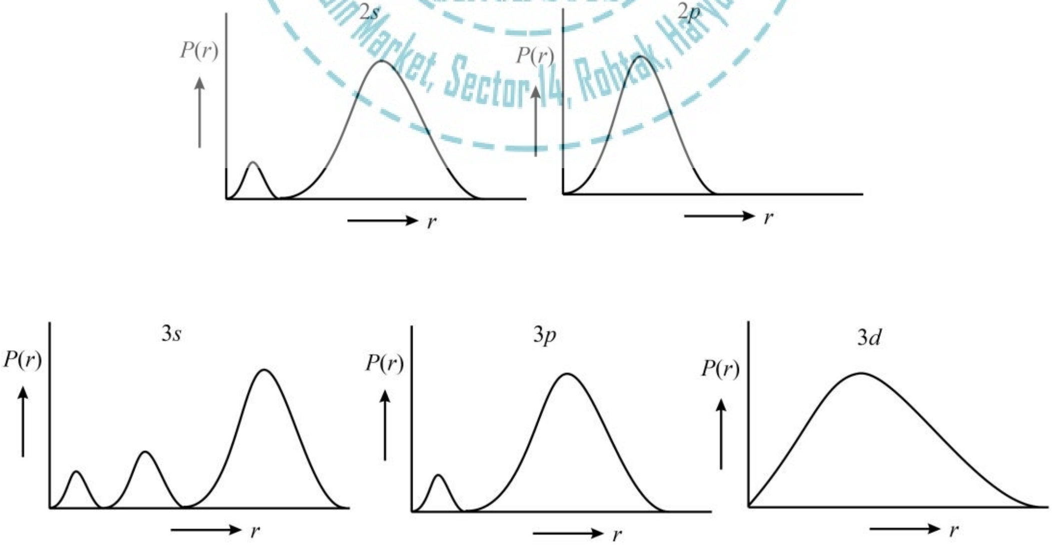


Figure 25. The variation of radial probability as a function of distance from the center of the nucleus.

❖ Shape of Atomic Orbitals (*s*, *p* & *d*)

The wave mechanical model of atom says that there is a non-zero probability of finding the electron almost everywhere in space excepting the angular and radial nodes. This means that primitive diagrams that depict the orbital shapes are intended to describe the region encompassing 90−95% probability density. In a typical drawing of orbital, we first plot the radial wave function and the angular part is superimposed. The shapes of some typical orbitals are discussed below.

➢ *Shape of s-Orbitals*

In order to draw the shape of s-orbital, we first need to recall the radial part of the same and then we will have to superimpose the angular part. For instance, the radial part of 1*s* orbital is

$$R_{1,0} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \tag{443}$$

It is obvious from the equation (443) that the radial part of the wave function has the largest magnitude when *r* = 0, and it decreases as we move away from the nucleus. The function will become zero only at infinite distance and will never change its sign. All this leads to a spherical-shaped cloud without any radial node. The angular part of every *s*-orbital is

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} = 0.28 \tag{444}$$

Hence, after multiplying radial wave function by a constant value of the angular part, the magnitude of function at all the points in space will reduce to 28% of the initial value.

