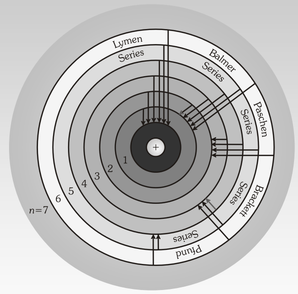


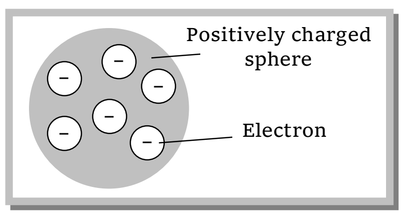
Atomic Structure

Important Atomic Models

(1) **Thomson's model**

J.J. Thomson gave the first idea regarding structure of atom. According to this model.

(i) An atom is a solid sphere in which entire and positive charge and it's mass is uniformly distributed and in which negative charge (*i.e.* electron) are embedded like seeds in watermelon.



Success and failure

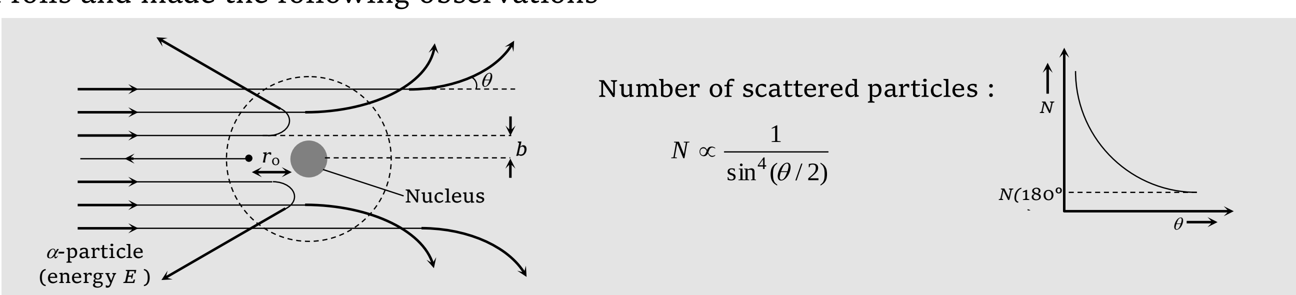
Explained successfully the phenomenon of thermionic emission, photoelectric emission and ionization.

The model fail to explain the scattering of α- particles and it cannot explain the origin of spectral lines observed in the spectrum of hydrogen and other atoms.

(2) **Rutherford's model**

Rutherford's α-particle scattering experiment

Rutherford performed experiments on the scattering of alpha particles by extremely thin gold foils and made the following observations



(i) Most of the α-particles pass through the foil straight away undeflected.

(ii) Some of them are deflected through small angles.

(iii) A few α-particles (1 in 1000) are deflected through the angle more than 90°.

(iv) A few α -particles (very few) returned back *i.e.* deflected by 180°.

(v) Distance of closest approach (Nuclear dimension)

The minimum distance from the nucleus up to which the α-particle approach, is called the distance of closest approach (r_0). From figure $r_0 = \frac{1}{4\pi\varepsilon_0}.\frac{Ze^2}{E}$; $E = \frac{1}{2}mv^2 =$ K.E. of α-particle

(vi) Impact parameter (b) : The perpendicular distance of the velocity vector ($\vec{v}$) of the α-particle from the centre of the nucleus when it is far away from the nucleus is known as impact parameter. It is given as

$$b = \frac{Ze^2 \cot(\theta/2)}{4\pi\varepsilon_0\left(\frac{1}{2}mv^2\right)} \Rightarrow b \propto \cot(\theta/2)$$

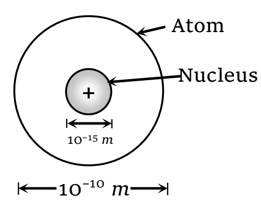
Note : ❑ If t is the thickness of the foil and N is the number of α-particles scattered in a particular direction (θ = constant), it was observed that $\frac{N}{t}$ = constant $\Rightarrow \frac{N_1}{N_2} = \frac{t_1}{t_2}$.

After Rutherford's scattering of α-particles experiment, following conclusions were made as regard as atomic structure :

(a) Most of the mass and all of the charge of an atom concentrated in a very small region is called atomic nucleus.

(b) Nucleus is positively charged and it's size is of the order of 10^{-15} $m \approx 1$ *Fermi*.

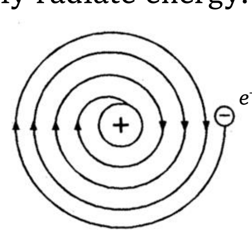
(c) In an atom there is maximum empty space and the electrons revolve around the nucleus in the same way as the planets revolve around the sun.



Size of the nucleus = 1 Fermi = 10^{-15} m

Draw backs

(i) Stability of atom : It could not explain stability of atom because according to classical electrodynamic theory an accelerated charged particle should continuously radiate energy. Thus an electron moving in an circular path around the nucleus should also radiate energy and thus move into smaller and smaller orbits of gradually decreasing radius and it should ultimately fall into nucleus.



Instability of atom

(ii) According to this model the spectrum of atom must be continuous where as practically it is a line spectrum.

(iii) It did not explain the distribution of electrons outside the nucleus.

(3) **Bohr's model**

Bohr proposed a model for hydrogen atom which is also applicable for some lighter atoms in which a single electron revolves around a stationary nucleus of positive charge *Ze* (called hydrogen like atom)

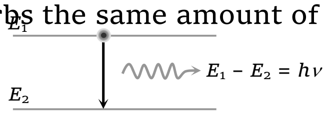
Bohr's model is based on the following postulates.

(i) The electron can revolve only in certain discrete non-radiating orbits, called stationary orbits, for which total angular momentum of the revolving electrons is an integral multiple of $\frac{h}{2\pi}\ (=\hbar)$

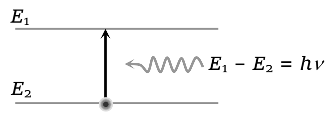
i.e. $L = n\left(\frac{h}{2\pi}\right) = mvr$; where n = 1, 2, 3, ...= Principal quantum number

(ii) The radiation of energy occurs only when an electron jumps from one permitted orbit to another.

