Hydrogen Atom

Theory of hydrogen atom is of fundamental importance as it provides the basis for the theory of many electron systems. This is the simplest atom, that contains one proton and one electron. This is the only atom for which exact solution of the schrödinger equation is possible. For discussion we shall consider hydrogen like atom which consists of nucleus of charge Ze and an electron of charge - e separated by a distance r. The potential is Coulombic and is given by

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} = \frac{kZe^2}{r} \text{ ------ (1)}$$

We have the schrödinger equation

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

Substituting the value of V(r) in the above equation.

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)\Psi = 0 \text{ --------- (2)}$$

Radial Equation

We have to express schrödinger equation in spherical polar coordinates (r,θ, Ø) and separating the variables

$$\Psi(r,\theta,\emptyset) = R(r)\,\Theta(\theta)\,\emptyset(\emptyset)$$

We get the radial equation as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left[E - \frac{l(l+1)\hbar^2}{2mr^2} + \frac{kZe^2}{r}\right]R = 0 \text{ ----------- (3)}$$

To solve the above equation let us introduce a variable ρ and a constant λ defined by

$$\rho = \sqrt{\frac{-8mE}{\hbar^2}}, \qquad \lambda = \frac{kZe^2}{\hbar}\sqrt{\frac{m}{-2E}}$$

As E is negative for bound states, ρ and λ are real quantities. In terms of the new variable. Equ (3) becomes

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

Solution of the radial equation

Its asymptotic solution can be found when ρ → ∞, equation reduces to

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

Its solutions are R = $e^{-\rho/2}$ and $e^{\rho/2}$. Out of this two solutions, only $e^{-\rho/2}$ is acceptable since $e^{\rho/2} \rightarrow \infty$ as $\rho \rightarrow \infty$. The exact solution of Equ (4) be

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

Substituting the value of R(ρ) gives the differential equation satisfied by F(ρ) as

$$\frac{d^2F}{d\,\rho^2} + \rho(2 - \rho)\frac{dF}{d\rho} + [\,\rho\lambda - l(\,l+1\,) - \rho\,]\,F(\rho) = 0 \text{ ---------- (5)}$$

When ρ = 0 we get

l(l+1) F(0) = 0 or F(0) = 0, $l \neq 0$

Therefore if we try a power series solution for F(ρ) it must not contain a constant term. Hence

$$F(\rho) = \sum_{k=0}^{\infty} a_k\, \rho^{c+k}$$

Then equ (5) reduces to

$$\sum_k a_k\,(\,\lambda - 1 - c - k\,)\,\rho^{c+k+1} + \sum_k a_k\,(\,c^2 + 2ck + k^2 + c + k - l^2 - l\,)\rho^{c+k} = 0 \text{ -------(6)}$$

The above equation is valid for all values of ρ only if the coefficient of each power of ρ vanishes separately. Equating the coefficient of ρ^c to zero. We have

$$a_0\,(\,c^2 + C - l^2 - l) = 0$$

Or as ($a_{0 \neq 0}$) $\quad (\,c^2 + C - l^2 - l) = 0$

Or (c - l) (c + l + 1) = 0

Therefore c = l or c = - (l + 1)

If c = - (l+1), the first term in F(ρ) would be a_0/ρ^{l+1} which tends to infinity as ρ → 0. Hence c = *l* is the only acceptable value. Setting the coefficient $\rho^{l+\rho+1}$ in equ (6), we get

$$a_{k+1} = \frac{l+k+1-\lambda}{(k+1)(k+2l+2)}\,a_k \text{ ------------ (7)}$$

As k → ∞, the series for F(ρ) behaves like $\rho^l e^{\rho/2}$ and

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

This value of R(ρ) is not acceptable and therefore the series break off after a certain value of k, say n'. For this to happen a_{n^1+1} must be zero. Then from equ (7)

$l + n' + 1 - \lambda = 0 \qquad n' = 0, 1, 2, \ldots.$

Energy Eigenvalues

Defining a new quantum number n by

$$n = l + n' + 1 = \lambda = \frac{kZe^2}{\hbar}\sqrt{\frac{m}{-2E}}$$

Squaring and simplifying

$$E_n = -\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = -\frac{mZ^2e^4}{32\varepsilon^2{}_0\pi^2\hbar^2 n^2}, \qquad n = 1, 2, 3, \ldots$$

As n ≥ l + 1, the highest possible value of l is n- 1. Thus

l = 0, 1, 2, 3, …. (n - 1)

The complete wave function for hydrogen like atom is given by

Ψ_{nlm} (r, θ, Ø) = $R_{nl}\, y_{lm}$ (θ,Ø)

Where n = 1, 2, 3, …. l = 0, 1, 2, 3,… m = 0, ±1, ±2 …..

The explicit form of the wave function for some of the states are

$$\Psi_{100} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-zr/a_0}$$

$$\Psi_{200} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/(2a_0)}$$

$$\Psi_{210} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a_0}\right)^{5/2} r\, e^{-Zr/(2a_0)}\text{Cos}\,\theta$$

It may be noted that the expressions for the l = 1 state contain the factor r^1. The l = 2 states will have the factor r^2 and so on. The presence of the factor r^l makes the wave function zero at r = 0 except for the s-states.

Quantum numbers

The set of numbers used to describe the position and energy of the electron in an atom are called quantum numbers.There are four quantum numbers.

1. Principal quantum number

- In the quantum theory of the hydrogen atom the electron energy is constant, but while it may have any positive value (corresponding to an ionized atom), the only negative values the electron can have are specified by the formula.

$$E_n = E_1/n^2$$

The quantization of electron energy in the hydrogen atom is therefore described by the principal quantum number .

2. Orbital quantum number

- Quantization of angular - momentum magnitude
- Electron angular momentum L = $\sqrt{l(l+1)}\hbar$

With the orbital quantum number l restricted to the values.

l = 0, 1, 2, ... (n-1)

The electron can have only the angular momentum L specified by equ (1) . Like total energy E , angular momentum is both conserved and quantized .

3. Magnetic quantum number

- Quantization of angular momentum direction.
- The orbital quantum number l determines the magnitude L of the electron's angular momentum L .
- However, angular momentum, like linear momentum, is vector quantity, and to describe it completely means that direction be specified as well as magnitude.
- An electron revolving about a nucleus is a minute current loop and has a magnetic field like that of a magnetic dipole.
- Hence an atomic electron that possesses angular momentum interacts with an external magnetic field B.
- The magnetic quantum number ml specifies the direction of L by determining the component of L in the field direction. This phenomenon is often referred to as space quantization.

4. Spin quantum number

- The spin quantum number represents the intrinsic angular momentum of an electron .
- Since the angular momentum is vector, the spin quantum number has both magnitude (1/2) and direction (+ or -).

Designation of Angular momentum states

It is customary to specify electron angular momentum states by a letter, with corresponding to l = 0, p to l = 1, and so on, according to the following scheme.

Angular momentum	l = 0	1	2	3	4	5	6 ……
States	s	p	d	f	g	h	i