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# ATOMIC STRUCTURE

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[DE – BROGLIE'S THEORY – B.sc – III (HONS)]



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DR. SHASHI KUMAR

[ASSOCIATE PROFESSOR G.J COLLEGE RAMBAGH BIHTA (PATNA) OF HOD DEPARTMENT OF CHEMISTRY]

## Atomic structure

### de – Broglie's Theory:-

This theory was given by Louis de – Broglie in 1924. According to Bohr's theory electron is particle only.

Now, according to de – Broglie theory:

“All moving particles of this universe have got both particle and wave character”.

That is why it is also called theory of Duality.

de – Broglie's was awarded to Nobel prize in Physics in 1929.

### de – Broglie equation:-

$$\lambda = \frac{h}{mu}$$

$$h = 6.625 \times 10^{-27} \text{ erg sec.}$$

$$= 6.625 \times 10^{-34} \text{ joule} \times \text{sec}$$

Here,  $\lambda$  = wave length.

$h$  = plank's constant.

$m$  = mass.

$u$  = velocity of the particle.

**Note:-** de – Broglie theory is applicable to those particles which are free any external or internal force.

**Proof:-** According to Einstein theory

$$E = mc^2 \longrightarrow (1)$$

$$C = 3 \times 10^8 \text{ m/sec}$$

Here,  $m$  = Lost mass

$C$  = velocity of light.

Now, according to plank's quantum theory.

$$E = h\nu \longrightarrow (2)$$

From equation (1) and (2)

$$h\nu = mc^2$$

$$\text{or, } h \times \frac{C}{\lambda} = mc^2$$

$$C = \nu\lambda, \quad \nu = C/\lambda$$

$$\frac{h}{\lambda} = mc \quad \text{or, } \lambda \times \frac{h}{mc} \longrightarrow (3)$$

In general  $\lambda \times \frac{h}{mc}$

Here,  $u$  = velocity of particle.

$$\text{or, } \lambda \propto \frac{1}{p} \longrightarrow (4)$$

Here,  $p = mu$  (momentum).

This proves de – Broglie's equation.

According to equation (4) it is quite clear, large the wave character of the particle smaller will be the mass of the particle and vice – versa. This principle can be utilised by the following examples.

Particles	Mass	Velocity cm/s	Wave length Å
Electron	$9.1 \times 10^{-28} \text{ gm}$	$1.2 \times 10^7 \text{ gm}$	61 Å
He	$6.6 \times 10^{-24} \text{ gm}$	$1.4 \times 10^5 \text{ gm}$	0.71 Å
Xe	$2.2 \times 10^{-22} \text{ gm}$	$2.4 \times 10^4 \text{ gm}$	0.12 Å

Proof of quantisation of Angular momentum of Bohr’s theory with the help of de – Broglie equation.



With the help of experiment, it has been observed that electron revolves round the nucleus in phase, that is in whole number of waves.

∴ Circumference :-

$$2\pi r = n\lambda \longrightarrow (1)$$

Here, n = no. of waves (In whole number)

Now, according to de – Broglie

$$\lambda \times \frac{h}{mu} \longrightarrow (2)$$

Now, after putting the value of  $\lambda$  from (2) to (1)

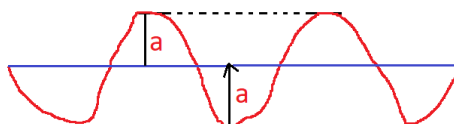
$$2\pi r = \frac{n \times h}{mu} \quad \text{or, } mur = \frac{nh}{2\pi} \text{ proved.}$$

This proves the quantisation of angular momentum of Bohr’s theory.

$\partial$  = Small delta (small charge).  
 $\Delta$  = Capital delta (Large charge).  
 de – Broglie theory and Heisenberg’s theory.

Schrodinger’s wave equation:-

In 1927 Schrodinger derived an equation for wave motion and with the help of this equation modern quantum mechanical concept of atom has been derived.



$$\Psi = A \sin \frac{2\pi}{\lambda} (x + ct) \longrightarrow (1)$$

Here,  $\Psi$  = Wave functions

A = Amplitude

$\lambda$  = Wave length  
 $X$  = Displacement  
 $C$  = Velocity of light  
 $t$  = time

After differentiating equation (1) with respect to  $x$  we have

$$\frac{\partial \Psi}{\partial x} = \frac{A2\pi}{\lambda} \cos \frac{2\pi}{\lambda} (x + ct)$$

Again, by double differentiating.

