# 7

# ATOMIC MODEL (II)

**7.1 Electron Spin-** In an attempt to explain the doublet character of spect emitted by alkali atoms and the phenomenon of anomalous Zeeman eff Dutch physicists Goudsmit and Uhlenbeck postulated that electron m rotating about its own axis. The name "spin" was given to this kind of m the electron. The angular momentum associated with the spin motion electron is called intrinsic spin angular momentum. It was this concept, was missing in the Schrodinger theory. Later in 1928, English physicist Dirac, showed that in relativistic formulation of Schrodinger equati hydrogen atom the intrinsic angular momentum of electron appeared in a way and the concept of electron spin got theoretical basis.

According to Goudsmit and Uhlenbeck hypothesis (1925) electron pos an intrinsic angular momentum due to its spin motion in addition to the a momentum resulting from its orbital motion. In classical picture elect regarded as a charged sphere, which rotates about its own axis. The motion electron in an atom may be compared with that of earth's motion. The a momentum of the earth due to its rotation about its own axis corresponds intrinsic spin angular momentum. The hypothesis of spinning electron proposed before the discovery of Schrodinger equation and had no theor basis. It was merely an ad-hoc hypothesis introduced to explain experim facts.

### 7.2 Quantum Numbers

When Schrodinger equation is applied to the motion of electron atom, it is found that the quantum state $\psi$ of electron is characterized by numbers called *quantum numbers*. These quantum numbers are prin **quantum number n, orbital quantum number $\ell$, magnetic quantum nu m $_\ell$, and spin quantum number m $_s$.** The solution $\psi$ of Schrodinger equation, called *wave function*, gives all kind of information about the electr the atom. The important characteristics and significance of these quantum numbers are as follows.

**Principal Quantum Number (n)** – This quantum number determines the total energy of electron in the atom. It can take integral values 1, 2, 3, ....The greater the value of n; greater is the energy of electron.

**Orbital (azimuthal) Quantum Number ($\ell$)** – This quantum number determines the orbital angular momentum of electron. The magnitude of orbital angular momentum of electron is given by

$$|\mathbf{L}| = \sqrt{\ell(\ell+1)}\,\hbar$$

where $\ell$ is a number, called *orbital quantum number*. For a given value of pricipal quantum numbern, the orbital quantum number can take integral values 0, 1, 2, ......(n-1). The quantum number $\ell$ also gives the shape of probability distribution curve. The electrons with $\ell$ = 0, 1, 2, 3.... are called s, p, d, f electrons respectively.

**Magnetic Quantum Number ($m_\ell$)** – The angular momentum vector **L** cannot take all orientations in space; only certain directions are allowed. This feature of vector **L** is called *space quantization.* The allowed orientations of vector **L** are such that its components along any fixed direction, say z-axis, are given by

$$|\mathbf{L}_z| = m_\ell \hbar$$

where $m_\ell$ is an integer called *magnetic quantum number*. For a given value of $\ell$, the quantum number $m_\ell$ can take integrally spaced values from $-\ell$ to $+\ell$.

The other components of vector **L** are uncertain which is in accord with the uncertainty principle. This means that the vector **L** traces out a cone in space about z-axis such that its projection onto z-axis is $m_\ell \hbar$. The average value of x and y components of L turns out to be zero.

**Spin Quantum Number ($m_s$)** - Relativistic quantum mechanics shows that electron possesses an intrinsic angular momentum **S** whose magnitude is given by

$$|\mathbf{S}| = \sqrt{s(s+1)}\,\hbar$$

where s is spin quantum number. It assumes only one value ½. The vector **S** can have only two directions. The projection of vector **S** onto any fixed axis, say z-axis, are given by

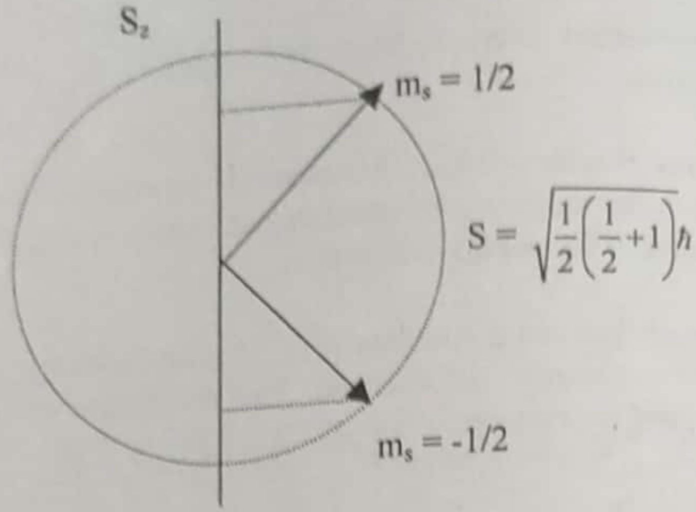



Fig ( 7.1 )

$$|S_z| = m_s\hbar = \pm\frac{1}{2}\hbar$$

where $m_s = \pm½$ is called the magnetic spin quantum number.

Thus the state of an electron, in an atom is described by four quantum numbers n, $\ell$, $m_l$ and $m_s$

Now we shall find the number of quantum states corresponding to various values of principal quantum number n.

Corresponding to the principal quantum number n = 1, we have $\ell = 0$, $m_l = 0$. $m_s = \pm ½$. Thus for n = 1, there are 2 states defined by the quantum numbers

$$n = 1, \ell = 0, m_l = 0, m_s = +1/2$$

$$n = 1, \ell = 0, m_l = 0, m_s = -½$$

Since not all the four quantum numbers are the same, each state is occupied by a single electron. The quantum states having the same value of principal quantum number n are said to constitute a shell. Shells are designated according to the following scheme

| | | | | | |
|---|---|---|---|---|---|
| n | 1 | 2 | 3 | 4 | 5 |
| Shell | K | L | M | N | O |

Thus K-shell contains two quantum states and hence two electrons. The quantum states, which have the same value of $\ell$ are said to constitute a **sub-shell**. The above two states have the same value of $\ell$ (= 0) and therefore form a sub-shell. The sub-shells are designated according to the following scheme.

| | | | | | | |
|---|---|---|---|---|---|---|
| Azimuthal quantum number | $\ell$ 0 | 1 | 2 | 3 | 4 | 5 |
| Sub-shell | s | p | d | f | g | h ......... |

The K shell contains only one sub-shell denoted by s.

For n = 2, $\ell$ = 0, 1. For $\ell$ = 0, the allowed value of $m_\ell$ is 0. For $\ell$ = 1, the allowed values $m_\ell$ are −1, 0, 1. For each value of $m_\ell$, $m_s = \pm½$. Thus the quantum states for n = 2 are as follows.

| n | $\ell$ | $m_\ell$ | $m_s$ | quantum states |
|---|---|---|---|---|
| 2 | 0 | 0 | +½ | (2,0,0,½) |
| | | | -½ | (2,0,0,-½) |
| 2 | 1 | -1 | +½ | (2,1,-1,½) |
| | | | -½ | (2,1,-1,-½) |
| | | 0 | ½ | (2,1,0,½) |
| | | | -½ | (2,1,0,-½) |
| | | 1 | ½ | (2,1,1,½) |
| | | | -½ | (2,1,1,-½) |

Thus the L shell (n = 2) contains one s-sub-shell and three p- sub-shells. In all there are eight quantum states. The pair of quantum states of a sub-shell differing in spin quantum numbers only, are called **orbital.** The s sub-shell contains one orbital and p-sub-shell contains three orbitals usually designated as $p_x$, $p_y$, $p_z$. Each orbital can accommodate two electrons with opposite spins.

The quantum states corresponding to principal quantum number n = 3 are shown in the table.

