Chapter = 18

Atomic Spectra

Atomic Spectroscopy:

The branch of physics which deals with the measurement of the wavelength and intensities of electromagnetic radiation emitted or absorbed by atoms is called Atomic spectroscopy.

Bohr Atomic Model of hydrogen:

In order to develop a quantitative theory for the spectrum off the hydrogen atom, Bohr put forward the following postulates.

- An electron moves only in those circular orbits for which its orbital angular momentum $\boldsymbol{L}$is an integral multiple of $\hbar = \left(\frac{h}{2\pi}\right)$.

$$\boldsymbol{L = n\hbar = \frac{nh}{2\pi}}$$

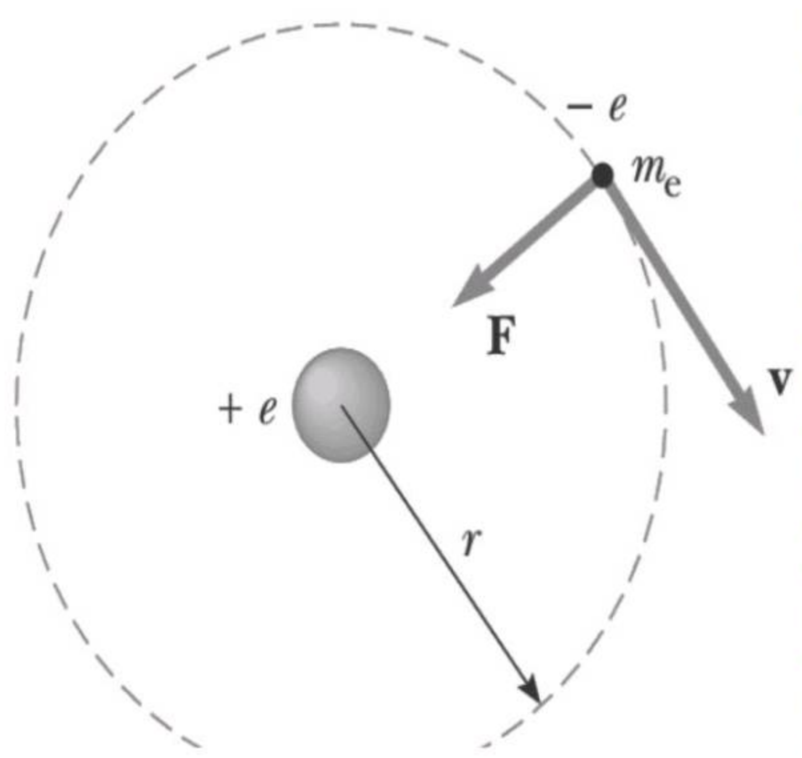
- Total energy of the electron remains constant as long as it remains in the same orbit.
- If an electron jumps from higher energy level (orbit) of energy $\boldsymbol{E_i}$ to the lower energy level (orbit) of energy $\boldsymbol{E_f}$ i-e ($\boldsymbol{E_i < E_f}$), a photon of is emitted. whose frequency is given by

$$\boldsymbol{f = \frac{E_i - E_f}{h}}$$

Determination of Atomic Radii:

Consider hydrogen atom as shown in figure as the electron revolving around the nucleus. Since the electro is positively charged and the nucleus is consisting of a single proton there is a columbic attractive force between these two particles given by

$$F_E = \frac{Kee}{r^2}$$



$$F_E = \frac{ke^2}{r^2}$$

As the electron is revolving in a circular orbit of radius the exists a centripetal force acting on it given by;

$$\boxed{F_c = \frac{m_e v^2}{r}}$$

This centripetal force is balanced by the Coulomb force

$$\boxed{\frac{ke^2}{r^2} = \frac{m_e v^2}{r}} --(a)$$

Now According to Bohr Atomic theory angular momentum of the electron can be written as

$$L = n\hbar$$

$$m_e vr = n\hbar$$

$$v = \frac{n\hbar}{m_e r}$$

Squaring on both sides we get

$$v^2 = \frac{n^2\hbar^2}{m_e^2 r^2}$$

Putting above in equation (a) we get

$$\frac{ke^2}{r^2} = \frac{m_e}{r} \times \frac{n^2\hbar^2}{m_e^2 r^2}$$

$$ke^2 = \frac{n^2\hbar^2}{m_e r}$$

Separating for $\boldsymbol{r}$ we get

$$r = n^2\left(\frac{\hbar^2}{m_e ke^2}\right)$$

$$\boxed{r = n^2 a_o}$$

Where $\boldsymbol{a_o}$ is called Bohr radius and its value is given by

$$a_o = \frac{\hbar^2}{m_e ke^2}$$

$$a_o = \frac{(1.05459 \times 10^{-34})^2}{9.11 \times 10^{-31} \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2}$$

$$\boxed{a_o = 0.53\text{Å}}$$

$\boldsymbol{n}$ is called principle quantum number and it represents orbit number for the electron.

For ground state($\boldsymbol{n = 1}$) radius $\boldsymbol{r_1}$of orbit will be

$$r_1 = (1)^2 \times 0.53\text{Å}$$

$$r_1 = 0.53\text{Å} = a_o$$

There for Bohr radius can be defined as

"It is the radius of obit of electron in of a hydrogen atom in ground state."

Determination of the Energy of an Electron in a "Stationary State":

According to Bohr atomic theory electron does not radiate energy as long as it remains in the same orbit or energy level.

