

Problems

Q1. Measurements on the line spectrum of certain atom show that the separations between adjacent energy levels of increasing energy in a multiple are in the ratio 3:5. Use the Lande interval rule to assign the quantum numbers S, L, J to these levels.

Q2. In an atom obeying L-S coupling, the components of a normal triplet state have separations 20 cm^{-1} and 40 cm^{-1} between adjacent components. There is a higher state for which the separations are 22 cm^{-1} and 33 cm^{-1} respectively. Determine the terms for the two states and show with the help of an energy level diagram the allowed transitions and the pattern of the spectrum.

Q3. The quantum numbers of the two optical electrons in a two valence electron atoms are

$$n_1=6, l_1=3, s_1=1/2$$

$$n_2=5, l_2=1, s_2=1/2$$

- (a) Assuming L-S
- (b) coupling find the possible values of L. and hence of J.
- (c) Assuming j-j coupling, find the possible value of J.

Q4. Write down the normal electronic configuration of carbon atom ($Z=6$) and obtain the spectral terms arising from equivalent electron.

Also write down its first excited configuration and obtain the spectral terms.

Indicate the allowed transition.

Table 2.2.1. Selected ionic properties of the rare-earth elements. The quantity G^* represents the De Gennes factor $G = (g_J - 1)^2 J(J + 1)$, normalized to the value for Gd^{3+}

Ion	$4f^n$ n	Ground term	L	S	J	g	$g\sqrt{J(J+1)}$	gJ	G^*
La^{3+}	0	$^1\text{S}_0$	0	0	—	0	0	0	0
Ce^{3+}	1	$^2\text{F}_{5/2}$	1/2	3	5/2	6/7	2.54	2.14	0.011
Pr^{3+}	2	$^3\text{H}_4$	1	5	4	4/5	3.58	3.20	0.051
Nd^{3+}	3	$^4\text{I}_{9/2}$	3/2	6	9/2	8/11	3.62	3.28	0.116
Pm^{3+}	4	$^5\text{I}_4$	2	6	4	3/5	2.68	2.40	0.217
Sm^{3+}	5	$^6\text{H}_{5/2}$	5/2	5	5/2	2/7	0.84	0.72	0.283
Eu^{3+}	6	$^7\text{F}_0$	3	3	0	0	0	0	0
Gd^{3+}	7	$^8\text{S}_{7/2}$	7/2	0	7/2	2	7.94	7	1
Tb^{3+}	8	$^7\text{F}_6$	3	3	6	3/2	9.72	9	0.667
Dy^{3+}	9	$^6\text{H}_{15/2}$	5/2	5	15/2	4/3	10.63	10	0.450
Ho^{3+}	10	$^5\text{I}_8$	2	6	8	5/4	10.60	10	0.286
Er^{3+}	11	$^4\text{I}_{15/2}$	3/2	6	15/2	6/5	9.59	9	0.162
Tm^{3+}	12	$^3\text{H}_6$	1	5	6	7/6	7.57	7	0.074
Yb^{3+}	13	$^2\text{F}_{7/2}$	1/2	3	7/2	8/7	4.54	4	0.020
Lu^{3+}	14	$^1\text{S}_0$	0	0	0	—	0	0	0

