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# ATOMIC MOLECULAR PHYSICS


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# Chapter 1

# Bohr's Model of Atom and Finite Mass Correction

**Atomic Physics -** Branch of Physics that deals with the Atom, its energy levels & its Interaction with electric &Magnetic fields.

**Rutherford Model –** This model suggests that the electrons are revolving around a very dense positive charged entity (Nucleus).

**Drawbacks of Rutherford Model –**

**(1) Instability of atom -** $e^-$ while revolving in a circular orbit is accelerated so, it must radiate out energy and must fall into the nucleus.

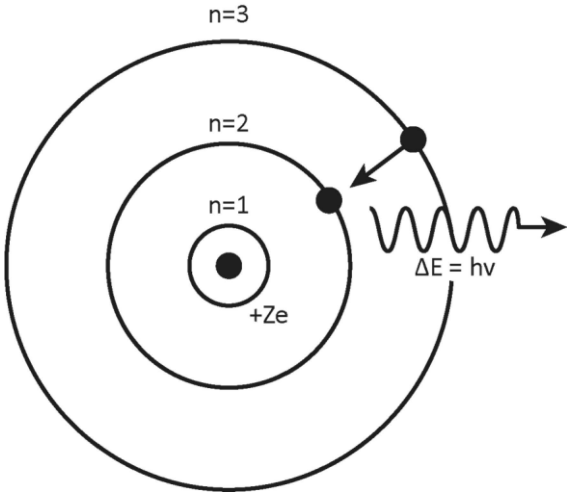
**(2) Continuous Spectrum –** According to the theory that accelerated charge radiates, there should be a continuous spectrum but in actual, energy levels are discrete.

**Bohr's Model (Applicable for Single $e^-$ species) –**

(1) $e^-$ revolves in circular orbits.

(2) These circular orbits are stationary orbits (which have fixed energy) and while revolving in such circular stationary orbits, $e^-$ does not emit radiation.

(3) The radiation is emitted only when an $e^-$ from excited state makes a transition to a lower energy state. Radiation energy corresponds to the energy gap b/w the two states.




(4) Only those orbits are allowed for which angular momentum of $e^-$ is integral multiple of $h/2\pi$

$m\,v\,r = \frac{n\,h}{2\pi}$ (Quantisation of Angular momentum)

**Derivations (Classical approach) -**

$\frac{KZe^2}{r^2} = \frac{mv^2}{r}$ (K= 1/4πϵ$_0$)

$\Rightarrow r = \frac{KZe^2}{mv^2}$ (1)

Also , $mvr = \frac{nh}{2\pi} \Longrightarrow r = \frac{nh}{2\pi\, mv}$ (2)

(1) = (2),

$\frac{KZe^2}{m\,v^2} = \frac{nh}{2\pi\, m\, v}$

$v = \frac{Ze^2}{2\epsilon_0 n h}$

For hydrogen, $Z = 1, n = 1$

$\Rightarrow v = \frac{e^2}{2\epsilon_0 h} = 2.18 \times 10^6\ m/s$

$v = \frac{e^2}{2\epsilon_0 h}\left(\frac{Z}{n}\right)$

$\Rightarrow v = 2.18 \times 10^6\ \left(\frac{Z}{n}\right)$

v $\alpha$ Z/n and velocity is independent of mass

For , $Z = 1, n = 1,$

$v_1 = \frac{e^2}{2\epsilon_0 h} = \frac{C}{137} = \alpha\ (fine\ structure\ constant\ tells\ about\ the\ strength\ of\ electromagnetic\ interaction.)$

$\alpha = \frac{C}{137}$ (Fine Structure constant is a dimensionless quantity)

Radius - $r = \frac{nh}{2\pi mv} = \frac{nh}{2\pi m\left(\frac{ze^2}{2\epsilon_0 nh}\right)} = \frac{\epsilon_0 n^2 h^2}{\pi m e^2 Z}$

$r = \left(\frac{\epsilon_0 h^2}{\pi m e^2}\right)\left(\frac{n^2}{z}\right)$

& $r\ \alpha \frac{1}{m}$ ⇒ more is the mass, smaller is the radius of orbit for eg. For $\mu = 200\ m_e . r_e > r_\mu$ because, $m_\mu > m_e$.