The total energy $\boldsymbol{E}$of the electron can be written as

$$\boxed{\boldsymbol{E = K.E + P.E}}$$

Kinetic Energy:

$$K.E = \frac{1}{2}m_e v^2$$

$$\frac{ke^2}{r^2} = \frac{m_e v^2}{r}$$

$$\frac{ke^2}{r} = m_e v^2$$

Separating for $\boldsymbol{v^2}$we get

$$v^2 = \frac{ke^2}{m_e r}$$

Putting in expression for kinetic energy we get

$$K.E = \frac{1}{2}\cancel{m_e}\frac{ke^2}{\cancel{m_e}r}$$

$$\boxed{\boldsymbol{K.E = \frac{ke^2}{2r}}}$$

Potential Energy:

Expression for electric potential is

$$V = \frac{W}{e}$$

$$P.E = -W$$

$$V = -\frac{P.E}{e}$$

$$P.E = -eV$$

Now Since

$$V = \frac{ke}{r}$$

Now potential energy can be written as

$$P.E = -e\frac{ke}{r}$$

$$\boxed{\boldsymbol{P.E = -\frac{ke^2}{r}}}$$

Total Energy:

Total energy can be written as

$$\boldsymbol{E = K.E + P.E}$$

$$E = \frac{ke^2}{2r} - \frac{ke^2}{r}$$

$$E = \frac{ke^2}{r}\left(\frac{1}{2} - 1\right)$$

$$\boxed{\boldsymbol{E = -\frac{ke^2}{2r}}}$$

Putting the value of $\boldsymbol{r}$ in above expression we get.

$$E_n = -\frac{ke^2}{2n^2 a_o}$$

$$E_n = -\frac{1}{n^2}\left(\frac{ke^2}{2a_o}\right)$$

Now putting values of constant and converting in to Electron-Volts we get

$$\frac{ke^2}{2a_o} = 13.6eV$$

Putting the values in expression for E_n we get

$$\boxed{E_n = -\frac{13.6eV}{n^2}}$$

Hydrogen Spectrum:

According to Bohr Atomic theory when an electron jumps from higher energy level (orbit) of energy E_i to the lower energy level (orbit) of energy E_f i-e ($E_i < E_f$), a photon of is emitted Whose frequency is given by

$$f = \frac{E_i - E_f}{h}$$

Here

$$E_i = -\frac{1}{n_i^2}\frac{ke^2}{2a_o}$$

$$E_f = -\frac{1}{n_f^2}\frac{ke^2}{2a_o}$$

Putting values, we get

$$f = \frac{1}{h}\left[-\frac{1}{n_i^2}\frac{ke^2}{2a_o} - \left(-\frac{1}{n_f^2}\frac{ke^2}{2a_o}\right)\right]$$

$$f = \frac{1}{h}\left(\frac{1}{n_f^2}\frac{ke^2}{2a_o} - \frac{1}{n_i^2}\frac{ke^2}{2a_o}\right)$$

$$f = \frac{ke^2}{2ha_o}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Now since

$$c = \lambda f$$

$$f = \frac{c}{\lambda}$$

Putting in above we get

$$\frac{c}{\lambda} = \frac{ke^2}{2ha_o}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{\lambda} = \frac{ke^2}{2cha_o}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) --- (b)$$

Now here

$$\frac{1}{\lambda} = |\bar{v}|$$

$|\bar{v}|$ is called wave number and

$$\frac{ke^2}{2hca_o} = R_H$$

Where R_H is called Rydberg constant and its numerical value is

$$\boldsymbol{R_H = 1.0970 \times 10^7 m^{-1}}$$

Now equation (b) will become

$$|\bar{v}| = \frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Series of hydrogen spectrum:

Electron emits its energy in the form of electromagnetic radiation when it jumps from higher energy level to lower energy level. Frequency of emitted EM radiation depends upon the difference in energy between these energy levels.

These frequencies belong to the different regions of EM spectrum depending upon in which energy state electron is after losing its energy. This phenomenon gives rise to the different series of hydrogen spectrum. These series are given below

1. Lyman Series:

If an electron falls from higher energy level to the ground state (n=1) it emits radiation which are in the **ultra violet region** of EM spectrum. $|\bar{v}|$ For Lyman series is written as

$$|\bar{v}| = \frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{n_i^2}\right)$$

2. Balmer Series:

If an electron falls from higher energy level to the 1st exited state (n=2) it emits radiation which are in the **visible region** of EM spectrum. $|\bar{v}|$ For Balmer series is written as

$$|\bar{\upsilon}| = \frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right)$$

3. Paschen Series:

If an electron falls from higher energy level to the 2nd exited state (n=3) it emits radiation which are in the **infrared region** of EM spectrum. $|\upsilon|$ For Paschen series is written as

$$|\bar{\upsilon}| = \frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{n_i^2}\right)$$

4. Brackett Series:

If an electron falls from higher energy level to the 3rd exited state (n=4) it emits radiation which are in the **far infrared region** of EM spectrum. $|\bar{\upsilon}|$ For Brackett series is written as

$$|\bar{\upsilon}| = \frac{1}{\lambda} = R_H\left(\frac{1}{4^2} - \frac{1}{n_i^2}\right)$$

5. Pfund Series:

If an electron falls from higher energy level to the 4th exited state (n=5) it emits radiation which are in the **far infrared region** of EM spectrum. $|\bar{\upsilon}|$ For Pfund series is written as