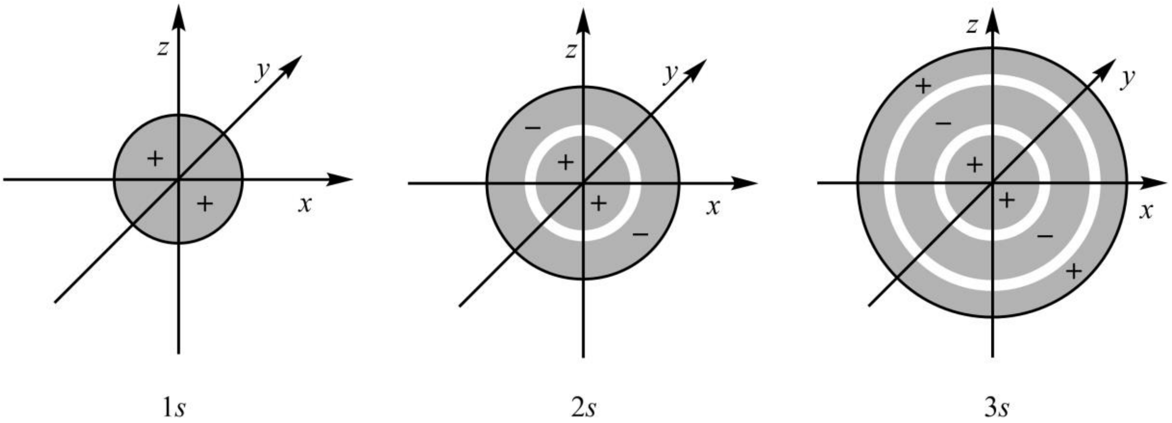


Figure 26. The shape of some lower energy *s*-orbitals.

Similarly, the shapes of some other s-orbitals are also given below to explain the concept more precisely. It is worthy to mention that the plots are easy to draw if we treat radial and angular parts consequently.

➢ *Shape of p-Orbitals*

In order to draw the shape of *p*-orbital, we first need to recall the radial part of the same and then we will have to superimpose the angular part. For instance, the radial part of 2*p* orbital is

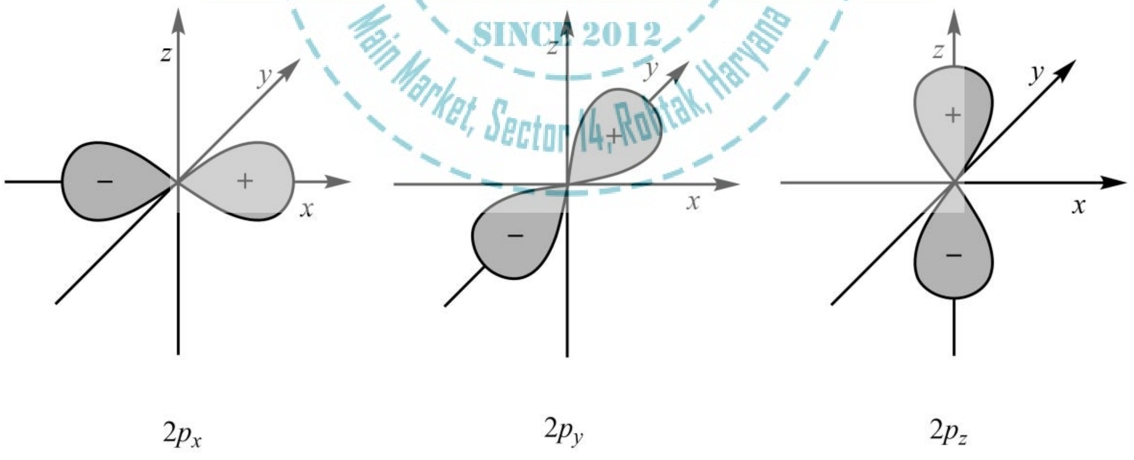
$$R_{2,1} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0} \tag{445}$$

It is obvious from the equation (445) that the radial part of the wave function has the zero magnitudes when $r = 0$; and it increases as we move away from the nucleus, reaches a maximum, and decreases afterward. The function becomes zero only at infinite distance and will never change its sign. All this leads to a spherical-shaped cloud without any radial node. The angular part of *p*-orbitals are

$$Y_{1,0} = \sqrt{\frac{3}{2}}\,Cos\,\theta.\frac{1}{\sqrt{2\pi}} \tag{446}$$

$$Y_{1,\pm1} = \sqrt{\frac{3}{2}}\,Sin\,\theta.\sqrt{\frac{1}{2\pi}}\,e^{\pm i\phi} \tag{447}$$

