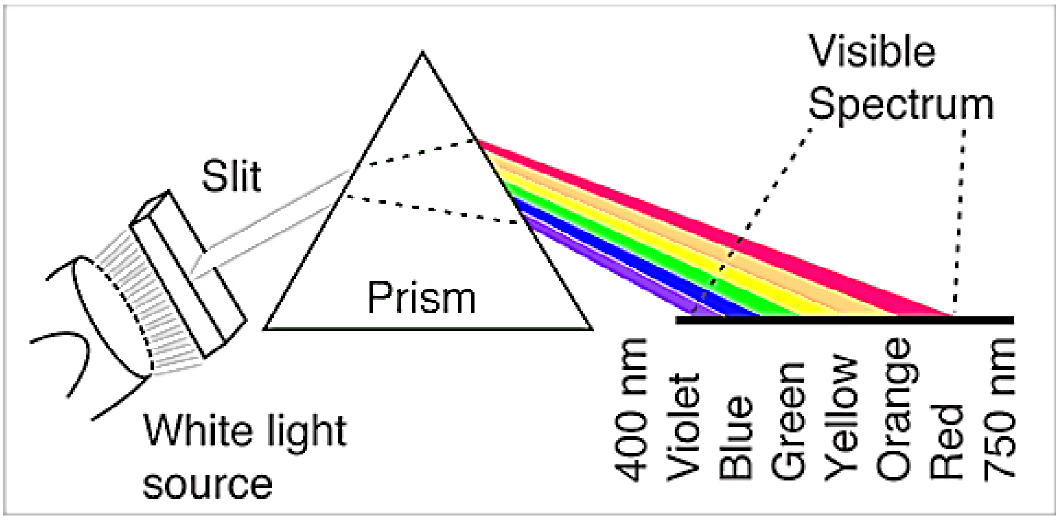
❖ *Types of Spectra*

- ❖ If white light falls on a prism, mounted in a spectrometer, the prism deviates the waves of varying wavelengths to different directions. The picture obtained in the telescope field of view is composed of a variety of colored slit images. That kind of picture is called a spectrum.

- ❖ For example, if the slit is illuminated with light from a sodium vapor lamp, two images of the slit are obtained in the yellow region of the spectrum. These images are the emission lines of sodium having wave lengths (5896 A^o) and (5890 A^o). This is known as the spectrum of sodium.



- ❖ **Emission Spectrum:** the spectrum of bright lines, bands or continuous radiation characteristic of a particular emitting material that is subject to a specific type of excitation.

- ❖ The emission spectrum is of three types.

1. **Continuous spectrum**. It consists of undivided, bright white bands of all wavelengths (from violet to red).

2. **Line spectrum**. It sharp lines of wavelengths specific. It is used to detect the gas. Arise from atom.

3. **Band spectrum**. Is a spectrum consisting of tightly spaced lines or bands. Arise from molecule

- **Absorption Spectrum**: Light shining on a sample causes electrons to be excited from the ground state to an excited state.

- Absorption spectra is also of three types

  1. Continuous absorption spectrum
  2. Line absorption spectrum and
  3. Band absorption spectrum

- **Line spectra**: Electron transitions between *energy levels* result in emission or absorption lines. So it divided to ***Emission*** spectra and ***Absorption*** spectra.

- Different elements produce different spectra due to differing atomic structure (discovered by Kirchhoff and Bunsen).

* Spectrum Of Hydrogen Atom

- One of the most important applications of early quantum theory was the interpretation of the ***atomic spectrum*** of hydrogen on the basis of the **Rutherford–Bohr model** of the atom.

- When an electric discharge occurs during a sample of hydrogen, the H_2 molecules dissociate into atoms, and the electron in a particular excited **H** atom may be promoted to one of many high energy levels.

- These levels or (states) are transient and the electron falls back to a lower energy state, emitting energy. The consequence is the observation of ***spectral lines*** in the emission spectrum of hydrogen; the spectrum consists of groups of discrete lines that have discrete energy corresponding to electronic transitions.

- At 1885 **Balmer** pointed out that the wavelengths of the spectral lines observed in the ***visible region*** of the atomic spectrum of hydrogen obeyed eq.(13):

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{.............................}\mathbf{(13)}$$

Where

R = ***Rydberg constant*** for hydrogen ($1.097*10^7$ m^{-1} **or** $1.097*10^5$ cm^{-1}).

