Bohr's atomic model

(1) This model was based on the quantum theory of radiation and the classical law of physics. It gave new idea of atomic structure in order to explain the stability of the atom and emission of sharp spectral lines.

(2) ***Postulates*** of this theory are:

(i) The atom has a central massive core nucleus where all the protons and neutrons are present. The size of the nucleus is very small.

(ii) The electron in an atom revolves around the nucleus in certain discrete orbits. Such orbits are known as *stable orbits* or *non – radiating* or *stationary orbits*.

(iii) The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

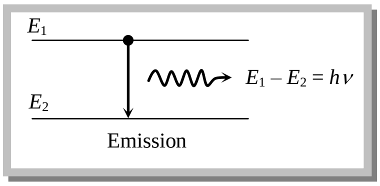
Force of attraction towards nucleus = centrifugal force

(iv) An electron can move only in those permissive orbits in which the angular momentum (mvr) of the electron is an integral multiple of $h/2\pi$. Thus, $\text{mvr} = n\frac{\text{h}}{2\pi}$

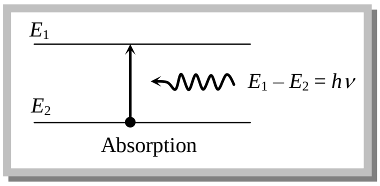
Where, m = mass of the electron, r = radius of the electronic orbit, v = velocity of the electron in its orbit.

(v) The angular momentum can be $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, ...\frac{nh}{2\pi}$. This principal is known as ***quantization of angular momentum***. In the above equation 'n' is any integer which has been called as *principal quantum number*. It can have the values $n=1,2,3,$ ------- (from the nucleus). Various energy levels are designed as $K(n=1)$, $L(n=2)$, $M(n=3)$ ------- etc. Since the electron present in these orbits is associated with some energy, these orbits are called energy levels.

(vi) The emission or absorption of radiation by the atom takes place when an electron jumps from one stationary orbit to another.



Emission



Absorption

(vii) The radiation is emitted or absorbed as a single quantum (photon) whose energy $h\nu$ is equal to the difference in energy ΔE of the electron in the two orbits involved. Thus, $h\nu = \Delta E$

Where 'h' =Planck's constant, ν =frequency of the radiant energy. Hence the spectrum of the atom will have certain fixed frequency.

(viii) The lowest energy state $(n=1)$ is called the *ground state*. When an electron absorbs energy, it gets excited and jumps to an outer orbit. It has to fall back to a lower orbit with the release of energy.

(3) **Advantages of Bohr's theory**

(i) Bohr's theory satisfactorily explains the spectra of species having one electron, *viz*. hydrogen atom, He^+, Li^{2+} etc.

(ii) *Calculation of radius of Bohr's orbit*: According to Bohr, radius of orbit in which electron moves is

$$\boxed{r = \left[\frac{h^2}{4\pi^2 me^2 k}\right] . \frac{n^2}{Z}}$$

Where, n =Orbit number, m =Mass number $\left[9.1 \times 10^{-31} kg\right]$, e =Charge on the electron $\left[1.6 \times 10^{-19}\right]$

Z =Atomic number of element, k = Coulombic constant $\left[9 \times 10^{9}\ Nm^2c^{-2}\right]$

After putting the values of m,e,k,h, we get.

$$\boxed{r_n = \frac{n^2}{Z} \times 0.529\ \text{Å}\ or\ r_n = \frac{n^2}{Z} \times 0.529\ nm}$$

(a) For a particular system [e.g., H, He^+ or Li^{+2}]

$r \propto n^2$ [Z = constant]

Thus we have $\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$ i.e., $r_1 : r_2 : r_3 .... :: 1 : 4 : 9.......\ r_1 < r_2 < r_3$

(b) For particular orbit of different species

$r \propto \frac{1}{Z}$ [Z =constant] Considering A and B species, we have $\frac{r_A}{r_B} = \frac{Z_B}{Z_A}$

Thus, radius of the first orbit H, He^+, Li^{+2} and Be^{+3} follows the order: $H > He^+ > Li^{+2} > Be^{+3}$

(iii) *Calculation of velocity of electron*

$$\boxed{V_n = \frac{2\pi e^2 ZK}{nh}, V_n = \left[\frac{Ze^2}{mr}\right]^{1/2}}$$

For H atom, $V_n = \frac{2.188 \times 10^8}{n} cm.\sec^{-1}$

(a) For a particular system [H, He^+ or Li^{+2}]

$V \propto \frac{1}{n}$ [Z = constant] Thus, we have, $\frac{V_1}{V_2} = \frac{n_2}{n_1}$

The order of velocity is $V_1 > V_2 > V_3.........$ or $V_1 : V_2 : V_3 .... :: 1 : \frac{1}{2} : \frac{1}{3}........$

(b) For a particular orbit of different species

$V \propto Z$ [n =constant] Thus, we have $H < He^+ < Li^{+2}$

(c) For H *or* He^+ or Li^{+2}, we have

$V_1 : V_2 = 2 : 1;\ V_1 : V_3 = 3 : 1;\ V_1 : V_4 = 4 : 1$

(iv) *Calculation of energy of electron in Bohr's orbit*

Total energy of electron = K.E. + P.E. of electron $= \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$

Substituting of r, gives us $E = \frac{-2\pi^2 mZ^2 e^4 k^2}{n^2 h^2}$ Where, n=1, 2, 3.........∞