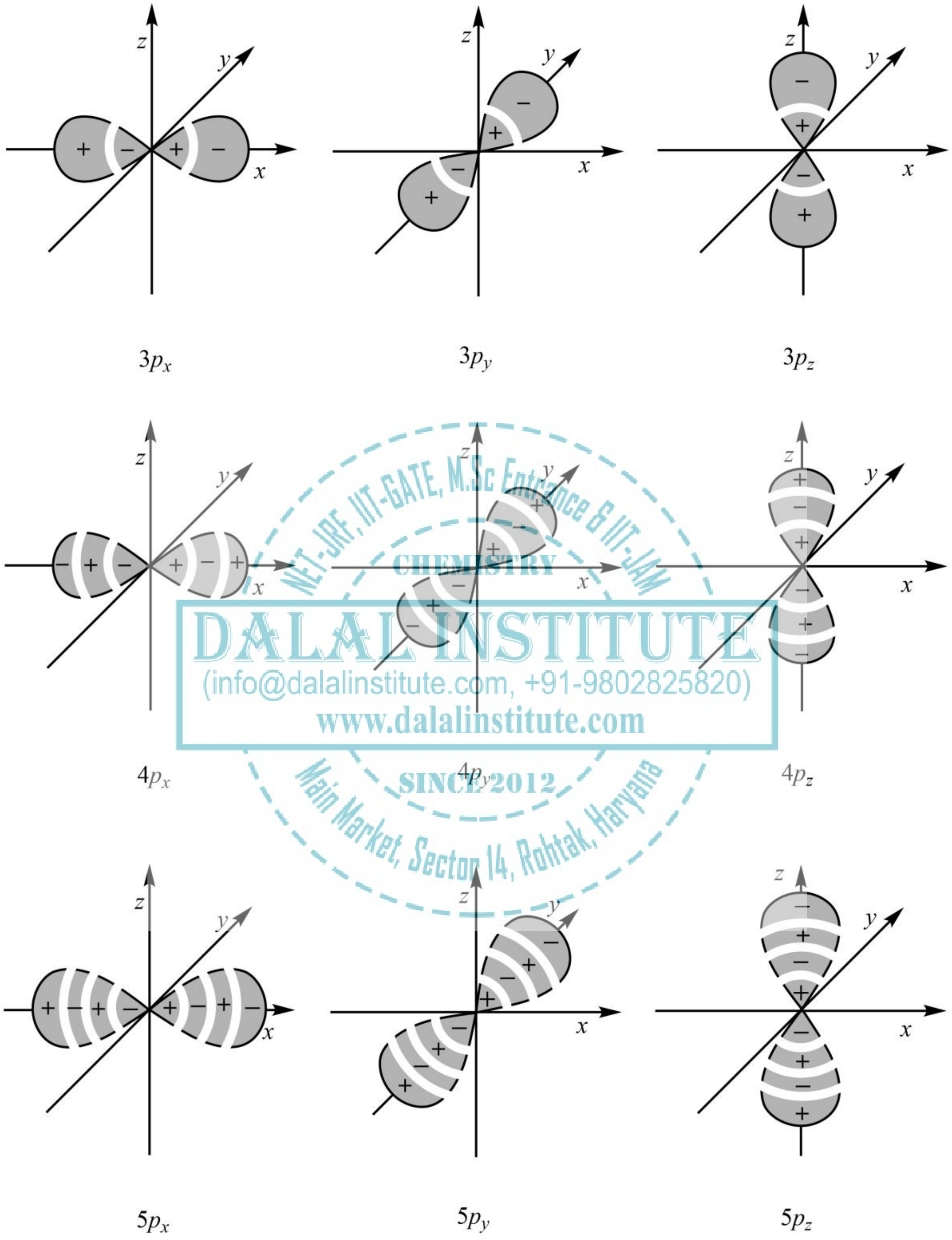
Hence, the full plot for p_z-orbital is obtained after multiplying radial wave function by angular part given by equation (446); and the sign of function above the *xy*-plane will remain positive whereas a negative sign will be obtained below *xy*-plane. Similarly, we can obtain the three-dimensional plots for p_x and p_y by multiplying equation (445) by equation (447).



$2p_x$ $2p_y$ $2p_z$

Figure 27. The shape of 2*p*-orbitals.

Similarly, the shapes of some other *p*-orbitals are also given below to explain the concept more precisely. It is worthy to mention that the plots are easy to draw if we treat radial and angular parts consequently.



$3p_x$ $3p_y$ $3p_z$

$4p_x$ $4p_y$ $4p_z$

$5p_x$ $5p_y$ $5p_z$

Figure 28. The shape of some 3p, 4p and 5p orbitals.

