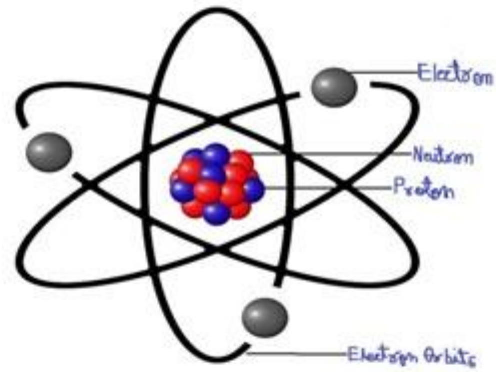
INTRODUCTION:

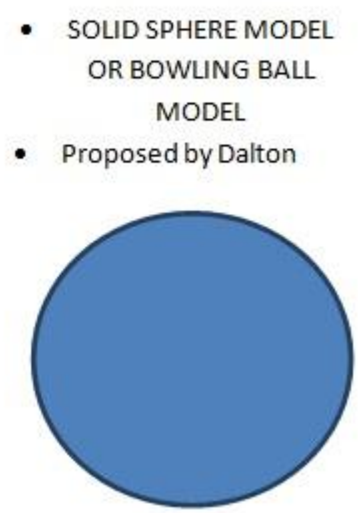
Atom is the fundamental building block of matter having a confined positively charged nucleus at the center, surrounded by negatively charged electrons. Every inorganic, organic, or even synthetic object is made up of atoms.



There were many atomic models given initially

DALTON'S ATOMIC THEORY:

- Atoms are the smallest constituents of matter and can't be divided further(indivisible)
- Atoms belonging to same matter have similar characteristics and mass; atoms of different matter have different properties and mass
- Atoms are reoriented in a chemical reaction (not generated or destructed)



Merits:

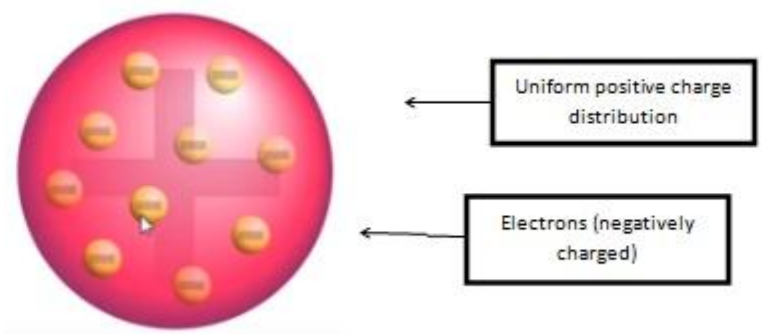
- It demonstrated laws of: a)mass conservation, b)fixed composition, c)multiple proportions

Demerits:

- It was unable to demonstrate experiments of electrostatics (dry paper bits sticking to comb) that showed charge exists.

THOMSON MODEL OF ATOM:

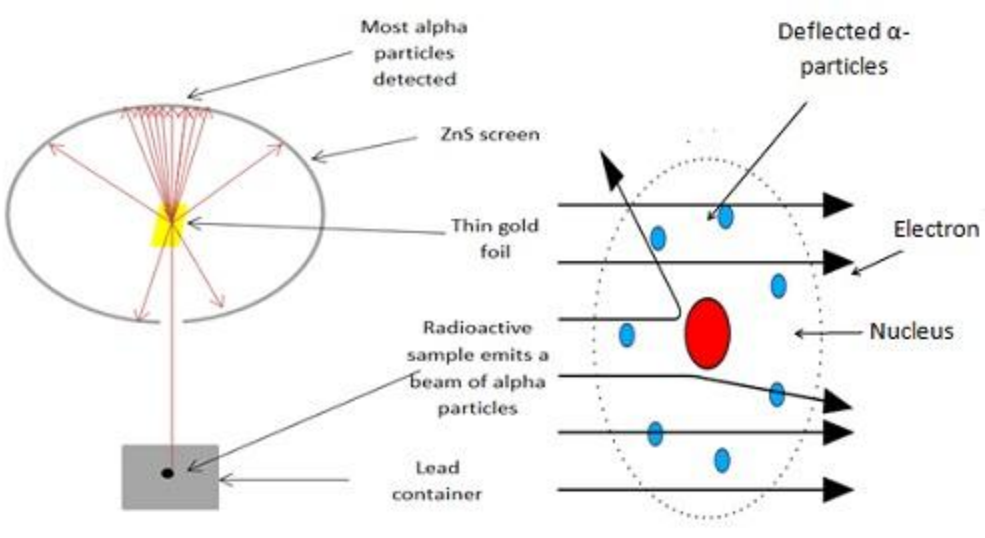
- Atom is like a sphere where positive charge has uniform distribution throughout
- Electrons are scattered inside in a way that most stable electrostatic arrangement is achieved, meaning that minimum possible energy of the system should is achieved
- Also known as watermelon model or plum pudding model or raisin bread model
- It positively illustrated the net neutrality(equal positive and negative charges, so no net charge) of atom
- It was inconsistent with the experiments conducted later and the discovery of neutron and proton.