When electron jumps from higher energy orbit (E_1) to lower energy orbit (E_2) then difference of energies of these orbits *i.e.* $E_1 - E_2$ emits in the form of photon. But if electron goes from E_2 to E_1 it absorbs the same amount of energy.



Emission



Absorptio

Note : ❑ According to Bohr theory the momentum of an e^- revolving in second orbit of H_2 atom will be $\frac{h}{\pi}$

❑ For an electron in the n^{th} orbit of hydrogen atom in Bohr model, circumference of orbit $= n\lambda$; where λ = de-Broglie wavelength.

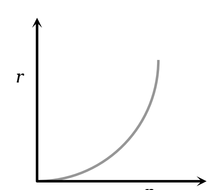
Bohr's Orbits (For Hydrogen and H_2-Like Atoms)

(1) **Radius of orbit**

For an electron around a stationary nucleus the electrostatics force of attraction provides the necessary centripetal force

i.e. $\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{mv^2}{r}$ .... (i) also $mvr = \frac{nh}{2\pi}$ ....(ii)

From equation (i) and (ii) radius of n^{th} orbit



$$r_n = \frac{n^2h^2}{4\pi^2kZme^2} = \frac{n^2h^2\varepsilon_0}{\pi mZe^2} = 0.53\frac{n^2}{Z}\,\mathring{A} \qquad \left[\text{where } k = \frac{1}{4\pi\varepsilon_0}\right]$$

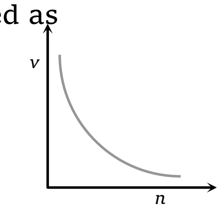
$$\Rightarrow \boldsymbol{r_n \propto \frac{n^2}{Z}}$$

Note : ❑ The radius of the innermost orbit (n = 1) hydrogen atom (z = 1) is called Bohr's radius a_0 *i.e.* $a_0 = 0.53\,Å$.

(2) **Speed of electron**

From the above relations, speed of electron in n^{th} orbit can be calculated as

$$v_n = \frac{2\pi kZe^2}{nh} = \frac{Ze^2}{2\varepsilon_0 nh} = \left(\frac{c}{137}\right).\frac{Z}{n} = 2.2\times 10^6\,\frac{Z}{n}\,m/sec$$



where (c = speed of light 3×10^8 m/s)

Note : ❑ The ratio of speed of an electron in ground state in Bohr's first orbit of hydrogen atom to velocity of light in air is equal to $\frac{e^2}{2\varepsilon_0 ch} = \frac{1}{137}$ (where c = speed of light in air)

(3) **Some other quantities**

For the revolution of electron in n^{th} orbit, some other quantities are given in the following table

Quantity	Formula	Dependency on n and Z
(1) Angular speed	$\omega_n = \frac{v_n}{r_n} = \frac{\pi mz^2e^4}{2\varepsilon_0^2 n^3 h^3}$	$\omega_n \propto \frac{Z^2}{n^3}$
(2) Frequency	$\nu_n = \frac{\omega_n}{2\pi} = \frac{mz^2e^4}{4\varepsilon_0^2 n^3 h^3}$	$\nu_n \propto \frac{Z^2}{n^3}$
(3) Time period	$T_n = \frac{1}{\nu_n} = \frac{4\varepsilon_0^2 n^3 h^3}{mz^2e^4}$	$T_n \propto \frac{n^3}{Z^2}$
(4) Angular momentum	$L_n = mv_n r_n = n\left(\frac{h}{2\pi}\right)$	$L_n \propto n$
(5) Corresponding current	$i_n = e\,\nu_n = \frac{mz^2e^5}{4\varepsilon_0^2 n^3 h^3}$	$i_n \propto \frac{Z^2}{n^3}$
(6) Magnetic moment	$M_n = i_n A = i_n(\pi r_n^2)$ (where $\mu_0 = \frac{eh}{4\pi m}$ = Bohr magneton)	$M_n \propto n$
(7) Magnetic field	$B = \frac{\mu_0 i_n}{2r_n} = \frac{\pi m^2 z^3 e^7 \mu_0}{8\varepsilon_0^3 n^5 h^5}$	$B \propto \frac{Z^3}{n^5}$

(4) **Energy**

(i) **Potential energy :** An electron possesses some potential energy because it is found in the field of nucleus potential energy of electron in n^{th} orbit of radius r_n is given by $U = k.\frac{(Ze)(-e)}{r_n} = -\frac{kZe^2}{r_n}$

(ii) **Kinetic energy :** Electron posses kinetic energy because of it's motion. Closer orbits have greater kinetic energy than outer ones.

As we know $\frac{mv^2}{r_n} = \frac{k.(Ze)(e)}{r_n^2}$ ⇒ Kinetic energy $K = \frac{kZe^2}{2r_n} = \frac{|U|}{2}$

(iii) **Total energy :** Total energy (E) is the sum of potential energy and kinetic energy *i.e.* $E = K + U$

⇒ $E = -\frac{kZe^2}{2r_n}$ also $r_n = \frac{n^2h^2\varepsilon_0}{\pi mze^2}$. Hence

$$E = -\left(\frac{me^4}{8\varepsilon_0^2h^2}\right).\frac{z^2}{n^2} = -\left(\frac{me^4}{8\varepsilon_0^2ch^3}\right)ch\frac{z^2}{n^2} = -Rch\frac{Z^2}{n^2} = -13.6\frac{Z^2}{n^2}eV$$

where $R = \frac{me^4}{8\varepsilon_0^2ch^3}$ = Rydberg's constant = 1.09×10^7 *per metre*

Note :
- Each Bohr orbit has a definite energy
- For hydrogen atom (Z = 1) ⇒ $E_n = -\frac{13.6}{n^2}eV$
- The state with n = 1 has the lowest (most negative) energy. For hydrogen atom it is $E_1 = -13.6$ eV.
- Rch = Rydberg's energy $\simeq 2.17 \times 10^{-18} J \simeq 31.6\,eV$.
- $E = -K = \frac{U}{2}$.

(iv) **Ionisation energy and potential :** The energy required to ionise an atom is called ionisation energy. It is the energy required to make the electron jump from the present orbit to the infinite orbit.

