QUANTUM CHEMISTRY

Planck's Quantum Theory

The main postulates of this theory are as under-

(1) The emission or absorption of radiant energy by a body does not occur continuously but occurs discontinuously in the form of small discrete packets of energy called quanta.

(2) The quanta of visible light are called photons.

(3) The energy of each quantum is directly proportional to the frequency of radiation. Thus,

$$E \alpha \nu$$

or $$E = h\nu$$

Where, h = Planck's constant

$= 6.626 \times 10^{-34}$ J -sec.

$$\because \quad \nu = \frac{c}{\lambda}$$

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

(4) The total energy emitted or absorbed by a body is integral multiple of the energy of one quantum of radiation. Thus,

$$E = nh\nu$$

$$= \frac{nhc}{\lambda}$$

Where, n = 1, 2, 3,---------(any integral number)

Dual Nature of Electron

According to De-Broglie, just like light, electrons have dual nature i.e. they have particle like as well as wave like nature. Their some of the properties like photo-electric effect and thermo-ionic emission can be explained by considering them to be particles, while some other properties like reflection, refraction, interference, diffraction etc. can only be explained if they are considered to be wave.

Thus, electrons have dual nature i.e. particle like as well as wave like nature.

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De-Broglie Equation

In order to calculate wavelength of matter waves, De-Broglie derived an equation by combining Planck's Quantum theory and Einstein's mass-energy relation which is called De-Broglie equation.

From Planck's Quantum theory-

$$E = h\nu$$

Here, $\nu = \frac{c}{\lambda}$

$$\therefore \quad E = \frac{hc}{\lambda} \qquad \text{---------} \quad (1)$$

Where, h = Planck's constant

ν = frequency of radiation

λ = Wavelength of radiation

From Einstein's mass-energy relation-

$$E = mc^2 \qquad \text{----------} \quad (2)$$

Where, c = velocity of light

Combing equation (1) and (2) we get-

$$\frac{hc}{\lambda} = mc^2$$

$$\text{or} \quad \frac{h}{\lambda} = mc$$

$$\text{or} \quad \lambda = \frac{h}{mc} \qquad \text{-----------} \quad (3)$$

For matter waves, velocity of light c of this equation should be replaced by velocity of particle v. Thus, we get-

$$\lambda = \frac{h}{mv} \qquad \text{------------} \quad (4)$$

$$\text{or} \quad \lambda = \frac{h}{p} \qquad \text{------------} \quad (5)$$

(mv = p , momentum of particle)

Here, equation (4) and (5) are called **De-Broglie equations**.

From these equations, it is clear that, the wavelength of the matter wave associated with a particle in motion is inversely proportional to the momentum of the particle.

- Since, Kinetic energy,

$$E_K = \frac{1}{2} mv^2$$

$$\therefore \quad mv^2 = 2E_K$$

$$\text{or} \quad m^2v^2 = 2mE_K$$

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or $mv = \sqrt{2mE_K} = p$

Thus,

$$\lambda = \frac{h}{\sqrt{2mE_K}}$$

- If a charged particle is accelerated with a potential difference of V then, kinetic energy of particle,

$\frac{1}{2}mv^2 = qV$ Where, q = charge of particle

or $m^2v^2 = 2qmV$

or $mv = \sqrt{2mE_K} = p$

Thus,

$$\lambda = \frac{h}{\sqrt{2mE_K}}$$

- For an electron,

$$\lambda = \frac{12.27}{\sqrt{V}} A^0$$

Hiesenberg's Uncertainty Principle

According to this principle,

"The simultaneous and exact determination of both position and momentum of an electron revolving around nucleus is impossible."

Mathematically, according to this principle, "The product of uncertainty in position (Δx) and that in momentum (Δp) of an electron revolving around nucleus is either equal to or greater than h/4π. "

Thus,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

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This is Mathematical form of Hiesenberg's uncertainty principle. From this expression, it is clear that, if uncertainty in position (Δx) is decreased i.e. position of electron is determined accurately, then uncertainty in momentum (Δp) gets increased and vice versa.

