Shivaji University - B.Sc. Part-III

Semester-V I

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ATOMIC AND MOLECULAR SPECTRA, ASTRONOMY AND ASTROPHYSICS

Physics paper- (XV)

Spectral series

(1) Sharp series : The sharp spectral line arises due to transition from ns level to the lowest p-level. In normal state, the configuration for sodium state is $1s^2$, $2s^2$, $2p^6$, $3s^1$. The lowest state is 3s and excited states are 3P, 4S, 4P, 4D, 5S, 5P, 5D, 5F ... etc. Therefore, sharp series is represented by $3p \leftarrow ns$, where n= 4, 5, 6 ... etc.

(2) Principal series : This is prominent series. This series arises due to transition from np level to the lowest s-level. For sodium this series is represented by $3s \leftarrow np$, where n = 3, 4, 5, ...

(3) Diffuse series : This series is rather wider, hence it is called diffuse. For sodium, this series corresponds to the transition of $3P \leftarrow nD$, where n = 3, 4, 5 ...

(4) Fundamental series : This series was detected in which the running term is nF. For sodium fundamental series corresponds to the transition of $3D \leftarrow nF$, where n = 4, 5, 6 ...

Sodium spectrum

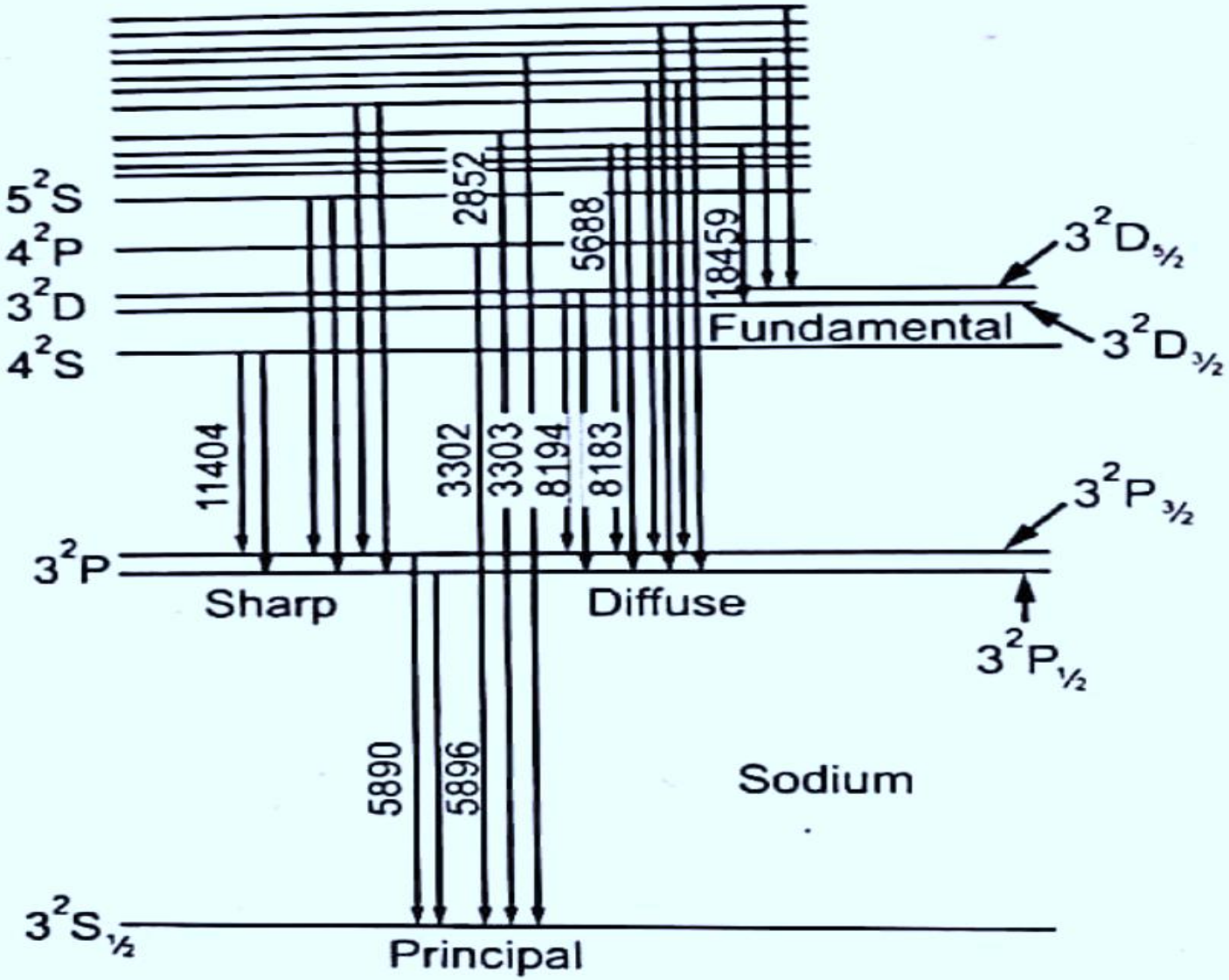
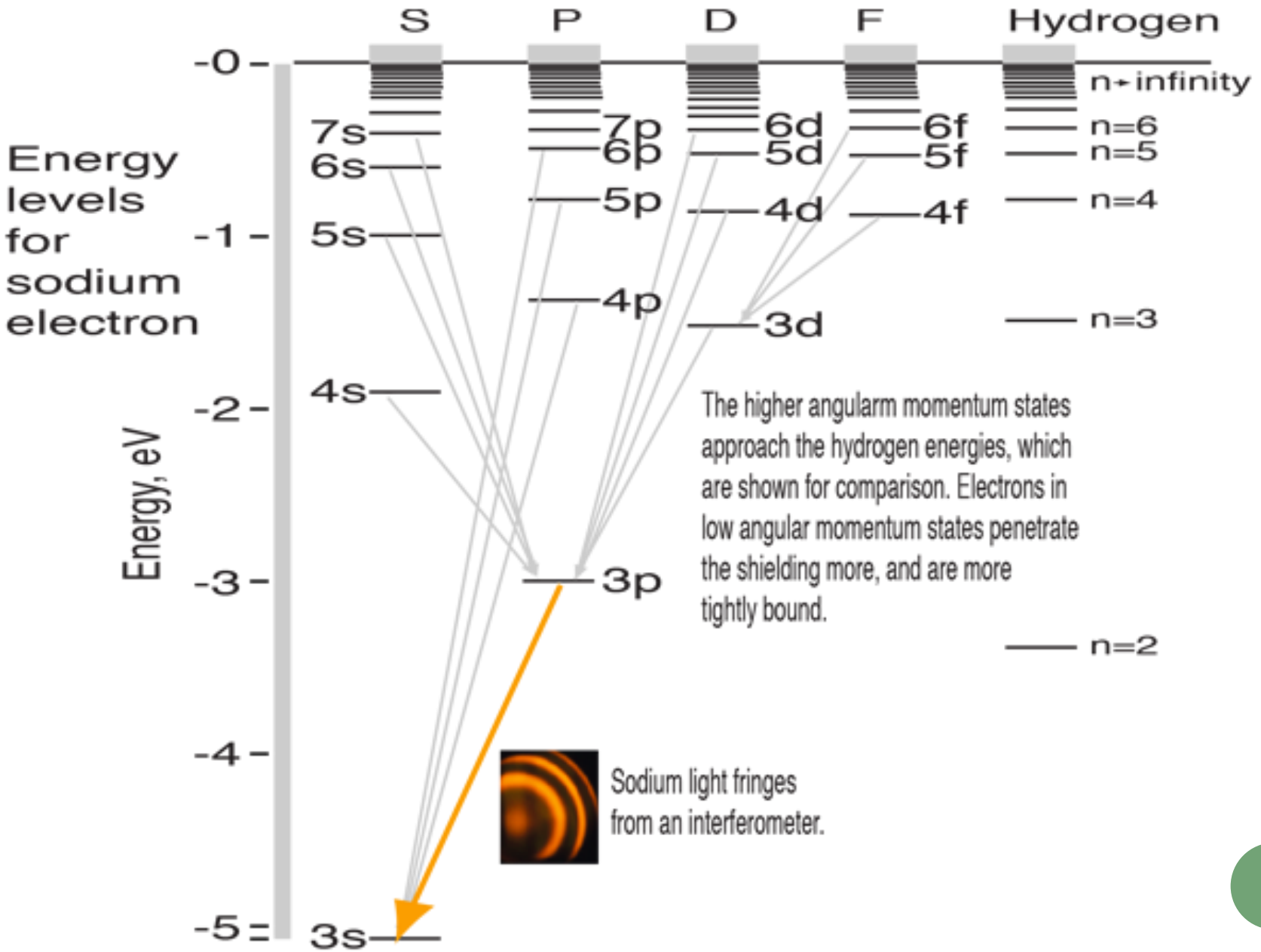


Fig. 1.1


S
P
D
F
Hydrogen
-0
-1
-2
-3
-4
-5
Energy, eV
Energy levels for sodium electron
n→infinity
n=6
n=5
n=4
n=3
n=2
7s
6s
5s
4s
3s
7p
6p
5p
4p
3p
6d
5d
4d
3d
6f
5f
4f
The higher angularm momentum states approach the hydrogen energies, which are shown for comparison. Electrons in low angular momentum states penetrate the shielding more, and are more tightly bound.
Sodium light fringes from an interferometer.

