

Bismah Noor

Batch I FSc

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# ATOMIC SPECTRA

→ Atomic Spectra: "Spectrum of frequencies of electromagnetic radiation emitted or absorbed during transitions of electrons between energy levels within an atom is called atomic spectra."

## Line Emission Spectrum vs. Line Absorption Spectrum

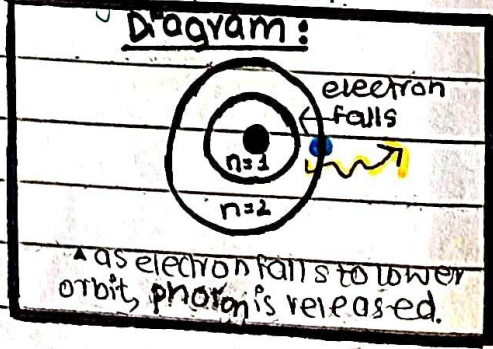
Spectrum of atoms	
(i) Definition :	
Spectrum of electromagnetic radiation emitted by a substance	Spectrum obtained by transmitting electromagnetic radiation through substance
(ii) Production	
Produced when atoms release energy	Produced when atoms absorb energy
(iii) Depiction	
Show colored lines	Show dark lines or gaps
(iv) Given when	
Given when an excited atom is excited and de-excited.	Given when atom obtains higher energy
(v) Accounts for	
wavelengths abs by a substance	wavelengths absorbed by a substance

## → Spectrum of hydrogen atom:

When hydrogen gas is heated in a sealed container atoms absorb energy and electrons move to higher levels. As electrons return to lower energy levels, they emit photons with specific energies creating a spectrum.

→ Spectral lines of Hydrogen: Spectral lines of hydrogen are grouped into various series each corresponding to electron transitions between different energy levels.

Prominent series include;



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- **Lyman Series**: Transitions to  $n=1$  energy level. Lie in **UV** part of spectrum
- **Balmer Series**: Transitions to  $n=2$  energy level. Lie in **visible** region
- **Paschen series**: Transitions to  $n=3$  energy level. Lie in **infrared** region
- **Bracket series**: Transitions to  $n=4$  energy level. Lie in **infrared** region
- **Pfund series**: Transitions to  $n=5$  energy level. Lie in **infrared** region

→ **Mathematically**:

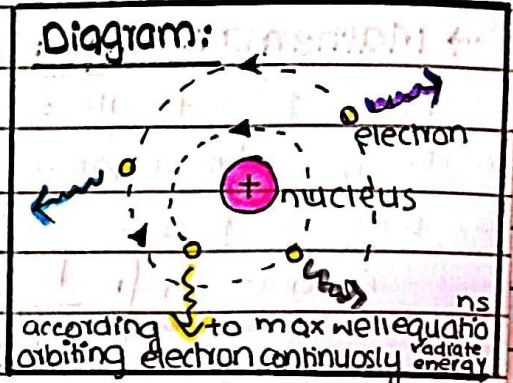
General mathematical form is called **Rydberg formula** and is given as

$$\frac{1}{\lambda_n} = R_H \left( \frac{1}{p^2} - \frac{1}{n^2} \right) \text{ where } R = 1.0974 \times 10^7 \text{ m}^{-1}, n = p+1, p+2, p+3 \dots$$

and  $p = 1, 2, 3, 4 \dots$

→ **Bohr Model of Hydrogen Atom**:

Bohr's model depicts an acceptable picture of atom which covers the defects of Neil Bohr's model. This model explains different states of an atom and why an atom doesn't collapse due to spin of electrons continuously.



→ **Quantization of angular momentum**: The angular momentum of electron has magnitude which is only integral multiple of  $h$  i.e.,  $1h, 2h, 3h$  and not values like  $1.5h, 2.5h$  etc where  $h$  is plank's constant.