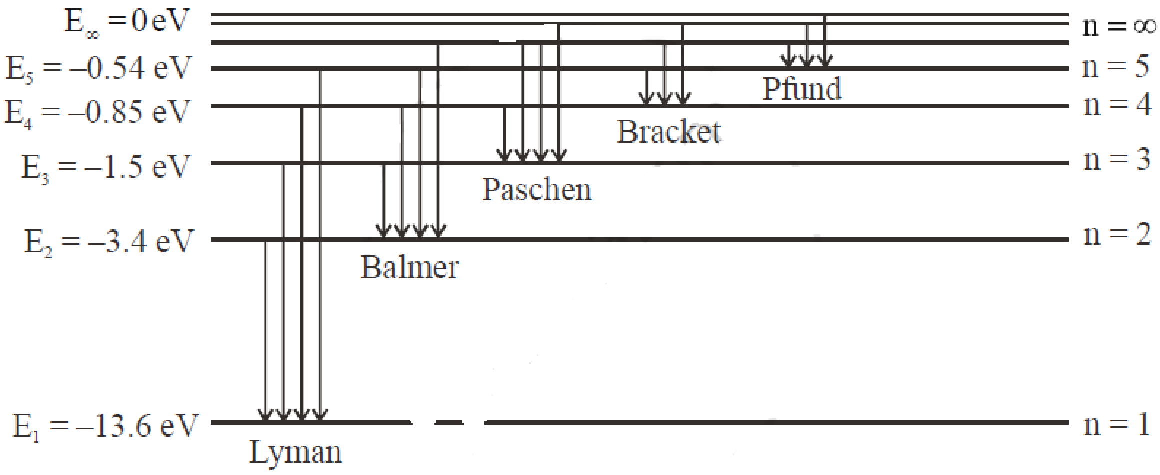
$\gamma^{-=}$ is the **wavenumber** (**reciprocal** of wavelength in $\mathbf{cm^{-1}}$).

($\mathbf{n_1 = 1, n_2}$ **)** are an integer numbers 1,2,3, 4, 5, 6. . . .

****For Balmer series** $\mathbf{n_1 = 2, n_2}$ **=** 3, 4, 5, 6,….

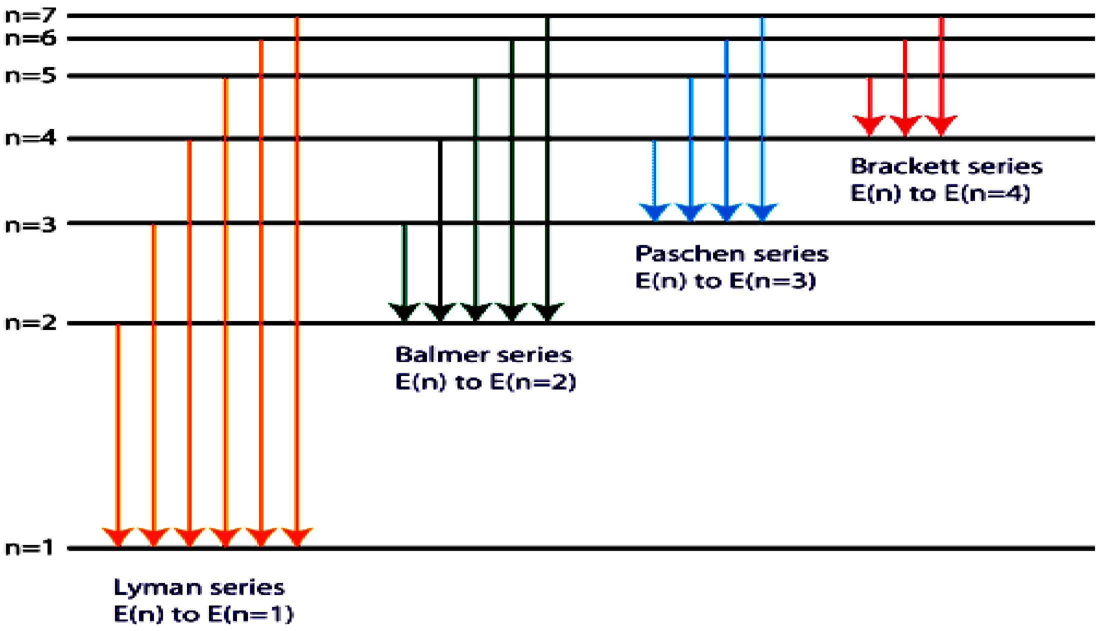
This series of spectral lines is known as the ***Balmer series***.