The M shell (n = 3) contains one s-sub-shell, three p-sub-shells and five d-sub-shells and in all eighteen quantum states. Thus it can accommodate 18 electrons. The number of electrons that can be accommodated in shell can be calculated as follows. Consider a shell characterized by a principal quantum number n. For this value of n, the orbital (*azimuthal*) quantum number $\ell$ can take integral values from 0 to n-1. For each value of $\ell$, magnetic quantum number $m_\ell$ assumes integrall spaced values from $-\ell$ to $+\ell$ i.e. in all $2\ell+1$ values. For each value of $m_\ell$, the spin quantum number takes two values +½ and -½. Thus the total number of quantum states is given by

$$\sum_{\ell=0}^{n-1} 2(2\ell+1) = 2[1+3+5+..........(2n-1)]$$

**Russel-Saunder's or L-S Coupling** – In light atoms containing many valence electrons, the electrostatic interaction between the electrons is large and by virtue of this interaction the individual orbital angular momenta of valence electrons add up to form a resultant **L**.

$$\mathbf{L}_1+\mathbf{L}_2+\mathbf{L}_3+....=\sum \mathbf{L}_i$$

where $\mathbf{L}_i$ are the orbital angular momenta of valence electrons. The magnitude of vector **L** is quantized and is given by

$$|\mathbf{L}|=\sqrt{L(L+1)}\,\hbar$$

where L is total orbital quantum number and is determined by

$$L=\ell_1\oplus\ell_2\oplus\ell_3\oplus....$$

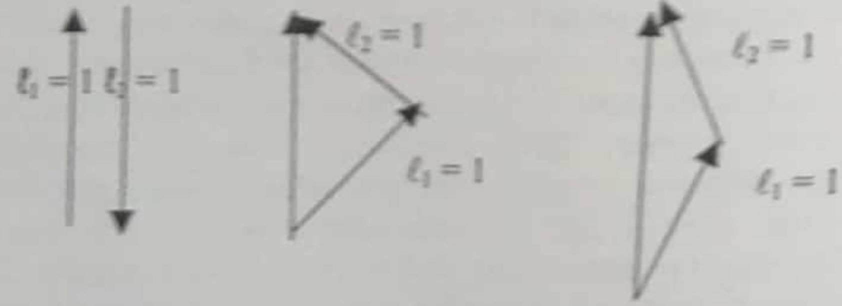
Here $\ell_1, \ell_2, \ell_3$ stand for orbital quantum number of valence electrons and $\oplus$ for quantized vector addition. For example, consider an atom with two valence electrons both in p-sub-shell i.e. $\ell_1=1, \ell_2=1$. Then

$$L=\ell_1\oplus\ell_2=1\oplus1=0,1,2$$

$(\ell_1\oplus\ell_2)$ takes on all integrally spaced values from $|\ell_1-\ell_2|$ to $(\ell_1+\ell_2)$. The allowed values of magnitude of the total orbital angular momentum **L** of these two valence electrons are:

$$|\mathbf{L}|=\sqrt{0(0+1)}\,\hbar=0$$
$$|\mathbf{L}|=\sqrt{1(1+1)}\,\hbar=\sqrt{2}\,\hbar$$
$$|\mathbf{L}|=\sqrt{2(2+1)}\,\hbar=\sqrt{6}\,\hbar$$

The geometrical addition of orbital angular momenta of the two electrons is shown in the figure (7.3).




L=0 $|\mathbf{L}|=0$ L=1 $|\mathbf{L}|=\sqrt{2}\hbar$ L=2 $|\mathbf{L}|=\sqrt{6}\hbar$

Fig (7.3) Addition of orbital angular momenta of two electrons with $\ell_1=1$ and $\ell_2=1$.

If one of the valence electrons is in p-sub-shell and the other is in d-sub shell i.e. $\ell_1 = 1, \ell_2 = 2$ then

$$L = \ell_1 \oplus \ell_2 = 1 \oplus 2 = 1,2,3$$

$$|L| = \sqrt{L(L+1)}\,\hbar = \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar$$

The geometrical addition of angular momenta are shown in the figure (7.4).

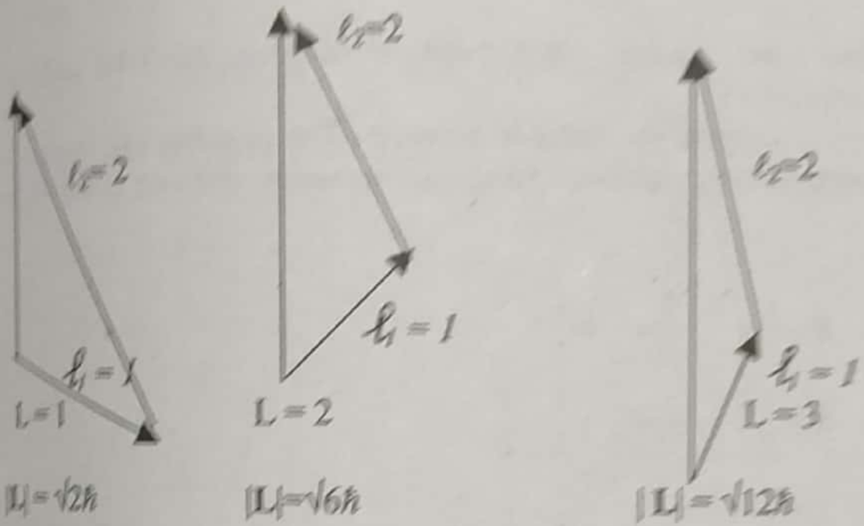



Fig (7.4) Addition of angular momenta of two electrons with $\ell_1=1$ and $\ell_2=2$

The total orbital angular momentum vector **L** can have only certain orientations in space. This implies that its projection along any fixed direction (z-axis) can have only discrete values given by

$$|\mathbf{L}_z| = M_L \hbar$$

where $M_L$, called *total orbital quantum number*, can take on integrally spaced values from $-L$ to $L$. In all $M_L$ can take $(2L + 1)$ values.

Each electron has spin angular momentum. Because of strong quantum mechanical effect, which has no classical analogue, the spin angular momenta of valence electrons are coupled to form a resultant spin angular momentum vector **S**.

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \ldots$$

The magnitude of vector **S** is quantized and is given by

$$|\mathbf{S}| = \sqrt{S(S+1)}\,\hbar$$

where S is *total spin quantum number* and is obtained from the following quantum sum.

$$S = s_1 \oplus s_2 \oplus s_3 \oplus .....$$
$$= \frac{1}{2} \oplus \frac{1}{2} \oplus \frac{1}{2} \oplus .....$$

The direction of vector **S** is quantized and its projection along any fixed direction has discrete values given by

$$|\mathbf{S}_Z| = M_S \hbar$$

where $M_S$ , *called total magnetic spin quantum number*, can take integrally spaced values from –S to S.

Let there be five valence electrons in an atom. The possible orientations of spin and the corresponding values of total spin quantum number S are shown below.

$$\uparrow\uparrow\uparrow\uparrow\uparrow \quad S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{5}{2}$$
$$\uparrow\uparrow\uparrow\uparrow\downarrow \quad S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = \frac{3}{2}$$
$$\uparrow\uparrow\uparrow\downarrow\downarrow \quad S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = \frac{1}{2}$$

Corresponding to S = 5/2, the allowed values of $M_S$ are –5/2, -3/2, -1/2, 1/2, 3/2, 5/2. Similarly the values of $M_S$ for S = 3/2 and S = 1/2 can be written.