➢ *Shape of d-Orbitals*

In order to draw the shape of *d*-orbital, we first need to recall the radial part of the same and then we will have to superimpose the angular part. For instance, the radial part of 3*d* orbital is

$$R_{3,2} = \frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^{3/2} - \left(\frac{Zr}{a_0}\right)^{2} e^{-Zr/3a_0} \tag{448}$$

It is obvious from the equation (448) that the radial part of the wave function has the zero magnitudes when $r = 0$; and it increases as we move away from the nucleus, reaches a maximum, and decreases afterward. The function becomes zero only at infinite distance and will never change its sign. All this leads to a spherical-shaped cloud without any radial node. The angular part of *d*-orbitals are

$$Y_{2,0} = \sqrt{\frac{5}{8}}(3Cos^2\,\theta - 1).\frac{1}{\sqrt{2\pi}} \tag{449}$$

$$Y_{2,\pm1} = \sqrt{\frac{15}{4}}\,Sin\,\theta\;Cos\,\theta.\sqrt{\frac{1}{2\pi}}e^{\pm i\phi} \tag{450}$$

$$Y_{2,\pm2} = \sqrt{\frac{15}{16}}\,Sin^2\,\theta.\sqrt{\frac{1}{2\pi}}e^{\pm i2\phi} \tag{451}$$

Hence, the full plot for d_{z^2}-orbital is obtained after multiplying radial wave function by angular part given by equation (449); and the sign of function in the *xy*-plane will become negative whereas a positive sign will be obtained in two opposite lobes along *z*-axis. It is also worthy to note that the function becomes completely zero in two conical surfaces (above and below) before changing its sign. Similarly, we can obtain the three-dimensional plots for p_x and p_y by multiplying equation (448) by equation (450, 451).

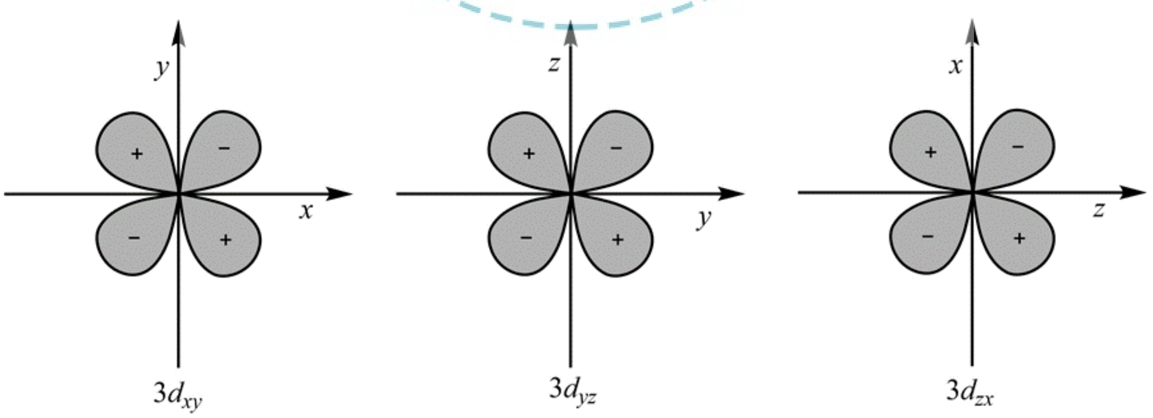


Figure 29. Continued on the next page…

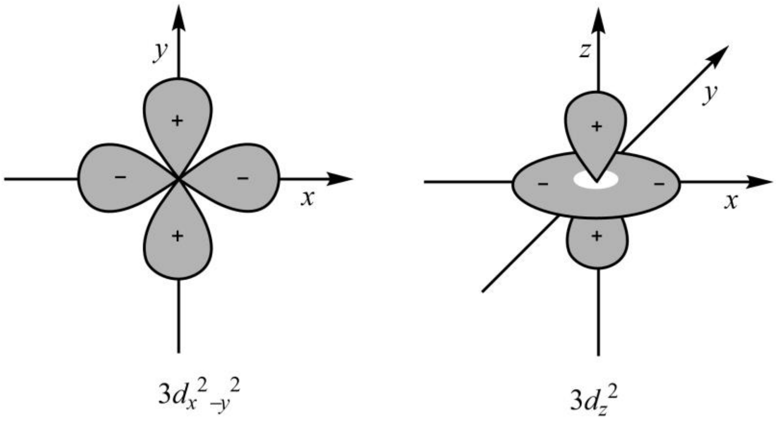


Figure 29. The shape of 3*d*-orbitals.