→ Kinetic energy - $K.E = \frac{1}{2}\ mv^2 = \frac{1}{2}m\ \left(\frac{Ze^2}{2\epsilon_0 nh}\right)^2$

$K.E = \frac{m\ z^2\ e^4}{8\epsilon_0{}^2 n^2 h^2} = \frac{me^4}{8\epsilon_0{}^2 h^2}\left(\frac{Z^2}{n^2}\right)$

$\Rightarrow K.E\ \alpha \frac{Z^2}{n^2}$

→ Potential energy - P.E = $-\frac{k\ Z\ e^2}{r} = -\frac{1}{4\ \pi\epsilon_0}\frac{ze^2}{\left(\frac{\epsilon_0 n^2 h^2}{\pi m e^2 z}\right)}$

$= \frac{-Ze^2 \times \pi\ me^2 Z}{4\pi\epsilon_0{}^2\ n^2 h^2}$

P.E = $-\frac{me^4\ Z^2}{4\epsilon_0{}^2 n^2 h^2}$ ; $P.E\ \alpha\ \frac{z^2}{n^2}$

→ Total energy

T.E = PE + K.E

$= \frac{-me^4 z^2}{4\ \epsilon_0{}^2 n^2 h^2} + \frac{me^4 z^2}{8\epsilon_0{}^2 n^2 h^2} = \frac{-me^4 z^2}{8\epsilon_0{}^2 n^2 h^2}$

$\Rightarrow T.E\ \alpha \frac{Z^2}{n^2}$

$\Rightarrow \#\ K.E = -T.E$

$\#\ P.E = -K.E \times 2\ \ or\ \ K.E = -\ {}^1/_2\ P.E.$

$T.E = -\frac{me^4 z^2}{8\epsilon_0{}^2 n^2 h^2} = -13.6\frac{z^2}{n^2}\ eV$

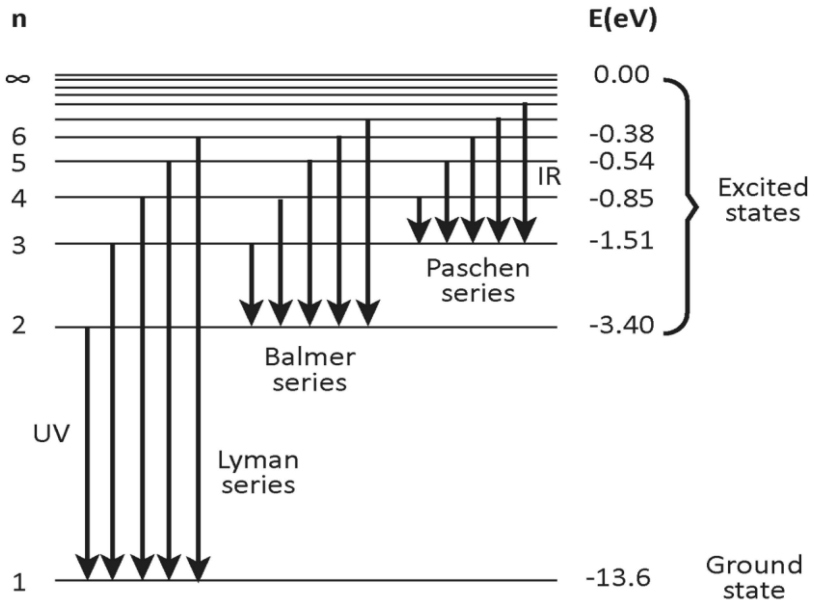
$T.E = -13.6\ \left(\frac{z^2}{n^2}\right)\ eV$

$E_1 = -\frac{13.6\ z^2}{n_1^2} eV, E_2 = -\frac{13.6\ z^2}{n_2^2} eV$

$\Rightarrow h\nu = E_2 - E_1 = +13.6\ z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV$

$\Rightarrow \Delta E = \frac{hc}{\lambda} = +13.6\ z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV$

**HYDROGEN SPECTRUM –**




Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.

