Unit – 02: Vector Atom Model & Optical Spectra

Syllabus: Vector atom model – model fundamentals, spatial quantization, spinning electron; Quantum numbers associated with vector atomic model; Coupling schemes – L-S and j-j schemes; Pauli's exclusion principle; Magnetic dipole moment due to orbital motion of electron – derivation; Magnetic dipole moment due to spin motion of electron; Lande g-factor and its calculation for different states; Stern-Gerlach experiment – Experimental arrangement and Principle; Fine structure of spectral lines with examples; Spin-orbit coupling/Spin-Orbit Interaction – qualitative; Optical spectra – spectral terms, spectral notations, selection rules, intensity rules; Fine structure of the sodium D-line; Zeeman effect: Types, Experimental study and classical theory of normal Zeeman effect, Zeeman shift expression (no derivation), examples; Stark effect: Experimental study, Types and examples. **[15 hour]**

Introduction:
VECTOR ATOM MODEL:

This model is an extension of Bohr-Sommerfeld atomic model. Following are the drawbacks of Bohr-Sommerfeld atomic model:

1) Original Bohr's theory was incapable of explaining the fine structure of the spectral lines even in the simplest hydrogen atom.
2) In case of complex atoms, Bohr's theory fails to calculate the energy of the system and frequencies of radiation emitted.
3) Sommerfeld modification, though gave a theoretical background of the splitting of individual spectral lines of hydrogen, still it could not predict the correct number of observed fine structure of these lines.
4) Both the models could not explain the distribution of and arrangement of electrons in atoms.
5) Both these models do not throw any light on the intensities of the spectral lines.
6) Both the models could not explain the anomalous Zeeman effect and Stark effect.

To overcome all these objections a new model known as ***vector atom model*** was proposed. The main contributors are Bohr, Sommerfeld, Uhelenbeck, Goudsmith, Pauli, Stern and Gerlach.

Concept of Vector Atom Model: The two concepts which characterize the vector atom model and differentiate it from other models are;

a) The concept of quantization of direction, i.e., spatial quantization, and
b) The concept of spinning electron.

Space Quantization: According to Bohr's theory, the electron moves in circular orbit. Since the radius of the orbit remains fixed, hence the electron has only one degree of freedom. In case of Sommerfeld's elliptical orbits, the electron possesses two degrees of freedom. The quantum numbers one corresponding to radius vector n_r and the other corresponding to angle n_ϕ are sufficient to describe the electron orbit. In general, the motion of an electron in an atom is three-dimensional and therefore possesses three degrees of freedom. Hence an additional quantum condition is required to describe the actual state of affairs. According to classical mechanics, when an electron moves in three-dimensional orbits it may have all orientations with respect to a fixed axis. In vector atom model, which is based on quantum theory, the orbits are assumed to be quantized in magnitude and direction (orientation of orbits in space) both. In this way the third condition quantizes the orientation of elliptical orbit in three dimensions and does not alter the original Sommerfeld orbits in regard to their size and shape. The introduction of such a spatial quantization makes the orbit vector quantized.

For the purpose of space quantization, we need a certain preferred direction with respect to which the orbits may receive their orientation. Such a direction may be received by an external field or force but that may deform the elliptical orbit. To avoid this situation, we choose the external field so small that it does not deform the orbits. For easiness the direction of field is taken along Z-axis. The angle between the field direction and the direction which is perpendicular to the plane of orbit is taken as θ. According to the rule of space quantization, the electron orbit can only set itself in certain discrete positions with respect to the field direction and not in all positions making all possible angles with the field direction as suggested by classical theory. This is known as spatial quantization and was proposed by Sommerfeld. The different permitted orientations of an electron orbit are determined by the fact that *the projection of quantized orbits on the field direction must themselves be quantized*.

Spinning Electron: In alkali spectra it was observed that many lines consist of a group of lines close to each other. To explain the multiple characters of spectral lines, Uhlenbeck and Goudsmith, in 1925 put forward their famous hypothesis of electron spin. According to this hypothesis the electron revolves not only in an orbit round the nucleus but also spins about its own axis. Thus electron has two types of motions viz., orbital motion and spin motion. The angular momentum of the atom will now be due to orbital motion and spin motion of electron. According to quantum theory, the spin motion, like orbital motion should be quantized. Hence a new quantum number, known as ***spin quantum number*** is introduced. The orbital and spin motions are quantized not only in magnitude but also in direction according to the concept of spatial quantization. The two are considered as quantized vectors and hence the atom model is called vector atomic model.

We know that a revolving body about an axis gives rise to a mechanical angular momentum. If the body is charged, it gives rise to a circuital current and hence to a magnetic moment. Now the electron will be endowed with two magnetic moments, one due to orbital motion, and the other due to spin motion. The magnetic moment of the atom will be resultant of two magnetic moments which are quantized vectors. Similarly the electron will now be endowed with two angular momenta – one due to orbital motion and other due to spin motion.

The two fundamental postulates of vector atom model have been experimentally verified by Stern and Gerlach while studying the behaviour of atoms in non-homogenous magnetic field.

Orbital Angular Momentum:

In Bohr's theory of hydrogen atom, it was assumed that the electron moves in circular orbit with an angular velocity ω. Due to this angular velocity the electron has a definite angular momentum. According to Bohr's theory, the angular momentum is an integral multiple of $\hbar$ and is represented by $n\frac{h}{2\pi}$. In Sommerfeld theory, the angular momentum is represented by $n_\phi \frac{h}{2\pi}$ where n_ϕ is the azimuthal quantum number. In vector atom model of atom, the quantum number n_ϕ is replaced by quantum number l which is known as **orbital quantum number**. The orbital angular momentum p_l associated with different orbits is

$$p_l = l\frac{h}{2\pi} \qquad \text{where } l = 0, 1, 2, 3, \cdots\cdots\cdots etc. \qquad (01)$$

Orbital quantum number is identical to azimuthal quantum number n_ϕ of Sommerfeld theory. The two are related by $l = (n_\phi - 1)$.

The orbital angular momentum is a vector quantity. This is represented by a straight line which is parallel to the axis of rotation as shown in fig (01). Its positive sense is taken by the direction of advance of a right hand screw rotated with motion.

According to quantum mechanical results, the value of orbital angular momentum p_l is not equal to $l\frac{h}{2\pi}$ i.e., $p_l \neq l\frac{h}{2\pi}$ but this is given by the following expression $p_l = \sqrt{[l(l+1)]} \cdot \frac{h}{2\pi}$
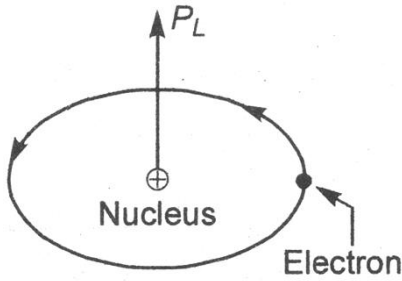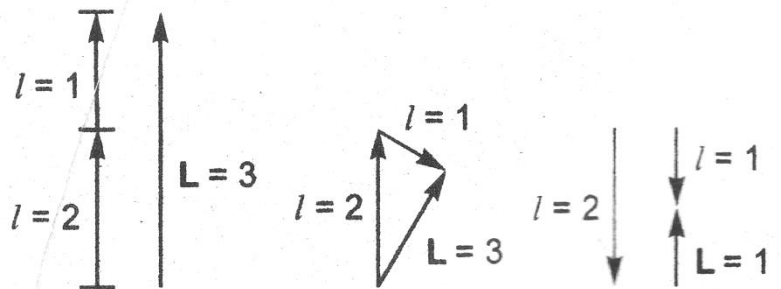

Fig (01)   Fig(02)

The value of l can take any integral number between 0 and $(n-1)$ where n is the principal quantum number. It is a common practice to assign letters to l values as shown below:

Orbital quantum number (l):	0	1	2	3	4	5
Electron designation:	s	p	d	f	g	h

Here the words $s, p, d, f, g, h, \cdots\cdots etc.$, stands for Sharp, Principal, Diffuse, Fundamental, etc.

When $n = 3 \qquad l = 0$ the electron is known as $3s$
$\qquad\quad n = 3 \qquad l = 1$ the electron is known as $3p$
$\qquad\quad n = 3 \qquad l = 2$ the electron is known as $3d$

The different sub-shells are tabulated below:

Shell n		Sub-shells					
		$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
K	1	$1s$					
L	2	$2s$	$2p$				
M	3	$3s$	$3p$	$3d$			
N	4	$4s$	$4p$	$4d$	$4f$		
O	5	$5s$	$5p$	$5d$	$5f$	$5g$	
P	6	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$

The maximum number of electrons allowed in a sub-shell is $2(2l + 1)$. The following table shows the distribution of electrons in different shells.

Shell	Principal quantum number	Orbital quantum number	Sub-Shell	Maximum number of electrons $2(2l + 1)$	Total $2n^2$
K	1	0	$1s$	2	2
L	2	0	$2s$	2	8
		1	$2p$	6	
M	3	0	$3s$	2	18
		1	$3p$	6	
		3	$3d$	10	
N	4	0	$4s$	2	32
		1	$4p$	6	
		2	$4d$	10	
		3	$4f$	14	
O	5	0	$5s$	2	50
		1	$5p$	6	
		2	$5d$	10	
		3	$5f$	14	
		4	$5g$	18	

The total orbital angular momentum in case of more complex atoms is denoted by L. This is a vector sum of all orbital angular momenta of individual electrons. This vector sum L is restricted by quantum conditions of integral values only. For example we consider the case of two electrons having orbital angular momentum $l = 1$ and $l = 2$ may have values from $L = 2 + 1 = 3$ to $L = 2 - 1 = 1$ and all integral values lie in between the two i.e., L may have values $3, 2 \text{ and } 1$. The method of addition of these vectors is shown in fig (02).

Electron Spin:

Experimentally it was observed that in the spectra of alkali metal all the lines were doublets. Bohr's theory as well as Sommerfeld theory could not explain the doublet nature of spectral lines. In order to explain this observed behaviour, Goudsmit and Uhlenbeck (Dutch

Physicists) in 1925 postulated that electron not only revolves round the nucleus but it spins round its own axis. Thus, the electron possesses spin motion as well as orbital motion. The spin angular momentum of the electron is given by

$$p_s = s\frac{h}{2\pi} \quad \text{where } s = \frac{1}{2} \tag{01}$$

According to wave mechanics, the spin angular momentum p_s of the electron is given by

$$p_s = \sqrt{[s(s+1)]} \cdot \frac{h}{2\pi} \tag{02}$$

The spin angular momenta of several electrons may be obtained as follows:
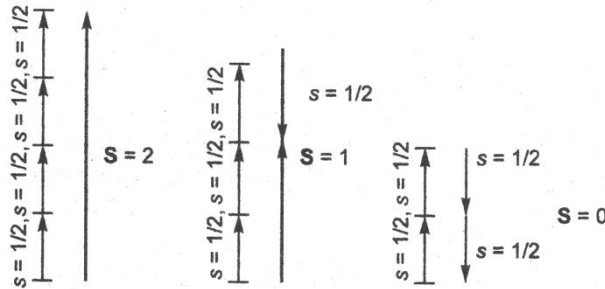

Fig (01)

Consider the case of four electrons. All the electrons may have the spin in one direction, i.e., total spin S may be 2. Out of these four electrons, three electrons may have spins in one direction and the fourth one may have spin in opposite direction. In this case the vector sum S will be 1. It is just possible that the two electrons have their spins in one direction and the rest two in opposite direction, now the vector sum S is 0. Thus in case of four electrons, the spin can have values $0, 1 \text{ or } 2$. This is shown in fig(01). In case of three electrons the spin values may be $1/2 \text{ or } 3/2$. In general, for an odd number of electrons, S must be an odd multiple of $1/2$ while for even number of electrons, S must be an even multiple of $1/2$.

Total Angular Momentum of Electron:

We have seen that an electron has orbital angular momentum p_l and spin angular momentum p_s. The total angular momentum of a single electron is the vector sum of the orbital and spin angular momenta of single electron. The total angular momentum is given by

$$p_j = j\frac{h}{2\pi} \tag{01}$$
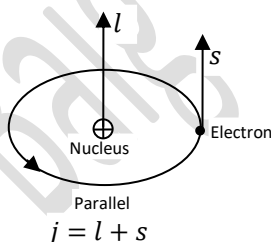
where j is called **total angular quantum number**.

Parallel $j = l + s$ Anti-Parallel $j = l - s$
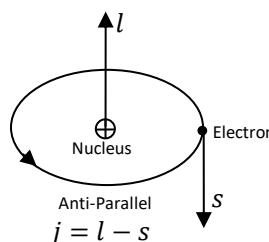
Fig (01)   Fig (02)

The value of j is $j = l + s$ and $j = l - s$ with the restriction that j must be positive. Here positive sign is taken when s is parallel to l and minus sign when s is antiparallel to l as shown in fig (01). Thus, for $l = 2$ and $s = \frac{1}{2}$, j can have values $\left(2 + \frac{1}{2}\right) = \frac{5}{2}$ and $\left(2 - \frac{1}{2}\right) = \frac{3}{2}$.

According to wave mechanics, the total angular momentum is given by

$$p_j = \sqrt{[j(j+1)]} \cdot \frac{h}{2\pi} \tag{02}$$

The spin angular momentum p_s and orbital angular momentum p_l couple vertically as shown in fig (02).