Now the total orbital angular momentum vector **L** and total spin angular momentum vector **S** interact magnetically through their associated magnetic moments and form a resultant **J** called the total angular momentum vector of the atom.

$$\mathbf{L} + \mathbf{S} = \mathbf{J}$$

The magnitude of vector **J** is quantized and is specified by

$$|\mathbf{J}| = \sqrt{J(J+1)}\,\hbar$$

where J is *total angular momentum quantum number* of the atom. The allowed values of J are given by

$$J = L \oplus S$$

i.e. J can take on integrally spaced values from L + S down to | L – S |.

The direction of vector **J** is quantized. Its projection onto any axis is given by

$$|J_z| = M_J \hbar$$

where $M_J$ called total magnetic quantum number of the atom. It can integrally spaced values from –J to +J. The other components of **J** viz $J_x$ and $J_y$ are uncertain. This means that vectors **L** and **S** precess about their resultant **J** as shown in the figure.

*If* $L=2$, *and* $S=1$ *then* $J = L \oplus S = 2 \oplus 1 = 1,2,3.$

*If* $L=2, S=3/2$ *then* $J = L \oplus S = 2 \oplus 3/2 = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}.$

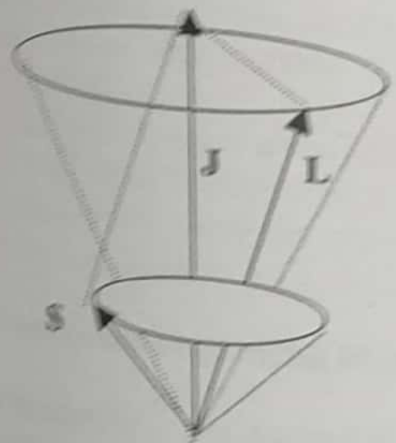



**Fig (7.5) Coupling of L and S to form J**

**j–j Coupling** – As the nuclear charge increases the magnetic spin orbit forces become stronger which dominate the electrostatic interactions. The LS coupling now breaks down. Under the influence of large spin orbit interaction, the orbital and the spin angular momenta of individual electron couple to form a resultant angular momentum **j**. The resultant angular momentum **j** of each electron combine to form a resultant **j** called total angular momentum vector of the atom. This coupling is known as j-j coupling and is summarized below

$$\mathbf{l}_1 + \mathbf{s}_1 = \mathbf{j}_1$$
$$\mathbf{j}_1 + \mathbf{j}_2 + \ldots = \Sigma \mathbf{j} = \mathbf{J}$$

## Atomic State or Term Symbol

The state of an atom is characterized by quantum numbers L,S and J and is represented by a symbol according to the following scheme

| L | = | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|
| symbol | | S | P | D | F | G | H |

Here S is not to be confused with total spin quantum number. The value of J ... written as post subscript and the multiplicity
r (= 2S + 1 if S ≤ L and = 2L + 1 if L < S) as pre-superscript. For example if ... atom is characterized by L = 2, S = 3/2 and J = 5/2 then it is designated as

$$^4D_{5/2} \qquad (r = 2S + 1 = 3 + 1 = 4)$$

**Ground State of hydrogen and alkali atoms-** The ground state configuration of valence electron is n $s^1$.
The valence shell has only one electron with $\ell = 0$

$$L = \ell = 0$$
$$S = s = 1/2$$
$$J = L \oplus S = 0 \oplus \frac{1}{2} = \frac{1}{2}$$
$$\text{Multiplicity } r = 2L + 1 = 1$$

The multiplicity is equal to the number of sublevels differing in the values of J.

The ground state symbol should be $^1S_{½}$ but it is written as $^2S_{1/2}$ because the term belongs a system, which is doublet. (In the excited state the valence goes to p or some other sub-shell. In all excited states L > S and the multiplicity r = 2S + 1 = 2. To specify this fact that these atoms belong the system whose excited states are doublet ( r = 2) we write the ground state system $^2S_{½}$.

**Excited States of alkali atoms-** If the valence electron in an alkali atom is promoted from s to p state then

$$L = \ell_1 = 1$$
$$S = s_1 = 1/2$$

$$r = 2S + 1 = 2$$
$$J = 1 \oplus \frac{1}{2} = \frac{3}{2}, \frac{1}{2}$$

Spectroscopic symbol $^2P_{1/2}$, $^2P_{3/2}$.

If the valence electron is promoted to d state then

$L = 2,\ S = 1/2,\ J = 2 \oplus \frac{1}{2} = \frac{5}{2}, \frac{3}{2}.$

Multiplicity $r = 2S + 1 = 2$

Spectroscopic symbol $^2D_{3/2},\ ^2D_{5/2}$.

Thus each term (except the ground state) split into two sets called multiplets (in present case doublet).

**Hund's Rule for determining the ground state of an atom –**

(i) Of the terms belonging to a given electronic configuration, the term with the greatest possible value S and greatest possible value of L at this S will have the lowest energy.

(ii) The multiplets formed by equivalent electrons are normal **i.e.** the energy of the state grows with increase in the value of J if not more than half of the sub-shell is filled.

(iii) The multiplets are inverted i.e. the energy diminishes with an increase in J if more than half of the sub-shell is filled.

In other words when not more than half of a sub-shell is filled, the component of the multiplet with $J = L - S$ has the lowest energy.

### 7.5 Applications of Vector Model

**Fine Structure of $H_\alpha$ Line** – The $H_\alpha$ line of hydrogen spectrum results from the transition of electron from the energy level corresponding to n = 3 to the energy level n = 2. The entire state of the atom is determined by its single valence electron.

Corresponding to n = 2, there are two sub-levels, s-sub-level ($\ell = 0$) and p-sub-level ($\ell = 1$). When electron is in s-sublevel ($\ell = 0$)

$$L = \ell = 0$$

$$S = s = ½$$

$$J = L \oplus S = 1 \oplus 1/2 = 1/2$$

This state is represented by $^2S_{1/2}$.

When the electron is in p-sublevel ($\ell = 1$)

$$L = \ell = 1$$

$$S = s = ½$$

$$J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$$

This state is represented by $^2P_{3/2}$, $^2P_{1/2}$.
Corresponding to n = 3 there are three sublevels, s, p and d sublevels. Whe... electron is in s-sublevel ($\ell = 0$)

$$L = \ell = 0$$

$$S = s = ½$$

$$J = L \oplus S = 0 \oplus 1/2 = 1/2$$

The corresponding state is $^2S_{1/2}$.
When the electron is in p-sublevel ($\ell = 1$)

$$L = \ell = 1$$

$$S = s = ½$$

$$J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$$

and the corresponding states are $^2P_{3/2}$ and $^2P_{1/2}$.
When the electron is in d-sublevel ($\ell = 2$)

$$L = \ell = 2$$

$$S = s = ½$$

$$J = L \oplus S = 2 \oplus 1/2 = 5/2, 3/2.$$

The corresponding states are $^2D_{5/2}$, $^2D_{3/2}$.

The energy levels corresponding to n = 3 and n = 2 are shown in the figure... can be shown that a state with lower value of J has smaller energy than the s... with higher value of J. In all fifteen transitions are possible but selection r... forbid some of them. Allowed transitions are those in which L changes by ±1 ... changes by 0 or ±1. i.e.

$$\Delta L = \pm 1, \Delta J = 0, \pm 1 \quad \text{(allowed)}$$

The selection rules permit only seven transitions. They are

$^2D_{5/2} \rightarrow {}^2P_{3/2}$, $^2D_{3/2} \rightarrow {}^2P_{1/2}$, $^2P_{1/2} \rightarrow {}^2S_{1/2}$, $^2D_{3/2} \rightarrow {}^2P_{3/2}$,

$^2P_{3/2} \rightarrow {}^2S_{1/2}$, $^2S_{1/2} \rightarrow {}^2P_{3/2}$, $^2S_{1/2} \rightarrow {}^2P_{1/2}$.

