

# **Important Atomic Models**

#### (1) Thomson's model

J.J. Thomson gave the first idea regarding structure of atom. According to this model.

(i) An atom is a solid sphere in which entire and positive charge and it's mass is uniformly distributed and in which negative charge (*i.e.* electron) are embedded like seeds in watermelon.



# Success and failure

Explained successfully the phenomenon of thermionic emission, photoelectric emission and ionization.

The model fail to explain the scattering of  $\alpha$ - particles and it cannot explain the origin of spectral lines observed in the spectrum of hydrogen and other atoms.

#### (2) Rutherford's model

# Rutherford's *a*-particle scattering experiment

Rutherford performed experiments on the scattering of alpha particles by extremely thin gold foils and made the following observations



(i) Most of the  $\alpha$ -particles pass through the foil straight away undeflected.

(ii) Some of them are deflected through small angles.





(iii) A few  $\alpha$ -particles (1 in 1000) are deflected through the angle more than 90°.

(iv) A few  $\alpha$  -particles (very few) returned back *i.e.* deflected by 180°.

(v) Distance of closest approach (Nuclear dimension)

The minimum distance from the nucleus up to which the  $\alpha$ -particle approach, is called the distance of closest approach ( $r_0$ ). From figure  $r_0 = \frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{E}$ ;  $E = \frac{1}{2}mv^2 = K.E.$  of  $\alpha$ -particle

(vi) Impact parameter (b) : The perpendicular distance of the velocity vector ( $\vec{v}$ ) of the  $\alpha$ -particle from the centre of the nucleus when it is far away from the nucleus is known as impact parameter. It is given as

$$b = \frac{Ze^2 \cot(\theta/2)}{4\pi\varepsilon_0 \left(\frac{1}{2}mv^2\right)} \implies b \propto \cot(\theta/2)$$

**Note** :  $\Box$  If t is the thickness of the foil and N is the number of  $\alpha$ -particles scattered in a

particular direction ( $\theta$  = constant), it was observed that  $\frac{N}{t}$  = constant  $\Rightarrow \frac{N_1}{N_2} = \frac{t_1}{t_2}$ .

After Rutherford's scattering of  $\alpha$ -particles experiment, following conclusions were made as regard as atomic structure :

(a) Most of the mass and all of the charge of an atom concentrated in a very small region is called atomic nucleus.

(b) Nucleus is positively charged and it's size is of the order of  $10^{-15} m \approx 1 Fermi$ .

(c) In an atom there is maximum empty space and the electrons revolve around the nucleus in the same way as the planets revolve around the sun.

# Size of the nucleus = 1 Fermi = $10^{-15} m$

Atom

#### **Draw backs**

(i) Stability of atom : It could not explain stability of atom because according to classical electrodynamic theory an accelerated charged particle should continuously radiate energy. Thus

an electron moving in an circular path around the nucleus should also radiate energy and thus move into smaller and smaller orbits of gradually decreasing radius and it should ultimately fall into nucleus.

(ii) According to this model the spectrum of atom must be continuous where as practically it is a line spectrum.

(iii) It did not explain the distribution of electrons outside the nucleus.

(3) Bohr's model



Instability of atom





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Bohr proposed a model for hydrogen atom which is also applicable for some lighter atoms in which a single electron revolves around a stationary nucleus of positive charge *Ze* (called hydrogen like atom)

Bohr's model is based on the following postulates.

(i) The electron can revolve only in certain discrete non-radiating orbits, called stationary orbits, for which total angular momentum of the revolving electrons is an integral multiple of  $\frac{h}{2\pi}$  (=  $\hbar$ )

*i.e.*  $L = n \left(\frac{h}{2\pi}\right) = mvr$ ; where  $n = 1, 2, 3, \dots = Principal$  quantum number

(ii) The radiation of energy occurs only when an electron jumps from one permitted orbit to another.

When electron jumps from higher energy orbit ( $E_1$ ) to lower energy orbit ( $E_2$ ) then difference of energies of these orbits *i.e.*  $E_1 - E_2$  emits in the form of photon. But if electron goes from  $E_2$  to  $E_1$  it absorbes the same amount of energy.



**Note** :  $\Box$  According to Bohr theory the momentum of an  $e^-$  revolving in second orbit of  $H_2$ 

atom will be  $\frac{h}{\pi}$ 

□ For an electron in the  $n^{\text{th}}$  orbit of hydrogen atom in Bohr model, circumference of orbit =  $n\lambda$ ; where  $\lambda$  = de-Broglie wavelength.

#### Bohr's Orbits (For Hydrogen and H<sub>2</sub>-Like Atoms)

#### (1) Radius of orbit

For an electron around a stationary nucleus the electrostatics force of attraction provides the necessary centripetal force

*i.e.* 
$$\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{mv^2}{r}$$
 .....(i) also  $mvr = \frac{nh}{2\pi}$  .....(ii)

From equation (i) and (ii) radius of  $n^{\text{th}}$  orbit

$$r_{n} = \frac{n^{2}h^{2}}{4\pi^{2}kZme^{2}} = \frac{n^{2}h^{2}\varepsilon_{0}}{\pi mZe^{2}} = 0.53 \frac{n^{2}}{Z} \mathring{A} \qquad \left[ \text{where } k = \frac{1}{4\pi\varepsilon_{0}} \right]$$

$$\Rightarrow r_{n} \propto \frac{n^{2}}{Z}$$



**Note**:  $\Box$  The radius of the innermost orbit (n = 1) hydrogen atom (z = 1) is called Bohr's radius  $a_0$  *i.e.*  $a_0 = 0.53$  Å.

