



Atomic Structure

Rutherford's nuclear model

Rutherford carried out experiment on the bombardment of thin (10^{-4} mm) Au foil with high speed positively charged α -particles.

He concluded that, an atom consists of

- (i) **Nucleus** which is small in size but carries the entire mass i.e. contains all the neutrons and protons.

Properties of the nucleus

- (i) The small, heavy and positively charged portion of the atom is known as **nucleus**. It is located at the centre of the atom and discovered in 1911 by Ernest Rutherford.
- (ii) Protons are positively charged particles.
- (iii) Neutrons and protons are present in the nucleus hence they are collectively known as **nucleons**.

Drawbacks of Rutherford's model

- (i) According to it “An electron moving around the nucleus continuously loses its energy and should set up spiral motion



ultimately falling into the nucleus”. Hence this **model does not able to explain** how the moving electrons could remain in its orbit.

(ii) It does not able to explain the discontinuous spectrum and the line spectra of $H -$ atom.

Planck's quantum theory

According to this theory, the energy of each quanta is directly proportional to the frequency (ν) of the radiation, i.e.

Lets,

$$E \propto \nu \quad \text{OR} \quad E = h\nu; \nu = \frac{c}{\lambda} \quad \text{Thus, } E = \frac{hc}{\lambda}$$

Where, h is proportionality constant also known as Planck's constant.

$$h = 6.626 \times 10^{-34} \text{ Joules sec.} \quad \text{or} \quad 6.626 \times 10^{-27} \text{ erg sec.}$$

Photoelectric effect

Einstein's photoelectric effect equation

According to Einstein,

Maximum kinetic energy of the ejected electron = absorbed energy – threshold energy

$$\frac{1}{2} m v_{\max}^2 = h\nu - h\nu_0 = hc \left[\frac{1}{\lambda} - \frac{1}{\lambda_0} \right]$$

Where, ν_0 and λ_0 are threshold frequency and threshold wavelength.



Bohr's atomic model

The Bohr postulates are,

- (1) An atom consists of positively charged nucleus
- (2) The electrons revolve around the nucleus in circular orbits
- (3) The circular orbits are those for which the angular momentum of an electron is an integral multiple of $\frac{h}{2\pi}$ where h is the Planck's constant.

$$L = mvr = \frac{nh}{2\pi}; n = 1, 2, 3, \dots, \infty$$

Where L is the orbital angular momentum and n is the number of orbit.

- (4) When electrons move in permitted discrete orbits they do not radiate or lose energy.

Advantages of Bohr's theory

- (i) Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen atom, He^+ , Li^{2+} etc.
- (ii) **Calculation of radius of Bohr's orbit:** According to Bohr, radius of n^{th} orbit in which electron moves is

$$r_n = \left[\frac{h^2}{4\pi^2 m e^2 k} \right] \cdot \frac{n^2}{Z}$$

Where, n = Orbit number, m = Mass number $[9.1 \times 10^{-31} \text{ kg}]$, e = Charge on the electron $[1.6 \times 10^{-19}]$ Z = Atomic number of element, k = Coulombic constant $[9 \times 10^9 \text{ Nm}^2 \text{c}^{-2}]$



After putting the values of m, e, k, h , we get.

$$r_n = \frac{n^2}{Z} \times 0.529 \text{ \AA}$$

(iii) Calculation of velocity of electron

$$V_n = \frac{2\pi e^2 ZK}{nh}, V_n = \left[\frac{Ze^2}{mr} \right]^{1/2}; V_n = \frac{2.188 \times 10^8 Z}{n} \text{ cm. sec}^{-1}$$

(iv) Calculation of energy of electron in Bohr's orbit

Total energy of electron = K.E. + P.E. of electron

$$= \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$$

Substituting of r , gives us $E = \frac{-2\pi^2 mZ^2 e^4 k^2}{n^2 h^2}$ Where, $n=1, 2, 3, \dots, \infty$

Putting the value of m, e, k, h, π we get

$$E = 21.8 \times 10^{-12} \times \frac{Z^2}{n^2} \text{ erg per atom}$$

$$= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J per atom} (1 \text{ J} = 10^7 \text{ erg})$$

$$E = -13.6 \times \frac{Z^2}{n^2} \text{ eV per atom} (1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$$

$$= -13.6 \times \frac{Z^2}{n^2} \text{ k.cal/mole} (1 \text{ cal} = 4.18 \text{ J})$$

or $\frac{-1312}{n^2} Z^2 \text{ kJmol}^{-1}$

When an electron jumps from an outer orbit (higher energy) n_2 to an inner orbit (lower energy) n_1 , then the energy emitted in form of radiation is given by

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

$$\Rightarrow \Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV / atom}$$

As we know that $E = h\bar{\nu}$, $c = \nu\lambda$ and $\bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E}{hc}$,



$$= \frac{2\pi^2 k^2 m e^4 Z^2}{ch^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

This can be represented as $\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

Where, $R = \frac{2\pi^2 k^2 m e^4}{ch^3}$; R is known as Rydberg constant.

