Unit 19

ATOMIC SPECTRA

Major Concepts (16 PERIODS)

- Atomic spectra
- Emission of spectral lines
- Ionization and excitation potentials
- Inner shell transitions and characteristics x-rays
- Laser

Conceptual Linkage

This chapter is built on Atomic Structure (Bohr Model) Chemistry XI

Students Learning Outcomes

After studying this unit, the students will be able to:

- describe and explain the origin of different types of optical spectra.
- show an understanding of the existence of discrete electron energy levels in isolated atoms (e.g. atomic hydrogen) and deduce how this leads to spectral lines.
- explain how the uniqueness of the spectra of elements can be used to identify an
- element.
- analyze the significance of the hydrogen spectrum in the development of Bohr's model of the atom.
- explain hydrogen atom in terms of energy levels on the basis of Bohr Model.
- determine the ionization energy and various excitation energies of an atom using an energy level diagram.
- Solve problems and analyze information using.

  $1/\lambda = R_H[1/p^2 - 1/n^2]$
- understand that inner shell transitions in heavy elements result into emission of characteristic X-rays.
- explain the terms spontaneous emission, stimulated emission, meta stable states, population inversion and laser action.
- describe the structure and purpose of the main components of a He-Ne gas laser.

INTRODUCTION

We have studied in the previous unit that a blackbody emits all radiations of all wavelengths with different intensities depending upon temperature. The set of all the emitted radiations of different wavelength is called spectrum and the study of spectrum is called spectroscopy. But in this unit, we observe and study the spectrum by another method of an atomic gas or vapors at less than atmospheric pressure are suitably excited by passing an electric current through it, they emit radiations. The emitted radiations have a spectrum which comprises of certain specific wavelengths known as atomic spectra. Each element has a characteristic line spectrum. Atomic structure and spectra have a reflective effect on revealing the inner mysteries of the structures of atoms. The existence of line emission spectra from atomic gases is used to reveal the structure of an atom in terms of discrete energy levels in atoms. J.J. Balmer in 1885 succeeded to devise an empirical formula which could explain the existence of the atomic spectra of hydrogen. Neil Bohr in 1913 provided a theoretical reasoning to Balmer formula explaining the emission of spectral lines by presenting a semi classical model of Hydrogen atom. Following this principle, the inner shells transition in heavy atoms should give rise to the emission of high energy photons i.e., x-rays. CAT (Computerized Axial Tomography) scanner is an improved technique of x-rays which can detect tumors and other anomalies too much small to be seen with older techniques. LASER is another triumph of research in this field. The laser beam is an intense, monochromatic, unidirectional and coherent source of light, which has many applications in medical, industry, telecommunication and other fields.

19.1 ATOMIC SPECTRA

When an atomic gas at much low pressure than the atmospheric pressure is excited by passing an electric current or by electric discharge through it, the excited gas emits radiation or light. If this emitted light is investigated using a spectrometer, then a series of discrete lines may be observed on screen. Each line corresponds to a different wavelength. This series of lines called an emission spectra. In general, when the electromagnetic radiation from a source is dispersed by a prism or diffraction grating into its various component

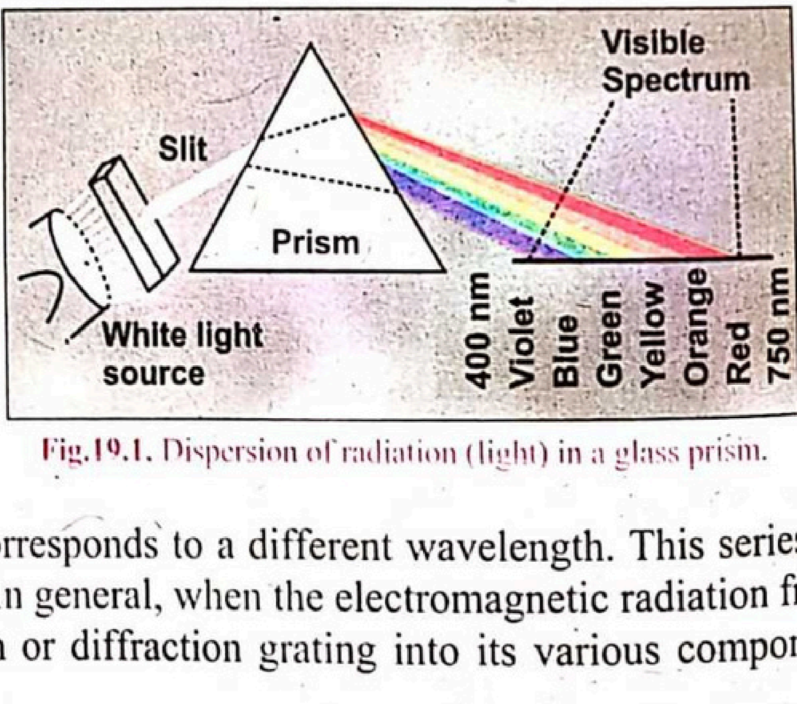


Fig.19.1. Dispersion of radiation (light) in a glass prism.

waves as shown in Fig.19.1 then the visible set of component waves have different wavelength known as visible spectrum.

Similarly, when a visible light is passed through a gas at low pressure, then we observe a spectrum with a few dark lines. These dark lines are absorbed by the molecules of the gas and such type of spectra is called absorption spectra.

The spectra can be classified into line, band or continuous as shown in Fig.19.2. Line spectra may be observed when the electrons of an excited atom, element or molecule move between energy levels, returning towards the ground state. As the spectra contains visible lines due to emission of radiation by the atoms is known as line spectra. The line spectra is not confined only to visible region. It is also observed in the ultraviolet and infrared regions of electromagnetic spectrum. If the spectra contain a series of bands closed to one another then it is called band spectra. The band spectra is formed due to the emission or absorption of radiation by the molecules. On the other hand, the spectrum in which there is a continuous region of radiation emitted or absorbed is a continuous spectrum. e.g., the spectrum of the sun or a blackbody is an example of a continuous spectrum.

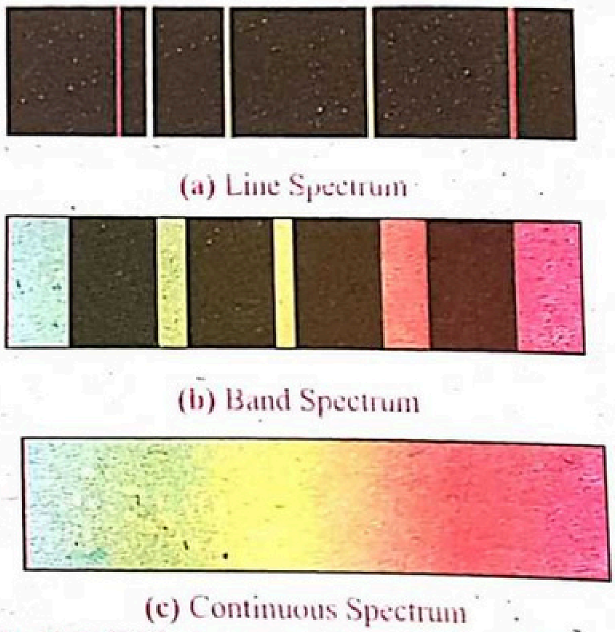


Fig.19.2. Different types of spectra of visible light.

Spectrum of hydrogen atom

Hydrogen atom produces the simplest line spectra. Balmer in 1885 identified the four prominent lines in the visible spectra of hydrogen atom i.e., H_α (red), H_β (blue-green), H_γ (blue-violet) and H_δ (violet). The wavelengths of these four lines are 656.3nm, 486.1nm, 434.1nm and 410.2nm respectively as shown in Fig.19.3. The set of these four lines is called Balmer series. The wavelength of these lines can be determined by the following equation which was modified by Rydberg of the Balmer's equation.

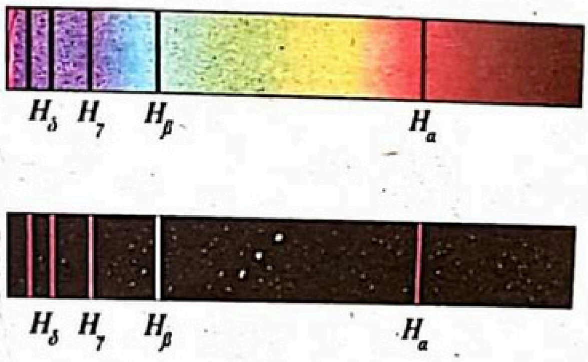


Fig.19.3. Spectrum of hydrogen atom.