# (2) Speed of electron

From the above relations, speed of electron in  $n^{\text{th}}$  orbit can be calculated as

$$v_n = \frac{2\pi kZe^2}{nh} = \frac{Ze^2}{2\varepsilon_0 nh} = \left(\frac{c}{137}\right) \cdot \frac{Z}{n} = 2.2 \times 10^6 \frac{Z}{n} m / sec$$

where (*c* = speed of light  $3 \times 10^8 m/s$ )

Note : 🗆 The ratio of speed of an electron in ground state in Bohr's first orbit of hydrogen

atom to velocity of light in air is equal to  $\frac{e^2}{2\varepsilon_0 ch} = \frac{1}{137}$  (where c = speed of light in

air)

# (3) Some other quantities

For the revolution of electron in  $n^{\text{th}}$  orbit, some other quantities are given in the following table

Quantity	Formula	Dependency on <i>n</i> and <i>Z</i>
(1) Angular speed	$\omega_n = \frac{v_n}{r_n} = \frac{\pi n z^2 e^4}{2\varepsilon_0^2 n^3 h^3}$	$\omega_n \propto \frac{Z^2}{n^3}$
(2) Frequency	$v_n = \frac{\omega_n}{2\pi} = \frac{mz^2 e^4}{4\varepsilon_0^2 n^3 h^3}$	$v_n \propto \frac{Z^2}{n^3}$
(3) Time period	$T_{n} = \frac{1}{v_{n}} = \frac{4\varepsilon_{0}^{2}n^{3}h^{3}}{mz^{2}e^{4}}$	$T_n \propto \frac{n^3}{Z^2}$
(4) Angular momentum	$L_n = m v_n r_n = n \left( \frac{h}{2\pi} \right)$	$L_n \propto n$
(5) Corresponding current	$i_n = e v_n = \frac{mz^2 e^5}{4\varepsilon_0^2 n^3 h^3}$	$i_n \propto \frac{Z^2}{n^3}$
(6) Magnetic moment	$M_n = i_n A = i_n \left( \pi r_n^2 \right)$	$M_n \propto n$
	(where $\mu_0 = \frac{eh}{4\pi m} = Bohr$	
	magneton)	
(7) Magnetic field	$B = \frac{\mu_0 i_n}{2r_n} = \frac{\pi m^2 z^3 e^7 \mu_0}{8\varepsilon_0^3 n^5 h^5}$	$B \propto \frac{Z^3}{n^5}$

# (4) Energy





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(i) **Potential energy :** An electron possesses some potential energy because it is found in the field of nucleus potential energy of electron in  $n^{\text{th}}$  orbit of radius  $r_n$  is given by  $U = k \cdot \frac{(Ze)(-e)}{r_n} = -\frac{kZe^2}{r_n}$ 

(ii) **Kinetic energy :** Electron posses kinetic energy because of it's motion. Closer orbits have greater kinetic energy than outer ones.

As we know  $\frac{mv^2}{r_n} = \frac{k.(Ze)(e)}{r_n^2} \Rightarrow$  Kinetic energy  $K = \frac{kZe^2}{2r_n} = \frac{|U|}{2}$ 

(iii) **Total energy :** Total energy (*E*) is the sum of potential energy and kinetic energy *i.e.* E = K + U

$$\Rightarrow \qquad E = -\frac{kZe^2}{2r_n} \qquad \text{also} \qquad r_n = \frac{n^2h^2\varepsilon_0}{\pi mze^2}. \qquad \text{Hence}$$

$$E = -\left(\frac{me^4}{8\varepsilon_0^2h^2}\right) \cdot \frac{z^2}{n^2} = -\left(\frac{me^4}{8\varepsilon_0^2ch^3}\right) ch\frac{z^2}{n^2} = -Rch\frac{Z^2}{n^2} = -13.6\frac{Z^2}{n^2}eV$$
where  $R = \frac{me^4}{2}$  = Rydberg's constant = 1.09 × 10<sup>7</sup> per metre

where  $R = \frac{mc}{8\varepsilon_0^2 ch^3}$  = Rydberg's constant = 1.09 × 10<sup>7</sup> per metre

Note : 🗖 Each Bohr orbit has a definite energy

- For hydrogen atom (Z = 1)  $\Rightarrow E_n = -\frac{13.6}{n^2} eV$
- □ The state with n = 1 has the lowest (most negative) energy. For hydrogen atom it is  $E_1 = -13.6 \text{ eV}$ .
- **C** Rch = Rydberg's energy  $\simeq 2.17 \times 10^{-18} J \simeq 31.6 \, eV$ .

$$\Box \quad E = -K = \frac{U}{2}.$$

(iv) **Ionisation energy and potential :** The energy required to ionise an atom is called ionisation energy. It is the energy required to make the electron jump from the present orbit to the infinite orbit.

Hence 
$$E_{ionisation} = E_{\infty} - E_n = 0 - \left(-13.6\frac{Z^2}{n^2}\right) = +\frac{13.6Z^2}{n^2}eV$$

For  $H_2$ -atom in the ground state  $E_{ionisation} = \frac{+13.6(1)^2}{n^2} = 13.6 \, eV$ 

The potential through which an electron need to be accelerated so that it acquires energy equal to the ionisation energy is called ionisation potential.  $V_{ionisation} = \frac{E_{ionisation}}{a}$ 

(v) **Excitation energy and potential :** When the electron is given energy from external source, it jumps to higher energy level. This phenomenon is called excitation.

The minimum energy required to excite an atom is called excitation energy of the particular excited state and corresponding potential is called exciting potential.

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$$E_{Excitation} = E_{Final} - E_{Initial}$$
 and  $V_{Excitation} = \frac{E_{excitation}}{e}$ 

(vi) **Binding energy (B.E.)**: Binding energy of a system is defined as the energy released when it's constituents are brought from infinity to form the system. It may also be defined as the energy needed to separate it's constituents to large distances. If an electron and a proton are initially at rest and brought from large distances to form a hydrogen atom, 13.6 *eV* energy will be released. The binding energy of a hydrogen atom is therefore 13.6 *eV*.

Note :  $\Box$  For hydrogen atom principle quantum number  $n = \sqrt{\frac{13.6}{(B.E.)}}$ .