Photo-Electric Effect

When light falls over the surface of certain metals, they start ejecting electrons. These electrons are called photo electrons and this phenomenon is called photo-electric effect. Ceasium shows this phenomenon in visible light, while most of the metals show it in ultra-violet light.

It has been observed that, for the phenomenon of photo-electric effect to take place, the frequency of incident light should be greater than a definite value. This frequency is called Threshold frequency (ν_0). The energy of photon corresponding to this frequency is called Threshold energy or work function (W_0). This energy is required to take valence electron to the last shell of the atom.

If a photon of frequency ν falls over an electron of a metal, a part of its energy is used up to take this electron to the last shell of the atom against nuclear attraction while rest is retained to the ejected electron as kinetic energy. Thus,

$$h\nu = W_0 + K.E$$

$$= h\nu_0 + \frac{1}{2}mv^2$$

Thus, kinetic energy of ejected electron,

$$\frac{1}{2}mv^2 = h(\nu - \nu_0)$$

$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

Where, h = Planck's constant

λ_0 = Threshold wavelength of radiation

If kinetic energy of ejected electron, is plotted against frequency, υ of incident light, then a straight line is obtained. It indicates that, the kinetic energy of ejected electron is directly proportional to the frequency of incident light.

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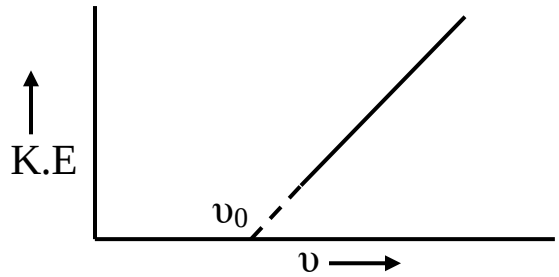


Fig.- Plot of kinetic energy of ejected electron against frequency of incident light

If kinetic energy of ejected electron, is plotted against intensity of incident light, then a straight line parallel to intensity axis is obtained. It indicates that, the kinetic energy of ejected electron is independent of intensity of incident light.

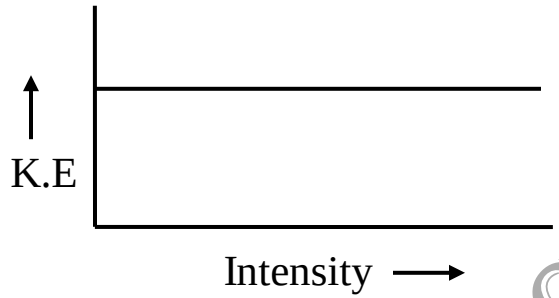


Fig.- Plot of kinetic energy of ejected electron against intensity of incident light

However, the number of electrons ejected is found to be directly proportional to the intensity of incident light.

Quantum Numbers

"The numbers which represent the position and energy of electrons in an atom are called Quantum numbers."

According to modern concept, following four quantum numbers are required to represent the position and energy of an electron in an atom completely-

(1) Principal quantum number (n)
(2) Azimuthal quantum number (l)
(3) Magnetic quantum number (m)
(4) Spin quantum number (s)

(1) Principal quantum number (n)

This quantum number represents Principal energy level or shell of electron. It is denoted by "n" and it can have any integral value except zero. Thus,

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Permitted values of n = 1, 2, 3, 4,-----(any integral value except zero)

Depending upon the value of n being 1, 2, 3, 4,------ etc. the shells are designated as K, L, M, N,-----shells respectively.

