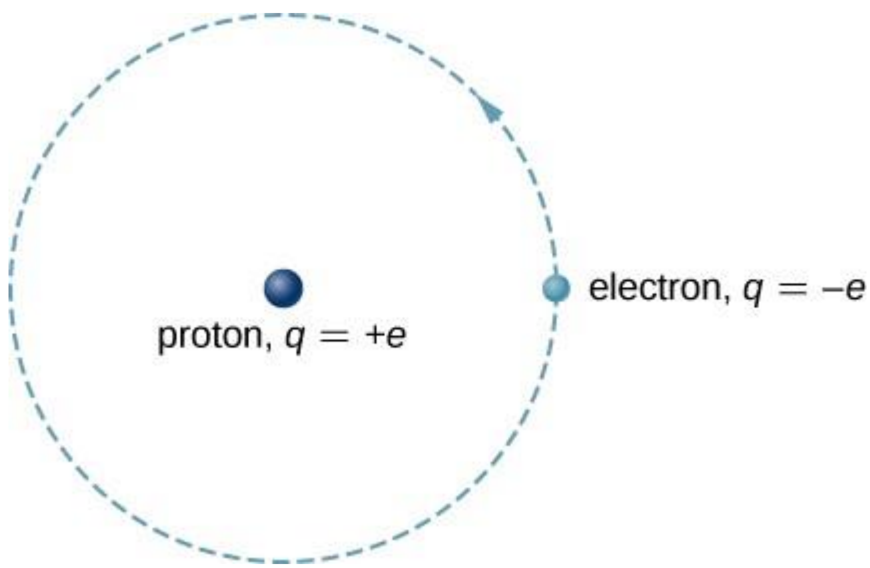
Lec 2 :Quantum mechanical description of the hydrogen atom Angular Momentum Atomic Spectra Time.

2.1 The hydrogen atom

The hydrogen atom is the simplest atom in nature and, therefore, a good starting point to study atoms and atomic structure. The hydrogen atom consists of a single negatively charged electron that moves about a positively charged proton ((Figure 1)). In Bohr's model, the electron is pulled around the proton in a perfectly circular orbit by an attractive Coulomb force. The proton is approximately 1800 times more massive than the electron, so the proton moves very little in response to the force on the proton by the electron. (This is analogous to the Earth-Sun system, where the Sun moves very little in response to the force exerted on it by Earth.) An explanation of this effect using Newton's laws is given in Photons and Matter Waves.

A representation of the Bohr model of the hydrogen atom.



hydrogen atom

2.2 Line Spectrum

You know that when we pass a beam of sunlight through a prism we get a range of colours from violet to red (VIBGYOR) in the form of a spectrum (like rainbow). This is called a continuous spectrum because the wavelengths of the light varies continuously that is without any break. Let us take another example. You are aware of the flame tests for identifying cations in the qualitative analysis. Compounds of sodium impart a bright yellow colour to the flame, copper gives a green flame while strontium gives a crimson red coloured flame. If we pass such a light through a prism it gets separated into a set of lines. This is called as a line spectrum. Fig. 5 differentiates between a continuous and a line spectrum.