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad ......(19.1)$$

where n = 3, 4, 5, ...and R_H is a Rydberg constant whose value is $1.097 \times 10^7\ m^{-1}$ for hydrogen atom.

Hydrogen spectral series of transitions resulting in visible emission lines spectra when an electron of the hydrogen atom makes a transition or jumps from $n \geq 3$ to $n = 2$.

The value of 'n' from 3 onward gives us the wavelengths of the Balmer's Series. On the other hand, the shortest wavelength in the series occurs at 364.6nm, corresponding to the series limit, $n \to \infty$:

The Balmer series contain wavelength in the visible region of the hydrogen spectrum, but the experiments show that there are also some other series in the hydrogen spectrum. i.e., the extreme ultraviolet section of the spectrum contains the Lyman series.

The remaining series, such as Paschen, Brackett and Pfund series are lying in the infrared region. All these series can be expressed in the form which is very similar to Equation.19.1.

Table 19.1 Different Wavelengths of different Spectral lines

Light Spectrum		
λ - nm	**Color**	**Group**
3000-10000	IRC	
1400-3000	IRB	Infrared
700-1400	IRA	
650-700	Deep Red	
623	Red	
596	Orange	
571	Yellow	
547	Green	
524	Blue-Green	Visible
501	Turguoise	
480	Blue	
460	Indigo	
440	Violet	
422-400	Deep Violet	
400-320	UVA	
320-280	UVB	Ultraviolet
280-200	UVC	

Lyman series: $$\frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad ......(19.2)$$

where n = 2, 3, 4, ...

i.e., hydrogen spectral series will be observed in the ultraviolet region when an electron of the hydrogen atom makes a transition or jumps from from $n \geq 2$ to $n = 1$.

Paschen series: $$\frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad ......(19.3)$$

where n = 4, 5, 6, ...

i.e., hydrogen spectral series will be observed in the infrared region when an electron of the hydrogen atom makes a transition or jumps from $n \geq 4$ to $n = 3$.

Brackett series: $$\frac{1}{\lambda} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad \text{......(19.4)}$$

where n = 5, 6, 7, ... The Bracket series is also in the infrared region.

Pfund series: $$\frac{1}{\lambda} = R_H\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \quad \text{......(19.5)}$$

where n = 6, 7, 8, ... The Pfund series is also in the infrared region.

The wavelength of all the hydrogen atom spectra lines can be represented by a single empirical formula as;

$$\frac{1}{\lambda} = R_H\left(\frac{1}{p^2} - \frac{1}{n^2}\right) \quad \text{......(19.6)}$$

This equation can be used for all the series of all wavelengths where $n > p$

Example 19.1

What wavelength does a hydrogen atom emit as its excited electron falls from the n = 5 to the n = 2 state.

Solution:

Wavelength = λ = ?

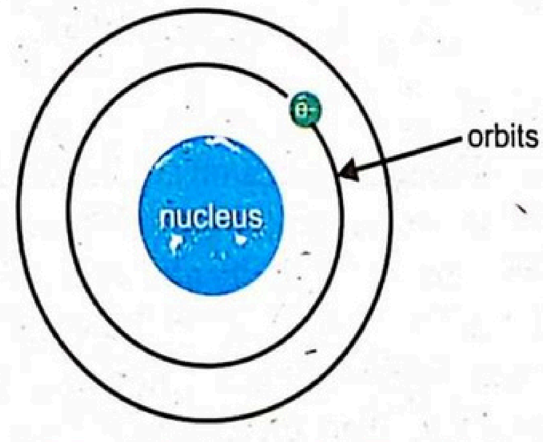
$$\frac{1}{\lambda} = R_H\left(\frac{1}{p^2} - \frac{1}{n^2}\right)$$

$$\frac{1}{\lambda} = 1.097\times10^7\left(\frac{1}{2^2} - \frac{1}{5^2}\right)$$

$$\lambda = 4.33\times10^{-7}\,\text{m} = 443\,\text{nm}$$

19.2 BOHR'S ATOMIC MODEL OF THE HYDROGEN ATOM

In order to modify Rutherford's model, Niels Bohr proposed his own model of atom and explained the empirical formula of atomic spectra in 1913 by using both classical and Planck's quantum theories. It gives an accurate account of the atomic spectrum of hydrogen as well as the stability of an atom. The Bohr's model is based on the following three postulates:



An electron in its allowed orbit around the nucleus

i:- An electron in an atom can move around the nucleus in certain circular stable orbit, without emitting energy. Electrons can exist only in certain discrete orbits called allowed orbits and electrons have definite energy values such as: E_1, E_2, E_3, etc. in these orbits.

ii:- An electron can revolve around nucleus only in those circular orbits in which its angular momentum is an integral multiple of $\frac{h}{2\pi}$ or $\hbar$ i.e.,

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

as

$$L = r \times P = mv_n r_n$$

$$mv_n r_n = \frac{nh}{2\pi} \quad ......(19.7)$$

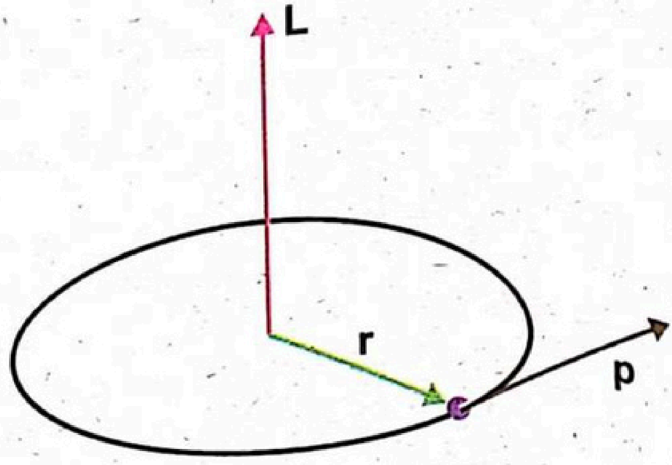
This relation is known as Bohr's quantization rule of angular momentum, where 'n' is the principle quantum number and n = 1, 2, 3, ... and 'h' is a Planck's constant.

iii:- An electron emits energy only when it makes a transition i.e., it jumps from higher allowed orbit to lower allowed orbit. If E_n be the total energy of an electron in the higher orbit and E_p be the total energy in the lower orbit then the energy emitted by an electron is given by

$$E_p - E_n = hf......(19.8)$$

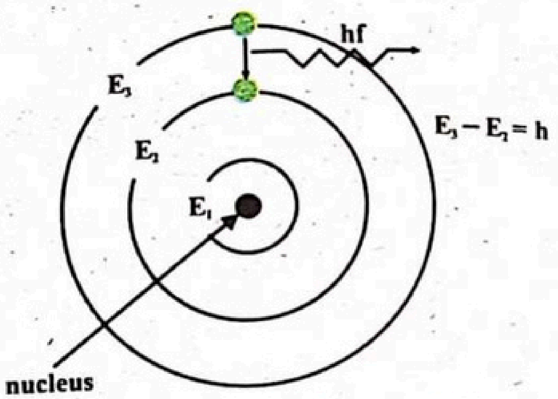
Radii of the quantized orbits

The hydrogen atom is the simplest atom. It has an electron of mass 'm' which is revolving in its allowed orbit of radius 'r_n' with velocity 'v_n' around the nucleus having a single proton as shown in Fig.19.4. The electrostatic force of attraction between the electron and proton provides the required centripetal force to the electron i.e.,



Angular momentum of an electron

Transitions between states



Electron emits energy when it jumps from higher orbit to lower.