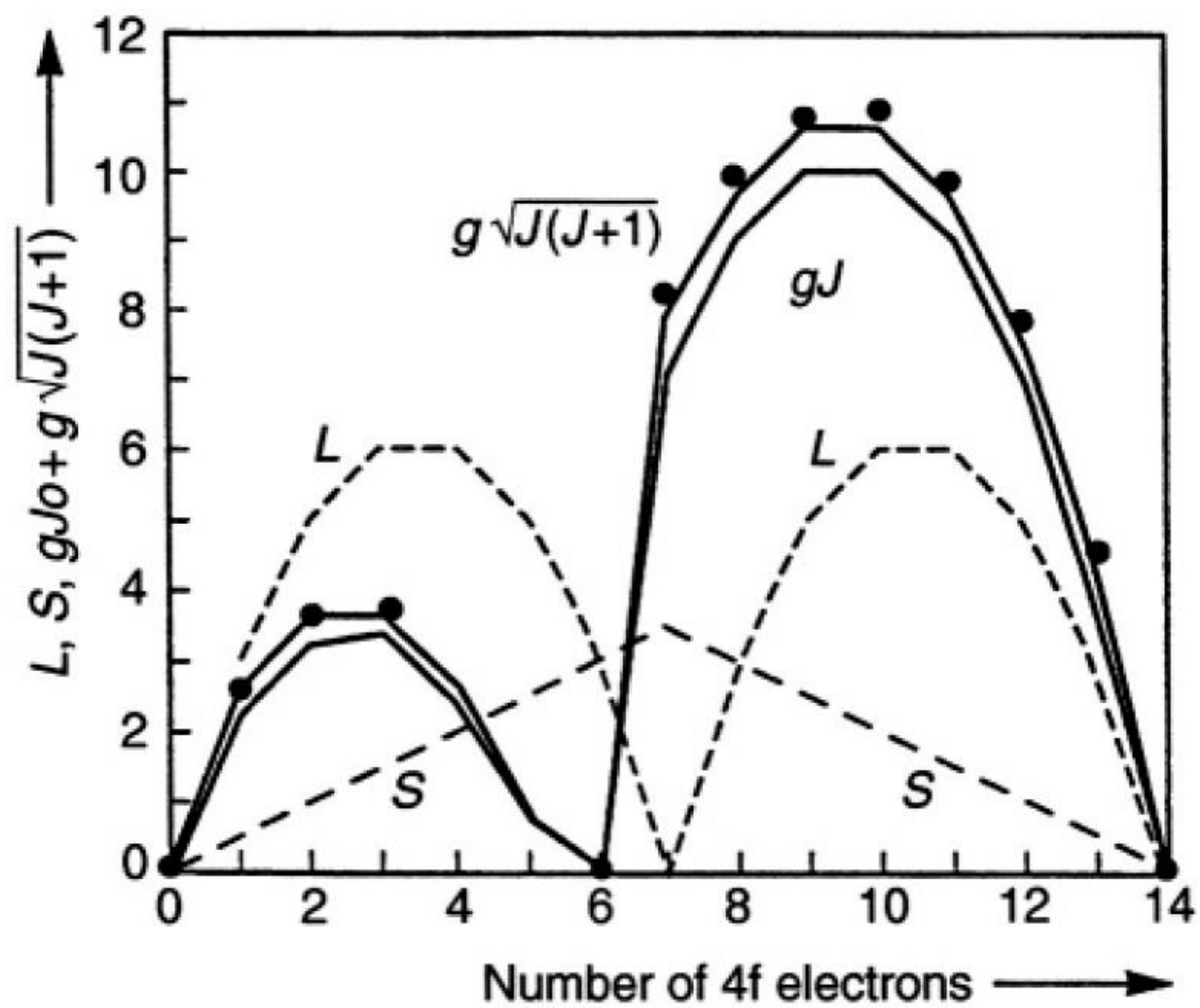


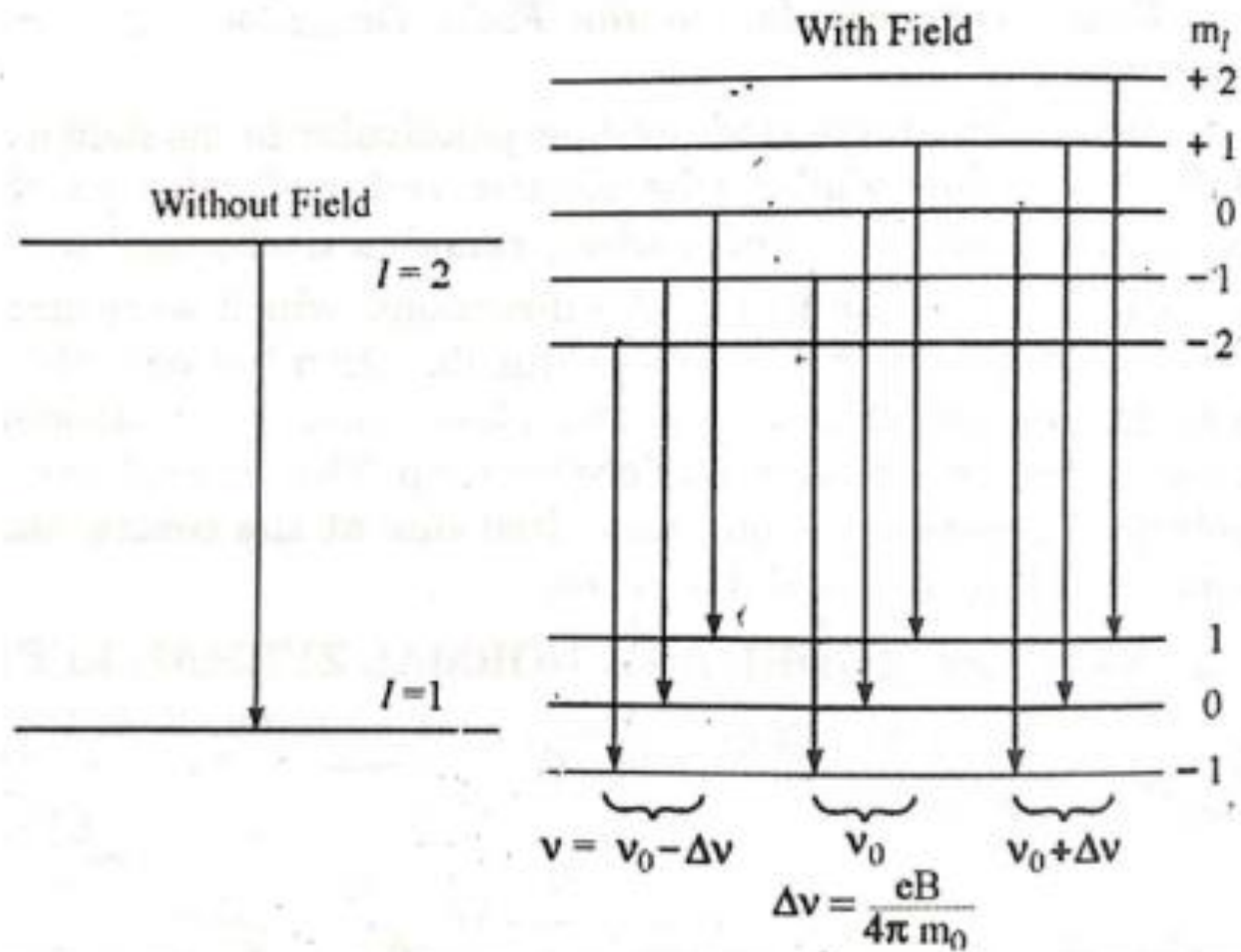
Table 2.2.2. Selected ionic properties of iron-group elements containing Z electrons

Z	Ion	Ground term	L	S	J	$M_{\text{eff,exp}}$	$g\sqrt{J(J+1)}$	$2\sqrt{S(S+1)}$	$g\sqrt{L(L+1)+4S(S+1)}$
18	K ⁺ , V ⁵⁺	¹ S ₀	0	0	0	diam.	0	0	0
19	Sc ²⁺ , Ti ³⁺ , V ⁴⁺	² D _{3/2}	2	1/2	3/2	1.73	1.55	3.01	1.78
20	Ti ²⁺ , V ³⁺	³ F ₂	3	1	2	2.83	1.63	4.49	2.83
21	V ²⁺ , Cr ³⁺ , Mn ⁴⁺	⁴ F _{3/2}	3	3/2	3/2	3.82	0.70	5.21	3.87
22	Cr ²⁺ , Mn ³⁺	⁵ D ₀	2	2	0	4.81	0	5.50	4.91
23	Mn ²⁺ , Fe ³⁺	⁶ S _{5/2}	0	5/2	5/2	5.85	5.92	5.92	5.92
24	Fe ²⁺	⁵ D ₄	2	2	4	5.52 – 5.22	6.71	5.50	4.91
25	Co ²⁺	⁴ F _{9/2}	3	3/2	9/2	5.20 – 4.43	6.63	5.21	3.87
26	Ni ²⁺	³ F ₄	3	1	4	3.23	5.59	4.49	2.83
27	Cu ²⁺	² D _{5/2}	2	1/2	5/2	2.02 – 1.81	3.55	3.01	1.73

ZEEMAN EFFECT

The Zeeman effect is a magneto-optical phenomenon in which spectral lines are affected by an applied magnetic field and split into several components. This was first observed by Zeeman in 1896 and hence called Zeeman effect. He found if a source of light giving line spectra be placed in a magnetic field, the lines were split into a number of component lines, symmetrically distributed about the original line. Doublets, triplets and even more complex system were observed.

It is observed that when magnetic field is applied, a single spectral line splits up into three components such that one line has got a larger frequency, other a lower frequency than the original line and the third one has the same frequency as that of the original line. This is called normal Zeeman effect.



The normal Zeeman effect is explained on the basis of Lorentz classical theory. According to this theory if a source of light is placed in a magnetic field, the frequency of motion of electron moving in a circular orbit gets modified.