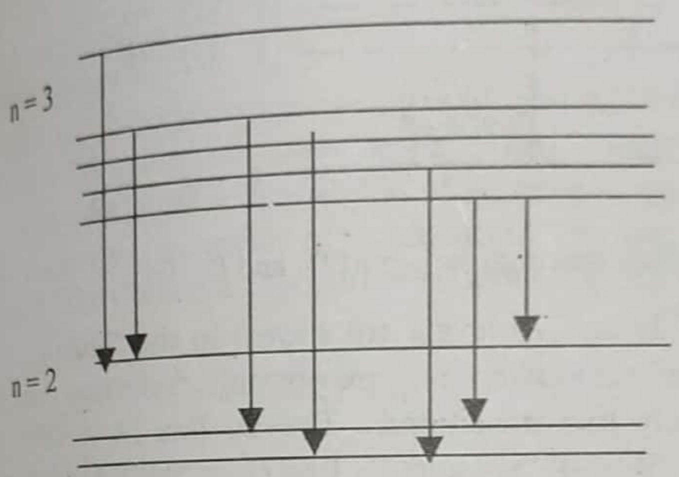



Fig (7.6 ) Fine Structure of $H_\alpha$ line.

States for which J values are the same but L values differ by unity are coincident. In the upper state the coincident pair of levels are ($^2D_{3/2}$, $^2P_{3/2}$) and ($^2P_{1/2}$, $^2S_{1/2}$). In the lower state the pair having the same energy are ($^2P_{1/2}$, $^2S_{1/2}$). Thus the transitions 4,4 and 5,5 are identical. The number of transitions then reduces to five. Experimentally only doublets are observed. This may be due to Doppler broadening (which arises due to thermal motion of atoms) the five components merge together and therefore it becomes difficult to record all the five lines.

**Fine Structure of Sodium D lines** – The D lines of sodium spectrum result from the transitions of electron from 3p to 3s level. In the ground state of Na atom the valence electron lies in 3s level. In this state

$$L = \ell = 0$$

$$S = s = ½$$

$$J = L \oplus S = 0 \oplus 1/2 = 1/2$$

The ground state is denoted by $^2S_{1/2}$. When the valence electron is excited to 3p level

$$L = \ell = 1$$

$$S = s = ½$$

$$J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$$

This state is denoted by $^2P_{3/2}$, $^2P_{1/2}$.

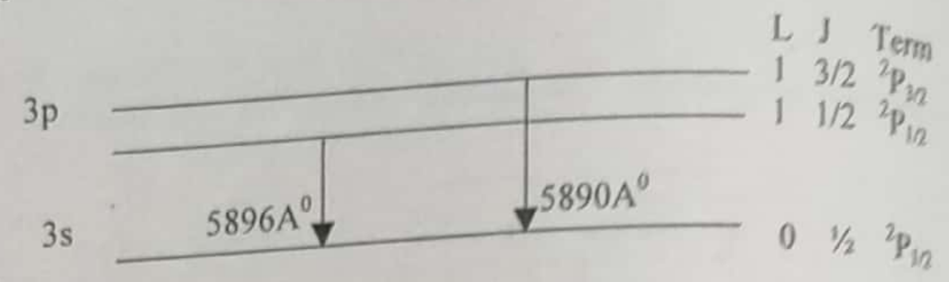



Fig (7.7 ) Fine Structure of sodium spectrum (origin of $D_1$ and $D_2$ lines

The energy level diagram of 3s and 3p levels are shown in the figure (7... Three transitions from upper level to lower level are possible. Selection rules ... $= \pm 1$, $\Delta J = 0, \pm 1$ allow only two transitions. The $D_1$ line ($\lambda = 5896$ ... originates from the transition $^2P_{1/2} \rightarrow {}^2S_{1/2}$ and $D_2$ line ($\lambda = 5890$ A$^0$) from ... transition $^2P_{3/2} \rightarrow {}^2S_{1/2}$.

### 7.6 Magnetic Moment of Atom

When a charged particle moves along a closed path or rotates about its ... axis, an electric current is associated with it. This current loop has magnetic moment associated with it. The magnetic moments of electron due to orbital ... spin motions are related to their corresponding angular momenta.

Consider an electron moving with velocity v in a circular orbit of radius r. The orbital current associated with this motion is

$$I = -\frac{ev}{2\pi r}$$

The magnetic moment associated with orbital motion is

$$|\vec{\mu}| = IA = -\left(\frac{ev}{2\pi r}\right)(\pi r^2) = -\left(\frac{e}{2m}\right)(mvr) = -\left(\frac{e}{2m}\right)|\mathbf{L}|$$

where $|\mathbf{L}| = mvr$ is the orbital angular momentum of electron. Eq.(2) expresses the fact that magnetic moment is associated with angular momentum of ... particle. The minus sign indicates that the direction of the magnetic moment ... opposite to that of the angular momentum. It is a remarkable fact that ... classical result is also valid in quantum mechanics. The ratio of magnetic moment to the angular momentum $\frac{\mu}{|\mathbf{L}|} = \frac{e}{2m}$ is called the *gyromagnetic ratio*. ... purely quantum mechanical reason, the magnetic moment associated with ... motion is related to its intrinsic (spin) angular momentum. The relation between them is

$$|\vec{\mu}| = -\frac{e}{m}|\mathbf{S}| \tag{3}$$

Notice that the *gyromagnetic ratio* of spin motion is not –e/2m but twice of it. For this reason the spin is said to have double magnetism.

The total angular momentum of an atom is equal to the vector sum of orbital and spin angular momenta of its electrons. The same is true for magnetic moment of atom. The magnetic moment of an atom is given by

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = -\frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) = -\frac{e}{2m}(\mathbf{J} + \mathbf{S}) \tag{4}$$

The projection of μ onto **J** is

$$\mu_J = \frac{\vec{\mu}.\mathbf{J}}{|\mathbf{J}|} = \left(-\frac{e}{2m}\right)\frac{(\mathbf{J}+\mathbf{S}).\mathbf{J}}{|\mathbf{J}|} = \left(-\frac{e}{2m}\right)\frac{\mathbf{J}.\mathbf{J}+\mathbf{J}.\mathbf{S}}{|\mathbf{J}|} \tag{5}$$

Now $\mathbf{L}.\mathbf{L} = (\mathbf{J}-\mathbf{S}).(\mathbf{J}-\mathbf{S}) = \mathbf{J}.\mathbf{J} + \mathbf{S}.\mathbf{S} - 2\,\mathbf{J}.\mathbf{S}$

$$\mathbf{J}.\mathbf{S} = \frac{\mathbf{J}.\mathbf{J}+\mathbf{S}.\mathbf{S}-\mathbf{L}.\mathbf{L}}{2}$$

$$\mu_J = \frac{\vec{\mu}.\mathbf{J}}{|\mathbf{J}|} = -\frac{e}{2m}\frac{\mathbf{J}.\mathbf{J} - \frac{1}{2}(\mathbf{J}.\mathbf{J}+\mathbf{S}.\mathbf{S}-\mathbf{L}.\mathbf{L})}{|\mathbf{J}|}$$

$$= -\frac{e}{2m}\frac{J(J+1)\hbar^2 - \frac{1}{2}\left\{J(J+1)\hbar^2 + S(S+1)\hbar^2 - L(L+1)\hbar^2\right\}}{\sqrt{J(J+1)}\,\hbar}$$

$$= -\frac{e}{2m}\left[1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)\hbar}\right]\sqrt{J(J+1)}\,\hbar$$

$$= -\frac{e}{2m}g\sqrt{J(J+1)}\,\hbar$$

$$= -\frac{e\hbar}{2m}g\sqrt{J(J+1)}$$

$$= -\mu_\beta\, g\sqrt{J(J+1)} \tag{6}$$

Where

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

g is called Lande' g-factor or spectroscopic splitting factor.

$$\mu_\beta = \frac{e\hbar}{2m} = 5.79 \times 10^{-5} \frac{eV}{T} = 9.27 \times 10^{-24}\ J/T$$

$\mu_\beta$ is called Bohr magneton and is a natural unit of magnetic moment of a... system.

