SOLVING HYDROGEN ATOM PROBLEM USING SPHERICAL POLAR COORDINATES: A QUALITATIVE STUDY

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Abstract

Quantum mechanics has completed century since its genesis. Quantum mechanics is taught at various levels-starting from school and colleges to universities. Regression methods are introduced at under graduate and post graduate levels to solve Schrodinger equation for finding solutions of various trivial and non-trivial physical problems. The common problems, which students encounter at UG level are- particle in a box, potential step and barriers, harmonic oscillator and hydrogen atom. It has been observed that students lack clarity in solving and grasping the hydrogen atom problem. Two reasons can be accounted for this. It is perhaps a lengthy derivation and students, many times, are not well acquainted with the requisite knowledge of Spherical Polar Co-ordinate system. In this article, a brief review on the birth of quantum mechanics is presented judiciously discussing the contribution of Schrodinger, before solving the hydrogen atom problem. Readers are first introduced to spherical-polar coordinate system. The radial solutions, radial probability distribution functions, and hydrogen orbital, are plotted using Mathematica software v.12, for the sake of visualization and understanding .

INTRODUCTION

The spectra of many elements have been known, since 19th century. The emission and absorption of different, but of definite wavelengths (i.e. color) radiations, work like a fingerprint to recognize chemical elements. In other words, the spectra of atoms are signatures of the electronic distribution inside atoms. But the emission and absorption of radiation, in visible spectra, had remained a mystery for a century, until Planck gave the idea of quanta and proposed that light travels in form of quanta. Quantum mechanics was born in the year 1900, when Max Planck derived a formula for black body radiation in order to explain it, for all possible wavelengths (Alain& Villain, 2017). Planck introduced the concept of quantization of energy. He proposed that radiation travels in form of quanta (i.e. a bundle of energy). In 1905, Einstein introduced the

notion of "Lichtquanten" (i.e. quantum of light). Twenty years later, it was named photon. He realized the importance of the idea of quantization to explain photoelectric effect. In the year 1905, also rendered as miraculous year in the history of science, Einstein published three historical papers; one dealing with special relativity, another with Brownian motion and the third one with photoelectric effect. He used quantum nature of light to explain photoelectric effect. Wave nature of light could already explain optical phenomena as interference, diffraction and polarization.

In 1913, the ground breaking discovery of Bohr atomic model further extended the idea of quantization, because Bohr postulated that electrons in atoms can move only in definite orbits, and it can emit or absorb radiation in form of definite quanta only. The experimental observation of hydrogen atom spectra Figure (1) was already reported by contemporary scientists. But, no satisfactory theory existed, which could explain it.These developments led Louis de Broglie to propose the idea of wave-particle duality in 1923, as a part of his doctoral dissertation. He wanted to introduce the idea of "Atom of Light", but his principal examiner Paul Lanevin consulted Einstein regarding this. Einstein, appreciated the idea of wave-particle duality, but could not agree with the idea of atom of light. Broglie removed the latter part and obtained his Ph.D degree.Broglie re-derived Bohr's quantization rules (Alain& Villain, 2017).

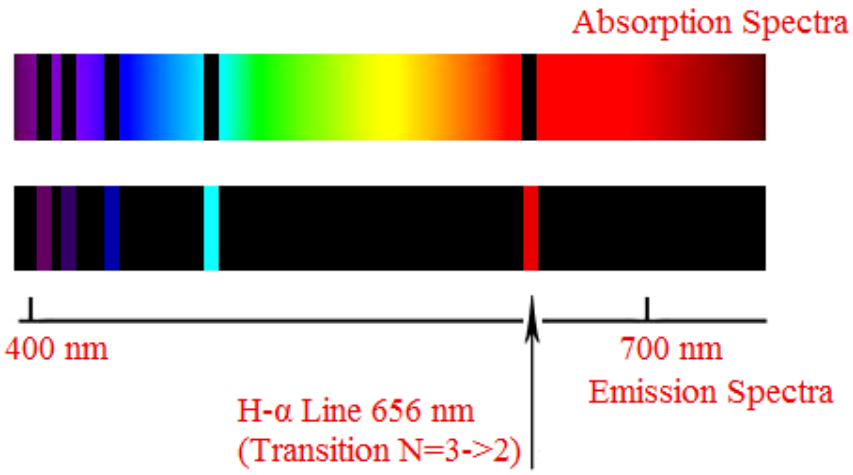


Figure 1.*Absorption and emission lines in hydrogen atom spectra (H-α lines are most intense)*

It had become quite natural for the contemporary physicists to raise question about the wave equation; that could be solved to obtain such solutions. In 1926, Schrodinger Figure (2) solved problems in a series of papers. In a co-parallel manner, Heisenberg (Heisenberg, 1925) Born and Jordan (Born & Jordan, 1925) published their matrix version of quantum mechanics in 1925 (Aschman & Keaney, 1989; Reiter &Yngvason, 2013; Fedak & Jeffrey 2009). Modern quantum mechanics was born, when Schrodinger demonstrated equivalence with their matrix formalism by exactly solving the hydrogen atom problem and explain it's spectra.

Figure 2. *Left: Erwin Schrodinger (1887-1961) (Courtesy: R. Braunizer 1926); Right: Tomb of Schrodinger and his wife with plaque imprinted with his famous equation (Courtesy: C. Joas 2008)*

A relativistic version of his equation came within a year. Klein, Gordon and Fock gave relativistic equation for a free particle. The relativistic treatment of hydrogen atom was introduced by P. A. M. Dirac in 1928.Opposite to matrix calculus of Heisenberg, Schrodinger's approach is quite simple. Schrodinger equation can be derived considering spatial distribution of the amplitude of the wave $\psi(x)$, at a fixed point in time as follows-

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{4\pi^2\psi(x)}{\lambda^2} = 0; \quad k = \frac{2\pi}{\lambda} \,\&\, \lambda = h/p \tag{1}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{4\pi^2 p^2\psi(x)}{h^2} = 0; \; p = \sqrt{2m(E-V)} \tag{2}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{8m\pi^2(E-V)\psi(x)}{h^2} = 0 \tag{3}$$

The premises of quantum mechanics have gotten developed tremendously, since its birth in the beginning of 20th century. Almost every walk of science needs it, especially when the problem is rooted at the bottom of the scale. From nanoscience to cosmology, its knowledge has become mandatory in order to fully narrate natures beauty in terms of mathematical formalism. Here, the exact solution of hydrogen atom, using Schrodinger equation is obtained in a greater detail in a pedagogical manner.

MATHEMATICAL ANALYSIS

Though, hydrogen atom problem has become a century old problem and numerous text books (Ghatak & Loknathan, 2004; Schiff & Bandhyopadhyay, 2017) (Feynman, 2015) and documents

are available to solve it including online references (Chapter-10 The Hydrogen Atom) we shall start with a fresh cumulative approach. We shall first convert three-dimensional Schrodinger equation from Cartesian coordinate system to spherical coordinate system.