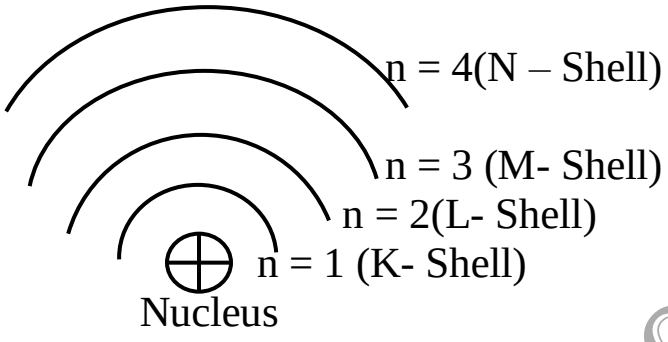


Fig- Different shells of an atom

Principal quantum number, n also represents the energy of electrons in an atom. For example, for hydrogen atom and hydrogen like ions containing only one electron, the energy of electron in n^{th} orbit is given by following formula-

$$E_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2}$$

Where, m = mass of electron
e = charge of electron
Z = atomic number
n = Principal quantum number
h = Planck's constant (6.62×10^{-34}Js)

It is clear that, the energy of electron increases with increase of the value of principal quantum number, n.

Principal quantum number, n also represents the average distance of electron from nucleus.

For example, for hydrogen atom and hydrogen like ions containing only one electron the radius of n^{th} orbit is given by following formula-

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

Thus, the average distance of electron from nucleus increases with increase of the value of principal quantum number, n.

(2)Azimuthal quantum number (l)-

This quantum number represents sub- energy level or sub-shell of electron. It is denoted by "l" and its value depends upon the value of principal quantum number, n. It can have any integral value from 0 to (n-1). Thus,

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Permitted values of l = 0 to (n-1) (any integer except zero)

Here, if n = 1 (K-shell), then l = 0

if n = 2 (L-shell), then l = 0, 1

if n = 3 (M-shell), then l = 0, 1, 2

if n = 4 (N-shell), then l = 0, 1, 2, 3

It is clear that, the total values of l is equal to the value of n.

Depending upon the value of l being 0, 1, 2, 3,------ etc., the sub-shells are designated as s, p, d, f,----- sub-shells respectively.

Value of 'l'	0	1	2	3
Designation of sub-shell	s	p	d	f

Each value of azimuthal quantum number, l represents a definite sub-shell. Hence, total number of sub-shells in a definite shell, corresponds to the total values of l for respective shell. For example,

For K-shell (n = 1), there is only one value of l i.e. 0. Hence K-shell contains only one sub-shell called s-sub-shell.

For L-shell (n = 2), there are two values of l i.e. 0 and 1. Hence, L-shell contains two sub-shells called s and p-sub-shells respectively.

Similarly, M-shell contains three sub-shells (s, p and d) and N - shell contains four sub-shells (s, p, d and f sub-shells).

Azimuthal quantum number, l also represents angular momentum (mvr) of an electron as per the following relation-

$$mvr = \frac{h}{2\pi}\sqrt{l(l+1)}$$

Hence, this quantum number is also called angular momentum quantum number.

(3)Magnetic quantum number (m)-

This quantum number represents the orbital of the electron. It is denoted by "m" and its value depends upon the value of azimuthal quantum number, l. It can have any integral value from -l through zero to +1. Thus,

Permitted values of m = -l ------- 0 -------- +l

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Here, if 1 = 0 (s sub-shell) then, m = 0
if l = 1 (p sub-shell) then, m = -1, 0, +1
if l = 2 (d sub-shell) then, m = -2, -1, 0, +1, +2
if l = 3 (f sub-shell) then, m = -3, -2,-1, 0, +1, +2, +3

It is clear that, the total values of m is equal to (2l + 1).

Each value of magnetic quantum number, m represents a definite orbital. Hence, total number of orbitals in a definite sub-shell, corresponds to the total values of m for respective sub-shell. For example,

For s- sub-shell (l = 0), there is only one value of m i.e. 0. Hence, s-sub-shell contains only one orbital called s- orbital.