Derivation of Expression for Bohr Magneton:

Consider an electron of mass m_e moving with constant speed v in a circular orbit of radius r about the nucleus, as shown in fig (01). Since the electron travels a distance $2\pi r$ (the circumference of the circle) in time T, its orbital speed is

$$v = \frac{2\pi r}{T} \tag{01}$$

The rotation of the electron in the orbit constitutes an electric current. The current I associated with this orbiting electron e is

$$I = \frac{e}{T} = \frac{e\omega}{2\pi} = \frac{ev}{2\pi r} \qquad \left(\because \ \omega = \frac{v}{r} \right) \tag{02}$$

Fig (01)

Such a current loop behaves like a **magnetic shell** having magnetic moment $\mu_l = IA$ where $A(= \pi r^2)$ is the area of the current loop.

$$\therefore \qquad \mu_l = IA = \left(\frac{ev}{2\pi r} \right) \pi r^2 = \frac{1}{2} evr = \frac{1}{2} e\omega r^2 \tag{03}$$

The magnetic moment μ of the electron has a direction perpendicular to the plane of the electron orbit as shown in fig (01). The magnetic moment μ and orbital angular momentum $\vec{p_l}$ of the electron point in opposite directions. The magnitude of $\vec{p_l}$ is given by

$$p_l = m_e \omega r^2 \tag{04}$$

Dividing equation (03) by equation (04), we have

$$\frac{\mu_l}{p_l} = \frac{e}{2m_e} \tag{05}$$

This ratio is known as the **gyromagnetic ratio**. The same expression for the gyromagnetic ratio is obtained if the electron is assumed to rotate in an elliptical orbit.

Since the orbital angular momentum is given by

$$p_l = l\frac{h}{2\pi} \qquad \text{where } l = 0, 1, 2, 3, \cdots\cdots\cdots \text{ we get}$$

$$\mu_l = \frac{e}{2m_e} \cdot p_l = l\frac{e}{2m_e} \cdot \frac{h}{2\pi}$$

$$\mu_l = l\mu_B \tag{06}$$

$$\boxed{\mu_B = \frac{eh}{4\pi m_e} = 9.2741 \times 10^{-24} \, JT^{-1}} \tag{07}$$

μ_B is known as the **Bohr magneton** which is the basic unit of magnetic moments. Thus, atomic magnetic moments can be expressed as multiples of the Bohr magneton.

Note:

1) $1 \, JT^{-1} = 1 \, A.m^2$.
2) The nucleus of an atom has a magnetic moment associated with its constituent protons and neutrons. However, the magnetic moment of a proton or neutron is much smaller than that of an electron and usually can be neglected.
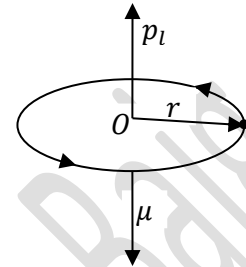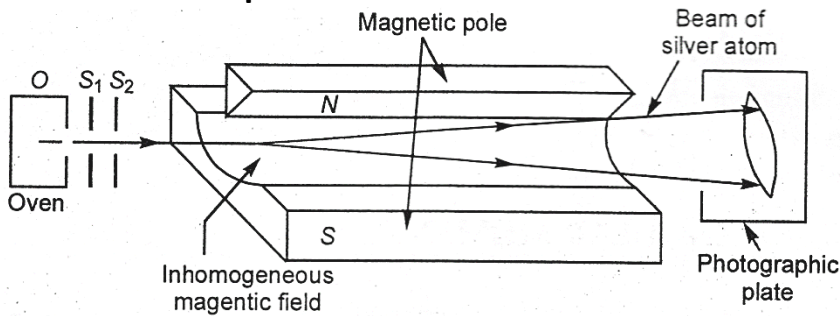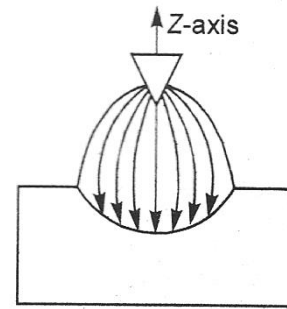

Stern-Gerlach Experiment:

Fig (01)

Fig (02)

In Stern and Gerlach experiment a beam of silver atoms is passed through an inhomogeneous magnetic field. The silver atoms beam is produced by heating silver in a small electric oven O [see fig (01)] and passing the beam through slits S_1 and S_2. The inhomogeneous magnetic field is produced having one of the pole pieces of magnet flat with a cylindrical groove and the other in the form of knife edge, parallel to the groove as shown in fig (01). Thus, the magnetic field is of much greater intensity near the knife edge than anywhere else in the gap, i.e., the intensity of the magnetic field increases as we go from the centre towards the upper knife edge pole and decreases as we go below towards the lower pole as shown in fig (02). A photographic plate P records the configuration of the beam after its passage through the field. To avoid the deflection of silver atoms by gas molecules, the whole arrangement is enclosed in a highly evacuated glass vessel.

In the absence of magnetic field, a trace of the form of a narrow strip is obtained as shown in fig (03a). In presence of the inhomogeneous magnetic field the strip splits up into two
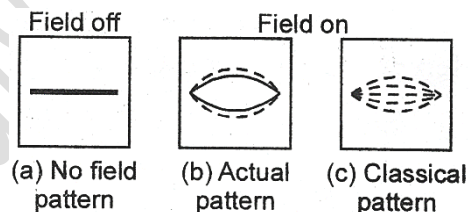

Fig (03)

components as shown in fig (03b). According to the classical concepts, the classical shape of the strip in inhomogeneous field is shown in fig (03c).

The splitting of beam into two components in inhomogeneous field verifies the existence of electron spin and the postulate of space quantization as shown in below:

Silver has an atomic number $z = 47$. According to Pauli's exclusion principle, all the inner shells and sub-shells are completely filled except the outermost electron in $5s$ state. Thus, silver is monovalent. So $5s$ electron is responsible for the magnetic moment of the atom. When all silver atoms possessing a magnetic moment μ_J pass through the inhomogeneous magnetic field, they experience different amounts of force in vertical direction depending on their orientation. This is due to the fact that when a bar magnet is placed in inhomogeneous magnetic field (let its north pole experiences a greater force than south pole) then the magnet experiences a resultant force $F_1 - F_2$ as shown in fig (04). The magnitude and direction of force F depends on the magnitudes of F_1 and F_2 i.e., orientation of the axis of magnet relative to the magnetic field. This force causes a deflection of silver atoms to varying degrees in a vertical direction. If the magnetic moment μ_J can have all possible orientations (according to the classical view), then the beam of silver atoms, consisting of millions of atoms having all possible

orientations of μ_J will be spread out into a broad continuous band on emerging from magnetic field. In this way it should produce a broad continuous patch on the photographic plate.
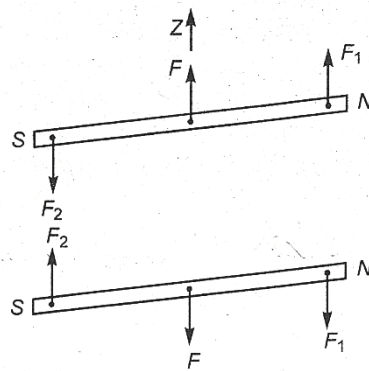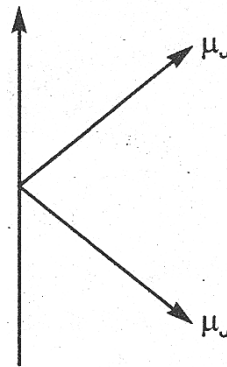

Fig (04)   Fig (05)

Experimentally only two narrow strips are obtained on the photographic plate. Therefore, the predictions of classical physics are not correct in this case. The two narrow strips show that μ_J cannot have all possible orientations, but only two possible orientations as shown in fig (05). We know that μ_J is proportional to angular momentum J and hence the direction of J relative to a well-defined direction should have only two values. According to the quantization rules, the magnitude of J is given by

$$J = \sqrt{[j(j-1)]} \cdot \frac{h}{2\pi}$$

There are $(2j + 1)$ possible orientations of J.

The Stern-Gerlach experiment shows that $(2j + 1) = 2$ 　　　or 　　 $j = \frac{1}{2}$

Thus 　　　　 $J = \frac{\sqrt{3}}{2} \cdot \frac{h}{2\pi}$

It is known that the angular momentum J of silver atoms is entirely due to spin of its valance electrons. Thus, we conclude that the electron has a spin angular momentum

$$S = \sqrt{[s(s+1)]} \cdot \frac{h}{2\pi} \qquad \text{where} \qquad s = \frac{1}{2}$$

Thus, Stern and Gerlach found that the initial beam split into two distinct parts, corresponding to two possible spin orientations in magnetic field that are permitted by space quantization.

Derivation of expression for the amount of deviation:
Suppose the magnetic field be non-homogenous along Y-direction. The field gradient is dB/dy and is positive. Let the atomic magnet with magnetic moment M, pole strength p and length l incline at an angle θ with the field direction is placed in such a field as shown in fig (06).

If the field strength at one pole is B then the field strength at another pole will be $B + (dB/dy)l\cos\theta$.

Force on one pole of atomic magnet is pB while on the other pole is $p[B + (dB/dy)l\cos\theta]$.

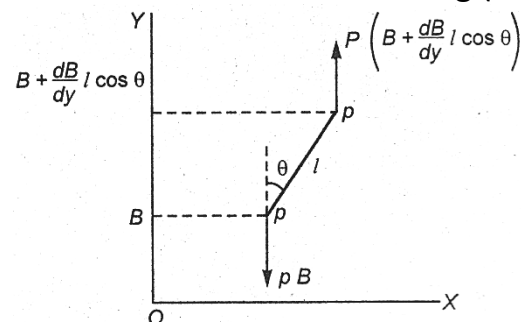The extra force $p(dB/dy)l\cos\theta$ on one pole displaces the atom as a whole. The force F_y is given by

Fig (06)

$$F_y = pl(dB/dy)\cos\theta = M\cos\theta\left(\frac{dB}{dy}\right) \tag{01}$$

where $M = pl$ is the magnetic moment.

Due to this force, the atomic magnet will be displaced from its straight path in the field direction. To find out this displacement, let the silver atom enters the non-homogenous field with velocity v and the length of path be L for which time taken is t. The displacement d_y of the atom along the field direction at the end of time t is given by

$$d_y = \frac{1}{2}\alpha_y t^2 \tag{02}$$

where α_y is the acceleration imparted to the atom along the field direction by the force F_y. Thus $\alpha_y = F_y/m$ where m is the mass of the atomic magnet.

$$d_y = \frac{1}{2}\frac{F_y}{m}t^2 = \frac{1}{2}\frac{F_y}{m}\left(\frac{L}{v}\right)^2 \qquad \because \ t = \left(\frac{L}{v}\right)$$

Substituting value of F_y from equation (01), we get

$$\boxed{d_y = \frac{1}{2}\frac{M\cos\theta}{m}\left(\frac{dB}{dy}\right)\left(\frac{L}{v}\right)^2} \tag{03}$$

where d_y is the most probable deflection of silver beam and can be determined from the maximum separation between the two traces obtained in the experiment. All other quantities are known. Therefore, the equation (03) can be verified by the experiment. The theoretical as well as experimental results are in excellent agreement. This strongly supports the postulate of space quantization and the existence of electron spin.

Quantum Numbers Associated with Vector Atom Model:

Quantum Numbers: "*The numbers that are required to completely specify the position of electron (its distance from the nucleus and its energy), orbital angular momentum of electron, configuration of electron in the presence of an external magnetic field and spin of electron, are known as quantum numbers or the quantum state of electron is characterized by four numbers called quantum numbers*".

Quantum Numbers Associated with Vector Atom Model:

1) **The Principal Quantum Number (n):** This quantum number belongs to the principal orbit (or shell) to which the electron belongs. Thus this quantum number $'n'$ is identical with the one used in Bohr-Sommerfeld atom model. The principal quantum number n can have only non-zero positive integral values $n = 1, 2, 3, \cdots$ and are denoted by the letters K, L, M, N, O, P, Q respectively. The number of electrons in a shell is limited to $2n^2$, where n is the principal quantum number concerned. The K-shell with $n = 1$ can have maximum of 2 electrons. L-shell with $n = 2$ can have maximum of 8 electrons and so on.

2) **The Orbital Quantum Number** (l):

This quantum number defines the shape of the orbital occupied by the electron and the orbital angular momentum of the electron. $P_l = l\dfrac{h}{2\pi} = l\hbar$

For any given value of $'n'$, l can take values from $0 \; to \; (n-1)$, each of which refers to an energy sub-shell or sub-level. The quantum numbers are denoted by the letters s, p, d, f, g, ... According to wave mechanics, orbital angular momentum $P_l \; or \; L$ of the electron is given by

$P_l = \sqrt{l(l+1)}\,\dfrac{h}{2\pi}$

n	l	Orbital
1	0	s
2	0	s
	1	p
3	0	s
	1	p
	2	d
4	0	s
	1	p
	2	d
	3	f

3) **The Spin Quantum Number** (s): The magnitude of s is always $1/2$. The spin angular momentum is $P_s = s\dfrac{h}{2\pi} = s\hbar$. According to wave mechanics, angular momentum due to spin motion is $P_s = \sqrt{s(s+1)}\,\dfrac{h}{2\pi} = \dfrac{\sqrt{3}}{2}\hbar$

Sometimes instead of P_s, S is also used.

4) **Total Angular Momentum Quantum Number** (j):

It represents the total angular momentum of the electron which is the vector sum of the orbital angular momentum and spin angular momentum.

The vector is defined by the equation

$$\vec{j} = \vec{l} \pm \vec{s} \qquad\qquad (01)$$

$\vec{j} = \vec{l} + \vec{s}$, plus sign when s is parallel to l and $\vec{j} = \vec{l} - \vec{s}$, minus sign when s is antiparallel to l.

The total angular momentum of the electron $p_j = j\hbar$.

