

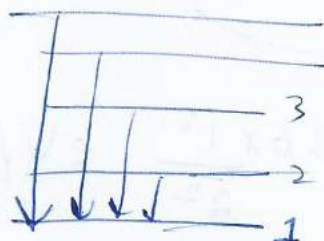
Solved Examples

Aspire One
Tutorial

⑥ $\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ $n_2 \rightarrow \infty$
 $n_1 \rightarrow 1$

$$\bar{\nu} = \frac{1}{\lambda} = R = 109678 \text{ cm}^{-1}$$

⑦ $\Delta E = \frac{hc}{\lambda}$



$$2 \rightarrow 1$$

$$\frac{1}{\lambda} = 109670 \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = 109670 \times \frac{3}{4} \text{ cm}^{-1}$$

$$\lambda = \frac{4}{109670 \times 3} \text{ cm} = 12158 \times 10^{-9} \text{ cm}$$

$$= \underline{1215.8 \text{ \AA}}$$

$$= 0.00001215768 = \underline{1215768} \times 10^{-11} \text{ cm}$$

$$= 12158 \times 10^{-11} \text{ cm}$$

$$= 12158 \times 10^{-13} \text{ m}$$

$$= 12158 \times 10^{-10} \times 10^{-3} \text{ m}$$

$$= 12.158 \text{ \AA}$$

$$= 1215800 \times 10^{-11} \text{ cm}$$

$$= 12158 \times 10^{-9} \text{ cm}$$

$$= 12158 \times \frac{10^{-9}}{100} \text{ m}$$

$$= 12158 \times 10^{-11} \text{ m}$$

$$= \underline{12158 \times 10^{-10} \times 10^{-1} \text{ m}}$$

\AA

$$\textcircled{B} \underline{1215.8 \text{ \AA}}$$

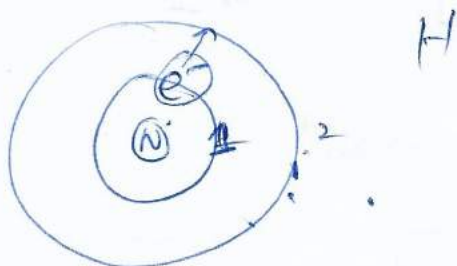
$$1215768 \times \frac{10^{-11}}{100} \text{ cm}$$

$$= 1215768 \times 10^{-13} \text{ m} = 1215.768 \text{ \AA}$$

⑧

$$E_n = -13.6 \times \frac{Z^2}{n^2}$$

⑨



$$E = -13.6 \times \frac{1^2}{2^2} \text{ eV/atom}$$

$$= -\frac{13.6}{4} \times 1.6 \times 10^{-19} \text{ J}$$

$$= -\frac{2.18 \times 10^{-18}}{4} \text{ J/atom}$$

$$1 \text{ atom} = -\frac{2.18 \times 10^{-18}}{4}$$

$$\frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ mole}} = ? = -\frac{2.18 \times 10^{-18}}{4} \times 6.023 \times 10^{23} \text{ J/mol}$$

$$= -\frac{1312}{4} \text{ kJ/mol}$$

$$= -328 \text{ kJ/mol}$$

$$= -328 \times 10^3 \text{ J/mol}$$

$$= -3.28 \times 10^5 \text{ J/mol}$$

$$(13) \quad \Delta E = E_3 - E_2 = \frac{hc}{\lambda}$$

$$\Rightarrow \left(\frac{-13.6 \times 1^2}{9} + \frac{13.6 \times 1^2}{4} \right) \text{eV} =$$

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

$$= 109678 \text{ cm}^{-1} \left[\frac{1}{4} - \frac{1}{9} \right] = 109678 \times \frac{5}{36} \text{ cm}^{-1}$$

$$\lambda = \frac{36}{5 \times 109678} \text{ cm}$$

$$= 6564671 \times 10^{-11} \text{ cm.}$$

$$= 6564671 \times 10^{-13} \text{ m.}$$

$$= 6564.671 \text{ \AA}$$

$$\approx 6600 \text{ \AA}$$

$$(14) \quad r_n = 0.53 \frac{n^2}{Z} \text{ \AA}$$

$$\boxed{n=2} \quad r_2 = 0.53 \times 4$$

$$= 2.12 \text{ \AA}$$

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$$PE = -\frac{kze^2}{r}, \quad KE = \frac{1}{2} \frac{kze^2}{r}$$

$$TE = -\frac{1}{2} \frac{kze^2}{r}$$

$$KE = x$$

$$PE = -2x$$

$$TE = -x = -3.4$$

$$x = 3.4$$

SOME SOLVED EXAMPLES

Example 1. Calculate the wavelength and energy of radiation emitted for the electronic transition from infinite to stationary state of hydrogen atom. (Given, $R = 1.09678 \times 10^7 \text{ m}^{-1}$, $h = 6.6256 \times 10^{-34} \text{ J-s}$ and $c = 2.9979 \times 10^8 \text{ ms}^{-1}$)

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

$$n_1 = 1 \text{ and } n_2 = \infty$$

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

or
$$\lambda = \frac{1}{R} = \frac{1}{1.09678 \times 10^7} = 9.11 \times 10^{-8} \text{ m}$$

We know that,

$$\begin{aligned} E = h\nu &= h \cdot \frac{c}{\lambda} = 6.6256 \times 10^{-34} \times \frac{2.9979 \times 10^8}{9.11 \times 10^{-8}} \\ &= 2.17 \times 10^{-18} \text{ J} \end{aligned}$$

Example 2. Calculate the velocity (cm/sec) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.