Putting the value of m, e, k, h, π we get

$$E = 21.8 \times 10^{-12} \times \frac{Z^2}{n^2} erg\ per\ atom = -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} J\ per\ atom\ (1J = 10^7 erg)$$

$$E = -13.6 \times \frac{Z^2}{n^2} eV\ per\ atom (1\text{eV} = 1.6 \times 10^{-19} J) = -313.6 \times \frac{Z^2}{n^2} kcal./mole \quad (1\ cal = 4.18J)$$

or $\frac{-1312}{n^2} Z^2 kJmol^{-1}$

(a) For a particular system[H, He^+ or Li^{+2}]

$E \propto -\frac{1}{n^2}$ [Z =constant] Thus, we have $\frac{E_1}{E_2} = \frac{n_2^2}{n_1^2}$

The energy increase as the value of n increases

(b) For a particular orbit of different species

$E \propto -Z^2$ [n =constant] Thus, we have $\frac{E_A}{E_B} = \frac{Z_A^2}{Z_B^2}$

For the system H, He^+ , Li^{+2}, Be^{+3} (n-same) the energy order is $H > He^+ > Li^{+2} > Be^{+3}$

The energy decreases as the value of atomic number Z increases.

When an electron jumps from an outer orbit (higher energy) n_2 to an inner orbit (lower energy) n_1, then the energy emitted in form of radiation is given by

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 k^2 me^4 Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \Delta E = 13.6 Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV/atom$$

As we know that $E = h\bar{\nu}$, $c = \nu\lambda$ and $\bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E}{hc}, = \frac{2\pi^2 k^2 me^4 Z^2}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

This can be represented as $\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where, $R = \frac{2\pi^2 k^2 me^4}{ch^3}$ R is known as Rydberg constant. Its value to be used is $109678\ cm^{-1}$.

(4) **Quantisation of energy of electron**

(i) *In ground state*: No energy emission. In ground state energy of atom is minimum and for 1st orbit of H-atom, $n=1$.

$\therefore E_1 = -13.6 eV$.

(ii) *In excited state*: Energy levels greater than n_1 are excited state. i.e. for H- atom n_2, n_3, n_4 are excited state. For *H*- atom first excitation state is $= n_2$

(iii) *Excitation potential*: Energy required to excite electron from ground state to any excited state.

$$\text{Ground state} \longrightarrow \text{Excited state}$$

Ist excitation potential = $E_2 - E_1 = -3.4 + 13.6 = 10.2\ eV$.

IInd excitation potential = $E_3 - E_1 = -1.5 + 13.6 = 12.1\ eV$.

(iv) *Ionisation energy* : The minimum energy required to relieve the electron from the binding of nucleus.

$$\boxed{E_{\text{ionisation}} = E_\infty - E_n = +13.6 \frac{Z_{\text{eff.}}^2}{n^2} eV.}$$

(v) *Ionisation potential* : $V_{\text{ionisation}} = \frac{E_{ionisation}}{e}$

(vi) *Separation energy* : Energy required to excite an electron from excited state to infinity.

$$\text{S.E.} = E_\infty - E_{excited}.$$

(vii) *Binding energy* : Energy released in bringing the electron from infinite to any orbit is called its binding energy (B.E.).

Note : ❑ Principal Quantum Number 'n' = $\sqrt{\frac{13.6}{(B.E.)}}$.

(5) **Spectral evidence for quantisation** (Explanation for hydrogen spectrum on the basis of bohr atomic model)

(i) The light absorbed or emitted as a result of an electron changing orbits produces characteristic absorption or emission spectra which can be recorded on the photographic plates as a series of lines, the optical spectrum of hydrogen consists of several series of lines called **Lyman, Balmar, Paschen, Brackett, Pfund** and **Humphrey.** These spectral series were named by the name of scientist who discovered them.

(ii) To evaluate wavelength of various H-lines Ritz introduced the following expression,

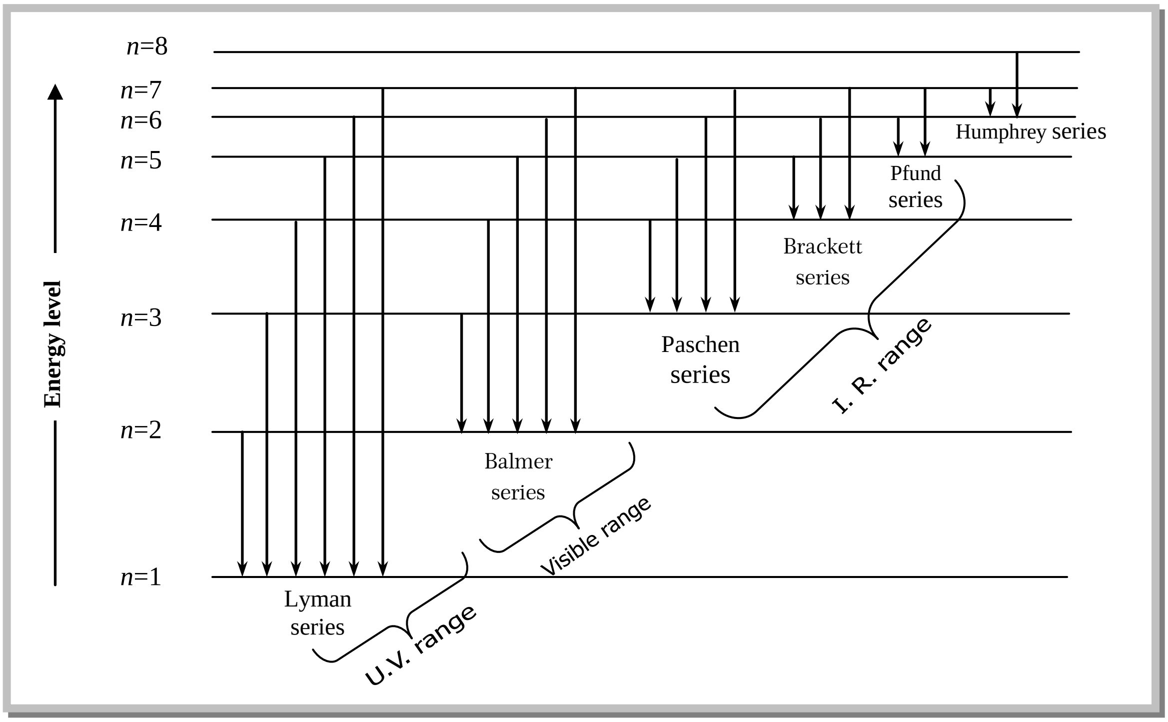
$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, R is $= \frac{2\pi^2 me^4}{ch^3}$ = Rydberg's constant