THOMSON'SATOMIC MODEL

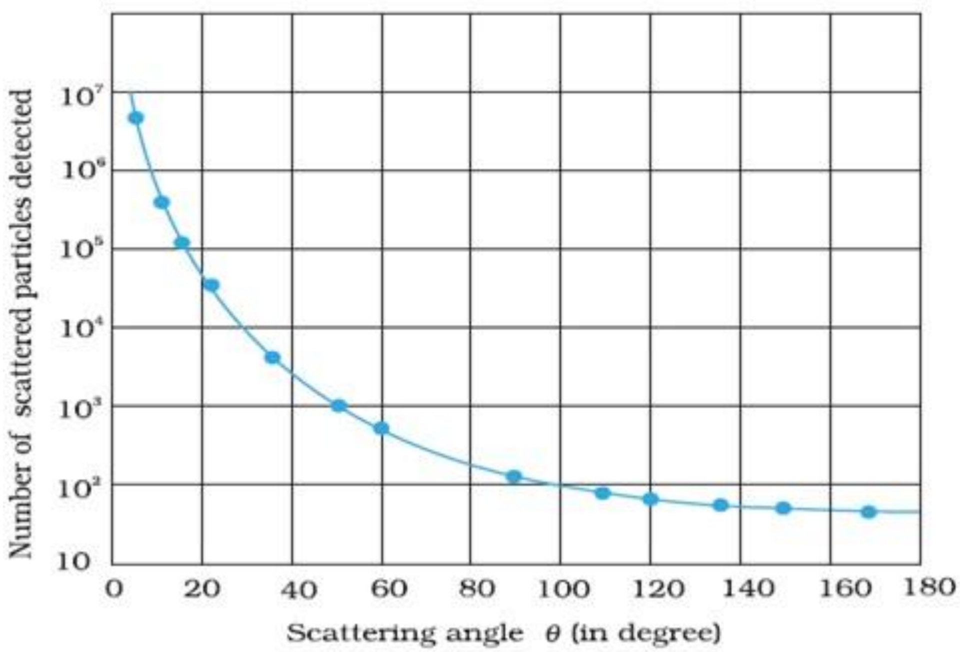
RUTHERFORD'S NUCLEAR MODEL OF ATOM:

- Geiger and Marsden carried out few experiments on the advice of Rutherford
- On a very thin gold foil, highly energetic ray of α-particles(that are positively charged with energy of 5.5MeV)was incident
- Scattered α-particles when strike zinc sulphide screen(surrounding the thin gold foil) produced light flashes(scintillations) which were observed via detector(microscope)



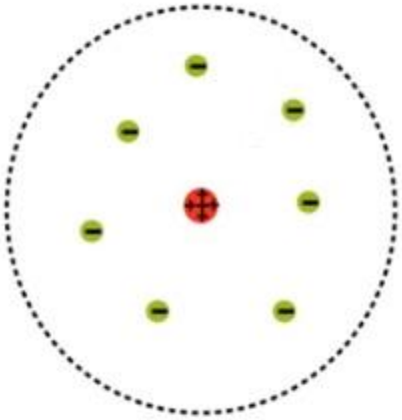
Geiger-Marsden Experiment

- Scattered α-particles' distribution as a function of scattering angle(θ) was analyzed and plotted as a graph