→ **Postulates**:

**Postulate 1** "Centripetal force required to keep the electron in the circular orbit is provided by the Coulomb force between the positively charged nucleus and negatively charged electron"

→ **Mathematically**:  $F_{\text{centripetal}} = F_{\text{Coulomb}}$  or  $m v^2 = k e^2$

**Postulate 2** "An electron revolve around the nucleus in any arbitrary circular orbit. Only those orbits are possible for which the angular momentum is the integral multiple of  $h/2\pi$ ."

→ **Mathematically**:  $L = n h$  or  $m v r = n h$   
 $2\pi$   $2\pi$

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**Postulate 3** "An electron in stable orbit does not radiate energy. Atom radiates energy only when it jumps from an allowed orbit of higher energy  $E_n$  to one of lower energy  $E_p$ . The difference in energy appears as a photon of energy  $E = hf$ ."

→ Mathematically:  $\Delta E = hf$   $hf = E_n - E_p$

## A. RADI OF QUANTIZED ORBITALS:

→ Electrons can orbit the nucleus only at certain specific distances from the nucleus. The orbits in an atom are quantized.

→ Mathematically:

From 1<sup>st</sup> postulate:  $\frac{mv^2}{r_n} = k \frac{e^2}{r_n^2}$  or  $mv^2 = k \frac{e^2}{r_n}$  (4)

From 2<sup>nd</sup> postulate:  $mv r_n = n \frac{h}{2\pi}$  or  $v = n \frac{h}{2\pi m r_n}$  (5)

Putting 5 in 4

We get  $m \left[ \frac{n h}{2\pi m r_n} \right]^2 = k \frac{e^2}{r_n}$  or  $\frac{n^2 h^2}{4\pi^2 m r_n} = k e^2$  isolating  $m$  we get

$r_n = n^2 \frac{h^2}{4\pi^2 m k e^2}$  here  $h = 6.626 \times 10^{-34}$  Js,  $\pi = 3.14$ ,  $m = 9.109 \times 10^{-31}$  kg,  $k = 8.988 \times 10^9$  Nm<sup>2</sup>/C<sup>2</sup> and  $e = 1.602 \times 10^{-19}$  C all constants can be collectively termed as  $r_0$  and can be calculated as  $r_0 = \frac{h^2}{4\pi^2 m k e^2}$  or  $r_0 = 0.53 \times 10^{-10}$  m

$n^{\text{th}}$  circular allowed orbit in the hydrogen atom can be written as

$r_n = n^2 r_0 = n^2 (0.53 \times 10^{-10} \text{ m})$

Bohr radii can be calculated as.

$r_1 = (1)^2 r_0 = 0.53 \times 10^{-10} \text{ m}$

$r_2 = (2)^2 r_0 = 2.12 \times 10^{-10} \text{ m}$

$r_3 = (3)^2 r_0 = 4.77 \times 10^{-10} \text{ m}$

## B. Energy OF ELECTRON IN QUANTIZED ORBITS:

Energy of an electron is quantized and depends on distance from nucleus. Each orbit corresponds to particular energy level for electrons.

→ **Mathematically**: Total energy  $E_n =$  sum of  $K.E$  and  $P.E$

$$E_n = K.E + P.E \quad (6) \quad \text{where}$$

$$K.E = \frac{1}{2}mv^2 \quad (4)$$

$$P.E = -k \frac{e^2}{r_n}$$

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Putting value of  $mv^2$  from (4)

$$K.E = \frac{1}{2}k \frac{e^2}{r_n} \quad (7)$$

$$P.E = -k \frac{e^2}{r_n} \quad (8)$$

Putting (7) and (8) in (6) →  $E_n = \frac{1}{2}k \frac{e^2}{r_n} - k \frac{e^2}{r_n}$  or  $E_n = -\frac{1}{2}k \frac{e^2}{r_n}$