$n_1 = 1, n_2 = n; n_2 > 1$ → Lyman series, UV region
$n_1 = 2, n_2 = n; n > 2$ → Balmer series, Visible region
$n_1 = 3, n_2 = n; n > 3$ → Paschen series, Infra Red region
$n_1 = 4, n_2 = n; n > 4$ → Brackett series, Infra Red region
$n_1 = 5, n_2 = n; n > 5$ → P-Fund series, Infra Red region
For $n_1 = 1, n_2 = 2$,
$\Delta E = +13.6\left(1 - {}^{1}/_{4}\right)eV$
$= +13.6 \times {}^{3}/_{4}\, eV$
$\Delta E = +10.2\ eV$

**Maximum and Minimum Wavelength for a series in Hydrogen Spectrum:-**

For Lymen series, minimum wavelength (means maximum energy difference) when $n_1 = 1$ & $n_2 = \infty$
$\Rightarrow \Delta E = 13.6\left(1 - \frac{1}{\infty}\right) = 13.6\ eV$
$\Rightarrow \lambda_{min} = \frac{12400\ eV-\text{Å}}{13.6\ eV} = 911.76\ \text{Å}$
For $\lambda_{max}$ (means minimum energy difference) , $n_1 = 1, n_2 = 2$
$\Delta E = 13.6\left(1 - {}^{1}/_{4}\right) = 13.6 \times {}^{3}/_{4}$
$= 10.2\ eV$
$\lambda_{max} = \frac{12400\ eV-\text{Å}}{10.2\ eV} = 1215.68\ \text{Å}$
We know, $E_1 = \frac{-mz^2e^4}{8\epsilon_0^2 n_1^2 h^2}$
And, $E_2 = \frac{-mz^2e^4}{8\epsilon_0^2 n_2^2 h^2}$
$\frac{hc}{\lambda} = \Delta E = \frac{mz^2e^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$
$\Rightarrow \frac{1}{\lambda} = \frac{mz^2e^4}{8\epsilon_0{}^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\frac{1}{\lambda} = R_\infty z^2 \left({}^1/_{n_1^2}, -{}^1/_{n_2^2}\right)$ $\quad (R_\infty = \frac{me^4}{8\epsilon_0^2 h^3 c} = = 1.097 \times 10^7\ m^{-1} =$ Rydberg constant)

For Hydrogen, $z = 1$

For $\lambda_{min}\ (\Delta E_{max})\ ; n_1 = 1, n_2 = \infty$

$\frac{1}{\lambda_{min}} = R_\infty (1 - 0)$

$\Rightarrow \lambda_{min} = \frac{1}{R_\infty}$

For $\lambda_{max}\ (\Delta E_{min})\ ; n_1 = 1, n_2 = 2$

$\frac{1}{\lambda_{max}} = R_\infty \left(1 - {}^1/_4\right) \Rightarrow \lambda_{max} = \frac{4}{3R_\infty}$

**FINITE MASS CORRECTION –**

If the mass of nucleus is comparable to the particle's mass which is revolving around the nucleus then we have to make the correction in Bohr's model.