- As the <u>scattering angle</u>(θ) got <u>higher</u>, count of <u>scattered α-particles</u> observed got <u>lower</u>, and vice versa
- Almost all of the α-particles passed through the gold foil undeflected, and infinitesimally small number of α-particles got deflected
- This proved that almost all the <u>space in an atom is empty</u> (<u>9999999999996%</u>), and the positive charge is confined to an extremely small region because very fewof the positively charged α-particles were repelled by gold foil proving positive charge is confined to a small region. This region was called nucleus.

- Atom has a structure analogous to our solar system where nucleus (like sun) is at center and all the electrons (like planets) revolving around it in a specified circular path at large speeds



Atomic Structure proposed by Rutherford

- Electrons and protons are bound together by electrostatic forces of attraction and atom, as a whole is electrically neutral
- Rutherford was the first to discover that atom has a nucleus and so his model was called as Rutherford's nuclear model of atom
- Electron Orbit:

Since electrons orbiting around the nucleus and are held to nucleus by electrostatic force of attraction, ergo, centripetal force (F_c) is provided by the electrostatic force (F_e) to keep electrons in the orbit.

$F_c = F_e$

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_o}\frac{Ze^2}{r^2}$$

Here r=radius of orbit, v= velocity of orbiting electron, e= charge of an electron, m= mass of an electron, Z=atomic mass of atom, $\mathcal{E}_o$=permittivity of free space

On solving, we get:

$$\boxed{r = \frac{Ze^2}{4\pi\varepsilon_o mv^2}}$$

- Kinetic Energy(K): putting the value of mv^2 from eq.(1), we get:

$$K = \frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_o r}$$

- Potential Energy(U): using the electrostatic potential between 2 charged body, we get:

$$U = \frac{1}{4\pi\varepsilon_o}\frac{-e \times +Ze}{r} = \frac{-Ze^2}{4\pi\varepsilon_o r}$$

- Negative sign here shows that there is a force of attraction and energy has to be given to the system to overcome this force of attraction
- Total Energy(T):

T = U + K

$$T = \frac{-Ze^2}{8\pi\epsilon_o r}$$

- Some important things to note:

Kinetic energy(K) = -(1/2)Potential energy(U)

Kinetic energy(K) = -Total energy(T)

Potential energy(U) = 2×Total energy(T)

Drawbacks of Rutherford's Model:

- Accelerated charged particle produces electromagnetic waves (Maxwell Theory), so orbital radius of electron should go on decreasing and finally electron should fall into the nucleus. But atoms are stable in nature and this stability of atoms could not be clarified by Rutherford's model
- The model didn't talk about electronic structure of atoms, viz. electrons orientation, their orbital motion and relative energy of electron in different orbits
- Dual character of electromagnetic radiation couldn't be elaborated by the model

Numerical Problems: Hydrogen atom has ground state energy of -13.6eV. What are the kinetic and potential energies of atom at this state?

Solution: Given: Total energy= -13.6eV

We know from the above equations: Kinetic energy(K)= -Total energy(T)

∴ K = -(-13.6eV) = 13.6eV (ans)

