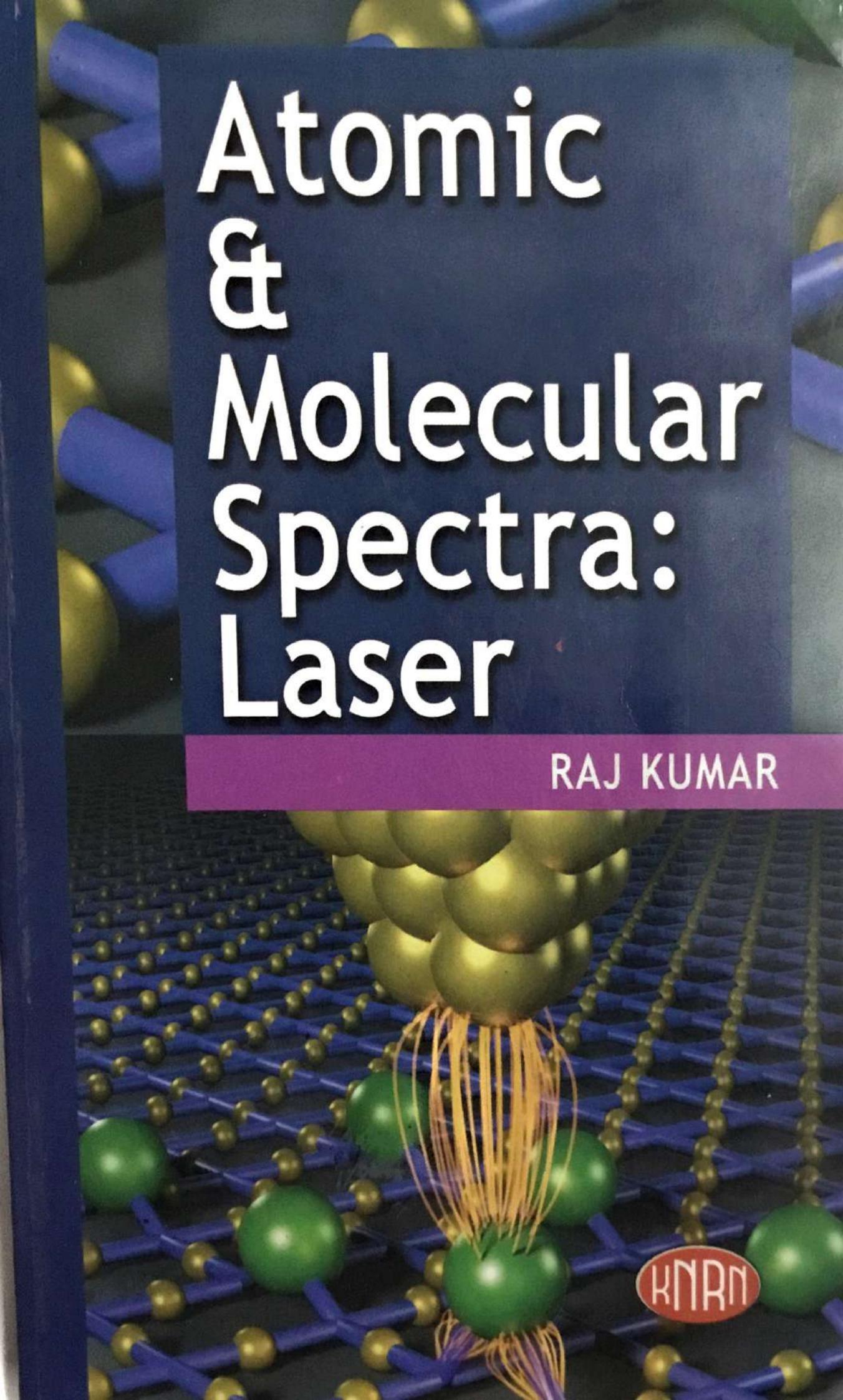


# Atomic & Molecular Spectra: Laser

RAJ KUMAR



KNKN

# CONTENTS

---

<i>Chapter</i>	<i>Page</i>
1. Introduction	1
2. Bohr-Sommerfeld Theory of Hydrogen Atom	6
3. Quantum Mechanics of Hydrogen Atom : Angular Momentum and Parity	48
4. Magnetic Dipole Moments, Electron Spin and Vector Atom Model	71
5. Spin-Orbit Interaction : Hydrogen Fine Structure	90
6. Identical Particles : Pauli's Exclusion Principle	103
7. Helium Atom and its Spectrum	111
8. Multi-electron Atoms : Hartree's Field : Atomic Ground States and Periodic Table	121
9. Spectroscopic Terms : L-S and j-j Couplings	138
10. Spectra of Alkali Elements	169
11. Spectra of Alkaline-Earth Elements and Complex Spectra	185
12. Zeeman Effect and Paschen-Back Effect	201
13. The Stark Effect	226
14. Hyperfine Structure of Spectral Lines	232
15. The Breadth of Spectral Lines	250
16. X-ray Spectra	255
17. Types of Molecular Spectra and Molecular Energy States	275
18. Pure Rotational Spectra	284
19. Vibrational-Rotational Spectra	302
20. The Raman Spectra	336
21. Electronic Spectra : Franck-Condon Principle	349
22. Isotope Effect on Electronic Spectra	380
23. Fluorescence and Phosphorescence	388
24. Classification of Molecular Electronic States	393
25. Symmetry Properties of Rotational Levels : Nuclear Spin and Intensity Alteration	400
26. Coupling of Rotational and Electronic Motions : Types of Electronic Transitions	416
27. Co-relation between Atomic and Molecular States : Building-up Principle	445
28. Molecules and Chemical Bonds : The Stability of Molecular States	474
29. Continuous and Diffuse Molecular Spectra : Dissociation and Predissociation	504
30. Temporal and Spatial Coherences	523
31. LASER : Einstein's Coefficients and Light Amplification	531
32. Types of Lasers : Characteristics and Applications of Lasers	541-555

## Introduction

Spectroscopy is that branch of Physics which deals with the observation and interpretation of radiation emitted and absorbed by atoms and molecules, and throws light on their structure. It provides information not only about the arrangement and motion of the outer electrons (optical spectroscopy), but also about the inner electrons (X-ray spectroscopy), and about the angular momentum, magnetic moment, distribution of charge and magnetism of the nucleus (study of hyperfine structure, nuclear magnetic resonance, etc.).

It was Sir Isaac Newton who originated spectroscopy by showing that a prism refracts blue light more than red light, thus forming a band of colours known as 'spectrum'. Today, we know that the visible spectrum is a very small part of the broad electromagnetic spectrum ranging from the  $\gamma$ -rays to the radio-waves. The wavelength  $\lambda$  and the frequency  $v'$  of a monochromatic wave are related as

$$v' \lambda = v, \quad \dots(i)$$

where  $v$  is the *phase velocity* in the medium. The phase velocity  $v$  of an electromagnetic wave in a medium is related to the phase velocity  $c$  in *vacuum* by

$$v = \frac{c}{\mu},$$

where  $\mu$  is the refractive index of the medium with respect to vacuum.

*The frequency of a wave remains unchanged as it propagates through various media.* Hence, for vacuum, eq. (i) may be written as

$$v' \lambda_{vac} = c,$$

and for a dispersive medium (say, air) we write

$$v' \lambda_{air} = v_{air} = \frac{c}{\mu_{air}}.$$

Thus, the frequency of an electromagnetic wave may be expressed as

$$v' = \frac{c}{\lambda_{vac}} = \frac{c}{\mu_{air} \lambda_{air}}.$$

The wavelength in the visible part of the spectrum is measured in Å (angstrom units), which is

$$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 10^{-1} \text{ nm (nanometer).}$$

Infra-red wavelengths longer than 10,000 Å are measured in microns ( $\mu$ ), which is

$$1 \mu = 10^{-4} \text{ cm} = 10^{-6} \text{ m} = 10^4 \text{ Å.}$$

A smaller unit is millimicron ( $m\mu$ ), which is

$$1 m\mu = 10^{-7} \text{ cm} = 10^{-9} \text{ m} = 10 \text{ Å.}$$

For the analysis of spectral lines, frequency is more fundamental than the wavelength because the frequency of monochromatic light does *not* alter in different media. However, frequency is numerically very large. For example, the frequency of visible light of wavelength 6000 Å is

$$\nu' = \frac{c}{\lambda_{vac}} = \frac{3 \times 10^8 \text{ m s}^{-1}}{6000 \times 10^{-10} \text{ m}} = 5 \times 10^{14} \text{ s}^{-1} \text{ (hertz).}$$

Therefore, in spectroscopy, 'wave numbers' (the number of waves per meter or per cm) rather than frequencies are usually employed. *The wave number  $\nu$  is the reciprocal of wavelength in vacuum*, and is expressed in  $\text{cm}^{-1}$  or in  $\text{m}^{-1}$ :

$$\nu = \frac{1}{\lambda_{vac}} = \frac{1}{\mu_{air} \lambda_{air}} = \frac{\nu'}{c}$$

To find the wave number for a wavelength measured in air, we must first convert the wavelength in air to the wavelength in vacuum by multiplying it by the refractive index of air for that wavelength, and then take the reciprocal value. Standard wave number tables are available for this computation.

After Newton, Joseph Fraunhofer in 1814 observed dark lines in the solar spectrum. Soon after, Kirchhoff and Bunsen found such dark lines, and similar bright lines, in the spectra of stars and laboratory flames and sparks. This brought into picture two types of spectroscopy, the emission spectroscopy and the absorption spectroscopy.

The main pieces of apparatus required in the study of spectroscopy are : a light source, a dispersing device and a receiver (eyepiece or camera).

The ways of producing light for spectroscopic studies are 'temperature radiation' and 'luminescence' (which includes electroluminescence, chemiluminescence, fluorescence and phosphorescence). In temperature radiation, the atoms and molecules of gases are excited by collision with other atoms and molecules at high temperature. The excited atoms and molecules emit light. This occurs in flames and electric furnaces. In electroluminescence, atoms or molecules are excited by collision with electrons or ions accelerated in an electric field. This occurs in all kinds of electric discharges (arcs, sparks and Geissler tubes). In chemiluminescence, energy is set free in a chemical reaction and is converted into light. This phenomenon takes place partly in flames. Photoluminescence (fluorescence and phosphorescence) results from excitation by absorption of light.

The light from the source is focussed on the entrance slit of a spectrograph which disperses it and forms an image of the slit in its focal plane. Images in different wavelengths occur at different points along the focal plane. The succession of images of the entrance slit is called the 'spectrogram'. The main observations in the spectrogram are as follows :

(i) Monoatomic gases (when heated to incandescence) give distinct bright emission lines; polyatomic gases give bands composed of closely spaced lines; and very dense gases or solids give continuum.

(ii) A continuous spectrum seen through a cool gas shows absorption lines or bands. This means that a cool gas absorbs from continuous light those very wavelengths which it emits when heated.

(iii) The positions (wavelengths) of spectral lines are characteristic of the atoms or molecules which produce them.

(iv) The intensity of spectral lines grows as the concentration of atoms increases.

(v) Intensities of spectral lines vary with the temperature of the source.

A particular spectral line may serve as a standard of length. In 1907, the red Cd line ( $6438 \text{ \AA}$ ) was adopted. Then, it was replaced by the green line ( $5460 \text{ \AA}$ ) of mercury isotope ( $\text{Hg}^{198}$ ), and in 1960, the orange line ( $6058 \text{ \AA}$ ) of krypton isotope ( $\text{Kr}^{86}$ ) was chosen. The wavelength of krypton orange line in vacuum is

$$\lambda_{vac} = 6057.802106 \text{ \AA.}$$

As reliable light sources and wavelength standards became available in the second half of the 19th century, spectroscopists began to note regularities in the spacing of spectral lines. In 1870's, Liveing and Dewar noticed that the spectral lines of various elements could be grouped into distinct 'series'. **In each series, the spacing and intensity decrease regularly towards shorter wavelengths**, until finally it becomes impossible to distinguish the individual lines (series limit). The various series in complicated spectra overlap. The simplest is the hydrogen spectrum. Its visible part shows a single series (Balmer series) which starts at 6563 Å in the red and proceeds toward a limit at 3646 Å in the violet. Besides this, there is a series in the ultraviolet (Lyman series); and a few series in the infra-red and far infra-red (Paschen, Brackett and Pfund series).

Balmer, in 1885, discovered a formula predicting the wavelengths of all the lines of the Balmer series, which is

$$\lambda = 3646 \frac{n^2}{n^2 - 4}; \quad n = 3, 4, 5, \dots$$

Subsequently, Rydberg found that Balmer's formula was a special case of the following more general wave-number formula for hydrogen :

$$v = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right];$$

where  $n_1$  and  $n_2$  are positive integers ( $n_2 > n_1$ ) and  $R_H$  is the Rydberg constant for hydrogen. From recent spectroscopic data, the value of  $R_H$  is known to be  $109677.576 \text{ cm}^{-1}$  (or  $10967757.6 \text{ m}^{-1}$ ). To obtain Balmer's formula, we set  $n_1 = 2$ ; and  $n_2 = 3, 4, 5, \dots$ . The series limit is derived by putting  $n_2 = \infty$ .

The above formula predicts all known series of the hydrogen spectrum. We thus conclude that the wave numbers of the hydrogen lines can be expressed as differences of two 'terms' of the form  $\frac{R_H}{n^2}$

The next simplest spectra are of the 'monovalent' atoms of alkalis Li, Na, K, ... which form the first column of the periodic table. The elements share many chemical properties and this is attributed to the presence of a single 'valence' electron in the outermost orbit. Spectroscopically, a typical alkali spectrum can be grouped into four distinct series. The strongest is the 'principal series' which, with the exception of its first member, lies in the ultra-violet. The other two, sharp and diffuse, series lie in the visible part, while the fourth one, the fundamental series, lies in the infra-red region. Rydberg represented the wave numbers of the lines of a particular series by the formula

$$v = R_A Z^2 \left[ \frac{1}{(n_1 - \Delta_1)^2} - \frac{1}{(n_2 - \Delta_2)^2} \right],$$

where  $R_A$  is the Rydberg constant for a particular element  $A$ ;  $n_1$  and  $n_2$  are positive integers, and  $\Delta_1$  and  $\Delta_2$  are quantum defects ( $< 1$ ). The integer  $n_1$  is fixed for the particular series, while  $n_2$  is a variable integer.

The lines of an alkali spectrum, under high resolution, show a fine structure and are termed as 'doublets'. The fine structure becomes more pronounced in the heavier elements.

Again, we find that the wave numbers of the lines can be expressed as difference of two 'terms' like  $\frac{R_A Z^2}{(n - \Delta)^2}$ .

From this we draw a final conclusion :

"The number of valence electrons determines the qualitative character of a spectrum (that is, the number and types of series), whereas the net atomic charge affects quantitative details (that is, the wavelengths of lines in series)."

**Wave number Units :** The wave number units are commonly used by spectroscopists as a measure of energy. When a *single* particle (atom or molecule) emits light, the emitted light quantum will have an energy given by,

$$E = h v', \quad (\text{Planck's photon theory})$$

where  $h$  is Planck's constant and  $v'$  is the frequency of emitted light.

But  $v' = c v$ , where  $v$  is the 'wave number' of the emitted light. Therefore,

$$E = h c v.$$

Substituting the known values (upto 4 significant figures) of the universal constants  $h$  and  $c$ , and taking  $v = 100 \text{ m}^{-1}$  ( $= 1 \text{ cm}^{-1}$ ), we have

$$\begin{aligned} E &= (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1}) (100 \text{ m}^{-1}) \\ &= 1.986 \times 10^{-23} \text{ J}. \end{aligned}$$

Thus

$$1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J/molecule} \quad \dots(\text{A})$$

Now, 1 mole contains  $6.023 \times 10^{23}$  molecules (Avogadro's number). Therefore, we can write

$$\begin{aligned} 1 \text{ cm}^{-1} &= (1.986 \times 10^{-23} \text{ J/molecule}) \times (6.023 \times 10^{23} \text{ molecules/mole}) \\ &= 11.962 \text{ J/mole}. \end{aligned}$$

Again 1 cal = 4.186 J. Therefore

$$1 \text{ cm}^{-1} = \frac{11.962 \text{ J/mole}}{4.186 \text{ J/cal}} = 2.858 \text{ cal/mole.}$$

Thus

$$1 \text{ cm}^{-1} = 2.858 \text{ cal/mole} = 2.858 \times 10^{-3} \text{ kcal/mole.} \quad \dots(\text{B})$$

We can also obtain interconversion between electron-volt and  $\text{cm}^{-1}$ . We know that

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J/molecule.}$$

$$\therefore 1 \text{ cm}^{-1} = \frac{1.986 \times 10^{-23} \text{ J/molecule}}{1.602 \times 10^{-19} \text{ J/(molecule-eV)}}.$$

or

$$1 \text{ cm}^{-1} = 1.239 \times 10^{-4} \text{ eV.} \quad \dots(\text{C})$$

$$\text{Conversely, } 1 \text{ eV} = \frac{1.602 \times 10^{-19} \text{ J/molecule}}{1.986 \times 10^{-23} \text{ J/molecule}} \times 1 \text{ cm}^{-1}$$

or

$$1 \text{ eV} = 8066 \text{ cm}^{-1}. \quad \dots(\text{D})$$

From relations (C) and (B) :

$$1.239 \times 10^{-4} \text{ eV} = 2.858 \times 10^{-3} \text{ kcal/mole}$$

$$\text{or } 1 \text{ eV} = \frac{2.858 \times 10^{-3} \text{ kcal/mole}}{1.239 \times 10^{-4}}$$

or

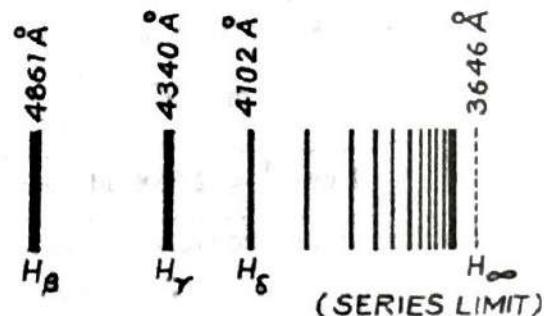
$$1 \text{ eV} = 23.06 \text{ kcal/mole.}$$

## Bohr-Sommerfeld Theory of Hydrogen Atom

### 1. Atomic Spectra

When an atomic gas or vapour is excited, say by the passage of an electric current through it, the emitted radiation after being dispersed by a suitable spectrometer becomes concentrated at a number of discrete wavelengths. Each of these wavelength components is called a 'spectral line', and the whole family of lines is called a 'line spectrum' or 'atomic spectrum'. Investigation of the spectra emitted from different kinds of atoms shows that each kind of atom has its own characteristic spectrum, that is, a characteristic set of wavelengths. This makes spectroscopy a useful tool for chemical analysis of an unknown substance.

A characteristic feature of line spectra is that the spectral lines can be grouped in one, or more, *series* in which the separation and intensity of lines decrease regularly toward shorter wavelengths. For example, in the line spectrum of hydrogen atom is observed a series of lines whose separation and intensity decrease in a perfectly regular manner toward shorter wavelengths, and the series converges to a limit at about 3646 Å (Fig. 1). The line with the longest wavelength, 6563 Å, is designated  $H_\alpha$ , the next of wavelength 4861 Å is designated  $H_\beta$ , and so on.



(BALMER SERIES OF HYDROGEN)

(Fig. 1)

Balmer, in 1885, discovered an empirical formula representing the wavelengths of the hydrogen lines. His formula is

$$\lambda = 3646 \frac{n^2}{n^2 - 4} \text{ Å},$$

where  $n = 3, 4, 5, \dots$  for  $H_\alpha, H_\beta, H_\gamma, \dots$  lines respectively. The series is therefore named as 'Balmer series'.

The formula is more generally written in the following form, which is due to Ritz and Rydberg :

$$v = \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right); \quad n = 3, 4, 5, \dots$$

Balmer

where  $\nu$  is the wave number of the line and  $R_H$  is the Rydberg constant for hydrogen and has the experimental value

$$R_H = 10967757.6 \text{ m}^{-1} = 1.097 \times 10^7 \text{ m}^{-1} (= 1.097 \times 10^5 \text{ cm}^{-1}).$$

The Balmer series contains only those spectral lines of hydrogen atom which occur in the visible and near ultra-violet parts of the spectrum. The spectral lines in the ultraviolet region form the 'Lyman series' which is specified by the formula

$$\nu = \frac{1}{\lambda} = R_H \left( \frac{1}{1^2} - \frac{1}{n^2} \right); n = 2, 3, 4, \dots \quad \text{Lyman}$$

In the infra-red, three spectral series have been found which are specified by the formula

$$\nu = \frac{1}{\lambda} = R_H \left( \frac{1}{3^2} - \frac{1}{n^2} \right); n = 4, 5, 6, \dots \quad \text{Paschen}$$

$$\nu = \frac{1}{\lambda} = R_H \left( \frac{1}{4^2} - \frac{1}{n^2} \right); n = 5, 6, 7, \dots \quad \text{Brackett}$$

$$\nu = \frac{1}{\lambda} = R_H \left( \frac{1}{5^2} - \frac{1}{n^2} \right); n = 6, 7, 8, \dots \quad \text{Pfund}$$

Similar regularities are found in the spectra of more complex atoms. The series formulae for those spectra are of the same general structure as for hydrogen spectrum.

## 2. Bohr's Postulates

Niels Bohr, in 1913, developed a model of atomic structure which was in accurate quantitative agreement with the observed hydrogen and hydrogen-like spectra. This model is based on certain postulates which are :

(i) *An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, according to the laws of classical mechanics.*

This postulate bases Bohr's model on the existence of the atomic nucleus and embodies some of the ideas concerning the stability of the nuclear atom.

(ii) *Out of the infinite number of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which the magnitude of its orbital angular momentum  $\vec{L}$  is an integral multiple of  $h/2\pi$ , where  $h$  is Planck's constant. That is,*

$$|\vec{L}| = \frac{n h}{2\pi}; \quad n = 1, 2, 3, \dots$$

This postulate introduces quantisation. We shall see that the quantisation of the orbital angular momentum of the atomic electron leads to the quantisation of its total energy.

(iii) *The electron, in spite of its accelerated motion, does not radiate electromagnetic energy while moving in an allowed orbit. Thus, its total energy remains stationary.*

This postulate removes the problem of the stability of the electron moving in a circular orbit, due to the emission of electromagnetic energy as demanded by classical theory.

(iv) *Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy  $E_i$ , discontinuously changes its motion so that it moves in a lower orbit of total energy  $E_f$ . The frequency  $\nu'$  of the emitted radiation is given by*

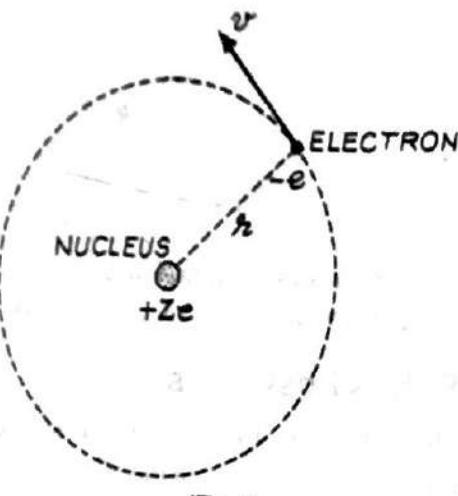
$$\nu' = \frac{E_i - E_f}{h}.$$

This postulate is closely related to Einstein's postulate ( $E = h\nu'$ ) that the frequency of a quantum (photon) of electromagnetic radiation is equal to the energy carried by the quantum divided by Planck's constant  $h$ .

These postulates mix up the classical and non-classical Physics. The electron moving in a circular orbit is assumed to obey classical mechanics, and yet the non-classical idea of quantisation of orbital angular momentum is included. The electron is assumed to obey one feature of classical electromagnetic theory (Coulomb's law), and yet not to obey another feature (emission of radiation of an accelerated charged body).

### 3. Bohr's Model of One-electron Atom : Explanation of Spectra of Hydrogen-like Atoms

Let us consider an atom consisting of a nucleus of charge  $+Ze$ , and a single electron of charge  $-e$  and mass  $m$  (Fig. 2). For a neutral hydrogen atom  $Z=1$ ; for a singly-ionised helium atom  $Z=2$ , for a doubly-ionised lithium atom  $Z=3$ , etc. We assume that the electron revolves in a circular orbit about the nucleus. Initially we also assume that the nucleus is infinitely heavy compared to the electron, and consequently assume that the nucleus remains fixed in space. The condition of mechanical stability of the electron is



(Fig. 2)

$$\frac{1}{4\pi\epsilon_0} \frac{Ze \times e}{r^2} = \frac{mv^2}{r}, \quad \dots(i)$$

(Coulomb's force) (centripetal force)  
where  $v$  is the speed of the electron in its orbit, and  $r$  is the radius of the orbit. Now, the orbital angular momentum of the electron,  $L = mvr$ , must be a constant, because the force acting on the electron is entirely in the radial direction. Applying the quantisation condition for  $L$ , we have

$$L = mvr = \frac{n\hbar}{2\pi}, \quad \dots(ii)$$

where  $n = 1, 2, 3, \dots$  and is called the 'principal quantum number'. Eq. (ii) gives

$$v = \frac{n\hbar}{2\pi mr}. \quad \dots(iii)$$

Substituting this value of  $v$  in eq. (i), we have

$$Ze^2 = 4\pi\epsilon_0 m v^2 r = 4\pi\epsilon_0 m r \left( \frac{n\hbar}{2\pi mr} \right)^2 = 4\pi\epsilon_0 \frac{n^2\hbar^2}{4\pi^2 m r}$$

so

$$r = \frac{n^2\hbar^2\epsilon_0}{\pi m Ze^2},$$

$$n = 1, 2, 3, \dots \dots(iv)$$

Substituting this value of  $r$  in eq. (iii), we have

$$v = \frac{Ze^2}{2n\hbar\epsilon_0},$$

$$n = 1, 2, 3, \dots \dots(v)$$

The application of the angular momentum quantisation condition restricts the possible circular orbits of radii given by eq. (iv). These radii are proportional to  $n^2$ . The radius of the smallest orbit ( $n = 1$ ) for a hydrogen atom ( $Z = 1$ ) works out to be  $0.53 \text{ \AA}^*$  which is in good agreement with the estimate made from other data (such as kinetic theory).

The orbital velocity of an electron in the smallest orbit of hydrogen atom works out to be, from eq. (v),  $v = 2.18 \times 10^6 \text{ m s}^{-1}**$  and this is the largest velocity possible for an electron in hydrogen atom. This is less than 1% of the velocity of light (about 1/137th of the velocity of light) and hence we are justified in using classical mechanics instead of relativistic mechanics in the Bohr model. For large values of  $Z$ , however, the electron velocity becomes relativistic. Eq. (v) also makes it clear why Bohr did not allow the quantum number  $n$  to assume the value of  $n = 0$ .

Let us now calculate the total energy of an atomic electron moving in one of the allowed orbits. Let us define the potential energy of the electron to be zero when the electron is infinitely distant from the nucleus. Then, the potential energy  $U$  at a finite distance  $r$  from the nucleus is equal to the work done in removing the electron from  $r$  to infinity *against the electrostatic attraction*  $\left( -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \right)$ , and is given by

$$U = \int_r^\infty -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} dr = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The kinetic energy of the electron is

$$K = \frac{1}{2} m v^2 = \frac{Ze^2}{8\pi\epsilon_0 r} \quad [\text{from eq. (i)}]$$

Hence the total energy of the electron is

$$E = K + U = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{8\pi\epsilon_0 r}.$$

Substituting for  $r$  from eq. (iv), we get for the total energy of the electron in the  $n$ th orbit, as

$$E_n = -\frac{m Z^2 e^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right). \quad n = 1, 2, 3, \dots \dots \dots \text{(vi)}$$

We see that the quantisation of the orbital angular momentum of the electron leads to quantisation of its total energy.

On substituting the values of  $m (= 9.1 \times 10^{-31} \text{ kg})$ ,  $e (= 1.60 \times 10^{-19} \text{ C})$ ,  $\epsilon_0 (= 8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)$  and  $h (= 6.63 \times 10^{-34} \text{ J s})$  in eq. (vi), the energies of the various allowed orbits of hydrogen atom ( $Z = 1$ ) work out to be

$$E_1 = -21.7 \times 10^{-19} \text{ J} = -13.6 \text{ eV} \quad [1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}]$$

$$E_2 = -5.42 \times 10^{-19} \text{ J} = -3.39 \text{ eV}$$

$$E_3 = -2.41 \times 10^{-19} \text{ J} = -1.51 \text{ eV}$$

\*Putting  $n = 1$ ,  $Z = 1$  and inserting the known values of  $h$ ,  $m$ ,  $e$  and  $\epsilon_0$  in eq. (iv), we have

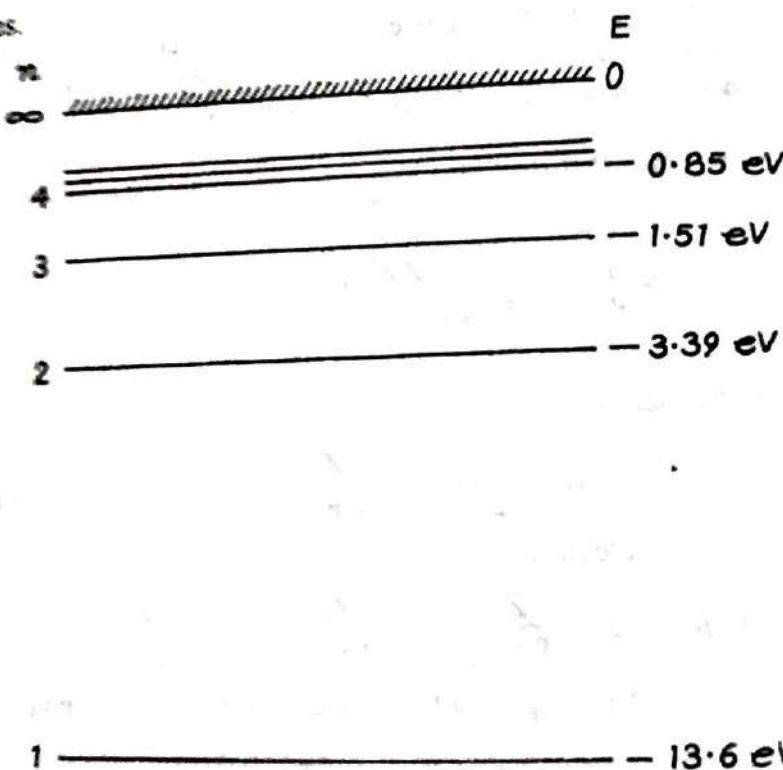
$$r = \frac{(1)^2 \times (6.63 \times 10^{-34} \text{ J s})^2 \times (8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)}{3.14 \times (9.1 \times 10^{-31} \text{ kg}) \times 1 \times (1.60 \times 10^{-19} \text{ C})^2} = 5.3 \times 10^{-11} \text{ m} = 0.53 \text{ \AA}.$$

\*\*Putting  $n = 1$ ,  $Z = 1$ , and inserting the known values of  $e$ ,  $h$  and  $\epsilon_0$  in eq. (v), we have

$$v = \frac{1 \times (1.60 \times 10^{-19} \text{ C})^2}{2 \times 1 \times (6.63 \times 10^{-34} \text{ J s}) \times (8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)} = 2.18 \times 10^6 \text{ m s}^{-1}$$

$$E_4 = -1.36 \times 10^{-19} \text{ J} = -0.85 \text{ eV}$$

The energies are all negative, signifying that the electron is bound to the nucleus. The lowest (most negative) energy occurs for the smallest quantum number  $n=1$  which corresponds to the innermost orbit. As  $n$  increases, the total energy of the quantum state becomes less negative, approaching zero as  $n$  approaches infinity. The electron is then no longer bound to the nucleus. This is represented in an energy-level diagram (Fig. 3). The lowest energy level  $E_1$  is called the 'ground' state or 'normal' state of the atom (being most stable for the electron), and the higher levels  $E_2, E_3, E_4, \dots$  are called 'excited' states.



(Fig. 3)

The ground-state energy  $E_1$  of the hydrogen ( $Z = 1$ ) atom is a convenient energy unit. It is called the 'rydberg' (ry), and its numerical value is

$$1 \text{ ry} = \frac{m e^4}{8 \epsilon_0^2 h^2} = 21.7 \times 10^{-19} \text{ J} = 13.6 \text{ eV}.$$

In order to remove the electron from its ground state  $n = 1$  to infinity, a minimum of 13.6 eV of energy is required. Thus, 13.6 eV is the binding energy of the hydrogen atom, the energy which binds the electron to the nucleus. The binding energy (or ionisation energy) is numerically equal to the energy of the ground state of the atom.

**Term Values :** The energy values of the various quantum states (energy levels) divided by  $-hc$  are called 'term values' of the states and are denoted by  $T_n$ . Thus, using eqn (3), we have

$$T_n = -\frac{E_n}{hc} = \frac{m Z^2 e^4}{8 \epsilon_0^2 h^3 c} \left( \frac{1}{n^2} \right), \quad n = 1, 2, 3, \dots$$

The quantity  $\frac{m e^4}{8 \epsilon_0^2 h^3 c}$  is defined as 'Rydberg constant'  $R_\infty$  for an infinitely heavy

$$R_{\infty} = \frac{m e^4}{8 \epsilon_0^2 h^3 c}$$

$R_{\infty}$  is a constant for all atoms. The last equation can now be written as

$$T_n = \frac{R_{\infty} Z^2}{n^2}$$

The lowest and the most stable energy level has the largest term value.

**Origin of One-electron (Hydrogen-like) Atomic Spectra :** The energy equation (vi) can be written, in term of  $R_{\infty}$ , as

$$E_n = - \frac{R_{\infty} Z^2 h c}{n^2}$$

Let us now calculate the frequency  $\nu'$  of the electromagnetic radiation emitted when the electron initially moving in an orbit of quantum number  $n_i$  drops to a lower orbit of quantum number  $n_f$ . If  $E_i$  and  $E_f$  be the initial and the final orbit energies respectively, then by Bohr's postulate, we have

$$\begin{aligned} \nu' &= \frac{E_i - E_f}{h} \\ &= R_{\infty} Z^2 c \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \end{aligned}$$

or

$$\frac{\nu'}{c} = R_{\infty} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

But  $\frac{\nu'}{c} = \frac{1}{\lambda} = \nu$ , where  $\nu$  is wave number. Thus

$$\nu = \frac{1}{\lambda} = R_{\infty} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \dots(vii)$$

We can now discuss the emission of electromagnetic radiation by a one-electron Bohr atom. The normal state of the atom is the state in which the electron has the lowest energy ( $n = 1$ ). When the atom receives energy from outside by some means, say by collisions in an electric discharge, the electron makes a transition to a state of higher energy ( $n > 1$ ). Now, as a common tendency of all physical systems, the atom emits its excess energy and returns to the ground state. This is accomplished by a series of transitions in which the electron drops to states of successively lower energy, finally reaching the ground state. In each transition, electromagnetic radiation is emitted with a wave number determined by eq. (vii). For example, if the electron is excited to the state  $n = 7$  and drops successively through the states  $n = 4$  and  $n = 3$  to the ground state  $n = 1$ ; then three lines are emitted with wave numbers given by eq. (vii) for  $n_i = 7$  and  $n_f = 4$ ;  $n_i = 4$  and  $n_f = 3$ ; and  $n_i = 3$  and  $n_f = 1$ .

For hydrogen  $Z = 1$ ; so that eq. (vii) is

$$\nu = \frac{1}{\lambda} = R_{\infty} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

This is identical with the series formula for the various series of the hydrogen spectrum, if  $R_{\infty} = R_H$ . According to the Bohr model

$$R_{\infty} = \frac{m e^4}{8 \epsilon_0^2 h^3 c}$$

Taking the known values of  $m$ ,  $e$ ,  $\epsilon_0$ ,  $h$  and  $c$  upto six significant figures, we obtain

$$R_{\infty} = 1.09737 \times 10^7 \text{ m}^{-1}$$

which is in good agreement with the experimental value of  $R_H$ .

According to the Bohr model, each of the five known series of the hydrogen spectrum arises from a set of transitions in which the electron drops to a certain final state  $n_f$ .

$$n_f = 1; n_i = 2, 3, 4, \dots$$

Lyman series

$$n_f = 2; n_i = 3, 4, 5, \dots$$

Balmer series

$$n_f = 3; n_i = 4, 5, 6, \dots$$

Paschen series

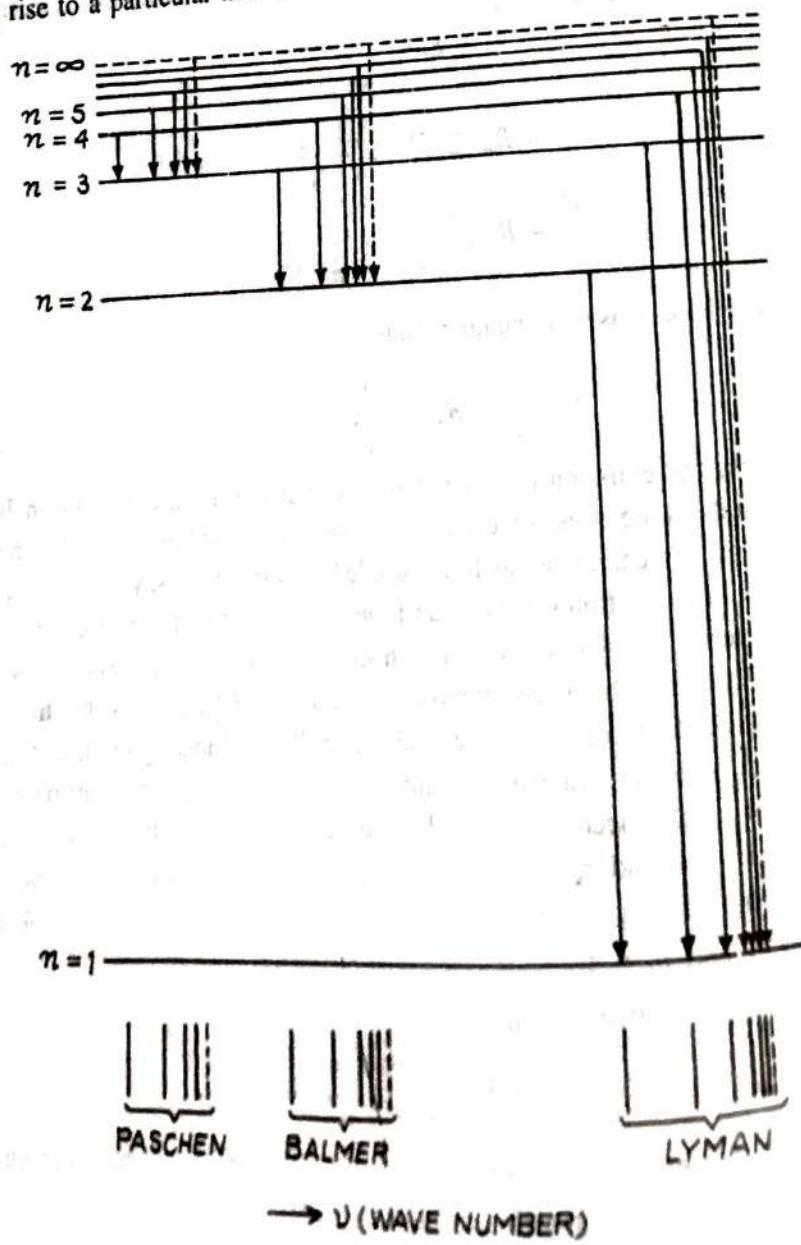
$$n_f = 4; n_i = 5, 6, 7, \dots$$

Brackett series

$$n_f = 5; n_i = 6, 7, 8, \dots$$

Pfund series

These series are illustrated in terms of the energy-level diagram (Fig. 4). The transition giving rise to a particular line of a series is indicated by an arrow going from an initial



(Fig. 4)

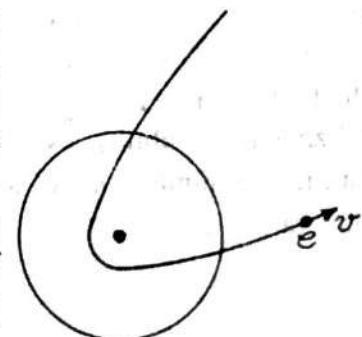
quantum state  $n_i$  to the final quantum state  $n_f$ . Since the distance between any two energy levels is proportional to the difference between the energy of the two levels, the length of any arrow is proportional to the wave number of the corresponding spectral line.

The theoretical explanation of Balmer series was a great success for Bohr's theory. The success was particularly impressive because the Lyman, Brackett, Pfund series had not been discovered at the time the theory was developed by Bohr. The existence of these series was predicted by the theory, and the series were observed experimentally in 1916, 1922, 1924 respectively at the predicted positions.

#### 4. Unquantized States and Continuous Spectra

In the spectrum of hydrogen, a continuous band is observed starting at the series limit and extending some little distance to higher wave numbers (or shorter wavelengths). This continuum is explained as due to 'unquantised' hyperbolic orbits on which the electron can move (Fig. 5). It can be shown from classical electrodynamics that an electron moving about a nucleus in an hyperbolic orbit has a *positive* energy. Further, since the orbits are unquantized, *all possible values of energy are possible*.

From an unquantised orbit, the electron can pass into one of the quantised orbits with emission of radiation. If the transition takes place when the electron has a velocity  $v$  and is at a distance  $r$  from the nucleus, the total initial energy (kinetic + potential) is  $\frac{1}{2} m v^2 - \frac{Z e^2}{4 \pi \epsilon_0 r}$ ; while



(Fig. 5)

the final energy (when it reaches a quantised orbit  $n$ ) is  $-\frac{m Z^2 e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right)$ . Hence, by

Bohr's postulate (which applies to all emission and absorption processes, whether the orbits are quantized or not) the frequency  $v'$  of the emitted radiation is given by

$$h v' = \frac{1}{2} m v^2 - \frac{Z e^2}{4 \pi \epsilon_0 r} + \frac{m Z^2 e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right).$$

This frequency is greater than that arising from transitions between orbits, both quantised. Hence, the spectrum will lie beyond the series limit. Since  $v$  and  $r$  can take all values, the spectrum will be continuous. These transitions can be shown in the energy-level diagram by arrows starting from any point in the continuum (which is above the energy level  $n = \infty$ ) and ending on any quantised level.

#### 5. Bohr's Model and Absorption Spectra

When a beam of continuous light is passed through a glass cell containing hydrogen gas in the atomic state and then sent into a spectrometer, a set of dark lines on a bright background is observed. This is the absorption spectrum of hydrogen. In terms of quantum theory, the incident light is considered to be a beam of quanta (photons) of all possible energies. According to Bohr's model, only those quanta are absorbed by the hydrogen atoms whose energies correspond to transitions between the allowed energy levels of the atoms. Hence discrete dark lines appear against the continuous background. The process of absorbing radiation is just the inverse of the emission process, since the absorption lines have exactly the same frequencies as the emission lines.

The dark lines in the absorption spectrum are never completely black, but only appear so by contrast with the bright background. The reason is that the atoms which are excited by absorbing radiation, re-radiate the absorbed energy almost at once, but these photons come off in random directions with only a few in the same direction as the original beam of continuous light.

**No Balmer Lines in the Absorption Spectrum of Hydrogen :** It is observed that for every line in the absorption spectrum there is a corresponding line in the emission spectrum of the substance. The reverse is, however, not true. Only certain emission lines appear in absorption. The reason is that normally the atom is initially in the ground state  $n = 1$ , and so absorption transitions can occur only from  $n = 1$  to  $n > 1$ . Therefore, lines of only the Lyman series appear in the absorption spectrum.

However, in absorption spectra of certain stars, lines of the Balmer series have been observed. This is due to the fact that, on account of the high temperature of the stellar atmosphere, a sufficient number of hydrogen atoms are in the first excited state  $n = 2$ .

We can, however, estimate the temperature of hydrogen gas in the atomic state at which the Balmer series will be observed in the absorption spectrum. According to Boltzmann probability distribution, the ratio of the number  $n_2$  of atoms in the first excited state to the number  $n_1$  of atoms in ground state, in a sample in thermal equilibrium at temperature  $T$  is

$$\frac{n_2}{n_1} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{(E_1 - E_2)/kT},$$

where  $k$  is Boltzmann's constant;

$$k = 1.38 \times 10^{-23} \text{ J/K} = 8.62 \times 10^{-5} \text{ eV/K.}$$

Now, for hydrogen, we have

$$E_1 = -13.6 \text{ eV}, E_2 = -3.39 \text{ eV, and so } E_1 - E_2 = -13.6 + 3.39 = -10.21 \text{ eV}$$

$$\therefore \frac{n_2}{n_1} = e^{-10.21 \text{ eV}/(8.62 \times 10^{-5} \text{ eV/K})T} = e^{-1.18 \times 10^5 \text{ K/T}}.$$

It is apparent that a significant fraction of the hydrogen atoms will initially be in the  $n = 2$  state provided  $T$  is of the order of  $10^5$  K.

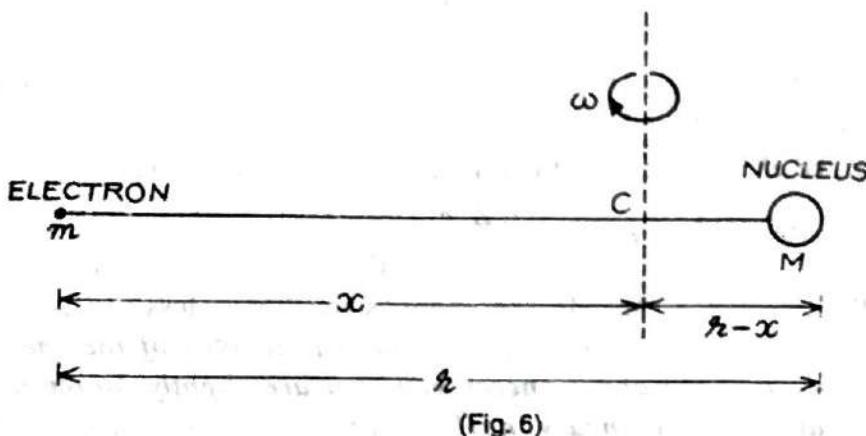
**Resonance Line :** When an atom in the ground state is excited to a higher state by the absorption of monochromatic radiation, it can fall directly back to the ground state, or after passing through other lower states. Therefore, the substance gives emission line of the same frequency as absorbed, and also lines of smaller frequencies. This phenomenon is called 'atomic fluorescence'.

If, however, hydrogen gas is illuminated with monochromatic radiation corresponding to the first line of the Lyman series, this radiation will be absorbed and atoms will rise from  $n = 1$  to  $n = 2$  state. The only possibility in this case is the transition back to the ground state  $n = 1$ , with the emission of the same line as absorbed. A spectral line with this property is called a 'resonance' line. Thus, the first (longest wavelength) line of Lyman series is the resonance line of hydrogen.

## 6. Correction for Finite Nuclear Mass

Let us now drop the assumption that the nucleus is infinitely heavy compared to the electron and so remains fixed in space. In fact, the nucleus has a finite mass, and the

electron and the nucleus both revolve about their common centre of mass  $C$  (Fig. 6) which remains fixed in space. We must make correction in Bohr theory for the finite mass (or motion) of the nucleus.



(Fig. 6)

Let  $m$  be the mass of electron,  $M$  the mass of nucleus, and  $r$  the distance between them. Let  $x$  be the distance of the electron from the centre of mass  $C$ . The distance of the nucleus from  $C$  will be  $(r - x)$ . Since the system is in equilibrium, the moments of  $m$  and  $M$  about  $C$  will be equal. That is,

$$m x = M(r - x).$$

This gives

$$x = \frac{M r}{m + M} \quad \text{and} \quad (r - x) = \frac{m r}{m + M}.$$

Since both the electron and the nucleus revolve around  $C$  with the same angular velocity  $\omega$ , the total orbital angular momentum of the atom,  $L$ , is the sum of the angular momenta of the electron and the nucleus. Thus

$$\begin{aligned} L &= m x^2 \omega + M(r - x)^2 \omega \\ &= m \frac{M^2 r^2}{(m + M)^2} \omega + M \frac{m^2 r^2}{(m + M)^2} \omega \\ &= \frac{m M (M + m) r^2 \omega}{(m + M)^2} \\ &= \frac{m M}{m + M} r^2 \omega. \end{aligned}$$

Let us write

$$\frac{m M}{m + M} = \mu,$$

where  $\mu$  is called the 'reduced mass' of the electron because it is less than  $m$  by a factor  $1/(1 + \frac{m}{M})$ . Then, the total angular momentum of the atom about the centre of mass is

$$L = \mu r^2 \omega.$$

To take nuclear motion into account, Bohr modified his second postulate and said that the electron can move only in those orbits for which the angular momentum of the atom is an integral multiple of  $\hbar/2\pi$ . Thus, from this quantisation condition, we have

$$\mu r^2 \omega = \frac{n \hbar}{2\pi}; \quad n = 1, 2, 3, \dots$$

or  $\mu v r = \frac{n h}{2\pi}$   $(\because v = r\omega)$

In the absence of nuclear motion, the corresponding equation is

$$m v r = \frac{n h}{2\pi}$$

A comparison of the last two equations shows that a replacement of  $m$  by  $\mu$  in Bohr's derivations takes into account the finite mass of the nucleus.

The energy of the electron in the  $n$ th orbit of a one-electron atom is now

$$E_n = -\frac{\mu Z^2 e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right)$$

Since  $\mu$  is slightly less than  $m$ , the electron energies are slightly less negative than if the nucleus were at rest (that is, infinitely heavy). **The wavelengths of the spectral lines computed on the basis of the above energy equation are slightly larger than those corresponding to an infinitely heavy nucleus,** and agree more closely with the experimental values.

## 7. Variation in Rydberg Constant due to Finite Nuclear Mass

The finite nuclear mass causes a slight variation in the Rydberg constant from atom to atom. The Rydberg constant for an atom having an infinitely heavy nucleus is

$$R_\infty = \frac{m e^4}{8 \epsilon_0^2 h^3 c}$$

and that for an atom having a nucleus of mass  $M$  is

$$R_M = \frac{\mu e^4}{8 \epsilon_0^2 h^3 c}$$

where  $\mu = \frac{m M}{m + M} = \frac{m}{1 + \frac{m}{M}}$ . Therefore,

$$R_M = \frac{m e^4}{8 \epsilon_0^2 h^3 c} \frac{1}{1 + \frac{m}{M}} = \frac{R_\infty}{1 + \frac{m}{M}}$$

Thus,  $R_M$  is less than  $R_\infty$  by a factor  $\frac{1}{1 + \frac{m}{M}}$ , and is different for different atoms,

depending upon their nuclear masses. Taking the known values of  $m$ ,  $e$ ,  $\epsilon_0$ ,  $h$  and  $c$ , upto six significant figures, we obtain

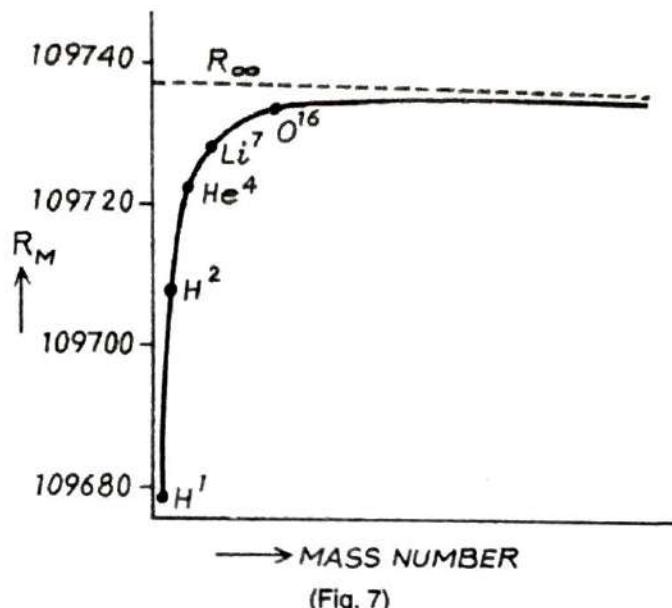
$$R_\infty = 1.09737 \times 10^7 \text{ m}^{-1} = 109737 \text{ cm}^{-1}$$

For the most extreme case of hydrogen,  $\frac{m}{M} = \frac{1}{1836}$ . The Rydberg constant for hydrogen is worked out to be

$$R_H = 109677 \text{ cm}^{-1}$$

Thus,  $R_H$  is less than  $R_\infty$  by about one part in 2000.

The variation of Rydberg constant from element to element against the mass number is shown in Fig. 7. The largest change occurs between  $H^1$  and  $H^2$ . With increasing mass number, the Rydberg constant approaches more and more closely to  $R_\infty$ .



(Fig. 7)

From Bohr's model, the expression for the series spectra of one-electron (hydrogen-like) atoms, assuming infinitely heavy nucleus, was obtained as

$$\nu = \frac{1}{\lambda} = R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

Taking into account the finite mass of the nucleus, this must be written as

$$\nu = \frac{1}{\lambda} = R_M Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

For hydrogen ( $H$ ),  $Z = 1$ . Hence writing  $R_H$  instead of  $R_M$ , the expression becomes

$$\nu = \frac{1}{\lambda} = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

For singly-ionised helium ( $He^+$ ),  $Z = 2$ , and so

$$\nu = \frac{1}{\lambda} = 4 R_{He} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

For doubly-ionised lithium ( $Li^{++}$ ),  $Z = 3$ , and so

$$\nu = \frac{1}{\lambda} = 9 R_{Li} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

For triply-ionised beryllium ( $Be^{+++}$ ),  $Z = 4$ , and so

$$\nu = \frac{1}{\lambda} = 16 R_{Be} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

The spectral lines of these atoms have been found at the calculated positions. It is found that Bohr's theory corrected for finite nuclear mass agrees with the experimental data to within 3 parts in 100,000.

The difference in the Rydberg constant for hydrogen and (ionised) helium can be utilised to compute the ratio of the mass  $m$  of the electron to the mass  $M_H$  of the hydrogen nucleus (that is, proton).

**Determination of  $m/M_H$ :** The Rydberg constant for hydrogen atom is given by

$$R_H = \frac{R_\infty}{1 + (m/M_H)}, \quad \dots(i)$$

where  $R_\infty$  is the Rydberg constant for an infinitely heavy nucleus,  $m$  is the mass of electron and  $M_H$  is the mass of hydrogen nucleus (that is, mass of proton). Similarly, the Rydberg constant for  $\text{He}^+$  is given by

$$R_{\text{He}} = \frac{R_\infty}{1 + (m/M_{\text{He}})},$$

where  $M_{\text{He}}$  is the mass of a helium nucleus. Since the mass of a helium nucleus is very nearly equal to four times the mass of a hydrogen nucleus ( $M_{\text{He}} \approx 4 M_H$ ), we write

$$R_{\text{He}} = \frac{R_\infty}{1 + (m/4 M_H)}. \quad \dots(\text{ii})$$

Dividing eq. (i) by (ii), we get

$$\frac{R_H}{R_{\text{He}}} = \frac{1 + (m/4 M_H)}{1 + (m/M_H)}$$

or

$$R_H \left( 1 + \frac{m}{M_H} \right) = R_{\text{He}} \left( 1 + \frac{m}{4 M_H} \right)$$

or

$$\frac{m}{M_H} (R_H - \frac{1}{4} R_{\text{He}}) = R_{\text{He}} - R_H$$

or

$$\frac{m}{M_H} = \frac{R_{\text{He}} - R_H}{R_H - \frac{R_{\text{He}}}{4}}.$$

$R_{\text{He}}$  and  $R_H$  can be found by measurements of wavelengths in the series of helium and hydrogen spectra. Hence  $m/M_H$ , the ratio of the mass of electron to the mass of proton (that is, hydrogen nucleus) can be determined.

Further, if  $e/M_H$  (specific charge of hydrogen ion or the charge required to liberate 1 gram-equivalent of any substance, known as Faraday constant) is given, we can evaluate the specific charge of electron  $(\frac{e}{m})$ .

$$\frac{e}{m} = \frac{e/M_H}{m/M_H}.$$

$e/M_H$  is 96500 coulomb/gram and  $m/M_H$  is 1/1836.

$$\therefore \frac{e}{m} = \frac{96500 \text{ C/g}}{1/1836} = 1.77 \times 10^8 \text{ C/g} = 1.77 \times 10^{11} \text{ C/kg.}$$

## 8. Discovery of Heavy Hydrogen

The variation of Rydberg constant with the (finite) mass of the nucleus resulted in the discovery of deuterium (heavy hydrogen). Deuterium is an isotope of hydrogen; its nucleus has a mass almost exactly double that of ordinary hydrogen. Therefore, the Rydberg constant for deuterium is slightly greater than that for hydrogen; as shown below :

$$R_H = \frac{R_\infty}{1 + \frac{m}{M_H}} = \frac{109737 \text{ cm}^{-1}}{1 + \frac{1}{1836}} = 109678 \text{ cm}^{-1}$$

and

$$R_D = \frac{R_\infty}{1 + \frac{m}{M_D}} = \frac{109737 \text{ cm}^{-1}}{1 + \frac{1}{2 \times 1836}} = 109707 \text{ cm}^{-1}.$$

Consequently, the wavelengths of the spectral lines of deuterium are slightly shorter than those of the corresponding spectral lines of hydrogen. The  $H_{\alpha}$  line of deuterium, for example, has a wavelength of 6561 Å, while that of hydrogen is 6563 Å; a small difference but sufficient for the identification of deuterium. The general nature of the two spectra is, however, exactly same because atoms of both hydrogen and deuterium have the same electron structure.

Urey, in 1932, photographed hydrogen spectrum by means of a large concave grating. He observed that each hydrogen line was accompanied by a very faint line slightly on the short wavelength side. He measured the wavelength difference and attributed the faint line to some heavier isotope of hydrogen. This isotope is now known as 'heavy hydrogen' or 'deuterium'. The relative abundance of deuterium in ordinary hydrogen was calculated to be approximately 1 part in 5000. This was taken another success of Bohr's model.

## 9. Comparison of H and $\text{He}^+$ Spectra

Pickering, in 1897, discovered a new series in  $\xi$ -Puppis star which was first attributed by Rydberg to some form of hydrogen since it could be represented by a formula similar to the Balmer's formula for hydrogen. Later on, the experimental work of Evans, Fowler and Paschen showed that this series arises due to ionised helium.

Putting  $Z = 2$  and  $R_{\text{He}}$  for the Rydberg constant in the Bohr's formula, all the four series of ionised helium can be represented as :

$$v = \frac{1}{\lambda} = 4 R_{\text{He}} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

Each series arises from a set of transitions in which the electron drops to a certain final state  $n_f$ :

$$n_f = 4 ; n_i = 5, 6, 7, \dots \quad \text{Pickering series}$$

$$n_f = 3 ; n_i = 4, 5, 6, \dots \quad \text{Fowler series}$$

$$\begin{aligned} n_f &= 2 ; n_i = 3, 4, 5, \dots \\ n_f &= 1 ; n_i = 2, 3, 4, \dots \end{aligned} \quad \left. \right\} \text{Lyman series in extreme ultraviolet}$$

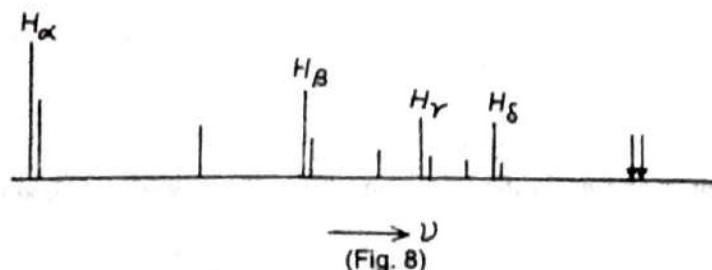
A comparison of the Balmer series formula for  $R_H$

$$v = \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n_i^2} \right), \quad n_i = 3, 4, 5, \dots$$

with the Pickering series formula for  $\text{He}^+$

$$v = \frac{1}{\lambda} = 4 R_{\text{He}} \left( \frac{1}{4^2} - \frac{1}{n_i^2} \right), \quad n_i = 5, 6, 7, \dots$$

shows that alternate members of the Pickering series ( $n_i = 6, 8, 10, \dots$ ) must coincide with members ( $n_i = 3, 4, 5, \dots$ ) of the Balmer series, provided  $R_{\text{He}} = R_H$ . A careful examination by Paschen has shown that Balmer lines of H are not exactly coincident with



→  $\nu$   
(Fig. 8)

alternate lines of the Pickering series of  $\text{He}^+$ , but are displaced by small intervals to lower wave numbers (longer wavelengths) as shown in Fig. 8. This small displacement is due to the difference in  $R_H$  and  $R_{\text{He}}$ , which arises due to the finite mass (motion) of the nucleus.

A careful observation shows that the series limits  $v_\infty$  of Balmer and Pickering series differ by about  $11 \text{ cm}^{-1}$ . Now

$$\text{For H : } (v_\infty)_H = \frac{R_H}{2^2} \quad (n_i \rightarrow \infty) \quad \text{Balmer}$$

$$\text{For } \text{He}^+ : (v_\infty)_{\text{He}^+} = \frac{4 R_{\text{He}}}{4^2} \quad (n_i \rightarrow \infty). \quad \text{Pickering}$$

$$\therefore R_{\text{He}} - R_H = 4 \left[ (v_\infty)_{\text{He}^+} - (v_\infty)_H \right] = 4 \times 11 \text{ cm}^{-1} = 44 \text{ cm}^{-1}.$$

This result is in excellent agreement with the value obtained from theory. This is a good example to establish the truth of the effect of the motion of the nucleus.

## 10. Wilson-Sommerfeld Quantisation Rules

Planck introduced his quantum theory by quantising the energy  $E$  of an atomic oscillator. According to Planck, an atomic oscillator can have only discrete energies which are multiples of  $h\nu'$  ( $E = n h \nu'$ ), where  $\nu'$  is the frequency of the oscillator. Bohr, on the other hand, quantised the angular momentum of the electron moving in a circular orbit. Wilson and Sommerfeld, in 1916, enunciated a set of rules for the quantisation of any physical system for which the coordinates are periodic functions of time. These are called 'Wilson-Sommerfeld quantisation rules', and include both the Planck and the Bohr quantisation as special cases. These rules can be stated as follows :

*For any physical system in which the coordinates are periodic functions of time, there exists a quantum condition for each coordinate. These quantum conditions are*

$$\oint p_i dq_i = n_i h, \quad \dots(i)$$

where  $q_i$  is one of the coordinates,  $p_i$  is the momentum associated with that coordinate, and  $n_i$  is a quantum number taking integral values.

The symbol  $\oint$  means that the integration is taken over a complete period of the coordinate  $q_i$ . The integral is called the 'phase integral' for the quantum number  $n_i$ .

**Derivation of Planck's Quantisation of Energy :** Let us apply Wilson-Sommerfeld quantum conditions to a one-dimensional simple harmonic oscillator. Its total (potential + kinetic) energy in terms of position  $x$  and linear momentum  $p_x$  is

$$E = U + K$$

$$= \frac{1}{2} k x^2 + \frac{1}{2} \frac{p_x^2}{m} \quad \left[ K = \frac{1}{2} m v^2, p_x = m v \right]$$

or

$$\frac{x^2}{2 E/k} + \frac{p_x^2}{2 m E} = 1.$$

The relation between  $x$  and  $p_x$  is the equation of an ellipse with semiaxes  $a$  and  $b$  given by

$$a = \sqrt{2E/k} \quad \text{and} \quad b = \sqrt{2mE}.$$

Any instantaneous state of motion of the oscillator is represented by some point on the ellipse, plotted on a two-dimensional space having coordinates  $x$  and  $p_x$ , as shown in Fig. 9. This plot is known as 'phase space diagram' of the oscillator. During one cycle of oscillation, the point  $(x, p_x)$  travels once around the ellipse,

so that the value of the integral  $\oint p_x dx$

is just equal to the area of the ellipse ( $\pi a b$ ). That is,

$$\oint p_x dx = \pi a b.$$

Putting the above values of  $a$  and  $b$ , and solving we get

$$\oint p_x dx = \frac{2\pi E}{\sqrt{k/m}}.$$

If  $v'$  be the frequency of oscillation, then  $v' = \frac{1}{2\pi} \sqrt{k/m}$ . Thus

$$\oint p_x dx = \frac{E}{v'}.$$

According to the Wilson-Sommerfeld quantisation rule, expressed by eq. (i), we have

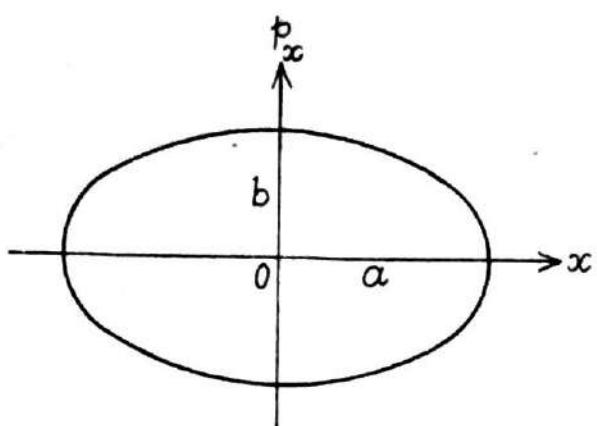
$$\oint p_x dx = n h, \quad n \text{ is an integer.}$$

Comparing the last two expressions,

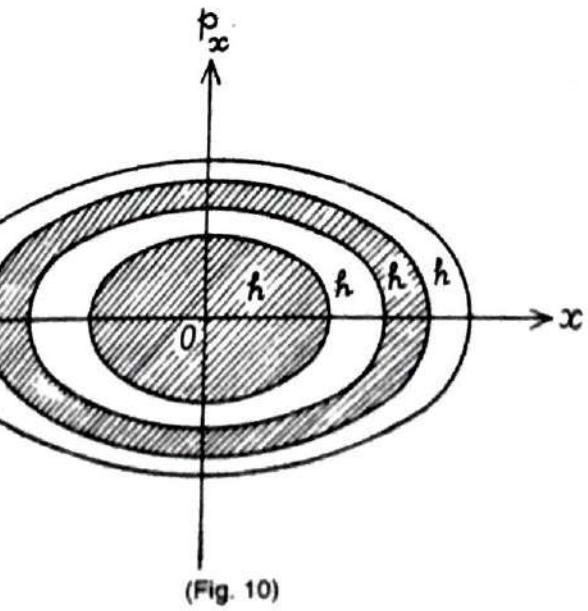
$$\frac{E}{v'} = n h$$

or  $E = n h v'$ ,  
which is Planck's quantisation law.

The allowed energy states of the oscillator can be represented by a series of ellipses in phase space, the area enclosed between successive ellipses always being  $h$ , as shown in Fig. 10.



(Fig. 9)



(Fig. 10)

**Derivation of Bohr's Quantisation of Angular Momentum :** Let us derive the Bohr's quantisation of angular momentum from the Wilson-Sommerfeld rule. The position of an electron moving in a circular orbit can be specified in terms of plane polar coordinates  $(r, \theta)$  which are periodic functions of time. The momentum associated with the radial coordinate  $r$  is  $p_r = m \frac{dr}{dt}$ , while that associated with the angular coordinate

$\theta$  is  $p_\theta = I \omega = m r^2 \frac{d\theta}{dt}$ , which is constant. For a circular orbit,  $r$  is constant so that  $p_r$  is zero. Hence, we apply the Wilson-Sommerfeld rule to the angular coordinate  $\theta$

only. The rule  $\oint p_i dq_i = n_i h$  becomes in this case

$$\oint p_\theta d\theta = n h$$

or

$$p_\theta \oint d\theta = n h$$

or

$$2\pi p_\theta = n h$$

or

$$p_\theta = \frac{n h}{2\pi}$$

The angular momentum of an electron is usually designated by  $\vec{L}$ , so that we may write the last expression as

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

which is Bohr quantisation law.

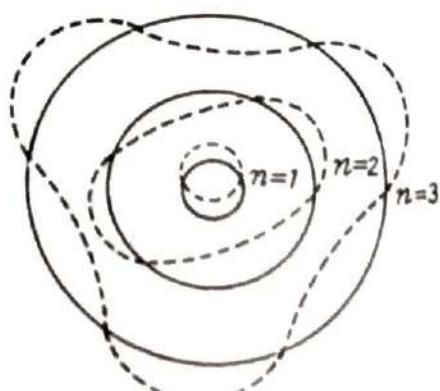
### 1.1. de Broglie's Interpretation of Bohr's Quantisation Law

According to de Broglie conception of matter waves, an electron of mass  $m$  moving with velocity  $v$  has associated with it a wave of wavelength given by

$$\lambda = \frac{h}{m v},$$

where  $h$  is Planck's constant. This wave-character of electron can account for the limited number of permissible orbits in an atom, and also enables us to deduce the quantised angular momentum of an electron in an atom.

We know that according to Bohr, an electron in an atom revolves in circular non-radiating orbits around the nucleus. Let us fit this idea with the wave-nature of electron. Since the electron does not radiate energy while moving in its orbit, the wave associated with it must be a 'stationary' wave in which there is no transfer of energy. Further, the electron wave can be adjusted around an orbit only when the circumference of the orbit can contain exactly an integral number of de Broglie wavelengths, as shown in Fig. 11 for the first three Bohr orbits. This means



(Fig. 11)

that only those orbits are permitted for which the radius  $r$  is given by

$$2\pi r = n\lambda. \quad n = 1, 2, 3, \dots$$

If this were not so, then the waves in each travel around the orbit will not be in phase, and in a large number of travels the waves would interfere with each other in such a way that their average intensity would be zero. This would mean that an electron cannot be found in such an orbit. Hence, the last expression is a necessary condition for the electron to exist in an orbit.

Substituting  $\lambda = h/mv$  in the last expression, we get

$$2\pi r = \frac{n h}{m v}$$

$$\text{or} \quad r = \frac{n h}{2\pi m v}.$$

Hence the magnitude of the angular momentum of the electron in its orbit must be

$$L = m v r = \frac{n h}{2\pi}.$$

This is Bohr's quantisation law.

## 12. Bohr's Correspondence Principle

According to the classical theory, an oscillating charged system would emit radiation of a particular frequency, namely, the frequency of the oscillator itself. According to quantum theory, however, radiation is emitted as a result of the system making a transition from a quantum state  $n_i$  to another quantum state  $n_f$ , and the frequency of radiation is determined by the difference in energy between the two states :

$$v' = \frac{E_i - E_f}{h}.$$

Bohr, in 1923, enunciated a principle which established a correspondence between the classical frequency and the quantum frequency. This principle consists of two parts :

(i) *The predictions of the quantum theory for the behaviour of any physical system must correspond to the predictions of the classical theory in the limit in which the quantum numbers specifying the state of the system become very large.*

(ii) *Any selection rules which are necessary to obtain the required correspondence in the limit of large quantum numbers also hold for small quantum numbers.*

Let us apply this principle to the hydrogen atom. Let  $v$  be the velocity of electron (mass  $m$ , charge  $e$ ) revolving in a Bohr orbit of radius  $r$  of the hydrogen atom. The condition of mechanical stability of the electron is

$$\frac{m v^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}.$$

The quantum condition is

$$m v r = \frac{n h}{2\pi}, \quad n = 1, 2, 3, \dots$$

These two equations give

$$v = \frac{e^2}{2n\hbar\epsilon_0}$$

$$r = \frac{n^2\hbar^2\epsilon_0}{\pi m e^2}.$$

and

The classical frequency of revolution of the electron in the orbit is

$$\begin{aligned} f &= \frac{\text{electron speed}}{\text{circumference of orbit}} = \frac{v}{2\pi r} \\ &= \frac{1}{2\pi} \frac{e^2/2n\hbar\epsilon_0}{n^2\hbar^2\epsilon_0/\pi m e^2} \\ &= \frac{m e^4}{4\epsilon_0^2 n^3 \hbar^3} = \left( \frac{m e^4}{8\epsilon_0^2 \hbar^3 c} \right) \frac{2c}{n^3}. \end{aligned}$$

Now,  $\frac{m e^4}{8\epsilon_0^2 \hbar^3 c} = R_\infty$ , the Rydberg constant for infinitely heavy nucleus.

$$\therefore f = \frac{2R_\infty c}{n^3} \quad \dots(i)$$

This is the frequency which must be radiated by the moving electron classically.

Now, the frequency radiated on the basis of quantum theory, when the electron drops from an initial orbit  $n_i$  to a final orbit  $n_f$ , is given by

$$v' = \frac{E_i - E_f}{h} = \frac{m e^4}{8\epsilon_0^2 \hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

Again, introducing  $R_\infty$ , we have

$$v' = R_\infty c \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

This may be written in the following form :

$$v' = R_\infty c \frac{(n_i - n_f)(n_i + n_f)}{n_f^2 n_i^2}.$$

Let us consider the transition  $\Delta n = n_i - n_f = 1$ , and write  $n_f = n$  and  $n_i = n_f + 1 = n + 1$ . Then, the radiated quantum frequency is

$$v' = R_\infty c \frac{2n+1}{n^2(n+1)^2}.$$

When  $n$  is very large, we can write

$$\frac{2n+1}{n^2(n+1)^2} \approx \frac{2n}{n^2(n^2)} \approx \frac{2}{n^3}.$$

Under this condition, the emitted quantum frequency is

$$v' = \frac{2R_\infty c}{n^3}. \quad \dots(ii)$$

Equations (i) and (ii) yield

$$v' = f.$$

If we consider transitions  $\Delta n = 2, 3, 4, \dots$  we shall have

$$v' = 2f, 3f, 4f, \dots$$

Thus, for very large quantum numbers  $n$ , the quantum-theory frequency  $v'$  of the radiation is identical with the classical frequency of the revolution (or its harmonics) of the electron in the orbits. This is in accordance with Bohr's correspondence principle.

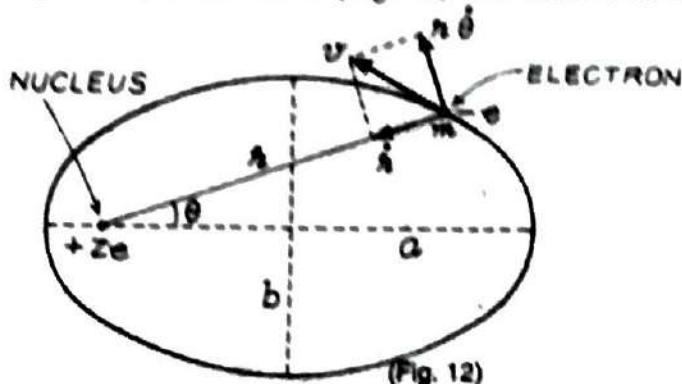
### 13. Sommerfeld's Extension of Bohr's Model

In Bohr's model of hydrogen atom, the electron could move only in *circular* orbits. This restriction was entirely arbitrary. Moreover, inspite of the striking numerical

agreements, the Bohr's model could not explain the "fine structure" of the hydrogen spectral lines. The fine structure is splitting of the spectral lines into several close, distinct components when observed under equipment of high resolution. This means that each Bohr's energy level in hydrogen atom actually consists of several components which are close together in energy.

Sommerfeld, in 1916, in an attempt to explain the fine structure, extended Bohr's model by assuming that the electron could move in *elliptic* orbits also, in addition to Bohr's circular orbits. He evaluated the size and shape of the allowed elliptic orbits, as well as the total energy of an electron moving in such an orbit.

Let us consider the motion of an electron (mass  $m$ , charge  $-e$ ) in an elliptic orbit, with nucleus (charge  $+Ze$ ) at one focus (Fig. 12). The instantaneous position of the electron



can be described in terms of the plane polar coordinates  $r$  and  $\theta$ , which, being periodic functions of time, must be quantised separately.

If  $p_r$  and  $p_\theta$  be the radial and the angular momenta of the electron, then according to Wilson-Sommerfeld quantisation rules, we have

$$\oint p_r dr = n \hbar \quad \dots(i)$$

and 
$$\int_0^{2\pi} p_\theta d\theta = k \hbar, \quad \dots(ii)$$

where  $n$  and  $k$  are integers, called 'radial' and 'azimuthal' quantum numbers respectively.

The second integral is easily evaluated because according to classical mechanics, the angular momentum  $p_\theta$  of any isolated system is *constant*. Thus,

$$p_\theta \int_0^{2\pi} d\theta = k \hbar$$

or 
$$p_\theta = \frac{k \hbar}{2\pi} \quad \dots(iii)$$

This restriction on the orbital angular momentum is the same as in Bohr circular orbit theory.

To evaluate the first integral, let us write

$$p_r = m r \dot{r} \quad \dots(iv)$$

and 
$$p_\theta = m r^2 \dot{\theta}, \quad \dots(v)$$

where  $r$  and  $r \dot{\theta}$  are the radial and the angular components of the velocity of the electron.

Now, the polar equation of the ellipse is

$$\frac{1}{r} = \frac{1}{a} \frac{1 - \epsilon \cos \theta}{1 - \epsilon^2}, \quad \dots (\text{vi})$$

where  $\sqrt{1 - \epsilon^2} = \frac{b}{a}$  (ratio of semi-minor to semi-major axis).

Taking logarithmic differentiation of  $r$  with respect to  $\theta$ , we get

$$-\frac{1}{r^2} \frac{dr}{d\theta} = \frac{1}{a} \frac{\epsilon \sin \theta}{1 - \epsilon^2}$$

or

$$-\frac{1}{r} \frac{dr}{d\theta} = -\frac{\epsilon \sin \theta}{1 - \epsilon \cos \theta} \quad [\text{from eq. (vi)}]$$

or

$$\left( \frac{1}{r} \frac{dr}{d\theta} \right)^2 = \frac{\epsilon^2 \sin^2 \theta}{(1 - \epsilon \cos \theta)^2}. \quad \dots (\text{vii})$$

Now,  $p_r = m \dot{r} = m \frac{dr}{dt} = m \frac{dr}{d\theta} \frac{d\theta}{dt} = m \frac{dr}{d\theta} \dot{\theta}$ . Using eq. (v), we have

$$p_r = \frac{p_\theta}{r^2} \frac{dr}{d\theta}. \quad \dots (\text{viii})$$

Also,

$$dr = \frac{dr}{d\theta} d\theta.$$

$$\therefore p_r dr = p_\theta \left( \frac{1}{r} \frac{dr}{d\theta} \right)^2 d\theta.$$

Using eq. (vii), we have

$$p_r dr = p_\theta \frac{\epsilon^2 \sin^2 \theta d\theta}{(1 - \epsilon \cos \theta)^2}.$$

Hence the integral in eq. (i) becomes

$$p_\theta \int_0^{2\pi} \frac{\epsilon^2 \sin^2 \theta d\theta}{(1 - \epsilon \cos \theta)^2} = n_r h.$$

The value of this definite integral is  $2\pi \left( \frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right)$ .

$$\therefore 2\pi p_\theta \left( \frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right) = n_r h.$$

But  $p_\theta = \frac{k h}{2\pi}$ , by eq. (iii).

$$\therefore k h \left( \frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right) = n_r h$$

or

$$\frac{1}{\sqrt{1 - \epsilon^2}} - 1 = \frac{n_r}{k}$$

or

$$\frac{1}{\sqrt{1 - \epsilon^2}} = \frac{n_r}{k} + 1 = \frac{n_r + k}{k}$$

or

$$\sqrt{1 - \epsilon^2} = \frac{k}{n_r + k}$$

But  $\sqrt{1 - \epsilon^2} = \frac{b}{a}$ , a property of ellipse.

$$\therefore \frac{b}{a} = \frac{k}{n_r + k} \quad \dots(\text{ix})$$

Since  $n_r$  and  $k$  are integers, we may put

$$n_r + k = n,$$

where  $n$  is called 'principal' or 'total' quantum number. In order to exclude "pendulum" orbits passing through the nucleus, Sommerfeld postulated that the azimuthal quantum number  $k \neq 0^*$ , that is,

$$k = 1, 2, 3, \dots$$

The radial quantum number  $n_r$ , however, takes the zero value for which the orbit is circular. That is

$$n_r = 0, 1, 2, 3, \dots$$

Therefore,  $n$  can take on the values :

$$n = 1, 2, 3, 4, \dots$$

For a given value of  $n$ , the  $k$  can assume only the values

$$k = 1, 2, 3, \dots, n.$$

The eq. (ix) now becomes

$$\boxed{\frac{b}{a} = \frac{k}{n}} \quad \dots(\text{x})$$

This is the quantum condition for the elliptic orbits. Out of all the classical possible ellipses, ***the electron can move only in those orbits for which the ratio of the minor to the major axis is the ratio of two integers.***

This quantises the size and the shape of the allowed elliptic orbits.

**Total Energy of Electron in allowed Orbit :** Let us now calculate the total energy  $E$  of an electron in a quantised elliptic orbit. The energy is the sum of the kinetic energy  $K$  and the potential energy  $U$ . That is

$$E = K + U$$

$$= \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2) - \frac{1}{4 \pi \epsilon_0} \frac{Z e^2}{r}.$$

Using eq. (iv) and (v), we have

$$E = \frac{1}{2m} \left\{ p_r^2 + \frac{p_\theta^2}{r^2} \right\} - \frac{1}{4 \pi \epsilon_0} \frac{Z e^2}{r}.$$

Again, using eq. (viii), we have

$$E = \frac{p_\theta^2}{2m r^2} \left[ \left( \frac{1}{r} \frac{dr}{d\theta} \right)^2 + 1 \right] - \frac{1}{4 \pi \epsilon_0} \frac{Z e^2}{r}$$

$$\text{or } \left( \frac{1}{r} \frac{dr}{d\theta} \right)^2 = \frac{2m E r^2}{p_\theta^2} - 1 + \frac{m Z e^2 r}{2 \pi \epsilon_0 p_\theta^2}. \quad \dots(\text{xii})$$

Now, from eq. (vi), we have

$$1 - \epsilon \cos \theta = \frac{a(1 - \epsilon^2)}{r}$$

\*If  $k = 0$ , then  $b = 0$  from eq. (ix), and the ellipse would become a straight line through the focus (nucleus).

or

$$\epsilon^2 \cos^2 \theta = \left\{ 1 - \frac{a(1 - \epsilon^2)}{r} \right\}^2$$

or

$$\epsilon^2 \sin^2 \theta = \epsilon^2 - \epsilon^2 \cos^2 \theta$$

$$= \epsilon^2 - \left\{ 1 - \frac{a(1 - \epsilon^2)}{r} \right\}$$

$$= \epsilon^2 - 1 - \frac{a^2(1 - \epsilon^2)^2}{r^2} + \frac{2a(1 - \epsilon^2)}{r}$$

$$\text{or } \frac{\epsilon^2 \sin^2 \theta}{(1 - \epsilon \cos \theta)^2} = \frac{r^2}{a^2(1 - \epsilon^2)^2} \left\{ - (1 - \epsilon^2) - \frac{a^2(1 - \epsilon^2)^2}{r^2} + \frac{2a(1 - \epsilon^2)}{r} \right\}$$

$$= - \frac{r^2}{a^2(1 - \epsilon^2)} - 1 + \frac{2r}{a(1 - \epsilon^2)}.$$

Substituting this in eq. (vii), we have

$$\left( \frac{1}{r} \frac{dr}{d\theta} \right)^2 = - \frac{r^2}{a^2(1 - \epsilon^2)} - 1 + \frac{2r}{a(1 - \epsilon^2)}.$$

This is identical with eq. (xi). Hence, we can compare the coefficients of  $r^2$  and  $r$  in these two equations. Then, we have

$$\frac{2mE}{p_\theta^2} = - \frac{1}{a^2(1 - \epsilon^2)}$$

and

$$\frac{mZe^2}{2\pi\epsilon_0 p_\theta^2} = \frac{2}{a(1 - \epsilon^2)}.$$

But  $1 - \epsilon^2 = \frac{b^2}{a^2}$ . Therefore, the last two eq. become

$$\frac{2mE}{p_\theta^2} = - \frac{1}{b^2} \quad \dots(\text{xii})$$

and

$$\frac{mZe^2}{2\pi\epsilon_0 p_\theta^2} = \frac{2a}{b^2}. \quad \dots(\text{xiii})$$

Dividing eq. (xii) by the square of eq. (xiii), we have

$$\frac{8\pi^2\epsilon_0^2 E p_\theta^2}{mZ^2 e^4} = - \frac{b^2}{4a^2}$$

or

$$E = - \frac{mZ^2 e^4 (b^2/a^2)}{32\pi^2\epsilon_0^2 p_\theta^2}.$$

But  $p_\theta = \frac{k\hbar}{2\pi}$  by eq. (iii), and  $\frac{b}{a} = \frac{k}{n}$  by eq. (x).

$$\therefore E = - \frac{mZ^2 e^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right). \quad \dots(\text{xiv})$$

This energy expression is exactly the same as for the Bohr's circular orbit. That is, the energy of the electron still depends only on the principal quantum number  $n$ , and is independent of the azimuthal quantum number  $k$ .

**Size and Shape of Sommerfeld's Elliptic Orbits :** From eq. (xiii), we have

$$a = \frac{m Z e^2 b^2}{4 \pi \epsilon_0 p_\theta^2}$$

Applying  $p_\theta = \frac{k h}{2 \pi}$ , and  $\frac{b}{a} = \frac{k}{n}$  so that  $b = \frac{a k}{n}$ , we have

$$a = \frac{\pi m Z e^2 a^2}{n^2 h^2 \epsilon_0}$$

or

$$a = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2}$$

...(xv)

Now,  $\frac{h^2 \epsilon_0}{\pi m e^2} = a_0$  (say), the radius of the smallest Bohr orbit of hydrogen atom. Hence, we may write

$$a = \frac{n^2}{Z} a_0$$

...(xvi)

Further, using  $b = \frac{a k}{n}$ , we have

$$b = \frac{n k}{Z} a_0$$

...(xvii)

Eq. (xvi) and (xvii) determine the size and shape of Sommerfeld's elliptic orbits.

Now, the theory predicts that for a given value of  $n (= k + n_r)$ ,  $k$  can take  $n$  possible different values ( $k = 1, 2, 3, \dots, n$ ). This means that for a given  $n$ , there are  $n$  orbits of *different eccentricities* (according to the condition  $\frac{b}{a} = \frac{k}{n}$ ) which can be occupied by the electron. Let us consider the first few cases of hydrogen atom ( $Z = 1$ ).

For  $n = 1$ ; we have  $k = 1$ ,

so that from eq. (xvi) and eq. (xvii), we have

$$a = a_0$$

and

$$b = a_0$$



This is a circular orbit of radius  $a_0$  (Fig. 13) which is exactly the same as the Bohr's orbit.

$n=1$

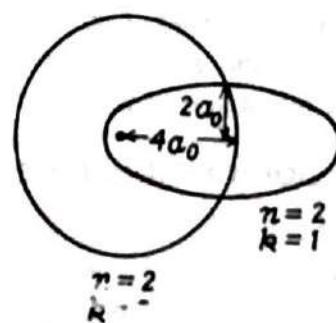
$k=1$

(Fig. 13)

For  $n = 2$ , we have

$$\begin{aligned} \text{(i)} \quad k = 2 \text{ so that } & \left. \begin{aligned} a &= 4 a_0 \\ b &= 4 a_0 \end{aligned} \right\} \\ \text{(ii)} \quad k = 1 \text{ so that } & \left. \begin{aligned} a &= 4 a_0 \\ b &= 2 a_0 \end{aligned} \right\} \end{aligned}$$

Thus, for  $n = 2$ , we have a Bohr's circular orbit of radius  $4 a_0$ , and an elliptic orbit with semi-major axis  $4 a_0$  and semi-minor axis  $2 a_0$  (Fig. 14).

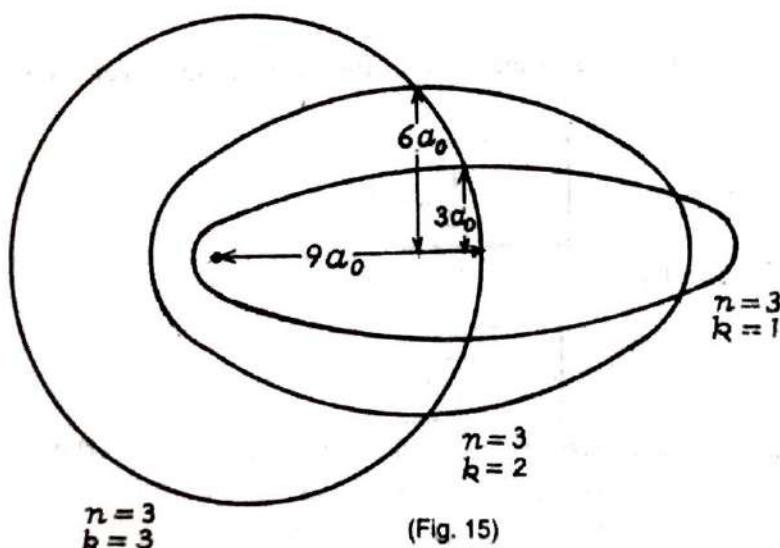


(Fig. 14)

For  $n = 3$ , there are three types of possible orbits :

$$\begin{aligned} \text{(i) } k = 3 & \text{ so that } \left. \begin{array}{l} a = 9 a_0 \\ b = 9 a_0 \end{array} \right\} \\ \text{(ii) } k = 2 & \text{ so that } \left. \begin{array}{l} a = 9 a_0 \\ b = 6 a_0 \end{array} \right\} \\ \text{(iii) } k = 1 & \text{ so that } \left. \begin{array}{l} a = 9 a_0 \\ b = 3 a_0 \end{array} \right\} \end{aligned}$$

Thus, out of the three possible orbits, one is the Bohr's circular orbit of radius  $9 a_0$ , the second is an elliptic orbit of semi-major axis  $9 a_0$  and semi-minor axis  $6 a_0$ , and the third is an elliptic orbit with semi-major axis  $9 a_0$  and semi-minor axis  $3 a_0$  (Fig. 15).



(Fig. 15)

We see that corresponding to each value of the principal quantum number  $n$ , there are  $n$  different allowed orbits. One of these is circular, just the orbit described by the original Bohr theory. The others are elliptic, all having the same semi-major axis as the radius of the circular orbit, but different semi-minor axes. The orbit having the lowest  $k$  is most elliptic.

But, despite the very different paths followed by the electron moving in different possible orbits for a given  $n$ , the total energy of the electron is the same. This means that Sommerfeld's introduction of elliptic orbits adds no new energy levels, and hence fails to explain the fine structure. The several orbits characterised by a common value of energy are said to be 'degenerate'.

To designate an orbit of given  $n$  and  $k$  values, the value of  $n$  is followed by one of the letters  $s, p, d, f, g, \dots$  according as  $k = 1, 2, 3, 4, 5, \dots$  respectively. For example, the state  $n = 3, k = 1$  is written as  $3s$ ; and that  $n = 3, k = 2$  as  $3p$ . It is seen that the  $s$ -electron orbit (lowest  $k$ ) is most elliptical in any family of orbits having same major axis (same  $n$ ).

#### 14. Sommerfeld's Relativistic Correction

Sommerfeld removed the degeneracy in the total energy of the electron moving in different  $k$ -orbits for a given  $n$  by introducing the relativistic variation of mass of the electron. For an electron in the innermost orbit of the hydrogen atom,  $\frac{v}{c} = 10^{-2}$ , or less

Although, this would give a relativistic correction to the total energy only of the order of  $10^{-4}$ , but it is just the order of the splitting of energy levels required to explain the observed fine structure of hydrogen spectral lines.

In an elliptic orbit, the velocity of electron varies and is largest near the perihelion. The actual size of the relativistic correction depends upon the average velocity of the electron which, in turn, depends on the ellipticity of the orbit. This means that the correction is different for different  $k$ -orbits of a given  $n$ , and thus the degeneracy is removed.

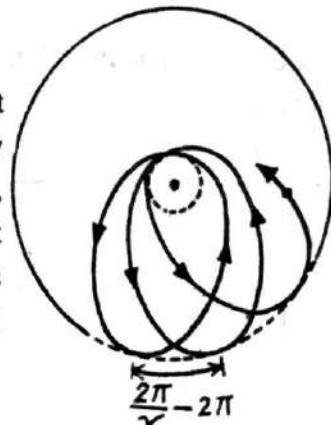
Using the relativistic expression for the kinetic energy of the electron,

$$K = m_0 c^2 \left( \frac{1}{\sqrt{1 - (v^2/c^2)}} - 1 \right),$$

where  $m_0$  is the rest mass of the electron, Sommerfeld obtained the following equation for the path of the electron :

$$\frac{1}{r} = \frac{1}{a} \frac{1 - \epsilon \cos(\gamma \theta)}{1 - \epsilon^2},$$

where  $\gamma (< 1)$  is a constant. This shows that  $r$  does not return to a given value when  $\theta$  increases by  $2\pi$ , but only when it increases by  $2\pi/\gamma$  which is greater than  $2\pi$ . Thus, the orbit of the electron is not a uniform rotating ellipse, but the perihelion of the orbit precesses in the same direction as the revolution of the electron. The advance of the perihelion per revolution is  $\frac{2\pi}{\gamma} - 2\pi$ , as shown in Fig. 16.



(Fig. 16)

Taking the effect of relativistic precession into account, Sommerfeld calculated the total energy of an electron in an orbit characterised by the quantum numbers  $n$  and  $k$  as

$$E = - \frac{m_0 Z^2 e^4}{8 \epsilon_0^2 n^2 h^2} \left[ 1 + \frac{Z^2 \alpha^2}{n} \left( \frac{1}{k} - \frac{3}{4n} \right) \right],$$

where the quantity  $\alpha \left( = \frac{e^2}{2 \epsilon_0 h c} \right)$  is a pure number called 'fine-structure constant'. Its value is about  $\frac{1}{137}$ . ( $\alpha$  is equal to the ratio of the velocity of electron in the first Bohr orbit of hydrogen to the velocity of light  $c$  in vacuum).

The last expression may also be written as

$$E = - \frac{R_\infty Z^2 h c}{n^2} \left[ 1 + \frac{Z^2 \alpha^2}{n} \left( \frac{1}{k} - \frac{3}{4n} \right) \right],$$

where  $R_\infty \left( = \frac{m_0 e^4}{8 \epsilon_0^2 h^3 c} \right)$  is the Rydberg constant for an infinitely heavy nucleus. The term values of the hydrogen-like atom are therefore

$$T = - \frac{E}{h c} = \frac{R_\infty Z^2}{n^2} \left[ 1 + \frac{Z^2 \alpha^2}{n} \left( \frac{1}{k} - \frac{3}{4n} \right) \right]$$

or

$$T = \frac{R_m Z^2}{n^2} + \frac{R_m Z^4 \alpha^2}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right).$$

The first term of this equation is the same as that derived by Bohr for circular orbits, and gives the major part of the energy. The second term is the relativity correction  $\Delta T$ , such that

$$\Delta T = \frac{R_m Z^4 \alpha^2}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right).$$

Now,

$$\begin{aligned} R_m \alpha^2 &= (1.097 \times 10^7 \text{ m}^{-1}) \left( \frac{1}{137} \right)^2 \\ &= 5.84 \times 10^2 \text{ m}^{-1} = 5.84 \text{ cm}^{-1}. \\ \therefore \Delta T &= 5.84 \frac{Z^4}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right) \text{ cm}^{-1}. \end{aligned}$$

which is positive since  $k \leq n$ . Since  $\Delta T$  depends on  $k$ , it is different for different  $k$ -orbits of the same  $n$ .

We can calculate the relativity shift in the energy levels of various  $k$  values for each Bohr energy level  $n$  with the help of the last expression. We do it for the Bohr levels  $n = 1, 2$  and  $3$  of hydrogen ( $Z = 1$ ).

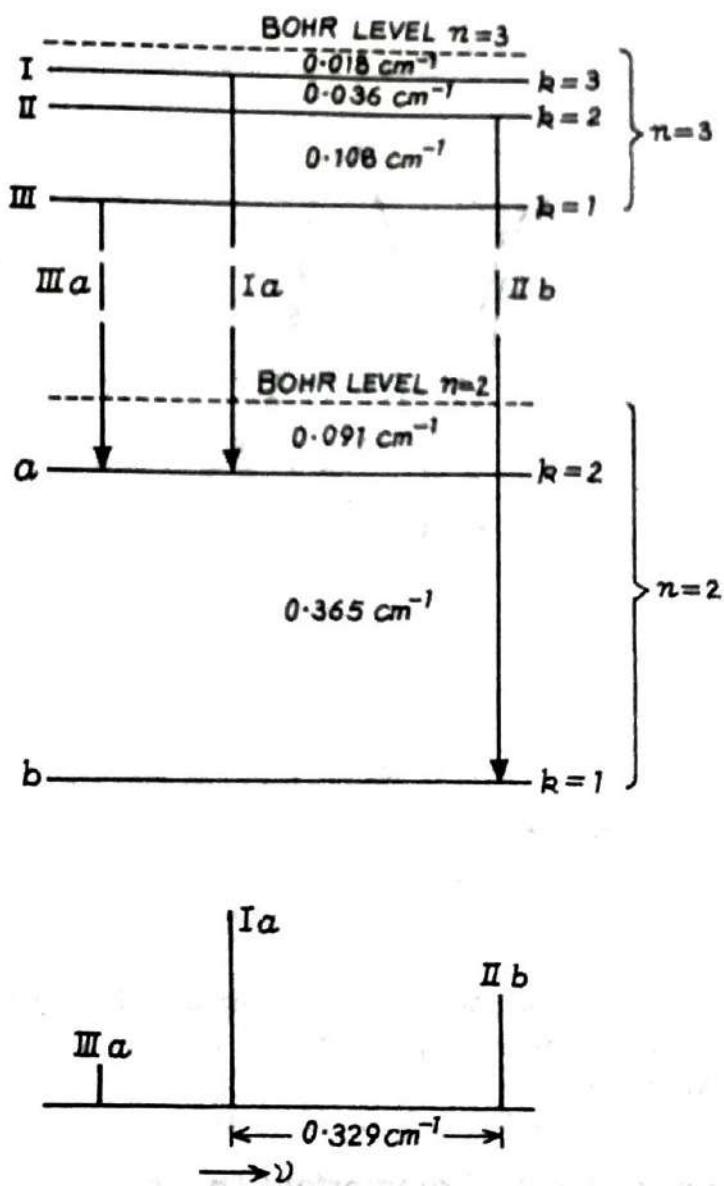
$n$	$k$	Shift from Bohr level $\Delta T$ (in $\text{cm}^{-1}$ )	Separation between $k$ -levels (in $\text{cm}^{-1}$ )
1	1	1.46	—
2	2	0.091	0.365
	1	0.456	
3	3	0.018	0.036
	2	0.054	
	1	0.162	0.108

Fig. 17 shows the energy states of the hydrogen atom corresponding to  $n = 2$  and  $n = 3$  in terms of an energy-level diagram.

The states  $n = 2$  and  $n = 3$  are involved in the emission of the  $H_\alpha$ -line. In the Fig.,  $a, b$  are the two  $k$ -levels corresponding to  $n = 2$ , and I, II, III are the three  $k$ -levels corresponding to  $n = 3$ . The separations between  $k$ -levels with a common  $n$  value are very much exaggerated for the sake of clarity. Emission transitions from the  $k$ -levels of  $n = 3$  to the  $k$ -levels of  $n = 2$  have been drawn according to the selection rule

$$\Delta k = \pm 1.$$

This rule was first introduced empirically but justified by correspondence principle, and later on by quantum mechanics. We expect in the  $H_\alpha$ -line two strong components I a and II b, and a faint component III a. The spacing between the two main components is worked out to be  $0.329 \text{ cm}^{-1}$  by Sommerfeld's formula.



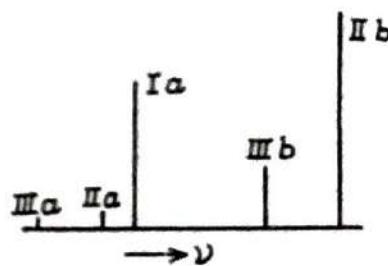
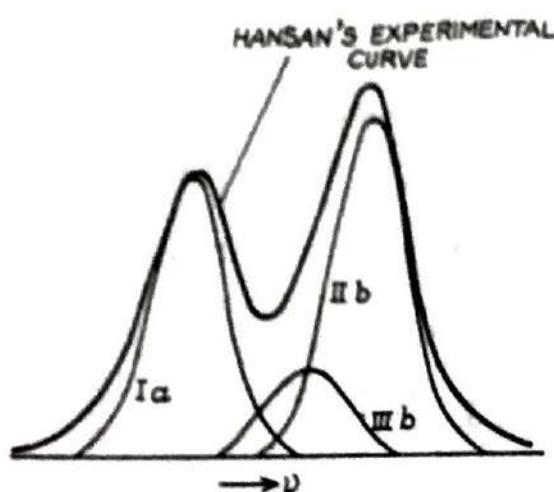
Fine-structure of  $H_{\alpha}$ -line as predicted by Sommerfeld Theory  
(Fig. 17)

Let us compare this result with experiment. Hansan obtained by experiment a photometric curve for the  $H_{\alpha}$ -line of hydrogen. An analysis of this curve indicated the presence of five components, two strong and three weaker ones (Fig. 18). The spacing between the two main components was found to be  $0.3297 \text{ cm}^{-1}$  which was in excellent agreement with Sommerfeld's theory. There were however, two serious disagreements :

(i) Experimentally, a rather strong component was observed on the small wave-number side of the main component II b. Calculation showed that this corresponds exactly to the transition  $n = 3, k = 1 \rightarrow n = 2, k = 1$  (III b), which is forbidden by the selection rule and hence not given by theory.

(ii) Experimentally, the component II b was stronger than the component I a, while reverse was the case in theory.

These discrepancies were removed by introducing the spin of the electron and adopting the quantum-mechanical relativistic correction. We shall return to the discussion of the hydrogen fine structure in a subsequent chapter.



Observed Fine-structure of H<sub>α</sub>-line  
(Fig. 18)

Note : From quantum mechanical considerations, the azimuthal quantum number  $k$  of Bohr-Sommerfeld theory has been replaced by  $l + 1$ , where  $l$  is a new quantum number, having possible values :

$$l = 0, 1, 2, 3, \dots, (n - 1).$$

## 15. Shortcomings of Bohr-Sommerfeld Theory

The Bohr-Sommerfeld theory was quite successful in explaining many experimental observations on the structure of atoms and simple spectra. Yet, it was not free from shortcomings.

(i) Although the theory told how to calculate the energies of the allowed states of an atom, and the frequency of radiation emitted or absorbed in transitions between allowed states; but it could not tell how to calculate the *rate* at which such transitions take place. As such, it could not explain the variation in intensity of the spectral lines.

(ii) The theory is applicable only to one-electron atoms like hydrogen, hydrogen isotopes, singly-ionised helium, etc. It fails when applied to the neutral helium atom which has only two electrons.

(iii) As we have seen, even in hydrogen-like atoms the theory become silent on the observed fine-structure of spectral lines.

(iv) No logical reason was given for the introduction of quantum numbers. The quantum numbers were introduced by Bohr as a postulate and adhoc selection rules were adopted to explain the observed lines.

(v) The theory did not throw any light on the distribution and arrangement of electrons in atoms.

(vi) The success of the theory in dealing with the effect of a magnetic field on spectral lines was only partial. It could not explain anomalous Zeeman effect.

These difficulties could not be resolved by further changes in Bohr's theory. It became apparent that the difficulties of the theory were caused by the failure of the atomic model then used. The solution to the problem came in 1925 and onwards in the form of quantum mechanics which yields all the correct results of the Bohr's theory, such as stationary states with the correct energy values, explanation of emission and absorption of radiation in terms of transitions between stationary states, the Ritz combination principle, etc. In quantum mechanics, the quantum numbers appear automatically in the mathematical solutions of the problems. The necessary selection rules also turn out to be a direct result of the mathematical treatment. Nevertheless, the so-called old quantum theory is still used as it is possible to go quite a long way with the Bohr's model without coming into disagreement with many experimental observations, without going through complicated and lengthy mathematics used in quantum mechanics.

### SOLVED PROBLEMS

1. Calculate the speed of electron in the  $n$ th orbit of hydrogen atom. If relativistic correction is important for  $v/c > 0.005$ , find for which orbit this correction is necessary. Given :  $e = 1.60 \times 10^{-19} \text{ C}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2$ .

**Solution.** Let  $v$  be the velocity of electron (mass  $m$ , charge  $e$ ) revolving in a Bohr orbit of hydrogen atom ( $Z = 1$ ) of radius  $r$ . The condition of mechanical stability of the electron is

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}. \quad \dots(i)$$

The quantum condition is

$$mv r = \frac{n h}{2\pi}, \quad n = 1, 2, 3, \dots \quad \dots(ii)$$

Dividing eq. (i) by eq. (ii), we get

$$v = \frac{e^2}{2n h \epsilon_0}.$$

Substituting the given values :

$$\begin{aligned} v &= \frac{(1.60 \times 10^{-19} \text{ C})^2}{2n(6.63 \times 10^{-34} \text{ Js})(8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)} \\ &= \frac{1}{n} (2.18 \times 10^6) \text{ m s}^{-1}. \end{aligned}$$

This is the required value. Now

$$\frac{v}{c} = \frac{1}{n} \frac{2.18 \times 10^6}{3.0 \times 10^8} = \frac{0.0073}{n}.$$

Thus, for  $n = 1, 2, 3, \dots$  we have

$$\frac{v}{c} = 0.0073, 0.0036, 0.0024, \dots$$

Hence the relativistic correction is necessary for  $n = 1$  orbit only.

2. How many revolutions does an electron in the  $n = 2$  state of a hydrogen atom make before dropping to the  $n = 1$  state? The average life time of an excited state is  $10^{-8}$  second. ( $R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$ )

**Solution.** Let  $v$  be the velocity of electron (mass  $m$ , charge  $e$ ) revolving in a Bohr orbit of hydrogen atom ( $Z = 1$ ) of radius  $r$ . The condition of mechanical stability of the electron is

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}.$$

The quantum conditions is

$$mv r = \frac{n\hbar}{2\pi},$$

$n = 1, 2, 3, \dots$

These two equation give  $v = \frac{e^2}{2n\hbar\epsilon_0}$  and  $r = \frac{n^2\hbar^2\epsilon_0}{\pi me^2}$ .

The number of revolutions of the electron in the orbit per second is

$$f = \frac{v}{2\pi r} = \frac{me^4}{4\epsilon_0^2 n^3 \hbar^3} = \frac{me^4}{8\epsilon_0^2 \hbar^3 c} \left( \frac{2c}{n^3} \right) = R_\infty \left( \frac{2c}{n^3} \right).$$

For the  $n = 2$  state, the frequency of revolution is

$$f = \frac{R_\infty c}{4}.$$

Substituting the given value of  $R_\infty$ , and the known value of  $c$ , we get

$$f = \frac{(1.097 \times 10^7 \text{ m}^{-1})(3.0 \times 10^8 \text{ m s}^{-1})}{4}$$

$$= 8.2 \times 10^{14} \text{ s}^{-1}.$$

Hence the number of revolutions of the electron in its life-time of  $10^{-8}$  second is

$$= (8.2 \times 10^{14} \text{ s}^{-1}) \times 10^{-8} \text{ s} = 8.2 \times 10^6.$$

3. The series limit wavelength of the Balmer series in hydrogen spectrum is 3646 Å. Calculate Rydberg constant for hydrogen atom.

**Solution.** The wavelengths of the lines of Balmer series are given by

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right); \quad n = 3, 4, 5, \dots$$

For the series limit wavelength,  $n = \infty$ . Thus,

$$\frac{1}{\lambda_{\infty}} = R_H \left( \frac{1}{2^2} \right)$$

or  $R_H = \frac{4}{\lambda_{\infty}} = \frac{4}{3646 \times 10^{-10} \text{ m}} = 1.097 \times 10^7 \text{ m}^{-1}$ .

4. Calculate the wavelength of the eighth line of the Balmer series of hydrogen atom. Given :  $R_\infty = 1.09737 \times 10^7 \text{ m}^{-1}$ .

**Solution.** The wavelengths of the lines of Balmer series are given by

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right); \quad n = 3, 4, 5, 6, 7, 8, 9, 10, \dots$$

For the 8th line,  $n = 10$ .

$$\therefore \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{10^2} \right) = \frac{6 R_H}{25}$$

or  $\lambda = \frac{25}{6 R_H}$  ... (i)

Now, the Rydberg constant for hydrogen is

$$R_H = \frac{R_\infty}{1 + \frac{m}{M_H}},$$

where  $R_\infty$  is Rydberg constant for infinitely heavy nucleus,  $m$  is the mass of electron, and  $M_H$  is the mass of hydrogen nucleus (that is, proton).

We know that  $m/M_H$  is  $1/1836$ .

$$\therefore R_H = \frac{1.09737 \times 10^7 \text{ m}^{-1}}{1 + (1/1836)} = 1.09677 \times 10^7 \text{ m}^{-1}.$$

Hence, from eq. (i) we have

$$\begin{aligned}\lambda &= \frac{25}{6 \times (1.09677 \times 10^7 \text{ m}^{-1})} \\ &= 3.799 \times 10^{-7} \text{ m} = 3799 \text{ Å}.\end{aligned}$$

**5. The wavelength of the first line of the Lyman series of hydrogen is  $1215 \text{ Å}$ .**

**Calculate the wavelength of the second line of the series, and the series limit.**

**Solution.** The wavelengths of the lines of the Lyman series of hydrogen atom are given by

$$\frac{1}{\lambda} = R_H \left( \frac{1}{1^2} - \frac{1}{n^2} \right); n = 2, 3, 4, \dots$$

For the first line ( $\lambda = 1215 \text{ Å}$ ),  $n = 2$ .

$$\therefore \frac{1}{1215 \text{ Å}} = \frac{3}{4} R_H$$

or  $R_H = \frac{4}{3 \times (1215 \text{ Å})}$ .

For the second line ( $\lambda = ?$ ),  $n = 3$ .

$$\begin{aligned}\therefore \frac{1}{\lambda} &= \frac{4}{3 \times (1215 \text{ Å})} \left( \frac{1}{1^2} - \frac{1}{3^2} \right) \\ &= \frac{4}{3 \times (1215 \text{ Å})} \times \frac{8}{9} \\ \lambda &= \frac{3 \times (1215 \text{ Å}) \times 9}{4 \times 8} = 1025 \text{ Å}.\end{aligned}$$

or

$$\therefore \lambda_{\infty} = \frac{1}{R_H} = \frac{3 \times (1215 \text{ Å})}{4} = 911 \text{ Å}.$$

**For the series limit,  $n = \infty$ .**

**6. (i) How much energy is required to remove an electron from a hydrogen atom in the ground state, and also in a state with  $n = 8$ ? (ii) Calculate the corresponding energies of the singly-ionised helium atom. ( $m = 9.11 \times 10^{-31} \text{ kg}$ ,  $e = 1.60 \times 10^{-19} \text{ C}$ ,  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{N m}^2$  and  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ ).**

**Solution.** (i) The energy required to remove an electron from the hydrogen atom in the ground state ( $n = 1$ ) to infinity (where the energy is zero) is numerically equal to the energy of the electron in the  $n = 1$  orbit. Now, the energy of the electron in  $n$  th orbit of hydrogen ( $Z = 1$ ) is given by

$$E_n = - \frac{m e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right), \quad n = 1, 2, 3, \dots$$

For the ground orbit,  $n = 1$ ,

$$\begin{aligned} E_1 &= - \frac{m e^4}{8 \epsilon_0^2 h^2} = - \frac{(9.11 \times 10^{-31}) \times (1.60 \times 10^{-19})^4}{8 \times (8.85 \times 10^{-12})^2 \times (6.63 \times 10^{-34})^2} \\ &= - 2.17 \times 10^{-18} \text{ J} \\ &= - \frac{2.17 \times 10^{-18} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = - 13.6 \text{ eV}. \end{aligned}$$

Hence the energy required to remove the electron from  $n = 1$  orbit to infinity is 13.6 eV. This is known as the binding energy of the hydrogen atom.

Again, for  $n = 8$  orbit,

$$\begin{aligned} E_8 &= - \frac{m e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{8^2} \right) = \frac{E_1}{64} \\ &= - \frac{13.6 \text{ eV}}{64} = - 0.213 \text{ eV}. \end{aligned}$$

Hence the energy required to remove an electron from  $n = 8$  orbit to infinity is 0.213 eV.

(ii) The energy expression for  $\text{He}^+$  ( $Z = 2$ ) is

$$\begin{aligned} (E_n)_{\text{He}^+} &= - \frac{m Z^2 e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right) \\ &= - \frac{4 m e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right) = - 4 (E_n)_H. \end{aligned}$$

That is, the energies for  $\text{He}^+$  are 4 times the corresponding energies for H. Thus, the results are

$$\begin{aligned} 4 \times 13.6 &= 54.4 \text{ eV} \\ \text{and} \quad 4 \times 0.213 &= 0.85 \text{ eV}. \end{aligned}$$

7. The wavelength of the first line of Balmer series of hydrogen is 6562.8 Å. Calculate (i) the ionisation potential, and (ii) the first excitation potential of the hydrogen atom. ( $\hbar = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ ).

**Solution.** (i) The wavelengths of the Balmer lines are given by

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \dots$$

For the first line  $n = 3$  and  $\lambda = 6562.8 \text{ Å} = 6562.8 \times 10^{-10} \text{ m}$ .

$$\frac{1}{6562.8 \times 10^{-10} \text{ m}} = R_H \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5 R_H}{36}$$

$$\text{or} \quad R_H = \frac{36}{5 \times (6562.8 \times 10^{-10} \text{ m})} = 1.097 \times 10^7 \text{ m}^{-1}$$

The ionisation potential of an atom is numerically equal to the (ionisation) energy required to remove an electron completely from the atom in the ground state. In hydrogen atom; the electron stays in the first orbit ( $n = 1$ ). Hence the energy required to remove this electron to infinity (where the energy is considered to be zero) is numerically equal to the energy of the electron in the first orbit. We know that electron energy in the  $n$ th orbit of hydrogen atom is given by

$$E_n = - \frac{m e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right), \quad n = 1, 2, 3, \dots$$

$$= - \frac{R_\infty h c}{n^2}.$$

$$\left[ R_\infty = \frac{m e^4}{8 \epsilon_0^2 h^3 c} \right]$$

Ignoring the effect of finite nuclear mass, we can take  $R_H = R_\infty$ .

$$\therefore E_n = - \frac{R_H h c}{n^2}.$$

For the ground orbit,  $n = 1$ .

$$\begin{aligned} \therefore E_1 &= - R_H h c \\ &= - (1.097 \times 10^7 \text{ m}^{-1}) (6.63 \times 10^{-34} \text{ J s}) (3.0 \times 10^8 \text{ m s}^{-1}) \\ &= - 21.8 \times 10^{-19} \text{ J} \\ &= - \frac{21.8 \times 10^{-19} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = - 13.6 \text{ eV}. \end{aligned}$$

Hence the energy required to remove the electron from  $n = 1$  orbit to infinity is 13.6 eV.

Obviously, the ionisation potential of the hydrogen atom is 13.6 volt.

(ii) The first excitation potential of the atom is the energy required to shift the electron from  $n = 1$  to  $n = 2$  orbit, that is,  $E_1 - E_2$ . Now,

$$E_1 = - 13.6 \text{ eV}$$

and

$$E_2 = \frac{E_1}{4} = - 3.4 \text{ eV}.$$

$$\left[ \because E_n \propto \frac{1}{n^2} \right]$$

$$\therefore E_1 - E_2 = 13.6 - 3.4 = 10.2 \text{ eV}.$$

Hence the first excitation potential is 10.2 volt.

**8. Calculate the ionisation potential of hydrogen atom.** Given :  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $e = 1.60 \times 10^{-19} \text{ C}$ ,  $m = 9.11 \times 10^{-31} \text{ kg}$ , and  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2$ .

**Solution.** The ionisation potential refers to the binding energy of the hydrogen atom (the energy binding the electron to the nucleus), which is numerically equal to the energy of the lowest state corresponding to  $n = 1$ . This is, with  $Z = 1$ ,

$$\begin{aligned} E_1 &= - \frac{m e^4}{8 \epsilon_0^2 h^2} \\ &= - \frac{(9.11 \times 10^{-31} \text{ kg})(1.60 \times 10^{-19} \text{ C})^4}{8 (8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)^2 (6.63 \times 10^{-34} \text{ J s})^2} \\ &= - 2.17 \times 10^{-18} \text{ J} \\ &= - \frac{2.17 \times 10^{-18} \text{ J}}{1.60 \times 10^{-19} \text{ J / eV}} = - 13.6 \text{ eV}. \end{aligned}$$

The ionisation potential is 13.6 V.

9. Find the energy, momentum, and wavelength of a photon emitted by a hydrogen atom making a direct transition from an excited state with  $n = 10$  to the ground state. Also, find the recoil speed of the hydrogen atom in this process. Given :  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $m_H = 1.67 \times 10^{-27} \text{ kg}$ .

**Solution.** The energy of electron in hydrogen atom ( $Z = 1$ ) in a state  $n$  is given by

$$E_n = -\frac{R_H h c}{n^2}$$

The energy of the photon emitted during an electron transition from  $n = 10$  to  $n = 1$  is

$$\begin{aligned} E_{10} - E_1 &= R_H h c \left( \frac{1}{1^2} - \frac{1}{10^2} \right) \\ &= (1.097 \times 10^7 \text{ m}^{-1})(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1}) \left( \frac{99}{100} \right) \\ &= 21.6 \times 10^{-19} \text{ J} \\ &= \frac{21.6 \times 10^{-19} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 13.5 \text{ eV.} \end{aligned}$$

The momentum of the photon is

$$p = \frac{E}{c} = \frac{21.6 \times 10^{-19} \text{ J}}{3.0 \times 10^8 \text{ m s}^{-1}} = 7.20 \times 10^{-27} \text{ kg m s}^{-1}$$

To find the wavelength of the photon, we see that the atom drops to the ground state ( $n = 1$ ). Hence the photon emitted belongs to the Lyman series. The wavelengths of the spectral lines in this series are given by

$$\frac{1}{\lambda} = R_H \left( \frac{1}{1^2} - \frac{1}{n^2} \right); \quad n = 2, 3, 4, \dots$$

For  $n = 10$ , we have

$$\text{or } \lambda = \frac{100}{99 R_H} = \frac{100}{99 \times (1.097 \times 10^7 \text{ m}^{-1})} = 9.21 \times 10^{-8} \text{ m} = 921 \text{ Å.}$$

Finally, after the emission of photon, the hydrogen atom recoils with a momentum of  $7.20 \times 10^{-27} \text{ kg m s}^{-1}$  (same as that of the photon). Hence the recoil speed of the hydrogen atom of mass  $m_H$  (say) is

$$v = \frac{p}{m_H} = \frac{7.20 \times 10^{-27} \text{ kg m s}^{-1}}{1.67 \times 10^{-27} \text{ kg}} = 4.31 \text{ m s}^{-1}$$

10. A photon ionises a hydrogen atom from the ground state. The liberated electron recombines with a proton into the first excited state, emitting a 466-Å photon. Find (i) the energy of the free electron, and (ii) the energy of the original photon. Given :  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ .

**Solution.** (i) The energy of the electron in hydrogen atom ( $Z = 1$ ) in the  $n$ th state is given by

$$\begin{aligned}
 E_n &= -\frac{R_H h c}{n^2} \\
 &= -\frac{(1.097 \times 10^7 \text{ m}^{-1})(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{n^2} \\
 &= -\frac{21.8 \times 10^{-19} \text{ J}}{n^2} \\
 &= -\frac{21.8 \times 10^{-19} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2}.
 \end{aligned}$$

The energy of electron in the first excited state ( $n = 2$ ) is

$$E_2 = -\frac{13.6 \text{ eV}}{(2)^2} = -3.40 \text{ eV}.$$

Further, the energy of the emitted 466-Å photon is

$$\begin{aligned}
 \frac{h c}{\lambda} &= \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{466 \times 10^{-10} \text{ m}} \\
 &= 42.7 \times 10^{-19} \text{ J} = 26.7 \text{ eV}.
 \end{aligned}$$

Hence, the total energy of the liberated electron is

$$-3.40 \text{ eV} + 26.7 \text{ eV} = 23.3 \text{ eV}.$$

(ii) The energy required to ionise hydrogen atom, that is, to remove the electron from the atom in the ground state ( $n = 1$ ) to infinity (where the energy is zero) is numerically equal to the energy of the electron in the  $n = 1$  state, that is,  $E_1$ , which is

$$E_1 = -\frac{13.6 \text{ eV}}{(1)^2} = -13.6 \text{ eV}.$$

The required energy of ionisation is then 13.6 eV. Hence, the energy of the original photon is the energy of ionisation plus the energy of the liberated electron, that is,

$$13.6 \text{ eV} + 23.3 \text{ eV} = 36.9 \text{ eV}.$$

**11. A beam of electrons bombards a sample of hydrogen. Through what minimum potential difference must the electrons have been accelerated if the first line of the Balmer series is to be emitted? Explain how many possible spectral lines can be expected if the atom finally attains the normal state. Given :  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ J s}$  and  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ .**

**Solution.** Normally the hydrogen atoms are in the ground state ( $n = 1$ ). The first Balmer line is emitted when the atom returns from  $n = 3$  to  $n = 2$  state. Hence in order to emit this line the atom must be first raised to the  $n = 3$  state by electron bombardment. Therefore, the energy of the bombarding electrons must be equal to the difference of energy between  $n = 1$  and  $n = 3$  states ( $E_1 - E_3$ ).

The energy of hydrogen atom in the  $n$ th state is

$$\begin{aligned}
 E_n &= -\frac{R_H h c}{n^2} \\
 \therefore E_1 - E_3 &= \frac{8}{9} R_H h c.
 \end{aligned}$$

Substituting the given values :

$$\begin{aligned}
 E_1 - E_3 &= \frac{8}{9} (1.097 \times 10^7 \text{ m}^{-1}) (6.63 \times 10^{-34} \text{ J s}) (3.0 \times 10^8 \text{ m s}^{-1}) \\
 &= 19.4 \times 10^{-19} \text{ J} \\
 &= \frac{19.4 \times 10^{-19} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} \\
 &= 12.1 \text{ eV.}
 \end{aligned}$$

[∴ 1 eV = 1.60 × 10<sup>-19</sup> J]

Hence the bombarding electrons must be accelerated by 12.1 volt.

If the atom finally attains the ground state, the possible number of spectral lines is 3 ( $3 \rightarrow 2, 3 \rightarrow 1, 2 \rightarrow 1$ ).

**12. Show that the ionisation potential of  $\text{He}^+$  is four times the value for hydrogen atom.**

**Solution.** The ionisation potential of an atom corresponds to the energy of the atom in the ground state. For one-electron atom, the ground-state energy is (ignoring effect of finite nuclear mass)

$$E_1 = - R_\infty Z^2 h c$$

$$E_1 \propto Z^2.$$

or

For  $\text{He}^+$  and H, we have  $Z = 2$  and 1 respectively.

$$\therefore \frac{E_{\text{He}^+}}{E_{\text{H}}} = 4.$$

Hence the ionisation potential of  $\text{He}^+$  is 4 times that of H.

**13. A positronium atom is a system consisting of a positron and an electron revolving about their common centre of mass, which lies half-way between them. Compare its ionisation energy and emission spectrum with those of the hydrogen atom (with infinitely heavy nucleus).**

(Meerut 98 sp. paper)

**Solution.** The positron has the same mass  $m$  as the electron and has equal but positive charge. The reduced mass of the electron-positron atom is therefore

$$\mu = \frac{(m)(m)}{m + m} = \frac{1}{2} m$$

while the reduced mass of electron in hydrogen is very nearly  $m$ .

The Rydberg constant  $\left( \frac{\mu e^4}{8 \epsilon_0^2 h^3 c} \right)$  for positronium,  $R_P$ , is therefore half that for hydrogen (with infinitely heavy nucleus). Thus

$$R_P = \frac{1}{2} R_\infty.$$

The energy states of the positronium atom would then be given by

$$(E_P)_n = - \frac{R_P Z^2 h c}{n^2} = - \frac{R_\infty Z^2 h c}{2 n^2}. \quad (i)$$

The corresponding expression for hydrogen atom (with infinitely heavy nucleus) is

$$(E_H)_n = - \frac{R_\infty Z^2 h c}{n^2}. \quad (ii)$$

Now,  $Z = 1$  for positronium atom as well as for hydrogen atom. Hence, we conclude from eq. (i) and (ii) that the **ionisation energy**, which is numerically equal to the energy of the lowest state ( $n = 1$ ), of positronium atom is half of that of hydrogen atom.

The wavelengths of the emitted spectral lines of positronium atom and hydrogen atom are given by

$$\frac{1}{\lambda_P} = R_P \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

and

$$\frac{1}{\lambda_H} = R_\infty \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

Thus

$$\frac{\lambda_P}{\lambda_H} = \frac{R_\infty}{R_P} = 2.$$

The wavelengths of positronium lines are double than those of hydrogen lines.

**14.** A  $\mu^-$  meson (charge  $-e$ , mass  $= 207 m$ , where  $m$  is mass of electron) can be captured by a proton to form a hydrogen-like "mesic" (or muonic) atom. Calculate the radius of the first Bohr orbit, the binding energy, and the wavelength of the first line in the Lyman series for such an atom.

The mass of the proton is 1836 times the mass of electron. The radius of first Bohr orbit and the binding energy of hydrogen are  $0.53 \text{ \AA}$  and  $13.6 \text{ eV}$  respectively.  $R_\infty = 109737 \text{ cm}^{-1}$ .

**Solution.** The reduced mass of the system is

$$\mu = \frac{(207 m)(1836 m)}{207 m + 1836 m} = 186 m.$$

From Bohr theory, the radius of the first orbit ( $n = 1$ ) of a hydrogen-like atom for  $Z = 1$ , is given by (taking finite mass of nucleus in consideration)

$$r_1 = \frac{h^2 \epsilon_0}{\pi \mu e^2} = \frac{h^2 \epsilon_0}{\pi (186 m) e^2} = \frac{1}{186} \left( \frac{h^2 \epsilon_0}{\pi m e^2} \right).$$

The quantity in the bracket is the first Bohr orbit of hydrogen atom which is  $0.53 \text{ \AA}$ . Therefore

$$r_1 = \frac{1}{186} \times 0.53 \text{ \AA} = 2.85 \times 10^{-3} \text{ \AA}.$$

The binding energy of an atom is equal to the energy of the lowest state ( $n = 1$ ). Now, from Bohr's theory, the ground-state energy of the hydrogen-like mesic atom with  $Z = 1$  is given by

$$E_1 = -\frac{\mu e^4}{8 \epsilon_0^2 h^2} = -186 \frac{m e^4}{8 \epsilon_0^2 h^2} = -186 \times 13.6 \text{ eV} = -2530 \text{ eV}.$$

Hence the binding energy is  $2530 \text{ eV}$ .

The wavelengths of the Lyman lines are given by

$$\frac{1}{\lambda} = R_M \left( \frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, 4, \dots$$

where  $R_M$  is the Rydberg constant for the mesic atom. For the first line,  $n = 2$ , so that

$$\lambda = \frac{4}{3 R_M}.$$

Now,

$$R_M = \frac{\mu e^4}{8 \epsilon_0^2 h^3 c} \quad \text{and} \quad R_\infty = \frac{m e^4}{8 \epsilon_0^2 h^3 c}.$$

$$\therefore R_M = \frac{\mu}{m} R_\infty = 186 R_\infty.$$

Hence

$$\lambda = \frac{4}{3 R_M} = \frac{4}{3 \times 186 R_\infty}.$$

Now,  $R_\infty = 109737 \text{ cm}^{-1}$  (given).

$$\therefore \lambda = \frac{4}{3 \times 186 \times 109737 \text{ cm}^{-1}} = 6.53 \times 10^{-8} \text{ cm} = 6.53 \text{ Å}.$$

Lyman series is in the X-ray region of the muonic atom spectrum.

**15. Calculate the radius of the first Bohr orbit in  $^{208}\text{Pb}$  ( $Z = 82$ ) for a  $\mu$ -mesic atom. The masses of  $\mu^-$  meson and proton are 207 times and 1836 times respectively the mass of electron. Given :  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $e = 1.60 \times 10^{-19} \text{ C}$ ,  $m = 9.1 \times 10^{-31} \text{ kg}$  and  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ . (Meerut sp. paper 98 S)**

**Solution.** The reduced mass of  $\mu$ -mesic atom (formed by a  $\mu^-$  meson and a proton) is

$$\mu = \frac{(207 m)(1836 m)}{207 m + 1836 m} = 186 m.$$

where  $m$  is mass of electron.

Now, from Bohr's theory, the radius of the first orbit ( $n = 1$ ) of a hydrogen-like mesic atom taking finite mass of nucleus in consideration is

$$r_1 = \frac{h^2 \epsilon_0}{\pi \mu Z e^2}.$$

Substituting the given values :

$$r_1 = \frac{(6.63 \times 10^{-34} \text{ J s})^2 (8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})}{3.14 (186 \times 9.1 \times 10^{-31} \text{ kg}) \times 82 \times (1.60 \times 10^{-19} \text{ C})^2}$$

$$= 3.49 \times 10^{-15} \text{ m}.$$

**16. A mixture of ordinary hydrogen and tritium (a hydrogen isotope whose nucleus is approximately three times more massive than ordinary hydrogen) is excited and its spectrum studied. Calculate the shift in wavelength for the  $\text{H}_\alpha$  lines of the two kinds of hydrogen. (Given :  $R_\infty = 109737 \text{ cm}^{-1}$ )**

**Solution.** The wavelengths of the  $\text{H}_\alpha$  lines ( $n = 3 \rightarrow n = 2$ ) of hydrogen ( ${}_1\text{H}^1$ ) and tritium ( ${}_1\text{H}^3$ ) are given by

$$\frac{1}{\lambda_H} = R_H \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_H \quad \dots(i)$$

and

$$\frac{1}{\lambda_T} = R_T \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_T, \quad \dots(ii)$$

where  $R_H$  and  $R_T$  are Rydberg constants for hydrogen and tritium respectively ( $Z = 1$  for both). Taking reciprocals and subtracting eq. (ii) from (i), we get

$$\begin{aligned} \lambda_H - \lambda_T &= \frac{36}{5} \left( \frac{1}{R_H} - \frac{1}{R_T} \right) \\ &= \frac{36}{5} \left\{ \frac{1 + \frac{m}{M_H}}{R_\infty} - \frac{1 + \frac{m}{M_T}}{R_\infty} \right\} = \frac{36 m}{5 R_\infty} \left( \frac{1}{M_H} - \frac{1}{M_T} \right). \end{aligned}$$

But  $M_T = 3 M_H$  (given).

$$\therefore \lambda_H - \lambda_T = \frac{36 m}{5 R_\infty} \left( \frac{1}{M_H} - \frac{1}{3 M_H} \right) = \frac{36 m}{5 R_\infty} \frac{2}{3 M_H} = \frac{24}{5} \frac{1}{R_\infty} \frac{m}{M_H}.$$

Now,  $R_\infty = 109737 \text{ cm}^{-1}$  and  $\frac{m}{M_H} = \frac{1}{1836}$  (we know).

$$\begin{aligned}\therefore \lambda_H - \lambda_T &= \frac{24}{5 \times (109737 \text{ cm}^{-1}) \times 1836} \\ &= 2.38 \times 10^{-8} \text{ cm} = 2.38 \text{ Å}.\end{aligned}$$

**17. Radiation from a helium ion  $\text{He}^+$  is nearly equal in wavelength to the  $H_\alpha$  line, first line of Balmer series. (a) Between what values of  $n$  does the transition in  $\text{He}^+$  occur? (b) Is the wavelength larger or smaller than that of  $H_\alpha$  line? (c) Calculate the wavelength difference. Given :  $R_H = 109677 \text{ cm}^{-1}$  and  $R_{\text{He}} = 109722 \text{ cm}^{-1}$ .**

**Solution.** (a) The wavelengths of the Balmer series of hydrogen (H), and those of the Pickering series of helium ion ( $\text{He}^+$ ) are given by

$$\frac{1}{\lambda_H} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right); \quad n = 3, 4, 5, 6, \dots \quad \dots(i)$$

and  $\frac{1}{\lambda_{\text{He}}} = 4 R_{\text{He}} \left( \frac{1}{4^2} - \frac{1}{n^2} \right); \quad n = 5, 6, 7, 8, \dots \quad \dots(ii)$

Eq. (ii) can be written as

$$\frac{1}{\lambda_{\text{He}}} = R_{\text{He}} \left( \frac{1}{2^2} - \frac{4}{n^2} \right); \quad n = 5, 6, 7, 8, \dots \quad \dots(iii)$$

A comparison of eq. (i) and (iii) shows that alternate lines of pickering series ( $n = 6, 8, 10, \dots$ ) nearly coincide with lines of Balmer series ( $n = 3, 4, 5, \dots$ ); nearly because  $R_{\text{He}} \approx R_H$  (not exactly). Thus, the transition in  $\text{He}^+$  corresponding to transition for  $H_\alpha$  line ( $n = 3 \rightarrow n = 2$ ) in H occurs for the following values :

$$n = 6, 4.$$

(b) Since  $R_{\text{He}} > R_H$ , we conclude that  $\lambda_{\text{He}} < \lambda_H$ .

(c) The wavelengths of the first line ( $n = 3$ ) of H and that of  $\text{He}^+$  ( $n = 6$ ) are given by

$$\frac{1}{\lambda_H} = R_H \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5 R_H}{36}.$$

and  $\frac{1}{\lambda_{\text{He}}} = R_{\text{He}} \left( \frac{1}{2^2} - \frac{4}{6^2} \right) = \frac{5 R_{\text{He}}}{36}.$

$$\begin{aligned}\therefore \lambda_H - \lambda_{\text{He}} &= \frac{36}{5} \left( \frac{1}{R_H} - \frac{1}{R_{\text{He}}} \right) \\ &= \frac{36}{5} \left( \frac{1}{109677 \text{ cm}^{-1}} - \frac{1}{109722 \text{ cm}^{-1}} \right) \\ &= \frac{36}{5} (9.1177 \times 10^{-6} \text{ cm} - 9.1139 \times 10^{-6} \text{ cm}) \\ &= \frac{36}{5} \times (3.8 \times 10^{-9} \text{ cm}) \\ &= 27.36 \times 10^{-9} \text{ cm} = 2.736 \times 10^{-8} \text{ cm} = 2.736 \text{ Å}.\end{aligned}$$

## QUESTIONS

1. State Bohr's postulates and deduce an expression for the allowed energies of the hydrogen atom. Show on an energy level diagram the observed transitions. What are the limitations of Bohr's theory?
2. Using Bohr's theory, calculate the radius of the first orbit of the electron moving around the proton.
3. Explain why lines of the Balmer series are not observed in absorption in terrestrial sources, but they have been observed in the absorption spectra of some stars.
4. Deduce the expression for the series spectra of a hydrogen-like atom, taking into account the finite mass of the nucleus.
5. Give postulates of Bohr's theory and derive an expression for the Rydberg constant. Explain why the value of this constant for helium is different than for hydrogen. How has this difference been used to determine the ratios  $m/M_H$  and  $e/m$ .
6. Apply Bohr's model to singly-ionised helium. What relationship exists between this spectrum and the hydrogen spectrum?
7. State and explain Wilson-Sommerfeld quantisation rules. Use them to deduce Planck's energy quantisation law, and Bohr's angular momentum quantisation law.
8. How de Broglie's concept of matter waves supports the quantisation of circular orbits of Bohr theory?
9. Explain Bohr's correspondence principle. Prove that for very large quantum numbers, the quantum theory frequency and the classical orbit frequency become equal.
10. Discuss analytically the Bohr-Sommerfeld theory of elliptical orbits of hydrogen atom and compare its results with those of Bohr's theory of circular orbits.
11. Discuss the characteristics of Sommerfeld's elliptical orbits. Show that the  $s$ -electron orbit is most elliptic in any family of orbits having the same major axis.
12. What is the meaning of degeneracy of elliptic orbits in Sommerfeld's theory of elliptic orbits? How is it removed by relativistic variation of electron mass? How far does it help in explaining the fine structure of  $H_\alpha$  line?

## PROBLEMS

(Use the following physical constants wherever required.)

$$h = 6.63 \times 10^{-34} \text{ Js}$$

$$c = 3.0 \times 10^8 \text{ m s}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$m_p = 1.67 \times 10^{-27} \text{ kg} \quad (\text{proton mass})$$

$$m/M_H = 1/1836$$

$$e = 1.60 \times 10^{-19} \text{ C}$$

$$R_\infty = 109737 \text{ cm}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

1. The angular momentum of the electron in a hydrogen-like atom is  $7.382 \times 10^{-34} \text{ J s}$ . Find the quantum number of the energy level occupied by the electron.

Ans. 7.

2. A hydrogen atom in the ground state absorbed a 20.0-eV photon. What is the speed of the liberated electron? The energy of electron in the ground state is  $-13.6\text{ eV}$ .  
**Ans.**  $1.5 \times 10^6 \text{ m s}^{-1}$ .
3. Find the wavelength of the photon emitted when a hydrogen atom goes from the  $n = 10$  state to its ground state.  
**Ans.**  $920 \text{ \AA}$ .
4. Calculate the wavelength of the transition from a level for which  $n = 7$  to a level for which  $n = 6$  for quadruply-ionised boron ( $\text{B}^{++++}$ ). The atomic number of boron is 5 and its Rydberg constant is  $1.0973 \times 10^5 \text{ cm}^{-1}$ .  
**Ans.**  $4946.4 \text{ \AA}$ .
5. The wavelength of the second member of Balmer series of hydrogen is  $4861 \text{ \AA}$ . Calculate the wavelength of the first member.  
**Ans.**  $6562.3 \text{ \AA}$ .
6. At what temperature will the average molecular kinetic energy in gaseous hydrogen be equal to the binding energy of hydrogen atom?  
**Ans.**  $1.05 \times 10^5 \text{ K}$ .
7. The wavelength of the second member of the Balmer series of hydrogen is  $4861 \text{ \AA}$ . Calculate the ionisation potential of hydrogen atom.  
**Ans.**  $13.6 \text{ volt}$ .
8. A  $12.1\text{-eV}$  photon is fully absorbed by a hydrogen atom in the ground state, and the atom is excited. What is the quantum number of the excited state? The ground state (negative) energy of hydrogen atom is  $13.6\text{ eV}$ .  
**Ans.** 3.
9. An electron is in  $n = 3$  level of hydrogen. Compute the energy required to ionise the atom.  
**Ans.**  $1.51 \text{ eV}$ .
10. Calculate the energy required to remove the electron from singly-ionised helium.  
**Ans.**  $54.4 \text{ eV}$ .
11. The spectroscopic values of Rydberg constant for hydrogen and ionised helium are  $109677.7 \text{ cm}^{-1}$  and  $109722.4 \text{ cm}^{-1}$  respectively. Calculate  $e/m$  of electron. The specific charge of hydrogen ion,  $e/M_H$ , is  $96490 \text{ C/g}$ .  
**Ans.**  $1.77 \times 10^{11} \text{ C/kg}$ .
12. In a transition to a state of excitation energy  $10.19 \text{ eV}$ , an hydrogen-like atom emits a  $4890\text{-\AA}$  photon. Find the binding energy of the initial state.  
*(Meerut special paper 2003)*  
**Ans.**  $-7.66 \text{ eV}$ .
13. A mixture of ordinary hydrogen and deuterium (whose nucleus is about two times more massive than ordinary hydrogen) is excited and its spectrum observed. How far apart in wavelength will the  $\text{H}_\alpha$  lines of two kinds of hydrogen be?  
**Ans.**  $1.78 \text{ \AA}$ .
14. Determine the mass ratio of deuterium and hydrogen atoms if their  $\text{H}_\alpha$  lines have wavelengths  $6561.01 \text{ \AA}$  and  $6562.80 \text{ \AA}$  respectively.  
**Ans.**  $2.00$

# Quantum Mechanics of Hydrogen Atom : Angular Momentum and Parity

---



---

## 1. Limitations of Classical Mechanics

Bohr model of the hydrogen atom accounts for the hydrogen line spectrum, but with a number of shortcomings. For example, it does not explain the fine structure of spectral lines and the intensity variation in them. Moreover, its use is limited to the (one-electron) hydrogen and hydrogen-like atoms; it cannot explain the spectra of complex atoms. Finally, but most important, it does not tell how electrons interact with atoms, and atoms with atoms, to give the observed properties of matter.

