The structure of hydrogenic atoms

The Coulomb potential energy of an electron in a hydrogenic atom of atomic number

Z (and nuclear charge Ze) is

$$V = -\frac{Ze^2}{4\pi\varepsilon_o r}$$

where r is the distance of the electron from the nucleus and ε_o is the vacuum permittivity.

The hamiltonian for the electron is therefore

$$\frac{-h^2}{8\pi^2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_o r} \quad \text{----------------------------------1}$$

Where μ is reduced mass.

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

The Schrödinger equation for the internal motion of the electron relative to the nucleus is

$$\left[\frac{-h^2}{8\pi^2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_o r}\right]\psi = E\psi$$

$$\left[\frac{h^2}{8\pi^2\mu}\nabla^2 + \frac{Ze^2}{4\pi\varepsilon_o r}\right]\psi = -E\psi$$

$$\left[\frac{h^2}{8\pi^2\mu}\nabla^2 + \frac{Ze^2}{4\pi\varepsilon_o r}\right]\psi + E\psi = 0$$

$$\left[\frac{h^2}{8\pi^2\mu}\nabla^2 + \frac{Ze^2}{4\pi\varepsilon_o r} + E\right]\psi = 0$$

$$[\nabla^2 + \frac{8\pi^2\mu}{h^2}(\frac{Ze^2}{4\pi\varepsilon_o r} + E)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2\mu}{h^2}(\frac{Ze^2}{4\pi\varepsilon_o r} + E)\psi = 0 \quad \text{---------------------2}$$

The exact solution of the above equation is difficult. Transforming equation 2 from Cartesian coordinates to spherical polar coordinates, it become easier to separate the variables and also become easier to solve the equation. The spherical polar coordinates are related to Cartesian coordinates as follows

$$x = r\,sin\theta\,cos\phi$$

$$y = r\,sin\theta\,sin\phi$$

$$z = r\,cos\theta$$

The values of x, y, z in the wave equation for hydrogenic atom can be substituted by polar coordinates which transforms the schrodinger equation as follows

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{r^2\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(\frac{sin\theta\,\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\times\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left(\frac{Ze^2}{4\pi\varepsilon_o r}+E\right)\psi(r,\theta,\phi)$$

=0 --------------------------------(3)

ψ will now function of r, θ and ϕ instead of x, y, z.

The variables r, θ and ϕ can be separated which gives the wave function multiplications of separated variables.

So,

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Where $R(r)$ is the function depends on r but independent of other coordinates, $\Theta(\theta)$ is the function of θ and independent of other coordinates and $\Phi(\phi)$ is the function of ϕ and independent of other coordinates.

The function $\psi(r,\theta,\phi)$ can be replaced by $R(r)\Theta(\theta)\Phi(\phi)$ in equation 3 which gives a complicated equation. Since the variables are independent to each other, so the resultant equation can be separated three independent equation as follows,

1) $\frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{r^2\partial R(r)}{\partial r}\right)+\frac{\beta}{r^2}R(r)+\frac{8\pi^2\mu}{h^2}\left(\frac{Ze^2}{4\pi\varepsilon_o r}+E\right)R(r)=0$ (4)
2) $\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(\frac{sin\theta\,\Theta(\theta)}{\partial\theta}\right)-\frac{m^2\Theta(\theta)}{r^2 sin^2\theta}+\beta\,\Theta(\theta=0$ (5)
3) $\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+m^2\,\Phi(\phi)=0$ (6)

Equation (4) is a function of r only and it is called radial equation for Schrodinger equation for hydrogen like atom. The solution of this equation is as given below. (No need to remember)

$$R_{n,l}(r)=\left(\frac{2Z}{na_o}\right)^{\frac{3}{2}}\left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{\frac{1}{2}}e^{\frac{Zr}{na_o}}\left(\frac{2Zr}{na_o}\right)^{i}L^{2l+1}_{n-l-1}\left(\frac{2Zr}{na_o}\right)$$

Where $n = 1, 2, 3, 4 \ldots$..etc and $l = 0, 1, 2, 3, 4 \ldots (n-1)$.

n is known as principal quantum number and l is known as angular momentum quantum number.

Quantum number l represents the subshell (letter designation) of orbital as 0 corresponds s orbital, 1 corresponds p orbital, 2 corresponds d orbital and 3 corresponds f orbital.

The radial wave functions are as given below

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

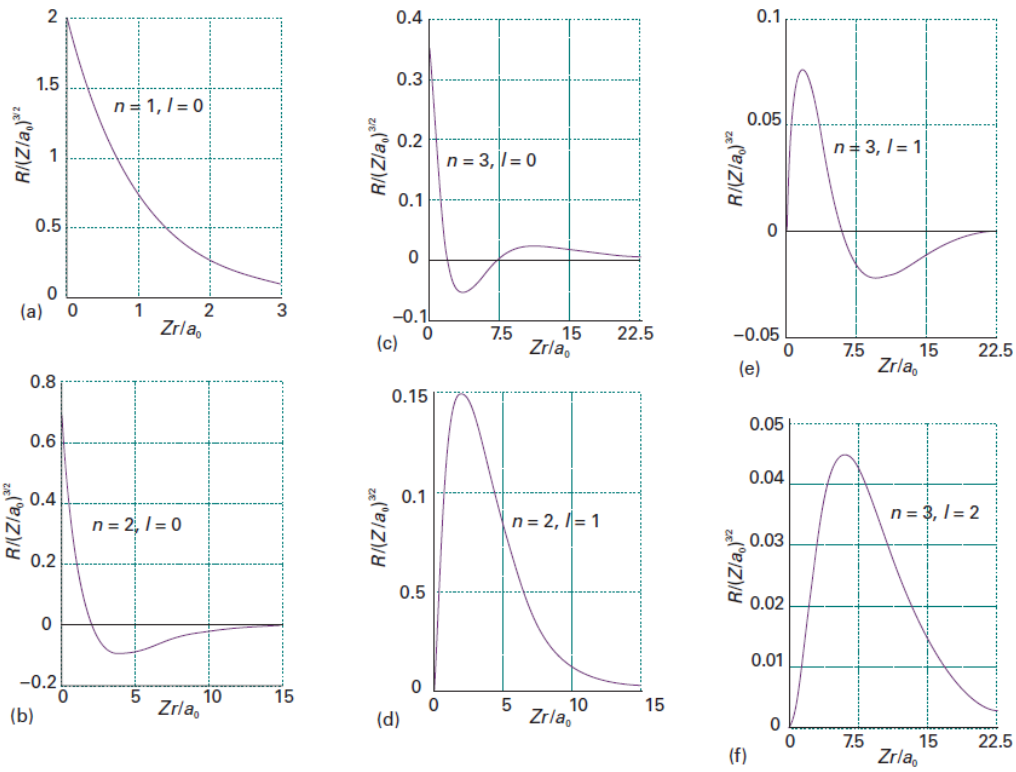
$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^{2} e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a_0}+\frac{2\left(Zr\right)^{2}}{27a_0^{2}}\right) e^{-Zr/3a_0}$$



Graphical representation of radial wave function of hydrogen atom. The point where the graph intercepts y axis is called a radial node. The number of radial node is equal to *n-l-1*.

Equation 5 and 6 represents angular wave equation. The solution of equation 5 gives the expression for $\Theta(\theta)$ which introduces magnetic quantum number m along with l. It gives the number of permitted orientation of subshells. The value of m varies from –l to +l through zero. For a given value of 'n' the total value of 'm' is equal to n^2. For a given value of 'l' the total value of 'm' is equal to (2l + 1).