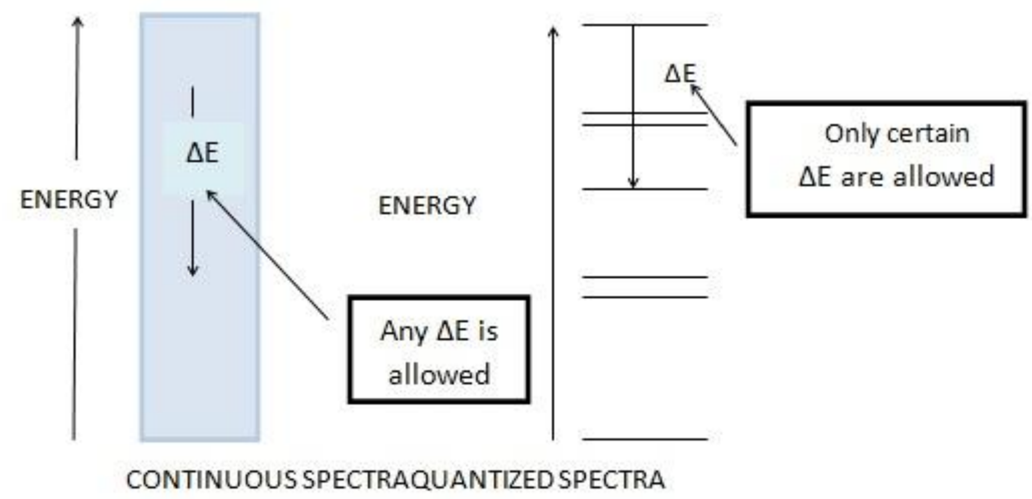
Potential energy(U) = 2×Total energy(T)

∴ U = 2×(-13.6eV) = -27.2eV (ans)

Note: Here negative sign shows that there is a force of attraction between electron and nucleus.

ATOMIC SPECTRA:

- When an electron jumps amongst energy levels in an atom, energy is emitted or absorbed in the form of electromagnetic radiations and these radiations produce a spectral lines of frequencies(or wavelength) associated with an atom, called atomic spectra
- Spectroscopy is the learning and examination emission and absorption spectra associated with an atom to determine its properties
- Spectral lines are the bright and dark line series that constitute the spectrum associated with an atom
- An atom has a discrete spectra(where exist a fixed specific lines of energy transition of electron with discrete energy gaps) also known as quantized spectra
- Another type is continuous spectra(where there is no specific lines of energy transition of electrons) which is the reverse of discrete spectra



- There are 3 types of atomic spectra: a)emission spectra, b)absorption spectra, c) continuous spectra

Emission spectra:

- Radiation spectrum produced due to absorption of energy by a matter
- When an electron of an atom, molecules or ions get to a higher energy state than their ground (stable) state due to radiation absorption, they are said to be excited
- Emission spectrum is produced when energy is supplied to a sample (through heating or irradiation) and the wavelength or frequency of radiation emitted by the sample is observed as a function of energy

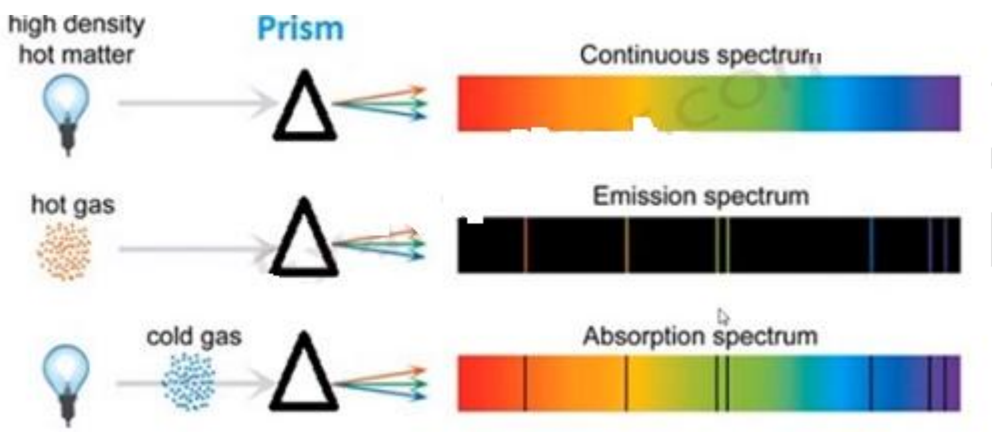
Absorption spectra:

- It is just the opposite of emission spectra
- Continuous radiation (energy) is directed through a sample which absorbs certain radiation of particular wavelengths and the remaining spectrum is recorded. Absorbed wavelengths correspond to the dark spaces in the spectrum
- Whatever absent(showed by dark lines) in the emission spectrum of an atom is actually present (showed by bright lines) in

the absorption spectrum of that atom

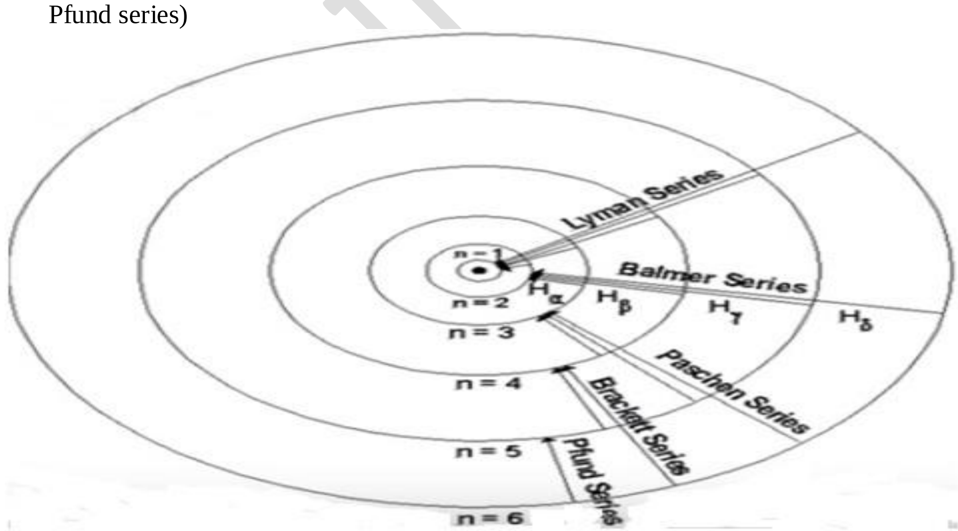
Continuous spectra:

- Formed when a ray of white light is passed through a prism(or water droplets) causing a continuous spectrum of visible light of different wavelength
- There are no discrete lines (separation) between any 2 adjacent wavelengths
- Speed of light changes with respect to the medium through which it passes, so as the medium changes, light with the longest wavelength (red)deviates the least and the light with the shortest wavelength (violet) deviates the most



SPECTRAL SERIES:

- On passing electric discharge through hydrogen gas, hydrogen molecules would dissociate giving rise to excited (highly energetic) hydrogen atoms that emit radiation of certain specified frequency while returning to its ground state
- Hydrogen spectra is constituted of 5 series of spectrum named after their discoverer(Lyman, Balmer, Paschen, Bracket and Pfund series)



TYPES OF SPECTRAL SERIES:

Balmer Series:

- First scientist to discover a spectral series of hydrogen atom
- It consist of visible radiation spectrum
- Experimentally, he found that these spectral lines could be expressed mathematically in the form of wavelength as:

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

- Here R= Rhydberg constant = 109677cm^{-1}(found experimentally), n= 3, 4, 5…… (higher discrete energy state from which electron jumps to 2nd energy state thus emitting radiation)

  λ = wavelength of emitted radiation in (cm)
- For maximum wavelength(λ_{max}) in the Balmer series, n=3 (has to be minimum):

$$\frac{1}{\lambda_{max}} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\lambda_{max} = \frac{36}{5R}$$

- For minimum wavelength (λ_{min}) in the Balmer series, n=∞(has to be minimum):

$$\frac{1}{\lambda_{min}} = R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$$

$$\lambda_{min} = \frac{4}{R}$$

Lyman Series:

- Spectral series when radiation emitted is due to jumping of electron from higher energy states to ground state
- Mathematically expressed as

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

- Here n= 2, 3, 4…
- For maximum wavelength in the Lyman series, n=2 (has to be minimum):

$\lambda_{max} = 4/3R$

- For minimum wavelength in the Lyman series, n=∞(has to be minimum):

$\lambda_{min} = 1/R$

Similarly, all other series could be expressed as:

Paschen Series:

- Mathematically expressed as

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

- Here n= 4, 5, 6…

Bracket Series:

- Mathematically expressed as

$$\frac{1}{\lambda} = \left(\frac{1}{4^2} - \frac{1}{n^2}\right)$$

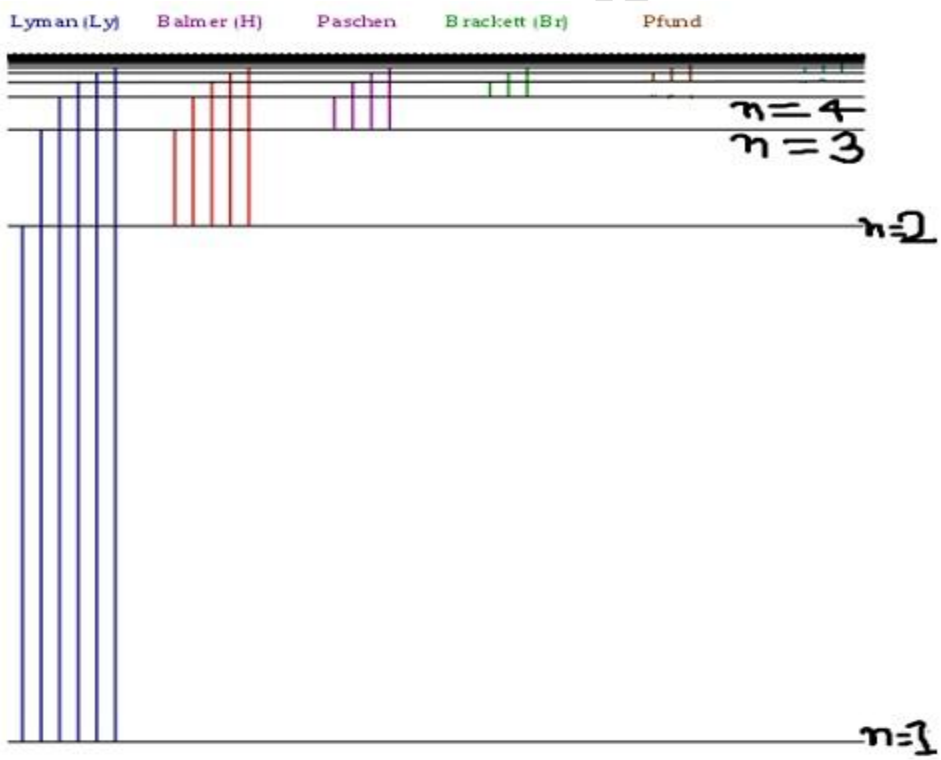
- Here n= 5, 6, 7…

PfundSeries:

- Mathematically expressed as

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

- Here n= 6, 7, 8…



- Atomic spectra has a huge scope in the study of electronic structures of various atoms, molecules and ions
- Elements have their own distinctive spectral series. So spectral series is used in the identification (even discovery) of unknown atoms
- Many elements were discovered by the spectroscopic methods, such as Rubidium(Ru), Caesium(Cs), Helium(He), Gallium(Ga), Thallium(Tl), Scandium(Sc).

***Numerical Problem*:**Evaluate the shortest and the longest wavelength corresponding to the following series of spectral lines:

1. Lyman series
2. Paschen series
3. Bracket series

Solution:

1. For Lyman series: $1/\lambda = R(1/1^2 – 1/n^2)$

For shortest wavelength (λ_{min}), n has to be maximum

$1/\lambda_{max} = R(1/1^2 – 1/\infty^2)$

$\lambda_{max} = 1/R = (1/109677)cm$

$\lambda_{min} = 9.118\times10^{-6}cm$ (Answer)

For longest wavelength (λ_{max}), n has to be minimum

$1/\lambda_{max} = R(1/1^2 – 1/2^2)$

$\lambda_{max} = 4/(3R) = 4/(3\times109677) = 1.216\times10^{-5}cm$

$\lambda_{max} = 1.216\times10^{-5}cm$ (Answer)

1. b) For Paschen series, similarly proceeding as above

For shortest wavelength , n has to be maximum

$1/\lambda_{min} = R(1/3^2 – 1/\infty^2)$

$\lambda_{min} = 9/R = 9/109677 = 8.206\times10^{-5}cm$ (ans)

For longest wavelength , n has to be minimum

$1/\lambda_{max} = R(1/3^2 – 1/4^2)$

$\lambda_{max} = 16\times9/7 =16\times9/106977 = 1.876\times10^{-4}cm$ (Answer)

c) For Bracket series, similarly proceeding as above

$1/\lambda_{min} = R(1/4^2 – 1/\infty^2)$

$\lambda_{min} = 16/R = 16/109677 =1.459\times10^{-4}cm$

For longest wavelength (λ_{max}), n has to be minimum

$\therefore 1/\lambda_{max} = R(1/4^2 - 1/5^2)$

$\lambda_{max} = 25\times16/(9R) = 4.052\times10^{-4}$cm (Answer)

Numerical Problem: A hydrogen atom on absorbing a photon, gets excited to the n=4 level from its ground level. What is the wavelength and frequency of the photon?