#### (5) Energy level diagram

The diagrammatic description of the energy of the electron in different orbits around the nucleus is called energy level diagram.

 0	, ,	, ,	0		
 $n = \infty$	Infinit	Infinite	$E_{\infty} = O \ eV$	0 eV	0 eV
	e				
 n = 4	Fourth	Third	$E_4 = -0.85 \ eV$	- 0.85 Z <sup>2</sup>	+ 0.85 eV
 <i>n</i> = 3	Third	Second	$E_3 = -1.51 \ eV$	- 1.51 $Z^2$	+ 1.51 eV
 n = 2	Second	First	$E_2 = -3.4 \ eV$	- 3.4 Z <sup>2</sup>	+ 3.4 eV
<i>n</i> = 1	First	Ground	$E_1 = -13.6 \ eV$	- 13.6 Z <sup>2</sup>	+ 13.6 eV
Principl e	Orbit	Excited state	Energy for <i>H</i> <sub>2</sub> – atom	Energy for <i>H</i> <sub>2</sub> – like atom	Ionisation energy
m number					(for $H_2$ – atom)

Energy level diagram of hydrogen/hydrogen like atom

**Note**: In hydrogen atom excitation energy to excite electron from ground state to first excited state will be  $-3.4 - (-13.6) = 10.2 \ eV$ .

and from ground state to second excited state it is  $[-1.51 - (-13.6) = 12.09 \ eV]$ .

□ In an  $H_2$  atom when  $e^-$  makes a transition from an excited state to the ground state it's kinetic energy increases while potential and total energy decreases.

#### (6) Transition of electron

When an electron makes transition from higher energy level having energy  $E_2(n_2)$  to a lower energy level having energy  $E_1(n_1)$  then a photon of frequency v is emitted

#### (i) Energy of emitted radiation

$$\Delta E = E_2 - E_1 = \frac{-Rc h Z^2}{n_2^2} - \left(-\frac{Rch Z^2}{n_1^2}\right) = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \qquad \underbrace{E_1 \qquad \qquad \Delta E, v, \lambda}_{\text{Emission}}$$

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#### (ii) Frequency of emitted radiation



 $E_2 n_2$ 

$$\Delta E = h \, v \Longrightarrow \, v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} = Rc \, Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

#### (iii) Wave number/wavelength

Wave number is the number of waves in unit length  $\overline{v} = \frac{1}{\lambda} = \frac{v}{c}$  $\Rightarrow \frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{13.6Z^2}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ 

(iv) **Number of spectral lines** : If an electron jumps from higher energy orbit to lower energy orbit it emits raidations with various spectral lines.

If electron falls from orbit  $n_2$  to  $n_1$  then the number of spectral lines emitted is given by

$$N_E = \frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$$

If electron falls from  $n^{\text{th}}$  orbit to ground state (*i.e.*  $n_2 = n$  and  $n_1 = 1$ ) then number of spectral lines emitted  $N_E = \frac{n(n-1)}{2}$ 

**Note** :  $\Box$  Absorption spectrum is obtained only for the transition from lowest energy level to higher energy levels. Hence the number of absorption spectral lines will be (n - 1).

(v) **Recoiling of an atom** : Due to the transition of electron, photon is emitted and the atom is recoiled

Recoil momentum of atom = momentum of photon =  $\frac{h}{\lambda} = hRZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ 

Also recoil energy of atom  $=\frac{p^2}{2m}=\frac{h^2}{2m\lambda^2}$  (where m = mass of recoil atom)

#### (7) Draw backs of Bohr's atomic model

(i) It is valid only for one electron atoms, e.g. : H,  $He^+$ ,  $Li^{+2}$ ,  $Na^{+1}$  etc.

(ii) Orbits were taken as circular but according to Sommerfield these are elliptical.

(iii) Intensity of spectral lines could not be explained.

(iv) Nucleus was taken as stationary but it also rotates on its own axis.

(v) It could not be explained the minute structure in spectrum line.

(vi) This does not explain the Zeeman effect (splitting up of spectral lines in magnetic field) and Stark effect (splitting up in electric field)

(vii) This does not explain the doublets in the spectrum of some of the atoms like sodium (5890Å & 5896Å)

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#### Hydrogen Spectrum and Spectral Series

When hydrogen atom is excited, it returns to its normal unexcited (or ground state) state by emitting the energy it had absorbed earlier. This energy is given out by the atom in the form of radiations of different wavelengths as the electron jumps down from a higher to a lower orbit. Transition from different orbits cause different wavelengths, these constitute spectral series which are characteristic of the atom emitting them. When observed through a spectroscope, these radiations are imaged as sharp and straight vertical lines of a single colour.



#### **Spectral series**

The spectral lines arising from the transition of electron forms a spectra series.

(i) Mainly there are five series and each series is named after it's discover as Lymen series, Balmer series, Paschen series, Bracket series and Pfund series.

(ii) According to the Bohr's theory the wavelength of the radiations emitted from hydrogen atom is given by

$$\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where  $n_2$  = outer orbit (electron jumps from this orbit),  $n_1$  = inner orbit (electron falls in this orbit)



(iii) First line of the series is called first member, for this line wavelength is maximum  $(\lambda_{max})$ 