Selection rules of doublets

(a) The selection rule for L : For this quantum number, the rule is $\Delta L = \pm 1$ i.e. transitions take place only between levels whose quantum number (L) differs by one.

(b) The selection rule for J : It is $\Delta J = \pm 1$ or 0 ($0 \leftrightarrow 0$ excluded) i.e. change in total quantum number (J) allowed is zero or ± 1.

(c) The selection rule for S : For this quantum number, the rule $\Delta S = 0$, which means that states with different S do not combine with one another i.e. there is no change in quantum number S.

(d) The selection rule for principal quantum number n : In Bohr's theory, there was no restriction on changes in 'n' for transitions of atoms from one energy level to other. Similarly, according to quantum theory, there is no restriction on changes in n. It can change by any positive integral rule, including zero.

(e) The selection rule for quantum number *l* : This rule is $\Delta l = \pm 1$; i.e. in any electron transition, it must change by +1 or −1.

(f) The selection rule for m_e and m_s : The orbital magnetic quantum number, m_e either does not change or changes by ± 1, i.e. $\Delta m_e = 0$ or ± 1.

The spin magnetic quantum number 'm_s' remains unchanged, i.e. $\Delta m_s = 0$.

These rules are useful in allotting proper quantum number to observe spectral lines in the series.

Intensity rules for fine structure doublets

- **The line which involving the largest J value, is the strongest.**

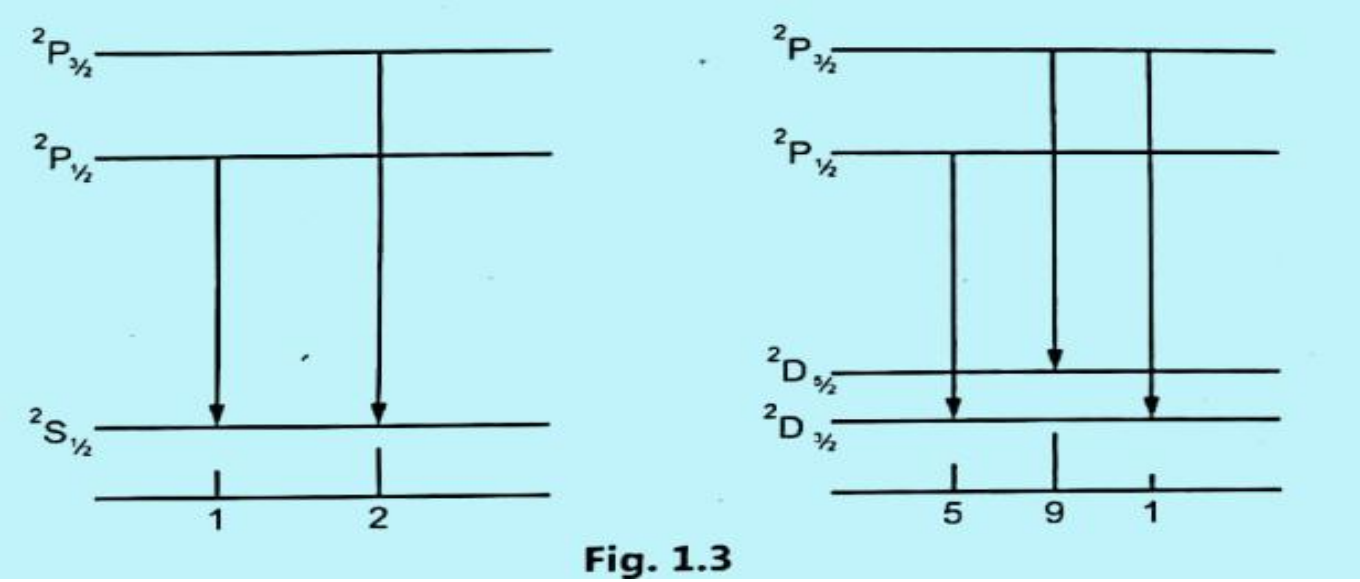


Fig. 1.3

For example : (1) In the first principal series doublet (Fig. 1.3) shows the line $^2S_{1/2} - {}^2P_{3/2}$ gives intense line than $^2S_{1/2} - {}^2P_{1/2}$.

(2) In diffuse series, there are two strong lines $^2P_{3/2} - {}^2D_{5/2}$ and $^2P_{1/2} - {}^2D_{3/2}$. But $^2P_{3/2} - {}^2D_{5/2}$ gives stronger line as it involves higher j value.

For qualitative aspects of the intensity of lines in doublet transition the following rules may be used :

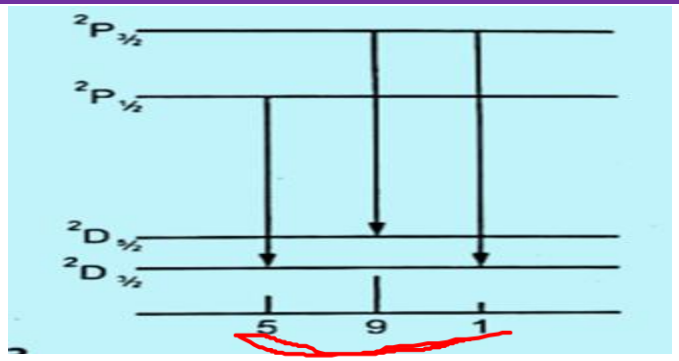
(a) The sum of the intensities of those lines of the doublet which come from common initial level is proportional to the quantum weight $(2j + 1)$ of that level.

(b) The sum of intensities of those lines of a doublet which end on a common level is proportional to the quantum weight $(2j + 1)$ of that level.

To apply the intensity rules :

1. Consider a simple case of principal series doublet, the transitions are $^2P_{1/2} - {}^2S_{1/2}$ and $^2P_{3/2} - {}^2S_{1/2}$. Here both the transitions end on the same common level $^2S_{1/2}$. Therefore, the intensities of 2P level are $2\left(\frac{3}{2}\right) + 1$ and $2\left(\frac{1}{2}\right) + 1$ which give intensity ratio as 2 : 1.

2. Consider diffuse series doublet which involves three spectrum lines. The transitions are $(^2P_{3/2} - {}^2D_{3/2})$, $(^2P_{1/2} - {}^2D_{3/2})$ and $(^2P_{3/2} - {}^2D_{3/2})$. A diffuse series doublet is written as



		$^2P_{3/2}$	$^2P_{1/2}$
		4	2
$^2D_{5/2}$	6	X	0
$^2D_{3/2}$	4	Y	Z

The number directly below and to the right of the term symbols are quantum weights $(2j + 1)$.

Let X, Y, Z represent unknown intensities of three allowed transitions and 0 represent the forbidden transition. From summation rules (a) and (b), the following relations are set up. The sum of lines starting from $^2D_{5/2}$ is to the sum starting from $^2D_{3/2}$ as 6 to 4.

$$\therefore \quad \frac{X + 0}{Y + Z} = \frac{6}{4} = \frac{3}{2} \quad \text{and} \quad \frac{X + Y}{0 + Z} = \frac{4}{2} = 2$$

$$\therefore \quad 2X = 3Y + 3Z \quad \text{and} \quad X + Y = 2Z$$

ie. x = 2z-y

$$\therefore \quad 2(2Z - Y) = 3Y + 3Z$$

$$\text{i.e.} \quad Z = 5Y$$

$$\therefore \quad X + Y = 10Y$$

$$\text{i.e.} \quad X = 9Y$$

$$\therefore \quad X : Y : Z = 9 : 1 : 5 \text{ is the intensity ratio.}$$

4z-2y=3y+3z
4z-3z=3y+2y
Z=5y

Fig. 1.3 shows allowed transitions and relative intensities. If 2D terms are very close, then satellite with very small intensity (y = 1) is not resolved and hence only two lines are observed with intensity ratio (9 + 1) : 5 i.e. 2 : 1.