It's theoritical value = 109,737 cm^{-1} and It's experimental value = $109{,}677.581 cm^{-1}$

This remarkable agreement between the theoretical and experimental value was great achievment of the Bohr model.

(iii) Although H- atom consists only one electron yet it's spectra consist of many spectral lines as shown in fig.



(iv) *Comparative study of important spectral series of Hydrogen*

S.No.	Spectral series	Lies in the region	Transition $n_2 > n_1$	$\lambda_{max} = \frac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R}$	$\lambda_{min} = \frac{n_1^2}{R}$	$\frac{\lambda_{max}}{\lambda_{min}} = \frac{n_2^2}{n_2^2 - n_1^2}$
(1)	Lymen series	Ultraviolet region	$n_1 = 1$ $n_2 = 2,3,4....\infty$	$n_1 = 1$ and $n_2 = 2$ $\lambda_{max} = \frac{4}{3R}$	$n_1 = 1$ and $n_2 = \infty$ $\lambda_{min} = \frac{1}{R}$	$\frac{4}{3}$
(2)	Balmer series	Visible region	$n_1 = 2$ $n_2 = 3,4,5....\infty$	$n_1 = 2$ and $n_2 = 3$ $\lambda_{max} = \frac{36}{5R}$	$n_1 = 2$ and $n_2 = \infty$ $\lambda_{min} = \frac{4}{R}$	$\frac{9}{5}$
(3)	Paschen series	Infra red region	$n_1 = 3$ $n_2 = 4,5,6....\infty$	$n_1 = 3$ and $n_2 = 4$ $\lambda_{max} = \frac{144}{7R}$	$n_1 = 3$ and $n_2 = \infty$ $\lambda_{min} = \frac{9}{R}$	$\frac{16}{7}$
(4)	Brackett series	Infra red region	$n_1 = 4$ $n_2 = 5,6,7....\infty$	$n_1 = 4$ and $n_2 = 5$ $\lambda_{max} = \frac{16 \times 25}{9R}$	$n_1 = 4$ and $n_2 = \infty$ $\lambda_{min} = \frac{16}{R}$	$\frac{25}{9}$
(5)	Pfund series	Infra red region	$n_1 = 5$ $n_2 = 6,7,8....\infty$	$n_1 = 5$ and $n_2 = 6$ $\lambda_{max} = \frac{25 \times 36}{11R}$	$n_1 = 5$ and $n_2 = \infty$ $\lambda_{min} = \frac{25}{R}$	$\frac{36}{11}$
(6)	Humphrey series	Far infrared region	$n_1 = 6$ $n_2 = 7,8....\infty$	$n_1 = 6$ and $n_2 = 7$ $\lambda_{max} = \frac{36 \times 49}{13R}$	$n_1 = 6$ and $n_2 = \infty$ $\lambda_{min} = \frac{36}{R}$	$\frac{49}{13}$

(v) If an electron from n^{th} excited state comes to various energy states, the maximum spectral lines obtained will be = $\boxed{\frac{n(n-1)}{2}}$. n= principal quantum number.

as n=6 than total number of spectral lines = $\frac{6(6-1)}{2} = \frac{30}{2} = 15$.

(vi) Thus, at least for the hydrogen atom, the Bohr Theory accurately describes the origin of atomic spectral lines.

(6) **Failure of Bohr Model**

(i) Bohr theory was very successful in predicting and accounting the energies of line spectra of hydrogen i.e. one electron system. It could not explain the line spectra of atoms containing more than one electron.

(ii) This theory could not explain the presence of multiple spectral lines.

(iii) This theory could not explain the splitting of spectral lines in magnetic field (Zeeman Effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.

(iv) This theory was unable to explain of dual nature of matter as explained on the basis of De broglies concept.

(v) This theory could not explain uncertainty principle.

(vi) No conclusion was given for the concept of quantisation of energy.