The g-factor depends on the atomic state (i.e. on L, S, J). For pure ... motion S = 0, L = J and hence g = 1. For pure spin motion L = 0, S = J and ... g = 2. The g-factor can also be calculated as follows.

The relation between orbital angular momentum vector L, spin an... momentum vector S and their resultant total angular momentum vector ... depicted by vector diagram as shown in the figure. Also shown are the associ... magnetic moments on the same diagram. Because of double magnetism of ... motion, the resultant of $\mu_L$ and $\mu_S$, which has been depicted as $\mu_{atom}$, i... collinear with J. The projection of $\mu_{atom}$ onto the direction of J is $\mu_J$. Let θ and φ be the angles defined in the figure. From the geometry of ... figure we have

$$\mu_J = |\bar{\mu}_L| \cos\theta + |\bar{\mu}_S| \cos\varphi$$

$$= -\frac{e}{2m}|\mathbf{L}|\cos\theta - 2\frac{e}{2m}|\mathbf{S}|\cos\varphi$$

$$= -\frac{e}{2m}\ \sqrt{L(L+1)}\hbar\cos\theta + 2\sqrt{S(S+1)}\hbar\cos\varphi$$

The cosine formula for angles θ and φ are

$$\cos\theta = \frac{|\mathbf{J}|^2 + |\mathbf{L}|^2 - |\mathbf{S}|^2}{2|\mathbf{J}||\mathbf{L}|} = \frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1}\sqrt{L(L+1)}}$$

$$\cos\varphi = \frac{|\mathbf{J}|^2 + |\mathbf{S}|^2 - |\mathbf{L}|^2}{2|\mathbf{J}||\mathbf{S}|} = \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)}\sqrt{S(S+1)}}$$

Substituting the expressions of cosθ and cosφ in Eq. (9) we have

$$\mu_J = -\frac{eh}{2m}\left[\frac{J(J+1)+L(L+1)-S(S+1)}{2\sqrt{J(J+1)}} + 2\frac{J(J+1)+S(S+1)-L(L+1)}{2\sqrt{J(J+1)}}\right]$$

$$= -\frac{eh}{2m}\left[\frac{3J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right]\sqrt{J(J+1)}$$

$$= -\frac{eh}{2m}\left[1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right]\sqrt{J(J+1)}$$

$$= -\frac{eh}{2m} g\sqrt{J(J+1)}$$

$$= -\mu_\beta g\sqrt{J(J+1)}$$

Thus the magnetic moment of an atom can be written as

$$\mu_J = -\frac{e}{2m} g|\mathbf{J}| = -\frac{eh}{2m} g\sqrt{J(J+1)} = -\mu_\beta g\sqrt{J(J+1)} \qquad (12)$$

The projection of $\mu_J$ onto z-direction is given by

$$(\mu_J)_z = -\frac{e}{2m} g|\mathbf{J}_z| = -\frac{eh}{2m} g M_J = -\mu_\beta g M_J \qquad (13)$$

where $M_J = 0, \pm1, \pm2, \pm3$......i.e. $M_J$ can take on integrally spaced values from $-J$ to $+J$. $M_J$ is called the magnetic quantum number of the atom.

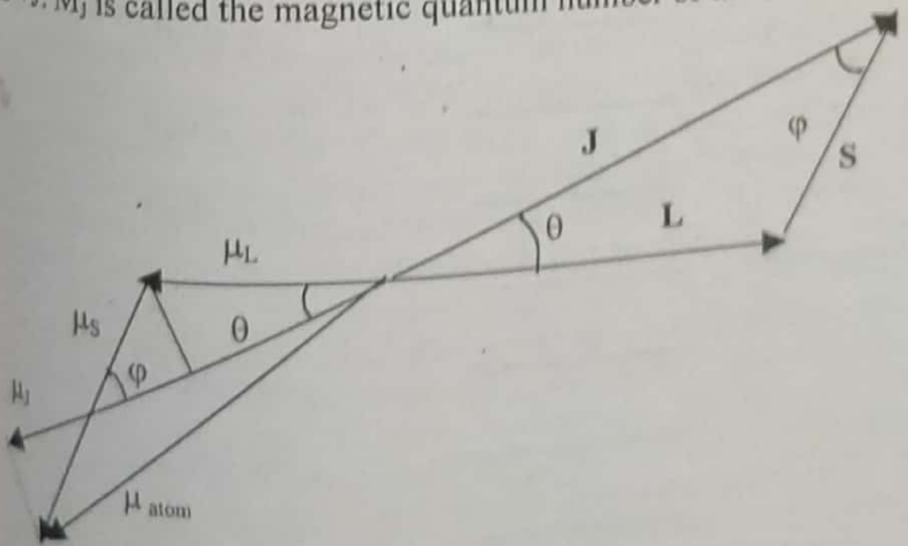



Fig ( 7.8 ) Addition of $\mu_L$ and $\mu_S$ to form $\mu_{atom}$.

## 7.7 Energy of an Atom in Magnetic Field

When an atom possessing magnetic moment is placed in a uniform mag... field, it experiences a torque equal to μ x B. Referred to a zero of pot... energy when μ and B are perpendicular to each other, the potential energy i... arbitrary orientation is given by - μ . B. Thus, in the magnetic field an a... acquires an extra energy - μ . B. If $E_0$ is the energy of an atom in absen... magnetic field, then the energy in presence of magnetic field is

$$E = E_0 - \vec{\mu}\cdot \mathbf{B}$$

If z-axis is chosen in the direction of the magnetic field i.e. $\mathbf{B} = B\,\mathbf{k}$, then energy of the atom can be written as

$$\begin{aligned} E &= E_0 - \mu_z B \\ &= E_0 - \left(-\frac{e}{2m}\right) g|\mathbf{J}_z| B \\ &= E_0 + g\left(\frac{e}{2m}\right) M_J \hbar B \\ &= E_0 + g\frac{e\hbar}{2m} BM_J \\ &= E_0 + g\mu_B BM_J \end{aligned}$$

where $M_J$ = J, J-1, ......0 .......-(J-1), J. Since $M_J$ can take on 2J+1 values... atomic energy level is splits into 2J+1 equally spaced sublevels as shown in... figure. The splitting of an energy level results from the interaction of magn... field with the magnetic moment of the atom. It is evident from equation (2) i... an atomic level with g = 0 does not split at all. For example, the state $^4D_{1/2}$ ha... = 0, S = 3/2, J = ½ and g = 0. Similarly for a state with J = 0 (called singlet)... splitting occurs. $^1S$ state is an example of this case.

