Lecture-1

ATOMIC STRUCTURE, QUANTUM THEORY AND BOHR ATOM

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TEXT

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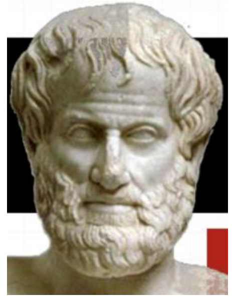
ATOMIC STRUCTURE

Landmarks in the evolution of atomic structure are:

1805	Dalton's atomic theory
1896	Thomson discovery of electron and proton
1909	Rutherford's nuclear atom
1913	Bohr's atomic model
1932	Chadwick's discovery of neutron

Democritus (400 BC)

Atomos= not to be cut



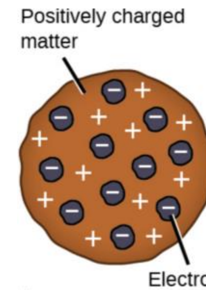
Aristotle (300 BC-1800’s)

Death to the field of chemistry

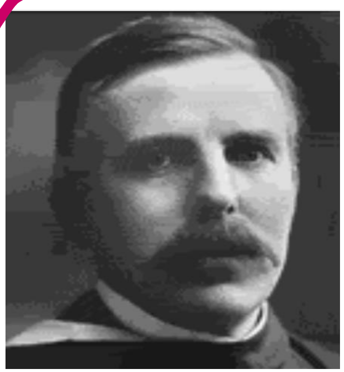
John Dalton (1803)

Atoms are uncuttable, too small to see and indestructible.

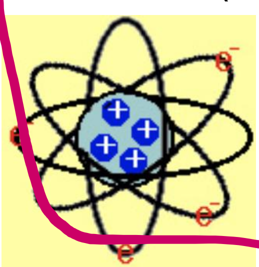
J.J Thomson (1897)

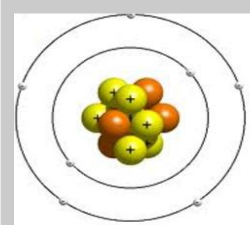


Plum pudding model

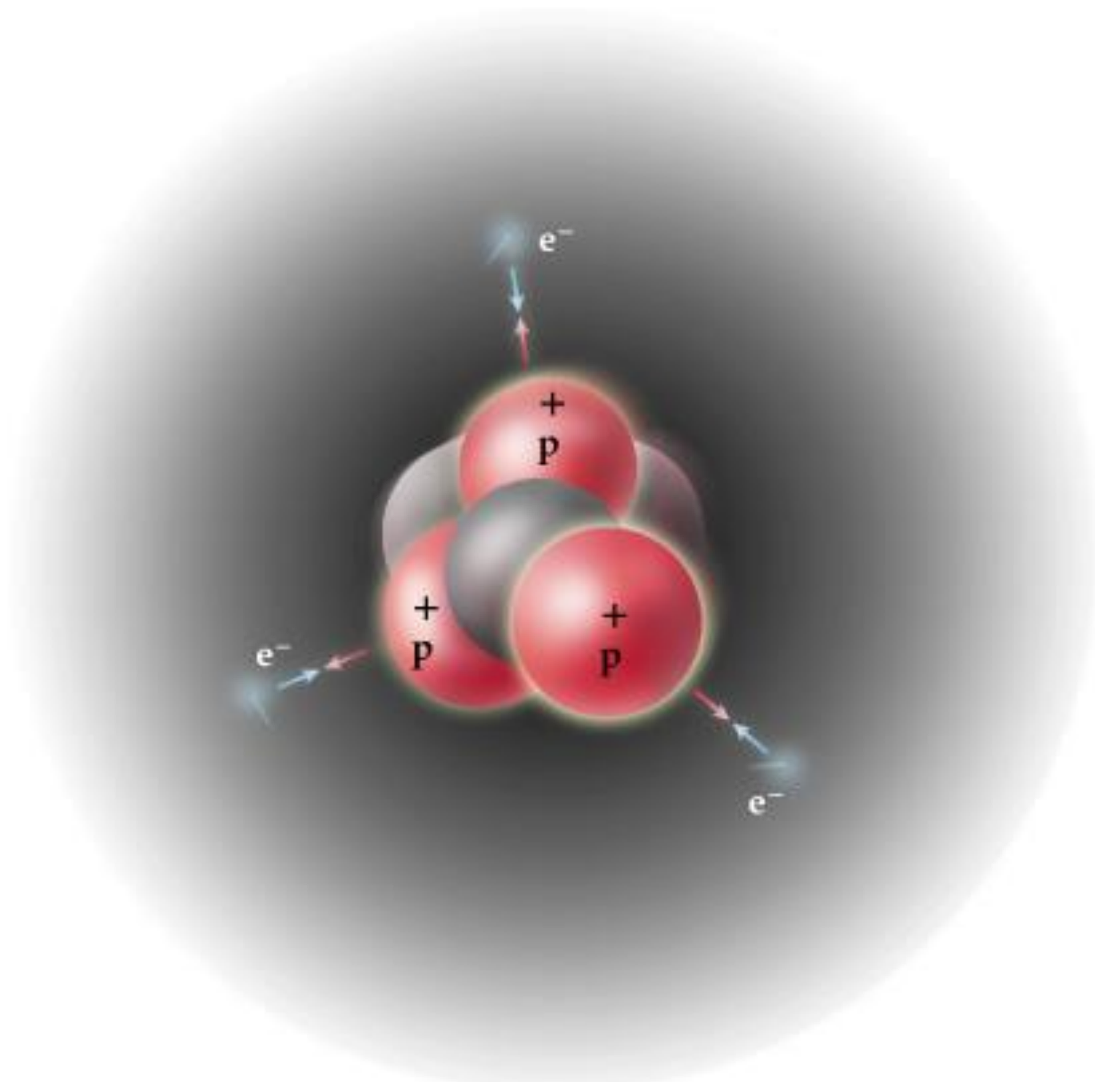


Rutherford(1908)



Atomic Model	Analogy
	Solar System 

Atomic Structure



Atomic Theory of Dalton: (1805)

- (1) All matter is composed of tiny particles called atom which can not be created, destroyed or split.
- (2) All atoms of any one element are identical, have same mass and chemical properties.
- (3) A compound is a type of matter composed of atoms of two or more elements.
- (4) A chemical reaction consists of rearranging atoms from one combination to another.

Dalton's Contribution:

British Chemist John Dalton provided the **basic theory**: all matter- whether element, compound, or mixture- is composed of small particles called atoms.

Limitations of Dalton's Model:

(1) Atom can be divided into subatomic particle namely electron, proton and neutron.

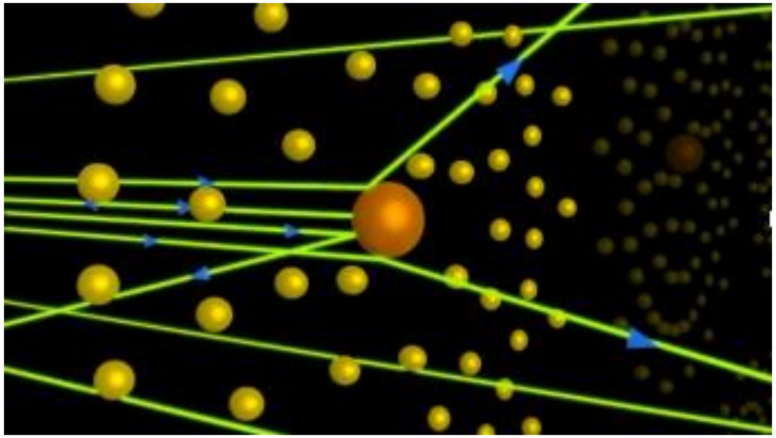
(2) All atoms of any elements are not identical, have different mass and chemical properties. This property is known as isotopes.