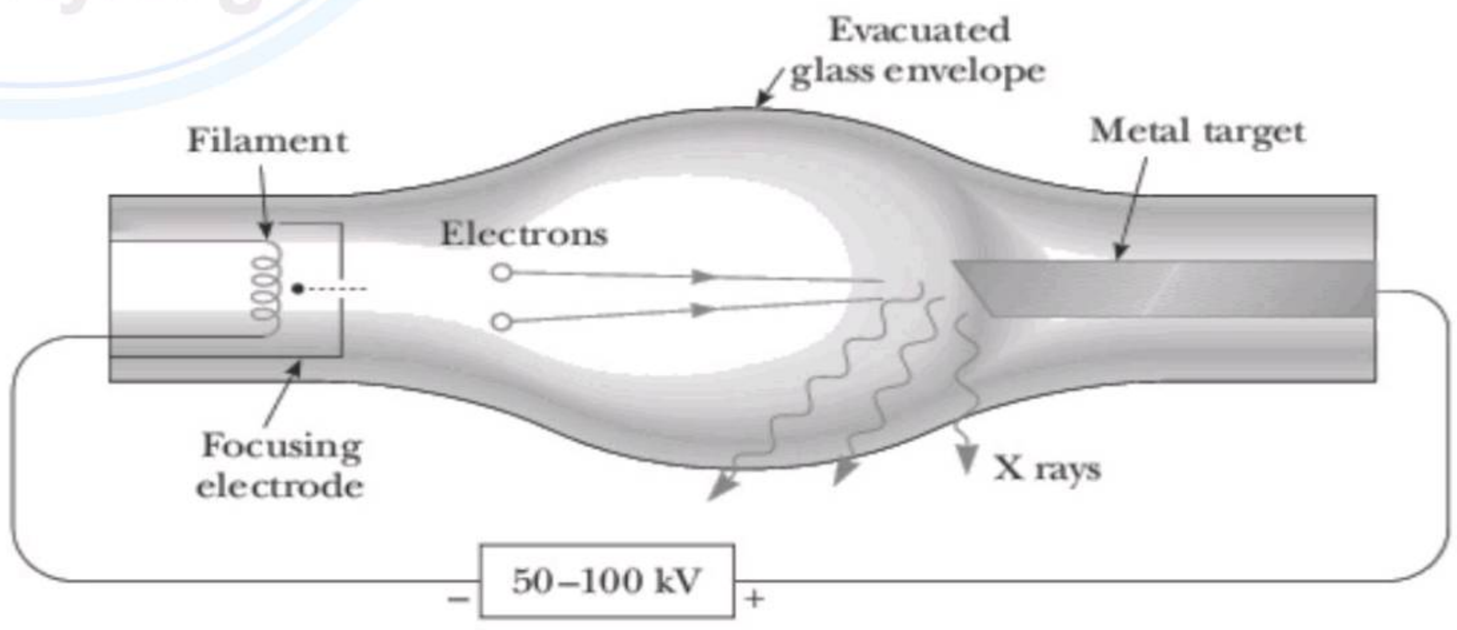
$$|\bar{\upsilon}| = \frac{1}{\lambda} = R_H\left(\frac{1}{5^2} - \frac{1}{n_i^2}\right)$$

X-Rays:

X-rays are high frequency (short wavelength) electromagnetic radiation. Frequency range of X-ray is from $10^{16}\ Hz$ to $10^{20} Hz$.

Generation of X-rays:

X-rays are generated by accelerating electron to high velocity and then suddenly stopping them by collision with a solid body of atomic number greater than 10.
Typical apparatus used for X-ray generation is shown in figure.



High amount of current is passed through highly resistive filament at cathode. Cathode emits electron by thermionic emission. These electrons are accelerated to high speed by high potential difference between anode and cathode. These high-speed electrons collide with Anode (of high atomic number). If potential difference is of several thousand of volt X-rays are emitted out of the anode.

X-Ray Spectra:

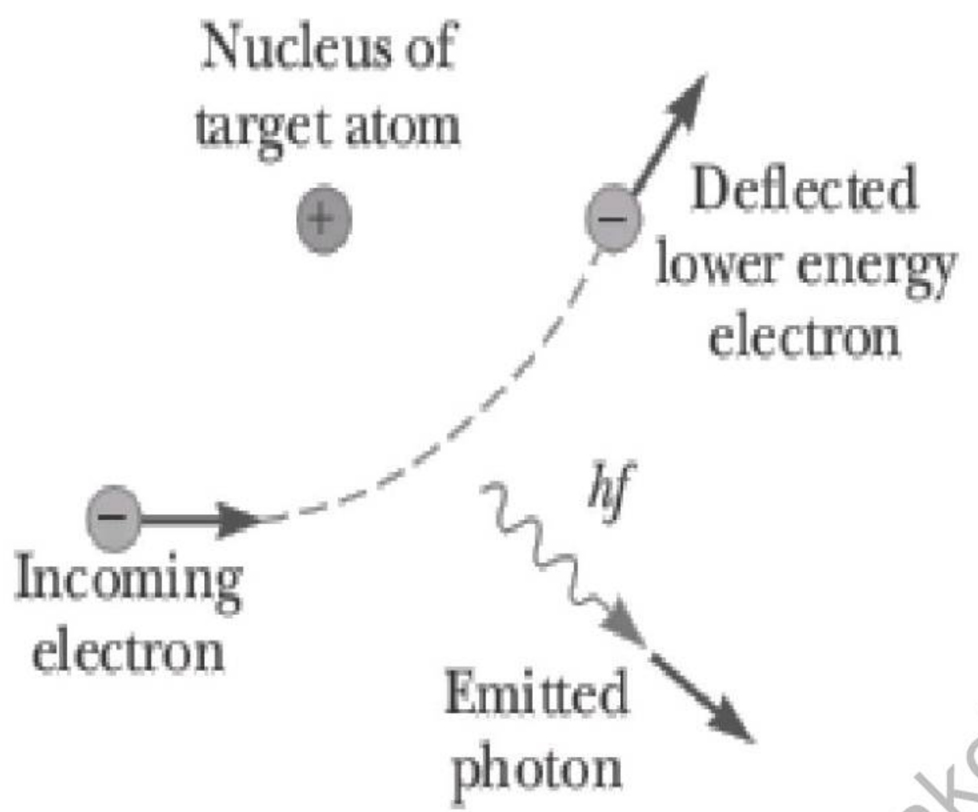
Spectral analysis of X-ray shows that

i. X-rays have continuous spectrum also called X-ray Bremsstrahlung.
ii. Under certain condition there is an additional line spectrum called Characteristic spectrum.

X-Ray Continuous Spectra (X-ray Bremsstrahlung):

In ordinary condition, continuous spectrum is emitted with maximum frequency directly proportional to the acceleration voltage and is nearly independent of material of which electrodes are made off.

Explanation:



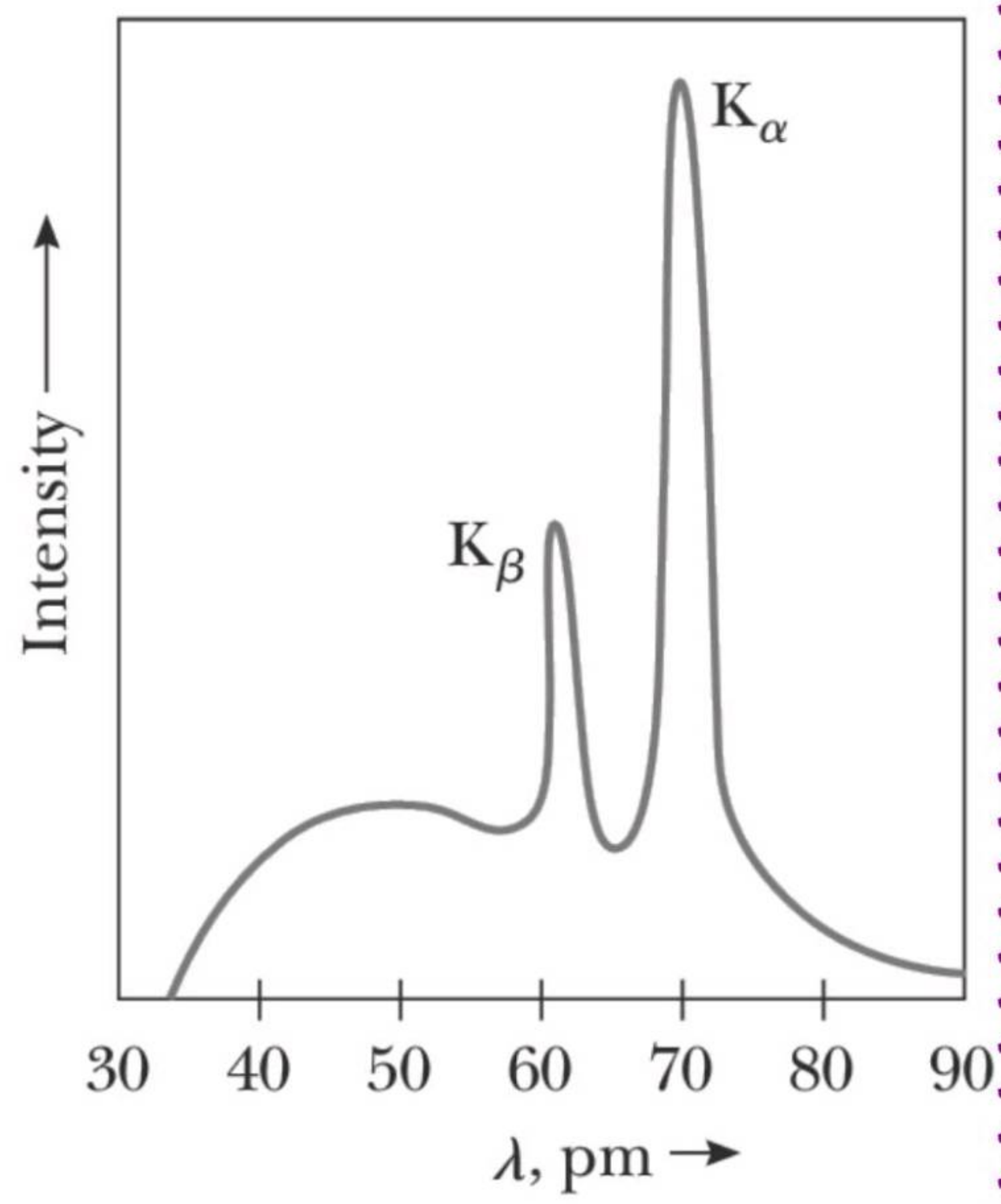
When fast moving electron from cathode passes near to the nucleus of atoms in anode nucleus attracted it toward itself by columbic force but due to the high speed of electron it passes away with some deflection due to this scattering process electron transfer some of its momentum to atom (or lose energy).Since electron can lose any amount of energy (from zero to its maximum energy eV) and therefore Continuous spectrum is obtain and whole process can be described by the equation

$$\boldsymbol{Atom + e^-(fast) \longrightarrow Atom + e^-(slow) + hf}$$

Here; hf is the energy of emitted X-ray photon.