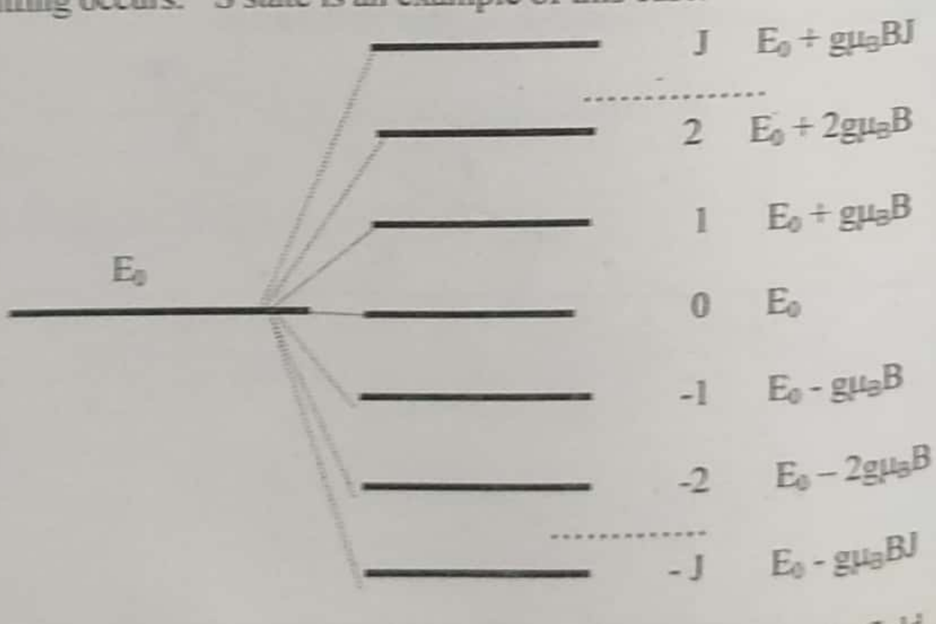



Fig (7.9) Splitting of a energy level in magnetic field.

In magnetic field the separation of two adjacent sub-levels is $g\mu_\beta B$ and the total splitting is given by

$$\Delta E = 2g\mu_\beta BJ \tag{16}$$

## 7.8 Stern and Gerlach Experiment (Space Quantization)

The confirming evidence of space quantization of angular momentum (and hence of magnetic moment) came from the celebrated atomic beam experiment of Stern and Gerlach (1922), which was originally devised to measure the magnetic moment of individual silver atoms. A well-defined beam of silver atoms was obtained by evaporating silver in a hot oven and letting the atoms through a series of holes as shown in the figure ( 7.10 ). The beam of silver atoms was allowed to pass through an *inhomogeneous* magnetic field B, which was produced between a sharp edged and a flat faced pole piece of a magnet. The emergent beam was received on photographic plate. The geometry of the experimental set up is shown in the figure. The magnetic field acts in z-direction and the atomic beam enters the field along x-axis.

Let $\mu$ be the magnetic moment of silver atom. In an *inhomogeneous* magnetic field having gradient in z-direction a magnetic dipole with magnetic moment $\mu$ experiences a translational force $F_z$ in z-direction.

$$F_z = \mu_z \frac{\partial B}{\partial z} = (\mu \cos\theta)\left(\frac{\partial B}{\partial z}\right) \tag{17}$$

where $\theta$ is the angle that magnetic moment vector makes with the field B. Classically the magnetic moment $\mu$ can take all possible orientations and hence $\theta$ is a continuous variable. Atoms for which $\cos\theta$ is positive, will be pulled up and those for which $\cos\theta$ is negative, will be pulled downward. Atoms whose magnetic moments are perpendicular to the magnetic field will be subjected to no force and hence they will go straight. Atoms with $\mu$ parallel to B will suffer maximum upward deflection and those with $\mu$ anti-parallel to B will suffer maximum downward deflection. Thus the beam of silver atoms, after emerging the field B will spread out; the spreading of atoms will be proportional to the z-component of $\mu$. Thus the classical physics predicts a *smeared out* pattern in vertical direction on the photographic plate. Stern and Gerlach, however, observed that the beam of silver atoms was split into two distinct parts.

**Quantum Mechanical Explanation** – The entire magnetic moment of silver atom comes from the spin of one of its electrons. That is, the spin of silver atom is ½. In magnetic field, the angular momentum and hence the magnetic moment can have only two orientations, parallel and anti-parallel to B. Atoms with $\mu$ parallel to B are deflected upward and those with $\mu$ anti-parallel to B are deflected downward and hence the beam gets split into two parts.

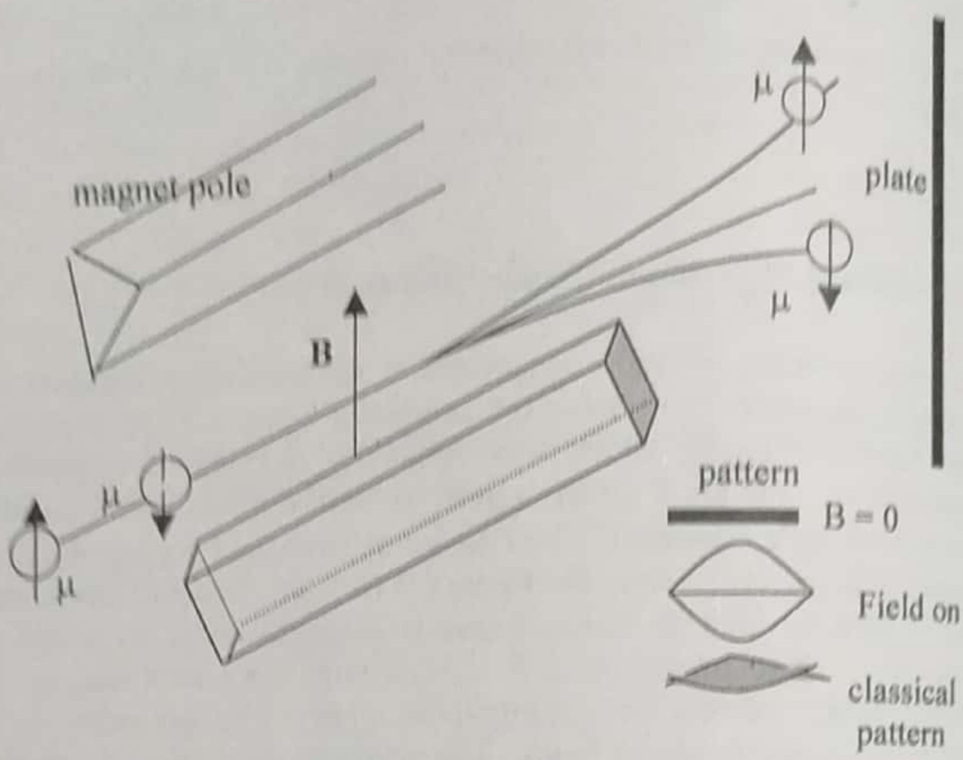



Fig ( 7.10 ) Stern-Gerlach experiment.

### 7.9 Zeeman Effect

In 1896 Peter Zeeman discovered that when a light source is placed in a magnetic field, the spectral lines emitted by the atoms split into a number of components. This phenomenon is called the *Zeeman Effect.* Suppose that a source emits a spectral line of frequency $\omega_0$ in absence of magnetic field. When magnetic field is switched on and the light emitted by the source is viewed transverse to the field, three equally spaced spectral lines of frequencies $\omega_0 - \Delta\omega$, $\omega_0$, and $\omega_0 + \Delta\omega$ are observed. The change in frequency of emitted light is called

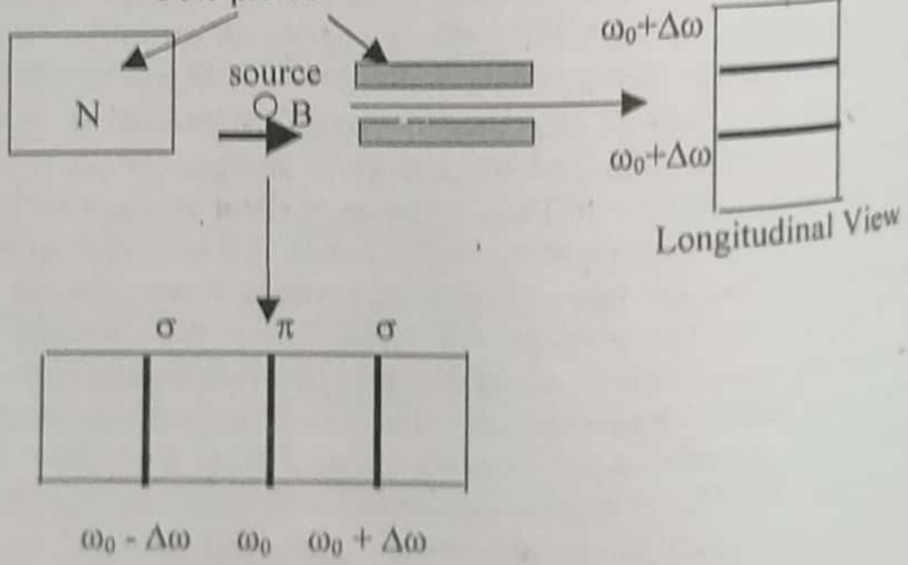



Fig (7.11) Zeeman Effect.