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		Wavelength ( $\lambda$ ) = $\frac{n_1^2}{(n_2^2 - n_1^2)}$	$\lambda_{max} (n+1)^2$		
Spectral series	Transition	Maximum wavelength $(n_1 = n \text{ and } n_2 = n + 1)$ $\lambda_{\max} = \frac{n^2(n+1)^2}{(2n+1)R}$	Minimum wavelength $(n_2 = \infty, n_1 = n)$ $\lambda_{\min} = \frac{n^2}{R}$	$\frac{\max}{\lambda_{\min}} = \frac{1}{(2n+1)}$	Region
1. Lymen series	$n_2 = 2, 3, 4$ $\infty$ $n_1 = 1$	$\lambda_{\max} = \frac{(1)^2 (1+1)^2}{(2 \times 1 + 1)R} = \frac{4}{3R}$	$n_1 = n = 1$ $\lambda_{\min} = \frac{1}{R}$	$\frac{4}{3}$	Ultraviolet region
2.Balmer series	$n_2 = 3, 4, 5$ $\infty$ $n_1 = 2$	$n_1 = n = 2, n_2 = 2 + 1 = 3$ $\lambda_{\text{max}} = \frac{36}{5R}$	$\lambda_{\min} = \frac{4}{R}$	$\frac{9}{5}$	Visible region
3. Paschen series	$n_2 = 4, 5, 6$ $\infty$ $n_1 = 3$	$n_1 = n = 3, n_2 = 3 + 1 = 4$ $\lambda_{\max} = \frac{144}{7R}$	$n_1 = n = 3$ $\lambda_{\min} = \frac{9}{R}$	$\frac{16}{7}$	Infrared region
4. Bracket series	$n_2 = 5, 6, 7 \dots$ $\infty$ $n_1 = 4$	$n_1 = n = 4, n_2 = 4 + 1 = 5$ $\lambda_{\text{max}} = \frac{400}{9R}$	$n_1 = n = 4$ $\lambda_{\min} = \frac{16}{R}$	$\frac{25}{9}$	Infrared region
5. Pfund series	$n_2 = 6, 7, 8 \dots$ $\infty$ $n_1 = 5$	$n_1 = \lambda = 5, n_2 = 5 + 1 = 6$ $\lambda_{\text{max}} = \frac{900}{11R}$	$\lambda_{\min} = \frac{25}{R}$	$\frac{36}{11}$	Infrared region

(iv) Last line of the series  $(n_2 = \infty)$  is called series limit, for this line wavelength is minimum  $(\lambda_{\min})$ 

#### **Quantum Numbers**

An atom contains large number of shells and subshells. These are distinguished from one another on the basis of their size, shape and orientation (direction) in space. The parameters are expressed in terms of different numbers called quantum number.

Quantum numbers may be defined as a set of four number with the help of which we can get complete information about all the electrons in an atom. It tells us the address of the electron *i.e.* location, energy, the type of orbital occupied and orientation of that orbital.

(1) **Principal Quantum number (***n***) :** This quantum number determines the main energy level or shell in which the electron is present. The average distance of the electron from the nucleus and the energy of the electron depends on it.  $E_n \propto \frac{1}{n^2}$  and  $r_n \propto n^2$  (in *H*-

atom)

The principal quantum number takes whole number values, n = 1, 2, 3, 4,....  $\infty$ 

(2) Orbital quantum number (l) or azimuthal quantum number (l)





This represents the number of subshells present in the main shell. These subsidiary orbits within a shell will be denoted as 1, 2, 3, 4 ... or s, p, d, f ... This tells the shape of the subshells.

The orbital angular momentum of the electron is given as  $L = \sqrt{l(l+1)} \frac{h}{2\pi}$  (for a particular value of *n*).

For a given value of *n* the possible values of *l* are l = 0, 1, 2, .... upto (n - 1)

(3) **Magnetic quantum number**  $(m_l)$  : An electron due to it's angular motion around the nucleus generates an electric field. This electric field is expected to produce a magnetic field. Under the influence of external magnetic field, the electrons of a subshell can orient themselves in certain preferred regions of space around the nucleus called orbitals.

The magnetic quantum number determines the number of preferred orientations of the electron present in a subshell.

The angular momentum quantum number m can assume all integral value between – l to +l including zero. Thus  $m_l$  can be – 1, 0, + 1 for l = 1. Total values of  $m_l$  associated with a particular value of l is given by (2l + 1).

(4) **Spin (magnetic) quantum number (** $m_s$ **) :** An electron in atom not only revolves around the nucleus but also spins about its own axis. Since an electron can spin either in clockwise direction or in anticlockwise direction. Therefore for any particular value of magnetic quantum

number, spin quantum number can have two values, *i.e.*  $m_s = \frac{1}{2}$  (Spin up) or

$$m_s = -\frac{1}{2}$$
 (Spin down)

This quantum number helps to explain the magnetic properties of the substance.

#### **Electronic Configurations of Atoms**

The distribution of electrons in different orbitals of an atom is called the electronic configuration of the atom. The filling of electrons in orbitals is governed by the following rules.

#### (1) Pauli's exclusion principle

"It states that no two electrons in an atom can have all the four quantum number (n, l,  $m_l$  and  $m_s$ ) the same."

It means each quantum state of an electron must have a different set of quantum numbers n, l,  $m_l$  and  $m_s$ . This principle sets an upper limit on the number of electrons that can occupy a shell.

 $N_{\text{max}}$  in one shell =  $2n^2$ ; Thus  $N_{\text{max}}$  in *K*, *L*, *M*, *N* .... shells are 2, 8, 18, 32,

*Note* :  $\Box$  The maximum number of electrons in a subshell with orbital quantum number *l* is 2(2l + 1).

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# (2) Aufbau principle



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Electrons enter the orbitals of lowest energy first.

As a general rule, a new electron enters an empty orbital for which (n + l) is minimum. In case the value (n + l) is equal for two orbitals, the one with lower value of *n* is filled first.

Thus the electrons are filled in subshells in the following order (memorize)

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, .....

#### (3) Hund's Rule

When electrons are added to a subshell where more than one orbital of the same energy is available, their spins remain parallel. They occupy different orbitals until each one of them has at least one electron. Pairing starts only when all orbitals are filled up.

Pairing takes place only after filling 3, 5 and 7 electrons in *p*, *d* and *f* orbitals, respectively.