Spectral series

S.No.	Spectral series	Lies in the region	Transition $n_2 > n_1$
(1)	Lyman series	Ultraviolet region	$n_1 = 1,$ $n_2 = 2, 3, 4, \dots, \infty$
(2)	Balmer series	Visible region	$n_1 = 2,$ $n_2 = 3, 4, 5, \dots, \infty$
(3)	Paschen series	Infra red region	$n_1 = 3,$ $n_2 = 4, 5, 6, \dots, \infty$



(4)	Brackett series	Infra red region	$n_1 = 4,$ $n_2 = 5, 6, 7, \dots, \infty$
(5)	Pfund series	Infra red region	$n_1 = 5,$ $n_2 = 6, 7, 8, \dots, \infty$

Dual nature of electron

According to the French physicist, Louis de Broglie, if light has an electron then it behaves as both a material particle and a wave.

The wavelength associated with a particle of mass m , moving with velocity v is given by the relation

$$\lambda = \frac{h}{mv}, \text{ where } h = \text{Planck's constant.}$$

According to Planck's equation, $E = h\nu = \frac{hc}{\lambda}$ ($\because \nu = \frac{c}{\lambda}$)

on the basis of Einstein's mass energy relationship, $E = mc^2$

on equating both $\frac{hc}{\lambda} = mc^2$ or $\lambda = \frac{h}{mc}$ which is same as de-Broglie relation. ($\because mc = p$)

Heisenberg's uncertainty principle



This principle states “It is impossible to specify at any given moment both the position and momentum (velocity) of an electron”.

Mathematically it is represented as, $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

Where Δx = uncertainty in position of the particle, Δp = uncertainty in the momentum of the particle

Now since $\Delta p = m \Delta v$

So equation becomes, $\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$ or $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

In terms of uncertainty in energy, ΔE and uncertainty in time Δt , this principle is written as, $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

Schrödinger wave equation

(1) Schrodinger wave equation based on the dual nature of electron, is given by **Erwin Schrödinger** in 1926.

(2) With the help of this wave equation, we can find the probability of an electron at any point around the nucleus.

The probability of an electron at any point around the nucleus is-

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

Here, x, y and z are the 3 space co-ordinates, m is the mass of electron, h is Planck's constant, E is Total energy, V is potential energy of electron, Ψ is amplitude of wave also called as wave function and ∂ is an infinitesimal change.



Quantum numbers

Orbital in an atom is specified by a set of three quantum numbers (n, l, m) and a set of four quantum numbers (n, l, m and s) is specified for each electron.

(1) Principle quantum number (n)

The **principal quantum number** proposed by *Bohr* and denoted by ' n '. It describes the energy of an electron in an orbit and the most probable distance between the electron and the nucleus. In other words, it denotes the size of orbital.

(2) Azimuthal quantum number (l)

Azimuthal quantum number proposed by *Sommerfeld* and denoted by ' l '. It is also known as angular momentum **quantum number** or secondary **quantum number**. It describes the shape and number of the orbital(sub shells) to which the electron belongs. The value of l is always equals to $(n-1)$. Where ' n ' is the number of principle shell.

Thus, the lowest possible value of l is 0, and its highest possible value, is $n - 1$. Following values of l are given below.

Value of l	=	0	1	2	3.....(n-1)
Name of subshell	=	s	p	d	f
Shape of subshell	=	Spher ical	Dumb bell	Doub le dumb bell	Com plex

It also represents the orbital angular momentum. That is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$

(3) Magnetic quantum number (m)

Magnetic quantum number denoted by ' m '. It describes the number of permitted orientation of the orbital(sub shell). The value of m varies from $-l$ to $+l$ through zero. For a given value of ' n ' the total value of ' $m = n^2$ ', for a given value of ' l ' the total value of ' $m = 2l+1$ ' and the number of degenerate orbitals of s subshell = 0.

(4) Spin quantum numbers (s)

Spin quantum number denoted by ' m '. It signifies the spin or rotation or direction of electron on it's axis during movement.



The value of it is either $+1/2$ or $-1/2$. If the spin of electron is clockwise then value of S will be $+1/2$ and if its direction is anticlockwise then value of S will be $-1/2$.

It represents the value of spin angular momentum. That is equal to $\frac{h}{2\pi}\sqrt{s(s+1)}$.

Rules for filling of electrons in various orbitals

The atom is built up by filling electrons in various orbitals according to the following rules,

(1) Aufbau's principle

This principle states that the electrons are added one by one to the various orbitals in order of their increasing energy starting with the orbital of lowest energy. The increasing order of energy of various orbitals is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p \dots\dots$$

(2) $(n+l)$ Rule

In neutral isolated atom, the lower the value of $(n + l)$ for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of $(n + l)$, the orbitals with lower value of n has lower energy.

(3) Pauli's exclusion principle



According to this principle “no two electrons in an atom will have same value of all the four quantum numbers”.

(4) Hund’s Rule of maximum multiplicity

“Electron pairing in p , d and f orbitals cannot occur until each orbitals of a given subshell contains one electron each or is singly occupied”.