Normal order of fine structure doublet

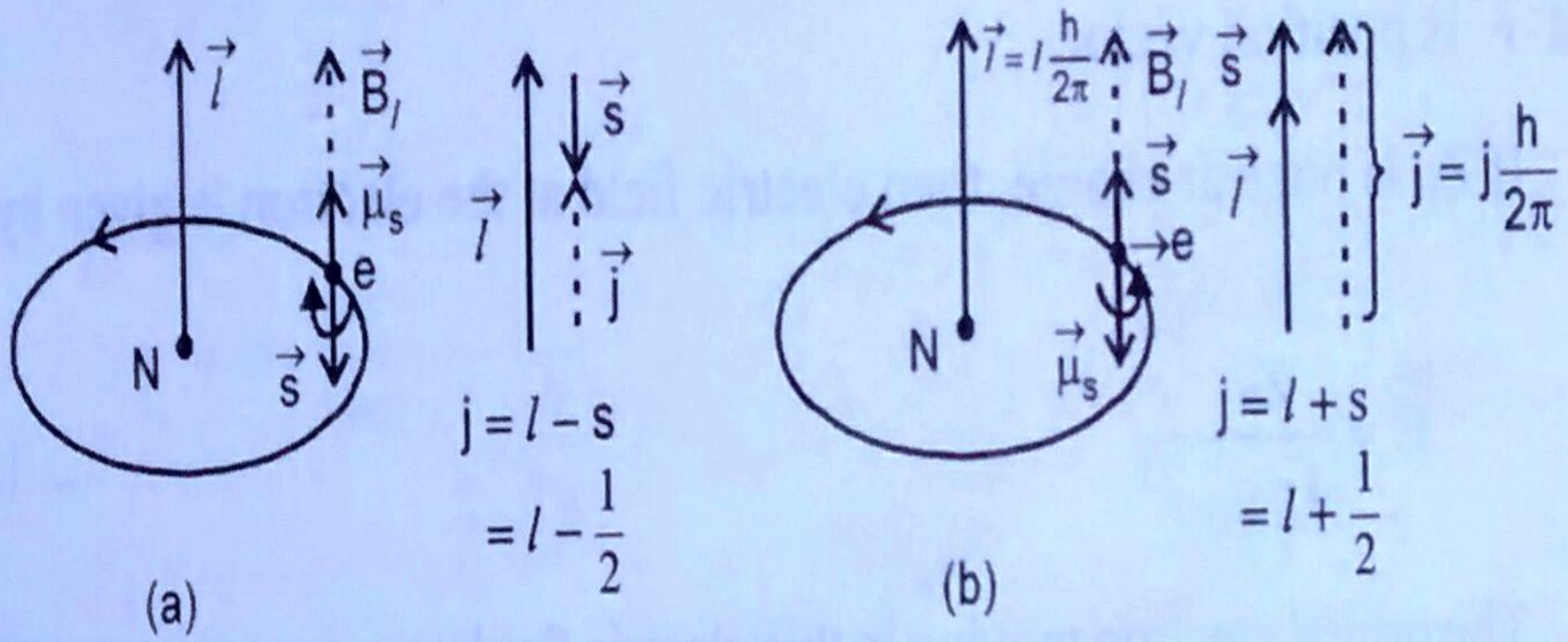


Fig. 1.4 : Total angular momentum $\vec{j} = j\frac{h}{2\pi}$ for fine-structure Doublets

$\vec{s} = s \cdot \frac{h}{2\pi} = \frac{1}{2}\frac{h}{2\pi}$, along with orbital angular momentum, $\vec{l} = l \cdot \frac{h}{2\pi}$ due to orbital motion of electron around the nucleus. Spin angular momentum is the intrinsic property of electron which may be thought of as due to spin motion of electron about its axis passing through the centre.

This produces a magnetic field $(\vec{B}_l)$ which is parallel to $\vec{l}$. If the spin magnetic moment $\vec{\mu}_s$ lines up in the direction of $\vec{B}_l$, then a state with total angular momentum quantum number $j = l - \frac{1}{2}$ results. On the other hand if $\vec{\mu}_s$ is antiparallel to $\vec{B}_l$, then, $j = l + \frac{1}{2}$ as shown in Fig. (1.4).

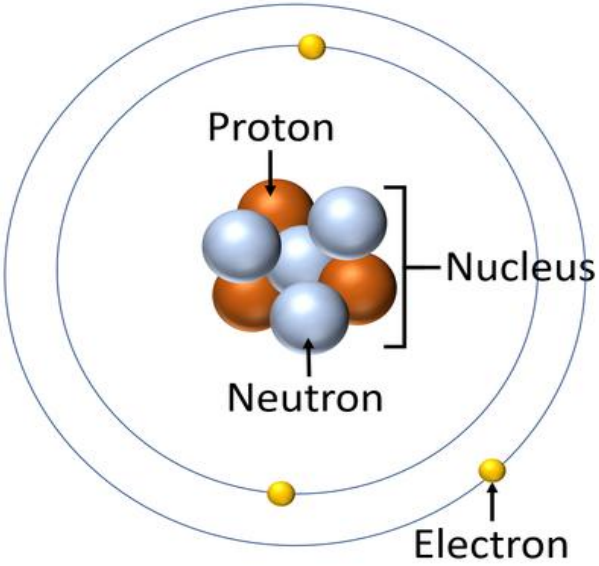
Here alignment of $\vec{\mu}_s$ along $\vec{B}_l$ is most probable and hence stable. Therefore, this arrangement corresponds to smaller energy. So a level with, $j = l - \frac{1}{2}$ lies deeper in a doublet as compared to a level with, $j = l + \frac{1}{2}$. This general feature is the *normal order* of the fine structure doublets. For example, in doublet ^2P levels, $^2P_{1/2}$ lies lower as compared to $^2P_{3/2}$.

However, there are certain exceptions in which the terms (levels) with higher *j*-value lie deeper and they are referred to as *inverted terms*.

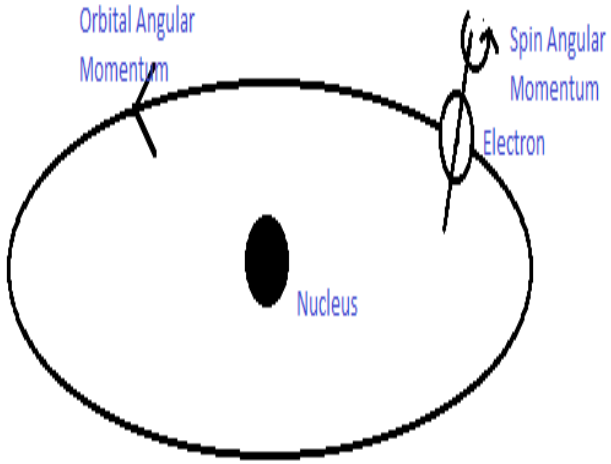
Electron Spin Orbit Interaction: Calculation of Term Value of Fine Structure Level

Spin Orbit Interaction:

It is interaction between spin magnetic moment and orbital magnetic moment of the atom.



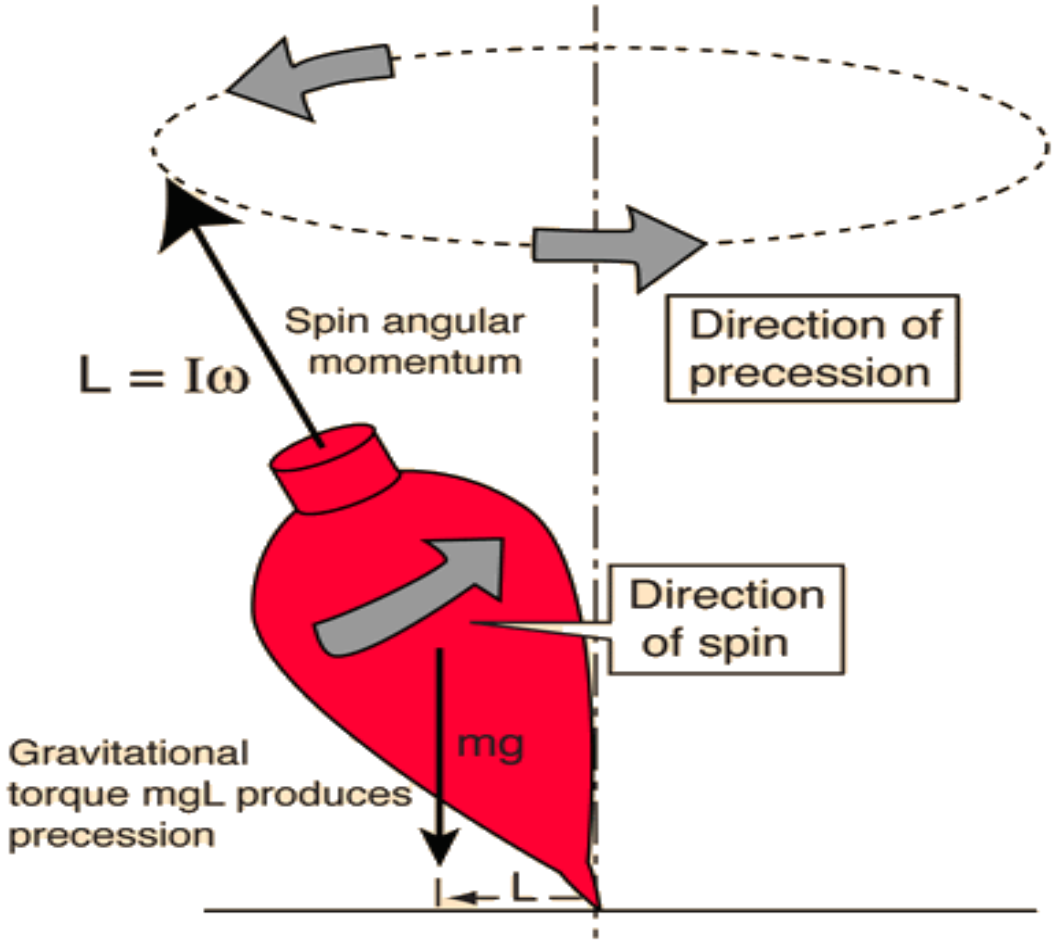
a



b

Precession:

Precession is a change in the orientation of the rotational axis of a rotating body. And the slow movement of the axis of a spinning body around another axis.