Replace $m \rightarrow \mu$

$\mu = \frac{m_N m_e}{m_N + m_e}$,

If $m_N \gg m_e \Rightarrow m_N + m_e \approx m_N$

$\mu = \frac{m_N m_e}{m_N} \Rightarrow \mu = m_e$

$\Rightarrow \frac{1}{\lambda} = \frac{\mu z^2 e^4}{8\epsilon_0{}^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{m_N \times m_e}{m_N + m_e} \underbrace{\frac{z^2 e^4}{8\epsilon_0{}^2 h^3 c}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\Rightarrow \frac{1}{\lambda} = \frac{m_N}{m_N + m_e} R_\infty z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\frac{1}{\lambda} = \frac{R_\infty z^2}{\left(1 + \frac{m_e}{m_N}\right)}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \Rightarrow \frac{1}{\lambda} = R z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$R = \frac{R_\infty}{1 + \frac{m_e}{m_N}} \Rightarrow \frac{R_\infty}{R} = 1 + \frac{m_e}{m_N} > 1$

$\Rightarrow R_\infty > R$

$\Rightarrow \lambda_\infty < \lambda$

$\Rightarrow \nu_\infty > \nu$

Thus, we can say that the whole spectrum will shift towards lower frequencies when the mass of the nucleus is considered to be finite as compared to the mass of the specie revolving about it.

**Example** - Find Time period, frequency angular momentum, magnetic moment dependency on z and n.

**Solution:**

(1) $T = \frac{2\pi r}{v}\ \alpha\ \frac{n^3}{z^2}$

(2) $v = \frac{1}{T} \Rightarrow v\ \alpha\ \frac{z^2}{n^3}$

(3) $mvr = \frac{nh}{2\pi}\ \alpha\ n$

(4) $\mu = IA = \frac{q}{T}\pi r^2\ \alpha \left(\frac{n^2}{z}\right)^2 \left(\frac{z^2}{n^3}\right)$

$\Rightarrow \mu\ \alpha\ n$

**Drawbacks or Bohr's Model –**

(1) Valid only for single $e^-$ species.

(2) Fine structure and hyperfine structure was not explained by Bohr's model.

(3) Cannot explain the splitting of lines in electric and magnetic field.

(4) Wave nature of $e^-$ was not considered.

**PREVIOUS YEAR QUESTIONS**

**[CSIR NET/JRF DEC-2011]**

1. Given that the ground state energy of the hydrogen atom is –13.6 $eV$, the ground state energy of positronium (which is a bound state of an electron and a positron) is

(a) + 6.8 eV (b) – 6.8 eV

(c) – 13.6 eV (d) – 27.2 eV

**Solution: (b)**

The energy of hydrogen atom in n[th] state is -

$E_n = \frac{-\mu e^4 Z^2}{8\epsilon_0{}^2 n^2 h^2}$

Reduced mass of positronium atom is given by –

$\mu = \frac{m_e \times m_e}{m_e + m_e} = \frac{1}{2} m_e$

So, energy of positronium atom in ground state is $\frac{1}{2}$ times the energy of Hydrogen atom in ground state.

$E = -6.8\ eV$

**[CSIR NET/JRF DEC-2011]**

2. An atom of mass M can be excited to a state of mass $(M + \Delta)$ by photon capture. The frequency of a photon which can cause this transition is

(a) $\frac{\Delta c^2}{2h}$ (b) $\frac{\Delta c^2}{h}$

(c) $\frac{\Delta^2 c^2}{2Mh}$ (d) $\frac{\Delta c^2}{2Mh}(\Delta + 2M)$

**Solution: (d)**

$Mc^2 + hv = [(M+\Delta)^2 c^4 + p^2 c^2]^{1/2}$

(Conservation of Energy) and $\frac{hv}{c} = p$ (Conservation of momentum)

$M^2 c^4 + h^2 v^2 + 2Mc^2 hv = M^2 c^4 + \Delta^2 c^4 + 2M\Delta c^4 + h^2 v^2$

$\Rightarrow 2Mc^2 hv = \Delta^2 c^4 + 2M\Delta c^4$

$\Rightarrow 2Mc^2 hv = 2M\Delta c^4 \left(1 + \frac{\Delta}{2M}\right)$

$\Rightarrow v = \frac{\Delta c^2}{h}\left(1 + \frac{\Delta}{2M}\right)$

$\Rightarrow v = \frac{\Delta c^2}{2Mh}(\Delta + 2M)$

**[CSIR NET/JRF JUNE-2013]**

3. A muon ($\mu^-$) from cosmic rays is trapped by a proton to form a hydrogen-like atom. Given that a muon is approximately 200 times heavier than an electron, the longest wavelength of the spectral line (in the analogue of the Lyman series) of such an atom will be

