

UNIT-3 ATOMIC SPECTRA

• BOHR ATOM MODEL:

Bohr assumed basically Rutherford nuclear-model of the atom and tried to overcome the defects of the model. He proposed the following two postulates.

Basic Postulates

- (1). An electron cannot revolve around the nucleus in all possible orbits as suggested by the classical theory. The electron can revolve around the nucleus only in those allowed or permissible orbits for which the angular momentum of the electron is an integral multiple of $\hbar$.

Here, $\hbar$ is the planck's constant — or rather, his original constant (h) divided by 2π .

$$\hbar = \frac{h}{2\pi} = \frac{6.62 \times 10^{-34} \text{ J-sec}}{2 \times 3.14} = 1.054 \times 10^{-34} \text{ J-sec}$$

where, $h = 6.62 \times 10^{-34} \text{ J-sec}$

These orbits are called stationary orbits and an electron revolving in these orbits does not radiate energy.

Explanation-

For an electron of mass ' m ', moving with a speed ' v ' in an orbit of radius ' r '. Therefore, angular momentum-

$$L = mvr = m r^2 \omega = n \hbar \quad \left\{ \because v = r\omega \right.$$

Here, $\hbar = \frac{h}{2\pi}$

$$L = mvr = m r^2 \omega = \frac{nh}{2\pi}$$

Where, n is called the Principal quantum number. It takes integral values, excluding zero; $n = 1, 2, 3, 4, \dots$

- (2). An atom radiates energy only when an electron jumps from a stationary orbit of higher energy to one of lower energy. If the electron jumps from an initial orbit of energy ' E_i ' to a final orbit of energy ' E_f ' ($E_i > E_f$), a photon of frequency

$$\nu = \frac{E_i - E_f}{h} \text{ is emitted.}$$

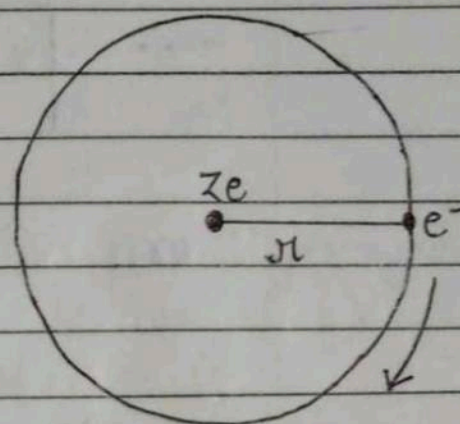
Where, h is the Planck's constant.

• The Bohr Formulae :

Based on the postulates, Bohr derived the formulae for-

- (i). the radii of the stationary orbits and
- (ii). the total energy of the electron in the orbit.

consider an atom whose nucleus has a positive charge ' Ze ' and ^{mass} M . Let an electron of charge ' $-e$ ' and mass ' m ' move around the nucleus in an orbit of radius ' r '.



The electrostatic force of attraction between the nucleus and the electron,

$$= \frac{1}{4\pi\epsilon_0} \frac{(Ze)(-e)}{r^2} \quad \text{----- (1)}$$

This force provides the necessary centripetal force $\left(= \frac{mv^2}{r} \right)$ to the electron to move in a circular orbit.

The centrifugal force on the electron -

$$= \frac{mv^2}{r} \quad \text{----- (2)}$$

The system will be stable if

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \quad \text{----- (3)}$$

According to Bohr's first postulate,

$$mvr = \frac{nh}{2\pi}$$

$$\therefore \boxed{v = \frac{nh}{2\pi mr}} \quad \text{----- (4)}$$

$$\text{or, } v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

Substituting this value of v^2 in eqs. (3)

$$\frac{m}{r} \left(\frac{n^2 h^2}{4\pi^2 m^2 r^2} \right) = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2}$$

$$\therefore r = \frac{n^2 h^2 \epsilon_0}{\pi Z e^2 m} \quad \text{----- (5)}$$

Thus, radius of the n^{th} permissible orbit,

$$\boxed{r_n = \frac{n^2 h^2 \epsilon_0}{\pi Z e^2 m}} \quad \text{----- (6)}$$

; $n = 1, 2, 3$ -----

where,

r_n = radius of the n^{th} orbit.

h = Planck's constant (6.62×10^{-34} J-sec)

ϵ_0 = Electric constant (8.85×10^{-12} F/m)

m = mass of the electron. (9.1×10^{-31} Kg)

$Z =$ Atomic number of the atom.

from eqs. (5) we find that

i.e; $r_n \propto n^2$; $n = 1, 2, 3, \dots$

The radii of the orbits are in the ratio of $1:4:9:16:25$ etc.

NOTE:

The radius of the first orbit for hydrogen atom -

For hydrogen atom $Z=1$, first orbit $n=1$

$$r_1 = \frac{h^2 \epsilon_0}{\pi e^2 m}$$

$$r_1 = \frac{(6.625 \times 10^{-34})^2 \times (8.854 \times 10^{-12})}{3.14 \times (1.6 \times 10^{-19})^2 (9.11 \times 10^{-31})} \text{ m}$$

$$r_1 = 0.053 \text{ nm}$$

This is called the Bohr radius.

$$\therefore r_1 = 0.053 \text{ nm}; r_2 = 2^2 r_1 \dots \dots \dots \text{ and } r_n = n^2 r_1$$

Now, from equations (4) and (5), we get -

$$v = \frac{nh}{2\pi m \left[\frac{n^2 h^2 \epsilon_0}{\pi m z e^2} \right]}$$

$$\therefore v = \frac{Ze^2}{2nh\epsilon_0}$$

Thus velocity of electron in the n^{th} permissible orbit,

$$v_n = \frac{Ze^2}{2nh\epsilon_0} \quad ; n = 1, 2, 3, \dots$$

i.e; $v_n \propto \frac{1}{n}$

Therefore speed of an electron in an orbit is inversely proportional to the principal quantum number.

- Calculation of Total Energy: [Energy of an e^- in an orbit]

The total energy of the electron in any orbit is the sum of its kinetic and potential energies. The potential energy of the electron is considered to be zero when it is at an infinite distance from the nucleus. Potential energy of an electron in an orbit is given by work done in bringing the electron from infinity to that orbit.

$\therefore$ Potential Energy of the electron,

$$= \int_{\infty}^{\infty} \frac{Ze^2}{4\pi\epsilon_0 r^2} dr$$

$$= \frac{ze^2}{4\pi\epsilon_0} \int_{\infty}^r \frac{1}{x^2} dx$$

$$= \frac{ze^2}{4\pi\epsilon_0} \left[-\frac{1}{x} \right]_{\infty}^r$$

$$= -\frac{ze^2}{4\pi\epsilon_0 r}$$

and Kinetic energy of the electron,

$$= \frac{1}{2} mv^2$$

Here, 'm' is the mass and 'v' is the velocity of the electron.

$$\text{As, } \frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{(ze)(e)}{r^2} \quad (\text{Centripetal Force})$$

where, r is the radius of the orbit.

$$\therefore mv^2 = \left[\frac{ze^2}{4\pi\epsilon_0 r} \right]$$

Therefore Kinetic energy of the electron,

$$= \frac{1}{2} \left[\frac{ze^2}{4\pi\epsilon_0 r} \right]$$

$$= \frac{ze^2}{8\pi\epsilon_0 r}$$

$\therefore$ Total energy of the electron in n^{th} orbit;

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

$$E_n = \frac{ze^2}{8\pi\epsilon_0 r} - \frac{ze^2}{4\pi\epsilon_0 r}$$

$$E_n = \frac{-ze^2}{8\pi\epsilon_0 r}$$

Since, $r = \frac{n^2 h^2 \epsilon_0}{\pi m z e^2}$

Thus,

$$E_n = \frac{-ze^2}{8\pi\epsilon_0 \left[\frac{n^2 h^2 \epsilon_0}{\pi m z e^2} \right]}$$

$$\therefore E_n = \frac{-m e^4 z^2}{8 \epsilon_0^2 n^2 h^2}$$

i.e; $E_n \propto -\frac{1}{n^2}$

As the values of n increases E_n increases.
Hence, the outer orbits have greater energies than the inner orbits.

NOTE:

The total energy of the electron in an orbit is negative. Negative energy tells us that electron and nucleus form a bound system. In other words, the electron can be taken away from the nucleus if energy is supplied to it.

- Bohr's Interpretation of the Hydrogen Spectrum

According to Bohr's Postulate, energy is radiated only if an electron jumps from higher energy orbit ' n_i ' to lower energy orbit ' n_f ', where $n_i > n_f$.

The energy of the emitted radiation is given by

$$E_{n_i} - E_{n_f} = h\nu$$

Therefore,

$$\nu = \frac{E_{n_i} - E_{n_f}}{h}$$

$$\left\{ \begin{array}{l} \text{As, } E_n = \frac{-me^4 z^2}{8\epsilon_0^2 n^2 h^2} \\ \text{For Hydrogen atom} \\ z = 1 \end{array} \right.$$

Since,

$$E_{n_i} = \frac{-me^4 z^2}{8\epsilon_0^2 n_i^2 h^2}$$

$$\text{and } E_{n_f} = \frac{-me^4 z^2}{8\epsilon_0^2 n_f^2 h^2}$$

Then,

$$\bar{\nu} = \frac{me^4 z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{h} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

The wave number of radiation emitted is,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Therefore,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{me^4 z^2}{8\epsilon_0^2 ch^3} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

The quantity $\frac{me^4}{8\epsilon_0^2 ch^3} = R$ and is known as

'Rydberg constant'.

Therefore, wavenumber of radiation emitted,

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

For Hydrogen atom $Z=1$

$$\therefore \bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

Here, $R = 1.097 \times 10^7 \text{ m}^{-1}$

• Spectral Series of Hydrogen Atom:

When an electron jumps from higher energy state (orbit) to the lower energy state (orbit), the radiation of a particular wavelength or frequency is emitted. This radiation is called Spectral line.

The wavelength of the Spectral line depends upon the energies between two energy states in which the transition of electron takes place.

The spectral lines arising from the transition of electron from the higher energy states to a particular lower energy state form a Spectral Series.

i). Lyman Series:

The spectral lines emitted due to the transition of an electron from any outer orbit ($n_i = 2, 3, 4, \dots, \infty$) to the first orbit ($n_f = 1$) form a spectral series known as Lyman Series.

The wavelengths of the spectral lines forming a Lyman series are given by-

$$\frac{1}{\lambda} = R \left[\frac{1}{1^2} - \frac{1}{n_i^2} \right] \quad \text{where } n_i = 2, 3, 4, \dots, \infty$$

This series lie in the ultraviolet region ($1000\text{\AA} - 4000\text{\AA}$) of the electromagnetic spectrum.

ii) Balmer Series:

The spectral lines emitted due to the transition of an electron from any outer orbit ($n_i = 3, 4, 5, \dots, \infty$) to the second orbit ($n_f = 2$) form a spectral series known as Balmer Series.

The wavelengths of the spectral lines forming Balmer series are given by-

$$\frac{1}{\lambda} = \frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n_i^2} \right] \quad \text{where, } n_i = 3, 4, 5, \dots, \infty$$

The series lies in the visible region ($4000\text{\AA} - 7000\text{\AA}$) of the electromagnetic spectrum. The first line in the series ($n_i = 3 \rightarrow n_f = 2$) is called 'H_α-line', the second line in the series ($n_i = 4 \rightarrow n_f = 2$) is called 'H_β-line', the third line is called 'H_γ-line' and so on.

iii) Paschen Series:

The spectral lines emitted due to the transition of an electron from any

outer ($n_i = 4, 5, \dots, \infty$) to the third orbit ($n_f = 3$) form a spectral series known as Paschen Series.