Substituting value of  $r_n$  from (A) we get  $E_n = -\frac{1}{2}k \frac{e^2}{\left(\frac{n^2 h^2}{4\pi^2 m k e^2}\right)}$

or  $E_n = -\frac{1}{2} \times \frac{4\pi^2 m k^2 e^4}{n^2 h^2}$  hence  $E_n = -\frac{1}{n^2} \times \frac{2\pi^2 m k^2 e^4}{h^2}$

all constants:  $\pi, m = 9.109 \times 10^{-31} \text{kg}, k = 8.988 \times 10^9 \text{Nm}^2/\text{C}^2, e$  and  $h$

are collectively termed as  $E_0$  calculated as:  $E_0 = \frac{2\pi^2 m k^2 e^4}{h^2}$

or  $E_0 = 2.17 \times 10^{-18} \text{J} = 13.6 \text{eV}$

Thus  $E_n = -\frac{E_0}{n^2} = -\frac{2.17 \times 10^{-18} \text{J}}{n^2} = -\frac{13.6 \text{eV}}{n^2}$

→ **Negative sign**: Shows that electron is bound to the nucleus!

→ **Ground state**: Lowest possible energy level is called ground state.

$$E_1 = -E_0/(1)^2 = -2.17 \times 10^{-18} \text{J} = -13.6 \text{eV}$$

$$E_2 = -E_0/(2)^2 = -0.54 \times 10^{-18} \text{J} = -3.4 \text{eV}$$

$$E_3 = -E_0/(3)^2 = -0.24 \times 10^{-18} \text{J} = -1.51 \text{eV}$$

## C. HYDROGEN EMISSION SPECTRUM

The hydrogen emission spectrum consists of discrete lines corresponding to transitions between different energy levels of the hydrogen atom. These lines result from the release of energy as electrons move from higher to lower energy levels.

Transition of an electron from higher to lower orbit releases a photon of energy =  $hf$ .

→ **Mathematically**:  $hf = E_n - E_p$  (9)

Where  $E_p$  is lower state =  $-\frac{E_0}{p^2}$  and  $E_n =$  higher state =  $-\frac{E_0}{n^2}$

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Putting values in eq ①  $\rightarrow hf = \left[-\frac{E^0}{n^2}\right] - \left[-\frac{E^0}{p^2}\right]$

Since  $f = \frac{c}{\lambda}$  therefore  $\frac{hc}{\lambda} = E^0_{p^2} - E^0_{n^2}$  or  $\frac{1}{\lambda} = \frac{E^0}{hc} \left(\frac{1}{p^2} - \frac{1}{n^2}\right)$

here  $E^0 = 2.17 \times 10^{-18} \text{ J}$

$$hc = 6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m s}^{-1}$$

hence  $E^0 = 1.0974 \times 10^7 \text{ m}^{-1} = R_H$  thus

$hc$

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

This equation resembles general form

of the spectral formula for hydrogen atom. Therefore Bohr model can be used to compute energies of the wavelengths in hydrogen spectra.

## D. EXCITATION AND IONIZATION POTENTIAL

**→ Excitation energy:** "The energy required to move an electron from its ground state ( $n=1$ ) to the excited state ( $n=2,3,4,\dots$ ) is called excitation energy."

**→ Mathematically**

**First Excitation Energy  $E_1 \rightarrow E_2$**

$$E_2 - E_1 = -\frac{E^0}{2^2} - \left[-\frac{E^0}{1^2}\right] \text{ or } E_2 - E_1 = -\frac{E^0}{4} + E^0$$

$$\text{or } E_2 - E_1 = \left(-\frac{1}{4} + 1\right)E^0 \text{ hence } E_2 - E_1 = \left(\frac{3}{4}\right)E^0 \text{ or } E_2 - E_1 = \frac{3}{4}E^0$$

$$\text{since } E^0 = 2.17 \times 10^{-18} \text{ J} = 13.6 \text{ eV} \text{ therefore } E_2 - E_1 = \frac{3}{4}E^0 = 1.02 \times 10^{-18} \text{ J}$$