According to wave mechanics,

$p_j(or\; j) = \sqrt{j(j+1)}\hbar$

5) **Magnetic Orbital Quantum Number** (m_l):

(a) $l = 1$　　(b) $l = 2$　　(c) $l = 3$
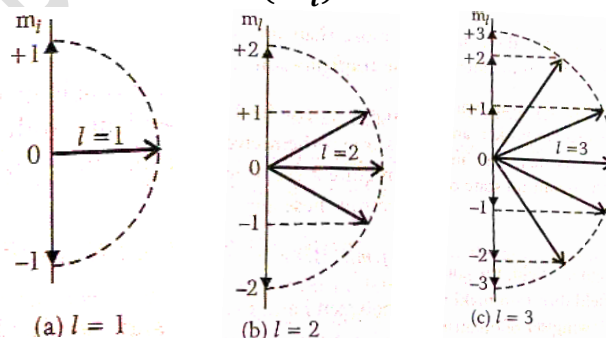
Fig (03)

The projection of the orbital quantum number l on the magnetic field is called magnetic orbital quantum number m_l. This is also called orientation quantum number. It gives information about the different possible orientations of the electron orbit in space. According to the concept of spectral quantization, the projection of l in the field direction must itself be

quantized. For a given l, m_l can have values from $+l\ to-l$. The permitted orientations are therefore equal to $(2l+1)$ as shown in fig (03).

The permitted orientations of d-orbital $(l=3)$ are $3, 2, 1, 0, -1, -2, -3$.

In the absence of magnetic field, all orientations have same energy and are called degenerate levels. Vector l is inclined to the field B at an angle θ such that its projection $m_l = l\cos\theta$ must be an integer.

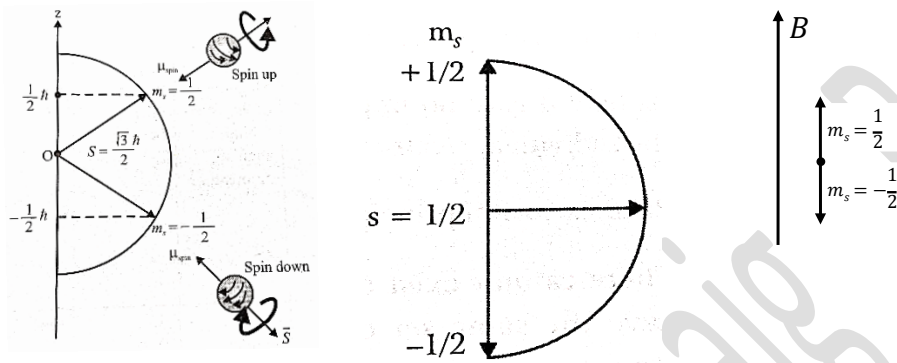### 6) Magnetic Spin Quantum Number (m_s):

Fig (04)

This is the projection of vector s on the external field direction. It can have $(2s+1)$ values from $-s\ to+s$ excluding zero. Since s is always equal to $1/2$ and never zero, m_s can have only two values $+1/2$ and $-1/2$ as shown in fig (04).

7) Magnetic Total Angular Momentum Quantum Number (m_j):

An electron in an atom has a certain orbital quantum number l and spin quantum number s; both of which contribute to the total quantum number j such that $j=l\pm s$. The projection of j on the field direction gives a numerical value called m_j, magnetic total angular momentum quantum number. m_j can have $(2j+1)$ values from $+j\ to-j$, zero excluded from space quantization.
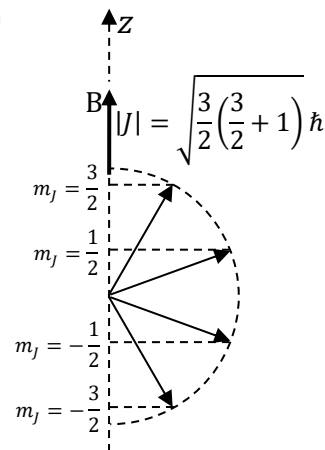
Example: For $j=3/2$ state $m_j=+\dfrac{3}{2}, +\dfrac{1}{2}, -\dfrac{1}{2}, -\dfrac{3}{2}$

Some important information regarding quantum numbers in tabular form:

Sl. No.	Quantum Number	Symbol	Constant of the motion	Possible values	Number of possible values	importance
1.	Principal quantum number	n	Energy	$1, 2, 3, \cdots \infty$	No limit (∞)	This quantum number is associated with the size of the orbits; radius and energy levels.
2.	Orbital quantum number	l	Magnitude of the orbital angular momentum	$0, 1, 2, 3, \cdots (n-1)$	n	This quantum number is associated with energy levels of orbitals, shape of orbits and orbitals and the orbital angular momentum of electron. $P_s = \sqrt{l(l+1)}\hbar$
3.	Spin quantum number	s	Spin angular momentum	$\dfrac{1}{2}$	One	This quantum number is associated with the direction of spin of the electron.
4.	Magnetic orbital quantum number	m_l	Z-component of the orbital angular momentum	i) $-l, -(l-1), \cdots, 0, +(l-1), \cdots (-l\ to +l)$ ii) $l\cos\theta$	$(2l+1)$	This quantum number is associated with moment of electrons and orientation of electron orbits with respect to magnetic field.
5.	Magnetic spin quantum number	m_s	Spin of electrons	i) from $(-s\ to +s)$ ii) $s\cos\theta$	$(2s+1)$	This quantum number is associated with the electrons in the presence of magnetic field.
6.	Total angular momentum quantum number	J	Resultant angular momentum	i) $(l \pm s)$ ii) $(L \pm S)$ iii) When l and s are parallel $j = l+s$ iv) When l and s are antiparallel $j = l-s$ $j = l \pm \frac{1}{2}$	$(2j+1)$	This quantum number is associated with the resultant angular momentum resulting from orbital and spin motions of the electrons. $P_j = \sqrt{j(j+1)}\hbar$

(i)   The state of an electron in an atom is completely specified by the four quantum numbers n, l, m_l and m_s.

(ii)   Note that all small letters l, s, j and $s, p, d, f, g\ etc.$ are used to describe the state of the electron and capital letters L, S, J and $S, P, D, F, G\ etc.$ are used to describe the states of the atom.

(iii)   Out of four quantum numbers only n and s are independent where as l and m_l depend upon n.

(iv)   For two electrons the values of three quantum numbers (n, l, m_l) may be same but not of s.

(v)   In weak magnetic fields n, l, j, m_j are used whereas in strong magnetic fields n, l, m_l and m_s are used.

Example: *Indicate the possible* (n, l, j) *values of electrons in the first three shells of an atom. The symbols have their usual significance*.

Solution: Case(01): First Shell i.e., $n = 1$

In this case $l = 0$ and $j = l \pm 1/2 = 0 \pm 1/2$ or $j = 1/2$ because negative of j is not permitted.
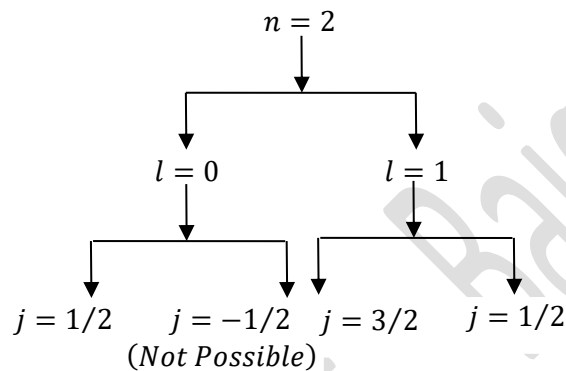
Case(02): Second Shell i.e., $n = 2$

In this case $l = 0$ & 1

Now $j = 0 \pm 1/2$ or $1/2$ and $j = 1 \pm 1/2$ i.e., $3/2, 1/2$

$\therefore \quad \boldsymbol{j} = 1/2 \ and \ 3/2, 1/2$

Hence three states are possible. They are $(2, 0, 1/2)$; $(2, 1, 3/2)$ and $(2, 1, 1/2)$. These three states are shown below in the form of a diagram.
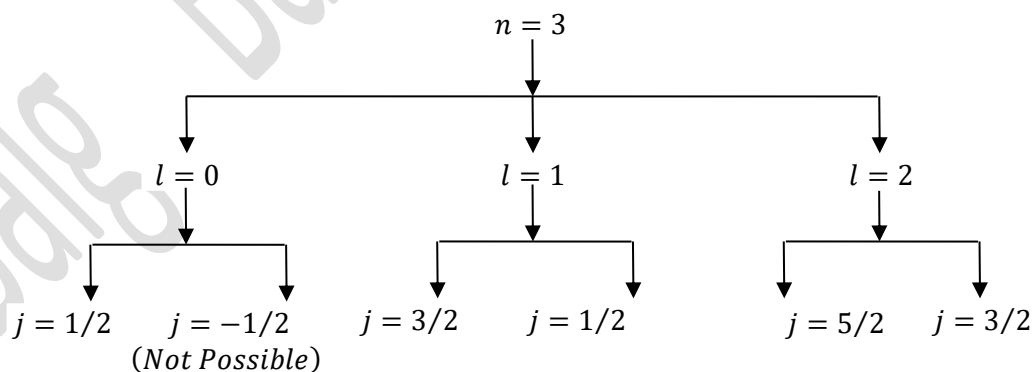
$$n = 2$$

$$l = 0 \qquad\qquad l = 1$$

$$j = 1/2 \quad j = -1/2 \quad j = 3/2 \quad j = 1/2$$
$$(Not\ Possible)$$

Case(03): Third Shell i.e., $n = 3$

In this case $l = 0, 1$ & 2

Now $j = 0 \pm 1/2$ or $1/2$; $j = 1 \pm 1/2$ i.e., $3/2, 1/2$ & $j = 2 \pm 1/2$ i.e., $5/2, 3/2$

$\therefore \quad \boldsymbol{j} = 1/2$; $(3/2, 1/2)$ and $(5/2, 3/2)$

Hence five states are possible. They are $(3, 0, 1/2)$; $(3, 1, 3/2)$; $(3, 1, 1/2)$; $(3, 2, 5/2)$ and $(3, 2, 3/2)$. These three states are shown below in the form of a diagram.

$$n = 3$$

$$l = 0 \qquad\qquad l = 1 \qquad\qquad l = 2$$

$$j = 1/2 \quad j = -1/2 \quad j = 3/2 \quad j = 1/2 \quad j = 5/2 \quad j = 3/2$$
$$(Not\ Possible)$$

Coupling Schemes:

There are two ways in which total angular momentum J of an atom containing two or more electrons, can be determined. They are

  i) $L - S$ Coupling or Russel-Saunders Coupling and

  ii) $J - J$ Coupling

L – S Coupling: In this type of coupling, the orbital angular momentum l_i of the various electrons are coupled together into a resultant L. The spin angular momenta s_i are also coupled together into a single resultant S.

The momenta L and S interact to form total angular quantum number J, mathematically,

$$L = \sum l_i \; ; \quad S = \sum s_i \quad \text{and} \quad J = L + S$$

When $L > S$, J can have $(2S + 1)$ values; when $L < S$, J can have $(2L + 1)$ values. L is always an integer including zero i.e., 0, 1, 2, 3, ……… The value of S depends on the number of electrons and the direction of their spin vectors.
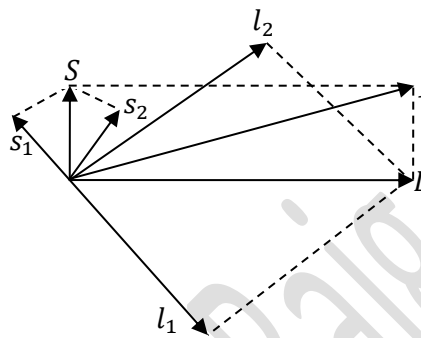

Fig (01)

S is an integer for an even number of electrons and half integer for an odd number of electrons.

$j - j$ Coupling: This type of coupling exists mainly in heavy atoms, in which interaction between spin and orbital vector is strong. In this case, the s_i and l_i of each electron are first coupled to form a j_i. The various j_i then coupled together to form the total angular momentum J. Mathematically,

$$j_i = l_i + s_i \; ; \qquad J = \sum j_i \; ; \text{ Total angular momentum } p_j = \sqrt{J(J + 1)}\hbar$$

Note: In spectroscopic notation, small letters l, s & j and s, p, d, f, g etc. are used to describe the state of the electron and capital letters L, S, J and S, P, D, F, G etc. are used to describe the state of the atom as a whole.
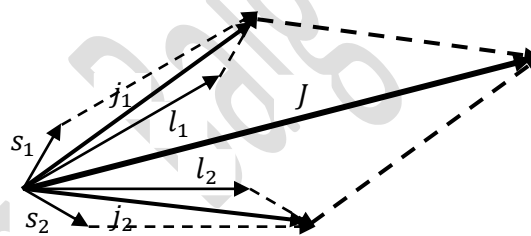
Pauli's Exclusion Principle:

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

　　　　The four quantum numbers n, l, m_l and m_s determine the state of an electron completely. Hence the principle may be state as

　　　　"***No two electrons in an isolated atom may have the same four quantum numbers***".

Explanation: The principle implies that each electron in an atom must have different set of quantum numbers n, l, m_l and m_s. If two electrons have all their quantum numbers identical, then one of those two electrons would be excluded from entering into the constitution of atom. Hence, the name ***exclusive principle***.

Application: This principle enables us to calculate the number of electrons that can occupy a given sub-shell.