The cause of these shortcomings goes back to the limitations of the classical mechanics itself which is usually applied to explain the properties of systems. The classical mechanics is based on the assumption that in any system of particles it is possible to measure precisely the quantities like position, velocity, momentum, acceleration, etc., which characterise the state of the system at any instant. The equations of motion then enable us to determine these quantities, and hence the state of the system, at all later instants. The assumption is valid in our everyday experience. This is why classical mechanics provides correct explanation for the behaviour of macroscopic systems.

<sup>1</sup> The assumption is, however, in conflict with the uncertainty principle which becomes important in the atomic domain. According to this principle, the position and momentum of a particle cannot be accurately measured at the same time. The measurement of one quantity introduces an uncertainty into the other. Therefore, classical mechanics which assumes both to have definite values at all instants, is not valid for atomic systems. This is the reason that the Bohr model, which was just a classical atomic model in which quantisation was introduced arbitrarily, failed to give a complete explanation of the behaviour of atomic systems. In fact, the success of classical mechanics in case of macroscopic systems is due to the fact that such systems consist of so many individual atoms that departures from average behaviour are unnoticeable. But, truly speaking, classical mechanics must be replaced by a theory of greater generality. Quantum mechanics, developed by Schrödinger, is a correct replacement.

## 2. Schrödinger's Time-independent Wave Equation

In 1926, Schrödinger presented his famous wave equation as a development of de Broglie ideas of the wave properties of matter. The Schrödinger's equation is the fundamental equation of quantum mechanics in the same sense as the Newton's second law of motion of classical mechanics. It is the differential equation for the de Broglie waves associated with moving particles, and describes the motion of particles.

Schrodinger introduced a mathematical function  $\psi$  which is the variable quantity associated with the moving particle, and is a complex function of the space co-ordinates of the particle and the time, that is,

$$\bar{\Psi} = \bar{\Psi}(x, y, z, t).$$

$\bar{\Psi}$  is called the "wave function" as it characterizes the (de Broglie) waves associated with the moving particle. It is postulated that  $\bar{\Psi}$  has the form of a solution of the classical wave equation.

The differential equation representing a three-dimensional wave motion is

$$\frac{\partial^2 \bar{\Psi}}{\partial x^2} + \frac{\partial^2 \bar{\Psi}}{\partial y^2} + \frac{\partial^2 \bar{\Psi}}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \bar{\Psi}}{\partial t^2}, \quad \dots(i)$$

where  $v$  is the wave velocity.

Now, the wavelength associated with a particle of mass  $m$  moving with velocity  $v$  is given by

$$\lambda = \frac{h}{m v}.$$

Applying Einstein's postulate  $E = h v'$  connecting the frequency  $v'$  of the de Broglie waves with the total energy  $E$  of the particle, we have

$$\frac{1}{v^2} = \frac{1}{v'^2 \lambda^2} = \frac{1}{(E/h)^2 (h/m v)^2} = \frac{m^2 v^2}{E^2}.$$

Making this substitution in eq. (i), we get

$$\frac{\partial^2 \bar{\Psi}}{\partial x^2} + \frac{\partial^2 \bar{\Psi}}{\partial y^2} + \frac{\partial^2 \bar{\Psi}}{\partial z^2} = \frac{m^2 v^2}{E^2} \frac{\partial^2 \bar{\Psi}}{\partial t^2}.$$

or

$$\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \bar{\Psi} = \frac{m^2 v^2}{E^2} \frac{\partial^2 \bar{\Psi}}{\partial t^2}. \quad \dots(ii)$$

The solution of this equation is of the form

$$\bar{\Psi} = \psi e^{-2\pi i E t / \hbar}, \quad \dots(iii)$$

where  $\psi$  is a function of space coordinates only (independent of time), that is,

$$\psi = \psi(x, y, z).$$

Differentiating eq. (iii) with respect to time twice, we get

$$\begin{aligned} \frac{\partial^2 \bar{\Psi}}{\partial t^2} &= \psi e^{-2\pi i E t / \hbar} (-2\pi i E / \hbar)^2 \\ &= -\frac{4\pi^2 E^2}{\hbar^2} \psi e^{-2\pi i E t / \hbar}. \end{aligned}$$

Substituting for  $\bar{\Psi}$  and  $\frac{\partial^2 \bar{\Psi}}{\partial t^2}$  in eq. (ii), we get

$$\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = -\frac{4\pi^2 m^2 v^2}{\hbar^2} \psi. \quad \dots(iv)$$

For non-relativistic motion of the particle, the particle's kinetic energy  $K = \frac{1}{2} m v^2$ . Thus, if  $V$  is the potential energy of the particle, then we can write

$$\frac{1}{2} m v^2 = K = E - V$$

$$\text{or } m^2 v^2 = 2 m (E - V).$$

Making this substitution in eq. (iv), we get

$$\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = -\frac{8\pi^2 m}{\hbar^2} (E - V) \psi.$$

Let us use the symbol

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

$\nabla^2$  is called 'Laplacian operator' or 'del squared' in rectangular coordinates. The last eq. is now written as

$$\boxed{\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0.}$$

This is Schroedinger's time-independent (steady-state) wave equation for a particle. Its (time-independent) solutions  $\psi$  are called "eigenfunctions". They determine the space dependence of the wave function  $\bar{\psi}$ .

### 3. Physical Interpretation of Wave Function $\bar{\psi}$

A satisfactory interpretation of the wave function  $\bar{\psi}$  associated with a moving particle was given by Born in 1926. Born postulated that the square of the magnitude of the wave function,  $|\bar{\psi}|^2$  (or  $\bar{\psi}\bar{\psi}^*$ , if  $\bar{\psi}$  is complex), evaluated at a particular point at any instant is proportional to the probability of finding the particle at that point. A large value of  $|\bar{\psi}|^2$  means a large possibility of the particle's presence, while a small value of  $|\bar{\psi}|^2$  means the slight possibility of its presence.  $|\bar{\psi}|^2$  is called the 'probability density', and  $\bar{\psi}$  is the 'probability amplitude'†.

According to this interpretation, the probability of finding the particle within an element of volume  $d\tau$  is  $|\bar{\psi}|^2 d\tau$ . Since the particle is certainly somewhere, the integral of  $|\bar{\psi}|^2 d\tau$  over the whole space must be unity, that is

$$\int_{-\infty}^{+\infty} |\bar{\psi}|^2 d\tau = 1.$$

A wave function that obeys this equation is said to be 'normalised'. Every acceptable wave function must be normalisable.

### 4. Required Properties of Eigenfunctions

To be an acceptable solution, an eigenfunction  $\psi$  must fulfil the following requirements :

(i)  **$\psi$  must be finite everywhere.** If, for instance,  $\psi$  is infinite for a particular point, the same would be true for the wave function  $\bar{\psi}$ . It would mean an infinitely large probability of finding the particle at that point. This would violate the uncertainty principle. Therefore,  $\psi$  must have a finite, or zero, value at any point.

(ii)  **$\psi$  must be single-valued.** If  $\psi$  has more than one value at any point, it would mean more than one value of probability of finding the particle at that point which is obviously ridiculous.

† If  $\bar{\psi}$  is complex, with both real and imaginary parts, then the probability is given by the product of  $\bar{\psi}$  and its complex conjugate  $\bar{\psi}^*$ . The complex conjugate of any function is obtained by replacing  $i(\sqrt{-1})$  by  $-i$  everywhere it appears in the function. Thus, if

$$\bar{\psi} = A + iB$$

$$\bar{\psi}^* = A - iB,$$

so that  $\bar{\psi}\bar{\psi}^* = A^2 - i^2 B^2 = A^2 + B^2$ . Thus,  $\bar{\psi}\bar{\psi}^*$  is always a positive real quantity.

(iii)  $\psi$  must be continuous and have a continuous first derivative everywhere. This is necessary from the Schroedinger equation itself which shows that  $d^2\psi/dx^2$  must be finite everywhere. This can be so only if  $d\psi/dx$  has no discontinuity at any boundary where potential changes. Furthermore, the existence of  $d\psi/dx$  as a continuous function implies that  $\psi$  too is continuous across a boundary.

These requirements which must be fulfilled by an acceptable eigenfunction carry great significance. When the Schroedinger steady-state equation for a given system is solved to obtain an eigenfunction which fulfills these requirements, then we find that the equation can be solved only for certain values of energy of the system. Thus, **energy quantisation appears in quantum mechanics as a natural feature of the solution of the wave equation**. The values of energy for which Schroedinger equation can be solved are called "eigenvalues".

## 5. Quantum Mechanical Treatment of One-electron Atom

**Schroedinger Equation :** One-electron atom, like hydrogen atom, is the simplest bound system that occurs in nature. It consists of a positively-charged nucleus and a negatively charged electron ( $-e$ ), moving under their coulomb attraction and bound together by that attraction. The nuclear charge is  $+Ze$  ( $Z = 1$  for neutral hydrogen atom,  $Z = 2$  for singly-ionised helium atom, etc.). The three-dimensional character of the system allows it to have angular momentum.

In one-electron atom, the electron of mass  $m$  and the nucleus of mass  $M$  move about their fixed centre of mass. We may replace this actual atom by an equivalent model atom in which the nucleus is infinitely massive and the electron has *reduced mass*  $\mu$  given by

$$\mu = \left( \frac{M}{m + M} \right) m.$$

The reduced-mass electron moves about the infinitely massive (hence stationary) nucleus with the same electron-nucleus separation as in the actual atom.

We consider, therefore, an electron of reduced mass  $\mu$  moving under the three-dimensional coulomb potential

$$V = V(x, y, z) = - \frac{Ze^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}},$$

where  $x, y, z$  are the rectangular coordinates of the electron relative to the nucleus, which is fixed at the origin. The square root  $\sqrt{x^2 + y^2 + z^2}$  in the denominator is just the electron-nucleus separation  $r$ .

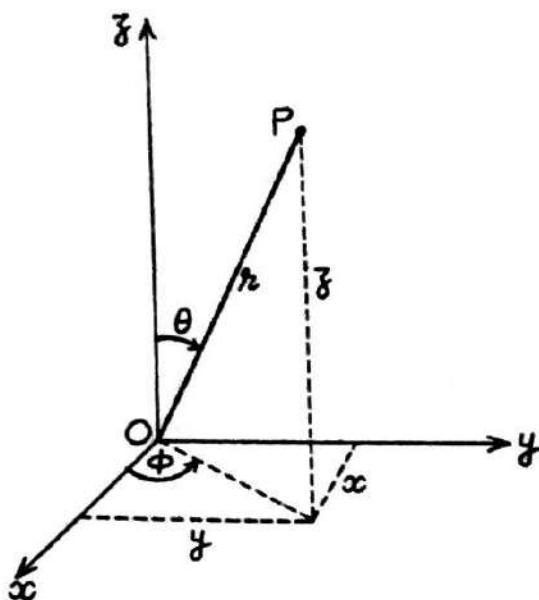
The Schroedinger equation for such a system is

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} (E - V) \psi = 0.$$

In cartesian coordinates, this is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2\mu}{h^2} (E - V) \psi = 0.$$

This equation can be solved by breaking it into three simpler equations, each involving only one variable coordinate. This is, however, not possible because the potential energy  $V$  is a function of all the three coordinates  $x, y, z$ . The difficulty is overcome by changing to spherical polar coordinates  $r, \theta, \phi$ .



(Fig. 1)

Fig. 1 illustrates the relations between the cartesian coordinates  $x, y, z$ , and the spherical coordinates  $r, \theta, \phi$  of a point  $P$ . These relation are

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta.$$

Thus, radius vector from origin  $O$  to point  $P$  is

$$r = \sqrt{x^2 + y^2 + z^2},$$

zenith (polar) angle is

$$\theta = \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}},$$

and azimuth angle is

$$\phi = \tan^{-1} \frac{y}{x}.$$

The Schroedinger's equation in spherical polar coordinates is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8 \pi^2 \mu}{h^2} (E - V) \psi = 0. \quad \dots(i)$$

The potential energy can now be expressed as a function of a single coordinate  $r (= \sqrt{x^2 + y^2 + z^2})$ , that is

$$V = V(r) = - \frac{Z e^2}{4 \pi \epsilon_0 r}. \quad \dots(ii)$$

Because of this simplification, it is possible to carry out the separation of variables in the Schroedinger equation.

**Separation of Variables :** We first separate the radial and the angular variables. For this, we substitute

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi);$$

where  $R(r)$  is the radial function depending upon  $r$  alone, and  $Y(\theta, \phi)$  is angular function depending upon  $\theta$  and  $\phi$ . Thus, eq. (i) can be written as

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) Y + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) R + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} R + \frac{8\pi^2 \mu}{h^2} [E - V(r)] R Y = 0.$$

Multiplying the entire equation by  $\frac{r^2}{R Y}$  and rearranging, we get

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} [E - V(r)] = - \frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right].$$

The left side of this equation depends on the variable  $r$ , while the right side depends upon the other variables  $\theta$  and  $\phi$ . Hence *this equation can be correct only if both sides of it are equal to the same constant*. Let this constant be  $l(l+1)$ . Thus, we get a radial equation

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} [E - V(r)] = l(l+1) \quad \dots(\text{iii})$$

and an angular equation

$$-\frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = l(l+1).$$

The last equation can be further separated by substituting

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi).$$

This gives

$$-\frac{1}{\Theta \Phi} \left[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \Phi + \frac{1}{\sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} \Theta \right] = l(l+1).$$

Multiplying the entire equation by  $\sin^2 \theta$  and rearranging, we get

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}.$$

Again, the two sides of this equation are functions of different variables; hence they must be equal to the same constant. Let this constant be  $m_l^2$ . Then, we get

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m_l^2 \quad \dots(\text{iv})$$

and

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2. \quad \dots(\text{v})$$

Equations (v), (iv) and (iii) are usually written as

$$\frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0, \quad \dots(\text{vi})$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad \dots(\text{vii})$$

and

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{8\pi^2 \mu}{h^2} \{ E - V(r) \} - \frac{l(l+1)}{r^2} \right] R = 0. \quad \dots(\text{viii})$$

Thus, we have broken the Schrödinger equation of hydrogen atom into three ordinary differential equations, each having a single variable  $\phi, \theta, r$  respectively. When we try to

find out 'acceptable' solutions of these equations, certain integral numbers, identified as quantum numbers, automatically come in.

### Solutions of the Equations : Entrance of Quantum Numbers :

I. The solution of  $\Phi(\phi)$  eq. (vi) is

$$\Phi_{m_l}(\phi) = A e^{im_l \phi}, \quad \dots \text{(ix)}$$

where  $A$  is the constant of integration. In order that it is an acceptable solution, the wave function  $\Phi_{m_l}$  must be a *single-valued* function of position, that is, it must have a single value at a given point in space. It is evident that the azimuth angles  $\phi$  and  $\phi + 2\pi$  are actually the same angle. Hence it must be true that

$$\Phi_{m_l}(\phi) = \Phi_{m_l}(\phi + 2\pi)$$

$$A e^{im_l \phi} = A e^{im_l(\phi + 2\pi)}$$

$$1 = e^{im_l 2\pi}$$

$$1 = \cos(m_l 2\pi) + i \sin(m_l 2\pi).$$

This can only happen when  $m_l$  is 0 or a positive or negative integer, that is

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots$$

The constant  $m_l$  is a quantum number of the atom.

II. The solution of  $\Theta(\theta)$  equation (vii) is known to be

$$\Theta_{l, m_l}(\theta) = N_{l, m_l} P_l^{|m_l|}(\cos \theta), \quad \dots \text{(x)}$$

where  $N_{l, m_l}$  is a constant and  $P_l^{|m_l|}$  is 'associated Legendre polynomial' which has different forms for different values of  $l$  and  $|m_l|$ . This solution is acceptable (remains finite) only if the constant  $l$  is an integer equal to or greater than  $|m_l|$ , that is

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots$$

This requirement can be expressed as a condition on  $m_l$  in the following form :

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l.$$

The constant  $l$  is another quantum number.

III. For solving equation (viii) we must specify  $V(r)$ . In the present case

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

Then, the solution of the equation is known to be

$$R_{n, l}(r) = N_{n, l} e^{-Zr/n a_0} \left( \frac{2Zr}{n a_0} \right)^l L_{n+1}^{2l+1} \left( \frac{2Zr}{n a_0} \right), \quad \dots \text{(xi)}$$

where  $N_{n, l}$  is a constant, and  $L_{n+1}^{2l+1}$  is 'associated Laguerre polynomial' which has different forms for different values of  $n$  and  $l$ . The parameter  $a_0$  is

$$a_0 = \frac{\hbar^2 \epsilon_0}{\pi \mu e^2},$$

which, in the old quantum theory, is the smallest Bohr orbit of hydrogen atom.

The above solution is acceptable (remains finite) only if the constant  $E$  in eq. (viii) is positive, or has one of the negative values  $E_n$  (which correspond to bound states), given by

$$E_n = -\frac{\mu Z^2 e^4}{8\epsilon_0^2 \hbar^2} \left( \frac{1}{n^2} \right),$$

where  $n$  is an integer; which must be equal to or greater than  $l+1$ . That is,

$$n = l + 1, l + 2, l + 3, \dots$$

This requirement may be expressed as a condition on  $l$  in the form

$$l = 0, 1, 2, \dots, (n - 1).$$

The constant  $n$  is also a quantum number.

The total eigenfunctions of the one-electron atom may now be written as

$$\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) \Theta_{l,m_l}(\theta) \Phi_{m_l}(\phi),$$

where  $R, \Theta, \Phi$  are given by eq. (xi), (x) and (ix) respectively. The constants  $N_{n,l}, N_{l,m_l}$  and  $A$  involved in  $R, \Theta$  and  $\Phi$  are adjusted so that each is normalised. The real form of the normalised eigenfunction for the ground state ( $n = 1, l = 0, m_l = 0$ ) of one-electron atom is

$$\Psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}.$$

**Interpretation of Quantum Numbers :** The three quantum numbers which arise in a natural way during search of acceptable solutions of the Schroedinger equation may be tabulated as follows :

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, (n - 1).$$

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l.$$

We can interpret these quantum numbers in the following way :

To interpret  $n$ , we note that according to the Schroedinger theory of one-electron atom, the total energy of the bound states of the atom can have *only* following values :

$$E_n = -\frac{\mu Z^2 e^4}{8 \epsilon_0^2 h^2} \left( \frac{1}{n^2} \right).$$

These eigenvalues which depend only on the quantum number  $n$ , are the same as obtained by old quantum theory (Bohr model). They are in excellent agreement with experiment. Thus,  $n$  quantises the total energy of the atom. Hence  $n$  is called the 'total' or 'principal' quantum number.

To interpret  $l$ , we consider the radial wave equation (viii) :

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{8\pi^2\mu}{h^2} \left\{ E - V(r) \right\} - \frac{l(l+1)}{r^2} \right] R = 0.$$

The total energy  $E$  of the atom consists of the kinetic energy  $K$  and the potential energy (electrostatic)  $V$  of its electron. The kinetic energy  $K$  has two parts,  $K_{radial}$  due to electron's motion toward or away from the nucleus and  $K_{orbital}$  due to the motion around the nucleus. Thus

$$E = K_{radial} + K_{orbital} + V(r).$$

Making this substitution in the radial eq., we obtain

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{8\pi^2\mu}{h^2} \left\{ K_{radial} + K_{orbital} - \frac{h^2}{8\pi^2\mu} \frac{l(l+1)}{r^2} \right\} \right] R = 0.$$

The *radial* equation is concerned only with the radial motion of the electron, hence it must be free from  $K_{orbital}$ . This is possible only when the last two terms cancel out each other, that is, when

$$K_{\text{orbital}} = \frac{h^2}{8\pi^2\mu} \frac{l(l+1)}{r^2}$$

If  $\vec{L}$  be the angular momentum of the electron, then

$$L = \mu v r$$

so that

$$K_{\text{orbital}} = \frac{1}{2}\mu v^2 = \frac{L^2}{2\mu r^2}$$

$$\therefore \frac{L^2}{2\mu r^2} = \frac{h^2}{8\pi^2\mu} \frac{l(l+1)}{r^2}$$

or

$$L^2 = l(l+1) \frac{h^2}{4\pi^2}$$

or

$$L = \sqrt{l(l+1)} \frac{h}{2\pi}$$

Since the quantum number  $l$  is restricted to the values

$$l = 0, 1, 2, \dots, (n-1)$$

the electron can have only discrete values of the angular momentum. Thus, like total energy  $E$ , the orbital angular momentum is also quantised (and conserved) and this quantisation is described by  $l$ . Hence  $l$  is called the 'orbital' quantum number.

The expression for the angular momentum is identical to that obtained in Bohr-Sommerfeld theory, provided  $k$  is replaced by  $\sqrt{l(l+1)}$ .

The various angular momentum states of the electron are denoted by letters  $s, p, d, f, \dots$  corresponding to  $l = 0, 1, 2, 3, \dots$ . The atomic states are denoted by writing the corresponding total quantum number alongwith these letters. Thus, a state for which  $n = 2$  and  $l = 0$  is a  $2s$  state, and one for which  $n = 3$  and  $l = 1$  is a  $3p$  state, and so on.

The interpretation of  $m_l$  comes when the atom is placed in an external magnetic field. We know that an electron revolving about a nucleus is a minute current-loop and behaves like a magnetic dipole in an external magnetic field. Its magnetic potential energy depends upon its magnetic moment and its orientation with respect to the field. But the magnitude and direction of the magnetic moment depends upon the magnitude and direction of the angular momentum  $\vec{L}$  of the electron which, therefore, determines the magnetic potential energy. As we shall see, the direction of  $\vec{L}$  is quantised with respect to an external magnetic field. If the field is along the  $z$ -axis, the component of  $\vec{L}$  in the  $z$ -direction is

$$L_z = m_l \frac{h}{2\pi},$$

where  $m_l$  is restricted to the values  $0, \pm 1, \pm 2, \dots, \pm l$ . Thus,  $m_l$  describes the quantisation of the orientation of  $\vec{L}$  in a magnetic field (known as space quantisation), and hence the quantisation of the magnetic energy of the electron. Hence  $m_l$  is called the magnetic quantum number.

Thus, each of the eigenfunctions of one-electron atom is specified by three quantum numbers  $n, l$  and  $m_l$ ; in which  $n$  determines the total energy (eigenvalue),  $l$  determines the angular momentum and  $m_l$  determines the  $z$ -component of the angular momentum of the electron. But for a given  $n$ , there are several different possible values of  $l$ , and for each  $l$  there are several possible values of  $m_l$ . Hence several different eigenfunctions

correspond to exactly the same eigenvalue  $E_n$ . Such eigenfunctions are said to be "degenerate".

## 6. Electron Probability Density

The quantum-mechanical description of the energy states of one-electron atom is similar in many respects to that from the old quantum theory. Yet there are striking differences regarding the motion of the electron within the atom. Quantum mechanically, the electron cannot be considered as moving around the nucleus in definite orbits. We can consider only the relative probability of finding the electron in volume elements at various locations.

The electron wave function in a one-electron atom is given by

$$\Psi_{n, l, m_l}(r, \theta, \phi) = R_{n, l}(r) \Theta_{l, m_l}(\theta) \Phi_{m_l}(\phi),$$

where  $R, \Theta, \Phi$  describe how  $\psi$  varies with  $r, \theta$  and  $\phi$  respectively. The three-dimensional electron probability density  $|\psi|^2$  may therefore be written as

$$|\psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2,$$

where  $|\psi|^2 = \psi\psi^*$ , etc.

The azimuthal probability density  $|\Phi|^2$ , however, does not play any part in determining the probability density  $|\psi|^2$ , because

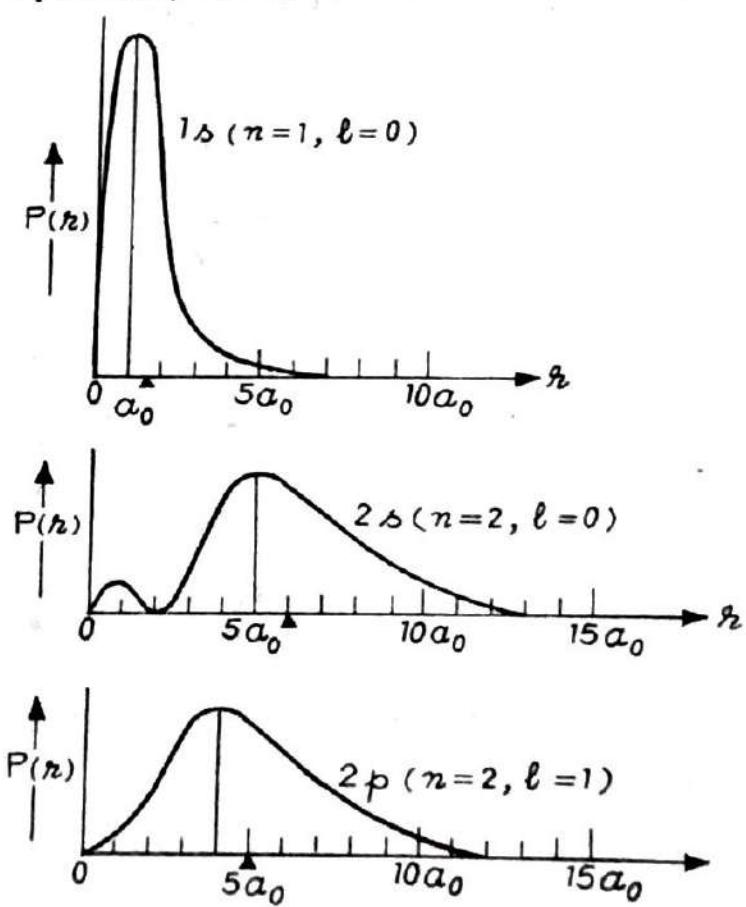
$$\begin{aligned} |\Phi|^2 &= \Phi \Phi^* \\ &= (A e^{im_l \phi})(A e^{-im_l \phi}) \\ &= A^2, \end{aligned}$$

which is a constant. This means that the probability density  $|\psi|^2$  does not depend on  $\phi$ . It is symmetrical about the  $z$ -axis, regardless of the quantum state of the electron. Thus,  $|\psi|^2$  is completely specified by  $|R|^2 |\Theta|^2$ .

Let us first consider the dependence of  $|\psi|^2$  on  $|R|^2$ . We define the radial probability density  $P(r)$ , such that  $P(r) dr$  is the probability of finding the electron at a distance between  $r$  and  $r + dr$  from the nucleus. It is given by

$$P(r) dr = |R|^2 (4\pi r^2 dr),$$

where  $4\pi r^2 dr$  is the volume enclosed between spheres of radii  $r$  and  $r + dr$ . The graphs of  $P(r)$  against  $r$  for certain values of  $n$  and  $l$  (states  $1s, 2s, 2p$ ) for the hydrogen atom ( $Z = 1$ ) are shown in Fig. 2. We see that for the states  $1s$  and  $2p$  the maxima of the curves fall exactly at  $a_0$  and  $4a_0$ , which are the radii of Bohr orbits



(Fig. 2)

corresponding to  $n = 1$  and  $n = 2$  respectively. For the state  $2s$ , however, the main maximum is a little deviated from  $4a_0$ , and a weaker maximum also exists. Thus, whereas **the electron is most likely to be found at the locations of Bohr orbits**, it has a finite probability of being found elsewhere also.

The average distance of the electron from the nucleus is given by

$$\bar{r} = \int_0^{\infty} r P(r) dr.$$

On evaluating the integral, we get

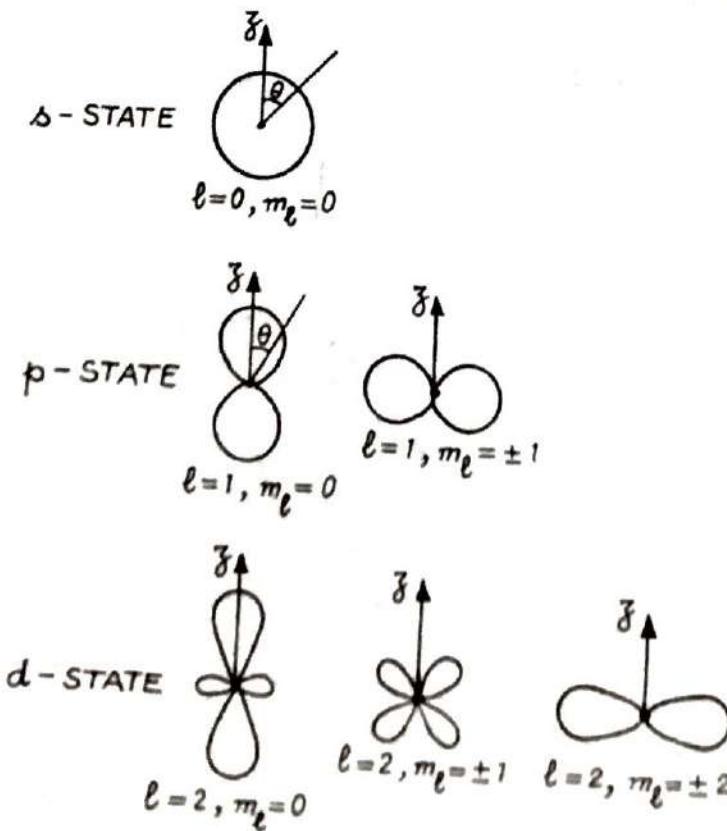
$$\bar{r} = \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left\{ 1 - \frac{l(l+1)}{n^2} \right\} \right],$$

where  $a_0$  is the smallest Bohr orbit. This is same as for the Bohr-Sommerfeld elliptic orbit, if  $k^2$  is replaced by  $l(l+1)$ .

The value of  $\bar{r}$  is evaluated to be  $1.5a_0$ ,  $6a_0$  and  $5a_0$  for  $1s$ ,  $2s$  and  $2p$  electrons respectively in hydrogen atom ( $Z = 1$ ). These values are somewhat larger than the corresponding values of  $r$  for maximum radial probability density. This is because of the asymmetrical nature of the probability density curve about its maximum (Fig. 2).

We also see that, except for  $n = 1$ , the probability of finding the electron near the nucleus is smaller than that at far away. This is in agreement with Sommerfeld elliptic orbits in which the electron moves faster when passing near the nucleus than when far away.

Finally, we consider the (directional) dependence of  $|\psi|^2$  on  $|\Theta|^2$ . In Fig. 3 is shown the form of  $|\Theta|^2$  in terms of polar diagrams in which the origin is at  $r = 0$  (the nucleus) and the  $z$ -axis is taken along the direction from which the angle  $\theta$  is measured.

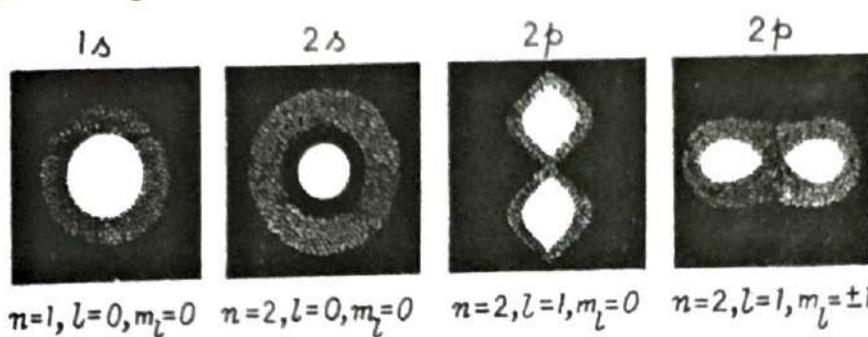


(Fig. 3)

The angular probability density  $|\Theta|^2$  is constant ( $= \frac{1}{2}$ , in fact) for an  $s$ -state ( $l = 0$ ). This means that, since  $|\Phi|^2$  is also a constant, the electron probability density  $|\psi|^2$  has the same value at a given  $r$  in all directions. In other words, *for s-states, the probability density  $|\psi|^2$  is spherically symmetrical about the nucleus* (independent of  $\theta$  and  $\phi$ ).

For other states, however,  $|\Theta|^2$  varies with  $\theta$  and takes on largest values in definite directions. In a given state (other than  $s$ -state), the concentration of probability density shifts from the  $z$ -axis to the plane perpendicular to the  $z$ -axis as the absolute value of  $m_l$  increases from 0 to  $l$ .

The three-dimensional character of  $|\psi|^2$  for a few states of one-electron atom has been shown in Fig. 4. Each figure, which is in fact an electron-cloud, is symmetrical about



(Fig. 4)

the  $z$ -axis which is vertical to the plane of paper. All  $s$ -states ( $l = 0$ ) are spherically-symmetric, with the maximum value of probability density function  $|\psi|^2$  at the origin and decreasing uniformly in all radial directions. The  $p$ -states ( $l = 1$ ), and also other higher states, show  $\theta$ -dependence.

The functions  $|\psi|^2$  displayed in these figures, in general, have spherical and conical nodal surfaces, defined by certain values of  $r$  and  $\theta$ , where they vanish, that is, the electron is never found there. For example, in the  $2s$ -state there is a spherical nodal shell between an inner sphere and an outer spherical shell. The nodal surfaces are a consequence of the fact that the wave functions for a bound particle must be standing waves with fixed nodes.

**Conclusion :** There are many points at which the quantum mechanical theory of the one-electron atom corresponds quite closely to the old quantum Bohr-Sommerfeld theory. For example, both theories result in the quantisation of the total energy of the atom, giving same energy values. Similarly, both agree on the quantisation of the angular momentum. But whereas in the old theory the quantum numbers are introduced as postulates, in quantum mechanics they appear automatically while finding the acceptable solutions of the wave equation.

As far as the actual motion of the electron within the atom is concerned, the two theories differ appreciably. In the old quantum theory, the electron traces fixed elliptic orbits whose size, shape and orientation are determined by quantisation rules. In quantum mechanics, on the other hand, the electron cannot be allotted definite orbits; it has only relative probabilities of being found at various locations. The probability is of course maximum at the locations of the Bohr-Sommerfeld orbits, but *not zero elsewhere*. Hence in quantum mechanics the electron is smeared out over the whole of space like an electron

cloud. This is clearly a consequence of the wave nature of the electron. As we shall see, the quantum mechanical theory has been very successful in explaining the spectra of multi-electron atoms and the relative intensity of spectral lines.

**A paradox regarding s-orbits :** According to Bohr-Sommerfeld theory, the angular momentum for an electron in the s-orbit is

$$L = k \frac{h}{2\pi} = \frac{h}{2\pi}, \quad (k=1)$$

whereas according to quantum mechanics it is

$$L = \sqrt{l(l+1)} \frac{h}{2\pi} = 0. \quad (l=0)$$

From measurements of atomic spectra, the quantum mechanical prediction of zero orbital angular momentum for the s-state comes out to be the correct one. The zero angular momentum means that the electron's motion is entirely radial. Therefore, in terms of Bohr theory, the s-orbit would be a radial oscillation (pendulum orbit) in which the electron would pass directly through the nucleus (which is actually impossible), and the oscillation could take place along any direction in space. This would correspond to a spherically symmetrical probability density (or charge distribution) about the nucleus. This is in agreement with quantum mechanics which predicts that all s-states are spherically symmetrical. Thus, the difficulty of the s-orbit passing through the nucleus was removed quantum mechanically.

## 7. Expectation Value

The expectation value of a dynamical quantity described by a wave function  $\bar{\Psi}$ , is the average value of the quantity weighted by the probability of observing that value.

As an example, let us consider a moving particle confined to the x-axis; and described by the wave function  $\bar{\Psi}(x, t)$ . According to Born's interpretation, the probability of finding the particle between  $x$  and  $x + dx$  at an instant  $t$  is given by

$$P(x, t) dx = |\bar{\Psi}(x, t)|^2 dx. \quad \dots(i)$$

Let us imagine that we measure experimentally the positions  $x$  of a large number of particles described by the same wave function  $\bar{\Psi}(x, t)$ , at same instant  $t$ . Then, the average of the observed values of  $x$  will be the expectation value of the position of the particle, indicated by  $\langle x \rangle$ . That is,

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x P(x, t) dx}{\int_{-\infty}^{\infty} P(x, t) dx}.$$

The denominator is the probability that the particle exists somewhere between  $x = -\infty$  and  $x = \infty$ , and is therefore equal to 1. Hence

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\bar{\Psi}(x, t)|^2 dx.$$

Using Born's interpretation given by eq. (i), we obtain

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\bar{\Psi}(x, t)|^2 dx.$$

This equation is customarily written in the equivalent form :

$$\langle x \rangle = \int_{-\infty}^{\infty} \bar{\Psi}^*(x, t) x \bar{\Psi}(x, t) dx.$$

The expectation value of any function of  $x$  designated by  $f(x)$ , can be expressed in a similar way :

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \bar{\Psi}^*(x, t) f(x) \bar{\Psi}(x, t) dx.$$

Even for a function which explicitly depends on time, such as potential energy  $V(x, t)$ , we can write

$$\langle V(x, t) \rangle = \int_{-\infty}^{+\infty} \bar{\Psi}^*(x, t) V(x, t) \bar{\Psi}(x, t) dx.$$

## 8. Orbital Angular Momentum

The quantum mechanical description of hydrogen atom has yielded the result that the angular momentum  $\vec{L}$  of an electron in its "orbital" motion about the centre of an atom is quantised both in magnitude and direction, with relations

$$L^2 = l(l+1) \frac{h^2}{4\pi^2}$$

and

$$L_z = m_l \frac{h}{2\pi},$$

where  $L^2$  is the square of the magnitude of the orbital angular momentum and  $L_z$  is the component of the angular momentum along the  $z$ -axis.  $l$  and  $m_l$  are quantum numbers which restrict  $L^2$  and  $L_z$  to certain specific values.

To prove the above relations for a one-electron atom we must show that the wave functions of the atom are eigenfunctions of the angular-momentum operators  $\hat{L}^2$  and  $\hat{L}_z$ , with eigenvalues  $l(l+1) \frac{h^2}{4\pi^2}$  and  $m_l \frac{h}{2\pi}$  respectively.

The angular momentum  $\vec{L}$  of a particle bound to and moving around a coordinate origin is defined by the equation

$$\vec{L} = \vec{r} \times \vec{p},$$

where  $\vec{r}$  is the position vector of the particle relative to the origin and  $\vec{p}$  is its linear momentum vector. The rectangular components of  $\vec{L}$  are, from the definition of the cross product,

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

and

$$L_z = x p_y - y p_x,$$

where  $x, y, z$  are the components of  $\vec{r}$ , and  $p_x, p_y, p_z$  are the components of  $\vec{p}$ .

Replacing  $p_x, p_y, p_z$  by their equivalent differential operators  $-\frac{i\hbar}{2\pi} \frac{\partial}{\partial x}, -\frac{i\hbar}{2\pi} \frac{\partial}{\partial y}, -\frac{i\hbar}{2\pi} \frac{\partial}{\partial z}$  respectively, we get the quantum mechanical operators for the rectangular components of angular momentum, which are

$$\hat{L}_x = -\frac{i\hbar}{2\pi} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -\frac{i\hbar}{2\pi} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

and

$$\hat{L}_z = -\frac{i\hbar}{2\pi} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right).$$

In spherical polar coordinates these operators become\*

$$\hat{L}_x = \frac{i\hbar}{2\pi} \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \quad \dots(i)$$

$$\hat{L}_y = \frac{i\hbar}{2\pi} \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \quad \dots(ii)$$

and

$$\hat{L}_z = -\frac{i\hbar}{2\pi} \frac{\partial}{\partial \phi}. \quad \dots(iii)$$

The square of the magnitude of the angular momentum vector  $\vec{L}$  is

$$L^2 = L_x^2 + L_y^2 + L_z^2.$$

The corresponding operator is

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2.$$

By substituting the squares of  $\hat{L}_x$ ,  $\hat{L}_y$ ,  $\hat{L}_z$  from eq. (i), (ii), (iii), we obtain

$$\begin{aligned} \hat{L}^2 &= -\frac{\hbar^2}{4\pi^2} \left[ \left\{ \sin^2 \phi \frac{\partial^2}{\partial \theta^2} + \cot^2 \theta \cos^2 \phi \frac{\partial^2}{\partial \phi^2} \right. \right. \\ &\quad + \sin \phi \frac{\partial}{\partial \theta} \left( \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \left( \sin \phi \frac{\partial}{\partial \theta} \right) \\ &\quad \left. \left. + \left\{ \cos^2 \phi \frac{\partial^2}{\partial \theta^2} + \cot^2 \theta \sin^2 \phi \frac{\partial^2}{\partial \phi^2} \right. \right. \right. \\ &\quad \left. \left. - \cos \phi \frac{\partial}{\partial \theta} \left( \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \left( -\cos \phi \frac{\partial}{\partial \theta} \right) \right\} + \left\{ \frac{\partial^2}{\partial \phi^2} \right\} \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ \frac{\partial^2}{\partial \theta^2} + (\cot^2 \theta + 1) \frac{\partial^2}{\partial \phi^2} + \sin \phi (-\operatorname{cosec}^2 \theta) \cos \phi \frac{\partial}{\partial \phi} \right. \\ &\quad \left. + \cot \theta \cos^2 \phi \frac{\partial}{\partial \theta} - \cos \phi (-\operatorname{cosec}^2 \theta) \sin \phi \frac{\partial}{\partial \phi} + \cot \theta \sin^2 \phi \frac{\partial}{\partial \theta} \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \cot \theta \frac{\partial}{\partial \theta} \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \end{aligned}$$

\*For this transformation, we use the relations

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

and

$$z = r \cos \theta$$

which connect the rectangular and spherical polar coordinates.

or  $\hat{L}^2 = -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \quad \dots(iv)$

This is the expression for the operator of the square of the angular momentum.

Let us now first apply the operator  $\hat{L}_z$  (eq. iii) to the one-electron atom wave function

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi).$$

This gives

$$\hat{L}_z \psi = -\frac{i\hbar}{2\pi} \frac{\partial\psi}{\partial\phi}$$

or  $\hat{L}_z \psi = -\frac{i\hbar}{2\pi} R \Theta \frac{d\Phi}{d\phi}.$

The function  $\Phi(\phi)$  for the atom is given by

$$\Phi = A e^{im_l \phi}.$$

Differentiating it,  $\frac{d\Phi}{d\phi} = A i m_l e^{im_l \phi} = i m_l \Phi.$

Substituting it in the above expression for  $\hat{L}_z \psi$ , we get

$$\hat{L}_z \psi = -\frac{i\hbar}{2\pi} i m_l R \Theta \Phi$$

or

$$\boxed{\hat{L}_z \psi = m_l \frac{\hbar}{2\pi} \psi.} \quad [\because \psi = R \Theta \Phi]$$

This result means that the wave functions  $\psi$  of the one-electron atom are the eigenfunctions of  $\hat{L}_z$  having eigenvalues given by

$$L_z = m_l \frac{\hbar}{2\pi}.$$

This is the expression for the quantised values of the  $z$ -component of the angular momentum of the atom. ( $L_x$  and  $L_y$ , however, do not obey quantisation relations).

We next apply the operator  $\hat{L}^2$  (eq. iv) to the wave function  $\psi = R \Theta \Phi$ . We have

$$\begin{aligned} \hat{L}^2 \psi &= -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] R \Theta \Phi \\ &= -\frac{\hbar^2}{4\pi^2} R \left[ \frac{\Phi}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \frac{\Theta}{\sin^2\theta} \frac{d^2\Phi}{d\phi^2} \right]. \end{aligned}$$

Differentiating the  $\Phi$ -equation :

$$\Phi = A e^{im_l \phi}$$

twice, we get

$$\frac{d^2\Phi}{d\phi^2} = A(i m_l)^2 e^{im_l \phi} = -m_l^2 \Phi.$$

This gives

$$\hat{L}^2 \psi = -\frac{\hbar^2}{4\pi^2} R \Phi \left[ \frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) - \frac{m_l^2}{\sin^2\theta} \Theta \right].$$

The function  $\Theta(\theta)$  is a solution of the equation

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m_l^2}{\sin^2\theta} \right] \Theta = 0$$

This means that the quantity in brackets in the above expression for  $\hat{L}^2 \psi$  is equal to  $-l(l+1)\Theta$ . Hence we get

$$\hat{L}^2 \psi = -\frac{\hbar^2}{4\pi^2} R \Phi \left[ -l(l+1)\Theta \right]$$

or

$$\hat{L}^2 \psi = l(l+1) \frac{\hbar^2}{4\pi^2} R \Theta \Phi$$

or

$$\boxed{\hat{L}^2 \psi = l(l+1) \frac{\hbar^2}{4\pi^2} \psi.}$$

Again, this result means that the wave functions  $\psi$  of one-electron atoms are the eigenfunctions of  $\hat{L}^2$  having eigenvalues given by

$$\hat{L}^2 = l(l+1) \frac{\hbar^2}{4\pi^2}.$$

This is the expression for the quantised values of the square of the angular momentum of the one-electron atom.

## 9. Parity of Eigenfunctions : Determination of Selection Rule

The parity of eigenfunction is the property which describes the behaviour of the eigenfunction when it is inverted about the origin of coordinates. In rectangular coordinates, the inversion about the origin means changing the signs of all the coordinates.

The eigenfunctions which satisfy the relation

$$\psi(-x, -y, -z) = +\psi(x, y, z)$$

are said to be of 'even parity', while those which satisfy the relation

$$\psi(-x, -y, -z) = -\psi(x, y, z)$$

are said to be of 'odd parity'

The parity of an eigenfunction can also be described in terms of its eigenvalue. Let us consider an operator which inverts the eigenfunction about the origin. It is called the 'parity operator'  $\hat{P}$ . If  $\epsilon$  be the eigenvalue of the parity operator, then we can write

$$\hat{P} \psi = \epsilon \psi.$$

Operating once again :

$$\hat{P}^2 \psi = \epsilon^2 \psi.$$

By definition, two operations by  $\hat{P}$  restore the function back into its original form, that is

$$\hat{P}^2 \psi = \psi.$$

Comparing the last two expression, we get

$$\epsilon^2 = 1$$

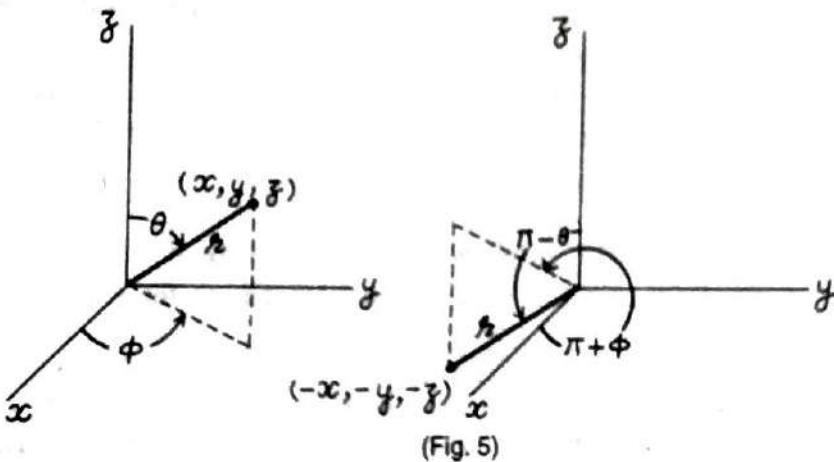
$$\epsilon = \pm 1.$$

The eigenvalues of the parity operator are  $\pm 1$ . An eigenfunction having an eigenvalue  $+1$  is of 'even' parity, while that having an eigenvalue  $-1$  is of 'odd' parity.

A system having an eigenfunction of even parity is said to be in a state of even parity ; while that having an eigenfunction of odd parity is said to be in a state of odd parity.

We can characterise the different states of a system by their parity. Let us consider the eigenfunctions for a one-electron atom. These eigenfunctions are described in spherical polar coordinates. When the rectangular coordinates  $(x, y, z)$  are changed to

$(-x, -y, -z)$ , the spherical polar coordinates  $(r, \theta, \phi)$  change to  $(r, \pi - \theta, \pi + \phi)$ , as illustrated in Fig. 5.



The one-electron angular eigenfunctions show following properties :

$$\Theta_{l, m_l}(\pi - \theta) = (-1)^{l+1} m_l \Theta_{l, m_l}(\theta)$$

and

$$\Phi_{m_l}(\pi + \phi) = (-1)^{|m_l|} \Phi_{m_l}(\phi).$$

Thus,

$$R_{n, l}(r) \Theta_{l, m_l}(\pi - \theta) \Phi_{m_l}(\pi + \phi) = (-1)^{l+2|m_l|}$$

$$R_{n, l}(r) \Theta_{l, m_l}(\theta) \Phi_{m_l}(\phi)$$

or

$$\psi_{n, l, m_l}(r, \pi - \theta, \pi + \phi) = (-1)^l \psi_{n, l, m_l}(r, \theta, \phi).$$

Thus, *the parity of one-electron atom eigenfunctions is determined by  $(-1)^l$* . The parity is even if the orbital angular momentum quantum number  $l$  is even, and odd if  $l$  is odd. This is true for all eigenfunctions of any spherically symmetric potential  $V(r)$ .

In a one-electron atom we have several (degenerate) eigenfunctions corresponding to the same eigenvalue, because of the several possible values of  $l$  for the same  $n$ . Obviously, these components differ in parity inspite of their having the same energy values.

We now show that *in an electric dipole transition, the parity of the state of the atom must change*. Let us consider the matrix element of the  $x$ -component of the electric dipole moment\*  $\sum_j e x_j$ . The matrix element is

$$(R_x)_{f, i} = \int \psi_f^* \left( \sum_j e x_j \right) \psi_i dx,$$

where  $\psi_f$  and  $\psi_i$  are the eigenfunctions corresponding to the final and the initial states respectively. The parity of  $\sum_j e x_j$  is odd because  $\sum_j e (-x_j) = -\sum_j e x_j$ . Therefore, if

the initial and the final eigenfunctions  $\psi_i$  and  $\psi_f$  are of the same parity, both even or both odd, the entire integrand will be of odd parity. In that case the contribution from any volume element will be cancelled by the contribution from the diametrically opposite

\*The electric dipole moment is the product of the electron charge and the expectation value of its displacement vector from the fixed massive nucleus, that is,  $e \vec{r}$ . It is a measure of the separation of the centre of the electron charge distribution from the nuclear centre of the atom. The  $x$ -component of electric dipole moment  $e \vec{r}$  is  $\sum_j e x_j$ .

volume element, and so the above integral will yield zero. Then, the transition rate will also be zero. This is true for the  $y$ - and the  $z$ -components also. Hence, for the electric dipole transition to take place, the parity of the final state eigenfunction  $\psi_f$  must be different from that of the initial state eigenfunction  $\psi_i$ , that is, **the parity must change**.

Since the parities are determined by  $(-1)^l$ , the transitions corresponding to  $\Delta l = 0, \pm 2, \pm 4, \dots$  are not allowed, because in these cases the parities of the initial and the final eigenfunctions would be the same. The transitions allowed by parity are

$$\Delta l = \pm 1, \pm 3, \pm 5, \dots$$

The selection rule  $\Delta m_l = 0, \pm 1$  disallows the transitions  $\Delta l = \pm 3, \pm 5, \dots$  because then  $\Delta m_l$  may be greater than 1. Hence, the selection rule for  $l$  is

$$\boxed{\Delta l = \pm 1.}$$

The electric dipole selection rule  $\Delta l = \pm 1$ , however, does not absolutely prohibit transitions that violate the rule, but only make such transitions very unlikely. Transitions disallowed by  $\Delta l = \pm 1$  have actually been observed, though with very small probability, due to oscillating *magnetic* dipole moment or oscillating electric *quadrupole* moment.

### SOLVED PROBLEMS

**1. Compute the value of the normalisation factor in the azimuthal wave function of hydrogen atom.**

**Solution.** The azimuthal wave function for a one-electron atom is

$$\Phi = A e^{im_l\phi},$$

where  $A$  is a constant and  $m_l$  is an integer, positive or negative. To normalise this wave function, we use the fact that the integral of  $|\Phi|^2$  over all angles must be equal to 1, because the electron certainly exists somewhere. Hence

$$\int_0^{2\pi} |\Phi|^2 d\phi = 1.$$

$$\text{Now, } |\Phi|^2 = \Phi \Phi^* = (A e^{im_l\phi}) (A e^{-im_l\phi}) = A^2.$$

$$\therefore A^2 \int_0^{2\pi} d\phi = 1$$

$$A^2 (2\pi) = 1$$

or

$$A = \frac{1}{\sqrt{2\pi}}.$$

This is the value of the normalisation factor. The normalised azimuthal wave function is therefore,

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}.$$

**2. Write the wave function for the ground state of hydrogen atom, and show that the most probable value of the distance  $r$  of the electron from the nucleus is the Bohr radius  $a_0$ , and the expectation (average) value of  $r$  is  $3a_0/2$ . Hence discuss the characteristics of the ground state of the atom.**

(Meerut 2004 special, 03 sp., 02 sp., 02 s, 00 sp.)

**Solution.** The ground state of one-electron atom corresponds to the quantum numbers  $n = 1$ ,  $l = 0$  and  $m_l = 0$ . The wave function for this state is

It is known that

$$\Psi_{1,0,0}(r, \theta, \phi) = R_{1,0}(r) \Theta_{0,0}(\theta) \Phi_0(\phi).$$

and

$$\Phi_0(\phi) = \frac{1}{\sqrt{2\pi}},$$

$$\Theta_{0,0}(\theta) = \frac{1}{\sqrt{2}}$$

$$R_{1,0}(r) = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0},$$

where  $a_0$  is the radius of the smallest Bohr orbit. Making these substitutions, and putting  $Z = 1$  for hydrogen, we obtain

$$\Psi_{1,0,0} = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}.$$

The probability density function for the electron relative to the nucleus is

$$|\psi|^2 = \psi \psi^* = \frac{1}{\pi a_0^3} e^{-2r/a_0}, \quad \dots(i)$$

which is independent of angles  $\theta$  and  $\phi$ . From this we conclude that *the ground state of the hydrogen atom is spherically symmetrical*.

The (radial) probability  $P(r)$  that the electron is found between the distances  $r$  and  $r + dr$  from the nucleus, regardless of angles  $\theta$  and  $\phi$ , is given by

$$P(r) dr = |\psi|^2 4\pi r^2 dr,$$

where  $4\pi r^2 dr$  is the volume enclosed between spheres of radii  $r$  and  $r + dr$ .

Substituting for  $|\psi|^2$  from eq. (i), we get

$$P(r) dr = \frac{4}{a_0^3} (e^{-2r/a_0}) r^2 dr.$$

The most probable distance  $r$  of the electron from the nucleus, that is, the maximum in  $P(r)$  is found by setting  $\frac{dP(r)}{dr}$  equal to zero. Thus,

$$\frac{dP(r)}{dr} = \frac{4}{a_0^3} \left\{ e^{-2r/a_0} \left( -\frac{2}{a_0} \right) r^2 + (e^{-2r/a_0}) 2r \right\} = 0$$

$$\text{or } \left( -\frac{2}{a_0} \right) r^2 + 2r = 0$$

$$\text{or } -\frac{r}{a_0} + 1 = 0$$

$$\text{or } r = a_0.$$

This is just the radius of the Bohr orbit in the ground state of the hydrogen atom. Thus, the electron is most likely to be found at the location predicted by Bohr theory. However, the probability of its being found elsewhere is *not* zero.

The expectation (average) value of the distance of the electron from the nucleus is

$$\begin{aligned} \bar{r} &= \int_0^\infty r P(r) dr \\ &= \frac{4}{a_0^3} \int_0^\infty (e^{-2r/a_0}) r^3 dr \end{aligned}$$

$$= \frac{4}{a_0^3} 3! \left( \frac{a_0}{2} \right)^4 \\ = \frac{3}{2} a_0.$$

This is larger than the value of  $r$  for maximum radial probability density. The reason is that the radial probability density is 'asymmetrical' about its maximum in such a way that there is a small but finite probability of finding fairly large values of  $r$  in measurement of the location of the electron in the atom.

The quantum mechanical value of the angular momentum  $\vec{L}$  is given by

$$L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}.$$

For the ground state ( $n = 1$ ),  $l = 0$  and so

$$L = 0.$$

Thus, a normal (ground-state) hydrogen atom has no orbital angular momentum. This is in conflict with old quantum theory which gives an angular momentum of  $h/2\pi$  to the ground state. Quantum mechanically, a zero angular momentum of the electron means that the electron cloud is spherically symmetrical about the nucleus.

**3. Consider two hypothetical shells centred on the nucleus of a hydrogen atom with radii  $r$  and  $r + dr$ . What is the probability  $P(r)$  that the electron will lie between these shells? Assume the wave function for the ground state of the hydrogen atom to be**

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi} a_0^{3/2}} (e^{-r/a_0}) \cos \omega t.$$

**Solution.** The volume between the two spherical shells is

$$dV = 4\pi r^2 dr.$$

The probability  $P(r)$  of the electron being found between these shells, as a function of  $r$ , is given by

$$P(r) dr = |\psi|^2 dV \\ = \left\{ \frac{1}{\pi a_0^3} (e^{-2r/a_0}) \cos^2 \omega t \right\} 4\pi r^2 dr.$$

The average probability is obtained by replacing  $\cos^2 \omega t$  by its average value over the time which is  $\frac{1}{2}$ . Thus, on arranging,

$$\overline{P(r)} = \frac{2r^2}{a_0^3} e^{-2r/a_0}.$$

**4. Compute the number of degenerate eigenfunctions for one-electron atom corresponding to a particular eigenvalue.**

**Solution.** The eigenvalues of one-electron atom are described by the total quantum number  $n$  alone. This means that the states of the atom having same  $n$ , but different values of  $l$  and  $m_l$ , have same energy, that is, they are degenerate.

Now, for a given  $n$ , there are  $n$  possible values of the orbital quantum number  $l$ , given by

$$l = 0, 1, 2, \dots, n-1;$$

and for each value of  $l$ , there are  $(2l + 1)$  values of the magnetic quantum number  $m_l$ , given by

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l.$$

Therefore, the number of degenerate energy states (eigenfunctions) for each value of  $n$  is

$$\begin{aligned} \sum_{l=0}^{n-1} (2l + 1) &= 1 + 3 + 5 + \dots + (2n - 1); \text{ a total of } n \text{ terms} \\ &= \frac{n}{2} [2(1) + (n - 1)2] \\ &= n^2. \end{aligned}$$

**5. Show that all eigenfunctions which are solutions to time-independent Schroedinger equation having spherically symmetrical potential have definite parities, either even or odd.**

**Solution.** A spherically-symmetrical potential is one which has the same value at points  $(x, y, z)$  and  $(-x, -y, -z)$ .

The time-independent Schroedinger equation is

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} (E - V) \psi = 0.$$

This may be written as

$$\left[ -\frac{\hbar^2}{8\pi^2\mu} \nabla^2 + V \right] \psi(x, y, z) = E \psi(x, y, z).$$

On changing the signs of the coordinates, remembering that  $V$  does not change, we have

$$\left[ -\frac{\hbar^2}{8\pi^2\mu} \nabla^2 + V \right] \psi(-x, -y, -z) = E \psi(-x, -y, -z).$$

Thus, both the eigenfunctions  $\psi(x, y, z)$  and  $\psi(-x, -y, -z)$  satisfy the same differential equation. Hence, it must be true that

$$\psi(-x, -y, -z) = K \psi(x, y, z),$$

where  $K$  is a constant. On changing the signs of the coordinates in this equation, we get

$$\psi(x, y, z) = K \psi(-x, -y, -z).$$

Multiplication of the last two equations gives

$$K^2 = 1$$

or

$$K = \pm 1.$$

Hence,

$$\psi(-x, -y, -z) = \pm \psi(x, y, z).$$

This equation means that the eigenfunction has a definite parity; even when  $\psi(-x, -y, -z) = + \psi(x, y, z)$  and odd when  $\psi(-x, -y, -z) = - \psi(x, y, z)$ .

#### 6. Determine the parity of the ground states of atoms N and O.

**Solution.** A given state of an atom is of even parity if the sum of the  $l$  values of all the electrons,  $\sum l$ , is even; and of odd parity if  $\sum l$  is odd. The ground state configuration of atom N ( $Z = 7$ ) is

$$1s^2 2s^2 2p^3.$$

$l = 0$  for  $s$ -electron and  $l = 1$  for  $p$ -electron. Therefore,

$$\sum l = 3.$$

Hence, the parity of N is odd.

$$= \frac{4}{a_0^3} 3! \left( \frac{a_0}{2} \right)^4 \\ = \frac{3}{2} a_0.$$

This is larger than the value of  $r$  for maximum radial probability density. The reason is that the radial probability density is 'asymmetrical' about its maximum in such a way that there is a small but finite probability of finding fairly large values of  $r$  in measurement of the location of the electron in the atom.

The quantum mechanical value of the angular momentum  $\vec{L}$  is given by

$$L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}.$$

For the ground state ( $n = 1$ ),  $l = 0$  and so

$$L = 0.$$

Thus, a normal (ground-state) hydrogen atom has no orbital angular momentum. This is in conflict with old quantum theory which gives an angular momentum of  $h/2\pi$  to the ground state. Quantum mechanically, a zero angular momentum of the electron means that the electron cloud is spherically symmetrical about the nucleus.

**3. Consider two hypothetical shells centred on the nucleus of a hydrogen atom with radii  $r$  and  $r + dr$ . What is the probability  $P(r)$  that the electron will lie between these shells? Assume the wave function for the ground state of the hydrogen atom to be**

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi} a_0^{3/2}} (e^{-r/a_0}) \cos \omega t.$$

**Solution.** The volume between the two spherical shells is

$$dV = 4\pi r^2 dr.$$

The probability  $P(r)$  of the electron being found between these shells, as a function of  $r$ , is given by

$$P(r) dr = |\psi|^2 dV \\ = \left\{ \frac{1}{\pi a_0^3} (e^{-2r/a_0}) \cos^2 \omega t \right\} 4\pi r^2 dr.$$

The average probability is obtained by replacing  $\cos^2 \omega t$  by its average value over the time which is  $\frac{1}{2}$ . Thus, on arranging,

$$\overline{P(r)} = \frac{2r^2}{a_0^3} e^{-2r/a_0}.$$

**4. Compute the number of degenerate eigenfunctions for one-electron atom corresponding to a particular eigenvalue.**

**Solution.** The eigenvalues of one-electron atom are described by the total quantum number  $n$  alone. This means that the states of the atom having same  $n$ , but different values of  $l$  and  $m_l$  have same energy, that is, they are degenerate.

Now, for a given  $n$ , there are  $n$  possible values of the orbital quantum number  $l$ , given by

$$l = 0, 1, 2, \dots, n-1;$$

and for each value of  $l$ , there are  $(2l + 1)$  values of the magnetic quantum number  $m_l$ , given by

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l.$$

Therefore, the number of degenerate energy states (eigenfunctions) for each value of  $n$  is

$$\begin{aligned} \sum_{l=0}^{n-1} (2l + 1) &= 1 + 3 + 5 + \dots + (2n - 1); \text{ a total of } n \text{ terms} \\ &= \frac{n}{2} [2(1) + (n - 1)2] \\ &= n^2. \end{aligned}$$

**5. Show that all eigenfunctions which are solutions to time-independent Schroedinger equation having spherically symmetrical potential have definite parities, either even or odd.**

**Solution.** A spherically-symmetrical potential is one which has the same value at points  $(x, y, z)$  and  $(-x, -y, -z)$ .

The time-independent Schroedinger equation is

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} (E - V) \psi = 0.$$

This may be written as

$$\left[ -\frac{h^2}{8\pi^2\mu} \nabla^2 + V \right] \psi(x, y, z) = E \psi(x, y, z).$$

On changing the signs of the coordinates, remembering that  $V$  does not change, we have

$$\left[ -\frac{h^2}{8\pi^2\mu} \nabla^2 + V \right] \psi(-x, -y, -z) = E \psi(-x, -y, -z).$$

Thus, both the eigenfunctions  $\psi(x, y, z)$  and  $\psi(-x, -y, -z)$  satisfy the same differential equation. Hence, it must be true that

$$\psi(-x, -y, -z) = K \psi(x, y, z),$$

where  $K$  is a constant. On changing the signs of the coordinates in this equation, we get

$$\psi(x, y, z) = K \psi(-x, -y, -z).$$

Multiplication of the last two equations gives

$$K^2 = 1$$

or

$$K = \pm 1.$$

Hence,

$$\psi(-x, -y, -z) = \pm \psi(x, y, z).$$

This equation means that the eigenfunction has a definite parity; even when  $\psi(-x, -y, -z) = + \psi(x, y, z)$  and odd when  $\psi(-x, -y, -z) = - \psi(x, y, z)$ .

**6. Determine the parity of the ground states of atoms N and O.**

**Solution.** A given state of an atom is of even parity if the sum of the  $l$  values of all the electrons,  $\sum l$ , is even; and of odd parity if  $\sum l$  is odd. The ground state configuration of atom N ( $Z = 7$ ) is

$$1s^2 2s^2 2p^3.$$

$l = 0$  for  $s$ -electron and  $l = 1$  for  $p$ -electron. Therefore,

$$\sum l = 3.$$

Hence, the parity of N is **odd**.

The ground state configuration of atom O ( $Z = 8$ ) is  
 $1 s^2 \ 2 s^2 \ 2 p^4$ .  
 $\therefore \Sigma l = 4$ .

Hence the parity of atom O is even.

## QUESTIONS

1. How do the predictions of the Bohr-Sommerfeld and the Schroedinger treatments of the hydrogen atom compare with regard to the location of the electron, its total energy, and its orbital angular momentum ?
2. Solve the Schroedinger radial wave equation for hydrogen atom and obtain its energy levels. Discuss the significance of quantum numbers involved.  
*(Meerut 92 special paper)*
3. Discuss the paradox that the  $s$ -orbit of an electron passes through the nucleus.
4. Explain the meaning of degeneracy. Show that the degree of degeneracy of  $n$  th energy level is given by  $n^2$ .
5. Write operators corresponding to the various rectangular components of angular momentum in spherical polar coordinates and show that

$$\hat{L}^2 = -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right].$$

Hence deduce expressions for the eigenvalues of the square of the total angular momentum  $\hat{L}^2$  and its  $z$ -component  $\hat{L}_z$ . *(Meerut 2002 special paper, 2000)*

6. What do you understand by parity of a state ? Show that for allowed transitions the parity changes. *(Meerut 90)*
7. Obtain selection rule for electric dipole transition in a single-electron atom and show that for allowed transitions, the parity changes. *(Meerut 89)*
8. Calculate the expectation value of  $r$  in the ground state of hydrogen atom.

*(Meerut 2001 special paper, 99)*

# Magnetic Dipole Moments, Electron Spin and Vector Atom Model

## 1. Orbital Magnetic Dipole Moment : Bohr Magneton

We continue our study of one-electron atom, in which the orbital quantum number  $l$  determines the *magnitude* of the electron's angular momentum. Now, an electron revolving in an orbit about the nucleus of an atom is a minute current-loop and produces magnetic field. It thus behaves like a magnetic dipole. We compute its magnetic moment.

Let us consider an electron of mass\*  $m$  and charge  $-e$  moving with velocity of magnitude  $v$  in a circular Bohr orbit of radius  $r$ , as shown in Fig. 1. It constitutes a current of magnitude.

$$i = \frac{e}{T},$$

where  $T$  is the orbital period of the electron. Now,  $T = 2\pi r/v$ , and so

$$i = \frac{e v}{2\pi r}.$$

From electromagnetic theory, the magnitude of the orbital magnetic dipole moment  $\vec{\mu}_l$  for a current  $i$  in a loop of area  $A$  is

$$\mu_l = i A$$

and its direction is perpendicular to the plane of the orbit, as shown. Substituting the value of  $i$  from above and taking  $A = \pi r^2$ , we have

$$\mu_l = \frac{e v}{2\pi r} \times \pi r^2 = \frac{e v r}{2}. \quad \dots(i)$$

Because the electron has a negative charge, its magnetic dipole moment  $\vec{\mu}_l$  is *opposite* in direction to its orbital angular momentum  $\vec{L}$ , whose magnitude is given by

$$L = m v r. \quad \dots(ii)$$

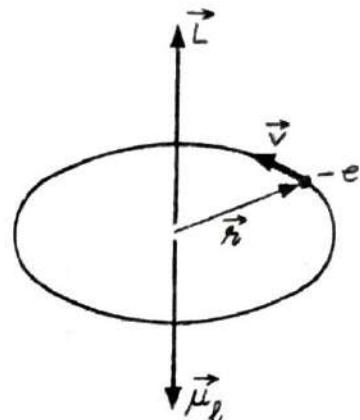
Dividing eq. (i) by eq. (ii), we get

$$\frac{\mu_l}{L} = \frac{e}{2m}. \quad \dots(iii)$$

Thus, the ratio of the magnitude  $\mu_l$  of the orbital magnetic dipole moment to the magnitude  $L$  of the orbital angular momentum for the electron is a constant, independent of the details of the orbit. This constant is called the 'gyromagnetic ratio' for the electron.

We can write eq. (iii) as a vector equation :

\* Here we are taking the mass  $m$  of the electron, not its reduced mass  $\mu$ . This will make little difference. The symbol  $\mu$  is being used for magnetic dipole moment.



(Fig. 1)

$$\vec{\mu}_l = - \left( \frac{e}{2m} \right) \vec{L}$$

The minus sign means that  $\vec{\mu}_l$  is in the opposite direction to  $\vec{L}$ .

The unit of electron magnetic dipole moment is ampere-meter<sup>2</sup> ( $A\ m^2$ ) or joule/tesla ( $J\ T^{-1}$ ).

It is usual to write the last relation as

$$\vec{\mu}_l = - g_l \left( \frac{e}{2m} \right) \vec{L}, \quad \dots(iv)$$

where

$$g_l = 1.$$

The quantity  $g_l$  is called the 'orbital  $g$  factor'. It is introduced here to preserve symmetry with further equations involving  $g$  factors which are different from 1.

**Bohr Magneton :** From quantum mechanics, the permitted scalar values of orbital angular momentum  $\vec{L}$  are given by

$$L = \sqrt{l(l+1)} \frac{h}{2\pi},$$

where  $l$  is the 'orbital quantum number'. Therefore, the magnitude of the orbital magnetic moment of the electron is

$$\mu_l = \sqrt{l(l+1)} \frac{e h}{4\pi m}.$$

The quantity  $\frac{e h}{4\pi m}$  forms a natural unit for the measurement of atomic magnetic dipole moments, and is called the 'Bohr magneton', denoted by  $\mu_B$ . Its value is

$$\mu_B = \frac{e h}{4\pi m} = \frac{(1.60 \times 10^{-19} C)(6.63 \times 10^{-34} J s)}{4 \times 3.14 \times (9.11 \times 10^{-31} kg)} = 9.27 \times 10^{-24} A\ m^2.$$

Thus,

$$\mu_l = \sqrt{l(l+1)} \mu_B.$$

Finally, equation (iv) can be written as

$$\vec{\mu}_l = - g_l \left( \frac{2\pi\mu_B}{h} \right) \vec{L}.$$

## 2. Behaviour of Magnetic Dipole in External Magnetic Field : Larmor Precession

An electron moving around the nucleus of an atom is equivalent to a magnetic dipole. Hence, when the atom is placed in an external magnetic field, the electron orbit precesses about the field direction as axis. This precession is called 'Larmor precession' and the frequency of this precession is called 'Larmor frequency'.

In Fig. 2 is shown an electron orbit in an external magnetic field  $\vec{B}$ . The orbital angular momentum of the electron is represented by a vector  $\vec{L}$  perpendicular to the plane of the orbit. Let  $\theta$  be the angle between  $\vec{L}$  and  $\vec{B}$ .

The orbital magnetic dipole moment  $\vec{\mu}_l$  of the electron is given by

$$\vec{\mu}_l = - \left( \frac{e}{2m} \right) \vec{L},$$

...(i)

where  $-e$  is the charge on the electron of mass  $m$ . The minus sign signifies that  $\vec{\mu}_l$  is directed opposite to  $\vec{L}$ . As a result of its interaction with magnetic field  $\vec{B}$ , the dipole experiences a torque  $\vec{\tau}$ , given by

$$\vec{\tau} = \vec{\mu}_l \times \vec{B}. \quad \dots (\text{ii})$$

According to eq. (i) and (ii), the torque  $\vec{\tau}$  acting on the dipole is always *perpendicular* to the angular momentum  $\vec{L}$ .

We know that a torque causes the angular momentum to change according to a form of Newton's law :

$$\vec{\tau} = \frac{d\vec{L}}{dt},$$

and the change takes place in the direction of the torque. The torque  $\vec{\tau}$  on the electron, therefore, produces a change  $d\vec{L}$  in  $\vec{L}$  in a time  $dt$ . **The change  $d\vec{L}$  is perpendicular to  $\vec{L}$**  (because the change is in the direction of torque, and the torque is perpendicular to  $\vec{L}$ ). Hence the angular momentum  $\vec{L}$  remains constant in magnitude, *but its direction changes*. As time goes on, the vector  $\vec{L}$  traces a cone around  $\vec{B}$ , such that the angle between  $\vec{L}$  and  $\vec{B}$  remains constant. This is the precession of  $\vec{L}$ , and hence of the electron orbit, around  $\vec{B}$ .

If  $\omega$  be the angular velocity of precession, then  $\vec{L}$  precesses through an angle  $\omega dt$  in time  $dt$ . From Fig. 2, we see that

$$\omega dt = \frac{dL}{L \sin \theta}$$

$$\left[ \text{angle} = \frac{\text{arc}}{\text{radius}} \right]$$

or

$$\omega = \frac{dL}{dt} \frac{1}{L \sin \theta} = \frac{\tau}{L \sin \theta}.$$

But from eq. (ii),  $\tau = \mu_l B \sin \theta$ .

$$\therefore \omega = \frac{\mu_l}{L} B.$$

Thus, the angular velocity of Larmor precession is equal to the product of the magnitude of the magnetic field, and the ratio of the magnitude of the magnetic moment to the magnitude of the angular momentum.

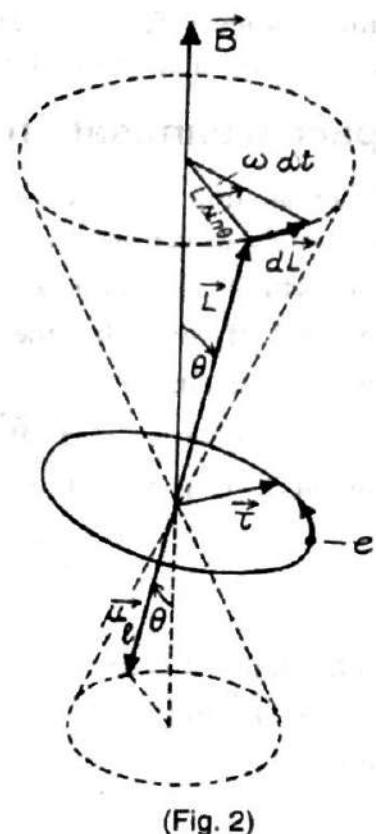
Again, from eq. (i),

$$\frac{\mu_l}{L} = \frac{e}{2m}.$$

$$\therefore \omega = \frac{e}{2m} B.$$

The Larmor frequency (frequency of precession) is therefore

$$f = \frac{\omega}{2\pi} = \frac{e}{4\pi m} B.$$



(Fig. 2)

It is independent of the orientation angle  $\theta$  between orbit normal ( $\vec{L}$ ) and field direction ( $\vec{B}$ ).

**Importance :** This theorem is of considerable importance in atomic structure as it enables an easy calculation of energy levels in the presence of an external magnetic field.

### 3. Space Quantisation

When an atom is placed in an external magnetic field  $\vec{B}$ , the electron orbit precesses about the field direction as axis (Larmor precession). The electron orbital angular momentum vector  $\vec{L}$  traces a cone around  $\vec{B}$  such that the angle  $\theta$  between  $\vec{L}$  and  $\vec{B}$  remains constant (Fig. 3).

If the magnetic field  $\vec{B}$  is along the z-axis, the component of  $\vec{L}$  parallel to the field is

$$L_z = L \cos \theta$$

or

$$\cos \theta = \frac{L_z}{L}$$

Quantum mechanically, the magnitude of the angular momentum  $\vec{L}$  and its z-component  $L_z$  are quantised according to the relations

$$L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$$

and

$$L_z = m_l \frac{\hbar}{2\pi},$$

where  $l$  and  $m_l$  are orbital and magnetic quantum numbers respectively. Hence the angle  $\theta$  between  $\vec{L}$  and the z-axis is determined by the quantum numbers  $l$  and  $m_l$ , according as

$$\cos \theta = \frac{L_z}{L} = \frac{m_l}{\sqrt{l(l+1)}}.$$

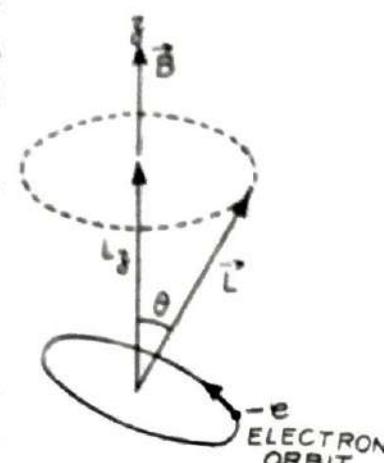
Since, for a given  $l$ , there are  $(2l+1)$  possible values of  $m_l$  ( $= 0, \pm 1, \pm 2, \dots, \pm l$ ), the angle  $\theta$  can assume  $(2l+1)$  discrete values. In other words, the angular momentum vector  $\vec{L}$  can have  $(2l+1)$  discrete orientations with respect to the magnetic field. This quantisation of the orientation of atoms in space is known as 'space quantisation'.

The space quantisation of the orbital angular momentum vector  $\vec{L}$  corresponding to  $l=2$  {or  $L=\sqrt{6}\ h/2\pi$ } is shown in Fig. 4. For  $l=2$ , we have

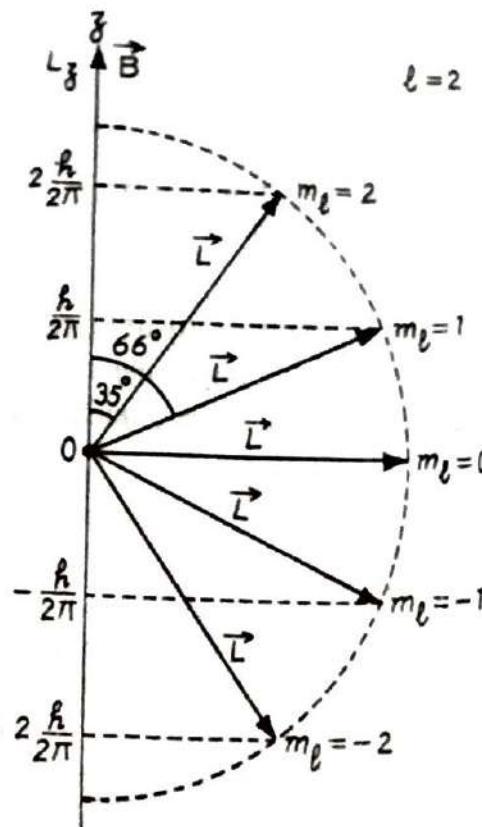
$$m_l = 2, 1, 0, -1, -2$$

so that  $L_z = 2 \frac{\hbar}{2\pi}, \frac{\hbar}{2\pi}, 0, -\frac{\hbar}{2\pi}, -2 \frac{\hbar}{2\pi}$ .

Alternatively, the orientations  $\theta$  of  $\vec{L}$  with respect to the field  $\vec{B}$  (z-axis) are given by



(Fig. 3)



(Fig. 4)

$$\begin{aligned}\cos \theta &= \frac{m_l}{\sqrt{l(l+1)}} \\&= \frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}}, 0, -\frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}} \\&= 0.8165, 0.4082, 0, -0.4082, -0.8165\end{aligned}$$

or  $\theta = 35^\circ, 66^\circ, 90^\circ, 114^\circ, 145^\circ.$

We note that  $\vec{L}$  can never be aligned exactly parallel or antiparallel to  $\vec{B}$ , since  $|m_l|$  is always smaller than  $\sqrt{l(l+1)}$ .

#### 4. Electron Spin

The Bohr-Sommerfeld quantum theory of elliptic orbits with relativity correction was in fair numerical agreement with the observed fine structure of hydrogen spectral lines. It, however, suffered from two major drawbacks : (i) Firstly, Sommerfeld's relativistic explanation could not be applied for the spectral lines of atoms other than hydrogen. For example, the spectral lines of alkali atoms are *doublets*, having two close fine-structure components. In alkali atoms the (single) optical electron moves in a Bohr-like orbit of large radius at low velocity. Therefore, the relativity effect would be too small to account for the large (compared with hydrogen) fine-structure splitting observed in alkali lines. (ii) Secondly, the simple quantum theory failed to explain anomalous Zeeman effect, that is, the splitting of atomic spectral lines into four, six or more components when the light source was placed in an external magnetic field.

In an effort to remove these two drawbacks of the theory, Goudsmit and Uhlenbeck proposed in 1925 that *an electron must be looked upon as a charged sphere spinning about its own axis, having an intrinsic (built-in) angular momentum and consequently an intrinsic magnetic dipole moment*. These are called 'spin angular momentum'  $\vec{S}$  and 'spin magnetic dipole moment'  $\vec{\mu}_s$  respectively. (These are in addition to the orbital angular momentum  $\vec{L}$  and orbital magnetic dipole moment  $\vec{\mu}_l$ ).

Let us write the magnitude  $S$  of the spin angular momentum of the electron in terms of a 'spin quantum number'  $s$ , as we do for the orbital angular momentum  $L$  in terms of orbital quantum number  $l$ . Thus

$$S = \sqrt{s(s+1)} \frac{h}{2\pi}.$$

The only value which the spin quantum number can be given is

$$s = \frac{1}{2},$$

which conforms to the observed fine-structure doubling\*. Thus

$$S = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \frac{h}{2\pi} = \frac{\sqrt{3}}{2} \frac{h}{2\pi}. \quad \dots(i)$$

The component of  $\vec{S}$  along a magnetic field parallel to the z-direction is\*\*

$$S_z = m_s \frac{h}{2\pi}, \quad \dots(ii)$$

\*It means that the  $2s + 1$  possible orientations of the spin angular momentum vector  $\vec{S}$  with respect to a certain direction must be equal to 2. Thus,  $2s + 1 = 2$  and so  $s = 1/2$ .

\*\*Let us note that  $S_x$  and  $S_y$  are not quantised, as is also the case for  $L_x$  and  $L_y$ .

where  $m_s$  is the 'spin magnetic quantum number' and takes  $(2s+1) = 2$  values which are  $+s$  and  $-s$ , that is

$$m_s = +\frac{1}{2} \text{ and } -\frac{1}{2} \quad \dots(\text{iii})$$

Thus  $S_z = +\frac{1}{2} \frac{\hbar}{2\pi}$  and  $-\frac{1}{2} \frac{\hbar}{2\pi}$ .

It has been concluded from experimental data that the gyromagnetic ratio for electron spin,  $\frac{\mu_s}{S}$ , is twice the corresponding ratio  $\frac{\mu_l}{L} \left( = \frac{e}{2m} \right)$  for the electron orbital motion. Thus, the spin magnetic moment  $\vec{\mu}_s$  of electron is related to the spin angular momentum  $\vec{S}$  by

$$\vec{\mu}_s = -2 \frac{e}{2m} \vec{S}.$$

The minus sign indicates that  $\vec{\mu}_s$  is opposite in direction to  $\vec{S}$  (because electron is negatively charged).

It is usual to write the last relation as

$$\vec{\mu}_s = -g_s \left( \frac{e}{2m} \right) \vec{S} \quad \dots(\text{iv})$$

where

$$g_s = 2.$$

The quantity  $g_s$  is called the 'spin g factor'.

We can express spin magnetic dipole moment in terms of Bohr magneton  $\mu_B (= e h / 4 \pi m)$ . Equation (iv) then becomes

$$\vec{\mu}_s = -\frac{g_s \mu_B}{(h/2\pi)} \vec{S}. \quad \dots(\text{v})$$

The possible component of  $\vec{\mu}_s$  along z-axis are given by

$$\begin{aligned} \mu_{sz} &= -\frac{g_s \mu_B}{(h/2\pi)} S_z \\ &= -\frac{g_s \mu_B}{(h/2\pi)} m_s \frac{\hbar}{2\pi} \quad [\text{by equation (ii)}] \\ &= -g_s \mu_B m_s. \end{aligned}$$

Now,  $g_s = 2$  and  $m_s = \pm \frac{1}{2}$  (by eq. iii).

$$\therefore \mu_{sz} = \pm \mu_B.$$

The spinning electron proved to be successful in explaining not only fine structure and the anomalous Zeeman effect but other atomic effects also. Although electron spin was introduced as a postulate, but in 1928 Dirac proved on the basis of *relativistic* quantum mechanics that an electron must have an intrinsic angular momentum and an intrinsic magnetic moment which were just the same as attributed to it by Goudsmit and Uhlenbeck. Thus, electron spin was put on a firm theoretical foundation. The practical evidence of its existence came from Stern-Gerlach experiment.

## 5. Vector Model of Atom : Coupling of Orbital and Spin Angular Momenta

The total angular momentum of an atom results from the combination of the orbital and the spin angular momenta of its electrons. Since angular momentum is a vector quantity, we can represent the total angular momentum by means of a vector, obtained by

the addition of orbital and spin angular momentum vectors. This leads to the vector model of the atom.

Let us consider an atom whose total angular momentum is provided by a single electron\*. The magnitude of the orbital angular momentum  $\vec{L}$  of an atomic electron is given by

$$L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$$

and its z-component is

$$L_z = m_l \frac{\hbar}{2\pi},$$

where  $l$  is orbital quantum number and  $m_l$  is the corresponding magnetic quantum number, with values

$$m_l = l, l-1, \dots, 0, \dots, -l+1, -l.$$

Similarly, the magnitude of the spin angular momentum  $\vec{S}$  is given by

$$S = \sqrt{s(s+1)} \frac{\hbar}{2\pi}$$

and its z-component is

$$S_z = m_s \frac{\hbar}{2\pi},$$

where  $s$  is the spin quantum number (which has the sole value  $+\frac{1}{2}$ ) and  $m_s$  is magnetic spin quantum number ( $m_s = \pm \frac{1}{2} = \pm s$ ).

The total angular momentum of the one-electron atom,  $\vec{J}$ , is the vector sum of  $\vec{L}$  and  $\vec{S}$ , that is

$$\vec{J} = \vec{L} + \vec{S}.$$

The magnitude and the z-component of  $\vec{J}$  are specified by two quantum numbers  $j$  and  $m_j$ . According to the usual quantisation conditions

$$J = \sqrt{j(j+1)} \frac{\hbar}{2\pi}$$

and

$$J_z = m_j \frac{\hbar}{2\pi}.$$

$j$  is called the 'inner quantum number' and  $m_j$  is the corresponding magnetic quantum number. The possible values of  $m_j$  range from  $+j$  to  $-j$  in integral steps :

$$m_j = j, j-1, \dots, 0, \dots, -j+1, -j.$$

Let us obtain the relationship among the various angular momentum quantum numbers. Since  $J_z$ ,  $L_z$  and  $S_z$  are scalar quantities, we may write

$$J_z = L_z \pm S_z.$$

This gives

$$m_j = m_l \pm m_s.$$

\*Atoms of H, Li, Na, etc are of this kind. They have single electron outside closed inner shells (except for hydrogen which has no inner electrons), the total angular momentum of a closed shell being zero. Ions He<sup>+</sup>, Be<sup>+</sup>, Mg<sup>+</sup>, B<sup>++</sup>, Al<sup>++</sup> etc also belong to this category.

Since  $m_l$  is an integer and  $m_s$  is  $\pm \frac{1}{2}$ , so  $m_j$  must be half-integral. The maximum values of  $m_j$ ,  $m_l$  and  $m_s$  are  $j$ ,  $l$  and  $s$  respectively. Therefore, from the last expression, we have

$$j = l \pm s.$$

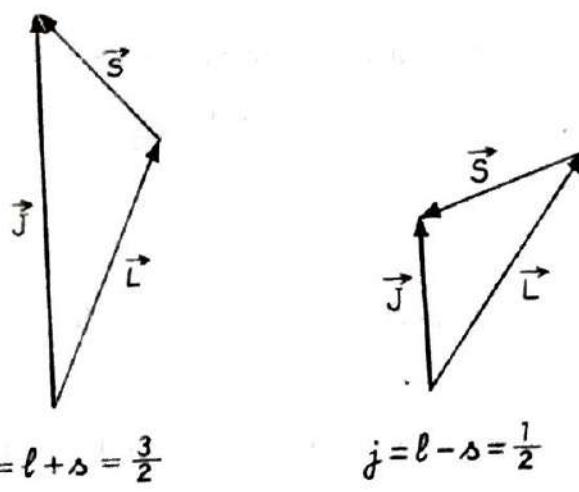
Like  $m_j$ ,  $j$  is always half-integral.

Since  $\vec{J}$ ,  $\vec{L}$  and  $\vec{S}$  are all quantised, they can have only certain specific relative orientations. In case of a one-electron atom, there are only two relative orientations possible, corresponding to

$$j = l + s, \quad \text{so that} \quad J > L$$

$$\text{and} \quad j = l - s, \quad \text{so that} \quad J < L.$$

The two ways in which  $\vec{L}$  and  $\vec{S}$  can combine to form  $\vec{J}$  (when  $l = 1$ ,  $s = \frac{1}{2}$ ) are shown in Fig. 5.



(Fig. 5)

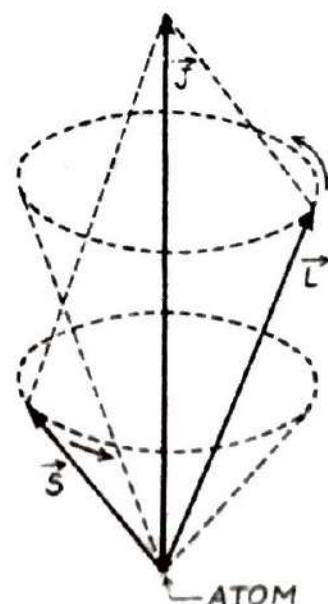
The angular momenta of the atomic electron,  $\vec{L}$  and  $\vec{S}$ , interact magnetically; which is known as 'spin-orbit interaction'. They exert torques on each other. These *internal* torques do not change the magnitudes of the vectors  $\vec{L}$  and  $\vec{S}$ , but cause them to precess uniformly around their resultant  $\vec{J}$  (Fig. 6). If the atom is in free space so that no external torques act on it, then the total angular momentum  $\vec{J}$  is conserved in magnitude and direction. Obviously, the angle between  $\vec{L}$  and  $\vec{S}$  remains invariant. From the cosine law, we have

$$J^2 = L^2 + S^2 + 2 LS \cos(\vec{L}, \vec{S}).$$

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

$$= \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}.$$

This is the vector model of one-electron atom. It can be extended to many-electron atoms. The vector model enables us to explain the phenomena which could not be understood from Bohr-Sommerfeld



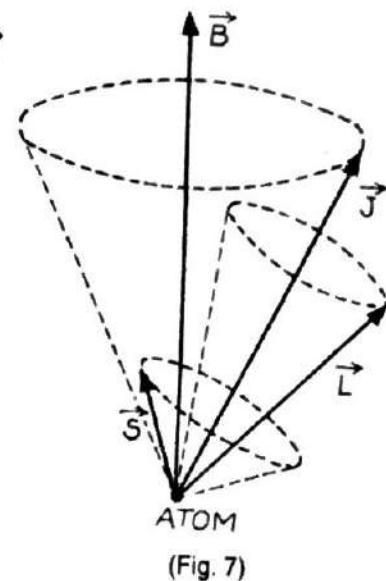
(Fig. 6)

theory such as fine structure of spectral lines, anomalous Zeeman effect and hyperfine structure.

The conception of spinning electron, which is a salient feature of the vector model, is responsible for the fine-structure doubling of the alkali spectral lines. The energy of an electron in a given quantum state will be higher or lower (depending upon the orientation of its spin vector  $\vec{S}$ ) than its energy in the absence of spin-orbit interaction. This means that each quantum state (except  $s$  state for which  $\vec{L}$  is zero) is splitted into two separated sub-states. This results in the splitting of every spectral line into two component lines. The numerical value of the splitting agrees with that experimentally observed. Similarly, spin-orbit interaction together with relativity correction explains the hydrogen fine-structure.

In the vector model,  $\vec{L}$  and  $\vec{S}$  precess around  $\vec{J}$ . When the atom is placed in an external magnetic field  $\vec{B}$ , then  $\vec{J}$  precesses about the direction of  $\vec{B}$ , while  $\vec{L}$  and  $\vec{S}$  continue precessing about  $\vec{J}$  (Fig. 7). The discrete orientations of  $\vec{J}$  relative to  $\vec{B}$ , which involve slightly different energies, give rise to anomalous Zeeman effect in agreement with experiment.

Like electrons, the atomic nuclei also have smaller intrinsic (spin) angular momenta and magnetic moments. When these vectors are added to the atomic model, the experimentally observed 'hyperfine structure' of spectral lines is explained.



## 6. Spectroscopic Terms and their Notations

The quantised energy states (simply called as quantum states) of an atomic electron are described in terms of the quantum numbers  $n, l, s$  and  $j$ . The electrons having orbital quantum number  $l = 0, 1, 2, 3, 4 \dots$  are named as  $s^*, p, d, f, g \dots$  electrons. The atomic states in the atom are specified by writing the corresponding principal quantum number alongwith these letters. Thus, an electron for which  $n = 2$  and  $l = 0$  is in a  $2s$  atomic state, and one for which  $n = 3$  and  $l = 1$  is in a  $3p$  atomic state, and so on.

The energy levels of electrons of an atom are called 'terms' of the atom. The corresponding energies, expressed in wave numbers, are called 'term values'. For a one-electron atom, the energy levels corresponding to  $l = 0, 1, 2, 3, 4, \dots$  are called  $S, P, D, F, G \dots$  terms respectively.

By spin-orbit interaction, each energy level of a given  $l$  is splitted into two sub-levels corresponding to

$$j = l + s = l + \frac{1}{2}$$

and

$$j = l - s = l - \frac{1}{2}.$$

\*This  $s$  should not be confused with the spin quantum number  $s$ .

with the exception of  $S$  term ( $l = 0$ ) for which  $j = \frac{1}{2}$  only. ( $j$ , which determines the total angular momentum of the electron, cannot be negative). The number of different possible orientations of  $\vec{L}$  and  $\vec{S}$  and hence the number of different possible values of  $j$  is known as the 'multiplicity' of the term. It is equal to  $(2s + 1)$ . Thus, the multiplicity of the terms of a one-electron atom is  $(2s + 1) = 2$ . It is added as a left superscript to the term symbol, thus :  $^2S, ^2P, ^2D$ , and so forth. These are called "doublet terms". In addition, the  $j$  value is added as a right subscript. Thus

Term	$l$	$j$	Full Notation
$S$	0	$1/2$	$^2S_{1/2}$
$P$	1	$3/2, 1/2$	$^2P_{3/2}, ^2P_{1/2}$
$D$	2	$5/2, 3/2$	$^2D_{5/2}, ^2D_{3/2}$

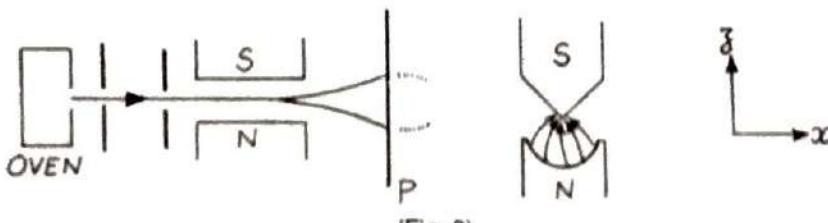
Sometimes the principal quantum number is also added to the term symbol, such as  $2^2P_{3/2}$ . Here  $n = 2, l = 1, s = \frac{1}{2}, j = 3/2$ .

In an atom containing several electrons, the orbital angular momenta  $\vec{L}_i, i = 1, 2, 3, \dots$  of the individual electrons couple among themselves to give a resultant electronic orbital angular momentum  $\vec{L}$  for the atom whose magnitude is  $\sqrt{(L(L+1)} h/2\pi$ , where  $L$  is the orbital quantum number for the atom. Similarly,  $\vec{S}_i, i = 1, 2, 3, \dots$  add up to give a resultant spin angular momentum  $\vec{S}$  of magnitude  $\sqrt{S(S+1)} \frac{h}{2\pi}$ , where  $S$  is spin quantum number for the atom. Finally,  $\vec{L}$  and  $\vec{S}$  couple to give the total electronic angular momentum  $\vec{J}$  for the atom, with magnitude  $\sqrt{J(J+1)} \frac{h}{2\pi}$ .  $J$  is the inner quantum number for the atom. The terms of the atom may now be singlets, doublets, triplets and so forth. They are denoted in the same way as the terms of a one-electron atom. We shall return to this point in a subsequent chapter.

## 7. Stern-Gerlach Experiment

Stern and Gerlach, in 1921, performed an experiment which demonstrated directly that an atom placed in a magnetic field can take only certain discrete orientations with respect to the field (space quantisation). It also demonstrated the existence of electron spin, thus providing an experimental verification of the vector model of atom.

The plan of the experiment is shown in Fig. 8. A beam of neutral silver atoms was formed by heating silver in an oven. It was collimated by a few fine slits and then passed



(Fig. 8)

\*For consistency, it is conventional to denote the  $S$ -term of one-electron atom as  $^2S$  indicating a doublet, even though there is only a single value of  $j$  since  $l = 0$ .

through a *non-homogeneous* magnetic field. The field was produced by specially-designed pole-pieces whose cross-sectional view is displayed separately. It shows that the field increases in intensity in the  $z$ -direction defined in the figure. The beam leaving the magnetic field was received on a photographic plate  $P$ . On developing the plate, no trace of the direct beam was obtained. Instead, two traces were obtained, symmetrically situated with respect to the direct beam. This meant that the beam of silver atoms splitted into two discrete components, one component being bent in the  $+z$ -direction and the other bent in the  $-z$ -direction. The experiment was repeated using other atoms, and in each case the beam was found splitted into two, or more, discrete components. This result is interpreted in the following way :

A magnet experiences a net *deflecting* force in a *non-homogeneous* magnetic field which depends on the orientation of the magnet in the field. Since atoms are tiny magnets, they experience deflecting force when passing through the field. If an atom could have *any* orientation in the magnetic field, then for the millions of atoms present in the beam, all possible orientations would be obtained and the beam would be deflected into a continuous band. In the experiment, however, there was no band, but discrete traces on the photographic plate. This showed that *the atoms passing through the field were oriented in space in discrete directions* so that the beam deflected in certain discrete directions only and gave discrete traces on the plate. Thus, the experimental results are, qualitatively, direct proof of the space quantisation of atoms.

Let us consider the experimental results quantitatively. The average transverse force experienced by an atomic magnet traversing the (inhomogeneous) magnetic field is

$$F_z = \frac{\partial B_z}{\partial z} \mu_{jz},$$

where  $\partial B_z / \partial z$  is the rate of change of field in the  $z$ -direction, and  $\mu_{jz}$  is the  $z$ -component of the total (orbital + spin) magnetic moment  $\vec{\mu}_j$  of the atom. The relation between the total magnetic dipole moment and the total angular momentum  $\vec{J}$  is

$$\begin{aligned} \vec{\mu}_j &= -g_j \left( \frac{e}{2m} \right) \vec{J} \\ &= -g_j \left( \mu_B \frac{2\pi}{h} \right) \vec{J}, \end{aligned}$$

where  $g_j$  is the corresponding  $g$  factor, and  $\mu_B (= e \hbar / 4\pi m)$  is Bohr magneton. The possible components of  $\vec{\mu}_j$  along  $z$ -axis are given by

$$\begin{aligned} \mu_{jz} &= -g_j \left( \mu_B \frac{2\pi}{h} \right) J_z \\ &= -g_j \left( \mu_B \frac{2\pi}{h} \right) m_j \frac{\hbar}{2\pi} \\ &= -g_j \mu_B m_j, \end{aligned}$$

where the magnetic quantum number  $m_j$  can assume a total of  $(2j + 1)$  values ranging from  $+j$  to  $-j$ . Thus

$$F_z = \frac{\partial B_z}{\partial z} g_j \mu_B m_j.$$

Because of this force the atoms (mass  $M$ ) have a transverse acceleration  $a_z$  given by

$$a_z = \frac{F_z}{M} = \frac{1}{M} \frac{\partial B_z}{\partial z} g_j \mu_B m_j.$$

If  $v_x$  be the longitudinal velocity of the atoms and  $d$  be the length of their path in the magnetic field, then the time  $t$  for which they experience the transverse force is

$$t = \frac{d}{v_x}.$$

But, from kinetic theory, the velocity  $v_x$  of an atom of mass  $M$  is evaluated by setting

$$\frac{1}{2} M v_x^2 = 2 k T,$$

where  $k$  is Boltzmann constant and  $T$  is kelvin temperature of the oven. From this, we have

$$v_x = \sqrt{\frac{4 k T}{M}}$$

and so

$$t = \frac{d}{v_x} = d \sqrt{\frac{M}{4 k T}}.$$

Therefore, the transverse deflection suffered by the atoms is given by

$$\begin{aligned} Z &= \frac{1}{2} a_t t^2 \\ &= \frac{1}{2} \left( \frac{1}{M} \frac{\partial B_z}{\partial z} g_j \mu_B m_j \right) d^2 \left( \frac{M}{4 k T} \right) \\ &= g_j m_j \frac{\frac{\partial B_z}{\partial z} \mu_B d^2}{8 k T}. \end{aligned}$$

The atomic beam would be deflected into  $(2j + 1)$  components corresponding to the  $(2j + 1)$  possible values of  $m_j$ , giving  $(2j + 1)$  traces on the plate.

For silver atoms two traces were obtained, and by measuring the separation between the traces it was found from the last expression that

$$g_j m_j = \pm 1.$$

At the temperature of the oven, the silver atoms were in their ground state, which is  ${}^2S_{1/2}$ , for which

$$l = 0$$

and

$$j = s = \frac{1}{2}$$

so that

$$(2j + 1) = 2.$$

Hence there were two traces. Further,

$$g_j = g_s = 2$$

and

$$m_j = m_s = \pm \frac{1}{2},$$

as postulated by spin hypothesis.

$$\therefore g_j m_j = 2 \left( \pm \frac{1}{2} \right) = \pm 1,$$

as experimentally observed.

\*According to kinetic theory, the hydrogen atoms in the oven have kinetic energy  $\left(\frac{3}{2}\right) k T$ ; but the atoms emitted in the beam have kinetic energy  $2 k T$ . The reason is that the more energetic atoms hit the walls of the oven more frequently and hence have a higher probability of falling on the hole in the wall through which the beam is emitted.

The ground state of atoms Zn, Cd, Hg is  $^1S_0$  and that of Sn and Pb is  $^3P_0$ . For these atoms,  $j = 0$  and hence  $g_j m_j = 0$ , that is, the beams of these atoms would not be deflected in the magnetic field. This was actually found to be the case.

The experiment is also an evidence for the existence of electron spin. This was shown most clearly in 1927 by Phipps and Taylor, who repeated the Stern-Gerlach experiment by using a beam of hydrogen atoms. This atom consists of a single electron and, the theory predicts, in the ground state the quantum number  $l$  is 0. If there were no spin, then we would have  $j = l = 0$  and  $g_j m_j = 0$  and the beam would be unaffected by the magnetic field, and only one trace would have been obtained on the plate. However, Phipps and Taylor found the beam to be splitted into two symmetrically deflected components, corresponding to  $g_j m_j = \pm 1$ . This is just the case when the existence of electron spin is admitted and a value  $\frac{1}{2}$  is assigned to the spin quantum number. Then

$$j = l \pm s = 0 \pm \frac{1}{2} = \frac{1}{2}$$

$$2j + 1 = 2.$$

so that

Hence two traces.

**Need of Inhomogeneous Magnetic Field :** If the field were homogeneous, then the atoms (tiny magnets) would have experienced only a turning moment, and no deflecting force. As such, we could not obtain the deflected components inspite of the orientation of the atoms relative to the field.

**Atoms, not Ions :** In the Stern-Gerlach experiment, a beam of 'neutral' atoms is passed through an inhomogeneous magnetic field, and each atom experiences a transverse force depending upon its orientation with respect to the field. If (charged) ions were used, they would be subjected to Lorentz force also and their deflection would no longer be transverse so that no traces would be obtained on the plate.

### SOLVED PROBLEMS

1. Calculate the two possible orientations of spin vector  $\vec{S}$  with respect to a magnetic field  $\vec{B}$ . (Meerut 2000 special paper, 89)

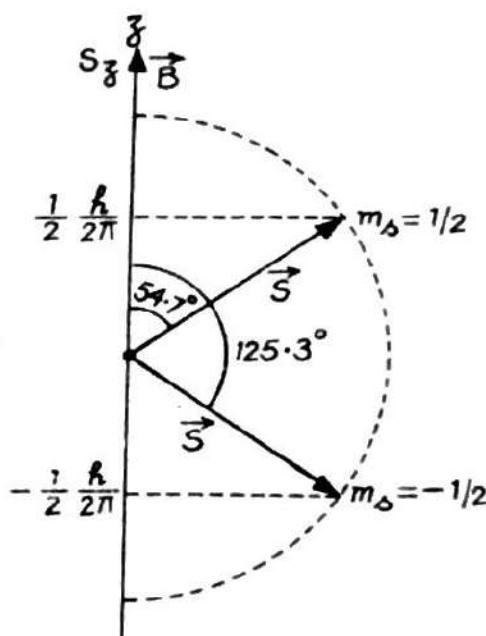
**Solution.** Let the magnetic field  $\vec{B}$  be along the  $z$ -axis. The magnitude of the spin angular momentum  $\vec{S}$  and its  $z$ -component are quantised according to the relations

$$S = \sqrt{s(s+1)} \frac{\hbar}{2\pi}, \quad s = \frac{1}{2}$$

$$\text{and} \quad S_z = m_s \frac{\hbar}{2\pi}, \quad m_s = \pm \frac{1}{2}$$

Hence, as clear from that figure, the angle  $\theta$  between  $\vec{S}$  and the  $z$ -axis is determined by the quantum numbers  $m_s$  and  $s$ , according as

$$\cos \theta = \frac{S_z}{S} = \frac{m_s}{\sqrt{s(s+1)}}$$



$$= \frac{2}{\sqrt{3}} m_s . \quad [ \because s = \frac{1}{2} ]$$

For  $m_s = +\frac{1}{2}$ , we have

$$\cos \theta = +\frac{1}{\sqrt{3}} = 0.577.$$

$$\therefore \theta = \cos^{-1}(0.577) = 54.7^\circ.$$

For  $m_s = -\frac{1}{2}$ , we have

$$\cos \theta = -\frac{1}{\sqrt{3}} = -0.577.$$

$$\therefore \theta = \cos^{-1}(-0.577) = 125.3^\circ.$$

These angles are indicated in the diagram.

**2. Obtain the magnitude of spin magnetic dipole moment of an electron in terms of Bohr magneton.**

**Solution.** The spin magnetic moment  $\vec{\mu}_s$  of electron is related to its spin angular momentum  $\vec{S}$  by

$$\vec{\mu}_s = -g_s \left( \frac{e}{2m} \right) \vec{S}.$$

The magnitude of spin magnetic moment is

$$\mu_s = g_s \frac{e}{2m} S.$$

$$\text{Now, } g_s = 2 \text{ and } S = \sqrt{s(s+1)} \frac{h}{2\pi} = \frac{\sqrt{3}}{2} \frac{h}{2\pi}, \text{ as } s = \frac{1}{2}.$$

$$\therefore \mu_s = 2 \left( \frac{e}{2m} \right) \frac{\sqrt{3}}{2} \frac{h}{2\pi} = \sqrt{3} \frac{e h}{4\pi m}.$$

But  $\frac{e h}{4\pi m} = \mu_B$ , the Bohr magneton.

$$\therefore \mu_s = \sqrt{3} \mu_B.$$

**3. A beam of electrons enters a uniform magnetic field of flux density 1.2 tesla. Calculate the energy difference between electrons whose spins are parallel and antiparallel to the field.**

**Solution.** An electron has an intrinsic (spin) angular momentum  $\vec{S}$  and an intrinsic magnetic dipole moment  $\vec{\mu}_s$ , which are related by

$$\vec{\mu}_s = -g_s \left( \frac{e}{2m} \right) \vec{S},$$

$$\text{where } g_s = 2, S = \sqrt{s(s+1)} \frac{h}{2\pi} \text{ and } s = \frac{1}{2}.$$

Let the magnetic field  $\vec{B}$  be along the  $z$ -axis. The magnitude of the  $z$ -component of the magnetic moment is

$$\mu_{sz} = g_s \left( \frac{e}{2m} \right) S_z,$$

where  $S_z$  is the  $z$ -component of the spin angular momentum and is given by

$$S_z = m_s \frac{\hbar}{2\pi},$$

where the quantum number  $m_s = \pm \frac{1}{2}$ , depending upon whether  $S_z$  is parallel or antiparallel to the z-axis. Thus

$$\begin{aligned}\mu_{eq} &= g_s \left( \frac{e}{2m} \right) m_s \frac{\hbar}{2\pi} \\ &= 2 \left( \frac{e}{2m} \right) \left( \pm \frac{1}{2} \right) \frac{\hbar}{2\pi} \\ &= \pm \frac{e\hbar}{4\pi m}.\end{aligned}$$

Now, the magnetic orientational potential energy of a dipole of moment  $\vec{\mu}_s$  in a magnetic field  $\vec{B}$  is given by

$$\begin{aligned}U_m &= - \vec{\mu}_s \cdot \vec{B} \\ &= - \mu_{sz} B,\end{aligned}$$

where  $\mu_{sz}$  is the scalar magnitude of  $\vec{\mu}_s$  in the direction of the magnetic field. Thus

$$U_m = \pm \frac{e\hbar}{4\pi m} B.$$

The difference in energy of electrons having spin parallel and antiparallel to the field is

$$\Delta U_m = \frac{e\hbar B}{4\pi m} - \left( - \frac{e\hbar B}{4\pi m} \right) = \frac{e\hbar B}{2\pi m}.$$

Substituting the known values of  $e$ ,  $\hbar$  and  $m$ ; and the given value of  $B$ , we get

$$\begin{aligned}\Delta U_m &= \frac{(1.60 \times 10^{-19} \text{ C}) \times (6.63 \times 10^{-34} \text{ Js}) \times (1.2 \text{ N/A-m})^*}{2 \times 3.14 \times (9.1 \times 10^{-31} \text{ kg})} \\ &= 2.23 \times 10^{-23} \text{ J}.\end{aligned}$$

But 1 eV =  $1.60 \times 10^{-19}$  J.

$$\therefore \Delta U_m = \frac{2.23 \times 10^{-23} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 1.39 \times 10^{-4} \text{ eV}.$$

4. An electron in a particular state of hydrogen atom has a magnetic potential energy of about  $10^{-23}$  J. Estimate the magnitude of the magnetic field acting on the spin magnetic moment of the electron which is of the order of 1 Bohr magneton.

**Solution.**

$$U_m = - \vec{\mu}_s \cdot \vec{B}.$$

So

$$|U_m| = \mu_s B.$$

Given :  $|U_m| = 10^{-23}$  J and  $\mu_s \sim \mu_B = 9.27 \times 10^{-24} \text{ A m}^2 \sim 10^{-23} \text{ A m}^2$ .

$$\begin{aligned}\therefore B &\sim \frac{10^{-23} \text{ J}}{10^{-23} \text{ A m}^2} \\ &\sim \frac{10^{-23} \text{ N m}}{10^{-23} \text{ A m}^2} \sim 1 \frac{\text{N}}{\text{A m}} \sim 1 \text{ tesla}.\end{aligned}$$

---

\* tesla =  $\frac{\text{weber}}{\text{m}^2} = \frac{\text{N}}{\text{A m}}$ .

**5. For an electron orbit with quantum number  $l = 2$ , state the possible values of the components of angular momentum along a specified direction.**

**Solution.** The component of total angular momentum along a specified direction ( $z$ -axis) is quantised, and takes values given by

$$J_z = m_j \frac{h}{2\pi},$$

where  $m_j$  is the magnetic quantum number corresponding to the inner quantum number  $j$ .

For the given electron, we have

$$l = 2 \text{ (d-electron)}$$

and, of course

$$s = \frac{1}{2}.$$

The two possible values of  $j$  are

$$j = l \pm s = 2 \pm \frac{1}{2} = 5/2 \text{ and } 3/2.$$

For  $j = 5/2$ , the possible values of  $m_j$  are

$$m_j = 5/2, 3/2, 1/2, -1/2, -3/2, -5/2.$$

For  $j = 3/2$ , the possible values of  $m_j$  are

$$m_j = 3/2, 1/2, -1/2, -3/2.$$

The values differ by integers. Thus, the possible values of the  $z$ -components of total angular momentum are

$$\pm \frac{5}{2} \left( \frac{h}{2\pi} \right), \pm \frac{3}{2} \left( \frac{h}{2\pi} \right), \pm \frac{1}{2} \left( \frac{h}{2\pi} \right).$$

**6. Calculate the possible orientations of the total angular momentum vector  $\vec{J}$  corresponding to  $j = 3/2$  with respect to a magnetic field along the  $z$ -axis.**

**Solution.** The magnitude of the total angular momentum and its  $z$ -component are quantised according to the relations

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

$$\text{and } J_z = m_j \frac{h}{2\pi}.$$

For  $j = 3/2$ , we have

$$m_j = 3/2, 1/2, -1/2, -3/2.$$

The angle  $\theta$  between  $\vec{J}$  and the  $z$ -axis is determined by  $m_j$  and  $j$ , according as

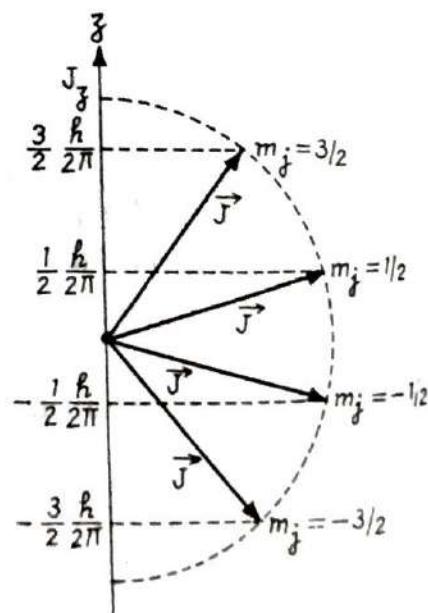
$$\cos \theta = \frac{J_z}{J} = \frac{m_j}{\sqrt{j(j+1)}}.$$

$$\text{Now } \sqrt{j(j+1)} = \sqrt{\frac{3}{2} \left( \frac{3}{2} + 1 \right)} = \frac{\sqrt{15}}{2}.$$

$$\therefore \cos \theta = \frac{2m_j}{\sqrt{15}}.$$

For  $m_j = 3/2, 1/2, -1/2, -3/2$ , we have

$$\cos \theta = 0.775, 0.258, -0.258, -0.775.$$



$$\therefore \theta = 39.2^\circ, 75.0^\circ, 105^\circ, 140.8^\circ.$$

The orientations of  $\vec{J}$  with respect to z-axis are shown in the figure.

**7. Determine the possible terms of a one-electron atom corresponding to  $n = 3$  and compute the angle between  $\vec{L}$  and  $\vec{S}$  vectors for the term  $^2D_{5/2}$ .**

**Solution.** For the principal quantum number  $n = 3$ , the orbital quantum number  $l$  can take the values :

$$l = 0, 1, 2,$$

and for an electron

$$s = \frac{1}{2},$$

so that the multiplicity is  $(2s + 1) = 2$ .

The possible values of the inner quantum number  $j$  are

$$j = l \pm s.$$

$$\text{For } l = 0, \quad j = 1/2$$

$$\text{For } l = 1, \quad j = 3/2, 1/2$$

$$\text{For } l = 2, \quad j = 5/2, 3/2.$$

Hence the possible terms are

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

For the state  $^2D_{5/2}$ , we have

$$l = 2, s = \frac{1}{2}, j = 5/2.$$

$$\therefore \cos(\vec{L}, \vec{S}) = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}$$

$$= \frac{\frac{35}{4} - 6 - \frac{3}{4}}{2\sqrt{6 \times \frac{3}{4}}} = 0.4714.$$

$$\therefore \text{angle}(\vec{L}, \vec{S}) = \cos^{-1}(0.4714) = 61.9^\circ.$$

**8. Calculate possible angles between  $\vec{L}$  and  $\vec{S}$  for a 'd' electron in one-electron atom.** (Meerut 2003 special paper)

**Solution.** For a 'd' electron, we have

$$l = 2$$

$$s = \frac{1}{2}.$$

and of course

The two possible values of  $j$  are

$$j = l \pm s = 5/2 \text{ and } 3/2.$$

The angle between  $\vec{L}$  and  $\vec{S}$  is given by

$$\cos(\vec{L}, \vec{S}) = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}.$$

For  $l = 2, s = \frac{1}{2}$  and  $j = 5/2$ , we have

$$\cos(\vec{L}, \vec{S}) = 0.4714 \quad (\text{as obtained in last problem})$$

$$\therefore \text{angle}(\vec{L}, \vec{S}) = \cos^{-1}(0.4714) = 61.9^\circ.$$

For  $l = 2$ ,  $s = \frac{1}{2}$  and  $j = 3/2$ , we have

$$\cos(\vec{L}, \vec{S}) = \frac{\frac{15}{4} - 6 - \frac{3}{4}}{2\sqrt{6}\sqrt{3/4}} = -\sqrt{\frac{1}{2}} = -0.7071.$$

$$\therefore \text{angle } (\vec{L}, \vec{S}) = \cos^{-1}(-0.7071) = 135^\circ.$$

The possible angles are  $61.9^\circ$  and  $135^\circ$ .

9. A beam of hydrogen atoms in a Stern-Gerlach experiment obtained from an oven heated to a temperature of 400 K passes through a magnetic field of length 1 meter and having a gradient of 10 tesla/m perpendicular to the beam. Calculate the transverse deflection of an atom of the beam at the point where the beam leaves the field. The value of the Bohr magneton  $\mu_B$  is  $9.27 \times 10^{-24} \text{ A m}^2$  and the Boltzmann constant  $k$  is  $1.38 \times 10^{-23} \text{ joule/K}$ .

**Solution.** The Stern-Gerlach deflection of an atom at a temperature of  $T$  kelvin in a magnetic field  $B$  of length  $d$  and transverse gradient  $\partial B_z / \partial z$  is

$$Z = g_j m_j \frac{\frac{\partial B_z}{\partial z} \mu_B d^2}{8 k T}.$$

At the oven temperature, the hydrogen atoms are in their ground state and have no orbital angular momentum ( $l = 0$ ), so that

$$j = s = \frac{1}{2},$$

$$m_j = m_s = \pm \frac{1}{2}$$

and

$$g_j = g_s = 2.$$

$$\therefore g_j m_j = \pm 1.$$

Hence

$$Z = \pm \frac{\frac{\partial B_z}{\partial z} \mu_B d^2}{8 k T}$$

$$= \pm \frac{10 \text{ N/A-m}^2 \times (9.27 \times 10^{-24} \text{ A m}^2) \times 1 \text{ m}^2}{8 \times (1.38 \times 10^{-23} \text{ J K}^{-1}) \times 400 \text{ K}}$$

$$= \pm 2.1 \times 10^{-3} \text{ m} = \pm 0.21 \text{ cm.}$$

The separation of the two components is 0.42 cm, which can be easily observed.

## QUESTIONS

- Derive an expression for the magnetic dipole moment of hydrogen atom, and find the value of Bohr magneton.
- Derive an expression for the Larmor precessional frequency. What is its importance? (Meerut 97, 90)
- Discuss the experimental evidence in support of electron spin. (Meerut 90)
- What is the basis of the origin of vector model of atom? What are its salient features. How are they experimentally verified? (Meerut 2003)

5. Discuss vector model of atom. What led to the assignment of quantum number  $1/2$  to the spin of electron ?  
 (Meerut 92)
6. Show that, if the angle between  $\vec{L}$  and  $\vec{S}$  vectors is  $\theta$ , then  

$$\cos \theta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}.$$
7. Describe Stern-Gerlach experiment. Discuss how it explained space quantisation and electron spin.  
 (Meerut 2003 special paper, 2001)

### PROBLEMS

1. An atomic magnetic dipole having orbital magnetic moment of 1 Bohr magneton is aligned parallel to an external magnetic field of 1 tesla. Calculate the energy required to turn the dipole to align it antiparallel to the field.

**Hint :**  $U = - \mu_l \cdot \vec{B}$ . The required energy is  $2 \mu_l B$ . The Bohr magneton is  $9.27 \times 10^{-24} \text{ A m}^2$ .

$$\text{Ans. } 1.16 \times 10^{-4} \text{ eV.}$$

2. Enumerate the possible values of  $j$  and  $m_j$  for states in which  $l = 3$  and  $s = 1/2$ .

**Ans.**  $j = 7/2; m_j = 7/2, 5/2, 3/2, 1/2, -1/2, -3/2, -5/2, -7/2$   
 and  $j = 5/2; m_j = 5/2, 3/2, 1/2, -1/2, -3/2, -5/2$ .

3. Write the values of quantum numbers  $l, s$  and  $j$  corresponding to each of the following one-electron terms :

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

**Ans.**  $(0, \frac{1}{2}, \frac{1}{2}), (1, \frac{1}{2}, \frac{1}{2}), (1, \frac{1}{2}, \frac{3}{2}), (2, \frac{1}{2}, \frac{3}{2}), (2, \frac{1}{2}, \frac{5}{2})$ .

4. Is  $^2D_{1/2}$  a possible term ? Why ?

**Ans.** No.

5. Compute the value of the total electronic angular momentum of a one-electron atom in the state  $^2D_{5/2}$ .

$$\text{Ans. } \frac{\sqrt{35}}{4\pi} h.$$

6. Calculate the angle between  $\vec{L}$  and  $\vec{S}$  vectors in the  $^2P_{3/2}$  state of a one-electron atom.

**Ans.**  $65.9^\circ$ .

7. Consider the states in which  $l = 4$  and  $s = \frac{1}{2}$ . Calculate the angle between  $\vec{J}$  and the + z-axis for the state with largest possible  $j$  and largest possible  $m_j$ .

**Ans.**  $25.2^\circ$ .

8. The lithium atom has one  $2s$  electron outside a filled inner shell. Its ground state is  $^2S_{1/2}$ . What are the term symbols of the other allowed states, if any ? Why would you think that the  $^2S_{1/2}$  state is the ground state ?

**Ans.** There are no other allowed states because for  $s$ -electron ( $l = 0$ ) there is only one possible value of  $j$ . This state corresponds to the lowest electron energy, hence it is the ground state.

9. Compute the field gradient of a 0.5 m-long Stern-Gerlach magnet that would produce a 1 mm separation at the end of the magnet between the two components of a beam of silver atoms emitted from an oven at  $960^\circ\text{C}$ . The magnetic dipole moment of silver is due to a single  $l = 0$  electron, just as for hydrogen. The Bohr magneton is  $0.928 \times 10^{-23} \text{ A m}^2$  and the Boltzmann constant is  $1.38 \times 10^{-23} \text{ J/K}$ .

**Ans.**  $29 \text{ T/m.}$

# Spin-Orbit Interaction : Hydrogen Fine Structure

Sommerfeld was the first who attempted to explain the observed fine-structure of hydrogen spectral lines by introducing the relativistic variation of mass of the electron moving in elliptic orbits. As we have seen, Sommerfeld was fairly successful in his mission. A more perfect account of the observed fine-structure is, however, given by quantum mechanics taking spin-orbit interaction as well as relativity correction into account. It is interesting to note that the quantum mechanical treatment leads to the same energy levels as the Sommerfeld orbital model.

## 1. Spin-Orbit Interaction

The spin-orbit interaction is an interaction between an electron's spin magnetic dipole moment and the *internal* magnetic field of an atom which arises from the orbital motion of the electron through the nuclear electric field. Since the internal magnetic field is related to the electron's orbital angular momentum, this is called the *spin-orbit interaction*. It is a relatively weak interaction but is responsible, partly, for the *fine-structure* of the excited states of one-electron atoms\*.

Let us write the electric field  $\vec{E}$ , in which the electron is moving, as a gradient of potential function  $V(r)$ ; where  $r$  is electron-nucleus distance.

$$\begin{aligned}\vec{E} &= \text{grad } V(r) \\ &= \frac{\vec{r}}{r} \frac{dV(r)}{dr}\end{aligned}$$

$\therefore \text{grad } r = \frac{\vec{r}}{r}$

The term  $\frac{\vec{r}}{r}$  is a unit vector in the radial direction which gives  $\vec{E}$  its proper direction.

The magnetic field in a reference frame fixed with the electron, arising from the orbital motion of the electron with velocity  $\vec{v}$  in the electric field  $\vec{E}$  (due to the nucleus) is given by

$$\begin{aligned}\vec{B} &= \frac{1}{c^2} (\vec{E} \times \vec{v}) \\ &= \frac{1}{c^2 r} \frac{dV(r)}{dr} (\vec{r} \times \vec{v}).\end{aligned}$$

Now, the orbital angular momentum of the electron is  $\vec{L} = m \vec{r} \times \vec{v}$ , so that the expression may be written as

$$\vec{B} = \frac{1}{m c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{L}$$

The electron and its spin magnetic moment  $\vec{\mu}_s$  can assume different orientations in the internal magnetic field  $\vec{B}$  of the atom, and its potential energy is different for different orientations. The expression for the magnetic potential energy of orientation is

\*The spin-orbit interaction occurs in multielectron atoms also, but in these atoms it is relatively strong because the internal magnetic field is quite strong.

$$\Delta E_{l,s} = - \vec{\mu}_s \cdot \vec{B}$$

But  $\vec{\mu}_s = -g_s \left( \frac{e}{2m} \right) \vec{S}$ , where  $g_s = 2$ . Therefore, the last expression can be written in terms of the electron's spin angular momentum  $\vec{S}$  as

$$\Delta E_{l,s} = \frac{e}{m} \vec{S} \cdot \vec{B}$$

Substituting for  $\vec{B}$  from above, we get

$$\Delta E_{l,s} = \frac{e}{m^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}$$

This is the energy in a frame of reference in which the electron is at rest. On relativistic transformation to the normal frame of reference in which the nucleus is at rest, the energy is reduced by a factor of 2. This is known as 'Thomas precession'. Taking this into account, the spin-orbit interaction energy is

$$\Delta E_{l,s} = \frac{e}{2m^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}$$

To express this in terms of quantum numbers  $l, s$  and  $j$ , we write

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

Taking the self dot product of this equality, we have

$$\begin{aligned} \vec{J} \cdot \vec{J} &= (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) \\ &= \vec{L} \cdot \vec{L} + \vec{S} \cdot \vec{S} + 2 \vec{S} \cdot \vec{L} \quad [\because \vec{L} \cdot \vec{S} = \vec{S} \cdot \vec{L}] \end{aligned}$$

So

$$\begin{aligned} \vec{S} \cdot \vec{L} &= \frac{1}{2} [\vec{J} \cdot \vec{J} - \vec{L} \cdot \vec{L} - \vec{S} \cdot \vec{S}] \\ &= \frac{1}{2} [J^2 - L^2 - S^2] \\ &= \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] \frac{\hbar^2}{4\pi^2} \end{aligned}$$

$$\text{Thus, } \Delta E_{l,s} = \frac{e\hbar^2}{16\pi^2 m^2 c^2} [j(j+1) - l(l+1) - s(s+1)] \frac{1}{r} \frac{dV(r)}{dr}$$

In general,  $\frac{1}{r} \frac{dV(r)}{dr}$  is not constant during the electron motion. Hence we must take its average value over the unperturbed motion. So

$$\Delta E_{l,s} = \frac{e\hbar^2}{16\pi^2 m^2 c^2} [j(j+1) - l(l+1) - s(s+1)] \overline{\frac{1}{r} \frac{dV(r)}{dr}} \quad \dots(i)$$

This is the general expression for the spin-orbit interaction energy of an atom. The average value  $\overline{\frac{1}{r} \frac{dV(r)}{dr}}$  is calculated by using the potential function  $V(r)$  for the given atom and the radial probability density for the state of interest.

For a hydrogen-like atom in which the electron moves in a Coulombian field, we have

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze}{r}$$

and so

$$\frac{dV(r)}{dr} = \frac{1}{4\pi\epsilon_0} \frac{Ze}{r^2}$$

Therefore, equation (i) can be written as

$$\Delta E_{l,s} = \frac{Z e^2 h^2}{4 \pi \epsilon_0 (16 \pi^2 m^2 c^2)} [j(j+1) - l(l+1) - s(s+1)] \frac{1}{r^3}$$

The average value of  $1/r^3$  is evaluated by using a generating function representation for the hydrogen radial eigenfunctions  $R_{n,l}(r)$ . The result is

$$\frac{1}{r^3} = \frac{Z^3}{a_0^3 n^3 l \left( l + \frac{1}{2} \right) (l+1)}, \text{ provided } l > 0$$

where  $a_0 \left( = 4 \pi \epsilon_0 \frac{h^2}{4 \pi^2 m e^2} \right)$  is the radius of the smallest Bohr orbit of the hydrogen atom. Introducing this value in the last expression, we get

$$\Delta E_{l,s} = \frac{Z e^2 h^2}{4 \pi \epsilon_0 (16 \pi^2 m^2 c^2)} \frac{Z^3}{a_0^3 n^3 l \left( l + \frac{1}{2} \right) (l+1)} [j(j+1) - l(l+1) - s(s+1)].$$

This equation is worked out to the following form :

$$\Delta E_{l,s} = \frac{R_\infty \alpha^2 Z^4 h c}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} [j(j+1) - l(l+1) - s(s+1)],$$

where  $R_\infty \left( = \frac{m e^4}{8 \epsilon_0^2 h^3 c} \right)$  is Rydberg constant for an infinitely heavy nucleus, and  $\alpha \left( = \frac{e^2}{2 \epsilon_0 h c} \right)$  is fine-structure constant.

The term shift due to spin-orbit interaction is

$$\begin{aligned} \Delta T_{l,s} &= - \frac{\Delta E_{l,s}}{h c} \\ &= - \frac{R_\infty \alpha^2 Z^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} [j(j+1) - l(l+1) - s(s+1)]. \quad \dots(ii) \end{aligned}$$

Now, for a hydrogen-like atom (single electron), we have

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

and so

$$j = l \pm s = l \pm \frac{1}{2}.$$

Making this substitution, we get

$$\begin{aligned} j(j+1) - l(l+1) - s(s+1) &= l && \text{for } j = l + \frac{1}{2} \\ &= -(l+1) && \text{for } j = l - \frac{1}{2} \end{aligned}$$

The term shifts corresponding to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  are

$$\Delta T_{l,s}' = - \frac{R_\infty \alpha^2 Z^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} l$$

and

$$\Delta T_{l,s}'' = \frac{R_\infty \alpha^2 Z^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} (l+1).$$

Thus, the spin-orbit interaction causes each term (energy level) of a given  $l$  to split into two terms of different  $j$ 's, one displaced upwards and the other downwards. The difference between them is

$$\begin{aligned}\Delta T &= \Delta T_{l,s}'' - \Delta T_{l,s}' \\ &= \frac{R_\infty \alpha^2 Z^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} (2l+1) \\ &= \frac{R_\infty \alpha^2 Z^4}{n^3 l (l+1)}.\end{aligned}$$

Taking  $R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$  and  $\alpha = 1/137$ , we get

$$\Delta T = 584 \frac{Z^4}{n^3 l (l+1)} \text{ m}^{-1}$$

$$\Delta T = 5.84 \frac{Z^4}{n^3 l (l+1)} \text{ cm}^{-1}$$

or  
Thus, the spin-orbit interaction splitting increases with increasing atomic number ( $Z$ ) and is smaller for higher  $n$  and higher  $l$ . It is zero for  $S$ -terms ( $l = 0$ ) for which  $j = \frac{1}{2}$  only.

## 2. Quantum Mechanical Relativity Correction

Besides the energy shifts due to spin orbit interaction, the relativistic effect is equally important as it produces energy shifts in the hydrogen atom comparable to those produced by spin-orbit interaction.

In order to calculate the relativistic shift, we consider the relativistic Hamiltonian function  $H$  of the electron. We know that

$$H = K + V,$$

where  $K$  is relativistic kinetic energy and  $V$  is potential energy. Now,  $K = (p^2 c^2 + m_0^2 c^4)^{1/2} - m_0 c^2$ , where  $p$  is linear momentum and  $m_0$  is rest mass of electron. Thus

$$\begin{aligned}H &= (p^2 c^2 + m_0^2 c^4)^{1/2} - m_0 c^2 + V \\ &= m_0 c^2 \left( 1 + \frac{p^2}{m_0^2 c^2} \right)^{1/2} - m_0 c^2 + V \\ &= m_0 c^2 \left( 1 + \frac{1}{2} \frac{p^2}{m_0^2 c^2} - \frac{1}{8} \frac{p^4}{m_0^4 c^4} + \dots \right) - m_0 c^2 + V \\ &= \frac{p^2}{2 m_0} - \frac{p^4}{8 m_0^3 c^2} + \dots + V.\end{aligned}$$

Thus, the change in Hamiltonian due to relativity is

$$-\frac{p^4}{8 m_0^3 c^2}.$$

This may be regarded as a perturbation term. The first-order energy shift can be found by evaluating its average value over the unperturbed wave function.

The equivalent differential operator of  $p$  is  $-\frac{i\hbar}{2\pi}\frac{\partial}{\partial q}$ . Therefore, the perturbed part of the quantum mechanical Hamiltonian operator would be

$$-\frac{1}{8m_0^3c^2}\left(-\frac{i\hbar}{2\pi}\frac{\partial}{\partial q}\right)^4$$

$$= -\frac{1}{8m_0^3c^2} \frac{\hbar^4}{16\pi^4} \nabla^4.$$

If  $\psi_0$  is the unperturbed wave function of the hydrogen atom, the first-order energy shift due to relativity is given by

$$\Delta E_r = - \int \psi_0^* \left( \frac{\hbar^4/16\pi^4}{8m_0^3c^2} \right) \nabla^4 \psi_0 d\tau.$$

On evaluating this integral, we obtain

$$\Delta E_r = -\frac{R_\infty \alpha^2 Z^4 h c}{n^3} \left( \frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right),$$

where  $R_\infty$  is the Rydberg constant and  $\alpha$  is the fine-structure constant. The relativistic term shift is

$$\Delta T_r = -\frac{\Delta E_r}{h c} = \frac{R_\infty \alpha^2 Z^4}{n^3} \left( \frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right).$$

### 3. Hydrogen Fine-structure

The first-order perturbation corrections due to different effects combine linearly. Therefore, the net term-shift due to spin-orbit interaction and the relativistic effect in a hydrogen-like atom is

$$\begin{aligned} \Delta T &= \Delta T_{l,s} + \Delta T_r \\ &= -\frac{R_\infty \alpha^2 Z^4}{2n^3 l \left( l + \frac{1}{2} \right) (l+1)} \left[ j(j+1) - l(l+1) - s(s+1) \right] \\ &\quad + \frac{R_\infty \alpha^2 Z^4}{n^3} \left( \frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right) \end{aligned}$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3} \left( \frac{1}{l + \frac{1}{2}} - \frac{j(j+1) - l(l+1) - s(s+1)}{2l \left( l + \frac{1}{2} \right) (l+1)} - \frac{3}{4n} \right)$$

where  $s = \frac{1}{2}$ . On substituting  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  in turn, we obtain

$$j(j+1) - (l+1) - s(s+1) = l$$

$$= -(l+1)$$

for  $j = l + \frac{1}{2}$

for  $j = l - \frac{1}{2}$

The net term-shifts corresponding to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  are therefore

$$\Delta T = \frac{R_{\infty} \alpha^2 Z^4}{n^3} \left( \frac{1}{l+1} - \frac{3}{4n} \right)$$

and

$$\Delta T = \frac{R_{\infty} \alpha^2 Z^4}{n^3} \left( \frac{1}{l} - \frac{3}{4n} \right).$$

Since  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$ , the last two equations can be replaced by a single equation

$$\Delta T = \frac{R_{\infty} \alpha^2 Z^4}{n^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right).$$

This equation is identical with Sommerfeld's relativistic equation for the energy levels of hydrogen-like atoms; namely

$$\Delta T = \frac{R_{\infty} \alpha^2 Z^4}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right),$$

except that  $k$  has been replaced by  $j + \frac{1}{2}$ . This equation was independently obtained by Dirac from a completely relativistic quantum mechanical treatment of the hydrogen-like atoms, and hence known as Dirac equation.