Let us consider an electron in an atom moving in a circular orbit of radius ‘r’ with a linear velocity ‘v’ and angular velocity ‘ω’. Let ‘e’ and ‘m’ be the charge and mass of electron respectively. The centripetal force acting on the electron towards the centre in the absence of the magnetic field,

$$F = \frac{mv^2}{r} = mr\omega^2 \dots\dots\dots(1)$$

Now, let an external magnetic field ‘B’ be applied in a direction perpendicular to the plane of the orbits of the two circular components. Then, an additional radial force of magnitude Bev acts on the electron. The direction of this force will be outwards from the center for clockwise

motion but inwards towards the center for anticlockwise motion. The resulting complex motion of the electron subjected to an additional radial force is called Larmor precession. This produces change in the angular velocity without any change in the form of the orbit.

Let $d\omega$ be the change in angular velocity caused by the magnetic field. For the circular motion in the clockwise direction, the additional radial force is directed away from the center,

Therefore
$$F - Bev = mr (\omega + d\omega)^2 \dots\dots\dots(2)$$

$$mr\omega^2 - mr (\omega + d\omega)^2 = Be\omega r$$

Or
$$-2mr\omega d\omega = Be\omega r \quad \text{neglecting } (d\omega)^2$$

Or
$$d\omega = -\frac{Be}{2m} \dots\dots\dots(3)$$

For the circular motion in the anticlockwise direction, the additional radial force is directed towards the centre.

Therefore
$$F + Bev = mr (\omega + d\omega)^2$$

Or
$$d\omega = + \frac{Be}{2m} \dots\dots\dots(4)$$

The two cases can be combined into the equation

$$d\omega = \pm \frac{Be}{2m} \dots\dots\dots(5)$$

If ν be the frequency of vibration of the electron,

Then
$$\omega = 2\pi\nu$$

Or
$$d\omega = 2\pi d\nu$$

Or
$$d\nu = \frac{d\omega}{2\pi}$$

Therefore, change in frequency of the spectral line,

$$d\nu = \pm \frac{Be}{4\pi m} \dots\dots\dots(6)$$

If ν and λ are the frequency and wavelength of the original line,

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

or

$$d\nu = - \frac{c}{\lambda^2} d\lambda$$

Therefore, the Zeeman shift

$$d\lambda = \pm \frac{Be\lambda^2}{4\pi mc} \dots\dots\dots(7)$$

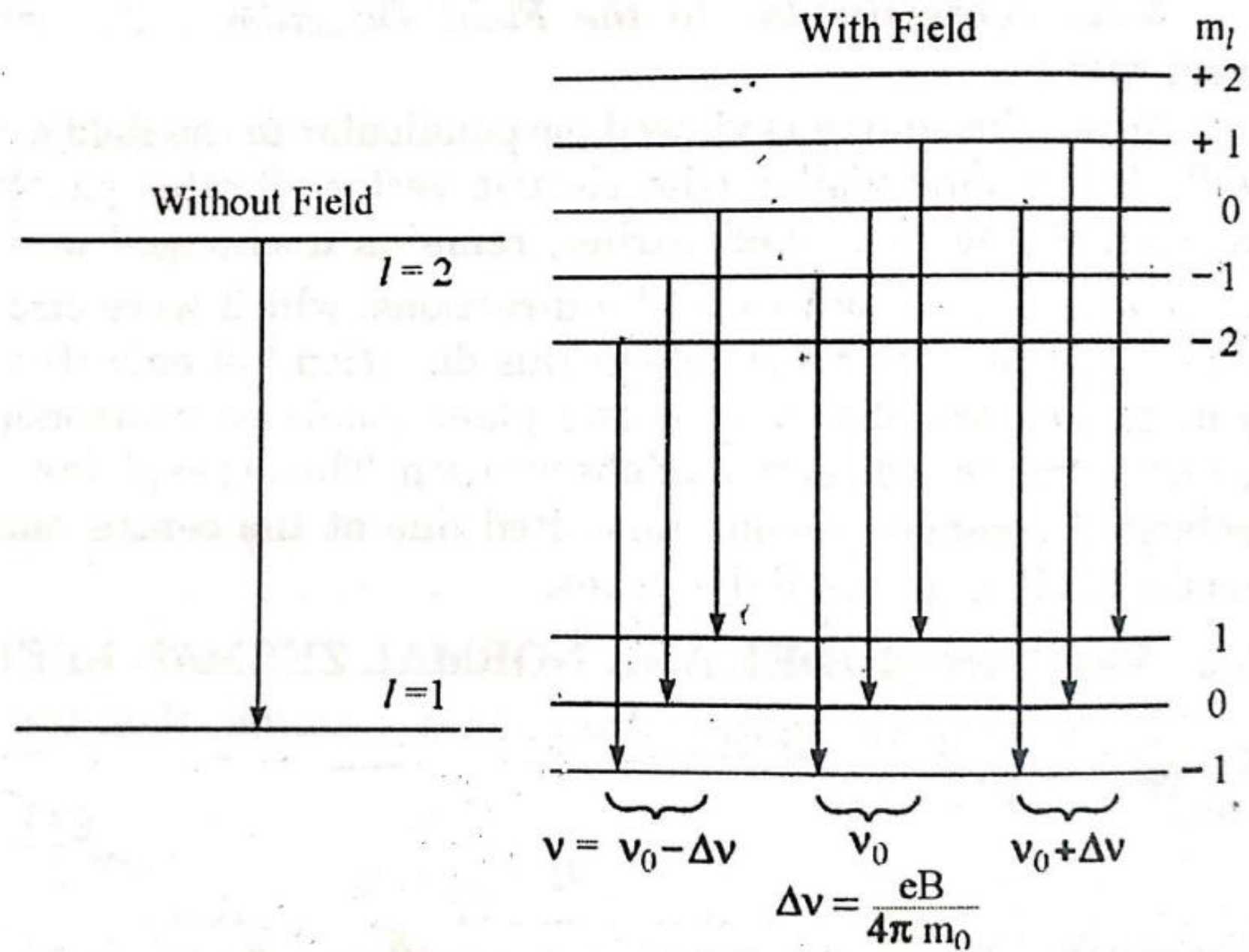
Taking a spectral line of known wavelength λ , and applying a magnetic field B , the Zeeman shift $d\lambda$ is measured.