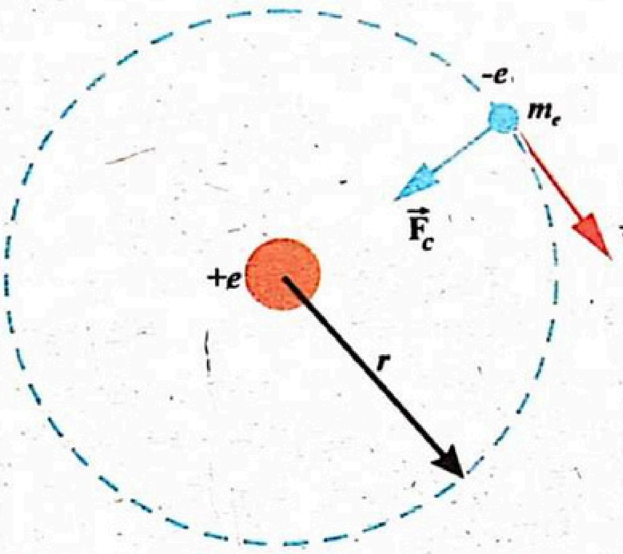


Fig.19.4 An electron is revolving in an orbit around the nucleus of hydrogen atom where the electrostatic force between nucleus and electron causes a centripetal force.

$$F_c = F_e$$

$$\frac{mv_n^2}{r_n} = \frac{ke^2}{r_n^2}$$

$$v_n^2 = \frac{ke^2}{mr_n} \quad \text{......(19.9A)}$$

According to the 2nd postulate or Eq.19.7

$$mv_n r_n = \frac{nh}{2\pi}$$

POINT TO PONDER

Why is the Bohr model of the hydrogen atom incompatible with uncertainty principle?

$$v_n = \frac{nh}{2\pi m r_n}$$

$$v_n^2 = \frac{n^2h^2}{4\pi^2m^2r_n^2} \quad \text{......(19.9B)}$$

Comparing the R.H.S.'s of Eq. 19.9A and 19.9B we get

$$\frac{n^2h^2}{4\pi^2m^2r_n^2} = \frac{ke^2}{mr_n}$$

$$r_n = \frac{n^2h^2}{4\pi^2kme^2} \quad \text{......(19.10)}$$

By substituting the values of 'h', k, m and e we get

$$r_n = \frac{n^2\left(6.625\times10^{-34}\right)}{4(3.14)^2\left(9\times10^9\right)\left(9.1\times10^{-13}\right)\left(1.6\times10^{-19}\right)}$$

$$r_n = \left(0.053\times10^{-9}n^2\right)\text{m} \quad \therefore \left(10^{-9}\text{m} = \text{nm}\right)$$

$$r_n = \left(0.53n^2\right)\text{nm} \quad \text{......(19.11)}$$

For the 1st orbit $\quad n = 1$

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

This is called Bohr's radius. Based on Eq.19.11, we can develop a general relation for Radii of the quantized orbits of hydrogen atom as;

$$r_n = n^2 r_1 \qquad \text{where} \quad r_1 = \frac{h^2}{4\pi^2kme^2}$$

As $\quad n = 1,2,3$

$\therefore \quad r_n = r_1, 4r_1, 9r_1, \cdots$

Energies of electron in the quantized orbits

When an electron is revolving in its allowed orbit, it possesses both the K.E. and P.E.. The sum of K.E. and P.E. is equal to the total energy 'E_n' of the electron i.e.,

$$E_n = \text{K.E.} + \text{P.E.}$$

$$E_n = \frac{1}{2}mv^2 + F \cdot r_n$$

As angle 'θ' between F and r_n is 180° so $F.r_n = Fr_n \cos 180^\circ = -Fr_n$

and
$$F = \frac{ke^2}{r_n^{\ 2}}$$

Thus
$$E_n = \frac{1}{2}m\left(\frac{ke^2}{mr_n}\right) - \frac{ke^2}{r_n^{\ 2}} r_n$$

$$E_n = \frac{ke^2}{2r_n} - \frac{ke^2}{r_n}$$

$$E_n = -\frac{ke^2}{2r_n} \quad \text{......(19.12)}$$

By substituting the value of r_n from Eq.19.10 we get

$$E_n = \frac{-2\pi^2k^2me^4}{n^2h^2}$$

$$E_n = \frac{2(3.14)^2\left(9\times10^9\right)^2\left(9.1\times10^{-31}\right)\left(1.6\times10^{-19}\right)^4}{n^2\left(6.625\times10^{-34}\right)^2}$$

$$E_n = -\frac{2.17\times10^{-18}}{n^2} J$$

$$E_n = -\frac{2.17\times10^{-18}}{n^2\left(1.6\times10^{-19}\right)} eV \qquad \therefore 1eV = 1.6\times10^{-19} J$$

$$E_n = \frac{-13.6}{n^2} eV \quad \text{......(19.13)}$$

For the 1st orbit, n =1

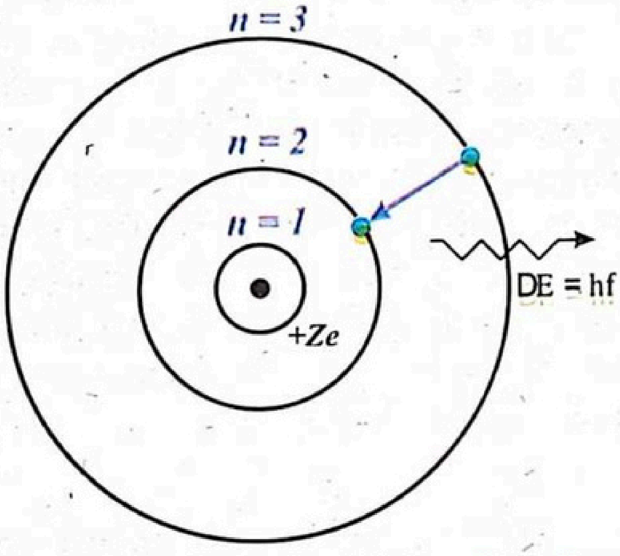
$$E_1 = -13.6eV$$

Based upon Eq.19.13, we can express a general relation for the energies of an electron in the quantized orbits as

$$E_n = -\frac{E_1}{n^2}$$

$$E_n = -E_1, \frac{-E_1}{4}, \frac{-E_1}{9}, \frac{-E_1}{16}, \ldots \frac{-E_2}{n^2}$$

Spectral lines of hydrogen atom



When electron jumps from higher orbit to lower orbit it emits energy in form of a spectral line.

Another most important result of Bohr's theory is the determination of spectrum of hydrogen atom. i.e., when an electron absorbs energy equal to the difference of energy between the two states then the electron jumps from lower energy state to higher energy state. At this position, the atom is said to be in the excited state. On de-excitation i.e., when the electron jumps from higher energy state to its ground state it emits the energy during this transition in the form of spectral lines. For example, if an electron in the hydrogen atom is in the excited state 'n' with energy E_n and it makes a transition to the lower state 'p' with energy E_p, where $E_n > E_p$, then according to the 3rd postulate

$$E_n - E_p = hf$$

$$\frac{-E_1}{n^2} - \left(\frac{-E_1}{p^2}\right) = hf$$

$$E_1\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = hf$$

But $\quad c = f\lambda \Rightarrow f = \frac{c}{\lambda}$

Therefore,

$$E_1\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{p^2} - \frac{1}{n^2}\right)$$

$$\frac{1}{\lambda} = R_H\left(\frac{1}{p^2} - \frac{1}{n^2}\right) \quad \ldots\ldots(19.14)$$

POINT TO PONDER

What is the energy of the photon emitted when a hydrogen atom makes a transition from the n = 2 state to n=1 state?

The relevant masses are:
$m\left({}_1^2H\right)=2.014102u$, $m\left({}_1^3H\right)=3.016049u$, $m\left({}_2^4He\right)=4.002603u$ and $m\left({}_0^1n\right)=1.008665u$

(17.6 MeV)

7. Calculate the amount of energy released in the nuclear fission reaction.

$${}_0^1n+{}_{92}^{235}U\rightarrow{}_{56}^{141}Ba+{}_{36}^{92}Kr+{}_0^1n+Q$$

The relevant masses are:
$m\left({}_0^1n\right)=1.008665u$, $m\left({}_{92}^{235}U\right)=235.043924u$, $m\left({}_{56}^{141}Br\right)=140.913740u$, and $m\left({}_{36}^{92}Kr\right)=91.926270u$.