Exercise

What is atom and how can you define the atomic number?

The number of protons in the nucleus of an atom is the atomic number of that atom

Rutherford's experiment



Observations

- A major fraction of the α-particles bombarded towards the gold sheet passed through the sheet without any deflection, and hence **most of the space in an atom is empty**.
- Some of the α-particles were deflected by the gold sheet by very small angles, and hence the **positive charge** in an atom **is not uniformly distributed**. **The positive charge** in an atom **is concentrated in a very small volume**.
- Very few of the α-particles were deflected back, that is only a few α-particles had nearly 180^{o} angle of deflection. So the **volume occupied by the positively charged particles in an atom is very small as compared to the total volume of an atom**

Postulates of Rutherford atomic model

- Most of the space in the atom is empty
- The positively charged particles and most of the mass of an atom were concentrated in an extremely small volume. He called this region of the atom as a *nucleus*.
- Rutherford's model proposed that the negatively charged electrons surround the nucleus of an atom. He also claimed that the electrons surrounding the nucleus revolve around it with very high speed in circular paths. He named these circular paths as orbits. Thus, ***Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.***
- Electrons being negatively charged and nucleus being a densely concentrated mass of positively charged particles are held together by strong electrostatic force of attraction.

Exercise

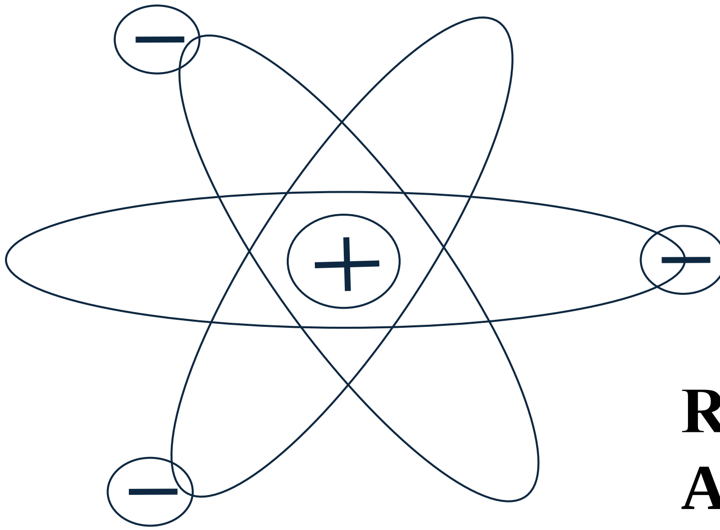
Question : Which sub-atomic particle was discovered by Rutherford through his Alpha (α) Particle Scattering Experiment?

Limitations of Rutherford atomic model

Although Rutherford's atomic model was based on experimental observations it failed to explain certain things.

- Rutherford proposed that the electrons revolve around the nucleus in fixed paths called orbits. According to Maxwell, **accelerated charged particles emit electromagnetic radiations** and hence an electron revolving around the nucleus should emit electromagnetic radiation. This radiation would carry energy from the motion of the electron which would come at the cost of shrinking of orbits. Ultimately the electrons would collapse in the nucleus. Calculations have shown that as per Rutherford's model an electron would collapse in the nucleus in less than 10-8 seconds. **So *Rutherford's model was not in accordance with Maxwell's theory and could not explain the stability of an atom.***
- **This model does not exactly same as the solar system because the planets are neutral but electrons are negatively charged.**
- **One of the drawbacks of Rutherford's model was also that he did not say anything about the arrangement of electrons in an atom which made his theory incomplete.**

Rutherford's Model of Atom (contd.):



Rutherford's Atomic Model

Contribution of Rutherford's model:

- Rutherford laid the foundation of the model picture of atom.

Three subatomic particles or principal fundamental particles:

Particle	Simbol	Mass		Charge	
		Amu	grams	Units	Coloumbs
Electron	e^-	1/1835	9.1×10^{-28}	-1	-1.6×10^{-19}
Proton	p^+	1	1.672×10^{-24}	+1	$+1.6\times10^{-19}$
Neutron	N or n^o	1	1.674×10^{-24}	0	0

Electrons are very small in mass compared with protons and neutrons. It takes more than 1,800 electrons to equal the mass of 1 proton. In fact, the mass of an electron is so small that it is usually considered to be zero.

Atomic Number, Mass Number & Isotopes

- An atom consists of three particles- electron, proton and neutron. The charge of proton is positive, electron is negative and neutron no charge.
- In a neutral atom, number of proton is equal to that of the electron and a proton has mass more than 1800 times that of the electron.
- The **atomic number** is the number of protons in the nucleus of an atom.

Atomic Number, Mass Number & Isotopes…

- The neutron is a nuclear particle having a mass almost identical to that of the proton.
- The **mass number** is the total number of protons and neutrons in a nucleus.
- All nuclei of the atoms of a particular element have the same atomic number, but the nuclei may have different mass numbers. These atoms are known as **Isotopes.**
- That is, isotopes have the same number of protons but different numbers of neutrons.

Quantum Theory and Bohr Atom: (1913)

To understand the Bohr theory, we need to learn-

- the nature of **electromagnetic radiations**,
- the **atomic spectra**

Electromagnetic Radiations:

Electromagnetic radiation can be described as a wave (carrier of energy) occurring simultaneously in electrical and magnetic fields and consists of particles called quanta or photons.

Energy can be transmitted through space by electromagnetic radiations.