The wavelengths of the spectral lines forming Paschen series are given by—

$$\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{3^2} - \frac{1}{n_i^2} \right] \quad \text{where } n_i = 4, 5, 6, \dots, \infty$$

This series lies in the Infrared region ($7000\text{\AA} - 10^7\text{\AA}$) of the electromagnetic spectrum.

iv). Brackett Series:

If $n_f = 4$ and $n_i = 5, 6, 7, \dots, \infty$, we get the Brackett Series.

$$\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{4^2} - \frac{1}{n_i^2} \right] \quad \text{where } n_i = 5, 6, 7, \dots, \infty$$

This series lies in the Infra-red region ($7000\text{\AA} - 10^7\text{\AA}$) of the electromagnetic spectrum.

NOTE: By putting $n_i = \infty$ (i - initial state) in each ^{one} of the series, we get the wave number ($\bar{\nu}$) or wavelength (λ) of the series.

limit, i.e; the last line of the series

- The Energy - level diagram:

The equation -

$$E_n = \frac{-me^4 z^2}{32 \pi^2 \epsilon_0^2 \hbar^2 n^2}$$

$$E_n = \frac{-me^4 z^2}{32 \pi^2 \epsilon_0^2 n^2 \left(\frac{h}{2\pi}\right)^2} \quad \left\{ \because \hbar = \frac{h}{2\pi} \right.$$

$E_n = \frac{-me^4 z^2}{8 \epsilon_0^2 \hbar^2 n^2}$
--

can be diagrammatically represented. Then, it is called energy - level diagram.

Substituting the values of m , e , ϵ_0 and h we get for hydrogen ($z=1$)

$$\frac{me^4 z^2}{8 \epsilon_0^2 \hbar^2} = \frac{(9.1 \times 10^{-31}) \times (1.6 \times 10^{-19})^4 \times (1)^2}{8 \times (8.85 \times 10^{-12})^2 \times (6.62 \times 10^{-34})^2}$$

$$= 21.76 \times 10^{-19} \text{ Joule}$$

$$= \frac{21.76 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

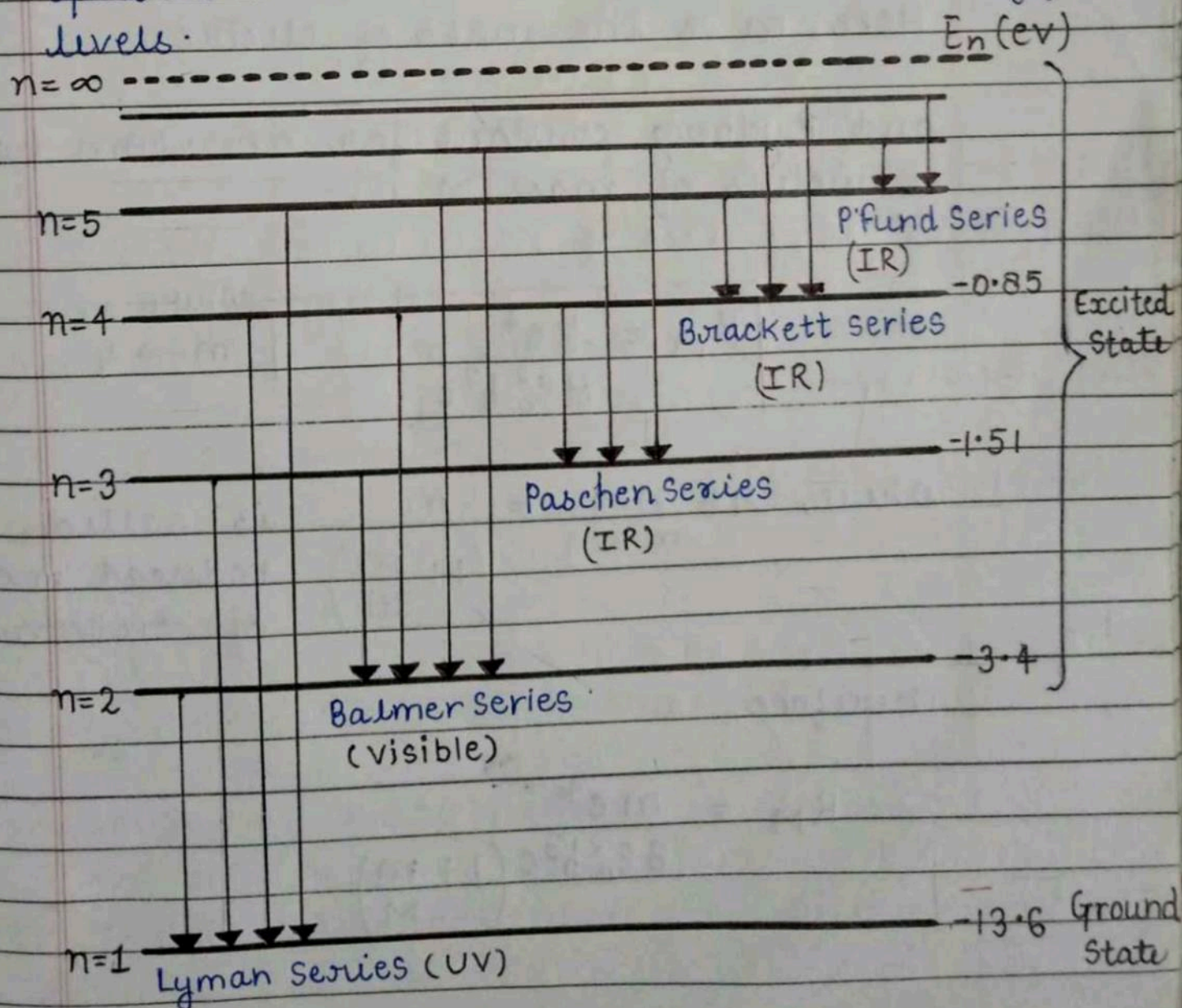
$$= 13.6 \text{ eV}$$

$$\therefore E_n = (-13.6/n^2) \text{ eV}$$

for $n=1, 2, 3, \dots$

The lowest energy level ' E_1 ' is called the normal or the ground state of the atom and the higher energy levels $E_2, E_3, E_4, \dots$ are called the excited states. As n increases, E_n increases.

In this energy-level diagram, the discrete energy states are represented by horizontal lines, and the electronic jumps between states by vertical lines. Figure shows schematically how spectral lines are related to atomic energy levels.



• Variation in Rydberg Constant due to finite Nuclear mass-

The finite nuclear mass causes a slight variation in the Rydberg constant from atom to atom. The Rydberg constant for an atom having an infinitely heavy nucleus is,

$$R_{\infty} = \frac{m e^4}{8 \epsilon_0^2 h^3 c}$$

Here, m is the mass of electron.

and Rydberg constant for an atom having a nucleus of mass ' M ' is,

$$R_M = \frac{\mu e^4}{8 \epsilon_0^2 h^3 c}$$

where
 $\left\{ \begin{array}{l} m \rightarrow \mu \end{array} \right.$

where, $\mu = \frac{mM}{m+M} = \frac{m}{\left(1 + \frac{m}{M}\right)}$ is called reduced mass of electron.

Therefore,

$$R_M = \frac{m e^4}{8 \epsilon_0^2 h^3 c \left(1 + \frac{m}{M}\right)}$$

$$\therefore R_M = R_\infty \left(\frac{1+m}{M} \right)$$

Thus ' R_M ' is less than R_∞ by a factor $\frac{1}{\left(\frac{1+m}{M} \right)}$ and is different for different atoms, depending upon their nuclear masses.

• NOTE :

(1). The Rydberg constant for Hydrogen (${}_1H^1$) is,

$$R_H = \frac{R_\infty}{1 + \frac{m}{M_H}}$$

for Hydrogen $\frac{m}{M_H} = \frac{1}{1836}$

and $R_\infty = 1.09737 \times 10^7 \text{ m}^{-1}$

$$\frac{m (\text{mass of } e^-)}{M_H (\text{mass of proton})}$$

$$= \frac{9.1 \times 10^{-31}}{1.67 \times 10^{-27}} = \frac{1}{1836}$$

$$\therefore M_H = m \times 1836$$

$$\therefore R_H = \frac{1.09737 \times 10^7}{\left(1 + \frac{1}{1836} \right)}$$

$$R_H = 1.09677 \times 10^7 \text{ m}^{-1}$$

(2). The Rydberg constant for deuterium (${}_1H^2$)

is,

$$R_D = \frac{R_\infty}{\left(1 + \frac{m}{M_D}\right)}$$

$$R_D = \frac{R_\infty}{\left(1 + \frac{m}{2M_H}\right)}$$

Since,

mass of deuterium (${}_1H^2$) nucleus is 2 times the mass of a hydrogen (${}_1H^1$) nucleus, i.e.,

$$M_D = 2M_H$$

(iii). The Rydberg constant for Tritium (${}_1H^3$) is,

$$R_T = \frac{R_\infty}{\left(1 + \frac{m}{M_T}\right)}$$

$\therefore M_T$ (Mass of Tritium nucleus, ${}_1H^3$)

= 3 times mass of Hydrogen nucleus (${}_1H^1$)

$$\therefore M_T = 3M_H$$

$$\therefore R_T = \frac{R_\infty}{\left(1 + \frac{m}{3M_H}\right)}$$

NUMERICALS

- (1). The series limit wavelength of the Balmer series in hydrogen spectrum is $3646 \text{ \AA}$. Calculate Rydberg constant for Hydrogen atom.

Solution - Given -

$$\lambda = 3646 \text{ \AA} = 3646 \times 10^{-10} \text{ m}$$

The wavelength of the lines of Balmer series are given by -

$$\frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{n_i^2} \right] \quad ; n_i = 3, 4, 5, \dots, \infty$$

For the series limit, $n_i = \infty$

Therefore,

$$\frac{1}{\lambda_{\infty}} = R_H \left[\frac{1}{2^2} - \frac{1}{\infty^2} \right]$$

$$\frac{1}{\lambda_{\infty}} = R_H \left[\frac{1}{4} \right]$$

$$\frac{1}{3646 \times 10^{-10} \text{ m}} = \frac{R_H}{4}$$

$$\text{or, } R_H = \frac{4}{3646 \times 10^{-10} \text{ m}}$$

$$R_H = 1.097 \times 10^7 \text{ m}^{-1}$$

Ans

(2). Calculate the wavelength of the eight line of the Balmer series of hydrogen atom. Given: $R_\infty = 1.09737 \times 10^7 \text{ m}^{-1}$.

Solution

Given-

$$R_\infty = 1.09737 \times 10^7 \text{ m}^{-1}$$

The wavelength of the lines of Balmer series are given by -

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right) ; n_i = 3, 4, 5, 6, 7, 8, 9, 10 \dots$$

for the eight line, ($n_i = 10 \rightarrow n_f = 2$)

$$\therefore \frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{10^2} \right]$$

$$\frac{1}{\lambda} = R_H \left[\frac{1}{4} - \frac{1}{100} \right]$$

$$\frac{1}{\lambda} = R_H \left[\frac{100 - 4}{400} \right]$$

$$\frac{1}{\lambda} = R_H \left[\frac{96}{400} \right]$$

$$\frac{1}{\lambda} = \frac{6}{25} R_H$$

$$\text{or, } \lambda = \frac{25}{6 R_H} \quad \text{--- (1)}$$

Now, the Rydberg constant for Hydrogen is,

$$R_H = \frac{R_\infty}{1 + \frac{m}{M_H}}$$

where,

R_∞ = Rydberg constant
for infinitely
heavy nucleus.

m = mass of electron.