Example: 18 If the radius of 2nd Bohr orbit of hydrogen atom is r_2. The radius of third Bohr orbit will be

(a) $\frac{4}{9}r_2$ (b) $4r_2$ (c) $\frac{9}{4}r_3$ (d) $9r_2$

Solution : (c) $r = \frac{n^2h^2}{4\pi^2mZe^2}$ $\therefore$ $\frac{r_2}{r_3} = \frac{2^2}{3^2}$ $\therefore$ $r_3 = \frac{9}{4}r_2$

Example: 19 Number of waves made by a Bohr electron in one complete revolution in 3rd orbit is

(a) 2 (b) 3 (c) 4 (d) 1

Solution : (b) Circumference of 3rd orbit = $2\pi r_3$

According to Bohr angular momentum of electron in 3rd orbit is

$mvr_3 = 3\frac{h}{2\pi}$ or $\frac{h}{mv} = \frac{2\pi r_3}{3}$

by De-Broglie equation, $\lambda = \frac{h}{mv}$

$\therefore \lambda = \frac{2\pi r_3}{3}$ $\therefore 2\pi r_3 = 3\lambda$

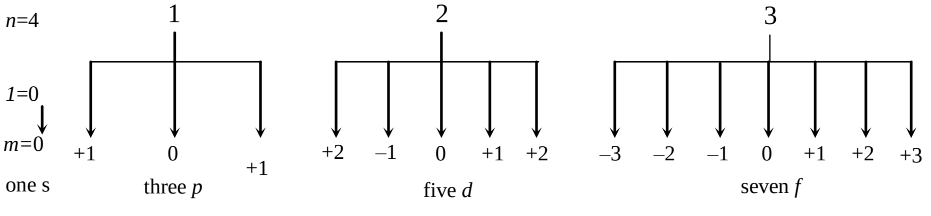
i.e. circumference of 3rd orbit is three times the wavelength of electron or number of waves made by Bohr electron in one complete revolution in 3rd orbit is three.

Example: 20 The degeneracy of the level of hydrogen atom that has energy $-\frac{R_{11}}{16}$ is

(a) 16 (b) 4 (c) 2 (d) 1

Solution : (a) $E_n = -\frac{R_H}{n^2}$ $\therefore$ $-\frac{R_H}{n^2} = -\frac{R_H}{16}$

i.e. for 4^{th} sub-shell



i.e. 1+3+5+7=16, $\therefore$ degeneracy is 16

Example: 21 The velocity of electron in the ground state hydrogen atom is $2.18 \times 10^8 ms^{-1}$. Its velocity in the second orbit would be

(a) $1.09 \times 10^8 ms^{-1}$ (b) $4.38 \times 10^8 ms^{-1}$ (c) $5.5 \times 10^5 ms^{-1}$ (d) $8.76 \times 10^8 ms^{-1}$

Solution : (a) We know that velocity of electron in nth Bohr's orbit is given by

$v = 2.18 \times 10^{6} \dfrac{Z}{n} m/s$

for $H, Z = 1$

$\Theta\ v_1 = \dfrac{2.18 \times 10^{6}}{1} m/s$

$\Theta\ v_2 = \dfrac{2.18 \times 10^{6}}{2} m/s = 1.09 \times 10^{6} m/s$

Example: 22 The ionization energy of the ground state hydrogen atom is $2.18 \times 10^{-18} J.$ The energy of an electron in its second orbit would be

(a) $-1.09 \times 10^{-18} J$ (b) $-2.18 \times 10^{-18} J$ (c) $-4.36 \times 10^{-18} J$ (d) $-5.45 \times 10^{-19} J$

Solution : (d) Energy of electron in first Bohr's orbit of H-atom

$E = \dfrac{-2.18 \times 10^{-18}}{n^2} J$ (Θ ionization energy of $H = 2.18 \times 10^{-18} J$)

$E_2 = \dfrac{-2.18 \times 10^{-18}}{2^2} J = -5.45 \times 10^{-19} J$

Example: 23 The wave number of first line of Balmer series of hydrogen atom is 15200 cm^{-1}. What is the wave number of first line of Balmer series of Li^{3+} ion.

(a) 15200 cm^{-1} (b) 6080 cm^{-1} (c) 76000 cm^{-1} (d) 1,36800 cm^{-1}

Solution : (d) For Li^{3+} $\bar{v} = \bar{v}$ for $H \times z^2 = 15200 \times 9 =$ 1,36800 cm^{-1}

Example: 24 The Bohr orbit radius for the hydrogen atom (n = 1) is approximately 0.530Å. The radius for the first excited state (n = 2) orbit is (in Å)

(a) 0.13 (b) 1.06 (c) 4.77 (d) 2.12

Solution : (d) The Bohr radius for hydrogen atom (n = 1) = 0.530Å

The radius of first excited state (n = 2) will be = $0.530 \times \dfrac{n^2}{Z} = 0.530 \times \dfrac{(2)^2}{1} = 2.120\ Å$

Example: 25 How many chlorine atoms can you ionize in the process $Cl \rightarrow Cl^{+} + e^{-}$, by the energy liberated from the following process :

$Cl + e^{-} \rightarrow Cl^{-}$ for 6×10^{23} atoms

Given electron affinity of $Cl = 3.61 eV$, and IP of $Cl = 17.422\ eV$

(a) 1.24×10^{23} atoms (b) 9.82×10^{20} atoms (c) 2.02×10^{15} atoms (d) None of these

Solution : (a) Energy released in conversion of 6×10^{23} atoms of Cl^{-} ions = 6×10^{23} × electron affinity