Similarly, the shapes of some other *d*-orbitals are also given below to explain the concept more precisely. It is worthy to mention that the plots are easy to draw if we treat radial and angular parts consequently.

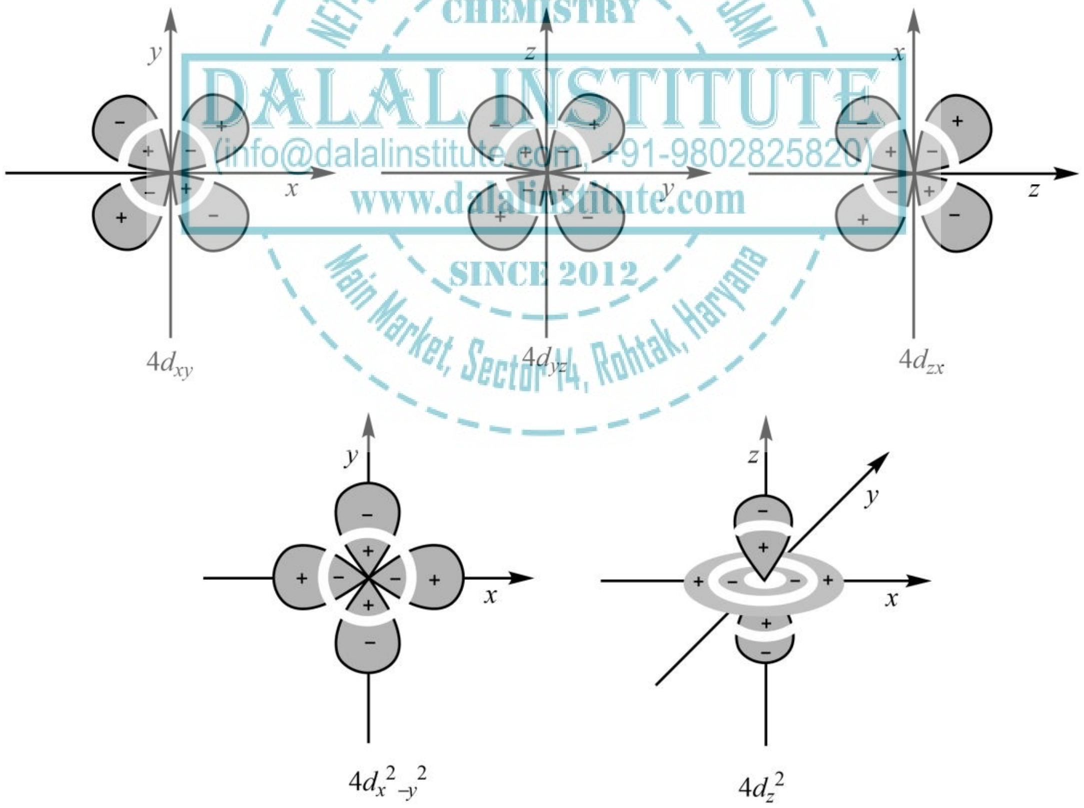


Figure 30. The shape of 4*d* orbitals.

It is also worthy to mention that the radii of maximum probability for 4*d* orbitals are larger than that of 3*d* orbitals. The same is true for *s* and *p* orbitals i.e. radius of maximum probability of *s* and *p* orbitals follow the order 3*s* > 2*s* > 1*s* and 4*p* > 3*p* > 2*p*, respectively.

❖ Problems

Q 1. Derive and discuss the Schrodinger wave equation for a particle of mass *m* trapped inside a cubical box with side *a*. Provided that the potential inside the box is zero while outside the box is infinite.

Q 2. Discuss the concept of the degeneracy of quantum mechanical states in a 3D box.

Q 3. What is the zero-point energy of a simple harmonic oscillator? How does it vary with force constant?

Q 4. Derive and discuss the Schrodinger wave equation for a diatomic rigid rotator. Also, draw the energy level diagram for the same.