M_H = mass of
proton

We know that, $\frac{m}{M_H} = \frac{1}{1836}$

$$\therefore R_H = \frac{1.09737 \times 10^7 \text{ m}^{-1}}{\left(1 + \frac{1}{1836}\right)}$$

$$R_H = 1.09677 \times 10^7 \text{ m}^{-1}$$

Hence, from equ. (1) we have

$$\lambda = \frac{25}{6 \times (1.09677 \times 10^7 \text{ m}^{-1})}$$

$$\lambda = 3.799 \times 10^{-7} \text{ m}$$

$$\lambda = 3799 \text{ \AA}$$

Ans

- (3). The wavelength of the first line of the Lyman series of hydrogen is $1215 \text{ \AA}$. Calculate the wavelength of the second line of the series, and the series limit.

Solution- Given -

The wavelength of the first line of the Lyman series of hydrogen (λ_1) = $1215 \text{ \AA}$

Now, the wavelength of the lines of the Lyman series of hydrogen atom are given by -

$$\frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{n_i^2} \right] ; n_i = 2, 3, 4, \dots \infty$$

For the first line of Lyman series, $n_i = 2$

$$\therefore \frac{1}{\lambda_1} = R_H \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\frac{1}{1215 \text{ \AA}} = R_H \left[\frac{1}{1} - \frac{1}{4} \right]$$

$$\frac{1}{1215 \text{ \AA}} = R_H \left[\frac{3}{4} \right]$$

$$\text{or, } R_H = \frac{4}{3 \times (1215 \text{ \AA})}$$

For the second line of Lyman series $n_i = 3$

$$\therefore \frac{1}{\lambda_2} = R_H \left[\frac{1}{1^2} - \frac{1}{3^2} \right]$$

$$\frac{1}{\lambda_2} = \frac{4}{3 \times (1215 \text{ Å}^{\circ})} \left[\frac{1}{1} - \frac{1}{9} \right]$$

$$\frac{1}{\lambda_2} = \frac{4}{3 \times (1215 \text{ Å}^{\circ})} \left[\frac{8}{9} \right]$$

$$\text{or, } \lambda_2 = \frac{3 \times (1215 \text{ Å}^{\circ}) \times 9}{8 \times 4}$$

$$\lambda_2 = 1025 \text{ Å}^{\circ}$$

Ans

For the series limit, $n_i = \infty$

$$\therefore \frac{1}{\lambda_{\infty}} = R_H \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right]$$

$$\frac{1}{\lambda_{\infty}} = R_H$$

$$\text{or, } \lambda_{\infty} = \frac{1}{R_H}$$

$$\lambda_{\infty} = \frac{3 \times (1215 \text{ Å}^{\circ})}{4}$$

$$\lambda_{\infty} = 911 \text{ Å}^{\circ}$$

Ans

(4). Calculate ratio of wavelengths for first

Spectral line in Balmer series for tritium (${}_1\text{H}^3$) and protium (${}_1\text{H}^1$).
(Given that: Mass of protium = $1836 \times$ mass of electron)

Solution

The wavelength of the spectral line of Balmer series are given by the formula-

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n_i^2} \right] ; n_i = 3, 4, 5, \dots, \infty$$

for the first line of Balmer series, ($n_i = 3$)

for tritium -

$$\frac{1}{\lambda_T} = R_T \left[\frac{1}{2^2} - \frac{1}{3^2} \right]$$

$$\frac{1}{\lambda_T} = R_T \left[\frac{1}{4} - \frac{1}{9} \right]$$

$$\frac{1}{\lambda_T} = R_T \left[\frac{9-4}{36} \right]$$

$$\frac{1}{\lambda_T} = R_T \left[\frac{5}{36} \right]$$

$$\frac{1}{\lambda_T} = \frac{5}{36} R_T \quad \text{--- (1)}$$

for Protium -

$$\frac{1}{\lambda_H} = R_H \left[\frac{1}{2^2} - \frac{1}{3^2} \right]$$

$$\frac{1}{\lambda_H} = R_H \left[\frac{1}{4} - \frac{1}{9} \right]$$

$$\frac{1}{\lambda_H} = \frac{5R_H}{36}$$

(2)

Dividing equation (2) by (1), we get,

$$\frac{1/\lambda_H}{1/\lambda_T} = \frac{R_H}{R_T}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{R_H}{R_T}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{R_\infty}{\left(1 + \frac{m}{M_H}\right)} \div \frac{R_\infty}{\left(1 + \frac{m}{M_T}\right)}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{\left(1 + \frac{m}{M_T}\right)}{\left(1 + \frac{m}{M_H}\right)}$$

Given:

Mass of protonium
= 1836 x mass of e^-

$$\frac{m}{M_H} = \frac{1}{1836}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{\left(1 + \frac{m}{3M_H}\right)}{\left(1 + \frac{m}{M_H}\right)}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{\left(1 + \frac{1}{3 \times 1836}\right)}{\left(1 + \frac{1}{1836}\right)}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{\left(1 + \frac{1}{5508}\right)}{\left(1 + \frac{1}{1836}\right)}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{5509}{5508} \times \frac{1836}{1837}$$

$$\frac{\lambda_T}{\lambda_H} = \frac{0.99963}{1}$$

$$\lambda_T : \lambda_H = 0.99963 : 1$$

Ans

AS-5

(5). Find out the ratio of limiting wavelength of Balmer series for Hydrogen atom with maximum wavelength of Lyman series.

Solution- Longest wavelength of the spectral line

of Lyman series is emitted when the transition of electron takes place from $(n_i=2 \rightarrow n_f=1)$, i.e., the first line of Lyman series.

$$\frac{1}{\lambda_{\max}} = R_H \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\frac{1}{\lambda_{\max}} = R_H \left[\frac{1}{1} - \frac{1}{4} \right]$$

$$\frac{1}{\lambda_{\max}} = R_H \left[\frac{4-1}{4} \right]$$

$$\frac{1}{\lambda_{\max}} = \frac{3R_H}{4}$$

limiting value means series limit, i.e., $(n_i=\infty \rightarrow n_f=2)$ for Balmer series,

$$\frac{1}{\lambda_{\text{limiting}}} = R_H \left[\frac{1}{2^2} - \frac{1}{\infty^2} \right]$$

$$\frac{1}{\lambda_{\text{limiting}}} = R_H \left[\frac{1}{4} \right]$$

$$\frac{1}{\lambda_{\text{limiting}}} = \frac{R_H}{4}$$

$$\therefore \frac{[\lambda_{\text{limiting}}]_B}{[\lambda_{\max}]_L} = \frac{[1/\lambda_{\max}]_L}{[1/\lambda_{\text{limiting}}]_B}$$

$$\frac{[\lambda_{\text{limiting}}]_B}{[\lambda_{\text{max}}]_L} = \frac{\frac{3}{4} R_H}{\frac{R_H}{4}}$$

$$\frac{[\lambda_{\text{limiting}}]_B}{[\lambda_{\text{max}}]_L} = \frac{3 R_H \times 4}{4 R_H}$$

$$\frac{[\lambda_{\text{limiting}}]_B}{[\lambda_{\text{max}}]_L} = \frac{3}{1}$$

$$[\lambda_{\text{limiting}}]_B : [\lambda_{\text{max}}]_L = 3 : 1$$

Ans

(6). The ground state energy of an electron in the H-atom is -13.6 eV . Calculate the energy of -

- (i). $n=3$ state for He^+
- (ii). $n=2$ state for Li^{++}

Solution- The energy of an electron in any orbit is,

$$E_n = -\frac{m z^2 e^4}{8 n^2 h^2 \epsilon_0^2} \text{ Joule}$$

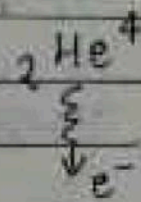
$$\therefore E_n = -\frac{13.6 \text{ eV } z^2}{n^2}$$

- (i). $n=3$ state for He^+

Since $\lambda = 2$

and $n=3$

$$\therefore E_n = -13.6 \times \frac{4}{9} \text{ eV}$$



$$E_3 = -6.04 \text{ eV}$$

APRIL

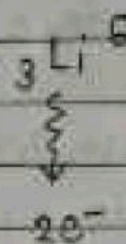
iii)

$n=2$ state for Li^{++}

Since $z = 3$

and $n = 2$

$$\therefore E_p = \frac{-13.6 \times 9}{4} \text{ eV}$$



$$E_2 = -30.4 \text{ eV}$$

Aug.

Hence,

(i) Energy, $n=3$ state for He^+

$$E_n = -6.04 \text{ eV}$$

(ii) Energy, $n=2$ state for Li^{++}

$$E_n = -30.4 \text{ eV}$$

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(156)

(7). Show that the speed of electron in the first hydrogen orbit is $c/137$, where c is the speed of light.

$$\text{Given } \frac{1}{4\pi\epsilon_0} = 9.0 \times 10^9 \text{ Nm}^2/\text{C}^2$$

$$e = 1.6 \times 10^{-19} \text{ coulomb and}$$

$$h = 6.63 \times 10^{-34} \text{ joule-sec}$$

Solution- Let ' v ' be the speed of the electron in the n^{th} orbit of radius r . The charge on hydrogen nucleus is $+e$. As the centripetal force provided by electrostatic attraction

we have,

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad \text{----- (1)}$$

{ $\because$ For Hydrogen atom, $z=1$ }

According to Bohr's first postulate -

$$mvr = \frac{nh}{2\pi}$$

$$\therefore mvr = \frac{h}{2\pi} \quad \text{----- (2)} \quad \left\{ \because \text{For first orbit, } n=1 \right.$$

Dividing eqs (1) by (2) we get

$$v = \frac{1}{4\pi\epsilon_0} \frac{2\pi e^2}{h}$$

$$v = \frac{e^2}{2\epsilon_0 h}$$

$$v = \frac{(1.6 \times 10^{-19})^2}{2 \times 8.85 \times 10^{-12} \times 6.6 \times 10^{-34}}$$

$$v = \frac{2.56 \times 10^{-38}}{116.8 \times 10^{-46}}$$

$$v = 2.18 \times 10^6 \text{ m/sec}$$

we know that,

$$\text{speed of light } (c) = 3 \times 10^8 \text{ m/sec}$$

$$\therefore \frac{v}{c} = \frac{2.18 \times 10^6}{3 \times 10^8}$$

$$\frac{v}{c} = \frac{1}{137}$$

$$v = \frac{c}{137}$$

Hence, the speed of electron (v) in the first hydrogen orbit is $c/137$.

• Drawbacks of Bohr's Atomic Model :

Bohr's atomic model has the following limitations:

- 1). It successfully explains the spectra of simple atoms (i.e; the atoms having only one electron).

For example, it can explain the spectra of hydrogen atom and hydrogen like atoms (He^+ , Li^{++} etc).

But, this model could not explain the spectra of complex atoms having more than one electron.

- 2). When the spectral lines of Balmer series was observed under a powerful microscope. It was found that each spectral line consists of closely spaced lines. Bohr's model of atom could not explained this fine structure of the spectral line of Balmer series.
- 3). Bohr's atomic model does not give any indication regarding the arrangement and distribution of electrons in an atom.
- 4). This model could not account for the wave nature of electrons.

- 5). This model could not explain the splitting of spectral line into a number of spectral lines under the effect of magnetic field (Zeeman effect).