Larmour precession:

In physics, Larmour precession is the precession of the magnetic moment of an object about an external magnetic field.

Theorem:

When a atom is placed in external magnetic field, the orbit precess the field direction of their axis, this precession is called Lamoure precession. And the frequency of precession is called Lamoure frequency.

By considering the spin angular momentum $s^* \frac{h}{2\pi}$, the energy level characterized by orbital angular momentum $l^* \frac{h}{2\pi}$ shows doublet except one with $l = 0$ i.e. 2s state.

We shall obtain the same result using vector atom model by semi-classical method. On the classical model of alkali atoms, the single electron moves in a central force field with an orbital angular momentum.

$$l^* \frac{h}{2\pi} = m\vec{r} \times \vec{v} \qquad \ldots (1.1)$$

Central force

$$\mathbf{r \times v = \frac{l*h}{2\pi m}}$$

where, $l^* = \sqrt{l\,(l+1)}$, m is the mass of the electron, v is the velocity of electron and r is the radius vector.

According to classical electro-magnetic theory, if Ze is nuclear charge, the electric field $\vec{E}$ is given by (CGS unit)

$$\vec{E} = \frac{Ze\,\vec{r}}{4\pi\varepsilon_0 r^3} \qquad \ldots (1.2)$$

The orbital electron moving in this electric field experiences a magnetic field given by

$$H = \frac{\vec{E} \times \vec{v}}{c}, \text{ where c is the velocity of light in free space}$$

$$= \frac{Ze}{4\pi\varepsilon_0 c}\frac{(\vec{r} \times \vec{v})}{r^3}$$

From equation (1.1), we get

$$H = \frac{Ze}{4\pi\varepsilon_0 c}\,\frac{1}{r^3}\left(\frac{l^* h}{2\pi m}\right)$$

$$= \frac{Ze\,l^* h}{8\pi^2\varepsilon_0 mc}\cdot\frac{1}{r^3} \qquad \ldots (1.3)$$

In this field the spinning electron undergoes Larmour precession around the field direction. It behaves like magnetic top. Dirac showed that due to spin motion, the electron possesses a magnetic moment

$$\mu_s = \frac{eh}{4\pi mc} \qquad \ldots (1.4)$$

From Larmour's theorem, the angular velocity of this precession is given by

$$\omega_L = \text{Magnetic field} \times \frac{\left[\begin{array}{c}\text{Magnetic moment of} \\ \text{spinning electron}\end{array}\right]}{\left[\begin{array}{c}\text{Mechanical moment of} \\ \text{spinning electron}\end{array}\right]}$$

$$= H \cdot \frac{\mu_s}{S \cdot \frac{h}{2\pi}} = H \cdot \frac{eh}{4\pi mc} \frac{1}{\frac{1}{2} \cdot \frac{h}{2\pi}}$$

$$\omega_L = \frac{He}{mc} \qquad \ldots (1.5)$$

By relativistic treatment, Thomas showed that, in addition to the Larmour precession (ω_L), there is a relativity precession (ω_T) which is one half of ω_L, but in the opposite direction.

$$\omega_T = -\frac{1}{2}\omega_L$$

$$\omega = \omega_L - \frac{1}{2}\omega_L$$

$$\omega = \frac{2\,\omega L - \omega_L}{2}$$

Therefore, the resultant precession of spinning electron is

$$\omega = \omega_L + \omega_T = \frac{1}{2}\omega_L = \frac{He}{2\,mc}$$

Using equation (1.3), $\omega = \dfrac{Ze^2\, h\, l^*}{16\pi^2\, \varepsilon_0\, m^2\, c^2} \cdot \dfrac{1}{r^3}$ ... (1.6)

Now the interaction energy is the product of precessional angular velocity ω and the projection of spin angular momentum on l^*.

$$\therefore \quad \Delta W = \omega \cdot s^* \frac{h}{2\pi} \cos(l^*\, s^*)$$

where, $\cos(l^*\, s^*)$ is cosine of the angle between l^* and s^*.

$$\therefore \quad \Delta W = \frac{Ze^2\, h^2\, l^*\, s^* \cos(l^*\, s^*)}{32\pi^3\, \varepsilon_0\, m^2\, c^2\, r^3} \qquad \ldots (1.7)$$

In field free space both orbit and spin are free to move so that l^* and s^* will precess around their resultant j^* as shown in Fig. 1.5. According to the law of conservation of angular momentum, the resultant j^* and hence the angle between l^* and s^* must remain invariant. If the angle is fixed, the cosine does not need to be averaged and therefore $l^* s^* \cos(l^* s^*)$ is calculated by using cosine law.

$$j^{*2} = l^{*2} + s^{*2} + 2l^* s^* \cos(l^* s^*)$$

$$\therefore \quad l^* s^* \cos(l^* s^*) = \frac{j^{*2} - l^{*2} - s^{*2}}{2} \qquad \ldots (1.10)$$

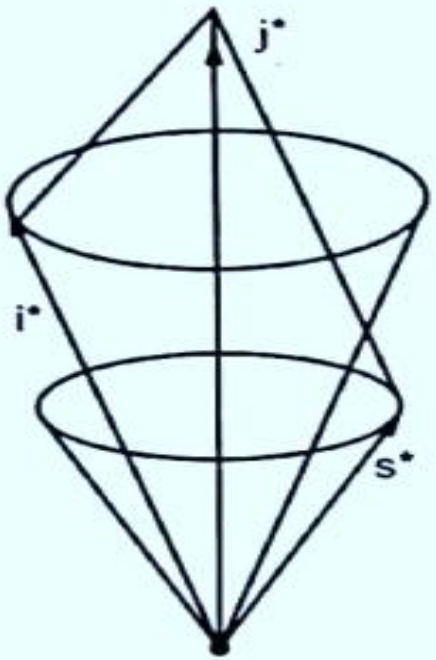


Fig. 1.5

For elliptic orbit, the distance of the electron from the nucleus changes continuously, hence it is necessary to calculate average interaction energy ΔW. In doing this only the average value $\left(\frac{\overline{1}}{r^3}\right)$ need to be calculated, since the interaction energy is very small as compared to the total energy of electron.

From perturbation theory and quantum mechanics,

$$\left(\frac{\overline{1}}{r^3}\right) = \frac{Z^3}{a_1^3\, n^3\, l\left(l+\frac{1}{2}\right)(l+1)} \qquad \ldots (1.8)$$

where, $a_1 = \frac{\varepsilon_0 h^2}{\pi m e^2}$ = radius of first Bohr-orbit.

Therefore, equation (1.7) becomes,

$$\Delta W = \frac{Ze^2 h^2}{32\pi^3 \varepsilon_0 m^2 c^2} \frac{Z^3 l^* s^* \cos(l^* s^*)}{a_1^3\, n^3\, l\left(l+\frac{1}{2}\right)(l+1)} \qquad \ldots (1.9)$$

Substituting the value of $a_1 = \frac{\varepsilon_0 h^2}{\pi m e^2}$ in equation (1.9), we get

$$\Delta W = \frac{Z^4 e^2 h^2}{32\pi^3 \varepsilon_0 m^2 c^2} \frac{(\pi m e^2)^3}{(\varepsilon_0 h^2)^3} \frac{l^* s^* \cos(l^* s^*)}{n^3 l\left(l + \frac{1}{2}\right)(l+1)}$$

$$= \frac{Z^4 m e^8}{32\varepsilon_0^4 c^2 h^4} \frac{l^* s^* \cos(l^* s^*)}{n^3 l\left(l + \frac{1}{2}\right)(l+1)}$$

Therefore, the term shift in wave number becomes

$$\Delta T = -\frac{(\Delta W)}{hc} = -\Gamma$$

$$\therefore \quad \Gamma = \frac{Z^4 me^8}{32\varepsilon_0^4 c^3 h^5} \cdot \frac{l^* s^* \cos(l^* s^*)}{n^3 l\left(l + \frac{1}{2}\right)(l+1)}$$

$$\Gamma = \frac{R\alpha^2 Z^4}{n^3 l\left(l + \frac{1}{2}\right)(l+1)} \; l^* s^* \cos(l^* s^*) \qquad \ldots (1.11)$$

where, $R = \frac{me^4}{8\varepsilon_0^2 ch^3}$ = Rydberg's constant

$\alpha = \frac{e^2}{2hc\varepsilon_0}$ = Fine structure constant

$\alpha^2 = \frac{e^4}{4h^2 c^2 \varepsilon_0^2}$ and using equation (1.10)

$$\therefore \quad \Gamma = a \cdot l^* s^* \cos(l^* s^*) = \frac{a}{2}(l^{*2} - l^{*2} - s^{*2}) \qquad \ldots (1.12)$$

where, $a = \frac{R\alpha^2 Z^4}{n^3 l\left(l + \frac{1}{2}\right)(l+1)}$

Thus, the term value of fine structure level is

$$T = T_0 - \Gamma$$

where, T_0 is the hypothetical term value for centre of gravity of doublet fine structure and Γ gives shift of each fine structure level from T_0.