$$E_2 - E_1 = 10.2 \text{ eV}$$

**Second Excitation Energy  $E_1 \rightarrow E_3$**

making similar calculations putting

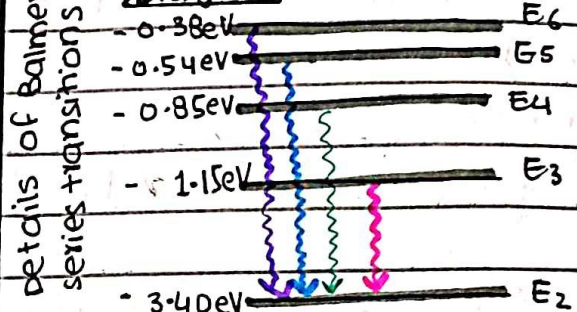
$$E_3 = \frac{E^0}{3^2} \text{ we get}$$

$$E_3 - E_1 = 12.1 \text{ eV}$$

**→ Excitation Potential:** "The potential difference required to move an electron from its ground state ( $n=1$ ) to the excited state ( $n=2,3,4,\dots$ ) is called excitation potential. Excitation energy must be equal to excitation potential."

**→ Ionization Energy:** "Minimum energy required to remove an electron from that atom in its ground state ( $n=1$ ) is called ionization energy."

**→ Diagram**



→ **Mathematically** : When an atom acquires enough energy to be raised to  $n = \infty$  where electron becomes freed from attractive force of nucleus it loses one or more  $e^-$ s and becomes ionized. Thus,

$$E_{\infty} - E_1 = -\frac{E_0}{\infty^2} - \left(-\frac{E_0}{1^2}\right) \text{ since } \frac{1}{\infty} = 0$$

hence  $E_{\infty} - E_1 = 0 + E_0$

$$E_{\infty} - E_1 = E_0 = 2.17 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$$

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Ionization energy for hydrogen atom is 13.6 eV.

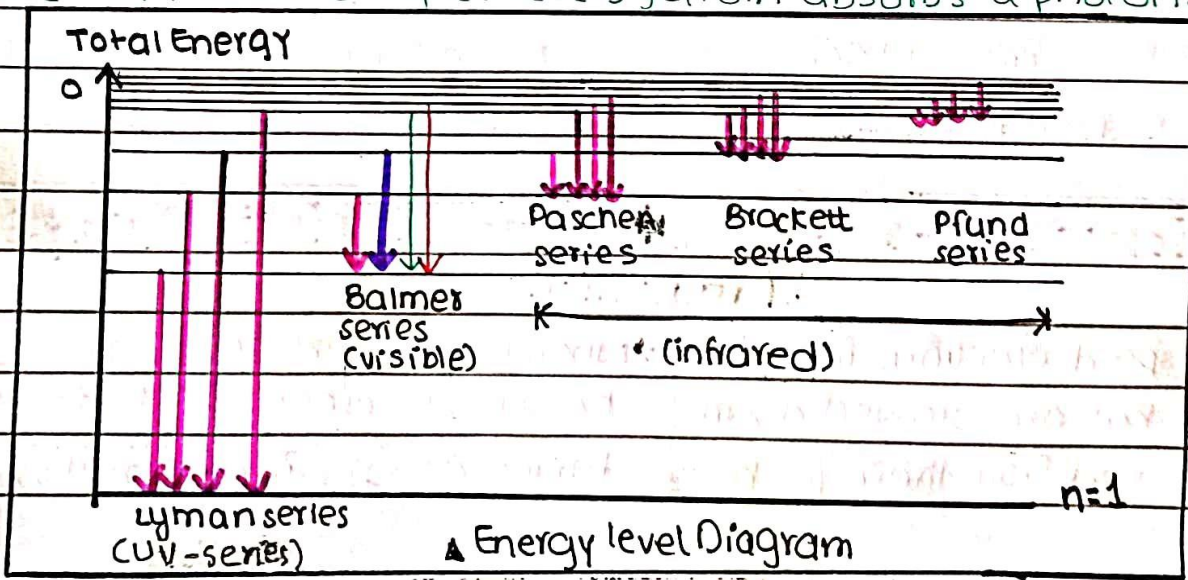
Ionization energy of an atom is numerically equal to ground state energy

→ **Ionization Potential**: "Minimum potential difference required to remove an electron from the atom in its ground state ( $n=1$ ) is called ionization potential. Ionization energy must be equal to ionization potential."