X-Rays

- X-Ray Spectra :

When fast moving electrons strike a target of high melting point and high atomic weight (tungsten, platinum etc), X-rays are produced. X-rays discovered by 'Roentgen' therefore, they are also known as 'Roentgen rays'.

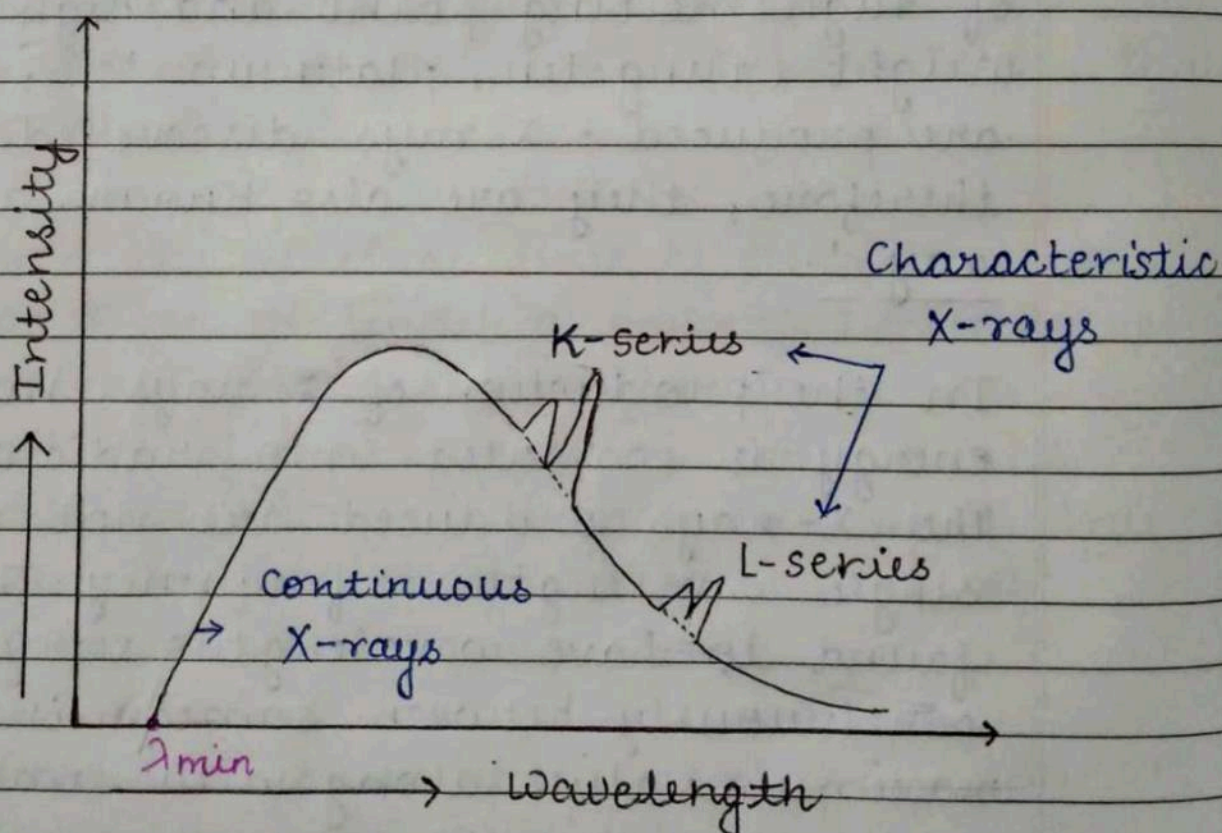
In the production of X-rays, mechanical energy is converted into radiant energy. The X-rays produced are not of a single wavelength or frequency. They are found to have wavelengths varying continuously between some minimum and maximum values along with some well defined wavelengths.

The intensity of the different wavelengths of the X-rays is found to be different as shown. It is called 'X-ray spectrum'. The X-ray spectrum consists of the following two distinct parts:

- (i). Continuous X-ray spectrum and
(ii). Characteristic (or line) X-ray spectrum.

(i). Continuous X-ray Spectrum:

It consists of radiations of all possible wavelengths within a certain wavelength range, starting from a minimum wavelength ' $\lambda_{\min}$ ' called the 'short wavelength limit'.



This limit is independent of the material of the target and depends on the voltage applied across the X-ray tube.

- Origin of Continuous X-rays Spectrum:

When high energetic electrons strike the target, they are deflected by the strong fields of force of the nuclei of the target atoms and get decelerated.

According to classical theory, an accelerated or decelerated charge radiates energy. Here the electrons are decelerated, hence they emit pulses of electromagnetic radiation of energy $h\nu$. Since the electrons suffer collision at all angles, they suffer varying deceleration. The nucleus, the greater is the loss in the energy of the electron. Due to different losses in the energy of the incident electrons, radiations of all possible wavelengths within a certain range are emitted which constitute Continuous X-ray Spectrum.

- Short Wavelength limit of Continuous X-rays and accelerating Potential:

Let an incident electron moving with velocity v be slowed down to velocity v' due to deceleration with nucleus in X-ray tube, then the frequency ' ν ' of emitted photon is given by -

$$\frac{1}{2}mv^2 - \frac{1}{2}mv'^2 = h\nu$$

If the incident electron is completely stopped, during a collision with the nucleus, i.e., $v' = 0$,

the emitted radiation has maximum frequency or minimum wavelength, called the short wavelength limit.

$$\text{i.e.; } \frac{1}{2} mv^2 = h\nu_{\max} \text{ ----- (1) } \left\{ \because v' = 0 \right.$$

If 'V' is the accelerating potential applied to a X-ray tube, then an electron of charge e emitted from the cathode, will gain kinetic energy eV.

$$\text{i.e.; } \frac{1}{2} mv^2 = eV \text{ ----- (2)}$$

If the electron loses all its Kinetic energy then it produces photon of maximum frequency $\nu_{\max}$ given by-

$$eV = h\nu_{\max} \quad \left\{ \text{from eqs. (1) and (2)} \right.$$

$$\nu_{\max} = \frac{eV}{h} \text{ ----- (3)}$$

If $\lambda_{\min}$ is the minimum wavelength corresponding to the maximum frequency then

$$\nu_{\max} = \frac{c}{\lambda_{\min}} \quad \left\{ c = \text{speed of light} \right.$$

Therefore,

$$\frac{c}{\lambda_{\min}} = \frac{ev}{h}$$

$$\lambda_{\min} = \frac{hc}{ev}$$

This relation gives the 'Short wavelength limit' of continuous X-ray spectrum.

Substituting,

$$h = 6.62 \times 10^{-34} \text{ J-sec (Planck's constant)}$$

$$c = 3 \times 10^8 \text{ m/sec (speed of light)}$$

$$\text{and } e = 1.6 \times 10^{-19} \text{ coulomb (charge of the electron)}$$

we get,

$$\lambda_{\min} = \frac{hc}{ev}$$

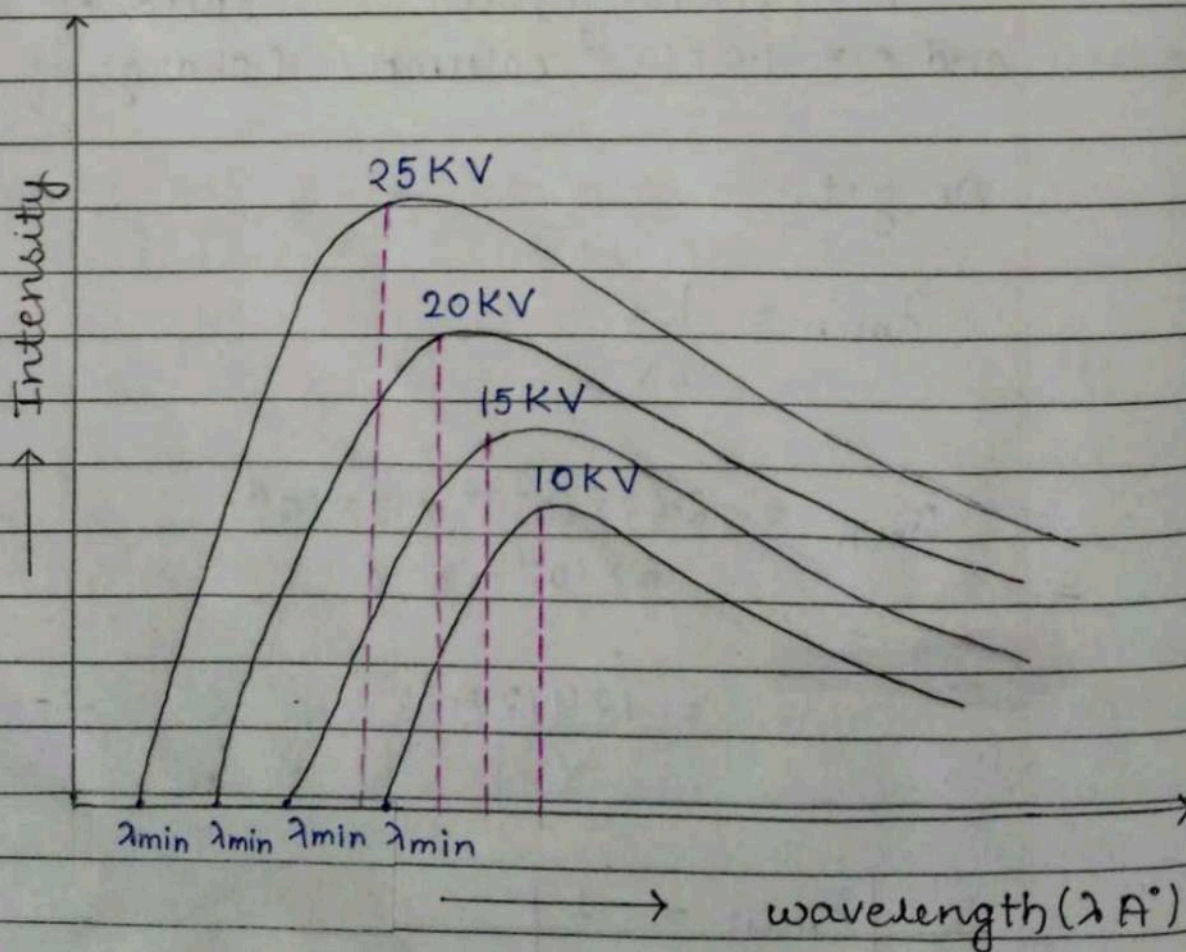
$$\lambda_{\min} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{1.6 \times 10^{-19} \times V}$$

$$\therefore, \lambda_{\min} = \frac{12412 \text{ \AA}}{V}$$

$$\therefore \lambda_{\min} \propto \frac{1}{V}$$

Thus, short wavelength limit ' $\lambda_{\min}$ ' is inversely proportional to potential difference ' V ' between cathode and target (anode) of the X-ray tube.