The separation between doublet states for s, p, d, f ... electrons may be calculated as follows by using equation (1.12).

(i) For s-electron, $l = 0$, $s = \frac{1}{2}$, $j = \frac{1}{2}$ $\therefore \Gamma = 0$

i.e. s-states are single.

(ii) For p-electron, $l = 1$, $s = \frac{1}{2}$ and $j = \frac{1}{2}, \frac{3}{2}$

$$\therefore \quad \Gamma_{j=1/2} = \frac{a}{2}\left[\frac{3}{4} - 2 - \frac{3}{4}\right] = -a$$

$$\Gamma_{j=3/2} = \frac{a}{2}\left[\frac{15}{4} - 2 - \frac{3}{4}\right] = +\frac{a}{2}$$

Here,
$l^* = l(l+1)$
$J^* = j(j+1)$
$S^* = s(s+1)$

(iii) For d-electron, $l = 2$, $s = \frac{1}{2}$ and $j = \frac{3}{2}, \frac{5}{2}$

$$\therefore \qquad \Gamma_{3/2} = \frac{-3a}{2} \text{ and } \Gamma_{5/2} = a \text{ ... etc.}$$

Here separation between the doublets goes on decreasing with l as shown in Fig. 1.6.

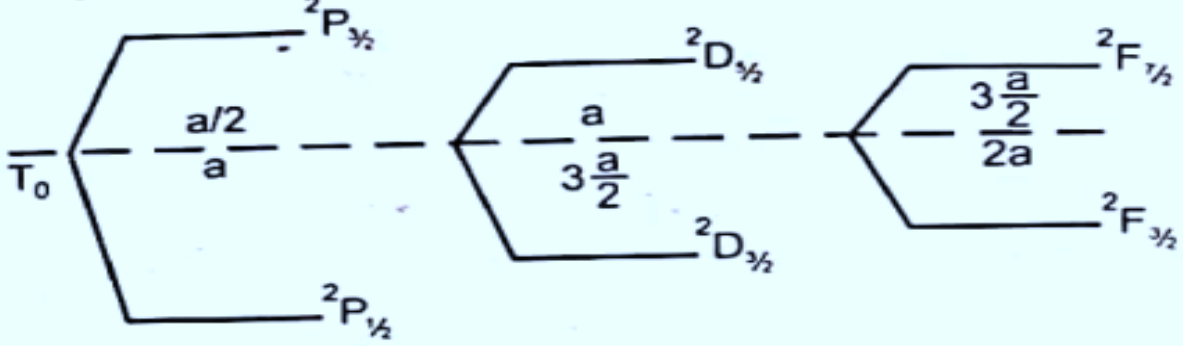


Fig. 1.6

From equation (1.11), the observed features of the doublets are :

1. Doublet separation increases with increasing atomic number.
2. Doublet separation decreases with increasing n i.e. in going to higher number of given series.
3. Doublet separation decreases with increasing l i.e. in going to different series p, d, f etc. At higher value of l, the doublet levels are not separated i.e. tends to zero.

Normal and anomalous Zeeman Effect:(Explanation using vector atom model) and also lande's 'g' factor

Zeeman effect:

When atomic sources are placed in external magnetic field, the optical spectral lines split into a number of polarised components. This was first observed by Zeeman, in 1896, and hence known as *Zeeman effect*.

Normal Zeeman effect:

The Zeeman effect that occurs for optical spectral lines resulting from transitions between singlet states (*i.e.* total spin angular momentum of the states is zero) is known as *normal Zeeman effect* and each spectral line splits into three components called *normal triplet*.

Zeeman effect are due to transitions between the singlet levels for which spin angular momentum, S = 0. Hence, to explain normal Zeeman effect, the concept of electron spin is not necessary. Thus, considering only the orbital motion of electron we can explain the normal Zeeman splitting using vector atom model. According to classical theory the magnetic moment due to orbital motion of electron is,

$$\mu_l = IA$$

where, $I = \frac{e}{T}$ is current in the orbit

$$\text{Area}(r) = \int_0^{2\pi r} \frac{1}{2} r \, du$$
$$= \left[\frac{1}{2} ru\right]_0^{2\pi r}$$
$$= \pi r^2.$$

and $A = \int_0^{2\pi} \frac{1}{2} r^2 d\theta$, is area of the orbit

Also, orbital angular momentum, $P_l = mr^2 \frac{d\theta}{dt}$ is conserved.

$$\therefore \quad A = \int_0^T \frac{1}{2} \frac{P_l}{m} dt$$

Therefore, $\mathbf{r^2 = \frac{pl}{m}}$

$$= \frac{1}{2} \frac{P_l}{m} T$$

$$\therefore \quad \mu_l = \frac{e}{T} \cdot \frac{1}{2} \frac{P_l}{m} T$$

$$\therefore \quad \boxed{\left|\vec{\mu}_l\right| = \left|\vec{P}_l\right| \cdot \frac{e}{2m}}$$

But, $P_l = \overset{*}{l}\frac{h}{2\pi}$, according to quantum mechanics.

Where $\overset{*}{l} = \sqrt{l(l+1)}$ and l is orbital angular momentum quantum number.

If $\vec{L}$ is the total orbital angular momentum of the valence electrons $\left(\vec{L} = \vec{l_1} + \vec{l_2} + \ldots\right)$, then total magnetic moment $\left(\vec{\mu}_L\right)$ due to orbital motion of electrons is,

$$\left|\vec{\mu}_L\right| = \left|\vec{L}\right| \cdot \frac{e}{2m}$$

where, e and m are charge and mass of an electron.

