T. Y. B. Sc. Physics (PH-354) Paper-IV Atomic and Molecular Physics (CBCS Pattern)

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T. Y. B. Sc. Physics PH-354(Paper IV) Atomic and Molecular Physics

Course contains five chapters

- 1. Atomic structure- (Revision of various atomic models- Dalton's atomic theory, Thomson's atomic model, Rutherford's and Bohr model of atom, Vector atom model, Pauli's exclusion principle and electronic configuration, quantum states, and its spectral notation)
- One and Two valence electron systems- (Spin-orbit interaction, Energy level of sodium atom, selection rule, Spectra of single valence electron, Sodium spectra, Spectral terms of two valence electrons, LS and JJ Couplings, singlet triplet separations for interactions energy of LS coupling, Interaction energy of LS Coupling, Helium spectra)
- Zeeman effect- (Zeeman effect, Experimental arrangement, Normal and Anomalous Zeeman effect, Normal Zeeman effect of single valence electron, Starks effect, Applications of Zeeman effect)
- 4. **Molecular spectroscopy-** (Introduction to molecular spectroscopy and its types, Rotational, Vibration and Electronic spectra of rigid diatomic molecules, Rotational and Vibration Energy levels, Electronic spectra of molecules, Applications of UV Vis-spectroscopy)
- 5. **Raman spectroscopy-** (History of Raman effect, Molecular polarizability, Classical and Quantum Theory of Raman effect, Experimental set up and Applications of Raman spectroscopy, Characteristics of Raman lines)

Chapter No.1 Atomic Structure

Introduction

Every atom consists of nucleus which is made up of proton and neutron and numbers of electrons are revolved around the nucleus. It was thought that electrons revolve around the nucleus like planets do around the sun. But classical electromagnetic theory rejected possibility of stable electron orbit. Neil Bohr applied quantum theory to understand atomic structure in 1913 and developed a model which is still a convenient model of an atom.

What is an atom?

- ✤ Atom is the smallest unit of matter that retains the identity of the substance.
- ✤ *Democritus* was the person who first suggested the existence of atoms.
- Atom consists of positively charged Nucleus at the centre and negatively charged electrons revolving around the nucleus
- ✤ Radius of an atom -10⁻¹⁰ m
- ✤ Radius of an nucleus- 10⁻¹⁵ m
- * Nucleus consist of **Protons and Neutrons** together called Nucleus

Revision of Various atomic models

In the study of atomic models, basically five models have been helped us to understand an atom. The five atomic models as described below.

- 1. John Dalton's atomic model
- 2. J.J. Thomson's atomic model
- 3. Ernest Rutherford's model
- 4. Niles Bohr's model
- 5. Erwin Schrodinger's model

1. Dalton's Atomic theory

John Dalton proposed a theory about nature of matter in 1808.

Postulates of Dalton's atomic theory

- 1. All matter is made up of tiny, indivisible particles called as atoms.
- 2. All atom of a specific element are similar in mass, size and other properties and it varies element to element.

- 3. Atoms are neither created nor destroyed i.e. it cannot be divided into smaller particles.
- 4. Atoms of different elements combine in fixed whole number ratios to form compound.
- 5. Atom can be rearranged, combined or separated in chemical reactions.



Limitations of Dalton's atomic model

Dalton theory does not discover subatomic particles (such as protons, electrons and neutrons)

It does not explain about isotopes and isobars, as per Daltons theory all elements have identical masses and densities.

2. Thomson's or Plum pudding model (1904)

Negative particles are scattered throughout an atom with a positively charged mass of matter



In this chapter we have discuss Rutherford's, Bohr's atomic model and energy levels.

3. Rutherford's Atomic model

According to the Rutherford's model, an atom is composed of tiny nucleus in which its positive charge and nearly all its mass are concentrated with electron some distance away. Rutherford used for fast moving alpha particles emitted by certain radioactive elements. Alpha particles are helium atoms that have lost tow electrons each leaving them with a charge of + 2e.

Rutherford's scattering experiment used to calculate radius of nucleus by distance of closest approach.

Rutherford's Alpha Scattering Experiment

- Rutherford's conducted an experiment by bombarding α-particles on thin gold foil and studied the trajectory of these particles after their interaction with the gold foil.
- In his experiment, α-particles from a radioactive source at a thin gold foil 100 nm thickness. In order to study the deflection caused to the α-particles, he placed a fluorescent zinc sulphide screen around the thin gold foil.