(174 MeV)

8. How much energy is released during following reaction?

$${}_1^1H+{}_3^7Li\rightarrow{}_2^4He+{}_2^4He+Q$$

The relevant nuclear masses are:
$m\left({}_1^1H\right)=1.007825u$, $m\left({}_3^7Li\right)=7.016005u$, and $m\left({}_2^4He\right)=4.002603u$

(17.3 MeV)

II Balmer Series

If the electrons of hydrogen atom jump from the outer orbits (n = 3, 4, 5, ...) to the 2^{nd} orbit (p = 2) then a set of spectral lines called Balmer series is obtained. The spectral lines of the Balmer series lie in the visible region. The wavelengths of the Balmer series are given by

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad \begin{array}{l} p = 2 \\ n = 3,4,5... \end{array}$$

III Paschen Series

When the electrons of hydrogen atom jump from the outer orbits (n = 4, 5, 6, ...) to the 3^{rd} orbit (p = 3), the set of spectral lines called Paschen series is obtained. Paschen series lie in the infrared region and corresponding wavelengths can be calculated as;

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \qquad \begin{array}{l} p = 3 \\ n = 4,5,6... \end{array}$$

IV Brackett Series

In Brackett series the transition of electrons take place from the outer orbits (n = 5, 6, 7, ...) to the 4^{th} orbit (p = 4). Therefore, the formula for the wavelength of the lines in the infrared region in this series is given by

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \qquad \begin{array}{l} p = 4 \\ n = 5,6,7... \end{array}$$

V Pfund Series

If the transition of electrons take place from the outer orbits (n = 6, 7, 8, ...) to the 5^{th} orbit (p = 5), then there are a number of spectral lines in the infrared region and this series is called Pfund series. The wavelengths of lines in the Pfund series are given by

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{p^2} - \frac{1}{n^2}\right) = R_H\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \qquad \begin{array}{l} P = 5 \\ n = 6,7,8... \end{array}$$

Example 19.2

An hydrogen atom is in its ground state. Using Bohr's theory calculate

(a) the radius of the orbit of the electron.

(b) the linear momentum of the electron

(c) the angular momentum of the electron

(d) the kinetic energy of the electron
(e) the potential energy of the electron
(f) the total energy of the electron

Solution:

Mass of electron = m = 9.1×10^{-31} Kg
Charge on an electron = e = 1.6×10^{-19} C
Planck's constant = h = 6.625×10^{-34} J – s
Number of orbit = n = 1
Coulomb's constant = k = $9 \times 10^{9}\ Nm^2C^{-2}$

(a) Radius (r) = ?
(b) Linear momentum = P = ?
(c) Angular momentum = $\overline{L}$ = ?
(d) K.E. = ?
(e) P.E. = ?
(f) T.E. = ?

(a) As
$$r_n = \frac{n^2h^2}{4\pi^2kme^2}$$

$$r_1 = \frac{(1)^2\left(6.63\times10^{-34}\right)^2}{4(3.14)^2\left(9\times10^{9}\right)\left(9.1\times10^{-31}\right)\left(6.1\times10^{-19}\right)^2}$$

$$r_1 = \frac{46.9\times10^{-68}}{8.3\times10^{-57}}$$

$$r_1 = 5.3\times10^{-11}\text{m} = 0.053\text{nm}$$

(b)
$$p = mv$$

As
$$v^2 = \frac{ke^2}{mr} \Rightarrow v = e\sqrt{\frac{k}{mr}}$$

$$p = me\sqrt{\frac{k}{mr}} = e\sqrt{\frac{mk}{r}}$$

$$p = 1.6\times10^{-19}\text{C}\sqrt{\frac{9.1\times10^{-31}\text{kg}\times9\times10^{9}\text{Nm}^2\text{C}^{-2}}{5.3\times10^{-11}\text{m}}}$$

$$p = 1.6\times10^{-19}\sqrt{15.45\times10^{-11}}$$

$$p = 1.6\times10^{-19}\sqrt{1.545\times10^{-10}}$$

$$p = 1.6\times10^{-19}\times1.243\times10^{-5}$$

$$p = 1.99\times10^{-24}\text{kg m s}^{-1}$$

(c) $$L = rp\sin\theta$$

If 'θ' between $\vec{r}$ and $\vec{p}$ is 90^0, then

$$L = 5.3\times10^{-11}\,\text{m}\times1.99\times10^{-24}\,\text{kg m s}^{-1}\times90^0$$

$$L = 1.05\times10^{-34}\,\text{kg m}^2\,\text{s}^{-1}$$

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

$$= \frac{1}{2}m\cdot\frac{ke^2}{mr} = \frac{1}{2}\frac{ke^2}{r}$$

$$= \frac{1}{2}\times\frac{\left(9\times10^9\,\text{Nm}^2\text{C}^{-2}\right)\left(1.6\times10^{-19}\,\text{C}\right)^2}{5.3\times10^{-11}\,\text{m}}$$

$$= \frac{23.04\times10^{-29}}{10.6\times10^{-11}}\,\text{J}$$

$$K.E. = 2.17\times10^{-18}\,\text{J} = 13.56\,\text{eV}$$

(e) $$P.E. = \frac{-ke^2}{r}$$

$$= \frac{\left(-9\times10^9\,\text{Nm}^2\text{C}^{-2}\right)\left(1.6\times10^{-19}\,\text{C}\right)^2}{5.3\times10^{-11}\,\text{m}}$$

$$= \frac{-14.4\times10^{-10}\times1.6\times10^{-19}}{5.3\times10^{-11}}$$

$$= -2.717\times10\times1.6\times10^{-19}$$

$$P.E. = -27.17\,\text{eV}$$

(f) $$T.E = K.E. + P.E.$$

$$= 13.56\,\text{eV} - 27.17\,\text{eV}$$

$$T.E = -13.61\,\text{eV}$$

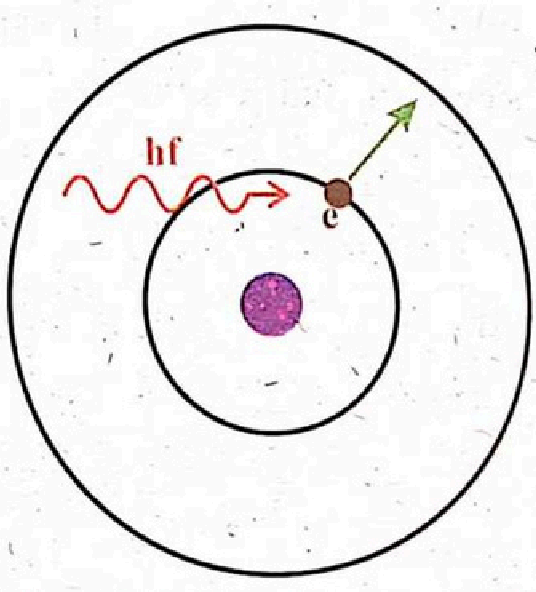
19.3 EXCITATION ENERGY AND EXCITATION POTENTIAL

We have studied an atom of hydrogen has quantized orbits called allowed orbits with discrete energy levels. The electrons can revolve around the nucleus without radiating energy in these allowed energy orbits. For example, hydrogen atom has a single electron and it is revolving in its lowest orbit called ground state. Let the electron absorbs some energy and it is excited from its ground state to the higher allowed orbits. The energy that absorbed by the electron to jump from the ground state to the excited states is known as excitation energy and it is equal to the difference of energies of the electrons in the two states. It is measured in terms of eV_o, where

'V_o' is the applied potential which provides the excitation energy to an electron. Therefore, it is called excitation potential.

As we know that in case of hydrogen atom, the total energy of an electron in its ground state is ($E_1=-13.6eV$). Similarly the total energy of an electron in the second state is ($E_2=-3.4eV$). Thus, the excitation energy of an electron from ground state to the 2nd state is given by

$$E = E_2 - E_1$$
$$E = -3.4-(-13.6)$$
$$= 10.2eV$$



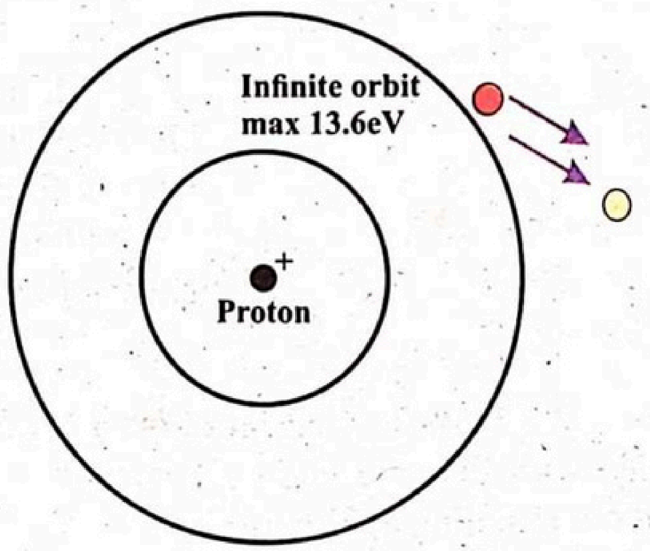
The electron excited by a photon's energy hf.