Q 5. Define space quantization with special reference to diatomic rigid rotator.

Q 6. What is the difference between the radial and angular wave function for hydrogen atom? Write down both parts for $3d_{z^2}$ orbital.

Q 7. What are quantum numbers in the modern wave mechanical model of the atom? Also, discuss the main significance of the principal quantum number.

Q 8. Write down a short note on "probability distribution functions".

Q 9. What are "radial distribution functions"? Also, explain how you would determine the radius of maximum probability for 1*s* orbital of the hydrogen atom.

Q 10. What are the formulas to find the number of angular and radial nodes?

Q 11. Draw and discuss the shape of $4d_{xy}$ and $3d_{z^2}$ in detail

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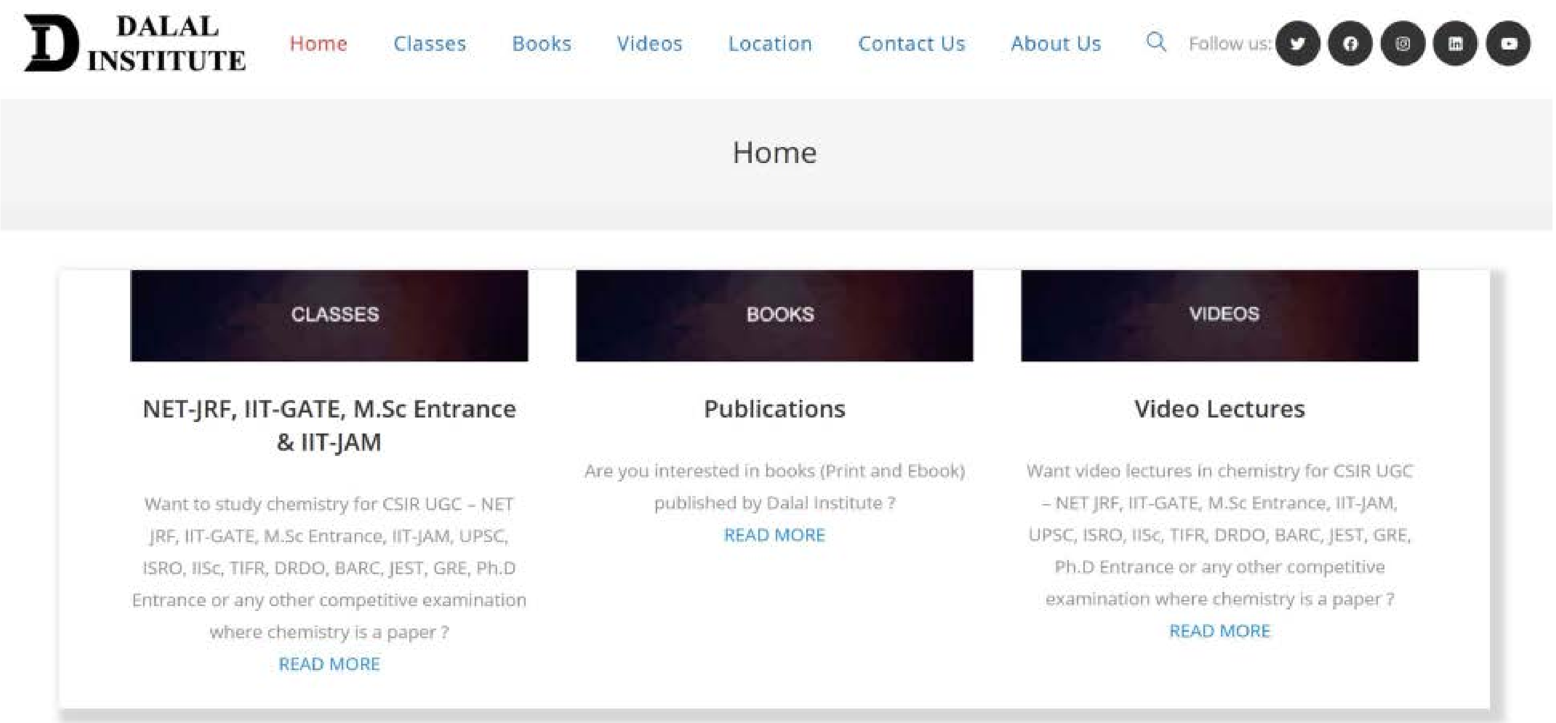