Rutherford scattering experiment

Observations of Rutherford's Alpha Scattering Experiment

- Large α -particles bombarded on the gold foil passed through it without any deflection, it means most of the space in an atom is empty.
- Some of the α-particles were deflected by the gold sheet by very small angles; it means 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° 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.

- Rutherford assumed that size of target nucleus is small as compared with minimum deviation R. So Rutherford's scattering gives us to find dimension of nucleus. Rutherford atomic model
- The positively charged particles and most of the mass of an atom were concentrated in an extremely small volume. i.e. **nucleus**
- Negatively charged electrons surround the nucleus of an atom. He claimed that the electrons surrounding the nucleus revolve around it with very high speed in circular paths. He named these circular paths as orbits
- Electrons being negatively charged and nucleus being a densely concentrated mass of positively charged particles are held together by a strong electrostatic force of attraction.



Limitations of Rutherford Atomic Model

- 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. So Rutherford model was not in accordance with Maxwell's theory and could not explain the stability of an atom.
- One of the drawbacks of the Rutherford model was also that he **did not say anything about the arrangement of electrons in an atom** which made his theory incomplete.

• Although the early atomic models were inaccurate and failed to explain certain experimental results, they were the base for future developments in the world of quantum mechanics.

Electron Orbit

- According to Rutherford's Atomic model, Atom is tiny, Massive and positively charged nucleus surrounded by electrons at some distance to make atom electrically neutral.
- In electron orbit, centripetal force holding electron in orbit of radius **r**.
- Centripetal force = Electrostatic force

$$\frac{Mv^2}{r} = \frac{1Ze^2}{4\pi\epsilon_0 r^2}$$

Hence, velocity of electron is, $V^2 = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{mr}$

The quantities have their usual meanings.



For hydrogen atom, Z=1 so,

$$V = \frac{e}{\sqrt{4\pi\varepsilon_0 mr}}$$

Total energy of hydrogen atom = Kinetic Energy + Potential Energy

$$E = \frac{1}{2}Mv^2 + \left[\frac{-e^2}{4\pi\varepsilon_0 r}\right]$$

By substituting the value of v equation becomes,

$$E = \frac{e^2}{8\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r}$$

Total energy of a hydrogen atom is,

$$E = \frac{e^2}{8\pi\varepsilon_0 r}$$

Total energy of hydrogen atom is negative means every electron bound to the nucleus. If E>0 means electron would not follow a closed path.

This analysis is an application of Newton's laws motion and Coulomb's law of electric field. According to EM theory the accelerating electric charges radiates energy in the form of wave. An electron pursuing a curved path is accelerated and so it loses energy into nucleus. But atoms do not collapse. i. e. classically electron spiral rapidly around the nucleus and it radiates energy due its acceleration.



Thus classical theory fails to for analysis of atomic structure.

4. Bohr atomic structure

Neil Bohr proposed the theory of hydrogen atom in 1913. This theory gave physical meaning to the experimental discovery that of frequency of spectral lines. Bohr modified the Rutherford's model by Plank's quantum theory of radiation. He assumes that hydrogen atom consists of nucleus at the centre of the atom and electron revolves around the nucleus. According to the Plank's quantum theory energy is radiated and absorbed.

E=hu

Where, **u** is frequency of radiation, h is Plank's constant ($h = 6.625 \times 10^{-34}$ Js)

This quantum energy is called photon.

Bohr's postulate

<u>Postulate 1:</u> An electron revolves in a certain allowed circular orbits about the nucleus due to Coulomb's force.



$$F_c = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2}$$

Z= Atomic number (Z=1 for hydrogen atom)

 \in_0 = Permittivity of free space

r = Distance between nucleus and electron

v = Velocity of electron

m = Mass of electron

At equilibrium condition,

Centripetal force = Electrostatic force

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2}$$

This gives,
$$v^2 = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{mr}$$

<u>Postulate 2</u>: Only those circular orbits of electrons are permitted for which the angular momentum (\overline{L}) is equal to the integral multiple of $h/2\pi$

Thus,
$$L^- = n \frac{h}{2\pi}$$

Where, n = 1, 2, 3,...

Orbital angular momentum of an electron in an orbit is,

 $mvr = n \frac{h}{2\pi}$ This orbit is called non radiating orbit.