Hence $E_{ionisation} = E_\infty - E_n = 0 - \left(-13.6\frac{Z^2}{n^2}\right) = +\frac{13.6Z^2}{n^2}eV$

For H_2-atom in the ground state $E_{ionisation} = \frac{+13.6(1)^2}{n^2} = 13.6\,eV$

The potential through which an electron need to be accelerated so that it acquires energy equal to the ionisation energy is called ionisation potential. $V_{ionisation} = \frac{E_{ionisation}}{e}$

(v) **Excitation energy and potential :** When the electron is given energy from external source, it jumps to higher energy level. This phenomenon is called excitation.

The minimum energy required to excite an atom is called excitation energy of the particular excited state and corresponding potential is called exciting potential.

$$E_{Excitation} = E_{Final} - E_{Initial} \text{ and } V_{Excitation} = \frac{E_{excitation}}{e}$$

(vi) **Binding energy (B.E.) :** Binding energy of a system is defined as the energy released when it's constituents are brought from infinity to form the system. It may also be defined as the energy needed to separate it's constituents to large distances. If an electron and a proton are initially at rest and brought from large distances to form a hydrogen atom, 13.6 *eV* energy will be released. The binding energy of a hydrogen atom is therefore 13.6 *eV*.

Note : ❑ For hydrogen atom principle quantum number $n = \sqrt{\frac{13.6}{(\text{B.E.})}}$.

(5) **Energy level diagram**

The diagrammatic description of the energy of the electron in different orbits around the nucleus is called energy level diagram.

Energy level diagram of hydrogen/hydrogen like atom

Principle quantum number	Orbit	Excited state	Energy for H_2 – atom	Energy for H_2 – like atom	Ionisation energy from this level (for H_2 – atom)
$n = \infty$	Infinite	Infinite	$E_\infty = 0\ eV$	$0\ eV$	$0\ eV$
$n = 4$	Fourth	Third	$E_4 = -0.85\ eV$	$-0.85\ Z^2$	$+0.85\ eV$
$n = 3$	Third	Second	$E_3 = -1.51\ eV$	$-1.51\ Z^2$	$+1.51\ eV$
$n = 2$	Second	First	$E_2 = -3.4\ eV$	$-3.4\ Z^2$	$+3.4\ eV$
$n = 1$	First	Ground	$E_1 = -13.6\ eV$	$-13.6\ Z^2$	$+13.6\ eV$

Note : ❑ In hydrogen atom excitation energy to excite electron from ground state to first excited state will be $-3.4 - (-13.6) = 10.2\ eV$.

and from ground state to second excited state it is [$-1.51 - (-13.6) = 12.09\ eV$].

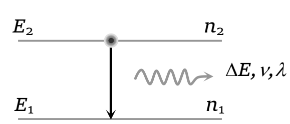
❑ In an H_2 atom when e^- makes a transition from an excited state to the ground state it's kinetic energy increases while potential and total energy decreases.

(6) **Transition of electron**

When an electron makes transition from higher energy level having energy $E_2(n_2)$ to a lower energy level having energy E_1 (n_1) then a photon of frequency ν is emitted

(i) **Energy of emitted radiation**

$$\Delta E = E_2 - E_1 = \frac{-Rc\,h\,Z^2}{n_2^2} - \left(-\frac{Rch\,Z^2}{n_1^2}\right) = 13.6 Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$



Emission

(ii) **Frequency of emitted radiation**

$$\Delta E = h\nu \Rightarrow \nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} = Rc\,Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

(iii) **Wave number/wavelength**

Wave number is the number of waves in unit length $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$

$$\Rightarrow \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{13.6Z^2}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

(iv) **Number of spectral lines** : If an electron jumps from higher energy orbit to lower energy orbit it emits raidations with various spectral lines.

If electron falls from orbit n_2 to n_1 then the number of spectral lines emitted is given by

$$N_E = \frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$$

If electron falls from n^{th} orbit to ground state (*i.e.* $n_2 = n$ and $n_1 = 1$) then number of spectral lines emitted $N_E = \frac{n(n-1)}{2}$

Note : ❑ Absorption spectrum is obtained only for the transition from lowest energy level to higher energy levels. Hence the number of absorption spectral lines will be (n – 1).

(v) **Recoiling of an atom** : Due to the transition of electron, photon is emitted and the atom is recoiled

Recoil momentum of atom = momentum of photon $= \frac{h}{\lambda} = hRZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Also recoil energy of atom $= \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$ (where m = mass of recoil atom)

(7) **Draw backs of Bohr's atomic model**

(i) It is valid only for one electron atoms, *e.g.* : H, He^+, Li^{+2}, Na^{+1} *etc.*

(ii) Orbits were taken as circular but according to Sommerfield these are elliptical.

(iii) Intensity of spectral lines could not be explained.

(iv) Nucleus was taken as stationary but it also rotates on its own axis.

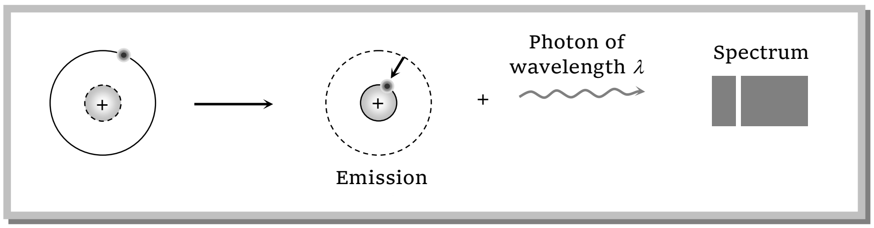
(v) It could not be explained the minute structure in spectrum line.

(vi) This does not explain the Zeeman effect (splitting up of spectral lines in magnetic field) and Stark effect (splitting up in electric field)

(vii) This does not explain the doublets in the spectrum of some of the atoms like sodium (5890$\mathring{A}$ & 5896$\mathring{A}$)

Hydrogen Spectrum and Spectral Series

When hydrogen atom is excited, it returns to its normal unexcited (or ground state) state by emitting the energy it had absorbed earlier. This energy is given out by the atom in the form of radiations of different wavelengths as the electron jumps down from a higher to a lower orbit. Transition from different orbits cause different wavelengths, these constitute spectral series which are characteristic of the atom emitting them. When observed through a spectroscope, these radiations are imaged as sharp and straight vertical lines of a single colour.