Schrödinger Equation in Spherical Polar Coordinates

The vector representations of unit vectors r, θ and ϕ are as shown in Figure (3).

$$d(\vec{r}) = d(r\hat{r}) = dr\hat{r} + rd\hat{r} \tag{4}$$

$$= dr\hat{r} + r\left[\frac{\partial \hat{r}}{\partial r}.dr + \frac{\partial \hat{r}}{\partial \theta}.d\theta + \frac{\partial \hat{r}}{\partial \phi}.d\phi\right] \tag{5}$$

$$\hat{r} = \frac{\frac{\partial \bar{r}}{\partial r}}{\left|\frac{\partial \vec{r}}{\partial r}\right|} \qquad \hat{\theta} = \frac{\frac{\partial \bar{r}}{\partial \theta}}{\left|\frac{\partial \bar{r}}{\partial \theta}\right|} \qquad \hat{\phi} = \frac{\frac{\partial \bar{r}}{\partial \phi}}{\left|\frac{\partial \bar{r}}{\partial \phi}\right|} \tag{6}$$

$$\bar{r} = r\sin\theta\cos\phi\ \hat{x} + r\sin\theta\sin\phi\ \hat{y} + r\cos\theta\ \hat{z} \tag{7}$$

$$\frac{\partial \bar{r}}{\partial r} = \sin\theta\cos\phi\ \hat{x} + \sin\theta\sin\phi\ \hat{y} + \cos\theta\ \hat{z} \tag{8}$$

$$\frac{\partial \bar{r}}{\partial \theta} = r\cos\theta\cos\phi\ \hat{x} + r\cos\theta\sin\phi\ \hat{y} - r\sin\theta\ \hat{z} \tag{9}$$

$$\frac{\partial \bar{r}}{\partial \phi} = -r\sin\theta\sin\phi\ \hat{x} + r\sin\theta\cos\phi\ \hat{y} + 0 \tag{10}$$

So, we have-

$$\hat{r} = \sin\theta\cos\phi\ \hat{x} + \sin\theta\sin\phi\ \hat{y} + \cos\theta\ \hat{z} \tag{11}$$

$$\hat{\theta} = \cos\theta\cos\phi\ \hat{x} + \cos\theta\sin\phi\ \hat{y} - \sin\theta\ \hat{z} \tag{12}$$

$$\hat{\phi} = \sin\theta\ \hat{x} + \cos\phi\ \hat{y} \tag{13}$$

Now, we have -

$$\frac{\partial \hat{r}}{\partial r} = 0;\ \ \frac{\partial \hat{r}}{\partial \theta} = \cos\theta\cos\phi\ \hat{x} + \cos\theta\sin\phi\ \hat{y} - \sin\theta\ \hat{z} = \hat{0} \tag{14}$$

$$\frac{\partial \hat{r}}{\partial \phi} = -\sin\theta\sin\phi\ \hat{x} + \sin\theta\cos\phi\ \hat{y} + 0 = \sin\theta\ \hat{\phi} \tag{15}$$

Substitution gives us:

$$d\bar{r} = dr\,\hat{r} + rd\theta\,\hat{\theta} + r\sin\theta d\phi\,\hat{\phi} \tag{16}$$

$$\bar{r} \to \bar{r} + d\bar{r} \Rightarrow \bar{f} + d\bar{f} \tag{17}$$

$$d\bar{f} = \frac{\partial \bar{f}}{\partial r}.d\bar{r} + \frac{\partial \bar{f}}{r\theta}.d\theta + \frac{\partial \bar{f}}{\partial \phi}.d\phi = \nabla \hat{f}.d\bar{r} \tag{18}$$

$$\nabla f.dr = \nabla fr.dr\,\hat{r} + \nabla f_0.r\,d\theta\,\hat{\theta} + \nabla f_\phi r\sin\theta\,d\phi\,\hat{\theta} \tag{19}$$

$$\nabla fr = \frac{\partial f}{\partial r}\nabla f\theta = \frac{1}{r}.\frac{\partial f}{\partial \theta}.\nabla f\phi = \frac{1}{r\sin\theta}.\frac{\partial f}{\partial \phi} \tag{20}$$

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{r\theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{21}$$

$$\nabla^2 f = \nabla.\nabla = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)f + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2} \tag{22}$$

The Hydrogen Atom Problem: The Cartesian coordinates x, y, z can be written in terms of Spherical polar coordinates as follows -

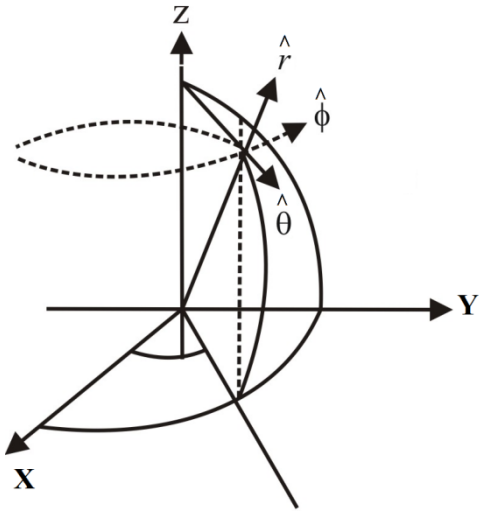


Figure 3.*Vector representations of unit vectors r, θ and ϕ*

$$x = r\sin\theta\cos\phi \tag{23}$$

$$y = r\sin\theta\sin\phi \tag{24}$$

$$z = r\cos\theta \tag{25}$$

Here, θ and ϕ are the angles made by the radial vector r, joining point P to the origin and its components along X, Y and Z axis respectively Figure (4).

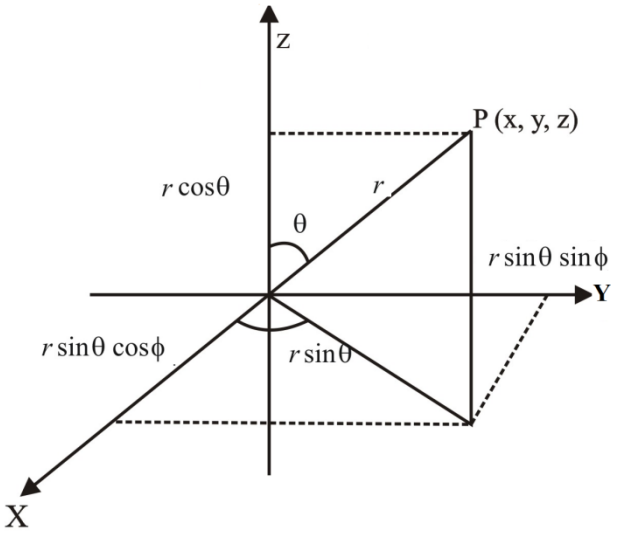


Figure 4. *Radial vector r joining point P to the origin and its components along X, Y and Z axis respectively*

The Schrodinger equation in Spherical coordinates is given by:

$$\frac{\partial\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{2m}{\hbar^2}(E-V)\Psi=0 \tag{26}$$

The above Schrodinger equation in spherical polar co-ordinate system can be written as:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}+\frac{2m}{\hbar^2}(E-V)=0 \tag{27}$$