(a) 5.62 Å (b) 6.67 Å

(c) 3.75 Å (d) 13.3 Å

**Solution: (b)**

The reduced mass for muonic atom is, $\mu = \frac{m_\mu m_p}{m_\mu + m_p} = 180 m_e$

$E_n = \left(\frac{\mu}{m_e}\right)\frac{E_1}{n^2} = 180\frac{E_1}{n^2}$

We know, $E_1 = -13.6eV$

$n = 1, E'_1 = 180E_1$ (Ground state for muonic atom)

$n = 2, E'_2 = 45E_1$

(First excited state of muonic atom)

The longest wavelength of the photon corresponds to the minimum energy difference **i.e**. from $n = 1$ to $n = 2$

The energy difference between first excited and ground state is

$\Delta E = E'_2 - E'_1 = -135E_1 = 1836eV$

$= 2938 \times 10^{-19} J$

In term of wavelength

$\Delta E = hv = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{2938 \times 10^{-19}}$

$= 6.67 \times 10^{-10} m = 6.67$ Å

**[CSIR NET/JRF DEC-2015]**

4. The first ionization potential of K is 4.34 eV, the electron affinity of Cl is 3.82 eV and the equilibrium separation of KCl is 0.3 nm. Then energy required to dissociate a KCl molecule into a K and a Cl atom is

(a) 8.62 eV (b) 8.16 eV

(c) 4.28 eV (d) 4.14 eV

**Solution: (c)**

The dissociation energy of KCl is –

$V = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r_{12}} = (9 \times 10^9)\frac{(1.6\times10^{-19})^2}{0.3\times10^{-9}} = 7.7 \times 10^{-19} J = 4.79\ eV$ (Given by Electrostatic potential energy)

To convert K into $K^+$, the dissociation energy is 4.34 eV which is to be given

And energy released in converting Cl to $Cl^-$ is 3.82 eV.

So the excess energy is 4.34 eV-3.82 eV=0.52 eV and this is utilized for dissociation

So, required dissociation energy = $4.79\ eV - 0.52 = 4.28\ eV$

**[CSIR NET/JRF JUN2020]**

5. The wavelength of the first Balmer line of hydrogen is 656nm. The wavelength of the corresponding line for a hydrogenic atom with Z= 6 and nuclear mass of 19.92 X10$^{-27}$ kg is

(a) 18.2nm (b) 109.3nm

(c) 143.5nm (d) 393.6nm

**Solution: (a)**

First Balmer line in Hydrogen atom is given by –

$\frac{1}{\lambda_H} = R_H\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$

Or $\frac{1}{\lambda_H} = R_H\left(\frac{1}{4} - \frac{1}{9}\right)$ (Eq.-1)

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

Similarly,

$\frac{1}{\lambda_C} = \frac{5}{36}R_C Z^2$ (Eq-2)

Also,

$R_H = R_\infty\left(\frac{\mu}{m_e}\right)$

$\because \mu = \frac{m_p \times m_e}{m_p + m_e}, m_p = 1836 m_e$ (Rydberg constant varies with the finite mass of nucleus)

$\Rightarrow R_H = R_\infty\left(\frac{m_p}{m_p + m_e}\right) = R_\infty\left(\frac{1836}{1837}\right)$

Where, $R_\infty$ is the Rydberg constant for infinite nuclear mass.