Solution: Given, n =4

From Balmer series, we can write

$1/\lambda = R(1/2^2 - 1/4^2) = 109677(1/4 - 1/16)$

$\lambda = 16/(3\times109677) = 4.86\times10^{-5}$cm (ans)

For frequency(υ), we know that it is given by the formula

$\upsilon = c/\lambda = 3\times10^8/(4.86\times10^{-7}) = 6.1\times10^{14}$Hz (ans)

Energy of Orbits:

The orbital energy of orbiting electron in the discrete energy levels in the Bohr's model is called as the energy of orbits.

We already know, from Rutherford's Model that total energy(T) is given by

$T = -Ze^2/(8\pi\varepsilon_o r)$

Putting the value of Bohr's radius, we get

$$T = \frac{-me^4}{8\pi\varepsilon_o^2 n^2 h^2}$$

- Putting the values of electron mass(m), charge(e), permittivity of free space(ε_o), Planck's constant(h); we get

$\mathbf{T = (-13.6/n^2)eV}$

- For the energy of innermost stationary orbit, put n=1

DRAWBACKS OF BOHR'S MODEL:

- It was primarily for hydrogen atom
- It couldn't elaborate spectra of multi-electron atoms
- Wave nature of electron was not justified by the model (inconsistent with the de Broglie's hypothesis of dual nature of matter)
- It didn't illustrated molecules making process of chemical reactions
- It violated Heisenberg's Principal($\Delta x\times \Delta p \geq nh/(2\pi)$) which said that it was impossible to evaluate theprecise position and

momentum of electron (and other microscopic particles) simultaneously.Only their probability could be estimated.

- Zeeman effect(spectral lines variation due to external magnetic field) and Stark Effect(spectral lines variation due to external electric field) couldn't be described by the model

Numerical Problem:The energy gap between the 2 energy levels is 2.3eV. What is the frequency of radiation emitted when the atom makes a transition from higher to lower energy levels?

Solution: Given, $\Delta E = 2.3eV$

Using Bohr's 2^{nd} postulate

$\Delta E = h\nu$

$$\therefore \nu = \frac{\Delta E}{h} = \frac{2.3 \times 10^{-19}}{6.6 \times 10^{-34}} = 3.485 \times 10^{14} Hz\ (ans)$$

Numerical Problem: Use the Bohr's model to calculate:

1. Electron speed in the n=1, 2, and 3 levels of the hydrogen atom
2. Bohr's radius of orbit in each of these levels.

Solution:

1. Velocity of orbiting electron as per Bohr's model is given by

$v = e^2/(2nh\varepsilon_o)$

For n = 1, velocity is given by

$$v = \frac{e^2}{2 \times 1 \times h \times \varepsilon_o} = \frac{(1.6 \times 10^{-19})^2}{2 \times 1 \times 6.6 \times 10^{-34} \times 8.85 \times 10^{-12}} ms^{-1}$$
$$\therefore v = 2.191 \times 10^6 ms^{-1}\ (ans)$$

For n = 2, velocity is given by

$$v = \frac{e^2}{2 \times 2 \times h \times \varepsilon_o} = \frac{(1.6 \times 10^{-16})^2}{2 \times 2 \times 6.6 \times 10^{-34} \times 8.85 \times 10^{-12}}$$
$$\therefore v = 1.096 \times 10^6 ms^{-1}\ (ans)$$