We have,

$$V=\frac{e^2}{4\pi\xi_0 r} \tag{28}$$

Multiply both sides of the above equation by $r^2\sin^2\theta$, we get

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{\partial^2\Psi}{\partial\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\xi_0 r}\right)=0 \tag{29}$$

Using separation of variable, we can write the wave function as follow:

$$\Psi(r,\theta,\phi)=\Psi(r)\Psi(\theta)\Psi(\phi) \tag{30}$$

Substituting Ψ as above and divide both sides of the equation by Ψ , we obtain -

$$\frac{\sin^2\theta}{\psi(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(r)}{\partial r}\right)+\frac{\sin\theta}{\Psi(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right)+\frac{1}{\Psi(\phi)}\frac{\partial^2\Psi(\phi)}{\partial\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\xi_0 r}\right)=0 \tag{31}$$

We can rearrange the terms as follows–

$$\frac{\sin^2\theta}{\psi(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(r)}{\partial r}\right)+\frac{\sin\theta}{\Psi(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\xi_0 r}\right) \tag{32}$$

$$=-\frac{1}{\psi(\phi)}\frac{\partial^2\Psi(\phi)}{\partial\phi^2}$$

The right hand side of the above equation is compared with the square of a quantum number m_e -

$$-\frac{1}{\Psi(\phi)}\frac{\partial^2\Psi(\phi)}{\partial\phi^2}=m_l^2 \tag{33}$$

$$\Rightarrow\frac{\partial^2\Psi(\phi)}{\partial\phi^2}+m_l^2\Psi(\phi)=0 \tag{34}$$

This yields a solution -

$$\Psi(\phi)=Ae^{im_l\phi} \tag{35}$$

Here, m_l is called magnetic quantum number.

$m_l=0,\ \pm1,\ \pm2,\ \pm3,\ \ldots\ldots\ldots\ldots$

We can re-write the Schrodinger equation as –

$$\frac{\sin^2\theta}{\Psi(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(r)}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\xi_0 r}\right)=m_l^2-\frac{\sin^2\theta}{\Psi(\theta)}\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial r}\right) \tag{36}$$

$$\frac{1}{\Psi(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(r)}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\xi r}\right)=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\sin\theta\,\Psi(\theta)}\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right) \tag{37}$$

In above equation, we have obtained L.H.S. and R.H.S. as a function for r and θ co-ordinates separately. Both sides give differential equations, which can be solved by comparing the equations with a constant. Here, in this case, it is $l(l+1)$. So, we have –

$$\frac{1}{r^2}\frac{1}{\Psi(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(\theta)}{\partial\theta}\right)+\left[\frac{2m}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\xi_0 r}\right)-\frac{l(l+1)}{r^2}\right]=0 \tag{38}$$

$$\frac{1}{\sin\theta\,\Psi(\theta)}\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]=0 \tag{39}$$

The above equations can be re-written as follows -

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(r)}{\partial r}\right)+\left[\frac{2m}{\hbar^2}\left(\mathrm{E}+\frac{e^2}{4\pi\xi_0 r}\right)-\frac{l(l+1)}{r^2}\right]\Psi(r)=0 \tag{40}$$

$$\frac{1}{\sin\theta}.\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]\Psi(\theta)=0 \tag{41}$$

Application to Hydrogen Atom

Radial Part

Now, we have the radial equation of Hydrogen atom given by –

$$\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\Psi(r)+\frac{2\gamma}{\hbar^2}\left(\mathrm{E}+\frac{ze^2}{r}-\frac{\hbar^2 l(l+1)}{2\mu r^2}\right)\Psi(r)=0 \tag{42}$$

Since, in atom electrons remain in bound state –

$\mathrm{E} < 0$, we can use $\mathrm{E} = -|\mathrm{E}|$

Let us introduce new variables:

$$\xi=\left(\frac{8\mu|\mathrm{E}|}{\hbar^2}\right)^{1/2}r \tag{43}$$

$$\lambda=\frac{ze^2}{\hbar}\left(\frac{\lambda}{2|\mathrm{E}|}\right)^{1/2} \tag{44}$$

Substituting ξ and λ from eq. (43) and (44) into (42) –

$$\frac{\partial^2\Psi(r)}{\partial\xi^2}+\frac{2}{\xi}\frac{\partial\Psi(r)}{\partial\xi}-\frac{l(l+1)}{\xi^2}\Psi(r)+\left(\frac{\lambda}{\xi}-\frac{1}{4}\right)\Psi(r)=0 \tag{45}$$

For the case of large ξ values, the equation (45) reduces to a simpler form as a special case.

$$\frac{\partial^2\Psi(r)}{\partial\xi^2}-\frac{1}{4}\Psi(r)=0 \qquad (46)$$

The solution for eq. (46) is $e^{\pm\xi/2}$, but the function must not diverge for $\xi \Rightarrow \pm\infty$, thus, the acceptable general solution for bound state can be taken as –

$$\Psi = e^{-\xi/2}.u(\xi) \qquad (47)$$

Substitution gives us –

$$\frac{\partial^2 u(\xi)}{2\xi^2}-\left(1-\frac{2}{\xi}\right)\frac{\partial u(\xi)}{\partial\xi}+\left[\frac{\lambda-1}{\xi}-\frac{l(l+1)}{\xi^2}\right]u(\xi)=0 \qquad (48)$$

Let us use a power series as a solution, such that –

$$u(\xi)=\sum_n a_n\xi^{n+r}=\xi^r F(\xi) \qquad (49)$$

Substitution of eq. (49) into eq. (48) yields –

$$\xi^2\frac{\partial^2F(\xi)}{\partial\xi^2}+\xi[2(r+1)-\xi]\frac{\partial F(\xi)}{\partial\xi}+[\xi(\lambda+r-1)+r(r+1)-(l-1)]F(\xi)=0 \qquad (50)$$

As a trivial case, $\xi=0$, which yields

$$r=l \text{ and } r=-(l-1) \qquad (51)$$

For finite solution at the origin, the acceptable solution is $r=l$ because r= (l-1) will make the
series singular at $\xi\to 0$

Now, eq. (50) becomes –

$$\frac{\partial^2F(\xi)}{\partial\xi^2}+\left(\frac{2l+2}{\xi}-1\right)\frac{\partial F(\xi)}{\partial\xi}+\frac{(\lambda-l-1)}{\xi}F(\xi)=0 \qquad (52)$$

Substitution of $F(\xi)$ in form of a series gives –

$$\sum_{n=0}^{\infty}\left[n(n-1)a_n\xi\left(\frac{(l+1)}{\xi}-1\right)+(\lambda-l-1)a_n\xi\right]=1 \qquad (53)$$

We obtain –

$$\sum_{n=0}^{\infty}[(n+1)(n+2l+2)a_{n+1}+(\lambda-1-l-n)a_n]\xi^{n-1}=0 \qquad (54)$$

Since, relation expressed by eq. (54) holds good for all value of ξ, we get the following recursion relation –

$$\frac{a_n+1}{a_n}=\frac{n+l+1-\lambda}{(n+1)(n+2l+2)} \tag{55}$$

For large n, we have

$$\frac{a_n+1}{a_n}\simeq\frac{1}{n}\Rightarrow 0 \tag{56}$$

Since, series given by eq. (55) must terminate for some value of n say n_r, we have.