<u>Postulate 3:</u> When an electron jumps from higher energy orbit to lower energy orbit and frequency of emitted radiation is proportional to the difference between two energy states.

Thus, $E = hv \text{ and } E = E_1 - E_2$

So,
$$hv = E_1 - E_2$$

Where, \cup is the frequency, E_1 and E_2 are energy of initial and final states.

Calculate the radius, velocity and energy of electron for hydrogen atom using Bohr's postulates.

According to 1st.postulates,

$$mv^{2} = \frac{1}{4\pi\varepsilon_{0}} \frac{Ze^{2}}{r}$$
$$m^{2}v^{2} = \frac{1}{4\pi\varepsilon_{0}} \frac{mZe^{2}}{r} - \dots - 1$$

But due to 2nd postulates $mvr = n\frac{h}{2\pi}$ $mv = n\frac{h}{2\pi r}$ Squaring on both side, $m^2v^2 = n^2\frac{h^2}{4\pi^2r^2}$ ------2

From equation 1 and 2,

$$r = \left[\frac{\varepsilon_0 h^2}{\pi m e^2 Z}\right] n^2$$

For hydrogen atom, Z=1. So radius of n^{th} orbit is given by,

$$r_n = \left[\frac{\varepsilon_0 h^2}{\pi m e^2}\right] n^2$$
 Where, n is principle quantum number
 $r_n \propto n^2$ n=1,2,3,...

Radius of the Bohr's orbit is proportional to square of the natural numbers.

Radius of first Bohr orbit n=1 is,

$$r_1 = 0.53 \times 10^{-10} \text{m} = 0.53 \text{A}^0$$

Put value of radius in Bohr's 2^{nd} postulates and gets **velocity of electron** i.e. use this equations,

$$r_n = \frac{\varepsilon_0 h^2}{\pi m e^2} n^2$$
 And $m v_n r_n = n \frac{h}{2\pi}$
 $v_n = \frac{e^2}{2\varepsilon_0 nh}$

Energy of electron in an atom

The total energy of an electron in n th orbit is sum of Kinetic and Potential energies.

Total energy (E) = K.E. + P.E.

$$\mathbf{E} = \frac{1}{2}mv^2 + \int_r^{\infty} F.\,dr$$

After putting value of velocity of nth electron and electrostatic force we get,

$$K.E. = \frac{me^4}{8\varepsilon_0^2 n^2 h^2}$$
$$P.E. = -\frac{me^4}{4\varepsilon_0^2 n^2 h^2}$$

$$E = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2}$$
 total energy of an electron in nth orbit

Total energy,

$$E_n \propto \frac{1}{n^2}$$

For first orbit n=1, E_1 = -2.18x10⁻¹⁸ J

$$E_1 = -\frac{2.18 \times 10^{-18}}{1.6 \times 10^{-19}} = -13.6 \text{ eV}.$$
 Thus 13.6eV energy is required to

remove the electron from first orbit of hydrogen atom. This is also called Binding energy. This is first orbit energy so called ground state energy.

In general,
$$E_n = -\frac{13.6}{n^2} eV$$

It indicates that total energy of an electron increases as it goes away from the nucleus. It also indicate that the energy different of electron in successive orbits decreases with increase in the value of n.

Origin of line spectra of the hydrogen atom

According to the third postulate, when there is transition of an electron from higher energy orbit to the lower energy orbit, a photon of energy hu is emitted.

$$h\nu = E_n - E_m$$

Where E_n is the energy of n^{th} orbit and E_m is the energy of m^{th} electron.

Using energy equations,

$$h\nu = -\frac{me^4}{860^2h^2n^2} - \left[-\frac{me^4}{860^2h^2m^2}\right]$$
$$\upsilon = \frac{me^4}{860^2h^3} \left[\frac{1}{m^2} - \frac{1}{n^2}\right]$$
$$c = \upsilon \lambda$$

Where λ is wavelength of spectral line, c is velocity of light. From above equation,

$$\frac{1}{\lambda} = \frac{me^4}{8\in 0^2 h^3 c} [\frac{1}{m^2} - \frac{1}{n^2}]$$

The quantity $\frac{1}{\lambda} = \nu^{-1}$

Bohr's model explains the spectral lines of the hydrogen atomic emission spectrum. The electron of the atom remains in the ground state, its energy is unchanged. When the atom absorbs photon energy, the electron moves from the ground state orbit to an excited state orbit, Energy levels are chosen with the variable E_n . The ground state is E_1 (n=1), the first excited state is E_2 (n=2), and so on. The energy that is gained by the atom is equal to the difference in energy between the two energy levels. When the atom relaxes back to a lower energy state, it releases energy that is again equal to the difference in energy of the two orbits as shown in fig.