## E. ENERGY LEVEL DIAGRAMS

→ **Excited states** : "Lowest energy level is called the ground state, to distinguish it from the higher levels which are called excited states."

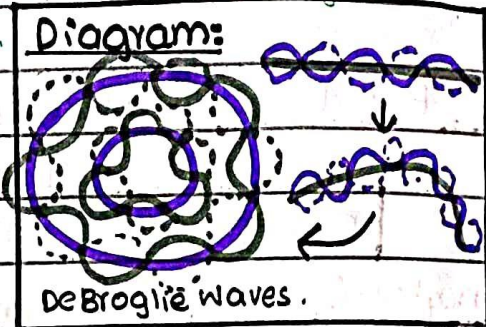
→ **Transitions** : When electrons move from higher to lower levels, photon is emitted. This transition can also be reversed. When electrons move from lower to higher levels, atom absorbs a photon.



## → De-Broglie Waves And Hydrogen Atom:

"Electron or any particle behaves like a wave as well as a particle."

De Broglie pointed out that his own theory for the wavelength of a moving particle could provide an answer to why only those orbits are possible for which angular momentum is the integral multiple of  $h/2\pi$ .



### → Mathematically:

$c = \lambda f$ ,  $p = h/\lambda$  or  $\lambda = h/p$  but  $p = mv$

$\lambda = h/mv$  ① circumference of orbit is associated with a wavelength

thus we can write  $2\pi r = n\lambda$  ② comparing ① and ②  $\frac{h}{mv} = \frac{2\pi r}{n}$

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

→ X-Rays: "X-rays are electromagnetic waves with wavelengths in the range of an Angstrom Å ( $10^{-10}$  m)."

### Production: X-rays are produced through an

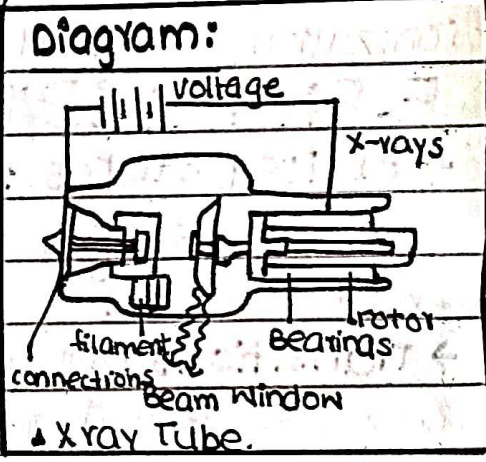
X-ray tube. It is a vacuum tube. It contains a filament heated by current supplied from battery which emits electrons. These electrons are accelerated towards rotating anode.

A high voltage power source for example

30 to 150 kilovolts is connected across

cathode and anode to accelerate electrons. When such high

energy electrons are suddenly stopped by a target, an intense beam of X-rays is produced.



### Types:

#### → Continuous X-rays | → Characteristic X-rays

##### (i) Production

→ When high speed electrons interact with atom but are slowed down and deviated from their path

→ When high speed electrons knock out electrons from target atom's inner shells,

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they emit radiation corresponding to their lost energy. These radiations are continuous x-rays

outer-shell electrons fill that place as a result of which photon or (x-ray characteristic) is omitted

### (ii) Also called

→ The radiation emitted is also called 'bremsstrahlung' (braking radiation)

→ can also be called 'inner shell transition x-rays'

### (iii) Spectrum

→ Broad continuous spectrum

→ Different peaks corresponding to specific energy levels

### (iv) Types

→ **Soft x-rays** (lower energy levels)

**Hard x-rays** (higher energy levels)

→ **Kshell x-rays**: when outer electron fills vacancy in kshell, **Lshell x-rays**:

when outer electron fall to L shell

**Mshell x-rays**: Mshell vacancy is filled.

### (v) Information Regarding Target

→ Not provided

→ spectrum provides information

### (vi) Applications

• **Medical Imaging**: Provides CT scans, detailed images of internal structures.