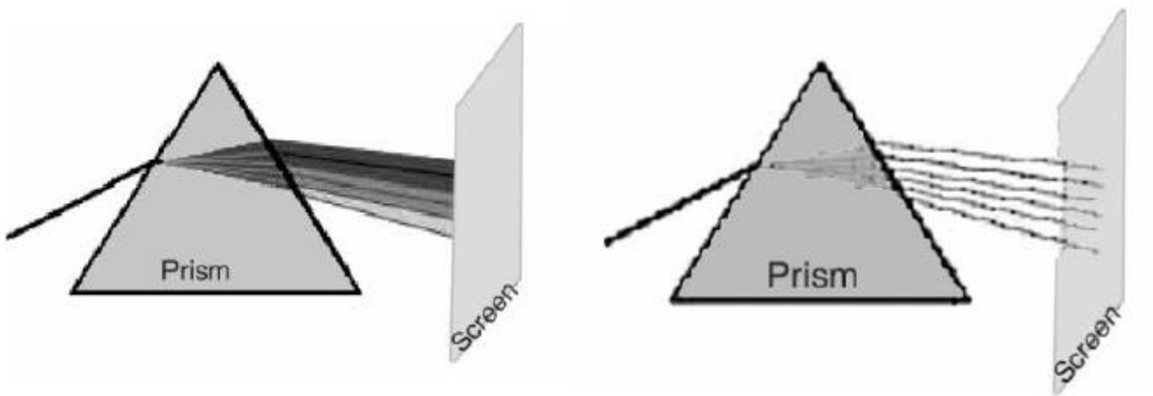


Fig. 5 : a) Continuous spectrum. b) Line spectrum.

2.3 Line Spectrum of Hydrogen Atom

When an electric discharge is passed through a discharge tube containing hydrogen gas at low pressure, it emits some light. When this light is passed through a prism it splits up into a set of five lines. This spectrum is called the line spectrum of hydrogen (Fig. 3.9).

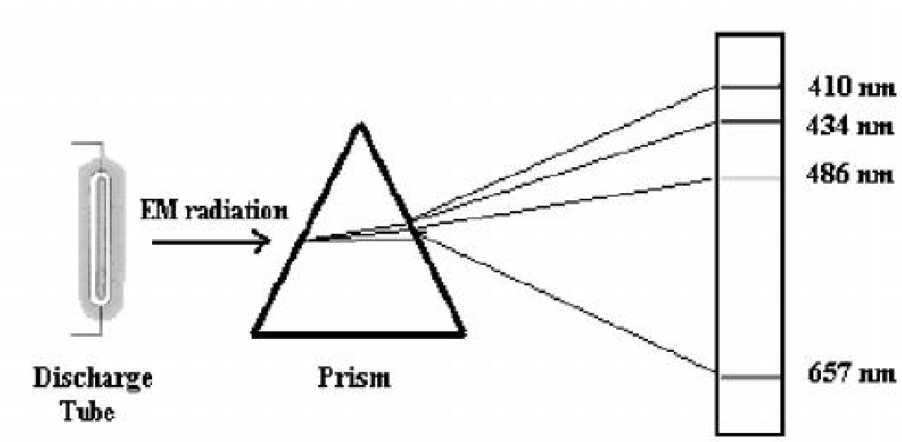


Fig. 6 : A schematic diagram showing line spectrum of hydrogen in the visible range.

On careful analysis of the hydrogen spectrum it was found to consist of a few sets of lines in the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. These spectral emission lines could be expressed in the form of a general formula as:

$$v = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad cm^{-1} \quad ; \quad R_H = 109677\ cm^{-1} \qquad \dots(1)$$

Where n_1 and n_2 are positive integers ($n_1 < n_2$) and RH is called Rydberg's constant. The different sets of lines observed in the hydrogen atom spectrum, their discoverers and the values of n_1 and n_2 are given in the Table 2.

Table 2 : Summary of the emission lines observed in hydrogen spectrum.

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4…..	Ultraviolet
Balmer	2	3,4,5…..	Visible
Paschen	3	4,5,6…..	Infrared
Bracket	4	5,6,7…..	Infrared
Pfund	5	6,7,8…..	Infrared

2.4 Bohr's Model

In 1913, Niels Bohr (1885-1962) proposed another model of the atom where electrons move around the nucleus in circular paths. Bohr's atomic model is built upon a set of postulates, which are as follows :

Bohr won the Nobel Prize in Physics in 1922 for his work.

1. The electrons move in a definite circular paths around the nucleus. He called these circular paths as orbits and postulated that *as long as the electron is in a given orbit its energy does not change* (or energy remains fixed). These orbits were therefore referred to as stationary orbits or stationary states or non-radiating orbits.
2. The *electron can change its orbit by absorbing or releasing energy*. An electron at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing (Fig 7) a single photon of energy given by

$$E = h\nu = E_f - E_i \qquad \dots(2)$$

Similarly, when electron changes its orbit from a higher initial state of energy E_i to a lower final state of energy E_f , a single photon of energy hν is released.