Spectral series

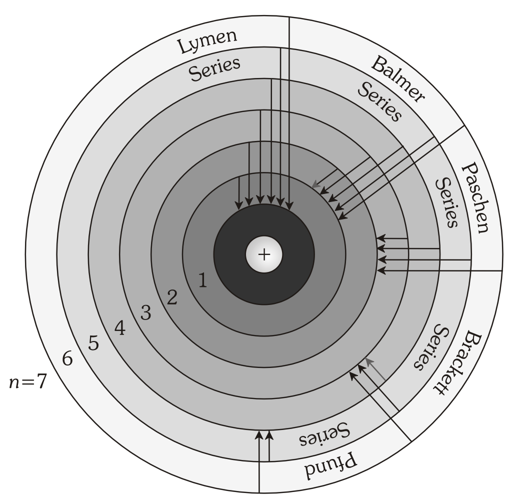
The spectral lines arising from the transition of electron forms a spectra series.

(i) Mainly there are five series and each series is named after it's discover as Lymen series, Balmer series, Paschen series, Bracket series and Pfund series.

(ii) According to the Bohr's theory the wavelength of the radiations emitted from hydrogen atom is given by

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where n_2 = outer orbit (electron jumps from this orbit), n_1 = inner orbit (electron falls in this orbit)



(iii) First line of the series is called first member, for this line wavelength is maximum (λ_{max})

(iv) Last line of the series ($n_2 = \infty$) is called series limit, for this line wavelength is minimum (λ_{min})

Spectral series	Transition	Wavelength (λ) $= \frac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R} = \frac{n_1^2}{\left(1 - \frac{n_1^2}{n_2^2}\right)R}$		$\frac{\lambda_{max}}{\lambda_{min}} = \frac{(n+1)^2}{(2n+1)}$	Region
		Maximum wavelength $(n_1 = n$ **and** $n_2 = n+1)$ $\lambda_{max} = \frac{n^2(n+1)^2}{(2n+1)R}$	**Minimum wavelength** $(n_2 = \infty, n_1 = n)$ $\lambda_{min} = \frac{n^2}{R}$		
1. Lymen series	n_2 = 2, 3, 4 ...∞ $n_1 = 1$	$\lambda_{max} = \frac{(1)^2 (1+1)^2}{(2 \times 1 + 1)R} = \frac{4}{3R}$	$n_1 = n = 1$ $\lambda_{min} = \frac{1}{R}$	$\frac{4}{3}$	Ultraviolet region
2.Balmer series	n_2 = 3, 4, 5 ...∞ $n_1 = 2$	$n_1 = n = 2$, $n_2 = 2 + 1 = 3$ $\lambda_{max} = \frac{36}{5R}$	$\lambda_{min} = \frac{4}{R}$	$\frac{9}{5}$	Visible region
3. Paschen series	n_2 = 4, 5, 6 ...∞ $n_1 = 3$	$n_1 = n = 3$, $n_2 = 3 + 1 = 4$ $\lambda_{max} = \frac{144}{7R}$	$n_1 = n = 3$ $\lambda_{min} = \frac{9}{R}$	$\frac{16}{7}$	Infrared region
4. Bracket series	n_2 = 5, 6, 7 ... ∞ $n_1 = 4$	$n_1 = n = 4$, $n_2 = 4 + 1 = 5$ $\lambda_{max} = \frac{400}{9R}$	$n_1 = n = 4$ $\lambda_{min} = \frac{16}{R}$	$\frac{25}{9}$	Infrared region
5. Pfund series	n_2 = 6, 7, 8 ... ∞ $n_1 = 5$	$n_1 = \lambda = 5$, $n_2 = 5 + 1 = 6$ $\lambda_{max} = \frac{900}{11R}$	$\lambda_{min} = \frac{25}{R}$	$\frac{36}{11}$	Infrared region

Quantum Numbers

An atom contains large number of shells and subshells. These are distinguished from one another on the basis of their size, shape and orientation (direction) in space. The parameters are expressed in terms of different numbers called quantum number.

Quantum numbers may be defined as a set of four number with the help of which we can get complete information about all the electrons in an atom. It tells us the address of the electron *i.e.* location, energy, the type of orbital occupied and orientation of that orbital.

(1) **Principal Quantum number (n) :** This quantum number determines the main energy level or shell in which the electron is present. The average distance of the electron from the nucleus and the energy of the electron depends on it. $E_n \propto \frac{1}{n^2}$ and $r_n \propto n^2$ (in *H*-atom)

The principal quantum number takes whole number values, n = 1, 2, 3, 4,..... ∞

(2) **Orbital quantum number (l) or azimuthal quantum number (l)**

This represents the number of subshells present in the main shell. These subsidiary orbits within a shell will be denoted as 1, 2, 3, 4 ... or *s*, *p*, *d*, *f* ... This tells the shape of the subshells.

The orbital angular momentum of the electron is given as $L = \sqrt{l(l+1)}\frac{h}{2\pi}$ (for a particular value of *n*).

For a given value of *n* the possible values of *l* are $l = 0, 1, 2, \ldots$ upto $(n - 1)$

(3) **Magnetic quantum number (m_l) :** An electron due to it's angular motion around the nucleus generates an electric field. This electric field is expected to produce a magnetic field. Under the influence of external magnetic field, the electrons of a subshell can orient themselves in certain preferred regions of space around the nucleus called orbitals.

The magnetic quantum number determines the number of preferred orientations of the electron present in a subshell.

The angular momentum quantum number *m* can assume all integral value between $-l$ to $+l$ including zero. Thus m_l can be – 1, 0, + 1 for $l = 1$. Total values of m_l associated with a particular value of *l* is given by $(2l + 1)$.

(4) **Spin (magnetic) quantum number (m_s) :** An electron in atom not only revolves around the nucleus but also spins about its own axis. Since an electron can spin either in clockwise direction or in anticlockwise direction. Therefore for any particular value of magnetic quantum number, spin quantum number can have two values, *i.e.* $m_s = \frac{1}{2}$ (Spin up) or

$m_s = -\frac{1}{2}$ (Spin down)

This quantum number helps to explain the magnetic properties of the substance.

Electronic Configurations of Atoms

The distribution of electrons in different orbitals of an atom is called the electronic configuration of the atom. The filling of electrons in orbitals is governed by the following rules.

(1) **Pauli's exclusion principle**

"It states that no two electrons in an atom can have all the four quantum number (n, l, m_l and m_s) the same."

It means each quantum state of an electron must have a different set of quantum numbers n, l, m_l and m_s. This principle sets an upper limit on the number of electrons that can occupy a shell.