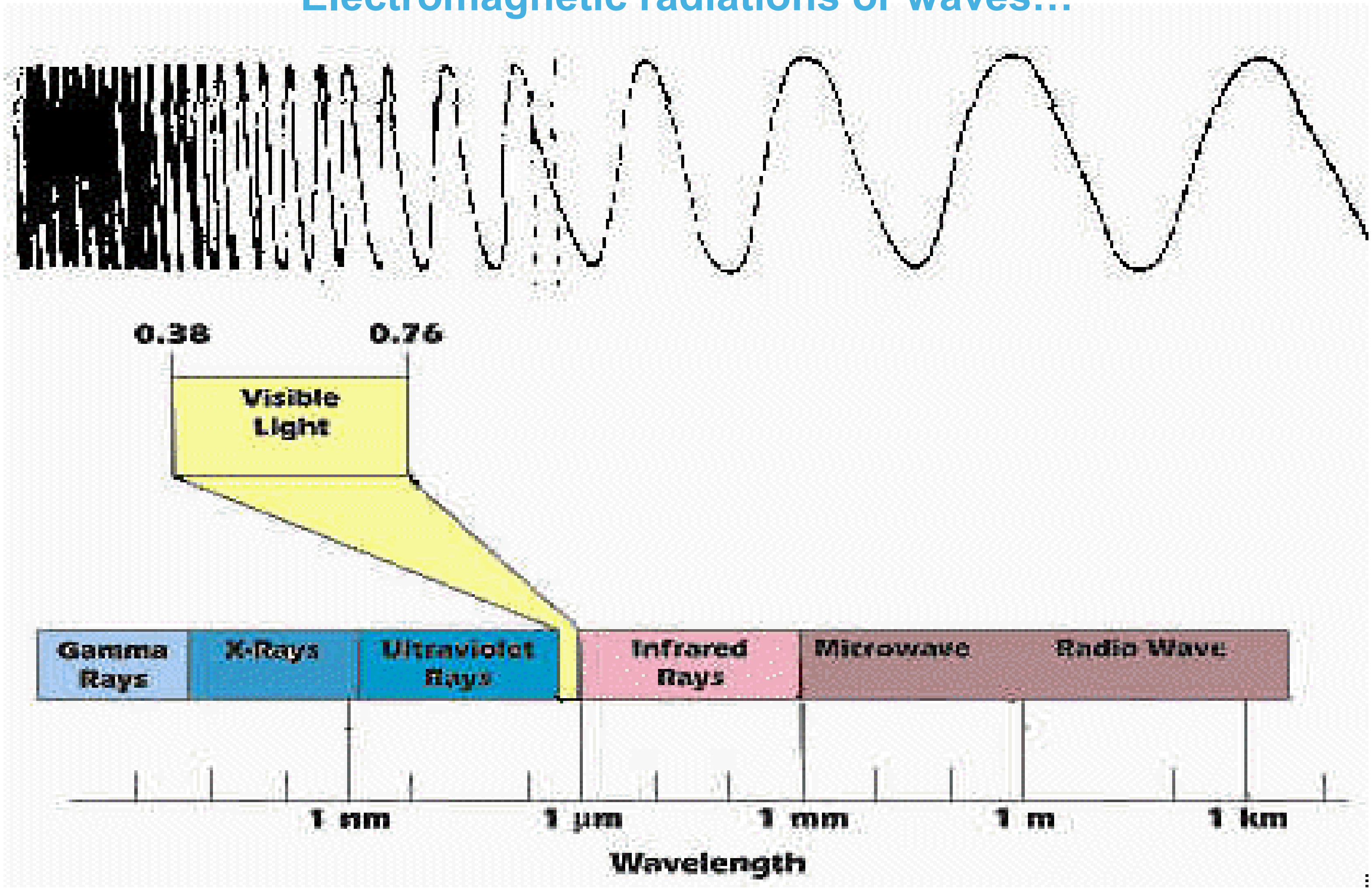
Some forms of electromagnetic radiations are:

Electromagnetic Radiations (contd.)

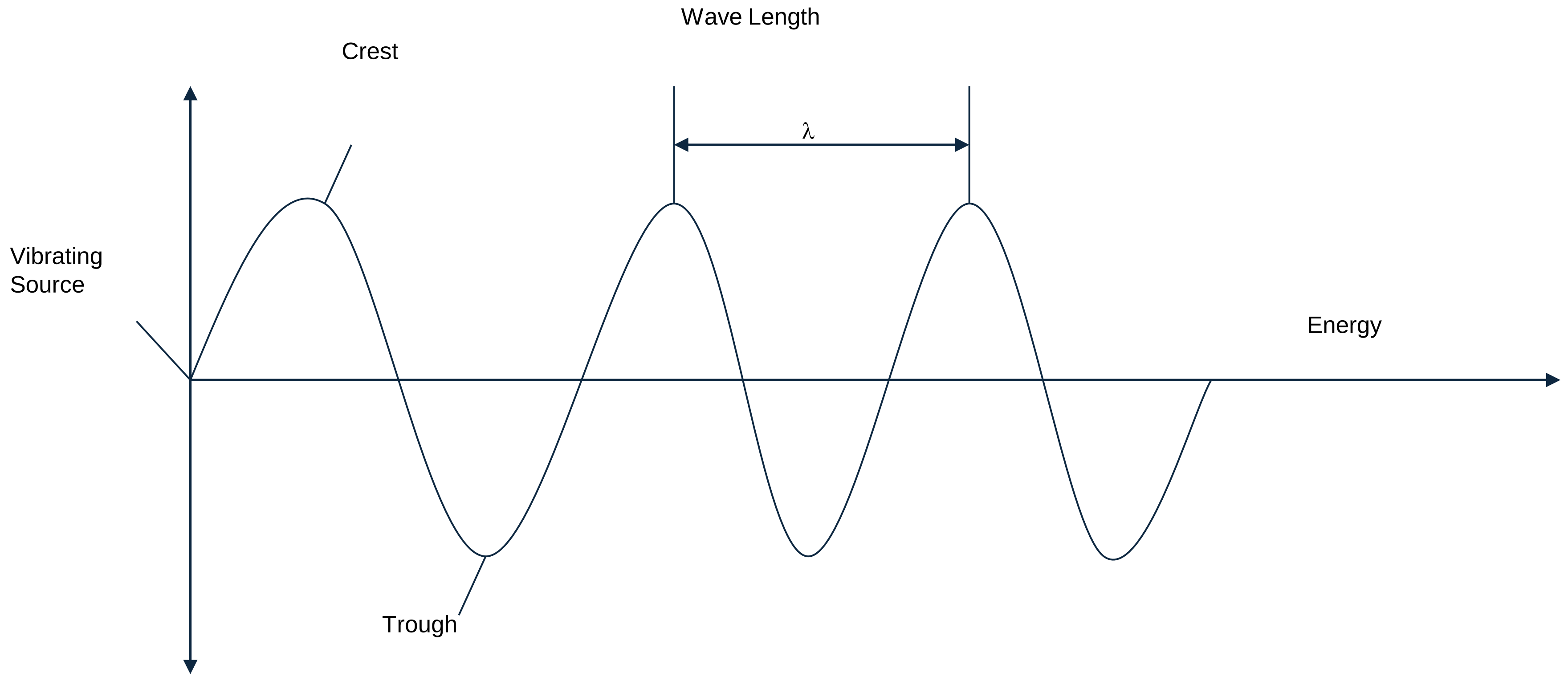
- **radio waves**
- **visible light**
- **infrared light**
- **ultraviolet light**
- **x-rays etc.**

These radiations have both the properties of a wave as well as a particle, now become familiar for their uses. The X-rays are used in medicine, the ultraviolet rays lead to sunburns and radio and radar waves used in communication and visible light.

Electromagnetic radiations or waves…



Characteristics of Waves:



Wavelength (λ, lambda):

The wavelength is defined as the distance between two successive crests or troughs of a wave.

<u>Units</u>: cm, m or Å (angstrom).

(1 Å = 10^{-8} cm = 10^{-10} m, 1 nm = 10^{-9} m)

Frequency (ν, nu):

The frequency is defined as the number of complete cycles (oscillations) per second.

<u>Units</u>: hertz (hz), one cycle per second.

A wave of high frequency has a shorter wavelength, while a wave of low frequency has a longer wavelength.

Speed (c):

The speed (or velocity) of a wave is the distance through which a particular wave travels in one second.

Speed = Frequency $\times$ Wavelength

i. e. $c = \nu \times \lambda$

Wave Number:

This is reciprocal of the wavelength and is given the symbol (nu bar). i. e. $\bar{\nu} = 1/\lambda$

Problems:

1# The wavelength of a violet light is 400 nm. Calculate its frequency and wave number. (Given, $c = 3\times10^{8}$ m sec^{-1}) (Answer: $\nu = 7.5 \times 10^{14}\ sec^{-1}$, $\bar{\nu} = 25 \times 10^{5}\ m^{-1}$)

2# The frequency of a strong yellow line in the spectrum of sodium is $5.09 \times 10^{14}\ sec^{-1}$. Calculate the wavelength of light in nanometers. (Answer: $\lambda = 589$ nm)

Spectra:

A spectrum is an arrangement of waves or particles spread out according to the increasing or decreasing of some property like wavelength or frequency.