　　1) Consider the K-shell with $n = 1, l = 0$ and hence $m_l = 0, m_s = \frac{1}{2}$. Since $s = \frac{1}{2}$, m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. Hence, the K-shell can have two electrons; electron 1 with quantum

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numbers $n = 1, l = 0$, $m_l = 0, m_s = \frac{1}{2}$ and electron 2 with quantum numbers $n = 1, l = 0$, $m_l = 0, m_s = -\frac{1}{2}$. If there were a third electron, its quantum numbers will be identical with those of the first or second electron, which is against Pauli's exclusion principle. Therefore the K-shell is completed or closed with two electrons.

2) For L-shell, $n = 2, l = 0 \; or \; 1$. For sub-shell $n = 2, l = 0$, m_l must be zero and $m_s = +\frac{1}{2} \; or \; -\frac{1}{2}$. Hence there can be only 2 electrons in this subshell. For the subshell $n = 2$, $l = 1$, m_l can have three values $-1, 0, +1$. For each of these three values of m_l, m_s may be either $+\frac{1}{2} \; or \; -\frac{1}{2}$. Hence there will be six possible sets of values for the quantum numbers characterizing the electrons. Therefore the maximum number of electrons in this sub-shell is 6. The L-shell with two subs-hells $[(n = 2, l = 0), \; and \; (n = 2, l = 1)]$ is therefore, completed when it contains $2 + 6 = 8$ electrons.

3) For the M-shell with $n = 3$, there can be three subshells with $l = 0, 1, 2$. The first and second sub-shells are completed by 2 and 6 electrons as explained above. The third sub-shell is completed with $2(2l + 1)$, i.e., 10 electrons since $l = 2$. Hence the total number of electrons required to complete the M-shell is 18.

4) Similarly, the N-shell can have a maximum of 32 electrons.

In general, we get the two following conclusions:

i) In the nth shell there are n subshells corresponding to the values $0, 1, 2, 3, \cdots (n - 1)$ of l. The maximum number of electrons in a sub-shell with a given value of l is $2(l + 1)$.

Orbital Quantum Number (l)	0	1	2	3	4	······
Number of possible electrons	2	6	10	14	18	······
Sub-shell symbols	s	p	d	f	g	······

ii) The number of electrons that can be accommodated in a shell with principal quantum number n = sum of the electrons in the constituent n sub-shells

$$= \sum_{l=0}^{l=n-1} 2(2l + 1) = 2 \sum_{l=0}^{l=n-1}(2l + 1)$$
$$= 2[1 + 3 + 5 + 7 + \cdots \cdots \cdots \cdots \{2(n - 1) + 1\}] = 2n^2$$

The following table shows the distribution of electrons according to this scheme.

Shell symbol	K	L	M	N	O
Quantum Number (n)	1	2	3	4	5
Number of electrons ($2n^2$)	2	8	18	32	50

The distribution of electrons in the various states (shells and sub-shells) according to

Pauli's exclusion principle is given in the following table:

n	l	m_l	m_s	Number of electrons in sub-shell with spectroscopic notations		Total number of electrons in shell $= 2n^2$
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$1s^2$	2
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$2s^2$	8
	1	$-1, 0, +1$	$+\frac{1}{2}, -\frac{1}{2}$	6	$2p^6$	
3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$3s^2$	18
	1	$-1, 0, +1$	$+\frac{1}{2}, -\frac{1}{2}$	6	$3p^6$	
	2	$-2, -1, 0, +1, +2$	$+\frac{1}{2}, -\frac{1}{2}$	10	$3d^{10}$	
4	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$4s^2$	32
	1	$-1, 0, +1$	$+\frac{1}{2}, -\frac{1}{2}$	6	$4p^6$	
	2	$-2, -1, 0, +1, +2$	$+\frac{1}{2}, -\frac{1}{2}$	10	$4d^{10}$	
	2	$-3, -2, -1, 0, +1, +2, +3$	$+\frac{1}{2}, -\frac{1}{2}$	14	$4f^{14}$	

Spectral Terms and their Notations:
Atoms are divided into two main classes:
   i) One electron system and
   ii) Many electron system

One Electron System: Atoms belonging to this class have only **one valence** or **optical electron** e.g., hydrogen and hydrogen like atoms, such as alkali metals. The alkali metals have a single valence electron. The valence electron in the alkali metals [Lithium (Li), Sodium (Na), Potassium (K), Rubidium (RB), Cesium (Cs), and Francium (Fr)] therefore behaves much like orbiting electron in the hydrogen atom. Therefore, *alkali metals have a hydrogen like spectra*. Hence, the spectrum of alkali metals is also known as the **one-electron spectra**.

Many Electrons System: Atoms belonging to this class have more than one electron i.e., several free electrons not interlocked in closed shells. Hence, they are responsible for fixing the spectral properties. The alkaline earths [The alkaline earth metals are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra)], belongs to the two-electron system, aluminum, scandium etc., belong to the three-electron system, titanium belong to the four-electron system.

Spectral Notations:

The electronic configuration of an atom is the distribution of electrons in various subshells around the nucleus of the atom. In describing the electron configuration, small letters are used to represent the values of l as follows:

$l =0$	1	2	3	4	5	....
s	p	d	f	g	h	

i.e., if an electron is in a shell for which $l = 0$, it is called an s electron, for $l = 1$, a p electron and so on. The value of the principal quantum number n is written as a prefix to the letter representing its value. For example, a state in which $n = 2, l = 0$ is a $2s - $ state; $n = 4, l = 2$ is a $4d - $ state and so on. The number of electrons having the same n and l values is indicated by an index written at the upper right of the letter representing their l value. Thus the 11 electrons of sodium in the normal state are designated as follows: $1s^2\ 2s^2\ 2p^6\ 3s$ i.e., there are two $1s$ electrons, two $2s$ electrons, six $3p$ electrons and one $3s$ electron. We shall now consider electron configuration of a few elements.

1) **Hydrogen $(z = 1)$:** The normal state of a an atom is one in which all the electrons are in the lowest possible energy levels. In hydrogen, the normal state is characterized by the quantum numbers $n = 1, l = 0, m_l = 0\ and\ m_s$ may be either $+\frac{1}{2}$ or $-\frac{1}{2}$. The symbolic representation is $1s$. The K-shell requires one electron to be completed. Hence atomic hydrogen is very active chemically.

2) **Helium $(Z = 2)$:** It has both its electrons in the shell $n = 1, l = 0,\ and\ m_s = +\frac{1}{2}$ for one electron and $-\frac{1}{2}$ for the second electron. The symbolic representation is $\boxed{1s^2}$. This shell is now complete or closed. The rectangular enclosure indicates that the electrons are interlocked in a closed shell. Therefore, helium may be expected to have a very stable configuration. This should be true of all other inert gases.

3) **Lithium $(Z = 3)$:** It has three electrons. Two electrons can be put in the shell $n = 1$. The third electron must be put into a new shell $n = 2, l = 0$. So the neutral lithium atom is represented by $1s^2\ 2s$. Lithium is one of the alkali elements and has a valence of unity. This means that the valance $2s$ electron can be detached easily form the atom to form the lithium ion Li^+. This is indicated by the fact that its ionization potential is only 5.9 volt, where as for He it is 54.58 volt. Lithium is chemically quite active and its monovalent. Similarly, all alkali metals (Na, K, Rb, Cs) have one electron in their outermost shell and hence are monovalent having similar chemical properties.

4) **Beryllium $(Z = 4)$:** It has two electrons in the completed K-shell (n=1). It has two additional electrons in the $(n = 2$ and $l = 0)$ subshell. It is represented by $1s^2\ 2s^2$. Beryllium is one of the alkaline earth elements with a valence of 2. Its optical spectrum is that of two electron atom. The atoms of the other elements of the group (Mg, Ca, Sr, Ba, Ra), should have similar structures. They have two electrons outside an inert gas or closed shell configuration. They have very similar chemical and physical properties.
   Similarly the electronic configuration from boron (Z=5) to neon (Z=10) are:
   a) Boron$(Z = 5)$: $1s^2\ 2s^2\ 2p$

b) Carbon $(Z = 6): 1s^2\, 2s^2\, 2p^2$
c) Nitrogen $(Z = 7): 1s^2\, 2s^2\, 2p^3$
d) Oxygen $(Z = 8): 1s^2\, 2s^2\, 2p^4$
e) Fluorine $(Z = 9): 1s^2\, 2s^2\, 2p^5$
f) Neon $(Z = 10): 1s^2\, 2s^2\, 2p^6$

In neon, both the $n = 1$ and $n = 2$ shells are completed. Neon is one of the inert gases and has a very stable configuration.

The next eight elements from sodium (Z=11) to argon (Z=18) are formed by adding the additional electrons to the M shell for which $n = 3$

a) Sodium $(Z = 11): \boxed{1s^2\, 2s^2\, 2p^6}\, 3s$. Sodium has an electron ($3s$ electron) outside a closed shell. The single electron, like that of lithium, is easily ionized; the valence is 1; the spectrum is that of one electron atom.

b) Magnesium $(Z = 12): \boxed{1s^2\, 2s^2\, 2p^6}\, 3s^2$. The two electrons in the outermost incomplete shell (n=3) are the valence electrons making Mg divalent.

Aluminium: $(Z = 13): \boxed{1s^2\, 2s^2\, 2p^6}\, 3s^3$. Al is trivalent.

Derivation of Total Magnetic Moment of an electron in an atom (or Lande's g-factor or Lande's splitting factor):

The total angular momentum $\vec{J}$ of an electron in an atom is the vector sum of the orbital angular momentum $\vec{L}$ and spin angular momentum $\vec{S}$ i.e.,

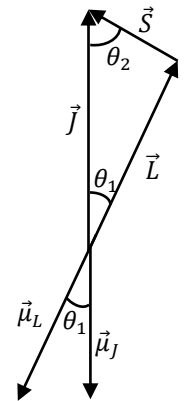$$\vec{J} = \vec{L} + \vec{S} \qquad (01)$$

where
$$|\vec{L}| = L = \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\hbar,$$
$$|\vec{S}| = S = \sqrt{s(s+1)}\,\frac{h}{2\pi} = \sqrt{s(s+1)}\hbar,$$
$$|\vec{J}| = J = \sqrt{j(j+1)}\,\frac{h}{2\pi} = \sqrt{j(j+1)}\hbar,$$

Let $\vec{\mu}_L$, $\vec{\mu}_S$ and $\vec{\mu}_J$ be the magnetic dipole moments associated with orbital angular momentum $\vec{L}$, spin angular momentum $\vec{S}$ and total angular momentum $\vec{J}$ respectively.

Now, $\vec{\mu}_J$ will be the sum of components of $\vec{\mu}_L$ and $\vec{\mu}_S$ in the direction of $\vec{\mu}_J$ i.e.,
$$\vec{\mu}_J = \vec{\mu}_L \cos\theta_1 + \vec{\mu}_S \cos\theta_2$$
Considering the magnitudes, we have
$$\mu_J = \mu_L \cos\theta_1 + \mu_S \cos\theta_2 \qquad (02)$$
From equation (01), we have
$$\vec{S} = \vec{J} - \vec{L}$$
$$\vec{S} \cdot \vec{S} = (\vec{J} - \vec{L}) \cdot (\vec{J} - \vec{L})$$
$$S^2 = \vec{J} \cdot \vec{J} - \vec{L} \cdot \vec{J} - \vec{J} \cdot \vec{L} + \vec{L} \cdot \vec{L}$$
$$S^2 = J^2 + L^2 - 2\vec{L} \cdot \vec{J}$$
$$S^2 = J^2 + L^2 - 2LJ \cos\theta_1$$
$$\cos\theta_1 = \frac{J^2 + L^2 - S^2}{2JL}$$

$$\cos\theta_1 = \frac{\left(\sqrt{j(j+1)}\hbar\right)^2 + \left(\sqrt{l(l+1)}\hbar\right)^2 - \left(\sqrt{s(s+1)}\hbar\right)^2}{2\sqrt{j(j+1)}\hbar \times \sqrt{l(l+1)}\hbar}$$

$$\cos\theta_1 = \frac{j(j+1) + l(l+1) - s(s+1)}{2\sqrt{j(j+1)} \times \sqrt{l(l+1)}} \qquad (04)$$

Again from equation (01), we have

$$\vec{L} = \vec{J} - \vec{S}$$
$$\vec{L} \cdot \vec{L} = (\vec{J} - \vec{S}) \cdot (\vec{J} - \vec{S})$$
$$L^2 = \vec{J} \cdot \vec{J} - \vec{S} \cdot \vec{J} - \vec{J} \cdot S + \vec{S} \cdot \vec{S}$$
$$L^2 = J^2 + S^2 - 2\vec{S} \cdot \vec{J}$$
$$L^2 = J^2 + S^2 - 2SJ\cos\theta_2$$
$$\cos\theta_2 = \frac{J^2 + S^2 - L^2}{2JS}$$

$$\cos\theta_2 = \frac{\left(\sqrt{j(j+1)}\hbar\right)^2 + \left(\sqrt{s(s+1)}\hbar\right)^2 - \left(\sqrt{l(l+1)}\hbar\right)^2}{2\sqrt{j(j+1)}\hbar \times \sqrt{s(s+1)}\hbar}$$

$$\cos\theta_2 = \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)} \times \sqrt{s(s+1)}} \qquad (05)$$

Orbital angular moment $\vec{\mu}_L$ is given by

$$\vec{\mu}_L = -\frac{e}{2m}\vec{L} \quad \text{or} \quad \mu_L = \frac{e}{2m}L$$
$$\mu_L = \frac{e}{2m}\sqrt{l(l+1)}\hbar = \frac{e\hbar}{2m}\sqrt{l(l+1)}$$
$$\mu_L = \mu_B\sqrt{l(l+1)} \qquad (06)$$

where $\mu_B = \frac{e\hbar}{2m} = \frac{eh}{4\pi m} = 9.2741 \times 10^{-24}\, JT^{-1}$ is Bohr's magneton.