$$n_p=\lambda=n_r+l+1 \tag{57}$$

Here, n_p is the principal quantum number. Now, we have the energy eigen value –

$$E_{n_p}=-\frac{\mu Z^2e^4}{2\hbar^2n_p^2} \tag{58}$$

Wave function

We have obtained the recursion relation –

$$a_{n+1}=\frac{n+l+1-\lambda}{(n+1)(n+2l+2)}a_n \tag{59}$$

$$a_{n+1}=\frac{n+l+1-n_p}{(l+1)(n+2l+2)} \tag{60}$$

$$a_{n+1}=(-1)^{n+1}\frac{n_p-(n+l+1)}{(n+1)(n+2l+2)}\cdot\frac{n_p-(n+l)}{n(n+2l+1)}\cdot\frac{n_p-(n+l-1)}{(n-1)(n+2l)}\cdots\cdots\cdots\frac{n-(l+1)}{1.(2l+2)}a_0 \tag{61}$$

This recursion relation determines the power series expansion of $F(\xi)$. If we try to obtain the first few terms of the series $F(\xi)$, We can observe that it closely matches with the terms of Associated Laguerre polynomials Laguerre polynomials can be represented by following expression –

$$L_r(x)=e^x\frac{d^r}{dx^r}\left(x^re^{-x}\right) \tag{62}$$

Associated Laguerre polynomials are defined by –

$$L_r^q(x)=\frac{d^2}{dx^2}L_q(x) \tag{63}$$

First few of the Laguerre polynomials are given as follows:

$$L_0(x)=1$$
$$L_1(x)=1-x$$
$$L_2(x)=2-4x+x^2$$
$$L_3(x)=6-18x+9x^2-x^3$$

Remember we have –

$$\lambda=\frac{Z_l^2}{\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2}=\frac{Ze^2}{\hbar c}\left(\frac{\mu e^2}{2|\mathrm{E}|}\right)^{1/2}=Z\alpha\sqrt{\frac{\mu c^2}{2|\mathrm{E}|}} \tag{64}$$

$$|\mathrm{E}|=\frac{Z^2x^2\mu c^2}{2n^2}\;\xi=\left(\frac{8b|E|}{e^2}\right)^{1/2}r=\sqrt{\frac{4\mu^2c^2Z^2\alpha^2}{\hbar^2ne^2}}r=\frac{2\mu cZ\alpha}{\hbar n_p}r=\frac{2Z}{n_pa_2}r \tag{65}$$

The solution $F(\xi)$ is given by –

$$F(\xi)=-L_{n+l}^{2l+1}(\xi) \tag{66}$$

$$\Psi_{n,l}(\xi)=-e^{-\xi/2}\xi^lL_{n+l}^{2l+1}(\xi) \tag{67}$$

The normalization of the wave function gives –

$$\int_0^\infty A^2\xi^2e^{-\xi}\xi^lL_{n+l}^{2l+1}(\xi)=1 \tag{68}$$

$$=A^2\frac{2n(\angle n+l)^3}{\angle n-l-1}=1$$

$$A=\left[\frac{\angle n-l-1}{2n(\angle n+l)^3}\right]^{1/2} \tag{69}$$

So, the normalized radial wave function can be written as –

$$\Psi_{n,l}(r)=-\left[\left(\frac{2Z}{na_0}\right)^3\frac{\angle n-l-1}{2n(\angle n+l)}\right]^{1/2}\left(\frac{2Zr}{na_0}\right)^le^{\frac{-zr}{na_0}}L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \tag{70}$$

Here, $\xi = \frac{2Zr}{na_0}$

The first radial wave functions for hydrogen atom are given by –

$$\Psi_{1,0}(r) = 2\left(\frac{z}{a_0}\right)^{3/2} e^{-Zr/a_0} \quad (71)$$

$$\Psi_{2,0}(r) = \left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{zr}{2a_0}\right)e^{-Zr/a_0} \quad (72)$$

$$\Psi_{2,1}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{zr}{2a_0}e^{-Zr/a_0} \quad (73)$$

$$\Psi_{3,0}(r) = \left(\frac{Z}{2a_0}\right)^{3/2}\left[1-\frac{2Zr}{3a_0}+\frac{2Z^2r^2}{27a_0^2}\right]e^{-Zr/3a_0} \quad (74)$$

The Polar Angle Equation

The angular part with θ can be re-written as –

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\frac{\partial}{\partial\theta}\right)\Psi(\theta) = \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right) \quad (75)$$

$$= \sin\theta\left(\cos\theta\frac{\partial\Psi(\theta)}{\partial\theta}+\sin\theta\frac{\partial^2\Psi(\theta)}{\partial\theta^2}\right) \quad (76)$$

$$= \sin^2\theta\frac{\partial^2\Psi(\theta)}{\partial\theta^2}+\sin\theta\cos\theta\frac{\partial\Psi(\theta)}{\partial\theta} \quad (77)$$

Now angular equation in θ becomes:-

$$\sin^2\theta\frac{\partial\Psi(\theta)}{\partial\theta^2}+\sin\theta\cos\theta\frac{\partial\Psi(\theta)}{\partial\theta}+l(l+1)\sin^2\theta\,\Psi(\theta)-m_l^2\,\Psi(\theta)=0 \quad (78)$$

Let us use a new variable, $x = \cos\theta$, we have -

$$\frac{\partial\Psi(\theta)}{\partial\theta} = \frac{\partial\Psi(\theta)}{\partial\theta}\cdot\frac{\partial x}{\partial\theta} = \frac{\partial\Psi(x)}{\partial x}(-\sin\theta) = -\sin\theta\frac{\partial\Psi(x)}{\partial x} \quad (79)$$

$$\frac{\partial^2\Psi(\theta)}{\partial\theta^2}=\frac{\partial}{\partial\theta}\left(-\sin\theta\frac{\partial\Psi(x)}{\partial x}\right)=-\cos\theta\frac{\partial\Psi(x)}{\partial x}-\sin\theta\frac{\partial}{\partial x}\frac{\partial\Psi(x)}{\partial x}.\frac{\partial x}{\partial\theta}$$

$$=-\cos\theta\frac{\partial\Psi(x)}{\partial x}+\sin^2\theta\frac{\partial^2\Psi(x)}{\partial x^2} \qquad (80)$$

Substitution gives us –

$$\sin^2\theta\left(\sin^2\theta\frac{\partial^2\Psi(x)}{\partial x}-\cos\theta\frac{\partial\Psi(x)}{\partial x}\right)+\sin\theta\cos\theta\left(-\sin\theta\frac{\partial\Psi(x)}{\partial x}\right) \qquad (81)$$

$$+b(l+1)\sin^2\theta\,\Psi(x)-m_e^2\Psi(x)=0 \qquad (82)$$

Dividing both sides by $\sin^2\theta$, we get –

$$(1+x^2)\frac{\partial\Psi(x)}{\partial x^2}-2x\frac{\partial\Psi(x)}{\partial x}+l(l+1)\Psi(x)-\frac{m_x^2}{(1-x^2)}\Psi(x)=0 \qquad (83)$$