- Other series of spectral lines occur in the ***ultraviolet*** (***Lyman series***) and ***infrared*** (***Paschen***, ***Brackett*** and ***Pfund*** series).



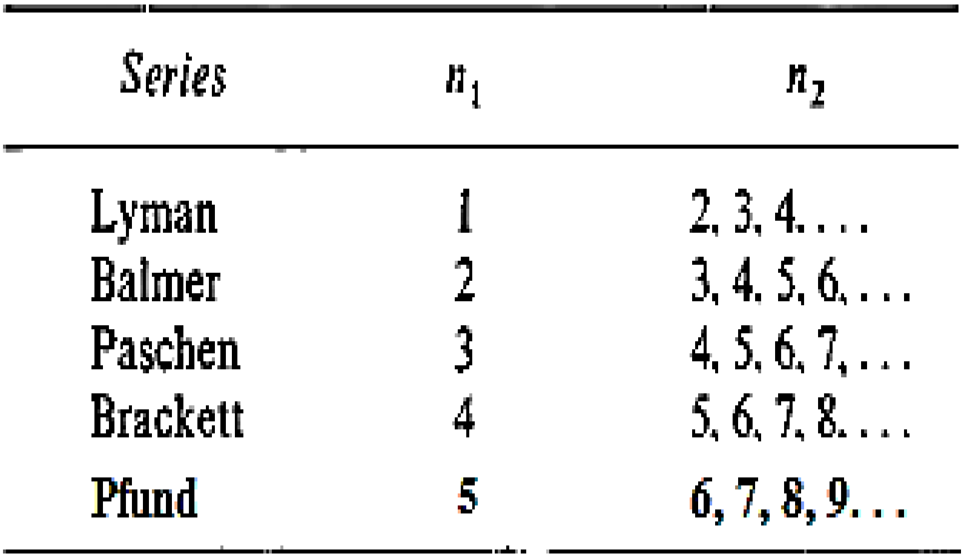
Energy level diagram for hydrogen atom

Electron transitions for the Hydrogen atom



- ❖ All lines in all the series obey the general expression given in eq.(**13**), where always ($\mathbf{n_2 > n_1}$).

- ❖ For the **Lyman** series, $\mathbf{n_1=1}$, for the **Balmer** series, $\mathbf{n_1=2}$, and for the **Paschen** series, $\mathbf{n_1=3}$, **Brackett** series, $\mathbf{n_1=4}$ and **Pfund** series, $\mathbf{n_1=5}$



Series	n_1	n_2
Lyman	1	2, 3, 4. . . .
Balmer	2	3, 4. 5, 6, . . .
Paschen	3	4, 5, 6, 7, . . .
Brackett	4	5, 6, 7, 8. . . .
Pfund	5	6, 7, 8, 9. . .

❖ Bohr's Theory of The Atomic Spectrum of Hydrogen

❖ In 1913, **Niels Bohr** combined elements of quantum theory and classical physics in a treatment of the hydrogen atom. He stated four postulates for an electron in an atom:

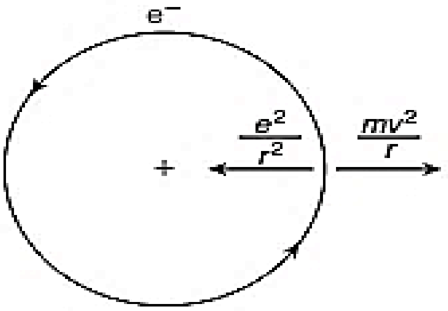
1- There were certain "allowed" orbits in which the electron could move without radiating electromagnetic energy.

2- Each orbital has certain radius and energy.

3- Electron could move around nucleus only in orbitals which have angular momentum of the electron is a multiple of ($h/2\pi$). Where for a rotating object angular momentum is expressed as (**mvr**), so ($mvr = nh/2\pi$); **m**=mass of electron, **v**=velocity of electron, **r**=radius of shell, **n**= integer, ***n*** is known as a ***quantum number*** or, more specifically, the ***principal* quantum number**.

4- Electromagnetic energy emitted as the electron moved from a higher orbital (larger *n* value) to a lower one and absorbed in the reverse process.

❖ In order for the electron to move in a stable orbit, the ***electrostatic attraction*** between it and the proton must be balanced by the ***centrifugal force*** that results from its circular motion. As shown in Figure below, the forces are actually in opposite directions, and equal in its magnitudes.