Similarly, spin angular moment $\vec{\mu}_S$ is given by

$$\vec{\mu}_S = -2\left(\frac{e}{2m}\right)\vec{L} \quad \text{or} \quad \mu_S = 2\left(\frac{e}{2m}\right)L$$
$$\mu_S = \frac{2e}{2m}\sqrt{s(s+1)}\hbar = \frac{2e\hbar}{2m}\sqrt{s(s+1)}$$
$$\mu_L = 2\mu_B\sqrt{s(s+1)} \qquad (07)$$

where $\mu_B = \frac{e\hbar}{2m} = \frac{eh}{4\pi m} = 9.2741 \times 10^{-24}\, JT^{-1}$ is Bohr's magneton.

Substituting equations (04), (05), (06) and (07) in equation (02), we get

$$\mu_J = \mu_B\sqrt{l(l+1)}\left\{\frac{j(j+1)+l(l+1)-s(s+1)}{2\sqrt{j(j+1)} \times \sqrt{l(l+1)}}\right\} + 2\mu_B\sqrt{s(s+1)}\left\{\frac{j(j+1)+s(s+1)-l(l+1)}{2\sqrt{j(j+1)} \times \sqrt{s(s+1)}}\right\}$$

$$\mu_J = \mu_B\left\{\frac{j(j+1)+l(l+1)-s(s+1)}{2\sqrt{j(j+1)}}\right\} + 2\mu_B\left\{\frac{j(j+1)+s(s+1)-l(l+1)}{2\sqrt{j(j+1)}}\right\}$$

$$\mu_J = \mu_B\left\{\frac{j(j+1)+l(l+1)-s(s+1)}{2\sqrt{j(j+1)}}\right\} + \mu_B\left\{\frac{2j(j+1)+2s(s+1)-2l(l+1)}{2\sqrt{j(j+1)}}\right\}$$

$$\mu_J = \mu_B\left\{\frac{2j(j+1)+j(j+1)-l(l+1)+s(s+1)}{2\sqrt{j(j+1)}}\right\}$$

$$\mu_J = \mu_B\left\{\frac{2j(j+1)+j(j+1)-l(l+1)+s(s+1)}{2\sqrt{j(j+1)}}\right\} \times \frac{\sqrt{j(j+1)}}{\sqrt{j(j+1)}}$$

$$\mu_J = \mu_B\sqrt{j(j+1)}\left\{\frac{2j(j+1)+j(j+1)-l(l+1)+s(s+1)}{2j(j+1)}\right\}$$

$$\mu_J = \mu_B\sqrt{j(j+1)}\left\{\frac{2j(j+1)}{2j(j+1)} + \frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)}\right\}$$

$$\mu_J = \mu_B\sqrt{j(j+1)}\left\{1 + \frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)}\right\}$$

$$\boxed{\mu_J = \mu_B\sqrt{j(j+1)}\,g_J}$$

where $g_J = \left\{1 + \frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)}\right\}$ is called **Lande's g-factor** or **Lande's splitting factor**.

Larmor's Theorem: "***The effect of a magnetic field on an electron moving in an orbit is to superimpose on the orbital motion a precessional motion of the entire orbit about the direction of the magnetic field with angular velocity ω given by $\omega = Be/2m$***" where B the magnetic field strength, e is the charge of electron and m the mass of electron.

Explanation: Fig (01) shows two positions of the vector $\vec{l}$ as it precesses about the magnetic field at constant inclination and the corresponding positions of the electronic orbit.

Fig (01)

Just as mechanical top precesses in a gravitational field, an electron in an orbit precesses in a magnetic field. This is called Larmor precession.
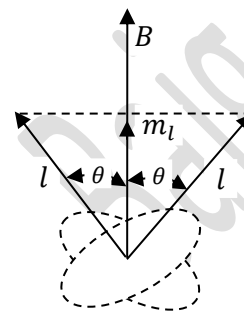
Zeeman Effect:

       Zeeman effect is a magneto-optical phenomenon discovered by Peter Zeeman in 1896. Zeeman discovered that if a source of light producing line spectrum is placed in strong magnetic field the spectral lines are split up into components – doublet or triplets or even more arrangement. This phenomenon is called Zeeman effect.

       "***The phenomenon of splitting of lines produced by a light source kept in an external magnetic field is called Zeeman effect***".

       "***When a source of radiation, giving line spectrum is placed in a magnetic field, the spectral lines are split up into a number of component lines, symmetrically distributed about the original line. Doublets, triplets and even more complex systems are observed. This phenomenon is called Zeeman effect***".

       If the magnetic field is very strong, each spectral line is split up into two components in the longitudinal view and in three components in transverse view. This is known as ***Normal Zeeman Effect***.

       If the magnetic field is comparatively weak, each line splits into more than three components. This is known as ***Anomalous Zeeman Effect***.

       If electron spin is involved in the Zeeman effect, then it is called the **Anomalous Zeeman Effect**.

       If electron spin is not involved, then it called the **Normal Zeeman Effect**. Normal Zeeman Effect is obtained from sources of elements like $Ca, Cu, Zn, Cd \ etc$.

Distinction is made between Normal and Anomalous Zeeman Effects, and also the **longitudinal** and **transverse effects**.

Experimental Study of Zeeman Effect:

An experimental arrangement to produce and observe Zeeman Effect is shown in fig (01). MM is an electromagnet capable of producing a very strong magnetic field. It has conical pole-pieces PP through which holes have been drilled lengthwise. A light source L emitting spectral lines (say, a sodium vapour lamp) is placed between the pole-pieces PP. The spectral lines are observed with a high resolving power spectrograph S. The Zeeman Effect may be observed into two ways:
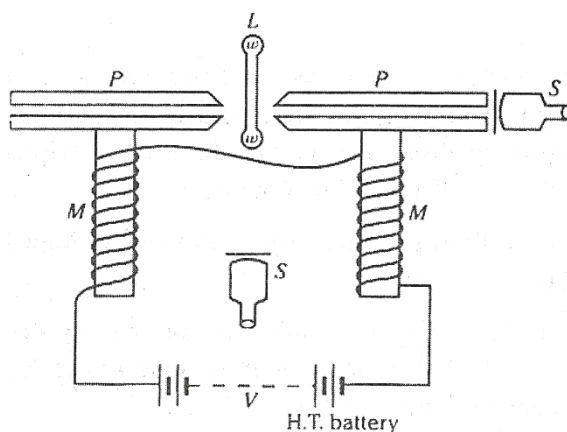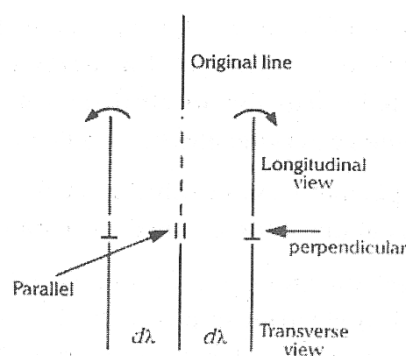

Fig (01)   Fig (02)

1) Perpendicular to the direction of magnetic field: In this case, a single spectral line is observed when no field is applied, and splits up into three components when magnetic field is applied i.e., a **triplet** is observed. The central line has the same wave length as the original line and is plane polarized with the vibrations parallel to the field. The displacement of either outer line from the central line is known as the **Zeeman Effect**. The outer two lines that are situated symmetrically on either side are also **plane polarized**, having vibrations in direction perpendicular to the field. This is also known as **Normal Transverse Zeeman Effect**.

2) Parallel to the direction of magnetic field: To observe the Zeeman Effect, a hole is drilled through one of the pole-pieces and light coming from the source through the hole is examined with the spectrograph. In this case, a single spectral line is split up into two components when the magnetic field is applied i.e., a **doublet** is observed. Both the lines are found to be symmetrically situated about the position of the parent line, and are **circularly polarized** in opposite directions. This is known as **Normal Longitudinal Zeeman Effect**.

The displacement in the two cases are proportional to the strength of the magnetic field and are equal for the same values of magnetic field as shown in fig (02).

Lorentz Classical Theory of Normal Zeeman Effect:

The emission of light by glowing gas is due to the vibratory motion of electrons. The electrons in the atom execute simple harmonic vibration about the centre of the atom. The frequency of spectral line is given by the frequency of vibration of the electron. Any linear motion of the electron can be resolved into three components – (i) a linear motion along the direction of magnetic field and (ii) two opposite circular motions perpendicular to the direction of the field. Since no force acts on the charged particle when its linear motion is along the direction of the field the frequency of this component remains the same by the magnetic field.

The other two circular components are affected by the magnetic field, one being retarded and the other being accelerated. Hence the frequency of one of these circular components is increased and that of the other is decreased by the same amount.

In longitudinal view, the unaltered linear component along the field gives no light waves along the direction of observation due to the transverse nature of light vibrations. Hence original line is not observed. The two altered components at right angles to the field produce **circularly polarized waves**. This explains the Longitudinal Zeeman Effect.

In the transverse view, the unaltered linear component sends out vibrations parallel to the field and perpendicular to the direction f observation. This gives the central line of the triplets. The two circular vibrations which are altered in frequency produce vibrations perpendicular to the field and when viewed sideways appear as **plane polarized vibrations** in opposite directions.
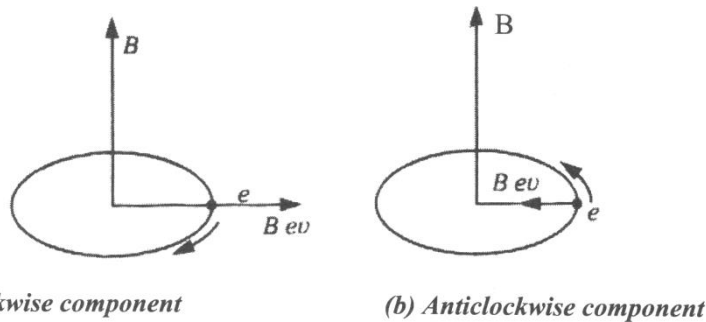
Expression for Normal Zeeman Shift:

(a) Clockwise component   *(b) Anticlockwise component*

Fig (03)

Consider an electron of mass m_e in the atom moving in a circular orbit of radius r with a linear velocity v and angular velocity ω.

The centripetal force acting on the revolving electron is given by

$$F = \frac{m_e v^2}{r} = m_e \omega^2 r \qquad (\because \ v = \omega r) \qquad (01)$$

Let a magnetic field of flux density B be applied in a direction perpendicular to the plane of the orbit. Then an additional force of magnitude $= Bev$ acts on the electron.

According to Flemming's left hand rule, the direction of this force will be towards or away from the centre, according as the election motion is clockwise or anti-clockwise. If the additional force is away from the centre, the orbit expands and hence frequency decrease. This force is added or subtracted from the attractive force, so that in the new state of dynamic equilibrium;

$$F \pm Bev = m_e(\omega + \delta\omega)^2 r \qquad (02)$$

For the circular motion in the anti-clockwise direction,

$$F - Bev = m_e(\omega + \delta\omega)^2 r$$
$$m_e \omega^2 r - Bev = m_e(\omega + \delta\omega)^2 r \qquad (\because \ F = m\omega^2 r)$$
$$m_e \omega^2 r - m_e(\omega + \delta\omega)^2 r = Be\omega r \qquad (\because \ v = \omega r)$$

Neglecting $(\delta\omega)^2$, we get

$$-2m_e r\omega\delta\omega = Be\omega r$$

or $\qquad \delta\omega = -\dfrac{Be}{2m_e} \qquad\qquad (03)$

For circular motion, in the anti-clockwise direction

$$F + Bev = m_e(\omega + \delta\omega)^2 r$$
$$m_e\omega^2 r + Bev = m_e(\omega + \delta\omega)^2 r \qquad (\because F = m\omega^2 r)$$
$$m_e\omega^2 r - m_e(\omega + \delta\omega)^2 r = -Be\omega r \qquad (\because v = \omega r)$$

Neglecting $(\delta\omega)^2$, we get
$$-2m_e r\omega\delta\omega = -Be\omega r$$
or $\qquad \delta\omega = +\dfrac{Be}{2m_e}$ $\hspace{4cm}$ (04)

Combining equations (03) and (04), we have
$$\delta\omega = \pm\frac{Be}{2m_e} \hspace{4cm} (05)$$

If ν is the frequency of vibration of the electron,
$$\nu = \frac{\omega}{2\pi} \qquad\text{or}\qquad \delta\nu = \frac{\delta\omega}{2\pi} \hspace{3cm} (06)$$

Change in frequency of spectral line is given by

Zeeman Shift $\qquad \delta\nu = \pm\dfrac{Be}{4\pi m_e}$ $\hspace{3.5cm}$ (07)

If ν and λ are the frequency and wavelength of the original line,
$$\nu = \frac{c}{\lambda} \qquad\text{or}\qquad \delta\nu = -\frac{c}{\lambda^2}\delta\lambda$$
$$\delta\lambda = -\frac{\delta\nu}{c}\lambda^2 \hspace{4cm} (08)$$

$\therefore$ $\qquad\boxed{\boldsymbol{Zeeman\ Shift\ \delta\lambda = \pm\dfrac{Be\lambda^2}{4\pi m_e c}}}$

The value of e/m determined by this method is $1.77 \times 10^{11}\ C\ kg^{-1}$. It is same as determined by J. J. Thomson for cathode rays.

Quantum Mechanical Explanation of Normal Zeeman Effect:

According to quantum theory, an electron around a nucleus describes a path characterized by
1) Principal quantum number (n)
2) Orbital angular quantum number (l)
3) Magnetic quantum number (m_l) and
4) Spin quantum number (s)

Debye explained the normal Zeeman effect on the basis of quantum theory without taking into consideration the electron spin.