For p- sub-shell (l = 1), there are three values of m i.e. -1, 0, +1. Hence, p-sub-shell contains three p-orbitals, namely p_x , p_y and p_z orbitals respectively.

For d- sub-shell (l = 2), there are five values of m i.e. -2, -1, 0, +1, +2. Hence, d-sub-shell will contains five d- orbitals, namely d_{xy} , d_{yz} , d_z^2 , d_{xz} and $d_{x^2-y^2}$ orbitals respectively.

Similarly, f-sub-shell having seven values of m, contains seven f-orbitals.

Magnetic quantum number, m also represents the orientation of orbitals in magnetic field. Hence, it is also called **orientation quantum number**.

(4) Spin Quantum number (s)-

This quantum number represents the direction of spin electron in an orbital. It is denoted by "s". Since, electrons can either have clockwise or anti-clockwise spin, the spin quantum number, s can have only two values i.e. +1/2 (for clockwise spin) and -1/2 (for anti-clockwise spin).

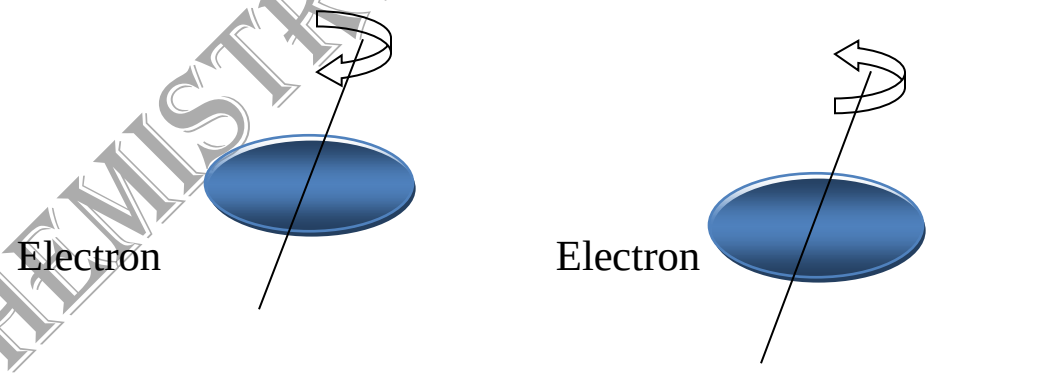


Fig- Different spin of electrons

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Electronic Configuration

The distribution of electrons in different shells, sub-shells and orbitals of an atom is called electronic configuration of the atom.

The electronic configuration of the atom is written using following rules-

(1) Pauli's Exclusion Principle

This principle governs all the four quantum numbers given to the electrons in an atom. According to this principle,

"No two electrons in an atom can have exactly same values of all the four quantum numbers."

or

" No two electrons in an atom can exist in same quantum state."

We know that, an orbital is characterized by three quantum numbers i.e. all the electrons residing in a definite orbital have exactly same values of three quantum numbers i.e. principal (n), azimuthal (l) and magnetic (m) quantum numbers. Hence, if Pauli's Exclusion Principle is correct then fourth quantum number i.e. spin quantum number (s) must be different for all the electrons residing in a definite orbital. Furthermore, spin quantum number (s) can have only two values i.e. +1/2 (for clockwise spin) and -1/2 (for anticlockwise spin). Hence, from Pauli's Exclusion Principle, it can be concluded that,

"Only a maximum of two electrons of opposite spin can reside in an orbital."

Thus, s-sub-shell containing only one s-orbital can accommodate only a maximum of 2 electrons. p-sub-shell containing three p-orbitals can accommodate a maximum of 6 electrons. d-sub-shell containing five d-orbitals can accommodate a maximum of 10 electrons and f-sub-shell containing seven f-orbitals can accommodate a maximum of 14 electrons.

Similarly, the maximum number of electrons present in different shells can also be determined using Pauli's Exclusion Principle.