An increase in frequency or a decrease in wavelength represents an increase in energy.

Continuous Spectrum:

White light is radiant energy coming from the sun or from incandescent lamps. It is composed of light waves in the range 4000-8000 Å.

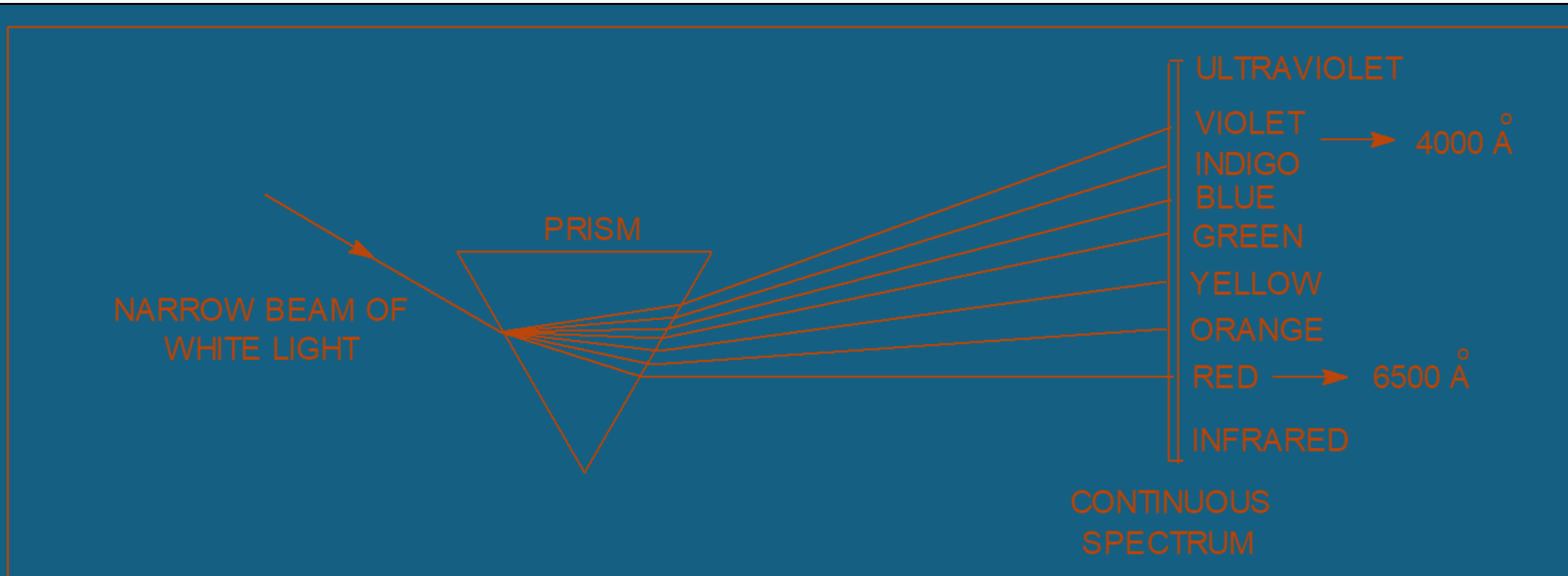


Figure: The continuous spectrum of white light

When a beam of white light is passed through a prism, a continuous series of colour bands (rainbow) is received on a screen with different wavelengths called *Continuous Spectrum*.

VIBGYOR -violet

-indigo

-blue

-green

-yellow

-orange and

-red

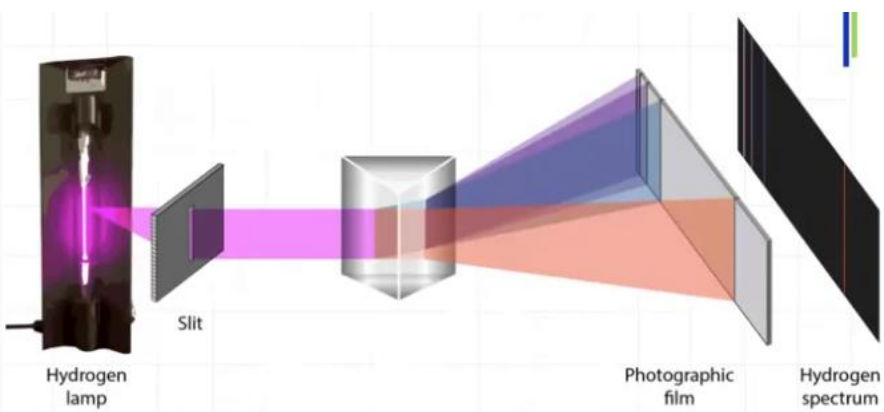
The violet component of the spectrum has shorter wavelengths (4000-4250Å) and higher frequencies.

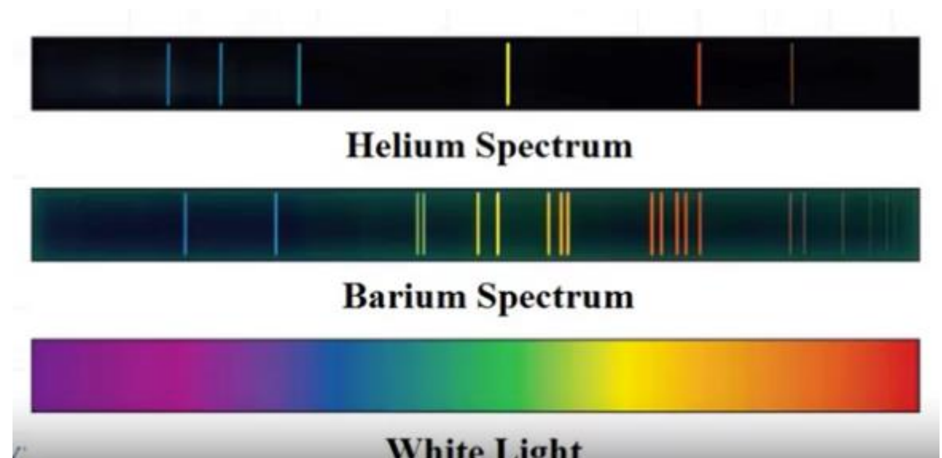
The red component has longer wavelengths (6500-7500Å) and lower frequencies.

The invisible region beyond the violet is called ultraviolet region and the one below the red is called infrared region.

Atomic Spectra:

When an element in the vapor or the gaseous state is heated in a flame or a discharge tube, the atoms are excited and emit light radiations of a characteristic colour. The colour of light produced indicates the wavelength of the radiation emitted. The spectrum obtained on the photographic plate is found to consists of bright lines.