Similarly, the excitation energy of an electron from the ground state (E_1) to the 3rd state (E_3) is given by

$$E = E_3 - E_1$$
$$E = -1.51-(-13.6) = 12.1eV$$

19.4 IONIZATION ENERGY AND IONIZATION POTENTIAL

When an electron is boosted from its ground state to infinity, such that the electron becomes free from the electrostatic force of the nucleus, then the atom is said to be ionized. The energy required to escape an electron completely from its ground state to infinity is known as ionization energy. It is measured in terms of eV_o, where 'V_o' is the applied potential which provides ionization energy to an electron so, it is called ionization potential. For example, in case of hydrogen atom, the total energy of an electron in its ground state is ($E_1 = -13.6eV$). Consider the case in which the electron has moved to infinity, the energy of the orbit at the infinity is zero ($E_\infty = 0$). Thus, the ionization energy of hydrogen atom is given by



Ionization of an atom by a photon of energy greater than $13eV_0$

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

This shows that the ionization energy of the hydrogen atom is 13.6eV and the ionization potential is 13.6 volts. It may be noted that there is only one value of ionization potential i.e. 13.6V for hydrogen atom because it has a single electron. There can be more than one value of ionization potentials for the atoms with several electrons.

19.5 INNER SHELL TRANSITIONS AND X-RAYS

We have discussed that when electrons make a transition from their higher orbits to lower orbits then they emit radiations in form of spectral lines in the range of infrared, visible or ultraviolet light.

In heavy atoms, electrons are arranged in concentric shells which are named as K, L, M, N, O...... shells, as shown in Fig.19.7(a). The electrons in the outer shells are loosely bound with the nucleus due to large distance and weak electrostatic force between electrons and the nucleus. Therefore, a small amount of energy is required for excitation of the electrons from the outer shells of such atoms. When the electrons return to their original states, they emit radiation of longer wavelength, which lie in the infrared region.

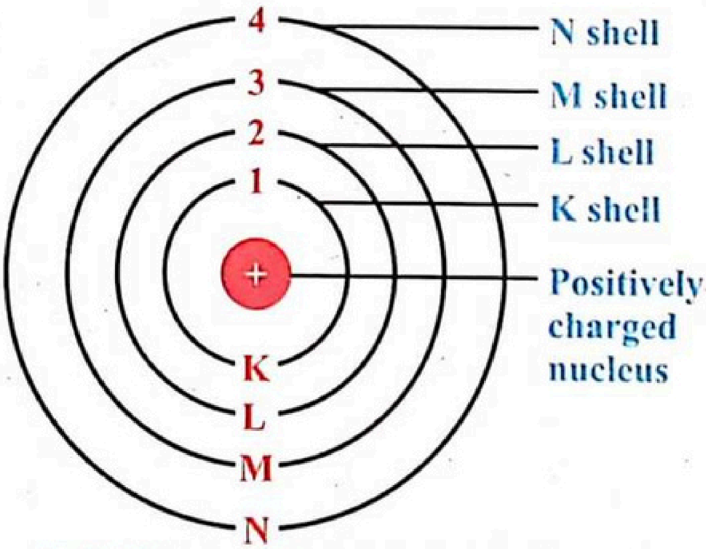


Fig.19.7(a). An isolated atom possessed a number of concentric shells.

On the other hand, the electrons in the inner shells are tightly bound with their nucleus due to a small distance and strong electrostatic force between the electrons and the nucleus. Therefore, a large amount of energy is required for excitation of these electrons. When the electrons return to their ground states, they emit highly energetic radiations of shorter wavelength, which are lying in the ultraviolet region. These highly energetic radiations are named as x-rays which are also known as characteristic x-rays.

In other words, characteristic x-rays are emitted from heavy elements due to inner shell transition, i.e., when their electrons make transitions between the different energy levels. As each element has a unique set of atomic energy levels, it emits a unique set of x-rays which are characteristic of that element. X-rays originate from atomic electrons and also from free electrons decelerating in the vicinity of heavy atoms (i.e., Bremsstrahlung).

Production of x-rays:

X-rays are electromagnetic waves which have extremely short wavelengths. They were discovered by Rontgen in 1895 when he was investigating cathode rays.

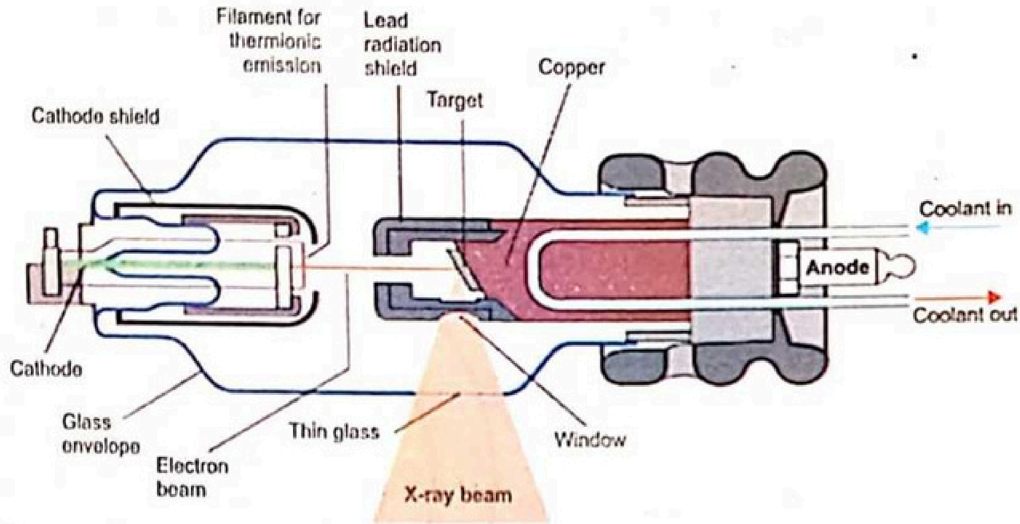


Fig.19.7(b). A schematic diagram for the production of x-rays, where electrons emitted by the hot filament are allowed to hit the target. The target then emits x-rays. .

In modern age, a tube called x-rays tube is used to produce x-rays as shown in Fig.19.7(b). Such tube consists of cathode and anode, where cathode is a heated filament and it acts as a source of electrons. The electrons emitted from the heated filament are accelerated through potential difference of the order 10^5V. When these high energy electrons strike the target anode (usually tungsten, molybdenum or copper), only a small fraction about 1% of the kinetic energy of the incident electrons is converted into x-rays while the remaining energy of the electrons is converted into heat at the anode. It is therefore, the target should be metal of high melting point. The target is cooled using cooling fans

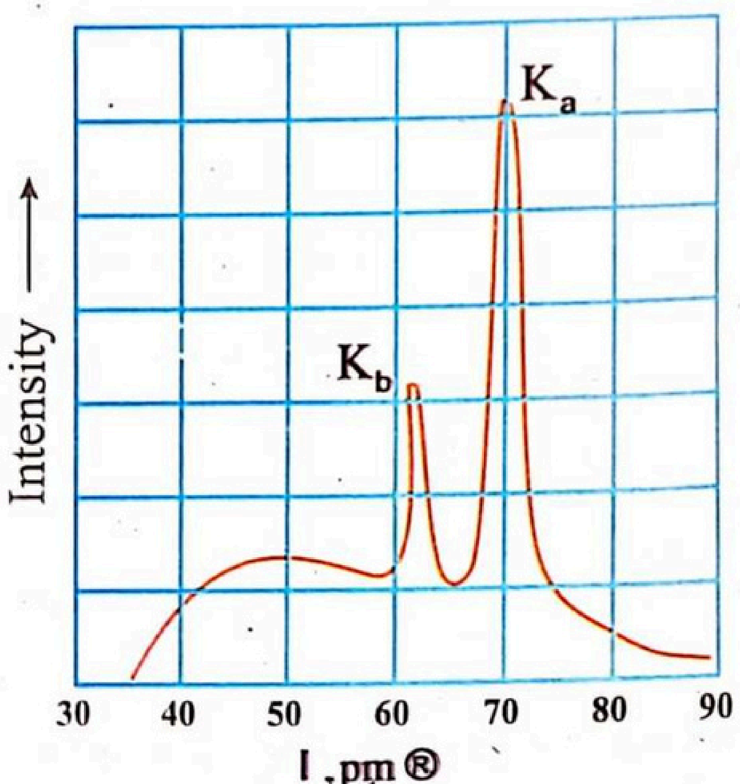


Fig.19.7(c). Graphical representation of x-rays spectrum.