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Radius 
$$r \propto n^2 \Rightarrow \frac{r_1^2}{r_2^2} = \frac{n_1^4}{n_2^4} \Rightarrow \frac{\pi r_1^2}{\pi r_2^2} = \frac{n_1^4}{n_2^4} \Rightarrow \frac{A_1}{A_2} = \frac{n_1^4}{n_2^4} = \frac{2^4}{1^4} = 16 \Rightarrow \frac{A_1}{A_2} = \frac{16}{1}$$

**Example: 2** The electric potential between a proton and an electron is given by  $V = V_0 \ln \frac{r}{r_0}$ , where  $r_0$  is a constant. Assuming Bohr's model to be applicable, write variation of  $r_n$  with n, n being the principal quantum number [IIT-JEE (Screening) 2003]

(a) 
$$r_n \propto n$$
 (b)  $r_n \propto 1/n$  (c)  $r_n \propto n^2$  (d)  $r_n \propto 1/n^2$ 

Solution : (a) Potential energy 
$$U = eV = eV_0 \ln \frac{r}{r_0}$$

$$\therefore \text{ Force } F = -\left|\frac{dU}{dr}\right| = \frac{eV_0}{r}. \text{ The force will provide the necessary centripetal force. Hence}$$
$$\frac{mv^2}{r} = \frac{eV_0}{r} \Rightarrow v = \sqrt{\frac{eV_0}{m}} \qquad \dots (i) \qquad \text{and} \qquad mvr = \frac{nh}{2\pi} \qquad \dots (ii)$$
Dividing equation (ii) by (i) we have  $mr = \left(\frac{nh}{2\pi}\right)\sqrt{\frac{m}{eV_0}} \text{ or } r \propto n$ 

**Example: 3** The innermost orbit of the hydrogen atom has a diameter 1.06 Å. The diameter of tenth orbit is

[UPSEAT 2002]  
(a) 5.3 
$$\mathring{A}$$
 (b) 10.6  $\mathring{A}$  (c) 53  $\mathring{A}$  (d) 106  $\mathring{A}$   
Solution : (d) Using  $r \propto n^2 \Rightarrow \frac{r_2}{r_1} = \left(\frac{n_2}{n_1}\right)^2$  or  $\frac{d_2}{d_1} = \left(\frac{n_2}{n_1}\right)^2 \Rightarrow \frac{d_2}{1.06} = \left(\frac{10}{1}\right)^2 \Rightarrow d = 106 \mathring{A}$   
Example: 4 Energy of the electron in  $n^{\text{th}}$  orbit of hydrogen atom is given by  $E_n = -\frac{13.6}{n^2} eV$ . The amount of energy needed to transfer electron from first orbit to third orbit is  
(a) 13.6  $eV$  (b) 3.4  $eV$  (c) 12.09  $eV$  (d) 1.51  $eV$   
Solution : (c) Using  $E = -\frac{13.6}{n^2} eV$   
For  $n = 1$ ,  $E_n = \frac{-13.6}{n^2} = -13.6 eV$  and for  $n = 2$ ,  $E_n = -\frac{13.6}{n^2} = -1.51 eV$ 

For 
$$n = 1$$
,  $E_1 = \frac{-13.6}{1^2} = -13.6 \, eV$  and for  $n = 3$   $E_3 = -\frac{13.6}{3^2} = -1.51 \, eV$   
So required energy  $= E_3 - E_1 = -1.51 - (-13.6) = 12.09 \, eV$ 

**Example: 5** If the binding energy of the electron in a hydrogen atom is 13.6 eV, the energy required to remove the electron from the first excited state of  $Li^{++}$  is (a) 122.4 eV (b) 30.6 eV (c) 13.6 eV (d) 3.4 eV

Solution : (b) Using 
$$E_n = -\frac{13.6 \times Z^2}{n^2} eV$$
  
For first excited state  $n = 2$  and for  $Li^{++}$ ,  $Z = 3$   
 $\therefore E = -\frac{13.6}{2^2} \times 3^2 = -\frac{13.6 \times 9}{4} = -30.6 eV$ . Hence, remove the electron from the first excited state of  $Li^{++}$  be 30.6  $eV$   
Example: 6 The ratio of the wavelengths for  $2 \rightarrow 1$  transition in  $Li^{++}$ ,  $He^+$  and  $H$  is [UPSEAT 2003]  
(a)  $1: 2: 3$  (b)  $1: 4: 9$  (c)  $4: 9: 36$  (d)  $3: 2: 1$ 

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Solution : (c) Using 
$$\frac{1}{\lambda} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow \lambda \propto \frac{1}{Z^2} \Rightarrow \lambda_{12} : \lambda_{14} : \frac{1}{2} + \frac{1}{2} : \frac{1}{4} : \frac{1}{1} - 4 : 9 : 36$$
  