N_{max} in one shell = $2n^2$; Thus N_{max} in *K*, *L*, *M*, *N* .... shells are 2, 8, 18, 32,

Note : ❑ The maximum number of electrons in a subshell with orbital quantum number *l* is $2(2l + 1)$.

(2) **Aufbau principle**

Electrons enter the orbitals of lowest energy first.

As a general rule, a new electron enters an empty orbital for which $(n + l)$ is minimum. In case the value $(n+l)$ is equal for two orbitals, the one with lower value of n is filled first.

Thus the electrons are filled in subshells in the following order (memorize)

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*, 7*p*, ...

(3) **Hund's Rule**

When electrons are added to a subshell where more than one orbital of the same energy is available, their spins remain parallel. They occupy different orbitals until each one of them has at least one electron. Pairing starts only when all orbitals are filled up.

Pairing takes place only after filling 3, 5 and 7 electrons in *p*, *d* and *f* orbitals, respectively.

Concepts

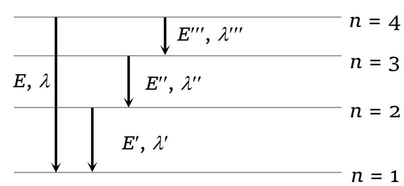
☞ *With the increase in principal quantum number the energy difference between the two successive energy level decreases, while wavelength of spectral line increases.*

$E' > E'' > E'''$

$\lambda' < \lambda'' < \lambda'''$

$E = E' + E'' + E'''$

$$\frac{1}{\lambda} = \frac{1}{\lambda'} + \frac{1}{\lambda''} + \frac{1}{\lambda'''}$$



☞ ***Rydberg constant is different for different elements***

R(=1.09 × 10^{7} *m*$^{-1}$*) is the value of Rydberg constant when the nucleus is considered to be infinitely massive as compared to the revolving electron. In other words, the nucleus is considered to be stationary.*

In case, the nucleus is not infinitely massive or stationary, then the value of Rydberg constant is given as

$$R' = \frac{R}{1 + \frac{m}{M}}$$ *where m is the mass of electron and M is the mass of nucleus.*

☞ ***Atomic spectrum is a line spectrum***

Each atom has it's own characteristic allowed orbits depending upon the electronic configuration. Therefore photons emitted during transition of electrons from one allowed orbit to inner allowed orbit are of some definite energy only. They do not have a continuous graduation of energy. Therefore the spectrum of the emitted light has only some definite lines and therefore atomic spectrum is line spectrum.

☞ *Just as dots of light of only three colours combine to form almost every conceivable colour on T.V. screen, only about 100 distinct kinds of atoms combine to form all the materials in the universe.*

Example

***Example*: 1** The ratio of areas within the electron orbits for the first excited state to the ground state for hydrogen atom is

(a) 16 : 1 (b) 18 : 1 (c) 4 : 1 (d) 2 : 1

Solution : (a) For a hydrogen atom

Radius $r \propto n^2 \Rightarrow \frac{r_1^2}{r_2^2} = \frac{n_1^4}{n_2^4} \Rightarrow \frac{\pi r_1^2}{\pi r_2^2} = \frac{n_1^4}{n_2^4} \Rightarrow \frac{A_1}{A_2} = \frac{n_1^4}{n_2^4} = \frac{2^4}{1^4} = 16 \Rightarrow \frac{A_1}{A_2} = \frac{16}{1}$

***Example*: 2** The electric potential between a proton and an electron is given by $V = V_0 \ln \frac{r}{r_0}$, where r_0 is a constant. Assuming Bohr's model to be applicable, write variation of r_n with n, n being the principal quantum number

[IIT-JEE (Screening) 2003]

(a) $r_n \propto n$ (b) $r_n \propto 1/n$ (c) $r_n \propto n^2$ (d) $r_n \propto 1/n^2$

Solution : (a) Potential energy $U = eV = eV_0 \ln \frac{r}{r_0}$

$\therefore$ Force $F = -\left|\frac{dU}{dr}\right| = \frac{eV_0}{r}$. The force will provide the necessary centripetal force. Hence

$\frac{mv^2}{r} = \frac{eV_0}{r} \Rightarrow v = \sqrt{\frac{eV_0}{m}}$ .....(i) and $mvr = \frac{nh}{2\pi}$ .....(ii)

Dividing equation (ii) by (i) we have $mr = \left(\frac{nh}{2\pi}\right)\sqrt{\frac{m}{eV_0}}$ or $r \propto n$

***Example*: 3** The innermost orbit of the hydrogen atom has a diameter 1.06 Å. The diameter of tenth orbit is

[UPSEAT 2002]

(a) 5.3 Å (b) 10.6 Å (c) 53 Å (d) 106 Å

Solution : (d) Using $r \propto n^2 \Rightarrow \frac{r_2}{r_1} = \left(\frac{n_2}{n_1}\right)^2$ or $\frac{d_2}{d_1} = \left(\frac{n_2}{n_1}\right)^2 \Rightarrow \frac{d_2}{1.06} = \left(\frac{10}{1}\right)^2 \Rightarrow d = 106$ Å

***Example*: 4** Energy of the electron in n^{th} orbit of hydrogen atom is given by $E_n = -\frac{13.6}{n^2} eV$. The amount of energy needed to transfer electron from first orbit to third orbit is

(a) 13.6 eV (b) 3.4 eV (c) 12.09 eV (d) 1.51 eV

Solution : (c) Using $E = -\frac{13.6}{n^2} eV$

For $n = 1$, $E_1 = \frac{-13.6}{1^2} = -13.6\, eV$ and for $n = 3$ $E_3 = -\frac{13.6}{3^2} = -1.51\, eV$

So required energy $= E_3 - E_1 = -1.51 - (-13.6) = 12.09\, eV$

***Example*: 5** If the binding energy of the electron in a hydrogen atom is 13.6 eV, the energy required to remove the electron from the first excited state of Li^{++} is

(a) 122.4 eV (b) 30.6 eV (c) 13.6 eV (d) 3.4 eV

Solution : (b) Using $E_n = -\frac{13.6 \times Z^2}{n^2} eV$

For first excited state $n = 2$ and for Li^{++}, $Z = 3$

$\therefore$ $E = -\frac{13.6}{2^2} \times 3^2 = -\frac{13.6 \times 9}{4} = -30.6\, eV$. Hence, remove the electron from the first excited state of Li^{++} be 30.6 eV