Let us now compare the energy levels of the hydrogen atom obtained from Sommerfeld's theory with those obtained from Dirac's theory. Taking  $R_{\infty} = 1.097 \times 10^7 \text{ m}^{-1}$ ,  $\alpha = 1/137$  and  $Z = 1$  (for hydrogen), we have

$$\Delta T = \frac{584}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right) \text{ m}^{-1} = \frac{5.84}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right) \text{ cm}^{-1} \quad \text{Sommerfeld Formula}$$

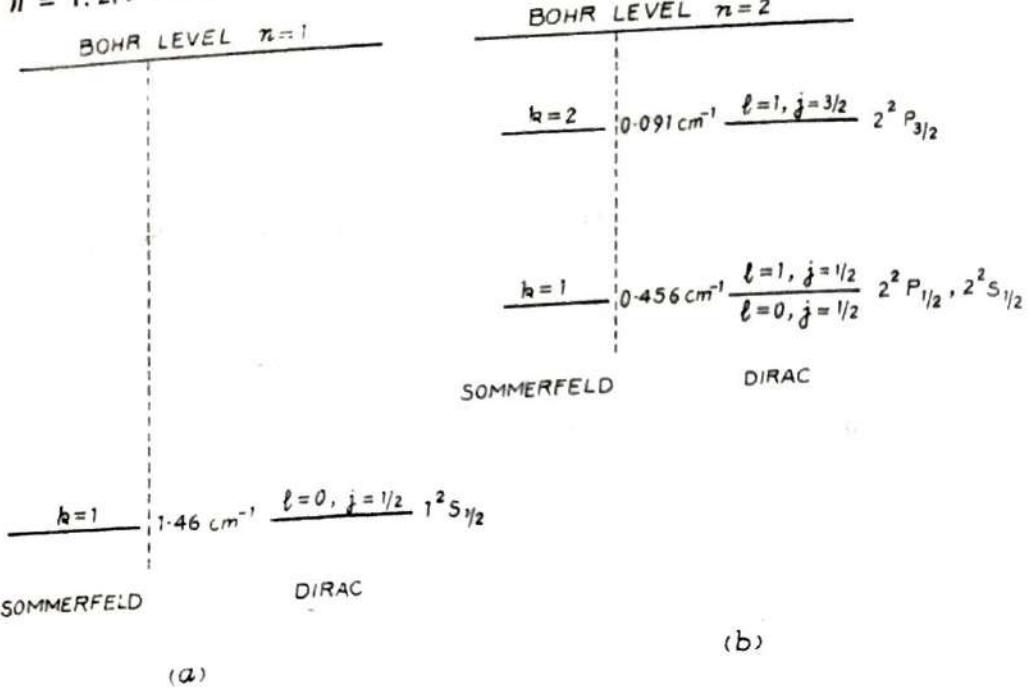
$$\text{and } \Delta T = \frac{584}{n^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \text{ m}^{-1} = \frac{5.84}{n^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \text{ cm}^{-1}. \quad \text{Dirac Formula.}$$

$\Delta T$  is the term-shift from the Bohr level. We consider Bohr levels corresponding to  $n = 1, 2, 3$ .

Bohr Level	Sommerfeld Levels		Dirac Levels		
	$n$	$k$	$\Delta T (\text{cm}^{-1})$	$l$	$j \left(= l \pm \frac{1}{2}\right)$
1	1	1	1.46	0	$\frac{1}{2}$
2	2	2	0.091	1	$\frac{3}{2}, \frac{1}{2}$
	1	1	0.456	0	$\frac{1}{2}$
3	3	3	0.018	2	$\frac{5}{2}, \frac{3}{2}$
	2	2	0.054	1	$\frac{3}{2}, \frac{1}{2}$
	1	1	0.162	0	$\frac{1}{2}$

The energy levels of hydrogen atom, as predicted by Bohr, Sommerfeld, and Dirac for  $n = 1, 2, 3$  are shown in Fig. 1 (a), (b) and (c) respectively. We see that the energy levels

BOHR LEVEL  $n=1$



(a)

BOHR LEVEL  $n=2$

$k=2$        $0.091 \text{ cm}^{-1}$        $\frac{l=1, j=3/2}{l=0, j=1/2}$        $2^2 P_{3/2}$

$k=1$        $0.456 \text{ cm}^{-1}$        $\frac{l=1, j=1/2}{l=0, j=1/2}$        $2^2 P_{1/2}, 2^2 S_{1/2}$

SOMMERFELD

DIRAC

SOMMERFELD

DIRAC

(b)

BOHR LEVEL  $n=3$

$k=3$        $0.018 \text{ cm}^{-1}$        $\frac{l=2, j=5/2}{l=2, j=3/2}$        $3^2 D_{5/2}$

$k=2$        $0.054 \text{ cm}^{-1}$        $\frac{l=2, j=3/2}{l=1, j=3/2}$        $3^2 D_{3/2}, 3^2 P_{3/2}$

$k=1$        $0.162 \text{ cm}^{-1}$        $\frac{l=1, j=1/2}{l=0, j=1/2}$        $3^2 P_{1/2}, 3^2 S_{1/2}$

SOMMERFELD

DIRAC

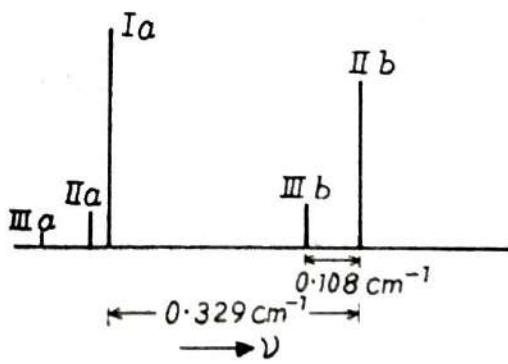
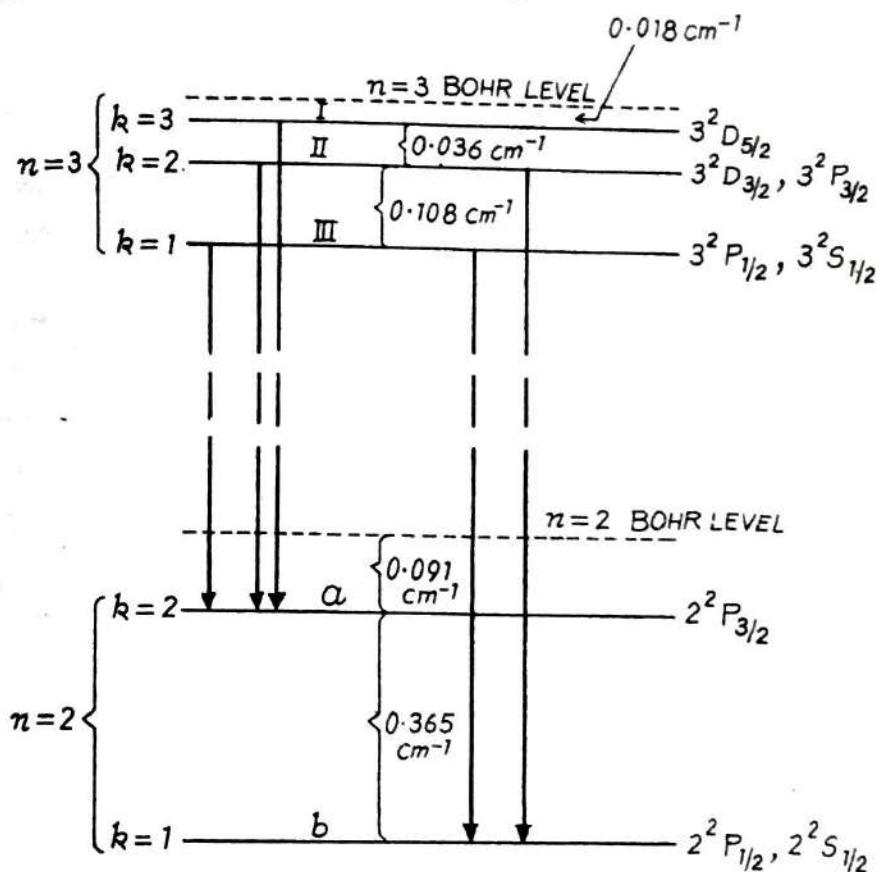
(c)

(Fig. 1)

due to Sommerfeld and those due to Dirac are essentially the same. This coincidence occurs for the hydrogen atom because the errors made by Sommerfeld in ignoring the spin-orbit interaction and in using classical mechanics to evaluate the energy shift due to relativity happen to cancel for the case of hydrogen atom.

The only difference between the results of the two theories is that Dirac, but not Sommerfeld, predicted a double-degeneracy of most levels, because the energy depends on the quantum numbers  $n$  and  $j$ , but not on the quantum number  $l$ . Generally there are two values of  $l$  corresponding to same  $j$ . Hence Dirac theory predicts that most levels are really double.

Let us now consider the fine-structure of  $H_{\alpha}$ -line ( $n = 3 \rightarrow n = 2$ ) on the basis of Dirac theory. The fine-structure energy levels, as deduced above, with proper spacings in terms of  $\text{cm}^{-1}$  and designations are drawn in Fig. 2.



(Theoretical Structure of  $H_{\alpha}$  as predicted by spin-relativity quantum-mechanical theory)

(Fig. 2)

The selection rules for dipole transitions are

$$\Delta l = \pm 1$$

$$\Delta j = 0, \pm 1 \text{ but } j = 0 \leftrightarrow j = 0.$$

These rules allow five transitions, resulting in five components spaced as shown in Fig. 2. The relative intensities of these components, as shown, have been calculated on the assumption that all the quantum states corresponding to  $n = 3$  are equally excited.

**Comparison with Experiment :** The theoretically deduced structure of the  $H_{\alpha}$  line has a general agreement with Hansan's observation. Still it is far from perfect agreement.

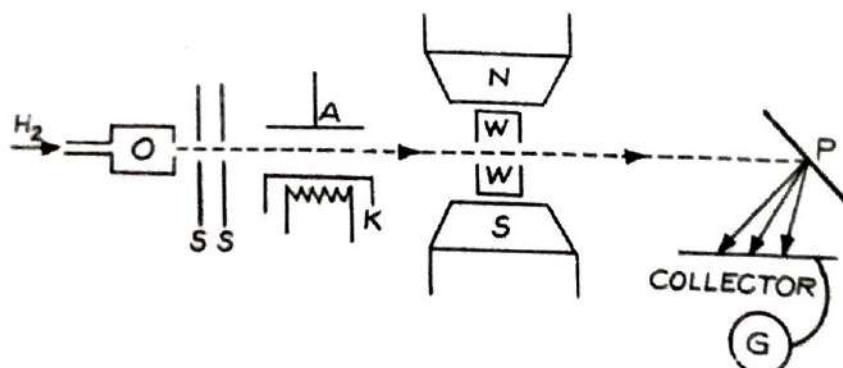
R.C. William extensively studied the fine-structure of the  $H_{\alpha}$  line, and also of the  $D_{\alpha}$  line, by using a triple-prism spectrograph and a microphotometer. He found two main differences between theory and experiment :

(i) The component I  $a$  was observed to be weaker than the component II  $b$ , which is in contradiction with theory. Similarly, the component III  $b$  was observed to be much more stronger than as predicted theoretically. These deviations could, however, be explained as due to unequal excitation of the  $n = 3$  levels.

(ii) The separation between the two main components I  $a$  and II  $b$  was observed to be  $0.319 \text{ cm}^{-1}$  against the theoretical separation of  $0.329 \text{ cm}^{-1}$ . Similarly, the separation between II  $b$  and III  $b$  was observed to be  $0.134 \text{ cm}^{-1}$  instead of  $0.108 \text{ cm}^{-1}$ .

**Lamb Shift** : Pasternack, in 1938, pointed out that the discrepancy in the separation between the main components of the  $H_{\alpha}$  line could be explained by assuming the state  $2^2S_{1/2}$  to be about  $0.03 \text{ cm}^{-1}$  higher than  $2^2P_{1/2}$ , in contradiction to Dirac's theory which had shown them to have exactly the same energy. Lamb and Rutherford, in 1947, proved the correctness of this assumption. They performed a microwave experiment on hydrogen atoms and showed that *for hydrogen-like atoms the states of a particular  $n$  value having terms with the same  $j$  value but different  $l$  values, such as  $2^2P_{1/2}$  and  $2^2S_{1/2}$ , are not degenerate, but are separated*. Such a separation is known as 'Lamb shift'.

The plan of the Lamb-Rutherford experiment is shown in Fig. 3. Molecular hydrogen ( $H_2$ ) entering an oven  $O$  was dissociated into atomic hydrogen which left the oven and



(Fig. 3)

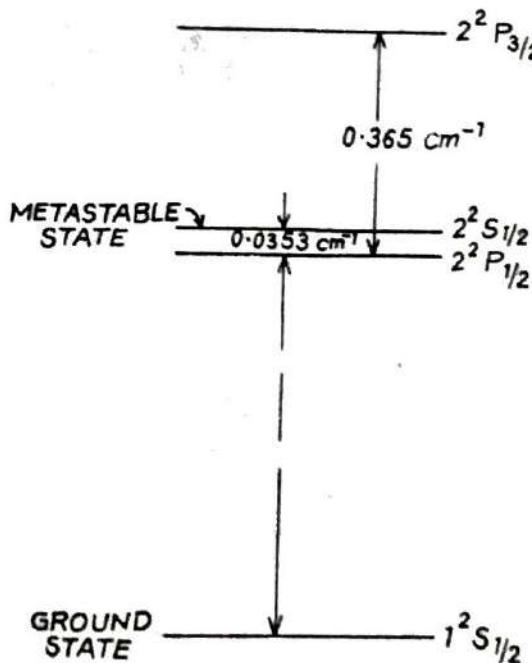
passed through slits  $S, S$ . This beam of hydrogen atoms passed through a vacuum diode in which electrons were being emitted from heated cathode  $K$  and accelerated toward anode  $A$ . Some of the normal atoms ( $1^2S_{1/2}$ ) passing through this region collided with the electrons and were excited into  $2^2S_{1/2}$ ,  $2^2P_{1/2}$  and  $2^2P_{3/2}$  states. These excited atoms proceeded toward a tungsten plate  $P$  and collided with it. During this journey the atoms in the  $2^2P_{1/2}$  and  $2^2P_{3/2}$  states returned to their ground state  $1^2S_{1/2}$ , but those in the (metastable) state  $2^2S_{1/2}^*$  could not do so because of the selection rule  $\Delta l \neq 0$ . These metastable atoms returned to their ground state by collision with the plate  $P$  from which,

\*The state  $2^2S_{1/2}$  is called a metastable state because decay from it to the ground state  $1^2S_{1/2}$  is forbidden by the selection rule  $\Delta l \neq 0$  and because all other states lie above it except the  $2^2P_{1/2}$  state which, according to the Dirac theory, coincides with it.

therefore, electrons were emitted. The stream of electrons so produced was collected and passed on to a galvanometer whose reading was a measure of the metastable atomic beam intensity.

Any mechanism which causes the metastable  $2^2S_{1/2}$  atoms to undergo a transition to the  $2^2P_{3/2}$  state will result in a fall in the galvanometer reading, which is sensitive only to metastable atoms. Such transitions were induced by passing the atoms through a waveguide WW in which microwaves of variable frequency were being generated.

It was found that at a certain frequency the metastable atomic beam intensity suddenly reduced. It was concluded that the microwaves of this frequency were absorbed by the  $2^2S_{1/2}$  atoms which were excited to the  $2^2P_{3/2}$  state from which they decayed at once to the ground state. Thus, the atoms reaching the tungsten plate were in their ground state and could not eject electrons from it. Hence this frequency was a measure of the term difference between  $2^2S_{1/2}$  and  $2^2P_{3/2}$  states. Such measurements showed that this difference was not  $0.365 \text{ cm}^{-1}$  (as predicted by Dirac) but  $0.0353 \text{ cm}^{-1}$  less. This meant that the state  $2^2S_{1/2}$  was higher than  $2^2P_{1/2}$  by  $0.0353 \text{ cm}^{-1}$  (Fig. 4).

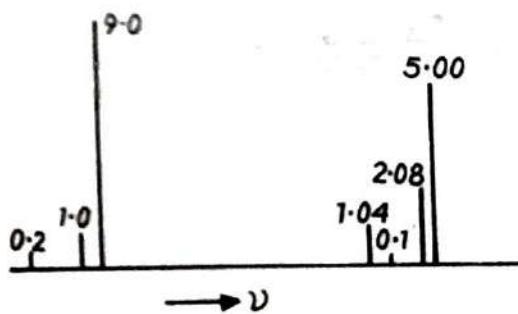
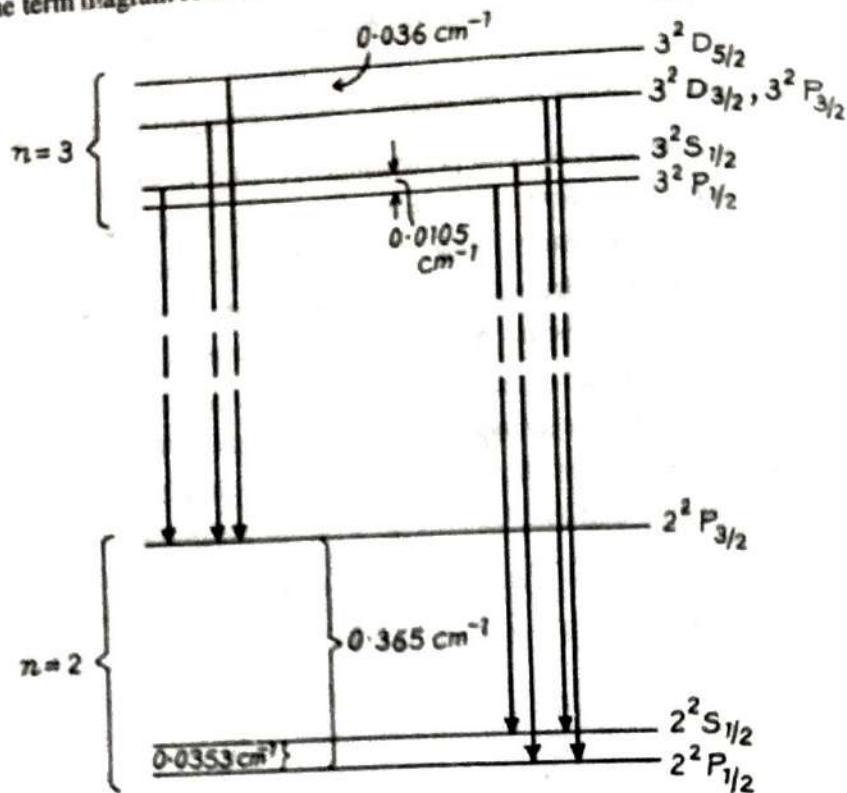


(Fig. 4)

In practice, instead of adjusting the frequency of the microwaves for maximum reduction in the metastable atomic beam intensity, the energy levels themselves are adjusted by means of a magnet NS, under Zeeman effect.

Soon after the discovery of this shift, Bethe showed that a revised theory of interaction between matter and radiation causes all S terms to be raised by an amount which agreed well with the experimental value for hydrogen. (Hence Lamb shift is also called as radiation shift).

The term diagram revised in the light of Lamb shift is drawn in Fig. 5.



(Fine structure of  $H_{\alpha}$  with Lamb shift)

(Fig. 5)

The line  $3^2P_{3/2} \rightarrow 2^2S_{1/2}$  thus no longer coincides exactly with  $3^2D_{3/2} \rightarrow 2^2P_{1/2}$ . If the  $3^2P_{3/2}$  and  $3^2D_{3/2}$  levels were equally excited, it can be calculated that the intensity ratio of these lines would be  $2.08 : 5.00$ , so that the two would actually be observed as a single line shifted by

$$\frac{2.08}{5.00} \times 0.0353 \text{ cm}^{-1} = 0.014 \text{ cm}^{-1},$$

which is in good agreement with William's observation of a separation of  $0.319 \text{ cm}^{-1}$  between the two main components I  $a$  and II  $b$  (Fig. 2).

## SOLVED PROBLEMS

- 1. If the doublet splitting of the first excited state,  ${}^2P_{3/2} - {}^2P_{1/2}$ , of  $\text{He}^+$  is  $5.84 \text{ cm}^{-1}$ , calculate the corresponding separation for H.** (Meerut 96 S, 90)

**Solution.** The doublet splitting (term difference) of a one-electron atomic state arising due to spin-orbit interaction is given by

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3 l(l+1)},$$

where  $R_\infty$  is Rydberg constant for infinitely heavy nucleus,  $\alpha$  is fine-structure constant and  $Z$  is atomic number.

For a given state ( $n, l$  constant), we have

$$\Delta T \propto Z^4.$$

Now, for  $\text{He}^+$ ,  $Z = 2$  and for H,  $Z = 1$

$$\therefore \frac{\Delta T_{\text{He}^+}}{\Delta T_{\text{H}}} = \frac{(2)^4}{(1)^4} = 16$$

or  $\Delta T_{\text{H}} = \frac{1}{16} \Delta T_{\text{He}^+} = \frac{1}{16} \times 5.84 \text{ cm}^{-1} = 0.365 \text{ cm}^{-1}$ .

- 2. The doublet splitting of the first excited state  ${}^2P_{3/2} - {}^2P_{1/2}$  of H atom is  $0.365 \text{ cm}^{-1}$ . Calculate the corresponding separation for  $\text{Li}^{++}$ .**

**Solution.**  $\Delta T \propto Z^4$ .

For  $\text{Li}^{++}$  and H,  $Z = 3$  and 1 respectively.

$$\therefore \frac{\Delta T_{\text{Li}^{++}}}{\Delta T_{\text{H}}} = \frac{(3)^4}{(1)^4} = 81$$

or  $\Delta T_{\text{Li}^{++}} = 81 \Delta T_{\text{H}} = 81 \times (0.365 \text{ cm}^{-1}) = 29.6 \text{ cm}^{-1}$ .

- 3. Calculate the spin-orbit interaction splitting of a level corresponding to  $n = 2$  and  $l = 1$  of hydrogen atom.**

**Solution.** The spin-orbit interaction splitting of an energy level is given by

$$\Delta T = 5.84 \frac{Z^4}{n^3 l(l+1)} \text{ cm}^{-1}.$$

Here  $n = 2, l = 1$  and  $Z = 1$  (for hydrogen atom).

$$\therefore \Delta T = 5.84 \left( \frac{1}{2^3 \times 1 \times 2} \right) = 0.365 \text{ cm}^{-1}.$$

## QUESTIONS

- Using first-order perturbation theory, derive an expression for the fine-structure splitting of an  $n/l$  level of a hydrogenic system due to spin-orbit interaction. (Meerut 96, special paper 92)
- Calculate the spin-orbit interaction energy for a single non-penetrating valence electron. (Meerut 2006, 02S, 00, special paper 92 S)
- The spin-orbit interaction causes each  $l$  level to split into two levels of different  $j$ . Calculate energy level shift in terms of  $l, s$  and  $j$  in case of one-electron atom. (Meerut 99 special paper)

4. How does the spin-orbit interaction when combined with the relativity correction, explain the hydrogen fine structure ? Discuss its limitations.  
(Meerut 2000 special paper, 90)
5. Derive an expression for the spin-orbit interaction energy. Draw energy level diagram for hydrogen atom, comparing the results of Bohr, Sommerfeld and Dirac theories.
6. Explain the effect of spin-orbit interaction on the structure of a spectral line. Discuss the fine structure of  $H_{\alpha}$  line.  
(Meerut 97 special paper)
7. Show the transitions from state  $n = 3$  to  $n = 2$  in case of hydrogen, following Bohr-Sommerfeld and Dirac theories.  
(Meerut 98 special paper)
8. Do  $2^2S_{1/2}$  and  $2^2P_{1/2}$  states of hydrogen atom have same energy ? Explain your answer.
9. What is Lamb shift ? Describe experimental arrangement to observe it. How is it explained ? What is its importance ?  
(Meerut 2002 special paper, 99)
10. Explain Lamb shift. How has it modified our knowledge about the spectrum of the hydrogen atom ?  
(Meerut 2002 special paper, 2000)

### PROBLEM

1. The doublet splitting for the first excited state  $^2P_{1/2} - ^2P_{3/2}$  of hydrogen atom is  $0.365 \text{ cm}^{-1}$ . Calculate the corresponding splitting for  $\text{He}^+$ .  
(Meerut 97, 96 special paper)

**Ans.**  $5.84 \text{ cm}^{-1}$

---

# 6

## Identical Particles : Pauli's Exclusion Principle

After hydrogen, we have to study the spectra of multielectron atoms starting from helium. For this, we must first consider the properties of quantum mechanical systems having several identical particles, such as electrons. This will lead us to the famous Pauli's exclusion principle which plays dominant part in determining the structure of multielectron atoms.

### 1. Identical Particles : Exchange Symmetry of Wave Functions

*If in a system of particles, on interchanging the position and the spin coordinates of any two particles, there is no physical way to know that a change has been made in the system, then the system is said to be consisted of 'identical' particles.*

There is a fundamental difference between the classical and the quantum mechanical descriptions of a system containing identical particles. In classical description we can assign labels to the identical particles. We can illustrate this by a specific example. Suppose a box contains two identical particles, say electrons. Classically, the electrons travel in sharply defined trajectories so that by observing the system constantly we can distinguish between them. That is, if at some instant we label the electrons as 1 and 2, we can constantly watch their motions without disturbing the system, and can tell at any later instant which electron is 1 and which is 2. This is, however, not possible in quantum-mechanical description of the system. The uncertainty principle does not allow us to observe constantly the motion of the electrons without disturbing the system. Any experiment can tell only that an electron was located at a given point at a certain instant but not *which one* it was. In other words, in quantum mechanics the finite extent of the wave function associated with each electron results in an overlapping of these wave functions and it becomes impossible to say which wave function was associated with which particle. Therefore, *a quantum-mechanical description of a system of identical particles should take into account the 'indistinguishability' of the 'identical' particles.* It should not depend on the assignment of labels to identical particles. This places a restriction upon the mathematical form of the wave functions required to describe a system of two or more identical particles.

Let us describe the above system (box with two electrons) quantum mechanically. We ignore the mutual interaction of the electrons. The Hamiltonian operator for the system can be written as the sum of the Hamiltonian operators for the individual electrons ( $\hat{H} = \hat{H}_1 + \hat{H}_2$ ), and the wave function can be written as a product of wave functions for the individual electrons. Thus,

$$\psi(1, 2) = \psi(1)\psi(2),$$

where 1, 2 represent the positional and the spin coordinates of electrons 1, 2 respectively. If the electron 1 is in a quantum state  $a$  (described by a particular set of space and spin

quantum numbers), and the particle 2 is in a state  $b$  (described by another set of quantum numbers), then the total wave function for the system would be

$$\psi(1, 2) = \psi_a(1)\psi_b(2).$$

We write it as

$$\Psi_{ab} = \psi_a(1)\psi_b(2). \quad \dots(i)$$

A wave function indicating that electron 1 is in state  $b$ , and electron 2 in state  $a$  would be

$$\Psi_{ba} = \psi_b(1)\psi_a(2). \quad \dots(ii)$$

The probability density functions for the systems described by the wave functions (i) and (ii) are

$$\Psi_{ab}^* \Psi_{ab} = \psi_a^*(1)\psi_b^*(2)\psi_a(1)\psi_b(2) \quad \dots(iii)$$

$$\text{and } \Psi_{ba}^* \Psi_{ba} = \psi_b^*(1)\psi_a^*(2)\psi_b(1)\psi_a(2). \quad \dots(iv)$$

But, since the two electrons are indistinguishable, we should be able to exchange their labels (that is, changing 1 into 2, and 2 into 1) without changing a physically measurable quantity such as the probability density. Let us make this change on the probability density function  $\Psi_{ab}^* \Psi_{ab}$  in eq. (iii). Then, we obtain

$$\psi_a^*(1)\psi_b^*(2)\psi_a(1)\psi_b(2) \xrightarrow[1 \rightarrow 2]{2 \rightarrow 1} \psi_a^*(2)\psi_b^*(1)\psi_a(2)\psi_b(1).$$

This leads to the probability-density function  $\Psi_{ba}^* \Psi_{ba}$  which is *different* from the original function  $\Psi_{ab}^* \Psi_{ab}$  [as is apparent from eq. (iii) and (iv)]. This means that a relabeling of the electrons *does* change the probability density function calculated from the wave function  $\Psi_{ab} = \psi_a(1)\psi_b(2)$ . The same is true for  $\Psi_{ba} = \psi_b(1)\psi_a(2)$ . Hence, the wave function described by eq. (i) and (ii) are *not* the proper wave functions for describing a system of two electrons.

We are in search of a proper form of the wave function that can describe accurately a system of identical particles. We shall just see that the total wave function describing a system of identical particles must be either symmetric or antisymmetric with respect to an exchange of the position and the spin coordinates of any two of them†. That is, the total wave function must possess the property of exchange-symmetry.

Let us consider a system of  $N$  identical particles with positional coordinates  $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_N, y_N, z_N)$ , and spin coordinates (z-components of spin angular momenta of particles)  $s_{z1}, s_{z2}, \dots, s_{zN}$ . The total (spatial + spin) wave function of the system is

$$\Psi(x_1, y_1, z_1, s_{z1}; x_2, y_2, z_2, s_{z2}; \dots; x_N, y_N, z_N, s_{zN}).$$

For abbreviation, we write it as

$$\Psi(1, 2, 3, \dots, N).$$

The Hamiltonian operator for the system will be

$$\hat{H} = -\frac{\hbar^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \dots + \nabla_N^2) + V(1, 2, 3, \dots, N).$$

If any two particles, say 1 and 2, are interchanged, the Hamiltonian becomes

† If the wave function remains unchanged or changes simply in sign on interchanging the position and the spin coordinates of any two particles, it is said to be symmetric or antisymmetric.

$$\hat{H}' = -\frac{\hbar^2}{8\pi^2 m} (\nabla_2^2 + \nabla_1^2 + \nabla_3^2 + \dots + \nabla_N^2) + V(2, 1, 3, \dots, N).$$

Since the potential energy must be same as before, (because the particles are identical in every way), we have

$$\hat{H}' \equiv \hat{H}$$

that is, *the Hamiltonian is invariant with respect to the positions and the spins of the particles*. This is called the 'exchange invariance' of the Hamiltonian.

Let us now define an exchange operator  $\hat{P}_{12}$  whose action is to interchange the position and the spin coordinates of any two particles, say 1 and 2, in any wave function of these coordinates, that is,

$$\hat{P}_{12} \psi(1, 2, 3, \dots, N) = \psi(2, 1, 3, \dots, N). \quad \dots(v)$$

Like parity-operator,  $\hat{P}_{12}$  also is a linear, Hermitian operator having eigenvalues  $\pm 1$  only, because

$$\hat{P}_{12} \psi = \alpha \psi \quad \dots(vi)$$

where  $\alpha$  is the eigenvalue. Operating once again

$$\hat{P}_{12}^2 \psi = \alpha^2 \psi.$$

But, by definition, the exchange operator applied twice brings the particles back to their original configuration and thus leaves the wave function unchanged, that is,

$$\hat{P}_{12}^2 \psi = \psi$$

so that

$$\alpha^2 = 1$$

or

$$\alpha = \pm 1.$$

Therefore, eq. (vi) is

$$\hat{P}_{12} \psi = \pm \psi$$

or

$$\hat{P}_{12} \psi(1, 2, 3, \dots, N) = \pm \psi(1, 2, 3, \dots, N).$$

Comparing this with eq. (v), we have

$$\psi(2, 1, 3, \dots, N) = \pm \psi(1, 2, 3, \dots, N).$$

Thus, the wave functions of  $\hat{P}_{12}$  have the property either of remaining unchanged or of changing sign when any two particles of the system are interchanged. That is, the wave functions are either symmetric or antisymmetric with respect to an exchange of the position and the spin coordinates of any two particles of the system. We have already seen that the Hamiltonian for a system of identical particles is invariant with respect to an exchange of any two of the particles. This means that the Hamiltonian and the exchange operator commute :

$$[\hat{H}, \hat{P}_{12}] \equiv \hat{H} \hat{P}_{12} - \hat{P}_{12} \hat{H} = 0.$$

Therefore, the wave functions of the Hamiltonian (that is, of the system) will also be the wave functions of  $\hat{P}_{12}$  and possess the property of exchange symmetry.

Those particles which can be described only by symmetric total wave functions are called 'Bose particles' or 'bosons'. Thus, for bosons, we have

$$\psi(1, 2, 3, \dots, N) = + \psi(2, 1, 3, \dots, N).$$

All particles having integral (including 0) spins are bosons. For example, photon (spin 1), deuteron (spin 1),  $\alpha$ -particle (spin 0), ground-state He atom (spin 0) are bosons.

On the other hand, those particles which can be described only by antisymmetric total wave functions are called 'Fermi particles' or 'fermions'. Thus, for fermions

$$\psi(1, 2, 3, \dots, N) = -\psi(2, 1, 3, \dots, N).$$

All particles having half-integral spins are fermions. Examples of fermions are electrons, protons, neutrons and  $\mu$ -mesons (all having spin  $\frac{1}{2}$ ).

This distinction between the two types of particles introduces many fundamental new physical effects such as superfluid state of liquid-helium, ferromagnetism, ortho and para hydrogen, and the Pauli's principle. We are interested in the last one.

## 2. Formulation of Pauli's Exclusion Principle

The very different chemical behaviours shown by elements whose atomic structures differ by just one electron (for example, F, Ne and Na which have 9, 10 and 11 electrons respectively) indicates that all the electrons of the atom cannot occupy the same quantum state; and that a given atom must have a certain electronic configuration. The fundamental principle governing the electronic configurations of atoms was discovered by Pauli (1925) according to which ***no two electrons in a multielectron atom can exist in the same quantum state***. This is known as Pauli's exclusion principle.

We can formulate the Pauli's principle on the basis of the exchange-symmetry of wave functions describing a system of identical particles. For simplicity, we consider a system of two identical particles and ignore their mutual interaction. The Hamiltonian operator for the system can be written as

$$\hat{H} = \left\{ -\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 + V(x_1, y_1, z_1, s_{z1}) \right\} + \left\{ -\frac{\hbar^2}{8\pi^2 m} \nabla_2^2 + V(x_2, y_2, z_2, s_{z2}) \right\} \\ = \hat{H}_1 + \hat{H}_2,$$

where  $\hat{H}_1$  and  $\hat{H}_2$  are the Hamiltonian operators for the separate *non-interacting* particles. The wave function for the 'system' can be expressed as a *product* of wave functions for the individual particles. Thus,

$$\psi(1, 2) = \psi(1)\psi(2).$$

Here the wave function  $\psi$  refers to the total wave function including both the spatial and the spin coordinates. If the particle 1 is in quantum state  $a$  and the particle 2 is in quantum state  $b$ , then the wave function of the system is

$$\psi_{ab}(1, 2) = \psi_a(1)\psi_b(2).$$

If the particle 1 is in state  $b$  and the particle 2 is in state  $a$ , then the wave function would be

$$\psi_{ba}(1, 2) = \psi_b(1)\psi_a(2).$$

Because the particles are *indistinguishable*, we cannot know whether at any moment  $\psi_{ab}$  or  $\psi_{ba}$  describes the system. Both have equal likelihood. Therefore, a linear combination of  $\psi_{ab}$  and  $\psi_{ba}$  is the proper description of the system. Thus

$$\psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)]$$

The factor  $\frac{1}{\sqrt{2}}$  is required to normalise the wave function  $\psi(1, 2)$ . This wave function describes a state of the system in which one particle is in state  $a$  and one in state  $b$ , but such that either of the two particles is equally likely to be found in either state. It satisfies the requirement of the wave function for identical particles because it is either symmetric (with + sign) or antisymmetric (with - sign) with respect to an exchange of coordinates of

the two particles. Thus, if the particles of the system are Bose particles, the proper wave function is

$$\Psi_{Bose}(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)], \quad \text{symmetric}$$

and if the particles are Fermi particles, the wave function is

$$\Psi_{Fermi}(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)], \quad \text{antisymmetric}$$

If we assume both particles to be in the same quantum state,  $a \equiv b$ , then we see that

$$\Psi_{Bose}(1, 2) \neq 0$$

but

$$\Psi_{Fermi}(1, 2) \equiv 0.$$

Thus, **whereas two Bose particles can exist in the same quantum state, two Fermi particles cannot**, because for Fermi particles the wave function vanishes identically. Therefore, we conclude that **two non-interacting Fermi particles cannot be in the same quantum state simultaneously, that is, they both cannot be described by the same set of quantum numbers**. Thus, Pauli's original statement of his exclusion principle that 'no two electrons in a multielectron atom can exist in the same quantum state' is a special case of the more general conclusion just drawn. (Electron is a Fermi particle).

We can alternatively say that if two particles are described by antisymmetric wave function, they cannot both be in the same quantum state. Thus, the property of electrons expressed by the exclusion principle is exactly the property of antisymmetric wave functions. This leads us to the statement that **a system containing several electrons must be described by an antisymmetric total wave function**. This is an alternative expression of the exclusion principle.

**Physical Significance :** If Pauli's principle were not obeyed, all electrons in an atom would have been in the lowest-energy state, having very high first-excited state. If this were so, all atoms would be inert and would not combine with other atoms to form molecules. Then the entire universe would be radically different. For instance, with no molecules there would be no compounds and hence no life.

### 3. Symmetry Character of Various Particles

The symmetry character of particles is settled by experiment. It is found that systems of electrons, protons, neutrons etc. must be described by antisymmetric total eigenfunctions; while systems of photons, helium atoms etc. must be described by symmetric total eigenfunctions. In the following table are listed several particles, their symmetry character and the values of their spin quantum number.

Particle	Symmetry	Generic Name	Spin ( $s$ )
electron	antisymmetric	fermion	1/2
positron	antisymmetric	fermion	1/2
proton	antisymmetric	fermion	1/2
neutron	antisymmetric	fermion	1/2
muon	antisymmetric	fermion	1/2
$\alpha$ -particle	symmetric	boson	0
He atom (ground state)	symmetric	boson	0
$\pi$ meson	symmetric	boson	0
photon	symmetric	boson	1
deuteron	symmetric	boson	1

We note that there is some connection between the symmetry character and spin. All antisymmetric particles have half-integral spin, while all symmetric particles have zero or integral spin. The symmetry character of a particle is a basic property (like mass, charge and spin) which is settled by experiment. However, the symmetry of a composite particle, like He atom, can be known from the symmetries of its constituents. If the composite particle has an even number of antisymmetric constituents, it is symmetric.

#### 4. Slater Determinant

An *antisymmetric* wave function for a system of two non-interacting (Fermi) particles can be written as a determinant :

$$\begin{aligned}\Psi_{\text{Fermi}}(1, 2) &= \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)] \\ &= \frac{1}{\sqrt{2}!} \begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix},\end{aligned}$$

where  $2! = 2 \times 1 = 2$ . Therefore, for a system of  $N$  non-interacting Fermi particles the antisymmetric energy wave function can be written as :

$$\Psi_{\text{Fermi}}(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \dots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \dots & \psi_b(N) \\ \vdots & \vdots & & \vdots \\ \psi_n(1) & \psi_n(2) & \dots & \psi_n(N) \end{vmatrix}$$

This is called a 'Slater determinant'. Since the value of this determinant consists of sums and differences of  $N!$  terms comprised of products of one-particle wave functions, such as  $\psi_a(1), \psi_b(2) \dots, \psi_n(N)$  and similar terms;  $\Psi_{\text{Fermi}}(1, 2, \dots, N)$  is simply a linear combination of degenerate wave functions. Hence  $\Psi_{\text{Fermi}}$  will also be a solution to the time-independent Schrodinger equation. The constant  $\frac{1}{\sqrt{N!}}$  is such that  $\Psi_{\text{Fermi}}$  will be normalised if each of the products of one-particle wave functions is normalised. Because a determinant vanishes if any two rows are identical, it is clear that  $\Psi_{\text{Fermi}}$  has the required property of vanishing if more than one particle are in the same quantum state (for example if  $a = b$ ).

If the interactions between the particles cannot be ignored, the antisymmetric wave function cannot be written as above, but can be obtained by taking sums and differences of the  $N!$  degenerate solutions to the time-independent Schrödinger equation. This wave function will still vanish identically if two particles are in the same quantum state.

#### SOLVED PROBLEMS

1. Let  $\Psi(1, 2) = A \left[ \psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2) \right]$ . Find the real value of  $A$  which normalises  $\Psi(1, 2)$  in this equation.

**Solution.** The general condition of normalisation is

$$\sum_{n=1}^{\infty} A_n^* A_n = 1.$$

Here there are two terms. Thus

$$\sum_{n=1}^2 A_n^* A_n = 1$$

or

$$A^* A + A^* A = 1.$$

For real values,  $A = A^*$ .

$$\therefore A^2 + A^2 = 1$$

or

$$A = \frac{1}{\sqrt{2}}.$$

**2. Determine the form of the normalised antisymmetric total wave-functions of three non-interacting particles.**

**Solution.** A two-particle normalised antisymmetric total wavefunction.

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)]$$

can also be written as a so called Slater determinant

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}!} \begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix},$$

where  $2! = 2 \times 1 = 2$ . The extension of this determinant to three particles 1, 2 and 3 is obvious :

$$\Psi_A(1, 2, 3) = \frac{1}{\sqrt{3}!} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) \\ \psi_c(1) & \psi_c(2) & \psi_c(3) \end{vmatrix}$$

where  $3! = 3 \times 2 \times 1 = 6$ .

**3. Write down the normalised wave function of a system of two Bose particles in the same quantum state, say  $a$ .**

(Meerut 98)

**Solution.** The total normalised wave function for two Bose particles 1 and 2 would be symmetric. Thus

$$\Psi_S(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)],$$

where  $\frac{1}{\sqrt{2}}$  is normalisation factor. If the particles are in the same quantum state  $a$ , then  $b = a$ , and we have

$$\begin{aligned} \Psi_S(1, 2) &= \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) + \psi_a(1)\psi_a(2)] \\ &= \sqrt{2}\psi_a(1)\psi_a(2). \end{aligned}$$

**4. Show that the total number of electrons in a shell is  $2n^2$ , where  $n$  is the principal quantum number of the shell.**

(Meerut 99)

**Solution.** The state of an electron can be described completely by a set of four quantum numbers such as  $n, l, m_l$  and  $m_s$ , where  $n$  is the principal quantum number.

For a given  $n$ , the azimuthal quantum number  $l$  can take the following values :

$$l = 0, 1, 2, 3, \dots, n-1.$$

For each  $l$ , the magnetic (orbital) quantum number  $m_l$  can take the values :

$$m_l = l, l-1, l-2, \dots, 0, \dots, -l,$$

that is, a total of  $(2l+1)$  values.

For each of these  $(2l + 1)$  values, the magnetic (spin) quantum number  $m_s$  can be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . Thus, for a given  $l$ , there are  $2(2l + 1)$  sets of quantum numbers  $m_l$  and  $m_s$ . Summing over the possible values of  $l$ , for a given  $n$ , the number of the possible sets of quantum numbers  $l$ ,  $m_l$  and  $m_s$

$$\begin{aligned} &= \sum_{l=0}^{n-1} 2(2l + 1) \\ &= 2[1 + 3 + 5 + 7 + \dots + 2(n - 1) + 1] \\ &= 2[1 + 3 + 5 + 7 + \dots + (2n - 1)] \\ &= 2 \times \frac{n}{2}[1 + (2n - 1)] \\ &= 2n^2. \end{aligned}$$

Since no two electrons can have the same set of quantum numbers, the maximum number of electrons for a given  $n$  is  $2n^2$ .

**5. If atoms could contain electrons with principal quantum numbers upto  $n = 6$ , how many elements would there be?** (Meerut 2000)

**Solution.** For a given  $n$ , the maximum number of electrons is  $2n^2$ .

$$\begin{array}{rcl} \text{For } n = 1, \text{ max. no. of electrons} &=& 2 \\ \text{For } n = 2, \text{ max. no. of electrons} &=& 8 \\ \text{For } n = 3, \text{ max. no. of electrons} &=& 18 \\ \text{For } n = 4, \text{ max. no. of electrons} &=& 32 \\ \text{For } n = 5, \text{ max. no. of electrons} &=& 50 \\ \text{For } n = 6, \text{ max. no. of electrons} &=& 72 \\ && \hline && 182 \end{array}$$

Hence, the number of elements would be 182.

## QUESTIONS

- What do you mean by identical particles? Show that the wave functions describing a system of identical particles must have the property of exchange-symmetry. (Meerut 2004 sp. paper, 2002, 96)
- Explain Pauli's exclusion principle in the light of antisymmetry of the wave function. (Meerut 99 sp. paper)
- What are symmetric and antisymmetric wave functions? State and Prove Pauli's exclusion principle on the basis of these functions. (Meerut 2003 sp. paper)
- State, explain and deduce Pauli's exclusion principle. What is its physical significance? (Meerut 2006, 02)
- State, explain and deduce Pauli's exclusion principle. Derive an expression for the maximum number of electrons that can go into a shell with its principal quantum number  $n$ . (Meerut 2004, 03, 02 sp. paper, 00 sp. paper, 96, 97)
- Write down a suitable wave function of an atom containing  $N$  electrons so that the wave function is completely antisymmetric and satisfies Pauli's principle. (Meerut 99, 98)

# Helium Atom and its Spectrum

## 1. Exchange Force

The quantum mechanical treatment of identical particles leads to a rather strange property of such particles which has no classical analogy. *Two identical particles, such as two electrons in the same atom or two neutrons (or protons) in the same nucleus, act as if they move under the influence of a force whose sign (attractive or repulsive) depends on the relative orientation of their spin.* This is called an 'exchange force'. For example, if in an atom the spins of two electrons are "parallel", the electrons act as if they repel each other. (This has nothing to do with the coulombian repulsion between the electrons). If, on the other hand, the spins are "antiparallel", the electrons act as if they attract each other.

Let us consider a system containing two electrons ; for example, He atom or  $\text{Li}^+$  ion. We ignore any interactions (like the coulomb interaction) between the electrons. According to Pauli's principle, the *total* wave function of the system must be antisymmetric with respect to the exchange of space and spin coordinates of the two electrons. The total wave function for the system can be written as a product of a space wave function and a spin wave function. That is

$$\Psi_{\text{total}} = \psi \beta,$$

where  $\psi$  is the space wave function\* and  $\beta$  is the spin wave function. The antisymmetry of the total wave function can be obtained by multiplying a symmetric space wave function with an antisymmetric spin wave function, or vice versa.

The normalised symmetric and antisymmetric *space* wave functions for a system of two electrons 1 and 2 have the *general* forms.

$$\frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)] \quad \text{symmetric}$$

and

$$\frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)], \quad \text{antisymmetric}$$

where the symbols  $a$  and  $b$  represent particular sets of *space* quantum numbers only.

We now write the forms of symmetric and antisymmetric spin wave functions. The spin coordinate is discrete (not continuous like space coordinate). For instance, the spin of a single electron can have only two discrete orientations relative to the  $z$ -axis, because its  $z$ -component has only two values given by

$$m_s \frac{\hbar}{2\pi}$$

where  $m_s = +\frac{1}{2}$  and  $= -\frac{1}{2}$ .

Therefore, for a system of two non-interacting electrons, each of which has only two possible spin wave functions  $\beta^+$  and  $\beta^-$  (say), there are only four possible spin states and

\*In the last chapter  $\psi$  was used for total wave function, but here it is being used for the space wave function alone.

so only four possible spin wave functions. We may write these wave functions in their normalised specific forms :

$$\left. \begin{aligned} & \beta_1^+ \beta_2^+ \\ & \frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- + \beta_1^- \beta_2^+]^\dagger \\ & \beta_1^- \beta_2^- \end{aligned} \right\} \text{symmetric (triplet states)}$$

$$\frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+]^\dagger \text{antisymmetric (singlet state)}$$

The first three are symmetric (interchanging the sub-scripts 1 and 2 makes no change in the wave function) and describe the so-called 'triplet' states of the system. The last one is antisymmetric (interchanging the sub-scripts 1 and 2 changes the sign) and describes the so-called singlet state.

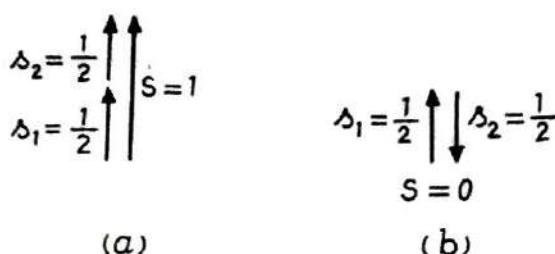
Let us have a physical interpretation of the triplet and the singlet states. The spin quantum number for each of the two electrons 1 and 2 is  $\frac{1}{2}$  ( $s_1 = \frac{1}{2}$ ,  $s_2 = \frac{1}{2}$ ). The magnitude of the spin angular momentum  $\vec{S}$  of the system is

$$|\vec{S}| = \sqrt{S(S+1)} \frac{\hbar}{2\pi},$$

where  $S$  takes all possible values from  $(s_1 + s_2)$  to  $(s_1 - s_2)$  differing by 1. Thus

$$S = 1, 0.$$

$S = 1$  corresponds to parallel electron spins (Fig. 1 a), while  $S = 0$  corresponds to antiparallel electron spins (Fig. 1 b).



(Fig. 1)

The  $z$ -component  $S_z$  of the spin angular momentum of the system is

$$S_z = M_S \frac{\hbar}{2\pi},$$

where the quantum number  $M_S$  takes all possible values from  $+S$  to  $-S$  differing by 1. That is,

$$M_S = 1, 0, -1 \quad \text{for } S = 1$$

$$\text{and} \quad M_S = 0 \quad \text{for } S = 0.$$

Thus, when the electron spins are parallel ( $S = 1$ ), there are three possible values of  $M_S$  which give rise to three possible spin states which are called 'triplet' states. When the electron spins are antiparallel ( $S = 0$ ), the only possible value for  $M_S$  is zero and the

†The wave functions  $\beta_1^+ \beta_2^-$  and  $\beta_1^- \beta_2^+$  have no definite symmetry. Hence we have made their linear symmetric and antisymmetric combinations.

spin state is called 'singlet' state. In other words, triplet states correspond to parallel spins, while the singlet state corresponds to antiparallel spins.

We can now explain the exchange force existing between two electrons of a system. If the spins of the two electrons are parallel, there are three possible spin wave functions which are all symmetric. In order to have the total wave function antisymmetric; the space wave function must therefore be antisymmetric, which is

$$\frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)],$$

where 1 and 2 represent the space coordinates of the electrons 1 and 2. Let us consider the situation when the electrons are close together, that is, their space coordinates have almost the same values. In this case,  $\psi_a(1) = \psi_a(2)$  and  $\psi_b(1) = \psi_b(2)$ . As a consequence

$$\psi_a(1)\psi_b(2) = \psi_b(1)\psi_a(2),$$

so that the antisymmetric space wave function has a value practically zero. The result is that the probability density will be very small. This means that there is little chance of finding two parallel-spin (triplet state) electrons close together, and the electrons act as if they repel each other.

On the other hand, if the spins of the two electrons are antiparallel, there is only one spin wave function which is antisymmetric. The corresponding space wave function must therefore be symmetric, which is

$$\frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)].$$

If the electrons happen to have almost the same space coordinates, that is,  $\psi_a(1) = \psi_a(2)$  and  $\psi_b(1) = \psi_b(2)$ , then the wave function becomes

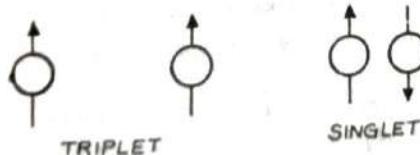
$$\sqrt{2} \psi_b(1)\psi_a(2).$$

Thus, the probability density will have the value

$$2 \psi_b^*(1)\psi_a^*(2)\psi_b(1)\psi_a(2),$$

which is twice the average probability density over all space. Thus, there is a large chance of finding two antiparallel-spin (singlet state) electrons close together, and the electrons act as if they attract each other.

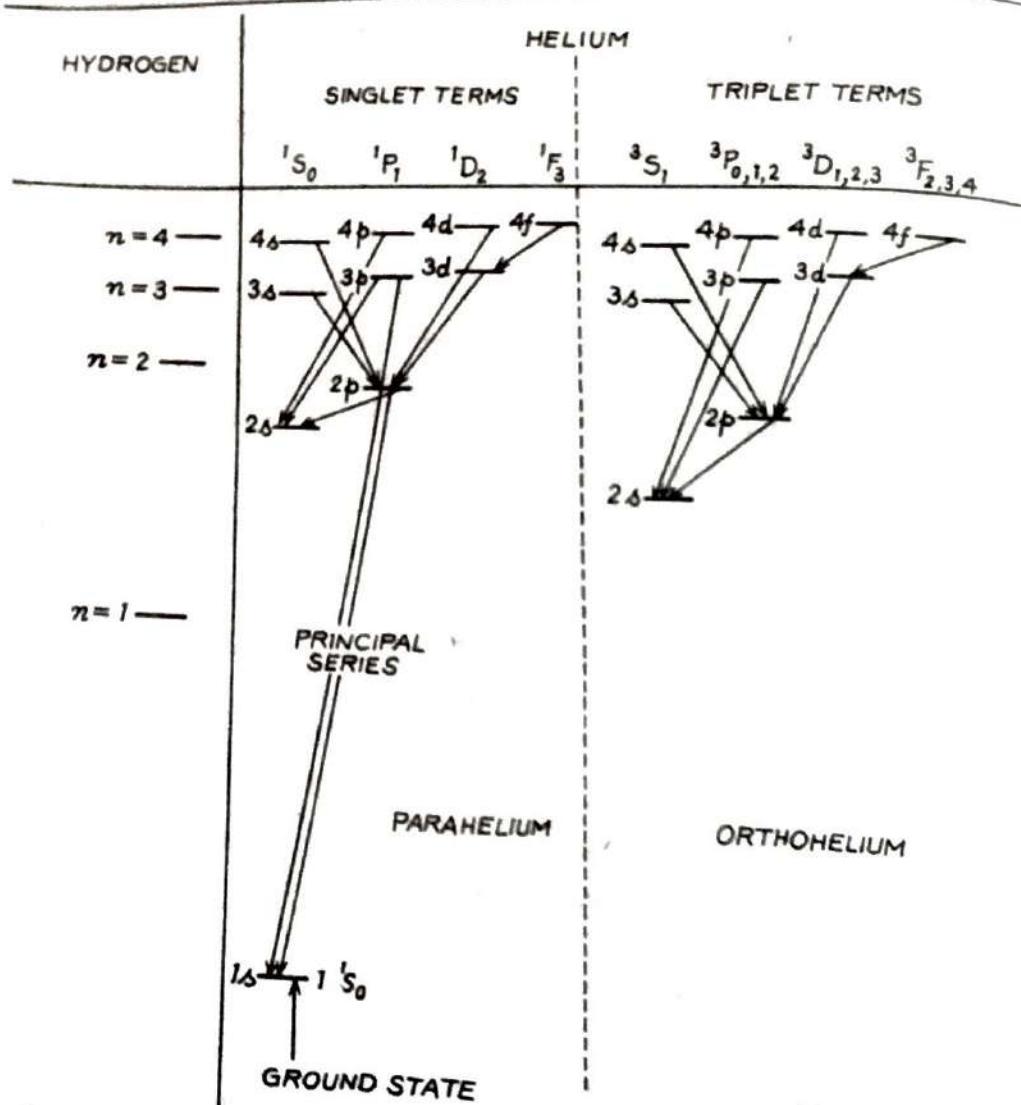
The triplet and the singlet cases for a system of two non-interacting electrons as He atom, are illustrated in Fig. 2. This quantum-mechanical effect is a consequence of the Pauli's principle that the total wave function of a system of two electrons must be antisymmetric.



(Fig. 2)

## 2. Spectrum of Helium

The emission spectrum of helium resembles the spectrum of a mixture of two alkali atoms. There are two each of the principal, sharp, diffuse and fundamental series, all having different limits. These can be analysed into two sets of terms, with no apparent relation between them. These are singlet and triplet terms, as shown in the energy-level diagram in Fig. 3.



(Fig. 3)

We note the following facts from this diagram :

- For each singlet energy state there is a corresponding triplet energy state, but there is no triplet state corresponding to the ground singlet state ( $1^1S_0$ ) of the He atom.
  - The triplet states lie a little deeper than the corresponding singlet states.
  - The energy difference between the ground state  $1^1S_0$  and the lowest excited state is relatively large.
  - The triplet states do not combine with the singlet states.
  - The experimental value of the ionisation potential of He, as obtained from the limit of the principal series ( $1^1S_0 - m^1P_1$ ) is 24.58 eV, and the total binding energy of the ground state of He is 78.98 eV.
- The division into non-combining singlet and triplet states gave rise to the idea that the helium occurs in two forms, parahelium and orthohelium. Atoms of the parahelium have antiparallel electron spins giving singlet states, while the atoms of the orthohelium have parallel electron spins giving triplet states. An orthohelium atom can lose excitation energy in a collision and become an atom of parahelium, while a parahelium atom can gain

excitation energy in a collision and become an atom of orthohelium. Ordinary helium is therefore a mixture of both. This explanation is partially correct. We now know that the splitting of the He terms into two practically non-combining systems follows from quantum mechanics.

### 3. Quantum-Mechanical Explanation of the Splitting of the Terms of He Atom

The He atom is a system of two electrons. The Pauli's requirement that its *total* wave function must be antisymmetric with respect to the exchange of the space and the spin coordinates of the two electrons, leads to a coupling between the two types of coordinates. The symmetric space function is coupled with the (single) antisymmetric spin function, and the antisymmetric space function is coupled with the (three) symmetric spin functions. Thus, the total wave functions of the He atom are of the form :

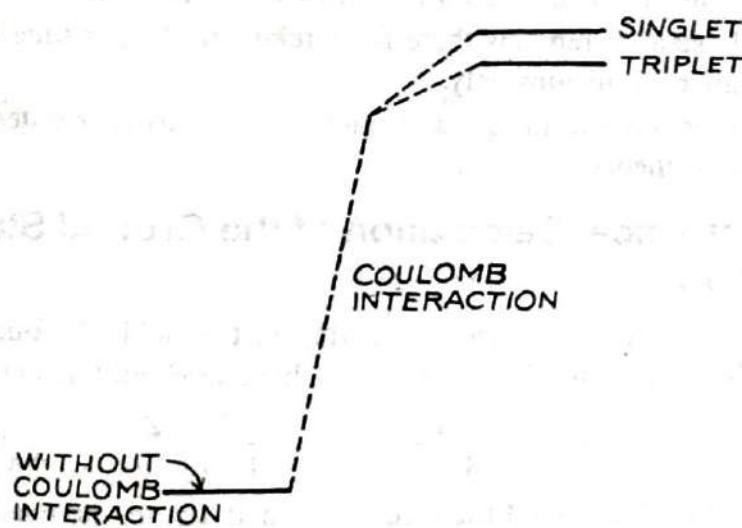
$$\frac{1}{\sqrt{2}} [\Psi_a(1) \Psi_b(2) + \Psi_b(1) \Psi_a(2)] \frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+] \quad \text{Singlet State (antiparallel spins)}$$

$$\frac{1}{\sqrt{2}} [\Psi_a(1) \Psi_b(2) - \Psi_b(1) \Psi_a(2)] \beta_1^+ \beta_2^+ \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Three Triplet States (parallel spins)}$$

$$\frac{1}{\sqrt{2}} [\Psi_a(1) \Psi_b(2) - \Psi_b(1) \Psi_a(2)] \frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- + \beta_1^- \beta_2^+] \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$\frac{1}{\sqrt{2}} [\Psi_a(1) \Psi_b(2) - \Psi_b(1) \Psi_a(2)] \beta_1^- \beta_2^- \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

The antisymmetric spin function gives rise to a singlet state, while the three symmetric spin functions give rise to three triplet states. All these four states are degenerate so long the coulomb interaction between the two electrons is ignored. This interaction, however, removes this so-called exchange-degeneracy. It *raises* (because the interaction energy is positive), and splits each state (except the ground state) into a singlet state and a 3-fold degenerate\* triplet state (Fig. 4). Thus, the singlet-triplet splitting of He terms is explained.



(Fig. 4)

For the ground state, however, both the electrons have the same space quantum numbers ( $a = b = 1s$ ) so that there is a single space wave function  $\Psi_{1s}(1) \Psi_{1s}(2)$

\*The triplet state is still 3-fold degenerate. This is spin-degeneracy which is removed when the atom is placed in an external magnetic field.

which is symmetric with respect to the exchange of electrons. This space function, to satisfy Pauli's principle, can be coupled only with the antisymmetric spin function  $\frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+]$ , which can give rise only to a singlet state. Hence, *the triplet state corresponding to the singlet ground state is missing*. Thus, the absence of triplet ground state is a consequence of Pauli's principle.

For all other states, triplet states exist along with the singlet states. In the triplet states, the electrons tend to keep apart, and in the singlet states they tend to keep together (Fig. 2). Therefore, the average distance between the two electrons,  $r_{12}$ , is larger in the triplet state than in the singlet state. Consequently, the coulomb interaction energy  $\frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{12}}$  is, on the average, less in the triplet state than in the singlet state. Hence, *the triplet energy states lie lower than the corresponding singlet states*.

Another feature of the He energy-level diagram is that the ground state level lies very much below the other energy levels. This is expected because in the ground state both electrons are in the innermost orbit and are attracted strongly by the nucleus. For all other states, one electron exists in a higher, approximately hydrogen-like, orbit. Thus, the inner electron moves in the field of the doubly-charged helium nucleus; whereas the outer electron moves in the field of a singly-charged nucleus (for the outer electron, the inner electron neutralizes one of the charges on the nucleus). Therefore, the ground helium level lies much deeper than the hydrogen ground level, but the excited helium levels agree closely with the corresponding hydrogen levels.

That the two sets of energy levels are non-combining, follows from the multiplicity selection rule  $\Delta S = 0$ . The lowest triplet state  $2^3S_1$  is highly metastable because an atom in this state cannot revert to the  $1^1S_0$  ground state by a spectroscopic transition because of the selection rules  $\Delta S = 0$  and  $\Delta l \pm 1$ . The  $2^1S_0$  state is also metastable because the selection rule  $\Delta l = \pm 1$  does not allow any transition to  $1^1S_0$ . Once the atom is in a metastable state, it remains there for a relatively longer time because it can return to the ground state by collisions only.

The energy of the He atom in the ground state and the various excited states can be calculated by perturbation theory.

#### 4. Quantum-Mechanical Calculation of the Ground State Energy of Helium Atom

For a system of two electrons, 1 and 2, moving in the field of a nucleus of charge  $+Ze$  (where  $Z = 2$  for helium), the quantum-mechanical Hamiltonian operator is

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_1} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_2} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{12}},$$

where  $r_1$  and  $r_2$  are the distances of the electrons 1 and 2 from the nucleus, and  $r_{12}$  is the distance between the electrons.  $\frac{e^2}{4\pi\epsilon_0 r_{12}}$  is the (positive) potential energy due to the coulomb (repulsive) interaction between the electrons. The magnetic spin-orbit and spin-spin interactions between the electrons have been ignored as these are very small compared to the coulomb interaction. The nuclear motion has also been neglected. The

terms  $-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_1}$  and  $-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_2}$  represent the potential energies of the two electrons due to their attraction by the nucleus. The wave equation for the helium-like atoms can thus be written as

$$\hat{H}\psi = \left[ -\frac{\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_1} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_2} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{12}} \right] \psi = E\psi. \quad \dots(i)$$

This equation can be solved by the perturbation method, where the term  $\frac{e^2}{4\pi\epsilon_0 r_{12}}$  may be chosen as perturbing potential. Thus, we put

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}} \text{ (perturbed part of the Hamiltonian).}$$

Now, we set

$$\hat{H} = \hat{H}^* + \hat{H}'.$$

The wave equation for the (unperturbed) ground state ( $1s\ 1s$ ) without electrostatic interaction, is

$$\hat{H}^* \psi^* = E^* \psi^*.$$

This is a non-degenerate state. Its wave function is the *product* of two ground-state hydrogen-like wave functions and its eigenvalue is the *sum* of the corresponding eigenvalues. That is,

$$\psi^* = \psi_{1s}^*(1) \psi_{1s}^*(2)$$

and

$$E^* = E_{1s}^*(1) + E_{1s}^*(2).$$

We know that the wave function for the ground state of hydrogen-like atom is

$$\psi_{1s}^* = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \text{ and the eigenvalue is } E_{1s}^* = -Z^2 E_H, \text{ where}$$

$$E_H = \frac{m e^4}{8 \epsilon_0^2 h^2} = 13.6 \text{ eV.}$$

Thus,

$$\psi^* = \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-\frac{Z}{a_0}(r_1 + r_2)}$$

and the unperturbed energy in the ground state is

$$\begin{aligned} E^* &= -2Z^2 E_H \\ &= -8 E_H, \text{ because } Z = 2 \text{ for He} \\ &= -8 \times (13.6 \text{ eV}) = -108.8 \text{ eV.} \end{aligned}$$

The experimental value of the ground state energy of He atom is  $-78.98 \text{ eV}$ , which is very much different from the calculated value ( $-108.8 \text{ eV}$ ) for the unperturbed ground state. This means that the unperturbed system provides a poor description of the energy levels, and the coulomb interaction between the two electrons plays an important role in the behaviour of He atom.

Let us now introduce the coulomb repulsion as a perturbation. The first-order perturbation energy, for non-degenerate states, is the quantum-mechanical average of the perturbed energy operator applied to the unperturbed wave function, and is given by

$$E' = \int \psi^* \hat{H}' \psi^* dt$$

$$\begin{aligned}
 &= \int \int \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-\frac{Z}{a_0}(r_1 + r_2)} \frac{e^2}{4\pi\epsilon_0 r_{12}} \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-\frac{Z}{a_0}(r_1 + r_2)} dr_1 dr_2 \\
 &= \frac{e^2}{\pi^2} \left( \frac{Z}{a_0} \right)^6 \int_0^\infty \int_0^\pi \int_0^{2\pi} \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{e^{-\frac{2Z}{a_0}(r_1 + r_2)}}{4\pi\epsilon_0 r_{12}} r_1^2 dr_1 \sin\theta_1 d\theta_1 d\phi_1 \\
 &\quad r_2^2 dr_2 \sin\theta_2 d\theta_2 d\phi_2.
 \end{aligned}$$

This integral, which represents the electrostatic energy of repulsion between two equal, spherically symmetrical charge-clouds, has been evaluated. It gives

$$\begin{aligned}
 E' &= \frac{5Ze^2}{32\pi\epsilon_0 a_0} = \frac{5}{4}Z \left( \frac{e^2}{8\pi\epsilon_0 a_0} \right) = \frac{5}{4}ZE_H^\dagger \\
 &= \frac{5}{4} \times 2 \times (13.6 \text{ eV}) = 34.0 \text{ eV}.
 \end{aligned}$$

Thus, to the first order perturbation correction, the total energy of the ground-state of helium-like atom is

$$\begin{aligned}
 E &= E^* + E' \\
 &= -108.8 \text{ eV} + 34.0 \text{ eV} \\
 &= -74.8 \text{ eV},
 \end{aligned}$$

which is in fair agreement with the experimental value (- 78.98 eV). There is an error of about 5%.

For the helium atom, the perturbation energy is  $\left(\frac{5}{16}\right)$ th of the zeroth-order energy :

$$\frac{E'}{E^*} = \frac{34.0 \text{ eV}}{108.8 \text{ eV}} = \frac{5}{16}.$$

This is not a 'small' perturbation. It means that the first-order perturbation theory cannot be expected to give very accurate results. For a greater accuracy, the variation method should be applied.

As we pass on to heavier two-electron helium-like atoms such as  $\text{Li}^+$ ,  $\text{Be}^{++}$ ,  $\text{B}^{+++}$ ,  $\text{C}^{++++}$ , the percentage error goes on decreasing. The reason is that as the nuclear charge increases, the interaction between the nucleus and the electrons becomes relatively more important than the mutual interaction between the electrons. So the perturbation becomes smaller and the perturbation calculation more accurate. For example, for  $\text{C}^{++++}$ , the theoretical value of 872.7 eV agrees very closely with the experimental value of 876.2 eV.

## 5. Prohibition of Intercombinations

For the lighter elements, in which the spin-orbit interaction is weak, the angular momentum vectors  $\vec{l}$  of individual electrons are tightly coupled to one another and form a resultant  $\vec{L}$ , and similarly the individual spin momentum vectors  $\vec{s}$  form a resultant  $\vec{S}$ . The vectors  $\vec{L}$  and  $\vec{S}$  are rather weakly coupled to form the total electronic angular momentum  $\vec{J}$  for the atom. In this case, the operator of the electric dipole moment, and

<sup>†</sup>  $E_H = \frac{m e^4}{8\epsilon_0^2 h^3}$  and  $a_0 = \frac{\hbar^2 \epsilon_0}{\pi m e^2}$ . Thus  $E_H = \frac{e^2}{8\pi\epsilon_0 a_0}$

also that of the electric quadrupole moment, commute with the spin operator and lead to the selection rule

$$\Delta S = 0,$$

both for the dipole and the quadrupole moments. This rule means that the states of different multiplicities cannot combine with one another. For He, which is a light element, this rule prohibiting intercombinations holds almost absolutely and as such no intercombination lines are observed in the helium spectrum.

In heavier elements, however, the spin-orbit interaction is large, so that the individual  $\vec{l}$  and  $\vec{s}$  vectors couple to give individual  $\vec{j}$  vectors which combine to give  $\vec{J}$ . In this case, the spin-orbit interaction term in the Hamiltonian is not negligible and is taken as a second order perturbation. It has the effect of "admixing" some of the singlet functions into the triplet functions (in case of two-electron atoms) and the selection rule  $\Delta S = 0$  forbidding intercombination of singlet and triplet terms tends to break down. The best known example of an intercombination line is the Hg resonance line of wavelength 2537 Å, corresponding to the transition  $^3P_1 \rightarrow ^1S_0$ . This is one of the strongest Hg lines, but it is considerably weaker than the corresponding non-intercombination line  $^1P_1 \rightarrow ^1S_0$  at  $\lambda = 1849$  Å. In Ca also, intercombination lines are observed.

## PROBLEM

**Construct the exchange symmetric wave functions (including spin) of the helium atom in the ground state and in the  $1s\ 2s$  excited state.**

**Solution.** The helium atom contains two electrons. Its ground-state electron configuration is  $1s\ 1s$  (or  $1s^2$ ). The normalised space wave function is

$$\frac{1}{\sqrt{2}} [\psi_{1s}(1)\ \psi_{1s}(2) + \psi_{1s}(1)\ \psi_{1s}(2)],$$

as both the electrons, 1 and 2, are in the  $1s$  quantum state. This can be written as

$$\sqrt{2} \psi_{1s}(1)\ \psi_{1s}(2).$$

This is a symmetric wave function. Hence it can be combined only with antisymmetric spin wave function so that the total wave function is antisymmetric as required by Pauli's principle. Thus, the total normalised wave function would be

$$\begin{aligned} & \left[ \sqrt{2} \psi_{1s}(1)\ \psi_{1s}(2) \right] \frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+] \\ &= [\psi_{1s}(1)\ \psi_{1s}(2)] [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+]. \end{aligned}$$

The excited state  $1s\ 2s$  can be described by two orthogonal, normalised symmetric and antisymmetric space wave functions of the following forms :

$$\frac{1}{\sqrt{2}} [\psi_{1s}(1)\ \psi_{2s}(2) + \psi_{2s}(1)\ \psi_{1s}(2)] \quad \text{symmetric}$$

$$\frac{1}{\sqrt{2}} [\psi_{1s}(1)\ \psi_{2s}(2) - \psi_{2s}(1)\ \psi_{1s}(2)] \quad \text{antisymmetric}$$

Now, according to Pauli's principle, the total wave function must be antisymmetric. Hence, the symmetric spatial wave function must be combined with antisymmetric spin wave function, and vice versa. Now, the total wave functions describing the  $1s\ 2s$  state have the following forms :

also that of the electric quadrupole moment, commute with the spin operator and lead to the selection rule

$$\Delta S = 0,$$

both for the dipole and the quadrupole moments. This rule means that the states of different multiplicities cannot combine with one another. For He, which is a light element, this rule prohibiting intercombinations holds almost absolutely and as such no intercombination lines are observed in the helium spectrum.

In heavier elements, however, the spin-orbit interaction is large, so that the individual  $\vec{l}$  and  $\vec{s}$  vectors couple to give individual  $\vec{j}$  vectors which combine to give  $\vec{J}$ . In this case, the spin-orbit interaction term in the Hamiltonian is not negligible and is taken as a second order perturbation. It has the effect of "admixing" some of the singlet functions into the triplet functions (in case of two-electron atoms) and the selection rule  $\Delta S = 0$  forbidding intercombination of singlet and triplet terms tends to break down. The best known example of an intercombination line is the Hg resonance line of wavelength 2537 Å, corresponding to the transition  $^3P_1 \rightarrow ^1S_0$ . This is one of the strongest Hg lines, but it is considerably weaker than the corresponding non-intercombination line  $^1P_1 \rightarrow ^1S_0$  at  $\lambda = 1849$  Å. In Ca also, intercombination lines are observed.

## PROBLEM

**Construct the exchange symmetric wave functions (including spin) of the helium atom in the ground state and in the  $1s\ 2s$  excited state.**

**Solution.** The helium atom contains two electrons. Its ground-state electron configuration is  $1s\ 1s$  (or  $1s^2$ ). The normalised space wave function is

$$\frac{1}{\sqrt{2}} [\psi_{1s}(1)\ \psi_{1s}(2) + \psi_{1s}(1)\ \psi_{1s}(2)],$$

as both the electrons, 1 and 2, are in the  $1s$  quantum state. This can be written as

$$\sqrt{2} \psi_{1s}(1)\ \psi_{1s}(2).$$

This is a symmetric wave function. Hence it can be combined only with antisymmetric spin wave function so that the *total* wave function is antisymmetric as required by Pauli's principle. Thus, the total normalised wave function would be

$$\begin{aligned} & [\sqrt{2} \psi_{1s}(1)\ \psi_{1s}(2)] \frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+] \\ &= [\psi_{1s}(1)\ \psi_{1s}(2)] [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+]. \end{aligned}$$

The excited state  $1s\ 2s$  can be described by two orthogonal, normalised symmetric and antisymmetric space wave functions of the following forms :

$$\frac{1}{\sqrt{2}} [\psi_{1s}(1)\ \psi_{2s}(2) + \psi_{2s}(1)\ \psi_{1s}(2)] \quad \text{symmetric}$$

and  $\frac{1}{\sqrt{2}} [\psi_{1s}(1)\ \psi_{2s}(2) - \psi_{2s}(1)\ \psi_{1s}(2)] \quad \text{antisymmetric}$

Again, according to Pauli's principle, the total wave function must be antisymmetric. Hence, the symmetric spatial wave function must be combined with antisymmetric spin wave function, and vice versa. Now, the total wave functions describing the  $1s\ 2s$  state have the following forms :

$$\frac{1}{\sqrt{2}} \left[ \psi_{1s}(1) \psi_{2s}(2) + \psi_{2s}(1) \psi_{1s}(2) \right] \frac{1}{\sqrt{2}} \left[ \beta_1^+ \beta_2^- - \beta_1^- \beta_2^+ \right] {}^1S_0$$

$$\frac{1}{\sqrt{2}} \left[ \psi_{1s}(1) \psi_{2s}(2) - \psi_{2s}(1) \psi_{1s}(2) \right] \left[ \beta_1^+ \beta_2^+ \right] \left. \begin{array}{l} \\ \\ \end{array} \right\} {}^3S_1$$

$$\frac{1}{\sqrt{2}} \left[ \psi_{1s}(1) \psi_{2s}(2) - \psi_{2s}(1) \psi_{1s}(2) \right] \frac{1}{\sqrt{2}} \left[ \beta_1^+ \beta_2^- + \beta_1^- \beta_2^+ \right]$$

$$\frac{1}{\sqrt{2}} \left[ \psi_{1s}(1) \psi_{2s}(2) - \psi_{2s}(1) \psi_{1s}(2) \right] \beta_1^- \beta_2^-$$

The first corresponds to the  ${}^1S_0$  term, while the remaining three correspond to the  ${}^3S_1$  term (3-fold spin degeneracy).

### QUESTIONS

1. Write down the symmetric and antisymmetric combinations of spin functions of a two-electron system. Set up an antisymmetric wave function for the ground state of helium atom. (Meerut 99 sp. paper)
2. Discuss the energy-level diagram of helium atom. Under what condition both the helium electrons would undergo transition to a higher state? (Meerut 2004 S, 92)
3. Discuss the salient features of the spectrum of the helium atom. How is the spectrum explained quantum mechanically? In what respect does it differ from the spectrum of hydrogen atom? (Meerut 2004, 03, 02S, 01, 00, 04 sp. paper)
4. State Pauli's principle and hence show that the helium atom in its ground state can exist only in singlet state. (Meerut 2006, 03, 01, 99, 96, 95, 04 sp. paper)
5. Explain the occurrence of ortho and para states of He atom. (Meerut 2002 sp. paper, 90)
6. Explain He atom spectrum quantum mechanically. Why does the ground He level lie much deeper than the H ground level, but the excited He levels agree closely with the corresponding H levels. (Meerut 95 sp. paper)
7. Calculate the energy of helium atom in its ground state. (Meerut 97 sp. paper)
8. Account for: The transition from  ${}^1P$  to  ${}^3S$  state in helium is forbidden.

# Multi-electron Atoms : Hartree's Field : Atomic Ground States and Periodic Table

## 1. Multi-electron Atoms in Schroedinger's Theory : Central Field Approximation : Hartree's Self-Consistent Field

A multi-electron atom of atomic number  $Z$  contains a nucleus of charge  $+Ze$ , surrounded by  $Z$  electrons, each of charge  $-e$ . Each electron moves under a strong attractive coulomb force exerted by the nucleus, and a comparatively weaker repulsive coulomb force exerted by the remaining  $(Z - 1)$  electrons, and also certain, still weaker spin forces. The Schroedinger's equation for such a system is too complicated to be solved exactly. The system can, however, be treated by using a method of successive approximations.

In the first approximation, each of the  $Z$  electrons in the atom is assumed to move *independently* in a spherically-symmetrical *net* potential  $V_i(r_i)$ , where  $r_i$  is the radial coordinate of the  $i$ th electron with respect to the nucleus. This is called 'central field approximation'. The net potential is the sum of the spherically-symmetrical potential due to the coulomb attraction by the nucleus, and the *spherically-averaged* potential due to the coulomb repulsion by the remaining  $Z - 1$  electrons. The latter, however, depends on the average radial probability densities of the electrons which are not known until solutions to the Schroedinger's equation of the system are obtained. This would make the determination of the net potential  $V_i(r_i)$  impossible.

Hartree, in 1928, overcame the difficulty by introducing a 'self-consistent field method' for determining the net potential. To understand this method, let us first write the Schroedinger's equation for a system of  $Z$  electrons moving *independently* in the atom :

$$-\frac{\hbar^2}{8\pi^2 m} \sum_{i=1}^Z \nabla_i^2 \psi + \sum_{i=1}^Z V_i(r_i) \psi = E \psi. \quad \dots(i)$$

Here  $E$  is the total energy of the atom and  $\psi$  is the wave function describing the motion of all the  $Z$  electrons, that is,  $\psi$  is

$$\psi(r_1, \theta_1, \phi_1, \dots, r_i, \theta_i, \phi_i, \dots, r_Z, \theta_Z, \phi_Z).$$

The spin has been ignored. Since the electrons have been assumed to move independently, the solution of equation (i) may be expected as a product of one-electron eigenfunctions :

$$\Psi = \Psi_1(r_1, \theta_1, \phi_1) \dots \Psi_i(r_i, \theta_i, \phi_i) \dots \Psi_Z(r_Z, \theta_Z, \phi_Z). \quad \dots(ii)$$

Thus, equation (i) can be splitted into  $Z$  one-electron equations, such as

$$-\frac{\hbar^2}{8\pi^2 m} \nabla_i^2 \Psi_i(r_i, \theta_i, \phi_i) + V_i(r_i) \Psi_i(r_i, \theta_i, \phi_i) = E_i \Psi_i(r_i, \theta_i, \phi_i). \quad \dots(iii)$$

Here  $\psi_i$  is the wave function for the  $i$  th electron and  $E_i$  its total energy. Initially  $V_i(r_i)$  is not known and so equation (iii) cannot be solved directly. It is here that the self-consistent method is employed in the following steps :

I. A set of trial eigenfunctions  $\psi_i^0$  is assumed for the atomic electrons on the basis of any previous knowledge, say Thomas Fermi model of the atom. The total eigenfunction is expressed as a product of these eigenfunctions :

$$\psi^0 = \psi_1^0 \psi_2^0 \dots \psi_i^0 \dots \psi_z^0.$$

II. From these approximate eigenfunctions, the approximate potential fields are evaluated. To evaluate, for example, the potential field  $V_i^0(r_i)$  acting on the  $i$  th electron, the spherically-symmetrical (that is, only  $r$ -dependent) charge density  $\rho_i(r)$  due to the remaining electrons is first found. This is equal to the product of the electronic charge  $e$  and the spherical average of the probability density  $\psi^0 * \psi^0$ . That is,

$$\rho_i(r) = \frac{e}{4\pi r^2} \int_0^\pi \int_0^{2\pi} \sum_{\substack{j=1 \\ j \neq i}}^Z \psi_j^0 * \psi_j^0 r^2 \sin \theta d\theta d\phi.$$

To this spherically-symmetrical electron charge density is added the spherically-symmetrical charge density due to the nucleus, to obtain the total charge density as seen by the  $i$  th electron in the atom. Gauss' law of electrostatics is then used to evaluate the approximate net potential  $V_i^0(r_i)$  experienced by the  $i$  th electron.

III. These approximate potentials  $V_i^0(r_i)$  are substituted in one-electron equations (iii) which are then solved by numerical integration. This yields a new eigenfunction  $\psi_i^1$  for each electron. The new set of eigenfunctions

$$\psi_1^1 \psi_2^1 \dots \psi_i^1 \dots \psi_z^1$$

is found to be different from the initial set  $\psi_1^0 \psi_2^0 \dots \psi_i^0 \dots \psi_z^0$ .

IV. The steps II and III are repeated starting with the new set  $\psi_1^1 \psi_2^1 \dots \psi_i^1 \dots \psi_z^1$ , obtaining more accurate net potentials  $V_i^1(r_i)$  and coming out with a fresh set  $\psi_1^2 \psi_2^2 \dots \psi_i^2 \dots \psi_z^2$ . Again, this is different from the starting set  $\psi_1^1 \psi_2^1 \dots \psi_i^1 \dots \psi_z^1$  but the difference is now smaller.

V. The above process is repeated again and again until the "output" eigenfunctions are identical with the "input" eigenfunctions. The final form of  $V_i(r_i)$  which leads to this result is the self-consistent net potential, and the eigenfunctions calculated from this potential describe the motion of the electrons in the ground state of the multi-electron atom.

Hartree's self-consistent field method (or central field approximation) is, however, not free from limitations. (i) Firstly, Hartree considered only the strongest interactions felt by the atomic electrons. The weaker interactions cannot always be ignored. (ii) Secondly, the (total) eigenfunction describing the motion of all the  $Z$  electrons in the atom must be antisymmetric (Pauli's condition). This would involve a linear combination of  $Z!$  terms, making the procedure extremely difficult. Hartree wrote the total eigenfunctions as a simple product (eq. ii) having no definite symmetry. Fock made calculations using antisymmetric total eigenfunctions for certain atoms and showed that **Hartree's results describe satisfactorily the ground state of complex atoms, but not the excited states.** As such Hartree's theory fails to explain the complex spectra of atoms.

## 2. Results of Hartree Theory

Hartree assumed that the electrons in a multi-electron atom move *independently* in a spherically symmetrical net potential field. The eigenfunctions for such an electron are found to be closely related to the eigenfunctions for the electron in a one-electron (hydrogen-like) atom. In fact, Hartree eigenfunctions can be written as

$$\Psi_{n, l, m_l, m_s}(r, \theta, \phi) = R_{n, l}(r) \Theta_{l, m_l}(\theta) \Phi_{m_l}(\phi) \beta_{m_s}$$

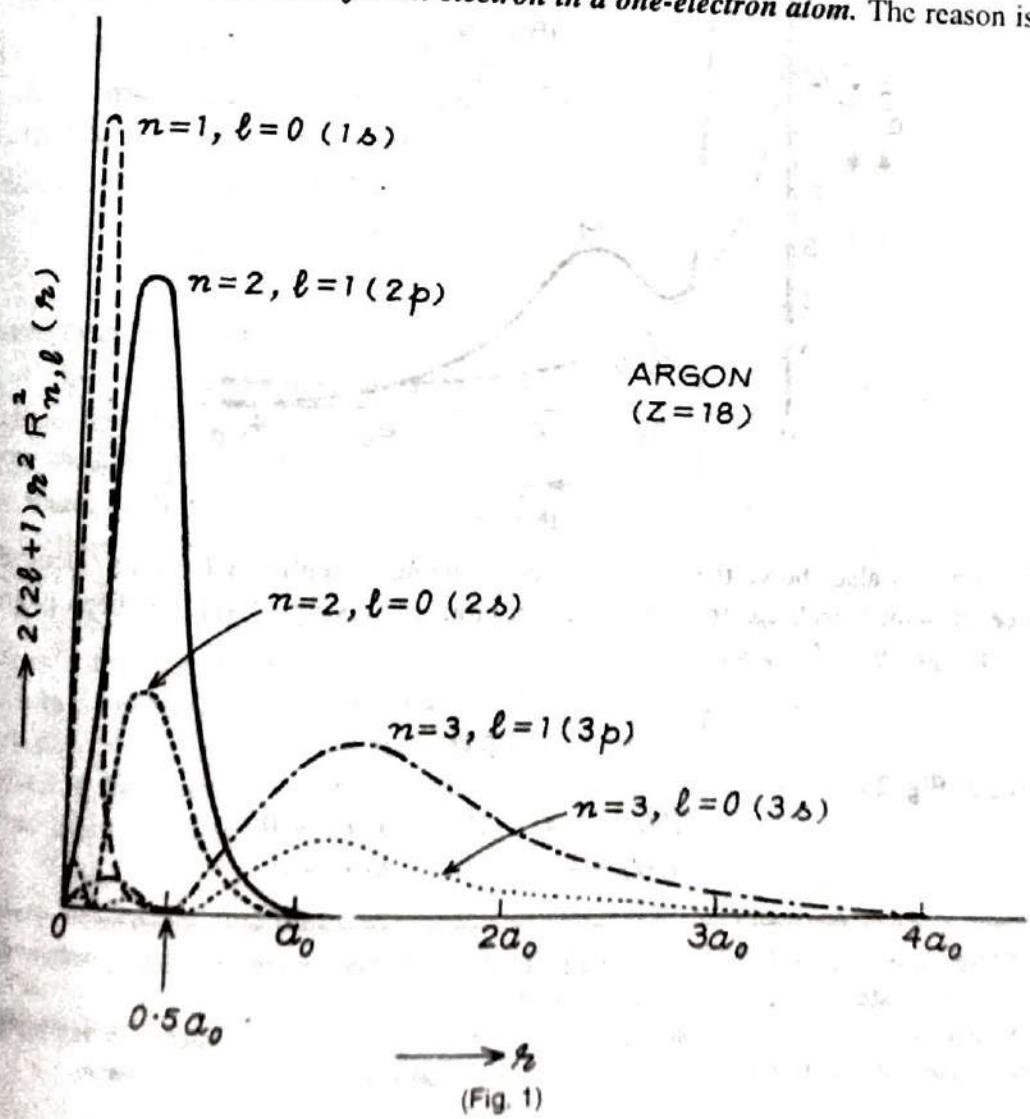
where  $n, l, m_l, m_s$  are the same quantum numbers as used for hydrogenic eigenfunctions. The angular eigenfunctions  $\Theta_{l, m_l}(\theta)$  and  $\Phi_{m_l}(\phi)$ , and the spin eigenfunction  $\beta_{m_s}$  are exactly the same as for a one-electron atom. Consequently,  $l$  determines the orbital angular momentum of the electron, the square of which is  $l(l+1)(\hbar^2/4\pi^2)$ ;  $m_l$  determines its  $z$ -component which is  $m_l(\hbar/2\pi)$  where

$$m_l = l, l-1, l-2, \dots, -l;$$

and  $m_s$  determines the  $z$ -component of the spin angular momentum of the electron which is  $m_s(\hbar/2\pi)$  where

$$m_s = \pm \frac{1}{2}.$$

The radial eigenfunctions  $R_{n, l}(r)$  for an electron in a multi-electron atom are, however, different than those for an electron in a one-electron atom. The reason is that

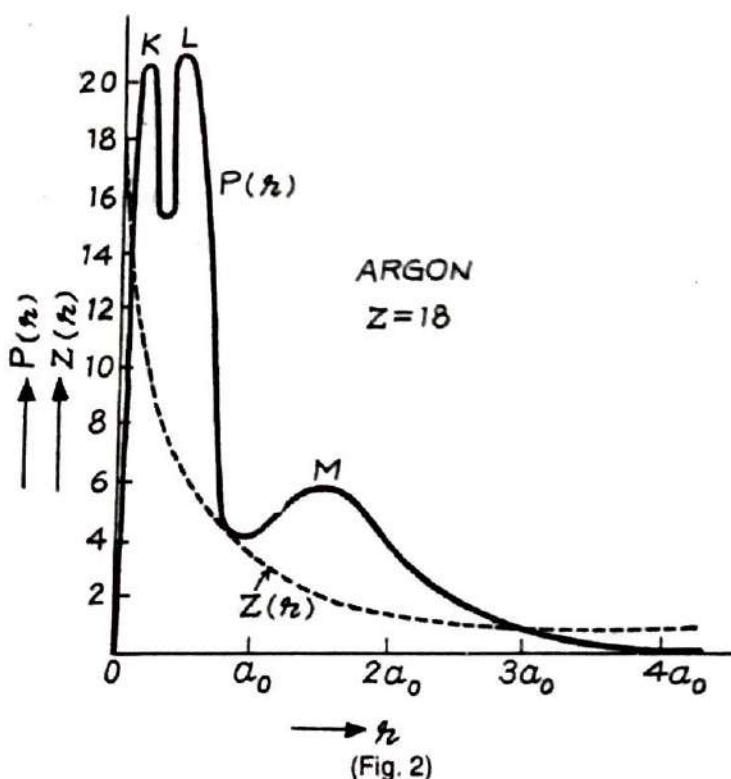


(Fig. 1)

the net potential  $V_i(r_i)$  appearing in the differential equation of a multi-electron atom does not have the same  $r$  dependence as the potential in a one-electron atom. The behaviour of  $R_{n,l}(r)$  for the electrons in the argon atom ( $Z = 18$ ) is shown in Fig. 1.

In Fig. 1, the quantities  $2(2l+1)r^2 R_{n,l}^2(r)$ , as calculated by Hartree for argon electrons with quantum numbers  $n = 1, l = 0$  ( $1s$ );  $n = 2, l = 0$  ( $2s$ );  $n = 2, l = 1$  ( $2p$ );  $n = 3, l = 0$  ( $3s$ ); and  $n = 3, l = 1$  ( $3p$ ) have been plotted against  $r$ . Here  $r^2 R_{n,l}^2(r)$  is the *radial probability density*\* and  $2(2l+1)†$  is the number of electrons possible in a given quantum state  $n, l$ .

In Fig. 2, is shown the *total radial probability density*  $P(r)$  for the argon atom. This is the sum of the quantities  $2(2l+1)r^2 R_{n,l}^2(r)$  taken over all the 18 electrons of the atom. That is,  $P(r)$  is the probability of finding *some* electron with a radial coordinate near  $r$ .



In Fig. 2 is also shown the  $r$ -dependence of the net potential  $V(r)$ , as calculated by Hartree, in which each electron of the argon atom is moving.  $V(r)$  has been plotted in terms of a quantity  $Z(r)$ , where

$$V(r) = - \frac{1}{4\pi\epsilon_0} \frac{Z(r)e^2}{r}.$$

We see in Fig. 2 that

$$Z(r) \longrightarrow Z(18) \quad \text{as } r \rightarrow 0$$

and

$$Z(r) \longrightarrow 1 \quad \text{as } r \rightarrow \infty.$$

\*This means that  $r^2 R_{n,l}^2(r) dr$  is the probability of finding an electron, with quantum numbers  $n$  and  $l$ , at a distance between  $r$  and  $r + dr$  from the nucleus.

†There are  $(2l+1)$  possible values of  $m_l$  for each  $l$ , and for each of these there are 2 possible values of  $m_s$ . Hence there are  $2(2l+1)$  possible electrons of a given  $l$  value.

This gives the idea that an electron very near the nucleus ( $r \rightarrow 0$ ) feels the full coulomb attraction of the nuclear charge  $+ Ze$ , while an electron very far from the nucleus ( $r \rightarrow \infty$ ) feels the attraction of a net charge  $+ e$ , because the nuclear charge is shielded by the charge  $- (Z - 1)e$  of the remaining  $(Z - 1)$  electrons surrounding the nucleus.

The plots in Fig. 1 shows that for all electrons of the same  $n$ , the probability densities are large only in essentially the same range of  $r$ . (This results in pronounced maxima in the resultant curve in Fig. 2). All these electrons are said to be in the same "shell". Furthermore, the range of  $r$  corresponding to large probability densities (the "thickness" of each shell) is quite narrow so that  $Z(r)$  has quite a well-defined value in that range. The shells are designated as  $K, L, M, N, \dots$  according as  $n = 1, 2, 3, 4, \dots$  respectively.

These observations lead to an approximate description of the results of Hartree theory. In this description, all the electrons in a shell (labeled by  $n$  value) of a multi-electron atom may be considered to be moving in a one-electron (hydrogen-like) potential field given by

$$V_n(r) = -\frac{1}{4\pi\epsilon_0} \frac{Z_n e^2}{r},$$

where  $Z_n$  is a constant equal to  $Z(r)$  evaluated at the average value of  $r$  for that shell (the "radius" of the shell). Thus, we may use one-electron atom equations for average distance, energy, etc to describe multi-electron atoms if we replace  $Z$  by  $Z_n$ . The quantity  $Z_n e$  is called the *effective nuclear charge* felt by the electrons in the shell  $n$ .

Let us now discuss the important results of Hartree theory :

(i) The equation for the average value of  $r$  (radius of shell), holding for a multi-electron atom would be\*

$$\bar{r} = \frac{n^2 a_0}{Z_n} \left[ 1 + \frac{1}{2} \left\{ 1 - \frac{l(l+1)}{n^2} \right\} \right] = \frac{n^2 a_0}{Z_n}.$$

Hartree calculations show that in all multi-electron atoms, for the shell  $n = 1$ , we have  $Z_n = Z - 2$ , because for this shell there is little shielding of the nucleus, and the electrons feel the full coulomb attraction of the highly-charged nucleus. Thus, Hartree theory predicts that ***in multi-electron atoms the radii of the inner shells of small n are very small.*** In fact, the radius of the  $n = 1$  shell of argon ( $Z_n = Z - 2 = 16$ ) is smaller than that of the  $n = 1$  shell of hydrogen by approximately a factor of 1/16. For atoms of higher  $Z$ , the radius is still smaller.

(ii) Electrons in the outer shells of large  $n$  are almost completely shielded from the nucleus by the inner electrons and feel only a small net attraction of the nucleus. Therefore, the mutual interactions of these electrons become more and more comparable with the interaction of an electron with the (shielded) nucleus. Hence the shell structure is less resolved in the outer parts of the atoms. For the outermost populated shell of an atom, Hartree calculations show that

$$Z_n \approx n,$$

and so the corresponding radius is

$$\bar{r} = \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left\{ 1 - \frac{l(l+1)}{n^2} \right\} \right].$$

\*We have read in quantum mechanics of hydrogen atom that the average distance of electron from the nucleus in one-electron atom is

$$\bar{r} \approx \frac{n^2 a_0}{Z_n} \approx \frac{n^2 a_0}{n} = n a_0.$$

Thus, the radius of the outermost shell of a multi-electron atom is roughly  $n$  times the radius of the smallest orbit of hydrogen.

(iii) Like radius, we can approximately express the total energy of an electron in a multi-electron atom by the energy equation of a one-electron atom, in which  $Z$  has been replaced by  $Z_n$ . That is,

$$E \approx -\frac{\mu Z_n^2 e^4}{8 \epsilon_0^2 h^2 n^2}.$$

For hydrogen atom,  $Z_n = Z = 1$ ; while for  $n = 1$  in all multi-electron atoms  $Z_n = Z - 2$ . Thus, Hartree theory predicts that *in multielectron atoms, the total energy of an electron in the  $n = 1$  shell is more negative than that of an electron in the  $n = 1$  shell of hydrogen atom by approximately a factor of  $(Z - 2)^2$ .*

(iv) For the outermost populated shell of an atom, we have

$$Z_n \approx n,$$

and so the corresponding energy is

$$E \approx -\frac{\mu e^4}{8 \epsilon_0^2 h^2 n^2}.$$

Thus, *the total energy of an electron in the outermost shell of any atom is comparable to that of an electron in the ground state of hydrogen atom.* The basic reason for this is the shielding of the outer-shell electron from the full nuclear charge by the charges of the intervening inner-shell electrons.

(v) The energy equation for a multi-electron atom contains  $Z_n^2$  in the numerator and  $n^2$  in the denominator. This means that *for a given atom, the total energy  $E$  becomes less negative with increasing  $n$ .* Infact,  $E$  becomes less negative very rapidly with increasing  $n$  for small  $n$ , but much less rapidly for large  $n$ . The behaviour for large  $n$  reflects the fact that the energy cannot become positive since the electron is bound. This prediction of the Hartree theory, and also all others, are verified by experiment.

(vi) The striking difference between one-electron atom and multi-electron atom is that *in a one-electron atom the total energy  $E$  depends only on the quantum number  $n$ , while in a multi-electron atom it depends on  $l$  as well as on  $n$ .* (So long we ignore spin-orbit and certain other weak interactions,  $E$  does not depend on  $m_l$  and  $m_s$ ). The  $l$ -independence of the energy of a one-electron atom is a consequence of the fact that its potential  $V(r)$  is exactly proportional to  $1/r$ . In a multi-electron atom, however, the electrons move in a net potential which is definitely not proportional to  $1/r$ .

The dependence of the total energy of a multi-electron atom on  $l$  can be understood from the behaviour of the electron probability density  $\psi^* \psi$  in the region of small  $r$  (near the nucleus). It can be seen from a study of eigenfunctions that in *all* atoms, for small  $r$ ,

$$\psi \propto r^l$$

so that

$$\psi^* \psi \propto r^{2l} \quad r \rightarrow 0.$$

From this it follows that the value of  $\psi^* \psi$  in a small volume near  $r = 0$  is relatively large only for  $l = 0$ , and decreases very rapidly with increasing  $l$ . The reason is that  $r^0 >> r^2 >> r^4 >> \dots$ , for  $r \rightarrow 0$ .

Thus, if we consider two electrons in the same shell  $n$  of a multi-electron atom, one with  $l = 0$  and the other with  $l = 1$ , there is much more chance of finding the  $l = 0$  electron in the region of small  $r$  (near the nucleus) than of finding the  $l = 1$  electron in that region. Similarly, the chance of finding an  $l = 1$  electron is much larger than the chance of finding an  $l = 2$  electron of the same  $n$  at small  $r$ . Since  $Z_n$  becomes very large at small  $r$ <sup>†</sup> the average potential energy  $V_n(r)$  of the  $l = 0$  electron will be more negative than that of the  $l = 1$  electron which, in turn, will be more negative than that of the  $l = 2$  electron, and so on. Hence *in a multi-electron atom, for a given  $n$ , the total energy of an electron is more negative for  $l = 0$  than for  $l = 1$ , more negative for  $l = 1$  than for  $l = 2$ , etc.* For outer shells with large values of  $n$ , where the  $n$ -dependence is not very strong<sup>††</sup>, the  $l$ -dependence of total energy actually predominates the  $n$ -dependence. But for a one-electron atom there is no  $l$ -dependence at all in the total energy because the electron *always* feels the full (unshielded) nuclear charge, and its average potential energy is independent of  $l$ .

Since in a multi-electron atom the total energy of an electron of a given shell does depend on  $l$ , we consider each shell as being composed of a number of *subshells*, one for each value of  $l$ . The subshells are designated as  $s, p, d, f, g, \dots$  according as  $l = 0, 1, 2, 3, 4, \dots$ . All the electrons in the same subshell have the same  $n$  and  $l$ , and hence exactly the same total energy (so long the spin-orbit and other weak interactions are ignored).

### 3. Atomic Orbitals and the Hund's Rule

We have just read that the electrons having the same value of  $l$  in a shell  $n$  are said to occupy the same "subshell". All of the electrons in a subshell have almost identical energies, since the dependence of electron energy upon  $m_l$  and  $m_s$  is comparatively minor.

Since  $l$  can take only the values  $0, 1, 2, \dots, n - 1$ ; the available subshells are :

1  $s$

2  $s$  2  $p$

3  $s$  3  $p$  3  $d$

4  $s$  4  $p$  4  $d$  4  $f$

.....

<sup>†</sup>At small  $r$  (near the nucleus) the electron feels nearly the full charge of the nucleus.

<sup>††</sup> $E \propto \frac{1}{r^2}$ ; hence as  $n$  increases, the  $n$ -dependence of  $E$  becomes weaker and weaker, that is, the energy difference between successive shells becomes smaller and smaller.

Since there are  $(2l + 1)$  possible values of the magnetic orbital quantum number  $m_l$  ( $= l, l - 1, \dots, 0, \dots, -l$ ) for each  $l$ , each of the above subshells has a spatial degeneracy\* of  $(2l + 1)$ . The electrons having the same value of  $m_l$  in a subshell  $n, l$  are said to occupy the same "atomic orbital". Thus, each subshell  $n, l$  consists of  $(2l + 1)$  spatially different degenerate atomic orbitals characterised by different  $m_l$  values.

For  $l = 0$ , there is one ( $s$ ) orbital corresponding to  
 $m_l = 0$ .

For  $l = 1$ , there are three ( $p$ ) orbitals corresponding to  
 $m_l = 1, 0, -1$ .

For  $l = 2$ , there are five ( $d$ ) orbitals corresponding to  
 $m_l = 2, 1, 0, -1, -2$ .

Thus, the available atomic orbitals are

$1s$

$2s \quad **2p_x, \quad 2p_y, \quad 2p_z$

$3s \quad **3p_x, \quad 3p_y, \quad 3p_z, \quad 3d_{xy}, \quad 3d_{yz}, \quad 3d_{zx}, \quad 3d_{x^2-y^2}, \quad 3d_{z^2}$

According to Pauli's principle, an atomic orbital  $n, l, m_l$  can have a maximum of two electrons having antiparallel spins ( $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ ). Two electrons having antiparallel spins are said to be paired off.

**Hund's rule :** According to Hund's rule, *one electron is placed in all the degenerate orbitals, such as  $p_x, p_y, p_z$ , before a second electron is placed in any one of them, and that the electrons in the singly-occupied orbitals have 'parallel' spins*. This means that the electrons in an atom have parallel spins as far as possible.

The origin of Hund's rule lies in the electrostatic repulsion of atomic electrons. Because of this repulsion, the farther apart the electrons in an atom, the lower the energy of the atom. Electrons in the same subshell  $n, l$  having parallel spins (same  $m_s$ ) would occupy *different* orbitals (different  $m_l$ ). Thus, they would be more separated in space (than if they had antiparallel spins and occupied the same orbital) and this arrangement, having less energy, is the more stable one.

\*This degeneracy is removed in the presence of an external magnetic field.

\*\*The three  $p$ -orbitals corresponding to  $m_l = 1, 0, -1$  are  $p_1, p_0, p_{-1}$ . These have been replaced by their linear combinations

$$p_x = \frac{1}{\sqrt{2}} [p_1 + p_{-1}],$$

$$p_y = -\frac{i}{\sqrt{2}} [p_1 - p_{-1}]$$

and

$$p_z = p_0.$$

Similarly, for  $d$ -orbitals,

## 4. The Periodic Table

The periodic table is an arrangement of elements listed in the order of atomic number. It has the characteristic that *the elements with similar chemical and physical properties recur at regular intervals*. The table was first constructed by Mendeleev in 1871, and perfected by Moseley and others from a study of X-ray spectra. A modern version of the periodic table of elements is shown in Fig. 3.

		Group																
		1	II															
Period	1																	
	H																He	
1	3	4																
2	Li	Be																
3	Na	Mg																
4	K	Ca																
5	Rb	Sr																
6	Cs	Ba																
7	Fr	Ra																
Transition Elements																		
	21	22	23	24	25	26	27	28	29	30								
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn								
	39	40	41	42	43	44	45	46	47	48								
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd								
	57	72	73	74	75	76	77	78	79	80								
	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg								
	89																	
Lanthanides* (Rare Earths)																		
	58	59	60	61	62	63	64	65	66									
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy									
	90	91	92	93	94	95	96	97	98									
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf									
Actinides†																		
	58	59	60	61	62	63	64	65	66									
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy									
	90	91	92	93	94	95	96	97	98									
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf									
	5	6	7	8	9	10												
	B	C	N	O	F	Ne												
	13	14	15	16	17	18												
	Al	Si	P	S	Cl	A												
	31	32	33	34	35	36												
	Ga	Ge	As	Se	Br	Kr												
	49	50	51	52	53	54												
	In	Sn	Sb	Te	I	Xe												
	81	82	83	84	85	86												
	Tl	Pb	Bi	Po	At	Rn												

(Fig. 3)

The table consists of seven horizontal rows which are called "periods", having 2, 8, 8, 18, 18, 32 and 17 elements respectively. The last period is rather incomplete. Across each period, there is a steady transition from an active metal, through less active metals and weakly active non-metals, to highly active non-metals, and finally to an inert gas.

As a consequence, elements with *similar* properties occur in vertical columns which are called "groups". For instance, group I consists of hydrogen plus the alkali metals all of which are highly active, while the (last) group VIII consists of noble gases all of which are inert.

In each period after the third, a series of "transition elements" appears between group II and group III elements. The elements of each series show chemical resemblance to one another, but are different from the elements of the preceding periods. The transition elements of period six include 14 "rare earth" elements called 'lanthanides' which are virtually indistinguishable in their properties. A similar group of closely related metals, called 'actinides' occurs in period seven.

A quantitative explanation of above characteristics is found in terms of Hartree's central field calculations.

Schroedinger's theory of multi-electron atoms led to the notion of electron shells and subshells in atoms which fits perfectly into the pattern of the periodic table. Pauli's exclusion principle that no two electrons can have the same set of quantum numbers, limits the number of electrons that can occupy a given subshell. A subshell is characterised by a certain total quantum number  $n$  and orbital quantum number  $l$ , where

$$l = 0, 1, 2, \dots, (n - 1).$$

There are  $2l + 1$  different values of the magnetic quantum number  $m_l$  for any  $l$ , since

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l,$$

and two possible values of the spin magnetic quantum number  $m_s$  ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ ) for any  $m_l$ . Hence each subshell can contain a maximum of  $2(2l + 1)$  electrons, and each shell a maximum of

$$\sum_{l=0}^{n-1} 2(2l + 1) = 2n^2$$

electrons. This leads to the following scheme :

Quantum Numbers	Shell	Sub-shells	Electron Capacity of Sub-shells $2(2l + 1)$	Electron Capacity of Shell $2n^2$
$n = 1$ $l = 0$	$K$	$1s$	2	2
$n = 2$ $l = 0, 1$	$L$	$2s, 2p$	2, 6	8
$n = 3$ $l = 0, 1, 2$	$M$	$3s, 3p, 3d$	2, 6, 10	18
$n = 4$ $l = 0, 1, 2, 3$	$N$	$4s, 4p, 4d, 4f$	2, 6, 10, 14	32

An atomic shell or subshell containing its full quota of electrons is said to be 'closed'. The total orbital and the total spin angular momenta of the electrons in a closed subshell are zero; and the subshell has a spherically symmetric distribution of charge\*. This is why the physical and the chemical properties of elements depend only on the electronic configuration outside closed subshells.

After having decided the maximum number of electrons permissible in the various subshells, we can determine the electronic structures of multi-electron atoms and then arrange them in a periodic system. For this, we require information about the ordering of subshells according to energy. This information is obtained from Hartree calculations, and from the experimental study of atomic spectra. On this basis, we can arrange the subshells in the order of increasing energy (becoming less negative) as follows :

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s,$

$4f, 5d, 6p, 7s, 5f, 6d, \dots$

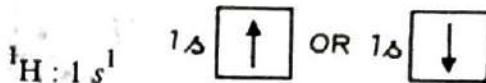
Hartree theory predicts that the energy of the subshell becomes less negative with increasing values of  $n$  and  $l$ . The  $1s$  subshell, which is the only subshell in the  $n = 1$  shell, has the lowest energy (most negative). The two subshells  $2s$  and  $2p$  of the  $n = 2$  shell are both of higher energy, of these the  $2s$  is lower. In the  $n = 3$  shell, the subshells  $3s, 3p, 3d$  are also ordered in energy according to the Hartree theory. However, the  $4s$  subshell is of lower energy than the  $3d$  subshell. This is because for outer subshells with large values of  $n$ , the  $l$ -dependence of energy becomes more important than the  $n$ -dependence. This tendency is seen as we continue with the above ordering. Near the end, the  $l$ -dependence of energy becomes so much stronger than the  $n$ -dependence that the energy of the  $7s$  subshell is lower than the energy of the  $5f$  subshell.

\*  $\sum_{l=0}^{+l} |1\Theta|^2 |\Phi|^2 = \text{constant (independent of } \theta \text{ and } \phi\text{)}.$  This is known as "unsoled's theorem".

The above energy ordering does not, however, hold for all the subshells of a particular atom, but only for the "outer" subshells of that atom. For example, the energy of the  $4s$  subshell is lower than that of the  $3d$  subshell for  $K$  atom ( $Z = 19$ ) and the next few atoms. But for atoms of very high  $Z$  the  $3d$  subshell is of lower energy than the  $4s$  subshell because for these atoms they are inner subshells and the  $n$ -dependence dominates the  $l$ -dependence.

**Building-up or aufbau Principle :** We can now allot subshells ( $n, l$  values) to the various electrons of an atom. The specification of the subshells occupied by the electrons of an atom is called the 'configuration' of the atom. **The configuration of any atom in its ground state is determined by filling the subshells in the order of increasing energy so that the total energy of the atom is a minimum\***. This is known as "building-up" or "aufbau" principle. Further, while allotting subshells, we must keep in view the capacity  $2(2l + 1)$  of any subshell and the Hund's rule regarding spin operating within the subshell.

Let us consider first the  $H$  atom ( $Z = 1$ ). The single electron occupies the lowest-energy subshell  $1s$ , with its spin either "up" or "down". The electron configuration of  $H$  in its ground state is written as :

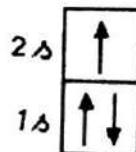
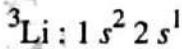


For the  $He$  atom ( $Z = 2$ ) both electrons are in the  $1s$  subshell, one with spin "up" and the other with spin "down". That is, the electrons are paired off. The configuration of  $He$  is written as :

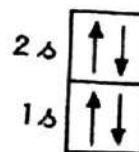
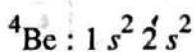


The  $1s$  subshell is complete and the atom is an inert gas atom. This also marks the closing of the  $K$ -shell ( $n = 1$ ) and also the closing of the first period.

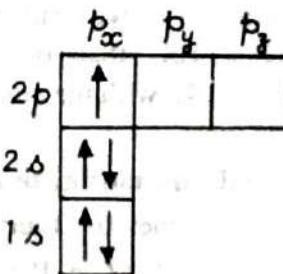
In the  $Li$  atom ( $Z = 3$ ) two electrons go into the  $1s$  subshell and close it, while the third goes into the next lowest subshell  $2s$  and it is the easily detachable valence electron. The configuration of  $Li$  atom is



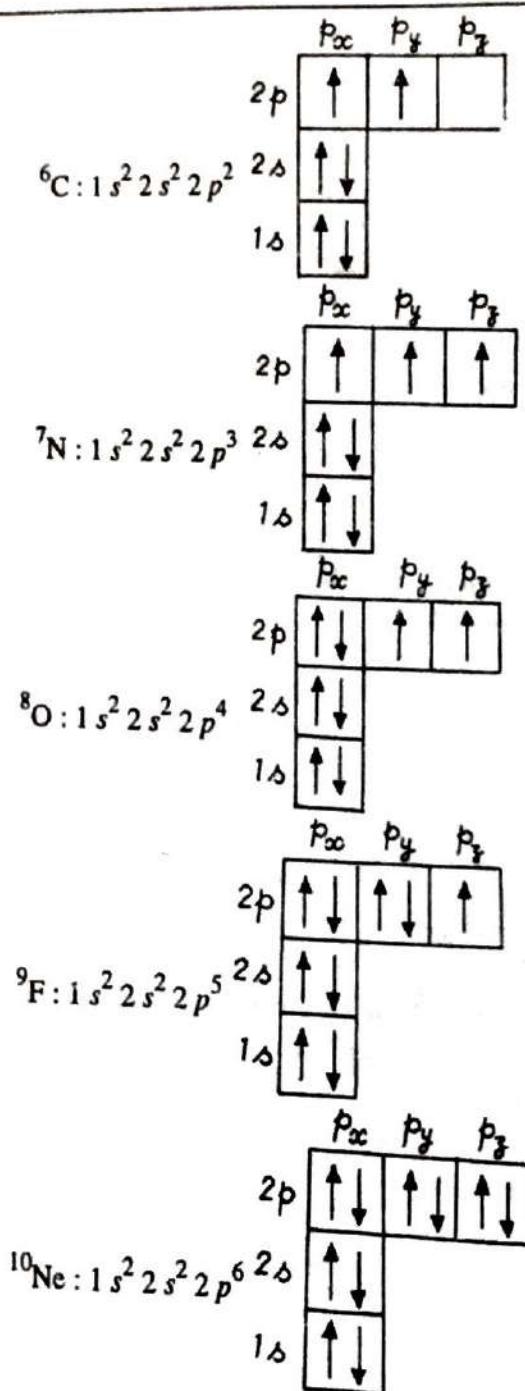
The  $Be$  atom ( $Z = 4$ ) completes the  $2s$  subshell and has the configuration



In the atoms from  $B$  ( $Z = 5$ ) to  $Ne$  ( $Z = 10$ ) the additional electrons fill the  $2p$  subshell according to the Hund's rule. Their configurations are

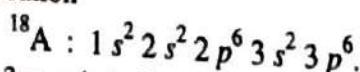


\* A system of particles is most stable when its total energy is a minimum.



The  $2p$  subshell is now complete with its quota of 6 electrons. This also marks the closing of the  $L$ -shell ( $n = 2$ ) and the closing of the second period.

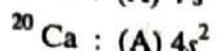
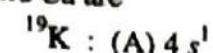
After Ne, we add one  $3s$  electron in Na ( $Z = 11$ ), two  $3s$  electrons in Mg ( $Z = 12$ ), then one  $3p$  electron in Al ( $Z = 13$ ) and so on, until we reach A ( $Z = 18$ ) with the configuration



This marks the closing of the  $3p$  subshell and also the closing of the third period.

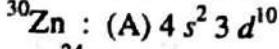
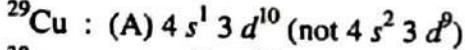
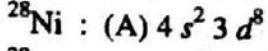
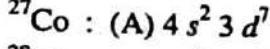
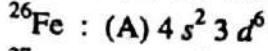
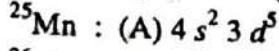
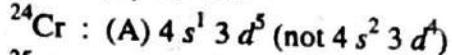
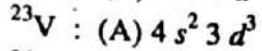
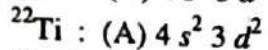
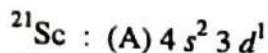
Now comes the fourth period which is larger than the periods so far. The elements after  ${}^{18}\text{A}$  are K ( $Z = 19$ ) and Ca ( $Z = 20$ ). For the first time a "cross-over" between two subshells takes place. The  $3p$  subshell is already complete in  ${}^{18}\text{A}$  and the  $3d$  falls next

in line. But for K and Ca the  $4s$  subshell is lower in energy than  $3d$ , and is therefore filled first. The configurations of K and Ca are



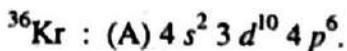
where (A) represents the argon core of 18 electrons having configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

After Ca, from Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ) the  $3d$  subshell is successively filled in the following way :



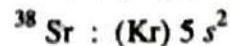
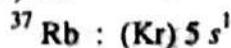
There are two irregularities, one at  $^{24}\text{Cr}$  and the other at  $^{29}\text{Cu}$ . In both these atoms, one of the electrons that could be in the  $4s$  subshell is actually in the  $3d$  subshell. This is because the energy difference between  $3d$  and  $4s$  subshells is small and the extra spin correlation frequently reverses the energy order. The elements from Sc to Zn have properties quite different from those occurring earlier, and form the first series of transition elements.

The following six elements from Ga ( $Z = 31$ ) to Kr ( $Z = 36$ ) are built up by the successive and regular filling of the  $4p$  subshell. The configuration of Kr which marks the close of  $4p$  subshell is



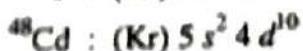
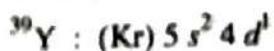
This marks the end of the fourth period.

The fifth period begins with Rb ( $Z = 37$ ). Although the  $4d$  and  $4f$  subshells are yet to be filled but the  $5s$  subshell, being of lower energy, is filled first. The configurations of Rb and Sr ( $Z = 38$ ) are



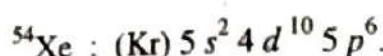
where (Kr) represents the krypton core of 36 electrons having configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ .

In the next ten elements from Y ( $Z = 39$ ) to Cd ( $Z = 48$ ) the  $4d$  subshell is filled, but with frequent irregularities of the same type as in the filling of  $3d$  subshell. The configurations of Y and Cd are



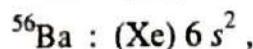
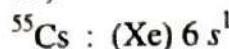
The elements from Y to Cd form the second series of transition elements.

The next six elements from In ( $Z = 49$ ) to Xe ( $Z = 54$ ) are built up by the regular filling of the  $5p$  subshell. The configuration of Xe which marks the close of the  $5p$  subshell is



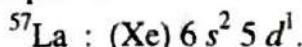
This marks the end of the fifth period.

The sixth period begins with Cs ( $Z = 55$ ). Although the  $4f$ ,  $5d$ ,  $5f$  subshells are yet to be filled but the  $6s$  subshell, being of lower energy, is filled first. The configurations of Cs and Ba ( $Z = 56$ ) are

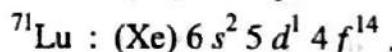
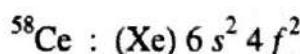


where ( $\text{Xe}$ ) represents the Xenon core of 54 electrons having configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ . The  $6s$  subshell is complete in Ba.

After the completion of the  $6s$  subshell the  $4f$  subshell should fill, but in La ( $Z = 57$ ) the last electron occupies the  $5d$  subshell. The configuration is

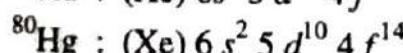
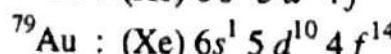
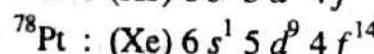
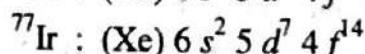
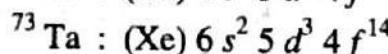
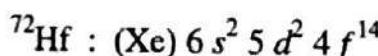


In the next element Ce ( $Z = 58$ ) the  $5d$  subshell remains vacant, the last two electrons go to the  $4f$  subshell. The electron capacity of the  $4f$  subshell is 14. Hence in 14 elements from Ce ( $Z = 58$ ) to Lu ( $Z = 71$ ) the  $4f$  subshell is successively filled. The electron configurations are



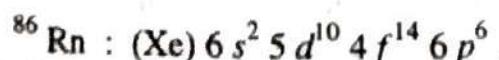
In  $^{64}\text{Gd}$  and  $^{71}\text{Lu}$ , however, there is one  $5d$  electron. This simply means that the energy differences between the  $5d$  and  $4f$  subshells are very small. The elements from  $^{58}\text{Ce}$  to  $^{71}\text{Lu}$  are known as 'lanthanides' or 'rare earths'.

In the elements from Hf ( $Z = 72$ ) to Hg ( $Z = 80$ ) the  $5d$  subshell is continuously filled. In Pt ( $Z = 78$ ) and Au ( $Z = 79$ ) this subshell is filled even at the cost of the  $6s$  subshell. The configurations are



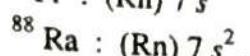
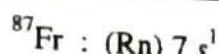
Again we conclude that the energy separations between  $5d$  and  $6s$  subshells are so small that the ordering is frequently reversed. At  $^{80}\text{Hg}$  the third transition series ends.

The next six elements from Tl ( $Z = 81$ ) to Rn ( $Z = 86$ ) are built up by the regular filling of the  $6p$  subshell. The configuration of Rn at which the  $6p$  subshell is complete is



This marks the end of the sixth period.

The seventh period starts with Fr ( $Z = 87$ ). Although the  $5f$  and  $6d$  subshells are still vacant, the  $7s$  subshell being of lower energy is filled first. The configurations of Fr and Ra ( $Z = 88$ ) are

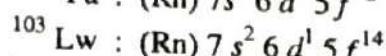
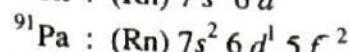
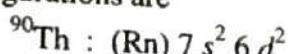


where  $(\text{Rn})$  is radon core of 86 electrons. The  $7s$  subshell is complete in  $^{88}\text{Ra}$ .

In the next element Ac ( $Z = 89$ ) the last electron occupies the  $6d$  subshell. The configuration is



The elements from Th ( $Z = 90$ ) to Lw ( $Z = 103$ ) are known as 'actinides'. In these elements the  $5f$  subshell is successively filled, except in Th in which the last electron goes to the  $6d$  subshell. The configurations are



Irregularities, however, occur in the filling of the  $5f$  subshell because it is very close in energy to the  $6d$  subshell.

We now interpret some of the prominent features of the periodic table in terms of the electron configurations of atoms :

**(i) Similarity of Group Elements :** The elements falling in the same vertical column (group) of the periodic table have similar chemical and optical properties. This is because such elements have similar electron configurations. For example, all the I group elements  $^1\text{H}$ ,  $^3\text{Li}$ ,  $^{11}\text{Na}$ ,  $^{19}\text{K}$ ,  $^{37}\text{Rb}$ ,  $^{55}\text{Cs}$ ,  $^{87}\text{Fr}$  have  $s^1$  configuration outside closed subshells. These are the well known 'alkalies' (except  $^1\text{H}$ ). They contain a single weakly bound electron in an  $s$  subshell. It is energetically very easy for these atoms to lose this electron and revert to the more stable configuration of completed subshells. Hence all alkalies are very active chemically. They have a valency of + 1.

At the other extreme are the halogens  $^9\text{F}$ ,  $^{17}\text{Cl}$ ,  $^{35}\text{Br}$ ,  $^{53}\text{I}$  and  $^{85}\text{At}$  falling in the VII group and having the same outer configuration  $p^5$ . These atoms have only one electron less than is required to complete their  $p$  subshell. Hence they are very eager to capture an electron, that is, they have a high electron affinity which accounts for their chemical behaviour. They have a valency of - 1.

**(ii) Noble Gases :** The last group elements  $^2\text{He}$ ,  $^{10}\text{Ne}$ ,  $^{18}\text{A}$ ,  $^{36}\text{Kr}$ ,  $^{54}\text{Xe}$  and  $^{86}\text{Rn}$  are known as 'noble gases'. They are monoatomic and chemically inert. The reason is easy to understand. In each of the noble gas atoms (except He) a  $p$  subshell is just completed, and the atom can have its first excitation only by going to the succeeding  $s$  subshell. But *every s subshell has a particularly large energy gap from the preceding p subshell*. As a result, these atoms are particularly difficult to excite\*. Furthermore, the total orbital and spin angular momenta of the electrons in completed subshells are zero (this yields zero total magnetic dipole moment), and their effective charge distributions are perfectly symmetrical. Therefore, the noble gas atoms produce no external magnetic fields in their ground state and also no external electric fields. Hence they have no tendency of interacting with other atoms to produce chemical compounds. They also have very low boiling and freezing points because they have little tendency to condense into liquids or solids.

\* Alternatively we can say that electrons in a completed subshell are very tightly bound because the positive nuclear charge is large relative to the negative charge of the inner shielding electrons.

The atom  ${}^2\text{He}$ , having configuration  $1s^2$ , is also a noble gas atom because for it also the first unfilled subshell is an  $s$  subshell ( $2s$ ) having a large energy gap from the preceding  $1s$  subshell, and because in its ground state the atom has completed shell and so produces no external fields. On the other hand, an atom like  ${}^{20}\text{Ca}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ ) is not a noble gas atom, even though it has completed subshells. The reason is that in the first excited state of the atom an electron goes to a  $3d$  subshell which is quite near in energy to the ground state.

(iii) **Transition Series Elements :** In the first three rows of the periodic table, the properties (valency, ionisation energy, etc) of the elements change uniformly from element to element. For the succeeding rows, however, this is not true. In the fourth row the elements from  ${}^{21}\text{Sc}$  to  ${}^{30}\text{Zn}$  have quite similar chemical properties and almost equal ionisation energies. They form the first transition series. This observation can be easily explained. These elements occur during the filling of the  $3d$  subshell whose radius is considerably less than that of the  $4s$  subshell which is completely filled for the transition elements (except  ${}^{24}\text{Cr}$  and  ${}^{29}\text{Cu}$ ). The filled  $4s$  subshell shields the  $3d$  electrons from external influence. Hence the chemical properties of these elements, which depend on the electrons in the outer subshells of their atoms, are quite similar, independent of the number of their  $3d$  electrons. The properties of  ${}^{24}\text{Cr}$  and  ${}^{29}\text{Cu}$  are somewhat different because they have only a single  $4s$  electron. Similar transition series occur during the filling of  $4d$  and  $5d$  subshells in 5th and 6th periods.

(iv) **Lanthanides and Actinides :** Lanthanides (or rare earths) are the elements from  ${}^{54}\text{Ce}$  to  ${}^{70}\text{Lu}$ . These are the elements in which the  $4f$  subshell is filling. This subshell lies deep within the outermost  $6s$  subshell, which is completed in all the rare earths. Thus, the  $4f$  electrons remain so well shielded from the external environment that they have virtually no effect on the chemical properties of the rare earths. Since the outer configuration, which is responsible for the chemical properties, is same ( $5s^2 5p^6 6s^2$ ) for these elements, the chemical properties of the rare earths are almost identical. The same is true for the actinides,  ${}^{90}\text{Th}$  to  ${}^{103}\text{Lw}$ , which occur during the filling of the  $5f$  subshell inside the filled  $7s$  subshell. They too have the same outer configuration ( $6s^2 6p^6 7s^2$ ) and hence identical chemical properties.

We end this topic by emphasising the importance of the 'exclusion principle'. If it were not obeyed, all the electrons in a multielectron atom would be in the lowest-energy  $1s$  subshell. In this case all atoms would have spherically symmetrical charge distributions of very small radii that would produce no external electric fields. Furthermore, they would also have very high first excited states. Then all atoms would be extremely inert and there would be no molecules, no chemical compounds, no life. In fact, the world would be completely different if electrons did not obey the exclusion principle.

## QUESTIONS

- Give an account of the Hartree's self-consistent field method. To what use the method has been put to? (Moorut 95 S)
- Discuss the postulates of the central field approximation. How does it fail to explain the complex spectra of atoms? How can you verify experimentally the validity of this approximation? (Moorut 2006 Qd. Q3, Q4, Q5)

3. Why is the angular dependence of multielectron eigenfunctions the same as for one-electron atom eigenfunctions? Why is the radial dependence different, except near the origin where it is the same?
4. What is the justification for using one-electron atom equations with an effective  $Z$  to discuss multielectron atoms?
5. What are quantum numbers? Give physical interpretation of various quantum numbers required to define the electronic configuration of atom. (Meerut 2003)
6. State the basic rules that determine electron configuration of many-electron atoms. Discuss briefly the sequence in which the electron subshells are filled in atoms. What is the maximum number of electrons that can occupy  $p$  subshell and  $d$  subshell? Write electronic configuration of K ( $Z = 19$ ).  
*(Meerut 93 special paper)*
7. Apply Pauli's principle to account for the periodic classification of elements.  
*(Meerut 2004 S, 97 special paper)*
8. How is the presence of a large number of elements in the fourth period of the periodic table explained?
9. Determine the configurations for the ground state of  ${}^6\text{C}$ ,  ${}^{17}\text{Cl}$ ,  ${}^{28}\text{Ni}$ ,  ${}^{29}\text{Cu}$ ,  ${}^{30}\text{Zn}$ ,  ${}^{86}\text{Rn}$ .
10. Write down the electronic configurations of  ${}_{11}\text{Na}^{23}$ ,  ${}_{20}\text{Ca}^{40}$ ,  ${}_{92}\text{U}^{235}$ .
11. Why is it difficult to separate mixtures of the rare earth elements by chemical means?

# Spectroscopic Terms : L-S and j-j Couplings

## 1. Terminology

We define some terminology associated with atomic energy levels.

**State** : The 'state' of an atom is the condition of motion of all the electrons. It is specified by listing four quantum numbers for each electron. If several states have same energy, they are said to be *degenerate*. The state with lowest energy is the *ground state*.

**Energy Level** : A collection of states having the same energy in the absence of external magnetic or electric field constitutes an 'energy level'. An energy level is characterised by a quantum number  $J$ , that is, by a particular value of the total angular momentum. The level with the lowest energy is the *ground level*.

**Sublevel** : An external field splits an energy level into several 'sublevels', each characterised by one or more magnetic quantum numbers.

**Term** : A collection of levels characterised by an orbital angular momentum and multiplicity (that is, spin) comprises a 'spectroscopic term'. For example a  $^3D$  term means the weighted average energy of the  $^3D_3$ ,  $^3D_2$  and  $^3D_1$  levels.

**Configuration** : The specification of the quantum numbers  $n$  and  $l$  for the orbitals of all the electrons of an atom is called the 'electron configuration' of the atom. For example, the electron configuration of the  ${}^6C$  atom is  $1s^2 2s^2 2p^2$ .

**Equivalent Orbitals** : Orbitals with same  $n$  and  $l$  values are said to be 'equivalent'. The electrons in equivalent orbitals are called 'equivalent electrons'.

**Statistical Weight** : The number of distinct states in a specified collection is the 'statistical weight'. The statistical weight of a level is  $2J + 1$ ; for a term it is  $(2S + 1)(2L + 1)$ ; for a single electron it is  $2n^2$ .

Spectral lines are categorised according to the following nomenclature :

**Component** : A transition between two sublevels is called a 'component'.

**Line** : A transition between two levels is a 'line'. Thus, a line is a blend of components.

**Multiplet** : A collection of transitions between two terms is called a 'multiplet'. Thus a multiplet consists of a number of lines.

**Resonance Line** : Among the lines arising from transitions between the ground level and higher levels, the line of lowest frequency is called the 'resonance line'.

## 2. Atoms with Several Optically Active Electrons

In the last chapter we determined the electron configuration ( $n$  and  $l$  values of the individual electrons) of the atoms by the application of Pauli's principle. This, however, does not tell us the term types associated with the ground and the excited electronic state.

configuration of the atom. The term type is obtained by adding together the angular momentum vectors  $\vec{l}$  and  $\vec{s}$  of the individual electrons. For this purpose, we have to first investigate the interactions (couplings) between the angular momentum vectors of the electrons.

Let us consider a multielectron atom (or ion) having a nuclear charge  $+Ze$ , surrounded by  $N$  electrons ( $N \leq Z$ ). The electrons constitute a 'core' of completely filled subshells surrounding the nucleus, and a few of them remain in a partially-filled outer subshell and are optically active. The Hamiltonian for such an atom must consist of the following terms :

- (i) The kinetic energy of the electrons, given by

$$\sum_{i=1}^N \frac{p_i^2}{2m},$$

where  $p_i$  is the momentum of the  $i$  th electron (mass  $m$ ).

- (ii) The electrostatic energy of the electrons due to their interaction with the nucleus, which is given by

$$-\sum_{i=1}^N \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i},$$

where  $r_i$  is the distance of the  $i$  th electron from the nucleus.

- (iii) The mutual (residual) electrostatic energy of the electrons, given by

$$\sum_{i=1}^N \sum_{j=1}^{N-1} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}},$$

where  $r_{ij}$  is the distance between the  $i$  th and the  $j$  th electrons.

- (iv) The spin-spin correlation energy. The spin-spin correlation makes electrons with parallel spins repel each other, and electrons with antiparallel spins attract each other. This effect arises because of the exchange-symmetry postulate which states that *the acceptable eigenfunctions for a system of electrons are antisymmetric with respect to an exchange of the space and the spin coordinates of any two electrons.*

- (v) The spin-orbit magnetic interaction energy of the electrons.

Besides above, there are a number of smaller interaction terms including relativistic correction.

In the Hartree central field approximation, each electron is treated as if it were moving independently in a spherically symmetrical net potential that describes the average of its coulombian interactions with the nucleus and with the other electrons. That is, the Hamiltonian includes from above only the terms (i), (ii) and a spherical average of (iii). The energy of each independently moving optically-active electron is determined by its quantum numbers  $n$  and  $l$ . The total energy of the atom is the constant total energy of the core\*, plus the sum of the total energies of the optical electrons. Consequently, in Hartree approximation, the energy of the atom is determined by the configuration ( $n, l$  values) of the optical electrons. Now, associated with each configuration are a number of different sets of quantum numbers  $m_l$  and  $m_s$ , that is, a number of different quantum

\*The energy of the core is constant because the core electrons do not take part in optical excitations.

states. Since the energy does not depend on  $m_l$  and  $m_s$ , the different quantum states are degenerate. Also, there is an exchange degeneracy because the energy does not depend on which of the electrons has a particular set of quantum numbers. Thus, in the Hartree approximation there are a number of degenerate energy levels associated with each configuration. Many of these degeneracies are removed when the remaining of the above terms are included as perturbations. The relative magnitudes of the remaining terms are different for different atoms. In general, we can divide the atoms into two main classes in this respect :

I. For most atoms, mainly the lighter ones, the residual (non-spherical) electrostatic interaction effect of the term (iii) and the spin-spin correlation effect of the term (iv) are the largest of the remaining terms; the spin-orbit magnetic interaction term (v) is considerably smaller, while the rest are negligible. Such atoms are governed by  $L-S$  coupling.

II. For some atoms, mainly the heavier ones, the spin-orbit term (v) predominates over others. Such atoms are governed by  $j-j$  coupling.

### 3. $L-S$ Coupling

The  $L-S$  coupling is also known as 'Russell-Saunders' coupling after the two astronomers who first used it in studying atomic spectra emitted by stars. In atoms which obey this coupling we introduce the various perturbations in the order : (a) spin-spin correlation, (b) residual electrostatic interaction, (c) spin-orbit interaction.

(a) As a result of spin-spin correlation effect, the individual spin angular momentum vectors of the 'optical' electrons are strongly coupled with one another to form a resultant spin angular momentum vector  $\vec{S}$  of magnitude  $\sqrt{S(S+1)} \frac{\hbar}{2\pi}$  which is a constant of motion. The quantum number  $S$  can take the values :

$$S = \left| \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \dots \right|_{\min}, \left| \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \dots \right|_{\min} + 1, \dots, \dots (s_1 + s_2 + s_3 + \dots)$$

The states with different values of  $S$  have considerable energy difference, the state of highest  $S$  being of lowest energy. It means that due to spin-spin correlation, an (unperturbed) energy level of the central field model is splitted into a number of well-separated levels, equal to the number of different values of  $S$  that can be formed from the individual spins of the optical electrons of the atom. The different levels are designated by their multiplicity,  $(2S + 1)$ . Thus :

$$\text{For one electron : } S = s = \frac{1}{2}$$

$$\therefore (2S + 1) = 2 \text{ (doublet level).}$$

$$\text{For two electrons : } s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$$

$$\therefore S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, (s_1 + s_2) = 0, 1$$

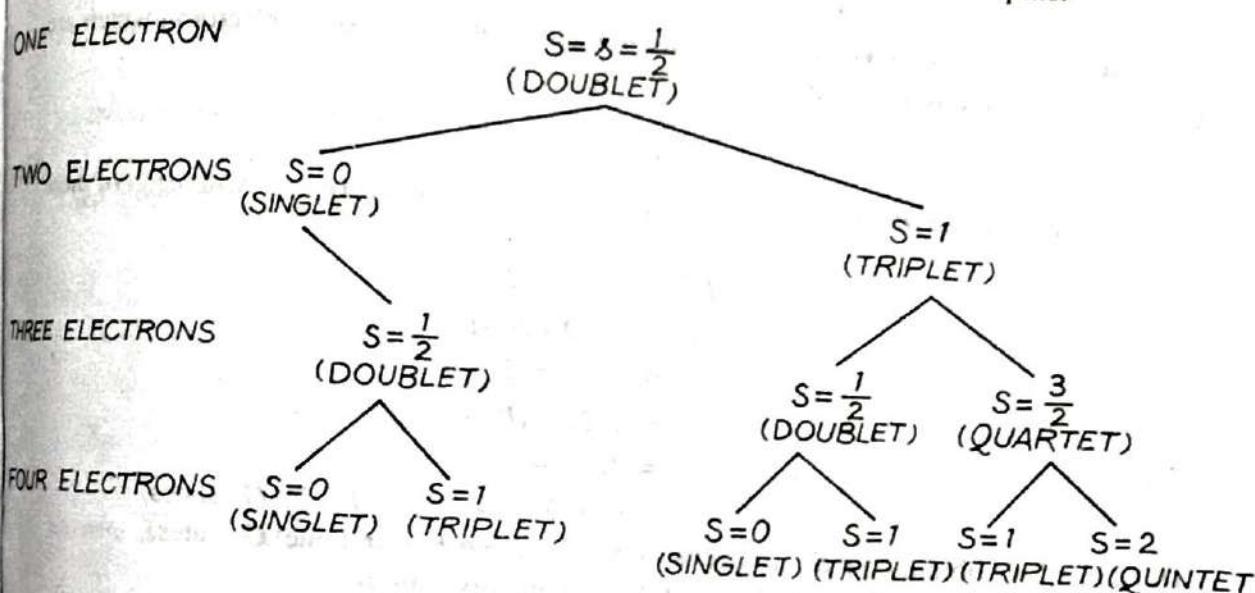
$$\therefore (2S + 1) = 1, 3 \text{ (singlet and triplet levels).}$$

$$\text{For three electrons : } s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, s_3 = \frac{1}{2}$$

To combine three spins, we first combine two of them to obtain  $S' = 0, 1$ , and then combine the third  $s_3 = \frac{1}{2}$  to each of them. Thus, if we couple  $s_3 = \frac{1}{2}$  to  $S' = 0$ ; we get  $S = \frac{1}{2}$ ; and if we couple  $s_3 = \frac{1}{2}$  to  $S' = 1$ , we get  $S = \frac{1}{2}, \frac{3}{2}$ . Thus, for three electrons, we get

$$S = \frac{1}{2}, \frac{1}{2}, \frac{3}{2} \quad (\text{two sets of doublets, and one set of quartets}).$$

The following branching diagram (Fig. 1) illustrates the possible total spin quantum numbers which can be obtained by combining several independent electron spins.