This is associated Legendre equation. Its solutions are given by associated Legendre polynomials as follows:

$$P_{em}(x)=(-1)^m\sqrt{(1-x^2)^m}\,\frac{d^m}{dx^m}P_e(x) \qquad (84)$$

Here, Legendre polynomials $P_e(x)$ are given by –

$$P_e(x)=\frac{(-1)^l}{2^l\angle l}\frac{d^l}{dx^l}(1-x^2)^l \qquad (85)$$

The first few associated Legendre polynomials are given by –

$$P_{0,0}(x)=1 \qquad P_{1,0}(x)=x \quad P_{1,1}(x)=-\sqrt{1-x^2}$$

$$P_{2,0}(x)=\frac{1}{2}(3x^2-1) \qquad P_{2,1}(x)=-3x\sqrt{1-x^2} \quad P_{2,2}(x)=3(1-x^2)$$

The complete wave function for angular parts can be written as –

$$Y_{l,m}(\theta,\phi)=\Psi(\theta)\Psi(\phi)=(-1)^m\sqrt{\frac{(2l+1)(l-m)}{4\pi L(l+m)}}P_{l,m}(\cos\theta)\,e^{im\phi}_{m>o} \qquad (86)$$

$$R_{1,0}(r) = 2a_0^{-3/2}e^{-r/a_0}$$

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

$$R_{2,1}(r) = \frac{1}{\sqrt{24}}a_0^{-3/2}\frac{r}{a_0}e^{-r/2a_0}$$

$$R_{3,0}(r) = \frac{2}{\sqrt{27}}a_0^{-3/2}\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$$

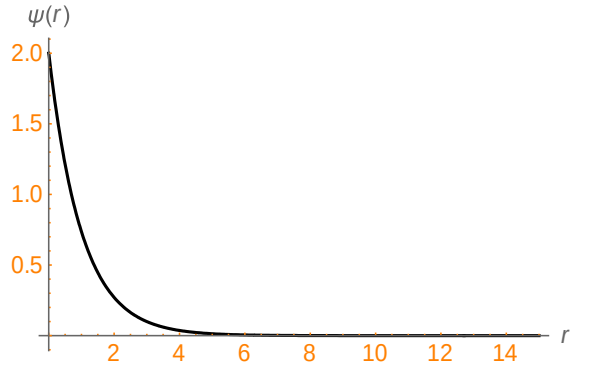
$$R_{3,1}(r) = \frac{8}{27\sqrt{6}}a_0^{-3/2}\left(1-\frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$$

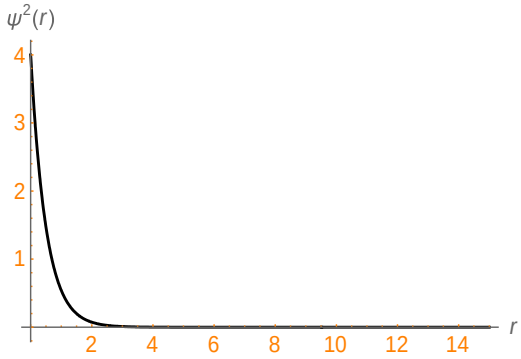
$$R_{3,2}(r) = \frac{4}{81\sqrt{30}}a_0^{-3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}$$

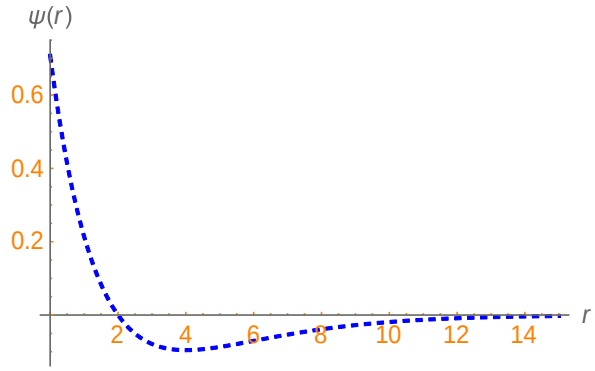
Table 1. *First six radial wave functions of hydrogen atom*

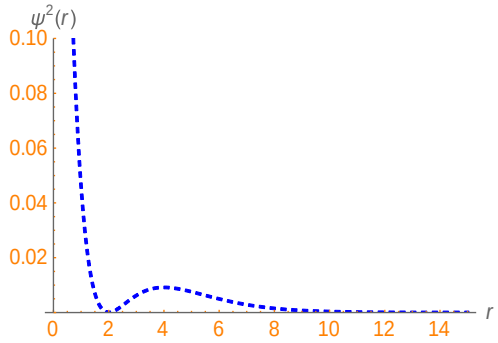
First six radial wave functions $\psi(r) \rightarrow R$ as shown in Table-1 and its square functions $\psi^2(r)$ (i.e. Radial probability distribution function) are plotted, respectively in Figure (5).