$= 6 \times 10^{23} \times 3.61 = 2.166 \times 10^{24} eV.$

Let x Cl atoms are converted to Cl^{+} ion

Energy absorbed $= x \times$ ionization energy

$x \times 17.422 = 2.166 \times 10^{24}$; $x = 1.243 \times 10^{23}$ atoms

Example: 26 The binding energy of an electron in the ground state of the He atom is equal to 24eV. The energy required to remove both the electrons from the atom will be

(a) 59eV (b) 81eV (c) 79eV (d) None of these

Solution : (c) Ionization energy of $He = \dfrac{Z^2}{n^2} \times 13.6 = \dfrac{2^2}{1^2} \times 13.6 = 54.4 eV$

Energy required to remove both the electrons

= binding energy + ionization energy

$= 24.6 + 54.4 = 79 eV$

Example: 27 The wave number of the shortest wavelength transition in Balmer series of atomic hydrogen will be

(a) 4215 Å (b) 1437Å (c) 3942Å (d) 3647Å

Solution : (d) $\dfrac{1}{\lambda_{\text{shortest}}} = RZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right) = 109678 \times 1^2 \times \left(\dfrac{1}{2^2} - \dfrac{1}{\infty^2}\right)$

$\lambda = 3.647 \times 10^{-5} cm = 3647\ Å$

Example: 28 If the speed of electron in the Bohr's first orbit of hydrogen atom is x, the speed of the electron in the third Bohr's orbit is

(a) $x/9$ (b) $x/3$ (c) $3x$ (d) $9x$

Solution : (b) According to Bohr's model for hydrogen and hydrogen like atoms the velocity of an electron in an atom is quantised and is given by $v \propto \frac{2\pi Ze^2}{nh}$ so $v \propto \frac{1}{n}$ in this cass $n = 3$

Example: 29 Of the following transitions in hydrogen atom, the one which gives an absorption line of lowest frequency is

(a) $n=1$ to $n=2$ (b) $n=3$ to $n=8$ (c) $n=2$ to $n=1$ (d) $n=8$ to $n=3$

Solution : (b) Absorption line in the spectra arise when energy is absorbed i.e., electron shifts from lower to higher orbit, out of a & b, b will have the lowest frequency as this falls in the Paschen series.

Example: 30 The frequency of the line in the emission spectrum of hydrogen when the atoms of the gas contain electrons in the third energy level are

(a) $1.268 \times 10^{14}\,Hz$ and $2.864 \times 10^{16}\,Hz$ (b) $3.214 \times 10^{10}\,Hz$ and $1.124 \times 10^{12}\,Hz$

(c) $1.806 \times 10^{12}\,Hz$ and $6.204 \times 10^{15}\,Hz$ (d) $4.568 \times 10^{14}\,Hz$ and $2.924 \times 10^{15}\,Hz$

Solution : (d) If an electron is in 3rd orbit, two spectral lines are possible

(a) When it falls from 3rd orbit to 2nd orbit.

In equation $v = 3.289 \times 10^{15}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$v_1 = 3.289 \times 10^{15}\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 3.289 \times 10^{15} \times \frac{5}{36} = 4.568 \times 14^{14}\,Hz$$

(b) When it falls from 3rd orbit to 1st orbit :

$$v_2 = 3.289 \times 10^{15} \times \left[\frac{1}{1} - \frac{1}{3^2}\right] = 3.289 \times 10^{15} \times \frac{8}{9} = 2.924 \times 10^{15}\,Hz$$

Example: 31 If the first ionisation energy of hydrogen is $2.179 \times 10^{-18}\,J$ per atom, the second ionisation energy of helium per atom is

(a) $8.716 \times 10^{-18}\,J$ (b) $5.5250\,kJ$ (c) $7.616 \times 10^{-18}\,J$ (d) $8.016 \times 10^{-13}\,J$

Solution : (a) For Bohrs systems : energy of the electron $\propto \frac{Z^2}{n^2}$

Ionisation energy is the difference of energies of an electron (E_∞), when taken to infinite distance and E_r when present in any Bohr orbit and E_α is taken as zero so ionisation energy becomes equal to the energy of electron in any Bohr orbit.

$E_H \propto \frac{Z_H^2}{n_H^2}$; $E_{He} \propto \frac{Z_{He}^2}{n_{He}^2}$ or $\frac{E_H}{E_{He}} = \frac{1}{2 \times 2}$ [as $Z_H = 1$, $Z_{He} = 2, n_H = 1, n_{He} = 1$]

or $E_{He} = E_H \times 4 = 2.179 \times 10^{-18} \times 4 = 8.716 \times 10^{-18}$ Joule per atom.