Solution: Radius of 3rd orbit

$$= 3^2 \times 0.529 \times 10^{-8} = 4.761 \times 10^{-8} \text{ cm}$$

We know that,

$$\begin{aligned} mvr &= \frac{nh}{2\pi} \quad \text{or} \quad v = \frac{nh}{2\pi mr} \\ &= \frac{3 \times 6.624 \times 10^{-27}}{2 \times 3.14 \times (9.108 \times 10^{-28}) \times (4.761 \times 10^{-8})} \\ &= 0.729 \times 10^8 \text{ cm/sec} \end{aligned}$$

$$\text{Time taken for one revolution} = \frac{2\pi r}{v}$$

Number of revolutions per second

$$\begin{aligned} &= \frac{1}{\frac{2\pi r}{v}} = \frac{v}{2\pi r} \\ &= \frac{0.729 \times 10^8}{2 \times 3.14 \times 4.761 \times 10^{-8}} \\ &= 2.4 \times 10^{14} \text{ revolutions/sec} \end{aligned}$$

Example 3. The electron energy in hydrogen atom is given by $E = -\frac{21.7 \times 10^{-12}}{n^2}$ erg. Calculate the energy required to remove an electron completely from $n=2$ orbit. What is the longest wavelength (in cm) of light that be used to cause this transition?

Solution:
$$E = -\frac{21.7 \times 10^{-12}}{n^2} \text{ erg}$$

Electron energy in the 2nd orbit, i.e., $n = 2$

$$E_2 = -\frac{21.7 \times 10^{-12}}{2^2} \text{ erg} = -5.425 \times 10^{-12} \text{ erg}$$

and $E_\infty = 0$

$$\Delta E = \text{Change in energy} = E_\infty - E_2 = 5.425 \times 10^{-12} \text{ erg}$$

Thus, energy required to remove an electron from 2nd orbit
 $= 5.425 \times 10^{-12} \text{ erg}$

According to quantum equation,

$$\Delta E = h \cdot \frac{c}{\lambda}$$

or

$$\lambda = \frac{hc}{\Delta E}$$

$$(h = 6.625 \times 10^{-27} \text{ erg-sec}; c = 3 \times 10^{10} \text{ cm/sec})$$

$$\text{and } \Delta E = 5.425 \times 10^{-12} \text{ erg}$$

$$\text{So, } \lambda = \frac{(6.625 \times 10^{-27}) \times (3 \times 10^{10})}{5.425 \times 10^{-12}} \\ = 3.7 \times 10^{-5} \text{ cm}$$

Thus, the longest wavelength of light that can cause this transition is $3.7 \times 10^{-5} \text{ cm}$.

Example 4. Calculate the shortest and longest wavelengths in hydrogen spectrum of Lyman series.

Or

Calculate the wavelengths of the first line and the series limit for the Lyman series for hydrogen. ($R_H = 109678 \text{ cm}^{-1}$)

Solution: For Lyman series, $n_1 = 1$.

For shortest wavelength in Lyman series (i.e., series limit), the energy difference in two states showing transition should be maximum, i.e., $n_2 = \infty$.

$$\text{So, } \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = R_H \\ \lambda = \frac{1}{109678} = 9.117 \times 10^{-6} \text{ cm} \\ = 911.7 \text{ \AA}$$

For longest wavelength in Lyman series (i.e., first line), the energy difference in two states showing transition should be minimum, i.e., $n_2 = 2$

$$\text{So, } \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4} R_H \\ \text{or } \lambda = \frac{4}{3} \times \frac{1}{R_H} = \frac{4}{3 \times 109678} = 1215.7 \times 10^{-8} \text{ cm} \\ = 1215.7 \text{ \AA}$$

Example 5. Show that the Balmer series occurs between 3647 Å and 6563 Å. ($R = 1.0968 \times 10^7 \text{ m}^{-1}$)

Solution: For Balmer series,

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

where, $n = 3, 4, 5, \dots \infty$

To obtain the limits for Balmer series $n = 3$ and $n = \infty$ respectively.

$$\lambda_{\max} (n = 3) = \frac{1}{R \left[\frac{1}{2^2} - \frac{1}{3^2} \right]} = \frac{36}{5R} \\ = \frac{36}{5 \times 1.0968 \times 10^7} \text{ m} \\ = 6563 \text{ \AA} \\ \lambda_{\min} (n = \infty) = \frac{1}{R \left[\frac{1}{2^2} - \frac{1}{\infty^2} \right]} = \frac{4}{R} \\ = \frac{4}{1.0968 \times 10^7} \text{ m} \\ = 3647 \text{ \AA}$$

Example 6. Light of wavelength 12818 Å is emitted when the electron of a hydrogen atom drops from 5th to 3rd orbit. Find the wavelength of the photon emitted when the electron falls from 3rd to 2nd orbit.

Solution: We know that,

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

When, $n_1 = 3$ and $n_2 = 5$,

$$\frac{1}{12818} = R \left[\frac{1}{9} - \frac{1}{25} \right] = \frac{16R}{9 \times 25}$$

$$\text{or } 12818 = \frac{9 \times 25}{16 \times R} \quad \dots (i)$$

When, $n_1 = 2$ and $n_2 = 3$,

$$\frac{1}{\lambda} = R \left[\frac{1}{4} - \frac{1}{9} \right] = \frac{5R}{36}$$

$$\lambda = \frac{36}{5R} \quad \dots (ii)$$

Dividing eqn. (ii) by eqn. (i),

$$\frac{\lambda}{12818} = \frac{36}{5R} \times \frac{16R}{9 \times 25} = \frac{64}{125}$$

$$\lambda = \frac{64}{125} \times 12818 = 6562.8 \text{ \AA}$$

Example 7. The ionisation energy of hydrogen atom is 13.6 eV. What will be the ionisation energy of He^+ and Li^{2+} ions?