(2) Aufbau's Principle

This principle governs the filling of electrons in orbitals of different energy belonging to different sub-shells.

According to this principle,

"In orbitals of different energy belonging to different sub-shells, electrons enter in increasing order of their energy ."

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Thus, electrons enter first in orbitals of lower energy and it is followed by orbitals of higher energy.

On experimental basis, the order of energy of different orbitals is found to be as under-

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < --------

This order of filling of electrons in orbitals of different energy can be graphically represented as under-

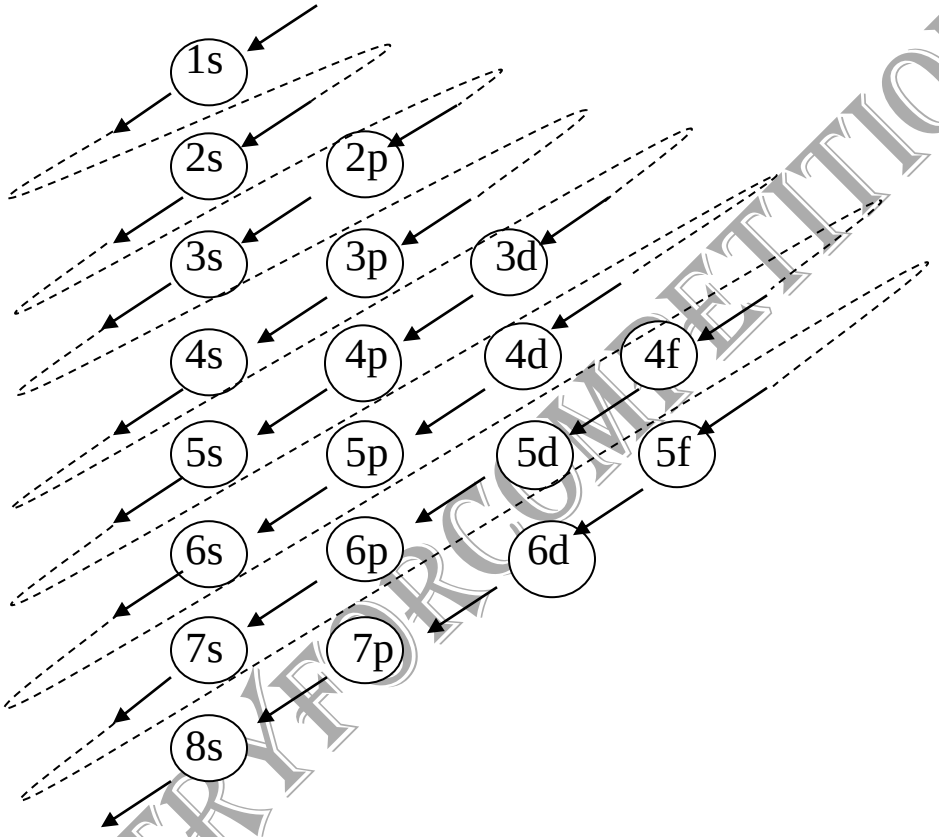


Fig- Sequence of filling of electrons in different orbitals

Following Aufbau's Principle, the electronic configuration of some important elements up to sub-shell level can represented as under-

H (1) = $1s^1$ He (2) = $1s^2$

Li(3) = $1s^2,2s^1$ Be (4) = $1s^2,2s^2$

B (5) = $1s^2,2s^2,2p^1$ C (6) = $1s^2,2s^2,2p^2$

N (7) = $1s^2,2s^2,2p^3$ O (8) = $1s^2,2s^2,2p^4$

F (9) = $1s^2,2s^2,2p^5$ Ne (10) = $1s^2,2s^2,2p^6$

Na (11) = $1s^2,2s^2,2p^6,3s^1$ Mg (12) = $1s^2,2s^2,2p^6,3s^2$

Al (13) = $1s^2,2s^2,2p^6,3s^2,3p^1$ P (15) = $1s^2,2s^2,2p^6,3s^2, 3p^1$

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- "Aufbau" is a German word meaning "building up or construction". Hence, this principle is also called building up or construction principle.