(Fig. 1)

In the general case of  $N$  electrons, the possible values of  $S$  are

$$S = 0, 1, 2, \dots, \frac{N}{2} \text{ for even } N.$$

$$S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots, \frac{N}{2} \text{ for odd } N.$$

That the state of largest  $S$  is of lowest energy can be understood by considering the case of two electrons. The spin correlation effect splits the unperturbed level into two : a singlet level and a triplet level. Because of the total eigenfunction being antisymmetric with respect to an exchange of the electrons, the average distance between the two electrons is larger in the triplet state (parallel spins) than it is in the singlet state (antiparallel spins). Therefore, the (positive) electrostatic repulsion energy is smaller in the triplet state than it is in the singlet state. Hence, triplet level lies deeper.

(b) As a result of the residual electrostatic interaction, the individual orbital angular momentum vectors of the 'optical' electrons are strongly coupled with one another to

form a resultant orbital angular momentum vector  $\vec{L}$  of magnitude  $\sqrt{L(L+1)} \frac{\hbar}{2\pi}$  which is a constant of motion. The quantum number  $L$  can take the values :

$$L = \left| \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots \right|_{\min}, \left| \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots \right|_{\min} + 1, \dots, \dots (l_1 + l_2 + l_3 + \dots).$$

The states with different values of  $L$  have fairly large energy difference, *the state of largest  $L$  being of lowest energy*. It means that each of the levels splitted by spin-spin corelation effect is further splitted by the residual electrostatic interaction into a number of less-separated levels, equal to the number of different values of  $L$  that can be formed from the individual orbital angular momenta of the optical electrons of the atom. The different levels are designated as  $S, P, D, F, G, \dots$  according as  $L = 0, 1, 2, 3, 4, \dots$

Thus :

**For  $3p\ 3d$  electrons :**  $l_1 = 1, l_2 = 2$ .

$$\therefore L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots (l_1 + l_2) \\ = 1, 2, 3 (P, D, F \text{ states}).$$

**For  $2p\ 3p\ 4d$  electrons :** Let us first combine the two  $p$  electrons which are more tightly bound to the atom. For this

$$l_1 = 1, l_2 = 1.$$

$$\therefore L' = 0, 1, 2.$$

Now, combining the  $d$  electron,  $l_3 = 2$ , which is less tightly bound, with each of these gives

$$L' = 0, l_3 = 2.$$

$$\therefore L = 2 (D \text{ states}),$$

$$L' = 1, l_3 = 2.$$

$$\therefore L = 1, 2, 3, (P, D, F, \text{ states}),$$

$$L' = 2, l_3 = 2$$

and

$$\therefore L = 0, 1, 2, 3, 4, (S, P, D, F, G, \text{ states})$$

Thus, in all we obtain one  $S$ , two  $P$ 's, three  $D$ 's, two  $F$ 's and one  $G$  states.

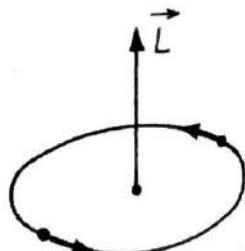
That the state of largest  $L$  is of lowest energy can be understood by considering two electrons in a Bohr atom. Because of the coulomb repulsion between the electrons, the electrostatic energy will be a minimum when the electrons stay at the opposite ends of a diameter, that is, at a maximum distance apart (Fig. 2). In this state, the two electrons would be revolving together "in the same direction" about the nucleus, that is, with their individual orbital angular momentum vectors parallel. The magnitude of the total orbital angular momentum vector,  $L$ , would clearly be a maximum in this state of lowest energy.

(c) The dominant spin-spin corelation and the residual electrostatic interaction having been taken into account as a first perturbation, the smaller spin-orbit interaction is included in  $L-S$  coupling as an additional perturbation.

As a result of smaller spin-orbit magnetic interaction, the resultant orbital angular momentum vector  $\vec{L}$  and the resultant spin angular momentum vector  $\vec{S}$  are less strongly coupled with each other to form a total angular momentum vector  $\vec{J}$  of the atom :

$$\vec{J} = \vec{L} + \vec{S},$$

the magnitudes of  $\vec{J}$ ,  $\vec{L}$  and  $\vec{S}$  remaining constant. The magnitude of  $\vec{J}$  is  $\sqrt{J(J+1)} \frac{\hbar}{2\pi}$ , where the quantum number  $J$  takes the values :



(Fig. 2)

$$J = |L - S|, |L - S| + 1, \dots, (L + S).$$

$J$  is integral or half-integral according as  $S$  is integral or half-integral. The number of  $J$  values is  $(2S + 1)$  when  $L > S$ , or  $(2L + 1)$  when  $S > L$ . This means that due to spin-orbit magnetic interaction; a level characterised by given values of  $L$  and  $S$  is further broken up into comparative closer  $(2S + 1)$  or  $(2L + 1)$  levels, each characterised by a different  $J$  value\*. The group of these  $J$ -levels forms a 'fine-structure multiplet'. The relative spacing of the fine-structure levels within a multiplet is governed by Lande interval rule.

#### 4. Lande Interval Rule

Under  $L-S$  coupling, the spin-orbit interaction energy is of the form

$$\Delta E_{s,l} = a (\vec{L} \cdot \vec{S}),$$

where  $a$  is an interaction constant. Let us write

$$\vec{J} = \vec{L} + \vec{S}.$$

Taking the scalar self product, we have

$$\begin{aligned} \vec{J} \cdot \vec{J} &= \vec{L} \cdot \vec{L} + \vec{S} \cdot \vec{S} + 2 \vec{L} \cdot \vec{S} \\ \text{or } |\vec{J}|^2 &= |\vec{L}|^2 + |\vec{S}|^2 + 2 \vec{L} \cdot \vec{S} \\ \text{or } \vec{L} \cdot \vec{S} &= \frac{1}{2} [|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2]. \end{aligned}$$

$$\therefore \Delta E_{s,l} = \frac{a}{2} [J(J+1) - L(L+1) - S(S+1)] \frac{\hbar^2}{4\pi^2},$$

because  $\vec{J} = \sqrt{J(J+1)} \frac{\hbar}{2\pi}$ , and so on. We can write it as

$$\Delta E_{s,l} = A [J(J+1) - L(L+1) - S(S+1)],$$

where  $A$  is another constant.

The various fine-structure levels of a Russell-Saunders multiplet have the same values of  $L$  and  $S$ , and differ only in the value of  $J$ . Hence, the energy difference between two fine-structure levels corresponding to  $J$  and  $J+1$  is

$$\begin{aligned} E_{J+1} - E_J &= A [(J+1)(J+2) - J(J+1)] \\ &= 2A(J+1). \end{aligned}$$

Thus, the energy interval (spacing) between consecutive levels  $J$  and  $J+1$  of a fine-structure multiplet is proportional to  $J+1$ , that is, to the larger of the two  $J$ -values involved. This is 'Lande interval rule.'

Let us take few examples. According to Lande interval rule, the fine-structure levels  ${}^3P_0, {}^3P_1, {}^3P_2$  have separations in the ratio  $1:2$ , the levels  ${}^3D_1, {}^3D_2, {}^3D_3$  in the ratio  $2:3$ ; the levels  ${}^4D_{1/2}, {}^4D_{3/2}, {}^4D_{5/2}, {}^4D_{7/2}$  in the ratio  $3:5:7$ ; and so on. The excellent agreement between the experimentally observed and the theoretically predicted ratios in lighter atoms provides evidence of  $L-S$  coupling in these atoms. Deviations from Lande interval rule occur with increasing deviation from  $L-S$  coupling.

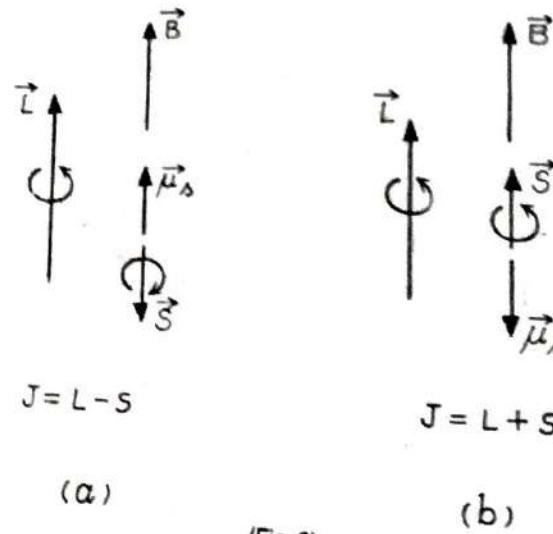
ly  
se

\*In fact each  $J$ -level has still a degeneracy of  $(2J+1)$  which can be removed by an external magnetic field.

## 5. Normal and Inverted Multiplets

Within a given multiplet, usually the level with smallest  $J$  value lies lowest. Such a multiplet is a 'normal' multiplet. There are, however, multiplets in which the largest  $J$  level lies lowest. Such multiplets are 'inverted' multiplets.

The reason why in a normal multiplet the smallest  $J$  level is lowest is easy to understand. The magnetic field  $\vec{B}$  produced by the orbital motion of the electron in the electric field of the nucleus is in the same direction as the orbital angular momentum  $\vec{L}$ . In this field the most stable state, that is, the state of lowest energy must be one in which the spin magnetic moment  $\vec{\mu}_s$  of the electron lines up in the direction of  $\vec{B}$  (Fig. 3 a). We



know that  $\vec{\mu}_s$  is directed opposite to  $\vec{S}$  because the electron is *negatively charged*. Thus, in the lowest energy state,  $\vec{L}$  and  $\vec{S}$  are in opposite directions and so the value of  $J$  is lowest. When  $\vec{L}$  and  $\vec{S}$  are in the same direction (Fig. 3 b), which corresponds to highest  $J$ , then  $\vec{\mu}_s$  is opposite to  $\vec{B}$  and the state is least stable.

The inverted multiplets arise due to some perturbing influences.

## 6. Determination of Spectral Terms for $L-S$ Coupling

We can now determine the spectral terms associated with the ground state and the excited states of atoms for which  $L-S$  coupling holds. Since the core electrons do not contribute to the angular momentum of the atom, we must consider only the (optical) electrons outside the completed subshells for computing the terms. The terms if computed from an odd electronic configuration are all odd; but if computed from an even electronic configuration are all even\*. The odd terms are denoted by a superscript  $o$ , following the  $L$  symbol. For example, a  $^3P$  term arising from an odd configuration  $2s\ 2p$  is denoted as  $^3P$ , while the same term arising from an even configuration  $2p\ 3p$  is written simply as

For the computation of terms we can divide the various atoms into three categories:

\*A given electronic configuration is said to be of 'odd' parity if the sum of the  $l$ 's of all the optical electrons,  $\sum l$ , is odd; and of 'even' parity if the sum  $\sum l$  is even. For example, the configuration  $2s\ 2p$  is of odd parity, while the configuration  $2p\ 3p$  is of even parity.

(1) Atoms with One Optical Electron : For a hydrogen-like atom, the ground state configuration is

$1s.$

For this, we have

$$s = \frac{1}{2} ; l = 0,$$

so that

$$S = s = \frac{1}{2}; \text{ multiplicity } 2S + 1 = 2,$$

$$L = l = 0 \text{ (S-state),}$$

and

$$J = |L - S|, \dots (L + S) = \frac{1}{2}.$$

Thus, the ground state term of a hydrogen-like atom is

$$^2S_{1/2}.$$

The excited state configurations and the corresponding terms for a hydrogen-like atom would be

$$2s, 3s, 4s, \dots ^2S_{1/2}$$

$$2p, 3p, 4p, \dots ^2P_{1/2}, ^2P_{3/2}$$

$$3d, 4d, \dots ^2D_{3/2}, ^2D_{5/2}.$$

The ground-state configuration of an alkali atom, say Li, is  $1s^2 2s$ . Hence, as for hydrogen, the ground state term of Li is  $^2S_{1/2}$ . This is so for all the alkalies.

(2) Atoms with Two or More Non-Equivalent Optical Electrons : Let us consider an atom having two optical electrons with outer configuration

For this, we have

$$4p\ 4d^*$$

$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}; l_1 = 1, l_2 = 2.$$

The possible values of  $S$  and  $L$  are:

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots (s_1 + s_2)$$

$$= 0, 1; \text{ multiplicity } (2S + 1) = 1, 3$$

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots (l_1 + l_2)$$

$$= 1, 2, 3, (P, D, F, \text{ states}).$$

Thus, we have in all six terms, three singlet terms and three triplet terms. All these terms are odd because the configuration  $4p\ 4d$  is odd ( $\sum l = 1 + 2 = 3$ ). We can write these terms as

$$^1P^*, ^1D^*, ^1F^*, ^3P^*, ^3D^*, ^3F^*.$$

To take into account spin-orbit interaction, let us combine  $L$  and  $S$  to form  $J$ . Now

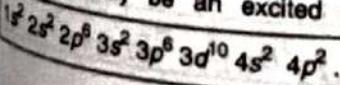
$$J = |L - S|, \dots (L + S).$$

For singlet terms, we have

$$\begin{cases} S = 0 \\ L = 1 \end{cases}; J = 1; ^1P_1^*.$$

$$\begin{cases} S = 0 \\ L = 2 \end{cases}; J = 2; ^1D_2^*.$$

\*This may be an excited state of Ge ( $Z = 32$ ) whose ground state configuration is

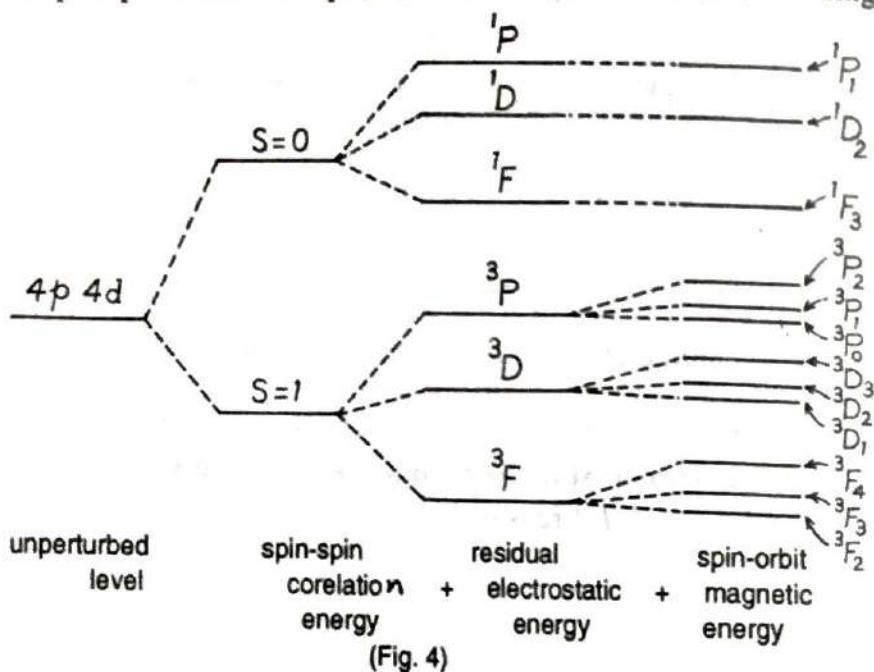


$$\begin{cases} S = 0 \\ L = 3 \end{cases} ; J = 3; \quad ^1F_3.$$

For triplet terms, we have

$$\begin{cases} S = 1 \\ L = 1 \end{cases} ; \quad J = 0, 1, 2; \quad ^3P_0^*, ^3P_1^*, ^3P_2^*. \\ \begin{cases} S = 1 \\ L = 2 \end{cases} ; \quad J = 1, 2, 3; \quad ^3D_1^*, ^3D_2^*, ^3D_3^*. \\ \begin{cases} S = 1 \\ L = 3 \end{cases} ; \quad J = 2, 3, 4; \quad ^3F_2^*, ^3F_3^*, ^3F_4^*. \end{cases}$$

Thus, a single degenerate level of configuration  $4p\ 4d$  is splitted into 12 levels as shown in Fig. 4. The spin-spin corelation splits this level into two levels, the singlet level



(Fig. 4)

( $S = 0$ ) and the triplet level ( $S = 1$ ); the triplet (higher multiplicity) level being lower. The residual electrostatic interaction splits each of these levels into three; the  $P$ ,  $D$  and  $F$  levels, the level of largest  $L$  (that is,  $F$  level) being lowest. Now each of the triplet levels is further splitted by the spin-orbit interaction into three fine-structure levels, each characterised by a  $J$  value. The spacings between each set of fine-structure levels is according to Lande rule, and the level with smallest  $J$  lies lowest (normal triplet).

Each of the  $J$  level is still  $(2J + 1)$ -fold degenerate and this degeneracy can be removed by an external magnetic field. The total degeneracy of  $4p\ 4d$  level is 60 (verify).

For practice, certain other electron configurations and their terms are given in the following table. Try these !

#### Terms of Non-Equivalent Electrons

Electron Configuration	Terms
$ss$	$^1S_0$ , $^3S_1$
$sp$	$^1P_1$ , $^3P_{0,1,2}$
$sd$	$^1D_2$ , $^3D_{1,2,3}$
$pp$	$^1S_0$ , $^1P_1$ , $^1D_2$ , $^3S_1$ , $^3P_{0,1,2}$ , $^3D_{1,2,3}$
$dd$	$^1S_0$ , $^1P_1$ , $^1D_2$ , $^1F_3$ , $^1G_4$ , $^3S_1$ , $^3P_{0,1,2}$ , $^3D_{1,2,3}$ , $^3F_{2,3,4}$ , $^3G_{3,4,5}$

For three non-equivalent electrons the terms are evaluated by combining the three spins and the three orbital angular momenta. The spin combinations are obtained by first combining the spins of two of the electrons and then combining the third spin with each of them. The orbital angular momenta combinations are obtained by first combining the orbital angular momenta of two more-tightly bound of the electrons and then couple the less-tightly bound electron with each of them.

For example, let us consider the configuration  $3d\ 4s\ 5p$ .

**Spin Combinations :**  $s_1 = \frac{1}{2}$ ,  $s_2 = \frac{1}{2}$ ,  $s_3 = \frac{1}{2}$ .

On combining  $s_1$  and  $s_2$  we obtain  $S' = 0, 1$ . Then, on combining  $s_3$  with each of these  $S'$  values, we obtain  $S = \frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ . Thus, the multiplicities ( $2S + 1$ ) are 2, 2 and 4 which correspond to two sets of 'doublet' states and one set of 'quartet' states.

**Orbital Angular Momenta Combinations :** We first combine  $3d$  and  $4s$  electrons. For them, we have

$$l_1 = 2, l_2 = 0.$$

$$\therefore L' = 2.$$

We now add  $5p$ -electron momentum to it, which is  $l_3 = 1$ . Thus,

$$L = 1, 2, 3 (P, D, F \text{ states})$$

Thus, we have two sets of three doublet terms, and one set of three quartet terms; in all nine terms. All these terms are odd because the configuration  $3d\ 4s\ 5p$  is odd ( $\sum l = 2 + 0 + 1 = 3$ ). We can write these terms as

$$^2P^{\circ}, ^2D^{\circ}, ^2F^{\circ}, ^2P^{\circ}, ^2D^{\circ}, ^2F^{\circ}, ^4P^{\circ}, ^4D^{\circ}, ^4F^{\circ}$$

that is,  $^2P^{\circ}(2), ^2D^{\circ}(2), ^2F^{\circ}(2), ^4P^{\circ}, ^4D^{\circ}, ^4F^{\circ}$ .

Including spin-orbit interaction, we can write the various levels as :

$$^2P_{1/2, 3/2}(2), ^2D_{3/2, 5/2}(2), ^2F_{5/2, 7/2}(2),$$

$$^4P_{1/2, 3/2, 5/2}, ^4D_{1/2, 3/2, 5/2, 7/2}, ^4F_{3/2, 5/2, 7/2, 9/2}.$$

Thus, we get a total of 23 distinct levels. We note that one of the quartet terms, namely  $^4P$ , has three (not four) fine-structure components. This is because for this term  $L (= 1)$  is less than  $S (= 3/2)$  and so the number of components is  $2L + 1$ , and not  $2S + 1$ .

**(3) Atoms with Two or More Equivalent Electrons :** For two equivalent electrons (same  $n$  and  $l$  values) the values of at least one of the remaining quantum numbers ( $m_l$  or  $m_s$ ) must differ to satisfy Pauli's exclusion principle. Hence certain terms which were possible for two non-equivalent electrons are now not allowed. For instance, two non-equivalent  $p$ -electrons, such as  $2p$  and  $3p$ , give rise to the terms  $^1S, ^1F, ^1D, ^3S, ^3P, ^3D$ ; but if the two electrons are equivalent, say  $2p^2$ , then the terms  $^3D, ^3S$  and  $^1P$  do not exist and we have only the terms  $^1S, ^1D$  and  $^3P$ . Let us now see how to obtain terms from a configuration involving equivalent electrons. Before we do so we must mention two important facts :

(i) A closed sub-shell, such as  $s^2, p^6, d^{10}, \dots$ , always forms a  $^1S_0$  term only. The closed sub-shell consists of maximum number,  $2(2l + 1)$ , of equivalent electrons in antiparallel pairs so that

$$\sum m_l = 0^*$$

$$\sum m_s = 0^*.$$

and

This means that

$$M_L = 0, M_S = 0$$

and so

$$L = 0 \text{ (S-State),}$$

$$S = 0, 2S + 1 = 1 \text{ (singlet)}$$

and

$$J = 0.$$

That is, the only possible term is  ${}^1S_0$ . Hence, we conclude that when a subshell is completely filled, the only allowed state is one in which the total spin angular momentum, total orbital angular momentum and total angular momentum are all zero. This also means that the subshell has no net magnetic dipole moment.

(ii) The terms of a configuration  $(n l)^r$  are the same as the terms of the configuration  $(n l')^{r'}$ , where  $r$  is the maximum number of electrons, that is  $2(2l+1)$ . For example, the terms of  $p^5$  are the same as those of  $p^1$ , the terms of  $p^4$  are the same as those of  $p^2$ , the terms of  $d^8$  are the same as those of  $d^2$ , and so on.

This simplification is based on the fact that a completed subshell like  $p^6$  gives only a  ${}^1S_0$  term (zero angular momentum). This means that the vector addition of the angular momenta of the terms of  $p^2$  (say) to the corresponding quantities for  $p^4$  must give zero. From this it follows that the quantum numbers  $S$  and  $L$  must be the same for  $p^2$  and  $p^4$ , that is, the terms of  $p^2$  are the same as those of  $p^4$ .

We now calculate the spectral terms arising from two equivalent  $p$ -electrons ( $p^2$ ). Let us imagine the atom to be placed in a very strong magnetic field where all the internal couplings are broken down. The individual  $\vec{l}$  and  $\vec{s}$  vectors then precess independently around the magnetic field with quantised components  $m_l h/2\pi$  and  $m_s h/2\pi$  respectively. The value of  $l$  for a  $p$ -electron is 1 and hence the values of  $m_l$  are 1, 0, -1; while those of  $m_s$  are  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . Now, all possible combinations of  $m_l$  and  $m_s$  for a single  $p$ -electron are :

$m_l = 1$	$0$	$-1$	$1$	$0$	$-1$
$m_s = \frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
(a)	(b)	(c)	(d)	(e)	(f)

Thus, there are six possible states (a), (b), (c), (d), (e), (f) in which a single  $p$ -electron can exist in an atom. The possible states for two (equivalent) electrons can be obtained by taking all possible combinations of the above six states taken two at a time, with no two alike (because by Pauli's principle, both  $m_l$  and  $m_s$  cannot be same for two equivalent electrons). There will be 15 such combinations  $\left({}^6C_2 = \frac{6!}{2!(6-2)!} = 15\right)$ . They are

\*For example, for the six  $p$ -electrons ( $l = 1$ ), we have

$$m_l = 1, 1, 0, 0, -1, -1$$

$$m_s = \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$$

$ab, ac, ad, ae, af;$   
 $bc, bd, be, bf;$   
 $cd, ce, cf;$   
 $de, df;$   
 $ef.$

For each of these 15 combinations of very strong field quantum numbers, we add two values of  $m_l$  to obtain the strong field values of  $M_L$ , and two values of  $m_s$  to form  $M_S$  [ $\sum m_l = M_L$  and  $\sum m_s = M_S$ ]. This leads to the following tabulation :

	$ab$	$ac$	$ad$	$ae$	$af$	$bc$	$bd$	$be$	$bf$	$cd$	$ce$	$cf$	$de$	$df$	$ef$
$M_L$	1	0	2	1	0	-1	1	0	-1	0	-1	-2	1	0	-1
$M_S$	1	1	0	0	0	1	0	0	0	0	0	0	-1	-1	-1

The highest value of  $M_L$  is 2 which indicates a  $D$  term ( $L = 2$ ). Since this value of  $M_L$  occurs only with  $M_S = 0$ , the term is  $^1D$  ( $S = 0$ ). Apart from  $M_L = 2$ ;  $M_L = 1, 0, -1, -2$  also belong to this term, each having  $M_S = 0$ . Thus, out of the above 15 combinations, the following combinations form  $^1D$  term.

$$\left. \begin{array}{ccccc} ad & ae & af & bf & cf \\ M_L = & 2 & 1 & 0 & -1 & -2 \\ M_S = & 0 & 0 & 0 & 0 & 0 \end{array} \right\} ^1D.$$

Of the remaining  $M_L$  and  $M_S$  values, the highest  $M_L$  is 1 and the highest  $M_S$  is 1. These values must belong to a  $^3P$  term ( $L = 1, S = 1$ ), because only for such a term can the highest values of  $M_L$  and  $M_S$  be 1. But  $L = 1$  corresponds to  $M_L = 1, 0, -1$ ; and  $S = 1$  corresponds to  $M_S = 1, 0, -1$ . Hence all the following nine combinations belong to the  $^3P$  term :

$$\left. \begin{array}{cccccccc} ab & ac & bc & bd & cd & ce & de & df & ef \\ M_L = & 1 & 0 & -1 & 1 & 0 & -1 & 1 & 0 & -1 \\ M_S = & 1 & 1 & 1 & 0 & 0 & 0 & -1 & -1 & -1 \end{array} \right\} ^3P.$$

Only one combination  $be$  is left for which  $M_L = 0$  and  $M_S = 0$ . Hence, it can give only a  $^1S$  term ( $L = 0, S = 0$ ).

$$\left. \begin{array}{c} be \\ M_L = 0 \\ M_S = 0 \end{array} \right\} ^1S.$$

Thus, two equivalent  $p$ -electrons give rise to  $^1D$ ,  $^3P$  and  $^1S$  terms; and no others. The fine-structure levels are  $^1D_2$ ,  $^3P_{0,1,2}$  and  $^1S_0$ .

The same terms are readily calculated from Breit's scheme. In this scheme we write in a table all the possible values of  $M_L$  which can be formed by the combination of  $m_{l_1}$  and  $m_{l_2}$  of the two electrons. For this we write the values of  $m_{l_1}$  and  $m_{l_2}$  in a row and in a column respectively. The sums  $M_L$  are written below  $m_{l_1}$  and to the left of  $m_{l_2}$ . These nine values of  $M_L$

$m_{l_1}$	1	0	-1	
$M_L$	2	1	0	1
$M_L$	1	0	-1	0
$M_L$	0	-1	-2	-1

(two equivalent  $p$ -electrons)  
 $l_1 = 1; l_2 = 1$

form three sets divided by the L-shaped (dotted) lines. These sets are :

2	1	0	-1	-2	(I set)
	1	0	-1		(II set)
		0			(III set)

These sets of  $M_L$ -values correspond to  $L = 2, 1$  and 0 respectively, that is, to one  $D$ , one  $P$ , and one  $S$  term.

The spins of the two electrons can be combined to form either  $S = 0$  (singlets) or  $S = 1$  (triplets). For  $S = 1$ , both electrons have the same spin quantum number  $m_s$  and hence they must differ in their values of  $m_l$ . We cannot, therefore, combine any of the  $M_L$ -values lying on the diagonal of the above table with  $S = 1$  (because the diagonal corresponds to equal values of  $m_{l_1}$  and  $m_{l_2}$ ). Also, we can use only the  $M_L$ -values from one side of the diagonal, as those on the other side merely correspond to a different numbering of the electrons (otherwise they are identical with, and are a mirror image of those on the first side). Thus, with  $S = 1$  (triplets), we are limited to the following  $M_L$ -values.

1	0	-1	(II set)
---	---	----	----------

which are the components of a term with  $L = 1$ . This corresponds to a  $^3P$  term or a  $^3P_{0,1,2}$  multiplet.

When  $S = 0$ , the electrons differ in their spin quantum numbers and there is no restriction on the values of  $M_L$  which may be combined with this value of  $S$ . As the II set of  $M_L$  values has already been used to form the  $^3P$  term, we have only the remaining I and III sets to combine with  $S = 0$  (singlets). These sets are the components of terms with  $L = 2$  and  $L = 0$  respectively. Hence, they correspond to  $^1D$  and  $^1S$  terms.

Thus, two equivalent  $p$ -electrons give  $^1S$ ,  $^1D$  and  $^3P$  terms or  $^1S_0$ ,  $^1D_2$  and  $^3P_{0,1,2}$  multiplets.

These will also be the terms for  $p^4$  configuration.

Let us now consider two equivalent  $d$ -electrons, that is,  $(nd)^2$  configuration. The Breit's scheme for the possible  $M_L$ -values is :

$m_{l_1} =$	2	1	0	-1	-2	
$M_L =$	4	3	2	1	0	2
$M_L =$	3	2	1	0	-1	1
$M_L =$	2	1	0	-1	-2	0
$M_L =$	1	0	-1	2	-3	-1
$M_L =$	0	-1	-2	-3	4	-2
	S	P	D	F	G	$m_{l_2}$

(two equivalent  $d$ -electrons)

$$l_1 = 2; l_2 = 2$$

There are 5 sets of  $M_L$ -values :

4 3 2 1 0 -1 -2 -3 -4 (I set)  
 3 2 1 0 -1 -2 -3 (II set)  
 2 1 0 -1 -2 (III set)  
 1 0 -1 (IV set)  
 0 (V set)

These sets correspond to  $L = 4, 3, 2, 1, 0$  respectively, that is, to  $G, F, D, P, S$  terms respectively. (V set)

The spins of the two electrons can be combined to form either  $S = 0$  (singlets) or  $S = 1$  (triplets). For  $S = 1$ , we are limited to the  $M_L$  values from one side of the diagonal, that is, to the following sets :

$$\begin{array}{ccccccc} 3 & 2 & 1 & 0 & -1 & -2 & -3 \\ & & 1 & 0 & -1 \end{array} \quad (\text{II set}) \quad (\text{IV set})$$

These sets correspond to  $L = 3$  and  $L = 1$  and give  $^3F$  and  $^3P$  terms or  $^3F_{2, 3, 4}$  and  $^3P_{0, 1, 2}$  multiplets.

The remaining I, III, and V sets of  $M_L$ -values are to be combined with  $S = 0$  (singlets). They yield  $^1G$ ,  $^1D$  and  $^1S$  terms. Thus, two equivalent  $d$ -electrons give

$$^1S_0, \ ^1D_2, \ ^1G_4, \ ^3P_{0,1,2}, \ ^3F_{2,3,4}.$$

These will also be the terms for  $d^8$  configuration.

As a final example, we now calculate the spectral terms arising from configuration. The six possible states for a single  $p$ -electron in a very strong field are

$m_l = 1$	$0$	$-1$	$1$	$0$	$-1$
$m_s = \frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
(a)	(b)	(c)	(d)	(e)	(f)

The possible states for three (equivalent) electrons can be obtained by taking all possible combinations of the above six states taken three at a time, with no two alike. There will be

20 such combinations  $\left( {}^6C_3 = \frac{6!}{3!(6-3)!} = 20 \right)$ . They are

*abc abd abe abf acd aceacf adeadf aef*

*bcd bce bcf bde bdf bef cde cdf cef def*

For each of these 20 combinations we obtain  $M_L$  ( $= \sum m_i$ ) and  $M_S$  ( $= \sum m_s$ ). This leads to the following tabulation :

The highest values of  $M_L$  are 2 which indicate a D-term ( $L = 2$ ). Since they occur with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$ , which are the magnetic field components of  $S = \frac{1}{2}$ , the term is  $^2D$ . Apart from  $M_L = 2$ ;  $M_L = 1, 0, -1, -2$  and each with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$  also belong to this term. Thus, out of the above 20 combinations those marked by a single star (\*) go to form the  $^2D$  term.

Of the remaining combinations, the highest  $M_L$  are 1, and again they occur with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$ . They indicate, therefore, a  $^2P$  term ( $L = 1, S = \frac{1}{2}$ ). Apart from  $M_L = 1; M_L = 0, -1$  and each with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$  also belong to this term. Hence the combinations marked by a double star (\*\*) belong to the  $^2P$  term.

The remaining four combinations are :

$$M_L = 0 \quad 0 \quad 0 \quad 0$$

$$M_S = \frac{3}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{3}{2}$$

These  $M_L$  and  $M_S$  values are the components of  $L = 0$  and  $S = \frac{3}{2}$  which correspond to a  $^4S$  term. Thus, the terms of  $p^3$  are

$$^2P^*, \quad ^2D^*, \quad ^4S^*$$

$$\text{or} \quad ^2P_{1/2, 3/2}; \quad ^2D_{3/2, 5/2}; \quad ^4S_{3/2}.$$

Some important results are as follows :

### Terms of Equivalent Electrons

Electron Configuration	Terms
$s^1$	$^2S_{1/2}$
$s^2, p^6, d^{10}$	$^1S_0$
$p^1, p^5$	$^2P_{1/2, 3/2}$
$p^2, p^4$	$^1S_0, ^1D_2, ^3P_{0, 1, 2}$
$p^3$	$^2P_{1/2, 3/2}, ^2D_{3/2, 5/2}, ^4S_{3/2}$
$d^1, d^9$	$^2D_{3/2, 5/2}$
$d^2, d^8$	$^1S_0, ^1D_2, ^1G_4, ^3P_{0, 1, 2}, ^3F_{2, 3, 4}$

If a given configuration contains both equivalent and non-equivalent electrons, then we can derive the spectral terms by starting with the equivalent electron terms and combining the other electrons, one by one, with them. Thus, suppose we have a configuration  $4p^2 5s$ , which is even.

The terms for  $4p^2$  are  $^1S, ^1D$  and  $^3P$ .

Let us add the  $5s$  electron to each of these :

$$\begin{array}{l}
 {}^1S + s = {}^2S = {}^2S_{1/2} \\
 (L' = 0, S' = 0) \quad \left( l = 0, s = \frac{1}{2} \right) \quad \left( L = 0, S = \frac{1}{2} \right) \\
 {}^1D + s = {}^2D = {}^2D_{3/2, 5/2} \\
 (L' = 2, S' = 0) \quad \left( l = 0, s = \frac{1}{2} \right) \quad \left( L = 2, S = \frac{1}{2} \right) \\
 {}^3P + s = {}^2P, {}^4P = {}^2P_{1/2, 3/2}, {}^4P_{1/2, 3/2, 5/2} \\
 (L' = 1, S' = 1) \quad \left( l = 0, s = \frac{1}{2} \right) \quad \left( L = 1, S = \frac{1}{2}, \frac{3}{2} \right)
 \end{array}$$

## 7. Order of Terms and Fine-structure Levels

The relative energies of the various terms and levels which arise from a given (equivalent) electron configuration may be deduced from a set of rules given by Hund. These rules are :

(1) Of the terms arising from equivalent electrons, those with largest multiplicity lie lowest.

(2) Of the terms with given multiplicity, and arising from equivalent electrons, that with largest  $L$  value lies lowest.

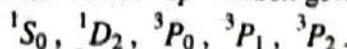
(3a) In the multiplets formed from equivalent electrons in a less than half-filled sub-shell, the level with lowest  $J$  lies lowest ("normal order").

(3b) In the multiplets formed from equivalent electrons in a more than half-filled sub-shell, the level with highest  $J$  lies lowest ("inverted order").

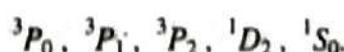
(3c) Terms arising from half-filled sub-shells show only very slight fine-structure splitting.

(3d) The lowest terms arising from the half-filled sub-shells are the  $S$ -terms and are specially stable. These terms are  ${}^2S_{1/2}$  for a half-filled  $s$  sub-shell,  ${}^4S_{3/2}$  for a half-filled  $p$  sub-shell,  ${}^6S_{5/2}$  for a half-filled  $d$  sub-shell, and  ${}^8S_{7/2}$  for a half-filled  $f$  sub-shell.

Hund was quite successful in predicting the lowest terms and levels of many atoms. However, exceptions do occur. Let us apply these rules to some examples. The normal configuration of the carbon atom is  $1s^2 2s^2 2p^2$  which gives rise to the following terms :



Applying Hund's set of rules and remembering that these terms arise from a less than half-filled sub-shell ( $p^2$ ), we find that these terms are in the following order of increasing energy :



The oxygen atom, on the other hand, has the configuration  $1s^2 2s^2 2p^4$ . The terms are again  ${}^1S_0, {}^1D_2, {}^3P_{0,1,2}$ ; the ground state being a  ${}^3P$  term. However, since the  $2p$  sub-shell is more than half-filled, the multiplet will be inverted and the state of lowest energy will now be the  ${}^3P_2$  term.

The nitrogen atom has the configuration  $1s^2 2s^2 2p^3$ , which gives rise to  $^2P^*$ ,  $^2D^*$ ,  $^4S^*$  terms. The  $^4S^*$  is the ground state, the next above it is  $^2D^*$  and then is  $^2P^*$ .

## 8. Normal Electron Configuration and Spectral Terms of Certain Atoms

We give below for certain important atoms the normal electron configurations and the terms (or levels) arising from them.

Atom	Configuration	Terms
$^1H$	$1s$	$^2S_{1/2}$
$^2He$	$1s^2$	$^1S_0$
$^3Li$	$1s^2 2s$	$^2S_{1/2}$
$^4Be$	$1s^2 2s^2$	$^1S_0$
$^5B$	$1s^2 2s^2 2p$	$^2P^*_{1/2}$ (ground), $^2P^*_{3/2}$
$^6C$	$1s^2 2s^2 2p^2$	$^1S_0$ , $^1D_2$ , $^3P_0$ (ground), $^3P_1$ , $^3P_2$
$^7N$	$1s^2 2s^2 2p^3$	$^2P^*_{1/2}$ , $^2P^*_{3/2}$ , $^2D^*_{3/2}$ , $^2D^*_{5/2}$ , $^4S^*_{3/2}$ (ground)
$^8O$	$1s^2 2s^2 2p^4$	$^1S_0$ , $^1D_2$ , $^3P_0$ , $^3P_1$ , $^3P_2$ (ground)
$^9F$	$1s^2 2s^2 2p^5$	$^2P^*_{1/2}$ , $^2P^*_{3/2}$ (ground)
$^{10}Ne$	$1s^2 2s^2 2p^6$	$^1S_0$
$^{11}Na$	$1s^2 2s^2 2p^6 3s$	$^2S_{1/2}$
$^{12}Mg$	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$
$^{17}Cl$	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^*_{1/2}$ , $^2P^*_{3/2}$ (ground)
$^{20}Ca$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$
$^{29}Cu$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$	$^2S_{1/2}$
$^{30}Zn$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	$^1S_0$
$^{80}Hg$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$	$^1S_0$

## 9. Selection Rules for Multi-electron Atoms in L-S Coupling

The selection rules for the electric-dipole transitions in multi-electron atoms are closely similar to the selection rules for the one-electron atom.

(i) Most of the transitions occur in which only one electron jumps at a time, and such that its  $l$ -value changes by one unit, that is,

$$\Delta l = \pm 1.$$

This is a special case of the more general Laporte rule that the parity\* of the configuration must change in an electric-dipole transition (odd  $\leftrightarrow$  even).

\*The parity is odd or even according as  $\sum l_i$  of the configuration is odd or even respectively.

In case more than one electron jumps, the Laporte rule requires that the sum of the individual  $l$ 's must change by an odd number of units. For example, if we have a transition involving two electrons simultaneously, then  $\Delta l$  must be even for one electron and odd for the other. Since we have  $\Delta l = \pm 1$  for a one-electron transition, for a two-electron transition we would have

$$\Delta l_1 = \pm 1; \Delta l_2 = 0, \pm 2.$$

Thus, a double electron jump may take place from the configuration  $3d\ 4d$  (even) to  $4s\ 4p$  (odd). There are two possibilities.  $4d$  may go to  $4p$  ( $\Delta l_1 = -1$ ) and  $3d$  to  $4s$  ( $\Delta l_2 = -2$ ); or  $3d$  to  $4p$  ( $\Delta l_1 = -1$ ) and  $4d$  to  $4s$  ( $\Delta l_2 = -2$ ).

(ii) There is no restriction on the total quantum number  $n$  of either electron.

(iii) For the atom as a whole, the quantum numbers  $L$ ,  $S$  and  $J$  must change as follows :

$$\Delta L = 0, \pm 1 \text{ (In one-electron atoms } \Delta L = 0 \text{ is not allowed)}$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1 \quad \text{but} \quad J = 0 \leftrightarrow J = 0.$$

The rules for  $L$  and  $S$  hold only when the spin-orbit (magnetic) coupling is weak, that is, when the splittings between the various fine-structure levels of a multiplet are very small compared with the separations between the various multiplets themselves. We know that the spin-orbit interaction increases rapidly as we go to heavier atoms. Hence the above rules for  $L$  and  $S$  hold quite accurately for light atoms but not well for heavy atoms. This is why there are no intercombination lines (singlet-triplet transitions) in the spectrum of helium, but they are quite strong in the spectrum of mercury. As a matter of fact, for heavy atoms the whole concept of  $L-S$  coupling breaks down and one approaches to  $j-j$  coupling.

## 10. $j-j$ Coupling

In its ideal form, the  $j-j$  coupling is an opposite extreme to the ideal  $L-S$  coupling and is approached by the heavier atoms, for which the spin-orbit (magnetic) interaction term in the Hamiltonian predominates over the residual electrostatic interaction and the spin-spin corelation. This means that the interaction between the orbital and the spin momenta of a single electron is much greater than the interaction between the orbital momenta of different electrons or between the spin momenta of different electrons. Therefore, in this case the splitting of the unperturbed energy level due to the introduction of the various perturbations takes place in the order : (a) spin-orbit interaction, (b) residual electrostatic interaction and spin-spin corelation.

(a) As a result of the stronger spin-orbit interaction, the orbital and the spin angular momentum vectors of each individual electron are strongly coupled together to form a resultant angular momentum vector  $\vec{j}$  of magnitude  $\sqrt{j(j+1)} \frac{\hbar}{2\pi}$ , where

$j = l - \frac{1}{2}$  and  $l + \frac{1}{2}$ , that is,  $j$  takes half-integral values only. This means that due to spin-orbit interaction, the unperturbed energy level is splitted into a number of well-spaced levels, each corresponding to a different combination of the possible  $j$ -values for the individual optical electrons; the level corresponding to all the electrons having their smaller  $j$ -value ( $j = l - \frac{1}{2}$ ) being lowest.

(b) As a result of the residual electrostatic interaction and spin-spin correlation, the resultant angular momentum vectors  $\vec{j}$  of the individual electrons are less strongly coupled with one another to form the total angular momentum vector  $\vec{J}$  of the atom, of magnitude  $\sqrt{J(J+1)} \frac{\hbar}{2\pi}$ . The total angular momentum quantum number takes the values :

$$J = \left| \vec{j}_1 + \vec{j}_2 + \dots \right|_{\min}, \left| \vec{j}_1 + \vec{j}_2 + \dots \right|_{\min} + 1, \dots \quad (j_1 + j_2 + \dots)$$

This means that each of the above levels is further splitted into a number of levels characterised by different values of  $J$ .

As an illustration, let us consider the terms for the electron configuration  $4p\ 4d$ , under  $j-j$  coupling. (We recall that under  $L-S$  coupling this configuration gives the terms  $^1P_1; ^1D_2; ^1F_3; ^3P_{0,1,2}; ^3D_{1,2,3}; ^3F_{2,3,4}$ .)

$$\text{For the } p\text{-electron: } l_1 = 1, s_1 = \frac{1}{2}; \text{ and so } j_1 = \frac{1}{2}, \frac{3}{2}.$$

$$\text{For the } d\text{-electron: } l_2 = 2, s_2 = \frac{1}{2}; \text{ and so } j_2 = \frac{3}{2}, \frac{5}{2}.$$

This gives four  $(j_1, j_2)$  combinations of the possible  $j_1$  and  $j_2$  values. These are

$$\left( \frac{1}{2}, \frac{3}{2} \right); \left( \frac{1}{2}, \frac{5}{2} \right); \left( \frac{3}{2}, \frac{3}{2} \right) \text{ and } \left( \frac{3}{2}, \frac{5}{2} \right).$$

Thus, the spin-orbit interaction splits the unperturbed energy level into four levels, of which  $\left( \frac{1}{2}, \frac{3}{2} \right)$  lies lowest and  $\left( \frac{3}{2}, \frac{5}{2} \right)$  lies highest.

Each of the above four levels is further splitted by residual electrostatic interaction and spin-spin correlation into a number of  $J$ -levels, equal to the number of integrally spaced values of  $J$  that can be formed out of the two  $j$ -values. The above four  $(j_1, j_2)$  combinations give  $J$  values as under :

$$\left( \frac{1}{2}, \frac{3}{2} \right) \text{ gives } J = 1, 2.$$

$$\left( \frac{1}{2}, \frac{5}{2} \right) \text{ gives } J = 2, 3.$$

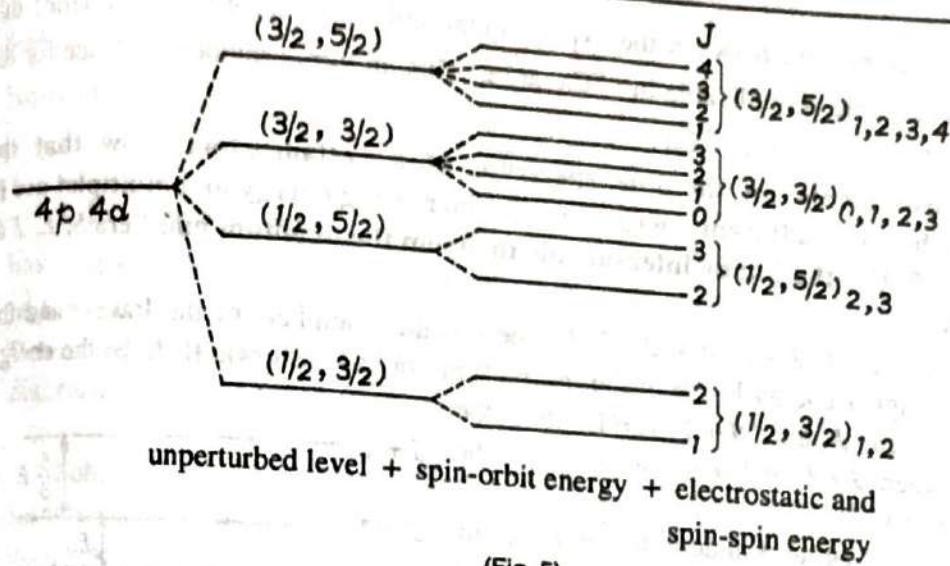
$$\left( \frac{3}{2}, \frac{3}{2} \right) \text{ gives } J = 0, 1, 2, 3.$$

$$\left( \frac{3}{2}, \frac{5}{2} \right) \text{ gives } J = 1, 2, 3, 4.$$

The complete splitting is shown in Fig. 5 (see next page).

We see that the total number of final levels is the same (12) as for the  $L-S$  coupling and that the  $J$  values also are the same.

Pure  $j-j$  coupling occurs relatively seldom. In fact, there is a gradual shift from  $L-S$  coupling for certain levels of lighter atoms toward  $j-j$  coupling for the heavier atoms. An example of such a transition is seen in the levels of the first excited state of the IV-group elements C, Si, Ge, Sn and Pb. Whereas C and Si have practically pure  $L-S$  coupling, Ge, Sn and Pb approach closer and closer to  $j-j$  coupling. For the ground state of these atoms however, it is the  $L-S$  coupling which holds.



(Fig. 5)

## 11. Selection Rules in $j-j$ Coupling

- (i) The parity of the configuration must change in an electric-dipole transition (Laporte rule). This means that if only one electron jumps in the transition (as is usually the case) then for this electron we must have  $\Delta l = \pm 1$ . If two electrons jump then  $\Delta l_1 = \pm 1$  and  $\Delta l_2 = 0, \pm 2$ . This rule is exactly same as in L-S coupling.
- (ii)  $\Delta j = 0, \pm 1$  for the jumping electron, and  $\Delta j = 0$  for all the other electrons.
- (iii) For the atom as a whole,

$$\Delta J = 0, \pm 1 \text{ but } J = 0 \leftrightarrow J = 0.$$

The selection rules  $\Delta S = 0$  and  $\Delta L = 0, \pm 1$  no longer hold, since  $L$  and  $S$  are no longer good quantum numbers.

## SOLVED PROBLEMS

1. In the  $3d\ 3d$  configuration of the  $^{20}\text{Ca}$  atom there is a normal triplet of levels :  $^3P_0, ^3P_1, ^3P_2$ . The measured energy interval between the  $^3P_1$  and  $^3P_0$  levels is  $16.7 \times 10^{-4}$  eV and that between the  $^3P_2$  and  $^3P_1$  levels is  $33.3 \times 10^{-4}$  eV. Show that these values verify the Lande interval rule.

**Solution.** By Lande interval rule, the interval between two consecutive fine-structure levels corresponding to  $J$  and  $J + 1$  is proportional to  $J + 1$ , that is,

$$E_{J+1} - E_J = 2A(J+1),$$

where  $A$  is some constant. Therefore, the energy interval between  $^3P_1$  and  $^3P_0$  levels is

$$E_1 - E_0 = 2A(1)$$

and that between  $^3P_2$  and  $^3P_1$  levels is

$$E_2 - E_1 = 2A(2).$$

Thus, the Lande interval rule predicts that

$$\frac{E_1 - E_0}{E_2 - E_1} = \frac{1}{2} = 0.500.$$

According to experiment, we have

$$\frac{E_1 - E_0}{E_2 - E_1} = \frac{16.7 \times 10^{-4} \text{ eV}}{33.3 \times 10^{-4} \text{ eV}} = 0.501.$$

The excellent agreement between the experimental and the predicted ratios verifies that Lande's interval rule is applicable in  $^{20}\text{Ca}$  atom. This, in turn, provides evidence for the presence of  $L\text{-}S$  coupling in  $^{20}\text{Ca}$ .

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

**Solution.** Let  $J, J+1$  and  $J+2$  be the quantum numbers of the lowest and the successively higher energy levels of the (normal) multiplet, as shown. If  $E$  be the energy interval between  $J$  and  $J+1$  levels, then the interval between  $J+1$  and  $J+2$  levels would be  $J+2$

$(5/3)E$ , as given.

Now, according to Lande interval rule, the energy interval between adjacent levels of a multiplet is proportional to the  $J$  value of the upper level. Thus,

$$E = 2A(J+1)$$

$$(5/3)E = 2A(J+2).$$

and

$$\frac{3}{5} = \frac{J+1}{J+2}.$$

Dividing :

$$J = \frac{1}{2}.$$

Solving :

Thus, the  $J$  values of the levels, in the order of increasing energy, are

$$J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}.$$

To determine the values of  $S$  and  $L$  for the multiplet, we use

$$J = |L - S|, |L - S| + 1, \dots, (L + S).$$

The minimum and the maximum values of  $J$  are  $\frac{1}{2}$  and  $\frac{5}{2}$ . Thus,

$$|L - S| = \frac{1}{2}$$

and

$$(L + S) = \frac{5}{2}.$$

Let us suppose that  $L > S$ . Then

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

and

$$L + S = \frac{5}{2}.$$

Addition and subtraction give

$$L = \frac{3}{2} \text{ and } S = \frac{1}{2}.$$

But, the total orbital angular momentum quantum number  $L$  cannot be half-integers. Hence, our supposition  $L > S$  is wrong.

Obviously,  $L < S$ . Then

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

and

$$S + L = \frac{5}{2}$$

Now, addition and subtraction give

$$S = \frac{3}{2} \text{ and } L = 1.$$

**3. In an atom, obeying L-S coupling, the components of a normal triplet state have separations } 20 \text{ cm}^{-1} \text{ and } 40 \text{ cm}^{-1} \text{ between adjacent components. There is a higher state for which the separations are } 22 \text{ cm}^{-1} \text{ and } 33 \text{ cm}^{-1} \text{ 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.}**

**Solution.** Let  $J, J+1, J+2$  be the quantum numbers of the lowest and the successively higher component levels of the lower *normal* triplet state. By Lande rule, the energy separation of adjacent levels of a multiplet is proportional to the larger of the two quantum numbers involved. Thus,

$$\frac{J+1}{J+2} = \frac{20 \text{ cm}^{-1}}{40 \text{ cm}^{-1}}$$

This gives  $J = 0$ . This means that the  $J$  values of the levels are, in the order of increasing energy,

$$J = 0, 1, 2.$$

To determine the values of  $S$  and  $L$  for the multiplet, we use

$$J = |L - S|, |L - S| + 1, \dots \quad (L + S).$$

Since the minimum value of  $J$  is 0 and the maximum value is 2, we have

$$|L - S| = 0$$

$$(L + S) = 2.$$

To handle the absolute value, we consider two cases. In this first case  $L > S$ , and the above two equations are

$$L - S = 0$$

$$L + S = 2.$$

$$S = 1, \text{ so that } 2S + 1 = 3$$

$$L = 1 \text{ (P state).}$$

The second case  $L < S$  would give the same result\*. Thus, the levels of the lower state term are

$${}^3P_0, {}^3P_1, {}^3P_2.$$

Proceeding as above for the higher state, we have

$$\frac{J+1}{J+2} = \frac{22 \text{ cm}^{-1}}{33 \text{ cm}^{-1}}$$

This gives  $J = 1$ . This means that the  $J$  values of the upper state levels, in the order of increasing energy, are

$$J = 1, 2, 3.$$

$$J = |L - S|, |L - S| + 1, \dots \quad (L + S).$$

$$|L - S| = 1$$

$$(L + S) = 3.$$

\*The value of  $S$  can alternatively be determined by the fact that the given multiplet is a 'triplet' so that  $2S + 1 = 3$  and hence  $S = 1$ .

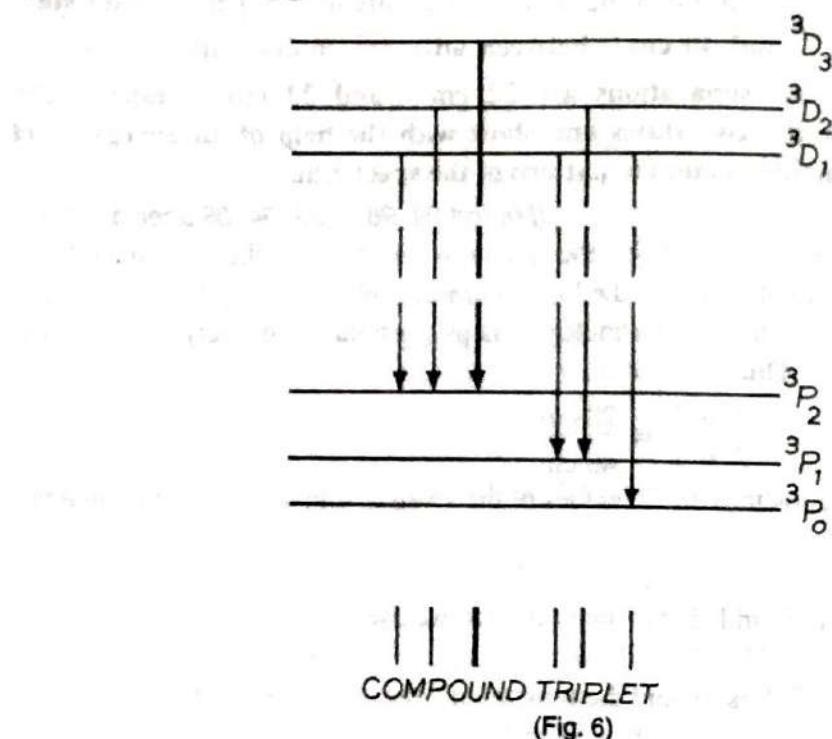
But  $S = 1$  (for triplet) and so

$$L = 2 \text{ (D state).}$$

The levels of the upper state are

$$^3D_1, ^3D_2, ^3D_3.$$

The energy level diagram has been drawn in Fig. 6.



Applying the selection rule

$$\Delta J = 0, \pm 1 \text{ but } J = 0 \leftrightarrow J = 0,$$

we obtain six transitions. The spectrum is a compound triplet.

**4. In a quartet transition for C<sup>+</sup> observed by Fowler and Selwyn, the separations between the upper state multiplet levels are found to be 14.72, 25.07 and 36.30 cm<sup>-1</sup>, while the separations between the lower state multiplet levels are found to be 23.84 and 45.0 cm<sup>-1</sup>. Obtain the term designation of the particular transition involved and draw the energy level diagram also. Which of the components would be most strong?**

(Meerut 95)

**Solution.** Let  $J, J+1, J+2, J+3$  be the  $J$ -values of the lowest, and the successive higher levels of the upper state multiplet. By Lande rule, the energy separation between two successive levels  $J$  and  $J+1$  of a multiplet is proportional to  $J+1$ . Thus,

$$\frac{J+1}{J+2} = \frac{14.72}{25.07} = \frac{2.944}{5.014} \approx \frac{3}{5}$$

and

$$\frac{J+2}{J+3} = \frac{25.07}{36.30} = \frac{5.014}{7.26} \approx \frac{5}{7}.$$

These give  $J = \frac{1}{2}$ . Thus, the  $J$ -values of the levels are

$$J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}.$$

To determine the values of  $S$  and  $L$  for the multiplet, we write

$$J = |L - S|, |L - S| + 1, \dots, (L + S).$$

The minimum and maximum values of  $J$  are  $\frac{1}{2}$  and  $\frac{7}{2}$ . Thus,

$$|L - S| = \frac{1}{2}$$

and

$$(L + S) = \frac{7}{2}.$$

Let us suppose that  $L > S$ . Then

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

and

$$L + S = \frac{7}{2}.$$

Solving :  $S = \frac{3}{2}$ , so that  $2S + 1 = 4$  (quartet)

and

$$L = 2 \text{ (D-state).}$$

The levels of the upper state are

$${}^4D_{1/2}, {}^4D_{3/2}, {}^4D_{5/2}, {}^4D_{7/2}.$$

If we suppose that  $L < S$ , then, we shall write

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

and

$$L + S = \frac{7}{2}.$$

These would give

$$S = 2, L = \frac{3}{2}.$$

But this is not possible because the total orbital angular momentum quantum number  $L$  cannot be half-integral. Hence, the assumption  $L < S$  is wrong.

Proceeding as above for the lower state multiplet levels, we have

$$\frac{J+1}{J+2} = \frac{23.84}{45.0} = \frac{2.65}{5} \approx \frac{3}{5}.$$

This gives  $J = \frac{1}{2}$ . The  $J$ -values of the levels are thus

$$J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}.$$

Again,

$$J = |L - S|, |L - S| + 1, \dots, (L + S).$$

Thus,

$$|L - S| = \frac{1}{2}$$

and

$$(L + S) = \frac{5}{2}.$$

Let us first suppose  $L > S$ . Then

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

and

$$L + S = \frac{5}{2}.$$

y

e

These would give  $L = \frac{3}{2}$  which is not possible. Hence, let us now suppose  $L < S$ . Then we shall write

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

and  $L + S = \frac{5}{2}$ .

These give  $S = \frac{3}{2}$ , so that  $2S + 1 = 4$  (quartet)

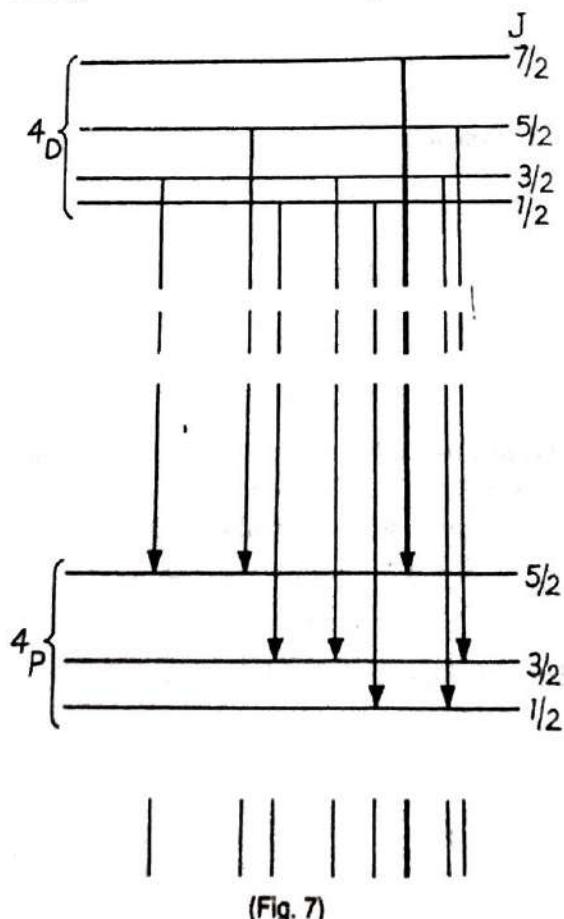
and  $L = 1$  ( $P$ -state).

The levels of the lower state are

$${}^4P_{1/2}, {}^4P_{3/2}, {}^4P_{5/2}.$$

We note that a  ${}^4P$  term has only three components (because  $L < S$ , hence the number of components is  $2L + 1$  and *not*  $2S + 1$ ).

The energy level diagram has been drawn in Fig. 7.



(Fig. 7)

#### Applying the selection rule

$$\Delta J = 0, \pm 1 (J = 0 \leftrightarrow J = 0)$$

we obtain eight transitions.

In a multiplet, those transitions for which  $J$  and  $L$  alter in the same sense are the most intense ; of these the most intense is that with greatest  $J$ . Thus, the transition  ${}^4D_{7/2} \rightarrow {}^4P_{5/2}$  is the most intense.

5. The quantum numbers of the two optical electrons in a two-valence electron atom are :

$$n_1 = 6, l_1 = 3, s_1 = \frac{1}{2}$$

$$n_2 = 5, l_2 = 1, s_2 = \frac{1}{2}$$

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

**Solution.** (a) Given that :

(Meerut 2003, 2000 special paper)

$$l_1 = 3, l_2 = 1,$$

$$\therefore L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots (l_1 + l_2) \\ = 2, 3, 4.$$

Again,

$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}.$$

$$\therefore S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots (s_1 + s_2) \\ = 0, 1.$$

The J-values are :

$$J = |L - S|, \dots (L + S).$$

For  $S = 0$  and  $L = 2, 3, 4$ , we have

$$J = 2, 3, 4.$$

For  $S = 1$  and  $L = 2, 3, 4$ , we have

$$J = 1, 2, 3; 2, 3, 4 \text{ and } 3, 4, 5.$$

(b)

$$l_1 = 3, s_1 = \frac{1}{2}.$$

$$\therefore j_1 = |l_1 - s_1|, |l_1 - s_1| + 1, \dots (l_1 + s_1) \\ = \frac{5}{2}, \frac{7}{2}.$$

Again

$$l_2 = 1, s_2 = \frac{1}{2}.$$

$$\therefore j_2 = \frac{1}{2}, \frac{3}{2}.$$

These give four  $j_1, j_2$  combinations :

$$\left(\frac{1}{2}, \frac{5}{2}\right); \left(\frac{1}{2}, \frac{7}{2}\right); \left(\frac{3}{2}, \frac{5}{2}\right); \left(\frac{3}{2}, \frac{7}{2}\right);$$

These combinations give the following J-values :

$$\left(\frac{1}{2}, \frac{5}{2}\right) \text{ gives } J = 2, 3,$$

$$\left(\frac{1}{2}, \frac{7}{2}\right) \text{ gives } J = 3, 4,$$

$$\left(\frac{3}{2}, \frac{5}{2}\right) \text{ gives } J = 1, 2, 3, 4,$$

$$\left(\frac{3}{2}, \frac{7}{2}\right) \text{ gives } J = 2, 3, 4, 5.$$

We see that J values (12 in number) are the same in both cases.

**6. Compute the possible terms and energy levels for a configuration with three optically active electrons  $2p\ 3p\ 4d$ .**

**Solution.** The configuration  $2p\ 3p\ 4d$  is even. Let us first compute spin combinations. We have

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

On combining  $s_1$  and  $s_2$ , we obtain  $S' = 0, 1$ . Then, on combining  $s_3$  with each of these  $S'$  values, we obtain

$$S = \frac{1}{2}, \ \frac{1}{2}, \ \frac{3}{2}$$

$$2S + 1 = 2, 2, 4,$$

so that

which correspond to two sets of doublet terms and one set of quartet terms.

Let us now compute orbital angular momenta combinations. We have

$$l_1 = 1, \ l_2 = 1, \ l_3 = 2.$$

On combining  $l_1$  and  $l_2$ , we obtain

$$L' = 0, 1, 2.$$

Combining  $l_3 = 2$  to each of these  $L'$  values, we obtain

$$L = 2; 1, 2, 3; 0, 1, 2, 3, 4;$$

which correspond to

$D, P, D, F; S, P, D, F, G$  states.

The possible terms are

$$\begin{aligned} & ^2D, ^2D, ^4D; ^2P, ^2P, ^4P, ^2D, ^2D, ^4D, ^2F, ^2F, ^4F; \\ & ^2S, ^2S, ^4S, ^2P, ^2P, ^4P, ^2D, ^2D, ^4D, ^2F, ^2F, ^4F, ^2G, ^2G, ^4G \end{aligned}$$

that is,

$^2S(2), ^2P(4), ^2D(6), ^2F(4), ^2G(2), ^4S(1), ^4P(2), ^4D(3), ^4F(2), ^4G(1)$ , where the numbers in parentheses indicate the number of the corresponding terms.

Including spin-orbit splitting, we can write

$$\begin{aligned} & ^2S_{1/2}(2), ^2P_{1/2, 3/2}(4), ^2D_{3/2, 5/2}(6), ^2F_{5/2, 7/2}(4), ^2G_{7/2, 9/2}(2), \\ & ^4S_{3/2}(1), ^4P_{1/2, 3/2, 5/2}(2), ^4D_{1/2, 3/2, 5/2, 7/2}(3), \\ & ^4F_{3/2, 5/2, 7/2, 9/2}(2), ^4G_{5/2, 7/2, 9/2, 11/2}(1); \end{aligned}$$

a total of 65 levels.

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

(Meerut special paper 2004, 03, 01, 00 S, 96, 90)

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

(Meerut 2000 S)

**Solution.** The normal (ground-state) electronic configuration of  ${}^6C$  is

$$\boxed{1s^2 \ 2s^2 \ 2p^2}.$$

We have to find spectral terms for two *equivalent p* electrons. These terms are (computed in § 6)

$$^1S, ^1D, ^3P.$$

The energy levels are

$^1S_0, ^1D_2, ^3P_0, ^3P_1, ^3P_2$ .

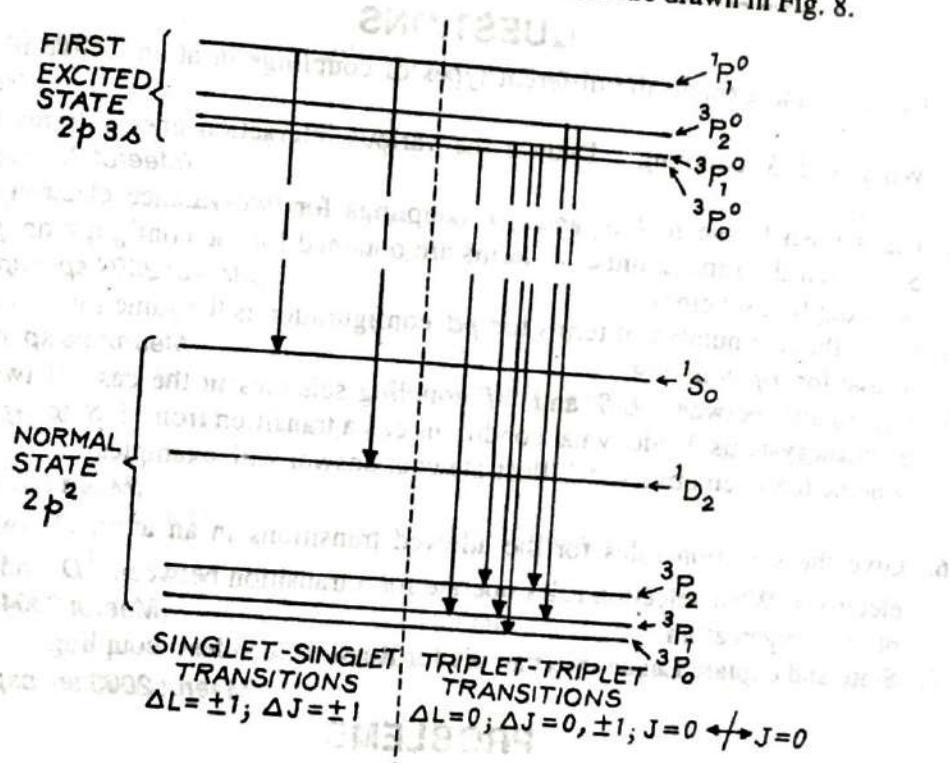
By Hund's rule, we may write them in the order of increasing energy as

$^3P_0, ^3P_1, ^3P_2, ^1D_2, ^1S_0$ .

The level  $^3P_0$  is of lowest energy (ground level). By Lande rule, the energy separations of the components of the triplet  $^3P$  are in the ratio

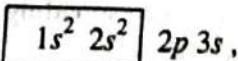
$$\frac{^3P_2 - ^3P_1}{^3P_1 - ^3P_0} = \frac{2}{1}$$

The energy levels for the normal state ( $2p^2$ ) of  ${}^6C$  atom are drawn in Fig. 8.



(Fig. 8)

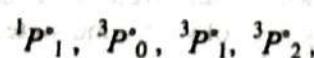
The first excited configuration is



which is odd. This configuration ( $ps$ ) would give the terms



The energy levels would be



the triplet levels being deeper.

The (first) excited-state ( $2p\ 3s$ ) energy levels are also drawn in Fig. 8.

Transitions are allowed under the following selection rules :

1. Transitions can occur only between configurations which differ in the  $n$  and  $l$  quantum numbers of a *single* electron. This means that two or more electrons cannot simultaneously make transitions between energy levels.
2. Transition can occur only between configuration in which the change in  $l$  of that electron satisfies the same restriction as for one-electron atoms, that is,

$$\Delta l = \pm 1.$$

even  $\leftrightarrow$  odd.

3. Transitions can occur only between states in these configurations for which the changes in  $L, S, J$  quantum numbers satisfy the following restrictions :

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

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1; \text{ but } J = 0 \leftrightarrow J = 0.$$

and

Transitions drawn according to the above rules are 8 in number, (2 + 6), as shown.

## QUESTIONS

1. Describe and explain the different types of couplings in atoms. Give illustrative examples. (Meerut 94)
2. What is  $L-S$  coupling ? Deduce the various interaction energy terms for  $L-S$  coupling. (Meerut 2001 sp. paper)
3. Distinguish between  $L-S$  and  $j-j$  couplings for two-valence electron systems. Show that the same number of terms are obtained for the configuration  $ps$  in the two coupling schemes. (Meerut 2004 sp. paper, 2000)
4. Prove that the number of terms for  $pd$  configuration is the same for  $L-S$  coupling as that for  $j-j$  coupling. (Meerut 96 sp. paper, 93)
5. Distinguish between  $L-S$  and  $j-j$  coupling schemes in the case of two-valence electron systems. Under what conditions can a transition from  $L-S$  to  $j-j$  coupling scheme has been observed ? Illustrate your answer with examples. (Meerut 99 sp. paper)
6. Give the selection rules for the allowed transitions in an atom for two valence electrons. What selection rules operate for a transition between  $^1D$  and  $^1S$  terms of the oxygen atom. (Meerut 2004 sp. paper)
7. State and explain Lande interval rule for Russell-Saunders' coupling. (Meerut 2003 sp. paper, 03, 92)

## PROBLEMS

1. Show that an atom having filled subshells has  $^1S_0$  ground state. (Meerut 98 sp. paper)
2. Find the values of  $l, s, j$  and the corresponding values of  $L, S, J$  for an atom having electron configuration  $1s^2 2s^2 2p^1$ . (Meerut 89 sp. paper)
- Ans.  $l = L = 1, s = S = \frac{1}{2}, j = J = \frac{1}{2}, \frac{3}{2}$ .
3. The aluminium atom has two  $3s$  electrons and one  $3p$  electron outside filled inner shells. Find the term symbol of its ground state.  
Hint :  $^{13}\text{Al} : 1s^2 2s^2 2p^6 3s^2 3p$ . Ans.  $^2P_{1/2}$ .
4. The lithium atom has one  $2s$  electron outside a filled inner shell. Its ground state is  $^2S_{1/2}$ . What are the term symbols of the other allowed states, if any ?  
Ans. There are no other allowed states.
5. The magnesium atom has two  $3s$  electrons outside filled inner shells. Find the term symbol of its ground state. Ans.  $^1S_0$ .

6. Express the following states in spectroscopic notation :

- (a)  $L = 1, S = \frac{1}{2}$ ; (b)  $L = 2, S = \frac{7}{2}$ ; (c)  $L = 3, S = 3$ .

**Ans.** (a)  $^2P_{1/2, 3/2}$ ; (b)  $^8D_{3/2, 5/2, 7/2, 9/2, 11/2}$ ; (c)  $^7F_{0, 1, 2, 3, 4, 5, 6}$ . (Meerut 92 sp. paper)

7. Find the values of  $L, S, J$  and the multiplicities of the following spectral levels :

- (a)  $^1S_0$ ; (b)  $^3D_2$ ; (c)  $^4P_{5/2}$ .

**Ans.** (a) 0, 0, 0, 1; (b) 2, 1, 2, 3; (c) 1,  $\frac{3}{2}, \frac{5}{2}, 4$ . (Meerut 92 sp. paper)

8. The term for a particular atomic state is  $^4D_{5/2}$ . What are the values of  $L, S$  and  $J$ ? What is the minimum number of electrons which could give rise to this state? (Meerut 2002, 92)

**Ans.**  $L = 2, S = \frac{3}{2}, J = \frac{5}{2}, 3$ .

9. Compute the allowed spectral terms for (i) two non-equivalent  $p$ -electrons ( $pp$  configuration), and (ii) two equivalent  $p$  electrons ( $p^2$  configuration) on the basis of Pauli's exclusion principle.

**Ans.** (i)  $^1S_0, ^1P_1, ^1D_2, ^3S_1, ^3P_{0, 1, 2}, ^3D_{1, 2, 3}$ ; (ii)  $^1S_0, ^1D_2, ^3P_{0, 1, 2}$ . (Meerut 2006, 04)

10. Which terms can be realised for the following two-electron systems?

- (i)  $np n'd$ , (ii)  $(np)^2$ , (iii)  $(nd)^2$ .

**Ans.** (i)  $^1P, ^1D, ^1F, ^3P, ^3D, ^3F$ , (ii)  $^1S, ^1D, ^3P$ , (iii)  $^1S, ^1D, ^1G, ^3P, ^3F$ . (Meerut 88 sp. paper)

11. Find out the spectral terms for two equivalent  $d$  electrons.

**Ans.**  $^1S_0, ^1D_2, ^1G_4, ^3P_{0, 1, 2}, ^3F_{2, 3, 4}$ .

12. Work out the different electronic terms obtainable from the following electronic configurations and state with reasons, which of these terms represents the ground state of the corresponding atoms :

- (a)  $1s^2 2s^2$ , (b)  $1s^2 2s^2 2p^2$ , (c)  $1s^2 2s^2 2p^3$ , (d)  $1s^2 2s^2 2p^6 3s^2 3p^4$ ,  
 (e)  $1s^2 2s^2 2p^6 3s^2 4p^5$ .

**Ans.** (a)  $^1S_0$ , (b)  $^1S_0, ^1D_2, ^3P_0$  (ground),  $^3P_1, ^3P_2$ ,

(c)  $^2P_{1/2}, ^2P_{3/2}, ^2D_{3/2}, ^2D_{5/2}, ^4S_{3/2}$  (ground)

(d)  $^1S_0, ^1D_2, ^3P_0, ^3P_1, ^3P_2$  (ground)

(e)  $^2P_{1/2}, ^2P_{3/2}$  (ground).

13. What spectral terms should be present in the odd configuration  $2p^2 3p$ ?

**Ans.**  $^2S_{1/2}, ^2P_{1/2, 3/2} (3), ^2D_{3/2, 5/2} (2), ^2F_{5/2, 7/2}; ^4S_{3/2}$ ,

$^4P_{1/2, 3/2, 5/2}, ^4D_{1/2, 3/2, 5/2, 7/2}$ .

14. Deduce terms of  $3p 4d$  configuration system in  $L-S$  and  $j-j$  couplings. Show them in a diagram.

15. The quantum numbers of two electrons in a two-valence electron atom are :

$$n_1 = 5, l_1 = 0, s_1 = \frac{1}{2},$$

$$n_2 = 4, l_2 = 1, s_2 = \frac{1}{2}.$$

nly  
use

- (a) Assuming  $L-S$  coupling, find possible values of  $L$  and hence of  $J$ .  
 (b) Assuming  $j-j$  coupling, find possible values of  $J$ . (Meerut 90)
- Ans.** (a)  $L = 1, J = 1; 0, 1, 2$ . (b)  $J = 0, 1; 1, 2$ .
16. Write down the normal electronic configurations of helium and lithium atoms and determine the states to which these configurations give rise.  
**Ans.**  ${}^2\text{He} : 1s^2, {}^1S_0$ ;  ${}^3\text{Li} : 1s^2 2s, {}^2S_{1/2}$ .
17. Show that the configuration  $2p^2$  in carbon atom gives  ${}^1S_0, {}^3P_{0,1,2}$  and  ${}^1D_2$  states. Draw energy level diagram and denote the ground state. (Meerut 2002 sp. paper)
- Hint :**  ${}^3P_0$  is ground state.
18. The atomic number of carbon is 6. (i) State its electronic configuration. (ii) Calculate the spectroscopic terms for this configuration. (iii) If one of the  $2p$  electrons gets excited to the  $M$ -shell what other spectroscopic terms will be possible? Carbon is governed by  $L-S$  coupling.  
**Ans.** (i)  $1s^2 2s^2 2p^2$ ; (ii)  ${}^1S, {}^1D, {}^3P$ ; (iii)  $2p 3s : {}^1P, {}^3P, 2p 3p : {}^1S, {}^1P, {}^1D; {}^3S, {}^3P, {}^3D, 2p 3d : {}^1P, {}^1D, {}^1F; {}^3P, {}^3D, {}^3F$ .
19. Explain equivalent and non-equivalent electrons. Write down normal electronic configuration of neutral nitrogen atom and spectral terms arising from it, and show that  ${}^2D^*$  is next state to  ${}^4S^*$  ground state. (Meerut 97)  
**Ans.**  $1s^2 2s^2 2p^3; {}^2P_{1/2,3/2}, {}^2D_{3/2,5/2}$  and  ${}^4S_{3/2}$ .
20. Write down the electronic configuration of  $\text{N}^+$  and obtain the spectral terms.  
**Ans.**  $1s^2 2s^2 2p^2; {}^1S_0, {}^1D_2, {}^3P_{0,1,2}$ .
21. Obtain the terms for the ground state of neutral oxygen atom. (Meerut 98 sp. paper)  
**Ans.**  ${}^1S_0, {}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2$  (ground).
22. Write down the normal electronic configuration of  $\text{O}^+$  ion and determine the spectral terms obtained from this configuration. State with reasons the ground term of  $\text{O}^+$  ion.  
**Ans.**  $1s^2 2s^2 2p^3; {}^2P, {}^2D, {}^4S$  (ground).
23. Write electronic configuration of Ca ( $Z = 20$ ). What are various spectral terms? (Meerut 92)  
**Ans.**  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2; {}^1S_0$ .

# Spectra of Alkali Elements

## 1. Broad Features of Alkali Spectra

After hydrogen, the simplest atoms to study with regard to their spectra are the 'alkali atoms';  ${}^3\text{Li}$ ,  ${}^{11}\text{Na}$ ,  ${}^{19}\text{K}$ ,  ${}^{37}\text{Rb}$ ,  ${}^{55}\text{Cs}$  and  ${}^{87}\text{Fr}$ . The experimental study of the spectra of alkali atoms was taken up by Liveing, Dewar, Rydberg and Bergmann. These investigators observed that the spectral lines in the emission spectrum of an alkali atom form four series : a 'principal' series of bright and most persistent lines, a 'sharp' series of fine lines, a 'diffuse' series of comparatively broader lines, and a 'fundamental' (or Bergmann) series in the infra-red region.

Taking clue from the Balmer's formula for hydrogen spectral series,  $v = v_{\infty} - \frac{R}{n^2}$ , Rydberg represented the alkali spectral series by similar formulae :

$$\text{Principal} \quad v_m^p = v_{\infty}^p - \frac{R}{(m+p)^2}, \quad m = 2, 3, 4, \dots, \infty$$

$$\text{Sharp} \quad v_m^s = v_{\infty}^s - \frac{R}{(m+s)^2}, \quad m = 2, 3, 4, \dots, \infty$$

$$\text{Diffuse} \quad v_m^d = v_{\infty}^d - \frac{R}{(m+d)^2}, \quad m = 3, 4, 5, \dots, \infty$$

$$\text{Fundamental} \quad v_m^f = v_{\infty}^f - \frac{R}{(m+f)^2}, \quad m = 4, 5, 6, \dots, \infty$$

where  $v_{\infty}$ 's are the wave numbers of the convergence limits of the corresponding series, and are called 'fixed terms'. In the so-called 'running terms';  $p, s, d$  and  $f$  represent Rydberg corrections for the corresponding series.

Rydberg noticed the following relations among different series of the same alkali atom :

(i) **The sharp and the diffuse series have a common convergence limit ( $v_{\infty}^s = v_{\infty}^d$ )**.

(ii) **The common convergence limit is equal to the first running term (with  $m = 2$ ) of the principal series :**

$$v_{\infty}^p = v_{\infty}^d = \frac{R}{(2+p)^2}$$

(iii) **The convergence limit of the principal series is equal to a running term (with  $m = 1$ ) of the sharp series :**

$$v_{\infty}^p = \frac{R}{(1+s)^2}$$

(iv) **The convergence limit of the fundamental series is equal to the first running term (with  $m = 3$ ) of the diffuse series :**

$$v_{\infty}^f = \frac{R}{(3+d)^2}$$

In view of these relations, the above formulae may be written in the following form :

$$\text{Principal} \quad v_m^p = \frac{R}{(1+s)^2} - \frac{R}{(m+p)^2}, \quad m = 2, 3, 4, \dots, \infty$$

$$\text{Sharp} \quad v_m^s = \frac{R}{(2+p)^2} - \frac{R}{(m+s)^2}, \quad m = 2, 3, 4, \dots, \infty$$

$$\text{Diffuse} \quad v_m^d = \frac{R}{(2+p)^2} - \frac{R}{(m+d)^2}, \quad m = 3, 4, 5, \dots, \infty$$

$$\text{Fundamental} \quad v_m^f = \frac{R}{(3+d)^2} - \frac{R}{(m+f)^2}, \quad m = 4, 5, 6, \dots, \infty$$

The following laws were found to hold in the alkali series :

**Rydberg-Schuster Law :** The wave number difference between the principal series limit and the sharp (or diffuse) series limit is equal to the wave number of the first line of the principal series :

$$v_{\infty}^p - v_{\infty}^{s(\text{or } d)} = \frac{R}{(1+s)^2} - \frac{R}{(2+p)^2} = v_2^p.$$

**Runge's Law :** The wave number difference between the diffuse series limit and the fundamental series limit is equal to the wave number of the first line of the diffuse series :

$$v_{\infty}^d - v_{\infty}^f = \frac{R}{(2+p)^2} - \frac{R}{(3+d)^2} = v_3^d.$$

## 2. Ritz Combination Principle

Ritz pointed out the possibility of occurrence of other series obtained by changing the fixed term in the formula for the chief series. Such additional series have actually been observed in many spectra including that of hydrogen.

As an example, the (chief) principal and sharp series of alkalies are represented in the abbreviated notation by

$$v_m^p = 1S - mP, \quad m = 2, 3, 4, \dots, \infty. \quad \dots(i)$$

$$v_m^s = 2P - mS, \quad m = 2, 3, 4, \dots, \infty. \quad \dots(ii)$$

The series predicted by Ritz are obtained by changing the fixed terms  $1S$  and  $2P$  to  $2S, 3S, \dots$  and  $3P, 4P, \dots$ . Thus, we obtain the combination principal series represented by

$$\begin{cases} 2S - mP, & m = 3, 4, 5, \dots, \infty \\ 3S - mP, & m = 4, 5, 6, \dots, \infty \end{cases} \quad \dots(iii)$$

and the combination sharp series represented by

$$\begin{cases} 3P - mS, & m = 4, 5, 6, \dots, \infty \\ 4P - mS & m = 5, 6, 7, \dots, \infty \end{cases} \quad \dots(iv)$$

We note that all fixed terms occurring in (iii) are included in the running terms of (ii); and the fixed terms occurring in (iv) are included in the running terms of (i). Thus, the predicted series are simply combinations (sum or difference) of the terms of the chief series. The resulting series are therefore called 'combination series', and the possibility of their occurrence is known as 'Ritz combination principle'.

## 3. Explanation of the Broad Features of Alkali Spectra

An alkali atom (of atomic number  $Z$ ) consists of an inert-gas core composed of the nucleus and a few completed subshells having  $Z - 1$  electrons, plus a single valence

electron in the outermost subshell. For example, the ground-state configurations of  ${}^3\text{Li}$ ,  ${}^{11}\text{Na}$  and  ${}^{19}\text{K}$  are

$$\boxed{1s^2} \quad 2s,$$

$$\boxed{1s^2 2s^2 2p^6} \quad 3s,$$

$$\boxed{1s^2 2s^2 2p^6 3s^2 3p^6} \quad 4s,$$

and

respectively. It is seen that, except for  $\text{Li}$ , the completed highest subshell is a  $p$  subshell, and the next  $s$  subshell is the outermost one. In the optical (low-energy) excitation processes, only the valence electron is excited which alone is responsible for the optical spectra\*. The inert-gas core having a spherically symmetrical distribution of charge does not play any part.

Let us take up the case of sodium ( ${}^{11}\text{Na}$ ). Its normal outer configuration is  $3s$ , and the corresponding term is an  $S$ -term. The various possible excited configurations and the corresponding terms are :

- $4s, 5s, 6s, \dots \dots \dots S\text{-terms}$
- $3p, 4p, 5p, \dots \dots \dots P\text{-terms}$
- $3d, 4d, 5d, \dots \dots \dots D\text{-terms}$
- $4f, 5f, 6f, \dots \dots \dots F\text{-terms}$

In excitation, the total energy of the core does not change. Therefore, the total energy of the atom is a constant plus the energy of the optically-active (valence) electron. For convenience, we take this constant as zero so that the total energy of the atom in a certain state is equal to the energy of the optically-active electron in that state.

Let us compare the energies of the alkali (sodium) atom in the various states with those of the hydrogen atom in the corresponding states.

In hydrogen atom, the electron in an orbit  $n$  (say) moves in the 'coulombian' field of the nucleus (point charge), and its energy is given by

$$E_n = -\frac{m(Ze)^2 e^2}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right); \quad (Z = 1 \text{ for hydrogen})$$

which depends upon  $n$  only. In alkali atom, on the other hand, the electron moves in the 'central' field of the nucleus plus core electrons, and its energy is given by

$$E_{n,l} = -\frac{m(Z_n e)^2 e^2}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right),$$

where  $Z_n e$  is the effective charge of the nucleus for the orbit  $n$ . The quantity  $Z_n e$  is always greater than  $e$  because the screening of a nucleus of charge  $Ze$  by the charge  $(Z-1)e$  of the core electrons is not perfect. Hence the energy of the alkali atom is more negative than the energy of the hydrogen atom in the same state  $n$ . This means that the energy levels of the alkali atom are lower than the corresponding levels of the hydrogen

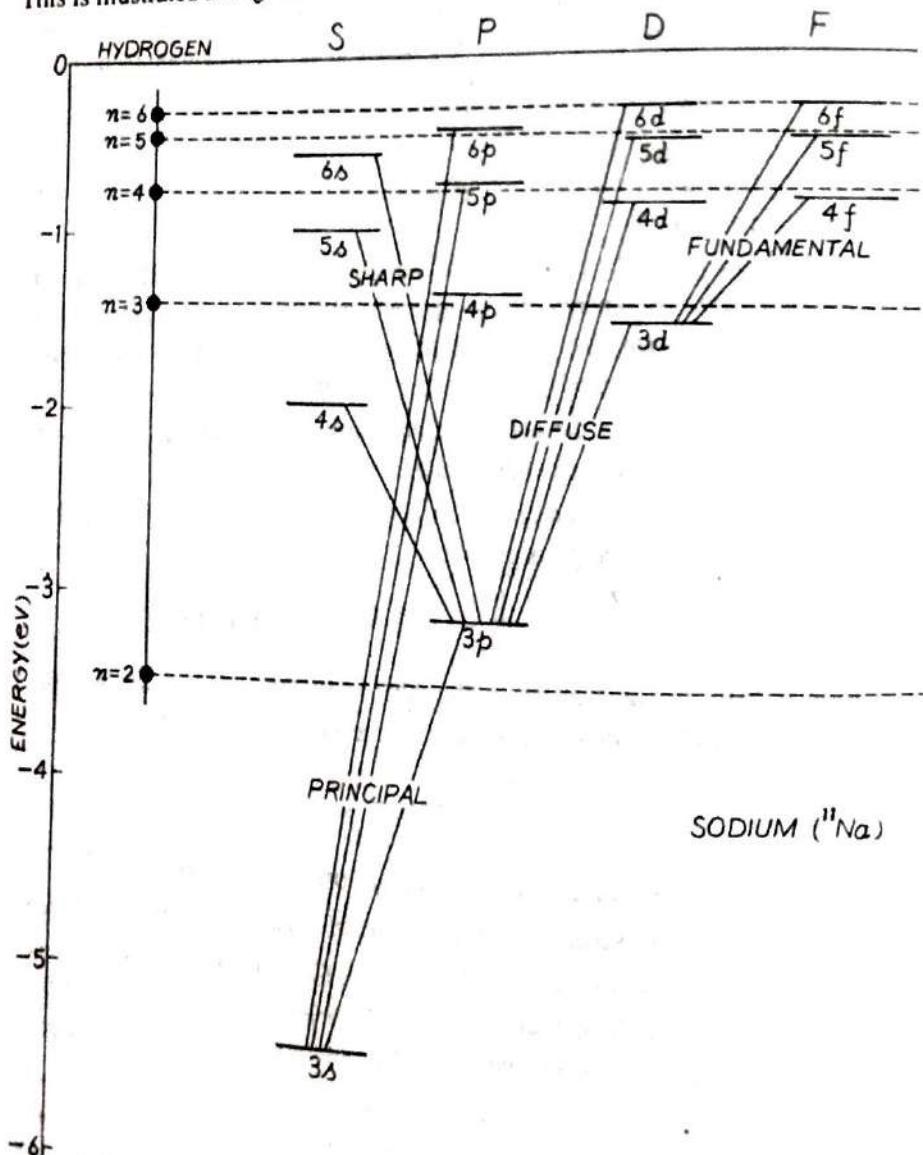
\*The alkali atoms Li, Na, K,..... readily give up one electron to form positive ions. The energy required to remove one electron from these atoms is small (5.1 eV in case of Na), but that required to remove a second electron is much larger (47.3 eV). This suggests that of all the electrons in an alkali atom, one electron is loosely-bound to the atom. The spectral lines of an alkali atom arise due to the transitions of this electron only which is called the 'optical' or the 'valence' electron.

atom. However, as  $n$  increases, the alkali levels approach the corresponding hydrogen levels because the screening becomes more and more perfect ( $Z_n e \rightarrow e$ ).

Secondly, in contrast to hydrogen, the energy of an alkali atom in a certain state depends not only upon  $n$  but also upon the  $l$  value of the optical electron. This is because the probability of finding the electron near the nucleus ( $r \rightarrow 0$ ) is

$$\psi^* \psi \propto r^{2l},$$

and is largest for  $l = 0$  (s-electron), and decreases very rapidly with increasing  $l$ . Thus, for a given  $n$ , the energy is most negative for the s-electron which spends more time near the nucleus and feels almost the full nuclear charge (at  $r \rightarrow 0, Z_n \rightarrow Z$ ); and becomes less and less negative for the  $p, d, f, \dots$  electrons. The  $l$ -dependence of energy is so important that in sodium the  $4s$  level is more negative than the  $3d$  level. Thus, all alkali levels of a given  $n$  are shifted lower than the corresponding levels of hydrogen; the shift being greatest for the  $s$  level and becoming smaller and smaller for the  $p, d, f, \dots$  levels. This is illustrated in Fig. 1.



(Fig. 1)

When the sodium atom is excited by some means, the (optical)  $3s$  electron is raised to any of the excited levels  $3p$ ,  $3d$ ,  $4s$ ,  $4p$ ,  $4d$ ,  $4f$ ,  $5s$ ,  $5p$ , .... etc. from which it jumps back through any selected path allowed by the following selection rules :

$$\Delta n = \text{any integer}$$

$$\Delta l = \pm 1.$$

The observed series in the emission spectrum arise from the following transitions :

$$np \rightarrow 3s, n > 2 \quad \text{Principal Series}$$

$$ns \rightarrow 3p, n > 3 \quad \text{Sharp Series}$$

$$nd \rightarrow 3p, n > 2 \quad \text{Diffuse Series}$$

$$nf \rightarrow 3d, n > 3 \quad \text{Fundamental Series}$$

A practical sodium source contains numerous atoms so that all possible excited states are available for the transitions which take place through all the allowed paths. Hence all the four series are simultaneously emitted in the spectrum. Since, ultimately, the electron returns to the ground state which involves the principal series, the lines of the principal series are most intense and persistent.

For hydrogen atom, the energy in different states  $S, P, D, \dots$  of the same  $n$  is same. Hence the four different series observed in the spectra of alkali atoms become identical in the spectrum of hydrogen atom.

The other observations in alkali spectra are also obvious in the energy level diagram (Fig. 1).

The sharp and the diffuse series have the same convergence limit ( $3p$  level)\*. The wave number difference \*\* between this limit ( $3p$  level) and the principal series limit ( $3s$  level) is equal to the wave number of the first line ( $3p \rightarrow 3s$ ) of the principal series. This is Rydberg-Schuster law.

Similarly, the wave number difference between the diffuse series limit ( $3p$  level) and the fundamental series limit ( $3d$  level) is equal to the wave number of the first line ( $3d \rightarrow 3p$ ) of the diffuse series. This is Runge's law.

#### 4. Absorption Spectra of Alkali Atoms

An absorption spectrum of an alkali atom, say sodium, is obtained when light from a continuous source is passed through a cooler sodium vapour. When this is the case, the optical electron in an atom absorbs quantised energy and passes to some higher level in accordance to the selection rule  $\Delta l = \pm 1$ . Thus, the continuous light is robbed off certain wave numbers which appear as dark lines in the continuous spectrum. Since at room temperature almost all atoms in the vapour are in the ground state  $3s$ , the only possible (absorption) transitions are  $3s \rightarrow np$ , where  $n > 2$ . These transitions give rise to the principal series. Hence it is only the principal series which appears in absorption as well as in emission. The sharp, diffuse and fundamental series appear in emission only.

The limit of the principal series corresponds to the complete removal of the electron from the  $3s$  level (in absorption), or jump of the electron from infinity to the  $3s$  level (in emission). Hence the wave number of this limit, converted to electron-volts \*\*\*, is the ionisation potential of the atom.

only  
luse

\* This limit corresponds to the jump of electron from infinity to the level  $3p$ .

\*\* The wave number difference corresponds to energy difference.

\*\*\* The unit of wave number is  $\text{cm}^{-1}$ , and  $1 \text{ cm}^{-1} = 1.239 \times 10^{-4} \text{ eV}$  or  $1 \text{ eV} = 8066 \text{ cm}^{-1}$

## 5. Resonance Line

When an atom in the ground state is raised to the 'first' excited state by absorbing monochromatic radiation, it can return to the ground state by emitting spectral line only of the same frequency as absorbed. Such a spectral line is known as 'resonance line' of the atom concerned.

For example, when continuous light is passed through sodium vapour, the optical electron in sodium atoms passes from the ground level  $3s$  to some higher level  $3p, 4p, \dots$ . From here it spontaneously falls to lower levels. In atoms, in which the electron passes from  $3s$  to  $3p$  level, the only possibility is the transition back to the ground level  $3s$ , emitting the same line as absorbed. Hence the line  $3s \rightarrow 3p$  is the (only) resonance line of sodium. It is the yellow D-line in emission, the first line of the principal series.

In the case of other absorption lines, part of the absorbed radiation is re-emitted with unchanged wave number, but lines of other wave numbers are also emitted at the same time. For example, if the absorbed light takes the electron from  $3s$  to  $4p$  then it has three possible paths to come back : (i)  $4p \rightarrow 3s$ ; (ii)  $4p \rightarrow 4s \rightarrow 3p \rightarrow 3s$ , and (iii)  $4p \rightarrow 3d \rightarrow 3p \rightarrow 3s$ ; thus emitting a number of other lines.

## 6. Fine Structure in Alkali Spectra : The Spinning Electron

When the spectral lines of an alkali atom are seen under high resolution, each of them is found to be made up of two close component lines, that is, each line is a close 'doublet'. For example, the yellow D-line of sodium consists of two close lines of wavelengths  $5890 \text{ \AA}$  and  $5896 \text{ \AA}$ . This is called the fine structure in alkali spectral lines.

The nature of fine structure is, however, different in the spectral lines of different series. All lines of the sharp series are close doublets having the same wave number separation. Similarly, each line of the principal series is a doublet but in this series the wave number separation between the two components decreases rapidly toward the lines of increasing wave number. The lines of diffuse and fundamental series show a three-component fine structure and are called 'compound doublets' (not triplets). The fine structure in the lines of the fundamental series is, however, negligible.

In general, the fine-structure splitting of spectral lines is small for the lighter atoms, but increases rapidly with increasing atomic number.

**Explanation of Fine Structure on the basis of Electron Spin :** The line-splitting (fine structure) in alkali spectra is traced back to level-splitting. An analysis of alkali spectra shows that the  $S$ -levels are single, but all others  $P, D, F, \dots$  are doublet levels. The level-splitting is the result of the "spin" of the electron. The spin magnetic moment of the optical electron interacts with the internal magnetic field arising due to the orbital motion of the electron in the nuclear electric field. This is known as spin-orbit interaction.\* Due to this interaction, the orbital angular momentum  $\vec{\Gamma}$  of the optical electron is coupled to the spin angular momentum  $\vec{s}$  to form a resultant  $\vec{j}$  about which both  $\vec{\Gamma}$  and  $\vec{s}$  precess.  $\vec{j}$  is also the total angular momentum of the (alkali) atom because the angular momentum of

\*The relativistic effect which is equally important in explaining the spectral fine-structure in the case of a one-electron atom, is negligible (compared with the spin-orbit interaction) for the optically active electrons in all multielectron atoms.

## 5. Resonance Line

When an atom in the ground state is raised to the 'first' excited state by absorbing monochromatic radiation, it can return to the ground state by emitting spectral line only of the same frequency as absorbed. Such a spectral line is known as 'resonance line' of the atom concerned.

For example, when continuous light is passed through sodium vapour, the optical electron in sodium atoms passes from the ground level  $3s$  to some higher level  $3p, 4p, \dots$ . From here it spontaneously falls to lower levels. In atoms, in which the electron passes from  $3s$  to  $3p$  level, the only possibility is the transition back to the ground level  $3s$ , emitting the same line as absorbed. Hence the line  $3s \rightarrow 3p$  is the (only) resonance line of sodium. It is the yellow D-line in emission, the first line of the principal series.

In the case of other absorption lines, part of the absorbed radiation is re-emitted with unchanged wave number, but lines of other wave numbers are also emitted at the same time. For example, if the absorbed light takes the electron from  $3s$  to  $4p$  then it has three possible paths to come back : (i)  $4p \rightarrow 3s$ ; (ii)  $4p \rightarrow 4s \rightarrow 3p \rightarrow 3s$ , and (iii)  $4p \rightarrow 3d \rightarrow 3p \rightarrow 3s$ ; thus emitting a number of other lines.

## 6. Fine Structure in Alkali Spectra : The Spinning Electron

When the spectral lines of an alkali atom are seen under high resolution, each of them is found to be made up of two close component lines, that is, each line is a close 'doublet'. For example, the yellow D-line of sodium consists of two close lines of wavelengths  $5890\text{ \AA}$  and  $5896\text{ \AA}$ . This is called the fine structure in alkali spectral lines.

The nature of fine structure is, however, different in the spectral lines of different series. All lines of the sharp series are close doublets having the same wave number separation. Similarly, each line of the principal series is a doublet but in this series the wave number separation between the two components decreases rapidly toward the lines of increasing wave number. The lines of diffuse and fundamental series show a three-component fine structure and are called 'compound doublets' (not triplets). The fine structure in the lines of the fundamental series is, however, negligible.

In general, the fine-structure splitting of spectral lines is small for the lighter atoms, but increases rapidly with increasing atomic number.

**Explanation of Fine Structure on the basis of Electron Spin :** The line-splitting (fine structure) in alkali spectra is traced back to level-splitting. An analysis of alkali spectra shows that the  $S$ -levels are single, but all others  $P, D, F, \dots$  are doublet levels. The level-splitting is the result of the "spin" of the electron. The spin magnetic moment of the optical electron interacts with the internal magnetic field arising due to the orbital motion of the electron in the nuclear electric field. This is known as spin-orbit interaction.\* Due to this interaction, the orbital angular momentum  $\vec{\Gamma}$  of the optical electron is coupled to the spin angular momentum  $\vec{s}$  to form a resultant  $\vec{j}$  about which both  $\vec{\Gamma}$  and  $\vec{s}$  precess.  $\vec{j}$  is also the total angular momentum of the (alkali) atom because the angular momentum of

\*The relativistic effect which is equally important in explaining the spectral fine-structure in the case of a one-electron atom, is negligible (compared with the spin-orbit interaction) for the optical active electrons in all multielectron atoms,

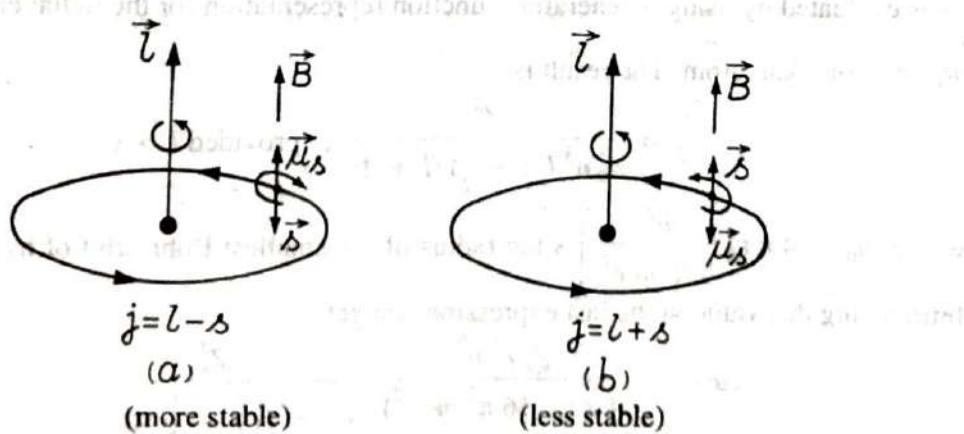
the core is zero. The quantum number  $j$ , called the 'inner quantum number', can take the following two values :

$$j = l \pm s = l \pm \frac{1}{2},$$

according as the spin and the orbital angular momenta are "parallel" or "antiparallel". The double possibility for the setting of the spin with respect to the orbit results in a splitting of each energy level ( $l$ -level) into two, one corresponding to  $j = l + \frac{1}{2}$  and the other corresponding to  $j = l - \frac{1}{2}$ , with the exception of  $S$ -levels, for which  $l = 0$ . The complete notation of the levels will be as below :

Level	$l$	$s$	Multiplicity ( $2s + 1$ )	$j (= l \pm s)$	Full Notation
$S$	0	$1/2$	2	$1/2$	$^2S_{1/2}$
$P$	1	$1/2$	2	$3/2, 1/2$	$^2P_{3/2}, ^2P_{1/2}$
$D$	2	$1/2$	2	$5/2, 3/2$	$^2D_{5/2}, ^2D_{3/2}$
$F$	3	$1/2$	2	$7/2, 5/2$	$^2F_{7/2}, ^2F_{5/2}$

In each doublet level the component corresponding to the smaller value of  $j$  lies deeper (more stable). This is because the more stable state is one in which the spin magnetic moment  $\vec{\mu}_s$  of the electron lines up in the direction of the magnetic field  $\vec{B}$  produced by the orbital motion of the electron in the electric field of the nucleus, and  $\vec{B}$  is in the same direction as the orbital angular momentum  $\vec{l}$ . The spin magnetic moment  $\vec{\mu}_s$  is opposite to spin angular momentum  $\vec{s}$ , because the electron is negatively charged. Since in the more stable state  $\vec{\mu}_s$  is in the same direction as  $\vec{l}$ , the vector  $\vec{l}$  is opposite to vector  $\vec{s}$  and the quantum number  $j$  is of lower value,  $j = l - s$  (Fig. 2 a). Obviously, the higher value of  $j$  corresponds to less stable state (Fig. b). Of course, exceptions do occur.



(Fig. 2)

## 7. Calculation of Level-Splitting due to Spin-Orbit Interaction

The splitting of the energy levels of an alkali atom due to the spin-orbit interaction acting on the optically-active electron can be calculated by considering the general expression for the interaction energy\*,

$$\Delta E_{l,s} = \frac{e h^2}{16 \pi^2 m^2 c^2} \left[ j(j+1) - l(l+1) - s(s+1) \right] \frac{1}{r} \frac{dV(r)}{dr}, \quad \dots(i)$$

provided the average value of  $\frac{1}{r} \frac{dV(r)}{dr}$  is calculated using the probability density obtained from the Hartree eigenfunctions.

The last expression shows that for  $l = 0$ , the interaction energy  $\Delta E_{l,s} = 0$  because  $j = s = \frac{1}{2}$ . For other values of  $l$ ,  $\Delta E_{l,s}$  assumes two different values, one positive and the other negative, as we shall see.

According to Hartree theory, in an alkali atom the optical electron in a shell  $n$  is considered to be moving in a potential field

$$V(r) = -\frac{1}{4 \pi \epsilon_0} \frac{Z_n e}{r},$$

where  $Z_n$  is a constant equal to  $Z(r)$  evaluated at the average value of  $r$  for the shell  $n$ . The  $Z(r)$  is such that

$$Z(r) \rightarrow Z, \quad \text{as } r \rightarrow 0$$

$$Z(r) \rightarrow 1, \quad \text{as } r \rightarrow \infty.$$

We have

$$\frac{dV(r)}{dr} = \frac{1}{4 \pi \epsilon_0} \frac{Z_n e}{r^2}.$$

The eq. (i) can now be written as

$$\Delta E_{l,s} = \frac{Z_n e^2 h^2}{4 \pi \epsilon_0 (16 \pi^2 m^2 c^2)} \left[ j(j+1) - l(l+1) - s(s+1) \right] \frac{1}{r^3}.$$

$\frac{1}{r^3}$  is evaluated by using a generating function representation for the radial eigenfunctions  $R_{n,l}(r)$  of alkali atom. The result is

$$\frac{1}{r^3} = \frac{Z_n^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)}, \quad \text{provided } l > 0$$

where  $a_0 = 4 \pi \epsilon_0 \frac{h^2}{4 \pi^2 m e^2}$  is the radius of the smallest Bohr orbit of hydrogen atom. Introducing this value in the last expression, we get

$$\Delta E_{l,s} = \frac{Z_n e^2 h^2}{4 \pi \epsilon_0 (16 \pi^2 m^2 c^2)} \frac{Z_n^3}{a_0^3 n^3 l \left( l + \frac{1}{2} \right) (l+1)} \left[ j(j+1) - l(l+1) - s(s+1) \right].$$

\*This expression has already been derived in chap. 5.

This equation is worked out to the following form :

$$\Delta E_{l,s} = - \frac{R_\infty \alpha^2 Z_n^4 h c}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} [ j(j+1) - l(l+1) - s(s+1) ],$$

where  $R_\infty \left( = \frac{m e^4}{8 \epsilon_0^2 c h^3} \right)$  is Rydberg constant for an infinitely heavy nucleus, and  $\alpha \left( = \frac{e^2}{2 \epsilon_0 h c} \right)$  is the fine-structure constant.

The term shift due to spin-orbit interaction is

$$\Delta T_{l,s} = - \frac{\Delta E_{l,s}}{h c} = - \frac{R_\infty \alpha^2 Z_n^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} [ j(j+1) - l(l+1) - s(s+1) ].$$

For the (single) optically-active electron of the alkali atom, we have

$$s = \frac{1}{2} \quad \text{and} \quad j = l \pm s = l \pm \frac{1}{2}.$$

Making this substitution, we get

$$\begin{aligned} j(j+1) - l(l+1) - s(s+1) &= l && \text{for } j = l + \frac{1}{2} \\ &= -(l+1) && \text{for } j = l - \frac{1}{2}. \end{aligned}$$

The term (level) shifts corresponding to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  are therefore

$$\Delta T_{l,s}' = - \frac{R_\infty \alpha^2 Z_n^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} l$$

$$\Delta T_{l,s}'' = \frac{R_\infty \alpha^2 Z_n^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} (l+1).$$

Thus, the spin-orbit interaction causes each term ( $l$ -level) to split into two levels of different  $j$ , one displaced upwards and the other downwards from the unperturbed level. The separation between them is

$$\begin{aligned} \Delta T &= \Delta T_{l,s}'' - \Delta T_{l,s}' \\ &= \frac{R_\infty \alpha^2 Z_n^4}{2 n^3 l \left( l + \frac{1}{2} \right) (l+1)} (2l+1) = \frac{R_\infty \alpha^2 Z_n^4}{n^3 l (l+1)}. \end{aligned}$$

Taking  $R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$  and  $\alpha = 1/137$ , we get

$$\Delta T = 584 \frac{Z_n^4}{n^3 l (l+1)} \text{ m}^{-1}$$

$$\Delta T = 5.84 \frac{Z_n^4}{n^3 l (l+1)} \text{ cm}^{-1}.$$

only  
ffuse

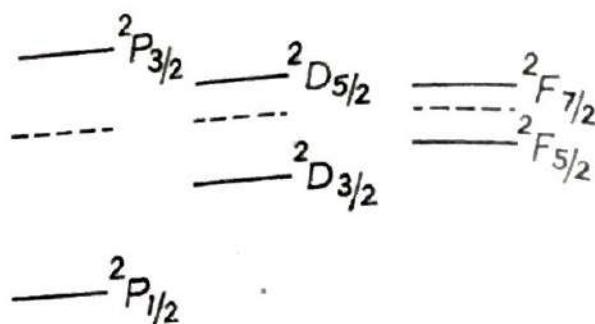
If  $\sigma$  be the screening constant, then  $Z_n = Z - \sigma$ , so that

$$\Delta T = 5.84 \frac{(Z - \sigma)^4}{n^3 l(l+1)} \text{ cm}^{-1}$$

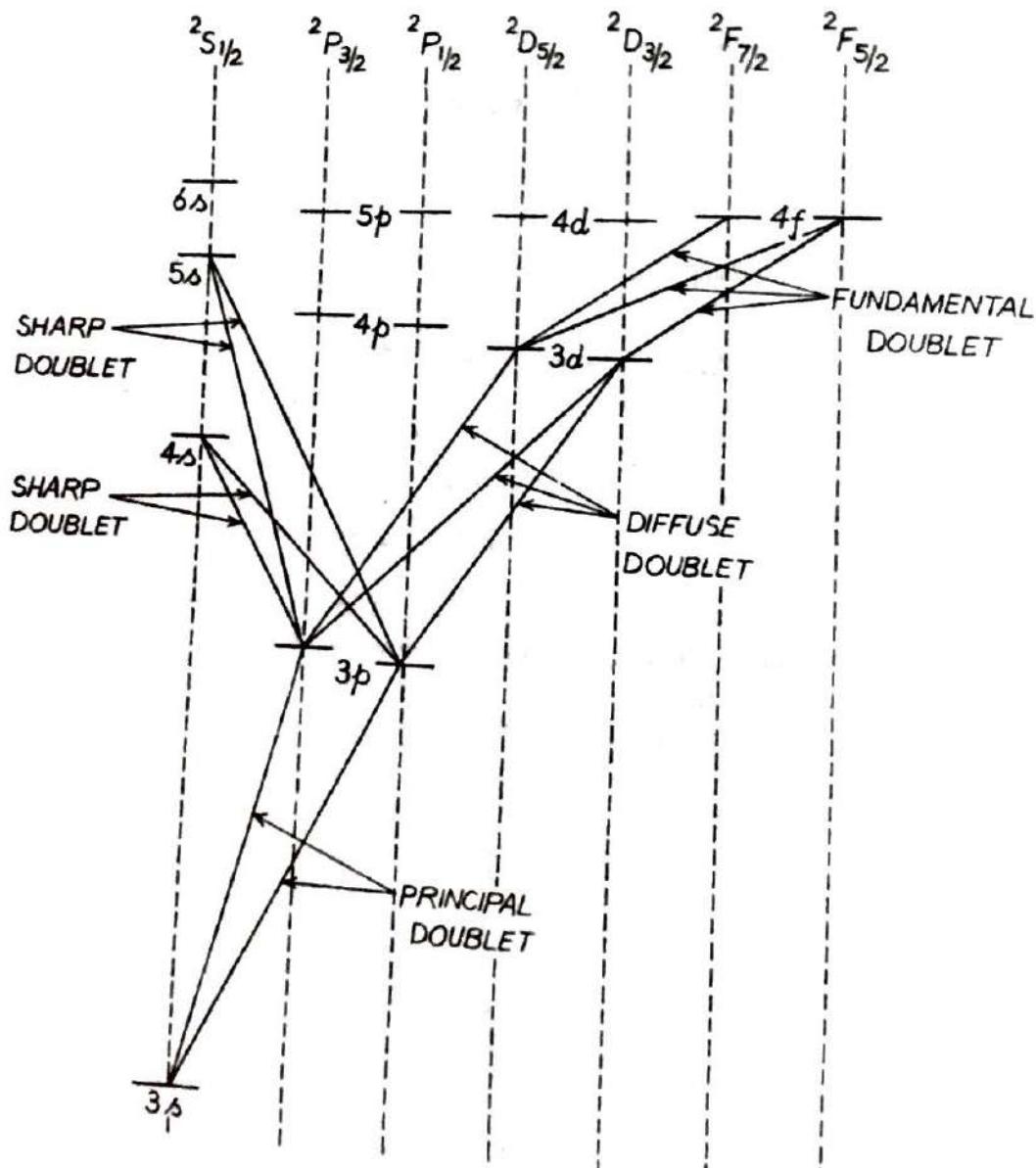
This formula gives doublet separation in remarkably good agreement with experimental observation. It shows that the level splitting for an alkali atom (i) increases with increasing atomic number, (ii) decreases with increasing  $n$  (for the same  $l$ ) and also (iii) decreases with increasing  $l$  (for same  $n$ ). As already seen, the splitting is zero for  $l = 0$  ( $S$ -levels).

The relative splitting of levels  $^2P$ ,  $^2D$ ,  $^2F$  of a given  $n$  value is illustrated in Fig. 3.

In Fig. 4 is shown the splitting of alkali levels involved in the emission of the lines of the four series. The  $^2S$  levels are single components  $^2S_{1/2}$ . The  $^2P$  levels are splitted as



(Fig. 3)



(Fig. 4)

$^2P_{3/2}$  and  $^2P_{1/2}$ , the latter ( $^2P_{1/2}$ ) being deeper, and the splitting decreases as  $n$  increases. Similarly, the  $^2D$  and  $^2F$  levels are splitted as  $^2D_{5/2}$ ,  $^2D_{3/2}$ , and  $^2F_{7/2}$ ,  $^2F_{5/2}$  but these splittings are much smaller.

The selection rules in operation are :

$$\Delta n = \text{any integer including zero}$$

$$\Delta l = \pm 1$$

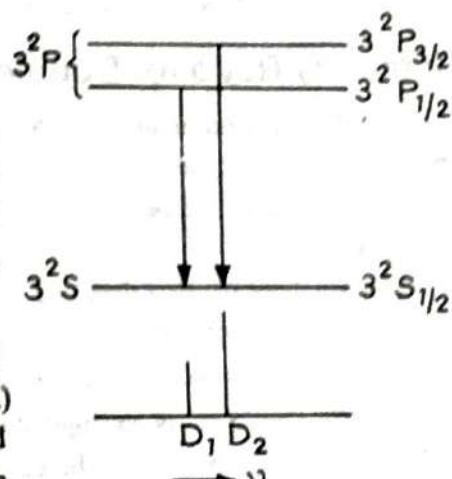
$$\Delta j = 0, \pm 1.$$

These rules explain the simple and compound doublet structure of spectral lines. For example, the principal resonance doublet of sodium ( $D_1$  and  $D_2$  lines) arise from the transitions  $3^2P \rightarrow 3^2S$ , which is equivalent to the following two transitions :

$$3^2P_{1/2} \rightarrow 3^2S_{1/2} \quad (D_1 \text{ } 5896 \text{ \AA})$$

$$3^2P_{3/2} \rightarrow 3^2S_{1/2} \quad (D_2 \text{ } 5890 \text{ \AA})$$

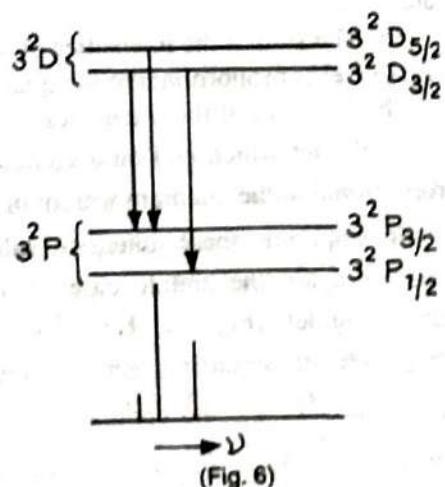
The wave number separation between  $D_1$  and  $D_2$  lines is equal to the separation between  $3^2P_{1/2}$  and  $3^2P_{3/2}$  levels (Fig. 5).



(Fig. 5)

The other lines, of higher wave numbers, of the principal series owe their doublet structure to the doubling of higher  $^2P$  levels such as  $4^2P$ ,  $5^2P$ , ..... levels. Since the splitting of these levels decreases with increasing  $n$ , the wave number separation between the doublet components of the principal series decreases in the lines of higher and higher wave numbers.

The doublets of the sharp series are formed by the transitions  $n^2S_{1/2} \rightarrow 3^2P_{3/2, 1/2}$ , where  $n = 4, 5, \dots$ . In this series the wave number separation between the doublet components of all the lines is the same and equal to the separation between  $3^2P_{3/2}$  and  $3^2P_{1/2}$  levels on which all the transitions terminate.



(Fig. 6)

The lines of the diffuse and the fundamental series show a three-component structure and are called 'compound' doublets. This is illustrated in Fig. 6 for a diffuse line arising from the transition  $3^2D_{5/2, 3/2} \rightarrow 3^2P_{3/2, 1/2}$ . Here both the  $^2D$  and  $^2P$  levels are splitted and the selection rules allow three transitions, as shown.

The splitting of the  $^2D$  level is, however, so small that under ordinary resolution only two components appear. If we ignore the  $^2D$ -splitting, then all the lines of the diffuse

series have the same doublet separation as the lines of the sharp series, that is, equal to the separation between  $3^2P_{3/2}$  and  $3^2P_{1/2}$  levels.

Although the lines of the diffuse and the fundamental series have three components but they are called 'doublets' (not triplets) because they arise from transitions between doublet levels. The name 'doublet' refers to the multiplicity of energy levels, and not to the number of components in the spectral lines.

## 8. Intensity Ratio for Doublets

General observations of line intensities in doublet spectra show that certain intensity rules hold. These rules are :

(i) The strongest line in any doublet arises from transition in which  $j$  and  $l$  change in the same way.

(ii) When there is more than one such line in the same doublet, the line involving the largest  $j$  values is strongest.

For example, in the principal-series doublet of Fig. 5, the line arising from the transition  $^2P_{3/2} - ^2S_{1/2}$  is stronger than that from  $^2P_{1/2} - ^2S_{1/2}$ ; since in the former both  $j$  and  $l$  change by  $-1$ , whereas in the latter  $j$  changes by zero and  $l$  changes by  $-1$ .

As a second example, let us consider the diffuse-series compound doublet of Fig. 6. For the two strong lines  $^2D_{5/2} - ^2P_{3/2}$  and  $^2D_{3/2} - ^2P_{1/2}$ , both  $j$  and  $l$  change by  $-1$ . The stronger of the two lines,  $^2D_{5/2} - ^2P_{3/2}$  involves the larger  $j$  values. For the faint satellite  $^2D_{3/2} - ^2P_{3/2}$ ,  $j$  changes by 0 while  $l$  changes by  $-1$ .

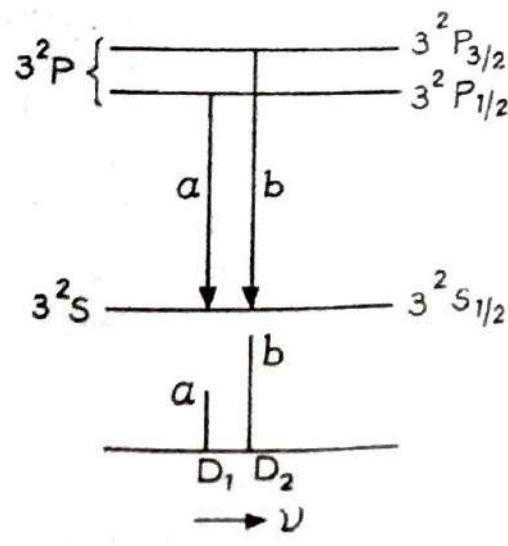
Quantitative intensity relations are also observed in doublet spectra. In sodium, the doublet components of the lines of sharp series show the intensity ratio  $2 : 1$ , and the same is true for the diffuse series if the splitting of the  $^2D$  level is unresolved, and for the principal series if self-absorption is avoided.

Quantitative rules for the relative intensities were discovered by Burger, Dorgelo and Ornstein. These rules apply not only to doublets but to all multiplets in general. They are stated as :

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

(b) The sum of the intensities of those lines of a multiplet which end on a common level is proportional to the quantum weight of that level.

In applying these intensity rules, let us consider again the simple case of a principal series doublet (Fig. 7). Here there are two component lines starting from the upper levels  $^2P_{3/2}$  and  $^2P_{1/2}$ , and ending on the common lower level  $^2S_{1/2}$ . The ratio of the intensities would be the same as the ratio of the quantum weights of the doublet levels. Thus



(Fig. 7)

$$\frac{I_b}{I_a} = \frac{2\left(\frac{3}{2}\right) + 1}{2\left(\frac{1}{2}\right) + 1} = \frac{4}{2} = 2 : 1.$$

The same holds for the members of the sharp series.

Let us now consider the diffuse-series compound doublet of Fig. 8. The line  $b$  starts from the level  ${}^2D_{5/2}$ , while  $a$  and  $c$  start from the level  ${}^2D_{3/2}$ . Therefore,

$$\frac{I_b}{I_a + I_c} = \frac{2\left(\frac{5}{2}\right) + 1}{2\left(\frac{3}{2}\right) + 1} = \frac{6}{4} = \frac{3}{2}. \quad \dots(i)$$

Again, the line  $c$  ends on the level  ${}^2P_{1/2}$ , while  $a$  and  $b$  end on the level  ${}^2P_{3/2}$ . Thus

$$\frac{I_c}{I_a + I_b} = \frac{2\left(\frac{1}{2}\right) + 1}{2\left(\frac{3}{2}\right) + 1} = \frac{2}{4} = \frac{1}{2}. \quad \dots(ii)$$

Solving (i) and (ii), we get

$$c = \frac{5}{9} b, \quad a = \frac{1}{9} b.$$

This means that

$$a : b : c = \frac{1}{9} : 1 : \frac{5}{9}$$

$$a : b : c = 1 : 9 : 5.$$

or If the satellite  $a$  is not resolved from  $b$ , then we shall see two lines having an intensity ratio

$$(1 + 9) : 5 = 2 : 1.$$

In the same way, the intensity ratio for a compound doublet of the fundamental series comes out to be  $1 : 20 : 14$ , that is, roughly  $3 : 2$ .

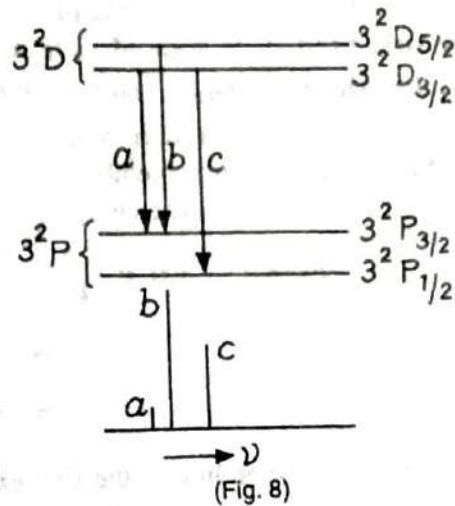
### SOLVED PROBLEMS

1. The mean position of the first pair of lines of the principal series of sodium is  $16960 \text{ cm}^{-1}$ . If the convergence limit of the sharp series lines is at  $24490 \text{ cm}^{-1}$ , calculate the ionisation potential of sodium. Given:  $1 \text{ eV} = 8066 \text{ cm}^{-1}$   
*(Meerut 2004 S, 99 S, 94; special paper 2004, 97, 90)*

**Solution.** The first line (ignoring doublet structure) of the principal series corresponds to the transition  $3s - 3p$ , and the convergence limit of the sharp series corresponds to the transition  $3p - \infty$  (Fig. 1). The sum of these two wave numbers is

$$16960 \text{ cm}^{-1} + 24490 \text{ cm}^{-1} = 41450 \text{ cm}^{-1},$$

which corresponds to  $3s - \infty$ , that is, the ionisation of the sodium atom. This wave number converted to electron-volts give the ionisation energy, which is



(Fig. 8)

$$\frac{41450 \text{ cm}^{-1}}{8066 \text{ cm}^{-1}/\text{eV}} = 5.14 \text{ eV},$$

because  $1 \text{ eV} = 8066 \text{ cm}^{-1}$ . Hence the ionisation potential of sodium atom is 5.14 volt.

**2. The first member of the principal series of sodium has a wavelength of  $5893 \text{ \AA}$ .** The first excited  $S$  state of sodium lies 3.18 eV above the ground state. Find the wavelength of the first member of the sharp series. Given :  $e = 1.60 \times 10^{-19} \text{ C}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $h = 6.63 \times 10^{-34} \text{ J s}$ . (Meerut 93 sp. paper)

**Solution.** The first member of the principal series corresponds to the transition  $3p - 3s$  (see Fig. 1). The energy corresponding to its wavelength of  $5893 \text{ \AA}$  is

$$\begin{aligned} E_1(3p - 3s) &= \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{5893 \times 10^{-10} \text{ m}} \\ &= 3.375 \times 10^{-19} \text{ J} \\ &= \frac{3.375 \times 10^{-19} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 2.11 \text{ eV}. \end{aligned}$$

The energy corresponding to the first excited state  $4s$  of sodium relative to the ground state  $3s$  is

$$E_2(4s - 3s) = 3.18 \text{ eV} \text{ (given).}$$

The first member of the sharp series corresponds to the transition  $4s - 3p$ . The corresponding energy is

$$\begin{aligned} E(4s - 3p) &= E_2(4s - 3s) - E_1(3p - 3s) \\ &= 3.18 \text{ eV} - 2.11 \text{ eV} = 1.07 \text{ eV}. \end{aligned}$$

The corresponding wavelength is

$$\begin{aligned} \lambda &= \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{1.07 \text{ eV}(1.60 \times 10^{-19} \text{ J/eV})} \\ &= 11.618 \times 10^{-7} \text{ m} = 11618 \text{ \AA}. \end{aligned}$$

**3. The sodium yellow line  $5893 \text{ \AA}$  arises from the transition  $3p \rightarrow 3s$ .** The  $3p$  level is splitted by spin-orbit interaction into two components separated by  $2.1 \times 10^{-3} \text{ eV}$ . Evaluate the wavelength separation between the two components of the yellow line. ( $1 \text{ eV} = 8066 \text{ cm}^{-1}$ ). (Meerut 98 S)

**Solution.** The splitting of sodium yellow line into two components ( $D_1$  and  $D_2$ ) arises due to the splitting of the  $3p$  level. The wave-number splitting of this level is

$$\Delta v = (2.1 \times 10^{-3} \text{ eV}) \times (8066 \text{ cm}^{-1}/\text{eV}) = 16.9 \text{ cm}^{-1}.$$

The mean wavelength of the sodium yellow line is  $\lambda = 5893 \text{ \AA} = 5893 \times 10^{-8} \text{ cm}$ . Now

$$v = 1/\lambda$$

$$\Delta v = -\frac{1}{\lambda^2} \Delta\lambda$$

$$|\Delta\lambda| = \Delta v \times \lambda^2$$

$$= 16.9 \text{ cm}^{-1} \times (5893 \times 10^{-8} \text{ cm})^2$$

$$= 5.87 \times 10^{-8} \text{ cm} = 5.87 \text{ \AA}.$$

**4. Calculate the doublet separation (in eV) of the  $3p$  state of sodium atom.** Given : for D lines of sodium,  $\lambda = 5890 \text{ \AA}, 5896 \text{ \AA}$ ;  $c = 2.99 \times 10^8 \text{ m s}^{-1}$ ,  $e = 1.60 \times 10^{-19} \text{ C}$  and  $h = 6.63 \times 10^{-34} \text{ J s}$ . (Meerut 92 sp. paper)

**Solution.** The splitting of sodium D line into two components  $D_1$  and  $D_2$  occurs due to the splitting of the  $3 p$  level of the sodium atom.

We know that the wave number  $\nu$  is reciprocal of wavelength  $\lambda$ , that is

$$\nu = \frac{1}{\lambda}$$

This gives

$$\Delta\nu = -\frac{\Delta\lambda}{\lambda^2}$$

or

$$\begin{aligned} |\Delta\nu| &= \frac{\Delta\lambda}{\lambda^2} = \frac{\Delta\lambda}{\lambda_1 \times \lambda_2} \\ &= \frac{(5896 - 5890) \text{ \AA}}{5890 \text{ \AA} \times 5896 \text{ \AA}} \\ &= 1.73 \times 10^{-7} (\text{\AA})^{-1} \\ &= 1.73 \times 10^{-7} (10^{-8} \text{ cm})^{-1} = 17.3 \text{ cm}^{-1} = 1730 \text{ m}^{-1}. \end{aligned}$$

The corresponding energy level separation (spin-orbit splitting) is

$$\begin{aligned} \Delta E &= h c (\Delta\nu) \\ &= (6.63 \times 10^{-34} \text{ J s}) (2.99 \times 10^8 \text{ m s}^{-1}) (1730 \text{ m}^{-1}) \\ &= 3.43 \times 10^{-22} \text{ J} = \frac{3.43 \times 10^{-22} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 2.14 \times 10^{-3} \text{ eV}. \end{aligned}$$

### POTASSIUM

5. The longest wavelength lines in the series  $(n, l) \rightarrow (4, 0)$  in potassium have wavelengths  $7699.0 \text{ \AA}$ ,  $7664.9 \text{ \AA}$ ,  $4047.2 \text{ \AA}$  and  $4044.1 \text{ \AA}$  respectively. Construct the relevant part of the energy level diagram ; and calculate the splitting between the levels with the same values of  $n$  and  $l$ , but different  $j$ .

**Solution.** The given wavelengths represent the first two doublets of the principal series of potassium, and arise from the transitions

$$4^2P_{3/2, 1/2} \rightarrow 4^2S_{1/2}$$

$$\text{and } 5^2P_{3/2, 1/2} \rightarrow 4^2S_{1/2}.$$

The line-splittings in wave number are the corresponding level-splittings with the same values of  $n$  and  $l$ , but different  $j$ .

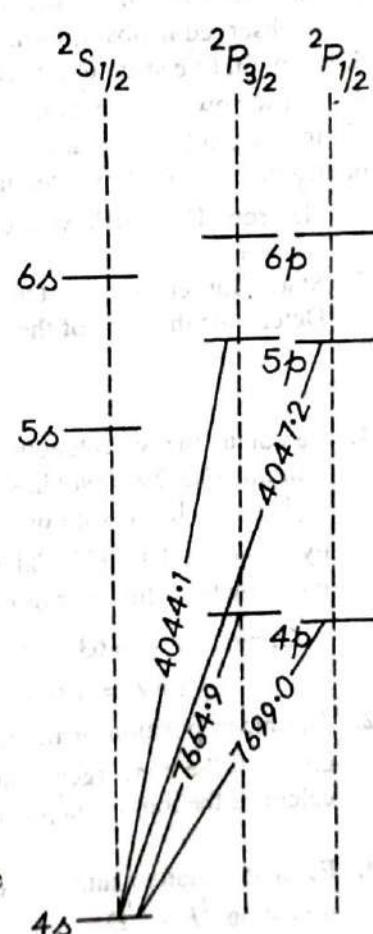
We know that the wave number  $\nu$  is reciprocal of wavelength  $\lambda$ ;

$$\nu = \frac{1}{\lambda}$$

$$\text{so that } \Delta\nu = -\frac{1}{\lambda^2} \Delta\lambda$$

$$\text{or } |\Delta\nu| = \frac{\Delta\lambda}{\lambda_1 \times \lambda_2}$$

For the wavelengths  $7699.0 \text{ \AA}$  and  $7664.9 \text{ \AA}$ , we have



$$\Delta v = \frac{(7699.0 - 7664.9) \times 10^{-8} \text{ cm}}{(7699.0 \times 10^{-8} \text{ cm}) \times (7664.9 \times 10^{-8} \text{ cm})}$$

$$= \frac{34.1}{7699.0 \times (7664.9 \times 10^{-8} \text{ cm})} = 57.8 \text{ cm}^{-1}.$$

This is the splitting between the levels  $4^2P_{3/2}$  and  $4^2P_{1/2}$ .

Again, for the wavelengths  $4047.2 \text{ \AA}$  and  $4044.1 \text{ \AA}$ , we have

$$\Delta v = \frac{(4047.2 - 4044.1) \times 10^{-8} \text{ cm}}{(4047.2 \times 10^{-8} \text{ cm}) \times (4044.1 \times 10^{-8} \text{ cm})}$$

$$= \frac{3.1}{4047.2 \times (4044.1 \times 10^{-8} \text{ cm})} = 18.9 \text{ cm}^{-1}.$$

This is the splitting between the levels  $5^2P_{3/2}$  and  $5^2P_{1/2}$ .

## QUESTIONS

- Describe the general features of spectra of alkali-like atoms. How are they explained ? *(Meerut 2004 S, 2002, 94, 89 sp. paper)*
- Distinguish between the spectra of hydrogen and sodium atoms. What makes the two spectra look so different even though both belong to the single valence electron system ? *(Meerut 2000)*
- Account for : Of the four series observed in alkali spectra, only the principal series is observed in absorption. *(Meerut 99 S, 98 S, 96 sp. paper)*
- Explain fine structure of alkali spectra. *(Meerut 88 sp. paper)*
- Show how the conception of spinning electron accounts for the doubling of levels in the spectra of alkalies. *(Meerut 2003, 02, 98, 95, 90 sp. paper)*
- Calculate the spin-orbit interaction energy for a single non-penetrating valence electron. How will you explain the separation of  $^2P$  and  $^2D$  terms of alkali spectra ? *(Meerut 2006, 04, 03, 01, 00 S)*
- State Burger-Dorgelo-Ornstein rule for the relative intensity of spectral lines. Determine the ratio of the intensities of a principal-series doublet of sodium. *(Meerut 96 sp. paper)*

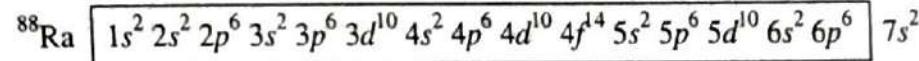
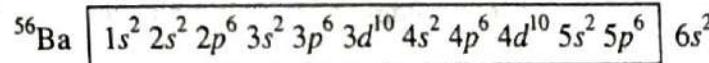
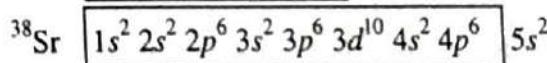
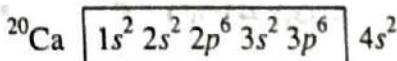
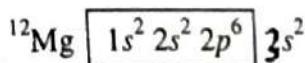
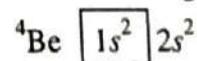
## PROBLEMS

- Calculate the wavelength of the line corresponding to  $2p - 2s$  transition in lithium. The  $2p$  level lies  $1.85 \text{ eV}$  higher than the  $2s$  level. The  $2p$  level is splitted by spin-orbit interaction into two components separated by  $0.042 \times 10^{-3} \text{ eV}$ . Calculate the wavelength difference of the two components into which the line is splitted.  
Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  
 $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} = 8066 \text{ cm}^{-1}$ . *Ans. 6719 \text{ \AA}, 0.153 \text{ \AA}*.
- The mean position of the first pair of lines of the principal series of Li is  $14904 \text{ cm}^{-1}$ . If the convergence limit of the sharp series lines is at  $28583 \text{ cm}^{-1}$ , calculate the ionisation potential of Li. *(Meerut sp. paper 2003, 02, 01, 96)* *Ans. 5.39 \text{ eV}*.
- Estimate relative intensities of lines of the compound doublet arising from the transition  $^2F - ^2D$ . *(Meerut 2004 sp. paper)*

# Spectra of Alkaline-Earth Elements and Complex Spectra

## 1. Essential Features of Spectra of Alkaline-Earth Elements

The elements placed in the second group of the periodic table are known as alkaline-earth elements, having similar chemical and physical properties. These elements, and the electronic configurations of their atoms are :



Thus, an alkaline-earth atom contains two valence electrons, outside *closed* shells or subshells. These two electrons are optically-active and are responsible for the alkaline-earth spectra. The spectrum of an alkaline-earth atom consists of two types of spectral lines; singlets and triplets. The lines of each type can be grouped into four chief series : principal, sharp, diffuse and fundamental. A number of relations are noticed among these series :

(i) The singlet sharp ( ${}^1S$ ) and the singlet diffuse ( ${}^1D$ ) series have a common convergence limit; and similarly the triplet sharp ( ${}^3S$ ) and the triplet diffuse ( ${}^3D$ ) series have another common limit.