**Example:** 7 Energy *E* of a hydrogen atom with principal quantum number *n* is given by  $E = \frac{-13.6}{n_1^2} e^{V}$ . The energy of a photon ejected when the electron jumps *n* = 3 state to *n* = 2 state of hydrogen is approximately **CENE PAT/PDT Screening 2004**  
(a) 1.9 eV (b) 1.5 eV (c) 0.85 eV (d) 3.4 eV  
Solution : (a)  $\Delta E = 13.6 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 13.6 \times \frac{5}{36} = 1.9 eV$   
**Example:** 3 In the Bohr model of the hydrogen atom, let *R*, *v* and *E* represent the radius of the orbit, the speed of electron and the total energy of the electron respectively. Which of the following quantity is proportional to the quantum number *n*  
(a) *R/E* (b)  $E/V$  (c) *RE* (d) *vR*  
Solution : (d) Rydberg constant  $R = \frac{e_{10}n^2h^2}{mt/2^2}$   
Velocity  $v = \frac{Ze^2}{2e_{0}nh}$  and energy  $E = -\frac{mZ^2e^4}{8k_0^2n^2h^2}$   
Now, it is clear from above expressions  $R.v \propto n$   
**Example:** 9 The energy of hydrogen atom in *n*th orbit is  $E_n$ , then the energy in *n*th orbit of singly ionised helium atom will be  
(a)  $4E^{E}$  (b)  $E/V$  (c)  $2E^{E}$  (d)  $E/Z$   
Solution : (a) By using  $E = -\frac{13.6 T^2}{n^2} \Rightarrow \frac{E_{14}}{E_{16}} = \left(\frac{1}{2}\right)^2 \Rightarrow E_{16} = 4E_n$ .  
**Example:** 10 The wavelength of radiation emitted is  $\lambda_n$  when an electron jumps from the third to the second orbit of hydrogen atom. For the electron jump from the fourth to the second orbit of hydrogen atom. For the electron jump from the fourth to the second orbit of hydrogen atom. For the electron jump from the fourth to the second orbit of  $\frac{1}{2}e^2 - \frac{1}{a^2} = \frac{1}{a}e^2 R \left(\frac{1}{2}e^2 - \frac{1}{3}\right) = R \left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}R$  .....(1)  
and  $\frac{1}{\lambda} = R \left[\frac{1}{22} - \frac{1}{4^2}\right] = R \left[\frac{1}{2} - \frac{1}{3^2}\right] = R \left[\frac{1}{4} - \frac{1}{9}\right] = \frac{5}{36}R$  .....(1)  
From equation (1) and (11)  $\frac{X}{\lambda} = \frac{5R}{36} \times \frac{16}{3R} = \frac{20}{27} \lambda_0$   
**Example:** 11 If scattering particles are 56 for 90° angle then t

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$$N \propto \frac{1}{\sin^4(\theta/2)} \Rightarrow \frac{N_2}{N_1} = \left[\frac{\sin\left(\frac{\theta_1}{2}\right)}{\sin\left(\frac{\theta_2}{2}\right)}\right]^4 \Rightarrow \frac{N_2}{N_1} = \left[\frac{\sin\left(\frac{90^\circ}{2}\right)}{\sin\left(\frac{60^\circ}{2}\right)}\right]^4 = \left[\frac{\sin 45^\circ}{\sin 30^\circ}\right]^4 = 4 \Rightarrow N_2 = 4N_1 = 4 \times 56 = 224$$

**Example: 12** When an electron in hydrogen atom is excited, from its  $4^{\text{th}}$  to  $5^{\text{th}}$  stationary orbit, the change in angular momentum of electron is (Planck's constant:  $h = 6.6 \times 10^{-34} J_{-s}$ )

(a) 
$$4.16 \times 10^{-34}$$
 J-s (b)  $3.32 \times 10^{-34}$  J-s (c)  $1.05 \times 10^{-34}$  J-s (d)  $2.08 \times 10^{-34}$  J-s

Solution : (c) Change in angular momentum

(a) 13.2 E

$$\Delta L = L_2 - L_1 = \frac{n_2 h}{2\pi} - \frac{n_1 h}{2\pi} \Rightarrow \Delta L = \frac{h}{2\pi} (n_2 - n_1) = \frac{6.6 \times 10^{-34}}{2 \times 3.14} (5 - 4) = 1.05 \times 10^{-34} J-s$$

**Example: 13** In hydrogen atom, if the difference in the energy of the electron in n = 2 and n = 3 orbits is *E*, the ionization energy of hydrogen atom is

# Solution : (b) Energy difference between n = 2 and n = 3; $E = K \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = K \left( \frac{1}{4} - \frac{1}{9} \right) = \frac{5}{36} K$ .....(i)

Ionization energy of hydrogen atom  $n_1 = 1$  and  $n_2 = \infty$ ;  $E' = K \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = K$  .....(ii)

(c) 5.6 E

From equation (i) and (ii) 
$$E' = \frac{36}{5}E = 7.2E$$

(b) 7.2 *E* 

**Example: 14** In Bohr model of hydrogen atom, the ratio of periods of revolution of an electron in n = 2 and n = 1 orbits is

[EAMCET (Engg.) 2000]

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(d) 3.2 E

Solution : (c) According to Bohr model time period of electron  $T \propto n^3 \Rightarrow \frac{T_2}{T_1} = \frac{n_2^3}{n_1^3} = \frac{2^3}{1^3} = \frac{8}{1} \Rightarrow T_2 = 8T_1.$ 

**Example: 15** A double charged lithium atom is equivalent to hydrogen whose atomic number is 3. The wavelength of required radiation for emitting electron from first to third Bohr orbit in  $Li^{++}$  will be (Ionisation energy of hydrogen atom is 13.6 *eV*)

(a) 182.51 
$$\mathring{A}$$
 (b) 177.17  $\mathring{A}$  (c) 142.25  $\mathring{A}$  (d) 113.74  $\mathring{A}$ 

Solution : (d) Energy of a electron in *n*th orbit of a hydrogen like atom is given by

$$E_n = -13.6 \frac{Z^2}{n^2} eV$$
, and  $Z = 3$  for *Li*

Required energy for said transition

$$\Delta E = E_3 - E_1 = 13.6Z^2 \left(\frac{1}{1^2} - \frac{1}{3^2}\right) = 13.6 \times 3^2 \left[\frac{8}{9}\right] = 108.8 \ eV = 108.8 \times 1.6 \times 10^{-19} \ J$$

Now using  $\Delta E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} \Rightarrow \lambda = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{108.8 \times 1.6 \times 10^{-19}} = 0.11374 \times 10^{-7} m \Rightarrow \lambda = 113.74 \text{ Å}$ 

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**Example: 16** The absorption transition between two energy states of hydrogen atom are 3. The emission transitions between these states will be