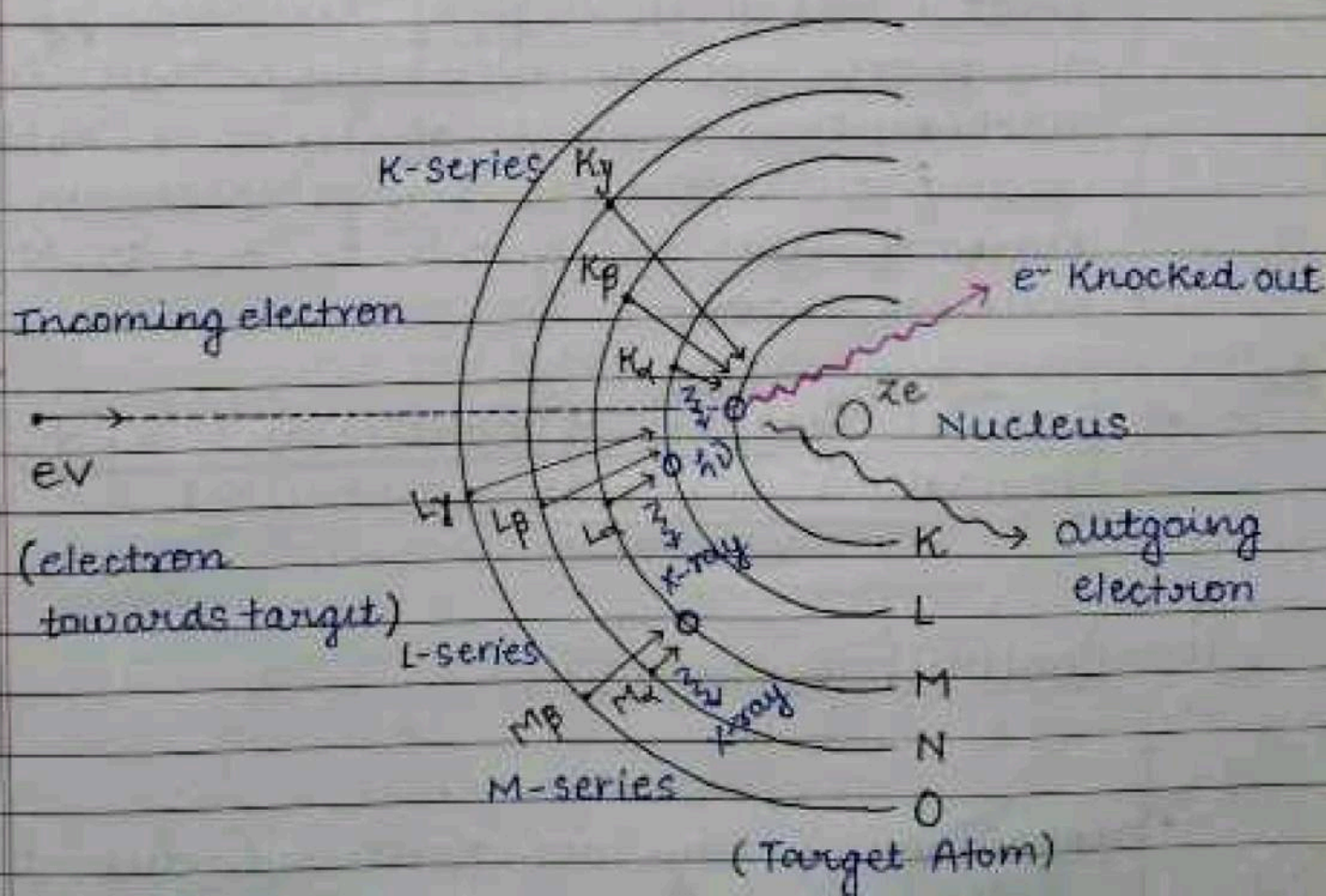
This relation is known as Duane and Hunt's Law. This relation was verified experimentally by Duane and Hunt who plotted the intensity with wavelength in continuous X-ray spectrum at different accelerating voltage applied to the X-ray tube. The experimental curves show that the short wavelengths limit of continuous X-ray spectrum varies inversely as the accelerating voltage across the tube.



(ii) Characteristic (or line) X-rays Spectrum:

It consists of few peaks superimposed on the continuous X-ray spectrum, indicating the enhanced production of X-rays. The positions of these peaks depends only on the material of the target. They occur in groups known as K, L, M----- series. The group of lines nearest to the shortwavelength region is called K-series, the next groups in the direction of increasing wavelength are called L-series, M series----- respectively. These series are characteristic of material and hence known as Characteristic X-ray spectrum.

• Origin of Characteristic X-rays spectrum:



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Sometimes it happens that the incident high energetic electron penetrate through the outer shells of the target atom and strike with an electron in inner shell. The collision is so strong that an electron from inner shell is knocked out. Thus a vacancy is created and to fill it an electron from higher energy state jumps into this vacancy. The energy difference between the energy states is emitted as X-rays photon of energy $\Delta E = h\nu$. This process further creates a vacancy in higher state which is again filled up by an other electron jumping from next higher state.

In this way another photon of X-ray is emitted out with slightly less energy. This process goes on till highest shell is reached. Thus a series of lines is obtained giving characteristic X-rays spectrum. The series of lines are known as K, L, M, N ----- series as shown.

ps-3

- Salient features of Continuous and Characteristic X-ray spectrum:

(i). Continuous Spectrum:

- Continuous X-rays are produced due to

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Slowing down of energetic electrons while passing near a positively charged nucleus.

- Continuous X-rays spectrum has a sharply defined minimum wavelength given by following relation,

$$\lambda_{\min} = \frac{hc}{eV}$$

- The value of ' $\lambda_{\min}$ ' depends upon the potential difference between the cathode and target of X-ray tube and is independent of the nature of the target material.
- The maximum intensity position (Peak) of Continuous X-rays shift towards short wavelength side as potential differences increases.

(ii) Characteristic or line Spectrum:

- Characteristic (or line) spectrum is produced when high velocity electrons completely knock out the inner most electrons, i.e., electrons from K, L, M----- shells.
- line spectrum consists of discrete spectral lines which forms, K-series, L-series, M-series etc.

- The line spectrum is the characteristic of the target material as the distribution of electrons in different shells and their binding with nucleus is different in all materials.
- The number of lines presents in the spectrum of a material depends upon the nature of target and the energy of the bombarded electrons (i.e; the potential difference).

• Mosley's Law:

Mosley plotted the square roots of frequencies of a given line (say K_{α} and K_{β}) against the atomic number 'Z' of the elements emitting that spectral lines. Mosley obtained a straight line and conclude that -

"The square root of the frequency ($\sqrt{\nu}$) of a spectral line in an X-ray spectrum is proportional to the atomic number of element emitting it." This result is known as Mosley's Law.

i.e;

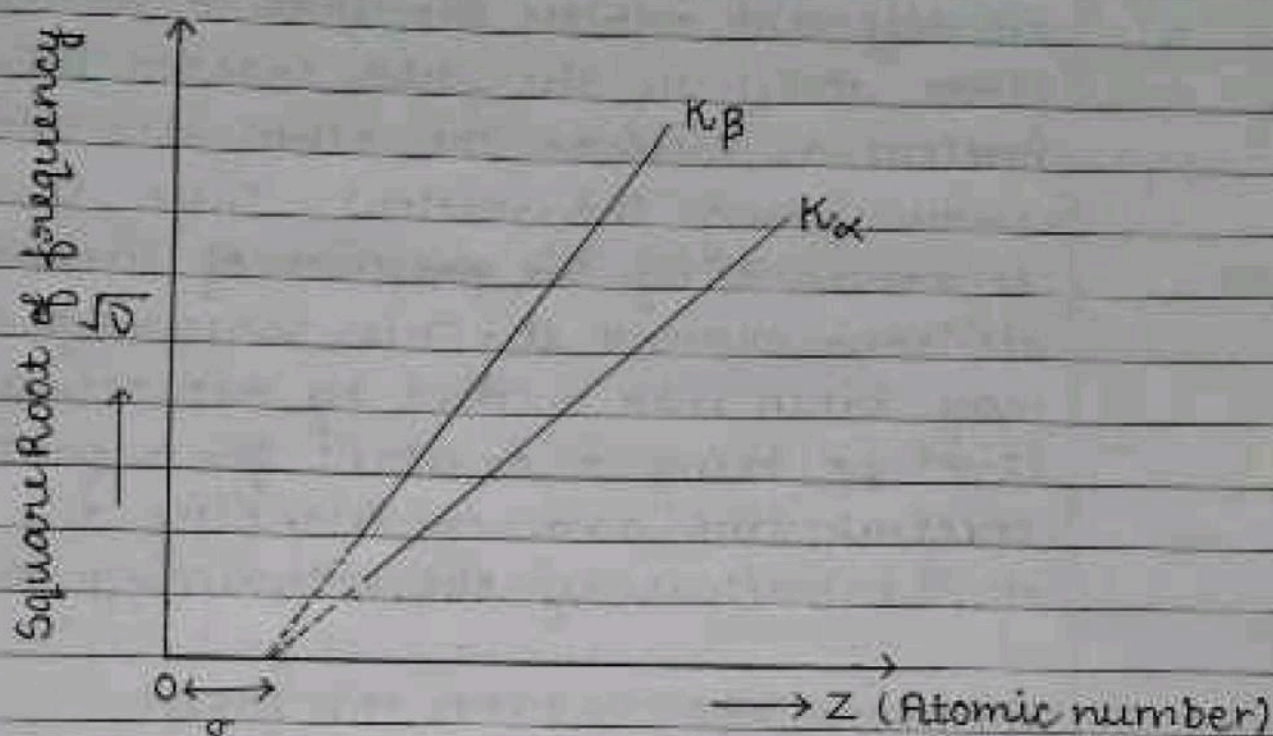
$$\sqrt{\nu} \propto Z$$

or,

$$\sqrt{\nu} = a(Z - \sigma) \quad \text{----- (1)}$$

where 'a' and ' σ ' are constants for a given
(Note) σ = Screening or shielding factor

transition (i.e; spectral line) and 'Z' is the atomic number of the element of the target



The graph is known as 'Moseley diagram'.

Proof:

According to Bohr's theory, the frequency of a spectral line for transition from state of higher energy ' n_i ' to the state of lower energy ' n_f ' is given by-

$$\frac{1}{\lambda} = \frac{\nu}{c} = RZ^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

$$\therefore \nu = RZ^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{ ----- (2)}$$

Here, R is Rydberg constant.

Now in heavier atoms electrons are situated in different orbits, therefore a certain electron finds itself in the field created by the nucleus as well as the other electrons surrounding the nucleus. Thus the nucleus is screened by the presence of remaining electrons around it. This screening effect may be taken into account by replacing Z with $(Z - \sigma)$, σ being a constant for a particular spectral line and representing the shielding of the nucleus by the remaining electrons.

Therefore, eqs. (3) takes the form

$$\nu = Rc(Z - \sigma)^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

$$\text{or, } \nu = a^2 (Z - \sigma)^2$$

$$\text{where, } a^2 = Rc \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

$$\therefore \boxed{\sqrt{\nu} = a(Z - \sigma)}$$

This is Mosley's law.

• Importance of Mosley's Law:

- 1) Before discovery of Mosley's law elements in periodic table were arranged according to their atomic weight but Mosley established that it is the atomic number which determines the physical and chemical properties of an element, hence they must be arranged according to their atomic number in the periodic table.
- 2) This law also helped in discovering new elements like rhenium, hafnium, illinium etc and fixing their position in periodic table.
- 3) This law also corrected the positions of many elements like cobalt, argon and tellurium in the periodic table according to their atomic numbers.

• Properties of X-Rays:

- (1) X-rays are not deflected by electric and magnetic fields which shows that they do not consist of charged particles.
- (2) They are electromagnetic radiations of very short wavelength ($\approx 1 \text{ \AA}$).
- (3) They affect photographic plate like light, but the effect is much more intense than light.

- (4). They travel in straight lines with the velocity of light i.e; $3 \times 10^8 \text{ m/sec}$.
- (5). They produce fluorescence in several materials like barium-platino cyanide, zinc sulphide and cadmium tungstate.
- (6). X-rays ionize the gas through which they pass.
- (7). X-rays are highly penetrating and can pass through many solids (e.g., wood, flesh etc.) which are opaque to ordinary light.
- (8). They produce photoelectric effect and thus exhibit a corpuscular nature also.
- (9). They show interference, diffraction and polarization similar to light rays.