Zeeman shift. All the three lines are plane polarized and are usually named σ components. The plane of vibration of the central line is parallel to the magnetic field and that of the remaining lines is perpendicular to the magnetic field. When viewed parallel to the magnetic field (longitudinal view) only two spectral lines with frequencies $\omega_0 - \Delta\omega$ and $\omega_0 + \Delta\omega$ are observed. Both of the lines are circularly polarized, the line of higher frequency shows left hand polarization and that with lower frequency shows right hand polarization.

**Quantum Mechanical Explanation** – When an atom possessing magnetic moment is subjected to a magnetic field, its energy levels are split into a number of components, called magnetic sublevels. Obviously, the transitions between the two sets of sublevels will result in splitting of spectral lines.

In magnetic field, an atom having magnetic moment $\mu_J$ acquires additional energy $\Delta E$ given by

$$\Delta E = -\mu_J \cdot B = -g\mu_B B M_J \qquad (18)$$

where $M_J = J, J-1, \ldots\ldots 0 \ldots\ldots\ldots -J$.

Thus the energy level characterized by quantum number $J$ is split into $2J+1$ equally spaced sublevels. The amount of splitting depends on the Landé g-factor (i.e. L, S, J). In absence of magnetic field, the sublevels with different $M_J$ have the same energy i.e. they were degenerate. Application of the magnetic field, the degeneracy is removed and the sublevels with different $M_J$ now possess different energy.

We shall now first consider the *normal Zeeman effect* in which a spectral line is split into three equally spaced spectral lines in magnetic field. Normal Zeeman effect is observed when the pair of energy levels involved in the transition leading to the emission lines is *singlet* (characterized by $S = 0, g = 1$).

(i) Consider the splitting of spectral line resulting from the transition $^1P_1 \rightarrow {}^1S_0$. For lower level ($^1S_0$), $L = 0, S = 0, g = 1, M_J = 0$. This level does not split in the magnetic field.

For the upper level ($^1P_1$), $L = 1, S = 0, J = 1, g = 1, M_J = -1, 0, 1$. This level splits into three sublevels. The allowed transitions are shown in the figure. It is evident from the figure that the original line will split into three components.

The displacement of the spectral line relative to the original line in energy unit is

$$\Delta E = g\mu_B B = \mu_B B \qquad (19)$$

and in frequency unit is

$$\Delta\omega_0 = \frac{\Delta E_0}{\hbar} = \frac{\mu_B B}{\hbar} \qquad (20)$$

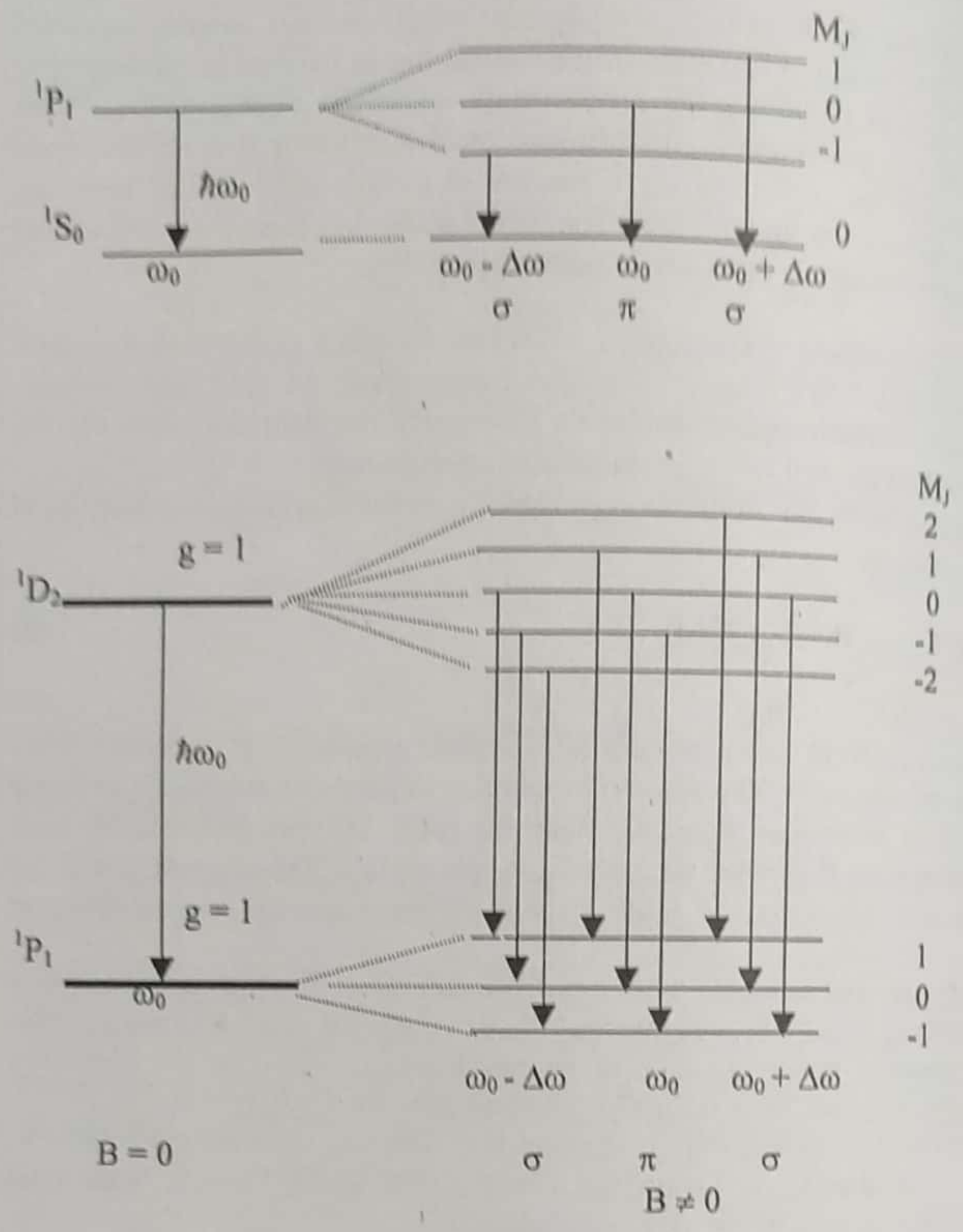



Fig ( 7.12 ) Zeeman Splitting of a spectral line.