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	(a) 3	(b) 4	(c) 5	(d) 6		
Solution : (d)	Number of absorption	n lines = $(n - 1) \Rightarrow 3 = (n - 1)$	$(n-1) \Rightarrow n = 4$			
	Hence number of emitted lines $=\frac{n(n-1)}{2}=\frac{4(4-1)}{2}=6$					
Example: 17	The energy levels o respectively. A photo wavelength of emission	f a certain atom for 1s n of wavelength $\lambda$ is em ons for transition 2 $\rightarrow$ 1	st, 2nd and 3rd leve itted for a transition	els are <i>E</i> , $4E/3$ and $2E$ $3 \rightarrow 1$ . What will be the		
				[CPMT 1996]		
	(a) λ/3	(b) $4\lambda/3$	(c) $3\lambda/4$	(d) 3λ		
Solution : (d)	For transition $3 \rightarrow 1$	$\Delta E = 2E - E = \frac{hc}{\lambda} \implies E =$	$\frac{hc}{\lambda}$ (i)			
	For transition $2 \rightarrow 1$	$\frac{4E}{3} - E = \frac{hc}{\lambda'} \Rightarrow E = \frac{3hc}{\lambda'}$	(ii)			
	From equation (i) and (	ii) $\lambda' = 3\lambda$				
Example: 18	Hydrogen atom emits Which colour of light	s blue light when it cha would the atom emit wh	nges from $n = 4$ ene en it changes from $n = 1$	rgy level to $n = 2$ level. = 5 level to $n = 2$ level		
	(a) Red	(b) Yellow	(c) Green	(d) Violet		
Solution : (d)	In the transition from orbits $5 \rightarrow 2$ more energy will be liberated as compared to transition from $4 \rightarrow 2$ . So emitted photon would be of violet light.					
Example: 19	A single electron orbits a stationary nucleus of charge $+Ze$ , where Z is a constant. It requires 47.2 <i>eV</i> to excited electron from second Bohr orbit to third Bohr orbit. Find the value of Z [IIT-JEE 1981]					
	(a) 2	(b) 5	(c) 3	(d) 4		
Solution : (b)	Excitation energy of l	nydrogen like atom for <i>n</i>	$_2 \rightarrow n_1$			
	$\Delta E = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) dz$	$eV \implies 47.2 = 13.6Z^2 \left(\frac{1}{2^2} - \frac{1}{2}\right)$	$\frac{1}{3^2} = 13.6 \times \frac{5}{36} Z^2 \implies Z$	$^{2} = \frac{47.2 \times 36}{13.6 \times 5} = 24.98 \approx 25$		
	$\Rightarrow$ Z = 5					
Example: 20	The first member of The short wavelength	the Paschen series in hy limit of Paschen series i	ydrogen spectrum is o is	of wavelength 18,800 Å. [EAMCET (Med.) 2000]		
	(a) 1215 Å	(b) 6560 Å	(c) 8225 Å	(d) 12850 Å		
Solution : (c)	First member of Pasc	hen series mean it's $\lambda_{\max}$	$=\frac{144}{7R}$			
	Short wavelength of Paschen series means $\lambda_{\min} = \frac{9}{R}$					
	Hence $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{16}{7} \implies \lambda$	$\gamma_{\min} = \frac{7}{16} \times \lambda_{\max} = \frac{7}{16} \times 18,800$	$0 = 8225  \text{\AA}$ .			
Example: 21	Ratio of the waveleng	ths of first line of Lymar	n series and first line [EAMCET	of Balmer series is (Engg.) 1995; MP PMT 1997]		
	(a) 1:3	(b) 27:5	(c) 5:27	(d) 4:9		

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Solution : (c) For Lyman series 
$$\frac{1}{\lambda_{i_{1}}} = R\left[\frac{1}{1^{2}} - \frac{1}{2^{2}}\right] = \frac{3R}{4}$$
 .....(i)  
For Balmer series  $\frac{1}{\lambda_{i_{1}}} = R\left[\frac{1}{2^{2}} - \frac{1}{3^{2}}\right] = \frac{5R}{36}$  .....(ii)  
From equation (i) and (ii)  $\frac{\lambda_{i_{1}}}{\lambda_{i_{1}}} = \frac{5}{27}$ .  
Example: 22 The third line of Balmer series of an ion equivalent to hydrogen atom has wavelength of to 8.5 m. The ground state energy of an electron of this ion will be  
(a) 3.4 eV (b) 13.6 eV (c) 54.4 eV (d) 122.4 eV  
Solution : (c) Using  $\frac{1}{4} = RZ^{\frac{1}{2}}\left(\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}}\right) \Rightarrow \frac{1}{108.5 \times 10^{-9}} = 1.1 \times 10^{7} \times Z^{2}\left(\frac{1}{2^{2}} - \frac{1}{5^{2}}\right)$   
 $\Rightarrow \frac{1}{108.5 \times 10^{-9}} = 1.1 \times 10^{7} \times Z^{2} \times Z^{\frac{1}{10}} = \frac{100}{118.5 \times 10^{-9}} \times Z^{\frac{1}{2}} = 4 \Rightarrow Z = 2$   
Now Energy in ground state  $E = -13.6Z^{2} eV = -13.6 \times 2^{2} eV = -54.4 eV$   
Example: 23 Hydrogen (H), deuterium (D), singly ionized helium (He<sup>1</sup>) and doubly ionized lithium (H<sup>1</sup>)  
all have one electron around the nucleus. Consider  $n = 1$  transition. The wavelengths of emitted radiations are  $A_{1,2,4}$  and  $A_{1}$  respectively. Then approximately  
(a)  $\lambda_{1} = \lambda_{2} = 4\lambda_{3} = 9\lambda_{4}$ . (b)  $4\lambda_{4} = 2\lambda_{2} = 2\lambda_{2} = \lambda_{4}$  (c)  $\lambda_{1} = \lambda_{2} = 2\lambda_{2} = 3\lambda_{3}^{2} \lambda_{4}$  (d)  $\lambda_{1} = \lambda_{2} = 2\lambda_{2} = 3\lambda_{4}^{2}$   
Solution : (a) Using  $\Delta E \propto Z^{2}$  (C)  $n_{1}$  and  $n_{2}$  are same)  
 $\Rightarrow \frac{h}{2} \frac{K}{2} \approx Z^{2} \Rightarrow \lambda Z^{2} = constant \Rightarrow \lambda_{1}Z_{1}^{2} = \lambda_{2}Z_{2}^{2} = \lambda_{2}Z_{3}^{2} = \lambda_{4} \times 1^{2} = \lambda_{3} \times 2^{2} = \lambda_{4} \times 3^{3} \Rightarrow \lambda_{4} = \lambda_{2} = 4\lambda_{3} = 9\lambda_{4}$ .  
Example: 24 Hydrogen atom in its ground state is excited by radiation of wavelength 975 Å. How many lines will be there in the emission spectrum  
(a) 2 (b) 4 (c) 6 (d) 8  
Solution : (c) Using  $\frac{1}{4} = R_{1}^{\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} ] \Rightarrow \frac{1}{975 \times 10^{-10}} = 1.07 \times 10^{2} \left(\frac{1}{1^{2}} - \frac{1}{n^{2}}\right\right) \Rightarrow n = 4$   
Now number of spectral lines  $N = \frac{n(n-1)}{2} = \frac{4(d-1)}{2} = 6$ .  
Example: 25 A photon of energy 12.4 eV is completely absorbed by a hydrogen atom initially in the ground state so