The change in energy, ΔE then translates to light of a particular frequency being emitted according to the equation $\Delta E = h u$, the atomic emission spectrum of hydrogen has spectral lines consisting of four different frequencies. This is explained in the Bohr model by the understanding that the electron orbits are not equally spaced. As the energy increases more and more from the nucleus, the spacing between the levels gets smaller and smaller.

Based on the wavelengths of the spectral lines, Bohr was able to calculate the energies that the hydrogen electron would have in each of its allowed energy levels. He then mathematically showed which energy level transitions correspond to the spectral lines in the atomic emission spectrum (see below).

 Lyman series- Transition of electron from initial orbit n=2, 3, 4, To final lower orbit m= 1. Wavelength of spectral lines of Lyman series lies in Ultra-violet region.

- Balmer series- Transition of electron from initial orbit n=3, 4, 5, To final lower orbit m= 2. Wavelength of spectral lines of Balmer series lies in Visible region.
- Pacshen series- Transition of electron from initial orbit n= 4, 5, 6, To final lower orbit m= 3. Wavelength of spectral lines of Pacshen series lies in near infra-red region.
- Brackett and Pfund series- Transition of electron from initial orbit n=4, 5, to final lower orbit m=4. And orbit n=5, 6,.... to final lower orbit m=5. Wavelength of spectral lines of Brackett and Pfund series lies in IR and far IR region respectively.



Electron transitions for the Hydrogen atom

The electron energy level diagram for the hydrogen atom

He found that the four visible spectral lines corresponded to transitions from higher energy levels down to the second energy level n=2. This is called the **Balmer** series. Transitions from higher energy levels down to the ground state n=1 are called the **Lyman** series, but the energies released are so large that the spectral lines are all in the ultraviolet region of the

energies released so large that the spectral lines are all in the ultraviolet region of the spectrum. The transitions called the **Paschen** series, the **Brackett** and **Pfund** series both result in spectral lines in the infrared region because the energies are too small.

Limitations of Bohr's theory:

- 1. It cannot explain intensity of spectral lines
- 2. It cannot explain the spectra of two or more electron atom.
- 3. It cannot explain fine structure of spectral lines.

Bohr-Sommerfeld's theory of hydrogen atom:



Sommerfeld atomic model

This model explains the fine spectrum of Hydrogen atom. The important postulates of Sommerfeld atomic model are-

1) The orbits may be both circular and elliptical.



 When path is elliptical, then there are two axis – major axis & minor axis. When length of major axis and minor axis become equal then orbit is circular.



Minor axis

3) The angular momentum of electron moving in an elliptical orbit is kh/2π.k is an integer except zero. Value of k = 1,2,3,4....n/k = length of major axis /length of minor axis, with increase in value of k, ellipticity of the orbit decreases. When n= k, then orbit is circular.



4) Sommerfeld suggested that orbits are made up of sub energy levels. These are s, p, d, f. These sub shells possess slightly different energies. Bohr gave a quantum number 'n', which determines the energy of electron. Sommerfeld introduced a new quantum number called Orbital or Azimuthal Quantum number (*l*) which determines the orbital angular momentum of electron.

Values of l = 0 to (n - l)

For, n=1 l=0, 1s sub shell ---- Only one circular orbit is possible.

- n=2 l=0, 1, 2, 2p sub shell ---Circular and elliptical orbit.
- n=3 l=0, 1, 2, 3s, 3p, 3d sub shell ----Circular and elliptical orbit.
- n=4 l=0, 1, 2, 3, 4s, 4p, 4d, 4f sub shell --- Circular and elliptical orbit.



- When an electron jumps from one orbit to another orbit, the difference of energy (ΔE) depends upon sub energy levels.
- It explains the splitting of individual spectral lines of hydrogen & thus fine spectrum. It could not predict the exact number of lines which are actually present in the fine spectrum.

Defects of Sommerfeld atomic model-

- 1. This model does not explain the behavior of system having more than one electron.
- 2. This model does not explain the Zeeman & Stark effect.