Solution: Ionisation energy = -(energy of the 1st orbit)

Energy of the 1st orbit of hydrogen = -13.6 eV

$$\text{Energy of the 1st orbit of } \text{He}^+ = -13.6 \times Z^2 \text{ (Z for } \text{He}^+ = 2) \\ = -13.6 \times 4 \text{ eV} = -54.4 \text{ eV}$$

So, Ionisation energy of $\text{He}^+ = -(-54.4) = 54.4 \text{ eV}$

$$\text{Energy of 1st orbit of } \text{Li}^{2+} = -13.6 \times 9 \text{ (Z for } \text{Li}^{2+} = 3) \\ = -122.4 \text{ eV}$$

$$\text{Ionisation energy of } \text{Li}^{2+} = -(-122.4) = 122.4 \text{ eV}$$

Example 8. If the energy difference between two electronic states is $46.12 \text{ kcal mol}^{-1}$, what will be the frequency of the light emitted when the electrons drop from higher to lower states? ($Nh = 9.52 \times 10^{-14} \text{ kcal sec mol}^{-1}$, where, N is the Avogadro's number and h is the Planck's constant)

Solution: $\Delta E = 46.12 \text{ kcal mol}^{-1}$

According to Bohr theory, $\Delta E = Nh\nu$

$$\text{or } \nu = \frac{\Delta E}{Nh} = \frac{46.12}{9.52 \times 10^{-14}}$$

$$= 4.84 \times 10^{14} \text{ cycle sec}^{-1}$$

Example 9. According to Bohr theory, the electronic energy of the hydrogen atom in the n th Bohr orbit is given by

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2} \text{ J}$$

Calculate the longest wavelength of light that will be needed to remove an electron from the 3rd orbit of the He^+ ion.

Solution: The electronic energy of He^+ ion in the n th Bohr orbit

$$= -\frac{21.76 \times 10^{-19}}{n^2} \times Z^2 \text{ J}$$

where, $Z = 2$

Thus, energy of He^+ in the 3rd Bohr orbit

$$= -\frac{21.76 \times 10^{-19}}{9} \times 4 \text{ J}$$

$$\Delta E = E_\infty - E_3$$

$$= 0 - \left[-\frac{21.76 \times 10^{-19} \times 4}{9} \right]$$

$$= \frac{21.76 \times 10^{-19} \times 4}{9}$$

We know that, $\lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4}$

$$= 2.055 \times 10^{-7} \text{ m}$$

Example 10. Calculate the ratio of the velocity of light and the velocity of electron in the first orbit of a hydrogen atom. (Given, $h = 6.624 \times 10^{-27} \text{ erg-sec}$; $m = 9.108 \times 10^{-28} \text{ g}$, $r = 0.529 \times 10^{-8} \text{ cm}$)

Solution: $v = \frac{h}{2\pi mr}$

$$= \frac{6.624 \times 10^{-27}}{2 \times 3.14 \times 9.108 \times 10^{-28} \times 0.529 \times 10^{-8}}$$

$$= 2.189 \times 10^8 \text{ cm/sec}$$

$$\frac{c}{v} = \frac{3 \times 10^{10}}{2.189 \times 10^8} = 137$$

Example 11. The wavelength of a certain line in Balmer series is observed to be 4341 \AA . To what value of ' n ' does the correspond? ($R_H = 109678 \text{ cm}^{-1}$)

Solution: $\frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{n^2} \right]$

$$\frac{1}{n^2} = \frac{1}{4} - \frac{1}{\lambda \times R_H}$$

$$= \frac{1}{4} - \frac{1}{4341 \times 10^{-8} \times 109678}$$

$$= 0.04$$

$$n^2 = \frac{1}{0.04} = 25$$

or $n = 5$

Example 12. Estimate the difference in energy between the first and second Bohr orbit for hydrogen atom. At what minimum atomic number would a transition from $n = 2$ to $n = 1$ energy level result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8} \text{ m}$? Which hydrogen-like species does this atomic number correspond to?

Solution: $\Delta E = h\nu = \frac{h \cdot c}{\lambda}$

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

$$\Delta E = R \cdot h \cdot c \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\Delta E = h \cdot c \cdot \frac{3}{4} R$$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 1.09678 \times 10^7 \times 3}{4}$$

$$= 1.635 \times 10^{-18} \text{ J}$$

For hydrogen-like species,

$$\Delta E = Z^2 R h c \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

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

$$\frac{1}{3.0 \times 10^{-8}} = Z^2 \times 1.09678 \times 10^7 \times \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$Z^2 = \frac{4}{3 \times 10^{-8} \times 1.09678 \times 10^7 \times 3} \approx 4$$

or $Z = 2$

The species is He^+ .

Example 13. What transition in the hydrogen spectrum have the same wavelength as Balmer transition $n = 4$ to $n = 2$ He^+ spectrum?

Solution: For He^+ ion,

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

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

For hydrogen atom,

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

So,

$$\frac{3R}{4} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

or

$$\text{i.e., } n_1 = 1 \text{ and } n_2 = 2$$

Example 14. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum. ($R_H = 1.1 \times 10^7 \text{ m}^{-1}$; $c = 3 \times 10^8 \text{ m s}^{-1}$; $h = 6.62 \times 10^{-34} \text{ J-s}$)

Solution: The transition occurs like Balmer series as spectral line is observed in visible region.

Thus, the line of lowest energy will be observed when transition occurs from 3rd orbit to 2nd orbit, i.e., $n_1 = 2$ and $n_2 = 3$.

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{5}{36} R$$

$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.62 \times 10^{-34} \times 3 \times 10^8 \times \frac{5}{36} \times 1.1 \times 10^7$$

$$= 3.03 \times 10^{-19} \text{ J per atom}$$

Energy corresponding to 1.0 g atom of hydrogen

$$= 3.03 \times 10^{-19} \times \text{Avogadro's number}$$

$$= 3.03 \times 10^{-19} \times 6.023 \times 10^{23} \text{ J}$$

$$= 18.25 \times 10^4 \text{ J}$$

Example 15. How many times does the electron go around the first Bohr's orbit of hydrogen in one second?