$R_C = R_\infty\left(\frac{\mu}{m_e}\right)$

$\because \mu = \frac{6m_p \times m_e}{6m_p + m_e}, m_p = 1836 m_e$

$\Rightarrow R_C = R_\infty\left(\frac{6m_p}{6m_p + m_e}\right) = R_\infty\left(\frac{6\times1836}{11017}\right)$

(On dividing eq. – 2 by eq. – 1)

$\Rightarrow \frac{1}{\lambda_C} = \frac{1}{\lambda_H R_H} R_C Z^2$

$\lambda_C = \frac{\lambda_H R_H}{R_C Z^2}$

Given, $Z = 6$ and $\lambda_H = 656\ nm$

$\Rightarrow \lambda_C = \frac{1836}{1837} \times \frac{11017}{6\times1836} \times \frac{656}{6^2} nm$

$\Rightarrow \lambda_C = 18.2nm$

**(GATE - 2017)**

6. Positronium is an atom made of an electron and a positron. Given the Bohr radius for the ground state of the Hydrogen atom to be 0.53 Angstroms, the Bohr radius for the ground state of positronium is.....Angstroms. (Up to two decimal places).

**Solution:**

The Bohr radius for ground state of positronium is

$= r_n = a_0\left(\frac{me}{\mu}\right)$

$\mu =$ reduced mass $= \frac{m_e m_e}{m_e + m_e} = \frac{m_e^2}{2m_e} = \frac{m_e}{2}$

$\Rightarrow r_n = 2a_0$

$r_n = 2 \times 0.53 = 1.06\ \text{Å}$

## PRACTICE QUESTIONS –

1. A positronium atom is a system consisting of a positron and an electron revolving about their common centre of mass, then the relation between radius of positronium atom $R_P$ and $R_H$ is :

(a) $R_P = 2\ R_H$ (b) $2\ R_P = R_H$

(c) $R_P = R_H$ (d) $R_P = 3\ R_H$

2. The relation between velocity of electron in ground state in a positronium atom $V_P$ and hydrogen atom $V_H$ is:

(a) $V_P = 4\ V_H$ (b) $V_P = 2\ V_H$

(c) $V_P = \frac{1}{2}V_H$ (d) $V_P = V_H$

3. The wavelength of first line of Balmer series of positronium atom is:

(a) 686 nm (b) 918 nm

(c) 1312 nm (d) 1826 nm

4. Which of the following statement is correct about binding energy of positronium atom $E_P$ and hydrogen atom $E_H$ :

(a) $E_P > E_H$ (b) $E_P < E_H$

(c) $E_P = E_H$ (d) None of the above

5. The energy of a positronium atom in second excited state is :

(a) -1.51 eV (b) -0.75 eV

(c) -3.4 eV (d) -1.7 eV

6. Suppose $\lambda_H$ be the spectral wavelength of hydrogen atom and $\lambda_P$ be the spectral wavelength of the positronium atom. Then which of the following statements is true?

(a) $\lambda_P = \frac{1}{2}\lambda_H$ (b) $\lambda_P = \lambda_H$

(c) $\lambda_P = 2\lambda_H$ (d) $\lambda_P = 4\lambda_H$

7. The relation between Rydberg constant of a positronium atom $R_P$ and of Hydrogen atom $R_H$ is :

(a) $R_P = \frac{1}{2}R_H$ (b) $R_P = \frac{3672}{1837}R_H$

(c) $R_P = \frac{1836}{1837}R_H$ (d) $R_P = \frac{1837}{3672}R_H$

8. The shortest wavelength for Lyman series of a positronium atom is :

(a) 91.1 nm (b) 45.5 nm

(c) 182.2 nm (d) 22.75 nm

9. Energy of a photon making direct transition from an excited state n=5 of a positronium atom to ground state is:

(a) 6.256 eV (b) 13.056 eV

(c) 6.528 eV (d) 13.328 eV

10. Atomic radius of a positronium atom in first excited state is:

(a) 4.24 Å (b) 0.265 Å

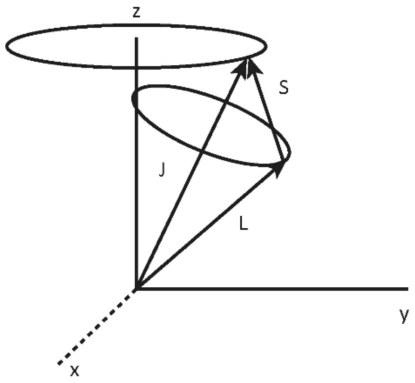
(c) 2.12 Å (d) 0.53 Å

| ANSWER KEY | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
| a | d | c | b | b | c | d | c | c | a |