Vector atom model

The vector atom model basically deals with the total angular momentum of an atom, which is result of the combination of orbital and spin angular momentum. The two fundamental features of the vector atom model are (1) space quantization of orbits and (2) spinning electron hypothesis.

1. Space Quantization

The angular momentum is a vector quantity; hence its direction must be specified to describe it completely. To specify the orientation or direction of an orbit, a reference is required. The direction of the magnetic field applied to the atom is a reference line.

The rotating electron about the nucleus forms a current loop which has a magnetic moment $\mu = IA$, where I is the current in the loop and A is the area vector.

The energy of loop-field system is given by,

 $\mathbf{U} = -\boldsymbol{\mu}. \ \mathbf{B} = - |\boldsymbol{\mu}| \ |\mathbf{B}| \ \cos \boldsymbol{\theta}$

Where, θ is the angle between the magnetic moment μ and magnetic field B.

Classically, energy value between $-\mu B$ to $+\mu B$ is possible for the loop. An electron revolves around the nucleus in an atom possess angular momentum L which interacts with external applied magnetic field B. According to quantum theory, there are fixed directions of

magnetic moment μ and magnetic dipole (formed by closed loop motion of electron about nucleus) with respect to the magnetic field B. The magnetic moment μ and angular momentum L can be related as

$$\mu = \left[\frac{e}{2m_e}\right] L$$

$$|L| = \sqrt{\iota(\iota+1)} \qquad L = \text{Orbital angular momentum}$$

$$\frac{1}{\mu} = \frac{1}{\mu} L$$

This relationship is true from both classical and quantum mechanical point of view. Since discrete directions of μ are allowed, as such the direction of L also quantized in space. Here, the quantization refers the projection of L along the Z-direction (L_z). The orbital magnetic quantum number m₁ gives the direction of L and the possible components of L in the Z-direction (the field direction). The phenomenon of quantization of L in the direction of magnetic field B is known as **space quantization**. The direction of B is along the Z axis. As such the component of L along Z-direction is given as L_Z = m_l h, the m_l has values from $-\iota$ to $+\iota$ including zero. Space quantization of orbits and possible components of L can be understood with the following example.

Space quantization of the orbital angular momentum for L=2



The possible values of m_1 for $\iota = 2$ can be -2, -1, 0, 1, 2 hence $L_Z = m \iota h = -2h - h$, 0, h, 2h. Above figure shows space quantization of L for $\iota = 2$.

 $M_i = 21 + 1$

2. Spin Quantization

Goudsmit and Uhlenbeck in 1925 proposed that electron 'spins' about an axis through its centre of mass and further it has both angular momentum and a magnetic moment. The spin of electron is analogous to the planetary motion about the Sun in our solar system. Quantum mechanical treatment has demonstrated that the spin of electron should be quantized. The spin angular momentum S is related with spin quantum number s as,

$$S = \frac{1}{2}$$

The spin can be either clockwise or anticlockwise as such s can have two values *i.e.*, $\pm \frac{1}{2}$

$$S = \sqrt[2]{s(s+1)h}$$

$$S_z = m_s h, \qquad M_S = 2S + 1$$

Where as m_s has two values. $\pm \frac{1}{2}$ so, $S_z = \pm \frac{1}{2}h$

$$S = \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1\right)} h = \frac{\sqrt{3}}{2} h$$

S is along the direction of magnetic field which gives spin magnetic quantum number m_s , the orbital and spin motions of an electron are quantized in magnitude as well as in direction. These motions are represented by vectors quantization so the atomic model is called as vector atom model.

The Quantum 'Numbers

The Bohr-Somerfield atomic theory uses four quantum numbers which are,

- 1. Principal quantum number (n)
- 2. Orbital quantum number (*l*)
- 3. Spin quantum number (s) and
- 4. Total angular momentum quantum number (j).

In addition to these, three other quantum numbers have been introduced in vector atom model which are,

- 1. Magnetic orbital quantum number (m_i),
- 2. Magnetic spin quantum number (m_s) and
- 3. Magnetic total momentum quantum number (m_j).

The general description and possible values of these quantum numbers is given below.

1) **Principal Quantum Number (n):** Principle quantum number represents the orbit number, size of the orbit and the energy of the state.

 $E_n \propto \frac{1}{n^2}$ The value of n are, n= 1, 2, 3, ... which represent energy levels or shells K, L, M, N... Respectively the serial number of shell starts from innermost shell.