(ii) The wave number difference between the common limit of  ${}^1S$  and  ${}^1D$  series, and the limit of the singlet principal ( ${}^1P$ ) series is equal to the wave number of the first member of the  ${}^1P$  series. Similarly, the wave number difference between the common limit of  ${}^3S$  and  ${}^3D$  series and the limit of  ${}^3P$  series is equal to the wave number of the first member of the  ${}^3P$  series. This is Rydberg-Schuster law.

(iii) The wave number difference between the common limit of  ${}^1S$  and  ${}^1D$  series and the limit of the  ${}^1F$  series is equal to the wave number of the first member of the  ${}^1D$  series. The same holds for the respective triplet series. This is Runge Law.

(iv) The above relations are also observed to hold when the fine structure is taken into account.

The lines of all triplet series show a fine structure.

- (a) All lines of the principal series show a three-component fine structure with decreasing wave number separations and approach a single limit.
- (b) All lines of the sharp series also show a three-component structure but with same wave number separations and approach a triple limit.
- (c) All lines of the diffuse and the fundamental series are composed of six components, three strong ones and three satellites, and approach triple limits. These are known as 'compound' triplets, in contrast to the 'simple' triplets of the principal and the sharp series.
- (d) Some lines show a fine structure with characteristics different from the normal simple and compound triplets. These are called 'anomalous' triplets which arise as a result of excitation of both valence electrons.

Certain alkaline-earth spectra show lines which do not fit in any of the above chief series. These are 'combination' and 'intercombination' lines.

All these broad and fine-structure features can be explained by the vector model of the atom.

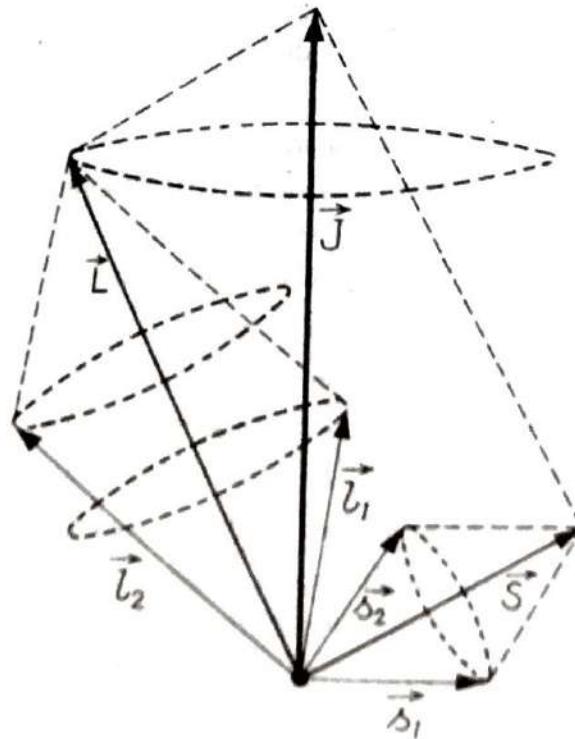
## 2. Vector Model For Two-Valence Electron Atom : Application to Spectra

Many atomic spectra can easily be described by a vector model of the atom, in which the various angular momenta occurring in the atom and their combinations are shown by vectors and their quantum numbers alone.

In the vector model, the orbital angular momentum of each electron is represented by a vector  $\vec{l}$ , and the spin angular momentum by  $\vec{s}$ . Under varying circumstances, vectors  $\vec{l}$  and  $\vec{s}$  combine to form resultant vectors, in terms of which the spectral properties of the atom may be expressed.

For alkaline-earth atoms, with two (optically active) electrons to be considered, the vector model consists of four vectors  $\vec{l}_1, \vec{l}_2, \vec{s}_1, \vec{s}_2$ , and their resultant  $\vec{J}$ . The formation of  $\vec{J}$  may take place by two different coupling schemes. These are known as *L-S* coupling and *j-j* coupling.

**L-S Coupling :** This is a common type of coupling which occurs in most of the lighter atoms. In the vector model for *L-S* coupling (Fig. 1), the individual orbital angular momentum vectors  $\vec{l}_1$  and  $\vec{l}_2$  of the two electrons are strongly coupled to each other to form a resultant orbital angular momentum vector  $\vec{L}$  about which both



(Fig. 1)

$\vec{l}_1$  and  $\vec{l}_2$  precess rapidly. The corresponding quantum number  $L$  can take the values

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots (l_1 + l_2).$$

This gives the various terms of the atom. These terms are designated as  $S, P, D, \dots$  terms according as  $L = 0, 1, 2, \dots$

Similarly, the individual spin angular momentum vectors  $\vec{s}_1$  and  $\vec{s}_2$  of the two electrons are strongly coupled to each other to form a resultant spin angular momentum vector  $\vec{S}$  about which both  $\vec{s}_1$  and  $\vec{s}_2$  precess rapidly. The quantum number  $S$  can take the values

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots (s_1 + s_2).$$

Since  $s_1 = s_2 = \frac{1}{2}$ , we have

$$S = 0, 1.$$

Thus, the multiplicity  $(2S + 1)$  has values 1 and 3; that is, the two (valence) electrons lead to singlet and triplet terms.

Finally, as a result of spin-orbit interaction,  $\vec{L}$  and  $\vec{S}$  are rather less strongly coupled with each other to form a total angular momentum vector  $\vec{J}$  of the atom, that is

$$\vec{J} = \vec{L} + \vec{S}.$$

Both  $\vec{L}$  and  $\vec{S}$  precess slowly around  $\vec{J}$ . The quantum number  $J$  can take the values

$$J = |L - S|, |L - S| + 1, \dots (L + S).$$

Thus, the spin-orbit interaction breaks each level characterised by an  $L$ -value in a number of fine-structure levels, each characterised by a  $J$ -value. The collection of fine-structure levels is known as a 'multiplet'.

**Case of Calcium Atom :** We can now apply the vector model to explain the spectrum of a two-electron atom, say Ca ( $Z = 20$ ). The ground-state configuration of Ca is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2.$$

For the two optically-active electrons, we have

$$l_1 = 0, l_2 = 0, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}.$$

Thus

$$L = 0 \text{ (S-term)}$$

$$S = 0, 1 \text{ so that } (2S + 1) = 1, 3$$

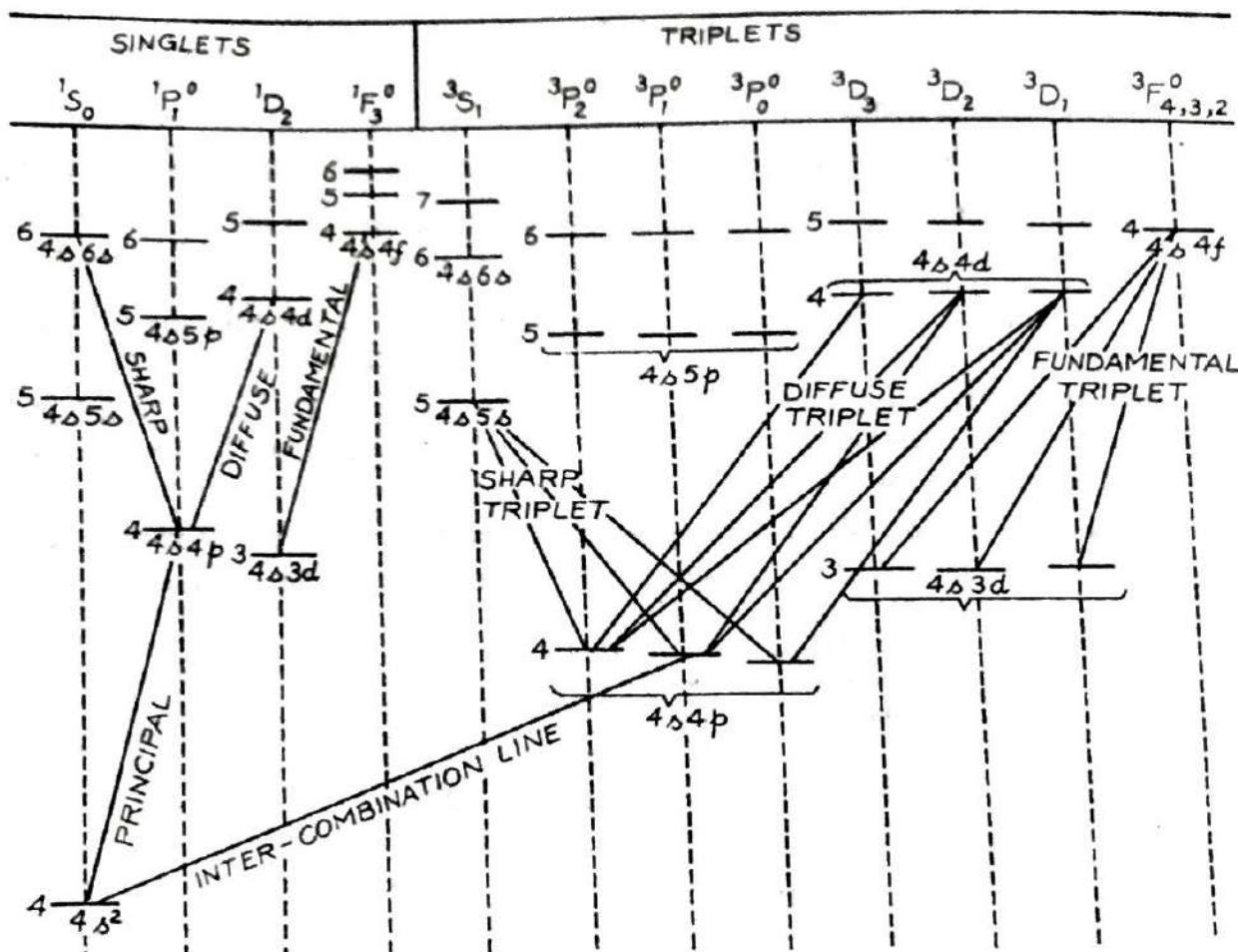
$$\text{and } J = 0, 1.$$

The terms are  ${}^1S_0$  and  ${}^3S_1$ . Since the two valence electrons ( $4s^2$ ) are equivalent, the term  ${}^3S_1$  is excluded by Pauli's principle. Hence the normal atom gives rise to a singlet-S term  ${}^1S_0$  only.

When the atom is excited, either or both of the optical electrons may be raised to higher states. It turns out that *lines of all the eight chief series of the spectrum result from the excitation of 'only one' of the optical electrons*. The various (single-electron) excited-state configurations and the corresponding terms are:

Configurations	Terms
$4s\ 5s, 4s\ 6s, \dots$	$5^1S_0, 6^1S_0, \dots$ and $5^3S_1, 6^3S_1, \dots$
$4s\ 4p, 4s\ 5p, \dots$	$4^1P_1, 5^1P_1, \dots$ and $4^3P_{2,1,0}; 5^3P_{2,1,0} \dots$
$4s\ 3d, 4s\ 4d, \dots$	$3^1D_2, 4^1D_2, \dots$ and $3^3D_{3,2,1}; 4^3D_{3,2,1}, \dots$
$4s\ 4f, \dots$	$4^1F_3, \dots$ and $4^3F_{4,3,2}, \dots$

The energy levels corresponding to the above terms are displayed in Fig. 2. An analytical investigation of spin-orbit interaction shows that the triplet-splitting of levels of



(Fig. 2)

same  $L$  converges rapidly with increasing  $n$ , and that the  $^3P$  intervals are wider than the corresponding  $^3D$  intervals, and the  $^3D$  intervals are wider than the corresponding  $^3F$  intervals.

The different spectral series are emitted as a result of the excited electron jumping back through any of the paths allowed by the selection rules

$$\Delta S = 0$$

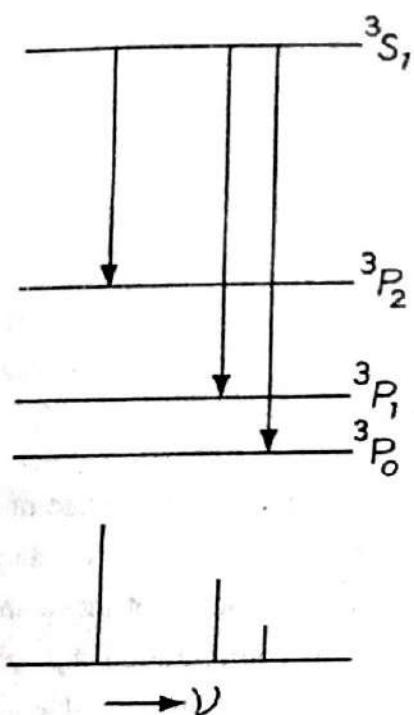
$$\Delta L = \pm 1$$

$$\Delta J = 0, \pm 1, \text{ but } J = 0 \leftrightarrow J = 0.$$

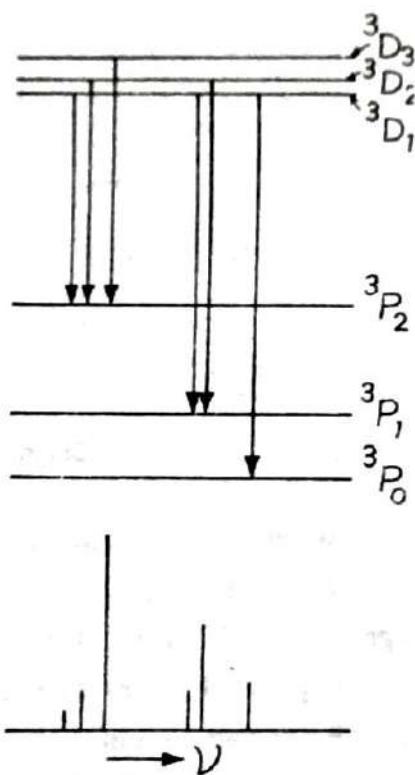
Some of the allowed transitions have been shown in Fig. 2. The singlet principal series arises due to transitions from the  $^1P_1$  levels into the lowest (normal) level  $4^1S_0$ . The triplet sharp series arises from transitions starting from the series of  $^3S_1$  levels and ending on the lowest  $4^3P_{2,1,0}$  levels; the triplet diffuse series from the  $^3D_{3,2,1}$  levels to the lowest  $4^3P_{2,1,0}$  levels, and the triplet fundamental series from the  $^3F_{4,3,2}$  levels to the lowest  $3^3D_{3,2,1}$  levels.

In some spectra, lines arising from transitions between levels higher up on the energy-level diagram are observed. These lines do not belong to the chief series, and are called 'combination lines'. Occasionally, transitions between singlet and triplet levels such as  $^3P_1 - ^1S_0$ , are also observed. They correspond to 'intercombination lines'.

Fig. 3 and 4 show the structure of simple ( $^3S \rightarrow ^3P$ ) and compound ( $^3D \rightarrow ^3P$ ) triplets respectively. Not only is the order of the levels regular (the lower- $j$  level lies



Simple Triplet  
(Fig. 3)



Compound Triplet  
(Fig. 4)

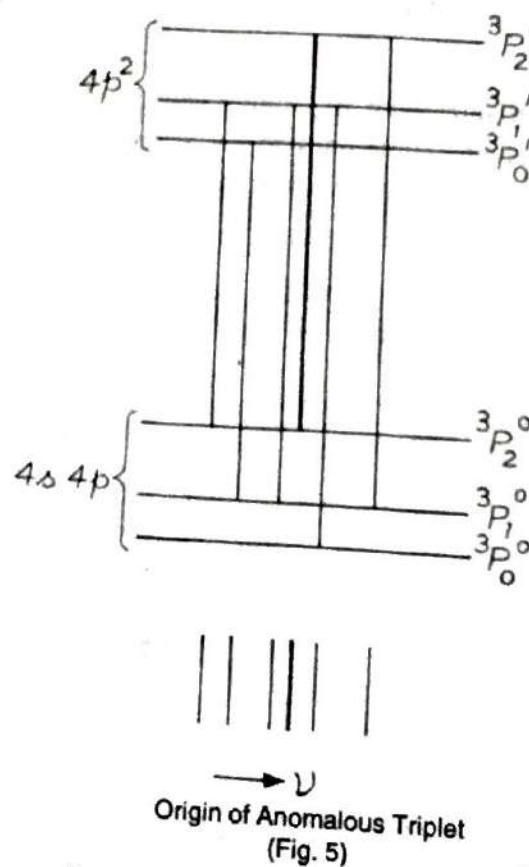
lower), but also their spacings obey the Lande's interval rule. The intervals  $^3P_2 - ^3P_1$  and  $^3P_1 - ^3P_0$  are in the ratio 2 : 1, and the intervals  $^3D_3 - ^3D_2$  and  $^3D_2 - ^3D_1$  in the ratio 3 : 2.

Relative intensities of spectral lines are governed by the following rules : The stronger lines arise where  $\Delta L$  changes in the same way as  $\Delta J$ . Of these the strongest line arises from the transition involving the largest values of  $L$  and  $J$ .

**Anomalous Triplets :** The spectra of alkaline earth elements and alkaline-earth-like ions show some prominent multiplets which have a structure different both in relative

separations and relative intensities, from that of a normal simple or compound triplet. These multiplets are known as 'anomalous' triplets and arise as a result of excitation of both of the optical electrons.

A particularly striking illustration is the multiplet at 4300 Å in Ca, which forms a group of six lines (Fig. 5). An analysis of the multiplet suggests that it arises from

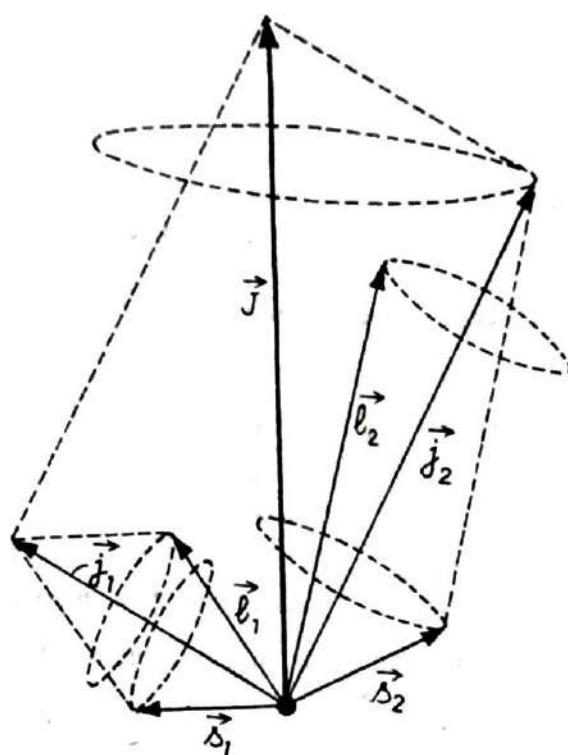


transitions between two  ${}^3P$  terms having nearly same splitting. The lower state of the multiplet is the lowest  $4s\ 4p\ {}^3P^*$  state. The upper state is an anomalous term (or dashed term) designated as  ${}^3P'$  which does not belong to the normal term series of the atom. In this term, both optical electrons are excited to  $4p$  subshell. The configuration  $4p^2$  gives three terms  ${}^3P$ ,  ${}^1D$  and  ${}^1S$  out of which only  ${}^3P$  will combine at all strongly due to the selection rule  $\Delta S = 0$ . Writing the symbols in full, we have the transitions

$$4p^2 \ {}^3P' \rightarrow 4s\ 4p\ {}^3P^*$$

When this is the case,  $\Delta L = 0$  is also possible, provided that  $\Delta l = \pm 1$  (even  $\leftrightarrow$  odd) for the one electron which jumps.

**j-j Coupling :** In the vector model of a two-electron atom under  $j-j$  coupling scheme, the orbital and the spin vectors  $\vec{l}_1$  and  $\vec{s}_1$  of one electron are strongly coupled to each other to form a resultant  $\vec{j}_1$  about which  $\vec{l}_1$  and  $\vec{s}_1$  precess rapidly. Similarly,  $\vec{l}_2$  and  $\vec{s}_2$  of the other electron form  $\vec{j}_2$ . The vectors  $\vec{j}_1$  and  $\vec{j}_2$  are less strongly coupled to each other and form the total angular momentum vector  $\vec{J}$  of the atom. The vectors  $\vec{j}_1$  and  $\vec{j}_2$  precess rather slowly about  $\vec{J}$  (Fig. 6).



(Fig. 6)

The number of terms and the  $J$  values for the  $j-j$  coupling are the same as for the  $L-S$  coupling. The  $j-j$  coupling occurs relatively seldom.

### 3. Interaction Energy (Triplet Separations) in L-S and j-j Couplings

As a result of spin-orbit interaction the atomic terms consist of multiplet components of slightly different energy, each corresponding to a different value of  $J$ . The interaction, and hence the multiplet splitting, increases rapidly with atomic number  $Z$ , and is specially large in excited states of heavier atoms.

We have already seen in chapter 5 that for a single-electron atom, the interaction energy, that is, the shift of each fine-structure level from the hypothetical centre is given by

$$\begin{aligned} -\Delta T_{l,s} &= \frac{R_\infty \alpha^2 Z^4}{2 n^3 l \left(l + \frac{1}{2}\right)(l+1)} \left[ j(j+1) - l(l+1) - s(s+1) \right] \\ &= a \frac{j^{*2} - l^{*2} - s^{*2}}{2}, \end{aligned}$$

where  $a = \frac{R_\infty \alpha^2 Z^4}{n^3 l \left(l + \frac{1}{2}\right)(l+1)}$ ,  $j^* = \sqrt{j(j+1)}$ ,  $l^* = \sqrt{l(l+1)}$  and  $s^* = \sqrt{s(s+1)}$ .

Using cosine law,  $j^{*2} = l^{*2} + s^{*2} + 2 l^* s^* \cos(l^*, s^*)$ , the last expression may be written as

$$-\Delta T_{l,s} = a l^* s^* \cos(l^*, s^*) \quad \dots(i)$$

In the case of two optical electrons there are four angular momenta  $l_1^*$ ,  $l_2^*$ ,  $s_1^*$  and  $s_2^*$  with six possible interactions :

$$(1) s_1^* \text{ with } s_2^*, \quad (2) l_1^* \text{ with } l_2^*, \quad (3) l_1^* \text{ with } s_1^*,$$

$$(4) l_2^* \text{ with } s_2^*, \quad (5) l_1^* \text{ with } s_2^*, \quad (6) l_2^* \text{ with } s_1^*.$$

In  $L\text{-}S$  coupling, the interactions (1) and (2) predominate over (3) and (4); while (5) and (6) are negligibly small.

Applying eq. (i), the energies corresponding to the interactions (1), (2), (3), (4) are

$$\left. \begin{aligned} \Delta T_1 &= a_1 s_1^* s_2^* \cos(s_1^*, s_2^*) \\ \Delta T_2 &= a_2 l_1^* l_2^* \cos(l_1^*, l_2^*) \\ \Delta T_3 &= a_3 l_1^* s_1^* \cos(l_1^*, s_1^*) \\ \Delta T_4 &= a_4 l_2^* s_2^* \cos(l_2^*, s_2^*) \end{aligned} \right\} \dots(ii)$$

Again, in  $L\text{-}S$  coupling,  $s_1^*$  and  $s_2^*$  precess rapidly with fixed angles around their resultant  $S^*$ , which remains invariant in magnitude. Therefore, by cosine law :

$$S^{*2} = s_1^{*2} + s_2^{*2} + 2 s_1^* s_2^* \cos(s_1^*, s_2^*).$$

This gives

$$\Delta T_1 = \frac{1}{2} a_1 (S^{*2} - s_1^{*2} - s_2^{*2}). \dots(iii)$$

Similarly,  $l_1^*$  and  $l_2^*$  precess rapidly with fixed angles around their resultant  $L^*$ , so that

$$\Delta T_2 = \frac{1}{2} a_2 (L^{*2} - l_1^{*2} - l_2^{*2}). \dots(iv)$$

Now,  $L^*$  and  $S^*$  precess around their resultant  $J^*$  in the same way as  $l^*$  and  $s^*$  of a single electron precess around their resultant  $j^*$ . The interaction energy corresponding to this precession is due to couplings between  $l_1^*$  and  $s_1^*$ , and between  $l_2^*$  and  $s_2^*$ , that is,  $\Delta T_3$  and  $\Delta T_4$ . Here the average values of the cosines must be evaluated since the angles between the vectors are continually changing. The average values are given by

$$\overline{\cos(l_1^*, s_1^*)} = \cos(l_1^*, L^*) \cos(L^*, S^*) \cos(S^*, s_1^*)$$

$$\text{and } \overline{\cos(l_2^*, s_2^*)} = \cos(l_2^*, L^*) \cos(L^*, S^*) \cos(S^*, s_2^*).$$

Using these average values of the cosines in eq. (ii), we get

$$\begin{aligned} \Delta T_3 + \Delta T_4 &= \left[ a_3 l_1^* s_1^* \cos(l_1^*, L^*) \cos(S^*, s_1^*) \right. \\ &\quad \left. + a_4 l_2^* s_2^* \cos(l_2^*, L^*) \cos(S^*, s_2^*) \right] \cos(L^*, S^*).$$

Applying cosine law for the various terms, we get

$$\begin{aligned} \Delta T_3 + \Delta T_4 &= \left[ a_3 l_1^* s_1^* \cdot \frac{l_1^{*2} + L^{*2} - l_2^{*2}}{2 l_1^* L^*} \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2 S^* s_1^*} \right. \\ &\quad \left. + a_4 l_2^* s_2^* \cdot \frac{l_2^{*2} + L^{*2} - l_1^{*2}}{2 l_2^* L^*} \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2 S^* s_2^*} \right] \frac{J^{*2} - L^{*2} - S^{*2}}{2 L^* S^*} \end{aligned}$$

$$= \left[ a_3 \frac{l_1^{*2} + L^{*2} - l_2^{*2}}{2L^{*2}} \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2S^{*2}} \right. \\ \left. + a_4 \frac{l_2^{*2} + L^{*2} - l_1^{*2}}{2L^{*2}} \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2S^{*2}} \right] \frac{J^{*2} - L^{*2} - S^{*2}}{2}.$$

This may be written as

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} (a_3 \alpha_3 + a_4 \alpha_4) (J^{*2} - L^{*2} - S^{*2}), \quad \dots(v)$$

where

$$\alpha_3 = \frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2L^{*2}} \frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2S^{*2}} \quad \dots(vi)$$

and

$$\alpha_4 = \frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2L^{*2}} \frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2S^{*2}}. \quad \dots(vii)$$

For any given triplet  $l_1^*, l_2^*, s_1^*, s_2^*, L^*, S^*$  etc. are fixed in magnitude so that  $a_3, a_4, \alpha_3, \alpha_4$  are constants. Writing

$$a_3 \alpha_3 + a_4 \alpha_4 = A, \quad \dots(viii)$$

eq. (v) becomes

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} A (J^{*2} - L^{*2} - S^{*2}). \quad \dots(ix)$$

We may now write any fine-structure term by the formula

$$T = T_0 - \Delta T_1 - \Delta T_2 - \Delta T_3 - \Delta T_4, \quad \dots(x)$$

where  $T_0$  is a hypothetical term value for the centre of gravity of the entire electron configuration.

As an example, let us consider a  $p\,s$  configuration. We have

$$l_1 = 1, l_2 = 0; \therefore L = 1 (P \text{ term})$$

$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}; \therefore S = 0, 1.$$

For  $S = 0$  (singlet state)

$$J = |L - S|, |L - S| + 1, \dots (L + S) \\ = 1$$

and for  $S = 1$  (triplet state)

$$J = 0, 1, 2.$$

The configuration gives a singlet term  ${}^1P_1$ , and a triplet term  ${}^3P_{0,1,2}$ . The shift of each term from the centre of gravity is  $\Delta T_1 + \Delta T_2$ . Now,

$$\Delta T_1 + \Delta T_2 = \frac{1}{2} a_1 (S^{*2} - s_1^{*2} - s_2^{*2}) \\ + \frac{1}{2} a_2 (L^{*2} - l_1^{*2} - l_2^{*2}).$$

Putting  $S = 0, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, L = 1, l_1 = 1, l_2 = 0$ , we get

$$\Delta T_1 + \Delta T_2 = - \frac{3a_1}{4}.$$

Thus, the singlet term is shifted *up* the hypothetical centre by  $3a_1/4$ , as shown in Fig. 7.

Again, putting

$$S = 1, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, L = 1, l_1 = 1, l_2 = 0,$$

we get

$$\Delta T_1 + \Delta T_2 = \frac{a_1}{4}.$$

The triplet term is shifted *down* the hypothetical centre by  $a_1/4$ , as shown in Fig. 7. This has been so chosen because singlet levels lie above the corresponding triplet levels of the same electron configuration.

Now, the shift of each fine-structure level of the triplet term from the hypothetical centre is  $\Delta T_3 + \Delta T_4$ . Now,

$$\Delta T_3 + \Delta T_4 = \frac{1}{2}A(J^{*2} - L^{*2} - S^{*2}).$$

Putting  $L = 1, S = 1$  and  $J = 0, 1, 2$ ; we get

$$\Delta T_3 + \Delta T_4 = -2A, -A, A.$$

Taking it a regular triplet, the levels  ${}^3P_0$  and  ${}^3P_1$  are *lowered* by  $2A$  and  $A$  from the centre, while the level  ${}^3P_2$  is *raised* up by  $A$  (Fig. 7).

The total  ${}^3P$  separation, that is, the  ${}^3P_0 - {}^3P_2$  interval is  $3A$ .

By eq. (vi), (vii) and (viii), we have

$$\begin{aligned} A &= a_3 \alpha_3 + a_4 \alpha_4 \\ &= a_3 \frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2L^{*2}} \frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2S^{*2}} \\ &\quad + a_4 \frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2L^{*2}} \frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2S^{*2}}. \end{aligned}$$

Putting  $l_1 = 1, l_2 = 0, L = 1, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, S = 1$ , we get

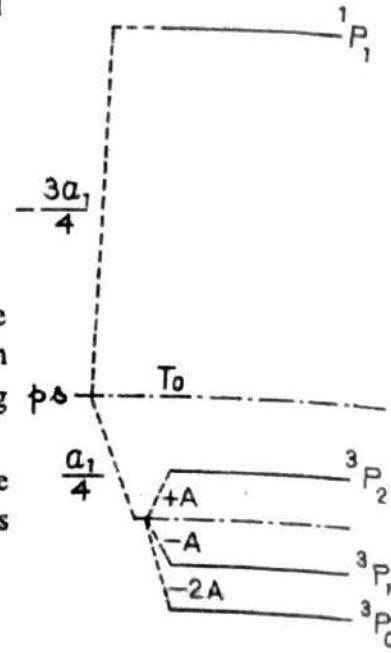
$$A = \frac{a_3}{2}.$$

Thus, in  $ps$  configuration the total  ${}^3P$  separation is  $3a_3/2$ .

In  $jj$  coupling, the interaction between  $l_1^*$  and  $s_1^*$ , and that between  $l_2^*$  and  $s_2^*$  are stronger than the interaction between  $l_1^*$  and  $l_2^*$ , and that between  $s_1^*$  and  $s_2^*$ . Hence in this case  $\Delta T_3$  and  $\Delta T_4$  predominate over  $\Delta T_1$  and  $\Delta T_2$  in eq. (ii).

Since the angles between  $l_1^*$  and  $s_1^*$ , and between  $l_2^*$  and  $s_2^*$  are fixed,  $\Delta T_3$  and  $\Delta T_4$  are readily calculated from the cosine law :

$$\Delta T_3 = \frac{1}{2}a_3(l_1^{*2} - l_1^{*2} - s_1^{*2}) \quad \dots (xi)$$



(Fig. 7)

f<sub>1</sub> → Al X

and  $\Delta T_4 = \frac{1}{2} a_4 (j_2^{*2} - l_2^{*2} - s_2^{*2})$ , ... (xii)

But the angles between  $s_1^*$  and  $s_2^*$ , and between  $l_1^*$  and  $l_2^*$  are continually changing, and so the cosines in  $\Delta T_1$  and  $\Delta T_2$  must be averaged. The average values are given by

$$\overline{\cos(s_1^*, s_2^*)} = \cos(s_1^*, j_1^*) \cos(j_1^*, j_2^*) \cos(j_2^*, s_2^*)$$

and  $\overline{\cos(l_1^*, l_2^*)} = \cos(l_1^*, j_1^*) \cos(j_1^*, j_2^*) \cos(j_2^*, l_2^*)$ .

Using these average values in eq. (ii), we get

$$\begin{aligned}\Delta T_1 + \Delta T_2 &= \left[ a_1 s_1^* s_2^* \cos(s_1^*, j_1^*) \cos(j_2^*, s_2^*) \right. \\ &\quad \left. + a_2 l_1^* l_2^* \cos(l_1^*, j_1^*) \cos(j_2^*, l_2^*) \right] \cos(j_1^*, j_2^*) \\ &= \frac{1}{2} (a_1 \beta_1 + a_2 \beta_2) (J^{*2} - j_1^{*2} - j_2^{*2}),\end{aligned}\text{... (xiii)}$$

where

$$\beta_1 = \frac{s_1^{*2} + j_1^{*2} - l_1^{*2}}{2 j_1^{*2}} \frac{s_2^{*2} + j_2^{*2} - l_2^{*2}}{2 j_2^{*2}} \text{... (xiv)}$$

and

$$\beta_2 = \frac{l_1^{*2} + j_1^{*2} - s_1^{*2}}{2 j_1^{*2}} \frac{l_2^{*2} + j_2^{*2} - s_2^{*2}}{2 j_2^{*2}} \text{... (xv)}$$

Writing

$$a_1 \beta_1 + a_2 \beta_2 = B,$$
 ... (xvi)

eq. (xiii) becomes

$$\Delta T_1 + \Delta T_2 = \frac{1}{2} B (J^{*2} - j_1^{*2} - j_2^{*2}). \text{... (xvii)}$$

We may again write any fine-structure term by the formula

$$T = T_0 - \Delta T_1 - \Delta T_2 - \Delta T_3 - \Delta T_4,$$

where  $T_0$  represents the hypothetical centre.

A good example of a  $ps$  configuration having  $jj$  coupling is found in tin. For  $ps$  configuration, we have

$$l_1 = 1, s_1 = \frac{1}{2}; \therefore j_1 = \frac{1}{2}, \frac{3}{2}$$

$$l_2 = 0, s_2 = \frac{1}{2}; \therefore j_2 = \frac{1}{2}.$$

This gives rise to two  $(j_1, j_2)$  combinations, namely  $\left(\frac{1}{2}, \frac{1}{2}\right)$  and  $\left(\frac{3}{2}, \frac{1}{2}\right)$ . We know that

$$J = |j_1 - j_2|, |j_1 - j_2| + 1, \dots (j_1 + j_2).$$

Therefore, the  $J$ -values corresponding to the above combinations are 0, 1 and 1, 2 respectively. Thus, we have the terms

$$\left(\frac{1}{2}, \frac{1}{2}\right)_{0,1} \text{ and } \left(\frac{3}{2}, \frac{1}{2}\right)_{1,2}.$$

The shift of each term from the centre of gravity is  $\Delta T_3 + \Delta T_4$ . Now,

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} a_3 (j_1^{*2} - l_1^{*2} - s_1^{*2}) + \frac{1}{2} a_4 (j_2^{*2} - l_2^{*2} - s_2^{*2}).$$

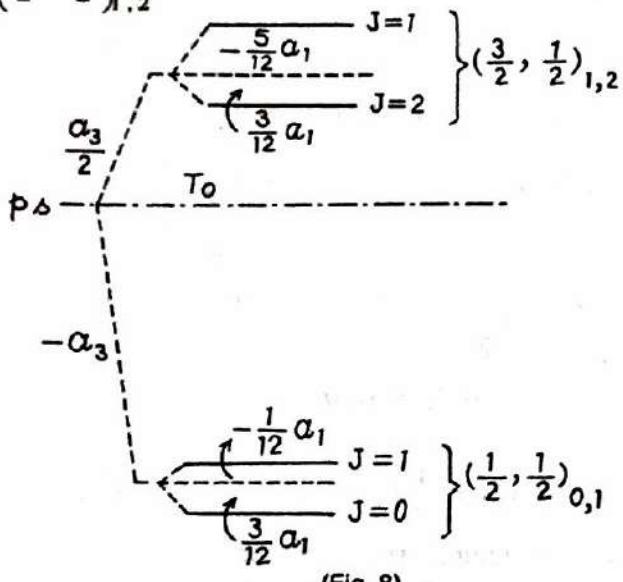
Putting  $j_1 = \frac{1}{2}$ ,  $j_2 = \frac{1}{2}$  and the values of  $l_1, s_1, l_2, s_2$ , we get  
 $\Delta T_3 + \Delta T_4 = -a_3$ .

Thus, the term  $\left(\frac{1}{2}, \frac{1}{2}\right)_{0,1}$  is shifted down the hypothetical centre by  $a_3$ .

Again, putting  $j_1 = \frac{3}{2}$ ,  $j_2 = \frac{1}{2}$  and the same other values, we get

$$\Delta T_3 + \Delta T_4 = \frac{a_3}{2}.$$

Thus, the term  $\left(\frac{3}{2}, \frac{1}{2}\right)_{1,2}$  is shifted up by  $a_3/2$ . This has been shown in Fig. 8.



(Fig. 8)

For the separation of fine-structure levels, we calculate  $\Delta T_1 + \Delta T_2$ , which is

$$\Delta T_1 + \Delta T_2 = \frac{1}{2} B (J^{*2} - J_1^{*2} - j_2^{*2}).$$

For the term  $\left(\frac{3}{2}, \frac{1}{2}\right)_{1,2}$ , we have

$$B = \frac{1}{3} a_1$$

and

$$\begin{aligned} \Delta T_1 + \Delta T_2 &= -\frac{5}{4} B, \quad \frac{3}{4} B \\ &= -\frac{5}{12} a_1, \quad \frac{3}{12} a_1. \end{aligned}$$

For the terms  $\left(\frac{1}{2}, \frac{1}{2}\right)_{0,1}$  we have

$$B = -\frac{1}{3} a_1$$

and

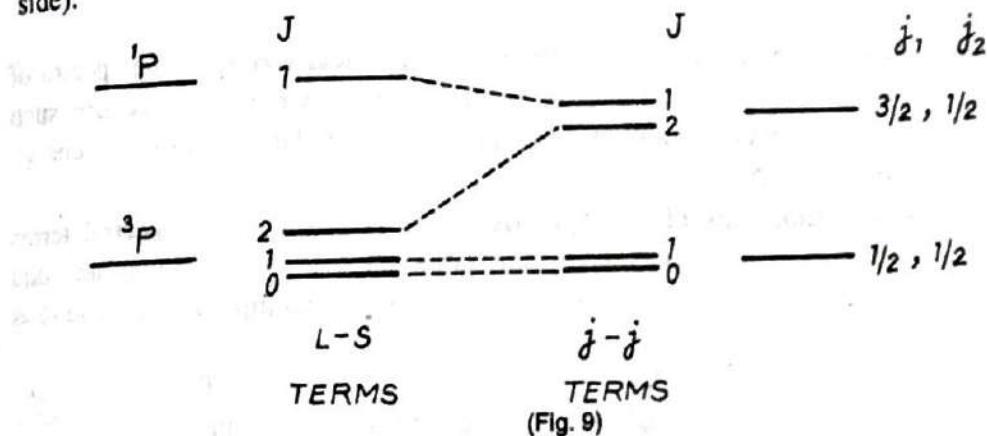
$$\begin{aligned} \Delta T_1 + \Delta T_2 &= -\frac{3}{4} B, \quad \frac{1}{4} B \\ &= \frac{3}{12} a_1, \quad -\frac{1}{12} a_1. \end{aligned}$$

These Separations are also shown in Fig. 8. It can be seen in Fig. 8 that the total  $^3P$  separation, that is, the interval between  $J = 0$  level and  $J = 2$  level is

$$a_3 + \frac{a_3}{2} = 3a_3/2, \text{ which is the same as in } L-S \text{ coupling.}$$

#### 4. Comparison of Terms in $L-S$ and $j-j$ Couplings

We have considered above the configuration  $ps$ . In  $L-S$  coupling, it gives a singlet term  $^1P$  and a triplet term  $^3P$ , with a relatively large energy difference. The small spin-orbit interaction splits the triplet term into three closely spaced components. Thus in all, there are four possible states  $^1P_1$ ,  $^3P_0$ ,  $^3P_1$  and  $^3P_2$  having  $J = 1$  and 0, 1, 2. (Fig. 9, left side).



In  $j-j$  coupling, the same configuration gives widely-separated ( $j_1, j_2$ ) terms  $\left(\frac{3}{2}, \frac{1}{2}\right)$  and  $\left(\frac{1}{2}, \frac{1}{2}\right)$ . When the small  $j-j$  interaction is taken into account, each term is splitted into two close components. For  $\left(\frac{3}{2}, \frac{1}{2}\right)$ ,  $J$  is 2, 1; for  $\left(\frac{1}{2}, \frac{1}{2}\right)$ ,  $J$  is 1, 0 (Fig. 9, right side).

Thus, we see that the number of terms is eventually the same for both types of coupling and that the  $J$  values are also the same. Hence the terms in the two couplings can be correlated as shown by dotted lines in Fig. 9.

Coupling intermediate between the two extremes can occur, but terms can always be identified by their  $J$  values since the total angular momentum of the atom is conserved, when the coupling is changed.

#### 5. Regularities in Complex Spectra

Several regularities can be observed in atomic spectra of complex atoms :

(i) **The Rydberg-series Relationships** : Rydberg observed that the spectral lines of a complex atom may be divided into a number of different series, and many observed series can be represented by a formula similar to the Balmer's formula of the hydrogen series. For example,

$$v_m = v_{\infty} - \frac{R}{(m + \mu)^2}; \quad \begin{aligned} \mu &< 1 \\ m &= 2, 3, 4, \dots, \infty \end{aligned}$$

where  $v_{\infty}$  (convergence limit) and  $\mu$  are constants which vary from series to series.

This can be explained from Schrödinger theory according to which a single electron far way from the nucleus moves in a potential field which approaches the field due to a singly-charged nucleus (like that of hydrogen) due to the screening effect of the inner electrons. Hence the higher excited states of a neutral atom in which only a single electron is excited approach those for hydrogen.

(ii) **Hartley Law of Constant Doublet Separation** : Hartley, in 1883, discovered that the wave-number separation between corresponding components of the multiplets of a spectral series is constant. For example, all the doublet lines of the sharp series of a given alkali atom have the same wave-number separation. This law is an obvious consequence of the idea of energy levels. All transitions that begin from, or end on, a doublet level yield two sets of lines, separated by just the energy interval between the two components of the level.

(iii) **Similarity between Members of the same Chemical Group** : The spectra of chemically-similar atoms show considerable similarity. This is expected because such atoms have similar electron configuration which give rise to similar sets of excited energy levels, resulting in similar spectra.

(iv) **The Alternation Law of Multiplicities** : This law states that spectral terms arising from successive elements in the periodic table alternate between even and odd multiplicities. For example, in the elements of fourth period, the multiplicities are found as under :

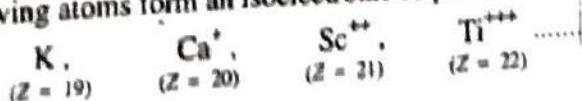
K	Ca	Sc	Ti
doublets	singlets	doublets	singlets
	triplets	quartets	triplets
			quintets

This law is a consequence of the combining properties of the spins of the various valence electrons. An even number of electrons (spins) yields odd multiplicity, while an odd number yields even multiplicity.

one electron	:	doublet
two electrons	:	singlet, triplet
three electrons	:	doublet, quartet
four electrons	:	singlet, triplet, quintet.

(v) **The Displacement Law** : This law was first stated by Kossel and Sommerfeld in 1919. It states that the spectrum and the energy levels of any neutral atom of atomic number  $Z$  resemble closely the spectrum and the energy levels of the singly-ionized atom of atomic number  $Z + 1$  succeeding it in the periodic table. This follows from the fact that the electron configurations of two such atoms would be the same. Thus, the hydrogen spectrum resembles the  $\text{He}^+$  spectrum, and the doublet series of  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ , ... (alkali metals) resemble the doublet series of  $\text{Be}^+$ ,  $\text{Mg}^+$ ,  $\text{Ca}^+$ , ..., (ionised alkaline earths).

(vi) **Isoelectronic Sequences** : The displacement law can also be applied to a 'series' of adjacent elements, each ionized to a successively greater degree. Such a series of atoms, whose electron configurations are identical, is called an 'isoelectronic sequence'. For example, the following atoms form an isoelectronic sequence :



These are also written as

K I, Ca II, Sc III, Ti IV, .....

The energy levels and the spectrum lines arising from each of these atoms show remarkable similarities, for example, same type of fine-structure splitting, similar relative intensities for the various corresponding transitions, etc.

### SOLVED PROBLEMS

1. Show that the total  $^3D$  multiplet separation for a  $d-s$  electron configuration is the same in both  $L-S$  and  $j-j$  couplings. (Meerut 2000, S.sp. paper, 89)

**Solution.** For  $d-s$  configuration, we have

$$l_1 = 2, l_2 = 0, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$$

$L-S$  Coupling :

$$L = 2 \text{ (D term)}$$

$$S = 0, 1$$

$$J = 2, (1, 2, 3).$$

The configuration gives a singlet term  $^1D_2$ , and a triplet term  $^3D_{1,2,3}$ .

The shift of each fine-structure level from the hypothetical centre of the triplet term  $^3D$  is  $\Delta T_3 + \Delta T_4$ , where

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} A (J^{*2} - L^{*2} - S^{*2}).$$

Putting  $L = 2, S = 1$  and  $J = 1, 2, 3$ ; we get

$$\Delta T_3 + \Delta T_4 = -3A, -A, 2A.$$

The levels  $^3D_1$  and  $^3D_2$  are lowered by  $3A$  and  $A$  respectively, while the level  $^3D_3$  is raised by  $2A$  from the centre. The total  $^3D$  separation, that is, the  $^3D_1 - ^3D_3$  interval is  $5A$ . Now,

$$A = a_3 \alpha_3 + a_4 \alpha_4$$

$$= a_3 \frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2L^{*2}} \frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2S^{*2}}$$

$$+ a_4 \frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2L^{*2}} \frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2S^{*2}}.$$

Putting  $l_1 = 2, l_2 = 0, L = 2, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, S = 1$ , we get

$$A = \frac{a_3}{2}.$$

Thus, in  $d-s$  configuration the total  $^3D$  separation is  $\frac{5}{2}a_3$ .

$j-j$  coupling :

$$j_1 = \frac{3}{2}, \frac{5}{2}$$

$$j_2 = \frac{1}{2}.$$

This gives rise to two  $(j_1, j_2)$  combinations, namely,  $\left(\frac{3}{2}, \frac{1}{2}\right)$  and  $\left(\frac{5}{2}, \frac{1}{2}\right)$ . The  $j$ -values corresponding to these combinations are 1, 2 and 2, 3 respectively. Thus, we have the terms

$$\left(\frac{3}{2}, \frac{1}{2}\right)_{1,2} \text{ and } \left(\frac{5}{2}, \frac{1}{2}\right)_{2,3}.$$

The shift of each term from the centre of gravity is  $\Delta T_3 + \Delta T_4$ , where

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} a_3 (j_1^{*2} - l_1^{*2} - s_1^{*2}) + \frac{1}{2} a_4 (j_2^{*2} - l_2^{*2} - s_2^{*2}).$$

Putting  $j_1 = \frac{3}{2}$ ,  $j_2 = \frac{1}{2}$  and the values of  $l_1, s_1, l_2, s_2$ , we get

$$\Delta T_3 + \Delta T_4 = -\frac{3}{2} a_3.$$

This is the shift of the term  $\left(\frac{3}{2}, \frac{1}{2}\right)_{1,2}$  from the centre.

Again, putting  $j_1 = \frac{5}{2}$ ,  $j_2 = \frac{1}{2}$  and the same other values, we get

$$\Delta T_3 + \Delta T_4 = a_3.$$

This is the shift of the term  $\left(\frac{5}{2}, \frac{1}{2}\right)_{2,3}$  from the centre in the *opposite* direction.

The separation between the two terms is thus  $\frac{3}{2} a_3 + a_3 = \frac{5}{2} a_3$ .

On calculating the separations of fine-structure levels, we can see that this is also the separation between  $J = 1$  and  $J = 3$  levels.

Thus, the total  $^3D$  separation, that is, the interval between  $J = 1$  and  $J = 3$  levels is  $\frac{5}{2} a_3$  both in  $L-S$  and  $j-j$  couplings.

## QUESTIONS

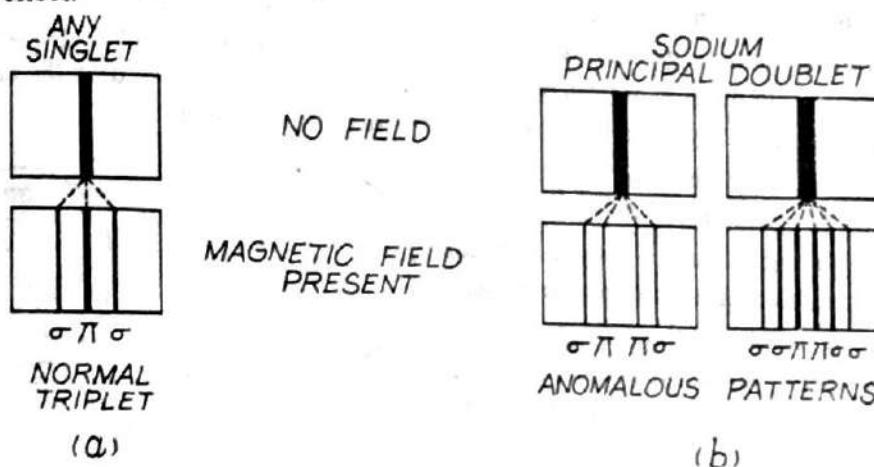
- Outline the essential features of the spectra of alkaline-earth elements. How are they explained theoretically ?  
*(Meerut 2006, 02 S, 01, 00 S, 98, special paper 2003, 02, 01, 00, 98)*
- Discuss the vector model of an atom consisting of two valence electrons in terms of  $L-S$  and  $j-j$  couplings. Show that the same number of terms is obtained for the configuration  $p-s$  in the two coupling schemes.  
*(Meerut 95 S sp. paper)*
- Discuss the salient features of the spectrum of the neutral calcium atom. How is the anomalous nature of the spectrum explained ?  
*(Meerut sp. paper 2003, 99)*
- Write electronic configuration of Ca ( $Z = 20$ ). What are various spectral terms ? Compare the observed spectrum of Ca with that of Na.  
*(Meerut 2002 S, 92)*
- Find an expression for triplet separations for two-valence electrons in  $L-S$  coupling.  
*(Meerut 96, 2004 sp. paper)*
- Calculate interaction energy in two-valence electron of complex atoms on the basis of  $L-S$  coupling with  $p-s$  configuration.  
*(Meerut 2004 sp. paper)*
- Mention regularities in atomic spectra of complex atoms.  
*(Meerut 2002 sp. paper)*

# Zeeman Effect and Paschen-Back Effect

## 1. Normal and Anomalous Zeeman Effects

Zeeman, in 1896, observed that when a light-source giving line spectrum is placed in an *external* magnetic field, the spectral lines emitted by the atoms of the source are split into a number of polarised components. For fields less than several tenths of 1 tesla, the splitting is proportional to the strength of the field. This effect of magnetic field on the atomic spectral lines is called 'Zeeman effect'.

A singlet spectral line viewed at right angles to the magnetic field direction is split into three plane-polarised components ; a central unshifted line with electric vector vibrating parallel to the magnetic field (called  $\pi$  component), and two other lines equally displaced on either side with electric vector vibrating perpendicular to the magnetic field (called  $\sigma$  components). This is called a 'normal triplet' (Fig. 1 a), and the effect is called 'normal' Zeeman effect.



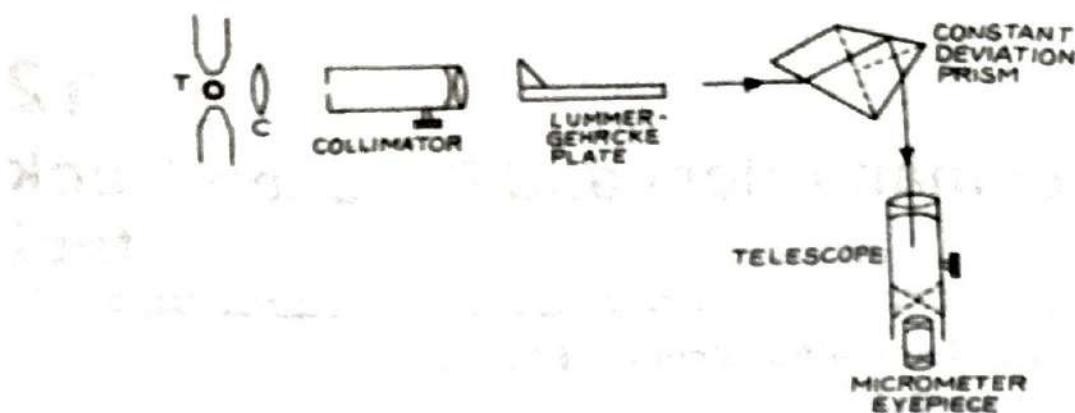
(Fig. 1)

The fine-structure components of a multiplet spectral line, however, show a complex Zeeman pattern. For example, the  $D_1$  and  $D_2$  components of sodium yellow doublet give four and six lines respectively in the Zeeman pattern (Fig. 1 b). This is 'anomalous' Zeeman effect. *The Zeeman splitting is smaller than the fine-structure splitting.*

## 2. Experimental Set-up for studying Zeeman Effect

The experimental arrangement for observing Zeeman effect should be of high resolving power and large light-gathering power. One arrangement using a constant-deviation prism spectrometer is shown in Fig. 2.

T is a neon discharge tube (line source) with its capillary part placed between the poles of an electromagnet, and C is a condensing lens. The light from the capillary part of the tube is condensed by the lens C on the slit of the collimator of the spectrometer. A Lummer-Gehrcke plate (a high-resolving optical device) is placed between the collimator



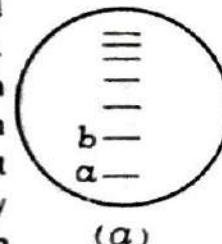
(Fig. 2)

and the constant-deviation prism. The light emerging from the prism at right angles to its initial direction is received in the telescope fitted with a micrometer eyepiece.

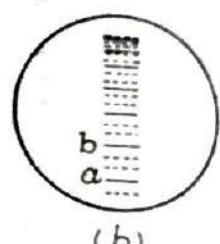
**Adjustment and Procedure :** (i) In the beginning, the current in the electromagnet is kept off. The condensing lens *C*, the L-G plate and the micrometer eyepiece are removed. The slit of the collimator is kept fairly wide opened. On looking through the telescope, the images of the pole-pieces and the neon tube are seen. The pole-pieces and the neon tube are so adjusted that the image of the pole-pieces appear central in the field of view and the neon tube symmetrical between the pole-pieces.

(ii) The condensing lens *C* is placed between the electromagnet and the slit of the collimator such that its aperture is fully illuminated and the image of the aperture fills the field of view. The micrometer eyepiece is put in position and focussed on the crosswires. Now, on looking through it, a bright spectrum of neon light is seen.

(iii) The L-G plate mounted on its stand is placed in position on the spectrograph. Now, on looking through the eyepiece, each spectral line shows a few orders, as shown in Fig. 3 (a). The screws permitting adjustment of the plate in various directions are finely rotated to obtain a bright and sharp fringe-system.



(a)



(b)

(Fig. 3)

(iv) The singlet yellow line ( $\lambda = 5852 \text{ \AA}$ ) of the spectrum is recognised, and by setting the cross-wire on a few successive orders (fringes) the readings of the micrometer are taken.

(v) The electromagnet is now switched-on and the current in it is adjusted so as to give a field of about 4000 gauss. Each order, say *a* and *b*, is splitted into three components, one undisplaced component and two symmetrically displaced components on either side of it (Fig. 3 b). The cross-wire is set, turn by turn, on the displaced components and the readings of the micrometer are taken.

(vi) The measurements are repeated for different fields, such as 7000 gauss and 10,000 gauss; and also for the singlet red line ( $\lambda = 6266 \text{ \AA}$ ) of the neon spectrum.

### 3. Explanation of Normal Zeeman Effect

The normal Zeeman effect which is shown by all lines due to transitions between the singlet ( $S = 0$ ) states of an atom, can be explained from the classical electron theory, and also from the quantum theory without taking note of electron spin.

In terms of quantum theory, a polyelectronic atom possesses an orbital angular momentum  $\vec{L}$  and an orbital magnetic moment  $\vec{\mu}_L$ , with gyromagnetic ratio given by

$$\frac{|\vec{\mu}_L|}{|\vec{L}|} = \frac{e}{2m},$$

where  $e$  and  $m$  are the charge and mass of electron. The vector  $\vec{\mu}_L$  is directed opposite to the vector  $\vec{L}$ , because the electron is *negatively charged*.

When the atom is placed in an external magnetic field  $\vec{B}$ , say along the Z-axis, the vector  $\vec{L}$  precesses around the field direction (Fig. 4), with quantised components given by

$$L_z = M_L \frac{h}{2\pi},$$

where the magnetic orbital quantum number  $M_L$  takes the values :

$$M_L = L, L-1, \dots, -L,$$

that is, a total of  $(2L+1)$  values. This precession is known as 'Larmor precession'. It means that in a magnetic field, each  $L$ -level is split in  $(2L+1)$  levels, each characterised by a  $M_L$  value.

By Larmor's theorem, the angular velocity of precession is given by

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

The interaction energy of such a precession is equal to the product of the angular velocity and the projection of  $\vec{L}$  along the field, that is,

$$\Delta E = \omega L_z = \frac{e}{2m} B M_L \frac{h}{2\pi}$$

or 
$$\Delta E = \frac{e h}{4\pi m} B M_L.$$

In wave numbers, the interaction energy is

$$-\Delta T = \frac{\Delta E}{h c} = \frac{e B}{4\pi m c} M_L.$$

Since the field  $B$  is same for all levels of a given atom, we can write

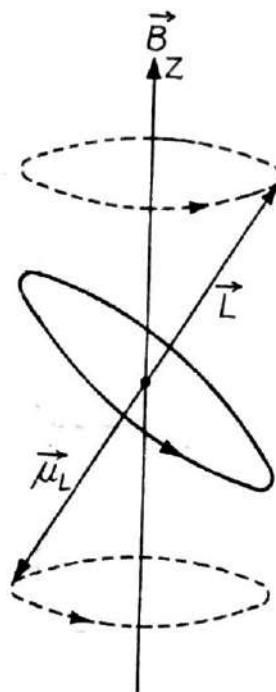
$$\frac{e B}{4\pi m c} = L',$$

where  $L'$  is called the 'Lorentz unit'. Thus

$$-\Delta T = M_L L'.$$

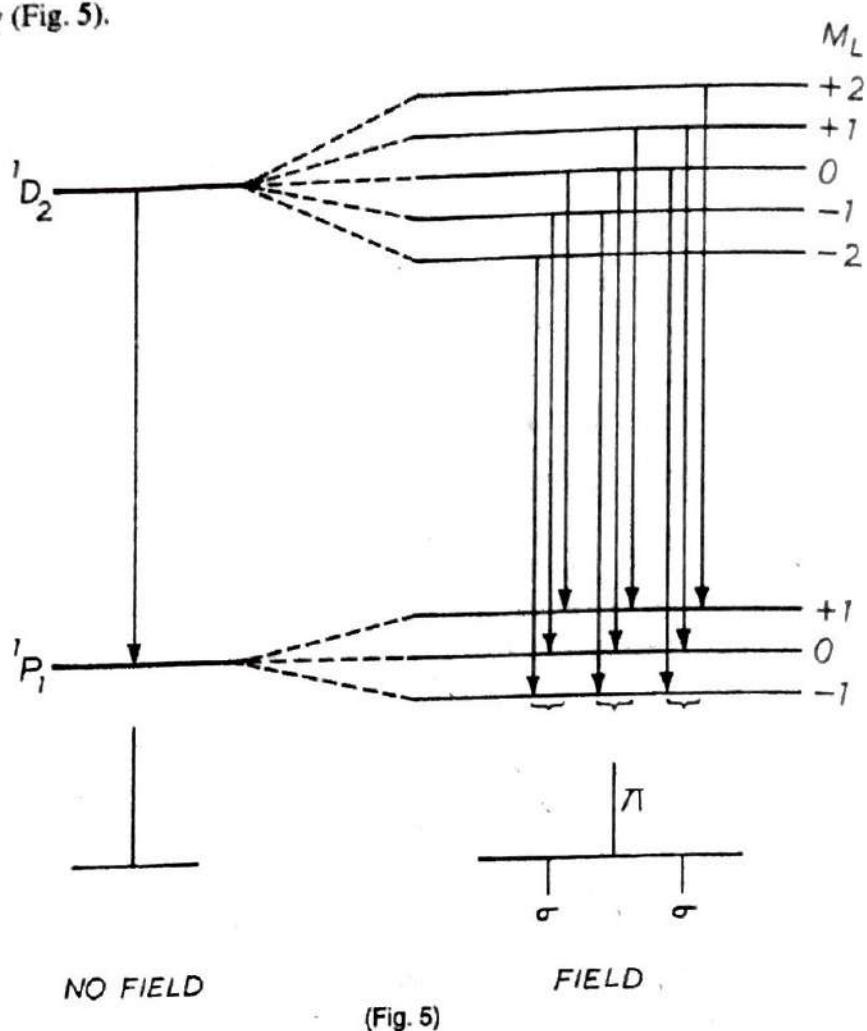
$\Delta T$  is the change in energy for each  $M_L$  level from the original level, and the shift is proportional to the magnetic field  $B$ . The wave-number separation between any two consecutive Zeeman levels is  $L'$ , whatever be the value of  $L$ .

Let us consider the transition  ${}^1D_2 - {}^1P_1$ . These terms correspond to  $L = 2$  and  $L = 1$  and so, in a weak magnetic field, break into  $(2L+1) = 5$  and 3 equispaced



(Fig. 4)

components respectively. The  $M_L$  values are 2, 1, 0, -1, -2; and 1, 0, -1 respectively (Fig. 5).



(Fig. 5)

The selection rule for the magnetic quantum number, as derived by quantum mechanics and also by correspondence principle, is

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

This allows nine transitions. But since the Zeeman splitting is same for all components of both terms, all transitions corresponding to same  $\Delta M_L$  coincide in wave number. This gives the normal triplet pattern, with three component lines. The rule  $\Delta M_L = 0$  gives the  $\pi$  component in the position of the field-free line, while  $\Delta M_L = \pm 1$  give the two symmetrically displaced  $\sigma$  components. The wave-number separation between consecutive components is equal to the separation between consecutive Zeeman levels, and is given by

$$\Delta v = L' = \frac{eB}{4\pi mc}.$$

Putting  $e = 1.6 \times 10^{-19}$  C,  $m = 9.1 \times 10^{-31}$  kg and  $c = 3.0 \times 10^8$  m s<sup>-1</sup>, we get

$$\Delta v = 46.7 B \text{ m}^{-1},$$

where  $B$  is in tesla (N/A-m).

Quantum mechanics leads not only to selection rules but also to the polarisation rules. For observation at right angles to the magnetic field, the transition  $\Delta M_L = 0$  results in spectral line polarised with the electric vector parallel to the field ( $\pi$  component), while the transitions  $\Delta M_L = \pm 1$  result in lines polarised with the electric vector perpendicular to the field ( $\sigma$  components).

The intensity ratio of the components can be derived from the correspondence principle which leads to the result that both  $\sigma$  components together have the same intensity as the  $\pi$  component.

Thus, the normal Zeeman effect is fully explained.

#### 4. Explanation of Anomalous Zeeman Effect

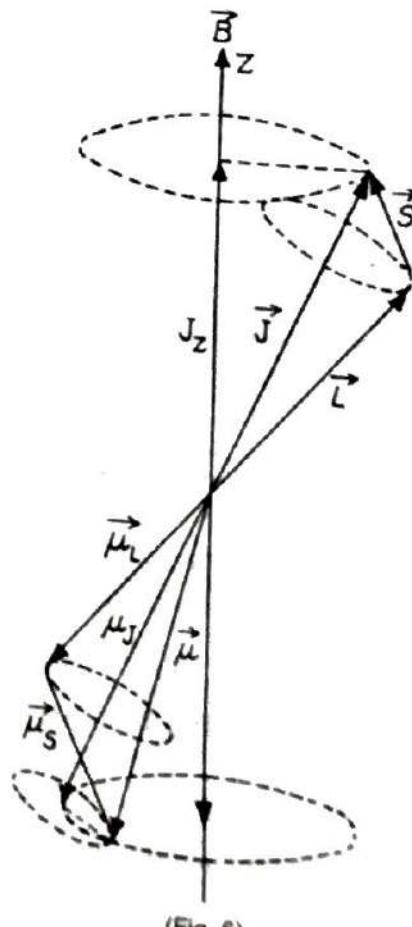
The spectral lines which arise from transitions between components of multiplet levels produce a complex Zeeman pattern. The explanation of this anomalous Zeeman effect is found in the "spin" of the electron.

In the vector model of atom, the orbital angular momentum vector  $\vec{L}$  and the spin angular momentum vector  $\vec{S}$  precess rapidly around the total angular momentum vector  $\vec{J}$ . When the atom is placed in a weak\* magnetic field  $\vec{B}$  along the Z-axis, the magnetic moment of the atom associated with the total angular momentum causes the vector  $\vec{J}$  to precess slowly around the field (Larmor precession). The motion is quantised such that the projection of  $\vec{J}$  along the field direction,  $J_z$ , takes

discrete values given by  $M_J \frac{\hbar}{2\pi}$ , where

$M_J = J, J - 1, J - 2, \dots, -J$ ,  
that is, in all  $2J + 1$  values. The discrete orientations of the atom in space and the small change in energy due to the precession of  $\vec{J}$  around  $\vec{B}$  break each (fine-structure)  $J$ -level into  $(2J + 1)$  Zeeman levels. The separations between the Zeeman levels is determined by the strength of the magnetic field and the total magnetic moment of the atom which we now calculate.

Let us consider the simplest case of a single valence-electron atom in which the valence electron alone is responsible for the angular momentum and the magnetic moment of the atom. Classically, the ratio of the orbital magnetic moment  $|\vec{\mu}_L|$  to the orbital angular momentum  $|\vec{L}|$  is  $e/2m$ . Anomalous Zeeman effect requires, and quantum mechanics confirms, that the ratio of the spin magnetic moment  $|\vec{\mu}_S|$  to the spin angular momentum  $|\vec{S}|$  is twice as large, that is,  $2e/2m$ . Because of this inequality of the two ratios, the total magnetic moment  $\vec{\mu}$  ( $= \vec{\mu}_L + \vec{\mu}_S$ ) is not exactly antiparallel to  $\vec{J}$  (Fig. 6).



(Fig. 6)

\*The field is weak in the sense that it does not decouple  $\vec{L}$  and  $\vec{S}$ .

Since  $\vec{J}$  is invariant,  $\vec{L}$ ,  $\vec{S}$ ,  $\vec{\mu}_L$ ,  $\vec{\mu}_S$  and  $\vec{\mu}$  precess around  $\vec{J}$ . In this precession, the component of  $\vec{\mu}$  perpendicular to  $\vec{J}$ , owing to the continual change in direction, averages to zero. Only the component parallel to  $\vec{J}$  remains a constant of magnitude  $\mu_J$  which contributes to the magnetic moment of the atom. Thus

$$\begin{aligned}\mu_J &= \text{component of } \vec{\mu}_L \text{ along } \vec{J} + \text{component of } \vec{\mu}_S \text{ along } \vec{J} \\ &= |\vec{\mu}_L| \cos(\vec{L}, \vec{J}) + |\vec{\mu}_S| \cos(\vec{S}, \vec{J}) \\ &= \frac{e}{2m} |\vec{L}| \cos(\vec{L}, \vec{J}) + \frac{2e}{2m} |\vec{S}| \cos(\vec{S}, \vec{J}).\end{aligned}$$

$$\text{But } |\vec{L}| = \sqrt{L(L+1)} \frac{h}{2\pi} \text{ and } |\vec{S}| = \sqrt{S(S+1)} \frac{h}{2\pi}.$$

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

Using the obtuse-angled triangle formed by  $\vec{L}$ ,  $\vec{S}$  and  $\vec{J}$ , we have by cosine law

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

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

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

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

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

The quantity inside the brackets is defined as 'Lande g-factor', that is

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

The importance of this  $g$  factor is that it gives directly the relative separations of the Zeeman levels for the different terms. The expression for  $g$ -factor for a multielectron atom under  $L-S$  coupling is same as above.

The expression for the total magnetic moment of the atom now becomes

$$\mu_J = g \frac{e}{2m} \sqrt{J(J+1)} \frac{h}{2\pi} = g \frac{e}{2m} |\vec{J}|.$$

Let us now calculate the magnetic interaction energy. From the last expression, we have

$$\frac{\mu_J}{|\vec{J}|} = g \frac{e}{2m}.$$

Thus,  $g$  determines the ratio of the total magnetic moment to the total angular momentum in states where the angular momentum is partly orbital and partly spin. (For  $S = 0$  and  $J = L$ ,  $g = 1$ ; for  $L = 0$  and so  $J = S$ ,  $g = 2$ ).

By Larmor's theorem, the angular velocity of precession of  $\vec{J}$  around the field  $\vec{B}$  is

$$\omega = \frac{\mu_J}{|\vec{J}|} B = g \frac{e}{2m} B.$$

The energy of precession is equal to product of the angular velocity and the projecton of  $\vec{J}$  along  $\vec{B}$  which is  $J_Z = M_J \frac{h}{2\pi}$ . Thus

$$\Delta E = \omega J_Z = g \frac{e}{2m} B M_J \frac{h}{2\pi}$$

$$\text{or } \Delta E = g M_J \frac{e h}{4\pi m} B.$$

In wave numbers, the interaction energy is

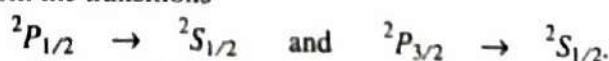
$$- \Delta T = \frac{\Delta E}{h c} = g M_J \frac{e B}{4\pi m c}.$$

$\frac{e B}{4\pi m c}$  is the Lorentz unit  $L'$ . Thus

$$- \Delta T = g M_J L'.$$

This is the expression for the weak-field magnetic interaction energy, or the Zeeman shift, of a single valance electron system\*. It shows that each  $J$ -level is split into  $(2J + 1)$  equispaced Zeeman levels corresponding to the possible values of  $M_J$ . **The Zeeman splitting is different for different  $J$ -levels, depending upon the value of  $g$  for that level.** This also means that the relative separations of the Zeeman levels of one term and those of another are determined by the  $g$ -factor alone.

Let us consider the Zeeman splitting of the resonance lines  $D_1$  and  $D_2$  of sodium. These lines arise from the transitions



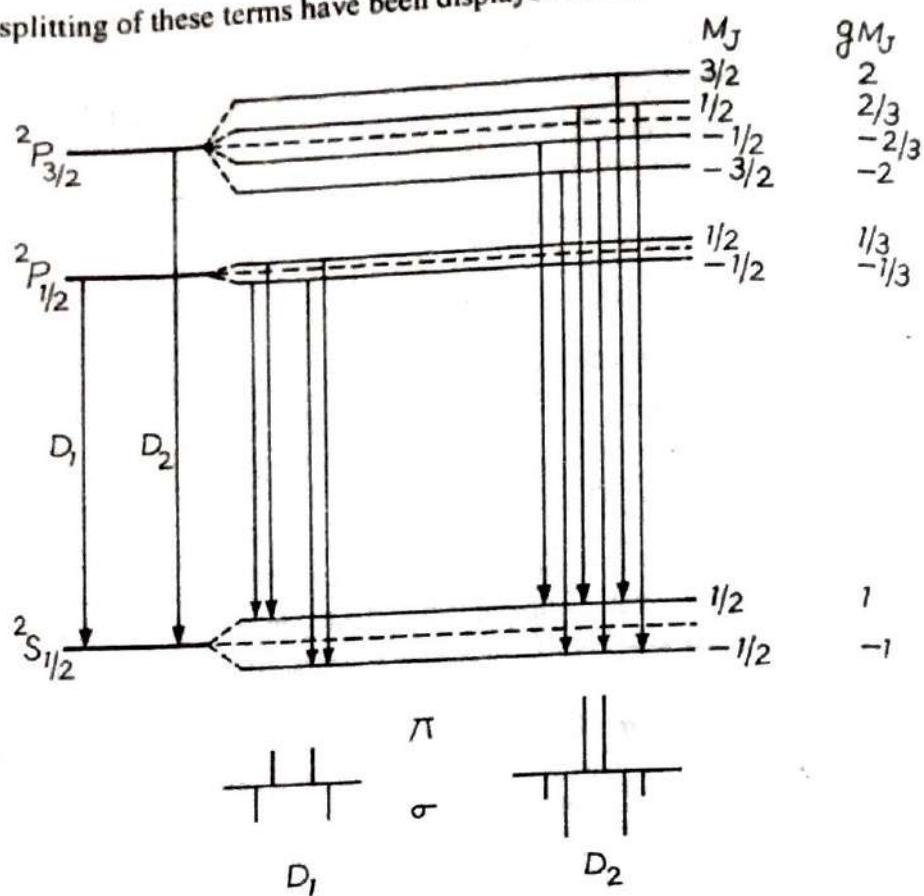
The Zeeman levels,  $g$ -factors and the Zeeman shifts for the various terms involved in these transitions are as follows : We know that

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

Terms	No. of Zeeman levels $(2J + 1)$	$g$	$M_J$ $(+J, \dots, -J)$	Shift in Lorentz unit $\pm M_J$
$^2S_{1/2}$ $(L = 0, S = \frac{1}{2}, J = \frac{1}{2})$	2	2	$\pm \frac{1}{2}$	$\pm 1$
$^2P_{1/2}$ $(L = 1, S = \frac{1}{2}, J = \frac{1}{2})$	2	$\frac{2}{3}$	$\pm \frac{1}{2}$	$\pm \frac{1}{3}$
$^2P_{3/2}$ $(L = 1, S = \frac{1}{2}, J = \frac{3}{2})$	4	$\frac{4}{3}$	$\pm \frac{3}{2}, \pm \frac{1}{2}$	$\pm 2, \pm \frac{2}{3}$

\*The expression for atoms having two or more valence electrons under  $L-S$  coupling is the same as that for a one-electron atom.

The splitting of these terms have been displayed in Fig. 7.



(Fig. 7)

Applying the selection rules

$$\Delta M_J = 0, \pm 1 \quad (\text{but } M_J = 0 \leftrightarrow M_J = 0 \text{ if } \Delta J = 0)$$

we obtain four Zeeman components for the D<sub>1</sub> line and six components for the D<sub>2</sub> line. The components corresponding to  $\Delta M_J = 0$  are polarised with electric vector perpendicular to the field ( $\sigma$ -components).

The intensities of the Zeeman components are governed by the following rules :

- (i) The sum of all the transitions starting from any initial Zeeman level is equal to the sum of all transitions starting from any other level having the same  $n$  and  $l$  values.
- (ii) The sum of all transitions arriving at any Zeeman level is equal to the sum of all transitions arriving at any other level having the same  $n$  and  $l$  values.

The relative intensities are indicated by the heights of the lines drawn at the bottom of the figure.

## 5. Paschen-Back Effect

In the Zeeman effect, the external magnetic field is weak as compared with the internal fields due to the spin and the orbital motions of the valence electron. When, however, the strength of the external field is increased, the separations between Zeeman components increase until they become greater than the separations between multiplet fine-structure components. The anomalous Zeeman pattern then changes over to like a normal Zeeman pattern. This phenomenon is known as "Paschen-Back effect". It can be explained in the following way :

When the external field  $\vec{B}$  becomes stronger as compared with the internal fields, the magnetic coupling between  $\vec{J}$  and  $\vec{B}$  exceeds that between  $\vec{L}$  and  $\vec{S}$ , and the precession of  $\vec{J}$  about  $\vec{B}$  becomes faster than that of  $\vec{L}$  and  $\vec{S}$  about  $\vec{J}$ . Under these conditions the coupling between  $\vec{L}$  and  $\vec{S}$  is partially broken down and  $\vec{J}$  is no longer fixed in magnitude. As the field  $\vec{B}$  is further increased,  $\vec{L}$  and  $\vec{S}$  start precessing independently about  $\vec{B}$  with quantised components  $L_z$  and  $S_z$  along the field direction (Z-axis), as shown in Fig. 8. The magnitudes of these components are  $M_L \frac{h}{2\pi}$  and  $M_S \frac{h}{2\pi}$  respectively, where the magnetic quantum numbers  $M_L$  and  $M_S$  take the following discrete values :

$$M_L = L, L-1, L-2, \dots, -L$$

and

$$M_S = S, S-1, S-2, \dots, -S.$$

By Larmor's theorem, the angular velocities of precession of  $\vec{L}$  and  $\vec{S}$  about the field  $\vec{B}$  are given by the product of  $B$  and the corresponding ratios of the magnetic moments with the angular momenta. That is,

$$\omega_L = \frac{e}{2m} B$$

and

$$\omega_S = 2 \frac{e}{2m} B.$$

The energy of each precession is equal to the product of the angular velocity and the projection of the corresponding angular momentum vector along the field direction. That is,

$$\Delta E_L = \omega_L L_z = \frac{e}{2m} B M_L \frac{h}{2\pi}$$

and

$$\Delta E_S = \omega_S S_z = 2 \frac{e}{2m} B M_S \frac{h}{2\pi}.$$

The sum of these two interaction energies is the main energy shift  $\Delta E$  from the unperturbed energy level. Thus

$$\begin{aligned} \Delta E &= \Delta E_L + \Delta E_S \\ &= (M_L + 2M_S) \frac{e h}{4\pi m} B. \end{aligned}$$

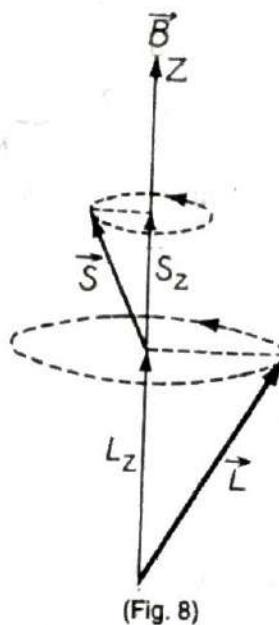
The shift in wave numbers is

$$-\Delta T = \frac{\Delta E}{hc} = (M_L + 2M_S) \frac{e B}{4\pi m c},$$

or in Lorentz unit of  $e B / 4\pi m c$ ,

$$-\Delta T = (M_L + 2M_S) L'.$$

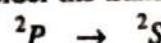
This is the expression for the strong-field magnetic interaction energy, ignoring spin-orbit interaction at all. It shows that each of the field-free level is split into  $(2L+1)(2S+1)$  magnetic levels\*.



(Fig. 8)

\* Because  $M_L$  can take  $(2L+1)$  values and  $M_S$  can take  $(2S+1)$  values.

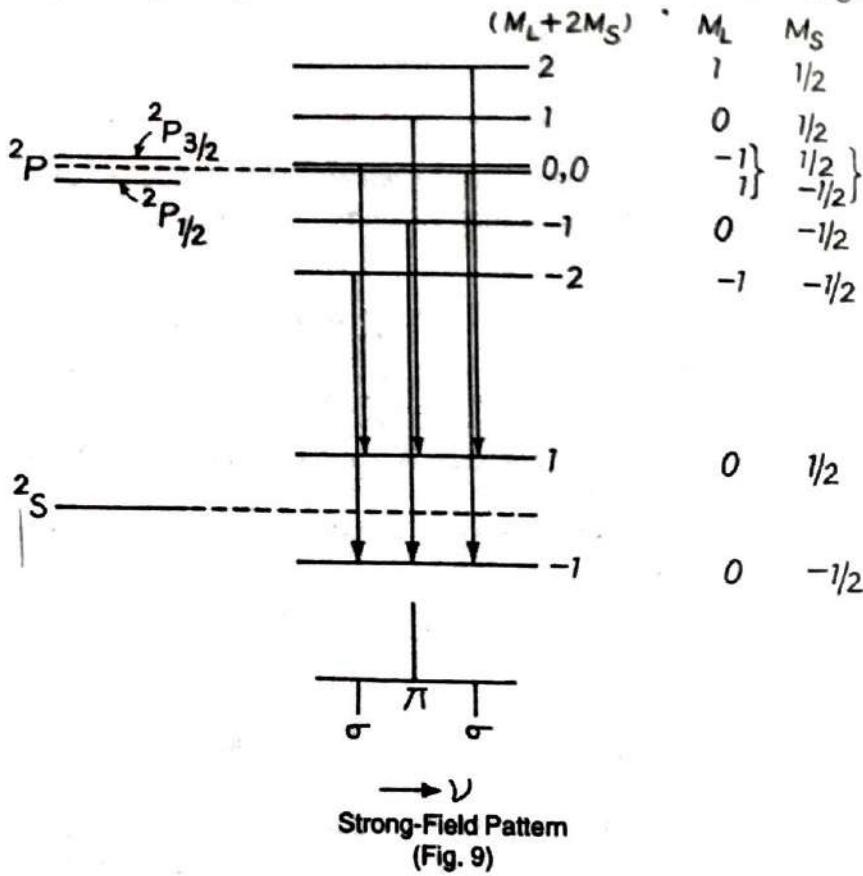
As a specific example, let us consider the transition



in a strong magnetic field. This transition is responsible for the  $D_1$  and  $D_2$  lines of sodium ( $^2P_{1/2, 3/2} \rightarrow ^2S_{1/2}$ ). The strong-field levels and the magnetic shifts for the multiplet terms  $^2P$  and  $^2S$  are as follows :

Term	No. of Strong-Field levels ( $2L + 1$ ) ( $2S + 1$ )	$M_L$	$M_S$	Shift in Lorentz unit ( $M_L + 2M_S$ )
$^2P$ $(L = 1, S = \frac{1}{2})$	6	1	$\frac{1}{2}, -\frac{1}{2}$	2, 0
		0	$\frac{1}{2}, -\frac{1}{2}$	1, -1
		-1	$\frac{1}{2}, -\frac{1}{2}$	0, -2
$^2S$ $(L = 0, S = \frac{1}{2})$	2	0	$\frac{1}{2}, -\frac{1}{2}$	1, -1

The strong-field splittings of the terms  $^2P$  and  $^2S$  have been shown in Fig. 9.



In a strong field, the selection rules for transitions are

$$\Delta M_L = 0 \text{ (components polarised } \parallel \text{ to the field)}$$

$$\Delta M_L = \pm 1 \text{ (components polarised } \perp \text{ to the field)}$$

$$\Delta M_S = 0.$$

When these selection rules are applied they lead to a pattern same as a normal Zeeman triplet.

**Spin-Orbit Correction :** In practice, the *residual* spin-orbit coupling changes the relative energies of the components of different terms. This can be allowed for by adding a small coupling term  $a M_L M_S$  in the expression for the magnetic interaction energy, which now becomes

$$-\Delta T = (M_L + 2M_S) L' + a M_L M_S.$$

As a result of this, each of the two  $\sigma$ -components of the normal triplet splits into narrow doublet, triplet, etc., according as the original field-free transition was a doublet, triplet, etc., transition. In the present field-free transition  $^2P \rightarrow ^2S$ , each  $\sigma$ -component splits into a doublet with a separation just two-thirds that of the field-free doublet (Fig. 10).

The Paschen-Back effect has experimentally been observed for very narrow multiplets only, such as the Li doublet having a field-free separation of  $0.34 \text{ cm}^{-1}$ . The reason is that the effect occurs when the magnetic splitting exceeds the fine-structure (field-free) splitting. The ordinarily available fields, for example, a

field of 4.3 tesla can produce a magnetic splitting of about  $2 \text{ cm}^{-1}$ , which is larger than the fine-structure splitting of Li doublet, and Paschen-Back effect can easily be observed. On the other hand, this magnetic splitting is much less than the fine-structure splitting of sodium resonance doublet ( $17 \text{ cm}^{-1}$ ). Hence a field of 4.3 tesla cannot produce Paschen-Back effect in sodium doublet. Instead, an abnormally large field is required.

So far we have considered the cases when the external field is either very weak (Zeeman effect) or very strong (Paschen-Back effect), as compared to the internal field in the atom. For intermediate fields (comparable with internal field) complicated patterns are obtained.

## 6. Transition from Weak to Strong Field

The number of magnetic levels into which a given state is split, is just the same whatever the field strength. This number is called the 'quantum weight'.

In a weak field, a level with a given inner quantum number  $J$  is split into  $(2J + 1)$  levels where  $(2J + 1)$  is the number of orientations of  $J$  in the external field. In case of an atom with one valence electron,  $J$  can have only two values  $L + \frac{1}{2}$  and  $L - \frac{1}{2}$ , so that a level is split into

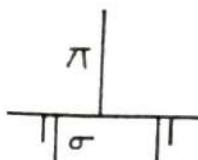
$$\left\{ 2\left(L + \frac{1}{2}\right) + 1 \right\} + \left\{ 2\left(L - \frac{1}{2}\right) + 1 \right\} = 4L + 2$$

levels. In a strong field,  $L$  alone has  $(2L + 1)$  orientations and for each of these,  $S$  has  $(2S + 1)$ , giving altogether

$$(2L + 1)(2S + 1) = 4L + 2 \quad \left[ \because S = \frac{1}{2} \right]$$

levels, same as in a weak field.

In a weak field, each of the magnetic levels is characterised by the quantum numbers  $J$  and  $M_J$ , while in a strong field the characteristic quantum numbers are  $M_L$  and  $M_S$ . We may now inquire which of the levels with  $J$  and  $M_J$  goes over to a particular level



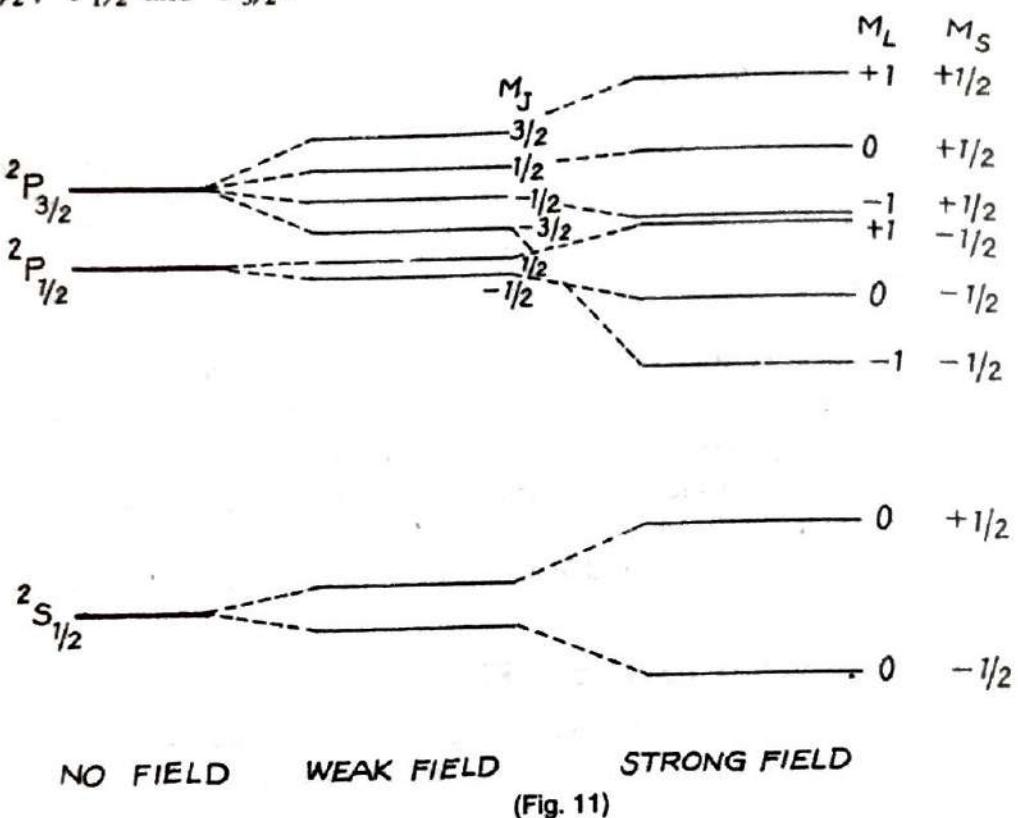
Strong-Field Pattern  
with Spin-Orbit Coupling  
(Fig. 10)

with  $M_L$  and  $M_S$  when the field is increased. As a first rule, the transition takes place in such a way that the sum of the projections of the angular momentum vectors on  $\vec{B}$  does not change. In a weak field this projection is  $M_J$ , in a strong field it is  $M_L + M_S$ . Hence the first rule of transition is

$$M_J = M_L + M_S .$$

This rule alone is, however, insufficient to correlate all weak and strong-field levels, since there are cases when there are more than one levels with the same value of  $M_J$ . Hence the further restriction is that no two levels with the same  $M_J$  cross each other.

In Fig. 11 is shown the transition of the magnetic levels corresponding to the states  $^2S_{1/2}$ ,  $^2P_{1/2}$  and  $^2P_{3/2}$ .



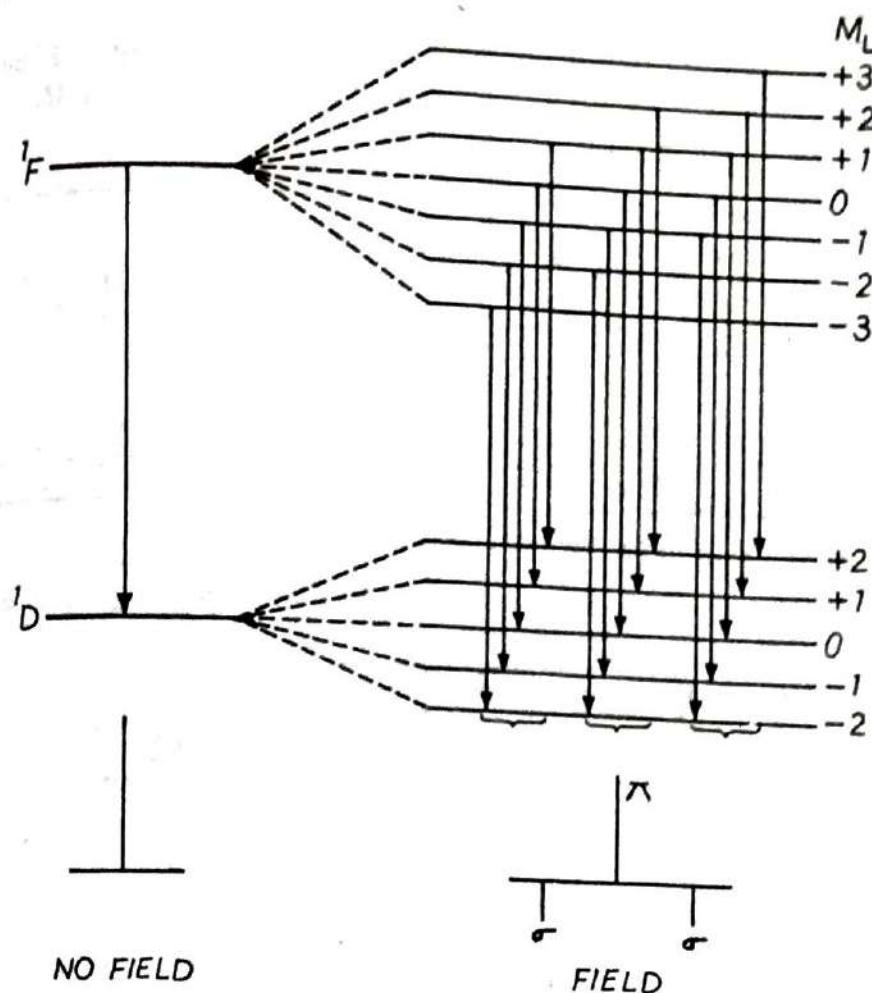
(Fig. 11)

## 7. Examples of Zeeman Effect in Some Transitions

(i)  $^1F_3 - ^1D_2$  : It is a singlet-singlet transition and would give rise to a normal Zeeman triplet.

The terms  $^1F$  and  $^1D$  correspond to  $L = 3$  and  $L = 2$  respectively and in a weak magnetic field, break into  $(2L + 1) = 7$  and 5 Zeeman components respectively. The  $M_L$  values characterising the Zeeman levels are  $3, 2, 1, 0, -1, -2, -3$  and  $2, 1, 0, -1, -2$  respectively.

Since for singlet terms ( $S = 0, J = L$ ) the lande  $g$ -factor is 1, the separation between consecutive Zeeman levels is the same for both terms, equal to one Lorentz unit. The splitting of the terms is shown in Fig. 12.



(Fig. 12)

The selection rules

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

allow 15 transitions. Since the Zeeman splitting is same for both terms, all transitions corresponding to same  $\Delta M_L$  coincide in wave number. Hence we obtain only three Zeeman component lines; the  $\pi$  component corresponding to  $\Delta M_L = 0$  and two  $\sigma$  components corresponding to  $\Delta M_L = \pm 1$ . This is the normal Zeeman triplet.

(ii)  $^2D_{3/2} - ^2P_{1/2}$ : It is a doublet-doublet transition so that the Zeeman pattern would be anomalous. The weak-field interaction energy of a one-electron atom is given by

$$- \Delta T = g M_J L'$$

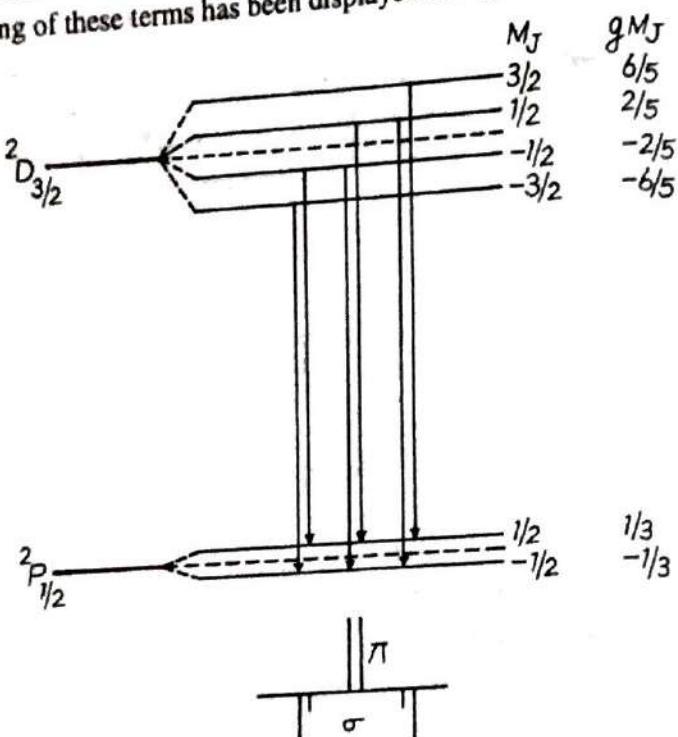
where  $L'$  is the Lorentz unit. The Lande  $g$ -factor is

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

The Zeeman levels,  $g$ -factors and the Zeeman shifts for the given terms  $^2P_{1/2}$  and  $^2D_{3/2}$  are as follows :

Term	No. of Zeeman levels ( $2J + 1$ )	$g$	$M_J$ ( $+J, \dots, -J$ )	Shift in $L'$ unit $g M_J$
$^2P_{1/2}$ $\left( L = 1, S = \frac{1}{2}, J = \frac{1}{2} \right)$	2	$\frac{2}{3}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{3}, -\frac{1}{3}$
$^2D_{3/2}$ $\left( L = 2, S = \frac{1}{2}, J = \frac{3}{2} \right)$	4	$\frac{4}{5}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$\frac{6}{5}, \frac{2}{5}, -\frac{2}{5}, -\frac{6}{5}$

The splitting of these terms has been displayed in Fig. 13.



(Fig. 13)

The selection rule is

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

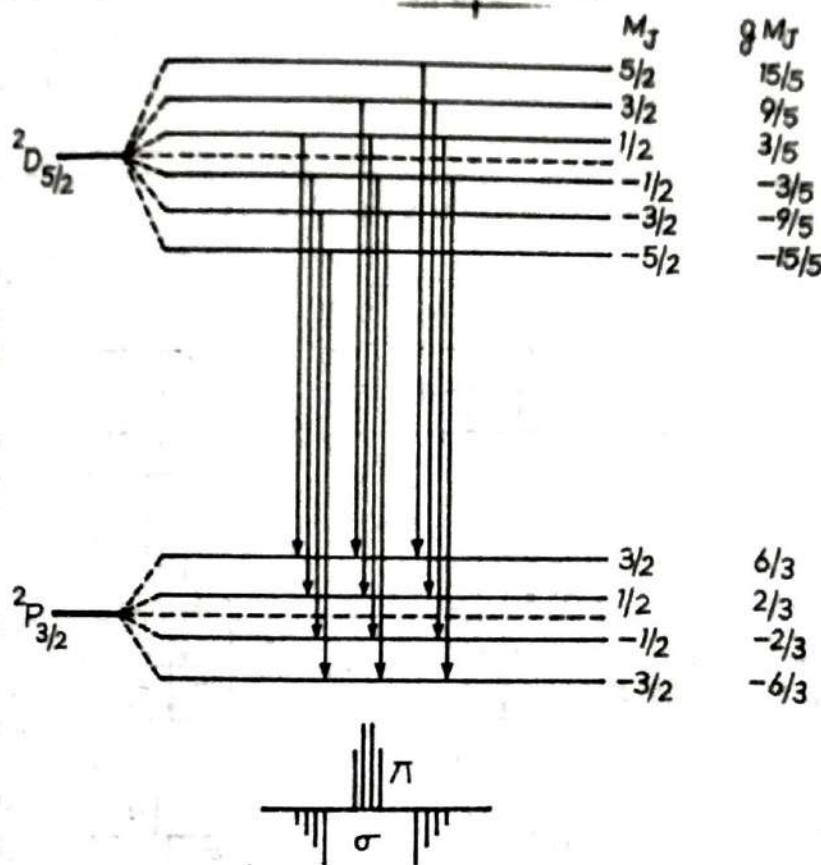
There are in all six allowed transitions, hence six Zeeman components. Transitions corresponding to  $\Delta M_J = 0$  give  $\pi$  components polarised parallel to the magnetic field, and transitions corresponding to  $\Delta M_J = \pm 1$  give  $\sigma$  components polarised perpendicular to the field, as shown below the energy level diagram.

(iii)  $^2D_{5/2} - ^2P_{3/2}$ : It is again a doublet-doublet transition so that the Zeeman pattern would be anomalous.

The Zeeman levels,  $g$ -factors and the Zeeman shifts for the given terms  $^2P_{3/2}$  and  $^2D_{5/2}$  are as follows :

Term	No. of Zeeman levels ( $2J + 1$ )	$g$	$M_J$ ( $+J, \dots, -J$ )	Shift in Lorentz unit L' $g M_J$
$^2P_{3/2}$ ( $L = 1, S = \frac{1}{2}, J = \frac{3}{2}$ )	4	$\frac{4}{3}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$\frac{6}{3}, \frac{2}{3}, -\frac{2}{3}, -\frac{6}{3}$
$^2D_{5/2}$ ( $L = 2, S = \frac{1}{2}, J = \frac{5}{2}$ )	6	$\frac{6}{5}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	$\frac{15}{5}, \frac{9}{5}, \frac{3}{5}, -\frac{3}{5}, -\frac{9}{5}, -\frac{15}{5}$

The splitting of these terms has been displayed in Fig. 14.



(Fig. 14)

The selection rule in operation is

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

The four allowed transitions corresponding to  $\Delta M_J = 0$  give  $\pi$  components, while, the four each corresponding to  $\Delta M_J = \pm 1$  give  $\sigma$  components. The complete Zeeman pattern of 12 components is shown below the energy level diagram.

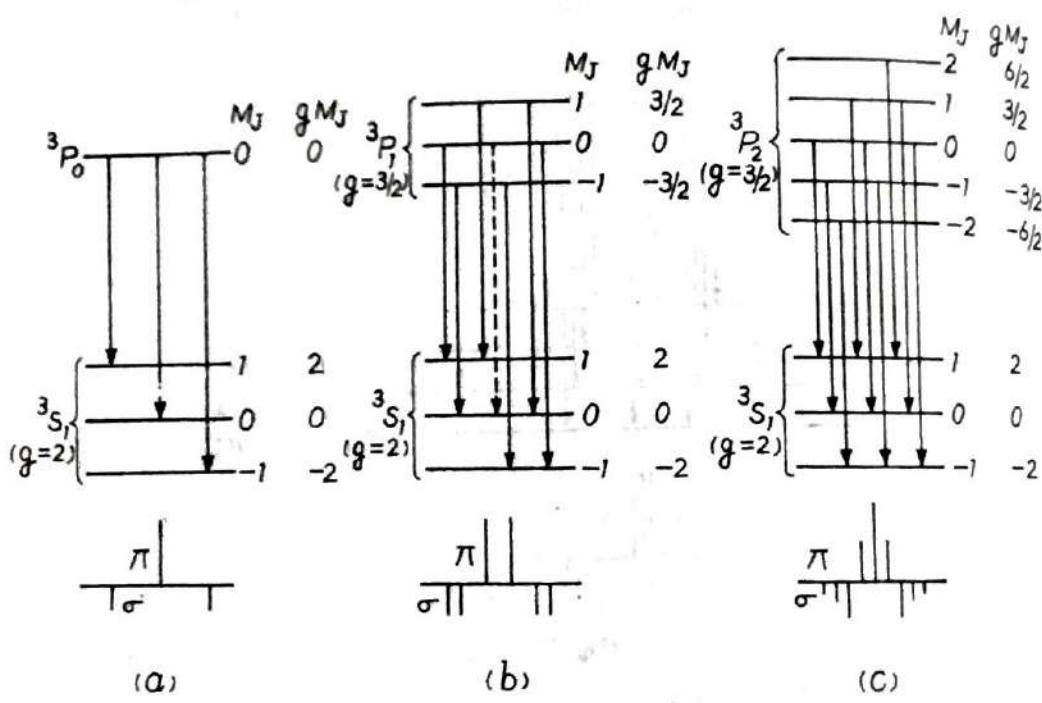
(iv) Principal Series Triplet  $^3P - ^2S$  or  $^3P_{0,1,2} - ^3S_1$  : The fine-structure transitions are

$$^3P_0 - ^3S_1; ^3P_1 - ^3S_1; ^3P_2 - ^3S_1.$$

The g-factors and Zeeman shifts for the unperturbed levels  $^3P_0$ ,  $^3P_1$ ,  $^3P_2$  and  $^3S_1$  are as follows :

Unperturbed level	No. of Zeeman levels ( $2J + 1$ )	$g$	$M_J (+J, \dots -J)$	Shift in Lorentz unit $g M_J$
$^3P_0$ ( $L = 1, S = 1, J = 0$ )	1	0	0	0
$^3P_1$ ( $L = 1, S = 1, J = 1$ )	3	$\frac{3}{2}$	1, 0, -1	$\frac{3}{2}, 0, -\frac{3}{2}$
$^3P_2$ ( $L = 1, S = 1, J = 2$ )	5	$\frac{3}{2}$	2, 1, 0, -1, -2	$\frac{6}{2}, \frac{3}{2}, 0, -\frac{3}{2}, -\frac{6}{2}$
$^3S_1$ ( $L = 0, S = 1, J = 1$ )	3	2	1, 0, -1	2, 0, -2

The magnetic splitting of levels is shown in Fig. 15 (a, b, c).



(Fig. 15)

#### The selection rules

$\Delta M_J = 0, \pm 1$  (but  $M_J = 0 \leftrightarrow M_J = 0$  if  $\Delta J = 0$ ) allow three Zeeman components in the transition  $^3P_0 - ^3S_1$ ; six in  $^3P_1 - ^3S_1$  and nine in  $^3P_2 - ^3S_1$ . The Zeeman transition  $M_J = 0 \rightarrow M_J = 0$  in  $^3P_1 - ^3S_1$  is forbidden since at the same time  $\Delta J = 0$ . (This transition is indicated by a dotted line.)

The Zeeman patterns are shown below the energy-level diagrams. While the qualitative structure of each pattern depends only on the values of  $J$  of the two unperturbed levels, the spacings depend on  $g$  and hence on other properties such as coupling conditions and on other quantum numbers.

All the three patterns are symmetrical with regard to wave number, intensity and polarisation of the components. The  $\pi$ -components form a central group, the  $\sigma$ -components form two symmetrically displaced groups, and the components are equidistant in each. The  $\pi$ -components are polarised with electric vector parallel to the magnetic field, the  $\sigma$ -components with electric vector perpendicular to the field. The sum of the intensities of the  $\pi$ -components is equal to that of the  $\sigma$ -components.

(v)  $^3P_1 - ^3D_2$  : It is a triplet-triplet transition and would give an anomalous Zeeman pattern in a 'weak' external magnetic field. The Zeeman shifts of the various levels from an unperturbed level are given by

$$-\Delta T = g M_J L'$$

where  $L'$  is the Lorentz unit, and  $g$  is given by

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

The Zeeman levels,  $g$ -factors and the shifts from the given unperturbed levels  $^3D_2$  and  $^3P_1$  are as follows :

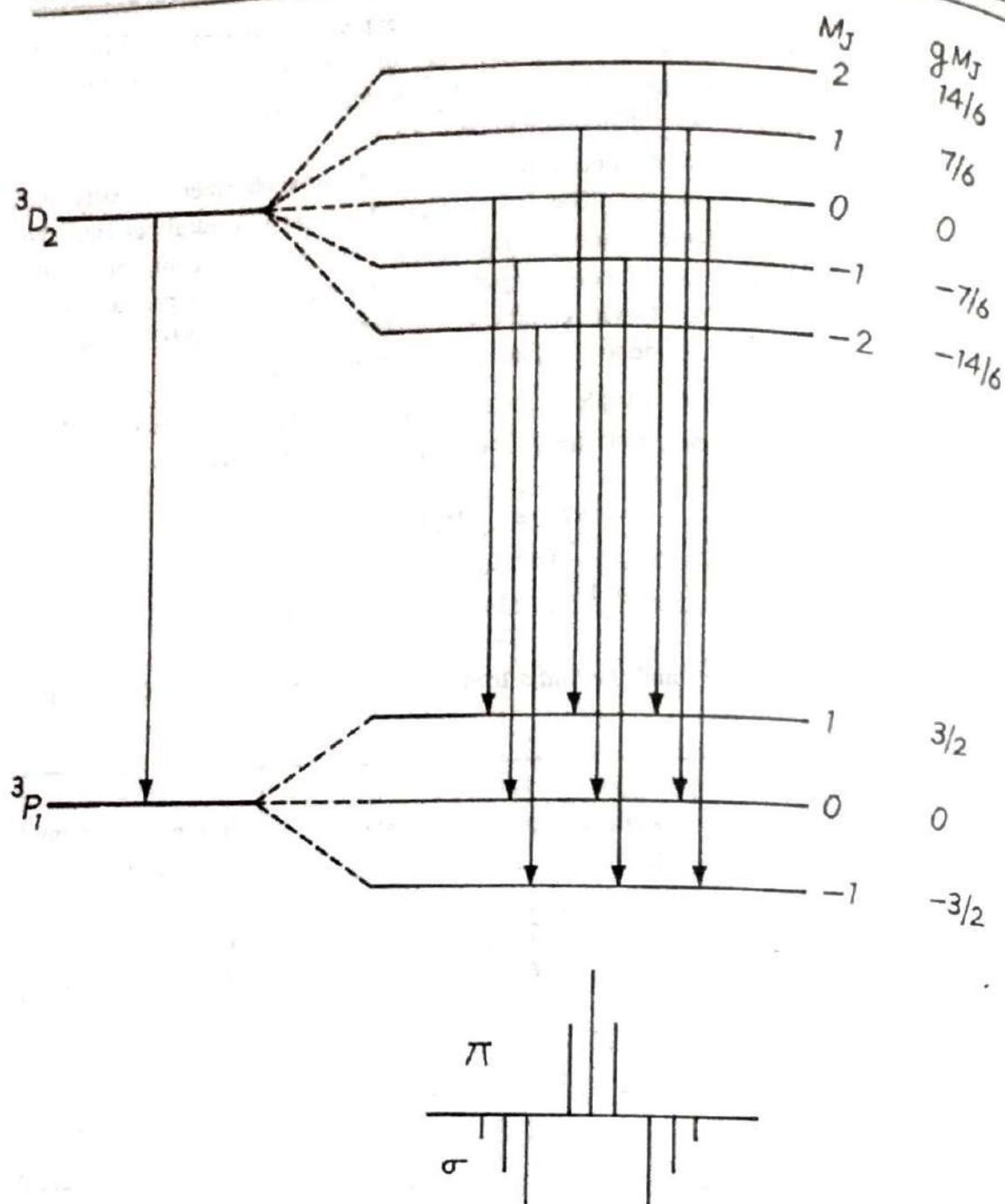
Unperturbed level	No. of Zeeman levels ( $2J+1$ )	$g$	$M_J$ ( $+J, \dots, -J$ )	Shift in Lorentz unit $g M_J$
$^3D_2$ ( $L=2, S=1, J=2$ )	5	$\frac{7}{6}$	2, 1, 0, -1, -2	$\frac{14}{6}, \frac{7}{6}, 0, -\frac{7}{6}, -\frac{14}{6}$
$^3P_1$ ( $L=1, S=1, J=1$ )	3	$\frac{3}{2}$	1, 0, -1	$\frac{3}{2}, 0, -\frac{3}{2}$

The Zeeman splitting of the levels  $^3D_2$  and  $^3P_1$  is shown in Fig. 16.

The selection rules

$$\Delta M_J = 0, \pm 1 \quad (M_J = 0 \leftrightarrow M_J = 0 \text{ if } \Delta J = 0)$$

allow 9 transitions.  $\Delta M_J = 0$  corresponds to the three  $\pi$  components, while  $\Delta M_J = \pm 1$  each give three  $\sigma$  components. The complete pattern is shown in Fig. 16 below the energy level diagram.



(Fig. 16)

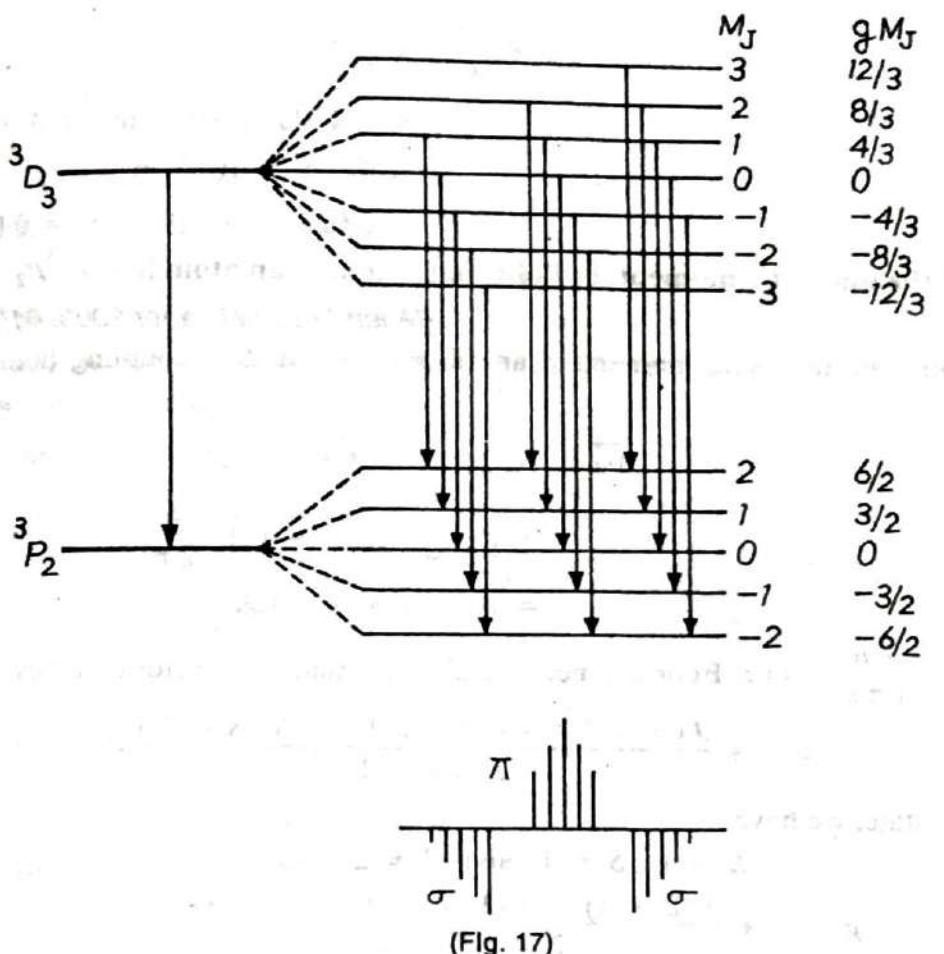
(vi)  $^3D_3 - ^3P_2$  : It is again a triplet-triplet transition and would give an anomalous Zeeman pattern in a 'weak' external magnetic field.

Zeeman levels,  $g$  factors and the shifts from the unperturbed levels  $^3D_2$  and  $^3P_1$  are as follows :

Unperturbed level	No. of Zeeman levels ( $2J + 1$ )	$g$	$M_J$ $(+ J, \dots, - J)$	Zeeman Shift in Lorentz Unit $g M_J$
$^3D_3$ $(L = 2, S = 1, J = 3)$	7	$\frac{4}{3}$	3, 2, 1, 0 - 1, - 2, - 3	$\frac{12}{3}, \frac{8}{3}, \frac{4}{3}, 0$ $-\frac{4}{3}, -\frac{8}{3}, -\frac{12}{3}$

$^3P_2$ $(L = 1, S = 1, J = 2)$	5	$\frac{3}{2}$	2, 1, 0, -1, -2	$\frac{6}{2}, \frac{3}{2}, 0, -\frac{3}{2},$ $-\frac{6}{2}$
------------------------------------	---	---------------	-----------------	--

The splitting of these levels is shown in Fig. 17.



(Fig. 17)

The selection rules

$$\Delta M_J = 0, \pm 1 (M_J = 0 \leftrightarrow M_J = 0 \text{ if } \Delta J = 0)$$

allow 15 transitions. The rule  $\Delta M_J = 0$  gives rise to five  $\pi$  components, while  $\Delta M_J = \pm 1$  each give five  $\sigma$  components. The complete pattern is shown below the energy-level diagram.

### SOLVED PROBLEMS

1. A sample of a certain element is placed in a magnetic field of flux density 0.3 tesla. How far apart is the Zeeman component of a spectral line of wavelength 4500 Å? Given :  $e/m = 1.76 \times 10^{11} \text{ C/kg}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ . (Meerut 2003)

**Solution.** The wave number separation between the components of a normal Zeeman triplet is given by

$$\Delta v = \frac{e B}{4 \pi m c} = \frac{(e/m) B}{4 \pi c}$$

Putting the given values :

$$\Delta v = \frac{(1.76 \times 10^{11} \text{ C/kg})(0.3 \text{ N/A-m})}{4 \times 3.14 \times (3.0 \times 10^8 \text{ m/s})}$$

$$= 14.0 \text{ m}^{-1}$$

Now,

or

or

$$v\lambda = 1$$

$$v\Delta\lambda + \lambda\Delta v = 0$$

$$|\Delta\lambda| = \frac{\lambda\Delta v}{v} = \lambda^2 \Delta v$$

$$= (4500 \times 10^{-10} \text{ m})^2 (14.0 \text{ m}^{-1})$$

$$= 283.5 \times 10^{-14} \text{ m}$$

$$= 0.02835 \times 10^{-10} \text{ m} = 0.02835 \text{ Å}$$

**2. Find the magnetic moment, in Bohr magneton, of an atom in the  ${}^3P_2$  state.**

(Meerut special paper 2003, 01, 99, 98 S)

**Solution.** The magnetic moment of an atom in which  $LS$  coupling holds has the magnitude

$$|\vec{\mu}_J| = g \frac{e}{2m} |\vec{J}|$$

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

$$= g \sqrt{J(J+1)} \mu_B$$

where  $\mu_B \left( = \frac{e\hbar}{4\pi m} \right)$  is the Bohr magneton, and  $g$  is Lande's  $g$ -factor given by

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

For the  ${}^3P_2$  state, we have

$$L = 1, S = 1 \text{ and } J = 2, \text{ so that}$$

$$g = 1 + \frac{2(2+1) - 1(1+1) + 1(1+1)}{2 \times 2(2+1)} = \frac{3}{2}$$

$$\therefore |\vec{\mu}_J| = \frac{3}{2} \sqrt{2(2+1)} \mu_B = 3 \sqrt{\frac{3}{2}} \mu_B$$

**3. The ground state of chlorine atom is  ${}^2P_{3/2}$ . Find its magnetic moment. Into how many substates will the ground state split in a weak magnetic field?**

**Solution.** The magnetic moment of an atom in which  $LS$  coupling holds has the magnitude

$$|\vec{\mu}_J| = g \frac{e}{2m} |\vec{J}|$$

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

$$= g \sqrt{J(J+1)} \mu_B$$

where  $\mu_B \left( = \frac{e\hbar}{4\pi m} \right)$  is the Bohr magneton, and  $g$  is Lande's  $g$ -factor given by

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

For the given state  ${}^2P_{3/2}$ , we have

$L = 1, S = \frac{1}{2}$  and  $J = \frac{3}{2}$ , so that

$$g = 1 + \frac{\frac{3}{2} \left( \frac{3}{2} + 1 \right) - 1(1+1) + \frac{1}{2} \left( \frac{1}{2} + 1 \right)}{2 \times \frac{3}{2} \left( \frac{3}{2} + 1 \right)} = \frac{4}{3}.$$

$$\therefore |\vec{\mu}_J| = \frac{4}{3} \sqrt{\frac{3}{2} \left( \frac{3}{2} + 1 \right)} \mu_B \\ = \frac{2}{3} \sqrt{15} \mu_B.$$

The number of weak-field sub-states is

$$(2J + 1) = 4.$$

4. Evaluate the Lande  $g$ -factor for the  ${}^3P_1$  level in the  $2p\ 3s$  configuration of the  ${}^6C$  atom, and use the result to predict the splitting of the level when the atom is in an external magnetic field of 0.1 tesla.

**Solution.** For the  ${}^3P_1$  level, we have

$$L = 1, S = 1, J = 1, \text{ and so}$$

$$\text{So } g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \\ = 1 + \frac{1(1+1) - 1(1+1) + 1(1+1)}{2 \times 1(1+1)} = 1 + \frac{1}{2} = \frac{3}{2}.$$

For  $J = 1$ , the possible values of  $M_J$  are 1, 0, -1 and so the level is split into three components. The wave-number shift of the components is given by

$$\Delta T = g M_J \frac{eB}{4\pi mc}.$$

The Zeeman level corresponding to  $M_J = 0$  remains unshifted while those corresponding to  $M_J = \pm 1$  are shifted by

$$\begin{aligned} \Delta T &= \pm g \frac{eB}{4\pi mc} \\ &= \pm \frac{3}{2} \frac{(1.6 \times 10^{-19} C)(0.1 \text{ N/A-m})}{4 \times 3.14 \times (9.1 \times 10^{-31} \text{ kg})(3.0 \times 10^8 \text{ m/s})} \\ &= \pm 7.0 \text{ m}^{-1} \\ &= \pm 0.07 \text{ cm}^{-1}. \end{aligned}$$

5. The Zeeman pattern of a line consists of six equidistant components. The upper state term is known to be  ${}^2P_{3/2}$ . Determine the lower state term and draw a schematic diagram showing the transitions.

**Solution.** The upper state term is  ${}^2P_{3/2}$ , that is,  $J = 3/2$  and so

$$M_J = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}.$$

Since there are 6 Zeeman components, only 6 transitions do occur. In view of the selection rule

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

the lower state term must split into only two components corresponding to

$$M_J = \frac{1}{2}, -\frac{1}{2};$$

because with no other choice of  $M_J$  value it is possible to have only 6 transitions. These values of  $M_J$  correspond to

$$J = \frac{1}{2}.$$

The selection rule  $\Delta S = 0$  indicates that the lower state term is also a doublet, that is,

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

The values  $J = \frac{1}{2}$  and  $S = \frac{1}{2}$  lead to

$$L = 0.$$

Hence the lower state term is  $^2S_{1/2}$ .

The transition  $^2P_{3/2} \rightarrow ^2S_{1/2}$  corresponds to sodium D<sub>2</sub> line. The Zeeman transitions are shown in Fig. 7.

**6. The Zeeman pattern of a line consists of nine equidistant components. The upper state is known to be  $^3P_2$  ( $L-S$  coupling). Determine the lowest state term and draw a schematic diagram showing the transitions.**

**Solution.** The upper state term is  $^3P_2$ , that is  $J = 2$  and so

$$M_J = 2, 1, 0, -1, -2.$$

There are 9 Zeeman transitions. According to the selection rule

$$\Delta M_J = 0, \pm 1 (M_J = 0 \leftrightarrow M_J = 0 \text{ if } \Delta J = 0)$$

the lower state term must split into only three components corresponding to

$$M_J = 1, 0, -1;$$

because with no other choice of  $M_J$  values it is possible to have only nine transitions

These values of  $M_J$  correspond to

$$J = 1.$$

The multiplicity selection rule  $\Delta S = 0$  demands the lower state term also to be a triplet term, that is,

$$S = 1.$$

The values  $J = 1$  and  $S = 1$  lead to

$$L = 0.$$

Hence the lower state term is  $^3S_1$ .

The Zeeman transitions for the terms  $^3P_2 - ^3S_1$  are shown in Fig. 15 (c).

**7. Illustrate with the help of diagrams the splitting of  $^2D$  levels of sodium when (Meerut 2000)**

(i) a weak magnetic field, (ii) a strong magnetic field is applied.

**Solution.** (i) The weak-field magnetic interaction energy of an atom is given by

$$- \Delta T = g M_J L'.$$

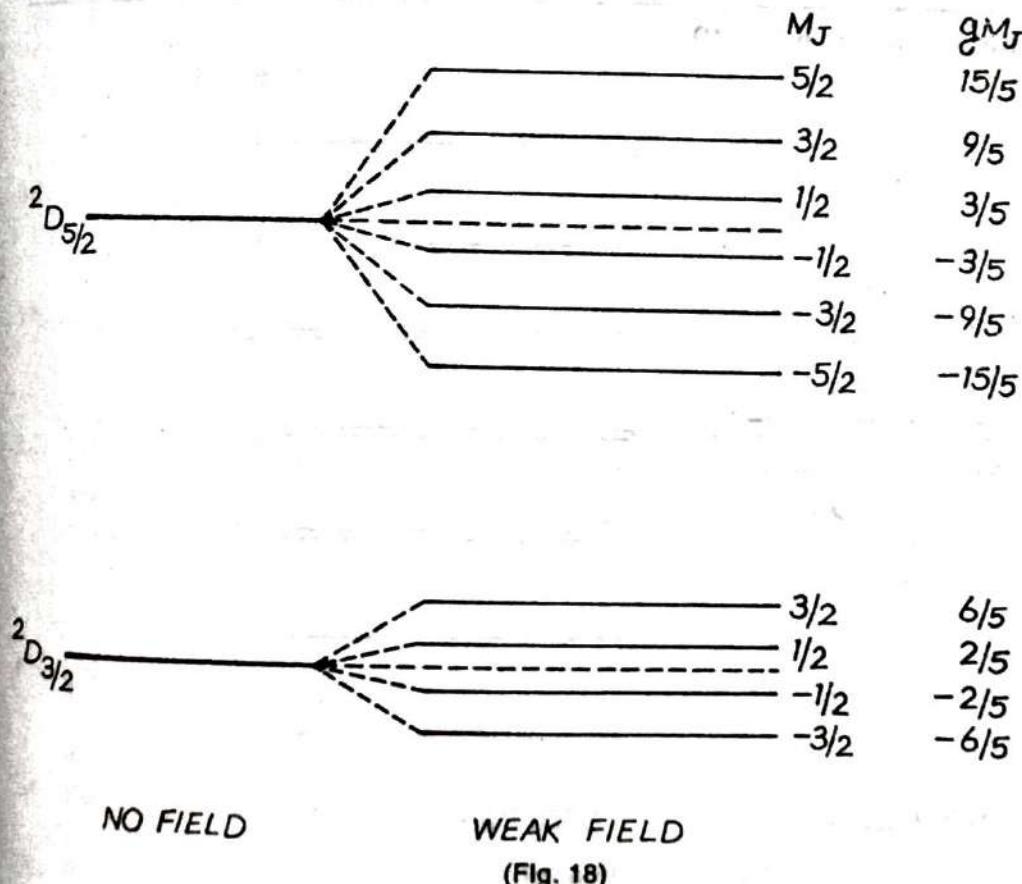
where  $L'$  is the weak-field Lorentz unit. The Lande  $g$ -factor is

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

The given term  $^2D$  has two fine-structure component levels  $^2D_{3/2}$  and  $^2D_{5/2}$ . The number of weak-field levels and their shifts are as follows :

Fine-structure levels	No. of weak-field levels ( $2J + 1$ )	$g$	$M_J$ (+J, ..... -J)	Shift in $L'$ units $g M_J$
$^2D_{3/2}$ $(L = 2, S = \frac{1}{2}, J = \frac{3}{2})$	4	$\frac{4}{5}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$\frac{6}{5}, \frac{2}{5}, -\frac{2}{5}, -\frac{6}{5}$
$^2D_{5/2}$ $(L = 2, S = \frac{1}{2}, J = \frac{5}{2})$	6	$\frac{6}{5}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	$\frac{15}{5}, \frac{9}{5}, \frac{3}{5}, -\frac{3}{5}, -\frac{9}{5}, -\frac{15}{5}$

The splittings are shown in Fig. 18.



(ii) The strong-field magnetic interaction energy of atom is

$$- \Delta T = (M_L + 2M_S) L',$$

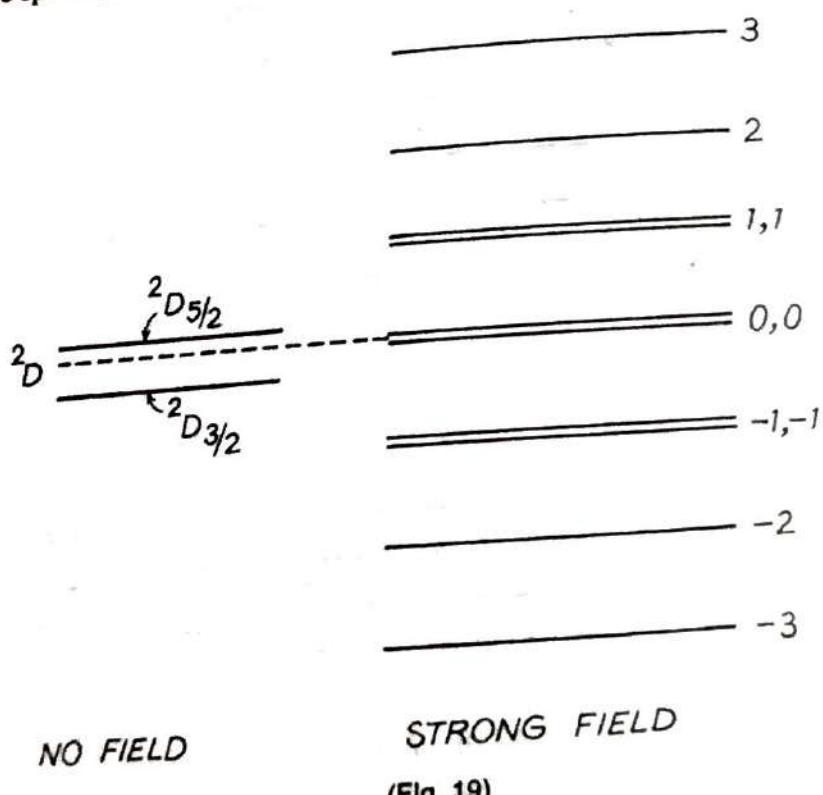
where  $L' \left( = \frac{eB}{4\pi mc} \right)$  is the strong-field Lorentz unit.

The strong-field levels and their shifts for the given term  $^2D$  are as follows :

224

Term	No. of strong-field levels $(2L + 1)(2S + 1)$	$M_L$	$M_S$	Shift in $L'$ units $(M_L + 2M_S)$
$^2D$ $(L = 2, S = \frac{1}{2})$	10	2	$\frac{1}{2}, -\frac{1}{2}$	3, 1
		1	$\frac{1}{2}, -\frac{1}{2}$	2, 0
		0	$\frac{1}{2}, -\frac{1}{2}$	1, -1
		-1	$\frac{1}{2}, -\frac{1}{2}$	0, -2
		-2	$\frac{1}{2}, -\frac{1}{2}$	-1, -3

The splitting is shown in Fig. 19.

 $(M_L + 2M_S)$ 


## QUESTIONS

1. Describe an experimental set-up to study Zeeman effect.  
(Meerut 2003, special paper 2003, 02, 01, 98)
2. Distinguish between normal and anomalous Zeeman effects. Derive expression for the magnetic interaction energy (Zeeman energy splitting) for a single valence electron atom given as  $\Delta E = g M_J \mu_B B$ , where symbols have usual meanings.  
(Meerut 99 special paper, 98)

3. What is anomalous Zeeman effect? Discuss the Zeeman pattern of the resonance ( $D_1, D_2$ ) lines of sodium. (Meerut 2002S, 99, special paper 96)
4. Derive an expression for Lande's splitting g-factor and explain with its help the Zeeman effect of the sodium doublet components  $D_1$  and  $D_2$ . (Meerut 2003, 02, 01, 00; 94 special paper 2003, 02)
5. Discuss with necessary theory the splitting of sodium lines when (a) a weak magnetic field, (b) a strong magnetic field is applied. (Meerut 2004 S, 00, 95 S)
6. Calculate the Zeeman pattern for the spectral lines arising from  $^2P_{3/2} - ^2S_{1/2}$  and  $^2P_{1/2} - ^2S_{1/2}$  transitions. Comment on the polarisability of Zeeman component lines.
7. State the rules for polarisation and intensities of the Zeeman components. (Meerut special paper 2003, 02, 00)
8. Discuss the Zeeman pattern of a line due to transition  $^2P_{3/2} - ^2S_{1/2}$ . (Meerut 2006, 00 S)
9. Why is  $^4D_{1/2}$  term not split in a magnetic field. Explain. (Meerut 98 special paper)  
Hint :  $L = 2, S = 3/2, J = 1/2$ ; for these values the lande g-factor is zero.  
Hence  $\Delta E = g M_J \mu_B B = 0$ .
10. Calculate Zeeman pattern for  $^2D_{3/2} - ^2P_{3/2}$  transition in one-electron atom. (Meerut special paper 2001, 99)

**Ans.** 10 components

11. Calculate Zeeman pattern for  $^2D_{5/2} - ^2P_{3/2}$  transition in one-electron atom. (Meerut 2003 S)

**Ans.** 12 components.

12. Distinguish between normal Zeeman, anomalous Zeeman and Paschen-Back effects. Determine the Lande g-values for the various levels of  $^3P$  and  $^3D$  multiplets. (Meerut 2004, 03, 00 S, special paper 2004)

**Ans.** For  $^3P_{0, 1, 2}; g = 0/0, 3/2, 3/2$  and

For  $^3D_{1, 2, 3}; g = 1/2, 7/6, 4/3$ .

13. Obtain the Zeeman pattern arising from a principal series triplet  $^3S - ^3P$  and show diagrammatically the different transitions involved. Comment on the intensities and polarisation of these transitions. (Meerut 95)
14. Deduce the Zeeman effect of the component  $^3P_2 - ^3S_1$  in a spectral multiplet in terms of Lorentz unit.
15. Explain with a diagram the Zeeman splitting of a spectral line corresponding to the transition  $sp\ ^3P_1 - sd\ ^3D_2$ .
16. Calculate the Zeeman pattern arising from the transition  $^3D_3 - ^3P_2$ .

### PROBLEM

1. Calculate the Lande g-factor for (i)  $^3S_1$  and (ii)  $^3P_1$  levels, and find energy splitting of the two levels if an external magnetic field of 1 tesla is applied. Use known values of  $e, m$  and  $c$ .  
**Ans.** (i)  $2, 0.934 \text{ cm}^{-1}$ , (ii)  $\frac{3}{2}, 0.70 \text{ cm}^{-1}$ .

## The Stark Effect

### 1. Observed Stark Effect in Hydrogen

In 1913, J. Stark discovered that the Balmer lines emitted by hydrogen atoms placed in an *electric field* of the order of  $10^5 \text{ V/cm}$  are split into a number of polarised components. When viewed perpendicular to the field, some of the components of each line are plane-polarised with the electric vector parallel to the field ( $\pi$  components), and the others are polarised with electric vector perpendicular to the field ( $\sigma$  components). When viewed parallel to the field, only the  $\sigma$  components appear which are now unpolarised. This splitting of spectral lines in an electric field is known as 'Stark effect'. It plays an important part in the theories of molecule formation from atoms, broadening of spectral lines, and dielectric constants.

**Main Features :** The main features of the observed Stark effect are :

(i) All hydrogen lines form symmetrical patterns, but the pattern depends markedly on the quantum numbers  $n$  of the terms involved. The number of Stark lines, and the total width of the pattern increase with  $n$ . This line  $H_\beta$  shows a larger number of Stark components than  $H_\alpha$ , the line  $H_\gamma$  showing still more larger number.

(ii) The wave-number shifts are integral multiples of a unit which is proportional to the strength of the electric field, and is same for all hydrogen lines.

(iii) Except for the absence of circular polarisation in longitudinal observation, the polarisation properties of Stark lines resemble those of the Zeeman lines. But, in contrast to Zeeman lines, the  $\pi$ -components show greater shifts than the  $\sigma$ -components.

(iv) The hydrogen lines involving the lower energy states (small  $n$ ), such as  $H_\alpha$ ,  $H_\beta$ , show only a symmetrical splitting proportional to the field strength about their field-free positions. This is known as the 'first-order' or the 'linear' Stark effect.

For the lines involving the higher states, such as  $H_\gamma$ ,  $H_\delta$ , the Stark components show unidirectional displacements proportional to the square of the field strength. This is known as the 'second-order' Stark effect.

The first-order Stark effect is restricted to hydrogen-like atoms, and occurs only in fields large enough for the fine structure to become negligible. Other atoms show a second-order or quadratic effect which is generally very small.

### 2. Weak-Field Stark Effect in Hydrogen

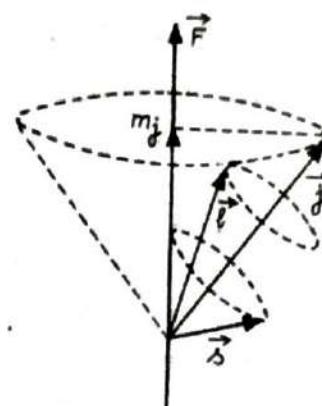
A weak electric field for hydrogen is one for which the interaction energy between the electron's total angular momentum  $\vec{j}$  and the field  $\vec{F}$  is less than the magnetic interaction energy between orbital momentum  $\vec{l}$  and spin momentum  $\vec{s}$ , that is, for which the Stark splitting is smaller compared with the fine-structure splitting. In such a

field, as shown Fig. 1,  $\vec{l}$  and  $\vec{s}$  couple to form  $\vec{j}$  which precesses around  $\vec{F}$  with projection  $m_j h/2\pi$ , where

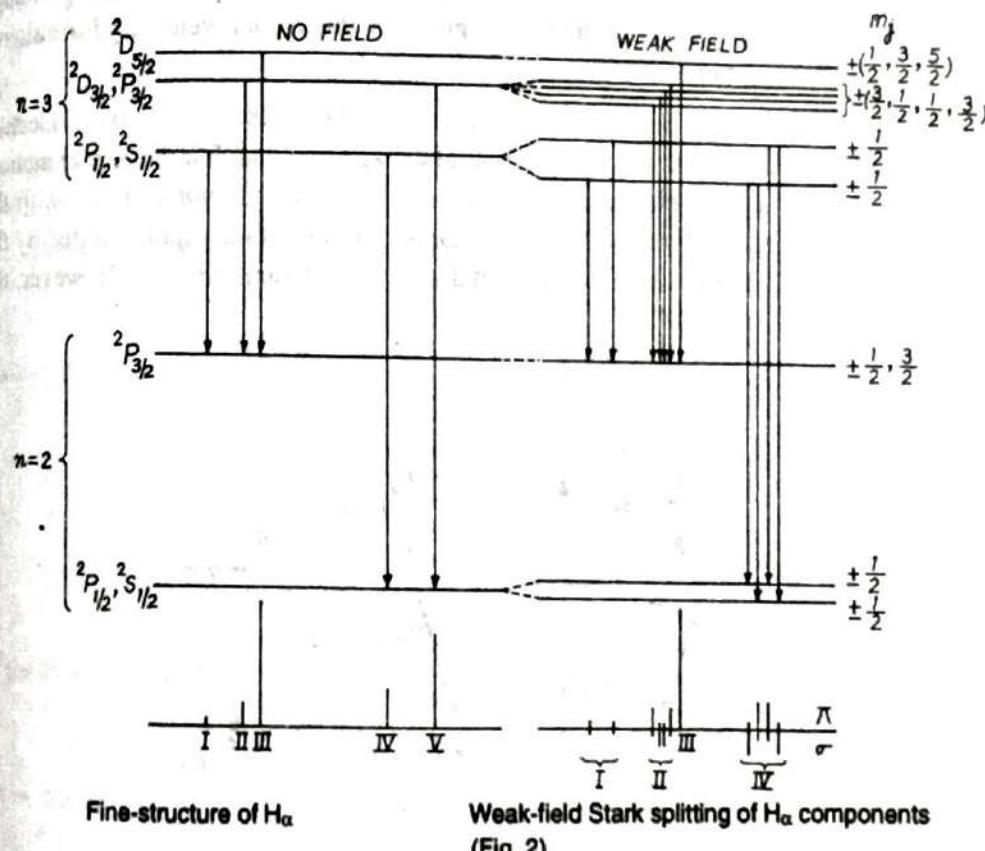
$$m_j = +j, j-1, j-2, \dots, -j.$$

However, in contrast to Zeeman levels, the Stark levels  $+m_j$  and  $-m_j$  arising from a given unperturbed level have the same energy.