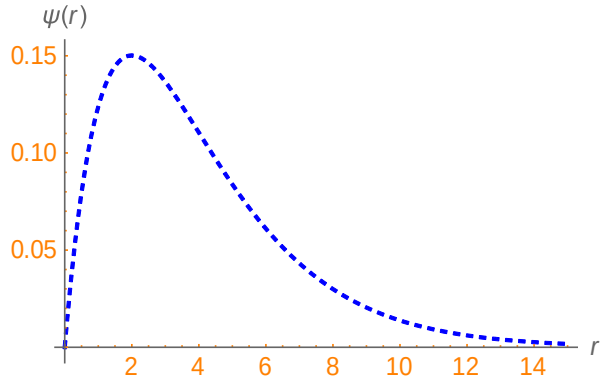
Visualization of Radial Function

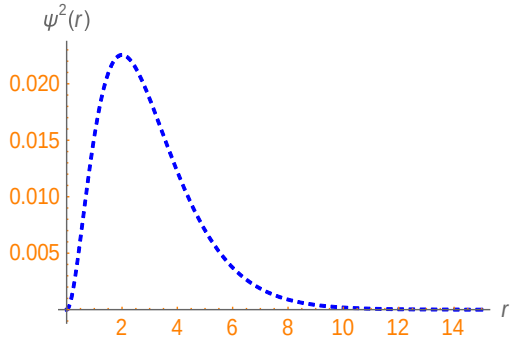


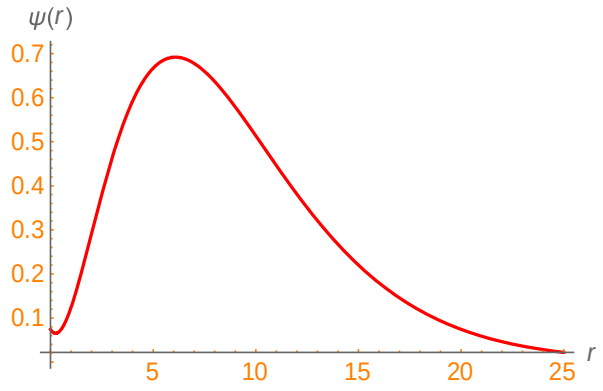


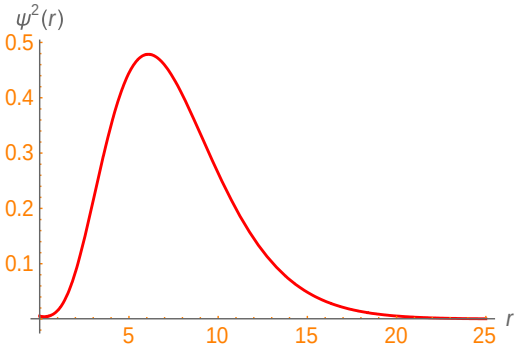


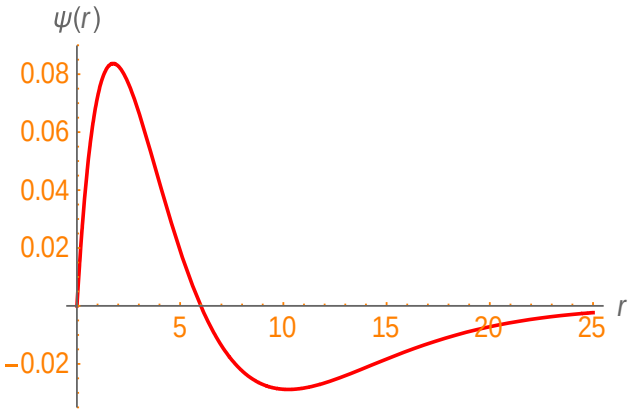


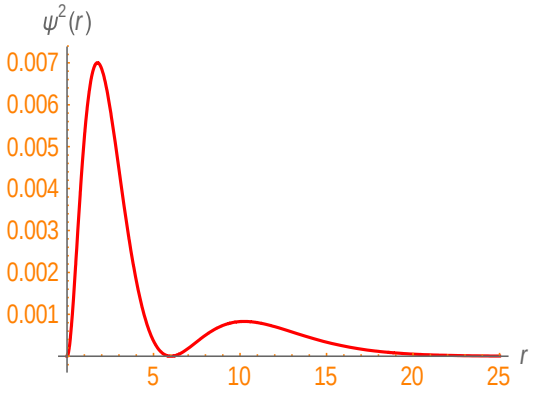


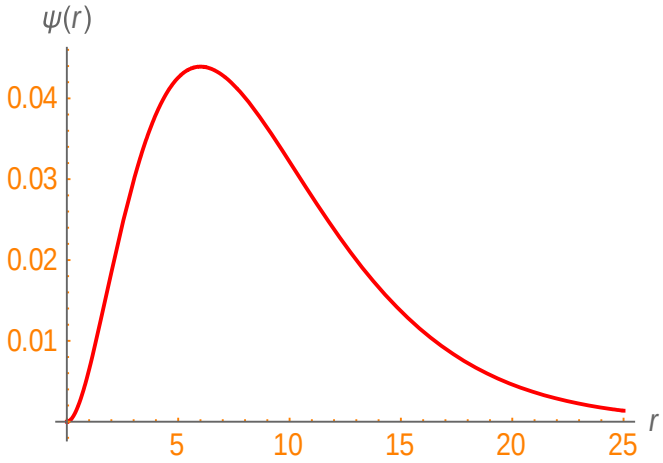


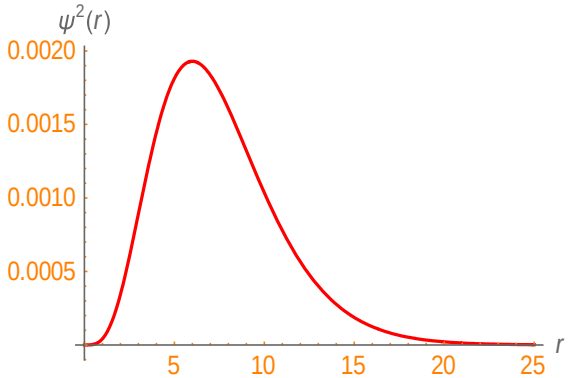


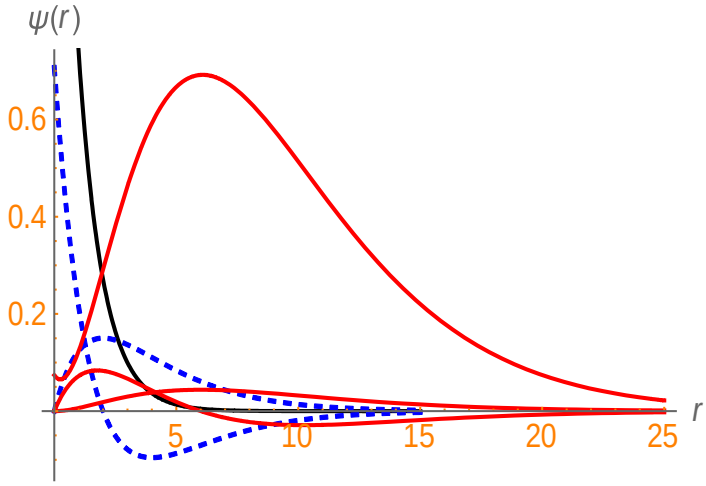



ψ(r)
0.08
0.06
0.04
0.02
−0.02
5
10
15
20
25
r


ψ²(r)
0.007
0.006
0.005
0.004
0.003
0.002
0.001
5
10
15
20
25
r


ψ(r)
0.04
0.03
0.02
0.01
5
10
15
20
25
r


ψ²(r)
0.0020
0.0015
0.0010
0.0005
5
10
15
20
25
r


ψ(r)
0.6
0.4
0.2
5
10
15
20
25
r

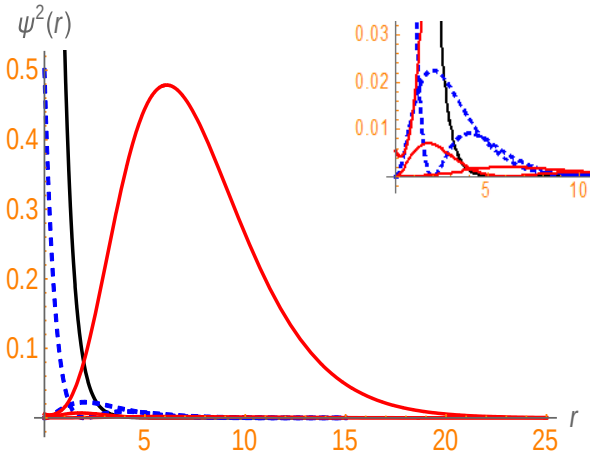
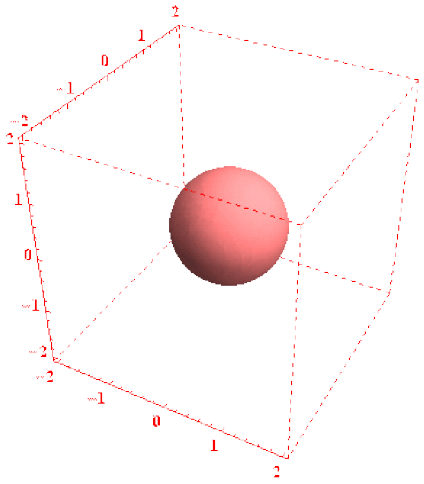
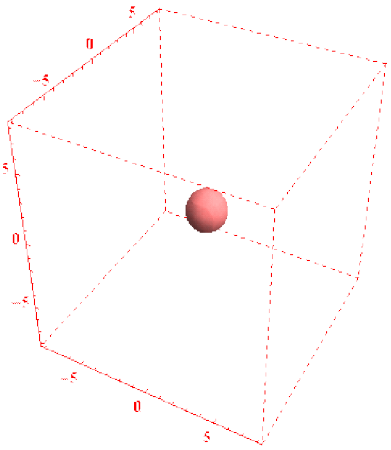