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(a) 5,099 cm<sup>-1</sup> (b) 20,497 cm<sup>-1</sup> (c) 40,994 cm<sup>-1</sup> (d) 81,998 cm<sup>-1</sup>  
Solution : (d) Using 
$$\frac{1}{\lambda} = \overline{v} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow \overline{v} \propto Z^3 \Rightarrow \frac{\overline{v}_3}{\overline{v}_3} = \left( \frac{Z_3}{L_1} \right)^3 = \left( \frac{Z_3}{1} \right)^2 = 4 \Rightarrow \overline{v}_3 = \overline{v} \times 4 = 81588 \text{ cm}^{-1}$$
.  
**Example: 27** In an atom, the two electrons move round the nucleus in circular orbits of radii *R* and 4*R*. the ratio of the time taken by them to complete one revolution is  
(a) 1/4 (b) 4/1 (c) 8/1 (d) 1/8  
Solution : (d) Time period  $T \propto \frac{n^3}{Z^2}$   
For a given atom (*Z* = constant) So  $T \propto n^3$  .....(i) and radius  $R \propto n^2$  .....(ii)  
 $\therefore$  Prom equation (i) and (ii)  $T \propto R^{3/2} \Rightarrow \frac{T_1}{T_2} = \left(\frac{R_1}{R_2}\right)^{3/2} = \left(\frac{R}{4R}\right)^{3/2} = \frac{1}{8}$ .  
**Example: 28** tonisation energy for hydrogen atom in the ground state is *E*. What is the ionisation energy of  $L^{z^*}$  atom  
in the  $2^{a4}$  excited state  
(a)  $\overline{v}$  (b)  $3\overline{v}$  (c)  $6\overline{v}$  (d)  $9\overline{v}$   
Solution : (a) Ionisation energy of atom in *n*th state  $F_n = \frac{Z^3}{n^2}$ .  
For hydrogen atom in ground state (*n* = 1) and  $Z = 1 \Rightarrow E = E_0$  .....(i)  
For  $L^{z^*}$  atom in  $2^{z6}$  excited state  $n = 3$  and  $Z = 3$ , hence  $E' = \frac{E_0}{3^2} \times 3^2 = E_0$  .....(ii)  
From equation (i) and (ii)  $E' = E$ .  
**Example: 29** An electron jumps from  $n = 4$  to  $n = 1$  state in *H*-atom. The recoil momentum of *H*-atom (in  $eV/C$ ) is  
(a)  $12.75$  (b)  $6.75$  (c)  $14.45$  (d)  $0.85$   
Solution : (a) The H-atom before the transition was at rest. Therefore from conservation of momentum  
Photon momentum = Recoil momentum of *H*-atom or  
 $P_{roosil} = \frac{hv}{c} = \frac{E_4 - E_1}{c} = -0.85 eV - (-13.6 eV)} = 12.75 \frac{eV}{c}$   
**Example: 30** If elements with principal quantum number  $n > 4$  were not allowed in nature, the number  
of possible elements would be  
IIIT-JEE 1983; CBSE PMT 1993; SM PPET 1993; 2001; RPMT 1993, 2003; J & K CET 2004]  
(a)  $60$  (b)  $32$  (c)  $4$  (d)  $64$   
Solution : (a) Maximum value of  $n = 4$   
So possible (maximum) no. of elements  
 $N = 2 \times 1^2 + 2 \times 2^2 + 2 \times 3^2 + 2 \times 4^2 = 2 + 8 + 18 + 32 =$ 

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	radius, then find <i>n</i>					
				[IIT-JEE (Screening) 2003]		
	(a) 100	(b) 200	(c) 4	(d) 1/4		
Solution : (d)	(d) $(r_m) = \left(\frac{m^2}{Z}\right)(0.53 \text{ Å}) = (n \times 0.53 \text{ Å}) \implies \frac{m^2}{Z} = n$					
	$m = 5$ for $_{100} Fm^{257}$ (the outermost shell) and $z = 100$					
	$\therefore \qquad n = \frac{(5)^2}{100} = \frac{1}{4}$					
	An energy of 24.6 <i>eV</i> is required to remove one of the electrons from a neutral helium atom. The energy (in <i>eV</i> ) required to remove both the electrons from a neutral helium atom is					
	(a) 79.0	(b) 51.8	(c) 49.2	(d) 38.2		
Solution : (a)	a) After the removal of first electron remaining atom will be hydrogen like atom.					
	So energy required to remove second electron from the atom $E = 13.6 \times \frac{2^2}{1} = 54.4  eV$					
	$\therefore$ Total energy required = 24.6 + 54.4 = 79 eV					