or a specially designed cold water summing system. The x-rays emitted from x-ray tube consist of various wavelengths and forms a spectrum. Graphically, it is shown in Fig.17.7(c). The x-ray spectrum produced by x-ray sources consists of continuous spectra and the line or characteristic x-ray spectra but no band spectra. **Continuous spectra or continuum radiation also called white radiation or bremsstrahlung.** Bremsstrahlung refers to "braking radiation" derived from German word bremsen "to brake" and Strahlung "radiation". Line spectra or characteristic X ray corresponds to quantum energies of inner shell transition of electrons.

x-rays are most commonly produced by bombardment of a metal target with a beam of high energy electrons. When highly energetic electrons from cathode strikes the target they knocks out one of the electrons from innermost K-shell. The atom is then raised to an excited state, producing a vacancy in the K-shell. If the vacancy in the K shell is filled by an electron from L-shell, then a photon of x-ray K_α is emitted. If the vacancy in the K shell of atom is filled by an electron from M-shell, then K_β is emitted. The series of x-ray produced due to transition of electron from L shell (K_α) or M shell (K_β) is known as K-characteristic x-ray.

The characteristic L series are produced when vacancies in the L-shell are filled by electrons from the higher energy states. The shorter-wavelength group is called the K series (from 1s orbital) and the L series (from 2s or 2p), even longer then L lines are M-series. Elements with atomic numbers smaller than 23 produce only a K series.

19.6 LASER

The term LASER is an acronym for 'light amplification by stimulated emission of radiation'. A laser is a device which produces intense, monochromatic and coherent beam of visible or infrared light. The fundamental principle of laser is that, the excited atoms are stimulated by the incident photon in order to emit another photon of same frequency as that of the frequency of incident photon. Thus, the emitted and the incident photons having same frequencies will travel away in phase. In order to understand the working of a laser, we explain some phenomenon related to it.

Spontaneous and stimulated emissions

Consider an atom has an electron in its ground state as shown in Fig.19.8(a). Suppose a photon of energy hf equal to the energy difference between two energy levels is incident on this atom then the photon can be absorbed by the atom. This process is called stimulated absorption because the photon stimulates the atom to transfer the electron from its ground state to the excited state as shown in Fig.19.8(b).

After the excitation, the electrons make a transition back to a lower energy state, because the electrons can remain in an excited state typically for 10^{-8}s. Moreover, during the transition when the electrons come back to the ground state, then it emits a photon of energy hf as shown in Fig.19.9. This process is known as spontaneous emission.

Now consider an atom which is in an excited state E_2 with lifetime 10^{-3}s, this lifetime is much longer than 10^{-8}s. Therefore, the excited state E_2 is called metastable state. Metastable state is an abnormally excited state of an atom with a longer lifetime than the other ordinary excited states. Thus, for an electron in its metastable state E_2 if a photon of energy $hf = E_2 - E_1$ is incident, it induces the electron returns to the ground state by emitting a second photon with energy $hf = E_2 - E_1$. **The phenomenon when an incident photon induce transition electron to make downward transition with the release of photon of same frequency is known as stimulated emission.** These two photons i.e., incident and emitted are in phase and travel in the same direction as shown in Fig.19.10.

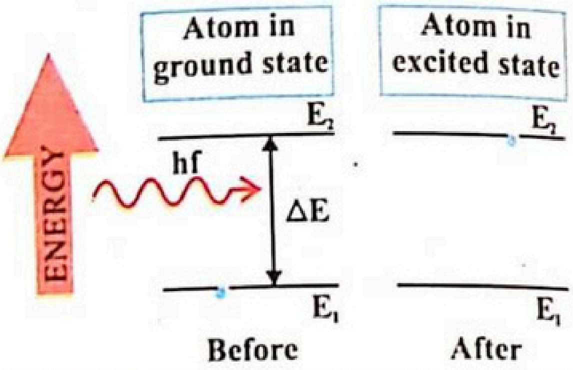


Fig.19.8(a). the electron of an atom in its ground state (b) the process of stimulated absorption, where the transition of electron from the ground state to the excited state when the atom absorbs the photon of energy hf.

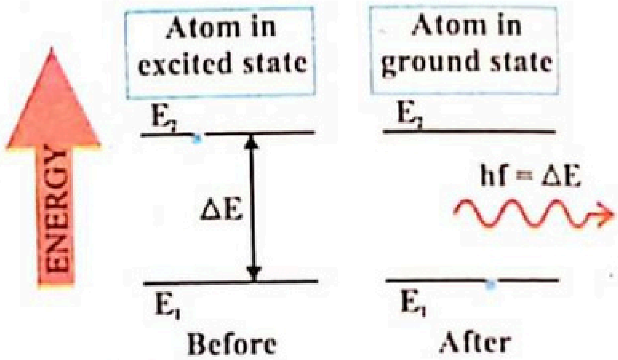


Fig.19.9. the process of spontaneous emission of photon due to the transition of electron from the excited state to the ground state.

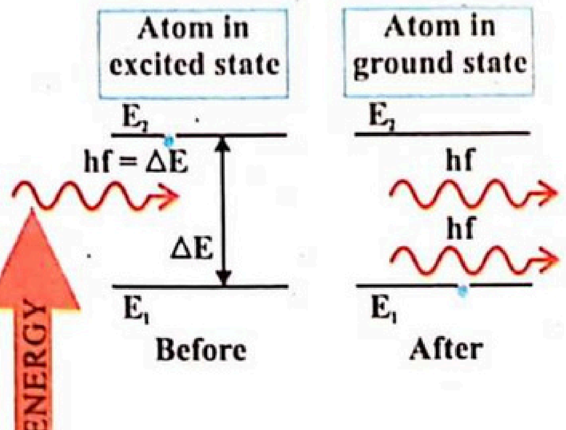


Fig.19.10. Stimulated emission of photon by incident of photon.

Population inversion

When there are more atoms in the ground state than in the excited state this is known as normal population as shown in Fig.19.11(a). On the other hand, when there are more atoms in their excited states than the ground state as shown in Fig.19.11(b), this condition is called population inversion. If the number of atoms in the excited state becomes more than number of atoms in the ground state, then more stimulated emissions occur. Population inversion can be achieved if there exists metastable state. This is the most important principle that involves in the action of a laser. One method of achieving population inversion is 'optical pumping' i.e., illuminating the laser material with light. The process of light stimulated emission is fundamental to laser operation.

Laser is produced by an active medium or gain medium inside the laser optical cavity. The active medium is a collection of atoms, or molecules that can undergo stimulated emission. The active medium can be in a gaseous, liquid or solid form.

Hence the essential components of a LASER are medium, pump (source of energy) and resonant cavity.

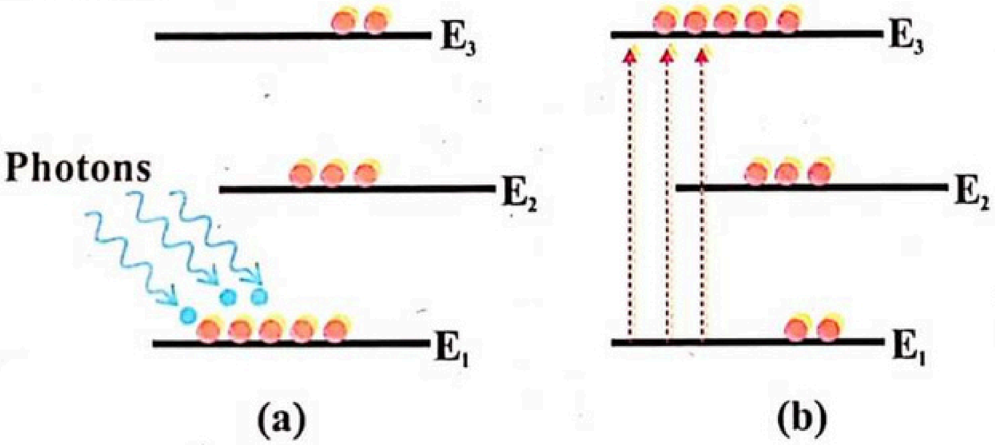


Fig.19.11(a). Normal population (b) Population inversion.