Solution: Number of revolutions per second = $\frac{v}{2\pi r}$... (i)

$$v = \frac{2.188 \times 10^8}{n} \text{ cm/sec}$$

$$v = \frac{2.188 \times 10^8}{1} = 2.188 \times 10^8 \text{ cm/sec}$$

$$r = \frac{n^2}{Z} \times 0.529 \text{ \AA}$$

$$= \frac{1^2}{1} \times 0.529 \times 10^{-8} \text{ cm}$$

$$= 0.529 \times 10^{-8} \text{ cm}$$

$$\therefore \text{Number of revolutions per sec} = \frac{2.188 \times 10^8}{2 \times 3.14 \times 0.529 \times 10^{-8}}$$

$$= 6.59 \times 10^{15}$$

Example 16. Calculate the wavelength of radiations emitted, produced in a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom. to ground state ($R_H = 1.1 \times 10^7 \text{ m}^{-1}$)

Solution:
$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$
$$= 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2} \right)$$
$$= 969.6 \times 10^{-10} \text{ metre}$$
$$\therefore \lambda = 969.6 \text{ \AA}$$

Example 17. What is the degeneracy of the level of the hydrogen atom that has the energy $\left(-\frac{R_H}{9} \right)$?

Solution:
$$E_n = -\frac{R_H}{n^2} = -\frac{R_H}{9}$$
$$\therefore n = 3$$

Thus, $l = 0$ and $m = 0$ (one 3s-orbital)

$l = 1$ and $m = -1, 0, +1$ (three 3p-orbitals)

$l = 2$ and $m = -2, -1, 0, +1, +2$ (five 3d-orbitals)

Thus, degeneracy is nine ($1 + 3 + 5 = 9$ states).

Example 18. Calculate the angular frequency of an electron occupying the second Bohr orbit of He^+ ion.

Solution: Velocity of electron (v) = $\frac{2\pi Ze^2}{nh}$... (i)

Radius of He^+ ion in an orbit (r_n) = $\frac{n^2 h^2}{4\pi^2 mZe^2}$... (ii)

Angular frequency or angular velocity (ω)

$$= \frac{v}{r_n} = \frac{2\pi Ze^2}{nh} \times \frac{4\pi^2 mZe^2}{n^2 h^2} = \frac{8\pi^3 mZ^2 e^4}{n^3 h^3}$$

Given, $n = 2$, $m = 9.1 \times 10^{-28} \text{ g}$, $Z = 2$, $e = 4.8 \times 10^{-10} \text{ esu}$

$$h = 6.626 \times 10^{-27} \text{ erg-sec}$$

$$\therefore \omega = \frac{8 \times \left(\frac{22}{7} \right)^3 \times 2^2 \times 9.1 \times 10^{-28} \times (4.8 \times 10^{-10})^4}{(2)^3 \times (6.626 \times 10^{-27})^3}$$
$$= 2.067 \times 10^{16} \text{ sec}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. If the speed of electron in first Bohr orbit of hydrogen be 'x', then speed of the electron in second orbit of He^+ is:

- (a) $x/2$ (b) $2x$ (c) x (d) $4x$

[Ans. (c)]

[Hint: $v_n = \frac{v_1 \times Z}{n} = \frac{x \times 2}{2} = x$]

2. If first ionisation energy of hydrogen is E , then the ionisation energy of He^+ would be:

- (a) E (b) $2E$ (c) $0.5E$ (d) $4E$

[Ans. (d)]

[Hint: $I_2(\text{He}^+) = Z^2 I_1(\text{H})$
 $= 2^2 \times E = 4E$]

3. The number of spectral lines that are possible when electrons in 7th shell in different hydrogen atoms return to the 2nd shell is:

(a) 12 (b) 15 (c) 14 (d) 10
 [Ans. (b)]

[Hint: Number of spectral lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$
 $= \frac{(7 - 2)(7 - 2 + 1)}{2} = 15$]

4. The ratio of radii of first orbits of H, He^+ and Li^{2+} is:

(a) 1:2:3 (b) 6:3:2 (c) 1:4:9 (d) 9:4:1
 [Ans. (b)]

[Hint: $r = \frac{n^2}{Z} \times 0.529 \text{ \AA}$

$$r_{\text{H}} : r_{\text{He}^+} : r_{\text{Li}^{2+}}$$

$$1 : \frac{1}{2} : \frac{1}{3}$$

$$6 : 3 : 2]$$

5. The energy of second orbit of hydrogen is equal to the energy of:

(a) fourth orbit of He^+ (b) fourth orbit of Li^{2+}
 (c) second orbit of He^+ (d) second orbit of Li^{2+}

[Ans. (a)]

[Hint: $E = -\frac{Z^2}{n^2} \times 13.6 \text{ eV}$

$$E_2 = -\frac{13.6}{4} \text{ for 'H'}$$

$$E = -\frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

$$-\frac{13.6}{4} = -\frac{Z^2}{n^2} \times 13.6$$

$$\frac{Z^2}{n^2} = \frac{1}{4} \quad (Z = 2, n = 2)$$

6. What is the energy in eV required to excite the electron from $n = 1$ to $n = 2$ state in hydrogen atom? ($n =$ principal quantum number)
 [CET (J&K) 2006]

(a) 13.6 (b) 3.4 (c) 17 (d) 10.2

[Ans. (d)]

[Hint: $\Delta E = E_2 - E_1$

$$= \left(-\frac{13.6}{2^2} \right) - \left(-\frac{13.6}{1^2} \right)$$

$$= 13.6 \left(1 - \frac{1}{4} \right) = \frac{3}{4} \times 13.6 = 10.2 \text{ eV}]$$