X-ray line spectra (Characteristic Spectra):

In X-Ray spectra certain peaks high intensity peaks appear that are called X-ray line spectra (Characteristic Spectra).



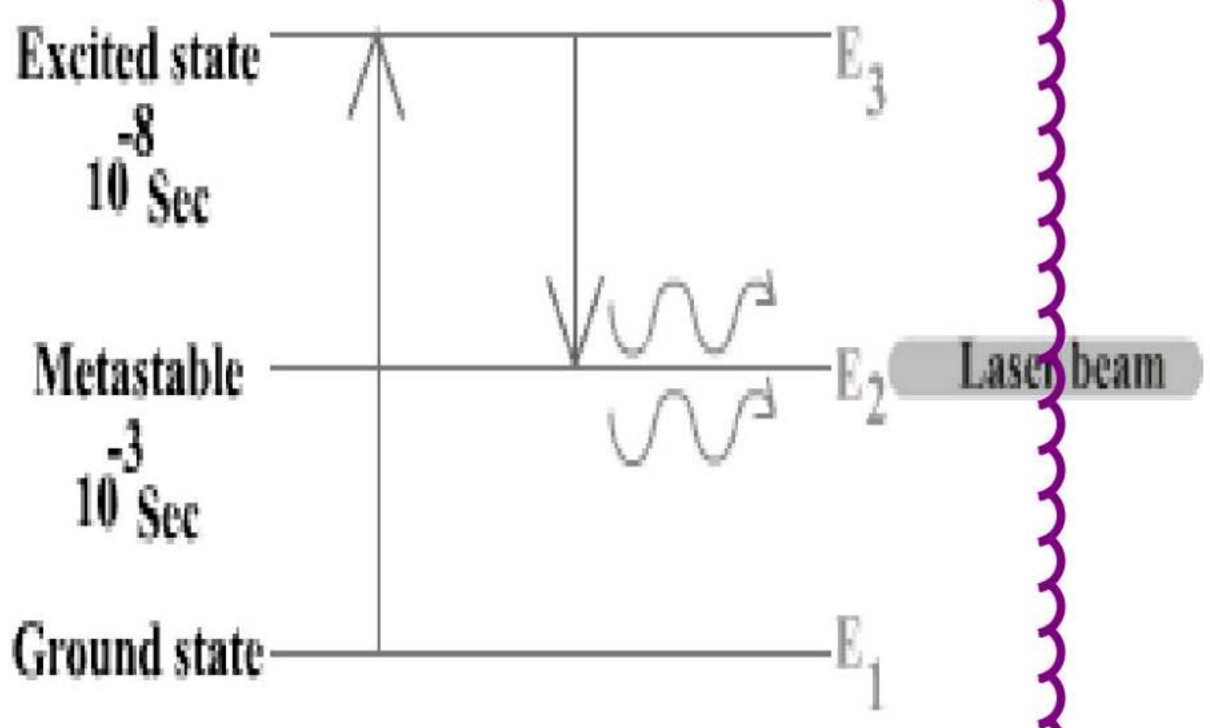
Explanation:

The process of emission of characteristic spectra takes place as follows. When a highly energetic incident electron knocks an electron from the k-shell, a vacancy occurs in that shell. This vacancy is filled by the arrival of an electron from outside the k-shell, emitting excess amount of energy in the form of photon. If the electron jumps only one shell and returns with the emission of X-rays to Y shell, then X-rays are termed as '$\boldsymbol{Y_\alpha}$' X-rays. If the electron jumps two shells and returns with emission of X-rays to suppose 'Y' shell, then X-rays are termed as '$\boldsymbol{Y_\beta}$' rays and so on, where Y may be K, L, M, ...

LASER

LASER stands for *Light **A**mplification by **S**timulated **E**mission of **R**adiation*.
Laser is a device used to produce very intense, highly directional, coherent and monochromatic beam of light.