***Example*: 6** The ratio of the wavelengths for $2 \rightarrow 1$ transition in Li^{++}, He^+ and H is **[UPSEAT 2003]**

(a) 1 : 2 : 3 (b) 1 : 4 : 9 (c) 4 : 9 : 36 (d) 3 : 2 : 1

Solution : (c) Using $\frac{1}{\lambda}=RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \Rightarrow \lambda \propto \frac{1}{Z^2} \Rightarrow \lambda_{Li}:\lambda_{He^+}:\lambda_H=\frac{1}{9}:\frac{1}{4}:\frac{1}{1}=4:9:36$

***Example*: 7** Energy E of a hydrogen atom with principal quantum number n is given by $E=\frac{-13.6}{n^2}eV$. The energy of a photon ejected when the electron jumps n = 3 state to n = 2 state of hydrogen is approximately

[CBSE PMT/PDT Screening 2004]

(a) 1.9 eV (b) 1.5 eV (c) 0.85 eV (d) 3.4 eV

Solution : (a) $\Delta E=13.6\left(\frac{1}{2^2}-\frac{1}{3^2}\right)=13.6\times\frac{5}{36}=1.9\,eV$

***Example*: 8** In the Bohr model of the hydrogen atom, let R, v and E represent the radius of the orbit, the speed of electron and the total energy of the electron respectively. Which of the following quantity is proportional to the quantum number n

(a) R/E (b) E/v (c) RE (d) vR

Solution : (d) Rydberg constant $R=\frac{\varepsilon_0 n^2 h^2}{\pi mZe^2}$

Velocity $v=\frac{Ze^2}{2\varepsilon_0 nh}$ and energy $E=-\frac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2}$

Now, it is clear from above expressions $R.v \propto n$

***Example*: 9** The energy of hydrogen atom in nth orbit is E_n, then the energy in nth orbit of singly ionised helium atom will be

(a) $4E_n$ (b) $E_n/4$ (c) $2E_n$ (d) $E_n/2$

Solution : (a) By using $E=-\frac{13.6\,Z^2}{n^2} \Rightarrow \frac{E_H}{E_{He}}=\left(\frac{Z_H}{Z_{He}}\right)^2=\left(\frac{1}{2}\right)^2 \Rightarrow E_{He}=4E_n$.

***Example*: 10** The wavelength of radiation emitted is λ_0 when an electron jumps from the third to the second orbit of hydrogen atom. For the electron jump from the fourth to the second orbit of the hydrogen atom, the wavelength of radiation emitted will be

(a) $\frac{16}{25}\lambda_0$ (b) $\frac{20}{27}\lambda_0$ (c) $\frac{27}{20}\lambda_0$ (d) $\frac{25}{16}\lambda_0$

Solution : (b) Wavelength of radiation in hydrogen atom is given by

$$\frac{1}{\lambda}=R\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] \Rightarrow \frac{1}{\lambda_0}=R\left[\frac{1}{2^2}-\frac{1}{3^2}\right]=R\left[\frac{1}{4}-\frac{1}{9}\right]=\frac{5}{36}R \qquad .....(i)$$

and $$\frac{1}{\lambda'}=R\left[\frac{1}{2^2}-\frac{1}{4^2}\right]=R\left[\frac{1}{4}-\frac{1}{16}\right]=\frac{3R}{16} \qquad .....(ii)$$

From equation (i) and (ii) $\frac{\lambda'}{\lambda}=\frac{5R}{36}\times\frac{16}{3R}=\frac{20}{27} \Rightarrow \lambda'=\frac{20}{27}\lambda_0$

***Example*: 11** If scattering particles are 56 for 90^o angle then this will be at 60^o angle

(a) 224 (b) 256 (c) 98 (d) 108

Solution : (a) Using Scattering formula

$$N \propto \frac{1}{\sin^4(\theta/2)} \Rightarrow \frac{N_2}{N_1} = \left[\frac{\sin\left(\frac{\theta_1}{2}\right)}{\sin\left(\frac{\theta_2}{2}\right)}\right]^4 \Rightarrow \frac{N_2}{N_1} = \left[\frac{\sin\left(\frac{90°}{2}\right)}{\sin\left(\frac{60°}{2}\right)}\right]^4 = \left[\frac{\sin 45°}{\sin 30°}\right]^4 = 4 \Rightarrow N_2 = 4N_1 = 4 \times 56 = 224$$

***Example*: 12** When an electron in hydrogen atom is excited, from its 4th to 5th stationary orbit, the change in angular momentum of electron is (Planck's constant: $h = 6.6 \times 10^{-34}$ $J\text{–}s$)

(a) 4.16×10^{-34} $J\text{-}s$ (b) 3.32×10^{-34} $J\text{-}s$ (c) 1.05×10^{-34} $J\text{-}s$ (d) 2.08×10^{-34} $J\text{-}s$

Solution : (c) Change in angular momentum

$$\Delta L = L_2 - L_1 = \frac{n_2 h}{2\pi} - \frac{n_1 h}{2\pi} \Rightarrow \Delta L = \frac{h}{2\pi}(n_2 - n_1) = \frac{6.6 \times 10^{-34}}{2 \times 3.14}(5-4) = 1.05 \times 10^{-34} J\text{-}s$$

***Example*: 13** In hydrogen atom, if the difference in the energy of the electron in n = 2 and n = 3 orbits is E, the ionization energy of hydrogen atom is

(a) 13.2 E (b) 7.2 E (c) 5.6 E (d) 3.2 E

Solution : (b) Energy difference between n = 2 and n = 3; $E = K\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = K\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}K$ .....(i)

Ionization energy of hydrogen atom $n_1 = 1$ and $n_2 = \infty$; $E' = K\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = K$ .....(ii)

From equation (i) and (ii) $E' = \frac{36}{5}E = 7.2\,E$

***Example*: 14** In Bohr model of hydrogen atom, the ratio of periods of revolution of an electron in n = 2 and n = 1 orbits is

[EAMCET (Engg.) 2000]

(a) 2 : 1 (b) 4 : 1 (c) 8 : 1 (d) 16 : 1

Solution : (c) According to Bohr model time period of electron $T \propto n^3 \Rightarrow \frac{T_2}{T_1} = \frac{n_2^3}{n_1^3} = \frac{2^3}{1^3} = \frac{8}{1} \Rightarrow$ $T_2 = 8T_1$.