We know that the atom is equivalent to tiny magnet. When the atom is placed in a magnetic field, it experiences a torque which causes the electron orbit to precess about the direction of field $\vec{B}$. This precession is known as Larmor's precession and its angular frequency is given by
$$\omega_l = \frac{Be}{2m_e} \hspace{4cm} (01)$$

So, the new angular frequency of the electron becomes
$$\omega_0 + \omega_l = \omega_0 + \frac{Be}{2m_e} \hspace{3.5cm} (02)$$

where ω_0 is the angular frequency of the electron in absence of magnetic field. The K.E. of the electron in absence of magnetic field is

$$E_0 = \frac{1}{2}m_e v_0^2 = \frac{1}{2}m_e r^2 \omega_0^2 \tag{03}$$

In presence of magnetic field, the kinetic energy of electron is given by

$$E_B = \frac{1}{2}m_e r^2 \left(\omega_0 + \frac{Be}{2m_e}\right)^2 \tag{04}$$

Therefore, the change in K.E. due to Larmor's precession is

$$\delta E = E_B - E_0 = \frac{1}{2}m_e r^2 \left(\omega_0 + \frac{Be}{2m_e}\right)^2 - \frac{1}{2}m_e r^2 \omega_0^2$$

$$= \frac{1}{2}m_e r^2 \omega_0^2 \left(1 + \frac{Be}{2m_e \omega_0}\right)^2 - \frac{1}{2}m_e r^2 \omega_0^2$$

$$\delta E \approx \frac{1}{2}m_e r^2 \omega_0^2 \left(1 + \frac{2Be}{2m_e \omega_0}\right) - \frac{1}{2}m_e r^2 \omega_0^2$$

$$\approx \frac{1}{2}m_e r^2 \omega_0^2 + m_e r^2 \omega_0^2 \frac{Be}{2m_e \omega_0} - \frac{1}{2}m_e r^2 \omega_0^2$$

$$\delta E \approx m_e r^2 \omega_0 \frac{Be}{2m_e} \approx p_l \frac{Be}{2m_e} \tag{05}$$

where $p_l = m_e r^2 \omega_0$ is the original angular momentum.

Here we have assumed that the axis of p_l is parallel to the magnetic field $\vec{B}$. But if the direction of p_l makes an angle θ with $\vec{B}$, then

$$\delta E = p_l \frac{Be}{2m_e} \cos\theta \tag{06}$$

We know that magnetic quantum number $m_l = l \cos\theta$ and $p_l = l(h/2\pi)$

$$\delta E = \frac{lh}{2\pi} \cdot \frac{Be}{2m_e} \cdot \frac{m_l}{l} = m_l \frac{h}{2\pi} \cdot \frac{Be}{2m_e} = m_l \left(\frac{eh}{4\pi m_e}\right) B \tag{07}$$

Here m_l can take $(2l + 1)$ values in all. This shows that an external magnetic field split a single energy level into $(2l + 1)$ levels. The amount of splitting is proportional to $\vec{B}$. This is Normal Zeeman Effect.

Selection Rules:

According to selection rules only those transitions are allowed for which m_l changes by 0 or ± 1, i.e., $\Delta m_l = 0, \pm 1$. Accordingly, from equation (07), we have

$$\delta E = 0, \pm \left(\frac{eh}{4\pi m_e}\right) B$$

$$\delta\nu = \frac{\Delta E}{h} = 0, \pm \left(\frac{e}{4\pi m_e}\right) B$$

Thus original line of frequency ν_0 splits up into three components in transverse view

$$\nu_0, \quad \nu_1 = \nu_0 + (e/4\pi m_e)B \quad and \quad \nu_2 = \nu_0 - (e/4\pi m_e)B$$

one being the original one and the other two are on either side of it at equal distances.

Application of Zeeman Effect:

Using Zeeman effect, the specific charge (e/m_0) of the electron can be obtained. When the source is placed in the magnetic field, the change in frequency $d\nu$ of the spectral line is given by

$$\delta\nu = \frac{eB}{4\pi m_e}$$

If λ be the wavelength of spectral line, then $\nu = c/\lambda$ and $d\nu = -\left(\frac{c}{\lambda^2}\right) d\lambda$

$$\therefore \quad \delta\lambda = \frac{\lambda^2}{c}\delta\nu = \frac{\lambda^2}{c} \times \frac{eB}{4\pi m_e} = \frac{eB\lambda^2}{4\pi m_e c} \qquad \text{(numerically)}$$

so
$$\frac{e}{m_e} = \frac{4\pi c}{B}\left(\frac{d\lambda}{\lambda^2}\right)$$

Hence by measuring the wavelength change, e/m_0 can be calculated. The calculated value comes out to be 1.757×10^{11} $coulomb\ per\ kg$. This is in agreement with the value obtained by Thomson's experiment.

Anomalous Zeeman Effect:

The Anomalous Zeeman Effect is observed when the energy levels involved in the emission of spectral lines have fine structure (i.e., when they are not singlet). A spectral line is found to split up into three components under the influence of weak magnetic field. This type of splitting is known as **Anomalous Zeeman Effect**.

"***The phenomenon of splitting up of a single line into four or more spectral lines when observed in a direction perpendicular to the magnetic field, is known as Anomalous Zeeman Effect***".

It is called Anomalous Zeeman Effect, because it could not be explained on the basis of classical physics. Anomalous Zeeman Effect is obtained from sources of elements like $Na, Cr\ etc.$

Quantum Theory of Anomalous Zeeman Effect:

The quantum mechanical explanation of anomalous Zeeman Effect is based upon the concept of 'spin of the electron'. An atom possesses a magnetic moment, because of its electrons have orbital (L) and spin (S) angular momenta and associated magnetic moments. The resultant angular momentum $\vec{J} = \vec{L} + \vec{S}$ precesses about the direction of magnetic field.

The magnetic moment due to orbital motion of the electron is given by

$$\overrightarrow{\mu_L} = \vec{L}\frac{eh}{4\pi m_e} = \left(\frac{e}{2m_e}\right)\overrightarrow{p_L} \qquad (01)$$

Fig (01)

where $\overrightarrow{\mu_L}$ is directed opposite to $\vec{L}$ because of the negative charge of electron.

Similarly, the magnetic moment due to spin of the electron is given by

$$\overrightarrow{\mu_S} = 2\vec{S}\frac{eh}{4\pi m_e} = \left(\frac{e}{m_e}\right)\overrightarrow{p_S} \qquad (02)$$

$\overrightarrow{\mu_S}$ is oppositely directed to $\vec{S}$ because of the negative charge of the electron.

The resultant magnetic moment is not along $\vec{J}$. Since $\vec{L}$ and $\vec{S}$ precess about $\vec{J}$, $\overrightarrow{\mu_L}$ and $\overrightarrow{\mu_S}$ also precess about $\vec{J}$. Each of the magnetic moments $\overrightarrow{\mu_L}$ and $\overrightarrow{\mu_S}$ is resolved into two components, one along J and the other perpendicular to J as shown in fig (01). The value of perpendicular component of each vector, averaged over a period of the motion will be zero, since it is continuously changing direction. The resultant magnetic moment of electron is given by

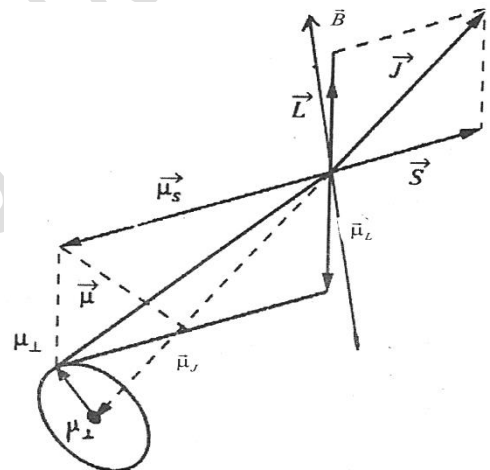$$\begin{Bmatrix} Resultant\ magnetic \\ moment\ of\ the\ electron \\ \mu_J \end{Bmatrix} = \begin{Bmatrix} Component\ of\ \mu_L\ along \\ the\ direction\ of\ \vec{J} \end{Bmatrix} + \begin{Bmatrix} Component\ of\ \mu_S\ along \\ the\ direction\ of\ \vec{J} \end{Bmatrix}$$

$$\mu_J = \mu_L \cos(\vec{L},\vec{J}) + \mu_S \cos(\vec{S},\vec{J})$$

$$\mu_J = \frac{eh}{4\pi m_e}\left[\vec{L}\cos(\vec{L},\vec{J}) + 2\vec{S}\cos(\vec{S},\vec{J})\right] \qquad (03)$$

But according to cosine law,

$$\cos(\vec{L},\vec{J}) = \frac{L^2 + J^2 - S^2}{2LJ}$$

and

$$\cos(\vec{S},\vec{J}) = \frac{S^2 + J^2 - L^2}{2SJ}$$

hence

$$\mu_J = \frac{eh}{4\pi m_e}\left[\frac{L^2 + J^2 - S^2}{2J} + \frac{S^2 + J^2 - L^2}{J}\right]$$

$$= \frac{eh}{4\pi m_e}\left[\frac{L^2 + J^2 - S^2 + 2S^2 + 2J^2 - 2L^2}{2J}\right]$$

$$= \frac{eh}{4\pi m_e}\left[\frac{3J^2 + S^2 - L^2}{2J}\right]$$

$$= \frac{eh}{4\pi m_e}J\left[\frac{3J^2 + S^2 - L^2}{2J^2}\right]$$

$$= \frac{eh}{4\pi m_e}J\left[\frac{J^2 + 2J^2 + S^2 - L^2}{2J^2}\right]$$

$$= \frac{eh}{4\pi m_e}J\left[1 + \frac{J^2 + S^2 - L^2}{2J^2}\right] \qquad (04)$$

$$\mu_J = \frac{eh}{4\pi m_e}Jg \qquad (05)$$

where

$$g = 1 + \frac{J^2 + S^2 - L^2}{2J^2} = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad (06)$$

is called **Lande 'g' factor**. It determines the splitting of energy levels in presence of a weak magnetic field and shows that the splitting is determined by the values of $\vec{L}, \vec{S}$ & $\vec{J}$.

Note that $J^2 = J(J+1)$, $S^2 = S(S+1)$ and $L^2 = L(L+1)$

When atom is placed in weak magnetic field, the total angular momentum vector $\vec{J}$ precesses about the direction of the magnetic field axis.

The change in energy under the action of magnetic field is given by

$$\Delta E = \mu_J B \cos(\vec{J},\vec{B})$$

$$\Delta E = \frac{eh}{4\pi m_e}JgB\cos(\vec{J},\vec{B}) \qquad (07)$$

Since, $J\cos(\vec{J},\vec{B})$ = projection of vector $\vec{J}$ on the direction of the magnetic field = m_J

∴

$$\Delta E = \frac{eh}{4\pi m_e}gBm_J \qquad (08)$$

The quantity $\frac{eh}{4\pi m_e}B$ is called **Lorentz unit**. It is a unit of energy used for expressing the splitting of the energy levels in a magnetic field.

Since m_J has $(2J+1)$ values, a given energy level is split up into $(2J+1)$ sub energy levels with the application of magnetic field. The transitions between the split energy levels are governed by the selection rule:

$$\Delta m_J = 0, \pm 1$$

The give rise the magnetic splitting of spectral lines. The number of components into which a spectral line splits up is in general different from that expected (two or three) when the electron spin is not considered (normal Zeeman effect). Hence it is known as **anomalous Zeeman effect**.

Stark Effect:

Soon after the discovery of Zeeman effect, a similar resolution of spectral lines in an electric field was looked for. The action of an electric field on the spectrum of hydrogen was discovered by Stark (in 1913) who observed the splitting of Balmer lines.

"***The splitting of spectral lines due to the action of external electric field is called Stark effect***".

The Stark effect was discovered many years after the Zeeman effect. The main practical difficulty with the earlier investigators was the absence of a proper technique. The chief aim was to subject hydrogen atoms emitting spectral lines to a powerful electric field. This was not possible with ordinary Geissler tube containing hydrogen since the gas in such a tube is comparatively a good conductor and hence incapable of maintaining a strong electric field. Stark overcame this difficulty with a specially designed apparatus.

Experimental Arrangement:

The experimental arrangement is shown in fig (01). Stark placed an auxilliary electrode F close behind the cathode C at a distance of few millimeters. The canal rays are produced in an ordinary discharge tube whose cathode is perforated. A high potential difference is applied between cathode C and electrode
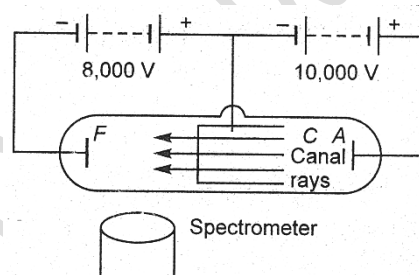

Fig (01)

F to produce a strong electric field of about 10^7 V/m between F and C. The spectrum is studied by a high resolving power spectrometer.

The main features observed in case of Balmer series of hydrogen spectrum are:

1) Every line splits up into a number of sharp components.
2) All hydrogen lines form symmetrical pattern. The pattern depends markedly on the quantum number n of the term involved. The number of lines and total width of the pattern increases with increase of n. Thus, the number of components of H_β line is greater than those of H_α; similarly the number components of H_γ is greater than those of H_β.
3) The wave number differences are integral multiples of a unit which is proportional to E. It is same for all hydrogen lines.
4) Observations perpendicular to the direction of electric field show that the components are polarized, some parallel to the direction of field strength and the other perpendicular to field strength.
5) Up to the electric fields of about 10^7 V/m, the resolution increases in proportional to the field strength. In this region, we have linear Stark effect. In case of more intense field, more complicated effects, so called quadratic Stark effect and even higher orders are observed in addition to linear effect.

