Radial probability density :

The probability of finding the electron in volume element $d\tau$ is given by

$$|\psi_{nlm}|^2 d\tau = |\psi_{nlm}|^2 r^2 \sin\theta dr d\theta d\phi$$

Therefore, the probability of finding the electron in a spherical shell of radius *r* and thickness *dr* is,

$$P(r)dr = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} |\psi_{nlm}|^2 r^2 \sin\theta dr d\theta d\phi = |R_{nl}|^2 r^2 dr$$

Here, $P(r)$ is called the radial probability density.

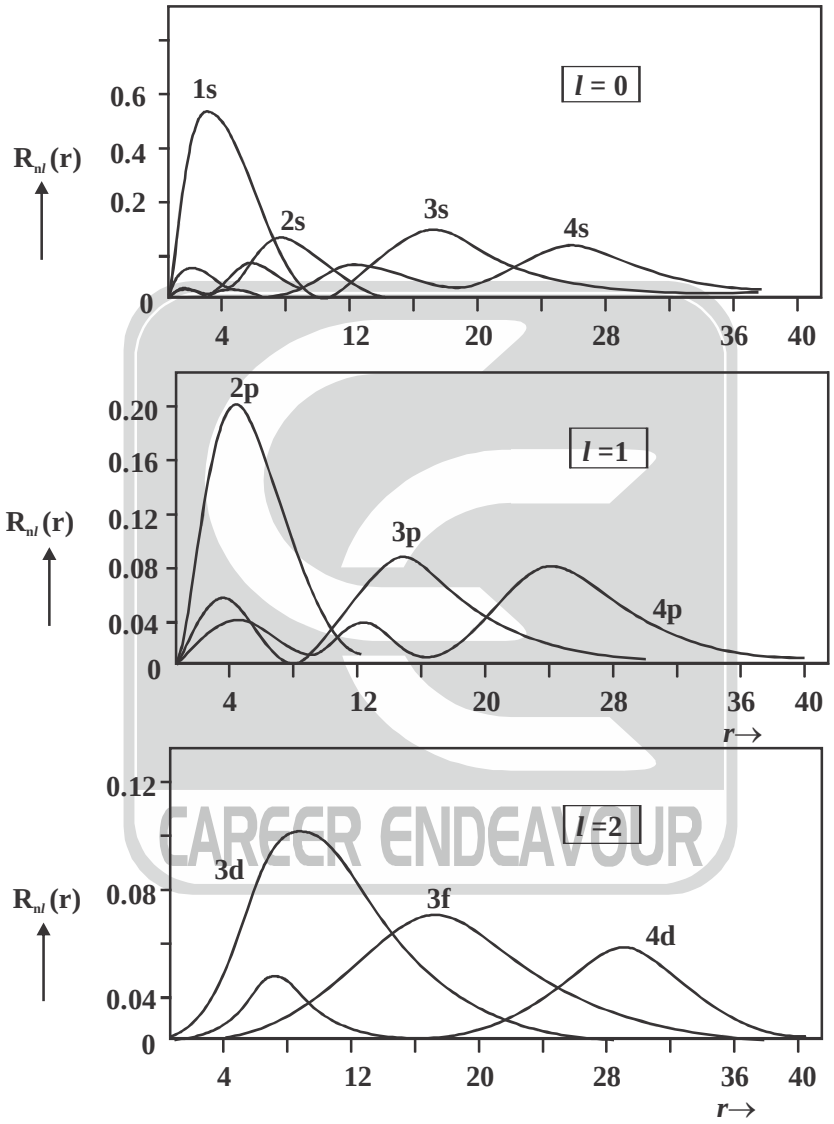

Figure : Variation of $R_{n\ell}(r)$ with *r* in units of a_0

Energy values for the hydrogen atom:

Energy eigenvalues of n^{th} state of hydrogen atom $E_n = -\dfrac{\mu z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}$

For the hyrogen atom *z* = 1 and hence, $E_n = -\dfrac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2} = -\dfrac{13.6}{n^2} eV$

where, *n* = 1, 2, 3, ... and is called the principal quantum number.