Example: 32 The ionization energy of hydrogen atom is $13.6eV$. What will be the ionization energy of He^+

(a) 13.6eV (b) $54.4eV$ (c) $122.4eV$ (d) Zero

Solution : (b) I.E. of $He^+ = 13.6eV \times Z^2$

$13.6eV \times 4 = 54.4eV$

Example: 33 The ionization energy of He^+ is $19.6 \times 10^{-18}\,J$ atom^{-1}. Calculate the energy of the first stationary state of Li^{+2}

(a) $19.6 \times 10^{-18}\,J$ atom $^{-1}$ (b) $4.41 \times 10^{-18}\,J$ atom^{-1}

(c) $19.6 \times 10^{-19}\,J$ atom $^{-1}$ (d) $4.41 \times 10^{-17}\,J$ atom $^{-1}$

Solution : (d) I.E. of $He^+ = E \times 2^2 (Z$ for $He = 2)$

I.E. of $Li^{2+} = E \times 3^3$ (Z for Li=3)

$$\therefore \frac{I.E.(He^+)}{I.E.(Li^{2+})} = \frac{4}{9} \text{ or I.E. } (Li^{2+}) = \frac{9}{4} \times I.E.(He^+) = \frac{9}{4} \times 19.6 \times 10^{-18} = 4.41 \times 10^{-17}\ J \text{ atom}^{-1}$$

Bohr – Sommerfeld's model

(1) In 1915, Sommerfield introduced a new atomic model to explain the fine spectrum of hydrogen atom.

(2) He gave concept that electron revolve round the nucleus in *elliptical orbit*. Circular orbits are formed in special conditions only when major axis and minor axis of orbit are equal.

(3) For circular orbit, the angular momentum = $\frac{nh}{2\pi}$ where n= principal quantum number only one component i.e. only angle changes.

(4) For elliptical orbit, angular momentum = vector sum of 2 components. In elliptical orbit two components are,

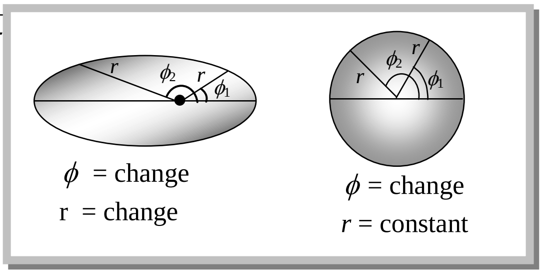
(i) Radial component (along the radius) $= n_r \frac{h}{2\pi}$

Where, n_r = radial quantum number

(ii) Azimuthal component $= n_\phi \frac{h}{2\pi}$

Where, n_ϕ = azimuthal quantum number

So angular momentum of elliptical orbit $= n_r \frac{h}{2\pi} + n_\phi \frac{h}{2\pi}$



Angular momentum $= (n_r + n_\phi)\frac{h}{2\pi}$

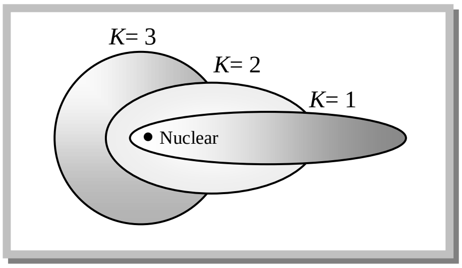
(5) Shape of elliptical orbit depends on,

$$\frac{\text{Length of major axis}}{\text{Length of minor axis}} = \frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi}$$

(6) n_ϕ can take all integral values from l to 'n' values of n_r depend on the value of n_ϕ. For $n = 3$, n_ϕ can have values 1, 2, 3 and n_r can have (n –1) to zero i.e. 2,1 and zero respectively.

Thus for n = 3, we have 3 paths

n	n_ϕ	n_r	Nature of path
3	1	3	elliptical
	2	1	elliptical
	3	0	circular



The possible orbits for n = 3 are shown in figure.

Thus *Sommerfield* showed that Bohr's each major level was composed of several sub-levels. therefore it provides the basis for existence of subshells in Bohr's shells (orbits).

(7) **Limitation of Bohr sommerfield model:**

(i) This model could not account for, why electrons does not absorb or emit energy when they are moving in stationary orbits.

(ii) When electron jumps from inner orbit to outer orbit or vice –versa, then electron run entire distance but absorption or emission of energy is discontinuous.

(iii) It could not explain the attainment of expression of $\frac{nh}{2\pi}$ for angular momentum. This model could not explain *Zeeman effect* and *Stark effect.*

Dual nature of electron

(1) In 1924, the french physicist, ***Louis de Broglie*** suggested that if light has both particle and wave like nature, the similar duality must be true for matter. Thus an electron, behaves both as a material particle and as a wave.

(2) This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

(3) According to de-broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation

$\boxed{\lambda = \frac{h}{mv},}$ where h = Planck's constant.

(4) This can be derived as follows according to Planck's equation, $E = h\nu = \frac{h.c}{\lambda} \left(\Theta \ \nu = \frac{c}{\lambda}\right)$

energy of photon (on the basis of Einstein's mass energy relationship), $E = mc^2$

equating both $\frac{hc}{\lambda} = mc^2$ *or* $\lambda = \frac{h}{mc}$ which is same as de-Broglie relation. $(\Theta \ mc = p)$

(5) This was experimentally verified by ***Davisson and Germer*** by observing diffraction effects with an electron beam. Let the electron is accelerated with a potential of V than the Kinetic energy is

$$\frac{1}{2}mv^2 = eV\ ;\quad m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = P\ ;\quad \lambda = \frac{h}{\sqrt{2eVm}}$$

(6) If Bohr's theory is associated with de-Broglie's equation then wave length of an electron can be determined in bohr's orbit and relate it with circumference and multiply with a whole number

$$2\pi r = n\lambda \text{ or } \lambda = \frac{2\pi r}{n}$$

From de-Broglie equation, $\lambda = \frac{h}{mv}$. Thus $\frac{h}{mv} = \frac{2\pi r}{n}$ or $mvr = \frac{nh}{2\pi}$

Note : ❑ For a proton, electron and an α-particle moving with the same velocity have de-broglie wavelength in the following order : Electron > Proton > α - particle.