2) Orbital Quantum Number (ℓ): The orbital quantum number l' can have the values. $\ell = 0, 1, 2, 3, ... (n - 1)$ where 'n' is the principal quantum number, This gives the orbital angular momentum of electron on basis of classical theory,

 $L = m(\bar{v} \times \bar{r})$

m=mass of electron, \overline{v} =velocity and \overline{r} = orbital radius of electron. \overline{L} is perpendicular to the plane of electron orbit.



According to the Bohr's 2^{nd} postulate, orbital angular momentum \overline{L} of electron is,

$$L^{-} = n \frac{h}{2\pi}$$

If, L=0, motion of electron along the straight line through the nucleus.

For example, if n = 3, then $\iota = 0, 1, 2$.

- $\ell = 0$ s electron $\ell = 1$ p electron $\ell = 2$ d electron $\ell = 3$ f electron
- 3) Spin Quantum Number (s): Spin quantum number s has only one value
 - $i.e. \ \frac{1}{2} \quad \Rightarrow \quad s = \frac{1}{2}$

- 4) Total Angular Momentum Quantum Number (j): The total angular momentum quantum number *j* is the sum of orbital angular momentum *l* and spin quantum number's'. As such *j* can have $l \pm s$ or $l \pm \frac{1}{2}$ values.
- 5) Magnetic Orbital Quantum Number (m_l): If atom is placed in a weak magnetic field H_{τ} , then the orbital angular momentum L of an electron interacts with H_{τ} , i.e. $l_z = m_l \frac{h}{2\pi}$ where, m_l is magnetic orbital quantum number, its allowed values are $m_l = 2l + 1$ for example, l = 2, m_l can have -2, -1, 0, 1, 2 *i.e.*, total 5 values.
- 6) Magnetic Spin Quantum Number m_s : The magnetic spin quantum number takes (2s + 1) values. We know that $s = \frac{1}{2}$ and hence m_{ss} can take $(2 \times \frac{1}{2} + 1) = 2$ in total. The values of m_s are -s and +s or $-\frac{1}{2}$ and $+\frac{1}{2}$.

Spin angular momentum of electron is given by equation, $S = \sqrt{s(s+1)} \frac{h}{2\pi}$ where s is spin quantum number. The spin angular momentum \overline{S} is also quantized, like \overline{L} , in space. It has two orientations with respect to applied external magnetic field \overline{H} . The component of \overline{S} along the field direction is given by,

$$S_z = m_s \frac{h}{2\pi}$$
 m_s is spin magnetic quantum number. It has two possible values $m_s = \pm \frac{1}{2}$
 $m_s = \pm \frac{1}{2}$ corresponds to up-spin and $m_s = -\frac{1}{2}$ corresponds to down-spin

7) Magnetic Total Angular Momentum Quantum Number m_j : The total momentum J of an atom is a vector quantity and is the vector sum of orbital momentum L and spin angular momentum S *i.e.*, J = L + S. We define quantum number m_j which is known as the magnetic total angular mom quantum number and specify the orientation of J in space with respect to Z-axis.

According to quantum mechanics,

$$J = \sqrt{J(J+1)}$$
 And $J_s = m_j h$

The possible values of m_j are 2j + 1 i.e., m_j can take values from -j to +j including zero in integral steps. Now $J_z = L_z \pm S_z$ Which implies that $m_j = m_1 \pm m_s$. Now m_l is an integer and m_s is $\pm \frac{1}{2}$ as such m_j will have the half integral values only. The m_j , m_l and m_s can have the maximum value j, l and s respectively.

Pauli's Exclusion Principle:

Pauli's exclusion principle states that "No two electrons in the same atom can have same four quantum numbers." Or it also states that "every completely specified quantum state in an atom can be occupied by only one electron." Number of electrons in orbit can be specified by principal quantum number n, there can be $2n^2$ electrons where n= 1, 2, 3, integers. There can also subshells which are specified by orbital quantum number ℓ and total number of electron in sub shell can be finding by $2(2\ell-1)$ with the given value of $\ell=0,1,2,.(n-1)$

n	1	1
ł	0	0
m_{ℓ}	0	0
ms	$+\frac{1}{2}$	$-\frac{1}{2}$

For example consider n=1 i.e. there are only **two** electrons. $1s^2$

M{=2 {+1, M {=3, M{=-1, 0,0,+1.}}}			
For n=2 there are eight electrons.	ls ²	$2s^2$	2p ⁴

n	1	1	2	2	2	2	2	2
ł	0	0	0	0	1	1	1	1
m_{ℓ}	0	0	0	0	-1	0	0	+1
ms	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

Using Pauli's exclusion principles we can find the maximum number of electrons in a given groups or subgroups using following rules.