# Chapter 2

# Vector Model of Atom

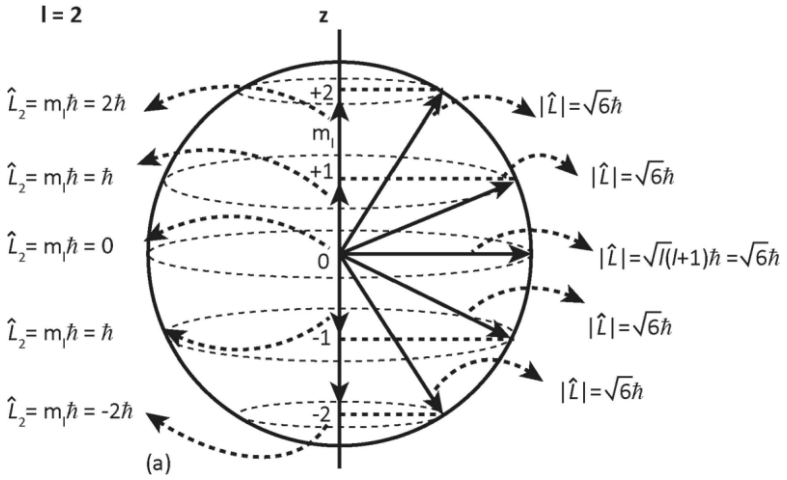
In bohr's model, spin was not considered. In Vector model of atom, spin was considered along with the orbital motion of electron. Here, there are two angular momentum vectors, one is orbital angular momentum and the other is spin angular momentum. Their resultant gives the total angular momentum vector **i.e.** J




$\vec{L}$ → orbital angular momentum

$\vec{S}$ → spin angular momentum

$\vec{J}$ → total angular momentum




$\vec{L} = \sqrt{l(l+1)}\hbar$ l → Orbital quantum no.

$\vec{S} = \sqrt{s(s+1)}\hbar$ s → Spin quantum no.

$\vec{J} = \sqrt{j(j+1)}\hbar$ j → Total quantum no.

$\vec{J}$ *is the vector sum of* $\vec{L}$ *and* $\vec{S}$.

Now we know , $L_z = m_l\hbar$

$m_l = -l$ to $l$

For Example , $l = 1$ (P Orbital)

$m_l = -1, 0, 1$

$\Rightarrow L_z = -\hbar, 0, \hbar$

For $l = 2, m_l = -2, -1, 0, 1, 2$

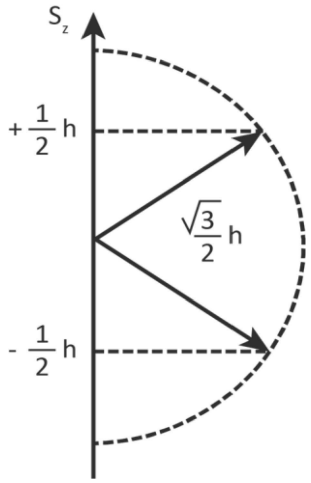
$\Rightarrow L_z = -2\hbar, -\hbar, 0, \hbar, 2\hbar$

Similarly,

$S_z = m_s\hbar$

$m_s = \pm {}^1/_2$

$\Rightarrow S_z = + {}^\hbar/_2 - {}^\hbar/_2$




Similar is for $J_z$,

$m_j = -j$ to $j$

j = $|l - s|$ to $|l + s|$

Therefore, these angular momenta will precise about the magnetic field only at the certain values of its z-component ( $L_z$, $S_z$ and $J_z$ ). This is called the Quantisation of Angular Momentum.