ψ²(r)
0.5
0.4
0.3
0.2
0.1
5
10
15
20
25
r
0.03
0.02
0.01
5
10

Figure 5.*First six radial wave functions $\psi(r) \rightarrow R$ as shown in Table-1 and it's square functions; $\psi^2(r)$ (i.e. Radial probability distribution function), respectively. These curves are plotted using Mathematica Software.*

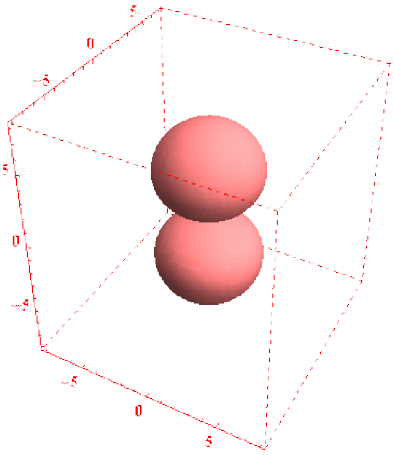
Twenty hydrogen orbitals are plotted using Mathematica Software for visualization as shown in Figure (6).



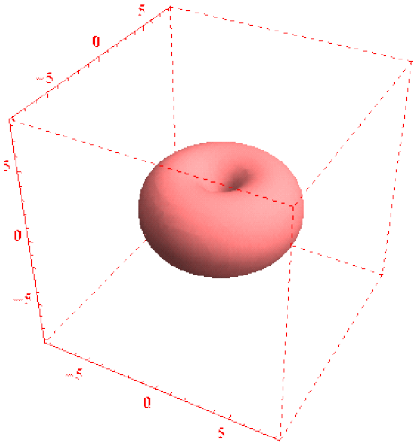
n=4, l=3, m=3



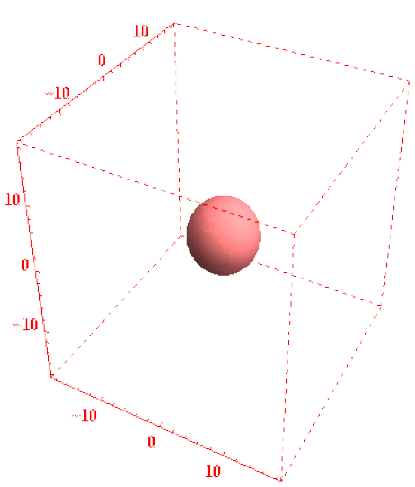
n=2, l=0, m=0



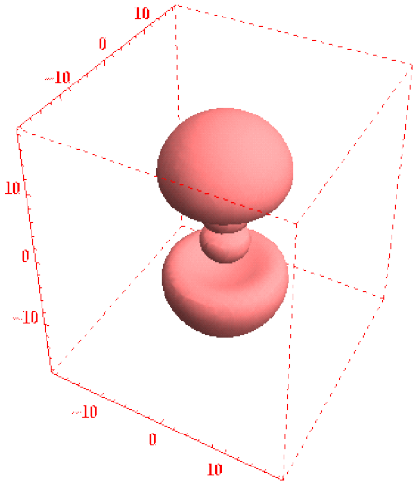
n=2, l=1, m=0



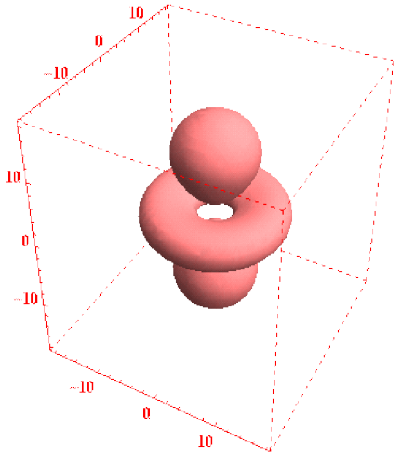
n=2, l=1, m=1



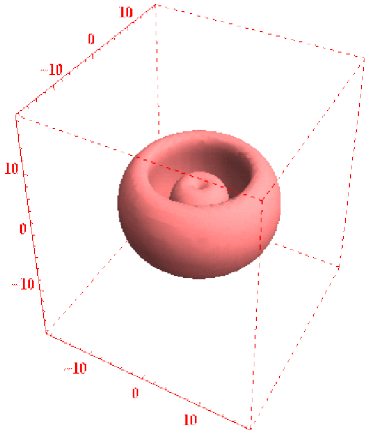
n=3, l=0, m=0



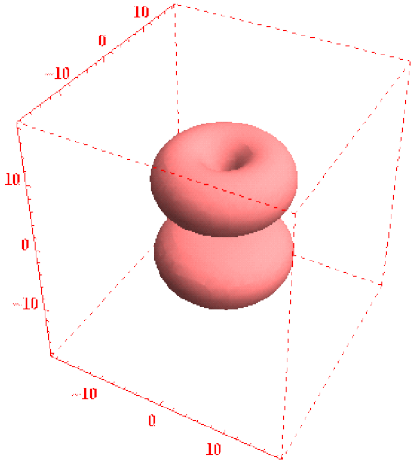
n=3, l=1, m=0



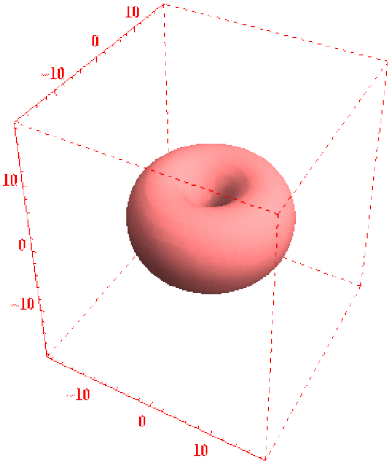
n=3, l=3, m=0



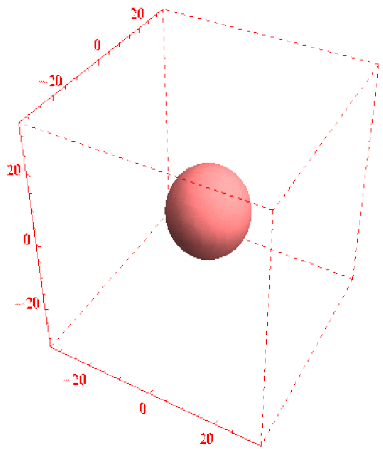
n=3, l=1, m=1



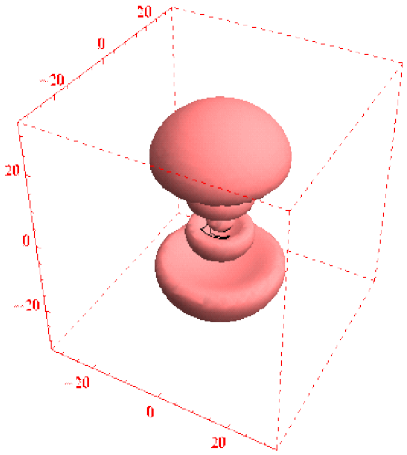
n=3, l=2, m=1



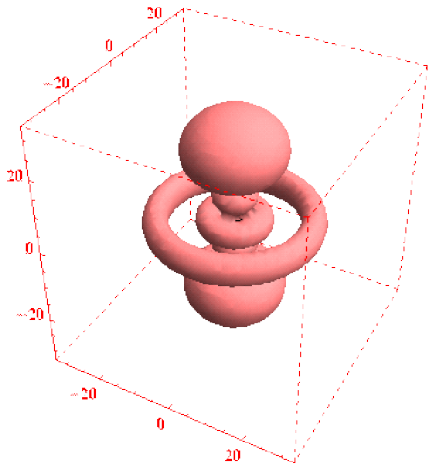
n=3, l=2, m=2



n=4, l=0, m=0



n=4, l=1, m=0



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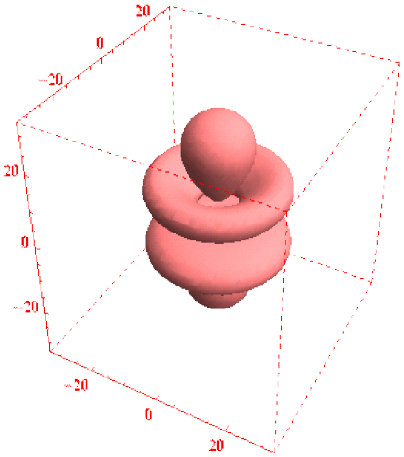