***Example*: 15** A double charged lithium atom is equivalent to hydrogen whose atomic number is 3. The wavelength of required radiation for emitting electron from first to third Bohr orbit in Li^{++} will be (Ionisation energy of hydrogen atom is 13.6 eV)

(a) 182.51 $Å$ (b) 177.17 $Å$ (c) 142.25 $Å$ (d) 113.74 $Å$

Solution : (d) Energy of a electron in nth orbit of a hydrogen like atom is given by

$E_n = -13.6\frac{Z^2}{n^2}eV$, and Z = 3 for Li

Required energy for said transition

$$\Delta E = E_3 - E_1 = 13.6Z^2\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = 13.6 \times 3^2\left[\frac{8}{9}\right] = 108.8\,eV = 108.8 \times 1.6 \times 10^{-19}\,J$$

Now using $\Delta E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} \Rightarrow \lambda = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{108.8 \times 1.6 \times 10^{-19}} = 0.11374 \times 10^{-7}\,m \Rightarrow \lambda = 113.74\,Å$

***Example*: 16** The absorption transition between two energy states of hydrogen atom are 3. The emission transitions between these states will be

(a) 3 (b) 4 (c) 5 (d) 6

Solution : (d) Number of absorption lines = $(n - 1) \Rightarrow 3 = (n - 1) \Rightarrow n = 4$

Hence number of emitted lines $= \frac{n(n-1)}{2} = \frac{4(4-1)}{2} = 6$

***Example*: 17** The energy levels of a certain atom for 1st, 2nd and 3rd levels are E, $4E/3$ and $2E$ respectively. A photon of wavelength λ is emitted for a transition $3 \to 1$. What will be the wavelength of emissions for transition $2 \to 1$

[CPMT 1996]

(a) $\lambda/3$ (b) $4\lambda/3$ (c) $3\lambda/4$ (d) 3λ

Solution : (d) For transition $3 \to 1$ $\Delta E = 2E - E = \frac{hc}{\lambda} \Rightarrow E = \frac{hc}{\lambda}$ .....(i)

For transition $2 \to 1$ $\frac{4E}{3} - E = \frac{hc}{\lambda'} \Rightarrow E = \frac{3hc}{\lambda'}$ .....(ii)

From equation (i) and (ii) $\lambda' = 3\lambda$

***Example*: 18** Hydrogen atom emits blue light when it changes from $n = 4$ energy level to $n = 2$ level. Which colour of light would the atom emit when it changes from $n = 5$ level to $n = 2$ level

(a) Red (b) Yellow (c) Green (d) Violet

Solution : (d) In the transition from orbits $5 \to 2$ more energy will be liberated as compared to transition from $4 \to 2$. So emitted photon would be of violet light.

***Example*: 19** A single electron orbits a stationary nucleus of charge $+Ze$, where Z is a constant. It requires 47.2 eV to excited electron from second Bohr orbit to third Bohr orbit. Find the value of Z **[IIT-JEE 1981]**

(a) 2 (b) 5 (c) 3 (d) 4

Solution : (b) Excitation energy of hydrogen like atom for $n_2 \to n_1$

$$\Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV \Rightarrow 47.2 = 13.6 Z^2 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 13.6 \times \frac{5}{36} Z^2 \Rightarrow Z^2 = \frac{47.2 \times 36}{13.6 \times 5} = 24.98 \simeq 25$$

$\Rightarrow Z = 5$

***Example*: 20** The first member of the Paschen series in hydrogen spectrum is of wavelength 18,800 Å. The short wavelength limit of Paschen series is **[EAMCET (Med.) 2000]**

(a) 1215 Å (b) 6560 Å (c) 8225 Å (d) 12850 Å

Solution : (c) First member of Paschen series mean it's $\lambda_{max} = \frac{144}{7R}$

Short wavelength of Paschen series means $\lambda_{min} = \frac{9}{R}$

Hence $\frac{\lambda_{max}}{\lambda_{min}} = \frac{16}{7} \Rightarrow \lambda_{min} = \frac{7}{16} \times \lambda_{max} = \frac{7}{16} \times 18,800 = 8225\ Å$.

***Example*: 21** Ratio of the wavelengths of first line of Lyman series and first line of Balmer series is

[EAMCET (Engg.) 1995; MP PMT 1997]

(a) 1 : 3 (b) 27 : 5 (c) 5 : 27 (d) 4 : 9

Solution : (c) For Lyman series $\frac{1}{\lambda_{L_1}} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3R}{4}$ .....(i)

For Balmer series $\frac{1}{\lambda_{B_1}} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5R}{36}$ .....(ii)

From equation (i) and (ii) $\frac{\lambda_{L_1}}{\lambda_{B_1}} = \frac{5}{27}$.

***Example*: 22** The third line of Balmer series of an ion equivalent to hydrogen atom has wavelength of 108.5 *nm*. The ground state energy of an electron of this ion will be

(a) 3.4 *eV* (b) 13.6 *eV* (c) 54.4 *eV* (d) 122.4 *eV*

Solution : (c) Using $\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \frac{1}{108.5 \times 10^{-9}} = 1.1 \times 10^7 \times Z^2\left(\frac{1}{2^2} - \frac{1}{5^2}\right)$

$\Rightarrow \frac{1}{108.5 \times 10^{-9}} = 1.1 \times 10^7 \times Z^2 \times \frac{21}{100} \Rightarrow Z^2 = \frac{100}{108.5 \times 10^{-9} \times 1.1 \times 10^{-7} \times 21} = 4 \Rightarrow Z = 2$

Now Energy in ground state $E = -13.6Z^2\ eV = -13.6 \times 2^2\ eV = -54.4\ eV$

***Example*: 23** Hydrogen (H), deuterium (D), singly ionized helium (He^+) and doubly ionized lithium (Li^{++}) all have one electron around the nucleus. Consider $n=2$ to $n=1$ transition. The wavelengths of emitted radiations are $\lambda_1, \lambda_2, \lambda_3$ and λ_4 respectively. Then approximately

(a) $\lambda_1 = \lambda_2 = 4\lambda_3 = 9\lambda_4$ (b) $4\lambda_1 = 2\lambda_2 = 2\lambda_3 = \lambda_4$ (c) $\lambda_1 = 2\lambda_2 = 2\sqrt{2}\lambda_3 = 3\sqrt{2}\lambda_4$ (d) $\lambda_1 = \lambda_2 = 2\lambda_3 = 3\lambda_4$

Solution : (a) Using $\Delta E \propto Z^2$ ($\because$ n_1 and n_2 are same)

$\Rightarrow \frac{hc}{\lambda} \propto Z^2 \Rightarrow \lambda Z^2 = \text{constant} \Rightarrow \lambda_1 Z_1^2 = \lambda_2 Z_2^2 = \lambda_3 Z_3^2 = \lambda_4 Z^4 \Rightarrow \lambda_1 \times 1 = \lambda_2 \times 1^2 = \lambda_3 \times 2^2 = \lambda_4 \times 3^3$

$\Rightarrow \lambda_1 = \lambda_2 = 4\lambda_3 = 9\lambda_4$.