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{A2\pi}{\lambda} \cdot \frac{2\pi}{\lambda} \cdot \sin \frac{2\pi}{\lambda} (x + ct)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{A4\pi^2}{\lambda^2} \times \sin \frac{2\pi}{\lambda} (x + ct)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \Psi$$

$$\frac{\partial^2 \Psi}{\partial x^2} = +\frac{4\pi^2}{\lambda^2} \Psi = 0 \longrightarrow (2)$$

From de – Broglie's equation known that.

$$\lambda = \frac{h}{mu} \longrightarrow (3)$$

Again, we know –

$$E' = K \cdot E + P \cdot E$$

$$\text{Or, } E = \frac{1}{2} mu^2 + P \cdot E \quad \text{Here, } [U = P \cdot E]$$

$$\text{Or, } (E-U) = \frac{1}{2} mu^2$$

$$\text{Or, } 2(E-U) = mu^2$$

After multiply by  $m$  both side of above equation:

$$2m(E-U) = m^2u^2$$

$$\text{Or, } mu = \sqrt{2m(E-U)} \longrightarrow (4)$$

Now, putting the value of  $mu$  from equation (4) to (3)

$$\lambda = \frac{h}{\sqrt{2m(E-U)}} \longrightarrow (5)$$

Now, putting the value of  $\lambda$  from equation (5) to (2) we have:

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{4\pi^2}{-h^2} \frac{2m(E-U)}{2m(E-U)} \Psi = 0$$

$$\text{Or, } \frac{\partial^2 \Psi}{\partial x^2} + \frac{8m\pi^2(E-U)}{h^2} \Psi = 0$$

This is the Schrodinger equation in  $X$  – axis in the same way Schrodinger wave equation be derived from  $x, y, z$  three axes ( $X, Y, Z$ ).

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m(E-U)}{h^2} \Psi = 0 \longrightarrow (6)$$

Equation (6) is the Schrodinger wave equation for any wave particle.

Application:-

Now, when above equation (6) is solved by complicated mathematical operations for electron of an atom we get numbers solutions for energy E. but most of the solutions are useless except one. This meaningful value of E is called eigen value.

Eigen value (E) :- This is the meaningful value of energy of electron in an atom which is solved from Schrodinger wave equation.

Eigen function :- Meaningful value of  $\Psi$  in Schrodinger wave equation for eigen value (E) is called eigen function or wave function of electron.

#### Concept of orbital (Application) 1 :-

The value of  $\Psi$  has not any specific significance except it represents the amplitude of wave.

But  $\Psi^2$  has got Significance and it is called as orbital.

Definition of orbital :- It is that three dimensional area in which there is maximum probability of finding the electron.

#### Value of energy (Application) 2 :-

With the help of Schrodinger wave equation, the value of energy has been derived without the help of Bohr model.

$$E = \frac{-2\pi^2 m e^4 z^2 k^2}{-n^2 h^2}$$

During the derivation of above equation three quantum numbers l, n, m has been taken.

#### Significance of Schrodinger wave equation:-

##### (1) Concept of eigen value and eigen functions :-

The Schrodinger wave equation being a second order differential equation, has innumerable solutions, many of them being without any significance.

##### Quantum mechanical model of Atom :-

The solutions will have significance only for certain definite values of the total energy, E. these value are known as eigen values.

In other words, the occurrence of definite energy levels in an atom follows directly from the wave mechanical concepts. The solution of Schrodinger wave equation, substituting proper value of E, give the values of the wave function ( $\Psi$ ) or eigen function.

##### (2) Concept of atomic orbitals :-

The wave function  $\Psi$  by itself has no physical significance (except that it represents the amplitude of the wave). However, its square ( $\Psi^2$ ) given the probability of finding an electron of a given energy E. Thus an atomic orbital represent a definite region in three dimensional space around the nucleus where there is high probability of finding an electron of specific energy.