(3)Hund's Rule of Maximum Multiplicity

This principle governs the filling of electrons in orbitals of same energy belonging to same sub-shell. According to this principle,

"In orbitals of same energy belonging to same sub-shell, the pairing of electrons does not occur, until all the orbitals are singly filled."

or

"As long as possible the number of unpaired electrons in orbitals of same energy is maximum and all these electrons have same spin."

Following this rule the filling of electrons in different orbitals of p-sub-shell can be represented as under-

Number of electrons	Distribution in p-orbitals
	p_x p_y p_z
1	↑
2	↑ ↑
3	↑ ↑ ↑
4	↑↓ ↑ ↑
5	↑↓ ↑↓ ↑
6	↑↓ ↑↓ ↑↓

Following Hund's rule, the electronic configuration of some important elements up to orbital level can represented as under-

B (5) = $1s^2,2s^2,2p_x^1,2p_y^0,2p_z^0$

C (6) = $1s^2,2s^2,2p_x^1,2p_y^1,2p_z^0$

N (7) = $1s^2,2s^2,2p_x^1,2p_y^1,2p_z^1$

O (8) = $1s^2,2s^2,2p_x^2,2p_y^1,2p_z^1$

F (9) = $1s^2,2s^2,2p_x^2,2p_y^2,2p_z^1$

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(4) **Bohr-Bury's Rule or (n+l) Rule-**

On experimental basis, Bohr-Bury found that in multi-electron atoms, energy of an orbital does not depend only upon principal quantum number (n) but also depends upon azimuthal quantum number (l). In order to decide relative energies of different orbitals they gave following two rules, which are collectively called Bohr-Bury's rule or (n+l) rule or (n+l) rule.

(1) If two orbitals have different values of (n+l), then the orbital having lower values of (n+l) has lower energy and electron enters first in this orbital.

For example, amongst 4s and 3d orbitals, 4s orbitals has lower value of (n+l) and therefore, has lower energy.

Value of (n+l) for 4s orbitals = (4+0)
= 4

Value of (n+l) for 3d orbitals = (3+2)
= 5

Thus , electron will enter first in 4s orbital and it will be followed by 3d orbitals.

(2) If two orbitals have same value of (n+l), then the orbital having lower values of n has lower energy and electron enters first in this orbital.

For example, amongst 3d and 4p orbitals, 3d orbitals have lower value of n and therefore have lower energy.

Value of (n+l) for 3d orbitals = (3+2)
= 5

Value of (n+l) for 4p orbitals = (4+1)
= 5

Thus , electron will enter first in 3d orbitals and it will be followed by 4p orbitals.

Exceptional Electronic Configuration of Chromium and Copper-

The electronic configuration of Chromium and Copper should be as under-

Cr (24) = $1s^2,2s^2,2p^6,3s^2,3p^6,4s^2,3d^4$

Cu (29) = $1s^2,2s^2,2p^6,3s^2,3p^6,4s^2,3d^9$

However, in practice, the electronic configuration of these elements is found to be as under-

Cr (24) = $1s^2,2s^2,2p^6,3s^2,3p^6,4s^1,3d^5$

Cu (29) = $1s^2,2s^2,2p^6,3s^2,3p^6,4s^1,3d^{10}$

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In fact, half-filled and full-filled configuration of orbitals have extra stability because of their more symmetry and more value of exchange energy. Hence, in Chromium one of the 4s electrons is transferred to the vacant 3d orbital, so that, it acquires comparatively more stable half-filled configuration of d-sub-shell.

Similarly, in Copper one of the 4s electron is transferred to the half-filled 3d orbital, so that, it acquires comparatively more stable full-filled configuration of d-sub-shell.

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