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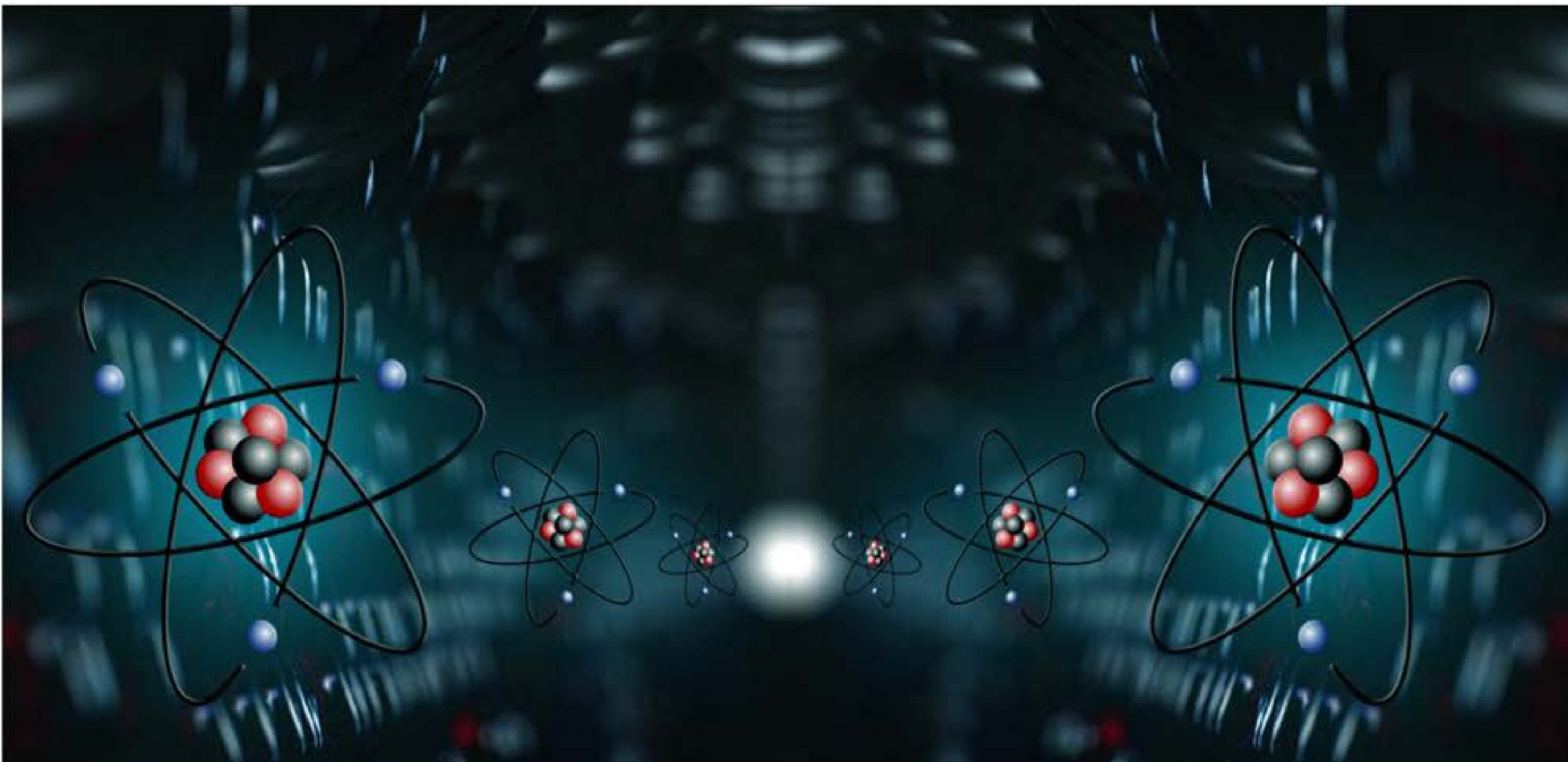

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