***Example*: 24** Hydrogen atom in its ground state is excited by radiation of wavelength 975 *Å*. How many lines will be there in the emission spectrum

(a) 2 (b) 4 (c) 6 (d) 8

Solution : (c) Using $\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{975 \times 10^{-10}} = 1.097 \times 10^7\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \Rightarrow n = 4$

Now number of spectral lines $N = \frac{n(n-1)}{2} = \frac{4(4-1)}{2} = 6$.

***Example*: 25** A photon of energy 12.4 *eV* is completely absorbed by a hydrogen atom initially in the ground state so that it is excited. The quantum number of the excited state is

(a) $n = 1$ (b) $n = 3$ (c) $n = 4$ (d) $n = \infty$

Solution : (c) Let electron absorbing the photon energy reaches to the excited state *n*. Then using energy conservation

$\Rightarrow -\frac{13.6}{n^2} = -13.6 + 12.4 \Rightarrow -\frac{13.6}{n^2} = -1.2 \Rightarrow n^2 = \frac{13.6}{1.2} = 12 \Rightarrow n = 3.46 \simeq 4$

***Example*: 26** The wave number of the energy emitted when electron comes from fourth orbit to second orbit in hydrogen is 20,397 cm^{-1}. The wave number of the energy for the same transition in He^+ is **[Haryana PMT 2000]**

(a) 5,099 cm^{-1} (b) 20,497 cm^{-1} (c) 40,994 cm^{-1} (d) 81,998 cm^{-1}

Solution : (d) Using $\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \bar{\nu} \propto Z^2 \Rightarrow \frac{\bar{\nu}_2}{\bar{\nu}_1} = \left(\frac{Z_2}{Z_1}\right)^2 = \left(\frac{Z}{1}\right)^2 = 4 \Rightarrow \bar{\nu}_2 = \bar{\nu} \times 4 = 81588\ cm^{-1}$.

***Example*: 27** In an atom, the two electrons move round the nucleus in circular orbits of radii R and $4R$. the ratio of the time taken by them to complete one revolution is

(a) 1/4 (b) 4/1 (c) 8/1 (d) 1/8

Solution : (d) Time period $T \propto \frac{n^3}{Z^2}$

For a given atom (Z = constant) So $T \propto n^3$ .....(i) and radius $R \propto n^2$ .....(ii)

$\therefore$ From equation (i) and (ii) $T \propto R^{3/2} \Rightarrow \frac{T_1}{T_2} = \left(\frac{R_1}{R_2}\right)^{3/2} = \left(\frac{R}{4R}\right)^{3/2} = \frac{1}{8}$.

***Example*: 28** Ionisation energy for hydrogen atom in the ground state is E. What is the ionisation energy of Li^{++} atom in the 2nd excited state

(a) E (b) $3E$ (c) $6E$ (d) $9E$

Solution : (a) Ionisation energy of atom in nth state $E_n = \frac{Z^2}{n^2}$

For hydrogen atom in ground state (n = 1) and Z = 1 $\Rightarrow E = E_0$ .....(i)

For Li^{++} atom in 2nd excited state n = 3 and Z = 3, hence $E' = \frac{E_0}{3^2} \times 3^2 = E_0$ .....(ii)

From equation (i) and (ii) $E' = E$.

***Example*: 29** An electron jumps from n = 4 to n = 1 state in H-atom. The recoil momentum of H-atom (in eV/C) is

(a) 12.75 (b) 6.75 (c) 14.45 (d) 0.85

Solution : (a) The H-atom before the transition was at rest. Therefore from conservation of momentum

Photon momentum = Recoil momentum of H-atom or

$P_{recoil} = \frac{h\nu}{c} = \frac{E_4 - E_1}{c} = \frac{-0.85\,eV - (-13.6\,eV)}{c} = 12.75\ \frac{eV}{c}$

***Example*: 30** If elements with principal quantum number $n > 4$ were not allowed in nature, the number of possible elements would be

[IIT-JEE 1983; CBSE PMT 1991, 93; MP PET 1999; RPET 1993, 2001; RPMT 1999, 2003; J & K CET 2004]

(a) 60 (b) 32 (c) 4 (d) 64

Solution : (a) Maximum value of n = 4

So possible (maximum) no. of elements

$N = 2\times1^2 + 2\times2^2 + 2\times3^2 + 2\times4^2 = 2 + 8 + 18 + 32 = 60$.

Tricky example: 1

If the atom ${}_{100}Fm^{257}$ follows the Bohr model and the radius of ${}_{100}Fm^{257}$ is n times the Bohr radius, then find n

[IIT-JEE (Screening) 2003]

(a) 100 (b) 200 (c) 4 (d) 1/4

Solution : (d) $(r_m) = \left(\frac{m^2}{Z}\right)(0.53\,Å) = (n \times 0.53\,Å) \Rightarrow \frac{m^2}{Z} = n$

$m = 5$ for ${}_{100}Fm^{257}$ (the outermost shell) and $z = 100$

$\therefore \quad n = \frac{(5)^2}{100} = \frac{1}{4}$

An energy of 24.6 eV is required to remove one of the electrons from a neutral helium atom. The energy (in eV) required to remove both the electrons from a neutral helium atom is

(a) 79.0 (b) 51.8 (c) 49.2 (d) 38.2

Solution : (a) After the removal of first electron remaining atom will be hydrogen like atom.

So energy required to remove second electron from the atom $E = 13.6 \times \frac{2^2}{1} = 54.4\,eV$

$\therefore$ Total energy required = 24.6 + 54.4 = 79 eV