This shows that the energy values for different quantum states are discrete which is in agreement with old quantum theory and experiment.

Degeneracy:

For a particular value of n, $\ell = (n-1), (n-2), -2, -1, 0$, i.e. ℓ can take (n) values. Also for a particular value of l, $m = \ell, (\ell-1), (\ell-2), ..., 0, ..., -(\ell-1), -\ell$, i.e., m can take $(2\ell+1)$ values. Thus degeneracy of a particular energy level is, $\sum_{l=0}^{n-1}(2l+1) = n^2$

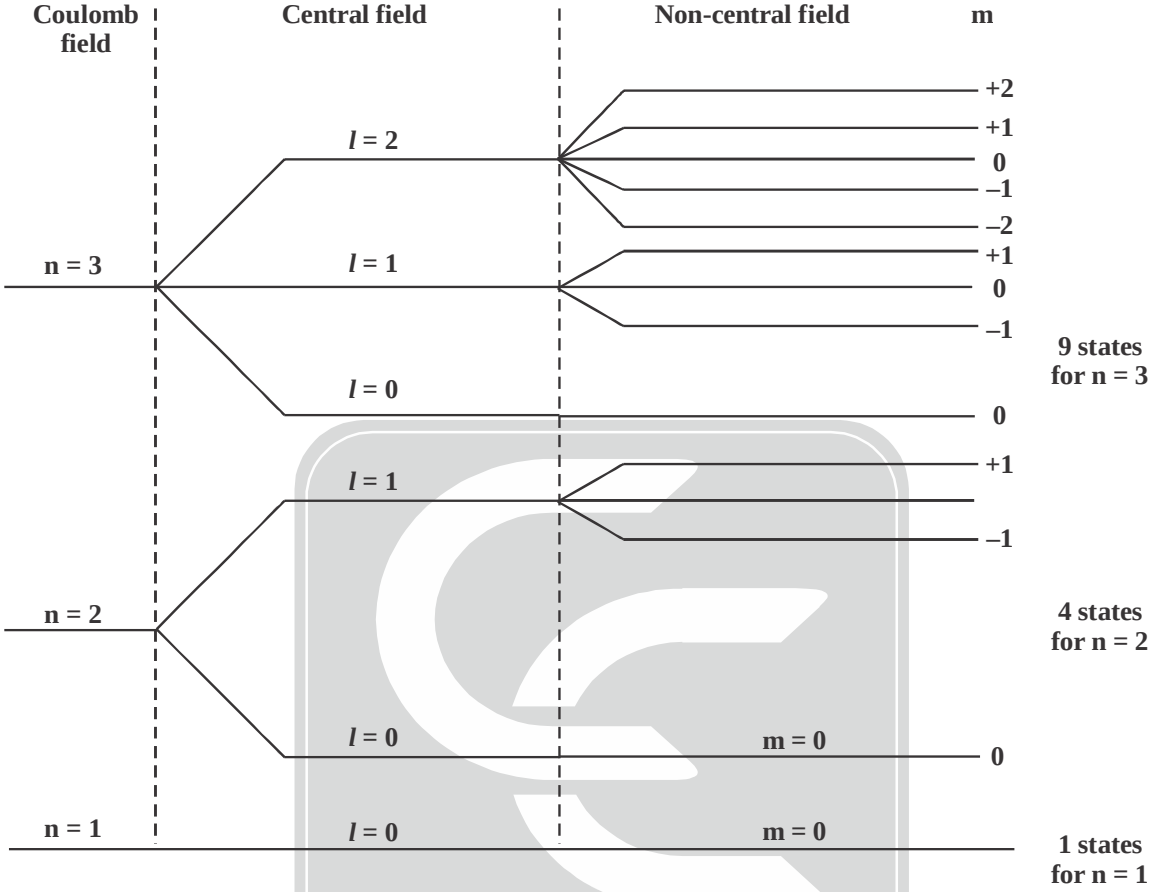

Figure : Degeneracy of hydrogenic atom

Virial theorem for hydrogen atom:

The statement of Virial theorem has been expressed in the previous chapter. Applying it to the case of Hydrogen atom results in the following.