7. An electron in an atom undergoes transition in such a way that its kinetic energy changes from x to $\frac{x}{4}$, the change in potential energy will be:

[Hint: $\text{PE} = -2\text{KE}$

$$\therefore \text{PE will change from } -2x \text{ to } -\frac{2x}{4}$$

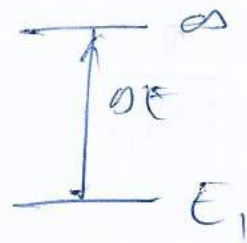
$$\text{Change in potential energy} = \left(-\frac{2x}{4} \right) - (-2x)$$

$$= -\frac{x}{2} + 2x = \frac{3x}{2}]$$

Solved Examples

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

$\Delta E = \frac{hc}{\lambda} = Rhc \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$



$$\Delta E = E_{\infty} - E_1 = 0 - (-13.6) = 13.6 \text{ eV}$$

(2) $V_n = 2.188 \times 10^8 \frac{\text{cm}}{\text{s}}$

$\nu_0 = 6.66 \times 10^{15} \frac{\text{cm}^2}{\text{s}^3} \text{ s}^{-1}$

$$= \frac{6.66 \times 10^{15}}{27} \text{ s}^{-1} =$$
$$= 2.467 \times 10^{14} \text{ rev/s}$$

(3) $\lambda = \frac{4}{R} = 36474 \times 10^{-9} \text{ cm}$

$$\approx 3.7 \times 10^{-5} \text{ cm.}$$

(4) $\frac{1}{12818} = R \left[\frac{1}{9} - \frac{1}{25} \right] \text{ --- (i)}$

$$\frac{1}{n} = R \left[\frac{1}{4} - \frac{1}{9} \right] \text{ --- (ii)}$$

$$\frac{1}{12818} = R \times \frac{16}{25 \times 9} \text{ --- (i)}$$

(i) / (ii)

$$\frac{1}{n} = R \times \frac{5}{9 \times n} \text{ --- (ii)}$$

$$\frac{x}{12818} = \frac{16 \times 4 \times 4}{25 \times 15}$$

$$x = \frac{12818 \times 16 \times 4}{125} = 6562.8 \text{ \AA}$$

Illustrations of Objective Questions

$$\textcircled{1} \quad V = \frac{V_0}{n} \times \frac{Z}{n} \quad V = x \times \frac{1}{2} = \underline{x}$$

$$\textcircled{4} \quad \frac{1}{1} : \frac{1}{2} : \frac{1}{3} \quad \frac{n^2}{Z}$$

$$6 : 3 : 2$$

$$\textcircled{5} \quad E_n = -13.6 \frac{Z^2}{n^2} = \frac{-13.6 \times 4}{4}$$

$$\textcircled{7} \quad KE \quad x \rightarrow \frac{x}{4}$$

$$P.E. \quad -2x \rightarrow -\frac{2x}{4}$$

$$-2x \rightarrow -\frac{x}{2} + 2x = \frac{3x}{2}$$

Particle & wave nature of electron

De Broglie

Like light all particles have wave nature as well.

$$E = \frac{h\nu}{\lambda} = \frac{hc}{\lambda} \quad (\text{for light})$$

$$E = \underline{mc^2} \quad (\text{Einstein's mass-energy equivalence})$$

$$\Rightarrow \frac{hc}{\lambda} = mc^2$$

mc \rightarrow momentum (mv)

$$\Rightarrow \frac{h}{mc} = \lambda = \frac{h}{p}$$

$p \rightarrow$ symbol for momentum

By analogy for other particles with mass m & velocity v ,

$$\boxed{\lambda = \frac{h}{mv}} \quad (\text{for other particles})$$

or

$$\boxed{\lambda = \frac{h}{p}} \rightarrow \text{De Broglie equation}$$

$$\lambda = \frac{6.626 \times 10^{-34}}{100 \times 100 \times 10^3 \text{ m/s}}$$

~ 0 (For bigger objects λ can be ignored)

For an e^-

$$\lambda = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2 \times 10^6 \text{ m/s}}$$