##### (3) Calculation of energy equation :-

The Schrodinger wave equation when solved fully with the help of advanced

mathematical treatment given the following expression for the energy of the electron in the level for H – atom.

$$E_n = \frac{-2\pi^2 e^4 m k^2}{n^2 h^2}$$

Thus, expression is identical with Bohr's equation for H – atom derived on the bases of classical mechanical for H – atom the energies calculated by both the methods agree with experimental value. Thus, Schrodinger's wave equation proves Bohr's theory of atom. For more complicated atoms, however the wave mechanical treatment is superior.

#### (4) Concept of Quantum numbers :-

It may be mentioned that three constant n, l and m are involved in solving the Schrodinger wave equation for the derivation of expression giving the energy of electron in a H – atom.

(Q) Write down the Schrodinger's equation for H – atom explaining the terms involved therein.

Answer :- In case of H – atom in which a single electron of charge -e is revolving round the nucleus of charge +e, the potential energy  $U = \frac{-e^2}{r}$ . Therefore, when applied to H – atom, the Schrodinger wave equation takes the form.

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left( E + \frac{e^2}{r} \right) \Psi = 0$$

Here,  $\Psi$  = Wave function.

m = Mass of electron.

E = Total energy.

$\frac{-e^2}{r}$  = Potential energy of H – atom.

e = Charge of electron or proton.

r = Radius of orbit 1<sup>st</sup>.

$$U = \frac{-kze^2}{r}$$

In C.G.S K= 1 dyx cm<sup>2</sup>/esu<sup>2</sup>

In 1<sup>st</sup>, K = 9×10<sup>9</sup> Nm<sup>2</sup>/C<sup>2</sup>.

#### Normalisation of wave function :-

The Schrodinger wave equation is a homogeneous differential equation whose solution gives a value for "Ψ". But Ψ multiplying by a constant factor would give the same differential equation. It is therefore necessary to find some conditions which will indicate which constant factor is to be used.

As the electron must be found somewhere, one can say that the probability of finding the electron in the whole of the space considered in a particular problem is unity. This may be written mathematically as given below.

$$\int_{-\infty}^{+\infty} |\Psi|^2 d\Gamma = 1 \quad , d\Gamma = dx, dy, dz$$

Here, 'Γ' is the volume of the whole space. This integral determines by what constant "Ψ" must be multiplied for the solution of the particular problem. This constant is known as the normalisation constant. As eigen function which has been completely evaluation in the way is said to have been normalised.

### Orthogonality or Orthogonal wave function:-

It we consider two wave functions  $\Psi_p$  and  $\Psi_q$  which corresponding to two value of energy  $E_p$  and  $E_q$  and if there, wave functions are separate solutions of the seldom Schrodinger's equation then.

$\int \Psi_p \cdot \Psi_q d\Gamma = 0$  and the wave function  $\Psi_p$  and  $\Psi_q$  are said to be orthogonal. This property will be proved for one dimension only. A proof extended to three dimension is out of the scope here.

Let us consider two Schrodinger equations which are written in one dimension only for the motion of "0" particle in a straight line.

$$\frac{d^2\Psi_q}{dx^2} + \frac{8\pi^2m}{h^2} (E_q - U_q)\Psi_q = 0 \quad \longrightarrow (1)$$

$$\frac{d^2\Psi_p}{dx^2} + \frac{8\pi^2m}{h^2} (E_p - U_p)\Psi_p = 0 \quad \longrightarrow (2)$$

After multiplying equation (1) by  $\Psi_q$  and equation (2) by  $\Psi_p$  on subtracting the above two equation we get.

$$\frac{d}{dx} \left( \Psi_q \frac{d\Psi_p}{dx} - \Psi_p \frac{d\Psi_q}{dx} \right) + \frac{8\pi^2m}{h^2} (E_p - E_q - U_p + U_q)\Psi_p \cdot \Psi_q = 0 \quad \longrightarrow (3)$$

Now, after integrating with respect to x over the whole of the space from  $-\infty$  to  $+\infty$ , we get the following relation.

$$\frac{8\pi^2m}{h^2} (E_p - E_q) \int_{-\infty}^{+\infty} \Psi_p \cdot \Psi_q dx = 0 \quad \longrightarrow (4)$$

Here,  $\Psi$  and  $U$  are taken as zero at infinity. Now, since

$$E_p \neq E_q$$

$$\text{So, } \frac{8\pi^2m}{h^2} (E_p - E_q) \neq 0$$

$$\text{Then, } \int_{-\infty}^{+\infty} \Psi_p \cdot \Psi_q dx = 0$$

This proves the orthogonality of two wave functions I,e. linear combination of orthogonal function is possible.