Basic Conditions to Produce Laser

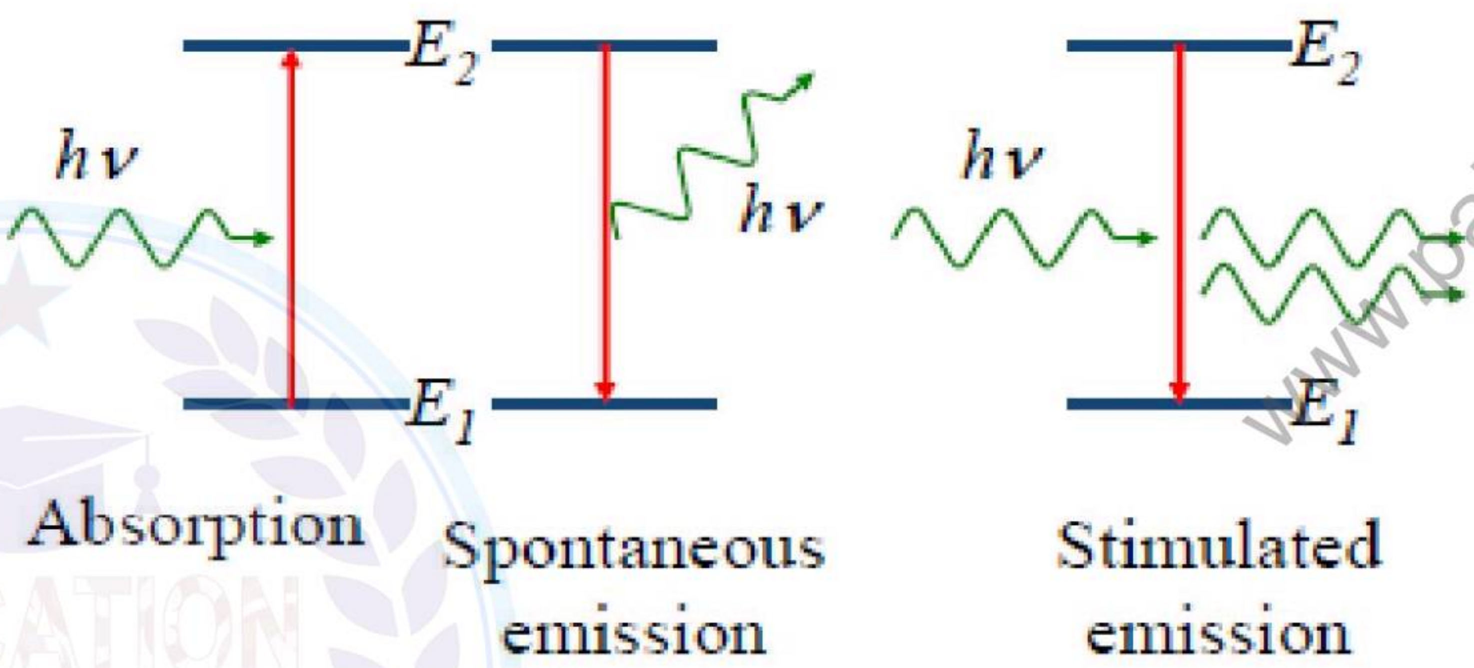


- There must be a Meta stable state in the system.
- The system must achieve population inversion.
- The photons emitted must be confined in the system for a time to allow them further stimulated emission.

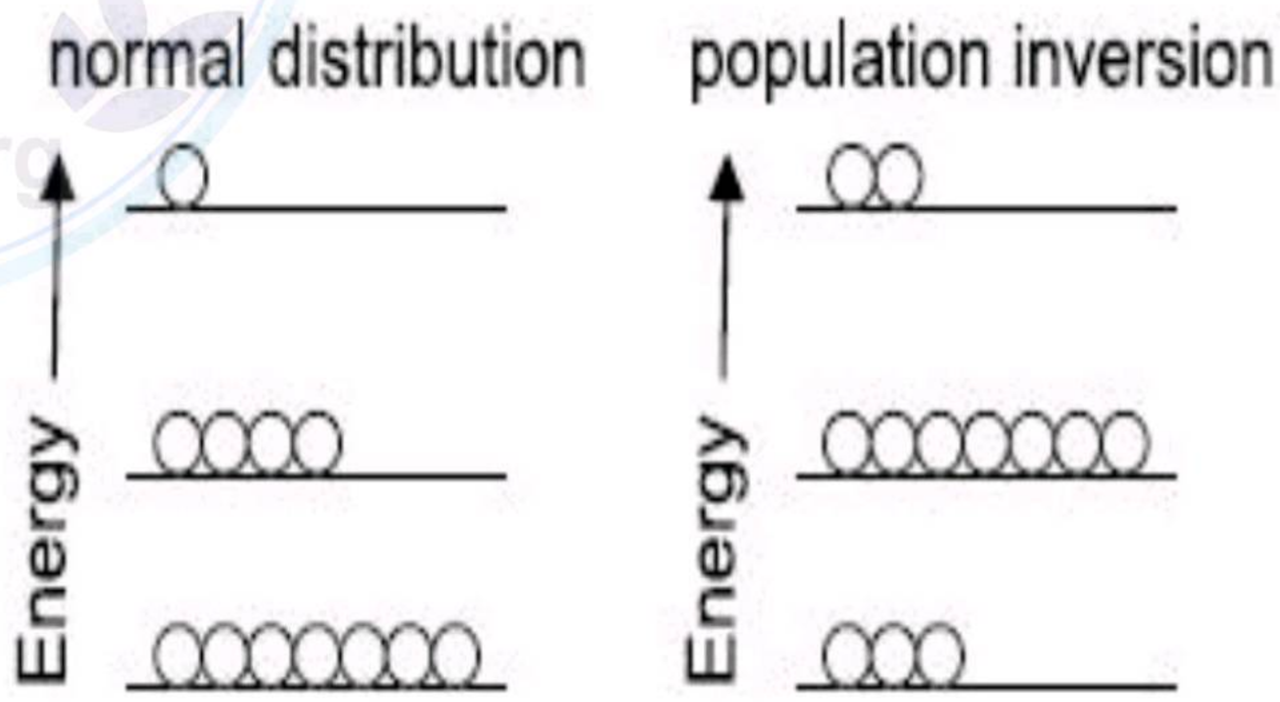
Principle of Laser

The principle of laser production is based on the fact that atoms of a material have a number of energy levels in which at least one is Meta stable state.