Atomic Spectra:

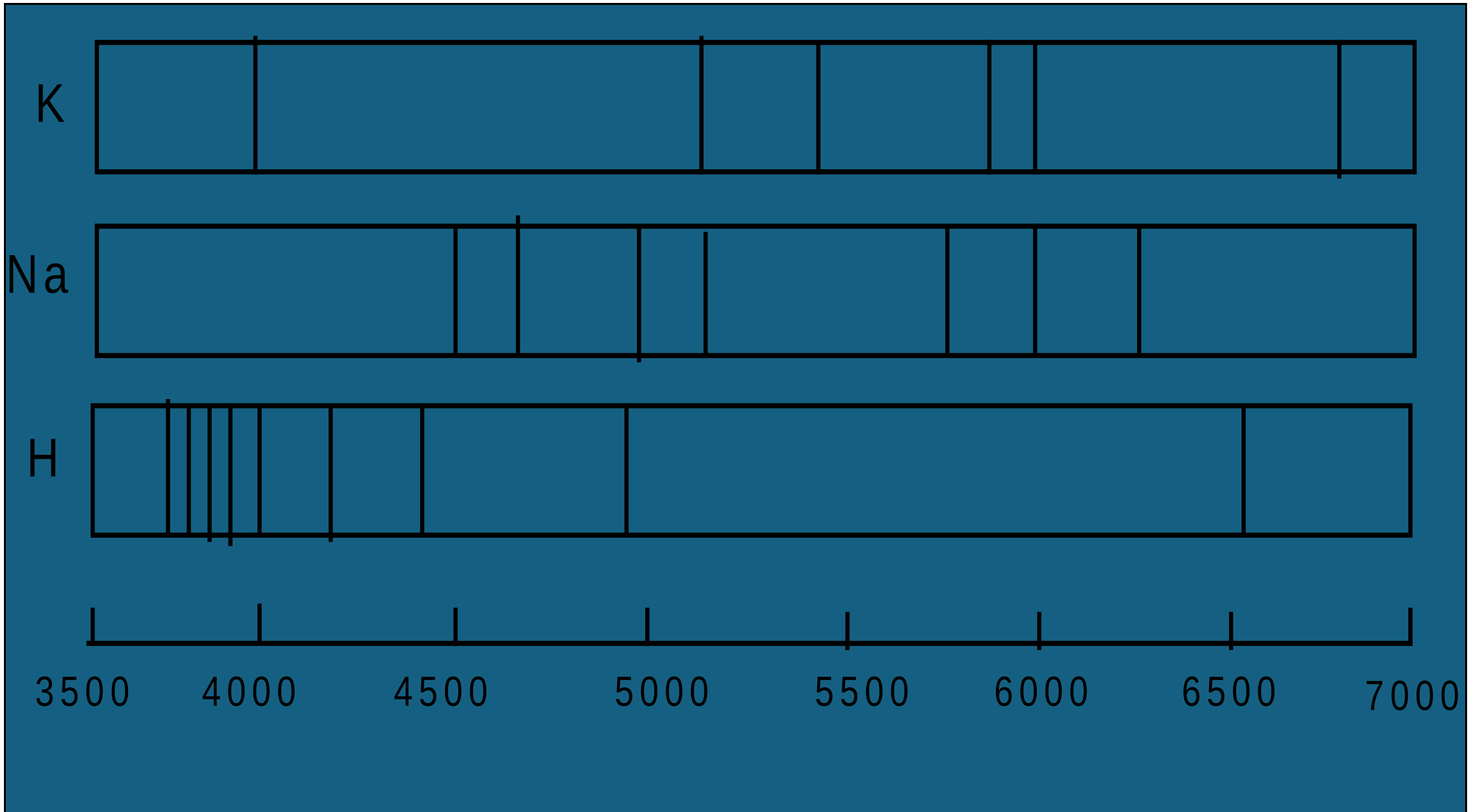


Fig. Emission spectra of K, Na and H

Atomic Spectrum of Hydrogen:

In 1884 J. J. Balmer observed the following four prominent coloured lines in the visible hydrogen spectrum:

(1) a red line with a wavelength of 6563 Å

(2) a blue-green line with a wavelength of 4861 Å

(3) a blue line with a wavelength of 4340 Å

(4) a violet line with a wavelength of 4102 Å

The series of four lines in the visible spectrum of hydrogen is known as Balmer series.

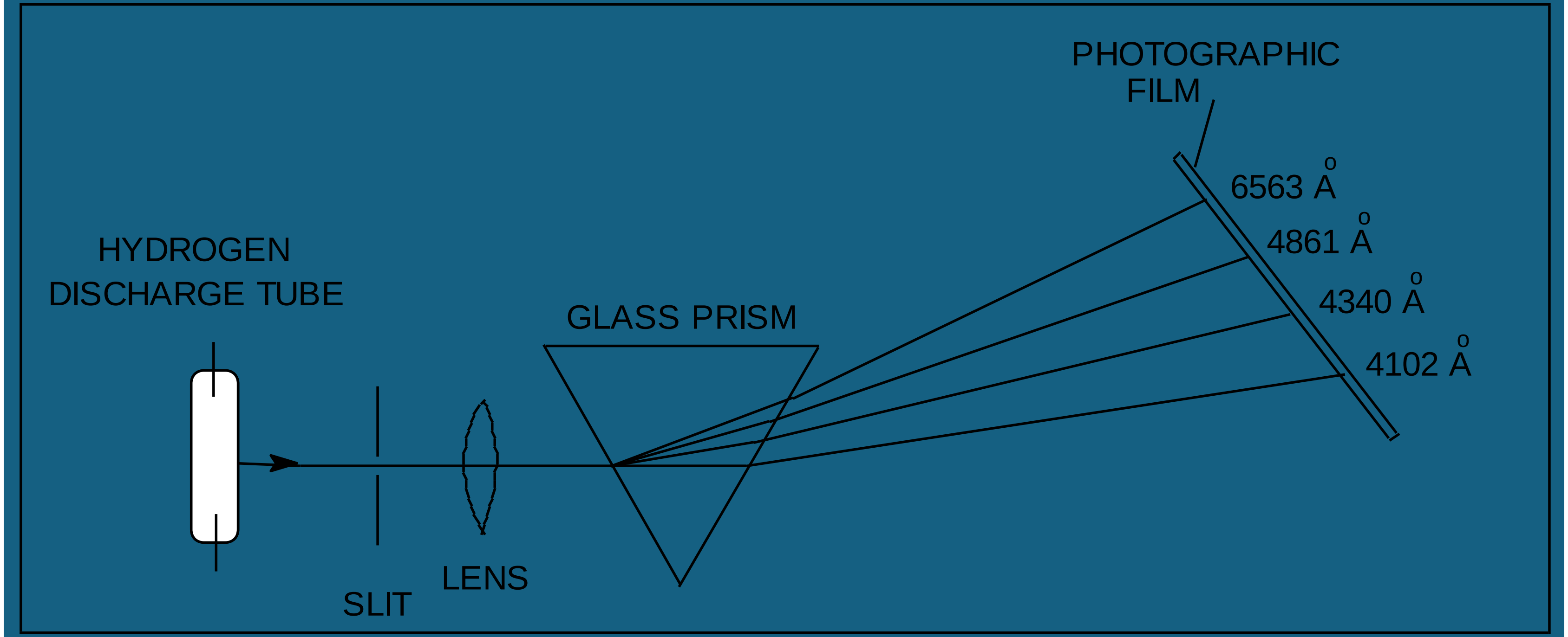


Figure: The examination of the atomic spectrum of hydrogen with a spectroscope.

Balmer equation:

Balmer was able to give an equation which relate the wavelengh (λ) of the observed lines. The Balmer equation is,

where R is a constant called **Rydberg constant** which has the value 109,677 cm^{-1} and n = 3, 4, 5, 6, etc.