From equation (7),

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

From above equation, $\frac{e}{m}$ can be calculated. $\frac{e}{m}$ is found to be $1.757 \times 10^{11} \text{ CKg}^{-1}$ which is in agreement with the value of $\frac{e}{m}$ of the electron obtained from Thomson's experiment.

$$\begin{aligned} \nu_1 &= \nu_0 \\ \nu_2 &= \nu_0 + \frac{eB}{4\pi m} \\ \nu_3 &= \nu_0 - \frac{eB}{4\pi m} \end{aligned}$$



QUANTUM MECHANICAL EXPLANATION OF NORMAL ZEEMAN EFFECT

The magnetic moment of an electron moving in its orbit is given by

$$\mu_L = \frac{e}{2m_0} L$$

This magnetic moment interacts with external magnetic field and gives the perturbing Hamiltonian as

$$H' = - \mu_L \cdot B$$

$$= \frac{e}{2m_0} L \cdot B$$

To calculate the splitting of spectrum lines, the operator forms of H' is used in the perturbation theory. The first order interaction energy is

$$\Delta E = \int \Psi^* \hat{L} \Psi d\tau$$

$$\Delta E = \frac{e}{2m_0} \int \Psi^* \hat{L} \hat{B} \Psi d\tau$$

Let us assume that B is directed towards z axis; then

$$B = B_z$$

$$\Delta E = \frac{e}{2m_0} B_z \int \Psi^* \hat{L} \Psi d\tau$$

But the average value of z-component of angular momentum is $M_L h$. Hence, change in energy value is (changing B_z to B)

$$\Delta E = \frac{eh}{2m_0} B_z M_L$$

Therefore, the energy of the having the orbital quantum number M_{L1} is

$$E_1 = E^{(1)} + \frac{eh}{2m_0} B M_{L1}$$

And

$$E_2 = E^{(2)} + \frac{eh}{2m_0} B M_{L2}$$

$$(E_2 - E_1) = (E^2 - E^1) + \frac{eh}{2m_0 c} B \Delta M_L$$

$$h\nu = h\nu_0 + \frac{eh}{2m_0} B \Delta M_L$$

$$\nu = \nu_0 + \frac{eB}{4\pi m_0} \Delta M_L$$

The expression when subjected to selection rule $\Delta M_L = 0, \pm 1$ gives rise to Zeeman normal triplet. $\Delta M_L = 0$ corresponds to π components and $\Delta M_L = \pm 1$ gives σ components