This shift in frequency relative to the original line is called normal Zeeman shift (some time also called Lorentz shift). In terms of wavelength, the Zeeman shift is expressed as

$$d\lambda = \frac{\mu_\beta B\lambda^2}{2\pi\hbar c} = \frac{eB\lambda^2}{4\pi mc} \tag{21}$$

Quantum mechanical analysis shows that the spectral line with σ polarization results from the transitions in which $\Delta M_J = \pm 1$ and π polarization from the transitions in which $\Delta M_J = 0$ (excluding 0→0 transitions 0.

(ii) Now consider the normal Zeeman splitting of the spectral line resulting from the transition $^1D_2 \rightarrow {}^1P_1$.
For the lower level L = 0, S = 0, J = 1, g = 1, $M_J$ = -1, 0, 1. This level splits into three sublevels.
For the upper level, L = 2, S = 0, J = 2, g = 1, $M_J$ = -2, -1, 0, 1, 2. This level splits into five components. Allowed transitions are those, which satisfy the selection rules

$$\Delta M_J = 0, \pm 1.$$

The transitions for which $\Delta M_J = 0$ lead to emission line of a single line with frequency $\omega_0$; those for which $\Delta M_J = 1$ lead to a single of frequency $\omega_0 - \Delta\omega$ and those for which $\Delta M_J = -1$ correspond to frequency $\omega_0 + \Delta\omega$. These transitions with their frequencies are shown in the figure

## 7.10 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). In the magnetic field, the spectral lines split into more than three components and the magnitude of splitting is a rational fraction of the normal splitting $\Delta\omega_0$.

$$\Delta\omega = \left(\frac{p}{q}\right)\Delta\omega_0, \quad \text{p and q being integers.}$$

We shall explain the anomalous Zeeman effect with two examples; the splitting of sodium D lines. The $D_1$ line 5896A$^0$ arises from the transition $^2P_{1/2} \rightarrow {}^2S_{1/2}$ and the $D_2$ line 5890A$^0$ from transition $^2P_{3/2} \rightarrow {}^2S_{1/2}$.
The level $^2S_{1/2}$ (for which L = 0, S = ½, J = ½ , $g' = 2$) splits into two sublevels. The shift in energy is given by

$$\Delta E' = g' \mu_B B M_J', \qquad M_J' = -1/2\ ,\ 1/2 \tag{22}$$

The level $^2P_{1/2}$ (for which L = 1, S = ½, J = ½ .$g'' = 2/3$.) splits into two sublevels. The shift in energy is given by

$$\Delta E'' = g'' \mu_B B M_J'', \qquad M_J'' = -1/2\ ,\ 1/2\ . \tag{23}$$

The level $^2P_{3/2}$ (for which L = 1, S = ½ , J = 3/2, $g''' = 4/3$) splits into four sublevels. The shift in energy is given by

$$\Delta E''' = g''' \mu_B B M_J''', \qquad M_J''' = -3/2, -1/2, 1/2, 3/2. \tag{24}$$

The splitting of these energy levels and the allowed transitions, which satisfy the selection rules $\Delta M_J = 0, \pm 1$ are shown in the figure. The selection rule $\Delta M_J$ = ... leads to $\pi$ polarization and $\Delta M_J = \pm 1$ to $\sigma$ polarization. For the transition $^2P_{1/2}$ ... $^2S_{1/2}$ the shift of lines relative to the original line is

$$\Delta\omega = \frac{\Delta E'' - \Delta E'}{\hbar} = \frac{\mu_\beta B}{\hbar}\left(g'' M_J'' - g' M_J''\right) = \Delta\omega_0\left(g'' M_J'' - g' M_J''\right)$$

The value of $(g'' M''_J - g' M'_J)$ for each line is given beside the vertical ... showing the transitions in the figure. See that the original line disappears w... the magnetic field is switched on. The shift of the observed four lines in term... normal shift is given by

$$\Delta\omega = -\frac{4}{3}\Delta\omega_0,\ -\frac{2}{3}\Delta\omega_0,\ \frac{2}{3}\Delta\omega_0,\ \frac{4}{3}\Delta\omega_0$$

In the adjacent figure, the splitting of level $^2P_{3/2}$ and $^2S_{1/2}$ along with allo... transitions are also shown. The shifts of the six lines in terms of normal shift ... are

$$\Delta\omega = \left(-\frac{5}{3}, -\frac{3}{3}, -\frac{1}{3}, \frac{1}{3}, \frac{3}{3}, \frac{5}{3}\right)\Delta\omega_0$$

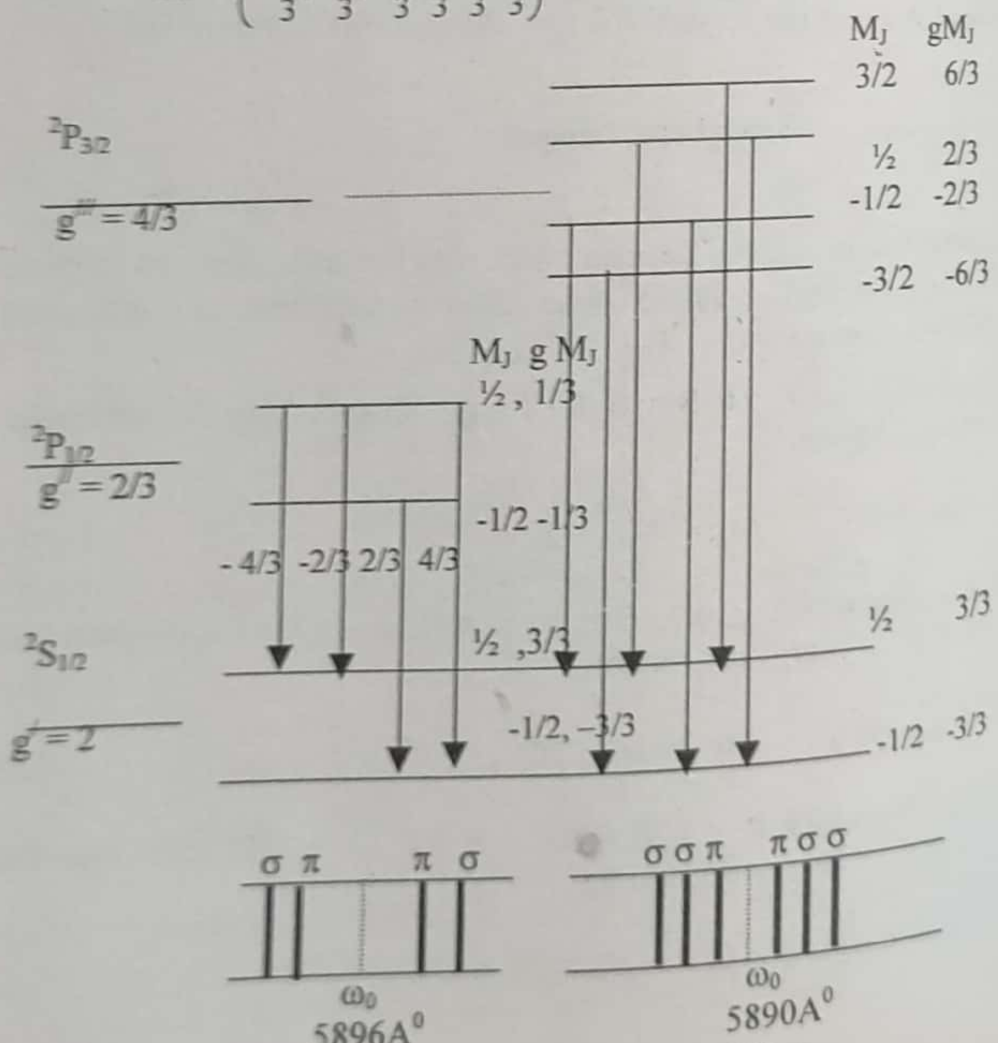



Fig (7.13 ) Anomalous Zeeman Effect