### Degeneracy :-

We know that for every wave function "Ψ", there must be a corresponding energy value E. That is for every eigen function there will be one eigen value. It means that each energy state must have a wave function which will be the characteristics of the system.

Thus, found if for two different Ψ. The same value energy be obtained, there two states will be called as degenerate states.

For example :-

- (i) 2p – sub – shell has got three degenerate states of orbitals (2P<sub>x</sub>, 2P<sub>y</sub>, 2P<sub>z</sub>).
- (ii) d – sub – shell has got five degenerate states of orbitals (d<sub>xy</sub>, d<sub>xz</sub>, d<sub>z<sup>2</sup></sub>, d<sub>yz</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub>).

Probability Density Pattern For Distribution Of Electrons. In Hydrogen Atom:-

In an atomic orbital, there is probability of finding the electron in particular region at a given radial distance and in a particular direction from the nucleus. This gives rise to two types of probability of finding the electrons.

- (1) Radial probability of electron.
- (2) Angular probability of electron.

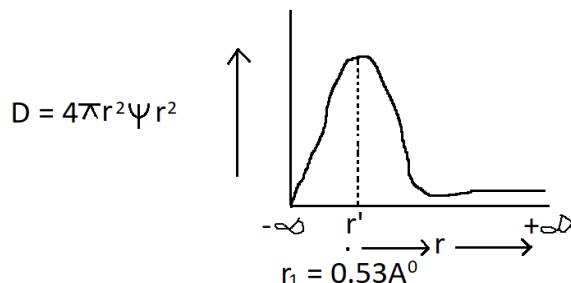
(1) Radial probability of finding the electron:-

The radial probability of finding the electron outside the nucleus of an atom is represented by radial probability distribution occurs of electrons. These curves give the probability of finding the electron at different radial distance (r) from the nucleus and are obtained by plotting the radial distribution function D against the electron nucleus distance (r).

Here,  $D = 4\pi r^2 \Psi^2 r$

These curves for 1s, 2s, 3s, 2p, 3p, and 3d electrons in H – atom are shown as below –

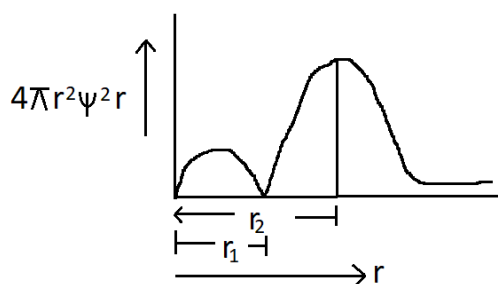
For 1s orbital :-



From this curve, it is evident that when  $r = 0$ ,  $d = 0$  I.e. at nucleus the density of electron is zero. Now, as 'D' increases, 'r' also increases from 'O' and reaches a maximum electron value of electron density, it begins to decrease and finally the electro density becomes 'zero' at infinity. Here, nodal area is equal to zero.

Total Nodal area =  $(n - l - 1) = 1 - 0 - 1 = 0$

For 2s orbital:-  $(n-l-1)$

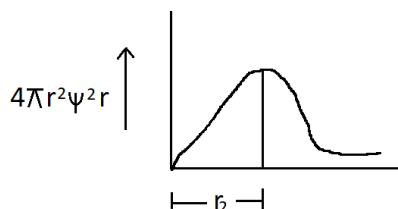




Total nodal area =  $2-0-1 = 1$ . For 2s electron, the value of electron density is zero at  $r = 0$ . Now, the value of D (density) increases as the value of 'r' increases, passes through a low maximum at  $r = 0.53A^0$  ( $r_1$ ) and falls to zero (nodal area). Again, the electron density begins to increase and passes through second higher maximum ( $r_2$ ). After that, the electron density decreases slowly and gradually it becomes zero at infinity.