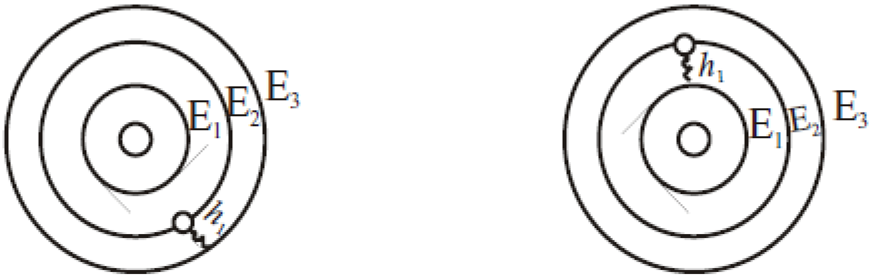


Fig. 7 : Absorption and emission of photon causes the electron to change its energy level.

3. The angular momentum of an electron of mass me moving in a circular orbit of radius r and velocity *v* is an integral multiple of $h/2\pi$.

$$m_e vr = \frac{n\hbar}{2\pi} \quad \text{... (3)}$$

where *n* is a positive integer, known as the principal quantum number. Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates :

Energy of the orbit,

$$E_n = -R_H\left(\frac{1}{n^2}\right) \quad \text{... (4)}$$

The negative sign in the energy expression means that the there is an attractive interaction between the nucleus and the electron. This means that certain amount of energy (called ionisation energy) would be required to remove the electron from the influence of the nucleus in the atom. You may note here that the energies of the Bohr orbits are inversely proportional to the square of the quantum number *n*. As *n* increases the value of the energy increases (becomes lesser negative or more positive). It means that as we go farther from the nucleus the energy of the orbit goes on increasing.

Example : A photon is emitted as an atom makes a transition from n = 4 to n = 2 level What is the frequency, wavelength and energy of the emitted photon?

Answer 1

we are given that,

Initial orbit of electron = n_i = 4

Final orbit of electron = n_f = 2:

Also we know that,

Speed of electromagnetic waves = $c = 3 \times 10^{8}\ m/s$

Planck's constant = $h = 6{:}63 \times 10^{34}\ J.s$

We want to calculate the frequency, wavelength and energy of the emitted photon, when the atom makes a transition from n_i = 4 to n_f = 2.

Frequency of the emitted photon can be calculated by using the equation,

$$E = hf \quad \Longrightarrow \quad f = \frac{E}{h}$$

Let's at _rst calculate E by using the following relation,

$$E = -13.6\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]\ eV$$

$$E = -13.6\left[\frac{1}{2^2} - \frac{1}{4^2}\right]\ eV$$

$$E = -13.6\left[\frac{1}{4} - \frac{1}{16}\right]\ eV$$

$$E = -13.6 \times \frac{3}{16}\ eV$$

$$E = -2.55\ eV$$

Thus frequency of photon will be,

$$f = \frac{E}{h} = \frac{2.55\ eV}{6.63 \times 10^{-34}\ J.s}$$

$$= \frac{2.55 \times 1.6 \times 10^{-19}\ J}{6.63 \times 10^{-34}\ J.s}$$

$$= 6.15 \times 10^{14}\ \ Hz.$$

Wavelength of the emitted photon can be calculated by using the following equation.

$$c = f\lambda$$

$$\Longrightarrow\ \lambda = \frac{c}{f} = \frac{3 \times 10^{8}\ \ m/s}{6.15 \times 10^{14}\ Hz}$$

$$= 4.875 \times 10^{-7}\ m$$

$$= 488\ nm$$

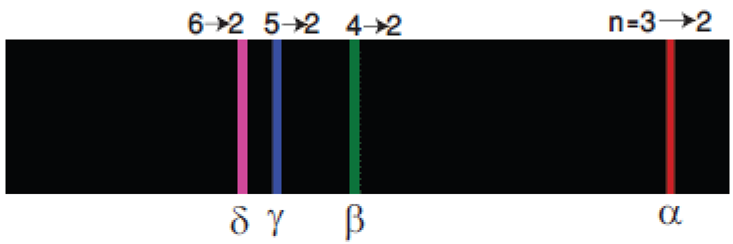
Example 2. For the Balmer series i.e., the atomic transitions where final state of the electron is n = 2, what is the longest and shortest wavelength possible? Is any of the frequency of Lyman series, which corresponds to transitions where electron ends up in n = 1 level, in the visible region?