Precession of L around B

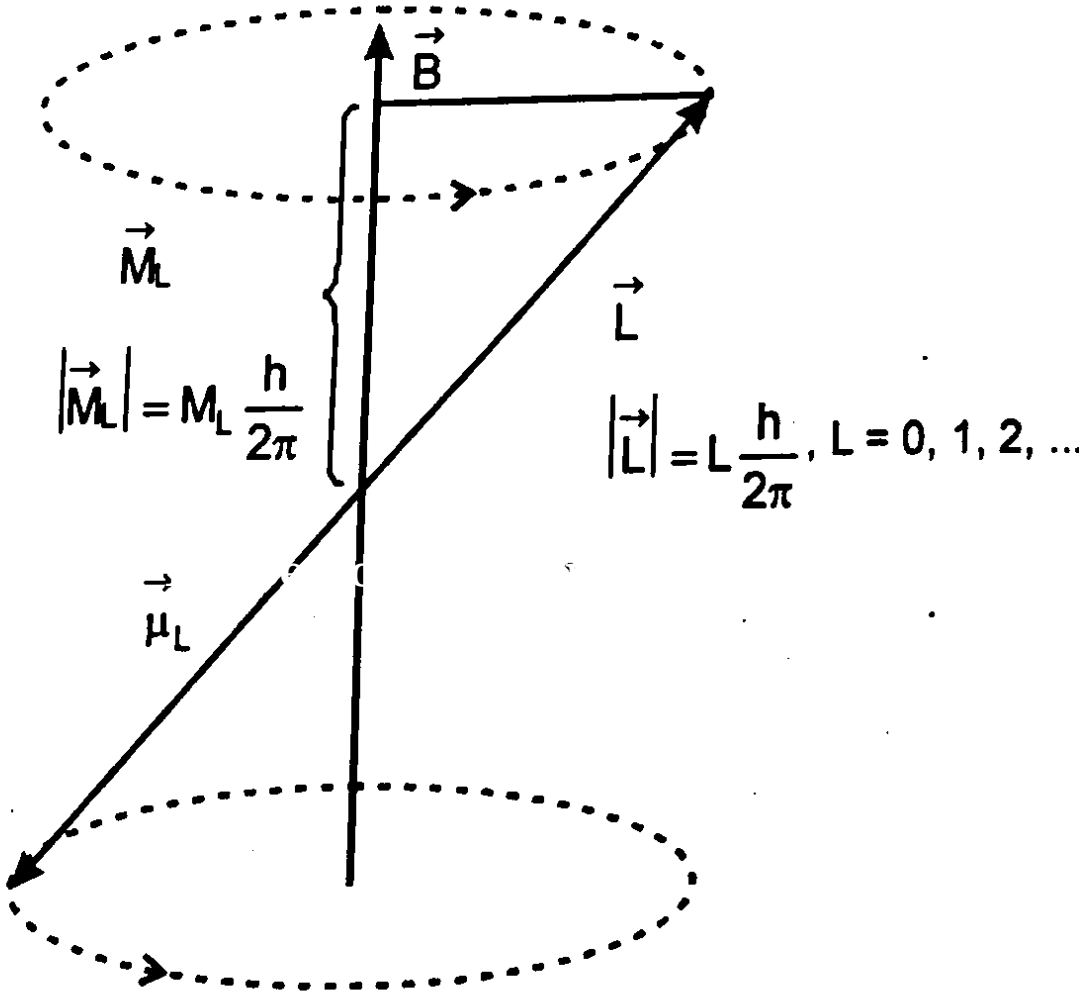


Fig. 1.7 : Precession of $\vec{L}$ around $\vec{B}$

When the atom is placed in an external magnetic field $\vec{B}$, the $\vec{L}$ vector precesses around the field direction as shown in Fig. (1.7). The orientation of $\vec{L}$ with respect to $\vec{B}$ is quantised, such that projection of $\vec{L}$ on $\vec{B}$ is $\vec{M}_L$, such that,

$$\left|\vec{M}_L\right| = M_L \frac{h}{2\pi} \quad \text{where, } M_L = L, L-1, \ldots . -L$$

This precession is known as *Larmor precession*, due to which each L-level splits into (2L + 1) levels characterised by M_L-values.

From Larmor theorem, the angular velocity of precession is given by,

$$\omega = \frac{\left|\vec{\mu}_L\right|}{\left|\vec{L}\right|} \cdot B = \frac{e}{2m} \cdot B$$

Where,

$$\left|\vec{\mu}_L\right| = \left|\vec{L}\right| \cdot \frac{e}{2m}$$

$\therefore$ The magnetic interaction energy on account of precession is obtained as the product of angular velocity ω and $\left|\vec{M}_L\right|$.

$$\therefore \quad \Delta W_m = \omega \cdot \left|\vec{M}_L\right| = \omega \cdot M_L \frac{h}{2\pi}$$

$$= \frac{e}{2m} B M_L \frac{h}{2\pi}$$

$$= \frac{eh}{4\pi m} \cdot B M_L$$

$\therefore$ Shift in the energy level in terms of wave numbers is,

$$-\Delta T_m = +\frac{\Delta W_m}{hc} = \frac{eB}{4\pi mc} \cdot M_L \equiv L' M_L$$

Since B is same for all levels, $L' = \frac{eB}{4\pi mc}$ is a constant called *Lorentz unit*. Hence, the Zeeman split levels are equispaced, for all the terms, with spacing equal to $\frac{eB}{4\pi mc} \cdot \Delta M_L = \frac{eB}{4\pi mc}$ ($\because \Delta M_L = 1$ for successive levels).

Thus, separation between successive Zeeman levels is equal to Lorentz unit, $L' = \frac{eB}{4\pi mc}$.

The spacing increases with strength of magnetic field (B). Let us consider, as an example, the fine structure spectral line corresponding to the transition $^1D_2 - {}^1P_1$.

The term (level) corresponding to L = 1 (*i.e.* $^1P_1$), splits into 3-equispaced levels, as (2L + 1) = 3. Similarly, the terms $^1D_2$ with L = 2, splits into 5 (= 2L + 1) equispaced levels. The spacing between successive levels is same and equal to Lorentz unit and is independent of L-value of field free state.

The selection rules for magnetic quantum number M_L are obtained from quantum mechanics as,

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

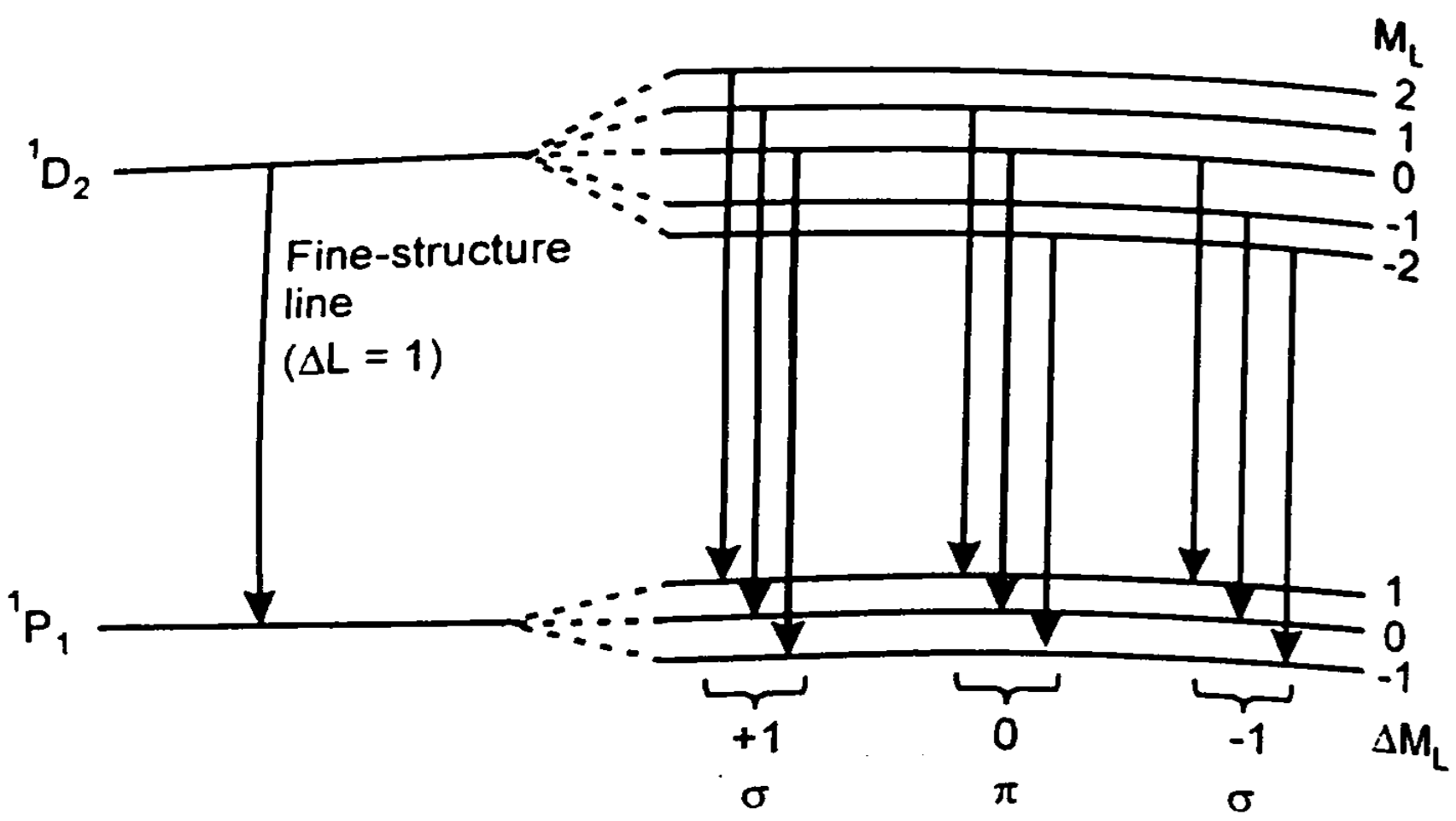


Fig. 1.8 : Energy level diagram showing Zeeman-splitting

$\therefore \Delta M_L = 0$, corresponds to undisplaced line (field free line), for which the electric vector is parallel to $\vec{B}$ and is called polarised π-component.