Potential, $V \propto r^{-1} \Rightarrow V \propto x^n \Rightarrow n = -1$

Therefore, $2\langle T\rangle = n\langle V\rangle \Rightarrow 2\langle T\rangle = -\langle V\rangle$

$$\Rightarrow \quad \frac{\langle T\rangle}{\langle V\rangle} = -\frac{1}{2} \Rightarrow \langle E\rangle = \langle T\rangle + \langle V\rangle$$

$$\Rightarrow \quad \frac{\langle E\rangle}{\langle V\rangle} = \frac{-\frac{1}{2}\langle V\rangle + \langle V\rangle}{\langle V\rangle} = \frac{1}{2} \Rightarrow \frac{\langle E\rangle}{\langle V\rangle} = \frac{1}{2}$$

where, E = total energy

T = kinetic energy

V = potential energy.

Some useful facts for the Hydrogen atom:

1. The eigenfunctions $\{\psi_{n,l,m}\}$ are simultaneous eigenstates of the Hamiltonian $(\hat{H})$, Angular momentum $(\hat{L}^2)$, and the *z*-component of angular momentum $(\hat{L}_z)$. The corresponding eigenvalues are as follows:

$\hat{H}\psi_{n,l,m} = E_n\psi_{n,l,m}$, where $E_n = -\frac{13.6}{n^2}$ eV; $\hat{L}^2\psi_{n,l,m} = \hbar^2 l(l+1)\psi_{n,l,m}$, and $\hat{L}_z\psi_{n,l,m} = m\hbar\psi_{n,l,m}$

2. The number of nodes in the radial part of the wavefunction $\left(R_{n,l}(r)\right)$ is equal to $(n-l-1)$.

3. The expectation values of some useful operators for the state $\psi_{n,l,m}$ are listed below:

(i) $\langle r\rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right]a_0$ (ii) $\langle r^2\rangle = \frac{n^2}{2}\left[5n^2 + 1 - 3l(l+1)\right]a_0^2$

(iii) $\langle r^{-1}\rangle = \frac{1}{n^2 a_0}$ (iv) $\left\langle \frac{1}{r^2}\right\rangle = \frac{2}{n^3(2l+1)a_0^2}$

4. The most probable distance of an electron in the *n*th state of Hydrogen atom with $l = 0$ is given by $r_{\text{most probable}} = n^2 a_0$.

Hartree Theory:

Hartree's method of self-consistent fields:

An important method for obtaining a suitable central field is due to Hartree. In this method, a suitable function $\bar{V}(r_i)$ is first chosen with property close to that given by equation

$$\left.\begin{aligned}\bar{V} &= -\frac{Ze^2}{r_i} + \text{constant} \quad (\text{for small } r_i)\\ \text{And, } \bar{V} &= -\frac{Ze^2}{r_i} \quad (\text{for large } r_i)\end{aligned}\right\} \quad \ldots (1)$$

The single particle states ψ_i are then obtained by solving the Schrodinger equation. Now, the part of the potential due to all electrons other than the i[th] is calculated by assuming that each of these electrons yields a charge distribution as given by their wavefunctions already worked out.

Consider the j[th] electron, $j \neq i$. The average charge in a volume element $d\tau_j$ due to this electron is $e\,d\tau_j\left|\psi(r_j)\right|^2$ and the potential energy of interaction with the i[th] electron is

$$e^2\int d\tau_j \frac{\left|\psi_j(r_j)\right|^2}{\left|r_i - r_j\right|} \quad \ldots (2)$$

Thus, the i[th] electron moves in a potential generated by all the other electrons,

Namely, $e^2\sum_{j\neq i}\int d\tau_j \frac{\left|\psi_j(r_j)\right|^2}{\left|r_i - r_j\right|}$

So, that the full potential is,