Five Spectral Series:

In addition to Balmer series, four other spectral series were discovered in the infrared (ir) and ultraviolet (uv) regions of the hydrogen spectrum. These bear the names of discoverers.

(1) Lyman series (uv)

(2) Balmer series (visible)

(3) Paschen series (ir)

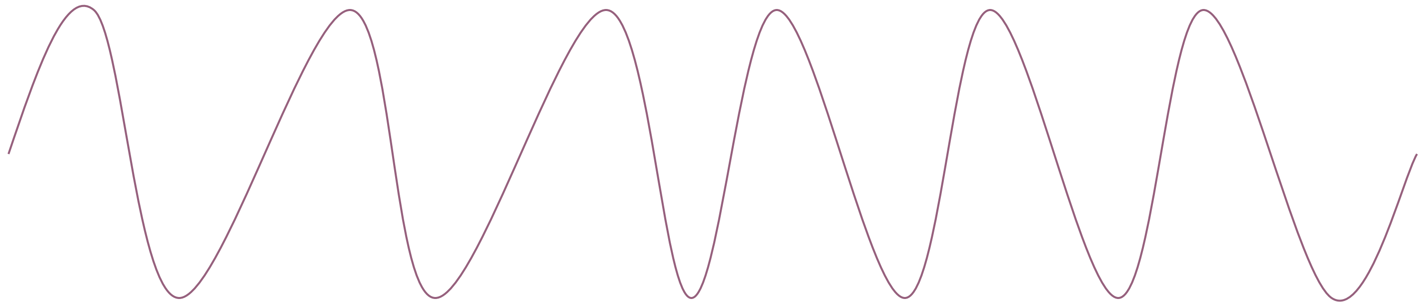
(4) Brackett series (ir)

(5) Pfund series (ir)

Quantum Theory of Radiation:

(1) When atoms or molecules absorb or emit radiant energy, they do so in separate 'units of waves' called **quanta** or **photons**.

Continuous Wave



Quantum Theory of Radiation (contd.):

(2) The energy, E, of a quantum or photon is given by the relation.

$E = h\nu$ (h, Planck's constant

$= 6.62 \times 10^{-27}$ erg sec.

or 6.62×10^{-34} J sec.)

$c = \lambda\nu$ (c = velocity of radiation)

$$\therefore E = \frac{hc}{\lambda}$$

Quantum Theory of Radiation (contd.):

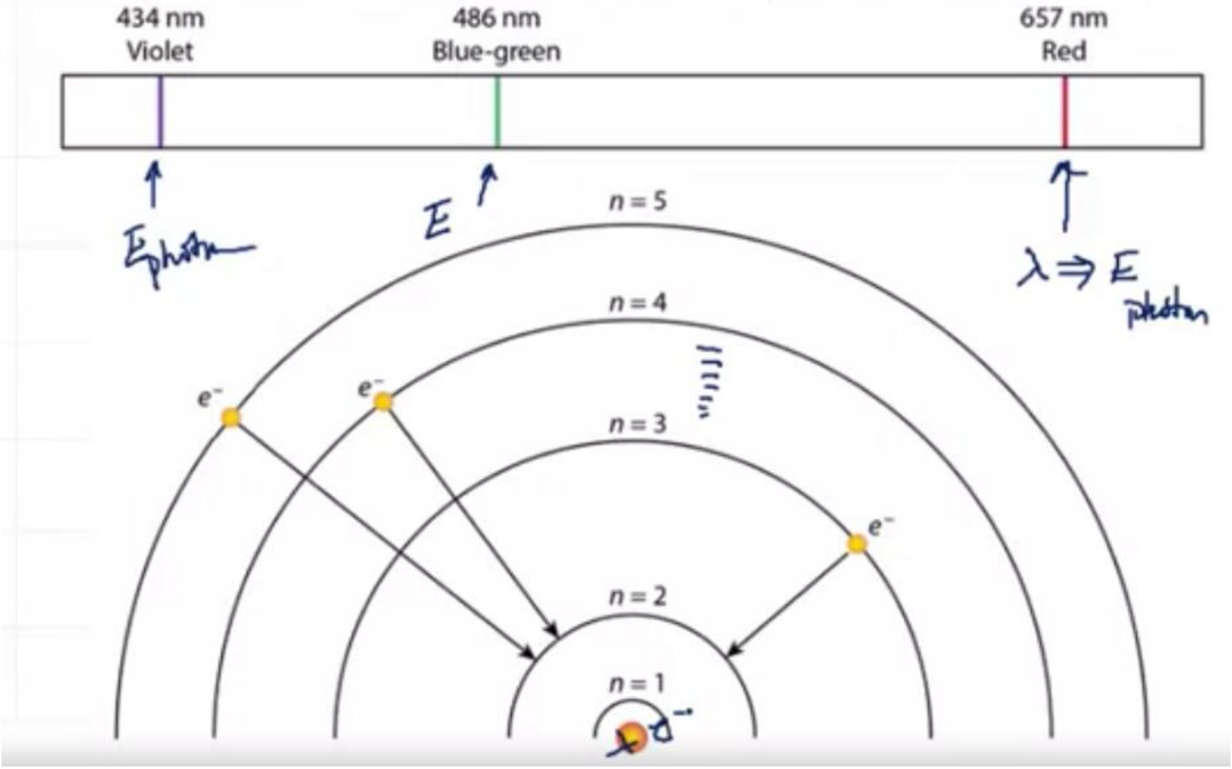
(3) An atom or molecule can emit (or absorb) either one quantum of energy ($h\nu$) or any whole number multiple of this unit.

Bohr's Model of the Atom (1913)