Numericals

- (1). The minimum wavelength of X-ray produced by X-ray tube is $0.25 \text{ \AA}$. At what voltage, it is working?

Solution

Given -

$$\begin{aligned} \text{minimum wavelength of X-ray } (\lambda_{\min}) &= 0.25 \text{ \AA} \\ &= 0.25 \times 10^{-10} \text{ m} \end{aligned}$$

Planck's constant (h) = 6.62×10^{-34} J-sec

speed of light (c) = 3×10^8 m/sec

charge of electron (e) = 1.6×10^{-19} coulomb

According to Duane and Hunt's law, short wavelength limit is,

$$\lambda_{\min} = \frac{hc}{eV}$$

$$\therefore V = \frac{hc}{e\lambda_{\min}}$$

$$V = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{1.6 \times 10^{-19} \times 0.25 \times 10^{-10}}$$

$$V = \frac{19.86 \times 10^{-26}}{4 \times 10^{-30}}$$

$$V = 4.95 \times 10^4 \text{ volt}$$

$$V = 49.5 \text{ KV}$$

Ans

(2) An X-ray machine uses accelerating potential of 50000 volts. Calculate the shortest wavelength present in X-ray produced.

(Given $h = 6.62 \times 10^{-34}$ J-sec, $c = 3 \times 10^8$ m/sec)

Solution - Given -

$$V = 50000 \text{ volts}$$

planck's constant (h) = 6.62×10^{-34} J-sec
 speed of Light (c) = 3×10^8 m/sec
 charge of electron(e) = 1.6×10^{-19} columb

According to Duane and Hunt's law, short wavelength limit is,

$$\lambda_{\min} = \frac{hc}{eV}$$

$$\lambda_{\min} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{1.6 \times 10^{-19} \times 50000}$$

$$\lambda_{\min} = \frac{19.86 \times 10^{-26}}{80 \times 10^{-16}}$$

$$\lambda_{\min} = 0.248 \times 10^{-10} \text{ meter}$$

$$\lambda_{\min} = 0.248 \text{ \AA}$$

Ans

- (3). The minimum wavelength recorded in the continuous of an X-ray tube operated at 30 kV is $0.414 \text{ \AA}$. Calculate the Planck's constant. (Given: $e = 1.6 \times 10^{-19}$ Columb, $c = 3 \times 10^8$ m/sec)

Solution -

Given -

$$\begin{aligned}
 V &= 30 \text{ kV} \\
 &= 30 \times 10^3 \text{ volts}
 \end{aligned}$$

$$\text{minimum wavelength } (\lambda_{\min}) = 0.414 \text{ \AA} \\ = 0.414 \times 10^{-10} \text{ m}$$

$$\text{Speed of light } (c) = 3 \times 10^8 \text{ m/sec}$$

$$\text{Charge of electron } (e) = 1.6 \times 10^{-19} \text{ Columb}$$

According to Duane and Hunt's law, short wavelength limit is,

$$\lambda_{\min} = \frac{hc}{eV}$$

$$\therefore h = \frac{\lambda_{\min} \cdot eV}{c}$$

$$h = \frac{0.414 \times 10^{-10} \times 1.6 \times 10^{-19} \times 30 \times 10^3}{3 \times 10^8}$$

$$h = \frac{19.872 \times 10^{-26}}{3 \times 10^8}$$

$$h = 6.62 \times 10^{-34} \text{ Joule-sec}$$

$$\text{Planck's constant, } h = 6.62 \times 10^{-34} \text{ Joule-sec}$$

Ans

- (4). Deduce the wavelength of K_{α} line for an atom of $Z = 92$, using Mosley law.
(Given: Rydberg constant, $R = 1.1 \times 10^5 \text{ cm}^{-1}$)

Solution - Given -

Atomic number, $Z = 92$

Rydberg constant, $R = 1.1 \times 10^5 \text{ cm}^{-1}$

The wavelength of K_{α} -line is related to atomic no. Z by Moseley's law,

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z - \sigma)^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

The spectral line K_{α} is emitted when an electron jumps from an orbit of principal quantum number, $n_i = 2$ to $n_f = 1$. Its wavelength is given by -

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z - \sigma)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z - 1)^2 \left[\frac{1}{1} - \frac{1}{4} \right] \quad \left\{ \text{for } K_{\alpha}\text{-line, } \sigma = 1 \right.$$

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z - 1)^2 \left[\frac{4 - 1}{4} \right]$$

$$\frac{1}{\lambda_{K_{\alpha}}} = \frac{3R}{4}(Z - 1)^2$$

$$\frac{1}{\lambda_{K_{\alpha}}} = \frac{3}{4} \times 1.1 \times 10^5 \times (92 - 1)^2 \text{ cm}^{-1}$$

$$\frac{1}{\lambda_{K\alpha}} = \frac{3 \times 1.1 \times 10^5 \times (91)^2}{4} \text{ cm}^{-1}$$

$$\frac{1}{\lambda_{K\alpha}} = \frac{3 \times 1.1 \times 8281 \times 10^5}{4} \text{ cm}^{-1}$$

$$\frac{1}{\lambda_{K\alpha}} = \frac{27327.3 \times 10^5}{4} \text{ cm}^{-1}$$

$$\frac{1}{\lambda_{K\alpha}} = \frac{27327.3 \times 10^7}{4} \text{ m}^{-1}$$

$$\text{or, } \lambda_{K\alpha} = \frac{4}{27327.3 \times 10^7 \text{ m}^{-1}} = \frac{4}{27327.3} \times 10^{-7} \text{ m}$$

$$\lambda_{K\alpha} = 0.146 \times 10^{-10} \text{ m}$$

$$\lambda_{K\alpha} = 0.146 \text{ \AA}$$

Ans

- (5). Estimate the value of the wavelength of the K_{α} -line of silver ($Z=47$). Given $R = 109737 \text{ cm}^{-1}$

Solution - Given -

Atomic number of silver, $Z = 47$

Rydberg constant, $R = 109737 \text{ cm}^{-1}$

The wavelength of K_{α} -line is related to atomic number Z by Moseley's law,

$$\frac{1}{\lambda_{K_{\alpha}}} = R (Z - \sigma)^2 \left| \frac{1}{1^2} - \frac{1}{2^2} \right|$$

$$\frac{1}{\lambda_{K_{\alpha}}} = R (Z - 1)^2 \left| \frac{1}{1^2} - \frac{1}{4} \right| \quad \left\{ \begin{array}{l} \text{for } K_{\alpha} \text{ line, } \sigma = 1 \\ (n_i = 2) \rightarrow (n_f = 1) \end{array} \right.$$

$$\frac{1}{\lambda_{K_{\alpha}}} = \frac{3}{4} R (Z - 1)^2$$

$$\frac{1}{\lambda_{K_{\alpha}}} = \frac{3}{4} \times 109737 \text{ cm}^{-1} \times (47 - 1)^2$$

$$\frac{1}{\lambda_{K_{\alpha}}} = \frac{3}{4} \times (46)^2 \times 109737 \text{ cm}^{-1}$$

$$\frac{1}{\lambda_{K_{\alpha}}} = 1.74 \times 10^8 \text{ cm}^{-1} = 1.74 \times 10^{10} \text{ m}^{-1}$$

or, $\lambda_{K_{\alpha}} = \frac{1}{1.74 \times 10^{10}} \text{ m}$

$$\lambda_{K_{\alpha}} = \frac{1}{1.74 \times 10^{10}} \text{ m}$$

$$\lambda_{K_{\alpha}} = 0.57 \times 10^{-10} \text{ m}$$

$$\lambda_{K_{\alpha}} = 0.57 \text{ \AA}$$

Ans

(6). What element has a K_{α} X-ray line of wavelength $1.785 \text{ \AA}$? of wavelength $0.712 \text{ \AA}$?

$$R = 109737 \text{ cm}^{-1}$$

Solution- Given,

Rydberg constant, $R = 109737 \text{ cm}^{-1}$

The wavelength of K_{α} -line is related to atomic number Z is given by Mosley's law,

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z-1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

For K_{α} -line,
 $n = 1$
 $n_i = 2 \rightarrow n_f = 1$

wavelength of K_{α} line, $\lambda_{K_{\alpha}} = 1.785 \text{ \AA}$
 $= 1.785 \times 10^{-8} \text{ cm}$

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z-1)^2 \left[\frac{1}{1^2} - \frac{1}{4} \right]$$

$$\frac{1}{\lambda_{K_{\alpha}}} = R(Z-1)^2 \left[\frac{3}{4} \right]$$

$$\frac{1}{\lambda_{K_{\alpha}}} = \frac{3R}{4} (Z-1)^2$$

$$\therefore (Z-1)^2 = \frac{4}{3R\lambda_{K_{\alpha}}}$$

$$(Z-1)^2 = \frac{4}{3 \times 109737 \text{ cm}^{-1} \times 1.785 \times 10^{-8} \text{ cm}}$$

$$3 \times 109737 \text{ cm}^{-1} \times 1.785 \times 10^{-8} \text{ cm}$$

$$(Z-1)^2 = \frac{4}{587641.6 \times 10^{-8}}$$

$$(Z-1)^2 = 680.7$$

$$Z-1 = \sqrt{680.7}$$

$$Z-1 = 26$$

or, $Z = 27$ (Cobalt) Ans

wavelength of K_{α} -line, $(\lambda_{K_{\alpha}}) = 0.712 \text{ \AA}$
 $= 0.712 \times 10^{-8} \text{ cm}$

$$\frac{1}{\lambda_{K_{\alpha}}} = R (Z-1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\therefore \frac{1}{\lambda_{K_{\alpha}}} = \frac{3}{4} R (Z-1)^2$$

$$\therefore (Z-1)^2 = \frac{4}{3 R \lambda_{K_{\alpha}}}$$

$$(Z-1)^2 = \frac{4}{3 \times 10987 \text{ cm}^{-1} \times 0.712 \times 10^{-8} \text{ cm}}$$

$$(Z-1)^2 = \frac{4}{234398.2 \times 10^8}$$

$$(Z-1)^2 = 1706.2$$

$$Z-1 = \sqrt{1706.2}$$

$$Z-1 = 41$$

$$Z = 42 \text{ (molybdenum)}$$

Ans

(7). If the K_{α} -radiation of Mo ($Z=42$) has a wavelength of $0.71 \text{ \AA}$, calculate the wavelength of the corresponding radiation of Cu ($Z=29$)

Solution Given

For Molybdenum (Mo),

$$Z_{Mo} = 42$$

$$\lambda_{Mo} = 0.71 \text{ \AA}$$

For Copper (Cu),

$$Z_{Cu} = 29$$

$$\lambda_{Cu} = ?$$

The wavelength of K_{α} -line is related to atomic number Z by Mosley's Law is given by -

$$\frac{1}{\lambda} = R(Z-\sigma)^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad \left\{ \begin{array}{l} \text{For } K_{\alpha} \text{-line} \\ \sigma = 1 \\ n_i = 2 \rightarrow n_f = 1 \end{array} \right.$$

$$\frac{1}{\lambda} = R(Z-1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\frac{1}{\lambda} = R(Z-1)^2 \left[\frac{1}{1} - \frac{1}{4} \right]$$

$$\frac{1}{\lambda} = \frac{3}{4} R (Z-1)^2$$

where, R is constant

from mosley's law, we have,

$$\frac{1}{\lambda} \propto (Z-1)^2$$

Then,

$$\frac{1}{\lambda_{Mo}} \propto (Z_{Mo}-1)^2 \quad \text{----- (1)}$$

and

$$\frac{1}{\lambda_{Cu}} \propto (Z_{Cu}-1)^2 \quad \text{----- (2)}$$

Dividing by (1) by (2), we get,

$$\frac{1/\lambda_{Mo}}{1/\lambda_{Cu}} = \frac{(Z_{Mo}-1)^2}{(Z_{Cu}-1)^2}$$

$$\frac{\lambda_{Cu}}{\lambda_{Mo}} = \frac{(42-1)^2}{(29-1)^2}$$

$$\frac{\lambda_{Cu}}{\lambda_{Mo}} = \frac{(41)^2}{(28)^2}$$

$$\frac{\lambda_{Cu}}{\lambda_{Mo}} = \frac{41 \times 41}{28 \times 28}$$

$$\lambda_{Cu} = \frac{41 \times 41}{28 \times 28} \times \lambda_{Mo}$$

$$\lambda_{Cu} = \frac{41 \times 41}{28 \times 28} \times 0.71 \text{ \AA}$$

$$\lambda_{Cu} = 1.52 \text{ \AA}$$

Ans

- (8). The copper ($Z=29$) target in X-rays tube has some impurity. In the spectrum of X-rays emitted from the tube, there appears a line of wavelength $0.54 \text{ \AA}$ in addition to the copper K_α line of wavelength $1.54 \text{ \AA}$. Use Mosley's law to detect the impurity.