• **Industrial Radiography**: Nondestructive testing of materials

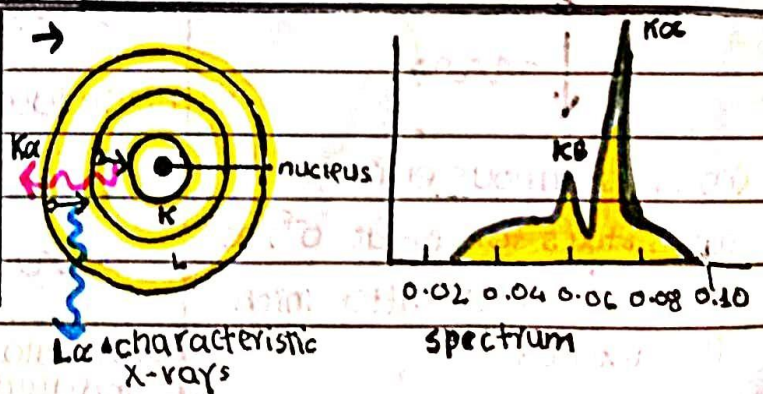
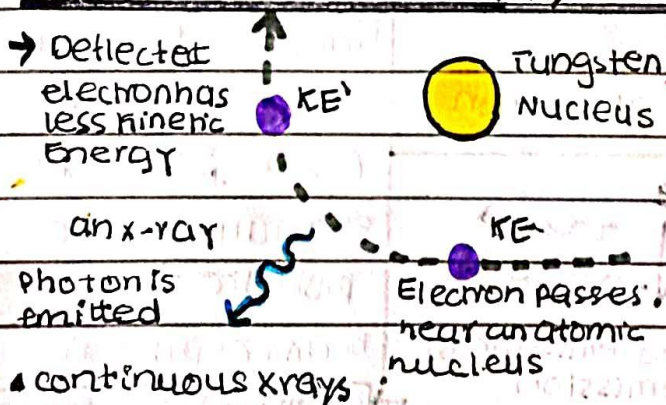
• **Airport security scanning**.

• **Elemental Analysis**: Used in XRF to determine elemental composition of materials

• **X-ray Crystallography**: Determining atomic and molecular structure of a crystal

• **Material Analysis Industry**: Helps to analyze materials in industrial settings

### (vii) Diagram





→ **Mathematical Derivation for continuous X-rays:** As electron

approaches target atoms decelerated and there is a decrease in its K.E.  
 Thus (i)  $K.E - K.E' = hf$  energy of photon emitted will be equal to loss of K.E of electron.

→ **Highest frequency, lowest wavelength photon / X-ray:** Such an X-ray must be produced due to an electron that gives up all its kinetic energy to produce one photon in a single collision.

initial K.E =  $q_e v$       final K.E when  $e^-$  reaches rest  $K.E' = 0$

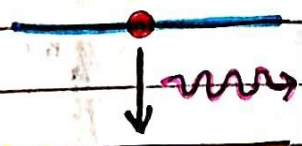
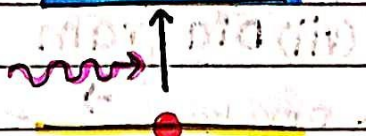
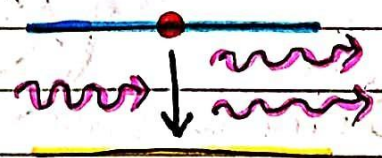
thus from eq (i),  $q_e v + 0 = hf$      $f = \frac{c}{\lambda}$      $q_e v = h \frac{c}{\lambda}$     or

$\lambda = \frac{hc}{q_e v}$  (ii)

→ **Validity of photon theory:** Eq (ii) shows X-rays are electromagnetic radiation and that photon theory of light is valid.