For n =3, velocity is given by

$$v = \frac{e^2}{2 \times 3 \times h \times \varepsilon_0} = \frac{(1.6 \times 10^{-19})^2}{2 \times 3 \times 6.6 \times 10^{-34} \times 8.85 \times 10^{-12}} ms^{-1}$$
$$\therefore v = 7.304 \times 10^5 ms^{-1}\ (ans)$$

1. Bohr's radius of orbit is given by

$r = n^2h^2\varepsilon_o/(\pi me^2)$

For n = 1, Bohr's radius will be

$$r = \frac{1^2 \times h^2 \times \varepsilon_o}{\pi me^2} = \frac{1^2 \times (6.6 \times 10^{-34})^2 \times 8.85 \times 10^{-12}}{\pi \times 9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^2} m$$
$$\therefore r = 5.27 \times 10^{-11} m\ (ans)$$

For n = 2, Bohr's radius will be

$$r = \frac{2^2 \times h^2 \times \varepsilon_o}{\pi me^2} = \frac{2^2 \times (6.6 \times 10^{-34})^2}{\pi \times 9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^2} m$$
$$\therefore r = 2.107 \times 10^{-10} m\ (ans)$$

For n = 3, Bohr's radius will be

$$r = \frac{3^2 \times h^2 \times \varepsilon_o}{\pi me^2} = \frac{3^2 \times (6.6 \times 10^{-34})^2 \times 8.85 \times 10^{-12}}{\pi \times 9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^2} m$$
$$\therefore r = 4.74 \times 10^{-10} m\ (ans)$$

Numerical Problem: Using Bohr's Model, find the quantum number associated with earth's revolution around the sun in an orbit of radius$5\times10^{11}m$, orbital speed of$3\times10^4 m/s$, and
mass of earth=$6\times10^{24}kg$

Solution:

Given, $r_n = 1.5\times10^{11}m$, $v_n = 3\times10^4 m/s$, and $m = 6\times10^{24}kg$

According to the Bohr's second postulate:

$mv_nr_n = nh/(2\pi)$

$$n = \frac{2\pi mv_nr_n}{h} = \frac{2\pi \times 6 \times 10^{24} \times 3 \times 10^4 \times 1.5 \times 10^{11}}{6.6 \times 10^{-34}}$$
$$\therefore n = 2.57 \times 10^{74}\ (ans)$$

DE-BROGLIE'S HYPOTHESIS:

- De Broglie's Hypothesis showed the wave particle duality of matter
- It showed that, like photons, electrons must also have mass or momentum() and wavelength(λ), given by the equation (here c= speed of light in air, v=frequency)

p = mv = h/λ = h/(c/λ)

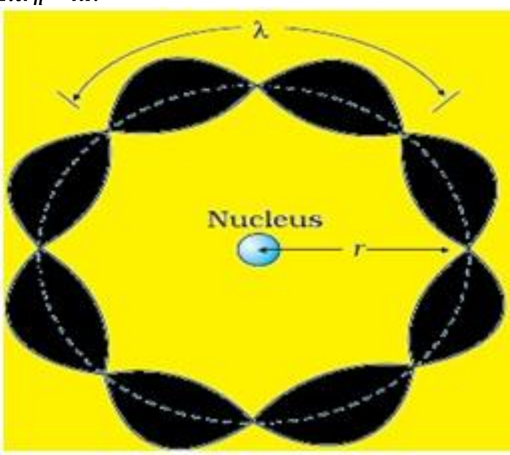
- It holds only for the subatomic (microscopic) particles like electron, proton etc. where mass is very small, so wavelength are large enough to be experimentally observable

- It does not hold for the macroscopic particles since mass there is very large, making wavelength too small to be experimentally observable

DE-BROGLIE'S EXPLANATION OF BOHR'S SECOND POSTULATE OF QUANTISATION:

- Electron orbiting in circular orbit can be considered as a particle wave
- Only those waves propagate and survive which form nodes at terminal point with integer multiple of wavelength(resonant standing waves), thus covering the whole circumferential distance of circular orbit

$2\pi r_n = n\lambda$



- From de Broglie's hypothesis: $\lambda = h/(mv)$
- So, ultimately we get: $mv_n r_n = nh/(2\pi)$
- This proved that wave-particle duality is the cause of quantized energy states