(7) The de-Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. Since, we come across macroscopic objects in our everyday life, de-broglie relationship has no significance in everyday life.

Example: 34 An electron is moving with a kinetic energy of 4.55×10^{-25} J. What will be de-Broglie wavelength for this electron

(a) $5.28 \times 10^{-7}\,m$ (b) $7.28 \times 10^{-7}m$ (c) $2 \times 10^{-10}m$ (d) $3 \times 10^{-5}m$

Solution : (b) $KE = \frac{1}{2}mv^2 = 4.55 \times 10^{-25}\ J$

$$v^2 = \frac{2 \times 4.55 \times 10^{-25}}{9.1 \times 10^{-31}} = 1 \times 10^6\ ;\quad v = 10^3\ m/s$$

De-Broglie wavelength $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} = 7.28 \times 10^{-7}\ m$

Example: 35 The speed of the proton is one hundredth of the speed of light in vacuum. What is the de Broglie wavelength? Assume that one mole of protons has a mass equal to one gram, $h = 6.626 \times 10^{-27}$ erg sec

(a) $3.31 \times 10^{-3}\ \text{Å}$ (b) $1.33 \times 10^{-3}\ \text{Å}$ (c) $3.13 \times 10^{-2}\ \text{Å}$ (d) $1.31 \times 10^{-2}\ \text{Å}$

Solution : (b) $m = \frac{1}{6.023 \times 10^{23}}\ g$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-27}}{1 \times 3 \times 10^8 cm\ \sec^{-1}} \times 6.023 \times 10^{23} = 1.33 \times 10^{-11}\ cm$$

Heisenberg's uncertainty principle

(1) One of the important consequences of the dual nature of an electron is the uncertainty principle, developed by ***Warner Heisenberg***.

(2) According to uncertainty principle "It is impossible to specify at any given moment both the position and momentum (velocity) of an electron".

Mathematically it is represented as , $\boxed{\Delta x.\Delta p \geq \frac{h}{4\pi}}$

Where $\Delta x =$ uncertainty is position of the particle, $\Delta p =$ uncertainty in the momentum of the particle

Now since $\Delta p = m\,\Delta v$

So equation becomes, $\Delta x.m\Delta v \geq \frac{h}{4\pi}$ or $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

The sign $\geq$ means that the product of Δx and Δp (or of Δx and Δv) can be greater than, or equal to but never smaller than $\frac{h}{4\pi}$. If Δx is made small, Δp increases and vice versa.

(3) In terms of uncertainty in energy, ΔE and uncertainty in time $\Delta t,$ this principle is written as,

$$\Delta E \,.\, \Delta t \geq \frac{h}{4\pi}$$

❑ Heisenberg's uncertainty principle cannot we apply to a stationary electron because its velocity is 0 and position can be measured accurately.

Example: 36 What is the maximum precision with which the momentum of an electron can be known if the uncertainty in the position of electron is $\pm 0.001 \mathring{A}$? Will there be any problem in describing the momentum if it has a value of $\frac{h}{2\pi a_0}$, where a_0 is Bohr's radius of first orbit, i.e., 0.529Å?

Solution : $\Delta x \,.\, \Delta p = \frac{h}{4\pi}$

$\Theta \;\; \Delta x = 0.001 \mathring{A} = 10^{-13} m$

$\therefore \;\; \Delta p = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 10^{-13}} = 5.27 \times 10^{-22}$

Example: 37 Calculate the uncertainty in velocity of an electron if the uncertainty in its position is of the order of a $1\mathring{A}$.

Solution : According to Heisenberg's uncertainty principle

$\Delta v \,.\, \Delta x \approx \frac{h}{4\pi m}$

$$\Delta v \approx \frac{h}{4\pi m.\Delta x} = \frac{6.625 \times 10^{-34}}{4 \times \frac{22}{7} \times 9.108 \times 10^{-31} \times 10^{-10}} = 5.8 \times 10^{5} m \;\; \sec^{-1}$$

Example: 38 A dust particle having mass equal to $10^{-11} g,$ diameter of $10^{-4} cm$ and velocity $10^{-4} cm \sec^{-1}$. The error in measurement of velocity is 0.1%. Calculate uncertainty in its positions. Comment on the result .

Solution : $\Delta v = \frac{0.1 \times 10^{-4}}{100} = 1 \times 10^{-7} cm \sec^{-1}$

$\Theta \;\; \Delta v \,.\, \Delta x = \frac{h}{4\pi m}$

$\therefore \;\; \Delta x = \frac{6.625 \times 10^{-27}}{4 \times 3.14 \times 10^{-11} \times 1 \times 10^{-7}} = 5.27 \times 10^{-10} cm$

The uncertainty in position as compared to particle size.

$= \frac{\Delta x}{diameter} = \frac{5.27 \times 10^{-10}}{10^{-4}} = 5.27 \times 10^{-6} cm$

The factor being small and almost being negligible for microscope particles.

PLANCK'S QUANTUM THEORY

Q.11 Calculate the wavelength of the radiation that would cause photo dissociation of chlorine molecule if the Cl- Cl bond energy is 243 KJ/mol.

Q.12 Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light (λ = 550 nm) are needed to generate this minimum amount of energy.