→ **Laser:** "A LASER (Light Amplification by Stimulated Emission of Radiation) is a device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation." Laser operating at microwaves and radio frequency is called MASER.

→ To understand how LASER works, we need to understand the following terms

Spontaneous Emission	Induced Absorption	Stimulated Emission
→ Atom in an excited state, spontaneously makes a transition to lower state.	→ Atom in ground state absorbs photon and makes a transition to higher state.	An atom already in excited state is induced by an external photon (having energy equal to difference of two levels) to make a transition to lower state emitting a photon joined with external photon to produce intense beam of photon.
→ $atom^* \rightarrow atom + photon$	→ $atom + photon \rightarrow atom^{excited}$	→ $atom^* + photon \rightarrow atom + 2 photons$
→ <b>Diagrams</b>		
		
(a) spontaneous emission: atom stays for about $10^{-8}$ sec in excited state after which it is excited.	(b) induced absorption	(c) stimulated emission or induced emission

→ Stimulated emission is used in Laser working but since atom stays for only  $10^{-8}$  sec in high energy level, we required to increase time interval for which we require a **metastable state and population inversion**. (important point)

## → Population Inversion & Meta-stable state:

→ What is metastable state? "Excited states in atom in which electrons stay for slightly longer period of time before spontaneously falling to ground state are called metastable states"

Meaning, rather than falling directly to ground state after excitation, electron enters metastable level where it spends a longer duration of  $10^{-3}$  sec.

→ What is population inversion? "When there are more atoms in excited state than in ground state is called population inversion."

→ Laser pumping: "Act of energy transfer from an external source producing excited states in its atoms is called Laser pumping."

→ conclusion **حاصل کلا**: For stimulated emission we require population inversion which

we acquire through laser pumping, achieving meta stable state.

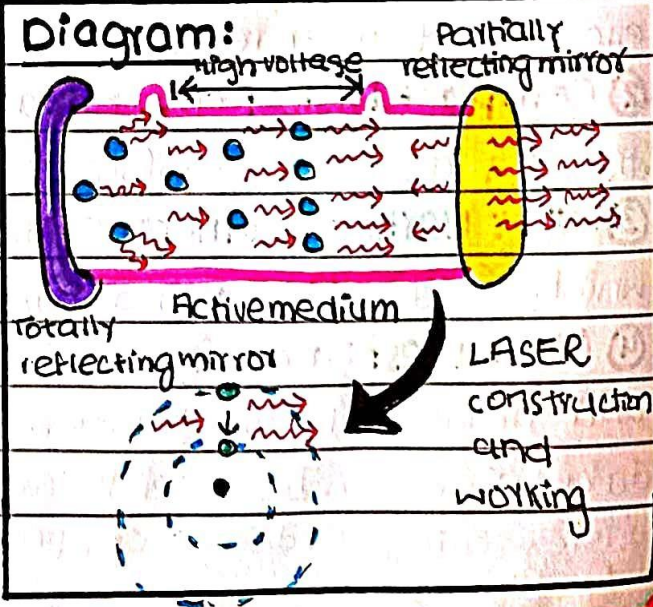
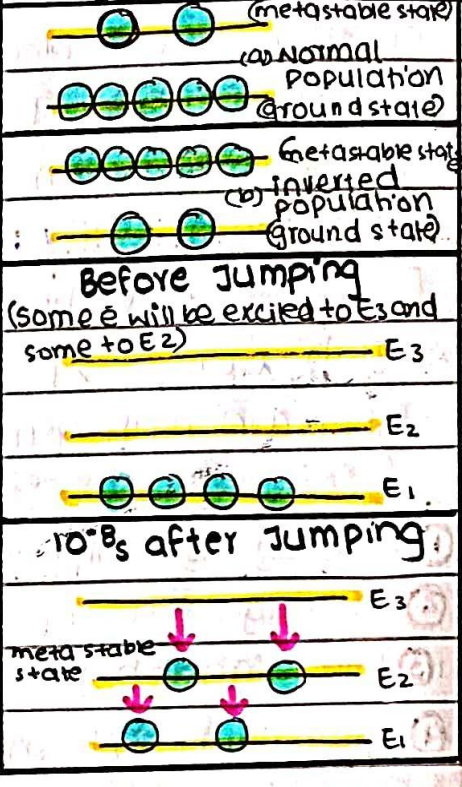
## → WORKING OF LASER: We shall discuss Helium - Neon