1. e⁻ can only have specific (quantized) energy values

2. light is emitted as e⁻ moves from one energy level to another

n (principal quantum number) = 1,2,3,…



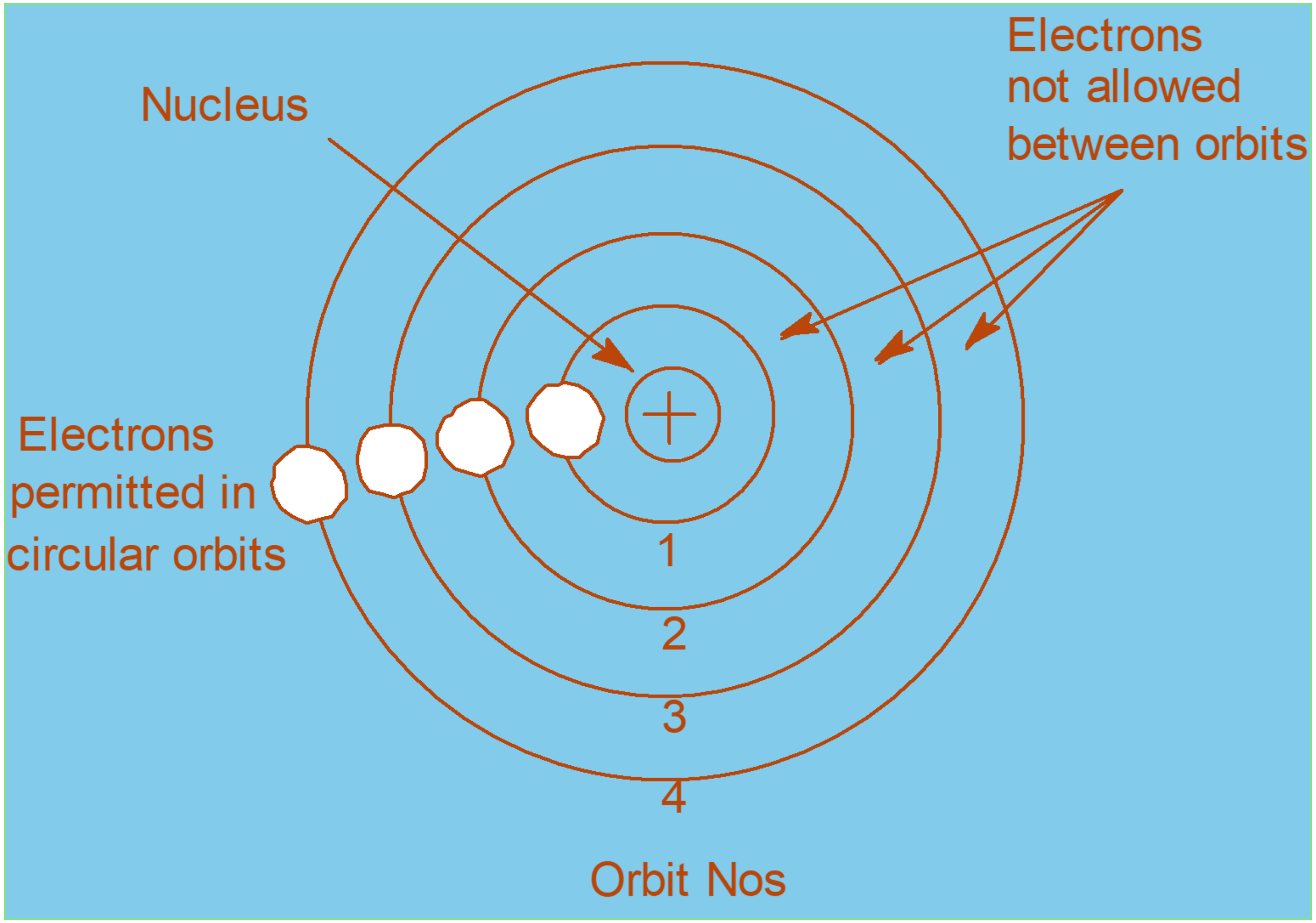
Bohr Model of the Atom:

1. Electrons travel around the nucleus in specific permitted circular orbits and in no others.
2. While in these specific orbits, an electron does not radiate (or lose) energy.
3. An electron can move from one energy level to another by quantum or photon jumps only.
4. The **angular momentum** (*mvr*) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by 2π.

$$\therefore mvr = \frac{nh}{2\pi}$$

where m = mass of electron,
v = velocity of electron,
r = radius of the orbit,
n = 1, 2, 3.....etc and
h = Planck's constant.

Bohr Model of the Atom (contd.):



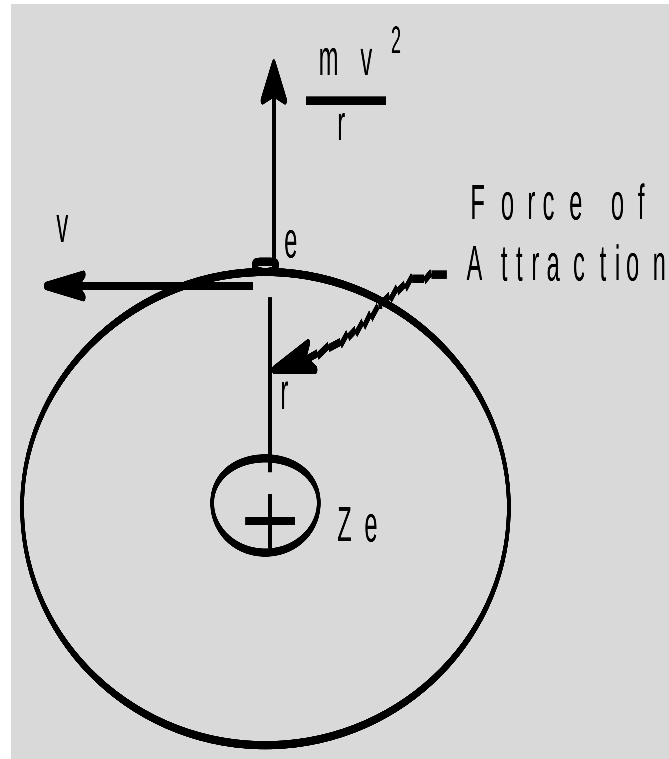
Shortcoming of the Bohr Atom:

- It is unsuccessful for every other atom containing more than one electron.
- In view of modern advances, like dual nature of matter, uncertainty principle etc. any mechanical model of the atom stands rejected.
- Bohr’s model of electronic structure could not account for the ability of atoms to form molecules through chemical bonds.
- Bohr’s theory could not explain the effect of magnetic field (Zeeman effect) and electric field (Stark effect) on the spectra of atoms.

Calculation of Radius of Orbits:

Calculation of Energy of Electron in each Orbit:

Consider, an electron of charge ***e*** revolving around a nucleus of charge ***Ze***, where ***Z*** is the atomic number and ***e*** the charge on a proton. Let ***m*** be the mass of the electron, ***r*** the radius of the orbit and ***v*** the tangential velocity of the revolving electron.



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Calculation of Radius of Orbits...

The electrostatic force of attraction between the nucleus and the electron (Coulomb's Law),

$$= \frac{Ze \times e}{r^2}$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r}$$

Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

Calculation of Radius of Orbits...

For hydrogen Z=1, therefore,

$$\frac{e^2}{r^2} = \frac{mv^2}{r}$$

multiplying both sides by r

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

According to Bohr's theory, angular momentum of the revolving electron is given by the expression:

$$mvr = \frac{nh}{2\pi} \qquad \text{or} \qquad v = \frac{nh}{2\pi\, mr} \qquad \text{--- --- --- (2)}$$

Calculation of Radius of Orbits...

Substituting the value of *v* in equation (1)

$$\frac{e^2}{r} = m\left(\frac{nh}{2\pi mr}\right)^2$$

1C= 3 x 10^9 esu
h= 6.626 x 10-27 erg s
e= 4.8 x 10^10 esu
m= 9.11 x 10^-28 g

Solving for r,

$$r = \frac{n^2h^2}{4\pi^2 me^2} \qquad \text{--- --- --- (3)}$$

Since the value of *h*, *m* and *e* had been determined experimentally, substituting these values in (3), we have

$$r = n^2 \times 0.529 \times 10^{-8}\, cm \qquad \text{--- --- --- (4)}$$

where *n* is the principal quantum number and hence the number of the orbit.

Calculation of Energy of Electron in each orbit...

For hydrogen atom, the energy of the revolving electron, E is the sum of its kinetic energy $\left(\frac{1}{2}mv^2\right)$ and potential energy. $\left(-\frac{e^2}{r}\right)$

(Hints: P.E.=kq_1q_2/r; attractive force, so negative)

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \qquad \text{--- --- --- (5)}$$

From equation (1) $mv^2 = \frac{e^2}{r}$

Substituting the value of mv^2 in (5),

$$E = \frac{1}{2}\frac{e^2}{r} - \frac{e^2}{r}, \qquad E = -\frac{e^2}{2r} \qquad \text{--- --- --- (6)}$$

Calculation of Energy of Electron in each orbit...