LASER action

Suppose population inversion has been achieved by some means and the atoms are gathered in the excited states E_2 and E_3 as shown in Fig.19.12. After the process of excitation, a spontaneous emission occurs due to the transition of atoms from the excited state E_3 to the excited state E_2 (metastable) because the lifetime of E_3 is only 10^{-8} s, and the lifetime of metastable (E_2) is 10^{-3} s which is much longer than 10^{-8}s.

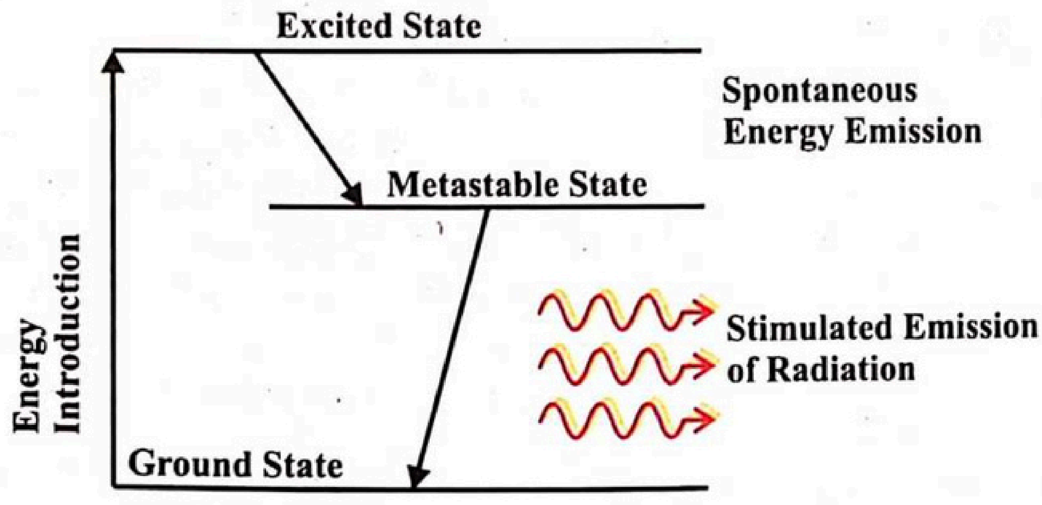


Fig.19.12. Energy level diagram showing stimulated absorption, spontaneous emission and stimulated emission.

In order to get the stimulated emission, a photon of energy $hf = E_2 - E_1$ is incident. This incident photon induces the stimulated emission. As a result, another photon is emitted having the same energy hf and travelling in the same direction. These two photons are in phase and they can stimulate other atoms to emit photons in a chain to similar processes. Thus, a chain of these emitted photons causes an intense, monochromatic and coherent beam of light i.e., laser.

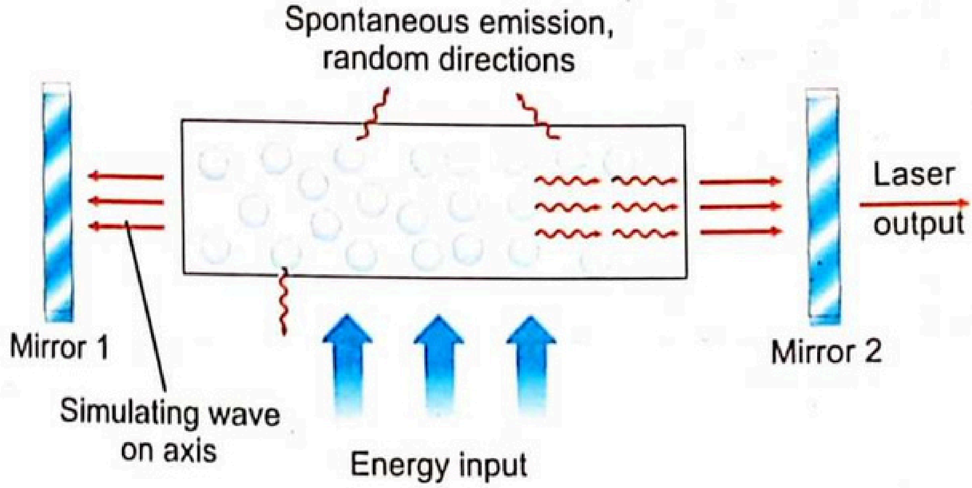


Fig.19.13. Schematic diagram of LASER action, the two mirrors keep the photons confined to the system.

The emitted photons must be confined in an optical cavity long enough to enable them to stimulate further emission from other excited atoms. It can be achieved by using two mirrors at the ends of this optical cavity as shown in Fig.19.13. One end of this assembly is made totally reflecting and the other is partially reflecting. The photons are reflecting back and forth between the two mirrors from the end of this optical cavity, so a very intense, monochromatic and coherent beam is setup and a small fraction of the beam passes through the partially reflecting mirror, producing the beam of the laser light.

Helium-neon laser

A familiar example of a laser is the helium-neon laser. It is a common and inexpensive laser that is available in physics laboratories. The helium-neon laser usually consists of a gas discharge tube containing a mixture of 85% helium and 15% neon gas at low pressure. The metastable states of helium and neon are identically located at 20.61eV and 20.66eV respectively, which are much closer to each other. When the helium-neon laser is electrically pumped then the electrical discharge excites the atoms of helium from the ground state to its metastable state with energy 20.61eV as shown in Fig.19.14.

Now these excited atoms of helium make inelastic collisions with the atoms of neon in the ground state. Therefore, there is transfer of energy from the excited helium atoms to the neon atoms in the ground state. As a result, the neon atoms are excited from the ground state to the metastable state with energy 20.66eV while the helium atoms return to their ground state. In this way, we have the necessary population inversion in neon. After population inversion, stimulated emission occurs during the transition of neon atoms from its metastable state of energy 20.66eV to the excited state of energy 18.70eV. Thus, it causes emission of highly coherent laser light of wavelength 632.8nm. Finally, spontaneous transition quickly takes place during the transition of neon atoms from the excited energy state 18.70eV to the ground state.

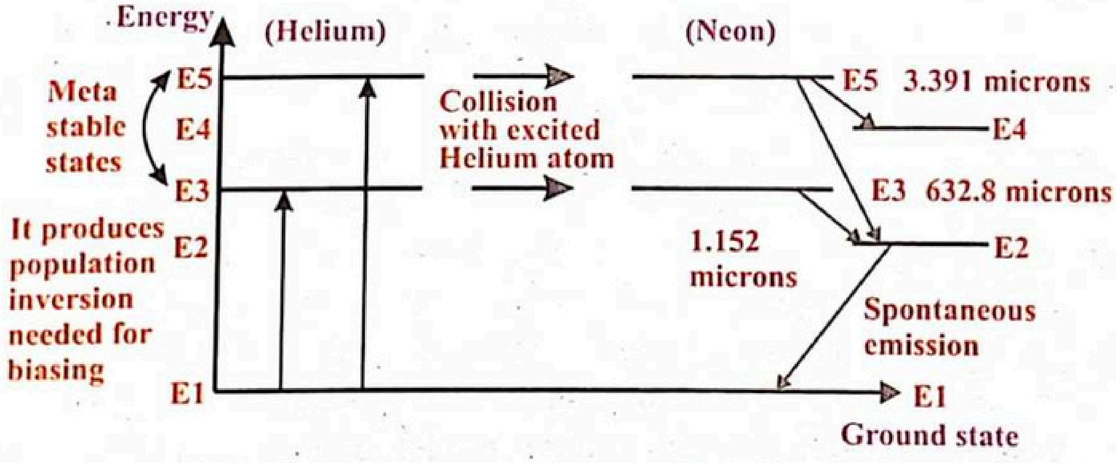


Fig.19.14. A schematic energy level diagram for Helium and Neon gas LASER.