* The **electrostatic force** is **(e^2/r^2)**, while the **centrifugal force** on the electron is **(mv^2/r)**. Therefore, we can write eq.(**14**)

$$\frac{mv^2}{r} = \frac{e^2}{r^2} \qquad \text{..............................(14)}$$

- From eq. (14) we can calculate the **velocit**y of the electron as follow, eq.(15).

$$v = \sqrt{\frac{e^2}{mr}} \qquad \text{..............................(15)}$$

- Since **(mvr= nh/2π**), we can write eq.(**16**)

$$v = \frac{nh}{2\pi mr} \qquad \text{..............................(16)}$$

- Because the moving electron has only one velocity, the values for ***v*** given in Eqs. (**15**) and (**16**) must be written as eq. (**17**).

$$\sqrt{\frac{e^2}{mr}} = \frac{nh}{2\pi mr} \qquad \text{..............................(17)}$$

- We can now solve for **r** to obtain, eq.(**18**)

$$r=\frac{n^2h^2}{4\pi^2me^2} \qquad \text{..............................}\mathbf{(18)}$$

* In Eq. (**18**), only **r** and **n** are variables. From the nature of this equation, we see that the value of **r**, the radius of the orbit, increases as the square of **n**. For the orbit with **n=2**, the radius is four times that when **n=1**, etc.

- From eq.(**14**), we can write eq.(**19**):-

$$mv^2=\frac{e^2}{r} \qquad \text{..............................}\mathbf{(19)}$$

- Multiplying both sides of the eq.(**19**), by 1/2 we obtain eq.(**20**):-

$$\frac{1}{2}mv^2=\frac{e^2}{2r} \qquad \text{..............................}\mathbf{(20)}$$

- Where the **left-hand side** is simply the ***kinetic energy*** of the electron. The ***total energy*** of the electron is the ***sum*** of the ***kinetic energy*** and the ***electrostatic potential energy***, (**$-e^2/r$**), eq.(**21**):-

$$E=\frac{1}{2}mv^2-\frac{e^2}{r}=\frac{e^2}{2r}-\frac{e^2}{r}=-\frac{e^2}{2r} \qquad \text{..............................}\mathbf{(21)}$$

- Substituting the value for *r* from Eq. (**18**) into Eq. (**21**) we obtain eq.(**22**)

$$E=-\frac{e^2}{2r}=-\frac{2\pi^2me^4}{n^2h^2} \qquad \text{..............................}\mathbf{(22)}$$

- From eq.(**22**), we see that there is an inverse relationship between the ***energy*** and the **square** of the value ***n***. The lowest value of *E* (and it is negative!) is for ***n* =1** while ***E*=0** when ***n*** has an infinitely large value that corresponds to complete removal of the electron. If the constants are assigned values in the cm-g-s system of units, the energy calculated will be in erqs. Of course **$1\ J = 10^7$ erq** and **1 cal = 4.184 J.**

- By assigning various values to***n***, we can evaluate the corresponding energy of the electron in the orbits of the hydrogen atom. When this is done, we find the energies of several orbits as follows:

$$n = 1, \qquad E = -21.7 \times 10^{-12}\ \text{erg}$$

$$n = 2, \qquad E = -5.43 \times 10^{-12}\ \text{erg}$$

$$n = 3, \qquad E = -2.41 \times 10^{-12}\ \text{erg}$$

$$n = 4, \qquad E = -1.36 \times 10^{-12}\ \text{erg}$$

$$n = 5, \qquad E = -0.87 \times 10^{-12}\ \text{erg}$$

$$n = 6, \qquad E = -0.63 \times 10^{-12}\ \text{erg}$$

$$n = \infty, \qquad E = 0$$

- Although the Bohr model successfully accounted for the line spectrum of the hydrogen atom, it could not explain the line spectrum of any other atom. It could be used to predict the wavelengths of spectral lines of other species that had only one electron such as $\mathbf{He^{+}}$, $\mathbf{Li^{+2}}$, and $\mathbf{Be^{+3}}$.
- Energy is ***absorbed*** or ***emitted*** only when an electron moves from one energy level to another and the energy change is given by eq.(**23**), where $\mathbf{n_1}$ and $\mathbf{n_2}$ are the principal quantum numbers referring to the energy levels $\mathbf{En_1}$ and $\mathbf{En_2}$ respectively.