Solution - Let,

Z_i = atomic number of the impurity atom.
 λ_i = the wavelength of its K_α -line.

Given,

for copper,

Atomic number of copper, $Z_{Cu} = 29$

wavelength of its K_α -line, $\lambda_{Cu} = 1.54 \text{ \AA}$

for impurity atom,

Atomic number of the impurity atom, $Z_i = ?$

wavelength of its K_α -line, $\lambda_i = 0.54 \text{ \AA}$

from Mosley's law for K_{α} -line, we have

$$\frac{1}{\lambda} \propto (Z-1)^2$$

then,

$$\frac{1}{\lambda_i} \propto (Z_i-1)^2$$

$$\text{and } \frac{1}{\lambda_{Cu}} \propto (Z_{Cu}-1)^2$$

Now,

$$\frac{1/\lambda_i}{1/\lambda_{Cu}} = \frac{(Z_i-1)^2}{(Z_{Cu}-1)^2}$$

$$\frac{\lambda_{Cu}}{\lambda_i} = \frac{(Z_i-1)^2}{(29-1)^2}$$

$$\frac{\lambda_{Cu}}{\lambda_i} = \frac{(Z_i-1)^2}{(28)^2}$$

$$\frac{\lambda_{Cu}}{\lambda_i} = \frac{(Z_i-1)}{28}$$

$$\frac{1.54 \text{ \AA}}{0.54 \text{ \AA}} = \frac{(Z_i-1)}{28}$$

$$1.69 = \frac{(Z_i-1)}{28}$$

$$(Z_i - 1) = 28 \times 1.69$$

$$(Z_i - 1) = 47.3$$

$$Z_i = 47.3 + 1 = 48.3$$

$$Z_i = 48.3 \approx 48$$

$$Z_i = 48$$

Thus, the impurity atom is of cadmium ($Z=48$).

Ans.

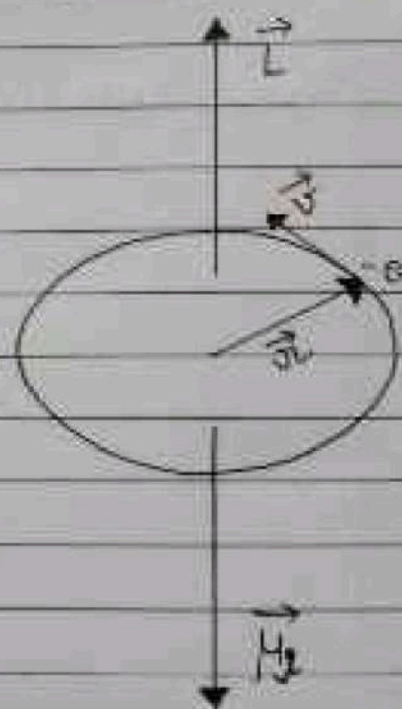
• Orbital Magnetic Dipole Moment:

Bohr Magneton

An electron revolving in an orbit about the nucleus of an atom is a tiny (so small) current loop and produces a magnetic field. It thus behaves like a magnetic dipole and possesses a magnetic moment. Let us calculate its magnetic moment.

Let us consider an electron of mass ' m ' and charge ' $-e$ ' moving with speed ' v ' in a circular Bohr orbit of radius ' r '. It constitutes a current of magnitude

$$i = \frac{e}{T}$$



where T is the orbital period of the electron whose charge has magnitude e .

Now, $T = \frac{2\pi r}{v}$, and so

$$i = \frac{ev}{2\pi r}$$

from electromagnetic theory, the magnitude

of the orbital magnetic dipole moment ' M_L ' for a current ' i ' in a loop of area A is,

$$M_L = iA$$

Its direction is perpendicular to the plane of orbit as shown.

Substituting the value of ' i ' from above,

$$M_L = \frac{evA}{2\pi r}$$

Area of the loop, $A = \pi r^2$

$$M_L = \frac{ev}{2\pi r} \cdot \pi r^2$$

$$\therefore M_L = \frac{evr}{2} \text{ ----- (1)}$$

Because the electron has negative charge, its magnetic dipole moment ' M_L ' is opposite in direction to its orbital momentum ' L ', whose magnitude is given by ^{angular}.

$$L = mvr \text{ ----- (2)}$$

Dividing eqs. (1) by eqs. (2), we get -

$$\boxed{\frac{M_L}{L} = -\frac{e}{2m}} \quad \text{----- (3)}$$

Thus the ratio of the magnitude M_L of the orbital magnetic dipole moment to the magnitude L of the orbital angular momentum for the electron is a constant, independent of the details of the orbit. This constant is called the 'gyromagnetic ratio' for the electron. Its value is $8.8 \times 10^{10} \text{ Coulomb Kg}^{-1}$.

We can write eqs. (3) in vector form.

$$\frac{\vec{M}_L}{\vec{L}} = -\frac{e}{2m}$$

$$\boxed{\vec{M}_L = -\left(\frac{e}{2m}\right) \vec{L}}$$

Thus, minus signs mean that $\vec{M}_L$ is in the opposite direction to $\vec{L}$.

The unit of electron magnetic moment is amp-m² or joule/tesla.

Bohr Magneton-

From quantum mechanics, the allowed magnitudes of $\vec{L}$ are given by,

$$L = \frac{\sqrt{l(l+1)} \cdot h}{2\pi}$$

where l = orbital quantum number.

Therefore, the magnitude of the orbital magnetic dipole moment of the electron is,

$$\mu_l = \frac{e}{2m} \cdot \frac{\sqrt{l(l+1)} \cdot h}{2\pi}$$

$$\mu_l = \frac{\sqrt{l(l+1)} \cdot eh}{4\pi m}$$

Here, $\hbar = \frac{h}{2\pi}$

$$\mu_l = \frac{\sqrt{l(l+1)} \cdot e\hbar}{2m}$$

The quantity $\frac{e\hbar}{2m} = \frac{eh}{4\pi m}$ forms a natural unit

for the measurement of atomic magnetic dipole moments, and is called the 'Bohr magneton', denoted by ' μ_B '. Thus

$$\mu_l = \sqrt{l(l+1)} \mu_B$$

where, $M_B = \frac{eh}{4\pi m}$

$$M_B = \frac{(1.6 \times 10^{-19} \text{ C}) \times (6.62 \times 10^{-34} \text{ Joule-sec})}{4 \times 3.14 \times (9.1 \times 10^{-31} \text{ Kg})}$$

$$M_B = 9.27 \times 10^{-24} \text{ amp} \cdot \text{m}^2$$

• Behaviour of Magnetic Dipole in External Magnetic field: Larmor Precession

An electron moving around the nucleus of an atom is equivalent to a magnetic dipole. Hence, when an atom is placed in an external magnetic field, the electron orbit precesses about the field direction as axis. This precession is called "Larmor precession" and the frequency of this precession is called "Larmor frequency".

The angular velocity of Larmor precession is equal to the product of the magnitude of the magnetic field, and the ratio of the magnitude of the magnetic moment ' M_B ' to the magnitude of the angular momentum L ,

i.e.,

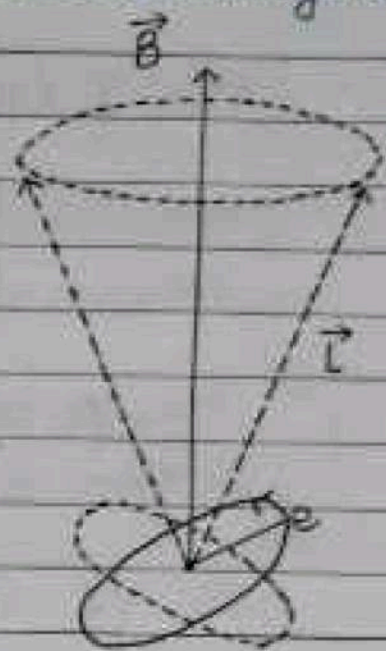
$$\omega = \frac{M_B \cdot B}{L}$$

Here, B is the magnitude of external magnetic field.

Since, $\frac{M_L}{L} = \frac{e}{2m}$

where, e is the charge on the electron of mass ' m '.

$$\therefore \omega = \frac{e}{2m} \cdot B$$



The Larmor frequency (frequency of precession) is therefore

$$f = \frac{\omega}{2\pi} = \frac{e}{4\pi m} \cdot B$$

$$\therefore \boxed{f = \frac{eB}{4\pi m}}$$

Numerical:

- 1) Calculate the precession frequency of an electron orbit in a magnetic field of 5 Tesla.

Solution- Given-

$$B = 5 \text{ Tesla}$$

Charge of the electron, $e = 1.6 \times 10^{-19}$ coulomb

mass of electron, $m = 9.1 \times 10^{-31} \text{ Kg}$

The frequency of precession (Larmor frequency)

$$f = \frac{eB}{4\pi m}$$

$$f = \frac{(1.6 \times 10^{-19} \text{ coulomb}) \times (5 \text{ Tesla})}{4 \times 3.14 \times (9.1 \times 10^{-31} \text{ Kg})}$$

$$f = 7 \times 10^{11} \text{ sec}^{-1}$$

Ans.

• L-S Coupling:

The L-S coupling occurs most frequently and hence it is also called the normal coupling. It is also known as Russell-Saunders coupling. In this coupling:

- (i) As a result of spin-spin correlation effect, the individual spin angular momentum vectors of the orbital electrons are strongly coupled with one another to form a resultant spin angular momentum vector $\vec{S}$ of magnitude $\frac{\sqrt{S(S+1)} h}{2\pi}$.