Substituting the value of *r* from equation (3) in (6),

$$E = -\frac{e^2}{2}\times\frac{4\pi^2 me^2}{n^2 h^2} = -\frac{2\pi^2 me4}{n^2 h^2} \quad \text{--- --- --- (7)}$$

Substituting the values of *m*, *e* and *h* in (7),

$$E = -\frac{2.179\times10^{-11}}{n^2} erg / atom ,$$

$$\text{or } E = -\frac{2.179\times10^{-18}}{n^2} J \; per \, atom \quad \text{--- --- --- (8)}$$

By using proper integer for n, we can get the energy for each orbit.

Problems:

- **Problem-3**: Calculate the first five Bohr radii of the hydrogen atom.
- **Problem-4**: Calculate the radius of the third orbit of hydrogen atom.
- **Problem-5**: Calculate the five lowest energy levels of the hydrogen atom.
- **Problem-6**: Calculate the energy of electron of the second orbit of the hydrogen atom.

Bohr Explanation of Hydrogen Spectrum:

- The solitary electron in hydrogen atom at ordinary temperature resides in the first orbit (n =1) and is in the lowest energy state (ground state).
- When energy is supplied to hydrogen gas in the *discharge tube*, the electron moves to higher energy levels viz., 2, 3, 4, 5, etc., depending on the quantity of energy absorbed.
- From these high energy levels, the electron returns by jumps to one or other lower energy level. In doing so the electron emits the excess energy as a photon.
- This gives an excellent explanation of the various spectral series of hydrogen.

Lyman series is obtained when the electron returns to the ground state i.e., n = 1 from higher levels (n_2 = 2, 3, 4, 5, etc.).

Similarly, **Balmer**, **Paschen**, **Brackett** and **Pfund series** are produced when the electron returns to the second, third, fourth and fifth energy levels respectively as shown in figure below:

Table: Spectral series of hydrogen

Series	n_1	n_2	Region	Wavelength λ (Å)
Lyman	1	2, 3, 4, 5, etc.	Ultraviolet	920-1200
Balmer	2	3, 4, 5, 6, etc.	Visible	4000-6500
Paschen	3	4, 5, 6, 7, etc.	Infrared	9500-18750
Brackett	4	5, 6, 7	Infrared	19450-40500
Pfund	5	6, 7	Infrared	37800-75000

Hydrogen spectral series:

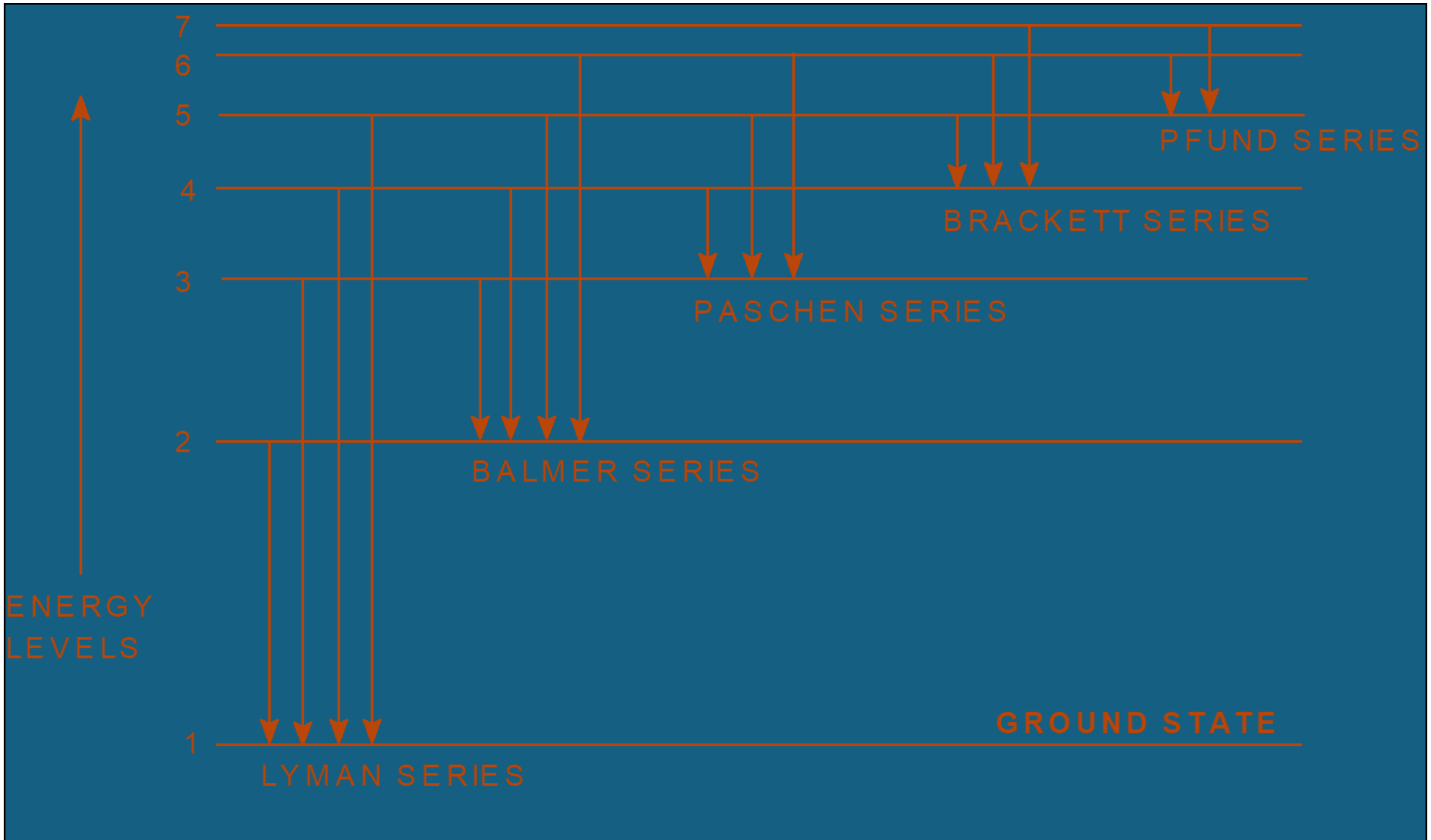

FIGURE. Hydrogen spectral series on a Bohr atom energy diagram.

Questions:

1. **Explain- ‘values of Rydberg’s constant is the same as in the original empirical Balmer’s equation’.**
2. **How do you calculate the wavelengths of the spectral lines of hydrogen in the visible region using Balmer equation?**

Problems:

Problem-7: Calculate the wavelength in Å of the line in Balmer series that is associated with drop of the electron from the fourth orbit. The value of Rydberg constant is 109,676 cm^{-1}.

Problem-8: Calculate the wavelength in Å of the third line in Balmer series that is associated with drop of the electron. (Rydberg constant =109,676 cm^{-1}).

Problem-9: The energy of the electron in the second and third orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wave length of the emitted radiation. (Hints: $\Delta E = hc/\lambda$, Answer: 6653Å)

Possible Question????

1. Discuss the contribution and limitation of each atomic model (Dalton, Rutherford & Bohr)

2.Extablish the Bohr atomic radius calculation equation for hydrogen atom.

3. Show the derivation of the Bohr atomic radius or energy expression equation.

4. What is spectrum and electromagnetic radiation.

5.Calculation of radius of certain orbit/ energy of electron orbiting in certain orbit. (Mathematical Problem)

6. Draw a labelled energy level diagram and explain the different series of spectral lines for hydrogen atom.

next class

QUIZ-1

Thank you