Answer 2

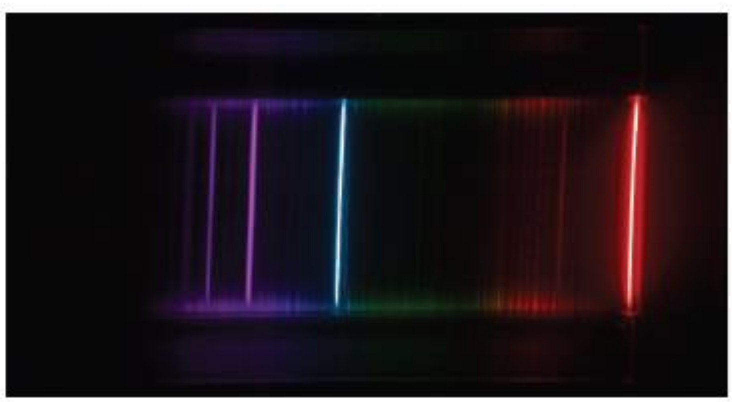
The atomic transitions where final state of the electron is n = 2, atoms emit a series of lines in the visible part of the spectrum. This series is called the Balmer Series. Balmer examined the four visible lines in the spectrum of the hydrogen atom. Wave length of this series can be calculated by using the equation,

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right], \quad where\ \ n = 3,4,5,\ldots$$

R is the Rydberg constant, whose value is $1.097 \times 10^{7}\ m^{-1}$. The number n is just an integer; the above formula gives the longest wavelength, when n = 3, and gives each of the shorter wavelengths as n increases. From Balmer's equation, it looks like when n gets bigger, the lines should start getting really close together. That's exactly right; as n gets larger, 1 over n squared gets smaller, so there's less and less difference between the consecutive lines. We can see that the series has a limit, that is, as n gets larger and larger, the wavelength gets closer and closer to one particular value. If n is infinity, then 1 over n squared is 0, and the corresponding wavelength is shortest. The individual lines in the Balmer series are given the names Alpha, Beta, Gamma, and Delta, and each corresponds to a n_i value of 3, 4, 5, and 6 respectively as shown in the figure below.



A picture from experimental demonstration is shown below.



The longest wavelength corresponds to the smallest energy difference between energy levels, which in this case will be between n = 2 and n = 3.

Wavelength for transition from n = 3

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

$$= 1.097 \times 10^7\ m^{-1} \times \left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

$$= 1.097 \times 10^7\ m^{-1} \times \left[\frac{1}{4} - \frac{1}{9}\right]$$

$$= 1.097 \times 10^7\ m^{-1} \times \frac{5}{36}$$

$$= 1.524 \times 10^6\ m^{-1}$$

$$\Longrightarrow \quad \lambda = 6.56 \times 10^{-7}\ m = 656\ nm$$

Thus the longest wavelength in the Balmer series is 656 nm.

The shortest wavelength corresponds to the largest energy difference between energy levels, which in this case will be between n = 2 and n = 1.

Wavelength for transition from $n = \infty$

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

$$= 1.097 \times 10^7\ m^{-1} \times \left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]$$

$$= 1.097 \times 10^7\ m^{-1} \times \left[\frac{1}{4} - \frac{1}{\infty}\right]$$

$$= 1.097 \times 10^7\ m^{-1} \times \frac{1}{4}$$

$$= 2.74 \times 10^6\ m^{-1}$$

$$\Longrightarrow \quad \lambda = 3.65 \times 10^{-7}\ m = 365\ nm$$

Thus the shortest wavelength in the Balmer series is 365 nm.