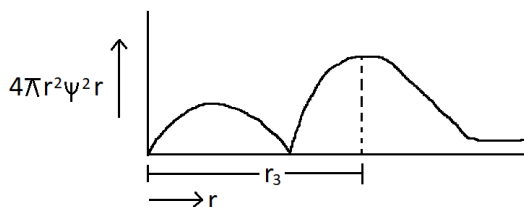
Curve for 2p orbital :-

Total nodal area =  $2-1-1 = 0$



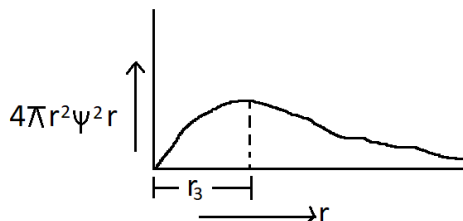
Curve for 3p orbital :-

Total nodal area =  $3-1-1 = 1$



Curve for 3d orbital :-

Total nodal area =  $3-2-1 = 0$

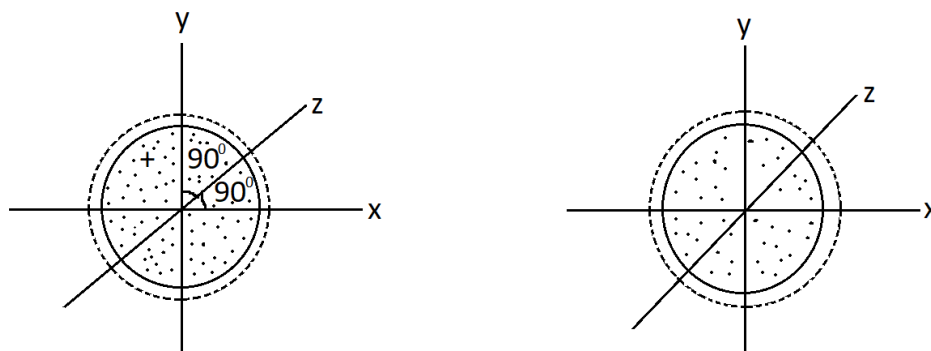


**(2) Angular probability of finding the electron :-**

The angular distribution of electron clouds around the nucleus is called as angular probability of finding the electron (wave function).

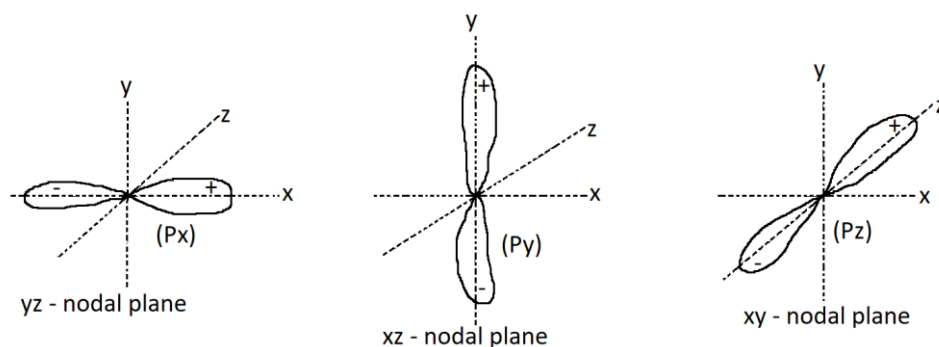
Angular probability of S – orbital :-

Since S – orbital are spherical in shape. The electron cloud in S orbital is found in all the three, axis x, y and z evenly (equally). Here, the nodal plane is found at all.



### Angular probability of P – orbital :-

P – orbital is dumbbell shape. There is two lobes in each orbital. Between two lobes the nucleus is situated so, there is one nodal plane in each P – orbital there are three P – orbital in a P – sub – shell ( $P_x$ ,  $P_y$ ,  $P_z$ ). The angular distribution of these orbitals can be represented as below.



### Angular probability of d – orbital :-

There are five degenerate d – orbital in d – sub – shell. All the five d – orbitals are arranged in different angles of the space. Hence, there are five angular distribution of electrons in the space around the nucleus for five d – orbitals. There are two nodal planes for each d – orbital. The angular distribution of five d – orbitals can be represented by as given below.