Explanation:



$h\nu = E_2 - E_1$



Consider three-level atomic system having energies E_1, E_2 and E_3, respectively. Let the atoms are at ground state E_1. If photons interact with an atom in ground state, the atom absorbs the photon and reaches the excited state E_3. We know that the excited state is an unstable state, therefore, electron must return back to ground state E_1 but such transitions are not allowed and the electron first reach the state E_2. Atoms in the state E_3 which has a life time of about 10^{-8} sec decay spontaneously from state E_3 to state E_2 which is Meta stable and has life time of 10^{-3}sec. This means that the atoms reach state E_2 much faster than they leave state E_2.
This results in an increase in number of atoms in state E_2, and hence population inversion is achieved.
After achieving population inversion, it is exposed to a beam of photons which causes induced emission of photons, and a beam of laser is produced.

Applications of Laser:

The lasers have widespread applications in industry, surgery, entertainment and in a number of other disciplines of life. However, some of them are as under: Generally speaking, a laser produces a very narrow and intense beam of light that can vaporize anything which comers in its way.

- **Laser as Accurate Cutter:**
  Precision cutting, welding and drilling of tiny holes into hardest materials can be performed by laser beam.

- **Application in Media**
  A very interesting application is the production of true three-dimensional images called "HOLOGRAM". A hologram records not only the intensity of the light but also the phase difference between two image-beams that cause the interference pattern to reconstruct an image suspended in air like a real object.

- **Application in Surgery**
  In surgery, the laser has proved a more delicate and accurate instrument than the finest scalpel. It has been used for bloodlessly removing small humors, cutting and delicate operations. Lasers are now widely used in the field of surgery. Laser can also be used to fragment gallstone, stones in kidney and eye-surgery.

- **Application as Range Finder**
  Laser beam is used as a range finder, lining up equipment accurately in surveying large distances.

- **Application in Electrical Devices**
  Tiny solid-state lasers are widely used in electrical devices. A laser beam replaces the phonographic needle in a compact disk audio system for music reproduction of extremely high fidelity. A laser can also be used for the photographic recording of output data of computer.

- **Application in Environmental Study**
  Laser is an important environmental monitoring instrument. Some types of laser can be tuned to a desired frequency. These lasers can be used as a very sensitive detector of pollutants in the atmosphere.

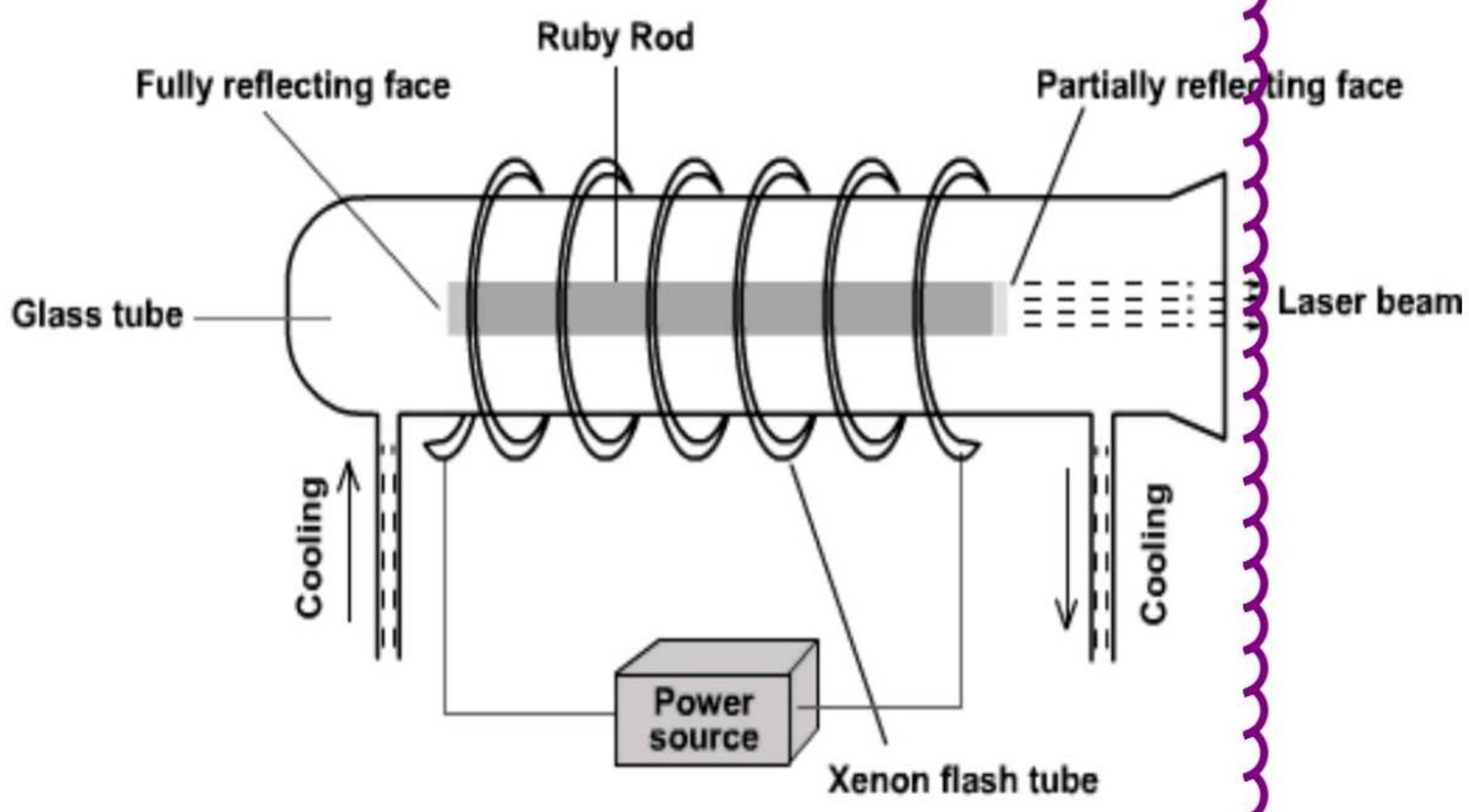
- **Application in Nuclear Fusion**
  A high-power laser is also a potential source to induce nuclear fusion reaction.