- 1. For given n, Orbital quantum No. ℓ can have values 0, 1, 2, 3, ...(n-1).
- For particular value of ℓ, magnetic orbital quantum no. mℓ has values ℓ, ..0, ..+ ℓ
 i. e. in all (2 ℓ+1) values.
- 3. For each m_s, spin quantum no m_s has two values $+\frac{1}{2}$ and $-\frac{1}{2}$.
- 4. Total no. of states for given n is $N=2n^2$ this is total no. of electron in the given shell.

Electronic Configuration:

Electron configuration is the arrangement of electrons around the nucleus of an atom based on their energy level. The electronic configuration of an atom is the distribution of electrons in various shells or subshells around the nucleus of the atom. The orbits or shells in an atom represented by the letters K, L, M, N, O, .. etc. corresponding to the principal quantum number n=1, 2, 3, 4, 5, ...etc. respectively.

Total electrons = atomic number (Z)

Electrons are added one at a time to the lowest energy levels first (Aufbau principle)

Level	n	ł	Sub-level	No. of electrons	Total no. of
				in sub-level =2(2ℓ +1)	electrons on level=2n ²
K	1	0	1s	2	2
L	2	0	2s	2	8
		1	2p	6	
Μ	3	0	3s	2	18
		1	3p	6	
		2	3d	10	
Ν	4	0	4s	2	32
		1	4p	6	
		2	4d	10	
		3	4f	14	

With these values of n, $\ell,\,m_\ell,$ and m_s we can have only two non- identical state of quantum numbers.

For K shell, n=1 and $\ell = 0$, $m_{\ell} = 0$, $m_{s} = +\frac{1}{2}$ n=1 and $\ell = 0$, $m_{\ell} = 0$, $m_{s} = -\frac{1}{2}$

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	The Hund's rul	A states th			1000	One Valer	tce Electron Syste			
	they are filled with electrons is such that a maximum number of electrons have unpair spins." Both, exclusion principle and Hund's rule can be illustrated through the electrons									
•	Let us consider the hydrogen atom 7 = 1									
•	It has only one electron. This electron									
	configuration is : 1 s1									
1	The superscript 1 indicates that one electron is associated and the									
1	Let us consider	neutral he	lium atom.	Z = 2	presentin	i the 15-Subshe	:11,			
	It has two ele	ctrons wh	ich enter in	nto 1s-su	hshall of	K shall (n -	1) The sheet			
	configuration is	1s ² .			USTIEN OF	k-snen (n =	I). The elecu			
	For neutral lithi	um, Z = 3,	there are 3	electrons			Variable Sec.			
	Electronic config	guration : 1	Ls ² 2s ¹							
	For beryllium a	tom, $Z = 4$, it has 4 ele	ctrons.			and the same			
	Electronic config	juration : 1	s ² 2s ²				and the second second			
	For boron atom	, Z = 5, it h	las 5 electro	ns.			a solid upor			
	Electronic config	uration : 1	s ² , 2s ² , 2p ¹				and the state of the state of the			
	For carbon aton	n, Z = 6, it	has 6 electro	ons.			A CARLES AND			
	In this case, elec	tronic conf	iguration is	152 252 2	m2		Constants of the			
•	Here two 2p-ele	ctrons can	not enter in	to only o	ne orbita	with paired a	the All hunde			
	enter into two s	eparate of	rbitals with	unpaired	spins (1	T) This is acc	pin (14), but t			
	rule. The electron	nic configu	ration of the	e above e	lements i	is shown in Fig	21			
	Shell	K		- L		Finale.	· 4.4.			
	Atom	- 15	2\$		2p	configur	ration			
	- t -	TA II	17.70			+	NTS ARADA			
	Z = 4, Be	1.+	11+	E.S.		1s ² , 2	s ²			
							- ALL OF THE PARTY			
	Z = 5, B	111	++	+		1.2 .	-2 -1			
						15,2	cs, zp			
		1000	- Errora	-	-	-	and the second second			
	Z = 6, C	1.4	1+	1	1	1s ² , 2	2s ² , 2p ²			
		-					and the second second			
	7 . 7 . 1	1	141		ET.	Ex-	and services			
	2=7, N	1		E	I	1 1s ² , 3	2s ² , 2p ³			