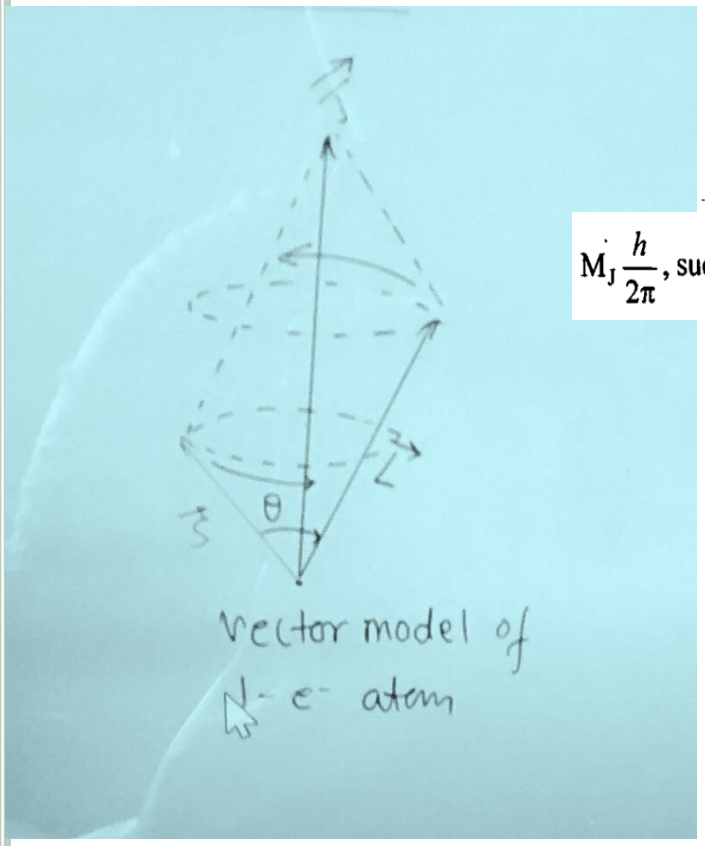
Similarly, for $\Delta M_L = \pm 1$, we get two symmetrically displaced components for which electric vector is perpendicular to $\vec{B}$ and they are called polarised σ-components.

$$\therefore \text{Zeeman (normal) splitting of lines} = \Delta\nu = L' = \frac{eB}{4\pi mc}.$$

Anamoulus Zeeman effect

The Zeeman effect that occurs for optical spectral lines resulting from transitions between multiplet states (*i.e.* states with non-zero spin) show Zeeman splitting into several components. Either one or both the states are multiplets. This is known as '**anomalous Zeeman effect.**

Zeeman splitting of the level (states) is much smaller than the fine structure splitting of the level.



$M_J \frac{h}{2\pi}$, such that, $M_J = J, J-1, \ldots -J$.

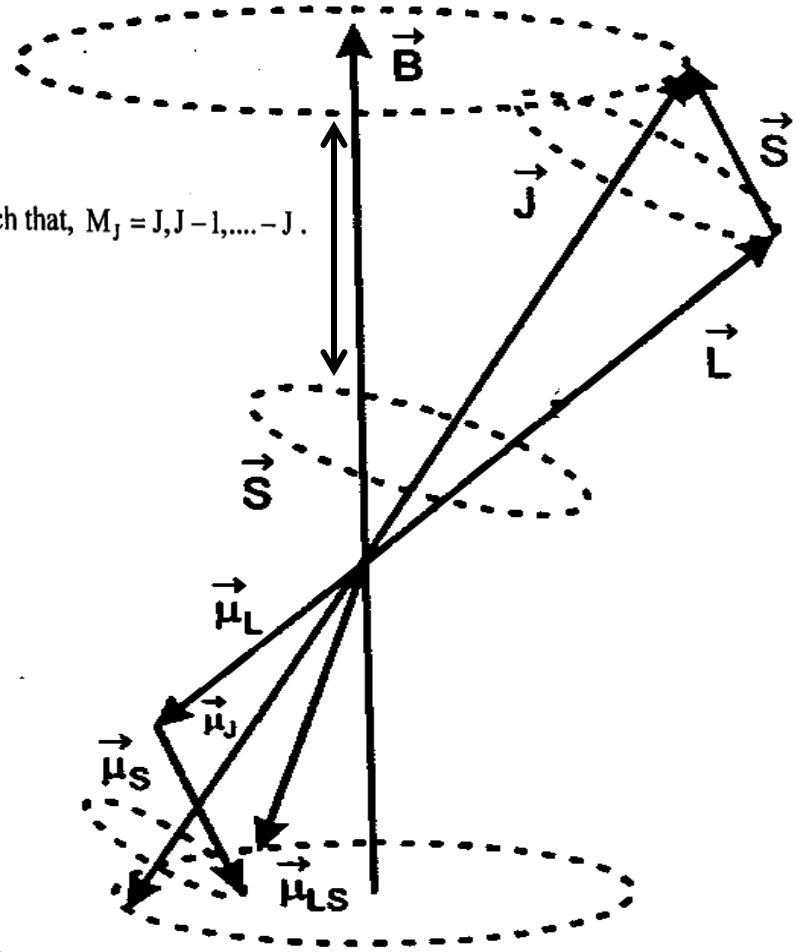


Fig. 1.9 : Vector diagram showing mechanical moments ($\vec{L}$, $\vec{S}$ and $\vec{J}$) and magnetic moments (μ_L, μ_S, μ_{LS} and μ_J) in $\vec{B}$.

According to vector atom model, the total orbital angular momentum $\vec{L}$ is the vector sum of orbital angular momenta of all the valence electrons (*i.e.* $\vec{L} = \vec{l}_1 + \vec{l}_2 + ...$). Similarly, the total spin angular momentum is $\vec{S}$ (*i.e.* $\vec{S} = \vec{S}_1 + \vec{S}_2 + ...$). Both $\vec{L}$ and $\vec{S}$ precess about total angular momentum $\vec{J}$ (where, $\vec{J} = \vec{L} + \vec{S}$). If the external applied magnetic field ($\vec{B}$) is weak enough that coupling between $\vec{L}$ and $\vec{S}$ is not broken, then $\vec{J}$ precesses slowly around $\vec{B}$ and is called **Larmor precession**. The orientation of $\vec{J}$ with respect to $\vec{B}$ is quantised, such that projection of $\vec{J}$ along $\vec{B}$ takes discrete values $M_J \frac{h}{2\pi}$, such that, $M_J = J, J-1, ... -J$.

Thus, a fine structure level with certain J-value splits into (2J + 1) Zeeman levels.

The magnetic moment μ_L, due to orbital motion of electrons is,

$$\mu_L = P_L \cdot \frac{e}{2m} \quad \text{... where, } P_L = \dot{L}\frac{h}{2\pi} = \sqrt{L(L+1)}\,\frac{h}{2\pi}.$$

Using quantum mechanics, Dirac showed that the magnetic moment μ_s due to spin motion of electrons is,

$$\mu_s = P_s \cdot 2 \cdot \frac{e}{2m} \quad \text{where, } P_s = \dot{S}\frac{h}{2\pi} = \sqrt{S(S+1)} \cdot \frac{h}{2\pi}.$$

Since charge on electron is negative, both $\vec{\mu}_L$ and $\vec{\mu}_S$ are oppositely directed to corresponding mechanical moments $\vec{P}_L$ and $\vec{P}_S$.

However, the components parallel to $\vec{J}$, remain constant in magnitude and direction and hence contribute to the total magnetic moment μ_J of the atom.

$$\therefore \quad \mu_J = \text{Component of } \vec{\mu}_L \text{ along } \vec{J} + \text{Component of } \vec{\mu}_S \text{ along } \vec{J}$$

$$= \left|\vec{\mu}_L\right| \cdot \cos(L, J) + \left|\vec{\mu}_S\right| \cdot \cos(S, L)$$

$$= \frac{e}{2m} P_L \cos(L, J) + 2 \cdot \frac{e}{2m} P_S \cos(S, L)$$

$$= \frac{e}{2m}\left[\sqrt{L(L+1)} \cdot \cos(L, J) + 2\sqrt{S(S+1)} \cdot \cos(S, L)\right] \cdot \frac{h}{2\pi}$$

Applying cosine rule for triangle formed by $\vec{L}$, $\vec{S}$ and $\vec{J}$, we get,

$$\cos(L, J) = \frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1)} \cdot \sqrt{L(L+1)}}$$

and $$\cos(S, J) = \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)} \cdot \sqrt{S(S+1)}}$$

$$= \frac{e}{2m}\left[\sqrt{L(L+1)} \cdot \frac{J(J+1)+L(L+1)-S(S+1)}{2\sqrt{J(J+1)} \cdot \sqrt{L(L+1)}} 2\sqrt{S(S+1)} \cdot \frac{J(J+1)+S(S+1)-L(L+1)}{2\sqrt{J(J+1)} \cdot \sqrt{S(S+1)}} \cdot \frac{h}{2\pi}\right.$$

$$\therefore \quad \mu_J = \frac{e}{2m} \cdot \frac{h}{2\pi}\left[\frac{J(J+1)+L(L+1)-S(S+1)}{2\sqrt{J(J+1)}}\right.$$

$$\left. + \frac{J(J+1)+S(S+1)-L(L+1)}{\sqrt{J(J+1)}}\right]$$

$$= \frac{eh}{4\pi m} \cdot \sqrt{J(J+1)} \left[\frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + \right.$$

$$\left. \frac{J(J+1) + S(S+1) - L(L+1)}{J(J+1)} \right]$$

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

$$= \left[1 + \frac{\overset{\bullet}{J}^2 + \overset{\bullet}{S}^2 - \overset{\bullet}{L}^2}{2\overset{\bullet}{J}^2} \right] \cdot \frac{e}{2m} \left[\vec{J} \right]$$

$$= g \frac{e}{2m} \left| \vec{J} \right| \equiv g \frac{e}{2m} \sqrt{J(J+1)} \frac{h}{2\pi} \equiv g \overset{\bullet}{J} \cdot \frac{e}{4\pi m} \qquad \ldots 1.15$$

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

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

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

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

where $g = \left[1 + \frac{\overset{*2}{J} + \overset{*2}{L} - \overset{*2}{S}}{2\overset{*2}{J}}\right]$, is called **Lande g-factor.**

The g-factor gives the relative separation of Zeeman levels for different terms (States).