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 m e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{.................(23)}$$

- ❖ Emitted radiation is expressed in terms of ***frequency*** (γ) or ***wave number*** ($\bar{\gamma}$). Eqs. (**24**) and (**25**), respectively :-

$$\nu = \frac{\mathbf{E}}{\mathbf{h}}$$

$$\nu = \frac{2\pi^2 m e^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{........................(24)}$$

$$\bar{\nu} = \frac{\nu}{c}$$

$$\bar{\nu} = \frac{2\pi^2 m e^4}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{........................(25)}$$

- ❖ The eq.(25), similar to that of ***Rydberg*** eq.(**13**), where:-

$$\mathbf{R}_H = \frac{2\pi^2 m e^4}{h^3 c}$$

- ❖ We can calculate the value of ***Rydberg*** constant from values of (m), (e), (c) and (h).
- ❖ So for hydrogen atom , where Z=1

$$\bar{\nu} = \mathbf{R}_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- While for ions similar to hydrogen atom, where Z larger than 1.

$$\bar{\nu} = R\, Z^{2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

- **Ex: Calculate the wave length of forth line (n=6), in Balmer series of hydrogen atom.**

Ans.

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$= 1.097*10^{5}\ \text{cm}^{-1} *[(1/2^{2}) - (1/6^{2})]$$

$$= \mathbf{\mathit{24372.88\ cm^{-1}}}$$

$$\lambda = 1/\gamma^{-}$$

$$\lambda = (1/24372.88\ \text{cm}^{-1}) = \mathbf{4.103*10^{-5}\ cm}$$

- **Ex: Calculate the radius of first, second and third Bohr orbitals of hydrogen atom.**

Ans:

$$r = \frac{n^{2}h^{2}}{4\pi^{2}me^{2}}$$

$r=[(1)^{2} *(6.626*10^{-27}\ \text{erq.seq})^{2}] / [4*(3.14)^{2} * (9.1072*10^{-28}\ \text{g}) * (4.8032*10^{-10}\ \text{erq. cm})^{2}]$

$r= 0.529 *10^{-8}$ cm

$r= 0.529\ A^{0}$

*This constant value of first Bohr orbital of hydrogen atom and referred as ($\mathbf{a_0}$).

*For second orbital $\mathbf{r= a_0 * n^2}$

$r=0.529 * 10^{-8}$ cm * 2^2

$r= 2.116 * 10^{-8}$ cm

*For third orbital

$r=0.529 * 10^{-8}$ cm * 3^2

$r= 4.761 * 10^{-8}$ cm

- **Ex: Find the velocity of electron for first Bohr orbital of hydrogen atom.**

Ans.

$\mathbf{V=nh / 2\pi mr}$

V= [(1) * ($6.626*10^{-27}$ erq. sec) / 2*(3.14)*($9.1072*10^{-28}$ g)*($0.529*10^{-8}$ cm)]

$V= 2.188 * 10^{8}$ cm.sec^{-1}

- **Ex: Calculate the electron's energy in the first and second orbits of the hydrogen atom.**

Ans:-

From eq.(17), $\mathbf{E= - e^2 / 2r}$

As $\mathbf{r=a_0 * n^2}$

So $E = \mathbf{- e^2 / (2\, a_0 * n^2)}$

*The energy of electron at first orbital;

$$E_{n=1} = -\,(4.8032 * 10^{-10}\ \text{e.s.u}) \,/\, (2*(0.529 * 10^{-8}\ \text{cm}) * (1)^2$$

$$= -2.17987 * 10^{-11}\ \text{erq}$$

*To calculate the energy in **Joule** unit

$$E_{n=1} = \ -2.17987 * 10^{-11}\ \text{erq}\ \ * (1\ \text{J} \,/\, 1*10^{7}\ \text{erq})$$

$$= -2.17987 * 10^{-18}\ \text{J}$$

*To calculate the energy in **e.v** unit

$$E_{n=1} = -2.17987 * 10^{-18}\ \text{J} * (1\ \text{e.v}/1.602 * 10^{-19}\ \text{J})$$

$$= \mathbf{-13.6\ e.v}$$

*The energy of electron at second orbital;

$$\mathbf{E_{n=2} = -\,(E_{n=1} \,/\, n^2)}$$

$$= -(13.6\ \text{e.v} \,/\, 2^2)$$

$$= \mathbf{-3.4\ e.v}$$

electrostatic unit of charge (e.s.u) , 1e.s.u= erq$^{1/2}$ * cm$^{1/2}$

The e.s.u of charge, also called the franklin or statcoulomb, is the charge such that two equal ***q*****=1** stat charges at a distance of **1cm** from each other exert an electrostatic force of **1dyn** on each other.