The energy levels of the hydrogen atom for the two states  $n = 2$  and  $n = 3$  are shown in Fig. 2. The field-free levels and theoretical pattern for  $H_\alpha$  are given at the left, and the weak-field levels and the Stark pattern at the right. The unpaired levels for each



(Fig. 1)



$n(2^2P_{3/2} \text{ and } 3^2D_{5/2})$  do not show Stark splitting because in these states the atom has no electric moment.

The selection rules for the weak-field Stark effect are the same as those for the Zeeman effect, that is

$$\Delta m_j = 0 \text{ gives } \pi \text{ components}$$

$$\Delta m_j = \pm 1 \text{ gives } \sigma \text{ components.}$$

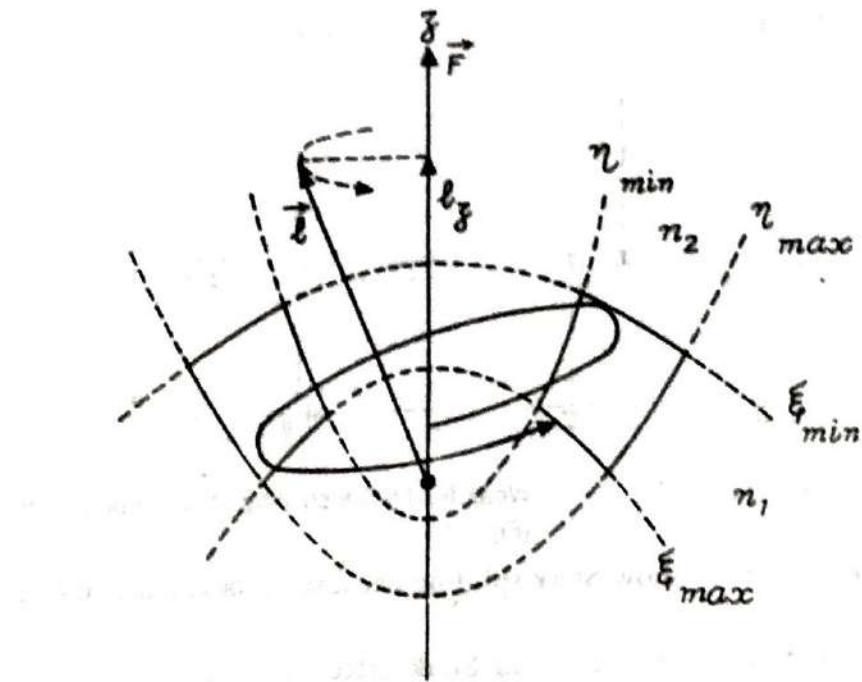
According to these rules, each of the fine-structure components I, II, III, IV, V in  $H_\alpha$  should show a symmetrical Stark pattern, as shown at the lower right. (The Stark pattern of the component V is too complicated to be shown). However, since the fine-structure components of  $H_\alpha$  have not been completely resolved, the weak-field Stark pattern has never been observed.

### 3. Strong-Field Stark Effect in Hydrogen

A strong electric field for hydrogen is one for which the interaction energy between the electron's total angular momentum  $\vec{J}$  and the field  $\vec{F}$  is greater than the magnetic interaction energy between electron's orbital momentum  $\vec{l}$  and spin momentum  $\vec{s}$ , that is, for which the (Stark) splitting of the energy levels due to the field is greater than the fine-structure splitting. It is this 'strong' field for which the first-order Stark effect in hydrogen has actually been observed. In such a field the magnetic coupling between  $\vec{l}$  and  $\vec{s}$  is broken down, and  $\vec{l}$  is quantised with respect to, and precesses independently around the field  $\vec{F}$ . The spin is, however, not acted on by  $\vec{F}$ .

Schwarzschild and Epstein, in 1916 (even before the discovery of electron spin), explained the observed first-order Stark effect in hydrogen and ionised helium by quantising a hydrogen-like atom in an electric field. This was taken an outstanding triumph for the old quantum theory because the results given by this theory were very little altered by quantum mechanical treatment.

The effect of a homogeneous electric field  $\vec{F}$ , parallel to the  $z$ -axis, on an electron moving in a Kepler ellipse is different from that of a magnetic field. For the Kepler motion, the centre of gravity of the electron averaged over its orbit does *not* coincide with the nucleus and thus forms an electric dipole. The torque on the orbital dipole exerted by the electric field causes a precession of the orbital about the  $z$ -axis (Fig. 3). However, the



(Fig. 3)

orbital angular momentum  $\vec{l}$  is not a constant (as it is in a magnetic field), and the orbital quantum number  $l$  is no longer a "good" quantum number. The projection of  $\vec{l}$  on the electric axis is  $l_z$ , given by  $m_l \frac{\hbar}{2\pi}$  where  $m_l$  is the electric quantum number.  $l_z$  is still a constant of motion and  $m_l$  retains its strict meaning. Calculation carried out in parabolic coordinates give the energy values as :

$$E = E_0 - \frac{3 a_0 e}{2 Z} F n (n_2 - n_1),$$

where  $E_0$  is the field-free energy of the atom,  $a_0$  is the Bohr radius,  $n$  is the usual total quantum number, and  $n_1$  and  $n_2$  are two new (parabolic) quantum numbers, subject to the condition

$$m_l = n - n_2 - n_1 - 1.$$

The allowed values are

$$n = 1, 2, 3, \dots, \infty$$

$$m_l = 0, \pm 1, \pm 2, \dots, \pm (n-1)$$

$$n_1 = 0, 1, 2, 3, \dots, n-1$$

$$n_2 = 0, 1, 2, 3, \dots, n-1$$

$n_1$  limits the electron's motion to the region between the two paraboloids of revolution  $\xi_{\min}$  and  $\xi_{\max}$ ; while  $n_2$  limits it to the region between the two paraboloids of revolution  $\eta_{\min}$  and  $\eta_{\max}$ . Thus, confined to the region intersected by the two pairs of paraboloids, the electron has three periodic motions, one around the field  $\vec{F}$  given by  $m_l$ , and one each along the  $\xi$  and  $\eta$  coordinates given by  $n_1$  and  $n_2$ . Since the last two periods are not necessarily the same, the orbit is not closed and the electron in time covers every point in the intersected region.

**Stark Shifting of Hydrogen Energy Levels :** The term shift is given by

$$-\Delta T = \frac{\Delta E}{h c} = \frac{3 a_0 e}{2 Z h c} F n (n_2 - n_1).$$

Putting the known values of  $a_0$ ,  $e$ ,  $h$  and  $c$ , we get

$$\begin{aligned} -\Delta T &= \frac{3 (0.53 \times 10^{-10} \text{ m}) (1.6 \times 10^{-19} \text{ C})}{2 Z (6.63 \times 10^{-34} \text{ Js}) (3.0 \times 10^8 \text{ m s}^{-1})} F n (n_2 - n_1) \\ &= \frac{6.40 \times 10^{-5} \text{ C/J}}{Z} F n (n_2 - n_1) \\ &= \frac{6.40 \times 10^{-5} \text{ V}^{-1}}{Z} F n (n_2 - n_1) \quad \left[ \because \frac{\text{J}}{\text{C}} = \text{V} \right] \end{aligned}$$

If the field  $F$  is expressed in V/cm, then this becomes

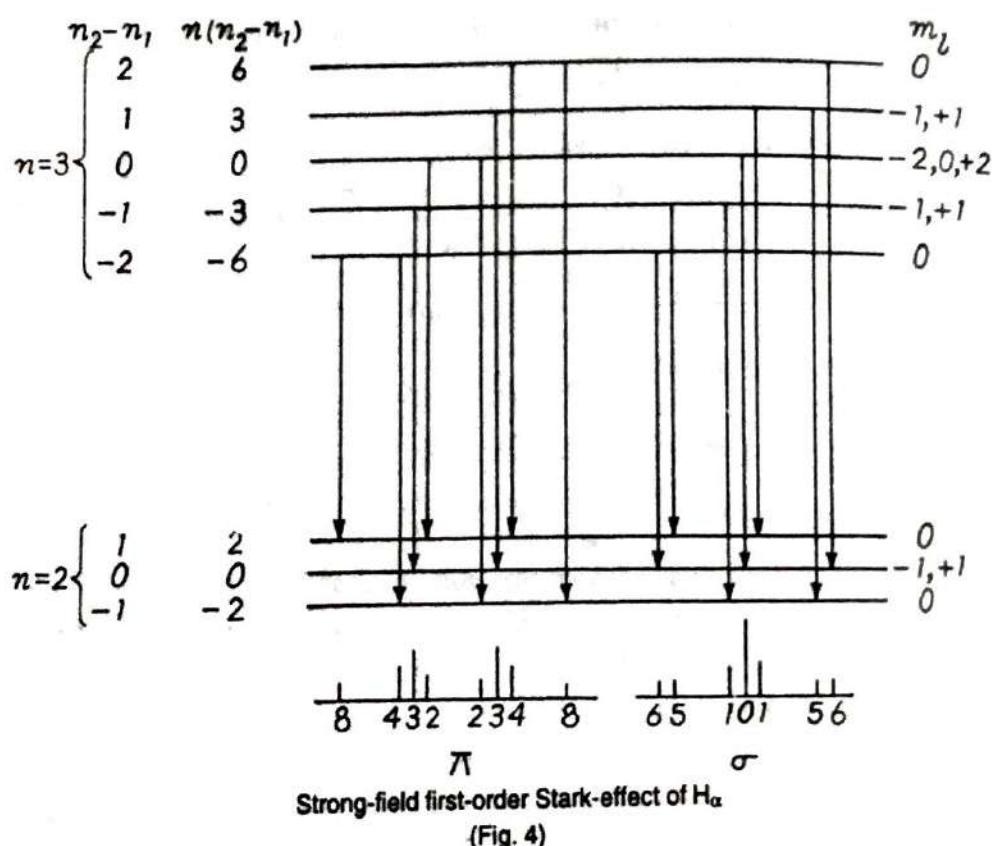
$$-\Delta T = \frac{6.40 \times 10^{-5}}{Z} F n (n_2 - n_1) \text{ cm}^{-1}.$$

Thus, the Stark-effect levels in a hydrogen-like atom are all shifted by integral multiples of a fundamental amount from the original level. We shall calculate the Stark shifting of the first three levels ( $n = 1, 2, 3$ ) of hydrogen ( $Z = 1$ ) and then compute the Stark-effect components of the  $H_\alpha$  line of the Balmer series.

The allowed values of  $n$ ,  $n_2$  and  $n_1$  are first written down in columns to ensure obtaining all possible combinations and then the quantities  $n(n_2 - n_1)$  representing Stark shifts are computed. The values of  $m_l$  are also obtained. We see from the table that there is exactly the same number ( $n^2$ ) of possible states of the atom as in the Zeeman effect. In the Stark effect, however, certain levels fall together. Further, the Stark-shift for the ground state ( $n = 1$ ) of hydrogen is zero.

$n$	$n_2$	$n_1$	$n_2 - n_1$	$n(n_2 - n_1)$	$m_l$ $(n - n_2 - n_1 - 1)$
1	0	0	0	0	0
	1	1	0	0	-1
2	1	0	1	2	0
	0	1	-1	-2	0
	0	0	0	0	1
	2	2	0	0	-2
	2	1	1	3	-1
3	2	0	2	6	0
	1	2	-1	-3	-1
	1	1	0	0	0
	1	0	1	3	1
	0	2	-2	-6	0
	0	1	-1	-3	1
	0	0	0	0	2

The Stark-effect levels for the states  $n = 3$  and  $n = 2$  are shown in Fig. 4.



The selection rules for a strong electric field are as follows :

$$\Delta m_l = 0 \quad \text{for } \pi \text{ components}$$

$$\Delta m_l = \pm 1 \quad \text{for } \sigma \text{ components.}$$

The transitions  $\Delta m_l = 1$  and  $\Delta m_l = -1$  give components circularly polarised in opposite sense. But a transition  $\Delta m_l = -1$  occurs for every transition  $\Delta m_l = 1$  and the

superposition of the two gives linearly-polarised components in transverse observation and unpolarised components in longitudinal observation.

The possible transitions for the  $H_{\alpha}$  line and the resulting Stark pattern have also been shown. This has been found in good agreement with experimental observation in both the relative shifts and the intensities. The intensities were calculated by Schrodinger quantum mechanically.

## QUESTIONS

1. What is Stark effect? Discuss the weak-field Stark effect and the strong-field Stark effect in hydrogen. *(Meerut 98 sp. paper)*
2. Show by actual transitions the Stark-effect components of  $H_{\alpha}$  line of hydrogen. *(Meerut sp. paper 2002, 01, 98)*
3. Discuss Stark effect and show that the first-order Stark effect for the ground state of hydrogen is zero. *(Meerut 2006, sp. paper 2003, 02, 01, 06)*

# Hyperfine Structure of Spectral Lines

## 1. Introduction

Many fine-structure components of spectral lines, when examined under instruments of highest possible resolution, are further splitted into components with separations of the order of  $1 \text{ cm}^{-1}$ , which is very much smaller than those of the ordinary multiplet structure. This splitting is called the 'hyperfine structure' and is caused by properties of the atomic nucleus.

For the experimental study of hyperfine structure, the light source must be one giving extremely sharp lines, such as Schuler lamp or a laser, and an interference spectroscope of the Fabry-Perot or Lummer-Gehrcke pattern or an echelon grating.

There are two types of nuclear effects that produce hyperfine structure. The first is due to the presence of different isotopic species in the element under investigation. The energy levels of isotopes are slightly displaced relative to each other, producing spectral transitions at slightly different wave numbers.

The second type of effect arises because the charged nucleus possesses as spin angular momentum and the associated magnetic dipole moment. *An interaction between the internal magnetic field produced by the orbital motion of the electrons in the atom and the spin magnetic dipole moment of the nucleus causes a hyperfine splitting of the spectral terms.* As nuclear magnetic dipole moments are smaller than electronic magnetic dipole moments by  $\sim 10^{-3}$ , the hyperfine splitting is smaller than the spin-orbit splitting by the same factor.

## 2. Isotope Effects

Many elements are composed of isotopic atoms. Different isotopes of an element have the same number and arrangement of extranuclear electrons, but differ from one another in mass. Since the nuclear mass enters into Rydberg constant for an atom (through the reduced mass of the atom), different isotopes have slightly different values of Rydberg constant. Correspondingly, the same transitions in different isotopes give rise to slightly different wave numbers.

The variation in Rydberg constant is particularly marked in hydrogen. Each of the first four members of Balmer series,  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$ , has a very weak companion on the short-wavelength side at distances of 1.79, 1.33, 1.19 and 1.12 Å respectively. These shifts agree with the theoretical values if the companions are attributed as due to presence of an isotope of mass 2 (deuterium), and it was in this way that the existence of heavy hydrogen was first established.

As an example, let us calculate the shift for  $H_\beta$  line (4861.33 Å). For this transition, we have from Balmer's formula

$$\frac{1}{\lambda_H} = R_H \left( \frac{1}{2^2} - \frac{1}{4^2} \right)$$

and

$$\frac{1}{\lambda_D} = R_D \left( \frac{1}{2^2} - \frac{1}{4^2} \right).$$

$$\therefore \frac{\lambda_D}{\lambda_H} = \frac{R_H}{R_D}$$

$$\text{or } \frac{\lambda_D - \lambda_H}{\lambda_H} = \frac{R_H - R_D}{R_D}.$$

$$\therefore \Delta\lambda = \lambda_D - \lambda_H = -\lambda_H \left( \frac{R_D - R_H}{R_D} \right)$$

$$= -4861.33 \text{ \AA} \left( \frac{109707.4 \text{ cm}^{-1} - 109677.6 \text{ cm}^{-1}}{109707.4 \text{ cm}^{-1}} \right)$$

$$= -1.32 \text{ \AA}.$$

Many cases of isotope-shift are not as simple as that for hydrogen. In fact, for the rare earths and heavier atoms, the main contribution to isotope shift is not due to a difference in mass but due to a change in nuclear radius with mass and the deviation of the nuclear magnetic field from being purely a coulombian one.

### 3. Nuclear Spin and Hyperfine Splitting

In many cases, the isotope effect fails to explain the hyperfine structure. The number of hyperfine components is often greater than the number of isotopes. On the other hand, certain elements have only one isotope, but still have hyperfine structure. For example, bismuth exists as a single isotope, but shows six hyperfine components in its line at wavelength 4722 Å. Likewise, the number of components of different lines is frequently quite different for one and the same element.

Pauli, in 1924, pointed out that hyperfine structure could be explained when it is assumed that *the atomic nucleus possesses an intrinsic spin angular momentum  $\vec{I}$  with which is associated a magnetic dipole moment  $\vec{\mu}_I$* . Just as in the case of spinning electron, the magnitude of the nuclear angular momentum is

$$|\vec{I}| = \sqrt{I(I+1)} \frac{h}{2\pi},$$

where  $I$  is the 'nuclear spin quantum number' which has different values for nuclei of odd mass numbers\*. Thus, the angular momentum has different magnitudes for different nuclei, and also for different isotopes of the same element.

Just as  $\vec{L}$ ,  $\vec{S}$  and  $\vec{J}$  have quantised components along an axis in space, the component of  $\vec{I}$  along the  $z$ -axis is

$$I_z = M_I \frac{h}{2\pi},$$

\*Values of  $I$  for some common isotopes are given in the following table :

Isotope	$I$	Isotope	$I$	Isotope	$I$
H <sup>1</sup>	1/2	N <sup>14</sup>	1	Cl <sup>35</sup>	3/2
H <sup>2</sup>	1	N <sup>15</sup>	1/2	Cl <sup>37</sup>	3/2
He <sup>4</sup>	0	O <sup>16</sup>	0	Ca <sup>40</sup>	0
C <sup>12</sup>	0	O <sup>17</sup>	5/2	Bi <sup>209</sup>	9/2
C <sup>13</sup>	1/2	F <sup>19</sup>	1/2		

where the nuclear magnetic quantum number  $M_I$  has  $2I + 1$  values given by

$$M_I = I, I - 1, I - 2, \dots - I.$$

The motions of the nuclear protons produce a magnetic moment  $\vec{\mu}_I$  which is proportional to the angular momentum, and which we shall write

$$\vec{\mu}_I = g_I \left( \frac{e}{2m_p} \right) \vec{I},$$

where  $e$  and  $m_p$  are respectively the charge and mass of proton. The quantity  $g_I$  is called the 'nuclear  $g$  factor'. The magnitude of the nuclear magnetic moment is

$$\begin{aligned} \mu_I &= g_I \left( \frac{e}{2m_p} \right) \sqrt{I(I+1)} \frac{h}{2\pi} \\ &= g_I \sqrt{I(I+1)} \frac{e h}{4\pi m_p}. \end{aligned}$$

The quantity  $\frac{e h}{4\pi m_p}$  forms a natural unit for the measurement of nuclear magnetic moment and is called the 'nuclear magneton'  $\mu_N$ . It is  $1/1836$  times the Bohr magneton (because mass of proton is  $1836$  times the mass of electron). Thus,

$$\mu_I = g_I \sqrt{I(I+1)} \mu_N.$$

The component of  $\mu_I$  along the  $z$ -axis is

$$\mu_{Iz} = g_I M_I \mu_N,$$

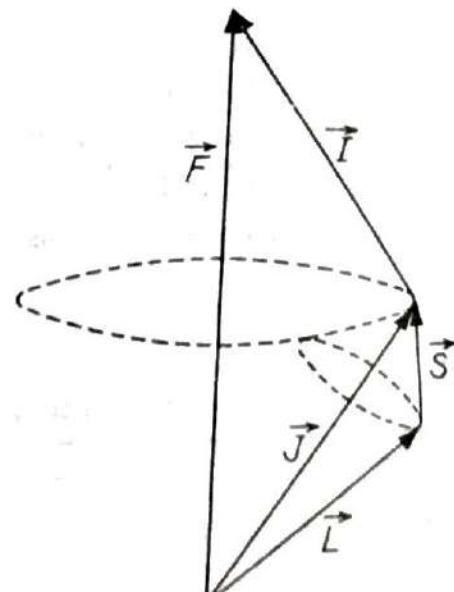
where  $M_I = I, I - 1, I - 2, \dots - I$ .

Since the maximum value of  $M_I$  is  $I$ , the maximum observable component of  $\mu_I$  is  $g_I I \mu_N$ , and is commonly called the 'nuclear magnetic moment'. It is roughly  $1000$  times smaller than electron magnetic moment.

**Atomic Vector Model :** Let us now construct the vector model with nuclear spin taken into account. The total angular momentum of the *whole atom* is the sum of three angular momenta : the electron orbital angular momentum  $\vec{L}$ , the electron spin angular momentum  $\vec{S}$  and the nuclear spin angular momentum  $\vec{I}$ . That is, the total angular momentum is

$$\vec{F} = \vec{L} + \vec{S} + \vec{I} = \vec{J} + \vec{I}.$$

As a result of interaction between electron orbit and spin,  $\vec{L}$  and  $\vec{S}$  precess rapidly around their resultant  $\vec{J}$ . Further, the interaction between the nuclear magnetic moment and the magnetic field produced by the orbital and spin motions of the atomic electrons couples  $\vec{I}$  with  $\vec{J}$  and causes these vectors to precess around their resultant  $\vec{F}$  (Fig. 1) This precession is, however, about  $1000$  times slower than that of  $\vec{L}$  and  $\vec{S}$  about  $\vec{J}$  (because nuclear magnetic moment is so much smaller than electron magnetic moment). Correspondingly the energy differences are very much smaller.



(Fig. 1)

The quantised values of the total angular momentum  $\vec{F}$  are  $\sqrt{F(F+1)} \frac{\hbar}{2\pi}$ .

where the hfs quantum number  $F$  can take the values :

$$F = J + I, J + I - 1, J + I - 2, \dots, |J - I|,$$

giving  $2J + 1$  values if  $I \geq J$ , or  $2I + 1$  values if  $I \leq J$ . This means that as a result of  $\vec{I} \cdot \vec{J}$  interaction, each fine-structure  $J$ -level splits into  $2J + 1$  (If  $I \geq J$ ) or  $2I + 1$  (if  $I \leq J$ ) hfs levels, each characterised by an  $F$  value.

**Interaction Energy :** The  $\vec{I} \cdot \vec{J}$  interaction energy can be shown to be given by

$$E_{I,J'} = \frac{1}{2} A' [F(F+1) - I(I+1) - J(J+1)],$$

where  $A'$  is a constant. The various hfs levels of a given term of a given atom have the same  $I$  and same  $J$ , but differ in  $F$ . Hence the separation between two hfs levels can be obtained by substituting first  $F+1$ , then  $F$ , in the above equation and taking the difference. This gives

$$\begin{aligned}\Delta E' &= \frac{1}{2} A' [(F+1)(F+2) - F(F+1)] \\ &= A' (F+1).\end{aligned}$$

Thus, the energy interval between consecutive hfs levels  $F$  and  $F+1$  is proportional to the larger of the  $F$  values (Lande's interval rule). The order of hfs levels in some hypermultiplets is normal (smallest  $F$  level deepest) while in others it is inverted (largest  $F$  level deepest).

The selection rule for  $F$  for electric dipole transitions is similar to that for  $J$ :

$$\Delta F = 0, \pm 1 \text{ but } F = 0 \leftrightarrow F = 0.$$

**Examples : (i)** As a first example,

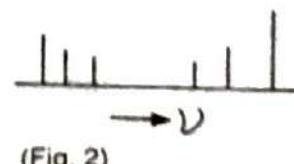
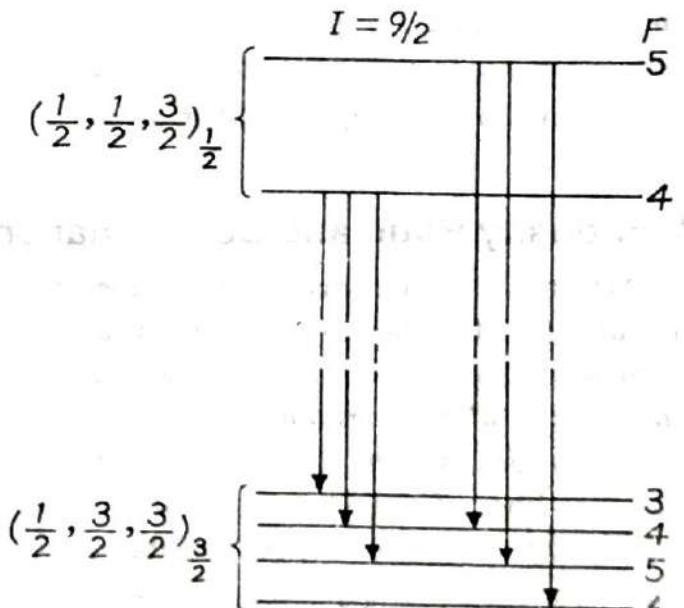
let us consider the hyperfine structure of the bismuth line 4722 Å. For bismuth,  $I = 9/2$ . The fine-structure in bismuth shows  $j-j$  coupling. The transition corresponding to this line is

$$6p^2 7s, \left( \frac{1}{2}, \frac{1}{2}, \frac{3}{2} \right)_{\frac{1}{2}} \longrightarrow$$

$$6p^3, \left( \frac{1}{2}, \frac{3}{2}, \frac{3}{2} \right)_{\frac{3}{2}}$$

With a nuclear spin  $I = 9/2$  and  $J = 1/2$ , the initial state is split into two hfs levels with  $F = 5, 4$  which are in normal order. Again, with  $I = 9/2$  and  $J = 3/2$ , the final state is split into four hfs levels with  $F = 6, 5, 4, 3$  which are in inverted order. This is shown in Fig. 2.

The selection rule  $\Delta F = 0, \pm 1$  (but  $F = 0 \leftrightarrow F = 0$ ) allows six transitions. Hence, the Bi line 4722 Å shows six hyperfine components.



(Fig. 2)

(ii) As a second example, we consider the hyperfine structure of the fine-structure component  $D_2$  (5890 Å) of Na ( $I = \frac{3}{2}$ ). The transition is  $^2P_{3/2} - ^2S_{1/2}$ .

For the  $^2P_{3/2}$  term, we have

$$J = \frac{3}{2}, I = \frac{3}{2}$$

$$\therefore F = 3, 2, 1, 0.$$

This term is splitted into four hfs components, as shown in Fig. 3.

For the  $^2S_{1/2}$  term, we have

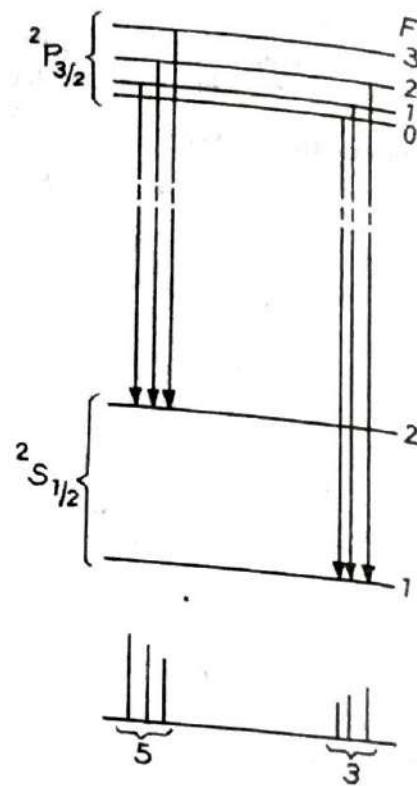
$$J = \frac{1}{2}, I = \frac{3}{2}$$

$$\therefore F = 2, 1.$$

This term is splitted into two hfs components, as shown in Fig. 3.

The selection rule  $\Delta F = 0, \pm 1$  allows six transitions. Hence the sodium 5890 Å line must show six hyperfine components.

However, since the factor  $A'$  for the  $^2P_{3/2}$  term is much smaller than that for the  $^2S_{1/2}$  term, the splittings of levels in the  $^2P_{3/2}$  term are comparatively very much smaller and remains unresolved. Hence, in practice, only two hfs components are seen as due to the splitting of the  $^2S_{1/2}$  term into two components with  $F = 2$  and  $F = 1$ .



(Fig. 3)

#### 4. Intensity Ratio and Determination of Nuclear Spin

When the hfs components are observed due to the splitting of only one of the terms, a measurement of the intensity ratios of the observed components leads to the determination of nuclear spin. This is based on the 'sum rule', according to which *the sum of the intensities of all the transitions starting from or ending on the same level is proportional to the statistical weight  $2F + 1$  of that level*. This situation arises in the hfs of the resonance lines of sodium (Fig. 3). In this case, the ratio of the intensities of the two observed hfs components is equal to the ratio of the weights ( $2F + 1$ ) of the hfs levels of the term  $^2S_{1/2}$ . When  $I$  is unknown, the  $F$  values of the two hfs levels of the term  $^2S_{1/2}$  ( $J = \frac{1}{2}$ ) would be  $I + \frac{1}{2}$  and  $I - \frac{1}{2}$ . Hence

$$\text{intensity ratio} = \frac{2\left(I + \frac{1}{2}\right) + 1}{2\left(I - \frac{1}{2}\right) + 1} = \frac{I + 1}{I}$$

The observed intensity ratio is 5 : 3. Thus,

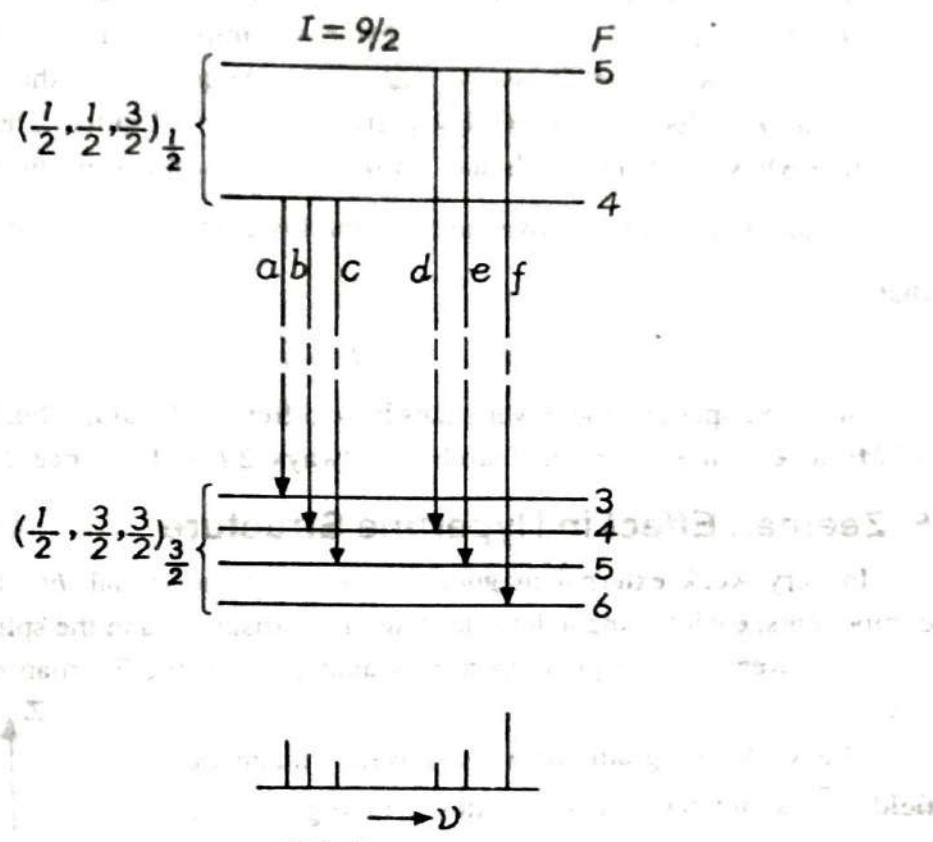
$$\frac{I+1}{I} = \frac{5}{3}$$

$$I = \frac{3}{2}$$

or  
Thus, the nuclear spin  $I$  is determined.

When  $I$  has been obtained, the  $g$ -factor and the magnetic moment of the nucleus can be derived from the magnitude of the  $hfs$  splitting by using the theoretical formulae.

When the  $hfs$  components are observed due to the splitting of both the terms, as in case of Bi line 4722 Å, then also an analysis of the hyperfine structure can also lead to the determination of nuclear spin. When all the hyperfine components are fully resolved, as in case of Bi (Fig. 4), then constant wave-number differences occur between pairs of components. For example, in Fig. 4, we have



(Fig. 4)

$$c - b = e - d$$

$$d - b = e - c$$

and

These differences correspond to level differences in the lower and the upper state respectively. We arrange the wave numbers of the hyperfine components in a square array such that along each row and along each column they increase (or decrease) regularly, and the differences between them in two successive rows and successive columns is constant. Then, all the components in any row correspond to the same upper  $hfs$  level, while all those in any column correspond to the same lower  $hfs$  level. This will enable us to construct  $hfs$  energy levels for the upper and the lower states. For example, in the above

case of Bi, when the wave numbers of the 6 observed components are filled in the square array, we obtain 2 hfs levels in the upper state and 4 in the lower state, as shown below :

$F_{lower}$	3		4		5		6
$F_{upper}$	4	$a$	$(b-a)$	$b$	$(c-b)$	$c$	
	5			$(q-p)$	$(e-d)$	$e$	$f$

Now, two cases may arise :

(i) The upper and the lower states have different  $J$  values (which are known from the fine-structure analysis), and have also different number of hfs levels. In this case, the number of hfs levels is always  $(2J + 1)$ . We may apply the Lande's interval rule to obtain the  $F$  values of the hfs levels from the interval ratios. Thus, all the  $F$  values of the state whose  $J$  value is already known are determined. From this the nuclear spin  $I$  can be calculated. In the above case, for the lower state  $F = 3, 4, 5, 6$  and  $J = \frac{3}{2}$ , so that

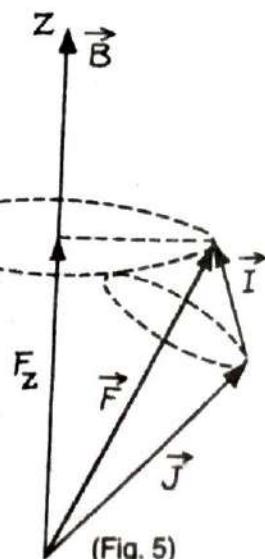
$$I = \frac{9}{2}.$$

(ii) The upper and the lower states have different  $J$  values, but have the same number of hfs levels. In this case this number is always  $2I + 1$ ; hence  $I$  may be evaluated.

## 5. Zeeman Effect in Hyperfine Structure

In very weak external magnetic fields, each individual hfs line splits into several components, each having a definite state of polarisation, and the splitting is proportional to the field strength. The phenomenon is analogous to the Zeeman effect in fine-structure lines.

The vector diagram for a (very weak) magnetic field  $\vec{B}$  along the  $z$ -axis is shown in Fig. 5. The electronic angular momentum vector  $\vec{J}$  and the nuclear angular momentum vector  $\vec{I}$  precess jointly about their resultant  $\vec{F}$ ; which in turn precesses more slowly about the direction of magnetic field  $\vec{B}$ . The projection of  $\vec{F}$  along the field,  $F_z$ , takes quantised values  $M_F \frac{\hbar}{2\pi}$ , where the magnetic quantum number can take only the following values :



$$M_F = F, F - 1, F - 2, \dots, -F.$$

These  $(2F + 1)$  values of  $M_F$  correspond to states of different energies in a magnetic field.

In order to calculate the energy differences of the  $(2F + 1)$  states with different  $M_F$ , let us first compute the magnetic moment  $\vec{\mu}_F$  of the atom as a whole. This moment consists of the electron magnetic moment  $\vec{\mu}_J$  and the nuclear magnetic moment  $\vec{\mu}_I$ . The magnitudes of these magnetic moments are given by

$$\mu_J = g_J \frac{e}{2m} \sqrt{J(J+1)} \frac{h}{2\pi}$$

$$\mu_I = g_I \frac{e}{2m_p} \sqrt{I(I+1)} \frac{h}{2\pi}$$

$$= g_I \frac{e}{2m} \frac{m}{m_p} \sqrt{I(I+1)} \frac{h}{2\pi}$$

and  
Because of the precession of  $\vec{J}$  and  $\vec{I}$  about  $\vec{F}$ , the direction of the electron and the nuclear magnetic moments lies, *on the average*, in the direction of  $\vec{F}$ . Hence, the magnitude of the resultant magnetic moment,  $\mu_F$ , of the atom is just the sum of the projections of  $\vec{\mu}_J$  and  $\vec{\mu}_I$  on  $\vec{F}$ . That is,

$$\mu_F = \mu_J \cos(\vec{J}, \vec{F}) - \mu_I \cos(\vec{I}, \vec{F}).$$

The difference in sign on the right-hand side appears because  $\vec{\mu}_I$  and  $\vec{I}$  are parallel (nucleus is positively charged), while  $\vec{\mu}_J$  and  $\vec{J}$  are antiparallel (electron is negatively charged). Substituting the values of  $\mu_J$  and  $\mu_I$ , we get

$$\mu_F = \left[ g_J \sqrt{J(J+1)} \cos(\vec{J}, \vec{F}) - g_I \frac{m}{m_p} \sqrt{I(I+1)} \cos(\vec{I}, \vec{F}) \right] \frac{e h}{4\pi m}.$$

Let us put the term in brackets equal to  $g_F \sqrt{F(F+1)}$ . Then, we get

$$\mu_F = g_F \sqrt{F(F+1)} \frac{e h}{4\pi m}. \quad \dots(i)$$

The value of  $g_F$  is given by

$$g_F = \frac{1}{\sqrt{F(F+1)}} \left[ g_J \sqrt{J(J+1)} \cos(\vec{J}, \vec{F}) - g_I \frac{m}{m_p} \sqrt{I(I+1)} \cos(\vec{I}, \vec{F}) \right].$$

Since the nuclear magnetic moment is much smaller than the electron magnetic moment, the second term may be omitted. Thus

$$g_F = g_J \sqrt{J(J+1)} \frac{\cos(\vec{J}, \vec{F})}{\sqrt{F(F+1)}}.$$

The cosine law applied to the triangle formed  $\vec{J}$ ,  $\vec{I}$  and  $\vec{F}$  gives

$$\cos(\vec{J}, \vec{F}) = \frac{F(F+1) + J(J+1) - I(I+1)}{2\sqrt{F(F+1)}\sqrt{J(J+1)}}.$$

$$\therefore g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}. \quad \dots(ii)$$

Now, from eq. (i), the ratio between the resultant magnetic moment and the resultant angular momentum of the atom is

$$\frac{\mu_F}{\sqrt{F(F+1)} \frac{h}{2\pi}} = g_F \frac{e}{2m}$$

By Larmor's theorem, the angular velocity of precession of  $\vec{F}$  along the direction of the magnetic field  $\vec{B}$  is  $B$  times the above ratio, that is,

$$\omega_F = B g_F \frac{e}{2m}$$

The energy of precession is equal to the product of the angular velocity and the projection of  $\vec{F}$  along  $\vec{B}$  which is  $F_Z = M_F \frac{h}{2\pi}$ . Thus

$$\begin{aligned}\Delta E &= \omega_F F_Z \\ &= B g_F \frac{e}{2m} M_F \frac{h}{2\pi} \\ &= g_F M_F \frac{e h}{4\pi m} B.\end{aligned}$$

In wave numbers, the interaction energy is

$$-\Delta T = \frac{\Delta E}{h c} = g_F M_F \frac{e B}{4\pi m c}.$$

$\frac{e B}{4\pi m c}$  is the Lorentz unit  $L'$ . Thus

$$-\Delta T = g_F M_F L',$$

where  $g_F$  is given by eq. (ii). This expression shows that the Zeeman levels are uniformly spaced.

As an example of the space quantisation of  $\vec{F}$  in a very weak magnetic field, let us consider the transition  $7^2P_{3/2} \rightarrow 7^2S_{1/2}$  in doubly-ionised thallium whose nuclear spin  $I = \frac{1}{2}$ . Each of the upper and the lower states has two hfs levels with  $F = 2, 1$  and  $1, 0$  respectively. These levels are  ${}^2P_{3/2}$ ,  ${}^2P_{3/2}$  and  ${}^2S_{1/2}$ ,  ${}^2S_{1/2}$  (Fig. 6).

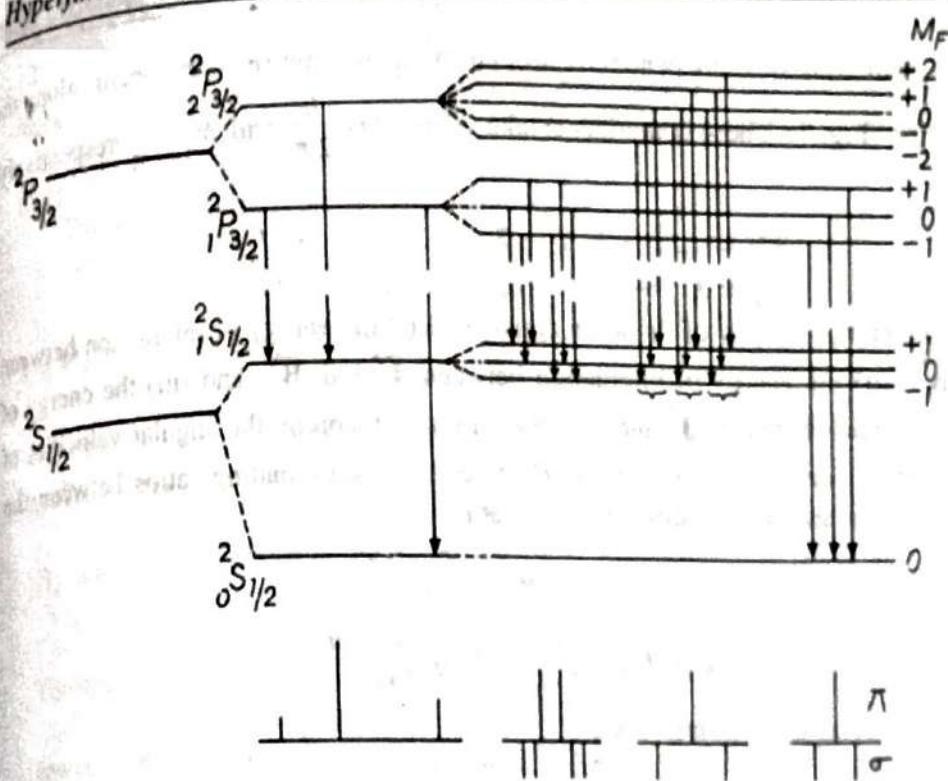
The selection rule  $\Delta F = 0, \pm 1$  allows three transitions. Hence, in the absence of magnetic field, three hfs components are observed.

When a very weak magnetic field is applied, each hfs level is further splitted into  $(2F + 1)$  Zeeman levels with  $M_F$  values as under :

hfs level	$M_F$ values
${}^2P_{3/2}$	+2, +1, 0, -1, -2
${}^2P_{3/2}$	+1, 0, -1
${}^2S_{1/2}$	+1, 0, -1
${}^2S_{1/2}$	0

This splitting is also shown in Fig. 6. The selection rules are :

$\Delta M_F = 0$  and  $\pm 1$ . (but  $M_F = 0 \leftrightarrow M_F = 0$  for  $\Delta F = 0$ ).  
 $\Delta M_F = 0$  gives  $\pi$  components, and  $\Delta M_F = \pm 1$  give  $\sigma$  components. The theoretical number of transitions in the presence of the field based on these rules is 12.



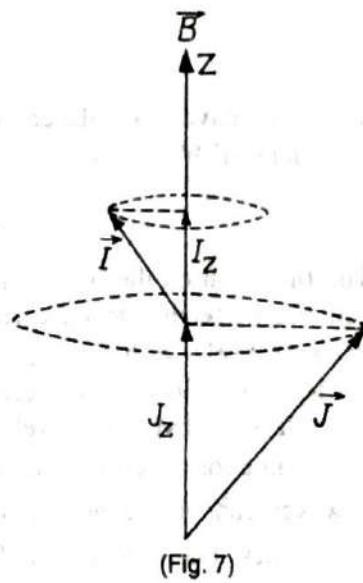
Thus, in a 'very weak' field each  $hfs$  line breaks up into a symmetrical Zeeman pattern similar to the anomalous pattern of fine-structure lines in a 'weak field'. The spacings between the Zeeman components lead to the values of  $g_F$  for the various  $hfs$  levels. Now,  $I$  can be derived from  $g_F$  by means of eq. (ii) since  $g_J$ ,  $J$  and  $F$  are known.

In actual practice, the so-called Zeeman effect of  $hfs$  lines has rarely been observed, because the hyperfine structure splitting itself is generally close to the limit of possible resolution. It is only with the atomic beam resonance technique that this effect can often be measured and used for determining  $I$ .

## 6. Back-Goudsmit Effect in Hyperfine Structure

When the magnetic field  $\vec{B}$  is so strong that the velocity of precession of  $\vec{F}$  about the field direction becomes greater than that of  $\vec{J}$  and  $\vec{I}$  about  $\vec{F}$ , a Paschen-Back like effect occurs in the  $hfs$  pattern. This is known as 'Back-Goudsmit effect'. However, on account of the weakness of the coupling between  $\vec{J}$  and  $\vec{I}$ , the Back-Goudsmit effect occurs at fields much lower than those at which Paschen-Back effect sets in fine-structure.

In fact, a magnetic field which is 'weak' for fine structure is a 'strong' field for hyperfine structure. In such a field the coupling between  $\vec{J}$  and  $\vec{I}$  breaks



(Fig. 7)

down, and each precesses independently around  $\vec{B}$  with quantised components along the field direction (Fig. 7). These components take values  $M_J \frac{h}{2\pi}$  and  $M_I \frac{h}{2\pi}$  respectively,

where

$$M_J = J, J-1, J-2, \dots -J$$

$$M_I = I, I-1, I-2, \dots -I.$$

and

The total interaction energy of the atom consists of (i) the energy of interaction between  $\vec{J}$  and  $\vec{B}$ , (ii) the energy of interaction between  $\vec{I}$  and  $\vec{B}$ , and (iii) the energy of residual interaction between  $\vec{J}$  and  $\vec{I}$ . By Larmor's theorem, the angular velocities of precession of  $\vec{J}$  and  $\vec{I}$  are given by  $B$  times the corresponding ratios between the magnetic moment and angular momentum. That is,

$$\omega_J = B g_J \frac{e}{2m}$$

and

$$\omega_I = B g_I \frac{e}{2m_p} = B g_I \frac{e}{2m} \frac{m}{m_p}.$$

The magnetic precessional energies are

$$\Delta E_{JB} = \omega_J J_Z$$

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

and

$$\Delta E_{IB} = -\omega_I I_Z$$

$$= -B g_I \frac{e}{2m} \frac{m}{m_p} M_I \frac{h}{2\pi}.$$

The total precessional energy is

$$\Delta E = \left( g_J M_J - g_I \frac{m}{m_p} M_I \right) B \frac{e h}{4\pi m}.$$

In wave numbers, the energy is

$$-\Delta T = \frac{\Delta E}{h c} = \left( g_J M_J - g_I \frac{m}{m_p} M_I \right) \frac{e B}{4\pi m c}.$$

$\frac{e B}{4\pi m c}$  is the Lorentz unit  $L'$ . Thus

$$-\Delta T = \left( g_J M_J - g_I \frac{m}{m_p} M_I \right) L'.$$

To this we have to add the energy of residual interaction between  $\vec{J}$  and  $\vec{I}$  which may be written as  $A' M_J M_I$ . Thus, the total magnetic interaction energy becomes

$$-\Delta T = \left( g_J M_J - g_I \frac{m}{m_p} M_I \right) L' + A' M_J M_I.$$

The first term on the right causes splitting of each fine-structure  $J$ -level into  $(2J+1)$  equidistant Zeeman levels corresponding to the different values of  $M_J$ . The separations of these levels, with sufficient field strength, are considerably greater than those of the field-free *hfs* levels. The second term predicts a further splitting of each Zeeman level into  $(2I+1)$  hyperfine levels corresponding to the different values of  $M_I$ . This number is the same for all terms of an atom, since  $I$  is constant for a given nucleus. This splitting, however, cannot be expected to be observed because the interaction of  $\vec{I}$  with  $\vec{B}$  is about 1000 times smaller than that of  $\vec{J}$  with  $\vec{B}$ . Yet, the splitting of each Zeeman level into

( $2J + 1$ ) hyperfine levels is observed. This is due to the third term  $A' M_J M_I$  representing  $\vec{J} \cdot \vec{I}$  interaction which is still present and determines the relative separations of the hyperfine components of each Zeeman level. These components are therefore equally spaced.

The selection rules for  $M_J$  and  $M_I$  are :

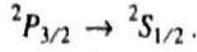
$$\Delta M_J = \begin{cases} 0, & \text{for } \pi \text{ components} \\ \pm 1, & \text{for } \sigma \text{ components,} \end{cases}$$

but  $M_J = 0 \leftrightarrow M_I = 0$  for  $\Delta J = 0$ ; and

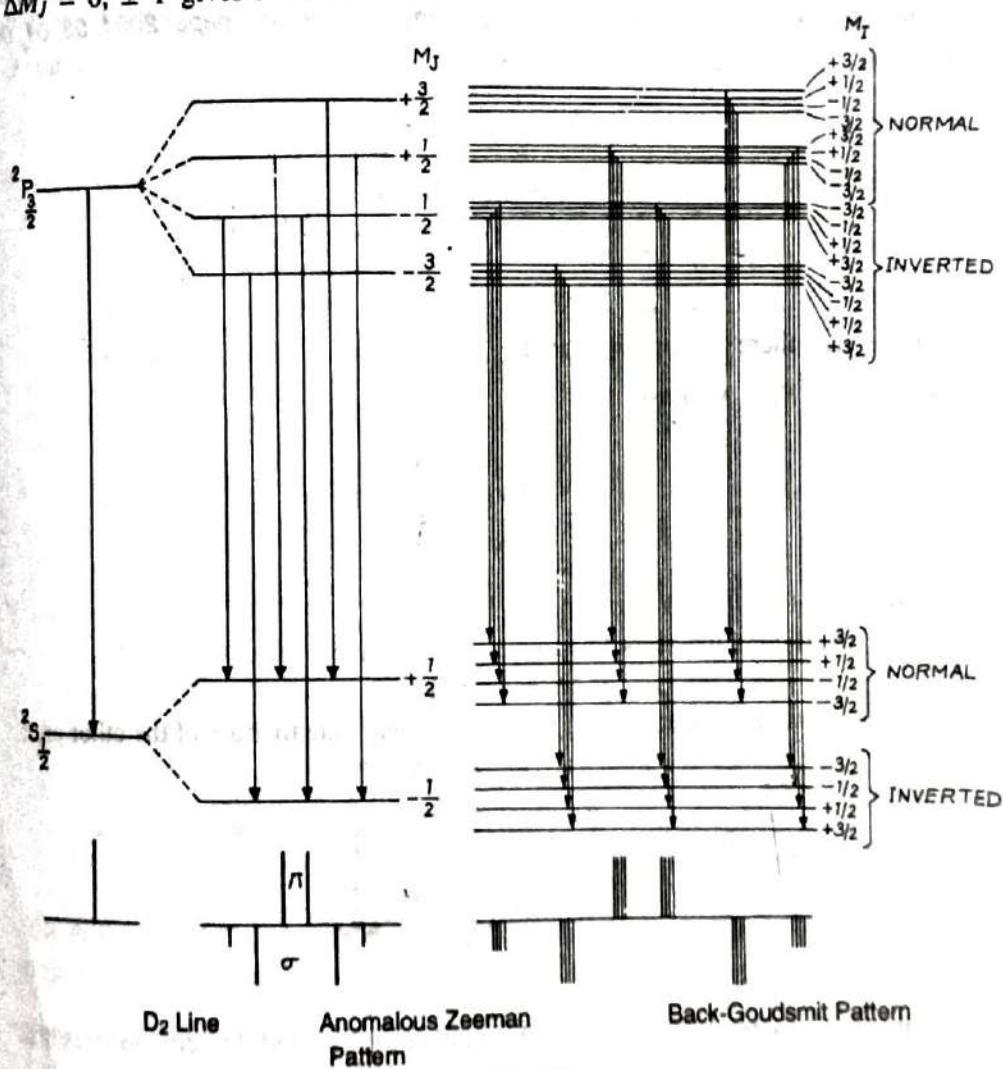
$$\Delta M_I = 0.$$

The rule for  $\Delta M_J$  gives the anomalous Zeeman line pattern, and that for  $\Delta M_I$  produces a hyperfine structure for each Zeeman line.

**Example :** As an example, let us consider the Back-Goudsmit effect for the sodium D<sub>2</sub> line which arises from the transition



The upper state is split into four Zeeman levels with  $M_J = +\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ , and the lower state in two levels with  $M_J = +\frac{1}{2}, -\frac{1}{2}$  (Fig. 8). The selection rule  $\Delta M_J = 0, \pm 1$  gives 6 Zeeman lines.



(Fig. 8)

Now for sodium,  $I = 3/2$ . Therefore, each of the Zeeman levels in both states is split into four hyperfine levels corresponding to  $M_I = +\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ . Each group of hyperfine levels is composed of equidistant levels, though the separation may differ from group to group. These hypermultiplet groups may be normal or inverted. The selection rule  $\Delta M_I = 0$  gives four hyperfine components for each Zeeman line. This number must be  $(2I + 1)$ . Thus, conversely

$$2I + 1 = 4$$

$$I = \frac{3}{2}$$

so that,

Thus, we have a very reliable method of determining the nuclear spin  $I$ . We have only to count the number of hyperfine components for any Zeeman line in a strong magnetic field, and this number is  $2I + 1$ . Hence,  $I$  is directly determined. Back and Goudsmit found that in a strong magnetic field each of the Zeeman components of Bi consists of 10 hyperfine components due to nuclear spin. Hence, they concluded that for Bi,  $I = \frac{9}{2}$ .

### SOLVED PROBLEMS

1. Two levels in an atom whose nuclear spin is  $I = 3$ , have the designations  $^2D_{3/2}$  and  $^2P_{1/2}$ . Find the expected number of components in the hyperfine structure of the corresponding spectral line. (Meerut 2003, 96, sp. paper 2004, 03, 01, 00)

**Solution.** For the state  $^2D_{3/2}$ , we have

$$J = \frac{3}{2}, I = 3.$$

The allowed values of the hfs quantum number  $F$  are

$$F = J + I, J + I - 1, \dots, |J - I|$$

$$= \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}.$$

Thus, for this state there are four hfs levels.

For the state  $^2P_{1/2}$ , we have

$$J = \frac{1}{2}, I = 3.$$

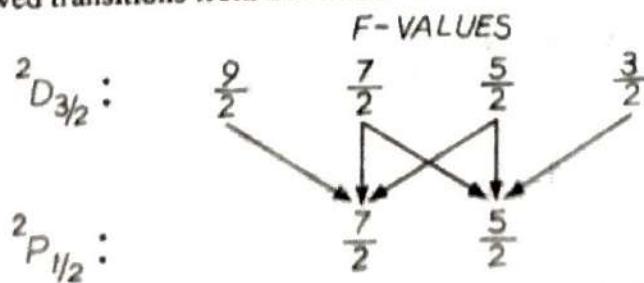
$$\therefore F = \frac{7}{2}, \frac{5}{2}.$$

This state has only two hfs levels.

The hfs levels combine according to the selection rule

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

Hence the allowed transitions from the levels of one state to those of the other are:



In all there are six transitions. Hence, the number of expected hfs components is 6.

2. In a vector diagram, illustrate graphically the Lande's interval rule for hfs of  $^2D_{5/2}$  level where the nuclear moment  $I = 9/2$ .

Solution. The  $I-J$  interaction energy can be expressed by

$$E'_{I,J} = \frac{1}{2} A' [F(F+1) - I(I+1) - J(J+1)], \quad \dots(1)$$

where  $A'$  is a constant and  $F$  is the hfs quantum number. This may, by using cosine law\*, also be written as

$$E'_{I,J} = A' \sqrt{I(I+1)} \sqrt{J(J+1)} \cos(\vec{I}, \vec{J}). \quad \dots(2)$$

Let us consider the hfs of  $^2D_{5/2}$  term. For this, we have

$$J = \frac{5}{2}, \quad I = \frac{9}{2} \text{ (given).}$$

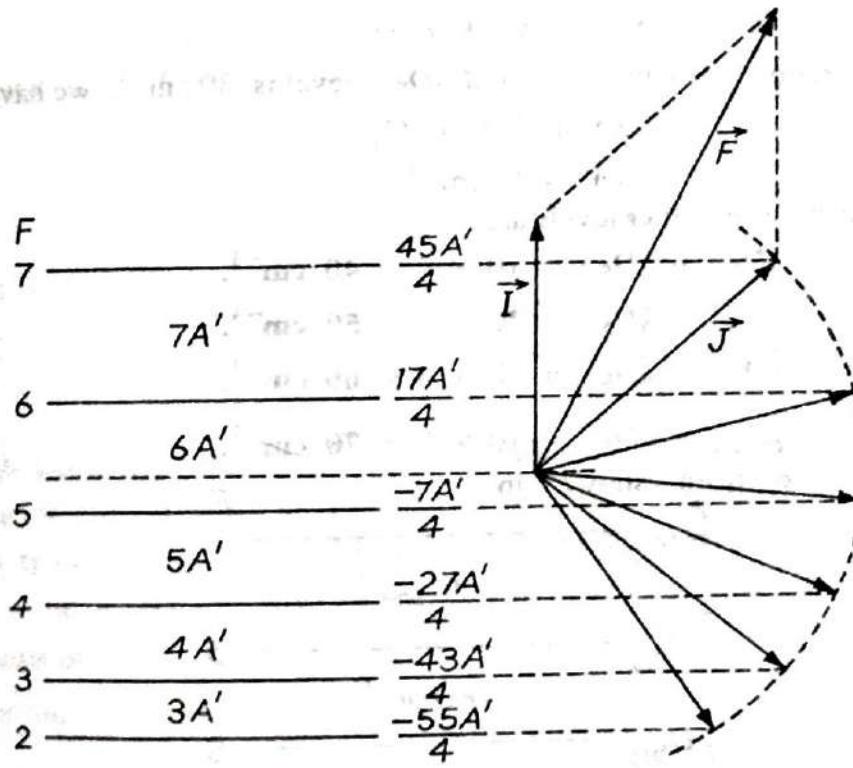
The allowed values of  $F$  are given by

$$\begin{aligned} F &= J + I, \quad J + I - 1, \quad \dots \quad |J - I| \\ &= 7, 6, 5, 4, 3, 2. \end{aligned}$$

The corresponding values of  $E'_{I,J}$  are, using eq. (i),

$$+ \frac{45}{4} A', \quad + \frac{17}{4} A', \quad - \frac{7}{4} A', \quad - \frac{27}{4} A', \quad - \frac{43}{4} A', \quad - \frac{55}{4} A'.$$

A graphical representation of the splitting is shown in Fig. 9. Also shown is the projection of  $\vec{J}$  on  $\vec{I}$ , giving  $\sqrt{J(J+1)} \cos(\vec{J}, \vec{I})$  which is proportional to  $E'_{I,J}$ .



(Fig. 9)

The differences between hfs levels are seen to be  $3A'$ ,  $4A'$ ,  $5A'$ ,  $6A'$ ,  $7A'$  which are proportional to the larger of the  $F$  values. This is Lande's interval rule. It can be

\*  $\cos(\vec{I}, \vec{J}) = \frac{J(J+1) + I(I+1) - F(F+1)}{2\sqrt{J(J+1)}\sqrt{I(I+1)}}$

derived by substituting first  $F + 1$ , then  $F$ , in eq. (i) and taking the difference. This gives

$$\Delta E' = A'(F + 1).$$

3. The nuclear spin of bismuth atom is  $9/2$ . Using this, find the number of levels in which the term  $^2D_{5/2}$  of bismuth will split due to  $\vec{I} - \vec{J}$  interaction. If the separation of the  $^2D_{5/2}$  and  $^3D_{5/2}$  levels is  $30 \text{ cm}^{-1}$ , calculate the separations of the rest of the adjacent levels.

(Meerut 2000, 90, sp. paper 2002, 96)

**Solution.** For bismuth atom, we have

$$I = \frac{9}{2}.$$

and for its state  $^2D_{5/2}$ , we have

$$J = \frac{5}{2}.$$

The allowed values of the hfs quantum number are

$$\begin{aligned} F &= J + I, J + I - 1, \dots, |J - I| \\ &= 7, 6, 5, 4, 3, 2, \end{aligned}$$

so that there are six hfs levels, which are designated as\*

$$^2D_{5/2}, ^2D_{5/2}, ^2D_{5/2}, ^2D_{5/2}, ^3D_{5/2}, ^2D_{5/2}.$$

The separation between two successive levels  $F$  and  $F + 1$  is given by Lande's interval rule, that is,

$$\Delta E' = A'(F + 1).$$

Therefore, as the separation between  $^2D_{5/2}$  and  $^3D_{5/2}$  level is  $30 \text{ cm}^{-1}$ , we have

$$30 \text{ cm}^{-1} = A'(3)$$

or

$$A' = 10 \text{ cm}^{-1}.$$

Hence the separations between other levels are :

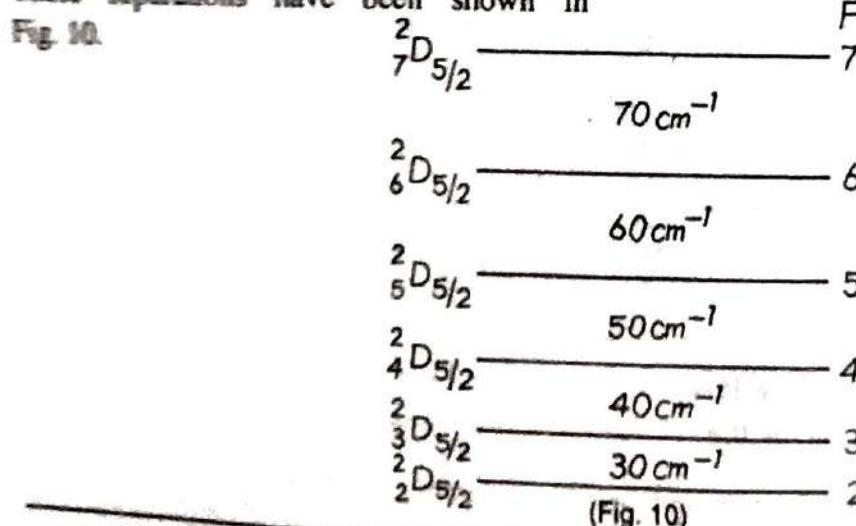
$$^2D_{5/2} - ^2D_{5/2} = 10 \times 4 = 40 \text{ cm}^{-1}.$$

$$^2D_{5/2} - ^2D_{5/2} = 10 \times 5 = 50 \text{ cm}^{-1}.$$

$$^2D_{5/2} - ^2D_{5/2} = 10 \times 6 = 60 \text{ cm}^{-1}.$$

$$^2D_{5/2} - ^2D_{5/2} = 10 \times 7 = 70 \text{ cm}^{-1}.$$

These separations have been shown in



\*The hfs quantum number  $F$  is written as a subscript to the left of the term type.

4. Bi has an excited state  ${}^2D_{3/2}$  which is split into six hfs levels. The distances between pairs of levels are 0.236, 0.312, 0.391, 0.471 and  $0.551\text{ cm}^{-1}$ . Find the spin quantum number  $I$ . What is its hyperfine structure constant?

(Moorut 98 sp. paper)

**Solution.** By Lande's interval rule, the distance between two successive hfs levels  $F$  and  $F + 1$  is proportional to higher quantum number, that is,

$$\Delta E' = A'(F + 1),$$

where  $A'$  is hyperfine structure constant. For the lowest pair of levels  $F$  and  $F + 1$ ,  $\Delta E'$  is  $0.236\text{ cm}^{-1}$ , as given. Therefore,

$$0.236\text{ cm}^{-1} = A'(F + 1). \quad \dots(i)$$

For the next pair of levels  $F + 1$  and  $F + 2$ ,  $\Delta E'$  is given to be  $0.312\text{ cm}^{-1}$ . Therefore,

$$0.312\text{ cm}^{-1} = A'(F + 2). \quad \dots(ii)$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{0.236\text{ cm}^{-1}}{0.312\text{ cm}^{-1}} = \frac{F + 1}{F + 2}.$$

Solving, we get

$$F = 2.10 \approx 2.$$

Thus, the hfs quantum numbers of the six hfs levels are

$$F = 2, 3, 4, 5, 6, 7.$$

Now,  $F = J + I, J + I - 1, \dots, |J - I|$

The largest value of  $F$  is  $J + I$ , and  $J = 5/2$ . Thus

$$J + I = \frac{5}{2} + I.$$

$$\therefore I = J - \frac{5}{2} = \frac{9}{2}.$$

By eq. (i), we have

$$0.236\text{ cm}^{-1} = A'(F + 1) = 3A'.$$

$$\therefore A' = \frac{0.236\text{ cm}^{-1}}{3} = 0.079\text{ cm}^{-1}.$$

5. We know that the  ${}^2S_{1/2}$  level of an atom is single and does not have any fine structure. If the nucleus of the atom has spin not equal to zero, what is the multiplicity of the  ${}^2S_{1/2}$  term? In a transition from a single hyperfine component of  ${}^2P_{1/2}$ , what is the relative intensity of transitions to the various hyperfine components of  ${}^2S_{1/2}$ ?

**Solution.** For the given level  ${}^2S_{1/2}$ , we have

$$J = \frac{1}{2}.$$

If the nuclear spin  $I$  is not zero, the number of hyperfine components will be  $(2J + 1)$  if  $I \geq J$  or  $(2I + 1)$  if  $I \leq J$ . Now  $I$  can either be integral or half-integral, that is, it can take values  $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots$ . Here  $J = \frac{1}{2}$  and  $I$  is not zero. Hence,

$I$  must be either equal to or greater than  $J$ . Therefore, the number of  $hfs$  components would be  $(2J + 1)$ , that is 2. In other words, the  $hfs$  multiplicity of  $^2S_{1/2}$  term is 2.

The hyperfine components of  $^2S_{1/2}$  term ( $J = \frac{1}{2}$ ) have the  $F$  values :

$$F = I + \frac{1}{2} \text{ and } I - \frac{1}{2}.$$

Now, according to the sum rule, within a  $hfs$  multiplet the ratio of the sums of the intensities of all transitions from  $I$  to two states with quantum numbers  $F$  and  $F'$  are in the ratio of their statistical weights  $(2F + 1) : (2F' + 1)$ . Hence, the intensities of transitions starting from a single level and ending on the hyperfine levels with  $F = I + \frac{1}{2}$  and  $I - \frac{1}{2}$  are in the ratio.

$$\frac{2\left(I + \frac{1}{2}\right) + 1}{2\left(I - \frac{1}{2}\right) + 1} = \frac{I + 1}{I}.$$

Thus, if  $I = \frac{3}{2}$ , the intensity ratio is 5 : 3.

6. A certain fine-structure multiplet of levels corresponding to  $L = 2$ ,  $S = 1$  and  $I = \frac{3}{2}$ . Find the number of components and write spectroscopic designations for the multiplet.

Find into how many components each of these fine-structure levels will be further split by hyperfine-structure splitting. Allowing for the degeneracy of each hyperfine level due to the quantum number  $M_F$ , what is the total degeneracy of each of the fine-structure levels ?

**Solution.** For the given multiplet, we have

$$L = 2, S = 1.$$

It is a  $D$  term whose multiplicity is  $(2S + 1) = 3$ , and the allowed values of the inner quantum number  $J$  are :

$$J = (L + S), (L + S - 1), \dots, |L - S| \\ = 3, 2, 1.$$

Thus, there are three fine-structure components whose designations are

$$^3D_3, ^3D_2, ^3D_1.$$

Let us consider the  $hfs$  of each of them for  $I = \frac{3}{2}$ .

**Fine-structure component  $^3D_3$  :**  $J = 3, I = \frac{3}{2}$ .

The allowed values of  $hfs$  quantum number  $F$  are

$$F = J + I, J + I - 1, \dots, |J - I| \\ = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}.$$

Thus, there are four  $hfs$  components whose designations are

$$^{9/2}D_3, ^{7/2}D_3, ^{5/2}D_3, ^{3/2}D_3.$$

The  $M_F$ -degeneracy ( $= 2F + 1$ ) of these hfs levels are 10, 8, 6, 4 respectively. Hence, the total degeneracy of the  $^3D_3$  level is 28.

**Fine-structure component  $^3D_2$  :**  $J = 2, I = \frac{3}{2}$ .

$$\therefore F = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$$

There are four hfs components whose designations are

$$\frac{7}{2}^3D_2, \frac{5}{2}^3D_2, \frac{3}{2}^3D_2, \frac{1}{2}^3D_2.$$

The  $M_F$ -degeneracies are 8, 6, 4, 2. The total degeneracy of  $^3D_2$  is 20.

Similarly, we can also see that there are three hfs components of fine-structure component  $^3D_1$ , and its total degeneracy is 12.

## QUESTIONS

- What is meant by hyperfine structure of spectral lines ? How could it be explained on the basis of nuclear spin ? (Meerut 2003, sp. paper 2003, 01)
- How will you account for the hyperfine structure of spectral lines ? (Meerut 2006, 03, 01)
- Discuss hyperfine structure of spectral lines. What light does this study throw on the spin and magnetic moment of atomic nuclei. (Meerut 2003 S, 02 S, sp. paper 89)
- Discuss the hfs of 4772 Å line of bismuth. The nuclear spin of bismuth is 9/2. (Meerut 2003, 93)
- Draw hfs components of the fine-structure component  $D_2$  of Na ( $I = 3/2$ ). (Meerut 98 sp. paper)
- Describe how from a study of the hyperfine structure of atomic spectral lines, one can determine nuclear spin. (Meerut 98 sp. paper)
- Give the theory of Back-Goudsmit effect and show how does it lead to the determination of nuclear spin. (Meerut sp. paper 2003, 00, 99, 97)
- Describe with theory an spectroscopic method for determining nuclear spin.

## PROBLEM

- In Bi atom, the nuclear spin is 9/2. Into how many levels  $^2D_{5/2}$  level will be split. If the  $^2D_{5/2} - ^2D_{5/2}$  interval is  $70 \text{ cm}^{-1}$ , find all other intervals.

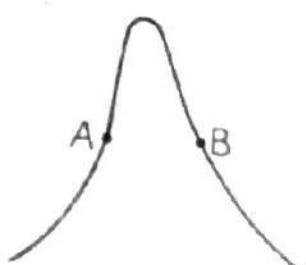
**Ans.** six;  $60 \text{ cm}^{-1}$ ,  $50 \text{ cm}^{-1}$ ,  $40 \text{ cm}^{-1}$ ,  $30 \text{ cm}^{-1}$ .

# The Breadth of Spectral Lines

## 1. Introduction

Many spectral lines have an observable breadth even when examined under the best optical system. In fact even the sharpest lines have a finite breadth, indicating that the corresponding photons have wavelengths which are not precisely defined but vary over a range of wavelengths. The intensity distribution of a typical spectral line may be expressed by an intensity versus frequency curve (Fig. 1).

*The breadth of a spectral line is defined as the separation, in  $\text{cm}^{-1}$ , between two points (A and B) whose intensities are half that of the maximum intensity.*



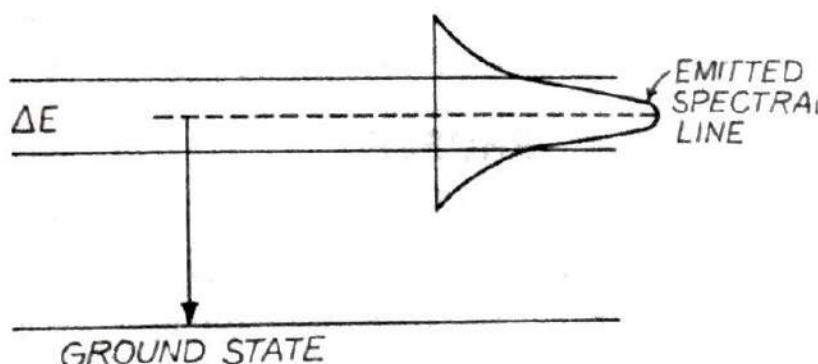
(Fig. 1)

The known causes of spectral-line breadths are the following :

- (i) natural breadth,
- (ii) Doppler effect,
- (iii) external effects : collision damping, pressure broadening, Stark effect, etc.

## 2. Natural Breadth

The spectral lines arise as a result of electron transitions between two energy levels. According to quantum mechanics, the energy levels of an atom are not discrete, but each has a finite energy-breadth,  $\Delta E$ , in which the probability distribution is concentrated in regions where the terms are observed (Fig. 2). A transition between two such levels cannot



(Fig. 2)

give an infinitely sharp spectral line. From Heisenberg uncertainty principle, the energy-spread  $\Delta E$  of a state and the mean time  $\Delta t$  for which the atom remains in that state are related by

$$\Delta E \Delta t \sim h.$$

Writing  $h \Delta v$  for the uncertainty  $\Delta E$  in energy (because  $E = h v$ , where  $v$  is frequency); and  $\tau$  (the mean life) for the time  $\Delta t$ , we get

$$(h \Delta v) \tau \sim h$$

$$\Delta v \sim \frac{1}{\tau}$$

or  
It thus follows that greater the mean life of the atom in a particular state, the smaller is the energy-breadth of that state. Hence, **the ground states, and the metastable states of atoms are sharp, whereas other states are broad.**

Thus, the inherent property of the atom that it remains only for a 'finite' time in an excited state gives a natural breadth to the spectral line, independent of all external effects.

Quantum mechanically, the half-intensity breadth of a spectral line due to transition from an excited state to the ground state is given by

$$\Delta v = \frac{1}{2\pi\tau}$$

For an ordinary excited state,  $\tau \approx 10^{-8}$  s.

$$\therefore \Delta v = \frac{1}{2 \times 3.14 \times 10^{-8} \text{ s}} = 10^7 \text{ s}^{-1}$$

For a visible line of  $\lambda = 6000 \text{ \AA}$ , this corresponds to a wavelength broadening of

$$\begin{aligned}\Delta \lambda &= \frac{\lambda^2}{c} \Delta v \\ &\approx \frac{(6000 \times 10^{-10} \text{ m})^2}{3.0 \times 10^8 \text{ m s}^{-1}} \times (10^7 \text{ s}^{-1}) \\ &\approx 1.2 \times 10^{-14} \text{ m} \\ &= 10^{-4} \text{ \AA}.\end{aligned} \quad [\because c = v \lambda]$$

This is a value many times too small to be measured by ordinary spectroscopic methods.

### 3. Doppler Effect

The observed frequency of a spectral line is different from its actual frequency, depending upon the velocity of the source relative to that of the observer. The observed frequency increases if the motion of the source is toward the observer, and decreases if the motion is away from the observer. This is known as Dopper effect and is an important cause of the broadening of spectral lines.

It can be shown that if a source of light of frequency  $v_0$  is moving in the line of sight with a velocity  $v$  relative to the observer, the apparent frequency  $v$  measured by the observer is given by

$$v = v_0 \left( 1 \pm \frac{v}{c} \right),$$

where  $c$  is the velocity of light. The plus sign applies for the motion toward the observer, and minus sign for the motion away from the observer. Thus, the change in frequency is given by

$$\Delta v = v - v_0 = \pm v_0 \frac{v}{c}.$$

In the case of gaseous sources (such as a discharge lamp) the centre of mass of the source is fixed, but the atoms emitting the light have velocities due to thermal agitation. The random motions of the atoms of the gas produce a net broadening of the spectral lines, with no apparent displacement of its central maximum. This means that the spectral line consists of a range of frequencies disposed about the natural frequency.

Assuming a Maxwellian distribution of velocities, the probability that the velocity of an atom of an ideal gas lies between  $v$  and  $v + dv$  is given by

$$dP = 4\pi \left( \frac{\mu}{2\pi RT} \right)^{3/2} \exp\left(-\frac{\mu v^2}{2RT}\right) v^2 dv,$$

where  $\mu$  is the atomic weight,  $R$  the universal gas constant and  $T$  the absolute temperature.

Now, the Doppler frequency shift is given by

$$\Delta v = v - v_0 = v_0 \frac{v}{c}$$

$$v = c \frac{v - v_0}{v_0}$$

so that

Substituting this value of  $v$ , we get the relative intensity  $I$  as a function of the frequency  $v$ , that is

$$I(v) = \text{constant} \exp\left[-\frac{\mu c^2 (v - v_0)^2}{2 R T v_0^2}\right]$$

The plot of this equation is shown in Fig. 3.

The two frequencies at which the intensity drops to half its maximum value are obtained by setting the exponential term in the last expression equal to one-half, that is,

$$\exp\left[-\frac{\mu c^2 (v - v_0)^2}{2 R T v_0^2}\right] = \frac{1}{2}$$

$$\text{or } \frac{\mu c^2 (v - v_0)^2}{2 R T v_0^2} = \log_e 2$$

$$\text{or } v - v_0 = \frac{v_0}{c} \sqrt{\frac{2 R T}{\mu} \log_e 2}.$$

Multiplying it by 2, we get the line-breadth  $\delta v$ . Thus,

$$\delta v = 2(v - v_0) = \frac{2v_0}{c} \sqrt{\frac{2 R T}{\mu} \log_e 2}.$$

Now,  $\sqrt{\log_e 2} = \sqrt{0.693} = 0.832$ .

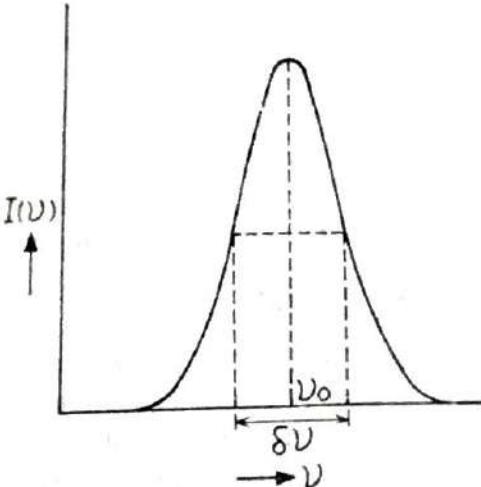
$$\therefore \delta v = 1.66 \frac{v_0}{c} \sqrt{\frac{2 R T}{\mu}}.$$

This equation shows that the Doppler broadening is (i) proportional to the square-root of the temperature, (ii) proportional to the frequency  $v_0$ , and (iii) inversely proportional to the square-root of the atomic weight.

$$\text{Now, } \frac{\delta v}{v} = \frac{\delta \lambda}{\lambda}.$$

Therefore, the half-intensity line breadth in terms of the wavelength is

$$\delta \lambda = 1.66 \frac{\lambda_0}{c} \sqrt{\frac{2 R T}{\mu}}.$$



(Fig. 3)

This shows that the line-breadth due to Doppler broadening increases with temperature and decreases with increasing atomic weight.

As an example of the application of this equation, the sodium line at 5893 Å is expected to have a half-intensity breadth of 0.02 Å at a temperature of 500 K, which is a value 200 times as large as the natural half-intensity breadth. Hence the natural breadth of a spectral line may be neglected in comparison with the Doppler breadth at ordinary temperatures.

In hydrogen, the Doppler effect has been the chief limiting factor to resolve the fine structure of the Balmer series lines. For  $H_{\alpha}$ , at temperatures between 250 K and 300 K, the Doppler half-intensity breadth is about 0.09 Å, a value of the same order of magnitude as the largest fine-structure interval. By operating a hydrogen-discharge tube in a liquid-air bath the  $H_{\alpha}$  and  $D_{\alpha}$  lines have been considerably sharpened. The effect of atomic weight on the Doppler breadth is clear by the fact that the  $H_{\alpha}$  line is 1.4 times as broad as  $D_{\alpha}$  line.

#### 4. External Effects

(a) **Collision Damping** : At high pressure, the life-time of a state is long compared to the time between successive collisions of the radiating atom with other atoms of the gaseous source. The radiating atom is thus disturbed by the collisions. The result is that the emitted photon is effectively a series of shorter, independent wave-trains. This causes broadening of the spectral line.

(b) **Pressure Broadening** : At high pressures, the time for which two atoms are in collision is large compared with the mean time between collisions. Then, the emitting or absorbing atom is subjected to a strong atomic field. This leads to a shift of the spectral line towards red, that is, the line is broadened asymmetrically.

(c) **Stark Broadening** : In electric discharge tubes, particularly those operating at high pressure and high voltage, an atom is subjected to an electric field due to a neighbouring ion. The energy levels of a radiating atom are therefore perturbed by the Stark effect and result in an average broadening of the spectral lines.

#### SOLVED PROBLEMS

1. A spectroscopic examination of the light from a certain star shows that the apparent wavelength of a certain line is 5001 Å, whereas the observer wavelength of the same line produced by a terrestrial source is 5000 Å. In what direction and with what speed the star is moving relative to the earth ? ( $c = 3 \cdot 0 \times 10^8$  m/s).

(Meerut sp. paper 2001)

**Solution.** The apparent wavelength is increased, indicating that the star is moving away from the observer situated on earth.

If  $\lambda$  the apparent wavelength and  $\lambda_0$  the actual wavelength (when the source is at rest), we have

$$\lambda = \lambda_0 \left[ 1 + \frac{v}{c} \right].$$

$$\frac{\lambda}{\lambda_0} = 1 + \frac{v}{c}.$$

or

$$\therefore v = c \left( \frac{\lambda}{\lambda_0} - 1 \right)$$

$$= 3.0 \times 10^8 \text{ m/s} \left( \frac{5001 \text{ Å}}{5000 \text{ Å}} - 1 \right)$$

$$= \frac{3.0 \times 10^8 \times 1}{5000} = 6.0 \times 10^4 \text{ m/s}$$

**2. Calculate the Doppler half-intensity breadth of the sodium D-lines at 5893 Å corresponding to a temperature of 500 K.  $R = 8.31 \text{ J/(mol-K)}$ ,  $c = 3.0 \times 10^8 \text{ m/s}$ , atomic weight of sodium = 22.99 g/mol.**

(Meerut sp. paper 2000)

**Solution.** The Doppler half-intensity breadth in terms of wavelength is given by

$$\delta\lambda = 1.66 \frac{\lambda_0}{c} \sqrt{\frac{2RT}{\mu}},$$

where  $R$  is universal gas constant,  $T$  is kelvin temperature and  $\mu$  is atomic weight. Putting the given values, we have

$$\begin{aligned}\delta\lambda &= 1.66 \frac{(5893 \times 10^{-10} \text{ m})}{(3.0 \times 10^8 \text{ m/s})} \sqrt{\frac{2 \times (8.31 \text{ J/mol-K}) \times 500 \text{ K}}{22.99 \times 10^{-3} \text{ kg/mol}}} \\ &= 1.96 \times 10^{-12} \text{ m} \\ &= 0.0196 \times 10^{-10} \text{ m} \\ &= 0.0196 \text{ Å} \approx 0.02 \text{ Å}.\end{aligned}$$

## QUESTIONS

1. Discuss the factors governing the breadth of spectral lines. Explain natural width.  
(Meerut sp. paper 2003, 01)
2. What do you understand by Doppler half-intensity breadth of spectral lines?  
(Meerut sp. paper 2002)
3. Write down the names of the causes of the breadth of the spectral lines. Deduce an expression for the Doppler half-intensity width.  
(Meerut sp. paper 2000)
4. Show that line width due to Doppler broadening increases with temperature and decreases with increasing atomic weight.
5. Account for : In hydrogen, the Doppler broadening has been the chief limiting factor to resolve the fine structure of the Balmer series.

## PROBLEMS

1. Estimate the fractional width of a spectral line of 5000 Å wavelength emitted from a level of a life-time of  $10^{-8} \text{ s}$ .  
(Meerut sp. paper 98)  
Ans.  $1.33 \times 10^{-4} \text{ Å}$
2. Calculate in Å the Doppler half-intensity breadth of mercury green line 5461 Å, the light source is at 1000 K. Given  $R = 8.31 \text{ J/(mol-K)}$ ,  $c = 3.0 \times 10^8 \text{ m/s}$ , atomic weight of mercury = 200.59 g/mol.  
(Meerut sp. paper 2000)  
Ans.  $0.0087 \text{ Å}$

# 16

## X-ray Spectra

### 1. X-ray Line Spectra

When the target of an X-ray tube is struck by energetic electrons, it emits two kinds of X-ray radiation. One of them has a continuous spectrum whose intensity distribution in wavelength depends entirely on the incident electron energy (tube voltage). The other type of radiation consists of *distinct spectral lines whose frequencies are characteristic of the material of the target*. This line spectrum is called the X-ray spectrum of the material of the target. The radiation forming the line spectrum is called as 'characteristic X-rays' \*. The frequencies of the characteristic X-rays are, in general, about 1000 times higher than the optical frequencies. Only the characteristic X-ray line spectrum is of direct interest for the study of atomic structure.

The characteristic X-ray spectra are distinguished by their simplicity. Most elements show in their X-ray spectra two series of lines, known as *K*-series and *L*-series. Each series contains a small number of lines designated as  $K_{\alpha}, K_{\beta}, \dots, L_{\alpha}, L_{\beta}, \dots$ . The wavelengths of *K*-series are generally less than 1 Å, while those of *L*-series are roughly ten times larger. Heavier elements ( $Z > 66$ ), however, show still more softer series known as *M*-, *N*-, *O*-, series.

The way in which the various series are emitted may be described by means of the example of a tungsten target used in an X-ray tube. When the tube is run at about 2500 volts, only the *M*-series appear. As the voltage is increased to 12000, the *L*-series also appear, while at 70,000 volts the (hardest) *K*-series is emitted. Thus, each series has a clearly-defined excitation potential.

### 2. Kossel's Explanation of Characteristic X-ray Spectra

Kossel was the first to explain the origin of the characteristic X-ray line spectrum on the basis of the shell structure of the atom. An atom is built up of a central positively-charged nucleus with discrete aggregates of electrons, known as *K*-shell, *L*-shell, *M*-shell, *N*-shell, etc. The maximum number of electrons which the *K*, *L*, *M*, *N*, ..... shells can hold are 2, 8, 18, 32, ..... In the normal state of the atom, the innermost shells have their full quota of electrons, while the outer shells are more or less incomplete. The electrons in the *K*-shell are attracted by the (positive) nucleus with the greatest force and as such maximum energy is required to eject them from the atom. Lesser energy is required to eject an electron from the *L*-shell, still lesser for the *M*-shell, and so on \*\*.

\* The characteristic X-rays of a material can be obtained by allowing a beam of X-rays from a hard X-ray tube to fall on that material. The material then emits secondary radiation, a part of which is the characteristic X-rays of the material.

\*\* This means that the binding energy of electron in the *K* shell is largest, and decreases in the *L*, *M*, *N*, .... shells.

Since higher quantum energies are required for the production of X-ray spectra, it can be inferred that X-ray spectra arise from the activity of the *inner* electrons. Now, an electron in one of the inner shells of an atom can only be excited to a quantum state which is not occupied by other electrons, that is, to one of the optical levels on the "surface" of the atom, or to the continuous states of positive energy. On the scale of X-ray energies, the entire energy range of optical levels is negligibly small. Thus, the condition for the excitation of an atom prior to its emission of X-ray spectra is almost the complete removal of an electron from one of the inner (closed) shells.

Now, in an X-ray tube an electron emitted from the cathode strikes the target with a tremendous velocity so that it penetrates well inside an atom of the target. If it ejects an electron from the *K*-shell of the atom, a vacancy is created in the *K*-shell. Immediately an electron from one of the outer shells, say *L*-shell, jumps to the *K*-shell, emitting an X-ray photon of energy equal to the difference in the binding energies of the electron in the *K* and *L* shells\*. Similarly, if an electron from the *M*-shell jumps to the *K*-shell, X-ray photon of higher energy is emitted. The X-ray photons emitted due to the jump of electron from the *L*, *M*, *N*, ..... shells to the *K*-shell give  $K_{\alpha}$ ,  $K_{\beta}$ ,  $K_{\gamma}$ ..... lines of the *K*-series of the spectrum.

If the electron striking the target ejects an electron from the *L*-shell of the target atom, an electron from the *M*, *N*, ..... shell jumps to the *L*-shell. In this process, X-ray photons of lesser energy are emitted. These photons form the *L*-series of the spectrum. Clearly, the frequencies of the *L*-series are smaller than those of the *K*-series. In a similar way, the formation of *M*-series, *N*-series etc. may be explained.

Whenever a vacancy is created in an inner shell, say *K*-shell, the electron from the next higher shell, the *L*-shell, is most likely to jump to the *K*-shell emitting a line of the *K*-series. The vacancy now created in the *L*-shell is filled by the jump of another electron from a still higher shell, so that a line of *L*-series is emitted. This process continues until the vacancy reaches the outermost shell where it is filled by some free electron. Thus, the emission of *K*-series is always accompanied by the emission of *L*, *M*, *N*, ..... series. Similarly, the emission of *L*-series is accompanied by the emission of *M*-, *N*-series, and so on. The *M*-and *N*-series appear only in atoms of medium and large *Z* in which the corresponding shells are filled.

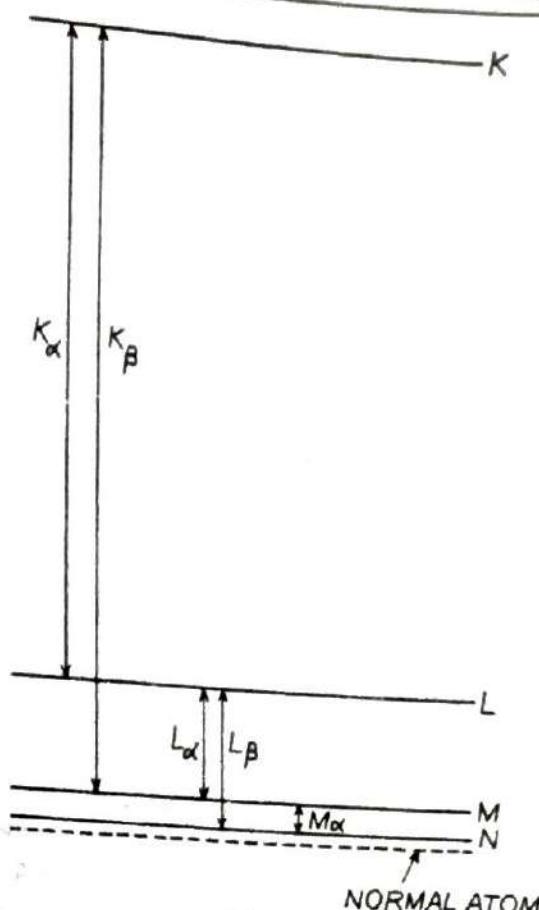
**Energy Level Diagram :** The emission of various X-ray series can be represented on an energy-level diagram (Fig. 1). It is customary in X-ray energy levels to assign zero energy to the normal state of the atom. The different levels represent the energies required to remove electrons from the different electron-shells. For example, if one of the most-firmly bound electrons of the *K*-shell is removed, the atom will be in the energy level marked *K* which we call the "*K*-level". An electron from any one of the outer levels *L*, *M*, *N*, ..... then falls into the *K*-level with emission of a *K*-series line. This follows with the emission of the other lines of the series.

The lines indicating transitions between X-ray levels are drawn with arrow-heads at each end to indicate that as an electron moves upwards, the atom moves in the down-state. Thus, in the emission of  $K_{\alpha}$  line, an electron goes from the *L* to *K* level, while the atom drops from the higher *K*-level to the lower *L*-level. Similarly, the  $K_{\beta}$  line arises

\* These binding energies are characteristics of the target atom. Hence the X-ray spectral lines have frequencies which are characteristics of the material of the target.

from the transition of the atom from the  $K$  to the  $M$ -level; the loss of energy in this case being greater. Hence the frequency of  $K_{\beta}$  line is higher than that of  $K_{\alpha}$  line. The transition of the atom from  $K$  level to the normal state, representing capture of a free electron from outside the atom into the vacancy of the  $K$ -level, would cause the emission of the series limit of the  $K$  lines. In a similar way, the lines belonging to  $L, M, N, \dots$  series may occur.

The above explanation of X-ray spectra clears up that why X-ray lines of a particular series are not emitted until the excitation potential exceeds a certain value, and that when this happens 'all' the lines of the series simultaneously appear. We have seen that the necessary condition for the emission of an X-ray line, say  $K_{\alpha}$ , is that a vacancy must be created in the  $K$ -shell by the removal of one of its electrons. This electron cannot stop in the  $L$ -shell because the latter is already full, nor in any other complete shell, but it has to go to an outer incomplete shell, or removed completely from the atom. This means that the energy involved in the ejection of the  $K$ -electron must be greater than that corresponding to any of the completed shells, roughly equal to the energy required to ionise the atom with respect to the  $K$ -electron. Since this energy is supplied by the excitation potential it is clear that the latter must be greater than that corresponding to any line of the  $K$ -series. Once the excitation potential is applied, all the lines of the  $K$ -series are emitted.

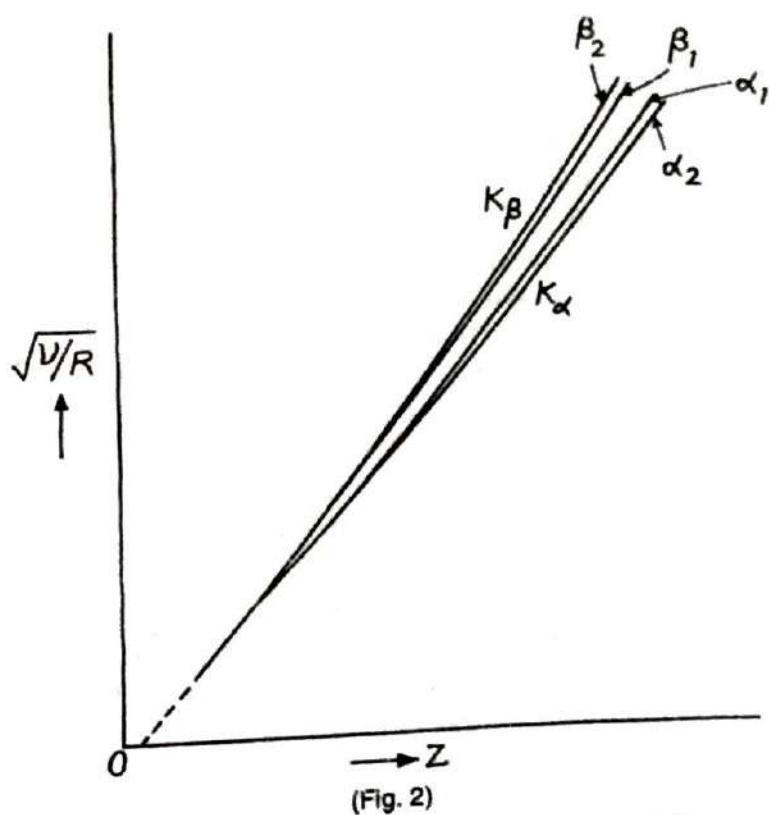


(Fig. 1)

### 3. X-ray Emission Spectra and the Moseley Law

In 1913, Moseley made a systematic study of the characteristic  $K$ -radiation. He photographed the  $K$ -spectra of a number of elements and found that the  $K$ -radiation consists of two distinct lines  $K_{\alpha}$  and  $K_{\beta}$ . Later investigators showed that in the heavier elements each of the  $K_{\alpha}$  and  $K_{\beta}$  lines is in itself a close doublet. These four lines are designated as  $K_{\alpha_1}, K_{\alpha_2}; K_{\beta_1}$  and  $K_{\beta_2}$ . Moseley found that the  $K$ -lines of elements shift toward higher frequency in a regular way with increasing atomic number. This is expressed in Moseley's law which states that ***the frequency of each corresponding K-line is approximately proportional to the square of the atomic number of the emitting element.***

Fig. 2 shows a plot of  $\sqrt{\nu/R}$  (where  $\nu$  is wave number and  $R$  is Rydberg constant) against the atomic number  $Z$ . These Moseley curves are very nearly straight lines, of which those for  $K_{\alpha_1}$  and  $K_{\alpha_2}$ , and similarly those for  $K_{\beta_1}$  and  $K_{\beta_2}$ , are very close and



approach each other toward lighter elements. From the nature of these curves, for each of them we may write :

$$\sqrt{\frac{\nu}{R}} = A(Z - \sigma)$$

$$\nu = RA^2(Z - \sigma)^2,$$

or where  $A$  and  $\sigma$  are constants for a given transition of the  $K$ -series. For the  $K_\alpha$  line,  $\sigma = 1$  and  $A^2 = \frac{3}{4}$ . By analogy with hydrogen-like atoms and Balmer's formula,

Moseley wrote

$$\nu = \frac{1}{\lambda} = R(Z - 1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right).$$

If, however, a graph be plotted between  $\sqrt{\nu/R}$  and atomic weight, there would be an appreciable departure from the straight line. Moseley therefore concluded that it is the **atomic number, and not the atomic weight, which is more fundamental to the atom.**

Like  $K$ -radiation, the  $L$ -radiation is also composed of a number of lines, and this number increases in going to heavier elements. It is remarkable that the  $L$ -lines can be divided into three groups which (group as a whole) appear successively as the excitation voltage is increased. This grouping of lines for each element and the regular shift in frequency with atomic number suggest that Moseley's law also holds for  $L$ -series lines.

For example, Moseley found that for  $L_{\beta_1}$  line,  $\sigma = 7.4$  and  $A^2 = \frac{5}{36}$ , and thus he wrote

$$\nu = \frac{1}{\lambda} = R(Z - 7.4)^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right).$$

Other series may also be represented in a similar way, using different values of  $\sigma$  and  $A^2$ .

**Explanation of Moseley's Law from Bohr Theory :** At about the same time when Moseley gave his law regarding characteristic X-ray spectra, Bohr presented his theory of the spectrum of hydrogen atom. It became evident that Bohr theory could also explain characteristic X-ray spectra if screening effects were taken into account. We know that for a  $K$ -electron the nuclear charge is partly screened off by the remaining  $K$ -electron, while for an  $L$ -electron the nuclear charge is screened off by the two  $K$ -electrons and the remaining  $L$ -electrons. Therefore, the energy state of an "inner" electron can be described by a hydrogen-like formula :

$$E_n = - \frac{R(Z - \sigma_0)^2 h c}{n^2},$$

or the energy of removal of this electron can be described by

$$E_n = + \frac{R(Z - \sigma_0)^2 h c}{n^2},$$

where  $\sigma_0$  is a measure of the screening effect of the remaining inner electrons.  $\sigma_0$  is nearly 1 for  $K$ -state and assumes larger values for higher states.

In addition to this internal screening, there is an external screening also due to the outer electrons which reduces the energy of removal of an inner electron\*. The outer shells can be considered as distributions of negative charge on spherical surfaces of suitable radii. We know that the potential energy of an electron within a spherical shell of radius  $\rho_i a_0$  and carrying a charge  $Z_i e$  is

$$U = - \frac{1}{4 \pi \epsilon_0} \frac{Z_i e^2}{\rho_i a_0}.$$

These energy terms, summed over all the outer shells, must be added to the main energy term, which is now written as

$$E_n = \frac{R(Z - \sigma_0)^2 h c}{n^2} - \frac{1}{4 \pi \epsilon_0} \sum_i \frac{Z_i e^2}{\rho_i a_0}.$$

The external screening is, however, much smaller than the internal screening and the two screenings can be included in a single screening constant  $\sigma$ , such that

$$E_n = \frac{R(Z - \sigma)^2 h c}{n^2},$$

where  $(Z - \sigma)^2 = (Z - \sigma_0)^2 - \frac{n^2}{R h c} \frac{1}{4 \pi \epsilon_0} \sum_i \frac{Z_i e^2}{\rho_i a_0}$ .

For the  $K$  and  $L$  electrons we have  $n = 1$  and  $n = 2$  respectively, so that

$$E_1 = \frac{R(Z - \sigma_1)^2 h c}{1^2}$$

$$E_2 = \frac{R(Z - \sigma_2)^2 h c}{2^2},$$

and where  $\sigma_2 > \sigma_1$ .

\*It is easy to understand that the energy required to carry an electron from an inner shell through the other outer shells to infinity is less than the energy required when the outer electrons are absent.

If an electron jumps from the  $L$ -shell to the  $K$ -shell, the energy radiated is given by

$$E_1 - E_2 = R h c \left[ \frac{(Z - \sigma_1)^2}{1^2} - \frac{(Z - \sigma_2)^2}{2^2} \right].$$

In terms of wave number, this may be written as

$$\nu = R \left[ \frac{(Z - \sigma_1)^2}{1^2} - \frac{(Z - \sigma_2)^2}{2^2} \right].$$

When  $Z$  is high enough, we may write

$$\sigma_1 = \sigma_2 = \sigma,$$

so that

$$\nu = R(Z - \sigma)^2 \left[ \frac{1}{1^2} - \frac{1}{2^2} \right].$$

Writing the constant  $\left[ \frac{1}{1^2} - \frac{1}{2^2} \right] = A^2$ , we have

$$\nu = R A^2 (Z - \sigma)^2$$

or

$$\sqrt{\frac{\nu}{R}} = A(Z - \sigma),$$

which is Moseley's law.

The application of Bohr theory to characteristics X-ray spectra was taken as one of the earliest confirmations of Bohr theory.

**Moseley's Law and the Periodic Table :** Mendeleev had arranged the elements in the periodic table in the order of increasing atomic weight. This table had a few anomalies. For example, the properties of argon, cobalt and tellurium were not in agreement with the properties of other elements of their groups.

Moseley's work on X-ray spectra indicated that an element is distinguished by the number of positive charges on the nucleus of its atom, that is, by the atomic number  $Z$ . Rutherford in the same year showed that the atomic number is the fundamental constant which decides the chemical properties of the atom. Moseley then pointed out that ***the elements in the periodic table must be arranged in the order of increasing atomic number*** (instead of atomic weight). From this point of view, he changed the positions of certain elements in the Mendeleev's periodic table. For instance, he found that the atomic number of cobalt ( $_{27}\text{Co}^{58.9}$ ) is less than that of nickel ( $_{28}\text{Ni}^{58.7}$ ) even though its atomic weight is greater. Therefore, he arranged them in the order Co, Ni instead of Ni, Co. Similarly, he placed argon ( $_{18}\text{A}^{40}$ ) before potassium ( $_{19}\text{K}^{39}$ ), and tellurium ( $_{52}\text{Te}^{127.6}$ ) before iodine ( $_{53}\text{I}^{127}$ ). When these changes were made, the anomalies of the Mendeleev's table disappeared.

While arranging the elements in the order of increasing atomic number, Moseley had to leave certain gaps such as at  $Z = 43$ , and  $Z = 72$ . He pointed out that the corresponding elements could exist but had not then been discovered. These elements were subsequently discovered; they are technetium (Tc) and hafnium (Hf) respectively.

#### 4. Fine Structure in X-ray Emission Spectra

The Kossel's explanation of X-ray line spectra in terms of electronic transitions in  $K, L, M, \dots$  levels is only a rough approximation to the facts. It does not explain the observed fine-structure in X-ray lines. In fact, when the characteristic X-ray spectral lines

are carefully examined, they are found not to be strictly single lines, but composed of a number of close components. For example, each of the lines  $K_{\alpha}, K_{\beta}, \dots$  of the  $K$ -series is a close doublet, designated as  $K_{\alpha_1}, K_{\alpha_2}, K_{\beta_1}, K_{\beta_2}, \dots$ . The lines of the other series are still more complex. This is called the 'fine structure' of X-ray characteristic lines.

**Explanation :** The X-ray line splitting is traced back to the splitting of X-ray energy levels. The structure of the absorption edges shows that although the  $K$ -level is single, but the  $L$ -level is 3-fold, the  $M$ -level is 5-fold, and so on. Higher levels which occur only in the heavier elements are even more complex.

The X-ray levels result from the removal of an electron from a given shell. It can easily be seen that a vacancy created in a completed shell produces the same levels as the presence of a single electron in that shell, *but in reverse order*. The X-ray levels therefore correspond closely to the alkali levels with their order reversed.

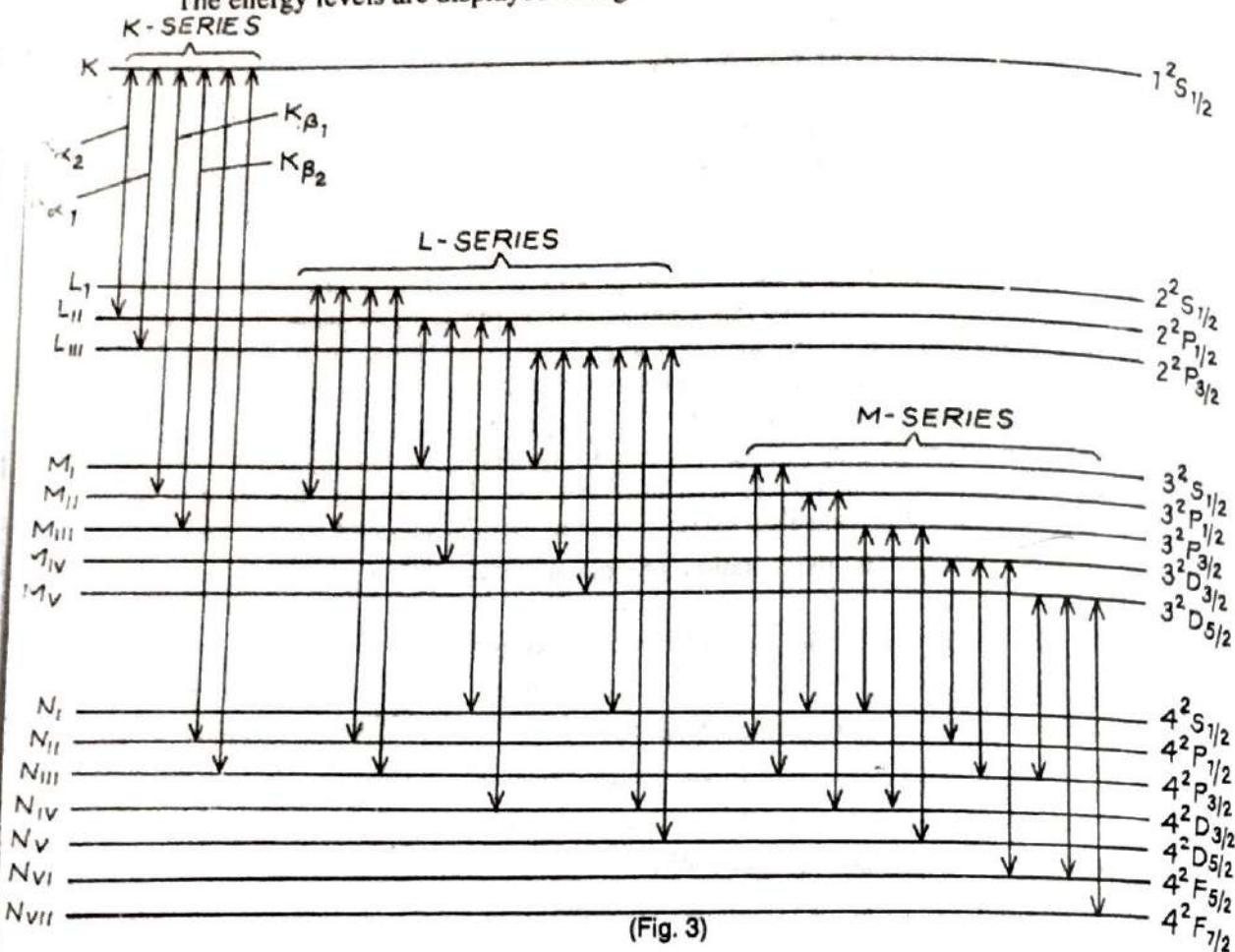
The X-ray notation of levels  $K, L, M, \dots$  represent the shells corresponding to the principal quantum number  $n = 1, 2, 3, \dots$  to which they are due by the removal of an electron. The removal of a  $1s$  electron from the neutral atom raises the atom to the highest energy state  $K$ . With one electron remaining in the  $1s$  sub-shell, this energy state is represented by  $1^2S_{1/2}$  in the notation of optical spectra. This corresponds to the  $K$ -level.

The  $2s$  electrons are the next tightly bound electrons. The removal of one  $2s$  electron again gives rise to a  $2^2S_{1/2}$  state. This corresponds to the  $L_I$  level. Next come the  $2p$  electrons, composing a completed sub-shell of six; and removal of one leaves the configuration  $2p^5$ . This gives rise to the same states as a singel electron in the  $p$  sub-shell gives. Hence the states are  $2^2P_{1/2}$  and  $2^2P_{3/2}$ . These states are inverted and correspond to  $L_{II}$  and  $L_{III}$  levels respectively.

Again the removal of a  $3s, 3p$  or  $3d$  electron leaves incomplete subshells  $3s, 3p^5$  or  $3d^9$ . These give rise to the states  $3^2S_{1/2}, 3^2P_{1/2}, 3^2P_{3/2}, 3^2D_{3/2}, 3^2D_{5/2}$  respectively. They are the  $M_I, M_{II}, M_{III}, M_{IV}, M_V$  levels respectively. A continuation of this process gives rise to  $7N$ -levels and so on. The scheme may be tabulated as below :-

Shell	$n$	Energy Level	Multiplicity of the Level	State
$K$	1	$K$	1	$1^2S_{1/2}$
$L$	2	$L_I$ $L_{II}, L_{III}$	3	$2^2S_{1/2}$ $2^2P_{1/2}, 2^2P_{3/2}$
$M$	3	$M_I$ $M_{II}, M_{III}$ $M_{IV}, M_V$	5	$3^2S_{1/2}$ $3^2P_{1/2}, 3^2P_{3/2}$ $3^2D_{3/2}, 3^2D_{5/2}$
$N$	4	$N_I$ $N_{II}, N_{III}$ $N_{IV}, N_V$ $N_{VI}, N_{VII}$	7	$4^2S_{1/2}$ $4^2P_{1/2}, 4^2P_{3/2}$ $4^2D_{3/2}, 4^2D_{5/2}$ $4^2F_{5/2}, 4^2F_{7/2}$

The energy levels are displayed in Fig. 3.



(Fig. 3)

The selection rules for X-ray spectra are the same as for optical spectra, that is,

$$\Delta n \text{ is arbitrary}$$

$$\Delta L = \pm 1$$

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

Thus, the lines  $K_{\alpha_1}, K_{\alpha_2}$  arise due to transitions from  $L_{III}$  and  $L_{II}$  to the  $K$ -level. Similarly, the three groups of lines in the  $L$ -series appear successively in transitions to the  $L_{III}, L_{II}$  and  $L_I$  levels when these levels are ionised. In this way, all the observed X-ray lines can be explained in terms of energy-level diagram.

The intensity rules derived and found to hold for optical spectra, are also found to hold in X-ray spectra. According to these rules, the theoretical intensities for the  $K_{\alpha_1}$  and  $K_{\alpha_2}$  lines have the ratio 2 : 1. Actual measurement shows that this is the case.

Certain relatively weak X-ray lines are often observed close to and on the high-frequency side of the chief lines. These are called "satellites" and arise from the removal of two or more inner electrons at the same time.

## 5. Screening Doublets and Spin-Relativity Doublets

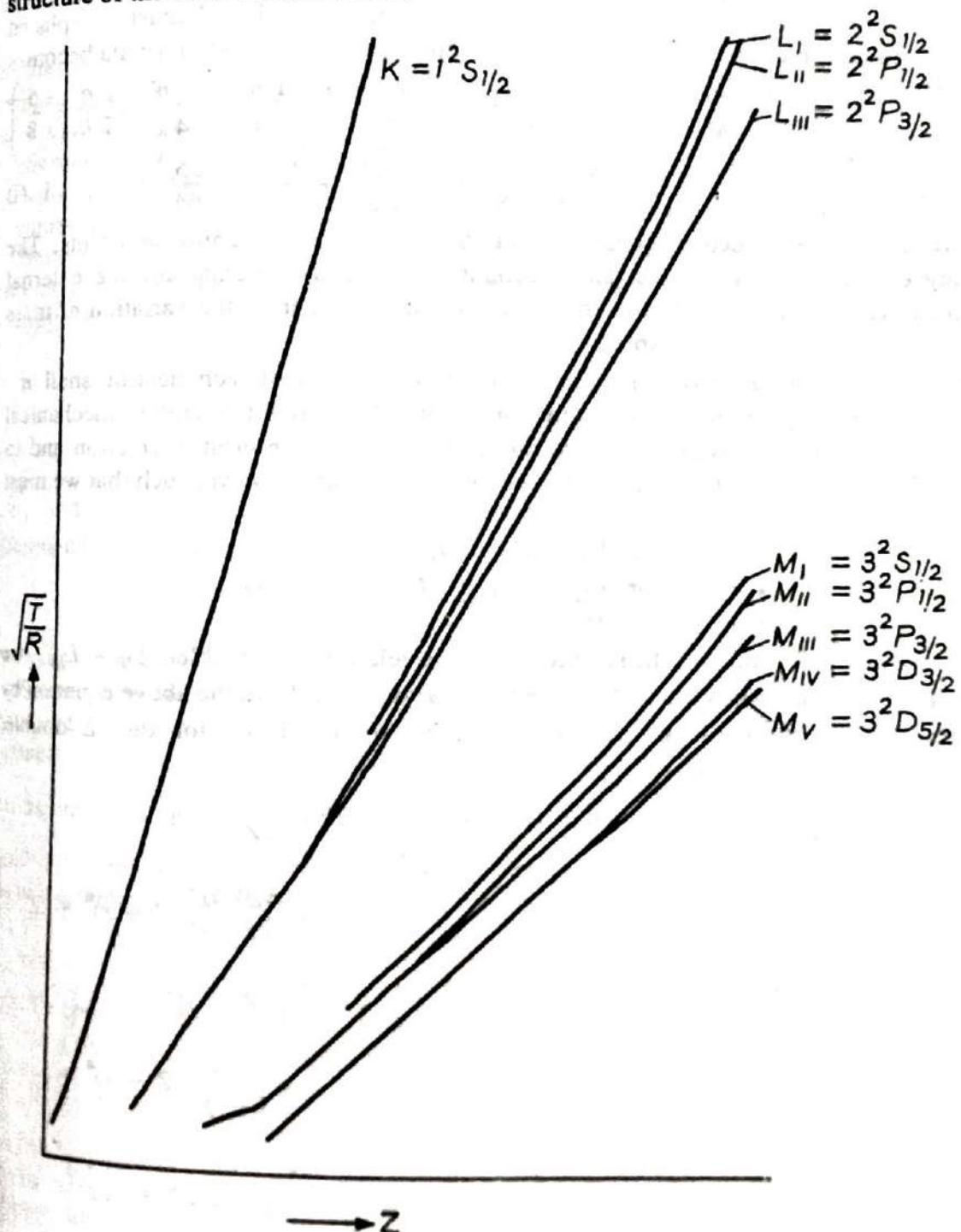
A better insight into the structure of X-ray levels is provided by Bohr-Coster diagram which is a plot between the term values, or  $\sqrt{T/R}$ , of the X-ray levels and the atomic number  $Z$  (Fig. 4).

The approximate straightness of these curves can be explained by a hydrogen-like term value formula

$$T = \frac{R(Z - \sigma)^2}{n^2}$$

Closer inspection shows that the curves are not quite straight. Their slope slightly increases with increasing  $Z$ . This can be ascribed to the external screening effects of the additional electrons.

The curves also show slight kinks at atomic numbers at which electrons begin to go into previously unoccupied sub-shells. These can be co-related with periodicities in the structure of the outer electron shells.



(Fig. 4)

It is further seen that the separations of the  $\sqrt{T/R}$  values for successive levels are of two kinds ; the separations  $L_I - L_{II}$ ,  $M_I - M_{II}$ ,  $M_{III} - M_{IV}$  etc. are independent of  $Z$  (the lines are parallel), while the separations  $L_{II} - L_{III}$ ,  $M_{II} - M_{III}$ ,  $M_{IV} - M_V$  etc. increase rapidly as  $Z$  increases (the lines diverge). The former are called 'screening doublets', and the later 'spin-relativity doublets'. The two levels belonging to a screening doublet have identical  $J$  but different  $L$ ; while those belonging to a spin-relativity doublet have identical  $L$  but different  $J$ . We shall first study the spin-relativity doublets and then the screening doublets.

**Spin-Relativity Doublets and the Regular Doublet Law :** Sommerfeld showed that an excellent agreement with the observed X-ray energy levels is obtained by using his relativistic formula for the energy of the hydrogenic atom, except that  $Z$  must be replaced by  $Z - \sigma$  in the first term, and by  $Z - s$  in the other terms, so that the formula becomes

$$T = \frac{R(Z - \sigma)^2}{n^2} + \frac{R\alpha^2(Z - s)^4}{n^4} \left( \frac{n}{k} - \frac{3}{4} \right) + \frac{R\alpha^4(Z - s)^6}{n^6} \left( \frac{1}{4} \frac{n^3}{k^3} + \frac{3}{4} \frac{n^2}{k^2} - \frac{3}{2} \frac{n}{k} + \frac{5}{8} \right) \\ + \frac{R\alpha^6(Z - s)^8}{n^8} \left( \frac{1}{8} \frac{n^5}{k^5} + \frac{3}{8} \frac{n^4}{k^4} + \frac{1}{8} \frac{n^3}{k^3} - \frac{15}{8} \frac{n^2}{k^2} + \frac{15}{8} \frac{n}{k} - \frac{35}{64} \right) + \dots \quad \dots(i)$$

where  $\alpha$  is the fine-structure constant, and  $\sigma$  and  $s$  are screening constants. The screening constant  $\sigma$  in the first term accounts for both the internal and the external screenings. The rest of the terms in the above equation arise from the variation of mass with velocity and from electron spin.

The first term in the above equation gives the main energy of each electron-shell  $n$ , and the other terms give the fine-structure corrections. According to quantum-mechanical derivation from Dirac's theory, they are due jointly to the spin-orbit interaction and to relativity. The quantum numbers given by the Dirac theory are however such that we must assign

$$k = 1 \text{ for } L_{II}, M_{II}, N_{II}, \dots$$

$$k = 2 \text{ for } L_{III}, M_{III}, M_{IV}, N_{III}, N_{IV}, \dots$$

$$k = 3 \text{ for } M_V, N_V, N_{VI}, \dots$$

Now, to obtain the formula for the separation of spin-relativity  $L$ -doublet,  $L_{II} - L_{III}$ , we must write down the term values of  $L_{II}$  and  $L_{III}$  as obtained from the above equation by substituting the values of  $k$  and  $n$  for these levels. Thus, for the  $L$ -doublet ( $2^2P_{1/2} - 2^2P_{3/2}$ ), we have

$$T_{L_{II}} = \frac{R(Z - \sigma)^2}{2^2} + \frac{R\alpha^2(Z - s)^4}{2^4} \left\{ \frac{5}{4} + \frac{21}{8} \frac{\alpha^2}{2^2} (Z - s)^2 + \frac{429}{64} \frac{\alpha^4}{2^4} (Z - s)^4 + \dots \right\}$$

and  $T_{L_{III}} = \frac{R(Z - \sigma)^2}{2^2} + \frac{R\alpha^2(Z - s)^4}{2^4} \left\{ \frac{1}{4} + \frac{1}{8} \frac{\alpha^2}{2^2} (Z - s)^2 + \frac{5}{64} \frac{\alpha^4}{2^4} (Z - s)^4 + \dots \right\}$

If  $\Delta\nu$  is the difference between these two equations, then

$$\Delta\nu = \frac{R\alpha^2(Z - s)^4}{2^4} \left\{ 1 + \frac{5}{2} \frac{\alpha^2}{2^2} (Z - s)^2 + \frac{53}{8} \frac{\alpha^4}{2^4} (Z - s)^4 + \dots \right\}$$

The introduction of the observed values of  $\Delta\nu$  in this eq. leads to values of  $s$  for the successive elements. It is observed that  $s$  is practically a constant, independent of  $Z$ . For some 40 elements from  $Z = 41$  to  $Z = 92$  Sommerfeld obtained for the  $L_{II} - L_{III}$  doublet, the average value of  $s$  as

$$s = 3.50 \pm 0.05.$$

In a similar way, we obtain for the  $M_{II} - M_{III}$  doublet ( $3^2P_{1/2} - 3^2P_{3/2}$ )

$$\Delta\nu = \frac{R\alpha^2(Z-s)^4}{3^4} \left\{ \frac{3}{2} + \frac{279}{32} \frac{\alpha^2}{3^2} (Z-s)^2 + \dots \right\}$$

From the observed doublet separations of the elements  $Z = 37$  to  $Z = 92$ , Wentzel showed that  $s$  is again a constant and has the average value

$$s = 8.5 \pm 0.4.$$

The above equations show that the doublet separation  $\Delta\nu$  for any spin-relativity doublet is approximately proportional to the fourth power of the effective atomic number  $(Z-s)$ . This is known as the 'regular-doublet law'.

**Screening Doublets and the Irregular Doublet Law :** The pairs of energy levels  $L_I - L_{II}$ ,  $M_I - M_{II}$ ,  $M_{III} - M_{IV}$  ..., characterised by the same  $J$  values but different  $L$  values are the screening doublets. The law followed by these doublets was announced by Hertz in 1920 which states that the difference between the  $\sqrt{T/R}$  values of a screening doublet is a constant independent of the atomic number  $Z$ . This is known as 'irregular doublet law' and can be formulated at once by the Moseley term values

$$T = \frac{R(Z-\sigma)^2}{n^2}$$

$$\text{or } \sqrt{\frac{T}{R}} = \frac{Z-\sigma}{n}.$$

If  $\sigma_1$  and  $\sigma_2$  are the screening constants for the two levels of a screening doublet, the difference is written as

$$\Delta \sqrt{\frac{T}{R}} = \frac{\sigma_1 - \sigma_2}{n} = \frac{\Delta\sigma}{n},$$

which is independent of  $Z$ . This is the irregular doublet law.

Sommerfeld showed that the irregular doublet law can be further refined by using the 'reduced term values' rather than the observed term values. The values of the screening constants  $s$  are determined from the spin-relativity doublets and substituted in eq. (i), and then the value of the term  $\frac{R(Z-\sigma)^2}{n^2}$  is calculated. This is known as the 'reduced term value'  $T'$ , and is the same for both levels of a spin-relativity doublet. Thus, taking the first two terms of eq. (i), we get

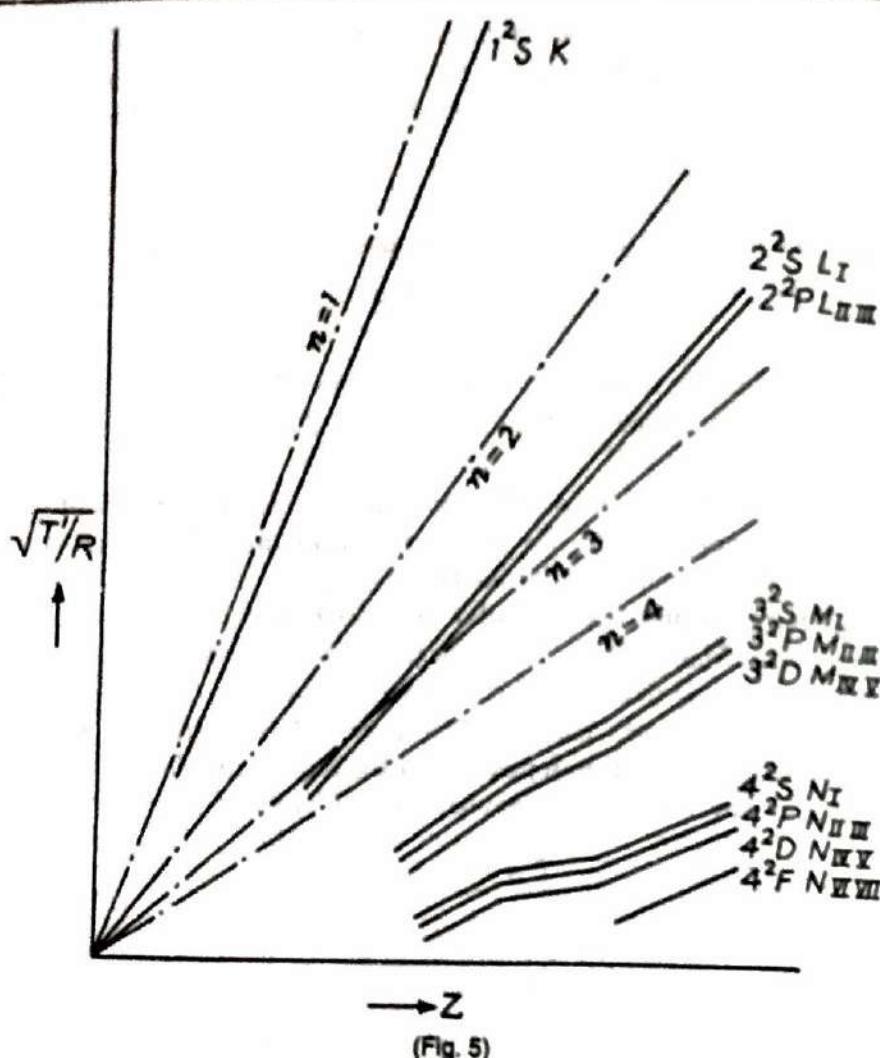
$$T' = T - \frac{R\alpha^2(Z-s)^4}{n^4} \left( \frac{n}{k} - \frac{3}{4} \right).$$

Here  $T$  represents the observed term values given directly by the absorption limit.

Using the reduced term values, the irregular doublet law may be written as

$$\Delta \sqrt{\frac{T'}{R}} = \frac{\Delta\sigma}{n} = \text{constant.}$$

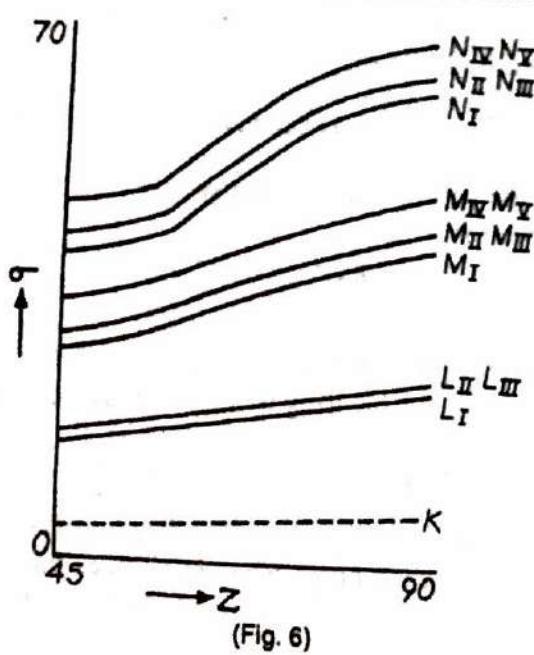
That this holds accurately is clear from the Moseley diagrams (Fig. 5) where the curves for a given  $n$  are quite parallel to each other. The dotted lines through the origin represent hydrogen-like atoms with no screening. The difference between these ideal curves and the



(Fig. 5)

corresponding reduced curves  $\left( \frac{Z}{n} - \frac{Z - \sigma}{n} \right)$ , multiplied by  $n$  gives directly the screening constant  $\sigma$  at various  $Z$ .

$\sigma$  has been plotted against  $Z$  in Fig. 6. The sudden change in the slope of the  $M$  and  $N$  curves at roughly  $Z = 57$  and  $Z = 71$  shows the increased screening effect of the



(Fig. 6)

$4f$  electrons added in the rare-earth elements. Their addition causes an increase in the external screening.

## 6. X-ray Absorption Spectra

When a beam of continuous X-rays is passed through the film of a substance and the transmitted beam is sent into an X-ray spectrograph, an X-ray absorption spectrum of that substance is obtained. The nature of this spectrum is quite different from the X-ray emission spectrum of the same substance. None of the emission lines  $K_{\alpha}, K_{\beta}, \dots$  appears in the absorption spectrum. Instead, the (absorption) spectrum shows a *continuous* region of absorption bounded by a *sharp edge* in the position of the limit of the emission  $K$ -series (Fig. 7). When successive elements in the periodic table are used as absorbers, the edge shifts toward higher frequency. Thus, these edges are characteristic of the absorber element and are called 'absorption edges'. In each case, the frequency  $\nu_K'$  of the absorption edge is called ' $K$ -absorption limit' of the particular element. Frequencies higher than  $\nu_K'$  are strongly absorbed; lower frequencies are almost transmitted.

**Explanation :** There are two features of the X-ray absorption spectrum which are to be explained:

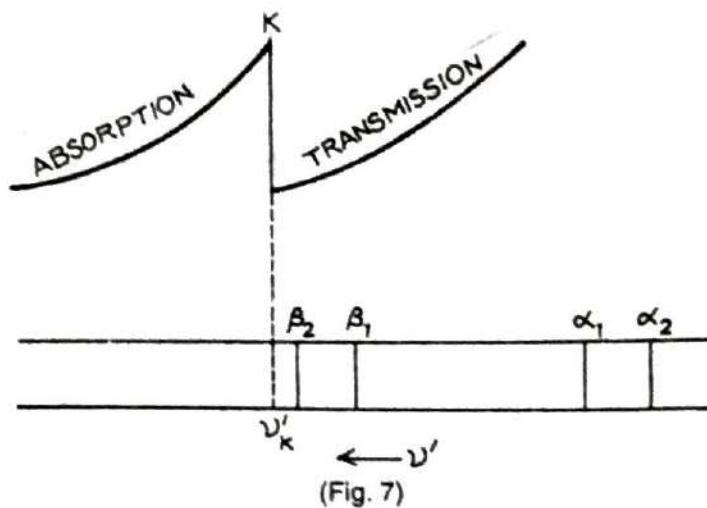
(i) **Absence of Discrete Absorption Lines :** The  $K_{\alpha}$ -line (for example) in emission occurs when an electron drops from the  $L$ -shell to the  $K$ -shell. In absorption, this line would occur only if an electron from the  $K$ -shell, after absorbing an X-ray photon of the required energy from the continuous beam, could go to the  $L$ -shell. But this does not happen because the  $L$ -shell has already its full quota of 8 electrons and so it cannot receive any further electron (Pauli's exclusion principle). Hence the  $K_{\alpha}$ -line cannot be observed as absorption line. This is true for all the X-ray emission lines that are commonly observed.

(ii) **Appearance of Sharp Absorption Edges :** An X-ray photon can, however, be absorbed by an atom if it has enough energy to remove an inner electron to infinity where the shells no longer exist. If  $W_K$  is the energy required to remove a  $K$ -electron, then a photon of frequency  $\nu'$  can eject a  $K$ -electron provided  $\nu' \geq \nu_K'$ , where

$$h\nu_K' = W_K.$$

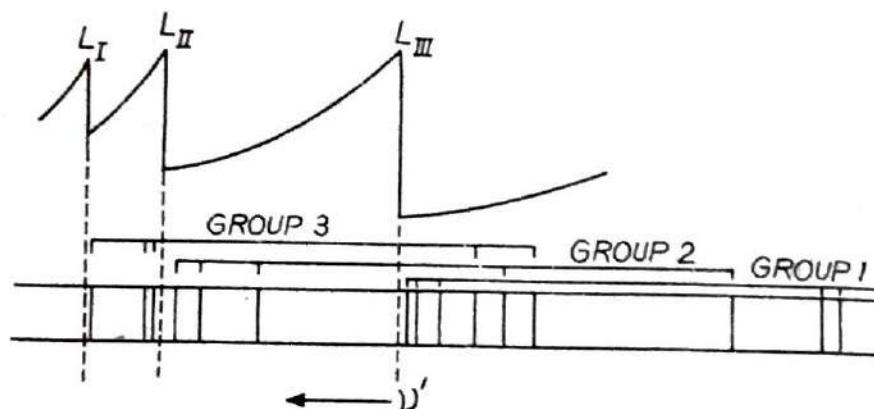
Photons of frequency lower than  $\nu_K'$  would be transmitted by the absorbing element. At the frequency  $\nu_K'$ , absorption in the  $K$ -shell suddenly starts and thereafter continues for all frequencies higher than  $\nu_K'$ . Hence an absorption continuum is observed.

As  $Z$  increases,  $W_K$  increases because of the increasing nuclear attraction, and so  $\nu_K'$  also increases. Hence for successive elements in the periodic table the absorption edge shifts towards higher frequency.



Thus, the  $K$ -absorption edge observed in X-ray spectra of elements corresponds to the photoelectric ejection of an electron from the  $K$ -shell of that element; its frequency  $v_K'$  gives exactly the required energy  $W_K$ . This means that the  $K$ -absorption edge directly gives the  $K$  energy level. Absorption beyond the edge indicates that the  $K$ -electron passes to infinity with kinetic energy  $E_K$  given by Einstein's photoelectric equation ( $E_K = h v' - W_K = h v' - h v_{K}'$ ). Since each element gives only one  $K$ -absorption edge, we conclude that the  $K$ -shell has only a single energy level.

**Importance of Absorption Edges :** When the X-ray absorption spectrum is taken in the  $L$ -region, again a continuum is observed but now with three absorption edges,  $L_I$ ,  $L_{II}$ ,  $L_{III}$  (Fig. 8.). We know that the  $L$ -emission lines form three groups according to



(Fig. 8)

their excitation voltages, indicating that the  $L$ -shell has three energy levels. The three edges  $L_I$ ,  $L_{II}$ ,  $L_{III}$  directly give these energy levels.

Similarly, the  $M$ -absorption spectra of heavier elements show five absorption edges which give the five energy levels of  $M$ -shell,  $N$ -spectra give seven edges, and so on. Thus, the absorption edges provide a direct means of determining the X-ray energy levels of elements.

## 7. Structure of X-ray Absorption Edges

X-ray absorption edges are not quite sharp and often show a complicated structure. On the low-frequency side of the absorption edge some close, fine absorption lines are observed ; while on the high-frequency side subsidiary edges appear.

Kossel, in 1920, suggested that the ejected electron, after absorbing the quantum of radiation, may sometimes not be removed completely from the atom but instead be simply raised to an unoccupied *outer* level. The softest X-radiation absorbed would then have a frequency corresponding to the energy required to lift an electron from an inner level to the most stable of the unoccupied outer levels. Such processes would lead to an absorption edge accompanied by absorption lines on the low-frequency side. The edge itself would constitute the series limit for these lines. These lines should be closely spaced because the energy differences between the outer levels are of the optical magnitudes.

It is also possible for the absorbed quantum of radiation to remove two electrons from the atom. This would give rise to a number of subsidiary edges close to and on the high-frequency side of the main absorption edge.

It is further found that the position and structure of the main absorption edge for a given element change with the chemical composition of the substance producing the edge. For example, the  $K$ -absorption edge of sulphur, as measured from different compounds, lies between  $4.987 \text{ \AA}$  and  $5.012 \text{ \AA}$ . Pauling has attributed this shifting of the edge to the difference in the electrostatic fields within the material used as absorber.

## 8. X-ray Spectra and Optical Spectra

There are many striking features of the characteristic X-ray spectra which are not found in optical spectra. The main differences between the two spectra are as follows :

(i) The frequencies in X-ray spectra are about a thousand times higher than those in optical spectra. This indicates that X-ray spectra arise from electron transitions among the inner completed shells of very firmly bound electrons. This is also in agreement with the fact that the X-ray spectra of a free element is same as that of its chemical compounds. The optical spectra, on the other hand, arise from transitions of the outermost electrons of the atom.

(ii) The X-ray spectra arise as a result of complete removal of an electron from an inner shell of the atom. In the emission of optical spectra, an outer electron is simply raised to a higher level, and is not completely removed.

(iii) The most striking feature of X-ray line spectra is that the frequencies of the lines increase steadily, not periodically, from element to element, that is, with increasing atomic number  $Z$ . This is because the characteristics of X-ray spectra depend on the binding energies of the electrons in the innermost shells. These energies increase uniformly from element to element owing to the increasing nuclear charge, and are not affected by the periodic changes in the number of outer electrons of the atom. This is why *the X-ray spectra of elements of nearby atomic numbers are qualitatively very similar*.

The optical spectra, on the other hand, show abrupt, periodic changes from one element to the next. This is because the electronic structure at the surface of the atom changes periodically from element to element.

(iv) Another striking feature of X-ray spectra is that X-ray emission spectra are entirely different from X-ray absorption spectra. The X-ray emission spectra consist of discrete lines, while the absorption spectra consist of continuous regions bounded by sharp edges. This is because in absorption spectra, the X-radiation of energy just sufficient to remove an electron from an inner shell as well as the radiation of higher energies are absorbed, but that of lower energies are not absorbed. Line absorption does not occur because the upper energy levels to which the electron would have to be raised are already occupied.

In case of optical spectra, emission and absorption spectra are identical. We get absorption lines at the same frequencies as the corresponding emission lines.

## 9. Auger Effect

When a  $K$ -electron is ejected from an atom say, by the absorption of an X-ray photon, the resulting vacancy in the  $K$ -shell is filled by the transition of an electron from an outer shell, for example, the  $L$ -shell which corresponds to a transition of the atom from the  $K$ -level to the  $L$ -level. This transition is usually accompanied by the emission of characteristic X-ray photon of energy

$$h\nu' = E_K - E_L$$

In some cases, however, the entire energy emitted in the transition is directly absorbed by another  $L$ -electron which is thereby ejected. Since there are now two vacancies in the  $L$ -shell, the resulting energy level of the atom will be different from the  $L$ -level and may now be called an  $LL$ -level, its energy being  $E_{LL}$ . The kinetic energy of the ejected **second** electron will be

$$\frac{1}{2} m v^2 = E_K - E_{LL}.$$

Such a *radiationless* transition resulting in the ejection of two electrons from the same atom is known as 'Auger transition'. The phenomenon is known as 'Auger effect' after the name of its discoverer Auger.

The Auger effect is competitive with X-ray emission in most atoms, but the resulting ejected electrons are usually absorbed in the target material, from which the X-rays readily emerge.

### SOLVED PROBLEMS

- 1. What are the most energetic X-rays emitted in each case when 40-keV electrons bombard (i) Mo target ( $Z = 42$ ), (ii) Cu target ( $Z = 29$ ) ?**

**Solution.** An X-ray photon of *maximum* energy is emitted when the electron loses the whole of its energy in a *single* collision with the target atom. Thus, the maximum energy of the emitted X-rays is 40 keV, whichever be the target.