Explanation of Stark Effect:

In 1916, Schwarzschild and Epstein explained Stark effect using Bohr-Sommerfeld atom model including the idea of spatial quantization. Accordingly, the circular and elliptical orbits of single electron revolving around the nucleus in hydrogen atom are described by three

quantum numbers referring to their, shape, size and orientation respectively. So, the total quantum number is made up of three component numbers. The external electric field distorts these electron orbits in a rather complicated way. Now the orbits are no longer circular or elliptical. When a hydrogen atom is in a homogenous electric field E along Z-direction, a perturbation energy $-eEz$ is added to the coulomb energy in the potential energy term of Schrödinger equation. This results in a first order change in energy given by $-eEz$ where z depends on the electric orbit and its eccentricity.

Solved Problems

1) The experimental value of the Bohr magneton is $\mu_B = 9.21 \times 10^{-24} \, JT^{-1}$ and Planck's constant is $h = 6.6 \times 10^{-34} \, Js$. Calculate the value of e/m of an electron.

Solu: Given: Bohr magneton is $\mu_B = 9.21 \times 10^{-24} \, JT^{-1}$

Planck's constant is $h = 6.6 \times 10^{-34} \, Js$

$e/m = ?$

Bohr magneton is given by

$$\mu_B = \frac{eh}{4\pi m}$$

or

$$\frac{e}{m} = \frac{4\pi \mu_B}{h}$$

or

$$\frac{e}{m} = \frac{4\pi \times 9.21 \times 10^{-24}}{6.6 \times 10^{-34}}$$

$\therefore \quad \boxed{\frac{e}{m} = 1.754 \times 10^{11} \, Ckg^{-1}}$

2) What magnetic field is required to observe normal Zeeman effect if a spectrometer can resolve spectral lines separated by $1 \, \mathring{A}$ at $10000 \, \mathring{A}$.

Solu: Given: Wavelength of spectral line $\lambda = 10000 \, \mathring{A} = 1 \times 10^{-6} \, m$

Change in wavelength $\Delta\lambda = 1 \, \mathring{A} = 1 \times 10^{-10} \, m$

Speed of light $c = 3 \times 10^8 \, ms^{-1}$

Magnetic field strength $B = ?$

We know that

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

$$dE = -\frac{hc}{\lambda^2} d\lambda$$

$$|d\lambda| = -\frac{\lambda^2 |dE|}{hc}$$

$$\frac{|d\lambda|}{\lambda} = -\frac{|dE|}{hc/\lambda} \qquad (01)$$

From the theory of Zeeman effect,

$$dE = \frac{ehB}{4\pi m} \qquad (02)$$

From equations (01) and (02), we can write

$$\frac{|d\lambda|}{\lambda} = -\frac{ehB/4\pi m}{hc/\lambda}$$

$$B = \frac{|d\lambda|}{\lambda} \times \frac{c}{\lambda} \times \frac{4\pi m}{e}$$

$$B = \frac{10^{-10}}{10^{-6}} \times \frac{3\times10^8}{10^{-6}} \times \frac{4\pi\times9.1\times10^{-31}}{1.6\times10^{-19}}$$

$$\boxed{B = 2.14\ T}$$

OR

Zeeman Shift is given by

$$B = \frac{4\pi m_e c\ d\lambda}{e\lambda^2}$$

$$B = \frac{4\pi\times9.1\times10^{-31}\times3\times10^8\times 10^{-10}}{1.6\times10^{-19}\times(10^{-6})^2}$$

$$\boxed{B = 2.14\ T}$$

3) Calculate the Zeeman effect shift observed in the normal Zeeman effect when a spectral line of wavelength $600\ nm$ is subjected to the magnetic field of $0.5\ T$. Given $e/m = 1.76 \times 10^{11}\ Ckg^{-1}$.

Solu: Given: Wavelength $\lambda = 600\ nm = 6 \times 10^{-7}\ m$

Magnetic field strength $B = 0.5\ T$

Speed of light $c = 3 \times 10^8\ ms^{-1}$

Specific charge of an electron $e/m = 1.76 \times 10^{11}\ Ckg^{-1}$

Zeeman shift $\Delta\lambda =?$

We known that Zeeman shift is

$$d\lambda = \frac{Be\lambda^2}{4\pi m_e c}$$

$$d\lambda = \frac{B(e/m_e)\lambda^2}{4\pi c}$$

$$d\lambda = \frac{0.5\times1.76\times10^{11}\times(6\times10^{-7})^2}{4\pi\times3\times10^8}$$

$$\boxed{d\lambda = 8.4 \times 10^{-12}\ m = 0.084\ Å}$$

4) Calculate the wavelength separation between two component lines which are observed in the normal Zeeman effect. The magnetic field is $0.4\ Wb\ m^{-2}$, the specific charge $e/m = 1.76 \times 10^{11}\ Ckg^{-1}$ and wavelength $\lambda = 4000\ Å$.

Solu: Given: Wavelength $\lambda = 4000\ Å = 4 \times 10^{-7}\ m$

Magnetic field strength $B = 0.4\ Wb\ m^{-2} = 0.4\ T$

Speed of light $c = 3 \times 10^8\ ms^{-1}$

Specific charge of an electron $e/m = 1.76 \times 10^{11}\ Ckg^{-1}$

Wavelength separation $2\Delta\lambda =?$

We known that Zeeman shift is

$$\Delta\lambda = \frac{Be\lambda^2}{4\pi m_e c}$$

$$\Delta\lambda = \frac{B(e/m_e)\lambda^2}{4\pi c} \quad \text{or} \quad \Delta\lambda = \frac{0.4\times1.76\times10^{11}\times(4\times10^{-7})^2}{4\pi\times3\times10^8}$$

$$\boxed{\Delta\lambda = 2.99 \times 10^{-12}\ m = 0.0299\ Å}$$

Therefore, wavelength separation between two component lines is

$$2\Delta\lambda = 5.98 \times 10^{-12}\, m = 0.0598\, \text{Å}$$

5) In a normal Zeeman effect, the sodium $422.6\, nm$ line splits into three components separated by $0.025\, nm$ in a magnetic field of $3\, T$. Calculate the value of specific charge of an electron.

Solu: Given: Wavelength $\lambda = 422.6\, nm = 4.226 \times 10^{-7}\, m$
Magnetic field strength $B = 3\, T$
Speed of light $c = 3 \times 10^8\, ms^{-1}$
Zeeman shift $\Delta\lambda = 0.025\, nm = 2.5 \times 10^{-11}\, m$
Specific charge of an electron $e/m =?$
We known that Zeeman shift is

$$d\lambda = \frac{Be\lambda^2}{4\pi m_e c}$$

$$e/m_e = \frac{4\pi c d\lambda}{B\lambda^2}$$

$$e/m_e = \frac{4\pi \times 3 \times 10^8 \times 2.5 \times 10^{-11}}{3 \times (4.226 \times 10^{-7})^2} \qquad \Rightarrow \qquad \boxed{e/m_e = 1.759 \times 10^{11}\, Ckg^{-1}}$$

6) Calculate the wavelength separation between the unmodified line of wavelength $6000\, \text{Å}$ and modified line when a magnetic induction of $1\, T$ is applied, in normal Zeeman effect.

Solu: Given: Wavelength $\lambda = 6000\, \text{Å} = 6 \times 10^{-7}\, m$
Magnetic field strength $B = 1\, T$
Speed of light $c = 3 \times 10^8\, ms^{-1}$
Specific charge of an electron $e/m = 1.76 \times 10^{11}\, Ckg^{-1}$ (assumed)
Zeeman shift $\Delta\lambda =?$
We known that Zeeman shift is

$$d\lambda = \frac{Be\lambda^2}{4\pi m_e c}$$

$$d\lambda = \frac{B(e/m_e)\lambda^2}{4\pi c}$$

$$d\lambda = \frac{1 \times 1.76 \times 10^{11} \times (6 \times 10^{-7})^2}{4\pi \times 3 \times 10^8}$$

$$\boxed{d\lambda = 1.68 \times 10^{-11}\, m = 0.168\, \text{Å}}$$

7) A spectral line of wavelength $4500\, \text{Å}$ when produced in a magnetic field of $10\, T$ is observed to be a normal Zeeman triplet. Calculate the wavelength of separation between components of this triplet.

Solu: Given: Wavelength $\lambda = 4500\, \text{Å} = 4.5 \times 10^{-7}\, m$
Magnetic field strength $B = 10\, T$
Speed of light $c = 3 \times 10^8\, ms^{-1}$

Specific charge of an electron $e/m = 1.76 \times 10^{11} \, Ckg^{-1}$ (assumed)

Zeeman shift $\Delta\lambda =?$

We known that Zeeman shift is

$$d\lambda = \pm \frac{\lambda^2}{c}\left(\frac{e}{4\pi m_e}\right) B$$

$$d\lambda = \pm \frac{(4.5\times10^{-7})^2}{3\times10^8}\left(\frac{1.76\times10^{11}}{4\pi}\right) 10$$

$$\boxed{d\lambda = 9.45 \times 10^{-11} \, m = 0.945 \, \text{Å}}$$

Hence the Zeeman triplets has wavelengths

i) $\lambda_1 = 4500 - 0.945 = 4499.055 \, \text{Å}$

ii) $\lambda_2 = 4500 - 0 = 4500 \, \text{Å}$

iii) $\lambda_3 = 4500 + 0.945 = 4500.945 \, \text{Å}$

8) The Zeeman components of a $500 \, nm$ spectral line are $0.0116 \, nm$ apart, when magnetic field is $1 \, T$. Find the specific charge of an electron.

Solu: Given: Wavelength $\lambda = 500 \, nm = 5 \times 10^{-7} \, m$

Magnetic field strength $B = 1 \, T$

Speed of light $c = 3 \times 10^8 \, ms^{-1}$

Zeeman shift $\Delta\lambda = 0.0116 \, nm = 1.16 \times 10^{-11} m$

Specific charge of an electron $e/m =?$

We known that Zeeman shift is

$$d\lambda = \frac{Be\lambda^2}{4\pi m_e c}$$

$$e/m_e = \frac{4\pi c d\lambda}{B\lambda^2}$$

$$e/m_e = \frac{4\pi\times3\times10^8\times1.16\times10^{-11}}{3\times(5\times10^{-7})^2} \quad \Rightarrow \quad \boxed{e/m_e = 1.749 \times 10^{11} \, Ckg^{-1}}$$

9) A spectrometer can resolve spectral lines separated by $0.03 \, nm$. How much magnetic field will have to be applied to a source of $422.7 \, nm$ line, so that the triplet is just resolved in normal Zeeman effect? Given $e/m = 1.76 \times 10^{11} \, Ckg^{-1}$

Solu: Given: Wavelength of spectral line $\lambda = 422.7 \, nm = 4.227 \times 10^{-7} \, m$

Change in wavelength $\Delta\lambda = 0.03 \, nm = 3 \times 10^{-11} \, m$

Speed of light $c = 3 \times 10^8 \, ms^{-1}$

Magnetic field strength $B =?$

Zeeman Shift is given by

$$B = \frac{4\pi m_e c \, d\lambda}{e\lambda^2} \qquad \text{or} \qquad B = \frac{4\pi c \, d\lambda}{e/m_e \lambda^2}$$

$$B = \frac{4\pi\times3\times10^8\times 3\times10^{-11}}{1.76\times10^{11}\times(4.227\times10^{-7})^2}$$

$$\boxed{B = 3.6 \, T}$$

Question Bank

Short Answer Questions:

1) Two features that characterize vector atom model are
2) Electron possesses an intrinsic angular momentum due to its _____ motion in addition to the angular momentum resulting from its orbital motion.
3) The state of an atom as a whole is described _____
4) According to Uhlenbeck and Goudsmith, the electron has a _____ like top.
5) The total angular momentum of an atom is the vector sum of _____ and _____
6) The ratio of magnetic moment and orbital angular momentum is called
7) What is the basic unit of atom magnetic moment?
8) Stern-Gerlach experiment is based on the behaviour of a _____ in _____
9) What are quantum numbers?
10) What is principal quantum number?
11) What is orbital quantum number?
12) What is spin quantum number?
13) What is total angular momentum?
14) What is magnetic orbital quantum number?
15) What is space quantization?
16) What is magnetic spin quantum number?
17) What does electron spin explain?
18) What are selection rules?
19) What is coupling?
20) Mention the types coupling schemes?
21) L-S coupling exists mainly in _____
22) j-j coupling exists mainly in _____
23) State Pauli's exclusion principle.
24) State Larmor's theorem.
25) What is vector atom model?
26) Mention the two essential features that characterize the vector atom model.
27) What is meant by spatial quantization?
28) What is meant by electron spin?
29) What is Bohr magneton?
30) Define gyromagnetic ratio.
31) What are quantum numbers?
32) Mention the quantum numbers.
33) Mention the quantum numbers in the presence of strong magnetic field.
34) What is principal quantum number?
35) What is orbital quantum number?