gas laser having gas as active medium

→ Construction: (i) Pumping source (ii) Gain medium containing 85% Helium and 15% Neon (iii) Resonant cavity (vacuum tube).

→ Metastable state of ;  
 Neon: located at  $20.66 \text{ eV}$   
 Helium: located at  $20.61 \text{ eV}$

### Diagrams:



LASER construction and working

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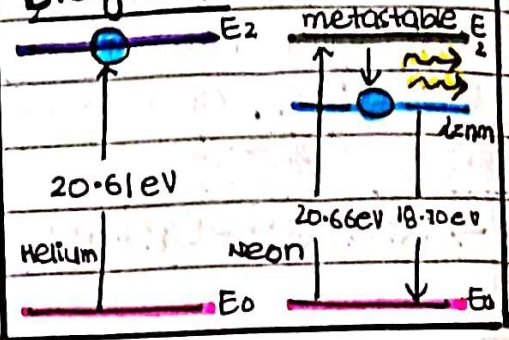
→ **Working:** High voltage electric discharge excites electrons in some of the helium atoms to 20.61 eV metastable states. These

excited helium atoms collide with neon atoms.

During the collision, He atoms de-excite to ground level by giving excitation energy of 20.61 eV and

some 0.05 eV energy due to its k.E to excite the Ne atoms to 20.66 eV metastable state. Stimulated

**Diagram:**



emission causes electrons to drop from 20.66 eV to 18.70 eV corresponding to 1.96 eV energy gap emitting a photon. This photon along with external photon form a concentrated photon beam called laser.

→ **Mathematically:** wavelength of emitted photon can be calculated as:

$E = E_2 - E_1 = 1.96 \text{ eV} = 1.6 \times 10^{-19} \text{ C} \times 1.96 \text{ J/C} = 3.14 \times 10^{-19} \text{ J}$ . since  $E = hf$ , but  $f = \frac{c}{\lambda}$  hence

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E} \text{ putting values } \lambda = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{3.14 \times 10^{-19}} \text{ m} = \lambda = 6.334 \times 10^{-7} \text{ m}$$

This wavelength corresponds to red colour in electromagnetic spectrum.

### → **Laser Vs Ordinary light:**

- ① Laser light is highly monochromatic whereas ordinary light spread over a range of wavelength.
- ② Laser light is highly coherent laser can travel several hundred kilometers.
- ③ Laser light is highly directional while ordinary light spreads in various directions.
- ④ Laser light can be sharply focused while focused spot of ordinary light is wide.

### → **Applications:**

→ ① **Lasers in the medical field:** Lasers are used in eye surgery, ulcer removal and disease prevention.

② **Compact Disks:** CDs contain laser which read the digital codes of information and translate them.

③ **Super Market scanners:** Scanners contain a laser which reads information on barcode of product.

④ **Other uses:** Laser fibre optics used by computer and the internet for transferring information and data. Lasers can be used for welding, cutting and for revealing hidden finger prints.

Side Box

1. How many types of laser are there?  
(i) continuous (ii) Pulsating

2. Why is one end of vacuum chamber partially polished? In order to allow only an intense beam of coherent photons out.