- 2. Calculate the minimum voltage that must be applied to an X-ray tube to produce X-ray photons of  $\lambda \sim 0.1 \text{ \AA}$ . (Given :  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $e = 1.6 \times 10^{-19} \text{ C}$ ).**

**Solution.** When electrons accelerated through a potential  $V$  strike a target, the maximum frequency  $v_{max}$  (or minimum wavelength  $\lambda_{min}$ ) of the emitted X-ray photon is given by

$$eV = h v_{max} = h \frac{c}{\lambda_{min}}.$$

The minimum voltage for 0.1-Å X-ray photon is

$$\begin{aligned} V &= \frac{hc}{e \lambda_{min}} \\ &= \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{(1.6 \times 10^{-19} \text{ C})(0.1 \times 10^{-10} \text{ m})} \\ &= 1.24 \times 10^5 \text{ J/C} = 1.25 \times 10^5 \text{ V}. \end{aligned}$$

- 3. If the series limit of the Balmer series for hydrogen is 364.6 nm, calculate the atomic number of the element which gives X-ray wavelength down to 0.1 nm (that is, of K-series).**

**Solution.** The Balmer's formula for hydrogen is

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \dots \dots \infty$$

For series limit ( $n = \infty$ ), we have

$$\frac{1}{\lambda_\infty} = \frac{R}{4}.$$

$$\therefore R = \frac{4}{\lambda_\infty} = \frac{4}{364.6 \text{ nm}}.$$

By Moseley's law, the X-ray wavelengths of  $K$ -series are given by

$$\frac{1}{\lambda} = R(Z - 1)^2 \left( \frac{1}{1^2} - \frac{1}{n^2} \right).$$

The minimum wavelength of this series would occur when  $n = \infty$ , and so

$$\frac{1}{\lambda} = R(Z - 1)^2.$$

Here minimum  $\lambda = 0.1$  nm.

$$\therefore \frac{1}{0.1 \text{ nm}} = \frac{4}{364.6 \text{ nm}} (Z - 1)^2$$

$$(Z - 1)^2 = \frac{364.6 \text{ nm}}{0.1 \text{ nm} \times 4} = 911.5$$

$$Z - 1 = 30.2.$$

$$\text{or} \quad \therefore Z = 31 \text{ (gallium).}$$

4. How much energy goes into the quantum emitted when an  $L$ -electron (that is, an electron from the  $n = 2$  state) drops into the empty  $K$ -state in copper ( $Z = 29$ )? Given  $R = 109737 \text{ cm}^{-1}$  and  $1 \text{ cm}^{-1} = 1.239 \times 10^{-4} \text{ eV}$ .

**Solution.** From Moseley's law, the X-ray wavelength emitted when an  $n = 2$  electron drops to  $n = 1$  state is

$$\frac{1}{\lambda} = R(Z - 1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right),$$

which corresponds to the  $K_{\alpha}$ -line. Thus

$$\frac{1}{\lambda} = \frac{3}{4} R(Z - 1)^2.$$

Putting the given values of  $R$  and  $Z$ :

$$\frac{1}{\lambda} = \frac{3}{4} (109737 \text{ cm}^{-1}) (29 - 1)^2 = 6.4525 \times 10^7 \text{ cm}^{-1}.$$

The corresponding energy emitted is

$$(6.4525 \times 10^7 \text{ cm}^{-1}) \times (1.239 \times 10^{-4} \text{ eV/cm}^{-1}) = 7994.6 \text{ eV}.$$

5. Estimate the value of the wavelength of  $K_{\alpha}$ -line of silver ( $Z = 47$ ). Given  $R = 109737 \text{ cm}^{-1}$ .

**Solution.** From Moseley's law, the wavelength of  $K_{\alpha}$ -line is given by

$$\begin{aligned} \frac{1}{\lambda} &= R(Z - 1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \\ &= \frac{3}{4} R(Z - 1)^2 \\ &= \frac{3}{4} \times 109737 \text{ cm}^{-1} \times (46)^2 = 1.74 \times 10^8 \text{ cm}^{-1}. \end{aligned}$$

$$\therefore \lambda = \frac{1}{1.74 \times 10^8} \text{ cm} = \frac{10^8}{1.74 \times 10^8} \text{ Å} = 0.57 \text{ Å}.$$

6. What element has a  $K_{\alpha}$  X-ray line of wavelength  $1.785 \text{ Å}$ ? Of Wavelength  $0.712 \text{ Å}$ ?  $R = 109737 \text{ cm}^{-1}$ .

**Solution.** From Moseley's law, the wavelength of  $K_{\alpha}$ -line is given by

$$\frac{1}{\lambda} = R(Z - 1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R(Z - 1)^2.$$

$$\therefore (Z - 1)^2 = \frac{4}{3R\lambda}$$

$$= \frac{4}{3 \times 109737 \text{ cm}^{-1} \times (1.785 \times 10^{-8} \text{ cm})}$$

$$= 680.7$$

or

$$Z - 1 = \sqrt{680.7} = 26$$

or

$$Z = 27 \text{ (cobalt).}$$

Similary, we can show that element having a  $K_{\alpha}$  X-ray line of  $0.712 \text{ \AA}$  is  $Z = 42$  (molybdenum).

**7. If the  $K_{\alpha}$ -radiation of Mo ( $Z = 42$ ) has a wavelength of  $0.71 \text{ \AA}$ , calculate the wavelength of the corresponding radiation of Cu ( $Z = 29$ ). (Meerut 99 S)**

**Solution.** From Moseley's law for  $K_{\alpha}$ -line, we have

$$\frac{1}{\lambda} \propto (Z - 1)^2.$$

$$\therefore \frac{\lambda_{Cu}}{\lambda_{Mo}} = \frac{(Z_{Mo} - 1)^2}{(Z_{Cu} - 1)^2} = \frac{(41)^2}{(28)^2}.$$

But  $\lambda_{Mo} = 0.71 \text{ \AA}$ .

$$\therefore \lambda_{Cu} = (0.71 \text{ \AA}) \times \frac{(41)^2}{(28)^2} = 1.52 \text{ \AA}.$$

**8. The copper ( $Z = 29$ ) target in an X-ray tube has some impurity. In the spectrum of X-rays emitted from the tube, there appears a line of wavelength  $0.54 \text{ \AA}$  in addition to the copper  $K_{\alpha}$  line of wavelength  $1.54 \text{ \AA}$ . Use Moseley's law to detect the impurity.**

**Solution.** Let  $Z_i$  be the atomic number of the impurity atom, and  $\lambda_i$  the wavelength of its  $K_{\alpha}$  line. Now, from Moseley's law for  $K_{\alpha}$ -line, we have

$$\frac{1}{\lambda} \propto (Z - 1)^2.$$

$$\therefore \frac{\lambda_{Cu}}{\lambda_i} = \frac{(Z_i - 1)^2}{(Z_{Cu} - 1)^2}$$

or

$$Z_i - 1 = (Z_{Cu} - 1) \sqrt{\frac{\lambda_{Cu}}{\lambda_i}}$$

$$= (29 - 1) \sqrt{\frac{1.54 \text{ \AA}}{0.54 \text{ \AA}}}$$

$$= 28 \times 1.69 = 47.3$$

or

$$Z_i = 47.3 + 1 = 48.$$

The impurity atom is of cadmium ( $Z = 48$ ).

**9. If the  $K$ -,  $L$ -,  $M$ -energy levels of platinum involved in the emission of the  $K$ -series of X-rays of this element are 78,000, 12,000 and 3,000 eV respectively, calculate the wavelengths of the  $K_{\alpha}$  and  $K_{\beta}$  lines of platinum ( $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ ).**

**Solution.** The  $K_{\alpha}$ -line is emitted when an electron drops from the  $L$ -shell to the  $K$ -shell. Hence the energy of a  $K_{\alpha}$ -photon is the difference in energies of these two shells, that is

$$\begin{aligned} h v_{K_{\alpha}}' &= 78000 - 12000 = 66000 \text{ eV} \\ &= 66000 \text{ eV} \times (1.6 \times 10^{-19} \text{ J/eV}) = 66000 \times 1.6 \times 10^{-19} \text{ J.} \\ \therefore v_{K_{\alpha}}' &= \frac{66000 \times 1.6 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ Js}} = 15.9 \times 10^{18} \text{ s}^{-1}. \end{aligned}$$

The corresponding wavelength is

$$\begin{aligned} \lambda_{K_{\alpha}} &= \frac{c}{v_{K_{\alpha}}'} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{15.9 \times 10^{18} \text{ s}^{-1}} \\ &= 0.189 \times 10^{-10} \text{ m} = 0.189 \text{ Å.} \end{aligned}$$

The  $K_{\beta}$ -line is emitted when an electron drops from the  $M$ -shell to the  $K$ -shell. Thus

$$h v_{K_{\beta}}' = 78000 - 3000 = 75000 \text{ eV.}$$

$$\therefore v_{K_{\beta}}' = \frac{75000 \times 1.6 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ Js}} = 18.1 \times 10^{18} \text{ s}^{-1}$$

$$\begin{aligned} \text{or } \lambda_{K_{\beta}} &= \frac{c}{v_{K_{\beta}}'} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{18.1 \times 10^{18} \text{ s}^{-1}} \\ &= 0.166 \times 10^{-10} \text{ m} = 0.166 \text{ Å.} \end{aligned}$$

10. If the  $K$ -absorption limit of uranium is  $0.107 \text{ Å}$ , find the minimum potential difference required across an X-ray tube to excite the  $K$ -series?

**Solution.** If  $v_K'$  be the frequency of the  $K$ -absorption limit for the target material, the critical voltage  $V_K$  required is given by

$$e V_K = h v_K' = \frac{h c}{\lambda_K}.$$

$$\therefore V_K = \frac{h c}{e \lambda_K}.$$

Putting the known values of  $h$ ,  $c$  and  $e$  and the given value of  $\lambda_K$ , we get

$$\begin{aligned} V_K &= \frac{(6.63 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ m s}^{-1})}{(1.6 \times 10^{-19} \text{ C})(0.107 \times 10^{-10} \text{ m})} \\ &= 116 \times 10^3 \text{ V} = 116 \text{ kV.} \end{aligned}$$

## QUESTIONS

- What is characteristic X-ray spectrum in emission? Explain its origin. Show it on an energy-level diagram.
- State and explain Moseley's law in X-rays. *(Meerut 2006, 04, 02)*
- Enumerate and deduce Moseley's law and show how it has been used in removing some of the defects in the periodic table. *(Meerut 2003, 99)*
- Describe and explain the fine structure observed in X-ray emission spectrum. *(Meerut 2004, 02)*
- What are spin-relativity and screening doublets in X-ray spectra. Explain their origin. Show that the doublet separation for spin-relativity doublet is proportional

- to the fourth power of the effective atomic number, whereas the separation for screening doublet is independent of atomic number. (Meerut 2000 S, 95 S)
6. What are regular and irregular doublet laws in X-ray spectra ? Discuss the light they throw on atomic structure. (Meerut 2003, 02 S 01, 95)
7. Explain the characteristic X-ray spectra in emission and absorption. How do they differ from optical spectra ? (Meerut 2004 S, 96)
8. Give the origin of X-ray spectra and explain why the absorption spectra are continuous with edges.
9. Explain why are emission and absorption X-ray spectra different. Give importance of absorption edges. How would you account for the finite width of absorption edges in X-ray spectra ? (Meerut 2000, 94)
10. In relation to  $L_I$ ,  $L_{II}$  and  $L_{III}$  levels in X-rays, discuss the screening doublets and spin-relativity doublets. State the laws governing their doublet separations with variation of  $Z$ .
11. Account for :
- (i) The X-ray spectra of elements of nearby atomic numbers are qualitatively very similar, while the optical spectra of these elements may differ considerably.
  - (ii) The optical spectra of elements show periodic characteristics with increasing  $Z$ , while X-ray characteristic spectra show continuous order through all  $Z$  values. (Meerut 96)
  - (iii) In optical atomic absorption generally discrete lines are observed whereas X-ray absorption show continua with edges. (Meerut 99 S, 90)
12. What is Auger effect ? Explain in brief.
-

## Types of Molecular Spectra and Molecular Energy States

### 1. Separation of Electronic and Nuclear Motion : The Born-Oppenheimer Approximation

A diatomic molecule is a stable arrangement of two atoms (nuclei and electrons), separated by a distance. If the two atoms forming the molecule are similar, the molecule is said to be a 'homonuclear' molecule, such as  $H_2$ ,  $N_2$ ,  $O_2$ , ..... molecules. On the other hand, if the two atoms are different, the molecule is said to be a 'heteronuclear' molecule, such as  $HCl$ ,  $CO$ ,  $CN$ , ..... molecules. The line joining the nuclei of the constituent atoms of a molecule is called the 'internuclear axis' of the molecule.

The emission and absorption spectra of molecules arise from transitions between the allowed energy states of the molecules. The energy-level scheme of molecules is, however, different from that of atoms, and is relatively complicated. There are two main reasons for this. Firstly, we cannot classify molecular energy states according to the electronic angular momentum  $L$  (as we do in atoms) which is not conserved in molecules. However, in diatomic molecules the total charge distribution is symmetrical about the internuclear axis so that the component of angular momentum about this axis is conserved and is used to classify molecular energy states. Secondly, the nuclear motion in molecules cannot be ignored (as we can do in atoms). In a diatomic molecule, the nuclei vibrate along the internuclear axis, and also the whole system rotates about its centre of mass. The energy of each of these vibrational and rotational motions is quantised. Hence the energy levels in a molecule are much more than in an atom.

Obviously, the quantum-mechanical Hamiltonian operator for a molecule, containing terms for electronic and nuclear motions and their interactions, is so complex that the exact solutions of the molecular Schrödinger's equation are not possible. However, in a molecule, the relatively much more massive nuclei move much more slowly than the electrons. Therefore, to a first approximation, the motion of the electrons at any instant is the same as if the nuclei were fixed in space. Born and Oppenheimer presented quantum-mechanical equivalent of this approximation. They showed that the molecular Schrödinger equation can be solved in two steps :

(1) firstly, the wave equation for the electronic motion alone is solved in which nuclear coordinates appear simply as parameters,

(2) then, the wave equation for the motion of the nuclei alone is solved in which the characteristic eigenvalue of the electronic equation occurs as part of the potential energy function of the nuclear motion.

Let us formulate this approximation :

The complete Hamiltonian operator  $\left( -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right)$  for a molecule consisting of  $a$  nuclei and  $i$  electrons is

$$H = - \sum_{\alpha} \frac{\hbar^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 - \sum_i \frac{\hbar^2}{8\pi^2 m} \nabla_i^2 + V_{nn} + V_{ne} + V_{ee}, \quad \dots(i)$$

where the first term represents the kinetic energy operator of all the nuclei with masses  $M_1, M_2, \dots, M_a$ ; the second term represents the kinetic energy operator of all the electrons; and  $V_{nn}$ ,  $V_{ne}$  and  $V_{ee}$  are the potential energy functions arising from nuclear-nuclear, nuclear-electronic, and electronic-electronic interactions respectively. The total eigenfunction  $\psi$  and the total eigenvalue  $E$  are given by the wave equation

$$H\psi = E\psi. \quad \dots(ii)$$

When the nuclei are assumed to be in fixed positions; the first term in eq. (i) is zero and the term  $V_{nn}$  is constant; so that the Hamiltonian for the electrons would be

$$H_e = - \sum_i \frac{\hbar^2}{8\pi^2 m} \nabla_i^2 + V_{ne} + V_{ee}. \quad \dots(iii)$$

The electronic eigenfunctions  $\psi_e$  and the corresponding electronic eigenvalues  $E_e'$  are given by the wave equation

$$H_e \psi_e = E_e' \psi_e. \quad \dots(iv)$$

Let us represent the remaining terms in eq. (i) by  $H_n$ , so that

$$H_n = - \sum_{\alpha} \frac{\hbar^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 + V_{nn}, \quad \dots(v)$$

and

$$H = H_n + H_e.$$

Now, following Born and Oppenheimer, let us make the assumption that the eigenfunction  $\psi$  for the whole system may be expressed as the product  $\psi_e \psi_n$ ; where  $\psi_e$  is a function of the coordinates of both the nuclei and the electrons, and  $\psi_n$  is a function of the coordinates of the nuclei only. Then, eq. (ii) can be written as

$$H\psi_e \psi_n = E\psi_e \psi_n$$

$$\text{or } - \sum_{\alpha} \frac{\hbar^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 \psi_e \psi_n - \sum_i \frac{\hbar^2}{8\pi^2 m} \nabla_i^2 \psi_e \psi_n + (V_{nn} + V_{ne} + V_{ee}) \psi_e \psi_n = E \psi_e \psi_n. \quad \dots(vi)$$

$$\text{Now, } \nabla_{\alpha}^2 \psi_e \psi_n = \psi_n \nabla_{\alpha}^2 \psi_e + \psi_e \nabla_{\alpha}^2 \psi_n + 2 \nabla_{\alpha} \psi_e \nabla_{\alpha} \psi_n$$

$$\text{and } \nabla_i^2 \psi_e \psi_n = \psi_n \nabla_i^2 \psi_e^*. \quad \dots$$

The electronic eigenfunction  $\psi_e$  is only a slowly-varying function of the nuclear coordinates, that is,  $\nabla_{\alpha} \psi_e \ll \nabla_{\alpha} \psi_n$ . Hence we can neglect the terms containing  $\nabla_{\alpha}^2 \psi_e$  and  $\nabla_{\alpha} \psi_e$  in the above two relations. This is the essential element in the Born-Oppenheimer approximation. Thus

$$\nabla_{\alpha}^2 \psi_e \psi_n \approx \psi_e \nabla_{\alpha}^2 \psi_n$$

$$\text{and } \nabla_i^2 \psi_e \psi_n = \psi_n \nabla_i^2 \psi_e.$$

Making these substitutions in eq. (vi), we get

\* Here  $\psi_n$  has been treated constant because in electronic wave equation involving  $\nabla_i$  the nuclear coordinates are assumed to be fixed.

$$-\Psi_e \sum_{\alpha} \frac{h^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 \Psi_n - \Psi_n \sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 \Psi_e + (V_{nn} + V_{ne} + V_{ee}) \Psi_e \Psi_n = E \Psi_e \Psi_n$$

or  $-\frac{\Psi_e}{\Psi_n} \sum_{\alpha} \frac{h^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 \Psi_n + \left[ - \sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 \Psi_e + (V_{ne} + V_{ee}) \Psi_e \right] + V_{nn} \Psi_e = E \Psi_e$

The term inside the brackets equals  $E_e' \Psi_e$  in view of eq. (iii) and (iv).

$$\therefore -\frac{\Psi_e}{\Psi_n} \sum_{\alpha} \frac{h^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 \Psi_n + E_e' \Psi_e + V_{nn} \Psi_e = E \Psi_e$$

$$\text{or } -\sum_{\alpha} \frac{h^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 \Psi_n + E_e' \Psi_e + V_{nn} \Psi_e = E \Psi_e$$

$$\text{or } \left[ -\sum_{\alpha} \frac{h^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 + E_e' + V_{nn} \right] \Psi_n = E \Psi_n \quad \dots(\text{vii a})$$

This, using eq. (v), can be written as

$$(H_n + E_e') \Psi_n = E \Psi_n, \quad \dots(\text{vii b})$$

Eq. (vii a) or (vii b) is the wave equation for the nuclear motion. The effective Hamiltonian is  $H_n + E_e'$  or  $\left[ -\sum_{\alpha} \frac{h^2}{8\pi^2 M_{\alpha}} \nabla_{\alpha}^2 + E_e' + V_{nn} \right]$ . It contains the characteristic eigenvalue  $E_e'$  of the electronic wave equation as part of the potential energy function for the nuclear motion. The other part of this function is provided by nuclear-nuclear interaction term  $V_{nn}$ .

Thus, the Born-Oppenheimer approximation enables us to solve the complete molecular wave equation in the following way :

(1) The electronic wave equation (iv) for a given electronic state of the molecule is solved for a range of values of nuclear coordinates (internuclear separations). This gives  $\Psi_e$  and  $E_e'$  as continuous functions of nuclear coordinates.

(2) Having obtained  $E_e'$ , the nuclear wave equation (vii) is solved. This gives a set of expressions for  $\Psi_n$  and  $E$ . The eigenvalues  $E$  are the characteristic energies for the whole molecule in the given electronic state. A different set of  $\Psi_n$  and  $E$  is obtained for each electronic state of the molecule.

(3) The complete wave functions are then obtained from  $\Psi = \Psi_e \Psi_n$ .

## 2. Types of Molecular Spectra

When light from a source containing a substance in 'molecular' state is sent into a spectrometer, more or less broad wavelength regions are observed in the spectrum. These regions are called 'bands', and the spectrum is called 'band spectrum' or 'molecular spectrum'.

The molecular spectra can be divided into three spectral ranges corresponding to the different types of transitions between molecular energy states.

**(i) Electronic Spectra :** These spectra are observed, both in emission and absorption, in the visible and the ultraviolet regions. Each spectrum consists of quite a large number of bands. Each individual band has a sharp edge, called band-head, where the intensity falls suddenly to zero; and from this edge the intensity falls off gradually to the other side of the band. Under high resolution, a band is found to be composed of a series of lines which draw farther apart as the distance from the band-head increases. The band is said to be 'degraded' toward the side opposite to the band-head. The electronic spectra are observed for the heteronuclear as well as for the homonuclear diatomic molecules.

**(ii) Vibrational-Rotational Spectra :** These spectra are observed in absorption, in the near infra-red region ( $1 \mu - 10^2 \mu$ ;  $1 \mu = 10^{-6} \text{ m} = 10^4 \text{ Å}$ ). Each spectrum consists of an intense band, called "fundamental" band which is accompanied by a few weak bands. These bands, like electronic bands, have a fine structure. They are observed only for the heteronuclear molecules. The homonuclear molecules like  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  do not produce vibrational-rotational bands.

**(iii) Pure Rotational Spectra :** These spectra are observed in absorption in the far infra-red ( $10^2 \mu - 10^3 \mu$ ) or in the microwave ( $10^3 \mu - 10^4 \mu$ ) region. Each spectrum is composed of a series of nearly equidistant lines. Like vibrational-rotational spectra, the pure rotational spectra are observed only for the heteronuclear diatomic molecules.

The origin of different molecular spectra lies in the different energy states of the molecule.

### 3. Types of Molecular Energy States and Associated Spectra

Like atomic spectra, molecular spectra are obtained by transitions between energy states of the molecules. Molecular energy states arise from the rotation of a molecule as a whole and from the vibrations of its constituent nuclei relative to one-another, as well as from changes in its electronic configuration. Rotational states are separated by quite small energy-intervals ( $\approx 10^{-3} \text{ eV}$ ) and the spectra arising from transitions between these states are in the far infra-red or microwave region. Vibrational states are separated by somewhat larger energy intervals ( $\approx 10^{-1} \text{ eV}$ ) and the vibrational spectra fall in the near infra-red region. The electronic states have higher energy separations ( $\approx 10 \text{ eV}$ ) and the corresponding spectra fall in the visible and ultraviolet regions.

According to the Born-Oppenheimer picture of a (diatomic) molecule, the electrons in the molecule move rapidly in the field of the two massive nuclei, and the nuclei move rather slowly under their mutual electrostatic repulsion and the electronic energy of attraction. When two atoms are brought nearer to form a stable molecule, the electronic (potential) energy of attraction decreases rapidly, while the energy of nuclear repulsion increases. For a certain internuclear separation, the total potential energy of the molecule becomes a minimum. This is the equilibrium internuclear separation. The two nuclei vibrate about their respective equilibrium positions along the internuclear axis, and the molecule rotates about the centre of mass.

The Schrödinger's equation for the nuclear motion in a diatomic molecule is

$$\left[ -\frac{\hbar^2}{8\pi^2 M_1} \nabla_1^2 - \frac{\hbar^2}{8\pi^2 M_2} \nabla_2^2 + V(r) \right] \psi = E \psi,$$

where  $M_1$  and  $M_2$  are the masses of the two nuclei, and  $V(r)$  is the potential energy function consisting of the instantaneous electronic energy and the electrostatic energy of the two nuclei.  $\psi$  is the "nuclear" eigenfunction\*, while  $E$  is eigenvalue for the whole molecule. The last equation may be written as

$$\frac{1}{M_1} \nabla_1^2 \psi + \frac{1}{M_2} \nabla_2^2 \psi + \frac{8\pi^2}{h^2} [E - V(r)] \psi = 0.$$

Eliminating the free-particle motion and retaining only the internal motions, the equation in the polar coordinates is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} [E - V(r)] \psi = 0,$$

where  $\mu = \frac{M_1 M_2}{M_1 + M_2}$ . This equation is similar to the equation of a one-electron atom. It can be splitted into an angular equation and a radial equation by writing

$$\psi(r, \theta, \phi) = Y(\theta, \phi) R(r).$$

The angular equation gives the solutions

$$\Phi_M(\phi) = \frac{1}{\sqrt{2\pi}} e^{iM\phi}; M = 0, \pm 1, \pm 2, \dots$$

and  $\Theta_{J, M}(\theta) = \sqrt{\frac{2J+1}{2}} \frac{(J-|M|)!}{(J+|M|)!} P_J^{|M|}(\cos \theta);$

where  $J = 0, 1, 2, \dots$ , so that  $M = -J, \dots, +J$ .

The quantum numbers  $J$  and  $M$  are associated with the angular momentum of the molecule.  $J(J+1) \frac{h^2}{4\pi^2}$  is the square of the total angular momentum, and  $M \frac{h}{2\pi}$  is

the  $z$ -component of the angular momentum.

The radial equation can be worked out to the following form :

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu}{h^2} \left[ E - V(r) - \frac{J(J+1)h^2}{8\pi^2 \mu r^2} \right] R = 0.$$

Substituting  $R(r) = \frac{1}{r} S(r)$ , we get

$$\frac{d^2 S}{dr^2} + \frac{8\pi^2 \mu}{h^2} \left[ E - V(r) - \frac{J(J+1)h^2}{8\pi^2 \mu r^2} \right] S = 0.$$

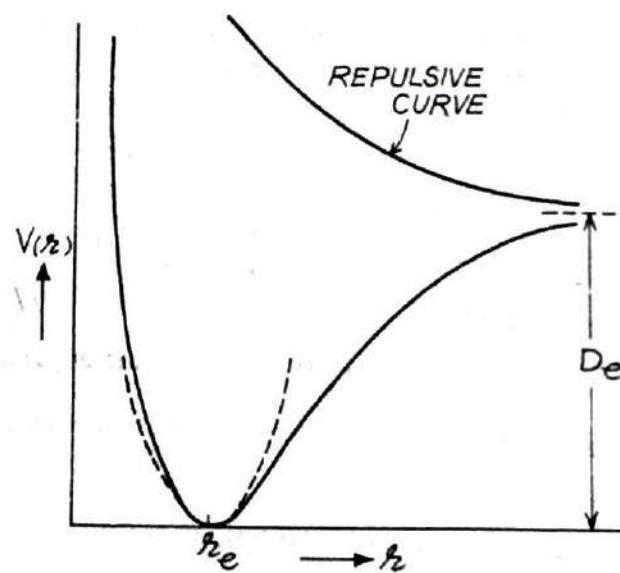
This is the same as the equation of a particle of mass  $\mu$  moving along a line under a potential energy function  $V(r) + \frac{J(J+1)h^2}{8\pi^2 \mu r^2}$ . The second term is the "centrifugal"

potential energy term indicating a rotational motion superimposed on the linear vibratory motion of the particle. The solution of the above equation, therefore, gives a set of vibrational eigenfunctions and eigenvalues, provided  $V(r)$  is known.

\* In the previous section the nuclear eigenfunction was denoted by  $\psi_n$  to distinguish it from the total eigenfunction  $\psi$ . Here we are concerned only with the nuclear eigenfunction and for simplicity we have denoted it by  $\psi$  (not by  $\psi_n$ ).

Now,  $V(r) = E_e' + V_{nn}$ , where  $E_e'$  is the eigenvalue of the electronic wave equation, and  $V_{nn}$  is the nuclear-nuclear interaction (repulsion) energy term.

We can understand that for a stable diatomic molecule, the potential energy must be minimum when the separation between the two nuclei has its equilibrium value  $r_e$ . In this position the attractive force due to the electronic binding and the repulsive force between the nuclei mutually balance. If the nuclei are brought closer than  $r_e$ , then the potential energy  $V(r)$ , say, must rise sharply due to the work done against the increasing repulsion between the nuclei. If the nuclei are drawn apart, then again the potential energy must rise, but much slowly, due to work against the now dominant electronic attractive force. If the separation between the nuclei is continued to increase, the potential energy must approach a limiting value  $D_e$  at which the molecule would dissociate into atoms.  $D_e$  is known as the 'dissociation energy' of the molecule. This physical picture of the molecule leads to a potential curve,  $V(r)$  against  $r$ , with a minimum at  $r_e$ , a sharp rise as  $r$  decreases from  $r_e$ , and a much less sharp rise to the dissociation limit as  $r$  increases to infinity (Fig. 1).



(Fig. 1)

A suitable expression for the potential energy curve can be obtained by a Taylor's series expansion of  $V(r)$  in terms of the powers of  $(r - r_e)$ ; because we are mainly interested in the part of the curve near the minimum. Thus

$$\begin{aligned} V(r) = V(r_e) + (r - r_e) \left( \frac{dV(r)}{dr} \right)_{r=r_e} &+ \frac{(r - r_e)^2}{2!} \left( \frac{\partial^2 V(r)}{\partial r^2} \right)_{r=r_e} \\ &+ \frac{(r - r_e)^3}{3!} \left( \frac{\partial^3 V(r)}{\partial r^3} \right)_{r=r_e} + \dots \end{aligned}$$

The first term  $V(r_e)$  is a constant and can be set zero if we measure the potential energy relative to the minimum of the curve. The second term is zero because at  $r = r_e$ ,  $V(r)$  is a minimum so that its first derivative is zero. Thus

$$V(r) = \frac{(r - r_e)^2}{2!} \left( \frac{\partial^2 V(r)}{\partial r^2} \right)_{r=r_e} + \frac{(r - r_e)^3}{3!} \left( \frac{\partial^3 V(r)}{\partial r^3} \right)_{r=r_e} + \dots$$

If we retain only the quadratic term; the expression is

$$V(r) = \frac{1}{2} k (r - r_e)^2,$$

where  $k = \frac{\partial^2 V(r)}{\partial r^2}$ , which represents a parabola.

Thus, the curve is parabolic near the minimum, and for small displacements ( $r - r_e$ ) the molecule may be treated as harmonic oscillator. The eigenfunctions  $S(r)$  must be similar to the eigenfunctions of a harmonic oscillator and the eigenvalues  $E$  must be approximately equal to the energy at the minimum of the curve plus the harmonic oscillator eigenvalues.

The retention of the cubic term gives a much better approximation for the potential curve for not too great values of  $(r - r_e)$ . The molecule comes out to be anharmonic oscillator. Morse and others have given still better expressions for the potential energy curves of actual molecules.

In Fig. 1 is also shown a curve which has no minimum. This corresponds to unstable molecules in which there is repulsion between the two nuclei at all separations.

Further, each electronic state of a molecule has its own potential energy curve, so that for any one molecule we have a number of curves.

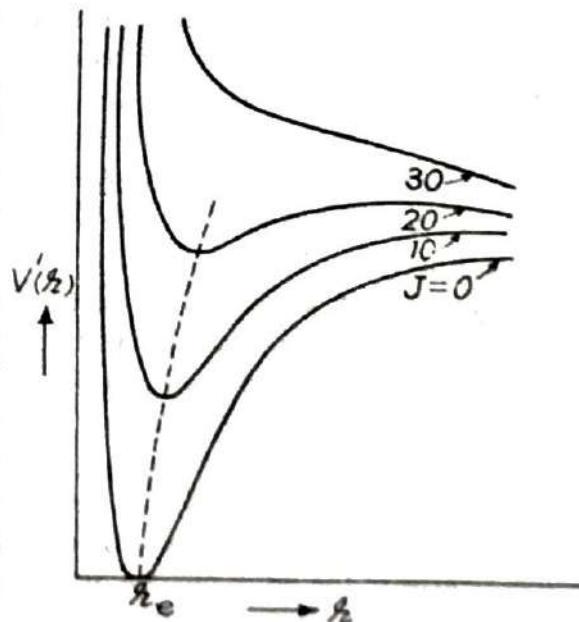
We have above considered the potential energy curve without taking note of molecular rotation. Since the molecule rotates also, the potential energy expression is

$$V'(r) = V(r) + \frac{J(J+1)h^2}{8\pi^2\mu r^2}.$$

The rotation adds a term containing  $\frac{1}{r^2}$ , so that the effective potential curve shows a maximum between the minimum and the dissociation limit (Fig. 2). Further as  $J$  (rotation) increases, the minimum moves upwards as well as outwards ( $r_e$  increases) and finally ceases to exist. That is, the molecule "stretches" as it rotates and becomes unstable for very rapid rotations.

We conclude that the eigenvalues of the system would consist of three quantised additive components : (i) energy at the minimum of  $V(r)$  function which is referred to as electronic energy  $E_e$ , (ii) energy of nuclear vibrations under the potential function  $V(r)$  which is referred to as vibrational energy  $E_v$ , and (iii) energy of rotation of the molecule as a whole referred to as rotational energy  $E_r$ . Thus

$$E = E_e + E_v + E_r.$$



(Fig. 2)

$E_e$  is the energy which the molecule would possess if nuclei were fixed, and consists of the kinetic and the potential energies of extranuclear electrons, and the potential energy of repulsion between the nuclei. It is defined by a group of quantum numbers

$\Delta$ ,  $\Sigma$  and  $\Omega$ .  $E_v$  is the additional (vibrational) energy which the molecule would possess if the nuclei executed vibrations and is defined by a single quantum number  $v$ .  $E_r$  is the additional (rotational) energy which the vibrating molecule would have if it rotated also. It is defined by a quantum number  $J$ .

In terms of wave number unit, the last equation is written as

$$\frac{E}{hc} = \frac{E_e}{hc} + \frac{E_v}{hc} + \frac{E_r}{hc}$$

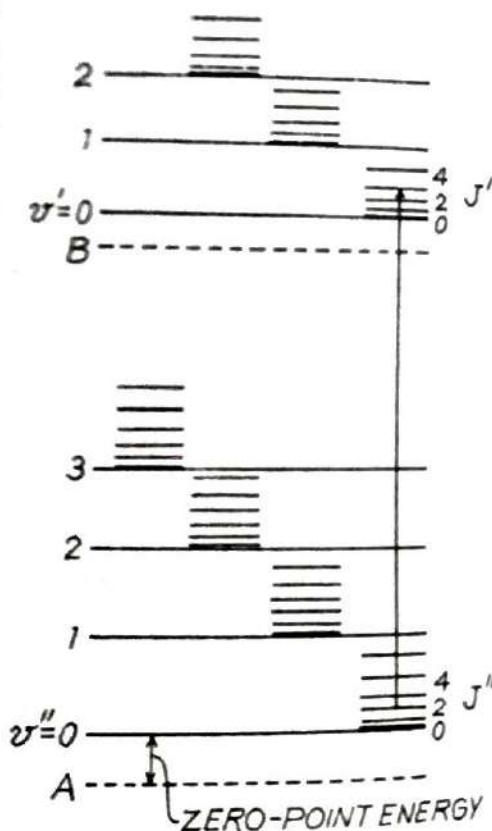
or

$$T = T_e + G(v) + F(v, J),$$

where  $T_e$  is the 'electronic term',  $G(v)$  is the 'vibrational term', and  $F(v, J)$  is the 'rotational term'. Thus, a molecule has a number of discrete electronic levels with separations of the same order as in atoms, and a transition between two electronic levels involve radiation falling in the visible or ultraviolet region. With each electronic level is associated a set of vibrational energy levels, with spacing decreasing slowly with increasing quantum number  $v$ , and a transition between two such levels associated with a given electronic level involves radiation falling in the near infra-red region. With each vibrational level is associated a set of rotational levels, with spacing increasing rapidly with increasing quantum number  $J$ , and a transition between two rotational levels associated with a given vibrational level of a given electronic level involves radiation falling in the far infra-red or microwave region.

For a 'single' (electronic) transition between electronic levels  $A$  and  $B$  (Fig. 3) of a molecule, there are a great number of permitted transitions between the vibrational and also between the rotational levels of  $A$  and  $B$  (One absorption transition is shown in Fig. 3). Hence a complicated molecular spectrum results. All the spectral lines arising from transitions between rotational levels  $J'$  and  $J''$  associated with a given pair of vibrational levels  $v'$  and  $v''$  of a given pair of electronic levels form a 'band'\*.

Thus, for a given band,  $J'$  and  $J''$  vary from line to line, while  $v'$  and  $v''$  are constants. All the bands which arise from transitions between vibrational (and rotational) levels of a given pair of electronic levels constitute a 'band-system', the values of  $v'$  and  $v''$  varying from band to band. Thus, a single electronic transition gives rise to a band-system, called electronic band-system. Each line in each band of the system arises due to a change in all the three energies  $E_e$ ,  $E_v$  and  $E_r$ . Thus



(Fig. 3)

\* The energy levels of an upper state are denoted by a single dash ( $J'$ ,  $v'$ ); while those of a lower state are denoted by double dash ( $J''$ ,  $v''$ ).

$$\begin{aligned}
 v &= T' - T'' \\
 &= [T'_e + G'(v') + F'(v', J')] - [T''_e + G''(v'') + F''(v'', J'')] \\
 &= (T'_e - T''_e) + [G'(v') - G''(v'')] + [F'(v', J') - F''(v'', J'')] \\
 &= v_e + v_v + v_r. \quad (v_e > v_v > v_r)
 \end{aligned}$$

For a given band,  $v_e$  and  $v_v$  are constants, while  $v_r$  changes from line to line in the band. The position in the band where  $v_r = 0$  is called "band-origin"; its wave number is  $v_e + v_v$ . The wave number corresponding to the band-origin represents the wave number for that particular band. For the given band-system,  $v_e$  is constant, whereas  $v_v$  varies from band to band. The position in the system where  $v_v = 0$  (and also  $v_r = 0$ ) is called the "system-origin"; its wave number is  $v_e$ . The electronic band-system lies in the visible or ultraviolet region.

Besides electronic bands, we have non-electronic bands also (for which  $v_e = 0$ ). These bands are of two types :

(i) **Vibrational-Rotational Bands** : A vibration-rotation band arises due to transitions between two vibrational levels associated with the same electronic level. The lines of the band result from the transitions between the rotational levels of one vibrational level and the rotational levels of the other, so that the wave number of a line is  $v_v + v_r$ . Such bands occur in the near infra-red.

(ii) **Pure Rotational Bands** : These are rather lines, each of which arises from transitions between two rotational levels associated with one and the same vibrational level of a given electronic state. They occur in the far infra-red or in the microwave region.

In subsequent chapters we shall investigate these three types of molecular spectra in the reverse order.

## QUESTIONS

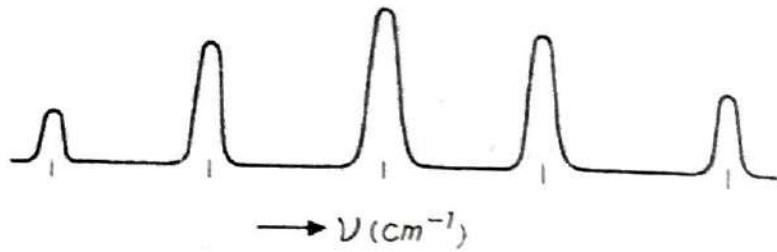
1. "The molecular wave function can be written as a product of electronic and nuclear wave functions." Elucidate this statement and discuss its limitations.  
*(Meerut 89, sp. paper 96, 94, 92)*
2. Account for : "The molecules have rotational and vibrational states but atoms do not".
3. Plot the potential energy curve for a harmonic oscillator and compare it with a typical potential energy curve of a diatomic molecule. What informations could be deduced from such a curve.
4.  $A$ ,  $B$  and  $C$  are three diatomic molecules such that  $A$  and  $B$  have same equilibrium internuclear separation but  $B$  has a larger dissociation energy ;  $C$  has a larger separation than  $A$  or  $B$  but same dissociation energy as  $A$ . Draw potential energy curves for  $A$ ,  $B$  and  $C$ .
5. What are the differences between atomic spectra and molecular spectra ? Discuss their origin.  
*(Meerut 2000 S)*
6. Discuss the origins of the various types of spectra obtained from a diatomic molecule.  
*(Meerut sp. paper 99, 95)*

## Pure Rotational Spectra

### 1. Salient Features of Rotational Spectra

Pure rotational molecular spectra arise from transitions between rotational energy states, and are observed in the far infra-red ( $\approx 10^2 \mu - 10^3 \mu$ ) or microwave ( $\approx 10^3 \mu - 10^4 \mu$ ) region of the electromagnetic spectrum. Only molecules that have permanent electric dipole moments can absorb or emit electromagnetic radiation in such transitions. It means that homonuclear diatomic molecules such as  $H_2, O_2, N_2$ ; symmetric linear molecules such as  $CO_2 (O = C = O)$ ; and spherical-top polyatomic molecules such as  $CH_4$  do not exhibit rotational spectra.

In practice, rotational spectra are observed in absorption. For heteronuclear diatomic molecules such as HF, HCl, HBr, CO, etc., *the rotational spectra consist of a simple series of absorption maxima which are very nearly equidistant on a wave number scale*



(Fig. 1)

(Fig. 1). A measurement of frequencies of these maxima leads to a determination of the moment of inertia and the internuclear distance of the molecule. (For homonuclear molecules, which do not give rotational spectra, the moment of inertia and the internuclear distance can be found from the rotational fine structure of electronic bands and from rotational Raman spectra).

### 2. Molecular Requirement for Rotational Spectra

As we have just read, the basic requirement for the emission or absorption of radiation by a transition between rotational energy states is that the molecule must have a permanent dipole moment. This is in agreement with the classical electrodynamics, according to which a rotating molecule can lead to emission of radiation provided a changing dipole moment is associated with the molecule. All (heteronuclear) diatomic molecules with "unlike" atoms, for which the centres of positive and negative charges do not coincide, have a permanent dipole moment. During the rotation of the molecule, the component of the dipole moment in a fixed direction changes periodically with the frequency of rotation,  $v_{rot}'$ , of the molecule so that, classically, the radiation of frequency  $v_{rot}'$  should

be emitted. Homonuclear molecules have no dipole moment and hence there is no emission of infra-red radiation.

Similarly, infra-red radiation can be absorbed by the rotating molecule, and thereby increase the rotation, only if a permanent dipole is present. Such a molecule interacts with the oscillating electric field of the incident radiation to absorb rotational energy and produce the absorption spectrum.

Suppose, at any instant, the molecule is in such a position that the electric field pushes the positive charge up and the negative charge down, thus making the molecule rotate faster (Fig. 2 a). Now, if a frequency of radiation coincides with that of the molecular rotation, then half a cycle later (Fig. 2 b), the electric field would still make the molecule rotate faster, thus keeping it pushed to a higher rotational energy and producing rotational spectrum. Thus, the production of absorption spectrum is due to the electric dipole moment of the molecule.

Homonuclear molecules have no dipole moment and hence there is no absorption of infra-red radiation.

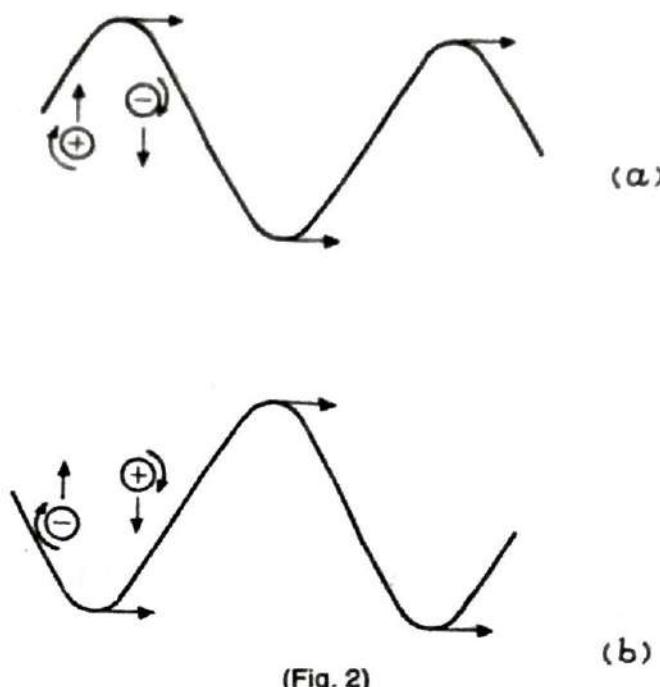
Homonuclear molecules, however, show rotational Raman spectra which is an effect arising due to the polarisability of the molecules.

### 3. Experimental Arrangement

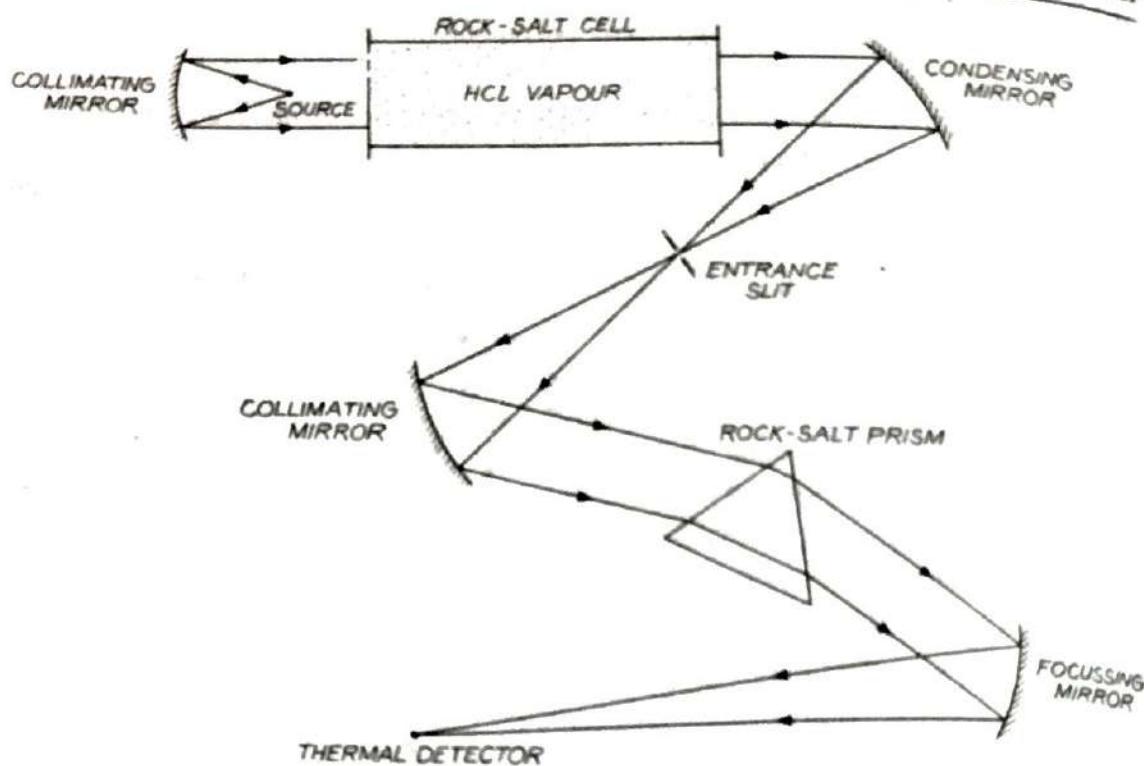
The basic requirements for observing pure rotational spectra in absorption are a source of continuous radiation in the proper infra-red region, a dispersing device and a detector.

Fig. 3 shows a plan for obtaining rotational spectrum of HCl in the form of vapour. The source is an electrically-heated ceramic element, the dispersing device is a rock-salt prism, and the detector is a thermopile connected to an amplifier and a sensitive galvanometer, or to a recorder.

Radiation from the source is taken, by means of a collimating mirror, as a parallel beam which passes through the HCl vapour filled in a rock-salt cell. The transmitted beam falls on a condensing mirror which directs it to an entrance slit placed at the focus of another collimating mirror. The collimated beam passes through a rock-salt prism and is brought to a focus at the thermal detector by means of a focussing mirror. Generally, two equivalent beams are taken from the source, one passing through an empty cell and the other through the filled cell. However, now a days most of the pure rotational studies are made by means of a microwave spectrometer.



(Fig. 2)

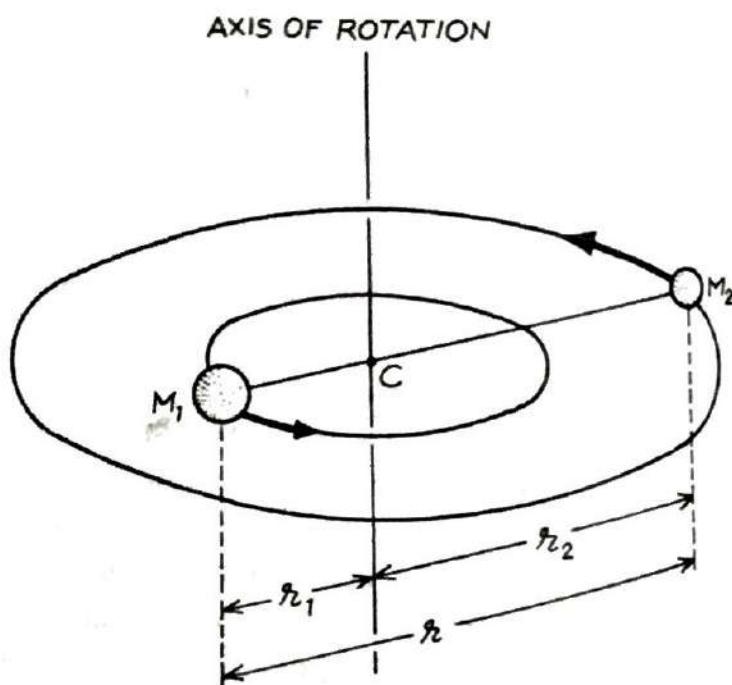


(Fig. 3)

#### 4. The Molecule as a Rigid Rotator : Explanation of Rotational Spectra

The simplest model of a rotating diatomic molecule is that of a 'rigid' rotator, that is, the internuclear separation is assumed to be fixed at the equilibrium value.

Let us consider two atoms of masses  $M_1$  and  $M_2$  which are chemically bonded to form a diatomic molecule (Fig. 4). The atoms may be treated as point-masses because their masses are concentrated in their nuclei which have a size ( $\approx 10^{-15}$  m) much smaller than the internuclear separation ( $= 10^{-10}$  m). Let  $r$  be the distance between the atoms  $M_1$  and  $M_2$ , and  $r_1$  and  $r_2$  the respective distances of the atoms from the molecular centre of mass  $C$ . The system is capable of rotation about an axis passing through its centre of mass  $C$  and perpendicular to the internuclear axis.



(Fig. 4)

By the definition of centre of mass, we have

$$M_1 r_1 = M_2 r_2.$$

$$r_1 + r_2 = r.$$

Also

From these two equations, we have

$$r_1 = \frac{M_2}{M_1 + M_2} r \quad \text{and} \quad r_2 = \frac{M_1}{M_1 + M_2} r.$$

Now, the moment of inertia of the molecule about the axis of rotation is given by

$$I = M_1 r_1^2 + M_2 r_2^2$$

$$= M_1 \left( \frac{M_2}{M_1 + M_2} r \right)^2 + M_2 \left( \frac{M_1}{M_1 + M_2} r \right)^2 = \frac{M_1 M_2}{M_1 + M_2} r^2.$$

But  $\frac{M_1 M_2}{M_1 + M_2}$  is the "reduced mass"  $\mu$  of the molecule. Then, we have

$$I = \mu r^2.$$

Thus, the diatomic molecule is equivalent to a single point-mass  $\mu$  at a fixed distance  $r$  from the axis of rotation. Such a system is called a rigid rotator.

In order to determine the possible energies of rotation of the molecule, we have to solve the Schroedinger equation of a rigid rotator, which is

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} E \psi = 0.$$

The potential energy term  $V$  has been taken zero because  $r$  is fixed.

In spherical polar coordinates, the equation can be written as

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2\mu}{h^2} E \psi = 0,$$

the derivatives with respect to  $r$  being set equal to zero. Substituting  $\frac{I}{r^2}$  for  $\mu$ , this equation becomes

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I E}{h^2} \psi = 0, \quad \dots(i)$$

Let us separate the variables  $\theta$  and  $\phi$  by making the substitution

$$\psi(\theta, \phi) = \Theta(\theta) \Phi(\phi).$$

Then

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) \Phi + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \Theta + \frac{8\pi^2 I E}{h^2} \Theta \Phi = 0,$$

Multiplying throughout by  $\frac{\sin^2 \theta}{\Theta \Phi}$ ; we get

$$\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{8\pi^2 I E}{h^2} \sin^2 \theta = - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2}.$$

The L.H.S. is a function of  $\Theta$  only, the R.H.S. a function of  $\Phi$  only. Let us put each side equal to a constant  $M^2$ . Then, we have two equations

$$\frac{d^2 \Phi}{d\phi^2} = - M^2 \Phi \quad \dots(ii)$$

and

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{8\pi^2 I E}{h^2} \sin^2 \theta = M^2.$$

On multiplying by  $\frac{\Theta}{\sin^2 \theta}$ , the last equation becomes

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( \frac{8\pi^2 I E}{h^2} - \frac{M^2}{\sin^2 \theta} \right) \Theta = 0. \quad \dots(iii)$$

The solution of the  $\Phi$ -equation (ii) can be written as

$$\Phi_M(\phi) = A e^{iM\phi}$$

$\Phi_M(\phi)$  will be 'single valued' at all values of  $\phi$ , provided  $M$  is a positive or a negative integer ( $M = 0, \pm 1, \pm 2, \dots$ ).

Now, the normalization condition

$$\int_0^{2\pi} \Phi_M^*(\phi) \Phi_M(\phi) d\phi = A^2 \int_0^{2\pi} e^{iM\phi} e^{-iM\phi} d\phi = A^2 \int_0^{2\pi} d\phi = A^2 (2\pi) = 1$$

gives  $A = \frac{1}{\sqrt{2\pi}}$ . Hence the normalized solution of eq. (ii) is

$$\Phi_M(\phi) = \frac{1}{\sqrt{2\pi}} e^{iM\phi}; \quad \dots(iv)$$

where  $M = 0, \pm 1, \pm 2, \dots$

Let us now consider the  $\Theta$ -equation (iii). We make the convenient substitutions:

$$x = \cos \theta; P(x) = \Theta(\theta)$$

so that  $\sin^2 \theta = (1 - x^2); \frac{d\Theta}{d\theta} = \frac{dP}{dx} \frac{dx}{d\theta} = - \frac{dP}{dx} \sin \theta$ .

Then, since  $\frac{d}{d\theta} = -\sin \theta \frac{d}{dx}$ ; eq. (iii) becomes

$$\frac{1}{\sin \theta} \left[ -\sin \theta \frac{d}{dx} \left\{ \sin \theta \left( -\frac{dP(x)}{dx} \sin \theta \right) \right\} \right] + \left( \frac{8\pi^2 I E}{h^2} - \frac{M^2}{\sin^2 \theta} \right) P(x) = 0$$

$$\text{or} \quad \frac{d}{dx} \left\{ (1 - x^2) \frac{dP(x)}{dx} \right\} + \left( \frac{8\pi^2 I E}{h^2} - \frac{M^2}{1 - x^2} \right) P(x) = 0$$

$$\text{or} \quad (1 - x^2) \frac{d^2 P(x)}{dx^2} - 2x \frac{dP(x)}{dx} + \left( \frac{8\pi^2 I E}{h^2} - \frac{M^2}{1 - x^2} \right) P(x) = 0.$$

This eq. is identical to the associated Legendre's differential equation, provided we put

$$\frac{8\pi^2 I E}{h^2} = J(J + 1)$$

$$\text{or} \quad E = \frac{h^2}{8\pi^2 I} J(J + 1),$$

where  $J$  is a positive integer. The function  $P(x)$  is then identified with the associated Legendre polynomial  $P_J^{(M)}(x)$  of degree  $J$  and order  $M$ . Then, the accepted solutions of the  $\Theta$ -equation are

$$\Theta_{J,M}(\theta) = N P_J^{(M)}(x) = N P_J^{(M)}(\cos \theta);$$

where  $J = 0, 1, 2, 3, \dots$

These functions are found to vanish except when  $|M| < J$ ; therefore  $M$  can take only the values

$$M = J, (J - 1), (J - 2), \dots, -J.$$

The normalization condition gives

$$\int_0^\pi \Theta_{J,M}^*(\theta) \Theta_{J,M}(\theta) \sin \theta d\theta = 1$$

$$\text{or } N^2 \int_{-1}^{+1} P_J^{|M|*}(x) P_J^{|M|}(x) dx = 1.$$

Using an orthogonal property of associated Legendre polynomial, we have

$$N^2 \frac{2}{2J+1} \frac{(J+|M|)!}{(J-|M|)!} = 1$$

$$\text{and so } N = \sqrt{\frac{2J+1}{2} \frac{(J-|M|)!}{(J+|M|)!}}.$$

Hence the normalized 'accepted' solutions of the  $\Theta$ -equation are

$$\Theta_{J,M}(\theta) = \sqrt{\frac{2J+1}{2} \frac{(J-|M|)!}{(J+|M|)!}} P_J^{|M|}(\cos \theta). \quad \dots(v)$$

The total eigenfunctions for the rigid rotator are then, combining (iv) and (v) :

$$\psi(\theta, \phi) = \sqrt{\frac{2J+1}{4\pi} \frac{(J-|M|)!}{(J+|M|)!}} P_J^{|M|}(\cos \theta) e^{iM\phi}. \quad \dots(vi)$$

Let us now calculate quantum-mechanically the eigenvalues for the square of the angular momentum,  $L^2$ , and its component  $L_z$  in the  $z$ -direction. The quantum-mechanical operators are :

$$\hat{L}^2 = -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad \dots(vii)$$

$$\text{and } \hat{L}_z = -\frac{i\hbar}{2\pi} \frac{\partial}{\partial \phi}. \quad \dots(viii)$$

The Schrödinger equation for the rotator, eq. (i), has been found to have acceptable solutions when  $\frac{8\pi^2IE}{\hbar^2}$  is replaced by  $J(J+1)$  where  $J$  is a positive integer. Making this replacement, the eq. (i) gives

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = -J(J+1)\psi$$

$$\text{or } -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = J(J+1) \frac{\hbar^2}{4\pi^2} \psi.$$

Substituting this in eq. (vii); we get

$$\boxed{\hat{L}^2 \psi = J(J+1) \frac{\hbar^2}{4\pi^2} \psi.}$$

Thus, the eigenvalues for the square of the angular momentum are  $J(J+1) \frac{\hbar^2}{4\pi^2}$ , where  $J = 0, 1, 2, \dots$

Let us now consider eq. (iv). Differentiating it, we have

$$\frac{d\Phi_M(\phi)}{d\phi} = \frac{1}{\sqrt{2\pi}} e^{iM\phi} (iM) = iM\Phi_M(\phi)$$

or

$$-\frac{i\hbar}{2\pi} \frac{d\Phi_M(\phi)}{d\phi} = \frac{M\hbar}{2\pi} \Phi_M(\phi).$$

Substituting the operator eq. (viii) in it, we get

$$\hat{L}_z \Phi_M(\phi) = \frac{M\hbar}{2\pi} \Phi_M(\phi).$$

Hence, we have also

$$\hat{L}_z \Psi = \frac{M\hbar}{2\pi} \Psi.$$

Thus, the eigenvalues for the  $z$ -component of the angular momentum are  $\frac{M\hbar}{2\pi}$ , where  $M = 0, \pm 1, \pm 2, \dots, \pm J$ .

The solving of the rigid-rotator Schrödinger equation gives the result that the eigenfunctions  $\Psi$  are single-valued, finite, and continuous only for certain values of  $E$ , given by

$$E = \frac{\hbar^2}{8\pi^2 I} J(J+1).$$

This is the expression for the rotational energy of a diatomic molecule.  $J$  is called the rotational quantum number which can take the integral values :

$$J = 0, 1, 2, 3, \dots$$

Thus, the rotator can have a discrete set of energy levels.

From classical mechanics, we have

$$E = \frac{1}{2} I \omega^2$$

and

so that

$$L = I \omega,$$

$$L = \sqrt{2EI}.$$

Thus, the angular momentum  $L$  of the system in the quantum state  $J$  is given by

$$L = \frac{\hbar}{2\pi} \sqrt{J(J+1)}.$$

This is a result agreeing with the general result for the angular momentum in quantum mechanics.

Since only certain discrete values of energy and angular momentum of the rigid rotator are possible, it follows that only certain rotational frequencies are possible. We have

$$\omega = \frac{L}{I} = \frac{\hbar}{2\pi I} \sqrt{J(J+1)}.$$

$$\therefore v_{rot} = \frac{\omega}{2\pi} = \frac{\hbar}{4\pi^2 I} \sqrt{J(J+1)}.$$

**Rotational Spectrum :** Let us now investigate the spectrum expected from a rigid rotator. In terms of wave-number, the energy equation can be written as

$$F(J) = \frac{E}{hc} = \frac{\hbar}{8\pi^2 I c} J(J+1).$$

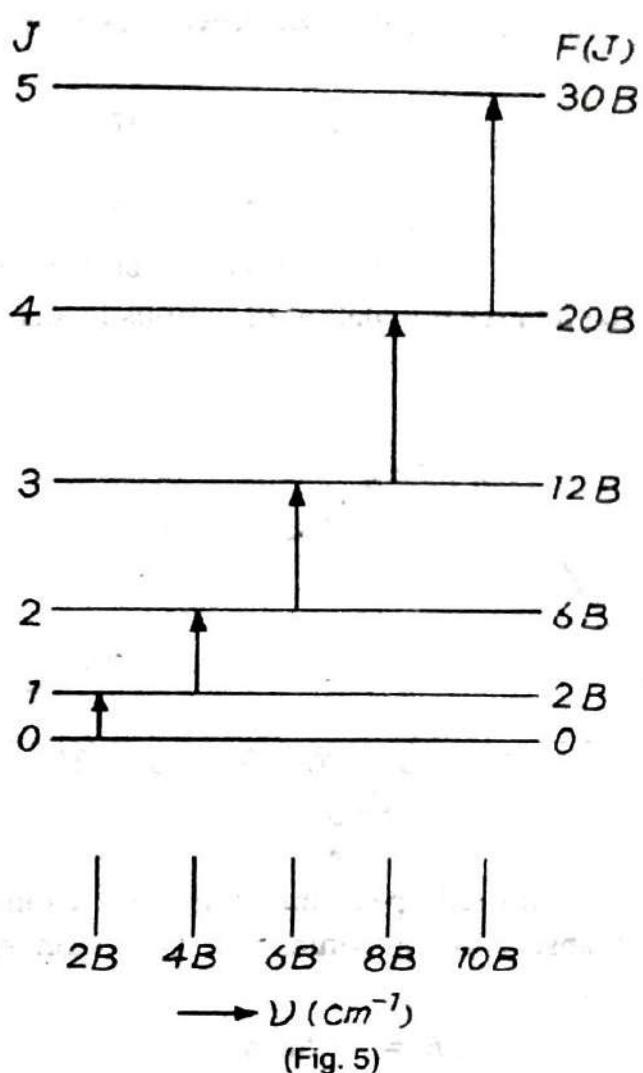
Let us put  $\frac{\hbar}{8\pi^2 I c} = B$ , known as 'rotational constant'. Then

$$F(J) = BJ(J + 1).$$

Substituting  $J = 0, 1, 2, \dots$ , we get

$$F(J) = 0, 2B, 6B, 12B, 20B, 30B, \dots$$

Thus, we have a series of discrete rotational energy levels whose spacings increase with increasing  $J$  (Fig. 5).



When a transition takes place between an upper level  $J'$  and a lower level  $J''$ , the wave number of the emitted or absorbed radiation would be given by

$$\begin{aligned} \nu &= F(J') - F(J'') \\ &= BJ'(J'+1) - BJ''(J''+1). \end{aligned}$$

A study of the matrix element of the dipole moment shows that the rotational transitions can only occur such that  $J$  changes by unity, so that the selection rule is

$$\Delta J = \pm 1.$$

Since we have chosen  $J' > J''$ , we have

$$J' = J'' + 1.$$

Thus

$$\nu = B(J'' + 1)(J'' + 2) - BJ''(J'' + 1) = 2B(J'' + 1).$$

In this formula, the  $J$  values of only the 'lower' state occur. Remembering this, we may write  $J$  for  $J''$  for simplicity. Thus

$$\nu = 2B(J + 1).$$

Substituting  $J = 0, 1, 2, \dots$

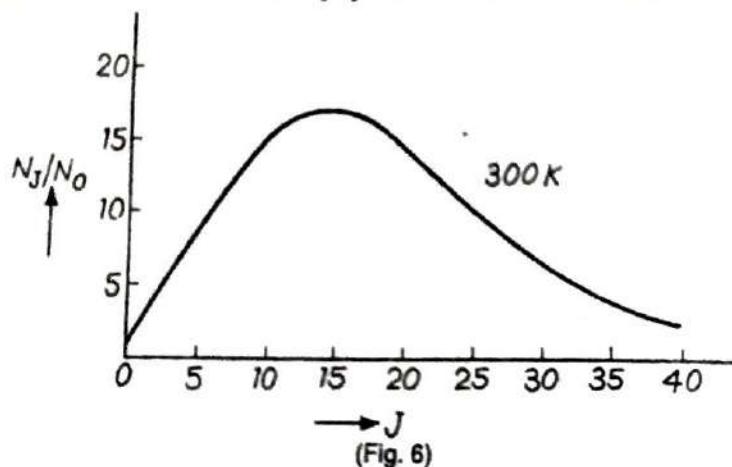
$$\nu = 2B, 4B, 6B, 8B, \dots$$

Thus, the absorption spectrum of a rigid rotator is expected to consist of a series of equidistant lines with constant separation  $2B$ , provided transitions start from various energy levels  $J = 0, 1, 2, 3, \dots$ , as shown. This, however, does not take place because quite a good number of rotational energy levels are well-populated even at ordinary temperatures.

The population in the  $J$ th level relative to the lowest level, in thermal equilibrium at a temperature of  $K$  kelvin is

$$\begin{aligned}\frac{N_J}{N_0} &= (2J + 1) e^{-(E_J - E_0)/kT} \\ &= (2J + 1) e^{-BJ(J+1)\hbar c/kT}.\end{aligned}$$

A graph between  $N_J/N_0$  and  $J$  for a typical molecule at room temperature (300 K) is drawn in Fig. 6. It shows the relative population of various levels.



Experimentally, the far infra-red spectrum of HF, for example, shows a series of approximately equidistant absorption maxima, and the mean spacing is found to be  $40.5 \text{ cm}^{-1}$ . From above, we have

$$2B = 40.5 \text{ cm}^{-1},$$

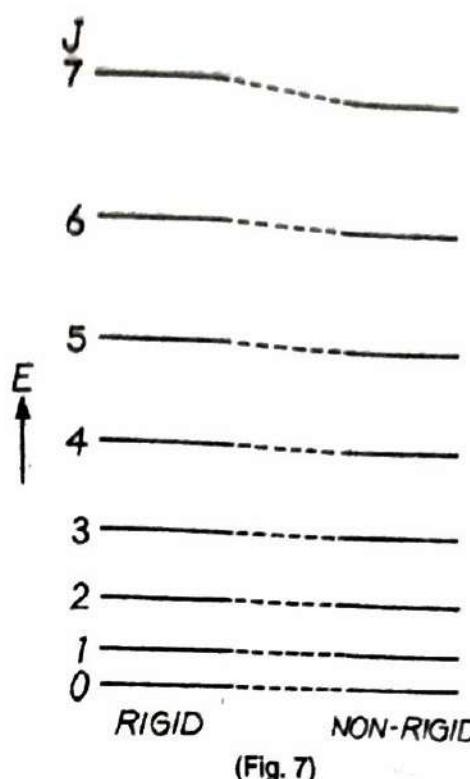
where  $B = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 (\mu r^2) c}$ . From this, the internuclear distance  $r$  works out to be  $0.937 \text{ \AA}$  which fairly agrees with the value obtained from gas viscosity and crystal structure measurements. Hence it is established that the far infra-red spectrum is a rotational spectrum.

## 5. The Non-rigid Rotator

In practice, the rotational lines are 'not' exactly equidistant; the separations decrease slightly with increasing  $J$ . This is attributed to the fact that the molecules are 'not' rigid. They stretch while in rotation, and the stretching (increase in bond-length) increases with increasing rotation. Taking this into account, the rotational terms come out to be

$$F(J) = BJ(J+1) - DJ^2(J+1)^2,$$

where  $D$  is the 'centrifugal distortion constant', and is much smaller than  $B$ . Due to the centrifugal term, the increase in spacing between successive rotational levels with increasing  $J$  becomes slightly less rapid (Fig. 7). The wave numbers of the rotational lines are now



$$\nu = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3.$$

This shows that the separations between lines decrease slightly with increasing  $J$ , slightly because  $D \ll B$ .

## 6. Isotope Effect on Rotational Spectrum

The reduced mass  $\mu$  and hence the rotational constant  $B \left( = \frac{\hbar}{8\pi^2 \mu r^2 c} \right)$  is different for different isotopic molecules. Since mass effects are negligible compared to electronic effects in the determination of equilibrium internuclear separation, this separation is the same in two isotopic molecules. Only reduced masses are different.

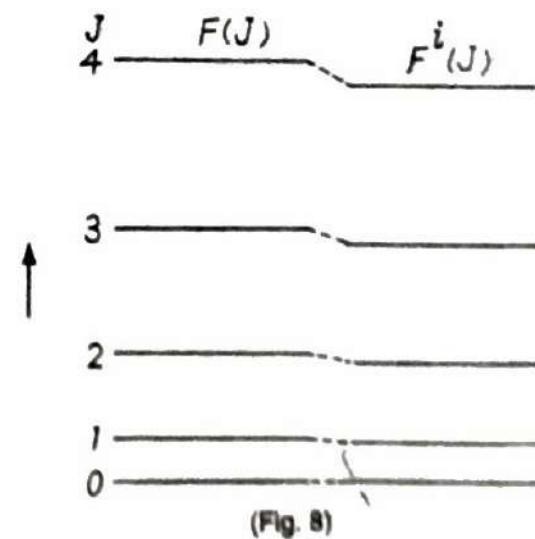
If  $B'$  be the rotational constant for the heavier isotope, then

$$B' < B$$

and so

$$F'(J) < F(J).$$

Thus, the separations of levels for the heavier isotope will be smaller than those of the corresponding levels of the lighter isotope (Fig. 8). Hence spectral lines will also be closer.



### SOLVED PROBLEMS

- 1.** The moment of inertia of the CO molecule is  $1.46 \times 10^{-46} \text{ kg}\cdot\text{m}^2$ . Calculate the energy (in eV), and the angular velocity in the lowest rotational energy level of the CO molecule. ( $\hbar = 6.63 \times 10^{-34} \text{ Js}$ ;  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ ).

(Meerut 2003, sp. paper 2004, 03, 00)

**Solution.** The quantum-mechanical energy of a rotating diatomic molecule is given by

$$E = \frac{\hbar^2}{8\pi^2 I} J(J+1),$$

where  $I$  is the moment of inertia of the molecule about the axis of rotation. The lowest rotational energy level corresponds to  $J = 1$ , and for this level in CO

$$E_{J=1} = \frac{\hbar^2}{4\pi^2 I}$$

Substituting the given values of  $\hbar$  and  $I$ , we have

$$\begin{aligned} E_{J=1} &= \frac{(6.63 \times 10^{-34} \text{ Js})^2}{4 \times (3.14)^2 \times (1.46 \times 10^{-46} \text{ kg}\cdot\text{m}^2)} \\ &= 7.63 \times 10^{-23} \text{ J}. \end{aligned}$$

Now,  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ .

$$\therefore E_{J=1} = \frac{7.63 \times 10^{-23} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 4.77 \times 10^{-4} \text{ eV}.$$

The angular velocity of CO molecule in the lowest energy level ( $J = 1$ ) is

$$\omega = \sqrt{\frac{2E}{I}} \quad (\because E = \frac{1}{2} I \omega^2)$$

$$= \sqrt{\frac{2 \times 7.63 \times 10^{-23} \text{ J}}{1.46 \times 10^{-46} \text{ kg}\cdot\text{m}^2}} = 1.02 \times 10^{12} \text{ rad/s.}$$

- 2.** The  $J = 0 \rightarrow J = 1$  absorption line in CO occurs at a frequency of  $1.153 \times 10^{11}$  cycles/s. Calculate the moment of inertia and the internuclear separation of CO molecule. ( $\hbar = 6.63 \times 10^{-34} \text{ Js}$ ,  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ ).

**Solution.** The rotational energy of a diatomic molecule is given by

$$E = \frac{\hbar^2}{8\pi^2 I} J(J+1).$$

The energy separation between  $J = 0$  and  $J = 1$  levels is

$$\Delta E = E_{J=1} - E_{J=0} = \frac{\hbar^2}{4\pi^2 I}.$$

The frequency  $v'$  absorbed in transition  $J = 0 \rightarrow J = 1$  is

$$v' = \frac{\Delta E}{\hbar} = \frac{\hbar}{4\pi^2 I}$$

and so  $I = \frac{\hbar}{4\pi^2 v'}$

$$= \frac{6.63 \times 10^{-34} \text{ Js}}{4 \times (3.14)^2 \times (1.153 \times 10^{11} \text{ s}^{-1})} = 1.46 \times 10^{-46} \text{ kg}\cdot\text{m}^2.$$

The reduced mass of the CO molecule is given by

$$\begin{aligned}\mu_{CO} &= \frac{M_C M_O}{M_C + M_O} \\ &= \frac{(12 \text{ g mol}^{-1} \times 16 \text{ g mol}^{-1}) / (6.023 \times 10^{23} \text{ mol}^{-1})^2}{(12 \text{ g mol}^{-1} + 16 \text{ g mol}^{-1}) / (6.023 \times 10^{23} \text{ mol}^{-1})} \\ &= \frac{192 \text{ g}^2 \text{ mol}^{-2} / (6.023 \times 10^{23} \text{ mol}^{-1})}{28 \text{ g mol}^{-1}} \\ &= 1.14 \times 10^{-23} \text{ g} = 1.14 \times 10^{-26} \text{ kg.}\end{aligned}$$

Therefore, the internuclear separation (bond length)  $r$  is

$$\begin{aligned}r &= \sqrt{\frac{I}{\mu}} \quad [\because I = \mu r^2] \\ &= \sqrt{\frac{1.46 \times 10^{-46} \text{ kg m}^2}{1.14 \times 10^{-26} \text{ kg}}} = 1.13 \times 10^{-10} \text{ m} = 1.13 \text{ Å}.\end{aligned}$$

3. The  $J = 0 \rightarrow J = 1$  rotational absorption line occurs at  $1.153 \times 10^{11}$  cycles/s in  $^{12}\text{C}^{16}\text{O}$ , and at  $1.102 \times 10^{11}$  cycles/s in  $^{13}\text{C}^{16}\text{O}$ . Calculate the mass number of the unknown carbon isotope.

**Solution.** As shown in the last problem, the frequency absorbed in the transition  $J = 0 \rightarrow J = 1$  is given by

$$v' = \frac{h}{4\pi^2 I}$$

$$v' \propto \frac{1}{I},$$

or

where  $I$  is the moment of inertia of the molecule. Thus

$$\frac{I^{12}\text{C}^{16}\text{O}}{I^{13}\text{C}^{16}\text{O}} = \frac{1.102}{1.153}.$$

The internuclear distance  $r$  remains unchanged on isotopic substitution ; and so the moment of inertia  $I$  is proportional to the reduced mass  $\mu$ .

$$\therefore \frac{\mu^{12}\text{C}^{16}\text{O}}{\mu^{13}\text{C}^{16}\text{O}} = \frac{1.102}{1.153}.$$

Let  $n$  be the mass number of the unknown isotope. Then

$$\frac{\mu^{12}\text{C}^{16}\text{O}}{\mu^{n}\text{C}^{16}\text{O}} = \frac{1.102}{1.153}$$

$$\text{or } \frac{(12 \times 16)/28}{(n \times 16)/(n + 16)} = \frac{1.102}{1.153}$$

$$\text{or } \frac{12}{28} \frac{n + 16}{n} = \frac{1.102}{1.153}$$

$$\text{or } \frac{n + 16}{n} = \frac{1.102}{1.153} \times \frac{28}{12} = 2.23$$

$$\text{or } n + 16 = 2.23 n$$

$$\text{or } 16 = 1.23 n$$

$$\text{or } n = \frac{16}{1.23} = 13.$$

**4.** The OH-radical has a moment of inertia of  $1.48 \times 10^{-47} \text{ kg m}^2$ . Calculate its internuclear distance. Also calculate, for  $J = 5$ , its angular momentum and angular velocity. Determine the energy absorbed in the  $J = 6 \leftarrow J = 5$  transition in  $\text{cm}^{-1}$  and in joule.

$$(h = 6.63 \times 10^{-34} \text{ Js}, c = 3.0 \times 10^8 \text{ m s}^{-1}, N_A = 6.023 \times 10^{23} \text{ mol}^{-1}).$$

(Meerut sp. paper 92)

**Solution.** The reduced mass of the OH-radical is given by

$$\begin{aligned}\mu_{OH} &= \frac{M_O M_H}{M_O + M_H} \\ &= \frac{(16 \times 1)/(6.023 \times 10^{23})^2}{(16 + 1)/(6.023 \times 10^{23})} = \frac{16}{17 \times (6.023 \times 10^{23})} \\ &= 1.56 \times 10^{-24} \text{ g} = 1.56 \times 10^{-27} \text{ kg}\end{aligned}$$

If  $I$  is the moment of inertia, then the internuclear distance  $r$  is

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.48 \times 10^{-47} \text{ kg m}^2}{1.56 \times 10^{-27} \text{ kg}}} = 0.97 \times 10^{-10} \text{ m} = 0.97 \text{ Å}.$$

The angular momentum of the radical, assumed as rigid rotator, is given by

$$L = \frac{\hbar}{2\pi} \sqrt{J(J+1)}.$$

For  $J = 5$ , we have

$$L = \frac{6.63 \times 10^{-34} \text{ Js}}{2 \times 3.14} \sqrt{5 \times 6} = 5.78 \times 10^{-34} \text{ Js}.$$

The angular velocity corresponding to the angular momentum  $L (= I\omega)$  is

$$\omega = \frac{L}{I} = \frac{5.78 \times 10^{-34} \text{ Js}}{1.48 \times 10^{-47} \text{ kg m}^2} = 3.90 \times 10^{13} \text{ s}^{-1}.$$

The wave number of the radiation absorbed (absorbed energy in  $\text{cm}^{-1}$ ) in transition from  $J$  to  $J + 1$  is given by

$$v = 2B(J+1),$$

where  $J$  refers to the lower state. Therefore, for the transition  $J = 6 \leftarrow J = 5$ , we have

$$v = 2B(5+1) = 12B.$$

$$\text{But } B = \frac{\hbar}{8\pi^2 I c}.$$

$$\therefore v = \frac{12\hbar}{8\pi^2 I c} = \frac{12 \times (6.63 \times 10^{-34} \text{ Js})}{8 \times (3.14)^2 \times (1.48 \times 10^{-47} \text{ kg m}^2) \times (3.0 \times 10^8 \text{ m s}^{-1})} \\ = 0.227 \times 10^5 \text{ m}^{-1} = 227 \times 10^2 \text{ m}^{-1} = 227 \text{ cm}^{-1}.$$

The energy  $E$  in joule is

$$\begin{aligned}E &= vhc = (0.227 \times 10^5 \text{ m}^{-1})(6.63 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ m s}^{-1}) \\ &= 4.51 \times 10^{-21} \text{ J}.\end{aligned}$$

**5.** The  $J = 1 \leftarrow 0$  transition in HCl occurs at  $20.68 \text{ cm}^{-1}$ . Regarding the molecule to be a rigid rotator, calculate the wavelength of the transition  $J = 15 \leftarrow 14$ .

(Meerut 2005 sp. paper)

**Solution.** The wave number of the radiation absorbed in a rotational transition from  $J$  to  $J + 1$  is given by

$$\nu = 2B(J + 1),$$

where  $J$  refers to the lower state.

For a transition from  $J = 0$  to  $J = 1$ , we have

$$\nu = 2B.$$

But  $\nu = 20.68 \text{ cm}^{-1}$  (given).

$$\therefore 2B = 20.68 \text{ cm}^{-1}$$

$$B = 10.34 \text{ cm}^{-1}.$$

or  
Again, the wave number of the radiation absorbed in the transition  $J = 15 \leftarrow 14$  is given by

$$\begin{aligned}\nu &= 2B(J + 1), \quad \text{where } J \text{ refers to lower state} \\ &= 2B(14 + 1) \\ &= 20.68 \text{ cm}^{-1} \times 15 = 310.2 \text{ cm}^{-1}.\end{aligned}$$

The corresponding wavelength is

$$\lambda = \frac{1}{\nu} = \frac{1}{310.2 \text{ cm}^{-1}} = 32 \times 10^{-4} \text{ cm} = 32 \mu\text{m}.$$

6. The transition  $J = 3$  to  $J = 4$  in HCl molecule is associated with radiation of  $83.03 \text{ cm}^{-1}$ . Use the rigid-rotator approximation to calculate the moment of inertia and internuclear distance (bond length) of HCl. Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ .

(Meerut 2002, sp. paper 95, 90)

**Solution.** The radiation absorbed in a rotational transition  $J \rightarrow J + 1$  is given by

$$\nu = 2B(J + 1),$$

where  $J$  refers to the lower state. For  $J = 3 \rightarrow J = 4$ , we have

$$\nu = 2B(3 + 1) = 8B.$$

But  $\nu = 83.03 \text{ cm}^{-1}$  (given).

$$\therefore 8B = 83.03 \text{ cm}^{-1}$$

$$B = 10.38 \text{ cm}^{-1} = 1038 \text{ m}^{-1}.$$

or

The rotational constant  $B$  is given by

$$B = \frac{h}{8\pi^2 I c}.$$

Therefore, the moment of inertia of the molecule is

$$\begin{aligned}I &= \frac{h}{8\pi^2 B c} = \frac{6.63 \times 10^{-34} \text{ Js}}{8 \times (3.14)^2 \times (1038 \text{ m}^{-1}) \times (3.0 \times 10^8 \text{ m s}^{-1})} \\ &= 2.7 \times 10^{-47} \text{ kg m}^2.\end{aligned}$$

The reduced mass of HCl molecule is

$$\begin{aligned}\mu_{HCl} &= \frac{M_H M_{Cl}}{M_H + M_{Cl}} \\ &= \frac{(1 \times 35)/(6.023 \times 10^{23})^2}{(1 + 35)/(6.023 \times 10^{23})} = 1.61 \times 10^{-24} \text{ g} = 1.61 \times 10^{-27} \text{ kg}.\end{aligned}$$

The internuclear distance (bond length) is therefore

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.7 \times 10^{-47} \text{ kg m}^2}{1.61 \times 10^{-27} \text{ kg}}} = 1.29 \times 10^{-10} \text{ m} = 1.29 \text{ \AA}.$$

7. The far infra-red spectrum of  $H^1Br^{79}$  consists of a series of lines spaced  $17\text{ cm}^{-1}$  apart. Find the internuclear distance of  $H^1Br^{79}$ . ( $\hbar = 6.63 \times 10^{-34}\text{ Js}$ ,  $c = 3.0 \times 10^8\text{ m s}^{-1}$ ,  $N_A = 6.023 \times 10^{23}$  per mol).

**Solution.** The wave numbers of the lines in a pure rotational spectrum are given by  
 $v = 2B(J + 1)$ .

where  $J$  refers to the lower rotational quantum number. The separation between two successive lines corresponding to  $J$  and  $J + 1$  is

$$\Delta v = 2B(J + 2) - 2B(J + 1) = 2B.$$

Here  $\Delta v = 17\text{ cm}^{-1}$ .

$$\therefore 2B = 17\text{ cm}^{-1}.$$

or

$$B = 8.5\text{ cm}^{-1} = 850\text{ m}^{-1}.$$

The moment of inertia of the molecule is

$$\begin{aligned} I &= \frac{\hbar}{8\pi^2 B c} \\ &= \frac{6.63 \times 10^{-34}\text{ Js}}{8 \times (3.14)^2 \times (850\text{ m}^{-1}) \times (3.0 \times 10^8\text{ m s}^{-1})} \\ &= 3.29 \times 10^{-47}\text{ kg m}^2. \end{aligned}$$

The reduced mass of  $H^1Br^{79}$  is

$$\mu_{HBr} = \frac{(1 \times 79)/(6.023 \times 10^{23})^2}{(1 + 79)/(6.023 \times 10^{23})} = 1.64 \times 10^{-24}\text{ g} = 1.64 \times 10^{-27}\text{ kg}.$$

Therefore, the internuclear distance is

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{3.29 \times 10^{-47}\text{ kg m}^2}{1.64 \times 10^{-27}\text{ kg}}} = 1.42 \times 10^{-10}\text{ m} = 1.42\text{ \AA}.$$

8. The spacing of a series of lines in the microwave spectrum of AlH is constant at  $12.604\text{ cm}^{-1}$ . Calculate the moment of inertia and the internuclear distance of the AlH molecule. What are the energy of rotation and the rate of rotation when  $J = 15$ ? ( $\hbar = 6.63 \times 10^{-34}\text{ Js}$ ,  $c = 3.0 \times 10^8\text{ m s}^{-1}$ ,  $\mu_{AlH} = 0.9718\text{ u}$ ,  $N_A = 6.023 \times 10^{23}$  per mole).

**Solution.** The spacing in the lines of a microwave (rotational) spectrum of a diatomic molecule, treated as rigid rotator, is  $2B$ , where  $B$  is the rotational constant. Thus, for AlH molecule, we have

$$2B = 12.604\text{ cm}^{-1}$$

or

$$B = 6.302\text{ cm}^{-1} = 630.2\text{ m}^{-1}.$$

But  $B = \frac{\hbar}{8\pi^2 I c}$ , where  $I$  is the moment of inertia of the rotating molecule. Therefore

$$\begin{aligned} I &= \frac{\hbar}{8\pi^2 B c} \\ &= \frac{6.63 \times 10^{-34}\text{ Js}}{8 \times (3.14)^2 \times (630.2\text{ m}^{-1}) \times (3.0 \times 10^8\text{ m s}^{-1})} \\ &= 4.44 \times 10^{-47}\text{ kg m}^2. \end{aligned}$$

The reduced mass of the AlH molecule is

$$\mu_{AlH} = 0.9718 \text{ u.}$$

But  $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg.}$

$$\therefore \mu_{AlH} = 0.9718 \text{ u} \times (1.66 \times 10^{-27} \text{ kg/u}) = 1.613 \times 10^{-27} \text{ kg.}$$

Therefore, the internuclear distance is

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{4.44 \times 10^{-47} \text{ kg m}^2}{1.613 \times 10^{-27} \text{ kg}}} = 1.66 \times 10^{-10} \text{ m} = 1.66 \text{ Å.}$$

The energy of rotation of the molecule is given by

$$E = \frac{h^2}{8 \pi^2 I} J(J+1) = B h c J(J+1).$$

For  $J = 15$ , we have

$$E = (630.2 \text{ m}^{-1}) \times (6.63 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ m s}^{-1}) \times 15 \times 16 \\ = 3.01 \times 10^{-20} \text{ J.}$$

Classically,  $E = \frac{1}{2} I \omega^2$ . Therefore, the frequency of rotation is

$$\omega = \sqrt{\frac{2E}{I}} = \sqrt{\frac{2 \times 3.01 \times 10^{-20} \text{ J}}{4.44 \times 10^{-47} \text{ kg m}^2}} = 3.68 \times 10^{13} \text{ rad/s.}$$

**9.** The wave numbers of the lines in a band are given by  $\nu = 1000(2n - 1)$  for  $n$  positive and by  $\nu = -1000(2n + 1)$  for  $n$  negative. Calculate the moment of inertia of the emitter molecule of the spectrum. *(Meerut sp. paper 2004, 03)*

**Solution.**  $\nu = 1000(2n - 1)$

$$= 1000, 3000, 5000, \dots \text{ cm}^{-1}; \quad \text{for } n = 1, 2, 3, \dots \\ \text{and} \quad \nu = -1000(2n + 1) \\ = 1000, 3000, 5000, \dots \text{ cm}^{-1}; \quad \text{for } n = -1, -2, -3, \dots$$

This means that the separation between any two consecutive lines is  $2000 \text{ cm}^{-1}$ ; so that

$$2B = 2000 \text{ cm}^{-1}$$

$$B = 1000 \text{ cm}^{-1} = 10^5 \text{ m}^{-1}.$$

The moment of inertia of the molecule is therefore

$$I = \frac{h}{8 \pi^2 B c} = \frac{6.63 \times 10^{-34} \text{ Js}}{8 \times (3.14)^2 \times (10^5 \text{ m}^{-1}) \times (3.0 \times 10^8 \text{ m s}^{-1})} \\ = 2.8 \times 10^{-49} \text{ kg m}^2.$$

## QUESTIONS

1. Discuss the condition under which the pure rotational spectrum of a diatomic molecule is observable. State, giving reasons, which of the molecules  $H_2$ ,  $N_2$ ,  $HCl$  and  $OH$  will give pure rotational spectrum and which will give rotational Raman spectrum. *(Meerut sp. paper 2006)*

**Hint :** Only  $HCl$  and  $OH$  will give pure rotational spectrum, all the four will give rotational Raman spectrum.

2. Describe a suitable experimental arrangement for the study of pure rotational spectrum of a diatomic molecule and explain how the moment of inertia of the molecule may be determined from such studies.

*(Meerut sp. paper 2006, 05, 04, 02, 00, 94)*

3. Obtain expression for the eigenvalues for the square of the angular momentum and for the component of the angular momentum in a fixed direction in the case of a rigid rotator.
  4. Obtain an expression for the rotational energy levels of a diatomic molecule. (Meerut 2003, Kanpur 2003)
  5. Write down the expression for the energy of a rigid-rotator model of a diatomic molecule and predict the pure rotational spectrum of the molecule. (Meerut 97 sp. paper)
  6. Give main features of the pure rotational band spectrum of a heteronuclear diatomic molecule. How are they explained, treating the molecule as a rigid rotator ? What information is provided by the study of this spectrum regarding the molecule ? (Meerut 2004, 99 S, 90)
  7. Discuss and explain briefly the principal features of the pure rotational band spectrum of a diatomic molecule. Show in a diagram the allowed rotational energy levels in terms of rotational constant. (Meerut 2002, sp. paper 2005, 02, 89)
  8. Show that the absorption spectrum of a rigid rotator is expected to consist of a series of equidistant lines. (Kanpur 2002)
  9. Show that for pure rotational spectrum of a diatomic molecule, the wave-number difference between the consecutive lines is  $h/4\pi^2 I c$ , where symbols have their usual meanings.
  10. Discuss rotational spectrum of a diatomic molecule, treated as a non-rigid rotator. (Meerut 2004 S)
  11. What effects will the presence of isotopic species such as  $H^1$ ,  $H^2$ ,  $Cl^{35}$ ,  $Cl^{36}$  and  $Cl^{37}$  have on the rotational spectrum of HCl ?
  12. What is the change in the value of the rotational constant  $B$  when  $H^2$  is substituted for  $H^1$  in the hydrogen molecule ?
- Ans.**  $B$  is decreased by a factor of 2.

## PROBLEMS

1. The rotational inertia of HCl molecule is  $2.66 \times 10^{-47} \text{ kg-m}^2$ . Estimate the energy difference between the lowest and the first excited rotational states of the molecule. Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ .  
**Ans.**  $4.2 \times 10^{-22} \text{ J} = 2.6 \times 10^{-3} \text{ eV}$
2. The internuclear distance in CO molecule is  $1.13 \text{ \AA}$ . Find the energy difference between  $J = 0$  and  $J = 1$  rotational levels of the molecule ( $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $\mu_{CO} = 1.14 \times 10^{-26} \text{ kg}$  and  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ ).  
**Ans.**  $4.79 \times 10^{-4} \text{ eV}$
3. The  $J = 0 \rightarrow J = 1$  transition in  $HCl^{35}$  occurs at  $6.264 \times 10^5$  megacycles/s. Calculate the moment of inertia and internuclear distance of  $HCl^{35}$  ( $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $N_A = 6.023 \times 10^{23}$  per mole).  
**Ans.**  $2.69 \times 10^{-47} \text{ kg m}^2$ ,  $1.29 \text{ \AA}$
4. How many revolutions per second does a  $C^{12}O^{16}$  molecule make when  $J = 1, J = 10$ ?  $r = 1.128 \text{ \AA}$ . ( $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $N_A = 6.023 \times 10^{23}$ )  
**Ans.**  $1.64 \times 10^{11}$ ,  $1.21 \times 10^{11}$

5. In the far infra-red spectrum of HCl molecule, the first line falls at  $20.68 \text{ cm}^{-1}$ . Calculate the moment of inertia and bond length of the molecule. Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ .

**Hint :** The first line falls at  $2B$ .

$$\text{Ans. } 2.71 \times 10^{-47} \text{ kg m}^2, 1.29 \text{ \AA.}$$

6. The separation of lines in the far infra-red spectrum of HCl molecule is  $20.68 \text{ cm}^{-1}$ . Calculate the moment of inertia and internuclear distance of the molecule. Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ .

**Hint :**  $B = 10.34 \text{ cm}^{-1} = 1034 \text{ m}^{-1}$ .

(Meerut 97 sp. paper)

$$\text{Ans. } 2.71 \times 10^{-47} \text{ kg m}^2, 1.29 \text{ \AA.}$$

7. The far infra-red spectrum of  $\text{H}^1\text{F}^{19}$  molecule consists of lines having a nearly constant separation of  $40.5 \text{ cm}^{-1}$ . Calculate the moment of inertia and the internuclear distance of the molecule. Take values of  $h, c, N_A$  from the last problem.

$$\text{Ans. } 1.38 \times 10^{-47} \text{ kg m}^2, 0.935 \text{ \AA.}$$

8. A  $\text{Hg}^{200}\text{Cl}^{35}$  molecule emits a 4.4-cm photon when it undergoes a transition from  $J = 1$  to  $J = 0$ . Find the internuclear distance in this molecule. The masses of  $\text{Hg}^{200}$  and  $\text{Cl}^{35}$  are respectively  $3.32 \times 10^{-25} \text{ kg}$  and  $5.81 \times 10^{-26} \text{ kg}$ .  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ .

$$\text{Hint. } 2B = \frac{1}{4.4 \text{ cm}} = 0.227 \text{ cm}^{-1} = 22.7 \text{ m}^{-1}$$

$$\text{Ans. } 2.25 \text{ \AA.}$$

9. The rotational spectrum of  $\text{H}^1\text{Cl}^{35}$  molecule contains the following wavelengths :

$$12.03 \times 10^{-5} \text{ m}$$

$$9.60 \times 10^{-5} \text{ m}$$

$$8.04 \times 10^{-5} \text{ m}$$

$$6.89 \times 10^{-5} \text{ m}$$

$$6.04 \times 10^{-5} \text{ m}$$

Find the internuclear distance of the molecule. The mass of  $\text{Cl}^{35}$  is  $5.81 \times 10^{-26} \text{ kg}$ .

$$\text{Ans. } 1.29 \text{ \AA.}$$

10. The rotational inertia of  $\text{H}_2$  molecule is  $4.5 \times 10^{-48} \text{ kg m}^2$ . Compute the temperature at which the average translational kinetic energy of an  $\text{H}_2$  molecule equals the energy difference between the ground rotational state and the first excited rotational state.  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ .

$$\text{Hint: } \frac{3}{2}kT = \frac{h^2}{4\pi^2 I}$$

$$\text{Ans. } 120 \text{ K.}$$

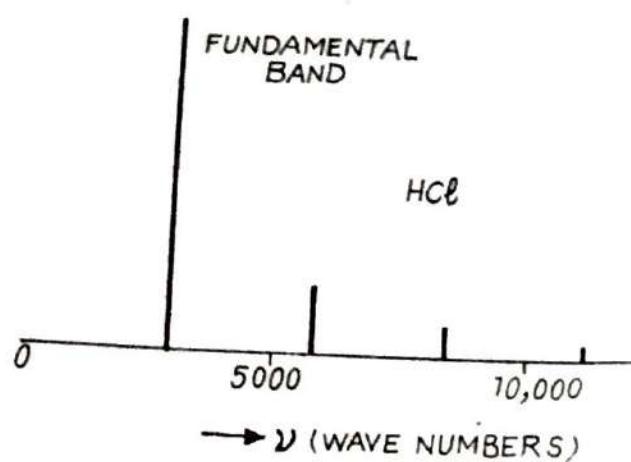
# Vibrational-Rotational Spectra

## 1. Salient Features of Vibrational-Rotational Spectra

Vibrational-rotational molecular spectra arise from transitions between vibration energy states associated with the same electronic state of the molecule, and are observed in the near infra-red ( $\approx 1 \mu - 10^2 \mu$ ) region of the electromagnetic spectrum. Like pure rotational spectra, the vibrational-rotational spectra are obtained only for molecules having permanent dipole moments; such as heteronuclear diatomic molecules. When the (unlike) nuclei of such a molecule vibrate relative to each other, the internuclear distance changes. Hence the dipole moment changes periodically with the frequency of vibration  $\nu_{osc}$  (say) of the molecule. Thus, a heteronuclear diatomic vibrating molecule is accompanied by an oscillating dipole moment. Such molecule, on the basis of classical electrodynamics, leads to the emission of radiation of frequency  $\nu_{osc}$ . Conversely, the molecule can interact with electromagnetic radiation and can absorb radiation of frequency  $\nu_{osc}$ .

Homonuclear diatomic molecules like  $H_2$ ,  $N_2$ ,  $O_2$ , which necessarily have zero dipole moment for all internuclear distances, fail to interact with radiation and so give no vibrational spectra. *The presence of an oscillating dipole moment is a must for an interaction with the oscillating electric field of radiation.* Such molecules, however, give Raman spectra.

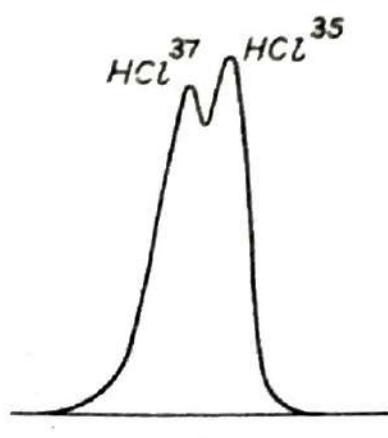
In practice, vibrational-rotational spectra are observed in absorption. The spectrum of a molecule like HCl consists of an intense band, known as fundamental band accompanied by a number of weak bands (overtones) at wave numbers approximately double, triple, ..... of the fundamental band (Fig. 1). On close



examination, the fundamental absorption band is found to consist of two close maxima, which is an isotope effect (Fig. 2). One maximum is due to  $\text{HCl}^{35}$  and the other (weaker) maximum is due to the rarer isotope  $\text{HCl}^{37}$ .

The overtone bands successively appear with rapidly decreasing intensity when the thickness of the layer of the absorbing diatomic gas is increased.

Under high resolution, a single band is found to consist of a large number of lines arranged in a particularly simple manner. This is the "fine structure" of infra-red bands.



(Fig. 2)

## 2. The Molecule as a Harmonic Oscillator

The near infra-red spectra are attributed to the vibrations of the nuclei in the diatomic molecule along the internuclear axis. The simplest possible assumption about the form of vibrations is to treat the molecule as a harmonic oscillator. The potential energy function under whose influence the nuclei vibrate is then parabolic, and of the form given by

$$V(r) = \frac{1}{2} k (r - r_e)^2 = \frac{1}{2} k x^2,$$

where  $k$  is the force constant,  $r_e$  is the equilibrium internuclear distance, and  $x$  is the displacement of the oscillator from the equilibrium position. The Schrödinger wave equation describing this motion would be

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2} \left( E - \frac{1}{2} k x^2 \right) \psi = 0,$$

where  $\mu$  is the reduced mass of the oscillator (diatomic molecule).

Substituting  $\alpha = \frac{8\pi^2\mu E}{h^2}$  and  $\beta = \sqrt{\frac{4\pi^2\mu k}{h^2}}$ , we get

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2) \psi = 0.$$

Let us introduce a dimensionless independent variable

$$\xi = \sqrt{\beta} x$$

so that

$$\frac{d^2}{dx^2} = \beta \frac{d^2}{d\xi^2}.$$

Then, we have

$$\beta \frac{d^2\psi}{d\xi^2} + \left( \alpha - \beta^2 \frac{\xi^2}{\beta} \right) \psi = 0$$

$$\frac{d^2\psi}{d\xi^2} + \left( \frac{\alpha}{\beta} - \xi^2 \right) \psi = 0. \quad \dots(i)$$

Let us try a solution of the following form to this equation :

$$\psi(\xi) = C U(\xi) e^{-\xi^2/2}. \quad \dots(ii)$$

Making this substitution in eq. (i), we get

$$\frac{d^2 U}{d\xi^2} - 2\xi \frac{dU}{d\xi} + \left( \frac{\alpha}{\beta} - 1 \right) U = 0.$$

If we replace  $\frac{\alpha}{\beta} - 1$  by  $2v$ , then this equation becomes the Hermite differential equation and we may put  $U(\xi)$  as  $H_v(\xi)$ . Then

$$\frac{d^2 H_v(\xi)}{d\xi^2} - 2\xi \frac{dH_v(\xi)}{d\xi} + 2v H_v(\xi) = 0.$$

This shows that the solution of eq. (i) is obtained by replacing  $U(\xi)$  by the Hermite polynomial  $H_v(\xi)$  in eq. (ii). That is

$$\Psi(\xi) = C H_v(\xi) e^{-\xi^2/2}.$$

These solutions are acceptable only for  $v = 0, 1, 2, \dots$ . The restriction on  $v$  gives a corresponding restriction on  $E$ . We have

$$\frac{\alpha}{\beta} = 2v + 1$$

or  $\frac{8\pi^2 \mu E/h^2}{2\pi \sqrt{\mu k/h}} = 2v + 1 = 2\left(v + \frac{1}{2}\right)$

or  $E = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2}\right).$

But  $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  =  $v_{osc}$  (classical frequency of oscillator).

$$\therefore E = h v_{osc} \left(v + \frac{1}{2}\right).$$

This gives the allowed energies for the harmonic oscillator.  $v$  is called the vibrational quantum number which can take the integral values :

$$v = 0, 1, 2, 3, \dots$$

A special feature of the quantum-mechanical oscillator is the existence of zero-point energy,  $\frac{1}{2} h v_{osc}$ .

**Spectrum :** Let us now investigate the expected spectrum of such an oscillator. The vibrational terms (energies in wave number unit  $m^{-1}$  or  $cm^{-1}$ ) are

$$G(v) = \frac{E}{h c} = \frac{v_{osc}}{c} \left(v + \frac{1}{2}\right).$$

$\frac{v_{osc}}{c}$  is the classical frequency in wave number unit and is known as vibrational constant, denoted by  $\omega$ . Thus

$$G(v) = \omega \left(v + \frac{1}{2}\right).$$

Substituting  $v = 0, 1, 2, \dots$ , we get

$$G(v) = \frac{1}{2} \omega, \frac{3}{2} \omega, \frac{5}{2} \omega, \frac{7}{2} \omega, \dots$$

Thus, we have a series of equispaced discrete vibrational levels, the common separation being  $\omega$  (Fig. 3).

When a transition takes place between an upper level  $v'$  and a lower level  $v''$ , the wave number of the emitted or absorbed radiation is

$$v = G(v') - G(v'') \\ = \omega \left( v' + \frac{1}{2} \right) - \omega \left( v'' + \frac{1}{2} \right).$$

Now, for a harmonically oscillating molecule of dipole moment  $M$ , the matrix element is found to be non-vanishing only when

$$\frac{dM}{dx} \neq 0 \text{ and } \Delta v = \pm 1,$$

that is, vibrational transition can only occur when the molecule has a permanent dipole moment which changes with distance. Further, the selection rule  $\Delta v = \pm 1$  gives

$$v' = v'' + 1.$$

$[\because v' > v'']$

The spacings between the vibrational levels are considerably larger than the spacings between the rotational levels of a molecule, infact larger than  $kT$  at room temperature. Hence most of the molecules in a sample exist in the  $v = 0$  state\*, with only their zero-point energies (except in case of very heavy molecules which have smaller vibrational spacings  $\omega$ ). Thus, the main vibrational transition in absorption is

$$v' = 1 \leftarrow v'' = 0.$$

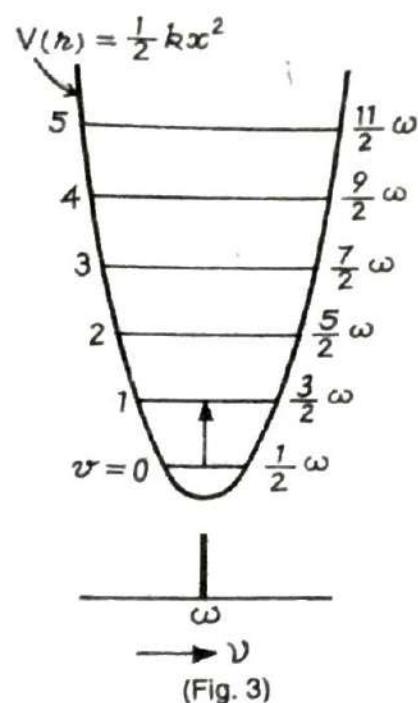
The absorbed wave number corresponding to this transition ( $v'' = 0, v' = 1$ ) is

$$v = \omega \left( v' + \frac{1}{2} \right) - \omega \left( v'' + \frac{1}{2} \right) \\ = \frac{3}{2} \omega - \frac{1}{2} \omega = \omega.$$

Thus, the vibrational spectrum is expected to consist of a single band at  $\omega$ . The observation of a very intense band in the infra-red spectrum thus leads to the conclusion that it is a vibrational spectrum, the nuclei carrying out harmonic vibrations along the internuclear axis. However, the weak occurrence of overtone bands at wave numbers nearly two, three times the wave number of the main band is still to be explained, and is connected with the deviations from the oscillations being "harmonic".

### 3. Molecule as Anharmonic Oscillator

A comparison of an observed near infra-red spectrum with that expected from a diatomic molecule treated as harmonic oscillator shows an important disagreement. The harmonic oscillator would give a single band at wave number  $\omega$ , which is the classical frequency of vibration of the molecule. The actual infra-red spectrum is, however, found to consist of an intense (fundamental) band at  $\omega$ , plus a number of weak bands (overtones)



(Fig. 3)

\* This situation is very different from that of rotational states, where the majority of the molecules at room temperature exist in higher (rotational) states.

at wave numbers slightly lesser and lesser than  $2\omega, 3\omega, \dots$ . The observation of overtones indicates that the selection rule  $\Delta v = \pm 1$  is not strictly obeyed, and transitions corresponding to  $\Delta v > 1$  do take place. This, in turn, is attributed to the fact that the dipole moment of the molecule is *not* strictly linear with respect to the internuclear displacement  $x (= r - r_e)$ . This is expressed as 'electrical anharmonicity' of the molecule. The observation that the overtones appear *not* exactly at  $2\omega, 3\omega, \dots$  but at lesser and lesser values indicates that the vibrational energy levels are not exactly equally-spaced, but converge slowly. This is attributed to the fact that for an actual molecule the potential energy curve is not strictly parabolic (except near the minimum). That is, the potential energy function  $V(r)$  is not harmonic and we must include terms higher than quadratic in the Taylor's series expansion of  $V(r)$ . This is expressed as 'mechanical anharmonicity' of the molecule.

To a first approximation, let us include the cubic term in  $V(r)$ , so that,

$$\begin{aligned} V(r) &= \frac{1}{2!} \left( \frac{\partial^2 V(r)}{\partial r^2} \right)_{r=r_e} (r - r_e)^2 + \frac{1}{3!} \left( \frac{\partial^3 V(r)}{\partial r^3} \right)_{r=r_e} (r - r_e)^3 \\ &= f(r - r_e)^2 - g(r - r_e)^3 \\ &= fx^2 - gx^3, \end{aligned}$$

where  $g \ll f$ . On substituting this value of  $V(r)$  in the Schrödinger equation and solving by perturbation method, it is found that the eigenvalues of the wave equation, that is, the energy values of the anharmonic oscillator are given by

$$E(v) = \hbar c \omega_e \left( v + \frac{1}{2} \right) - \hbar c \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \dots \quad (i)$$

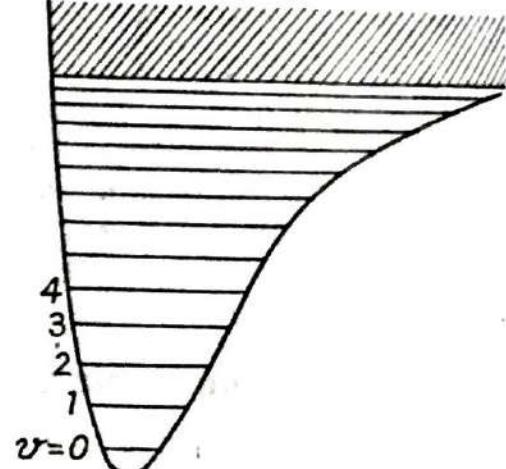
The corresponding term values are given by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \dots \quad (ii)$$

The quantity  $\omega_e$  is the wave-number spacing of energy levels that would occur if the potential curve were a parabola,  $\omega_e x_e$  is the 'anharmonicity constant' which is much smaller than  $\omega_e$  and is always positive. The eq. (ii) shows that the energy levels of the anharmonic oscillator are not equidistant, but that their separation decreases slowly with increasing  $v$  (Fig. 4).

When the molecule receives energy more than that corresponding to the uppermost vibrational level, it dissociates into atoms and the excess energy appears as (unquantised) kinetic energy of these atoms. Hence a continuum joins the uppermost level.

The zero-point energy of the anharmonic oscillator is obtained by putting  $v = 0$  in eq. (ii). Thus



(Fig. 4)

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \dots \quad \dots(\text{iii})$$

If the energy levels are referred to this lowest level as zero, then we shall re-write eq. (ii) as

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2 + \dots \quad \dots(\text{iv})$$

On equating the coefficients of like powers of  $v$  in eq. (ii) and (iv), we obtain the following relations :

$$\left. \begin{aligned} \omega_0 &= \omega_e - \omega_e x_e + \dots \\ \omega_0 x_0 &= \omega_e x_e - \dots \end{aligned} \right\} \quad \dots(\text{v})$$

Let us now investigate the infra-red spectrum for the anharmonic oscillator. Since the eigenfunctions of the anharmonic oscillator are very similar to those of the harmonic oscillator, the selection rule  $\Delta v = \pm 1$  still holds giving the most intense transitions. In addition, for the anharmonic oscillator, transitions corresponding to  $\Delta v = \pm 2, \pm 3, \dots$  also appear, even though with rapidly decreasing intensity. The possible transitions in absorption when all the molecules are initially in the  $v = 0$  state are shown in Fig. 5. This explains the appearance of observed weak overtone bands, together with the intense fundamental band.

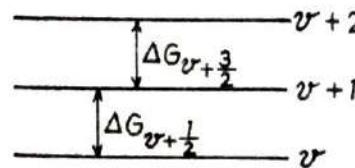
If it is also seen that transitions with  $\Delta v = 2, 3, 4, \dots$  have approximately, but not exactly, two, three, four, ..... times the wave number of the transition  $\Delta v = 1$ , in agreement with observation.

The absorbed wave numbers for the transition  $v \leftarrow 0$  are

$$\begin{aligned} v &= G(v) - G(0) &= G_0(v) - G_0(0) \\ &= \omega_e v - \omega_e x_e v^2 - \omega_e x_e v \dots &= \omega_0 v - \omega_0 x_0 v^2 \dots \quad \dots(\text{vi}) \end{aligned}$$

Thus, the observed absorption wave numbers give directly the positions of the vibrational levels above the lowest level.

The wave-number separation between two successive absorption bands (or levels) (Fig. 6) is given by



(Fig. 6)

$$\Delta G_{v+\frac{1}{2}} = G(v+1) - G(v) = G_0(v+1) - G_0(v)$$

$$= \omega_e - 2 \omega_e x_e - 2 \omega_e x_e v = \omega_0 - \omega_0 x_0 - 2 \omega_0 x_0 v. \quad \dots(\text{vii})$$

Thus, as  $v$  increases, the separation between successive bands (or levels) decreases very nearly linearly, in agreement with observation.

The second differences are given by

$$\begin{aligned}\Delta^2 G_{v+1} &= \Delta G_{v+\frac{1}{2}} - \Delta G_{v-\frac{1}{2}} \\ &= [\omega_r - 2\omega_r x_r - 2\omega_r x_r(v+1)] - [\omega_r - 2\omega_r x_r - 2\omega_r x_r(v)] \\ &= -2\omega_r x_r = -2\omega_0 x_0.\end{aligned}$$

Thus, the second difference directly determines the anharmonicity constant  $\omega_r x_r$  (or  $\omega_0 x_0$ ).

The values of  $\omega_r$  and  $\omega_0$  are then obtained from the observed wave number of the fundamental band, which is given by

$$\begin{aligned}v(0 \rightarrow 1) &= \Delta G_{\frac{1}{2}} = G(1) - G(0) = G_0(1) - G_0(0) \\ &= \omega_r - 2\omega_r x_r = \omega_0 - \omega_0 x_0.\end{aligned}$$

Since  $\omega_r$ ,  $x_r$ , and  $\omega_0 x_0$  have already been determined,  $\omega_r$  and  $\omega_0$  can be evaluated from the last expression. Thus, we can determine the vibrational constants  $\omega_r$  and  $\omega_r x_r$  (or  $\omega_0$  and  $\omega_0 x_0$ ) from the observed positions of the infra-red absorption bands of a diatomic molecule.

#### 4. Vibrational Frequency and Force Constant for Anharmonic Oscillator

The classical vibrational frequency for a harmonic oscillator is

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

where  $k$  is the force-constant and  $\mu$  is the reduced mass. The separation of successive vibrational levels is constant and is equal to  $\omega$  ( $= v_{osc}/c$ ) which is the classical wave-number frequency.

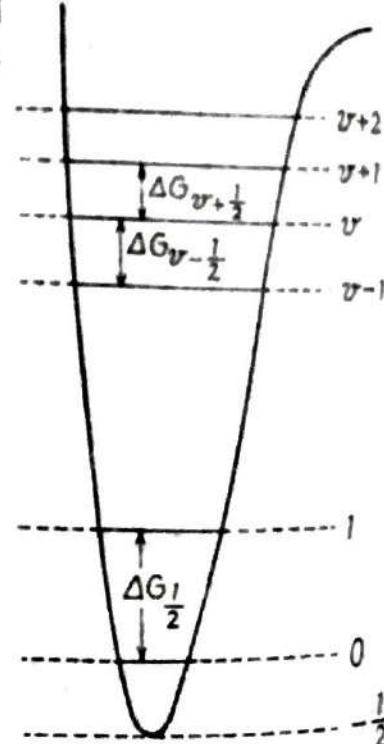
In case of anharmonic oscillator, the classical frequency as given above holds for very small amplitudes only. Infact, it decreases slowly as the amplitude (that is,  $v$ ) increases..

The exact classical expression for the vibrational frequency of anharmonic oscillator in the state  $v$  (Fig. 7) is given by

$$\begin{aligned}v_{osc}(v) &= c \Delta G_v \\ &= c \frac{\Delta G_{v+\frac{1}{2}} + \Delta G_{v-\frac{1}{2}}}{2} \\ &= \frac{1}{2} c [ \{G(v+1) - G(v)\} \\ &\quad + \{G(v) - G(v-1)\} ] \\ &= \frac{1}{2} c [ G(v+1) - G(v-1)].\end{aligned}$$

Now, we know that,

$$\begin{aligned}G(v) &= \omega_r \left( v + \frac{1}{2} \right) - \omega_r x_r \left( v + \frac{1}{2} \right)^2 \\ \therefore v_{osc}(v) &= \frac{1}{2} c \left[ \left\{ \omega_r \left( v + \frac{3}{2} \right) - \omega_r x_r \left( v + \frac{3}{2} \right)^2 \right\} \right. \\ &\quad \left. - \left\{ \omega_r \left( v - \frac{1}{2} \right) - \omega_r x_r \left( v - \frac{1}{2} \right)^2 \right\} \right]\end{aligned}$$



(Fig. 7)

$$\begin{aligned}
 &= \frac{1}{2} c \left[ \omega_e \left( v + \frac{3}{2} - v + \frac{1}{2} \right) - \omega_e x_e \left\{ \left( v + \frac{3}{2} \right)^2 - \left( v - \frac{1}{2} \right)^2 \right\} \right] \\
 &= \frac{1}{2} c [ 2 \omega_e - \omega_e x_e (4v + 2) ] \\
 &= c [ \omega_e - \omega_e x_e (2v + 1) ] \\
 &= c (\omega_e - \omega_e x_e - 2 \omega_e x_e v).
 \end{aligned}$$

Thus, as  $v$  increases, the classical vibrational frequency  $v_{osc}(v)$  decreases.

Let us imagine a hypothetical state with  $v = -\frac{1}{2}$  (for which the vibrational energy is zero). The frequency for this state is given by

$$v_{osc} \left( -\frac{1}{2} \right) = c \omega_e .$$

Thus,  $\omega_e$  represents the vibrational frequency (in wave numbers) that the anharmonic oscillator would have classically for an infinitesimal amplitude, that is, in the imaginary state  $v = -\frac{1}{2}$  at the very bottom of the potential curve.

From the vibrational frequency  $\omega_e$  for infinitesimal amplitude, the force-constant  $k_e$  of the anharmonic oscillator for the infinitesimal displacement may be determined. We know that

$$v_{osc} = c \omega_e = \frac{1}{2\pi} \sqrt{\frac{k_e}{\mu}}$$

$$k_e = 4\pi^2 \mu c^2 \omega_e^2 .$$

or

For the molecule HCl (say), we have

$$\mu = 1.61 \times 10^{-27} \text{ kg} \text{ and } \omega_e = 2989 \text{ cm}^{-1} = 298900 \text{ m}^{-1} .$$

$$\begin{aligned}
 \therefore k_e &= 4 \times (3.14)^2 \times (1.61 \times 10^{-27} \text{ kg}) \times (3.0 \times 10^8 \text{ m s}^{-1})^2 \times (298900 \text{ m}^{-1})^2 \\
 &= 510 \text{ N/m} .
 \end{aligned}$$

This is somewhat larger than the value of the force-constant ( $k = 480 \text{ N/m}$ ) obtained from the harmonic oscillator model of HCl, using  $k = 4\pi^2 \mu c^2 \omega^2$  where  $\omega = 2886 \text{ cm}^{-1}$ .

## 5. Isotope Effect on Vibrational Levels

Different isotopic molecules have different vibrational levels, and hence different vibrational frequencies. The classical frequency of a molecule, assumed as harmonic oscillator is given by

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} .$$

The force-constant "k" is determined by the electronic motion only and is therefore exactly the same for different isotopic molecules. The reduced mass is, however, different for different isotopes. If  $\omega^i$  is vibrational constant for the heavier isotope, we have

$$\frac{\omega^i}{\omega} = \frac{v_{osc}^i}{v_{osc}} = \sqrt{\frac{\mu}{\mu^i}} = \rho \text{ (say)} .$$

The heavier isotopic molecule has the smaller frequency ( $\rho < 1$ ).

The vibrational terms of two isotopic molecules (assuming harmonic vibrations) are given by

$$G(v) = \omega \left( v + \frac{1}{2} \right)$$

and

$$G^i(v) = \omega^i \left( v + \frac{1}{2} \right) = \rho \omega \left( v + \frac{1}{2} \right).$$

Therefore, the isotopic shift of a vibrational level  $v$  is

$$G^i(v) - G(v) = (\rho - 1) \omega \left( v + \frac{1}{2} \right).$$

Since  $\rho < 1$ ; we have

$$G^i(v) < G(v).$$

Thus, the vibrational levels of the heavier isotope are lower than the corresponding levels of the lighter isotope.

If anharmonicity be taken into account, the terms are given by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$$

and

$$G^i(v) = \rho \omega_e \left( v + \frac{1}{2} \right) - \rho^2 \omega_e x_e \left( v + \frac{1}{2} \right)^2,$$

so that we have

$$\omega_e^i = \rho \omega_e \quad \text{and} \quad \omega_e^i x_e^i = \rho^2 \omega_e x_e.$$

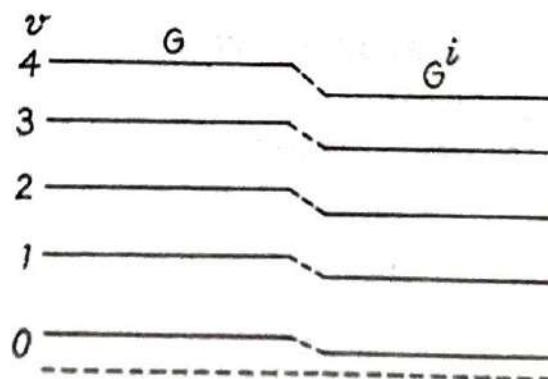
The isotopic shift of a vibrational level is now

$$G^i(v) - G(v) = (\rho - 1) \omega_e \left( v + \frac{1}{2} \right) - (\rho^2 - 1) \omega_e x_e \left( v + \frac{1}{2} \right)^2.$$

If  $\rho$  is only slightly different from 1, we can write  $\rho + 1 \approx 2$ , so that

$$G^i(v) - G(v) \approx (\rho - 1) \left( v + \frac{1}{2} \right) \left[ \omega_e - 2 \omega_e x_e \left( v + \frac{1}{2} \right) \right].$$

Since  $\rho < 1$ ;  $G^i(v) - g(v)$  is negative. Thus, the vibrations levels of the heavier isotope are lower than those of the lighter, and the shift between corresponding levels increases with increasing  $v$  (Fig. 8).



(Fig. 8)

The shifting in levels results in the doubling of the vibrational bands. The band-shift is (ignoring anharmonicity)

$$\begin{aligned} \Delta v &= v^i - v = (G^{i'} - G^{i''}) - (G' - G'') \\ &= (G^{i'} - G') - (G^{i''} - G'') \end{aligned}$$

$$\begin{aligned}
 &= \left\{ \rho \omega \left( v' + \frac{1}{2} \right) - \omega \left( v' + \frac{1}{2} \right) \right\} - \left\{ \rho \omega \left( v'' + \frac{1}{2} \right) - \omega \left( v'' + \frac{1}{2} \right) \right\} \\
 &= \left\{ (\rho - 1) \omega \left( v' + \frac{1}{2} \right) \right\} - \left\{ (\rho - 1) \omega \left( v'' + \frac{1}{2} \right) \right\} \\
 &= (\rho - 1) \omega (v' - v'').
 \end{aligned}$$

Thus, for the fundamental band ( $v' = 1, v'' = 0$ ), we obtain

$$\Delta v = (\rho - 1) \omega.$$

The shift increases as the order of the band (value of  $v'$ ) increases. As we have seen, in the infra-red spectrum of HCl each band is in fact a double band, one corresponding to  $\text{HCl}^{35}$  and the other to  $\text{HCl}^{37}$ . The band belonging to  $\text{HCl}^{37}$  is shifted by a small amount toward shorter wave number side with respect to the corresponding band belonging to  $\text{HCl}^{35}$ , and the shift increases with the order of the band. In fact, every line of each (rotation-vibration) band has a weaker companion on the shorter wave number side. To this (vibrational) shift of each line is added a rotational isotopic shift also.

For molecules like  $\text{HCl}^{35}$  and  $\text{DCl}^{35}$  (or  $\text{HCl}^{37}$  and  $\text{DCl}^{37}$ )  $\rho$  is nearly 0.7 (quite different from 1) and the shift is so great that the bands lie in quite different spectral regions.

## 6. Fine Structure of Infra-red Bands : Molecule as Vibrating Rotator

The near infra-red spectra of molecules consist of "bands" (not lines), each band being composed of close lines arranged in a particular manner. In the series of lines which are *not* equidistant, a line is missing at the centre of the band. The missing line is known as the 'null line' or 'zero gap'. Further, the lines show a rather poor tendency of convergence toward the high-wave number side, and the band is said to be degraded toward the low-wave number side, that is, toward the red.

The observed fine structure in infra-red band suggests that in a vibrational transition the molecule also changes its rotational energy state, that is, it must be treated as a vibrating-rotator.

Ignoring any interaction between vibration and rotation of the molecule, the term values of a vibrating-rotator would be given by the sum of the term values of the anharmonic oscillator and the (rigid) rotator, that is,

$$G(v) + F(J) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + BJ(J+1);$$

where  $B = \frac{\hbar}{8\pi^2 I c} = \frac{\hbar}{8\pi^2 \mu r^2 c}$ ,  $\mu$  being the reduced mass of the molecule. The gives a set of rotational levels, with similar spacings, associated with each vibrational level. (For example there are about 50 rotational levels of HCl associated with each vibrational level). A transition between two vibrational levels would therefore be accompanied by a number of transitions between the two corresponding sets of rotational levels. This would result in a number of (rotational) lines in the band. These lines would form two branches of equidistant lines. This is, however, not in agreement with observation. In fact, the spacing between the lines of one branch slowly decreases and of the other branch slowly increases as we move toward higher and higher lines of the branch. This is attributed to what is known as 'vibration-rotation interaction'.

We find from the shape of the potential curve (Fig. 9) that as  $v$  increases, the equilibrium internuclear separation  $r_e$ , and hence the moment of inertia of the molecule increases so that the rotational constant  $B$  decreases. Thus,  $B$ , which determines the spacings between the rotational levels, is different for different vibrational states. Therefore, the rotational constant associated with a vibrational state  $v$  is written as  $B_v$ , and not simply as  $B$ .

Also, in a given vibrational state, the internuclear distance and hence the rotational constant is changing during the vibration. Therefore, we must use a mean value for the rotational constant in a given vibrational state, namely,

$$B_v = \frac{\hbar}{8\pi^2 \mu c} \overline{\left( \frac{1}{r^2} \right)_v},$$

where  $\overline{\left( \frac{1}{r^2} \right)_v}$  is the mean value of  $\frac{1}{r^2}$  in the vibrational state  $v$  during the vibration. It can

be shown that the rotational constant  $B_v$  in the vibrational state  $v$  is given by

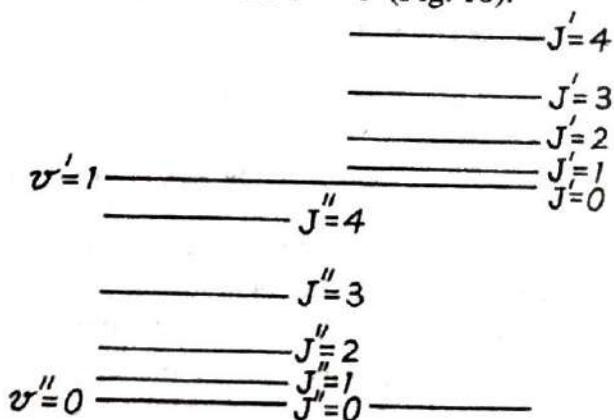
$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right) + \dots,$$

where  $\alpha_e$  is a constant depending upon the shape of the potential curve ( $\alpha_e \ll B_e$ ), and  $B_e$  is the rotational constant corresponding to the separation  $r_e$  at the minimum of the potential curve ( $B_e = \frac{\hbar}{8\pi^2 \mu r_e^2 c}$ ).

Now, the term values of a vibrating-rotator are

$$G(v) + F(v, J) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + B_v J(J+1),$$

and  $B_v' < B_v''$  (the factor  $B_v$  decreases slightly with increasing  $v$ ). The spacings between the rotational levels associated with  $v = 1$  are, for example, slightly smaller than those between the levels associated with  $v = 0$  (Fig. 10).



(Fig. 10)

Since the eigenfunctions of the vibrating-rotator are essentially the products of the eigenfunctions of the oscillator and the rotator, the selection rules are the same as for these systems individually, that is,

$$\Delta v = \pm 1, \pm 2 \dots$$

$$\Delta J = \pm 1.$$

For the main absorption, we have  $\Delta v = + 1$  and the most probable transition is  $v' = 1 \leftarrow v'' = 0$ .

For  $J$ , both the transitions  $\Delta J = \pm 1$  are now applicable in absorption, because the two  $J$ -levels involved now belong to *different* vibrational levels. For a given vibrational transition, the rotational transitions  $\Delta J = + 1$  give one set of lines called the '*R-branch*', while the rotational transitions  $\Delta J = - 1$  give the other set of lines called the '*P-branch*'. All the lines of both branches form a vibration-rotation band.

The wave numbers of the branch-lines of a particular band  $v', v''$  are given by

$$\begin{aligned} v &= [G(v') + F(v', J')] - [G(v'') + F(v'', J'')] \\ &= G(v') - G(v'') + B_v' J'(J' + 1) - B_v'' J''(J'' + 1) \\ &= v_0 + B_v' J'(J' + 1) - B_v'' J''(J'' + 1), \end{aligned}$$

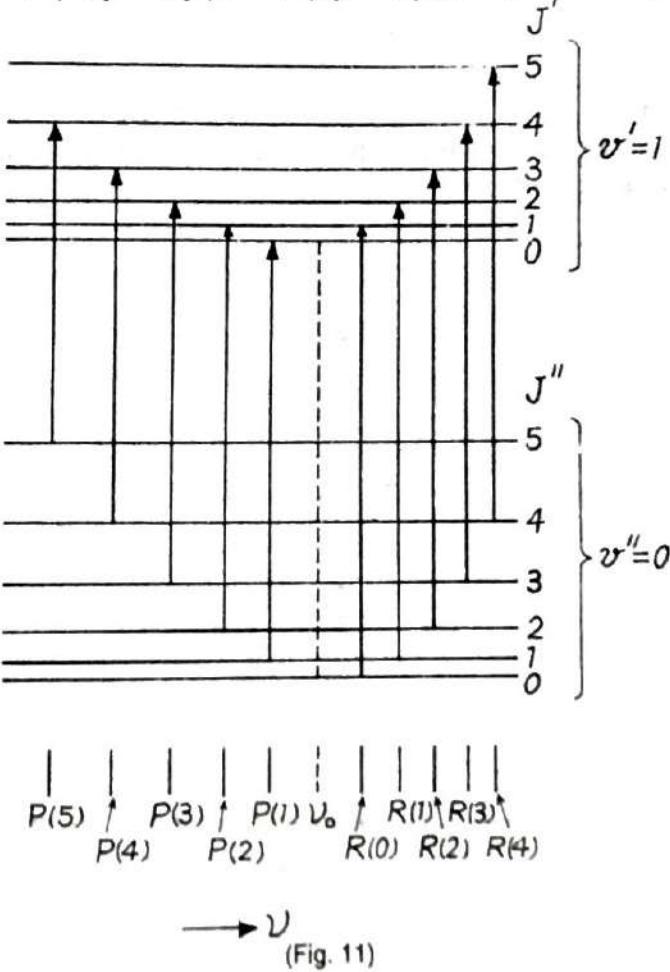
where  $v_0 \{= G(v') - G(v'')\}$  is the wave number of the pure vibrational transition (for which  $J' = J'' = 0$ ) which is unallowed ( $\Delta J \neq 0$ ) and corresponds to the missing line in the band.  $v_0$  is known as the wave number of the "band-origin".

*R-branch* : For  $\Delta J = J' - J'' = + 1$ , so that  $J' = J'' + 1$ , we obtain the lines of *R-branch* with wave numbers given by

$$\begin{aligned} v_R &= v_0 + B_v'(J'' + 1)(J'' + 2) - B_v'' J''(J'' + 1) \\ &= v_0 + B_v' J''^2 + 3B_v' J'' + 2B_v' - B_v'' J''^2 - B_v'' J'' \\ &= v_0 + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2, \quad \dots(i) \end{aligned}$$

where  $J''$ , the *lower* rotational quantum number, can take the values  $0, 1, 2, \dots$ . Thus, the *R-branch* consists of a series of lines named as  $R(0)$ ,  $R(1)$ ,  $R(2)$ , ..... corresponding to  $J'' = 0, 1, 2, \dots$  on the high wave-number side of the band-origin  $v_0$ .

Since  $B_v' < B_v''$ ;  $(B_v' - B_v'')$  is always negative, though small. The term  $(3B_v' - B_v'')$  is positive as  $B_v'$  is only slightly smaller than  $B_v''$ . Thus, the linear and quadratic terms in eq. (i) are of opposite signs. Hence the line-spacing decreases very slowly as  $J''$  takes on increasing values (Fig. 11).



(Fig. 11)

**P-branch :** For  $\Delta J = J' - J'' = -1$ , so that  $J' = J'' - 1$ , we obtain the lines of P-branch with wave numbers given by

$$\begin{aligned} v_p &= v_0 + B_v'(J'' - 1)J'' - B_v''J''(J'' + 1) \\ &= v_0 + B_v'J''^2 - B_v'J'' - B_v''J''^2 - B_v''J'' \\ &= v_0 - (B_v' + B_v'')J'' + (B_v' - B_v'')J''^2, \end{aligned} \quad \dots \text{(ii)}$$

where  $J''$ , the lower rotational quantum number, can take values 1, 2, 3, ..... ( $J''$  cannot be zero because the level  $J' = -1$  does not exist). Thus, the P-branch consists of a series of lines  $P(1), P(2), P(3), \dots$  corresponding to  $J'' = 1, 2, 3, \dots$  on the low wave-number side of the band-origin  $v_0$ .

Again, since  $B_v' < B_v''$ ,  $(B_v' - B_v'')$  is negative. Both the linear and the quadratic terms in eq. (ii) are now of the same sign so that the lines of this branch draw farther apart as  $J''$  takes on increasing values (Fig. 11).

If we neglect vibration-rotation interaction ( $B_v' = B_v'' = B$ ), the wave-numbers of R and P branches would be given by

$$v_R = v_0 + 2B + 2BJ'',$$

and

$$v_P = v_0 - 2BJ'';$$

that is, both the branches would have equispaced lines.

The exact equations for both branches, (i) and (ii), are the equations for parabolas. Since the two branches have common upper and lower states, they must be inter-related. Infact, they can be fitted to the same parabolic equation :

$$v = v_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2, \quad \dots \text{(iii)}$$

where

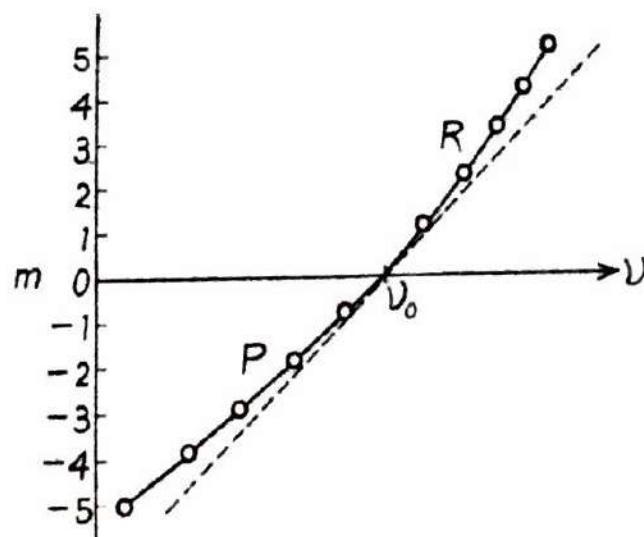
$$m = J'' + 1 = 1, 2, 3, \dots \text{ for lines } R(0), R(1), R(2), \dots,$$

$$m = -J'' = -1, -2, -3, \dots \text{ for lines } P(1), P(2), P(3), \dots,$$

and

$$m = 0 \text{ for the zero gap } v_0.$$

A plot of eq. (iii) is shown in Fig. 12. The dashed line indicates the corresponding plot if  $B_v' = B_v''$ .



(Fig. 12)

Since the constant  $\alpha_e$  is very small, the difference  $(B_v' - B_v'')$  is also very small. Hence the curve is only very slightly deviated from the straight line. This is why the vibration-rotation bands show a very poor tendency of head formation.

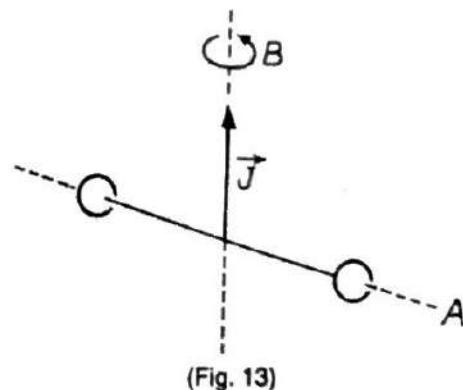
Further, for vibration-rotation bands, both the involved vibrational levels belong to the same electronic state. Therefore, the rotational constant for the upper vibrational state,  $B_v'$ , is always smaller than that for the lower vibrational state,  $B_v''$ , (since  $r_v' > r_v''$ ). In other words,  $(B_v' - B_v'')$  is always negative, though small. Hence, as the above eq. (iii) shows, the line-spacing decreases as  $m$  takes on increasing positive values. This means that the tendency of head formation is always seen in the R-branch. Conversely, the degradation of band is observed in the P-branch. This may be expressed by saying that **rotation-vibration bands are always degraded toward the lower wave-number side, that is, toward the red.**

In contrast, electronic bands show a strong tendency of head formation, and may be degraded either way.

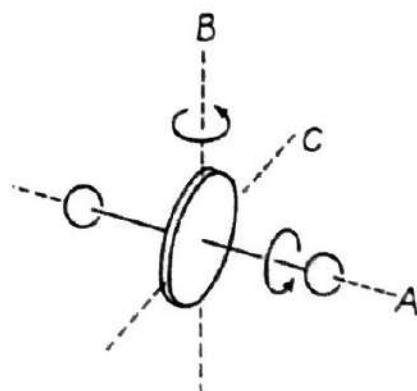
## 7. Diatomic Molecule as Symmetric Top

So far we have considered a diatomic molecule as a simple rotator whose moment of inertia about the internuclear axis (called A-axis) is zero. That is, the rotation of the molecule about the B-axis (Fig. 13) is responsible for the entire angular momentum (represented by the vector  $\vec{J}$ ) of the molecule. This is fairly true for the ground electronic state ( ${}^1\Sigma$ ) of the majority of stable diatomic molecules.

Actually, however, there are a number of electrons revolving about the two nuclei which contribute 'electronic' angular momentum. As a result, the moment of inertia about the internuclear axis (A-axis) is not, in general, exactly zero, though very small due to 'small' mass of electrons. For the  ${}^1\Sigma$ -state, for most diatomic molecules, the electron cloud surrounding the nuclei has cylindrical symmetry about the A-axis and hence the component of angular momentum along the A-axis is zero ( $\Lambda = 0$ ). For those diatomic molecules which are not in a  ${}^1\Sigma$ -state (that is,  $\Lambda \neq 0$ ), but in  ${}^1\Pi$  or  ${}^1\Delta$  (say) states, the electron cloud is not cylindrically symmetrical; that is, there is a 'net' rapid motion of the electrons about the A-axis. Hence there is a component of electronic angular momentum along the A-axis. Such molecules have a 'small' moment of inertia about the A-axis. A better model for such diatomic molecules is a 'symmetric top' which can be represented by a dumb-bell carrying a light flywheel on its axis, as shown in Fig. 14\*.