Q.13 A photon having λ = 854 Å causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ.

Q.14 Calculate the threshold frequency of metal if the binding energy is 180.69 KJ mol^{-1} of electron.

Q.15 Calculate the binding energy per mole when threshold frequency to the wavelength of 240 nm.

Q.16 A metal was irriadated by light of frequency 3.2×10^{15} S^{-1}. The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irriadated with a light of frequency 2.0×10^{15} S^{-1}. What is work function.

Q.17 U.V. light of wavelength 800 Å & 700 Å falls on hydrogen atoms in their ground state & liberates electrons with kinetic energy 1.8 eV and 4 eV respectively. Calculate planck's constant.

Q.18 The dissociation energy of H_2 is 430.53 KJ/mol. If H_2 is exposed to radiant energy of wavelength 253.7 nm, what % of radiant energy will be converted into K.E.

Q.19 A potential difference of 20 KV is applied across an X-ray tube. Find the minimum wavelength of X-ray generated.

Q.20 The K.E. of an electron emitted from tungstan surface is 3.06 eV. What voltage would be required to bring the electron to rest?

BOHR'S MODEL

Q.21 Calculate energy of electron which is moving in the orbit that has its rad. sixteen times the rad. of first Bohr orbit for H–atom.

Q.22 The electron energy in hydrogen atom is given by Calculate the energy required to remove an e^- completely from n = 2 orbit . What is the largest wavelength in cm of light that can be used to cause this transition.

Q.23 Calculate the wavelength in angstrom of photon that is emitted when an e^- in Bohr orbit n=2 returns to the orbit n=1. The ionization potential of the ground state of hydrogen atom is 2.17×10^{-11} erg/atom.

Q.24 The radius of the fourth orbit of hydrogen atom is 0.85 nm. Calculate the velocity of electron in this orbit.

Q.25 The velocity of e^- in a certain Bohr orbit of the hydrogen atom bears the ratio 1:275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition from the quatum state (n+1) to the ground state.

Q.26 Electrons of energy 12.09 eV can excite hydrogen atoms. To which orbit is the electron in the hydrogen atom raised and what are the wavelengths of the radiations emitted as it drops back to the ground state.

Q.27 A doubly ionised lithium atom is hydrogen like with atomic number z = 3. Find the wavelength of the radiation required to excite the electron in Li^{2+} from the first to the third Bohr orbit.

Q.28 Estimate the difference in energy between I and II Bohr Orbit for a hydrogen atom. At what minimum at no. a transition from n=2 to n=1 energy level would result in the emission of X–rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen like species does this at no correspond to.

Q.29 Find out the no. of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

Q.30 Iodine molecule dissociates into atoms after absorbing light of $4500A^0$. If one quantum of radiation is absorbed by each molecule, calculate the K.E. of iodine atoms
(Bond energy of I_2 = 240 KJ/mol)

Q.31 Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.

Q.32 Calculate the wave no. for the shortest wavelength transition in the Balmer series of atomic hydrogen.

GENERAL

Q.33 What is de-Broglie wavelength of a He-atom in a container at room temperature.(Use U_{avg})

Q.34 Through what potential difference must an electron pass to have a wavelength of 500 Å.

Q.35 A proton is accelerated to one- tenth of the velocity of light. If its velocity can be measured with a precision $\pm$ 1%. What must be its uncertainity in position.

Q.36 To what effective potential a proton beam be subjected to give its protons a wavelength of 1×10^{-10} m.

Q.37 Calculate magnitude of angular momentum of an e^- that occupies 1s, 2s , 2p , 3d , 3p.

Q.38 Calculate the number of exchange pairs of electrons present in configuration of Cu according to Aufbau Principle considering 3d & 4s orbitals.

Q.39 He atom can be excited to $1s^1\ 2p^1$ by $\lambda = 58.44$ nm. If lowest excited state for He lies 4857cm^{-1} below the above. Calculate the energy for the lower excitation state.

Q.40 Wave functions of electrons in atoms & molecules are called________.

Q.41 The outermost electronic conf. of Cr is___________.

Answer Key

PLANCK'S QUANTUM THEORY

Q.11 4.9×10^{-7} m Q.12 28 photons Q.13 1403 KJ/mol Q.14 4.5×10^{14} s^{-1}
Q.15 497 KJ/mol Q.16 319.2 KJ/mol Q.17 6.57×10^{-34} Js
Q.18 8.68 % Q.19 0.62 Å Q.20 3.06 V

BOHR'S MODEL

Q.21 -1.36×10^{-19} Joules Q.22 -5.425×10^{-12} ergs, 3.7×10^{-5} cm
Q.23 1220 Å Q.24 5.44×10^{5} m/s Q.25 2 ; 9.75×10^{4} cm^{-1}
Q.26 3 , 6563 Å , 1215 Å , 1026 Å Q.27 113.74 Å
Q.28 10.2 eV , z = 2 Q.29 3 Q.30 2.186×10^{-20} Joules
Q.31 9.7×10^{-8} m Q.32 27419.25 cm^{-1}

GENERAL

Q.33 0.79 Å Q.34 6.03×10^{-4} volt Q.35 1.05×10^{-13} m
Q.36 0.0826 volts Q.37 0 ; 0 ; ; ; Q.38 25
Q.39 3.3×10^{-18} J Q.40 orbitals Q.41 $3s^2\ 3p^6\ 3d^5\ 4s^1$