Where, S is total spin quantum number. It takes all the values between the maximum and minimum value corresponding to $S_1, S_2, \dots$

s_3 with a difference of 1.

$$\text{i.e.; } |s_1 + s_2 + s_3| \dots |_{\min}, |s_1 + s_2 + s_3| \dots |_{\min+1}, \dots \dots \dots (s_1 + s_2 + s_3 \dots)$$

(ii). As a result of the residual electrostatic interaction, the individual orbital angular momentum vectors of the orbital electrons are strongly coupled with one another to form a resultant orbital angular momentum vector $\vec{L}$ of magnitude $\sqrt{L(L+1)} \frac{h}{2\pi}$.

where, L is the total orbital quantum number and can take all values between the maximum and minimum values corresponding to l_1, l_2, l_3 with a difference of 1.

$$\text{i.e.; } |l_1 + l_2 + l_3| \dots |_{\min}, |l_1 + l_2 + l_3| \dots |_{\min+1}, \dots \dots \dots (l_1 + l_2 + l_3 \dots)_{\max}$$

(iii). As a result of smaller spin-orbit magnetic interaction, the resultant orbital angular momentum vector $\vec{L}$ and the resultant spin angular momentum vector $\vec{S}$ are less strongly coupled with each other to form a total angular momentum vector $\vec{J}$ of the atom.

$$\vec{J} = \vec{L} + \vec{S}$$

The magnitude of $\vec{J}$ is $\sqrt{J(J+1)} \cdot \frac{h}{2\pi}$, where the

quantum number J takes the values:

$$J = |L-S|, |L-S|+1, \dots, (L+S)$$

• Determination of Spectral terms for L-S Coupling:

(1). Atoms with one orbital (optical) Electron:

For a hydrogen-like atom, the ground state configuration is -

1s

For this, we have

$$s = \frac{1}{2}, \quad l = 0$$

So that, S = Total spin quantum number.

$$S = s = \frac{1}{2}; \quad \text{Multiplicity } 2S+1 = \left[2 \times \frac{1}{2} + 1\right] = 2$$

and L = Total orbital quantum number.

$$L = l = 0 \text{ (S-state)} \quad \left\{ \begin{array}{l} L = 0 \quad 1 \quad 2 \quad 3 \quad \dots \\ \quad \quad S \quad P \quad D \quad F \quad \dots \end{array} \right.$$

Then, J = Total quantum number.

$$J = |L-S|, \dots, (L+S)$$

$$J = \frac{1}{2}$$

Thus, the ground state term of a hydrogen-like atom is -

$$(2S+1) = 2 \quad S_{J=1/2} = {}^2S_{1/2}$$

(3) • Atoms with Two or more Non-Equivalent orbital (optical) electrons:

Let us consider an atom having two optical electrons with outer configuration (eg. excited state of Ge $Z=32$)

4p 4d

For this, we have

$$s_1 = \frac{1}{2}, \quad s_2 = \frac{1}{2}, \quad l_1 = 1, \quad l_2 = 2$$

The possible values of S (total spin quantum number) and L (total orbital quantum number) are:

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, (s_1 + s_2)$$

$$S = 0, 1$$

$$\text{Multiplicity of state} = 2S + 1$$

$$\text{For } S = 0, \quad 2(0) + 1 = 1 \quad (\text{Singlet})$$

$$\text{For } S = 1, \quad 2(1) + 1 = 3 \quad (\text{Triplet})$$

$$\text{and } L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, (l_1 + l_2)$$

$$L = 1, 2, 3 \text{ (P, D, F states)}$$

Then, total quantum number.

$$J = |L - S|, \dots, (L + S)$$

For singlet terms, we have.

$$\begin{cases} S=0 \\ L=1 \end{cases} ; J=1 ; \begin{matrix} (2S+1)=1 \\ P_{J=1} \end{matrix} ; {}^1P_1$$

$$\begin{cases} S=0 \\ L=2 \end{cases} ; J=2 ; {}^1D_2$$

$$\begin{cases} S=0 \\ L=3 \end{cases} ; J=3 ; {}^1F_3$$

For triplet terms, we have

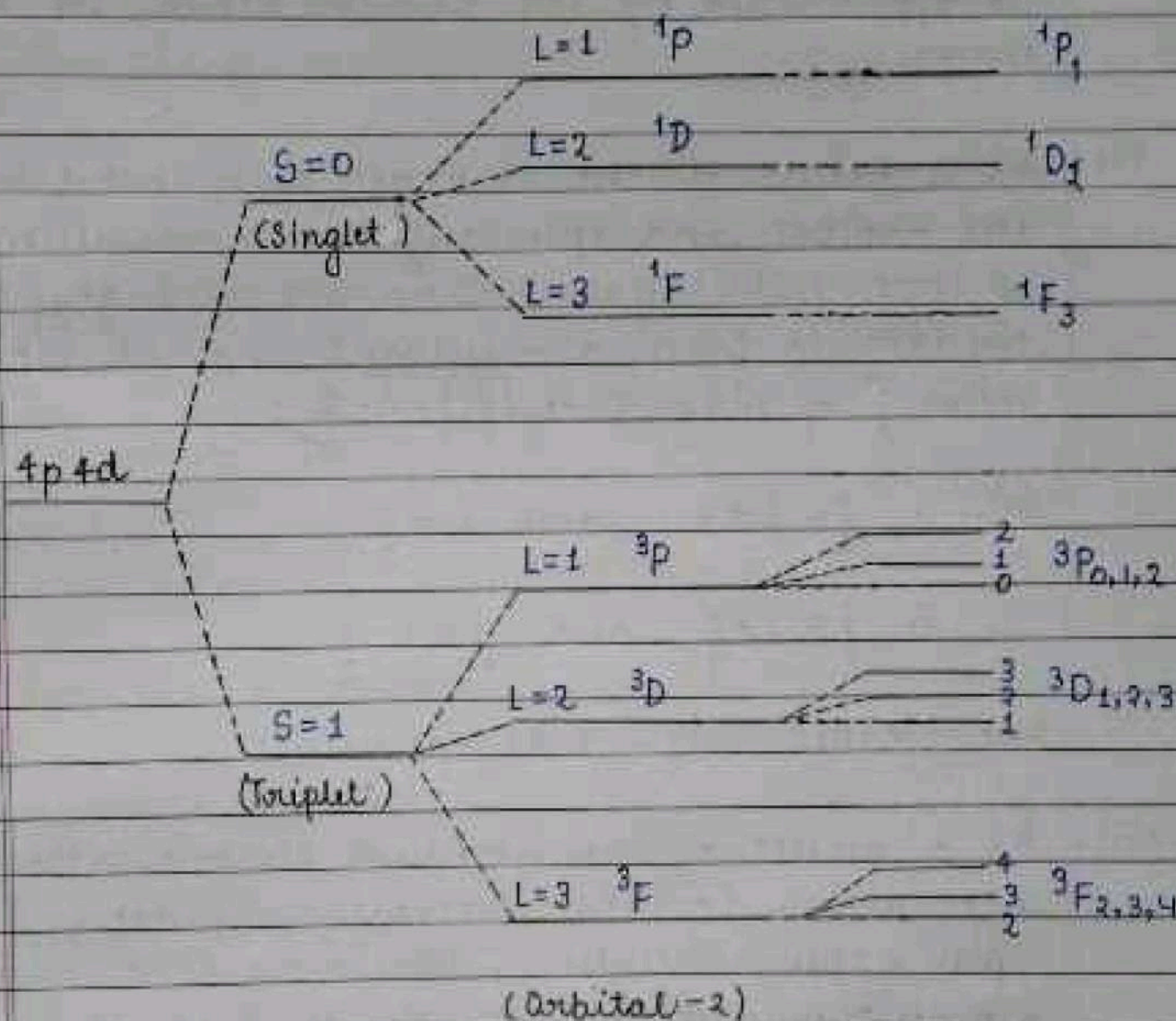
$$\begin{cases} S=1 \\ L=1 \end{cases} ; J=0, 1, 2 ; {}^3P_0, {}^3P_1, {}^3P_2$$

$$\begin{cases} S=1 \\ L=2 \end{cases} ; J=1, 2, 3 ; {}^3D_1, {}^3D_2, {}^3D_3$$

$$\begin{cases} S=1 \\ L=3 \end{cases} ; J=2, 3, 4 ; {}^3F_2, {}^3F_3, {}^3F_4$$

Thus, a single degenerate level of configuration

4p 4d is splitted into 12 levels as shown in figure. The spin-spin correlation splits this level into two levels.



unperturbed level	+	spin-spin correlation energy	+	residual electrostatic energy	+	spin-orbit magnetic energy
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• J-J Coupling:

In its ideal form, the j-j coupling is an opposite extreme to the ideal L-S coupling and is approached by the heavier atoms. In this coupling:

- (i). As a result of the stronger spin-orbit interaction the orbital and spin angular momentum vectors of each individual electron are strongly coupled together to form a resultant angular momentum vector $\vec{j}$ of magnitude $\sqrt{j(j+1)} \cdot \frac{h}{2\pi}$.

where, $j = l \pm s$ and $s = \frac{1}{2}$

$$\therefore j = l + \frac{1}{2} \text{ and } j = l - \frac{1}{2}$$

i.e; j takes half-integral values.

- (ii). As a result of the residual electrostatic interaction (orbital-orbital interaction) and spin-spin correlation, the resultant angular momentum vectors $\vec{j}$ of the individual electrons are less strongly coupled with one another to form the total angular momentum vector $\vec{J}$ of the atom, of magnitude $\sqrt{J(J+1)} \cdot \frac{h}{2\pi}$.

The total angular momentum quantum number takes the values;

$$J = |j_1 + j_2 + \dots|_{\min}, |j_1 + j_2 + \dots|_{\min} + 1, \dots, (j_1 + j_2 + \dots)_{\max}$$

Example:

Let us consider the terms for the electronic configuration $4p \ 4d$ under $j-j$ coupling.

for the p -electron:

$$l_1 = 1, \quad s_1 = \frac{1}{2}$$

$$j_1 = (l_1 \pm s_1)$$

$$j_1 = \left(1 \pm \frac{1}{2}\right) = \left(1 - \frac{1}{2}, 1 + \frac{1}{2}\right)$$

$$j_1 = \left(\frac{1}{2}, \frac{3}{2}\right)$$

for the d -electron:

$$l_2 = 2, \quad s_2 = \frac{1}{2}$$

$$j_2 = (l_2 \pm s_2)$$

$$j_2 = \left(2 \pm \frac{1}{2}\right) = \left(2 - \frac{1}{2}, 2 + \frac{1}{2}\right)$$

$$j_2 = \left(\frac{3}{2}, \frac{5}{2}\right)$$

This gives four (j_1, j_2) combinations of the possible j_1 and j_2 values. These are

$$\left(\frac{1}{2}, \frac{3}{2}\right); \left(\frac{1}{2}, \frac{5}{2}\right); \left(\frac{3}{2}, \frac{3}{2}\right) \text{ and } \left(\frac{3}{2}, \frac{5}{2}\right)$$

Thus, the spin-orbit interaction splits the unperturbed energy level into four levels, of which $\left(\frac{1}{2}, \frac{3}{2}\right)$ lies lowest and $\left(\frac{3}{2}, \frac{5}{2}\right)$ lies highest.

Each of the above four levels is further splitted by residual electrostatic interaction and spin-spin correlation into a number of J-levels. The above four (j_1, j_2) combinations give J values as under:

$$J = |j_1 + j_2|_{\min} \dots \dots \dots (j_1 + j_2)_{\max}$$

$$\left(\frac{1}{2}, \frac{3}{2}\right) ; J = 1, 2$$

$$\left(\frac{1}{2}, \frac{5}{2}\right) ; J = 2, 3$$

$$\left(\frac{3}{2}, \frac{3}{2}\right) ; J = 0, 1, 2, 3$$

$$\left(\frac{3}{2}, \frac{5}{2}\right) ; J = 1, 2, 3, 4$$

The complete splitting is shown in figure. The total number of final levels is the same (12) as for the L-S coupling and the J values also are the same.