When atom is placed in external magnetic field $\vec{B}$, which is weak enough so that the coupling between $\vec{L}$ and $\vec{S}$ is not broken *i.e.* $\vec{L}$ and $\vec{S}$ precess about their resultant $\vec{J}$ and in turn $\vec{J}$ precesses about $\vec{B}$ with angular velocity ω given by Larmor's theorem as,

$$\omega = \frac{\mu_J}{|\vec{J}|} B = g \frac{e}{2m} B \qquad \text{... from eq}^{n}\text{. (1.15)}$$

$$g \frac{e}{2m} \frac{|\vec{J}|}{|J|} B \qquad \text{...1.16}$$

The magnetic interaction energy, due to this precession, is given by the product of angular velocity ω and projection of $\vec{J}$ on $\vec{B}$ as,

$$\Delta W_m = \mu_J B \cos(J, B) = \vec{\mu}_J \cdot \vec{B}$$

$$= g \frac{e}{2m} \left|\vec{J}\right| B \cos(J, B)$$

$$= g \frac{eh}{4\pi m} \cdot B \cdot \sqrt{J(J+1)} \cdot \cos(J, B)$$

$$\sqrt{J(J+1)} \frac{h}{2\pi} \equiv |J|$$

$$= g \frac{eh}{4\pi m} \cdot B \cdot M_J \qquad \ldots 1.17$$

where, $M_J = \sqrt{J(J+1)} \cdot \cos(J, B) \equiv J \cos(J, B)$

$\therefore$ Interaction energy in wave number, *i.e.* term shift ΔT, due to magnetic interaction is,

$$-\Delta T_m = \frac{\Delta W_m}{hc} = g\frac{eB}{4\pi mc}M_J \quad (m^{-1})$$

$$= gL'M_J \quad (m^{-1}) \qquad \ldots 1.18$$

where L' is Lorentz unit *i.e.* $L' = \frac{eB}{4\pi mc}$.

Thus, each J-level splits into (2J + 1) equispaced Zeeman levels corresponding to possible M_J-values *viz.* $M_J = +J$ to $-J$. (*i.e.* $M_J = J, (J-1) \ldots -J$). The complete term value of a magnetic level characterised by M_J is,

$$T = T_0 - \Delta T - \Delta T_m$$

where T_0 is hypothetical centre of gravity , ΔT is fine-structure shift (no field) and ΔT_m is Zeeman shift (in magnetic field).

Significance of Lande g-factor

(i) The spacing between Zeeman levels depends upon the *g*-value for that level.

(ii) *g*-value for different J-level (value) is different *i.e.* the relative separations of Zeeman levels is determined by *g*-value.

(iii) For singlet levels, *i.e.* for $S = 0$, $J = L + S = L + 0 = L$,

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

$\therefore$ Eq^{n}. (1.18), reduces to classical Lorentz formula or term shift for normal Zeeman effect *i.e.* $-\Delta T_m = L' M_L$.

... in the transition.

Selection rules : The selection rules which govern the transitions among Zeeman levels are,

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

The state of polarisation of radiations emitted by atoms placed in magnetic field are given as,

(a) When viewed perpendicular to the magnetic field ($\vec{B}$)

(i) if $\Delta M_J = 0$, then plane polarised with electric vector parallel to $\vec{B}$, called π (or p)-components.

(ii) if $\Delta M_J = \pm 1$, then plane polarised with electric vector perpendicular to $\vec{B}$, called σ (or s)-components.

(b) When viewed parallel to magnetic field ($\vec{B}$) (*i.e.* along a hole drilled in the magnetic pole pieces).

(i) if $\Delta M_J = 0$, then forbidden transitions *i.e.* π-components are absent.

(ii) if $\Delta M_J = \pm 1$, then circularly polarised (σ-components).

D_1-line : $3^2S_{1/2} \leftarrow 3^2P_{1/2}$

and D_2-line : $3^2S_{1/2} \leftarrow 3^2P_{3/2}$

Term	L	S	J	g	M_J	gM_J (Shift in Lorentz unit)
$^2S_{1/2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	2	$\frac{1}{2}, -\frac{1}{2}$	$1, -1$
$^2P_{1/2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{3}, -\frac{1}{3}$
$^2P_{3/2}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{4}{3}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$2, \frac{2}{3}, -\frac{2}{3}, -2$

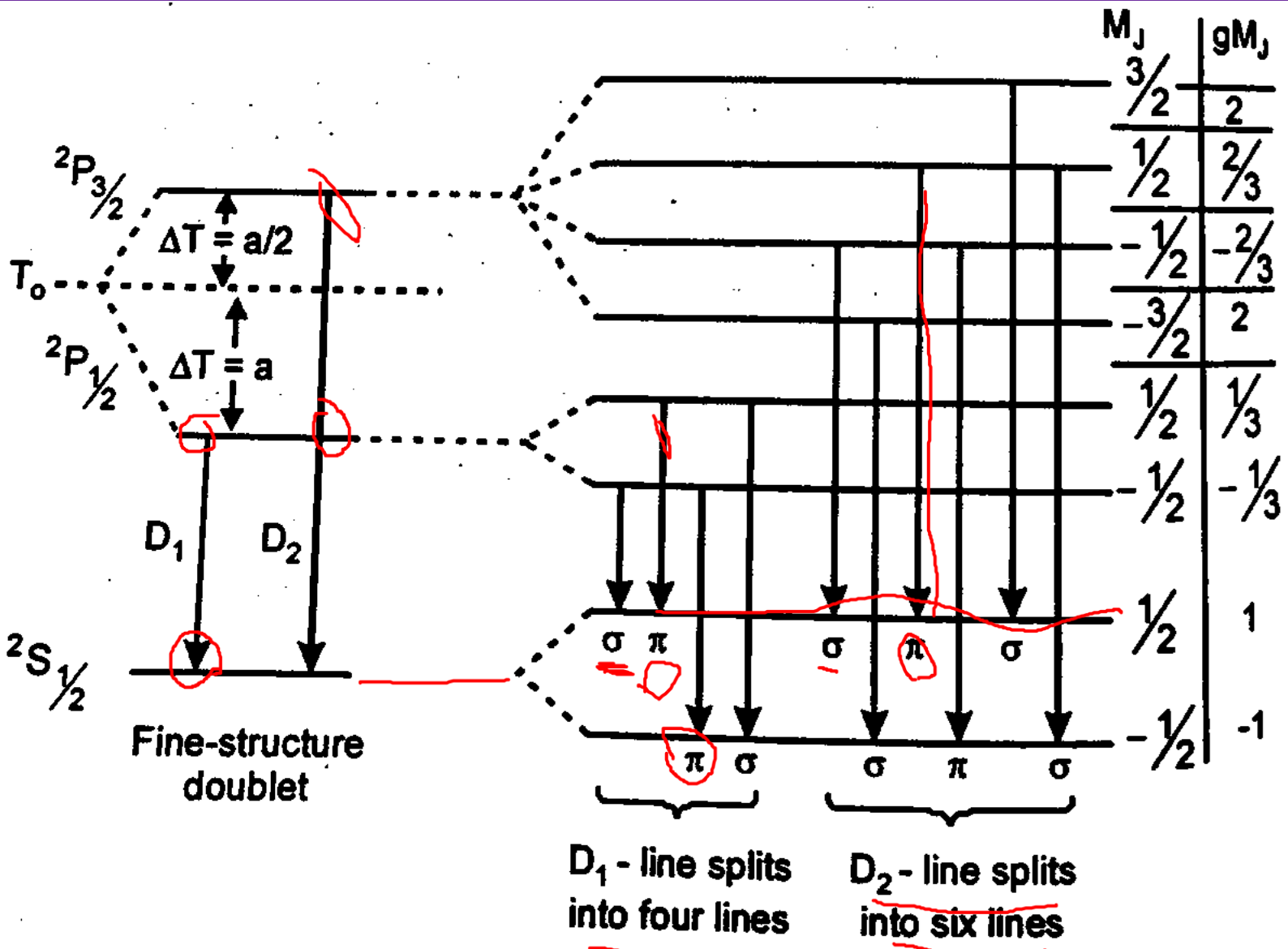


Fig. 1.10 : Zeeman (anomalous) splitting of Sodium D-lines

Thank You!!!!