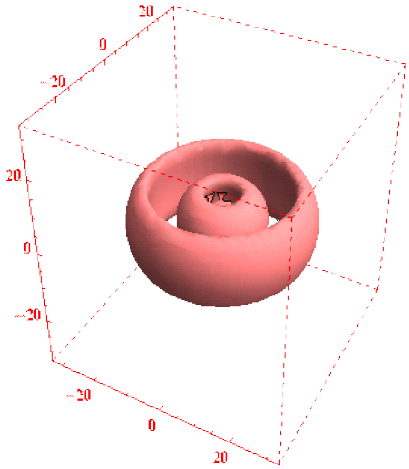
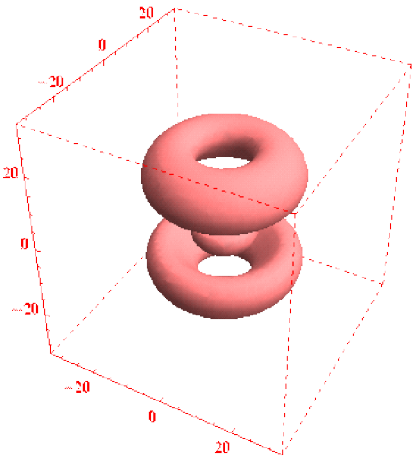


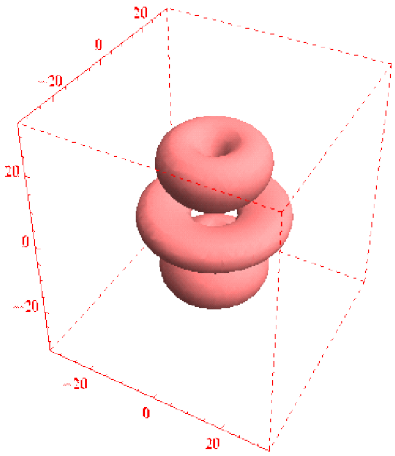
n=4, l=3, m=0



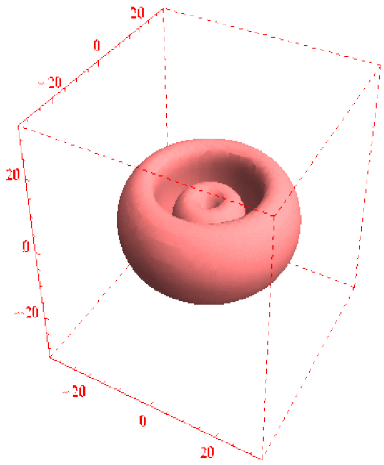
n=4, l=1, m=1



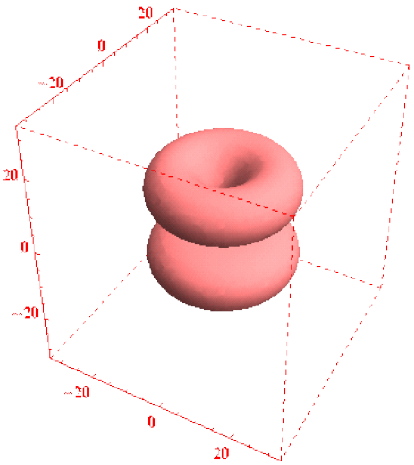
n=4, l=2, m=1



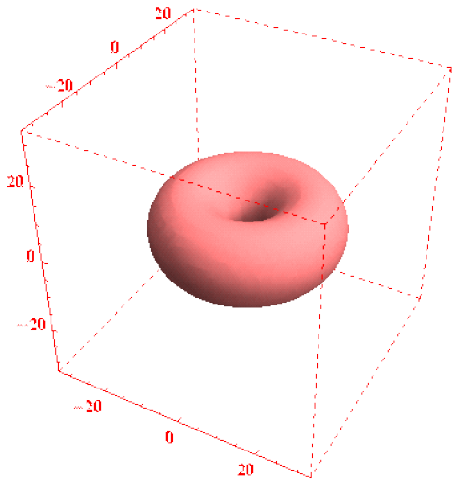
n=4, l=3, m=1



n=4, l=2, m=2



n=4, l=3, m=2



n=4, l=3, m=3

Figure 6. *Twenty hydrogen orbitals are plotted using Mathematica Software for visualization. Their respective quantum numbers n, l and m are below the figures.*

Readers may develop their own computer programs for Figure (5) and Figure (6) using available books (Wolfram 1996) on Mathematica Software .

CONCLUSION

The author hopes that the hierarchy of ideas systematically presented, will result into easy understanding of the problem,at under graduate level. The graphical presentations may encourage young students and their tutors to visualize the rigorous and comprehensive solutions, thus obtained, using Mathematica Software, and help them to grasp this important concept in order to apply quantum mechanics to more complicated physical problems.

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