Laser have several usage and applications, some of them are listed below:

i Lasers are used to destroy tumors and to fragment kidney stones and gallstones.

ii A detached retina of the eye can be welded back into place by using a laser beam.

iii Laser surgery is used to reshape the cornea of the eye to correct near sightedness (myopia).

iv Laser is used in the process of endoscope.

v Intense laser beam is being used for ranging i.e., to determine far distance between two objects accurately, such as, the distance between earth and moon.

vi A high intensity laser beam can drill a very small hole in hand objects such as diamond.

FOR YOUR INFORMATION

A patient undergoes laser eye surgery to correct his vision by modifying the shape of the surface of the eyeball. This process is called LASIK (laser assisted in situ keratomileusis).

vii A laser light is being used as a communication signal through a fiber optics and it can transmit both video and audio information.

viii Laser plays a dynamic role in the system of compact disc (CD) and digital video disc (DVD) players.

ix A laser beam is being used to draw three dimensional photography called holography.

x A laser light also used in the printing process called laser printing.

xi A laser beam has a potential to induce and control the fusion reaction.

xii Laser is being used for weapons guided system and submarine tracking.

SUMMARY

- **Spectrum:** A set of wavelengths or frequencies is known as spectrum (spectra). It can be classified into line, band and continuous spectra.
- **Emission Spectra:** The spectra due to the emission of light from excited atoms (gas) is called emission spectra, such spectra contain a series of visible lines.
- **Absorption Spectra:** The spectra due to the passing of visible light through a gas is called absorption spectra, such spectra contain few dark lines.
- **Bohr's Atomic Model:** Bohr's atomic model can be explained under the following postulates:
  i An electron does not radiate energy when it is revolving in its allowed orbit.
  ii Electrons are revolving in the allowed orbits for which their angular momenta is an integral multiple of $\frac{h}{2\pi}$.
  iii An electron radiates energy only when it jumps from higher orbit to lower orbit.
- **Spectrum of hydrogen atom:** When an electron in an excited hydrogen atom makes transition from higher orbits to lower orbits then it emits radiations in the form of spectral lines series.
- **Excitation energy and excitation potential:** The amount of energy which can raise an electron from its normal state to higher energy state is called excitation energy, and the potential which provides such energy is called excitation potential.
- **Ionization energy and ionization potential:** The amount of energy required to make an electron free from the electrostatic force of the nucleus is called ionization energy and the potential which provides such energy is known as ionization potential.
- **Characteristic X-rays:** Characteristic x-rays are emitted from heavy elements due to inner shell transition, i.e., when their electrons make transitions between the different energy levels.

- **LASER:** Laser is a device stands for light amplification by stimulated emission of radiation and it produces intense, monochromatic and coherent light.
- **Stimulated absorption:** Absorption of photon by electron that electron becomes excited from ground state to higher state energy level.
- **Spontaneous Emission:** Emission of photon by an atom during the transition from the higher orbit to the lower orbit.
- **Metastable State:** Second energy state (E_2) is known as metastable state because it has longer lifetime of 10^{-3}s.
- **Population Inversion:** If there are more atoms in a higher energy state or excited state than the ground state then this condition is called population inversion.
- **Stimulated Emission:** A process in which a photon is incident with the excited electron, causing the electron to jump from excited state to de-excited state by emitting a photon of same frequency is that of the incident photon.

EXERCISE

Select the best option of the following questions.

1. When light is passed through a gas at low pressure then we observe
   (a) Emission spectra (b) Absorption spectra
   (c) Band spectra (d) Molecular spectra
2. The spectra due to absorption or emission of radiation by atoms of a gas is known as
   (a) Line spectra (b) Band spectra
   (c) Continuous spectra (d) Molecular spectra
3. The band spectra is produced due to emission or absorption of radiation by
   (a) Atoms (b) Molecules (c) Electrons (d) Photons
4. Dark lines correspond to
   (a) Emission spectra (b) Absorption spectra
   (c) Band spectra (d) Continuous spectra
5. Name of the scientist who identified the four lines spectrum series for the first time
   (a) Lyman (b) Balmer (c) Paschen (d) Brackett
6. Which one of the following spectrum series is found in the visible region?
   (a) Brackett (b) Pfund (c) Balmer (d) Paschen
7. Lyman series lies in which region
   (a) Visible (b) Infrared (c) Violet (d) Ultraviolet
8. The dimensions of Rydberg constant are
   (a) $[M^0L^0T]$ (b) $[M^0LT^0]$ (c) $[M^0LT]$ (d) $[M^0L^{-1}T^0]$

9. When an electron in hydrogen atom is raised from the ground state to the 2nd energy state, how many times its radius is greater than the radius of its ground state

(a) Same (b) Half (c) Twice (d) Four time

10. When an electron in hydrogen atom is raised from the ground state to the excited state then its K.E. and P.E. will be

(a) K.E. increased and P.E. decreased (b) K.E. decreased and P.E. increased
(c) Both K.E. and P.E. increased (d) Both K.E. and P.E. decreased

11. The diameter of hydrogen atom is

(a) 0.35A° (b) 0.53A° (c) 0.70A° (d) 1.06A°

12. The ionization potential of hydrogen atom is

(a) 6.13eV (b) 6.13V (c) 13.6V (d) 13.6eV

13. Laser action cannot occur with the process of

(a) Spontaneous absorption (b) Spontaneous emission
(c) Normal population (d) Population inversion

14. Stimulated emission occurs only when the population inversion is in

(a) Ground state (b) Metastable state (c) 3rd energy state (d) Any energy state

15. Lifetime of metastable state is about

(a) 10^{-2} s (b) 10^{-3} s (c) 10^{-5} s (d) 10^{-8} s

16. Lifetime of higher excited states is

(a) Equal to the metastable state (b) Shorter than the metastable state
(c) Longer than the metastable state (d) Is not compare with metastable state

SHORT QUESTIONS

1. How can you produce atomic spectra?
2. What is the difference between absorption spectra and emission spectra?
3. How can you distinguish among line, band and continuous spectra?
4. What is the reason of dark lines in the line spectra?
5. Calculate the value of Rydberg constant.
6. How the stability of an atom is explained by Bohr's postulates?
7. What do you know about the quantization of orbits?
8. Under what condition an electron can emit energy?
9. What do you know about the Bohr's radius?
10. What is the significance of negative energy of electron in an orbit?
11. What do you know about excitation energy and excitation potential?
12. Calculate ionization energy and ionization potential for hydrogen atom.
13. What is the working principle of a laser?
14. Distinguish between spontaneous and stimulated emission.
15. What is the difference between normal population and population inversion?

16. What do you know about the metastable state?
17. Why population inversion in metastable state is necessary for the action of laser?

COMPREHENSIVE QUESTIONS

1. State and explain atomic spectra with its different kinds.
2. What do you know about spectrum of hydrogen atom? Discuss the Balmer's series with empirical formula.
3. State and explain Bohr's atomic model of the hydrogen atom with postulates. Also derive the empirical formulas for radii and energies of the quantized orbits of the atom.
4. Discuss the energy level diagram and various series due to the different transition of electrons in the excited atoms.
5. What do you know about the excitation and ionization of an atom? Also discuss the potentials which are being used for excitation and ionization of atoms?
6. Explain characteristic x-rays due to the transition of electrons in the excited atoms. Also explain the production of x-rays.
7. What is LASER action? Explain the various process which are related with laser, such as spontaneous and stimulated emission and population inversion.
8. Define Helium-Neon laser. Also write down the various applications of laser.

NUMERICAL PROBLEMS

1. Calculate the shortest wavelength of the Balmer series. **(3646A°)**
2. Determine the longest wavelength in the Lyman series. **(1216A°)**
3. Calculate the speed of an electron of hydrogen atom in the second orbit and also find its kinetic energy also **(1.23×10^{12} ms^{-1}, 3.4eV)**
4. Show that the Paschen series of spectral lines is entirely in the infrared region.
5. Determine the time period of the first Bohr's orbit in the hydrogen atom. **(1.53×10^{-16} s)**
6. An electron jumps from a level $E_i = -2.2$eV to $E_f = -7.5$eV. What is the wavelength of the emitted radiation? **(234nm)**
7. The ionization energy of hydrogen atom is 13.6eV. Calculate the wavelength of the 1st line of the Lyman series. **(1212A°)**
8. The wavelength of K X-ray from copper is 1.377×10^{-10} m. What is the energy difference between the two levels from which this transition occurs? **(9.025keV)**