= considerable value

$$= 0.364 \times 10^{-9} \text{ m}$$

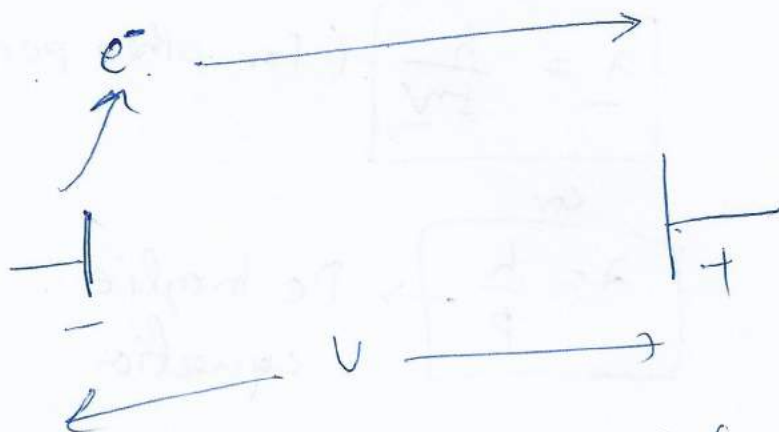
$$= 3.64 \text{ \AA}$$

$$\Rightarrow \frac{1}{2} m v^2 = K E$$

$$\Rightarrow m v^2 = 2 K \Rightarrow m^2 v^2 = 2 m K$$

$$m v = \sqrt{2 m K}$$

$$\lambda = \frac{h}{m v} = \frac{h}{\sqrt{2 m K E}}$$



$$K E = e \times V \quad (\text{for } e^-)$$

$$K E = q \times V$$

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

V is potential difference

$$\text{for } e^- \quad \lambda = \frac{h}{m v} = \frac{h}{\sqrt{2 m e V}}$$

For any charged particle with charge q -

$$KE = qV$$

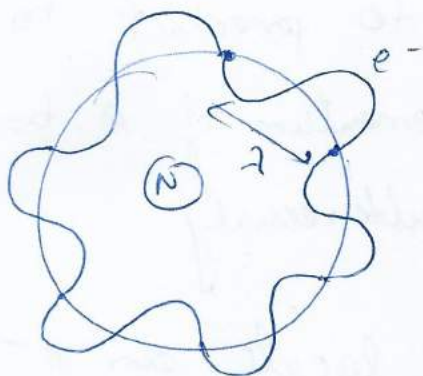
$$\lambda = \frac{h}{\sqrt{2mqV}}$$

⊗ $\lambda_{e^-} = \frac{h}{\sqrt{2meV}} = \frac{12.27}{\sqrt{V}} \text{ \AA}$

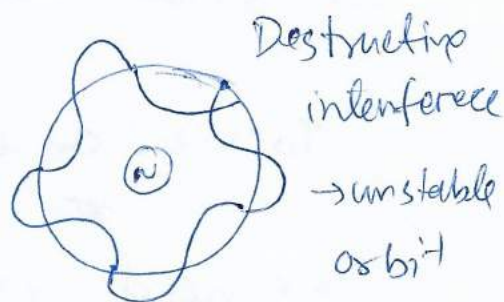
Bohr Theory v/s De Broglie equation

$$mvr = \frac{nh}{2\pi} \text{ (Bohr's theory)}$$

$e^- \rightarrow$ is a wave also



$$2\pi r = n\lambda$$



⊗ $2\pi r = n\lambda$ (from de Broglie)

— (i)

↓
concept of wave nature of e^-

$$\lambda = \frac{h}{mv} \text{ — (ii)}$$

$$2\pi r = n \frac{h}{mv} \Rightarrow \boxed{mvr = \frac{nh}{2\pi}}$$

→ This proves that de Broglie & Bohr concepts are in perfect agreement with each other

Heisenberg's Uncertainty principle

$e^- \rightarrow$ particle (Bohr theory)

$e^- \rightarrow$ wave (De Broglie)



$\rightarrow V, a$
 x

$$\underline{v} = \underline{u} + \underline{at}$$

$$\underline{x} = \underline{u}t + \frac{1}{2} \underline{a}t^2$$

→ It is impossible to predict both the exact position & exact momentum of a body as small as e^- simultaneously.

To view an e^- or to locate an e^- we need radiation of very short λ .

$$E = \frac{hc}{\lambda} \quad \begin{matrix} E \rightarrow \text{high} \\ \lambda \leftarrow \text{small} \end{matrix}$$

this changes the momentum of the e^-

→ If a higher wavelength radiation of lower energy is used

e^- momentum can be determined but its position cannot be determined precisely.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$\Delta x \rightarrow$ uncertainty in position

$\Delta p \rightarrow$ uncertainty in momentum.

$h \rightarrow$ planck's constant.

For e^-

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta mv \geq \frac{h}{4\pi}$$

$$m \Delta x \cdot \Delta v \geq \frac{h}{4\pi}$$

$$\Rightarrow \boxed{\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$\Delta x \cdot \Delta v \geq 0.57 \text{ erg-s g}^{-1} \text{ (For } e^-)$$

$\Delta x \cdot \Delta v \rightarrow$ uncertainty product.

For bigger particles $\Delta x \cdot \Delta v \sim 0$ (negligible)

For smaller particles

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}, \quad \begin{matrix} \Delta x = 0, \Delta v \rightarrow \infty \\ \Delta v = 0, \Delta x \rightarrow \infty \end{matrix}$$

other forms

$$p = mv = m \left(\frac{v}{t} \right) \times t$$

$$p = ma \times t$$

$$p = F \times t$$

$$n \cdot p = \underline{F \cdot x} \times t$$

$$n \cdot p = E \times t$$

$$\Delta n \cdot \Delta p = \Delta E \times \Delta t \quad \left(\begin{array}{l} \text{in terms of energy \& time} \end{array} \right)$$

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

⇒ Bohr picture of fixed orbit & fixed velocity is no longer applicable.

⇒ best we can think of is probability of locating an electron with a probable velocity in a given region of space at a given time.

Examples

$$(2) \quad (a) \quad \Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot 1 \times 10^{-3} \text{ g cm sec}^{-1} \geq \frac{6.626 \times 10^{-27} \text{ erg-s}}{4 \times 3.14}$$

$$\Delta x \geq 0.527 \times 10^{-24} \text{ cm}$$

Example 1. Calculate the wavelength associated with an electron moving with a velocity of 10^{10} cm per sec.

Solution: Mass of the electron = 9.10×10^{-28} g
Velocity of electron = 10^{10} cm per sec
 $h = 6.62 \times 10^{-27}$ erg - sec

According to de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}}{9.10 \times 10^{-28} \times 10^{10}} \\ = 7.22 \times 10^{-10} \text{ cm} \\ = 0.0722 \text{ \AA}$$

Example 2. Calculate the uncertainty in the position of a particle when the uncertainty in momentum is:

(a) 1×10^{-3} g cm sec $^{-1}$ (b) zero.

Solution: (a) Given,

$$\Delta p = 1 \times 10^{-3} \text{ g cm sec}^{-1} \\ h = 6.62 \times 10^{-27} \text{ erg - sec} \\ \pi = 3.142$$

According to uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

So,
$$\Delta x \geq \frac{h}{4\pi \Delta p} = \frac{6.62 \times 10^{-27}}{4 \times 3.142} \times \frac{1}{10^{-3}} \\ = 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of Δx will be infinity.

Example 3. Calculate the momentum of a particle which has a de Broglie wavelength of 2.5×10^{-10} m.