RUBY LASER:

Construction:

Ruby is a crystal of Al_2O_3, a small number of whose Al atoms are replaced by Cr^{+3} ions. A high intensity helical flash lamp surrounding the ruby rod is used as light source to raise **Cr** atoms from state E_1 to E_3.

The ruby laser is a cylindrical rod with parallel, flat reflecting ends. One end is partially reflecting. The flash light is attached with the high voltage.



Working:

- Electrons are raised from ground state E_1 to Excited state E_3(optical pumping) which has a lifetime 10^{-8} sec.
- The atoms from the state E_3 make transition to state E_2. Since E_2 is meta-stable state having life time equal to 10^{-3} sec.
- As atoms reach state E_2 much faster than they leave state E_2. This results in an increase in the number of atoms in state E_2 and hence population inversion is achieved.
- In this process few Cr atoms make spontaneous transition from E_2 to E_1 and emitted photons stimulate further transition. In this way we obtain an intense, coherent, monochromatic beam of red laser.

CHAPTER-18 **NUMERICALS**

FROM PAST PAPERS

1990

Q.7. (c) A blood corpuscle has diameter about 9 x 10^{-6} m. In which excited orbit should a hydrogen atom so that it is just about as big as the blood corpuscle. **(291)**

1993

Q.7. (c) The energy of the lowest level of hydrogen atom is –13.6 eV. Calculate the energy of the emitted photons in transition from n = 4 to n = 2. **(2.55eV)**

1995

Q.7. (c) Find the wavelength of light which is capable of ionizing a hydrogen atom. **(911.5A°)**

1997

Q.7. (c) The energy of an electron in an excited hydrogen atom is –3.4 eV. Calculate the angular momentum of the electron according to Bohr's Theory. **(2.1 x 10^{-34}Js)**

2000

Q.7. (c) What is the wavelength of the radiation that is emitted when hydrogen atom undergoes a transition from the state n_2 = 3 to n_1 = 2. **(6.5 x 10^{-7} m)**

2002 (Pre Med. group)

Q.8. (d) What is the longest wavelength of light capable of ionizing a hydrogen atom? What energy in electron volt is needed to ionize it? **(9.12 x 10^{-8} m/s, 13.6eV)**

2002 (Pre Engg. group)

Q.7. (d) A photon of 12.1 eV absorbed by a hydrogen atom originally in the ground state raises the atom to an excited state. What is the quantum number of this state? (E_1 = –13.6 eV) **(3)**

2003 (Pre Engg. group)

Q.7. (d) An electron in the hydrogen atom makes a transition from the n = 2 energy state to the ground state (corresponding to n = 1) find the wavelength in the ultraviolet region. **(1.21 x 10^{-7} m)**

2005

Q.7. (d) In a hydrogen atom an electron experiences transition from a state whose binding energy is 0.54 eV to the state whose excitation energy is 10.2 eV.

a) The quantum numbers of the two states

b) The wavelength of the photon emitted **(5, 2, 4.342 x 10^{-7} m)**

2007

Q.7. (d) Calculate the Binding Energy of a hydrogen atom. **(–13.6 eV)**

2008

Q.8. (d) Calculate the longest and shortest wavelengths of emitted photons where R_H = 1.097 x 10^7 m^{-1}. **(656.33 nm, 364.6nm)**

2010

Q.2. (xii) Find the shortest wavelength of photon emitted in the Balmer series and determine its energy in eV. ($R_H = 1.097 \times 10^7\ m^{-1}$). **(3646A°, 3.41eV)**

2011

Q.2. (xi) Calculate the energy of the longest wavelength radiation emitted in the Paschen series in hydrogen atom spectra. ($R_H = 1.0968 \times 10^7\ m^{-1}$, $h = 6.63 \times 10^{-34}$Js, m c = 3×10^8 m/s).

(1875.6 nm)

2012

Q2(xi) Find the value of shortest and the longest wavelength of emitted photon in hydrogen spectra in Balmer series. (Rydberg constant = $1.097 \times 10^7\ m^{-1}$)

2013

Q2(v) A hydrogen atom in the ground state gets excited by absorbing a photon of 12.15 eV. Find the Quantum number of this state,

2014

Q2. (x) Determine the longest and shortest wavelength of photons emitted in the Lyman series. (R_H=$1.097 \times 10^7\ m^{-1}$)

2015

Q2(xi) Find the shortest wavelength of photon emitted in the Balmer series and determine its energy in eV. ($R_H = 1.097 \times 10^7\ m^{-1}$). **(3646A°, 3.41eV)**