36) What is spin quantum number?
37) What is total angular quantum number?
38) What is magnetic orbital quantum number?
39) What is magnetic spin quantum number?
40) What is the expression for Bohr Magneton?
41) What is selection rule?
42) Give the value of Bohr Magneton.
43) What is meant by L-S coupling?
44) What is meant by j-j coupling?
45) Write an expression for the resultant total angular momentum of the atom.
46) State Pauli's exclusion principle.
47) State Larmor's Theorem?
48) Give the expression for Larmor's frequency.
49) What is Zeeman Effect?
50) What is Normal Zeeman Effect?
51) What is Anomalous Zeeman Effect?
52) If electron spin is involved in the Zeeman effect then it is called _____
53) If electron spin is not involved in the Zeeman effect then it is called _____
54) What is Lande 'g' factor?
55) Why does normal zeeman effect occurs only in atoms with an even number of electrons?
56) Is electron spin considered to explain normal Zeeman effect? Explain.
57) Write the expression for the Zeeman Shift when viewed in the longitudinal direction.
58) Write the expression for the Zeeman Shift when viewed in the transverse direction.
59) What is Stark Effect?

Long Answer Questions:
1) Mention the concepts that characterize the vector atom model. Explain.
2) What is meant by vector atom model? Explain.
3) What is meant by Bohr magneton? Derive an expression for it.
4) Describe with a diagram Stern and Gerlach experiment. Write the importance of the results of the experiment.
5) State and explain the significance of four quantum numbers. How are they interrelated?
6) What are the four quantum numbers assigned to an electron in an atom? What is the significance of each of these quantum numbers.
7) State the various quantum numbers and their significance associated with vector model of atom.
8) Write a note on; (a) spin quantum number, (b) total angular quantum number, (c) magnetic orbital quantum number and (d) magnetic spin quantum number.
9) Write a note on spectral terms and their notations.

10) List the set of quantum numbers for $n = 3$; hydrogen atom.
11) Mention different types of coupling.
12) Write a note of L-S coupling.
13) Write a note on j-j coupling.
14) State and explain Pauli's exclusion principle.
15) Write the important points related to Pauli's exclusion principle.
16) Derive an expression for maximum number of electrons in an orbit.
17) State and explain Larmor precession.
18) Derive and expression for Larmor frequency.
19) Write a note on spectral terms and spectral notations.
20) Derive an expression for the total magnetic moment of an electron in an atom.
21) Derive Lande's g-factor or Lande's splitting factor.
22) State and explain Zeeman effect.
23) What is Zeeman effect? Distinguish between normal Zeeman effect and anomalous Zeeman effect.
24) Describe the experimental arrangement for studying the normal Zeeman effect.
25) Explain the normal Zeeman effect in classical theory and obtain an expression for normal Zeeman shift.
26) What is normal Zeeman effect? On the basis of quantum theory explain the effect of magnetic field on energy levels of an atom and show that a spectral line splits into three spectral lines. Explain the splitting of spectral line in normal Zeeman effect.
27) Explain why normal Zeeman effect occurs only in atoms with even number of electrons.
28) Derive an expression for Zeeman shift. On the basis of quantum theory, explain the effect of magnetic field on energy levels of atom. Show that a spectral line splits into three spectral lines in Zeeman effect.
29) What is anomalous Zeeman effect? Explain the phenomenon of anomalous Zeeman effect on the basis of quantum theory. Derive an expression for change in energy.

Solutions to Short Answer Questions

1) Vector atom model is the extension of _____ model.
Ans. Bohr-Sommerfeld

2) Two features that characterize vector atom model are
Ans. Space quantization & Electron Spin

3) Electron possesses an intrinsic angular momentum due to its _____ motion in addition to the angular momentum resulting from its orbital motion.
Ans. Spin

4) The state of an atom as a whole is described _____
Ans. L, S and J

5) **According to Uhlenbeck and Goudsmith, the electron has a _____ like top.**

Ans. Spinning motion

6) **The total angular momentum of an atom is the vector sum of _____ and _____**

Ans. Orbital angular momentum and Spin angular momentum

7) **The ratio of magnetic moment and orbital angular momentum is called**

Ans. Gyromagnetic ratio

8) **What is the basic unit of atom magnetic moment?**

Ans. Bohr Magneton

9) **Stern-Gerlach experiment is based on the behaviour of a _____ in _____**

Ans. Magnetic dipole;   non-uniform magnetic field

10) **What are quantum numbers?**

Ans. The numbers that are required to completely specify the position of electron, orbital angular momentum of electron, configuration of electron in presence of an external magnetic field are called quantum numbers.

11) **What is principal quantum number?**

Ans. Principal quantum number (n) gives the position and energy of an electron in an orbit.

12) **What is orbital quantum number?**

Ans. Orbital quantum number (L) defines the shape of the orbit occupied by the electron and the orbital angular momentum of the electron.

13) **What is spin quantum number?**

Ans. Spin quantum number (s) defines the spin of an electron in an orbit.

14) **What is total angular momentum?**

Ans. Total angular momentum (j) of a single electron is the vector sum of the orbital angular momentum and spin angular momentum of the single electron.

15) **What is magnetic orbital quantum number?**

Ans. Magnetic orbital quantum number (m_l) is the projection of orbital quantum number (l) on the magnetic axis. It specifies the orientation of the electron orbit in presence of the magnetic field.

16) **What is space quantization?**

Ans. The quantization of the direction of $\vec{L}$ with respect to the external magnetic field is known as space quantization.

17) What is magnetic spin quantum number?

Ans. Magnetic spin quantum number (m_s) is the projection of spin quantum number on the magnetic axis. It specifies the orientation of the electron spin relative to the same frame of reference.

18) What does electron spin explain?

Ans. Electron spin accounts for the fine structure of the spectral lines and splitting of these lines in the magnetic field.

Electron spin also accounts for the magnetic properties of ferromagnetic substances.

19) What are selection rules?

Ans. Selection rules are specified in the form of relationships between the quantum numbers characterizing the initial and final states of the system in a transition due to the given perturbation.

20) What is coupling?

Ans. In an atom having two or more electrons the orbital angular momenta and the spin angular moments are added to obtaining total angular momentum. This process of adding orbital angular momentum and spin angular momentum is called coupling.

21) Mention the types coupling schemes?

Ans.   i) L-S Coupling or Russel & Saunders's Coupling
            ii) j-j Coupling

22) L-S coupling exists mainly in _____

Ans. Light atoms

23) j-j coupling exists mainly in _____

Ans. Heavy atoms

24) State Pauli's exclusion principle.

Ans. No two electrons in an atom can occupy the same quantum state

25) State Larmor's theorem.

Ans. The effect of a magnetic field on an electron moving in an orbit is to superimpose on the orbital motion a precessional motion of the entire orbit about the direction of the magnetic field with angular velocity ω given by $\omega = Be/2m$" where B the magnetic field strength, e is the charge of electron and m the mass of electron.

26) What is vector atom model?

Ans. Vector model of the atom is a model of the atom in terms of angular momentum involving space quantization and spin of an electron. It can be considered as the extension of the Rutherford-Bohr-Sommerfeld atom model to multi-electron atoms.

27) Mention the two essential features that characterize the vector atom model.

Ans. Space quantization and Electron Spin

28) What is meant by spatial quantization?

Ans. Quantization in respect to direction in space. The space quantization of an atom in a magnetic field whose quantum states correspond to a limited number of possible angles between the directions of the angular momentum and the magnetic intensity.

29) What is meant by electron spin?

Ans. The electron spin is one of the three inherent properties of the electrons; the others are mass and charge of the electron. The electron spin is described as the spinning of the electron around its own axis.

30) What is Bohr magneton?

Ans. Bohr magneton (μ_B) is the basic unit of magnetic moments. Atomic magnetic moments can be expressed as multiples of the Bohr magneton.   OR
Bohr magneton (μ_B) is a physical constant and the natural unit for expressing the magnetic moment of an electron caused by either its orbital or spin angular momentum.

31) Define gyromagnetic ratio.

Ans. Gyromagnetic ratio (also sometimes known as the magnetogyric ratio in other disciplines) of an electron is the ratio of its magnetic moment to its angular momentum, and it is often denoted by the symbol γ

32) What are quantum numbers?

Ans. The numbers that are required to completely specify the position of electron, orbital angular momentum of electron, configuration of electron in presence of an external magnetic field are called quantum numbers.

33) Mention the quantum numbers.

Ans. Principal Quantum Number (n), Orbital Quantum Number (l), Spin Quantum Number (s), Total Angular Momentum Quantum Number (j), Magnetic Orbital Quantum Number (m_l), Magnetic Spin Quantum Number (m_s), Magnetic Total Angular Momentum Quantum Number (m_j)

34) Mention the quantum numbers in the presence of strong magnetic field.

Ans. Magnetic Orbital Quantum Number (m_l), Magnetic Spin Quantum Number (m_s), Magnetic Total Angular Momentum Quantum Number (m_j)

35) What is principal quantum number?

Ans. The principal quantum number (n) represents the relative overall energy of each orbital. The energy level of each orbital increases as its distance from the nucleus increases. The sets of orbitals with the same (n) values are often referred to as electron shells or energy levels

36) What is orbital quantum number?

Ans. The orbital quantum number is a quantum number for an atomic orbital that determines its orbital angular momentum and describes the shape of the orbital. It is also sometimes known as the azimuthal quantum number, orbital quantum number or second quantum number, and is symbolized as ℓ.

37) What is spin quantum number?

Ans. The Spin Quantum Number (s) describes the spin angular momentum of an electron. An electron spins around an axis and has both spin angular momentum and orbital angular momentum.

38) What is total angular quantum number?

Ans. The total angular quantum number (j) is the sum of the orbital angular quantum number (l) and spin angular quantum number (s) given by $j = l + s$

39) What is magnetic orbital quantum number?

Ans. The magnetic orbital quantum number (m_l) is the projection of orbital quantum number (l) on the magnetic axis. It distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of orbital in space.

40) What is magnetic spin quantum number?

Ans. The magnetic spin quantum number (m_s) is the projection of spin quantum number (s) on the magnetic axis. It describes the spin magnetic moment of an electron.

41) What is the expression for Bohr Magneton?

Ans. $\mu_B = \dfrac{eh}{4\pi m_e} = 9.2741 \times 10^{-24} \, JT^{-1}$

42) What is selection rule?

Ans. A rule which describes whether particular quantum transitions in an atom or molecule are allowed or forbidden.

43) Give the value of Bohr Magneton.

Ans. $\mu_B = \dfrac{eh}{4\pi m_e} = 9.2741 \times 10^{-24} \, JT^{-1}$

44) What is meant by L-S coupling?

Ans. For multi-electron atoms where the spin-orbit coupling is strong (not independent of each other), it can be presumed that the total angular momentum and total spin angular momentum of all the electrons add to form a total orbital angular momentum. Then the total angular momentum is determined by using $L = \sum_{i=1}^{n} l_i$ $S = \sum_{i=1}^{n} s_i$ and $J = L + S$

45) What is meant by j-j coupling?

Ans. For multi-electron atoms where the spin-orbit coupling is weak (independent of each other), it can be presumed that the orbital angular momentum and spin angular

momentum of the individual electrons add to form a total orbital angular momentum. Then the total angular momentum is determined by using $J = \sum_{i=1}^{n} j_i$

46) Write an expression for the resultant total angular momentum of the atom.

Ans. $J = L + S$

47) State Pauli's exclusion principle.

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

The four quantum numbers n, l, m_l and m_s determine the state of an electron completely. Hence the principle may be state as

"No two electrons in an isolated atom may have the same four quantum numbers".

48) State Larmor's Theorem?

Ans. "The effect of a magnetic field on an electron moving in an orbit is to superimpose on the orbital motion a precessional motion of the entire orbit about the direction of the magnetic field with angular velocity ω given by $\omega = Be/2m$" where B the magnetic field strength, e is the charge of electron and m the mass of electron.

49) Give the expression for Larmor's frequency.

Ans. $\omega = Be/2m$

50) What is Zeeman Effect?

Ans. "The phenomenon of splitting of lines produced by a light source kept in an external magnetic field is called Zeeman effect".

"When a source of radiation, giving line spectrum is placed in a magnetic field, the spectral lines are split up into a number of component lines, symmetrically distributed about the original line. Doublets, triplets and even more complex systems are observed. This phenomenon is called Zeeman effect".

51) What is Normal Zeeman Effect?

Ans. If the magnetic field is very strong, each spectral line is split up into two components in the longitudinal view and in three components in transverse view. This is known as Normal Zeeman Effect.

52) What is Anomalous Zeeman Effect?

Ans. If the magnetic field is comparatively weak, each line splits into more than three components. This is known as Anomalous Zeeman Effect.

If electron spin is involved in the Zeeman effect, then it is called the Anomalous Zeeman Effect.

53) If electron spin is involved in the Zeeman effect then it is called _____

Ans. Anomalous Zeeman Effect

54) If electron spin is not involved in the Zeeman effect then it is called _____

Ans. Normal Zeeman Effect

55) **What is Lande 'g' factor?**

Ans. Lande 'g' factor determines the splitting of the energy levels in the presence of a weak magnetic field and shows that the splitting is determined by the values of $\vec{L}, \vec{S}$ & $\vec{J}$

56) **Why does normal Zeeman effect occurs only in atoms with an even number of electrons?**

Ans. Since the net spin (spin up + spin down) of even number of valence electrons is zero, normal Zeeman effect is observed for light emitted from sources of elements like Ca, Cu, Zn etc.

57) **Is electron spin considered to explain normal Zeeman effect? Explain.**

Ans. Yes

58) **Write the expression for the Zeeman Shift when viewed in the longitudinal direction.**

Ans. $Zeeman\ Shift\ \delta\lambda = \pm \dfrac{Be\lambda^2}{4\pi m_e c}$

59) **Write the expression for the Zeeman Shift when viewed in the transverse direction.**

Ans. $Zeeman\ Shift\ \delta\lambda = 0 \pm \dfrac{Be\lambda^2}{4\pi m_e c}$

60) **What is Stark Effect?**

Ans. "The splitting of spectral lines due to the action of external electric field is called Stark effect".