($h = 6.6 \times 10^{-34}$ kg m 2 s $^{-1}$)

Solution: Momentum = $\frac{h}{\lambda}$ (using de Broglie equation)

$$= \frac{6.6 \times 10^{-34}}{2.5 \times 10^{-10}} \\ = 2.64 \times 10^{-24} \text{ kg m sec}^{-1}$$

Example 4. What is the mass of a photon of sodium light with a wavelength of 5890 Å?

($h = 6.63 \times 10^{-27}$ erg - sec, $c = 3 \times 10^{10}$ cm/sec)

Solution: $\lambda = \frac{h}{mc}$

or $m = \frac{h}{\lambda c}$

So,
$$m = \frac{6.63 \times 10^{-27}}{5890 \times 10^{-8} \times 3 \times 10^{10}} \\ = 3.752 \times 10^{-33} \text{ g}$$

Example 5. The uncertainty in position and velocity of a particle are 10^{-10} m and 5.27×10^{-24} m s $^{-1}$ respectively. Calculate the mass of the particle. ($h = 6.625 \times 10^{-34}$ J - s)

Solution: According to Heisenberg's uncertainty principle,

$$\Delta x \cdot m \Delta v = \frac{h}{4\pi}$$

or

$$m = \frac{h}{4\pi \Delta x \cdot \Delta v} \\ = \frac{6.625 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 5.27 \times 10^{-24}} \\ = 0.099 \text{ kg}$$

Example 6. Calculate the uncertainty in velocity of a cricket ball of mass 150 g if the uncertainty in its position is of the order of 1 Å ($h = 6.6 \times 10^{-34}$ kg m 2 s $^{-1}$).

Solution: $\Delta x \cdot m \Delta v = \frac{h}{4\pi}$

$$\Delta v = \frac{h}{4\pi \Delta x \cdot m} \\ = \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 0.150} \\ = 3.499 \times 10^{-24} \text{ ms}^{-1}$$

Example 7. Find the number of waves made by a Bohr electron in one complete revolution in the 3rd orbit. (IIT 1994)

Solution: Velocity of the electron in 3rd orbit = $\frac{3h}{2\pi mr}$

where, m = mass of electron and r = radius of 3rd orbit.

Applying de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{h}{m} \times \frac{2\pi mr}{3h} = \frac{2\pi r}{3}$$

$$\text{No. of waves} = \frac{2\pi r}{\lambda} = \frac{2\pi r}{\frac{2\pi r}{3}} \times 3 = 3$$

Example 8. The kinetic energy of an electron is 4.55×10^{-25} J. Calculate the wavelength, ($h = 6.6 \times 10^{-34}$ J-sec, mass of electron = 9.1×10^{-31} kg).

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

or $\frac{1}{2} \times 9.1 \times 10^{-31} \times v^2 = 4.55 \times 10^{-25}$

or $v^2 = \frac{2 \times 4.55 \times 10^{-25}}{9.1 \times 10^{-31}}$

$v = 10^3 \text{ ms}^{-1}$

Applying de Broglie equation,

$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} = 0.72 \times 10^{-6} \text{ m}$

Example 9. The speeds of the Fiat and Ferrari racing cars are recorded to $\pm 4.5 \times 10^{-4} \text{ m sec}^{-1}$. Assuming the track distance to be known within $\pm 16 \text{ m}$, is the uncertainty principle violated for a 3500 kg car?

Solution: $\Delta x \Delta v = 4.5 \times 10^{-4} \times 16$

$= 7.2 \times 10^{-3} \text{ m}^2 \text{ sec}^{-1} \quad \dots (i)$

$\frac{h}{4\pi m} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 3500} \quad \dots (ii)$

$= 1.507 \times 10^{-38}$

Since, $\Delta x \Delta v \geq h/4\pi m$

Hence, Heisenberg uncertainty principle is not violated.

Example 10. Alveoli are tiny sacs in the lungs whose average diameter is $5 \times 10^{-5} \text{ m}$. Consider an oxygen molecule ($5.3 \times 10^{-26} \text{ kg}$) trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule.

Solution: Uncertainty in position $\Delta x = \text{Diameter of Alveoli} = 5 \times 10^{-5} \text{ m}$

$\Delta x \Delta v \geq \frac{h}{4\pi m}$

$\Delta v \geq \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 5.3 \times 10^{-26} \times 5 \times 10^{-5}}$

$\Delta v \approx 1.99 \text{ m/sec}$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. If the kinetic energy of an electron is increased 4 times, the wavelength of the de Broglie wave associated with it would become:

- (a) 4 times (b) 2 times
(c) $\frac{1}{2}$ times (d) $\frac{1}{4}$ times

[Ans. (c)]

[Hint: $\lambda = \frac{h}{\sqrt{2Em}}$, where, $E = \text{kinetic energy}$

When, the kinetic energy of electron becomes 4 times, the de Broglie wavelength will become half.]

2. The mass of photon having wavelength 1 nm is:

- (a) $2.21 \times 10^{-35} \text{ kg}$ (b) $2.21 \times 10^{-33} \text{ g}$
(c) $2.21 \times 10^{-33} \text{ kg}$ (d) $2.21 \times 10^{-26} \text{ kg}$

[Ans. (c)]

[Hint: $\lambda = \frac{h}{mc}$

$m = \frac{h}{\lambda c} = \frac{6.626 \times 10^{-34}}{1 \times 10^{-9} \times 3 \times 10^8} = 2.21 \times 10^{-33} \text{ kg}$

3. The de Broglie wavelength of 1 mg grain of sand blown by a 20 ms^{-1} wind is:

- (a) $3.3 \times 10^{-29} \text{ m}$ (b) $3.3 \times 10^{-21} \text{ m}$
(c) $3.3 \times 10^{-49} \text{ m}$ (d) $3.3 \times 10^{-42} \text{ m}$