Fig. 2.1 : Electronic configuration for some lighter atoms

1s², 2s², 2p⁴

1s2, 2s2, 2p5

Z = 8, O

Z = 9, F

t +

Quantum state of electron-

Every electron in an atom has its unique set of four quantum numbers n, ℓ , m_{ℓ} and m_s . this set of quantum numbers specify the state of electron in atoms is called as quantum state of electron. For example, quantum state of oxygen atom is given by,

In oxygen atom, Z= 8 so there are 8 electrons and electronic configuration is, $1s^22s^22p^4$

First 2 electrons enters in s-sub shell of K-shell (n=1)

 1^{st} electron: n=1, ℓ =0, m $_{\ell}$ =0, m $_{s}$ =+1/2

 2^{nd} electron: n=1, ℓ =0, m $_{\ell}$ =0, m $_{s}$ = -1/2

N=2n², Total no. of electron in sub shell =2(2 ℓ +1), M ℓ = - ℓ to + ℓ and M_S=+1/2 and -1/2

Similarly, we can write quantum state of 3rd and 4th electron, there exist two quantum states for 2s-subshell and remaining 4 electrons enters into 2p-subshell of L orbit.

Spectral notation of Quantum states

We know that the orbital angular momentum L, spin angular momentum S and total angular momentum J of an atom, so, $J = L + S^-$

Where $L^{-}=\sum li$ Total orbital angular momentum and $S^{-}=\sum si$ Total spin angular momentum

$$\mathbf{J} = \mathbf{j} \div \frac{h}{2\pi}$$
 or $\vec{j} = \sqrt{j(j+1)} \frac{h}{2\pi}$

Total angular momentum of an atom is decided by the last unpaired electrons in an atom. The core of electrons in an atom, do not contribute to the total angular momentum \vec{j} of an atom.

$$J=(L+S)$$
 to (L-S)

For example, L=3 and S= $\frac{3}{2}$ then J= 3+ $\frac{3}{2} = \frac{9}{2}$, $\frac{7}{2}$, $\frac{8}{2}$, $\frac{3}{2}$

Thus there are 4 values of J. In general, there are (2S+1) different values of j and each value of \vec{j} gives a separate atomic state. So there are (2S+1) different energy states for the atom.

The quantity (2S+1) is called multiplicity of atomic state.

(2S+1) = 1 represent the singlet energy level (S = 0)

(2S+1) = 2 represent the doublet energy level $(S = \frac{1}{2})$

(2S+1) = 3 represent the triplet energy level (S = 1)

The atomic states are denoted by the capital letters S, P, D, F, G...etc. which corresponds to the L= 0, 1, 2, 3, 4... respectively. Atomic state is denoted by, $^{(2S+1)}L_J$ For example, hydrogen atom Z=1, 1S¹ $n=1, l=0, ml=0 \text{ and } ms=\frac{1}{2}$

State of atom is ${}^{(2S+1)}L_J {}^2S_{1/2}$ Doublet S half.

Similarly, L= 3 and S= 1/2 Then the values J are, $J=\frac{7}{2},\frac{8}{2},\frac{3}{2},\frac{1}{2}$

The multiplicity = (2S + 1) = 2

L =3 indicate F state as ${}^{2}F_{7/2}$, ${}^{2}F_{5/2}$, ${}^{2}F_{3/2}$, ${}^{2}F_{1/2}$, These are spectral notation of L shell electrons.

Questions for exercise-

- 1. State four quantum numbers.
- 2. Explain Rutherford model of an atom.
- 3. Find expression for total energy and radius of hydrogen atom in electron orbit.
- 4. Discuss vector atom model.
- 5. Discuss energy levels and series transition of hydrogen atom.
- 6. Explain Frank and Hertz experiment. What conclusions are drawn from the experiment?

Numerical problems:

- 1. An electron collides with a hydrogen atom in its ground states and excites into state of n=2 .How much energy was given to hydrogen atom in this inelastic collision?
- 2. Calculate the linear velocity of an electron in the first, second and third orbit of hydrogen atom.
- 3. Determine the magnitude of orbital angular momentum L and allowed values of L_Z for the hydrogen atom in l = 3 states.