[Ans. (a)]

[Hint: $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{1 \times 10^{-6} \times 20} = 3.313 \times 10^{-29} \text{ m}$

4. In an atom, an electron is moving with a speed of 600 m sec^{-1} with an accuracy of 0.005%. Certainty with which the position of the electron can be located is:

($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$, mass of electron = $9.1 \times 10^{-31} \text{ kg}$)

(AIEEE 2009)

- (a) $1.52 \times 10^{-4} \text{ m}$ (b) $5.1 \times 10^{-3} \text{ m}$
(c) $1.92 \times 10^{-3} \text{ m}$ (d) $3.84 \times 10^{-3} \text{ m}$

[Ans. (c)]

[Hint: Accuracy in velocity = 0.005%

$\Delta v = \frac{600 \times 0.005}{100} = 0.03$

According to Heisenberg's uncertainty principle,

$\Delta x \Delta v \geq \frac{h}{4\pi m}$

$\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03}$
 $= 1.92 \times 10^{-3} \text{ m}$

5. Velocity of de Broglie wave is given by:

- (a) $\frac{c^2}{v}$ (b) $\frac{h\nu}{mc}$ (c) $\frac{mc^2}{h}$ (d) $v\lambda$

[Ans. (b)]

[Hint: $\lambda = \frac{h}{mv} = \frac{h}{p}$

$p = \frac{h}{\lambda}$
 $mv = \frac{h\nu}{c}$
 $v = \frac{h\nu}{mc}$

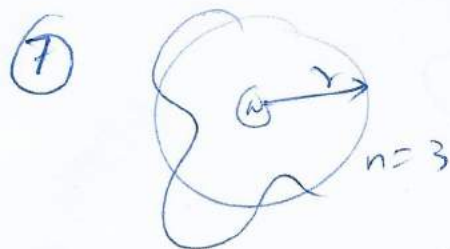
$$\textcircled{5} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

$$10^{-10} \times 5.27 \times 10^{-24} \geq \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times m}$$

$$m = \frac{6.625 \times 10^{-34}}{10^{-10} \times 5.27 \times 10^{-24} \times 4 \times 3.14} = 0.099 \text{ Kg}$$

$$\textcircled{6} \quad 1 \times 10^{-10} \times \Delta v = \frac{6.6 \times 10^{-34} \times 10^3}{4 \times 3.14 \times 150}$$

$$\Delta v = 3.499 \times 10^{-24} \text{ m s}^{-1}$$



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

$$mvr = \frac{nh}{2\pi} \quad n=3$$

$$\rightarrow \frac{2\pi r}{\lambda} = ?$$

$$2\pi r = \frac{nh}{mv}$$

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

$$\frac{2\pi r}{\lambda} = n = 3$$

$$\textcircled{8} \quad \lambda = \frac{h}{\sqrt{2mk.E.}} = \frac{6.6 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 4.55 \times 10^{-25}}} = 0.72 \times 10^{-6} \text{ m}$$

$$\textcircled{9} \quad \Delta x = \pm 16 \text{ m}, \quad \Delta v = \pm 4.5 \times 10^{-4}$$

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

$$16 \times 4.5 \times 10^{-4} \geq \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 3500}$$

$$\downarrow \qquad \qquad \qquad \downarrow$$

$$7.2 \times 10^{-3} > 1.507 \times 10^{-38}$$

$$\textcircled{5} \quad \lambda = \frac{h}{mv} \quad \text{Q}$$

$$v = \frac{h}{m\lambda}$$

$$c = v\lambda$$

$$= \frac{h\cancel{v}}{mc} \quad \checkmark$$

Probability

Atomic orbital

Wave - mechanical model of Atom

→ Based on wave as well as particle nature of e^-

→ Proposed by Erwin Schrodinger

→ This model describes the e^- as a three dimensional wave in the electronic field of positively charged nucleus

→ Schrodinger Equation

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (E - V) \psi = 0$$

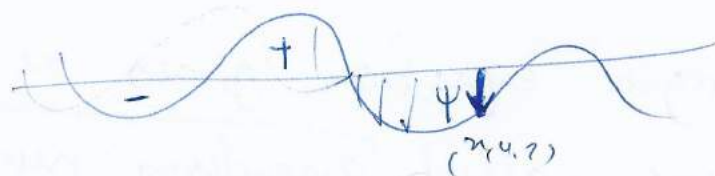
$x, y, z \rightarrow$ cartesian coordinates of e^-

$m \rightarrow$ mass of e^-

$E \rightarrow$ total energy of e^-

$V \rightarrow$ Potential energy of e^-

ψ (psi) = wave function of the e^-



Significance of ψ (wave function)

→ The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y, z

→ The main aim of Schrodinger's equation is to give a solution for the probability approach.

Ψ → + or -ve

Probability is always +ve

hence Ψ^2 is used, $\Psi^2 \rightarrow +ve$

Significance of Ψ^2

→ Ψ^2 is the probability factor.

→ It describes the probability of finding an e^- within a small space.

→ The space in which there is maximum probability of finding an e^- is termed as orbital.

→ Schrodinger's equation gives a set of numbers called quantum numbers, which describe energies of the electron in atoms, information about shape & orientation of most probable distribution of e^- around the nucleus.

Quantum Numbers (Four types)

(I) Principal Quantum number (n)
(orbit number)

→ Given by Bohr

→ represents the name, size & energy of the shell to which e^- belongs

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

K L M - - -

→ $E_n = -13.6 \times \frac{Z^2}{n^2}$, $E_1 < E_2 < E_3 \dots$

→ Higher is the n , greater is the distance of e^- from nucleus

$$r_1 < r_2 < r_3 < \dots$$

→ maximum no. of e^- in a shell $= 2n^2$

→ $mvr = \frac{nh}{2\pi}$

↑
angular momentum