(Fig. 13)



(Fig. 14)

\*For a rigid body there are three mutually perpendicular axes, all passing through the centre of mass about which the moment of inertia is maximum (or minimum). These are called 'principal axes' A, B and C. The corresponding moments of inertia are  $I_A$ ,  $I_B$  and  $I_C$  respectively.

If  $I_A = 0$ , and  $I_B = I_C$ , the rigid body is called a rotator. If  $I_A \neq 0$  (but less than  $I_B$ ), and  $I_B = I_C$ ; the body is called a 'symmetric top'.

According to quantum mechanics, the component of the electronic angular momentum along the internuclear axis (*A*-axis) is an integral multiple of  $\frac{h}{2\pi}$ , and indicated by the vector  $\vec{\Lambda}$ . Thus

$$|\vec{\Lambda}| = \Lambda \frac{h}{2\pi},$$

where  $\Lambda$  is the quantum number of the angular momentum of the electrons about the internuclear axis.

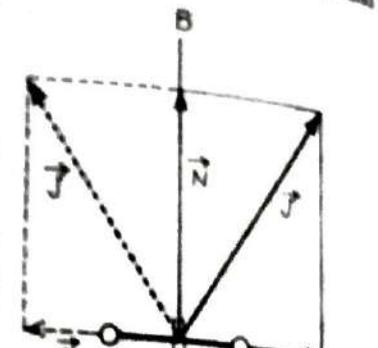
The rotation of the two nuclei about the *B*-axis results in an angular momentum vector  $\vec{N}$  along the *B*-axis.

The resultant angular momentum of the molecule is represented by the vector  $\vec{J}$  and is given by the vector sum of  $\vec{\Lambda}$  and  $\vec{N}$  (Fig. 15). It can take only the values

$$|\vec{J}| = \sqrt{J(J+1)} \frac{h}{2\pi}.$$

Thus, in general,  $\vec{J}$  subtends an angle ( $< 90^\circ$ ) with the internuclear (*A*) axis.

If the sense of rotation of the electrons is reversed,  $\vec{\Lambda}$  has the opposite direction and the vector diagram shown by dotted lines is obtained. The magnitude of  $\vec{J}$  remains unchanged. Both these orientations are equally probable for the molecules.



(Fig. 15)

It is clear from the figure that  $|\vec{J}| > |\vec{\Lambda}|$ . Therefore,  $J(J+1) > \Lambda^2$ , that is, for a given  $\Lambda$ , the possible values of the quantum number  $J$  are

$$J = \Lambda, \Lambda + 1, \Lambda + 2, \dots$$

This means that the rotational levels corresponding to  $J < \Lambda$  are missing, and this provides a means of identifying symmetric-top molecules.

**Energy Levels :** The total energy of rotation is given by

$$\begin{aligned} E &= \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \\ &= \frac{1}{2} I_A \omega_A^2 + I_B \omega_B^2 \quad [ \because I_B = I_C, \omega_B = \omega_C ] \\ &= \frac{L_A^2}{2I_A} + \frac{L_B^2}{I_B}, \end{aligned}$$

where  $L_A$  and  $L_B$  are angular momenta. Now,

$$L_A = \Lambda \frac{h}{2\pi}$$

and

$$\begin{aligned} L_B^2 + L_C^2 &= 2L_B^2 = N^2 \left( \frac{h}{2\pi} \right)^2 \\ &= \left[ J(J+1) - \Lambda^2 \right] \frac{h^2}{4\pi^2}. \end{aligned}$$

$$\therefore E = \frac{1}{2 I_A} \Lambda^2 \frac{\hbar^2}{4\pi^2} + \frac{1}{I_B} \frac{1}{2} [J(J+1) - \Lambda^2] \frac{\hbar^2}{4\pi^2}$$

$$= \left[ \frac{\Lambda^2}{2 I_A} + \frac{J(J+1) - \Lambda^2}{2 I_B} \right] \frac{\hbar^2}{4\pi^2}.$$

In wave-number units, we have

$$F(J) = \frac{E}{h c} = \left[ \frac{\Lambda^2}{I_A} + \frac{J(J+1) - \Lambda^2}{I_B} \right] \frac{\hbar}{8\pi^2 c}$$

$$= \left[ \frac{J(J+1)}{I_B} + \left( \frac{1}{I_A} - \frac{1}{I_B} \right) \Lambda^2 \right] \frac{\hbar}{8\pi^2 c}.$$

$$B = \frac{\hbar}{8\pi^2 c I_B} \text{ and } A = \frac{\hbar}{8\pi^2 c I_A}.$$

Let us put

$$\text{Then, we have } F(J) = BJ(J+1) + (A - B)\Lambda^2,$$

where  $A \gg B$ . For a given electronic state,  $\Lambda$  is constant. Thus, the rotational levels of a symmetric top are the same as those of the rigid rotator except that (i) they are shifted by an amount  $(A - B)\Lambda^2$ , which is constant for a given electronic state, and (ii) levels corresponding to  $J < \Lambda$  are missing. The energy level diagram of symmetric-top  $\Lambda = 2$  is shown in Fig. 16.

For the vibrating symmetric-top, the effective value  $B_v$  of the rotational constant has to be used which differs slightly for different vibrational levels. Thus, we have

$$G(v) + F(v, J) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$$

$$+ B_v J(J+1) + (A - B_v)\Lambda^2.$$

The selection rules obtained from the eigenfunctions of the symmetric-top are as under :

for  $\Lambda = 0$ ;  $\Delta J = \pm 1$  (simple rotator case)

for  $\Lambda \neq 0$ ;  $\Delta J = 0, \pm 1$ .

That is, for a molecule in an electronic state with  $\Lambda \neq 0$ , the transitions  $\Delta J = 0$  also appear. The  $\Delta J = \pm 1$  transitions produce an *R*- and a *P*-branch; while  $\Delta J = 0$  produces an additional branch called '*Q*' branch, with wave numbers given by

$$v_Q = \left[ G(v') + F(v', J') \right] - \left[ G(v'') + F(v'', J'') \right]$$

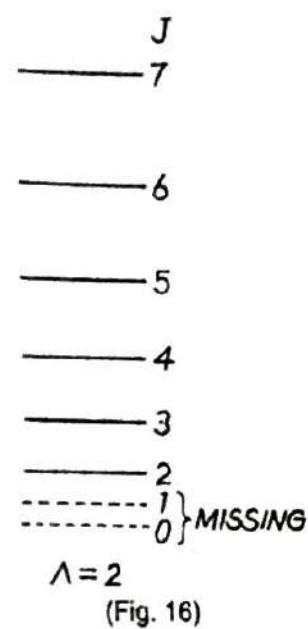
$$= \left[ G(v') - G(v'') \right] + \left[ B_v' J'(J'+1) + (A - B_v')\Lambda^2 \right]$$

$$- \left[ B_v'' J''(J''+1) + (A - B_v'')\Lambda^2 \right].$$

Putting  $G(v') - G(v'') = v_0$  (wave number of the pure vibrational transition\*\*) and  $J' = J'' = J$  (that is, applying  $\Delta J = 0$ ), we get

\*  $I_B$  is the ordinary moment of inertia of the molecule (referred so far) about the *B* axis; and  $I_A$  is the moment of inertia of the electrons about the *A* axis and is very small.

\*\*  $v_0$  corresponds to  $J' = 0 \leftarrow J'' = 0$ , which is now allowed by  $\Delta J = 0$ . But since levels  $J < \Lambda$  are missing; the levels  $J' = J'' = 0$  are absent for the  $\Lambda = 1$  state, the levels  $J' = J'' = 0, 1$  are absent for the  $\Lambda = 2$  state, and so on. Hence  $v_0$  is still missing.



$v_Q = v_0 + (B_v' - B_v'') J + (B_v' - B_v'') J^2 - (B_v' - B_v'') \Lambda^2$  ;  
where  $J = \Lambda, \Lambda + 1, \Lambda + 2, \dots$

Since  $B_v'$  is very nearly equal to  $B_v''$ , all the lines of the  $Q$  branch fall very near the band origin  $v_0$ , producing an intense 'line' which is usually unresolved.

The formation of  $R$  and  $P$  branches is same as in case of vibrating-rotator. Further in view of the fact that levels  $J < \Lambda$  are missing, one or more of the lines at the beginning of the  $R$  and  $P$  branches would be missing.

The only case of a diatomic molecule for which a  $Q$ -branch (that is, a central 'line') has been observed in the rotation-vibration infra-red bands is that of nitric oxide ( $\text{NO}$ ).

## 8. Thermal Distribution of Vibrational and Rotational Levels

**Vibrational Levels :** According to Maxwell-Boltzmann distribution law, the number of molecules in the  $v$  th state,  $N_v$ , relative to that in the lowest state,  $N_0$ , is given by

$$N_v = N_0 e^{-G_0(v) h c/k T},$$

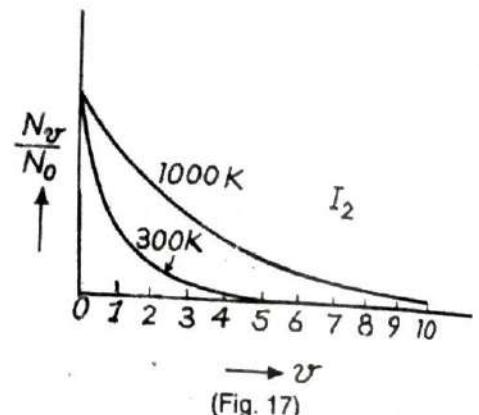
where  $k$  is Boltzmann constant and  $T$  is the absolute temperature of the gas.  $G_0(v)$  is the energy term in the  $v$  th state minus the zero-point energy, that is,

$$G_0(v) = G(v) - G(0),$$

where  $G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$ .

In Fig. 17, graphs are drawn between  $\frac{N_v}{N_0}$  and the vibrational quantum number  $v$  for

$\text{I}_2$  molecules at temperatures 300 K and 1000 K. It is seen that at room temperature the population of higher vibrational levels is very small compared to that of the lowest  $v = 0$  level. It is still smaller, even at higher temperatures, for lighter molecules  $\text{H}_2, \text{HCl}, \text{N}_2$  etc. Hence practically all the transitions observed in the infra-red absorption have  $v = 0$  in the initial state. The  $v = 1$  level has an appreciable population only in the heaviest diatomic molecules which have smaller vibrational quanta.



(Fig. 17)

**Rotational Levels :** The relative population of the various rotational levels associated with a given vibrational level is of a different nature. Unlike vibrational states, a rotational state with quantum number  $J$  is  $(2J + 1)$ -fold degenerate, and each of these degenerate states is accessible to molecules with equal probability. The frequency of occurrence of the state  $J$  is therefore  $(2J + 1)$  times than that of the state  $J = 0$ .

Let  $N_{v=0}$  be the total number of molecules in the lowest vibrational state ( $v = 0$ ). These molecules will be distributed among the rotational levels associated with this vibrational state according as

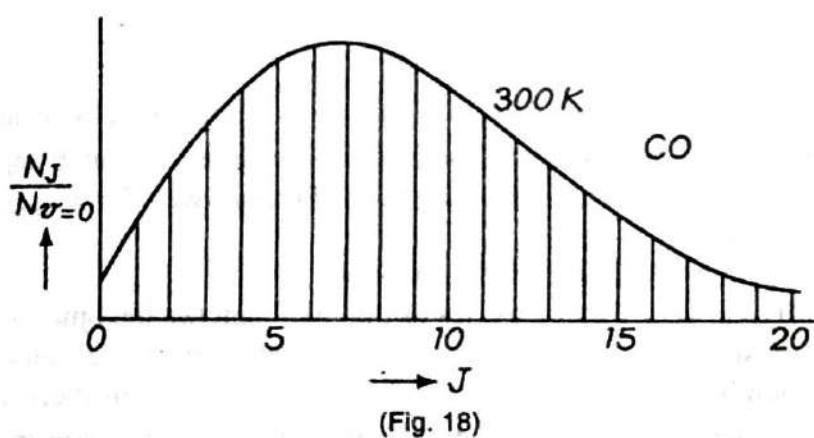
$$N_J = \frac{N_{v=0}}{Q_r} (2J + 1) e^{-F(J) h c/k T},$$

where  $Q_r$  is the rotational partition function, given by

$$\begin{aligned}
 Q_r &= \sum_{J=0}^{\infty} (2J+1) e^{-F(J)\hbar c/kT} \\
 &= \sum_{J=0}^{\infty} (2J+1) e^{-BJ(J+1)\hbar c/kT} \\
 &\approx \int_0^{\infty} (2J+1) e^{-BJ(J+1)\hbar c/kT} dJ \\
 &= \frac{kT}{\hbar c B} \\
 \therefore \frac{N_J}{N_{v=0}} &= \frac{\hbar c B}{kT} (2J+1) e^{-BJ(J+1)\hbar c/kT}.
 \end{aligned}$$

A graph of  $\frac{N_J}{N_{v=0}}$  against  $J$  for  $CO$  molecules at room temperature (300 K) is drawn in

Fig. 18. It is seen that as  $J$  increases, the population first rises to a maximum and then decreases.



The value of  $J$  at which the population is maximum is obtained by putting.

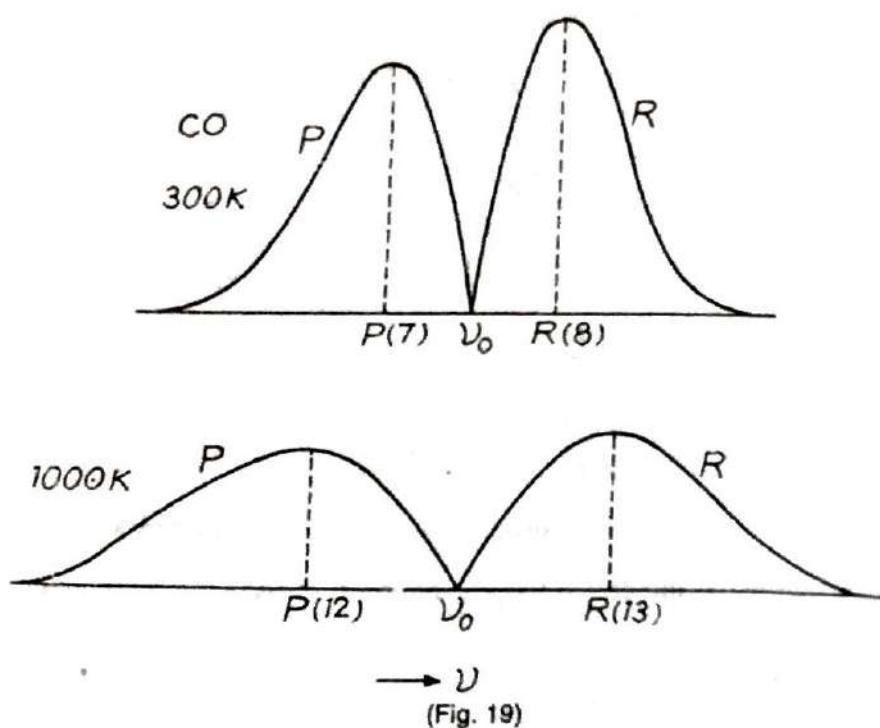
$$\frac{d}{dJ} \left( \frac{N_J}{N_{v=0}} \right) = \frac{d}{dJ} \left[ \frac{\hbar c B}{kT} (2J+1) e^{-BJ(J+1)\hbar c/kT} \right] = 0.$$

This would give

$$J_{\max} = \sqrt{\frac{kT}{2B\hbar c}} - \frac{1}{2}.$$

Thus, the value of  $J$  at which the population is maximum increases with decreasing  $B$  and with increasing  $T$ .

The experimentally observed intensity distributions in the rotational structure of  $1 \leftarrow 0$  vibrational band of  $CO$  in absorption at 300 K and 1000 K are shown in Fig. 19. We see that the intensity is zero at the band-origin  $v_0$ ; increases with increasing  $J$  on either side of it, reaches a maximum, and then slowly decreases. In both  $R$  and  $P$  branches the maximum occurs at about the same value of  $J$  at which the population is maximum. However, on the whole, the  $R$ -branch is stronger than the  $P$ -branch. (Reverse is the case in an emission band).



As the temperature of the molecular gas is raised, the following effects are observed :

- The band extends on both sides because more lines in each branch appear.
- The intensity maxima in both branches move farther away from  $\nu_0$ , that is, occur at higher  $J$  values.
- The height of the intensity maxima decreases.
- The inequality between the intensities of the two branches becomes less marked.

If the rotational structure of a band is not resolved, then the  $P$  and  $R$  branches appear as wings extending on either side of the band-origin  $\nu_0$ . In these wings, the  $P$  and  $R$  maxima can be recognised and their separation can be measured. From this separation, the rotational constant  $B$  for the molecule can be computed roughly if temperature is known.

The value of  $J$  at which maxima occur is given by

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

Now, ignoring vibration-rotation interaction, the wave numbers of  $R$  and  $P$  branch-lines are given by

$$\nu_R = \nu_0 + 2B + 2BJ; \quad J = 0, 1, 2, \dots$$

and

$$\nu_P = \nu_0 - 2BJ; \quad J = 1, 2, 3, \dots$$

Substituting the above maximum value of  $J$ , we obtain the wave numbers of  $R$  and  $P$  maxima :

$$\nu_R^{\max} = \nu_0 + 2B + 2B \left( \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \right)$$

$$\nu_P^{\max} = \nu_0 - 2B \left( \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \right).$$

and

$$\begin{aligned}\therefore v_R^{\max} - v_p^{\max} &= 2B + 4B \left( \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \right) \\ &= 4B \sqrt{\frac{kT}{2Bhc}} \\ &= \sqrt{\frac{8BkT}{hc}}.\end{aligned}$$

Hence measuring  $v_R^{\max} - v_p^{\max}$ , and using the known values of  $k$ ,  $h$  and  $c$ ,  $B$  may be computed if  $T$  is known.

### SOLVED PROBLEMS

- 1. The force constant of the bond in CO molecule is  $1870 \text{ N m}^{-1}$ . Find the energy of the lowest vibrational level. The reduced mass of CO molecule is  $1.14 \times 10^{-26} \text{ kg}$ . Given :  $\hbar = 6.63 \times 10^{-34} \text{ J s}$ ,  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ .**

(Meerut sp. paper 2000)

**Solution.** The frequency of vibration of CO molecule is

$$\begin{aligned}v_{osc} &= \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2 \times 3.14} \sqrt{\frac{1870 \text{ N m}^{-1}}{1.14 \times 10^{-26} \text{ kg}}} = 6.45 \times 10^{13} \text{ s}^{-1}.\end{aligned}$$

The vibrational energy of a diatomic molecule is given by

$$E_v = \hbar v_{osc} \left( v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots$$

The lowest level corresponds to  $v = 0$ . Its energy is

$$\begin{aligned}E_{v=0} &= \frac{1}{2} \hbar v_{osc} \\ &= \frac{1}{2} (6.63 \times 10^{-34} \text{ J s}) (6.45 \times 10^{13} \text{ s}^{-1}) \\ &= 21.4 \times 10^{-21} \text{ J} \\ &= \frac{21.4 \times 10^{-21} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.134 \text{ eV}.\end{aligned}$$

- 2. The force constant of the bond in CO molecule is  $1870 \text{ N m}^{-1}$ . Calculate the frequency of vibration of the molecule and the spacing between its vibrational energy levels in eV. Given that the reduced mass of CO =  $1.14 \times 10^{-26} \text{ kg}$ ,  $\hbar = 6.63 \times 10^{-34} \text{ J s}$  and  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ .**

(Meerut 2004 S, 01, 00 S, 98, 96, 93, sp. paper 2002 S, 98)

**Solution.** As above, the frequency of vibration of the CO molecule is

$$v_{osc} = 6.45 \times 10^{13} \text{ s}^{-1}.$$

The separation between two successive vibrational energy levels is

$$\begin{aligned}\Delta E &= E_{v+1} - E_v \\ &= \hbar v_{osc} \left( v + \frac{3}{2} \right) - \hbar v_{osc} \left( v + \frac{1}{2} \right) \\ &= \hbar v_{osc}\end{aligned}$$

$$\begin{aligned}
 &= (6.63 \times 10^{-34} \text{ Js}) \times (6.45 \times 10^{13} \text{ s}^{-1}) \\
 &= 42.8 \times 10^{-21} \text{ J} \\
 &= \frac{42.8 \times 10^{-21} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.2675 \text{ eV}.
 \end{aligned}$$

3. Assume that the  $\text{H}_2$  molecule behaves like a harmonic oscillator with a force constant  $k = 573 \text{ N/m}$  and find the vibrational quantum number corresponding to its 4.50-eV dissociation energy. Given : mass of hydrogen atom  $= 1.67 \times 10^{-27} \text{ kg}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$ .

(Meerut sp. paper 96)

**Solution.** The frequency of oscillation of the molecule is given by

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The reduced mass of  $\text{H}_2$  molecule is

$$\mu = \frac{M_H M_H}{M_H + M_H} = \frac{1}{2} M_H = \frac{1}{2} \times (1.67 \times 10^{-27} \text{ kg}) = 0.835 \times 10^{-27} \text{ kg}$$

$$\therefore v_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{573 \text{ N/m}}{0.835 \times 10^{-27} \text{ kg}}} = 1.32 \times 10^{14} \text{ s}^{-1}$$

The vibrational energy of the  $\text{H}_2$  molecule is

$$\begin{aligned}
 E_v &= h v_{osc} (v + \frac{1}{2}) \\
 &= (6.63 \times 10^{-34} \text{ Js}) (1.32 \times 10^{14} \text{ s}^{-1}) \left( v + \frac{1}{2} \right) \\
 &= 8.75 \times 10^{-20} \left( v + \frac{1}{2} \right) \text{ J} \\
 &= \frac{8.75 \times 10^{-20} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} \left( v + \frac{1}{2} \right) = 0.547 \left( v + \frac{1}{2} \right) \text{ eV}.
 \end{aligned}$$

For  $E_v = 4.50 \text{ eV}$ , we would have

$$4.50 = 0.547 \left( v + \frac{1}{2} \right)$$

$$\text{or } v + \frac{1}{2} = \frac{4.50}{0.547} = 8.2$$

$$\text{or } v = 8.$$

4. The force constant of a vibrating  $\text{HCl}$  molecule is  $480 \text{ N/m}$ . Find the energy difference between the lowest and the first vibrational level of  $\text{HCl}$ . Given :  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ .

Is the  $\text{HCl}$  molecule likely to be found in the first excited vibrational state at room temperature ? (Given : Boltzmann constant  $k = 1.38 \times 10^{-23} \text{ J/K}$ ).

**Solution.** The frequency of vibration of the molecule is given by

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The reduced mass of the  $\text{HCl}^{35}$  molecule is

$$\mu = \frac{(1 \times 35)/(6.023 \times 10^{23})^2}{(1 + 35)/(6.023 \times 10^{23})} = 1.61 \times 10^{-24} \text{ g} = 1.61 \times 10^{-27} \text{ kg}.$$

$$\therefore v_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ N m}^{-1}}{1.61 \times 10^{-27} \text{ kg}}} = 0.87 \times 10^{14} \text{ s}^{-1}$$

Now, the vibrational energy of a diatomic molecule is given by

$$E_v = h v_{osc} \left( v + \frac{1}{2} \right).$$

The energy difference between the lowest ( $v = 0$ ) and the first excited ( $v = 1$ ) vibrational levels of HCl molecule is

$$\begin{aligned} \Delta E &= E_{v=1} - E_{v=0} \\ &= \frac{3}{2} h v_{osc} - \frac{1}{2} h v_{osc} = h v_{osc} \\ &= (6.63 \times 10^{-34} \text{ J s}) (0.87 \times 10^{14} \text{ s}^{-1}) = 5.77 \times 10^{-20} \text{ J} \\ &= \frac{5.77 \times 10^{-20} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.36 \text{ eV}. \end{aligned}$$

This is the energy required for the molecule to rise to the first excited state.

The thermal energy of a molecule is of the order of  $kT$ , where  $k$  is Boltzmann constant. At room temperature (300 K) this energy is

$$\begin{aligned} kT &= (1.38 \times 10^{-23} \text{ J/K}) (300 \text{ K}) = 4.14 \times 10^{-21} \text{ J} \\ &= \frac{4.14 \times 10^{-21} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.026 \text{ eV}. \end{aligned}$$

Thus, at room temperature, collisions of molecules can transfer only 0.026 eV of kinetic energy to the internal energy, which is insufficient to excite even the  $v = 1$  state (the required energy is 0.36 eV). Hence the HCl molecule is not likely to be found vibrating in its first vibrational excited state at room temperature.

In case of rotational states, the energy difference between  $J = 0$  and  $J = 1$  levels is only 0.0026 eV. Hence, at room temperature, collisions of HCl molecules can transfer sufficient kinetic energy to the internal energy to excite many rotational states.

**5. In the near infra-red spectrum of HCl molecule, there is an intense band at  $2886 \text{ cm}^{-1}$ . Find the energies of the lowest and the first excited vibrational levels of the molecule. Also find the force constant. Given : mass of hydrogen atom,  $M_H = 1.67 \times 10^{-27} \text{ kg}$ ,  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ . (Kanpur 2005)**

**Solution.** The wave number of the fundamental vibrational band is  $\omega$ , the vibrational constant of the molecule. Thus

$$\omega = 2886 \text{ cm}^{-1}.$$

But  $\omega = \frac{v_{osc}}{c}$ , where  $v_{osc}$  is the fundamental frequency of vibration.

$$\begin{aligned} \therefore v_{osc} &= \omega c = 2886 \text{ cm}^{-1} \times (3.0 \times 10^8 \text{ cm s}^{-1}) \\ &= 8.66 \times 10^{13} \text{ s}^{-1}. \end{aligned}$$

Now, the vibrational energy of a diatomic molecule is given by

$$E_v = h v_{osc} \left( v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots$$

The energy of the lowest vibrational level ( $v = 0$ ) of the HCl molecule is

$$\begin{aligned}
 E_{v=0} &= \frac{1}{2} h v_{osc} \\
 &= \frac{1}{2} (6.63 \times 10^{-34} \text{ Js}) (8.66 \times 10^{13} \text{ s}^{-1}) \\
 &= 28.7 \times 10^{-21} \text{ J} \\
 &= \frac{28.7 \times 10^{-21} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.179 \text{ eV}.
 \end{aligned}$$

The energy of the first excited vibrational level ( $v = 1$ ) is

$$E_{v=1} = \frac{3}{2} h v_{osc} = 3 \times 0.179 \text{ eV} = 0.537 \text{ eV}.$$

Now,  $v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ , where  $k$  is the force constant and  $\mu$  is the reduced mass of the molecule. Therefore,

$$k = 4\pi^2 \mu v_{osc}^2.$$

The reduced mass of the  $\text{H}^1\text{Cl}^{35}$  molecule is

$$\begin{aligned}
 \mu &= \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{M_H \times 35 M_H}{M_H + 35 M_H} = \frac{35}{36} M_H \\
 &= \frac{35}{36} \times (1.67 \times 10^{-27} \text{ kg}) \\
 &= 1.62 \times 10^{-27} \text{ kg}.
 \end{aligned}$$

Substituting the values of  $\mu$  and  $v_{osc}$  in eq. (i), we get

$$\begin{aligned}
 k &= 4 \times (3.14)^2 \times (1.62 \times 10^{-27} \text{ kg}) \times (8.66 \times 10^{13} \text{ s}^{-1})^2 \\
 &= 479 \text{ kg/s}^2 = 479 \text{ N/m}.
 \end{aligned}$$

**6. Calculate the amplitude of vibration in the  $v = 0$  level of the molecule CO which has a stiff bond of 1870 N/m. Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ .**

(Meerut 95 S)

**Solution.** Let  $x_0$  be the maximum displacement (amplitude) from the equilibrium position. The potential energy at  $x = x_0$  is equal to the vibrational energy of the  $v = 0$  state, that is, the zero-point energy. Thus

$$\frac{1}{2} k x_0^2 = \frac{1}{2} h v_{osc}$$

$$x_0 = \sqrt{\frac{h v_{osc}}{k}}.$$

or

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

Now where  $k$  is force constant and  $\mu$  is reduced mass of the molecule.

The reduced mass of the  $\text{C}^{12}\text{O}^{16}$  molecule is given by

$$\mu = \frac{(12 \times 16)/(6.023 \times 10^{23})^2}{(12 + 16)/6.023 \times 10^{23}} = 1.14 \times 10^{-23} \text{ g} = 1.14 \times 10^{-26} \text{ kg}.$$

$$\therefore v_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{1870 \text{ N/m}}{1.14 \times 10^{-26} \text{ kg}}} = 6.45 \times 10^{13} \text{ s}^{-1}.$$

Putting this value of  $v_{osc}$ , and the given values of  $h$  and  $k$  in eq. (i), we get

$$x_0 = \sqrt{\frac{(6.63 \times 10^{-34} \text{ J s}) \times (6.45 \times 10^{13} \text{ s}^{-1})}{1870 \text{ N m}^{-1}}} \\ = 0.478 \times 10^{-11} \text{ m} = 4.78 \times 10^{-2} \text{ Å}.$$

7. Find the amplitude of vibration of HCl molecule in the first excited vibrational level. The force constant  $k$  of the vibrating HCl molecule is 480 N/m, and its reduced mass is  $1.62 \times 10^{-27}$  kg. ( $h = 6.63 \times 10^{-34}$  J s).

**Solution.** Let  $x_0$  be the maximum displacement (amplitude) from the equilibrium position. The potential energy at  $x = x_0$  is equal to the vibrational energy of the  $v = 1$  state\*. That is

$$\frac{1}{2} k x_0^2 = \frac{3}{2} h v_{osc}, \\ x_0 = \sqrt{\frac{3 h v_{osc}}{k}}. \quad \dots(i)$$

or

$$\text{Now, } v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \\ = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ N/m}}{1.62 \times 10^{-27} \text{ kg}}} = 0.87 \times 10^{14} \text{ s}^{-1}.$$

Putting this value of  $v_{osc}$ , and the given value of  $h$  and  $k$  in eq. (i), we get

$$x_0 = \sqrt{\frac{3(6.63 \times 10^{-34} \text{ J s})(0.87 \times 10^{14} \text{ s}^{-1})}{480 \text{ N m}^{-1}}} \\ = 0.190 \times 10^{-10} \text{ m} \\ = 0.190 \text{ Å}.$$

8. The vibrational constant  $\omega$  for O<sub>2</sub> molecule is  $1580 \text{ cm}^{-1}$ . Calculate the maximum displacement ( $r - r_e$ ) in Å as a percentage of  $r_e$  ( $= 1.207 \text{ Å}$ ), when  $v = 0$ ,  $v = 15$ . Assume that the molecule is a harmonic oscillator and  $r_e$  is the equilibrium internuclear distance.

( $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ .)

**Solution.** The energy of the molecular oscillator is given by

$$E = h v_{osc} \left( v + \frac{1}{2} \right).$$

In the  $v = 0$  state, we have

$$E(0) = \frac{1}{2} h v_{osc}.$$

Now, the potential energy of the oscillator at maximum displacement ( $r - r_e$ ) is equal to the vibrational energy in the  $v = 0$  state, that is

$$E_0 = h v_{osc} \left( v + \frac{1}{2} \right)$$

$$E_0 = 1,$$

$$E_1 = \frac{3}{2} h v_{osc}$$

$$\frac{1}{2} k (r - r_e)^2 = \frac{1}{2} h v_{osc}$$

or

$$r - r_e = \sqrt{\frac{h v_{osc}}{k}}$$

But

$$k = 4\pi^2 \mu v_{osc}^2$$

$$\left[ \because v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \right]$$

$$\therefore r - r_e = \frac{1}{2\pi} \sqrt{\frac{h}{\mu v_{osc}}} \quad \dots(i)$$

The reduced mass of  $O_2$  molecule is

$$\mu = \frac{(16 \times 16)/(6.023 \times 10^{23})^2}{(16 + 16)/(6.023 \times 10^{23})} = 1.33 \times 10^{-23} \text{ g} = 1.33 \times 10^{-26} \text{ kg}$$

Also,  $v_{osc} = \omega c = (158000 \text{ m}^{-1})(3.0 \times 10^8 \text{ m s}^{-1}) = 4.74 \times 10^{13} \text{ s}^{-1}$

Putting these values in eq. (i), we get

$$\begin{aligned} r - r_e &= \frac{1}{2 \times 3.14} \sqrt{\frac{6.63 \times 10^{-34} \text{ Js}}{(1.33 \times 10^{-26} \text{ kg})(4.74 \times 10^{13} \text{ s}^{-1})}} \\ &= 0.052 \times 10^{-10} \text{ m} = 0.052 \text{ \AA}. \\ \therefore \frac{r - r_e}{r_e} \times 100 &= \frac{0.052 \text{ \AA}}{1.207 \text{ \AA}} \times 100 = 4.31\%. \end{aligned}$$

In the  $v = 15$  state, we have

$$E(15) = h v_{osc} \left( 15 + \frac{1}{2} \right) = \frac{31}{2} h v_{osc}$$

Proceeding as above, eq. (i) gives

$$\begin{aligned} r - r_e &= \frac{1}{2\pi} \sqrt{\frac{31h}{\mu v_{osc}}} = \sqrt{31} \times 0.052 \text{ \AA} = 0.29 \text{ \AA}. \\ \therefore \frac{r - r_e}{r_e} \times 100 &= \frac{0.29 \text{ \AA}}{1.207 \text{ \AA}} \times 100 = 24\%. \end{aligned}$$

9. The values of  $\omega_e$  are 4395, 3817 and 3118  $\text{cm}^{-1}$  for  $H_2$ , HD and  $D_2$  molecules respectively. The values of  $\omega_e x_e$  are 118, 95 and 64  $\text{cm}^{-1}$  for the same molecules. Calculate the zero-point energies of the molecules in kcal/mole. Given :  $1 \text{ cm}^{-1} = 2.858 \times 10^{-3} \text{ kcal/mole}$ .

**Solution.** The term values of a diatomic molecule, treated as an anharmonic oscillator, are given by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$$

The (zero-point) energy corresponding to  $v = 0$  is

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e$$

For  $H_2$ ,  $\omega_e = 4395 \text{ cm}^{-1}$  and  $\omega_e x_e = 118 \text{ cm}^{-1}$ .

$$\begin{aligned}\therefore G(0) &= \frac{1}{2}(4395 \text{ cm}^{-1}) - \frac{1}{4}(118 \text{ cm}^{-1}) \\ &= 2197.5 \text{ cm}^{-1} - 29.5 \text{ cm}^{-1} = 2168 \text{ cm}^{-1} \\ &= 2168 \text{ cm}^{-1} \times (2.858 \times 10^{-3} \text{ kcal/mol} \cdot \text{cm}^{-1}) \\ &= 6.20 \text{ kcal/mol.}\end{aligned}$$

Similarly,  
and

10. The fundamental band for CO molecule is centered at  $2143.3 \text{ cm}^{-1}$ , and the first overtone at  $4259.7 \text{ cm}^{-1}$ . Calculate  $\omega_e$ ,  $\omega_e x_e$ , the vibrational frequency and the simple harmonic force constant for the molecule.

The reduced mass of CO molecule is  $1.14 \times 10^{-26} \text{ kg}$ . Take  $c = 3.0 \times 10^{10} \text{ cm s}^{-1}$ . (Meerut 95)

**Solution.** The vibrational terms of a diatomic molecule are given by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2;$$

so that

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e,$$

$$G(1) = \frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e,$$

$$G(2) = \frac{5}{2} \omega_e - \frac{25}{4} \omega_e x_e.$$

and

For the wave number of the fundamental band  $1 \leftarrow 0$ , we have

$$\begin{aligned}v &= G(1) - G(0) \\ &= \omega_e - 2 \omega_e x_e = 2143.3 \text{ cm}^{-1}. \quad \dots(i)\end{aligned}$$

For the first overtone band  $2 \leftarrow 0$ , we have

$$\begin{aligned}v &= G(2) - G(0) \\ &= 2 \omega_e - 6 \omega_e x_e = 4259.7 \text{ cm}^{-1}. \quad \dots(ii)\end{aligned}$$

Solving eq. (i) and (ii), we get

$$\omega_e = 2170.2 \text{ cm}^{-1}$$

$$\omega_e x_e = 13.45 \text{ cm}^{-1}.$$

and

The vibrational frequency is

$$v_{osc} = c \omega_e = (3.0 \times 10^{10} \text{ cm s}^{-1}) \times (2170.2 \text{ cm}^{-1}) = 6.51 \times 10^{13} \text{ s}^{-1}.$$

The S.H. force constant is

$$\begin{aligned}k &= 4 \pi^2 \mu v_{osc}^2 \\ &= 4 \times (3.14)^2 \times (1.14 \times 10^{-26} \text{ kg}) \times (6.51 \times 10^{13} \text{ s}^{-1})^2 \\ &= 1905 \text{ N m}^{-1}.\end{aligned}$$

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

11. The fundamental mode of HCl occurs at  $2886 \text{ cm}^{-1}$ . Predict the frequency of the corresponding mode of DCl.

**Solution.** The difference in frequency arises due to difference in masses of the isotopic molecules. We know that

$$v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The force constant  $k$  is same for both the molecules as it is determined by electronic motion. If  $\omega^i$  is vibrational constant for the heavier isotope, then

$$\frac{\omega^i}{\omega} = \frac{v_{osc}^i}{v_{osc}} = \sqrt{\frac{\mu}{\mu_i}} = \rho \text{ (say).}$$

Thus

$$\omega^i = \rho \omega.$$

$$\begin{aligned} \text{Here } \rho &= \sqrt{\frac{\mu_{HCl}}{\mu_{DCl}}} = \sqrt{\frac{(1 \times 35)/(1 + 35)}{(2 \times 35)/(2 + 35)}} = \sqrt{\frac{35}{36} \times \frac{37}{70}} \\ &= \sqrt{\frac{37}{72}} = 0.7168. \end{aligned}$$

Treating the molecule as harmonic oscillator, the fundamental band occurs at  $\omega \text{ cm}^{-1}$ , where  $\omega$  is the vibrational constant. Here  $\omega = 2886 \text{ cm}^{-1}$  for HCl. Therefore, the fundamental band for DCl occurs at  $\omega^i$  where

$$\omega^i = \rho \omega = 0.7168 \times 2886 \text{ cm}^{-1} = 2069 \text{ cm}^{-1}.$$

**12. If the fundamental band of  $H^1Cl^{35}$  lies at  $3.46 \mu$  (micron), calculate the wavelength of the corresponding band of  $H^2Cl^{37}$ .**

(Meerut 92)

**Solution.** If  $i$  stands for the heavier isotope, then

$$\frac{\omega^i}{\omega} = \sqrt{\frac{\mu}{\mu_i}} = \rho$$

or

$$\omega^i = \rho \omega.$$

In terms of wavelength, we write

$$\lambda^i = \frac{1}{\rho} \lambda.$$

$$\left[ \because \omega = \frac{1}{\lambda} \right]$$

$$\text{Here } \rho = \sqrt{\frac{(1 \times 35)/(1 + 35)}{(2 \times 37)/(2 + 37)}} = \sqrt{\frac{35}{36} \times \frac{39}{74}} = 0.7158$$

$$\text{and } \lambda = 3.46 \text{ micron}$$

$$\therefore \lambda^i = \frac{3.46 \text{ micron}}{0.7158} = 4.83 \text{ micron.} \quad [1 \text{ micron} = 10^{-4} \text{ cm}]$$

**13. The mean of the internuclear distances for  $HCl^{35}$  in the  $v = 0$  and  $v = 1$  levels is  $1.293 \text{ \AA}$ . Calculate the wave-number difference between the  $R(0)$  and  $P(1)$  lines of the fundamental band for  $HCl^{35}$ .**

**Given :**  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ . The reduced mass of HCl molecule is  $1.61 \times 10^{-27} \text{ kg}$ .

**Solution.** The internuclear distance has been taken same in  $v = 0$  and  $v = 1$  states. It means that the vibration-rotation interaction has been ignored.

The mean rotational constant for the molecule is

$$B = \frac{h}{8\pi^2 \mu r^2 c}$$

$$= \frac{6.63 \times 10^{-34} \text{ Js}}{8(3.14)^2 (1.61 \times 10^{-27} \text{ kg}) (1.293 \times 10^{-10} \text{ m})^2 (3.0 \times 10^8 \text{ m s}^{-1})} = 1041 \text{ m}^{-1}$$

When vibration-rotation interaction is ignored, the wave numbers of the *R*- and *P*-lines are given by

$$v_R = R(J) = v_0 + 2B + 2BJ; \quad J = 0, 1, 2, \dots$$

$$v_P = P(J) = v_0 - 2BJ; \quad J = 1, 2, 3, \dots$$

and

$$\therefore R(0) - P(1) = (v_0 + 2B) - (v_0 - 2B)$$

$$= 4B$$

$$= 4 \times 1041 \text{ m}^{-1} = 4164 \text{ m}^{-1} = 41.64 \text{ cm}^{-1}.$$

14. The  $2886\text{-cm}^{-1}$  fundamental band of HCl can be shown to fit in the empirical eq. :

$v(\text{cm}^{-1}) = 2885.90 + 20.577m - 0.3034m^2$ . Calculate the values of  $B_e$ ,  $B_0$  and  $B_1$ . Given :  $\alpha_e = 0.3019 \text{ cm}^{-1}$ . *(Meerut sp. paper 98, 96)*

**Solution.** The general equation for the rotational lines of a band is

$$v = v_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2.$$

Comparing it with the given equation for the fundamental ( $v'' = 0$ ,  $v' = 1$ ) band, we have

$$B_1 + B_0 = 20.577 \text{ cm}^{-1}$$

$$B_1 - B_0 = -0.3034 \text{ cm}^{-1}.$$

Solving we get :

$$B_1 = 10.1368 \text{ cm}^{-1}$$

$$B_0 = 10.4402 \text{ cm}^{-1}.$$

We know that the rotational constant corresponding to the vibrational state  $v$  is given by

$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right).$$

For the  $v = 0$  state, we would have

$$B_0 = B_e - \frac{1}{2} \alpha_e.$$

$$\therefore B_e = B_0 + \frac{1}{2} \alpha_e$$

$$= 10.4402 \text{ cm}^{-1} + \frac{1}{2}(0.3019 \text{ cm}^{-1}) = 10.5909 \text{ cm}^{-1}.$$

15. The vibration-rotation constants of HCl molecule in the three lowest vibrational levels of the ground electronic state are  $B_0 = 10.440 \text{ cm}^{-1}$ ,  $B_1 = 10.138 \text{ cm}^{-1}$  and  $B_2 = 9.836 \text{ cm}^{-1}$ . Calculate the equilibrium internuclear distance  $r_e$ . Given :  $\mu_{\text{HCl}} = 1.62 \times 10^{-27} \text{ kg}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$  and  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ .

**Solution.** The rotational constant  $B_v$  in the vibrational state  $v$  is given by

$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right),$$

where  $B_e$  is the rotational constant corresponding to the equilibrium internuclear distance  $r_e$  (at the minimum of the potential curve) and  $\alpha_e$  is a small constant determined by the shape of the potential curve.

According to the given data, we have

$$B_0 = B_e - \frac{1}{2} \alpha_e = 10.440 \text{ cm}^{-1}, \quad \dots(i)$$

$$B_1 = B_e - \frac{3}{2} \alpha_e = 10.138 \text{ cm}^{-1} \quad \dots(ii)$$

and  $B_2 = B_e - \frac{5}{2} \alpha_e = 9.836 \text{ cm}^{-1}. \quad \dots(iii)$

Solving any two equations, say (i) and (ii), we get

$$B_e = 10.597 \text{ cm}^{-1} = 1059.7 \text{ m}^{-1}.$$

Now,

$$B_e = \frac{h}{8 \pi^2 \mu r_e^2 c}$$

or

$$r_e^2 = \frac{h}{8 \pi^2 \mu B_e c} \\ = \frac{6.63 \times 10^{-34} \text{ Js}}{8(3.14)^2 (1.62 \times 10^{-27} \text{ kg}) (1059.7 \text{ m}^{-1}) (3.0 \times 10^8 \text{ m s}^{-1})} \\ = 1.632 \times 10^{-20} \text{ m}^2.$$

$$\therefore r_e = \sqrt{1.632 \times 10^{-20}} \text{ m}$$

$$= 1.277 \times 10^{-10} \text{ m} = 1.277 \text{ Å}.$$

**16.** A molecule is found to give an infra-red spectrum in which the first lines of both the P- and R-branches are missing, and a large asymmetric line occurs in the centre of the band. What is the electronic configuration of the molecule?

**Solution.** The appearance of P- and R-branches together with an asymmetric line (unresolved Q-branch) indicates that the state of the molecule corresponds to a symmetric top. The electronic configuration may be any one of the  ${}^1\Pi$ ,  ${}^1\Delta$ , ... (Symmetric top corresponds necessarily to singlet electronic states).

The first lines of P- and R- branches, which are missing, are P (1) and R (0); the digit in the bracket corresponds to the lower rotational quantum number  $J''$ .

R (0) corresponds to  $J'' = 0 \rightarrow J' = 1$

[ $J' = J'' + 1$ ]

P (1) corresponds to  $J'' = 1 \rightarrow J' = 0$

[ $J' = J'' - 1$ ]

R (1) corresponds to  $J'' = 1 \rightarrow J' = 2$

P (2) corresponds to  $J'' = 2 \rightarrow J' = 1$ .

The missing lines R (0) and P (1) indicate that  $J'' = 0$  and  $J' = 0$  are missing; whereas  $J'' = J' = 1, 2, \dots$  are present because lines R (1) and P (2) are present.

We know that in a symmetric top, levels  $J < \Lambda$  do not occur but  $J = \Lambda, \Lambda + 1, \dots$  occur. This means that

$$\Lambda = 1.$$

Hence the electronic state is  ${}^1\Pi$ .

**17.** At what temperature will the number of  $I_2$  molecules in the  $v = 1$  level be one-tenth of that in the  $v = 0$  level? Given :  $\omega_e = 214.6 \text{ cm}^{-1}$ ,  $\omega_e x_e = 0.6 \text{ cm}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $k = 1.38 \times 10^{-23} \text{ J/K}$ .

**Solution.** From Maxwell-Boltzmann distribution law, the number of molecules in the  $v$  th state relative to that in the  $v = 0$  (lowest) state at  $T$  kelvin temperature is given by

$$\frac{N_v}{N_0} = e^{-G_0(v) h c/k T}$$

$$= e^{-\{G(v) - G(0)\} h c/k T},$$

where  $G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$ .

$$\therefore \frac{N_v}{N_0} = e^{-(\omega_e v - \omega_e x_e v^2 - \omega_e x_e v) h c/kT}$$

For the  $v = 1$  level, we have

$$\frac{N_1}{N_0} = e^{-(\omega_e - 2\omega_e x_e) h c/kT}$$

Here  $\frac{N_1}{N_0} = \frac{1}{10}$ ,  $\omega_e = 214.6 \text{ cm}^{-1}$  and  $\omega_e x_e = 0.6 \text{ cm}^{-1}$  (given).

$$\therefore \frac{1}{10} = e^{-(214.6 \text{ cm}^{-1} - 1.2 \text{ cm}^{-1}) h c/kT}$$

$$10 = e^{(213.4 \text{ cm}^{-1}) h c/kT} = e^{(21340 \text{ m}^{-1}) h c/kT}$$

or

Taking natural logarithm :

$$\log_e 10 = (21340 \text{ m}^{-1}) h c/kT.$$

But  $\log_e 10 = 2.303$ .

$$\begin{aligned} \therefore T &= \frac{21340 \text{ m}^{-1}}{2.303} \frac{h c}{k} \\ &= (9266 \text{ m}^{-1}) \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{1.38 \times 10^{-23} \text{ J K}^{-1}} \\ &= 133.5 \text{ K}. \end{aligned}$$

18. The population of levels greater than  $v = 0$  is appreciable for  $I_2$  molecules at 300 K. Given that  $\omega_e = 215.0 \text{ cm}^{-1}$ ,  $\omega_e x_e = 0.61 \text{ cm}^{-1}$ , and that the population of levels greater than  $v = 3$  can be neglected, determine the relative population of the first four vibrational levels.

Given :  $h = 6.63 \times 10^{-34} \text{ J s}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ .

Solution. The relative population of the  $v$  th level is

$$\begin{aligned} \frac{N_v}{N_0} &= e^{-G_0(v) h c/kT} \\ &= e^{-(G(v) - G(0)) h c/kT}, \end{aligned}$$

where  $G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2$ .

$$\therefore \frac{N_1}{N_0} = e^{-(\omega_e - 2\omega_e x_e) h c/kT},$$

$$\frac{N_2}{N_0} = e^{-(2\omega_e - 6\omega_e x_e) h c/kT}$$

$$\frac{N_3}{N_0} = e^{-(3\omega_e - 12\omega_e x_e) h c/kT}.$$

and

$$\frac{h c}{k T} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}$$

$$= 4.80 \times 10^{-5} \text{ m.}$$

Also,  $\omega_e - 2\omega_e x_e = 215.0 \text{ cm}^{-1} - 1.22 \text{ cm}^{-1} = 213.78 \text{ cm}^{-1} = 21378 \text{ m}^{-1}$ .

$$\therefore \frac{N_1}{N_0} = e^{(-21378 \text{ m}^{-1})(4.80 \times 10^{-5} \text{ m})} = e^{-1.026}$$

or

$$\log_e \frac{N_1}{N_0} = -1.026$$

or

$$\frac{N_1}{N_0} = 0.358 \approx 0.36.$$

Similarly, we can show that

$$\frac{N_2}{N_0} = 0.13 \text{ and } \frac{N_3}{N_0} \approx 0.05.$$

$$\therefore N_0 : N_1 : N_2 : N_3 = 1 : 0.36 : 0.13 : 0.05.$$

**19. Use the data of the last problem to compute the average vibrational energy of I<sub>2</sub> at room temperature (300 K).**

**Solution.** The vibrational energy of a molecule in  $v$  th level is

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2.$$

At room temperature, only  $v = 0, 1, 2, 3$  levels are populated in the ratio  $1 : 0.36 : 0.13 : 0.05$ . Therefore,

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e = 107 \text{ cm}^{-1}.$$

$$G(1) = \frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e = 321 \text{ cm}^{-1}.$$

$$G(2) = \frac{5}{2} \omega_e - \frac{25}{4} \omega_e x_e = 534 \text{ cm}^{-1}.$$

$$G(3) = \frac{7}{2} \omega_e - \frac{49}{4} \omega_e x_e = 745 \text{ cm}^{-1}.$$

The average energy is therefore

$$\begin{aligned} & \frac{(107 \times 1) + (321 \times 0.36) + (534 \times 0.13) + (745 \times 0.05)}{1 + 0.36 + 0.13 + 0.05} \\ &= \frac{107 + 116 + 69 + 37}{1.54} = 214 \text{ cm}^{-1}. \end{aligned}$$

**20. Find the most populated rotational level for the molecule HCl at a temperature of 600 K. The moment of inertia of the molecule is  $2.71 \times 10^{-47} \text{ kg}\cdot\text{m}^2$ . Given :  $h = 6.63 \times 10^{-34} \text{ J s}$  and  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ .**

**Solution.** The value of the quantum number  $J$  for the maximum populated rotational level for a molecule at a temperature  $T$  is given by

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}, \quad \dots(i)$$

where  $B$  is rotational constant for the molecule.

Now,  $B = \frac{h}{8\pi^2 I c}$ , where  $I$  is the moment of inertia of the molecule about the rotational axis. Making this substitution in eq. (i) we get

$$J_{\max} = \frac{2\pi}{h} \sqrt{kTI} - \frac{1}{2}.$$

Putting the given values :

$$\begin{aligned}
 J_{\max} &= \frac{2 \times 3.14}{6.63 \times 10^{-34} \text{ Js}} \sqrt{(1.38 \times 10^{-23} \text{ JK}^{-1})(600 \text{ K})(2.71 \times 10^{-47} \text{ kg m}^2)} - \frac{1}{2} \\
 &= \frac{2 \times 3.14 \times 10^{-34}}{6.63 \times 10^{-34}} \sqrt{1.38 \times 6 \times 2.71} - \frac{1}{2} \\
 &= \left( \frac{2 \times 3.14}{6.63} \times 4.74 \right) - \frac{1}{2} \\
 &= 4.5 - 0.5 = 4.
 \end{aligned}$$

## QUESTIONS

- Give an account of the salient features of near infra-red spectrum of a diatomic molecule like HCl. Explain how these observations are accounted for quantum-mechanically. Why are such spectra not observed for homonuclear molecules like N<sub>2</sub>? *(Meerut 2004 S, 04, 03, 01, 00, 98)*
- Discuss the main features of the vibrational-rotational spectra of diatomic molecules. How are they explained? Why are such spectra not obtained for molecules having identical nuclei?
- Find the vibrational energy of a diatomic molecule when the potential energy is given by  $U = \frac{1}{2} k (r - r_e)^2$  where  $k$  is constant. *(Meerut 2006, 02 S, 02, 00, 99, 95 sp. paper 2006)*
- Write down the expression of energy for anharmonic oscillator model of a diatomic molecule. Show how from the infra-red absorption bands, the vibrational constants  $\omega_e$  and  $\omega_e x_e$  of the molecule can be determined. *(Meerut sp. paper 97)*
- Draw a schematic diagram to represent the energy levels of a diatomic molecule regarded as an anharmonic oscillator and show the allowed transitions and the expected spectrum.
- Discuss how the study of vibrational spectrum of a diatomic molecule enables us to determine anharmonicity constant and equilibrium frequency of vibration. *(Meerut sp. paper 95, Kanpur 2000)*
- Give the theory of isotope effect in relation to vibrational bands of a diatomic molecule and discuss the importance of its study. *(Meerut 2003, Kanpur 93)*
- Compare qualitatively the vibrational energy levels of H<sub>2</sub>, HD and D<sub>2</sub>.
- Discuss the fine structure of infra-red bands of diatomic molecules. Why are they all degraded toward red (longer wavelength side)? *(Meerut sp. paper 2004, 03, 00, 99, 98, 90)*
- What are P, Q and R branches in the vibration-rotation spectra? Explain their origin. *(Meerut 95 S, sp. paper 99)*
- Explain diatomic molecule as 'symmetric top'. Deduce expression for the rotational energy levels of a symmetric-top molecule and discuss the structure of their vibrational bands. *(Meerut sp. paper 2001)*
- How does the thermal distribution of the rotational levels of a diatomic molecule differ from that of the vibrational levels at a particular temperature?
- Discuss the intensity distribution in the rotational spectrum of a diatomic molecule. How would you obtain approximately the rotational constant  $B$  from the separation of the band maxima of the P and R branches of an unresolved band, if the temperature is known?

## PROBLEMS

1. The force constant of  $\text{HF}^{19}$  molecule is 966 N/m. Find the frequency of vibration of the molecule. ( $N_A = 6.023 \times 10^{23}$  per mole).  $\text{Ans. } 1.24 \times 10^{14} \text{ s}^{-1}$
2. The simple harmonic force constant for  $\text{DCl}^{35}$  is 490.3 N/m. Calculate the frequency ( $\text{cm}^{-1}$ ) of radiation absorbed by  $\text{DCl}$ . Is this dependent on  $v$ ? ( $N_A = 6.023 \times 10^{23} \text{ mole}^{-1}$ ,  $c = 3.0 \times 10^8 \text{ m/s}$ ).  $(\text{Meerut 2006})$   
 $\text{Ans. } 2097 \text{ cm}^{-1}$ , no.
3. The force constant of a vibrating  $\text{HCl}$  molecule is about 480 N/m. Estimate the energy difference between the lowest and the first vibrational state of  $\text{HCl}$ . ( $N_A = 6.023 \times 10^{23} \text{ mole}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ ).  $\text{Ans. } 0.36 \text{ eV.}$
4. In the near-ir spectrum of  $\text{C}^{12}\text{O}^{16}$  molecule there is an intense band at  $2144 \text{ cm}^{-1}$ . Calculate the fundamental vibration frequency, the force constant and the zero-point energy of the molecule. ( $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $h = 6.63 \times 10^{-34} \text{ Js}$  and  $N_A = 6.023 \times 10^{23}$  per mole.)  $\text{Ans. } 6.43 \times 10^{13} \text{ s}^{-1}$ ,  $1860 \text{ N m}^{-1}$ ,  $0.133 \text{ eV.}$
5. The most intense vibrational bands of  $\text{CO}$  and  $\text{HCl}$  molecules occur at wave numbers  $2.143 \times 10^5 \text{ m}^{-1}$  and  $2.886 \times 10^5 \text{ m}^{-1}$  respectively. Their reduced masses are  $1.14 \times 10^{-26} \text{ kg}$  and  $1.61 \times 10^{-27} \text{ kg}$  respectively. Find the force constants of  $\text{CO}$  and  $\text{HCl}$  molecules.  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ .  $\text{Ans. } 1858 \text{ N/m, } 476 \text{ N/m.}$
6. The molecule of  $\text{HCl}$  shows a strong absorption line of wavelength 3.465 microns. Assuming the origin of the line due to vibration, calculate the force constant of the molecule. ( $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ,  $N = 6.023 \times 10^{23} \text{ mole}^{-1}$ ).  
 $\text{Hint: } v = \frac{1}{\lambda} = \frac{1}{3.465 \times 10^{-4} \text{ cm}} = 2886 \text{ cm}^{-1}$ .  $\text{Ans. } 476 \text{ N/m.}$
7. The force constant of  $\text{HCl}$  molecule is 480 N/m. Find the energy required to increase the nuclear separation by  $1 \text{ \AA}$ .  
 $\text{Hint: } W = \frac{1}{2} k x^2$ .  $\text{Ans. } 15 \text{ eV.}$
8. The values of  $\omega_e$  and  $\omega_e x_e$  are  $1580.36 \text{ cm}^{-1}$  and  $12.073 \text{ cm}^{-1}$  respectively for the ground state of molecular oxygen. Compute the zero-point energy of  $\text{O}_2$  molecule. Given :  $1 \text{ cm}^{-1} = 1.24 \times 10^{-4} \text{ eV.}$   
 $\text{Hint: } G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e$ .  $\text{Ans. } 0.0976 \text{ eV.}$
9. Calculate the ratio of the vibrational frequencies of hydrogen iodide ( $\text{H}^1\text{I}^{127}$ ) molecule to deuterated hydrogen iodide ( $\text{D}^2\text{I}^{127}$ ) molecule.  $\text{Ans. } 1.41.$
10. The fundamental vibration of molecule  $\text{Cl}^{35}\text{Cl}^{35}$  occurs at  $2940.8 \text{ cm}^{-1}$ . Determine the corresponding vibration of  $\text{Cl}^{35}\text{Cl}^{37}$ . What is the separation between the fundamental bands due to this isotope effect ?  
 $\text{Ans. } 2900.8 \text{ cm}^{-1}$ ,  $40 \text{ cm}^{-1}$ .

11. The fundamental band for  $\text{DCl}^{35}$  is centred at  $2011\cdot00 \text{ cm}^{-1}$ . Assume that the internuclear distance is constant at  $1\cdot288 \text{ \AA}$ , and calculate the wave numbers of the first two lines of each of the *P*- and *R*-branches of  $\text{DCl}^{35}$ .

Given :  $h = 6\cdot63 \times 10^{-34} \text{ Js}$ ,  $c = 3\cdot0 \times 10^8 \text{ m s}^{-1}$ ,  $N_A = 6\cdot023 \times 10^{23} \text{ mol}^{-1}$ .

Ans.  $P(1)$ ,  $P(2)$ ,  $R(0)$ ,  $R(1)$  are  $2000\cdot24 \text{ cm}^{-1}$ ,  $1989\cdot48 \text{ cm}^{-1}$ ,  $2021\cdot76 \text{ cm}^{-1}$ ,  $2032\cdot52 \text{ cm}^{-1}$  respectively.

12. At what temperature would the number of HCl molecules in the first excited vibrational state ( $v = 1$ ) be equal to  $1/e$  (about 37%) of the number in the ground vibrational state. What fraction will be found in the first excited vibrational state at 1000 K? Take  $\omega_e = 2990 \text{ cm}^{-1}$  and ignore  $\omega_e x_e$ .

( $h = 6\cdot63 \times 10^{-34} \text{ Js}$ ,  $c = 3\cdot0 \times 10^8 \text{ m s}^{-1}$  and  $k = 1\cdot38 \times 10^{-23} \text{ J K}^{-1}$ )

— Ans.  $4309 \text{ K}$ ,  $\frac{1}{74\cdot4}$ .

---

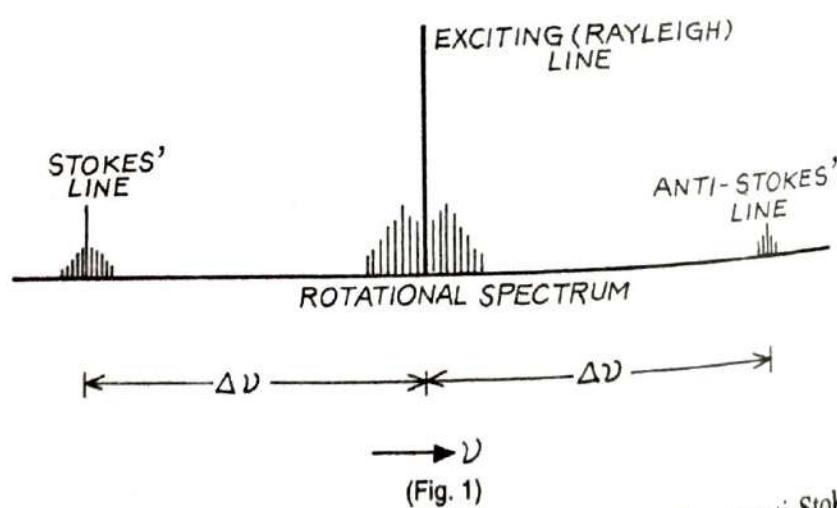
# The Raman Spectra

## 1. Nature of the Raman Spectra

When a strong beam of visible or ultra-violet line-spectral light illuminates a gas, liquid, or a transparent crystal, a small fraction of light is scattered in all directions. The spectrum of the scattered light is found to consist of lines of the same frequencies as the incident beam (Rayleigh lines), and also certain weak lines of *changed frequencies*. These additional lines are called 'Raman lines'. The Raman lines corresponding to each exciting (Rayleigh) line occur *symmetrically* on both sides of the exciting line. The lines on the low-frequency side of the exciting line are called 'Stokes' lines, while those on the high-frequency side are called 'anti-Stokes' lines. The anti-Stokes Raman lines are much weaker compared to the Stokes Raman lines. This phenomenon is called 'Raman effect'.

The wave-number displacements  $\Delta\nu$  of the Raman lines from the corresponding exciting line are independent of the frequency of the exciting line. If another light source with a different line-spectrum is used, other Raman lines are obtained for the same scattering substance. However, the displacements from the exciting lines are the same. For different scattering substances, however, the displacements are different. Thus, *the Raman displacements are characteristic of the scattering substance*.

**Vibrational and Pure Rotational Raman Spectra :** A typical Raman spectrum shown in Fig. 1. It has two important characteristics :



(Fig. 1)

(i) Under low resolution, there is one Stokes' Raman line and one anti-Stokes' Raman line, each having the same wave-number displacement,  $\Delta\nu$ , with respect to the exciting line. This is vibrational Raman spectrum. The Raman displacement  $\Delta\nu$  agrees exactly with the wave-number of the main vibrational-rotational absorption band in the near infrared spectrum of the molecule. This is found to be the case for all those diatomic molecules for which both the Raman spectra and the infra-red spectra are observed.\*

\*For homonuclear molecules  $H_2$ ,  $N_2$ ,  $O_2$ , ..... the infra-red spectrum does not occur. Raman spectrum does occur.

(ii) Under high resolution, the exciting line is found to have on both sides close, approximately equidistant lines. This is pure rotational Raman spectrum. The separation between successive rotational lines is very nearly twice the separation between successive lines in the far infra-red spectrum of the molecule. The Stokes' and anti-Stokes' lines referred above are also found to be bands composed of rotational fine structure. They constitute the vibrational (strictly vibrational-rotational) Raman spectrum of the molecule.

## 2. Experimental Arrangement for Raman Spectra

The basic requirements for photographing Raman spectrum are a proper source, a Raman tube and a spectrograph.

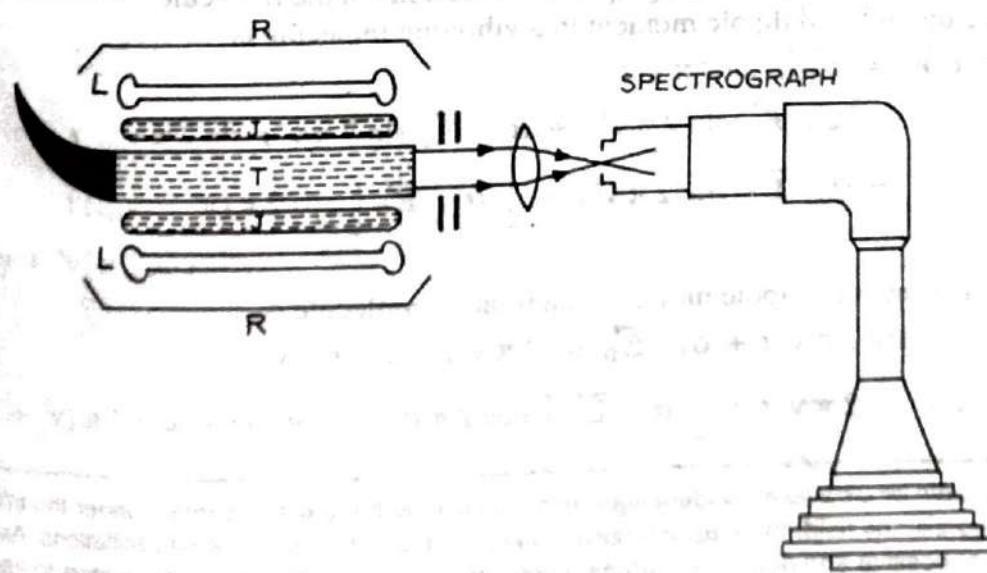
The source must be an intense line-source with distinct lines in the blue-violet region. A mercury arc or a discharge lamp is a proper source. Any one of its three prominent lines 2536, 4047 and 4358 Å may be used. The 4047 Å line may be isolated by using a 'noviol glass' and a solution of iodine in  $\text{CCl}_4$ ; while 4358 Å may be filtered by a thin sheet of pale noviol combined with quinine.

The most suitable Raman source is LASER as it gives an exceptionally intense and highly monochromatic beam of light which can be sharply focussed into a small sample of scattering material.

The Raman tube used for liquids is a thin-walled glass (or quartz) tube about 15 cm long and 2 cm in diameter, whose one end is closed with an optically-plane glass (or quartz) plate, and the other is drawn out into the shape of a horn and covered with black tape. The experimental liquid is filled in this tube. The flat end serves as the window through which the scattered light emerges, while the blackened horn-shaped end causes the total reflection of backward scattered light and provides a dark back-ground.

The spectrograph must be one of high light-gathering power combined with good resolution. This may be achieved in a good prism spectrograph with a short-focus camera.

A typical arrangement for obtaining Raman spectra of liquids is shown in Fig. 2. Two intense mercury discharge lamps  $L, L$ , are placed parallel and close to the Raman tube  $T$ . The Raman tube is surrounded by an annular jacket  $J$  through which is circulated the filtering solution to isolate one of the mercury lines. Light reflectors  $R, R$  are suitably placed to further enhance the intensity of illumination. The scattered light passing through



(Fig. 2)

the plane window of the Raman tube is focussed on the slit of a spectrograph which photographs the spectrum under a long exposure. A spectrophotometer may also be used as a recorder instead of a spectrograph.

The Raman spectra of gases are generally weaker than those of liquids. For gases, very long discharge lamps and Raman tubes are used. The tubes are fitted with mirrors so as to increase the effective length of the path of the light beam through the gas.

### 3. Classical Theory of Raman Effect

An elementary explanation of the Raman effect can be given from the classical theory. When a beam of *visible* or *ultraviolet* light falls upon a molecule, the rapidly-oscillating electric field of the beam *induces* an oscillating electric dipole moment in the molecule, irrespective of whether the molecule has a permanent dipole moment or not\*. The molecule is then said to be 'polarised'.

The field associated with a light beam of frequency  $v'$  ( $s^{-1}$ ) may be written as  

$$\vec{E} = \vec{E}_0 \sin 2\pi v' t,$$

and the induced dipole moment as

$$\vec{p} = \alpha \vec{E} = \alpha \vec{E}_0 \sin 2\pi v' t,$$

$\alpha$  is known as the 'polarisability' of the molecule. The molecule now behaves like a Hertzian oscillator and radiates energy in the form of electromagnetic waves of frequency  $v'$ , same as the incident frequency. This is Rayleigh scattering.

Now, the molecule has *internal* motions too, namely, the vibration and rotation of its nuclei. As a result of these motions, the polarisability  $\alpha$  of the molecule varies with time. The vibrational variation in  $\alpha$  may be written as

$$\alpha = \alpha_{0v} + \alpha_{1v} \sin 2\pi v_{osc} t,$$

where  $\alpha_{0v}$  is the value of  $\alpha$  in the equilibrium position, and  $\alpha_{1v}$  is the maximum change in  $\alpha$  during the vibration.

Similarly, for the rotational variation, we may write

$$\alpha = \alpha_{0r} + \alpha_{1r} \sin 2\pi 2v_{rot} t,$$

where  $\alpha_{0r}$  is the average value of  $\alpha$ , and  $\alpha_{1r}$  is the maximum change in  $\alpha$  during the rotation. The frequency with which  $\alpha$  changes during the rotation, is twice the rotational frequency; since  $\alpha$  is same along opposite directions in the molecule.

Hence the induced dipole moment in a vibrating molecule is

$$\begin{aligned}\vec{p}_v &= \alpha \vec{E} = \alpha \vec{E}_0 \sin 2\pi v' t \\ &= \alpha_{0v} \vec{E}_0 \sin 2\pi v' t + \alpha_{1v} \vec{E}_0 \sin 2\pi v' t \sin 2\pi v_{osc} t \\ &= \alpha_{0v} \vec{E}_0 \sin 2\pi v' t + \frac{1}{2} \alpha_{1v} \vec{E}_0 [\cos 2\pi (v' - v_{osc}) t \\ &\quad - \cos 2\pi (v' + v_{osc}) t]\end{aligned}$$

Similarly, the induced dipole moment in a rotating molecule is

$$\vec{p}_r = \alpha_{0r} \vec{E}_0 \sin 2\pi v' t + \alpha_{1r} \vec{E}_0 \sin 2\pi v' t \sin 2\pi 2v_{rot} t$$

$$= \alpha_{0r} \vec{E}_0 \sin 2\pi v' t + \frac{1}{2} \alpha_{1r} \vec{E}_0 [\cos 2\pi (v' - 2v_{rot}) t - \cos 2\pi (v' + 2v_{rot}) t]$$

\*For *visible* or *ultraviolet* incident light, essentially only the electrons move under the influence of the oscillating electric field, the massive nuclei being unable to follow the rapid oscillations. As a result, the centres of positive and negative charges (nuclei and electrons) are displaced relative to each other, producing an induced dipole moment in the molecule.

Thus, the induced dipole moment changes not only with the frequency  $v'$  of the incident light, but also with frequencies  $(v' - v_{osc})$ ,  $(v' + v_{osc})$ ,  $(v' - 2v_{rot})$  and  $(v' + 2v_{rot})$ . Hence in the spectrum of the scattered light, one obtains vibrational Raman lines at distances  $v_{osc}$  on either side of the Rayleigh line  $v'$ ; and also rotational Raman lines at distances  $2v_{rot}$  on either side of  $v'$ . It is thus clear that the molecule need not have a permanent dipole moment for its Raman spectrum to appear. Hence, besides the molecules like HCl, the homonuclear molecules like  $H_2$ ,  $N_2$ ,  $O_2$  also show Raman spectra although they do not show infra-red spectra.

The classical explanation of Raman effect has two discrepancies :

(i) According to the classical theory, the Raman lines on the two sides of the Rayleigh line must be of the same intensity. Actually, the Raman lines on the high-frequency side (anti-Stokes) are too weak to be observed.

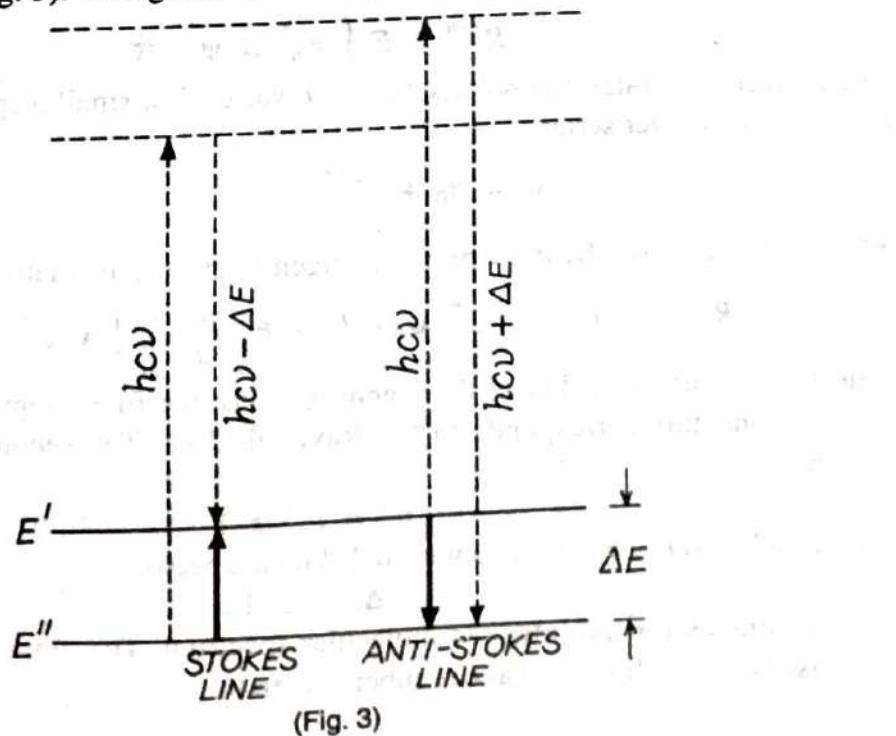
(ii) While  $v_{osc}$  has a fixed value,  $v_{rot}$  can, classically, take any value. Therefore, classically, the rotational Raman spectrum must be continuous on either side of the undisplaced line. This is contrary to observation.

#### 4. Quantum Theory of Raman Effect

Raman effect can be explained from quantum theory. According to this theory, light of wave number  $v$  is a bundle of 'photons', each of energy  $hcv$ . When light falls on a scatterer, the photons collide with the molecules of the scatterer. There are three possibilities in such a collision :

(i) The collision may be elastic, that is, the scatterer molecule maintains its initial energy state, and the photon is scattered (deflected off its path) with its energy unchanged giving rise to the Rayleigh line at wave number  $v$ .

(ii) The collision may be inelastic, in which the molecule in its initial (ground) energy state  $E''$  (say) takes energy from the photon and goes to a higher energy state  $E'$ , and the photon is consequently scattered with a smaller energy  $hcv - \Delta E$ , where  $\Delta E = E' - E''$  (Fig. 3). This gives rise to a Raman line with a frequency lower than that



of the incident spectral line at a wave number  $\frac{h c v - \Delta E}{h c}$ ; the wave number shift being  $\frac{\Delta E}{h c}$ . Such a Raman line is called a 'Stokes line'.

(iii) The photon may collide with a scatterer molecule already in the excited energy state  $E'$  and take energy  $\Delta E$  from it. In this case, the molecule is de-excited to the ground state  $E''$ , and the photon is scattered with increased energy  $h c v + \Delta E$ . This gives rise to a Raman line with a frequency higher than that of the incident spectral line at a wave number  $\frac{h c v + \Delta E}{h c}$ , the wave number shift again being  $\frac{\Delta E}{h c}$ . Such a Raman line is called an 'anti-Stokes line'.

Thus, Stokes and anti-Stokes Raman lines are symmetrically situated on either side of the Rayleigh line. The Raman-shifts  $\Delta v (= \Delta E/h c)$  gives directly the energy-difference between the stationary states of the molecule.

Since the number of molecules in the excited state is very small, the chances of this collision are very small. Hence anti-Stokes Raman line is much weaker than Stokes Raman line.

Now, in the case of free molecules causing scattering of light, the energy  $\Delta E$  which is added to or given up by the molecule may be the vibrational energy or the rotational energy. That is, we can have two different kinds of Raman spectra, namely, a vibrational Raman spectrum and a rotational Raman spectrum.

**Vibrational Raman Spectrum :** The vibrational Raman spectrum arises due to the transition of the molecule from one vibrational energy state to the other of the same electronic state. Quantum-mechanically, the origin of the Raman lines can be explained by considering the matrix elements of the scattering dipole moment :

$$R^{n'm} = \int \psi_n^* p \psi_m d\tau .$$

Now,  $p = \alpha E$ , where  $\alpha$  is the 'polarisability' of the molecule and  $E$  is the oscillating electric field of the incident radiation. Thus

$$R^{n'm} = E \int \psi_n^* \alpha \psi_m d\tau .$$

As the molecule vibrates, the polarisability  $\alpha$  varies. For small displacement  $x$ , we may express  $\alpha$  as a power series :

$$\alpha = \alpha_0 + \left( \frac{d\alpha}{dx} \right)_0 x + \dots$$

Replacing  $\psi_n$  and  $\psi_m$  by the vibrational eigenfunctions, the matrix elements become

$$R^{v'v''} = E \alpha_0 \int \psi_{v'}^* \psi_{v''} dx + E \left( \frac{d\alpha}{dx} \right)_0 \int x \psi_{v'}^* \psi_{v''} dx .$$

Because of the orthogonality of the eigenfunctions, the first integral is zero except when  $v' = v''$  and this corresponds to the Rayleigh line. The second integral is non-zero when only

$$v' = v'' \pm 1 .$$

Thus, the selection rule for the vibrational Raman spectrum is

$$\Delta v = \pm 1 ,$$

which is same as for the infra-red molecular spectrum. The vibrational Raman spectrum thus consists of two lines at wave numbers given by

$$\begin{aligned}\nu_{Raman}^v &= \nu \pm \{G(v+1) - G(v)\} \\ &= \nu \pm \left\{ \omega \left( v + \frac{3}{2} \right) - \omega \left( v + \frac{1}{2} \right) \right\} \\ &= \nu \pm \omega,\end{aligned}$$

where  $\nu$  is the wave number corresponding to the Rayleigh line and  $\omega$  is the vibrational constant of the molecule. At ordinary temperatures, most of the molecules in a sample are in the  $v = 0$  state, and only a very small number in the  $v = 1$  state. Hence the intensity of the anti-Stokes Raman line  $\nu + \omega$  ( $v = 1 \rightarrow v = 0$ ) is much smaller than that of the Stokes Raman line  $\nu - \omega$  ( $v = 0 \rightarrow v = 1$ ), as observed. Infact

$$\frac{\text{anti-Stokes intensity}}{\text{Stokes intensity}} = e^{-\omega h c/kT}.$$

The vibrational Raman shift is

$$\left| \Delta\nu \right|_{Raman}^v = \omega.$$

This is also the wave number corresponding to the main absorption band in the near infra-red spectrum of the molecule. Thus, there is agreement between the vibrational Raman shift and the infra-red absorption band of the molecule.

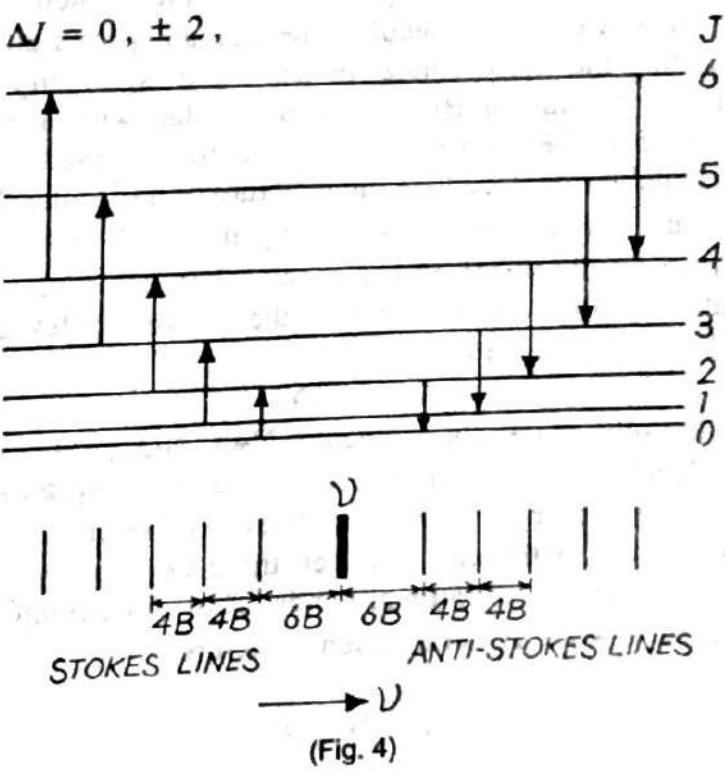
**Pure Rotational Raman Spectrum :** The pure rotational Raman lines appearing on both sides of the Rayleigh line arise from transitions of the molecule from one rotational energy state to the other, of the same vibrational state. The selection rules are derived by resolving the induced dipole moment along axes in space and calculating the corresponding matrix elements involving rotational eigenfunctions. Each of these components passes through two cycles for one revolution of the molecule since the molecular polarisability is the same along opposite directions in the molecule. Hence the matrix elements are non-zero only when

$$J' = J'' \text{ or } J' = J'' \pm 2.$$

This leads to the selection rule

$$\Delta J = 0, \pm 2,$$

which is different from the rule for the far infra-red spectrum. The  $\Delta J = 0$  corresponds to the Rayleigh line. The transitions  $J \rightarrow J + 2$  give Stokes rotational Raman lines, while the transitions  $J + 2 \rightarrow J$  give anti-Stokes rotational Raman lines. Now, even at room temperature, molecules with different  $J$  values are present. Hence a good number of Stokes as well as anti-Stokes lines of comparable intensity are obtained (Fig. 4).



(Fig. 4)

The wave numbers of the rotational Raman lines are given by

$$\begin{aligned}\nu_{\text{Raman}} &= \nu \pm [F(J+2) - F(J)] \\ &= \nu \pm [B(J+2)(J+3) - B(J(J+1))] \\ &= \nu \pm (4BJ + 6B) \\ &= \nu \pm 4B \left( J + \frac{3}{2} \right),\end{aligned}$$

where  $\nu$  is the wave number corresponding to the Rayleigh line and  $B$  is the rotational constant of the molecule.

The rotational Raman shift is

$$\left| \Delta\nu \right| = \left| \frac{\nu_{\text{Raman}}}{\nu_{\text{Rayleigh}}} \right| = 4B \left( J + \frac{3}{2} \right) = 6B, 10B, 14B, 18B,$$

Thus, the pure rotational Raman spectrum is expected to consist of a series of equidistant lines on either side of the exciting line, starting at a distance of  $6B$ , and having a separation of  $4B$  between two successive lines. The line separation ( $4B$ ) is twice as great as that in the far infra-red spectrum of the same molecule. This is in agreement with observation.

There is an additional characteristic of the rotational Raman spectra. In case of homonuclear molecules like  $H_2$ ,  $D_2$ ,  $N_2$ , ... the rotational lines are alternately weak and strong. In certain extreme cases like  $O_2$ , every alternate line is missing. This phenomenon arises from the symmetry properties of the rotational levels of homonuclear molecules. It will be discussed in a subsequent chapter.

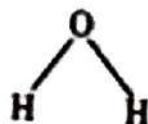
## 5. Raman Spectra and Molecular Structure

Raman effect is an important tool for determining information regarding the structure of diatomic and polyatomic molecules. The vibrational and rotational Raman spectra enable us to determine the force constant and bond-length respectively of those diatomic molecules which have no permanent dipole moment.

In polyatomic molecules, the Raman spectra and the infrared data give information regarding the shape (linear or bent) and symmetry of the molecules. According to the "Mutual Exclusion Rule", for molecules with a centre of symmetry the frequencies observed in the infra-red spectra are not observed in the Raman spectra, and vice-versa. This enables us to deduce the structure of molecules. For example, the molecules  $CO_2$  and  $CS_2$  are found to have two strong infra-red bands; neither of which coincides with a Raman displacement. Hence each of these molecules must have a centre of symmetry. For triatomic molecules this implies that the molecules are linear and symmetric. Hence  $CO_2$  and  $CS_2$  will have the structures



On the other hand, the molecules  $N_2O$ ,  $NO_2$ ,  $SO_2$  and  $H_2O$  show three strong infra-red bands which coincide in many cases with strong Raman bands. Hence these molecules do not have a centre of symmetry. They may be either bent or linear, but not symmetrical. It is possible to distinguish between these two possibilities by observation of the rotational structure of the vibrational bands. Thus, for example,  $N_2O$  has a non-symmetrical linear structure, while  $H_2O$  has a bent structure :



## 6. Infra-red Spectra Versus Raman Spectra

The wave number of the fundamental vibrational band in the near infra-red spectrum of a (heteronuclear) diatomic molecule is the same as the vibrational Raman shift in the Raman spectrum of the same molecule. The reason is that the fundamental infra-red absorption band of a diatomic molecule is observed as a result of vibrational transition  $v = 0 \rightarrow v = 1$ , which is the same as is responsible for the vibrational Stokes Raman band.

However, the mechanism of production of infra-red spectra is quite different from that of Raman spectra :

For the production of infra-red spectra, the energy of the absorbed radiation must be equal to the energy difference between two stationary states of the molecule; whereas no such relationship is required between the incident radiation and the scatterer molecule responsible for the Raman spectra. In Raman spectra, it is the *change* in energy rather than the energy itself which corresponds to the energy difference between the two states of the molecule. This is why Raman spectra arise for *visible* incident light.

Further, the infra-red bands occur when the molecular vibration causes a change in the electric dipole moment of the molecule. Hence the presence of a permanent dipole moment is a must for the production of infra-red spectra. On the other hand, Raman spectra arise due to the polarisability of the molecule which varies as a result of molecular vibration, no matter the molecule has a permanent dipole moment or not.

## SOLVED PROBLEMS

1. With exciting line  $2536 \text{ \AA}$  a Raman line for a sample is observed at  $2612 \text{ \AA}$ . Calculate the Raman shift in  $\text{cm}^{-1}$ .

**Solution.** The wave number  $v (= 1/\lambda)$  of the exciting line is

$$v = \frac{1}{2536 \times 10^{-8} \text{ cm}} = 39432 \text{ cm}^{-1}$$

and that of the Raman line is

$$v_{\text{Raman}} = \frac{1}{2612 \times 10^{-8} \text{ cm}} = 38285 \text{ cm}^{-1}.$$

Therefore, the Raman shift is

$$\Delta v = 39432 \text{ cm}^{-1} - 38285 \text{ cm}^{-1} = 1147 \text{ cm}^{-1}.$$

2. The exciting line in an experiment is  $5460 \text{ \AA}$  and the Stokes line is at  $5520 \text{ \AA}$ . Find the wavelength of the anti-Stokes line. (Meerut 2000 S, 97)

**Solution.** The Stokes and the anti-Stokes lines have the same wave-number displacement with respect to the exciting line. The wave-number of the exciting line is

$$v = \frac{1}{5460 \times 10^{-8} \text{ cm}} = 18315 \text{ cm}^{-1}$$

and that of the Stokes line is

$$\frac{1}{5520 \times 10^{-8} \text{ cm}} = 18116 \text{ cm}^{-1}.$$

Thus, the wave-number displacement is

$$\Delta v = 18315 \text{ cm}^{-1} - 18116 \text{ cm}^{-1} = 199 \text{ cm}^{-1}.$$

Therefore, the wave-number corresponding to the anti-Stokes line would be given by

$$\nu + \Delta\nu = 18315 \text{ cm}^{-1} + 199 \text{ cm}^{-1} = 18514 \text{ cm}^{-1}$$

The corresponding wavelength is

$$\lambda = \frac{1}{18514 \text{ cm}^{-1}} = 5.401 \times 10^{-5} \text{ cm} = 5401 \text{ Å}$$

3. A substance shows a Raman line at 4567 Å when exciting line 4358 Å is used. Deduce the positions of Stokes and anti-Stokes lines for the same substance when exciting line 4047 Å is used. (Meerut sp. paper 2006, 04, 03, 02 S, 95)

**Solution.** The wave number corresponding to the exciting line 4358 Å is

$$\nu = \frac{1}{4358 \times 10^{-8} \text{ cm}} = 22946 \text{ cm}^{-1}$$

and that corresponding to the Raman line at 4567 Å is

$$\frac{1}{4567 \times 10^{-8} \text{ cm}} = 21896 \text{ cm}^{-1}$$

Therefore, the Raman wave-number displacement is

$$\Delta\nu = 22946 \text{ cm}^{-1} - 21896 \text{ cm}^{-1} = 1050 \text{ cm}^{-1}$$

The Raman displacement is the characteristic of the substance, whichever be the exciting line.

Now, the wave number corresponding to the exciting line 4047 Å is

$$\nu = \frac{1}{4047 \times 10^{-8} \text{ cm}} = 24710 \text{ cm}^{-1}$$

Therefore, the wave numbers for the Stokes and the anti-Stokes lines are

$$\nu \mp \Delta\nu = 24710 \text{ cm}^{-1} \mp 1050 \text{ cm}^{-1} = 23660 \text{ cm}^{-1} \text{ and } 25760 \text{ cm}^{-1}$$

The corresponding wavelengths are

$$\lambda_{\text{Stokes}} = \frac{1}{23660 \text{ cm}^{-1}} = 4.2265 \times 10^{-5} \text{ cm} = 4226.5 \text{ Å}$$

$$\text{and } \lambda_{\text{antiStokes}} = \frac{1}{25760 \text{ cm}^{-1}} = 3.882 \times 10^{-5} \text{ cm} = 3882 \text{ Å}$$

4. For exciting light of 4358 Å, the Raman spectrum of benzene shows Raman lines for  $\Delta\nu = 608, 846, 995, 1178, 1599, 3064 \text{ cm}^{-1}$ . At what wavelengths would these Raman lines appear if benzene is irradiated with monochromatic light of 5461 Å.

**Solution.** The Raman displacements  $\Delta\nu$  are the same, whichever the exciting light. The wave number corresponding to exciting light of 5461 Å is

$$\nu = \frac{1}{5461 \times 10^{-8} \text{ cm}} = 18312 \text{ cm}^{-1}$$

The wave numbers corresponding to the Stokes Raman lines are

$$\begin{aligned} \nu - \Delta\nu &= 18312 \text{ cm}^{-1} - (608, 846, 995, 1178, 1599, 3064) \text{ cm}^{-1} \\ &= (17704, 17466, 17317, 17134, 16713, 15248) \text{ cm}^{-1} \end{aligned}$$

The corresponding wavelengths are

$$5648, 5725, 5775, 5836, 5983, 6558 \text{ Å}$$

5. When acetylene is irradiated with the 4358 Å mercury line, a Raman line attributed to the symmetrical stretching vibration is observed at 4768 Å. Calculate the fundamental frequency for this vibration. Given :  $c = 3.0 \times 10^{10} \text{ cm s}^{-1}$ .

(Meerut sp. paper 93)

**Solution.** The wave number corresponding to the exciting line is

$$\nu = \frac{1}{4358 \times 10^{-8} \text{ cm}} = 22946 \text{ cm}^{-1},$$

and that corresponding to the Stokes Raman line is

$$\frac{1}{4768 \times 10^{-8} \text{ cm}} = 20973 \text{ cm}^{-1}.$$

The vibrational Raman displacement is

$$\left| \Delta\nu \right|_{\text{Raman}}^{\nu} = 22946 \text{ cm}^{-1} - 20973 \text{ cm}^{-1} = 1973 \text{ cm}^{-1}.$$

This is the same as the vibrational constant  $\omega$  of the acetylene molecule, that is,

$$\omega = 1973 \text{ cm}^{-1}.$$

Hence the vibrational frequency is

$$\begin{aligned} v_{\text{osc}} &= \omega c = 1973 \text{ cm}^{-1} \times (3.0 \times 10^{10} \text{ cm s}^{-1}) \\ &= 5.92 \times 10^{13} \text{ s}^{-1}. \end{aligned}$$

**6.** In the vibrational Raman spectrum of HF, the Raman lines are observed at wavelengths 2670 Å and 3430 Å. Find the fundamental vibrational frequency of the molecule. Given :  $c = 3.0 \times 10^{10} \text{ cm s}^{-1}$ .

**Solution.** The wave numbers corresponding to Raman lines are

$$\frac{1}{2670 \times 10^{-8} \text{ cm}} = 37453 \text{ cm}^{-1} \text{ and } \frac{1}{3430 \times 10^{-8} \text{ cm}} = 29154 \text{ cm}^{-1}.$$

If  $\nu$  be the wave number of the exciting line, and  $\Delta\nu$  be the vibrational Raman displacement, then

$$\nu + \Delta\nu = 37453 \text{ cm}^{-1} \text{ and } \nu - \Delta\nu = 29154 \text{ cm}^{-1}.$$

$$\therefore \Delta\nu = \frac{37453 \text{ cm}^{-1} - 29154 \text{ cm}^{-1}}{2} = 4149.5 \text{ cm}^{-1}.$$

This is same as the vibrational constant  $\omega$  of the molecule HF, that is,

$$\omega = 4149.5 \text{ cm}^{-1}.$$

Hence the vibrational frequency of the molecule is

$$\begin{aligned} v_{\text{osc}} &= \omega c = 4149.5 \text{ cm}^{-1} \times (3.0 \times 10^{10} \text{ cm s}^{-1}) \\ &= 1.24 \times 10^{14} \text{ Hz}. \end{aligned}$$

**7.** The values  $\omega_e$  and  $\omega_e x_e$  are  $1580.36 \text{ cm}^{-1}$  and  $12.07 \text{ cm}^{-1}$  respectively for the ground state of  $\text{O}_2$  molecule. Calculate the zero-point energy and the expected Raman vibrational displacement.

**Solution.** The vibrational energy of a diatomic molecule is given by

$$G(\nu) = \omega_e \left( \nu + \frac{1}{2} \right) - \omega_e x_e \left( \nu + \frac{1}{2} \right)^2.$$

The zero-point energy is

$$\begin{aligned} G(0) &= \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e \\ &= \left( \frac{1}{2} \times 1580.36 \text{ cm}^{-1} \right) - \left( \frac{1}{4} \times 12.07 \text{ cm}^{-1} \right) \\ &= 790.18 \text{ cm}^{-1} - 3.02 \text{ cm}^{-1} = 787.16 \text{ cm}^{-1}. \end{aligned}$$

The vibrational Raman displacement is

$$|\Delta v|^v_{Raman} = G(v') - G(v'').$$

The molecules are normally in the ground state  $v'' = 0$ , and the selection rule is  $\Delta v = \pm 1$ . Therefore,

$$\begin{aligned} |\Delta v|^v_{Raman} &= G(1) - G(0) \\ &= \left( \frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e \right) - \left( \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e \right) \\ &= \omega_e - 2 \omega_e x_e \\ &= 1580.36 \text{ cm}^{-1} - (2 \times 12.07 \text{ cm}^{-1}) \\ &= 1580.36 \text{ cm}^{-1} - 24.14 \text{ cm}^{-1} \\ &= 1556.22 \text{ cm}^{-1}. \end{aligned}$$

8. In the rotational Raman spectrum of HCl the displacements from the exciting line are represented by

$$\Delta v = \pm (62.4 + 41.6 J) \text{ cm}^{-1}.$$

Calculate the moment of inertia of the HCl molecule ( $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ). (Meerut 2004, 03, 02, 99, sp. paper 98, 90)

**Solution.** The rotational Raman displacements of HCl molecule are given by

$$|\Delta v|^r_{Raman} = (62.4 + 41.6 J) \text{ cm}^{-1} = 41.6 \left( J + \frac{3}{2} \right) \text{ cm}^{-1}.$$

Comparing it with the theoretical formula

$$|\Delta v|^r_{Raman} = 4B \left( J + \frac{3}{2} \right),$$

we have

$$4B = 41.6 \text{ cm}^{-1}$$

or

$$B = 10.4 \text{ cm}^{-1} = 1040 \text{ m}^{-1}.$$

The rotational constant of the molecule is given by

$$B = \frac{h}{8\pi^2 I c},$$

where  $I$  is the moment of inertia of the molecule.

$$\begin{aligned} \therefore I &= \frac{h}{8\pi^2 B c} \\ &= \frac{6.63 \times 10^{-34} \text{ Js}}{8 \times (3.14)^2 \times (1040 \text{ m}^{-1}) \times (3.0 \times 10^8 \text{ m s}^{-1})} \\ &= 2.7 \times 10^{-47} \text{ kg m}^2. \end{aligned}$$

9. The small (rotational) Raman displacement for HCl molecule is  $41.6 \text{ cm}^{-1}$ . Find the internuclear distance between the atoms forming the molecule. Given :  $h = 6.63 \times 10^{-34} \text{ Js}$ ,  $c = 3.0 \times 10^8 \text{ m s}^{-1}$  and  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ .

(Meerut 2006)

**Solution.** Given :

$$4B = 41.6 \text{ cm}^{-1}.$$

Therefore, the rotational constant of the HCl molecule is

$$B = \frac{41.6 \text{ cm}^{-1}}{4} = 10.4 \text{ cm}^{-1} = 1040 \text{ m}^{-1}.$$

Now,  $B = \frac{h}{8\pi^2 I c}$ , where  $I$  is the moment of inertia of the molecule.

$$\begin{aligned}\therefore I &= \frac{h}{8\pi^2 B c} \\ &= \frac{6.63 \times 10^{-34} \text{ Js}}{8 \times (3.14)^2 \times (1040 \text{ m}^{-1}) \times (3.0 \times 10^8 \text{ m s}^{-1})} \\ &= 2.7 \times 10^{-47} \text{ kg m}^2.\end{aligned}$$

If  $\mu$  be the reduced mass, and  $r$  the internuclear distance for the molecule, then

$$I = \mu r^2$$

$$r = \sqrt{I/\mu}.$$

or  
The reduced mass of the HCl molecule is

$$\mu = \frac{(1 \times 35)/(6.023 \times 10^{23})^2}{(1 + 35)/(6.023 \times 10^{23})} = 1.61 \times 10^{-24} \text{ g} = 1.61 \times 10^{-27} \text{ kg.}$$

$$\therefore r = \sqrt{\frac{2.7 \times 10^{-47} \text{ kg m}^2}{1.61 \times 10^{-27} \text{ kg}}} = 1.29 \times 10^{-10} \text{ m} = 1.29 \text{ Å.}$$

## QUESTIONS

- What is Raman effect? Describe briefly the chief characteristics of vibrational and pure rotational Raman spectra.
- Describe an experimental arrangement for the study of Raman spectra in the laboratory. (Meerut 2002 S, 01, sp. paper 95)
- The occurrence of a Raman spectrum depends on the polarisability of the molecule but is entirely independent of the presence of a permanent dipole moment. Elucidate this statement with examples. (Meerut 2002 S)
- Consider  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{HCl}$  and  $\text{OH}$  molecules. State, giving reasons, which of these will show infra-red spectrum and which will give Raman spectrum.
- What is Raman effect? Give its quantum theory. What light does it throw on the structure of molecules? what are Stokes and anti-Stokes lines? (Meerut sp. paper 2006, 05)
- What is Raman effect? Explain theoretically the observed characteristics of the Raman spectrum of a diatomic molecule. How is it used to explain the structure of a molecule. (Meerut 2000, 99 S, sp. paper 2004, 03, 02, 00)
- Discuss the main features of the vibrational and the rotational Raman spectra of diatomic molecules. Give the necessary theory. What light does it throw on the structure of molecules? (Meerut 2004, 03, 02, 99, 93, sp. paper 2001, 94)
- Discuss about the salient features of the vibrational and rotational Raman spectra of a diatomic molecule and how they can be explained with the help of an appropriate theory. Hence obtain the selection rules that govern these transitions on the basis of appropriate matrix elements.
- Discuss origin of Raman effect. Obtain expression for frequency shift of rotational Raman lines. (Meerut 93 sp. paper)
- Discuss the quantum theory of Raman effect and describe the rotational structure of the Raman spectrum of a diatomic molecule. (Meerut 2000 S sp. paper)
- Discuss Raman spectra of diatomic molecules and point out the similarity and difference in infra-red and Raman spectra. (Meerut 2006, 00 S, 98; Kanpur 2002)

12. Describe the salient features of the Raman spectrum of a heteronuclear diatomic molecule and how you would explain it. In what way does it differ from the fluorescence spectrum ?
13. Explain how are infra-red and Raman spectra used to find out that  $\text{CO}_2$  is a linear molecule, while  $\text{H}_2\text{O}$  is bent.

(Meerut sp. paper 99, 95)

**PROBLEMS**

1. With exciting line  $4358 \text{ \AA}$ , a sample gives Stokes line at  $4458 \text{ \AA}$ . Deduce the wavelength of the anti-Stokes line.

(Meerut sp. paper 93)

Ans.  $4262 \text{ \AA}$ .

2. The Raman spectrum of gaseous HBr is produced by means of a mercury lamp and a filter which only transmits the mercury lines  $4358.3$ ,  $4046.6$  and  $4077.8 \text{ \AA}$ . Raman lines are found at  $4513.9$ ,  $4552.7$  and  $4905.1 \text{ \AA}$ . Analyse this observation.

Ans. Each exciting line produces a Stokes Raman line

$$4358.3 \text{ \AA} \rightarrow 4905.1 \text{ \AA}; 4046.6 \text{ \AA} \rightarrow 4513.9 \text{ \AA}; 4077.8 \text{ \AA} \rightarrow 4552.7 \text{ \AA}.$$

# Electronic Spectra : Franck-Condon Principle

## 1. Salient Features of Molecular Electronic Spectra

Among the molecular spectra, the electronic spectra are the most complex which appear in the visible and ultraviolet regions, and involve a change in all the three electronic, vibrational and rotational energies of the molecule. Such spectra are studied both in emission and absorption, and the (electronic) bands show a fine structure more complicated than in the vibrational-rotational bands. The tendency of head formation is much stronger, and the bands may be degraded either toward the red or toward the violet.

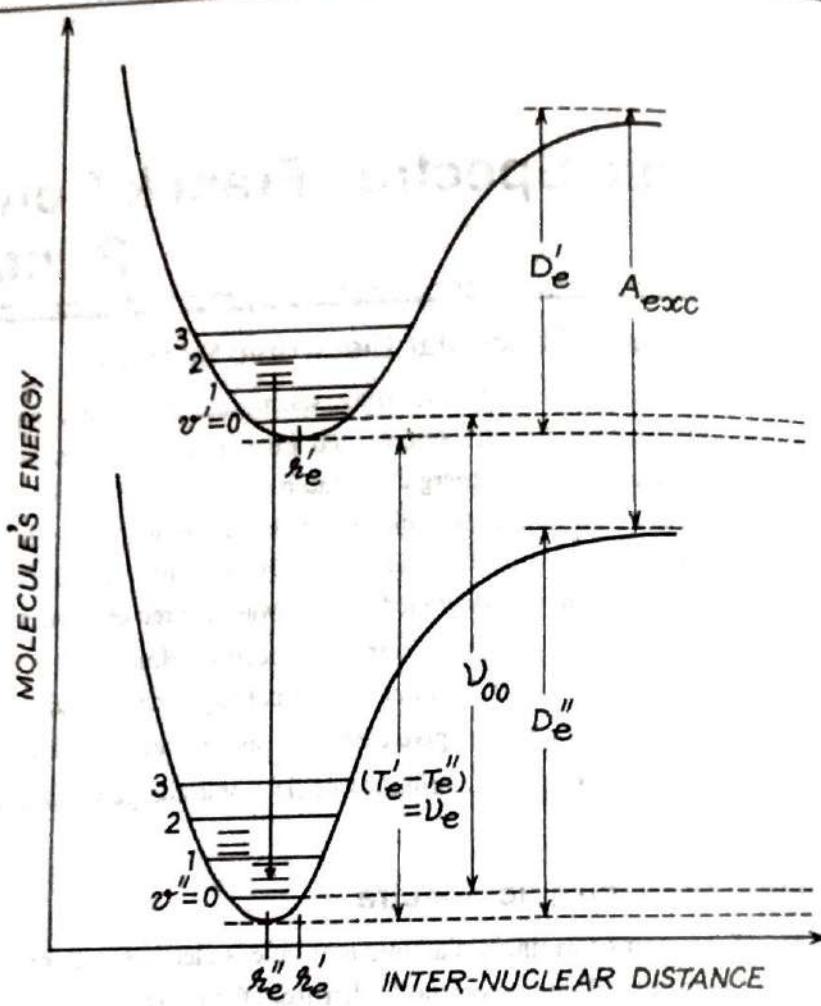
All diatomic molecules exhibit electronic spectra. Homonuclear molecules ( $H_2, N_2, O_2$ ) which give neither rotational nor vibrational-rotational spectra because they do not have permanent dipole moments, give electronic spectra because the instantaneous dipole moment\* changes during the redistribution of electronic charge which accompanies the electronic transition.

## 2. Formation of Electronic Spectra

When one of the atoms forming a diatomic molecule is electronically excited, that is, its valence electron is pushed into an orbital farther from the nucleus, the molecule is said to be in an electronically-excited state. The various possible electron arrangements for a given molecule form a pattern of allowed electronic states for the molecule. For each of the electronic states there is a different dependence of the molecule's energy on its internuclear separation. That is, *each electronic state of the molecule has a different potential energy curve* characterised by a minimum (provided the electronic state is stable) at an equilibrium internuclear distance  $r_e$ , a dissociation limit  $D_e$ , a set of discrete vibrational levels and sets of discrete rotational levels.

Two typical potential energy curves for a diatomic molecule are shown in Fig. 1, the lower one representing the ground state and the upper one an electronically-excited state of the molecule. The curves differ in shape as well as in position of minimum. Because the atoms are more loosely bound in the excited states, the curve showing the molecule's potential energy as a function of internuclear distance becomes shallower and broader, and the equilibrium internuclear distance increases with increasing electronic excitation, as illustrated in Fig. 1. Further, the asymptote of the upper curve is higher than that of the lower by the *electronic energy of excitation*,  $A_{exc}$ , of the atom. The *electronic energies* of the molecule in the upper and the lower states are  $T_e'$  and  $T_e''$  (in wave-number unit

\* In homonuclear molecules, it is the average value of the dipole moment which is zero.



(Fig. 1)

$\text{m}^{-1}$  or  $\text{cm}^{-1}$ ) and their difference  $\nu_e$  is the difference between the minima of the two curves.

When a transition of the molecule from one electronic state to the other takes place, the emitted or absorbed radiation falls in the visible or ultraviolet region (because the energy separation between different electronic states is from 1 to 10 eV). The electronic transition is accompanied by a number of transitions involving a vibrational level of the upper and a vibrational level of the lower electronic state. Each such vibrational transition is, in turn, accompanied by a number of transitions involving a rotational level of the upper and a rotational level of the lower vibrational state. (One such emission transition has been shown in Fig. 1). The rotational transitions give rise to a group of fine lines which constitute a "band". That is, a band arises from a particular vibrational transition, and the bands arising from all the vibrational transitions constitute a "band-system". Thus, a single electronic transition in a molecule gives rise to a band-system. The bands of the system which correspond to the same upper vibrational level ( $v'$ ) but different lower vibrational levels ( $v''$ ) are said to form a  $v''$ -progression; and similarly the bands corresponding to the same lower level ( $v''$ ) but different upper levels ( $v'$ ) form a  $v'$ -progression. In an emission band-system, a number of progressions appear.

### 3. Vibrational (Gross) Structure of Electronic Band-System in Emission

An electronic transition involves a change in all the three electronic; vibrational and rotational energies of the molecule. Therefore, the wave numbers arising from an electronic transition are given by

$$\nu = (T_e' - T_e'') + (G' - G'') + (F' - F'').$$

Now,  $T_e' - T_e'' = v_e$ , a constant for a given electronic transition.  $G'$  and  $G''$  correspond to vibrational levels associated with different electronic states and so have different  $\omega_e$  and  $\omega_e x_e$  values, and  $G'$  may be larger or smaller than  $G''$ .

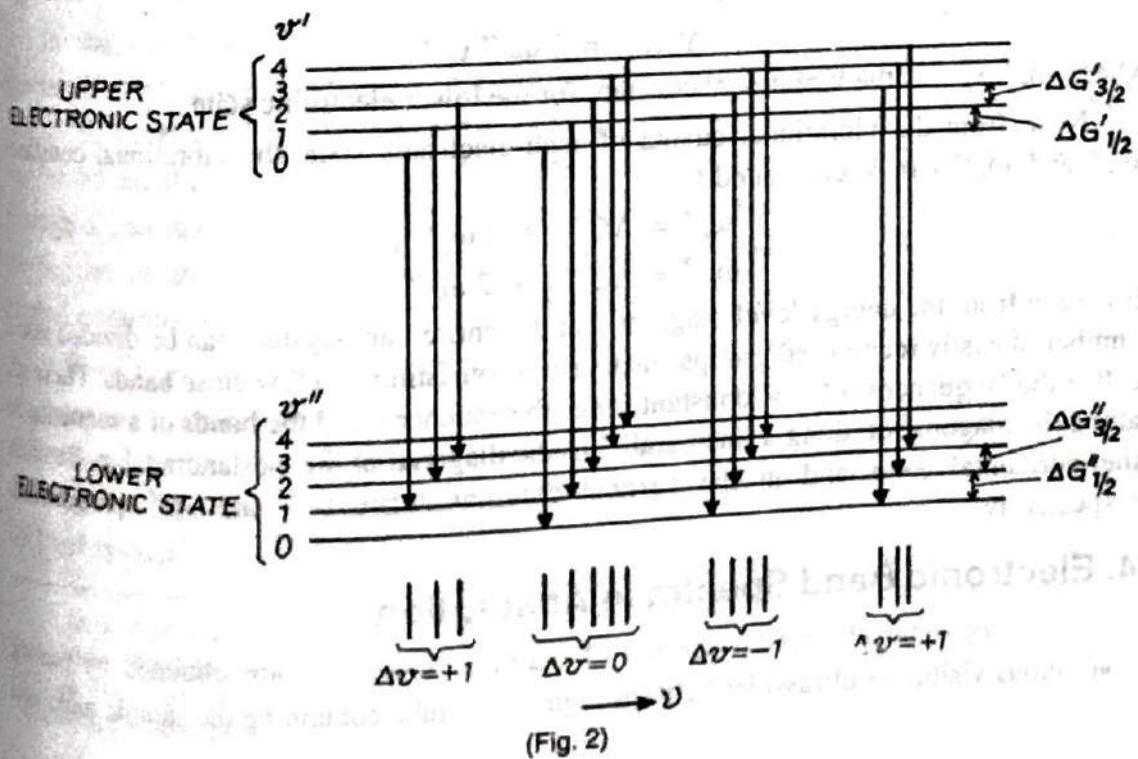
Let us ignore the rotational structure of the individual bands ( $F = F'' = 0$ ). Then, the wave numbers corresponding to the band-origins of the system are given by

$$\begin{aligned} \nu_0 &= v_e + G'(v') - G''(v'') \\ &= v_e + \left\{ \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e' x_e' \left( v' + \frac{1}{2} \right)^2 \right\} \\ &\quad - \left\{ \omega_e'' \left( v'' + \frac{1}{2} \right) - \omega_e'' x_e'' \left( v'' + \frac{1}{2} \right)^2 \right\}. \end{aligned}$$

For an electronic transition, there is no restriction on the change in the vibrational quantum number  $v$ , that is,

$$\Delta v = \text{unrestricted}.$$

This means that, in principle, transition from each vibrational level of the upper electronic state can take place to each of the vibrational levels of the lower electronic state (although the intensity of transition depends upon  $v'$  and  $v''$  involved). Thus, we can expect a large number of bands from a single electronic transition. As the temperature of the emission sources is much higher than the room temperature, a good number of vibrational levels of the upper electronic state are appreciably populated and hence quite a good number of emission bands are obtained. Some of the emission transitions are shown in the energy-level diagram drawn in Fig. 2.



(Fig. 2)

In order to analyse these bands, the wave numbers of the band-origins are arranged into an array between the values of  $v'$  and  $v''$  (Deslandre table), as shown below :

$v''$	0	1	2	3
$v'$	$v_e + G'(0) - G''(0)$	$v_e + G'(1) - G''(1)$	$v_e + G'(2) - G''(2)$	
0	$v_e + G'(1) - G''(0)$	$v_e + G'(2) - G''(1)$	$v_e + G'(3) - G''(2)$	
1			$v_e + G'(3) - G''(2)$	
2			$v_e + G'(3) - G''(2)$	
3				
4				

A comparison of this table with the energy level diagram (Fig. 2) shows that the *constant* separation between two successive 'rows' of the table is the separation (in wave-number unit  $m^{-1}$  or  $cm^{-1}$ ) between the corresponding vibrational levels (called vibrational quanta) of the 'upper' electronic state.

$$\Delta G'_{1/2} = G'(1) - G'(0) = \omega_e' - 2 \omega_e' x_e'$$

$$\Delta G'_{3/2} = G'(2) - G'(1) = \omega_e' - 4 \omega_e' x_e'$$

$$\Delta G'_{5/2} = G'(3) - G'(2) = \omega_e' - 6 \omega_e' x_e'$$

$$\dots \dots \dots \dots \dots$$

The second difference of successive vibrational quanta is the same and gives the vibrational constant  $\omega_e' x_e'$  (anharmonicity constant) for the upper state :

$$\Delta^2 G' = 2 \omega_e' x_e'.$$

Similarly, the *constant* separation between two successive 'columns' of the table is the separation between the corresponding vibrational levels of the 'lower' electronic state.

$$\Delta G''_{1/2} = G''(1) - G''(0) = \omega_e'' - 2 \omega_e'' x_e''$$

$$\Delta G''_{3/2} = G''(2) - G''(1) = \omega_e'' - 4 \omega_e'' x_e''$$

$$\Delta G''_{5/2} = G''(3) - G''(2) = \omega_e'' - 6 \omega_e'' x_e''$$

$$\dots \dots \dots \dots \dots$$

Again, the second difference gives

$$\Delta^2 G'' = 2 \omega_e'' x_e'',$$

where  $\omega_e'' x_e''$  is the vibrational constant for the lower electronic state

Now, from the vibrational quanta of each electronic state, the vibrational constants  $\omega_e'$  and  $\omega_e''$  can be calculated :

$$\omega_e' = \Delta G'_{1/2} + 2 \omega_e' x_e'$$

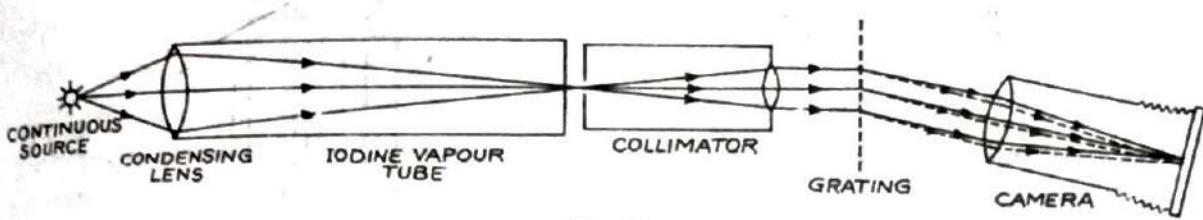
$$\omega_e'' = \Delta G''_{1/2} + 2 \omega_e'' x_e''$$

It is seen from the energy level diagram that the entire band-system can be divided into number of easily recognised groups, each group consisting of a few close bands. These are called the 'sequences' ( $\Delta v = \text{constant}$  for each sequence), and the bands of a sequence lie along the diagonal or along a line parallel to the diagonal of the Deslandre table. Bands in the horizontal rows and in the vertical columns form  $v''$ - and  $v'$  progressions respectively.

#### 4. Electronic Band Spectra in Absorption

The electronic absorption spectra of diatomic molecules are obtained by passing continuous visible or ultraviolet light through a long tube containing the sample molecule.

gas at room temperature and then directing it into a spectrograph. An experimental arrangement to record the absorption spectrum of  $I_2$  molecules is shown in Fig. 3. The apparatus consists of a source of continuous light, a condensing lens, a long tube having its ends closed by thin optical glass plates and filled with  $I_2$  vapour, and a grating spectrograph fitted with a collimator and a camera.



(Fig. 3)

Continuous light condensed by the lens passes through  $I_2$  vapour and then enters the collimator of the spectrograph. The light, robbed of the frequencies characteristics of  $I_2$  molecule, leaves the collimator as a parallel beam and enters the camera which is focussed for parallel beam. The absorption spectrum of  $I_2$  is recorded on the photographic plate properly placed in the camera.

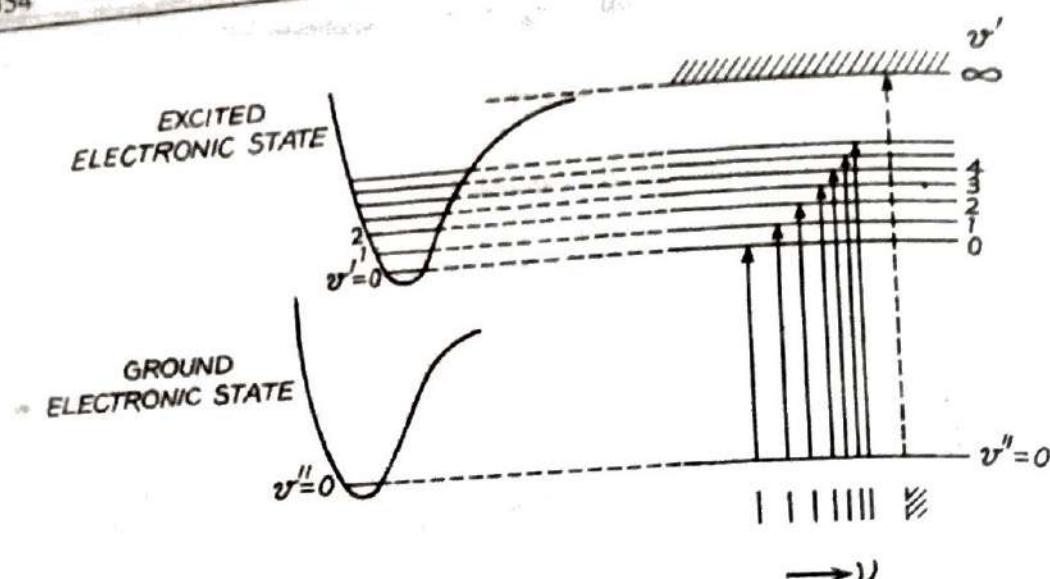
A typical absorption spectrum is found to consist of an extensive series of bands which come more and more closer toward high wave-number side and ultimately merge into a continuum.

#### Difference between Emission Band Spectrum and the corresponding Absorption Band Spectrum :

The emission sources of band spectra are usually at temperatures much higher than the room temperature and so a large number of vibrational levels of the excited electronic state are appreciably populated. Hence transitions from each of these  $v'$ -levels to various  $v''$ -levels of the lower electronic state do occur. Hence a large number of  $v''$  progressions (corresponding to  $v' = 0, 1, 2, 3, \dots$ ) of emission bands appear.

In the absorption experiment, on the other hand, the sample is at the room temperature. At such temperatures, according to Boltzmann's distribution law, most of the molecules are in the lowest vibrational level ( $v'' = 0$ ) of the ground electronic state, a very small number in the  $v'' = 1$  level, an extremely few in higher levels. Hence the passage of continuous light causes absorption transitions mostly from the  $v'' = 0$  level of the ground electronic state to the different vibrational levels  $v' = 0, 1, 2, 3, \dots$  of the excited electronic state. (Fig. 4) Therefore, only a single  $v'$ -progression (corresponding to  $v'' = 0$ ) of bands appear prominently in the absorption spectrum\*. (The ground-state progressions corresponding to  $v'' = 1, 2, \dots$  appear, if at all, with very poor intensities). The spectrum is shown below the energy-level diagram. The bands converge at a point corresponding to the transition  $v'' = 0 \rightarrow v' = \infty$ , where a continuum joins the band-system.

\* All emission band-systems are not observed in absorption. Infact, a band-system can be observed in absorption only when its lower electronic state is the ground electronic state of the molecule. Those emission band-systems which have excited electronic states as their lower states are not observed in absorption.



(Fig. 4)

**Importance of Absorption Band Spectra :** The analysis of absorption spectra gives useful information about the vibrational levels of excited electronic state of the molecule.

The wave numbers of the band-origins of a system are given by

$$\begin{aligned}v_0 &= \nu_e + G'(v') - G''(v'') \\&= \nu_e + \left\{ \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e' x_e' \left( v' + \frac{1}{2} \right)^2 \right\} \\&\quad - \left\{ \omega_e'' \left( v'' + \frac{1}{2} \right) - \omega_e'' x_e'' \left( v'' + \frac{1}{2} \right)^2 \right\}\end{aligned}$$

For the observed absorption progression of bands corresponding to  $v'' = 0$ , we have

$$v_0 = \nu_e + \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e' x_e' \left( v' + \frac{1}{2} \right)^2 - \frac{1}{2} \omega_e'' + \frac{1}{4} \omega_e'' x_e''.$$

For the first few bands of this progression, we have  $v' = 0, 1, 2, 3, \dots$ . The wave numbers of these bands are :

Wave numbers	First differences
$\nu_e + \frac{1}{2} \omega_e' - \frac{1}{4} \omega_e' x_e' - \frac{1}{2} \omega_e'' + \frac{1}{4} \omega_e'' x_e''$	$\omega_e' - 2 \omega_e' x_e'$
$\nu_e + \frac{3}{2} \omega_e' - \frac{9}{4} \omega_e' x_e' - \frac{1}{2} \omega_e'' + \frac{1}{4} \omega_e'' x_e''$	$\omega_e' - 4 \omega_e' x_e'$
$\nu_e + \frac{5}{2} \omega_e' - \frac{25}{4} \omega_e' x_e' - \frac{1}{2} \omega_e'' + \frac{1}{4} \omega_e'' x_e''$	$\omega_e' - 6 \omega_e' x_e'$
$\nu_e + \frac{7}{2} \omega_e' - \frac{49}{4} \omega_e' x_e' - \frac{1}{2} \omega_e'' + \frac{1}{4} \omega_e'' x_e''$	

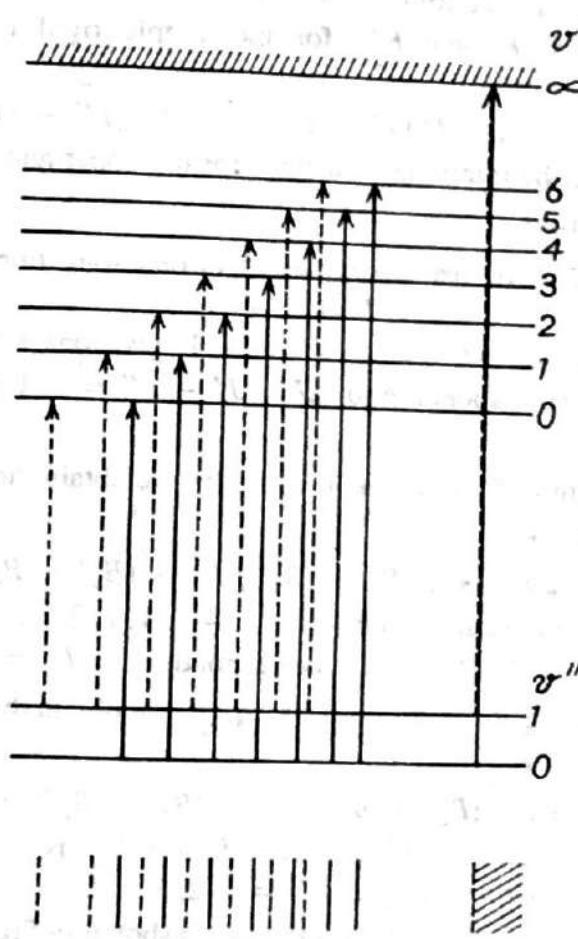
F  
h

Th

This shows that as  $v'$  increases, the wave-number separation (first difference) between successive bands decreases. This means that in the excited electronic state, the vibrational levels draw closer and closer. The second difference between adjacent bands is the same,  $2 \omega_e' x_e'$ , and gives directly the anharmonicity constant  $\omega_e' x_e'$ . Once  $\omega_e' x_e'$  is known, the vibrational constant  $\omega_e'$  is obtained from the first differences.

The absorption continuum which joins the discrete bands at the convergence limit, corresponds to the dissociation of the molecule. Therefore, a suitable extrapolation of bands enables us to compute the dissociation energy of the molecule. Thus, the study of absorption spectra, as compared to emission spectra, gives more information, with less elaborate computation, regarding the excited electronic states of molecules.

**Absorption Spectrum of  $I_2$  Molecule :** The absorption spectrum of  $I_2$  molecule shows progressions corresponding to  $v'' = 1$  and even higher, in addition to the progression  $v'' = 0$ , although with smaller intensity. The reason is that  $I_2$  is a very heavy molecule, so that it has *very small vibrational quanta\** in the ground state, that is, its vibrational levels are much closer. Therefore, even at room temperature, enough molecules occupy  $v'' = 1$  level, and higher. Hence, absorption transitions take place from  $v'' = 1, 2, \dots$  levels also (Fig. 5), and additional progressions appear in the absorption



(Fig. 5)

spectrum. The progression  $v'' = 1$  is indicated by broken lines in Fig. 5. The separations of bands in these additional progressions are exactly the same as in the progression  $v'' = 0$ . Bands with  $v'' = 1$  can also be observed at room temperature for molecules with large vibrational quanta if thick absorbing layers or high pressures are used.

$$*\omega = \frac{v_{osc}}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

## 5. Fine (Rotational) Structure of Electronic Bands

An electronic band of a molecule, when studied under high resolution, is found to be composed of a large number of lines arranged in a particular manner. This fine structure of individual bands is attributed to the rotation of the molecule. This, in turn, means that each line of a band corresponds to a change in all the three electronic, vibrational and rotational energies of the molecule. As such, the wave number of a line ( $J', J''$ ) of an electronic band is given by

$$\nu = \nu_e + (G' - G'') + (F' - F'')$$

$$= \nu_0 + F'(v', J') - F''(v'', J''),$$

where  $\nu_0 (= \nu_e + (G' - G''))$  is the band-origin.  $F'$  and  $F''$  are the rotational terms of the upper and the lower electronic states respectively, and hence they are widely different. Substituting for  $F'$  and  $F''$  for the simple rigid rotator case, the last expression is

$$\nu = \nu_0 + B_v' J'(J' + 1) - B_v'' J''(J'' + 1), \quad \dots(i)$$

where  $B_v'$  and  $B_v''$  are the rotational constants for the upper and the lower vibrational and electronic states involved.

The selection rule for  $J$ , in case of simplest electronic transition  ${}^1\Sigma - {}^1\Sigma$ , is

$$\Delta J = \pm 1.$$

Transitions corresponding to  $\Delta J = J' - J'' = + 1$  give one set of lines called the 'R-branch'; while those corresponding to  $\Delta J = J' - J'' = - 1$  give other set of lines called the 'P-branch'.

**R-branch :** Substituting  $J' = J'' + 1$  in eq. (i), we obtain the lines of the R-branch with wave numbers given by

$$\nu_R = \nu_0 + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2. \quad \dots(ii)$$

where the (lower) rotational quantum number  $J'' = 0, 1, 2, 3, \dots$ . Thus, the R-branch is a series of lines  $R(0), R(1), R(2), \dots$  corresponding to  $J'' = 0, 1, 2, \dots$

**P-branch :** Substituting  $J' = J'' - 1$  in eq. (i), we obtain the lines of the P-branch with wave numbers given by

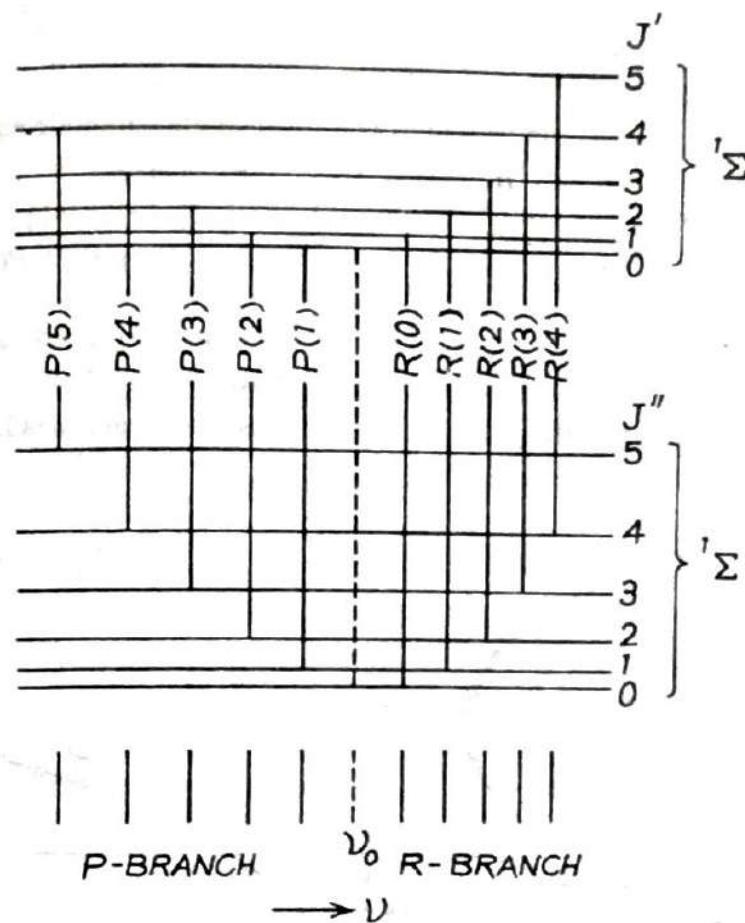
$$\nu_P = \nu_0 - (B_v' + B_v'')J'' + (B_v' - B_v'')J''^2, \quad \dots(iii)$$

where  $J'' = 1, 2, 3, 4, \dots$ . Thus, the P-branch is a series of lines  $P(1), P(2), P(3), \dots$  corresponding to  $J'' = 1, 2, 3, \dots$

The transitions and the resulting band-structure is shown in Fig. 6.

**Difference between Electronic Bands and Vibrational-Rotational Bands :** The structure of an electronic band differs from the structure of a vibrational-rotation (infra-red) band in two important respects :

- (1) In an electronic transition, the rotational constants  $B_v'$  and  $B_v''$  belong to different electronic states and so they are widely different. That is,  $(B_v' - B_v'')$  has value much larger than that in case of an infra-red transition (in which  $B_v'$  and  $B_v''$  belong to the vibrational levels of the same electronic state). Therefore, the coefficient of the quadratic ( $J''^2$ ) term in eq. (ii) and (iii) is quite large. As a result, with increasing  $J$ ,



(Fig. 6)

the line-spacing changes *rapidly*. As we move away from the band-origin, the lines rapidly converge in one branch and rapidly diverge in the other. In the converging branch, the line-spacing after diminishing to zero, changes sign with increasing  $J''$  and so this branch returns back after forming a *sharp* head at zero spacing. Thus, in electronic bands there is a strong tendency of head formation. On the contrary, in a vibrational-rotational band the head formation is not at all pronounced and usually the head is not observed.

(2) Again, because in electronic transition  $B_v'$  and  $B_v''$  belong to different electronic states,  $(B_v' - B_v'')$  may be negative or positive; whereas in case of infra-red transition it is necessarily negative. If  $(B_v' - B_v'')$  is negative, the quadratic term in eq. (ii) differs in sign with the linear term so that line-spacing decreases with increasing  $J''$  in the *R*-branch.\* That is, the head is formed in the *R*-branch. Conversely, the band is degraded in the *P*-branch, that is, toward the red (decreasing wave number), as indicated in Fig. 6. If  $(B_v' - B_v'')$  is positive, then it is in eq. (iii) that the quadratic term differs in sign with the linear term. In this case, the head is formed in the *P*-branch and the band is degraded toward the violet. Thus, ***both red-degraded and violet-degraded bands are observed in electronic band-systems ; whereas only red-degraded bands are observed in vibrational-rotational spectra.***

\* When  $(B_v' - B_v'')$  is negative, then in eq. (iii) both the terms are of the same (negative) sign. This means that line-spacing increases with increasing  $J''$  in the *P*-branch.

In the special case of  $B_v' = B_v''$  (vibration-rotation interaction zero), both the branches will have equi-spaced lines and the band would be headless.

Both the R-and P-branches can be represented by a single parabolic equation :

$$v = v_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2, \quad \dots(iv)$$

where

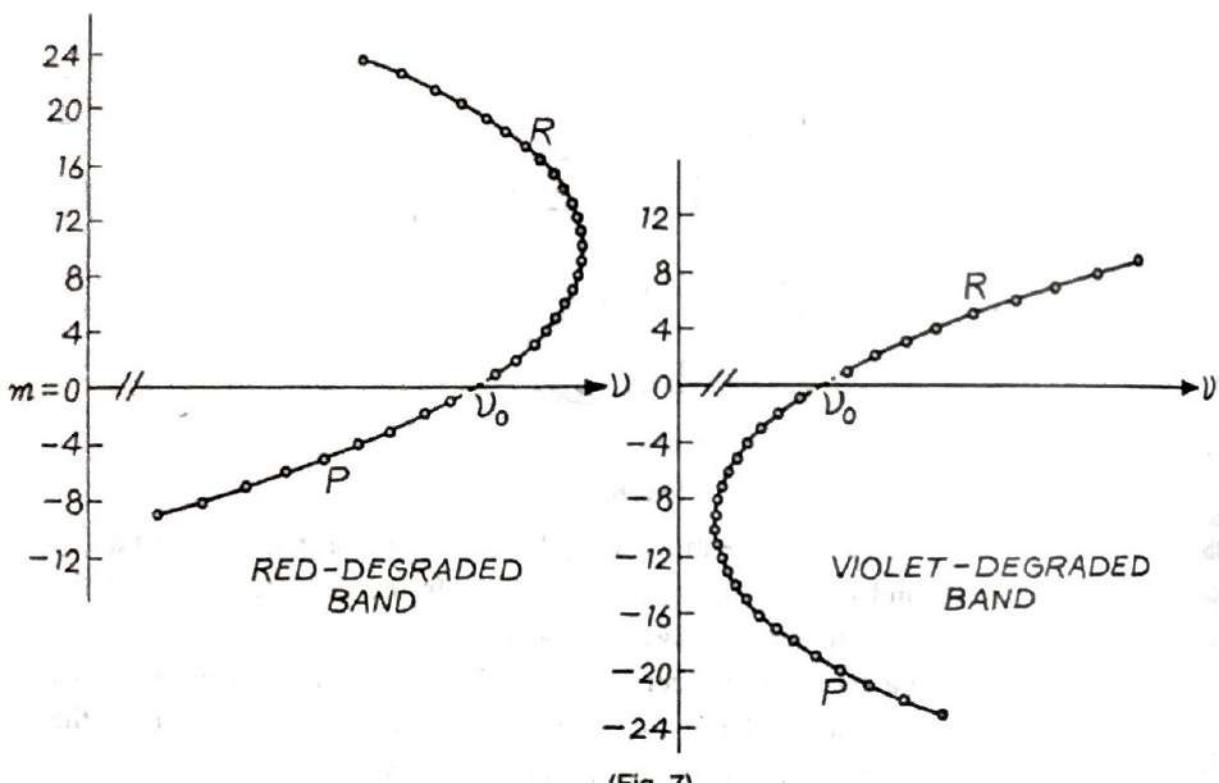
$$m = J'' + 1 = 1, 2, 3, \dots \text{ for lines } R(0), R(1), R(2), \dots$$

$$m = -J'' = -1, -2, -3, \dots \text{ for lines } P(1), P(2), P(3), \dots$$

and

$$m = 0 \text{ for the band-origin.}$$

The plot of eq. (iv), both when  $(B_v' - B_v'')$  is negative (red-degraded band) and when  $(B_v' - B_v'')$  is positive (violet-degraded band) are shown in Fig. 7. These are known as 'Fortrat' parabola. The vertex of the parabola corresponds to the band-head.



(Fig. 7)

The value of  $m$  at which the vertex of the Fortrat parabola (band-head) lies is obtained by differentiating eq. (iv) and equating  $\frac{dv}{dm}$  to zero. This gives

$$m_{\text{vertex}} = -\frac{B_v' + B_v''}{2(B_v' - B_v'')}$$

Substituting this value of  $m$  in eq. (iv), the wave-number separation between band-head and band-origin is given by

$$\begin{aligned} v_{\text{head}} - v_0 &= -(B_v' + B_v'') \frac{B_v' + B_v''}{2(B_v' - B_v'')} + (B_v' - B_v'') \frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')^2} \\ &= -\frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')} \end{aligned}$$

$v_{\text{head}} - v_0$  is positive for a band degraded to the red, and negative for the one degraded to the violet.

Since, for different bands of a band-system,  $B_v'$  and  $B_v''$  are different ; the distance of the band-head from the band-origin changes from band to band.

Again, in case of electronic bands, the difference ( $B_v' - B_v''$ ) is usually not very small, and has the same sign for all the bands (owing to the smallness of the rotational constant  $\alpha_e^*$ ). Therefore, *all the bands of a band-system are usually shaded in the same direction*. However, if the difference ( $B_v' - B_v''$ ) is very slight, it may actually change from positive values through zero to negative values from band to band in a long sequence. Then the bands with low values of  $v', v''$  would degrade towards the violet, and those with high values of  $v', v''$  towards the red, some of the intermediate bands being headless. An example of this rare phenomenon is found in the violet CN bands and  $N_2^+$  bands.

## 6. Rotational Structure of Three-Branch Bands

There are certain electronic states of molecules in which the electron cloud is not cylindrically symmetrical and has a component of angular momentum along the internuclear axis. In these states, the total angular momentum of the molecule is the resultant of the component of the electronic angular momentum along the internuclear axis and the nuclear rotation angular momentum perpendicular to the internuclear axis. The molecule then behaves as an axially-symmetric spinning top. In this case, the rotational levels are slightly shifted by an amount which is constant for the given electronic state and one or more of the initial  $J$ -levels are missing.

When, in an electronic transition, one of the electronic states belongs to a symmetric-top model, the resulting bands are found to have an additional branch of lines, known as *Q*-branch, besides the *R*- and *P*-branches. The *Q*-branch has its head very close to the band-origin. Also, more than one lines are found to be missing from the rotational structure.

The general expression for the wave number of a rotational line ( $J', J''$ ) of an electronic band is

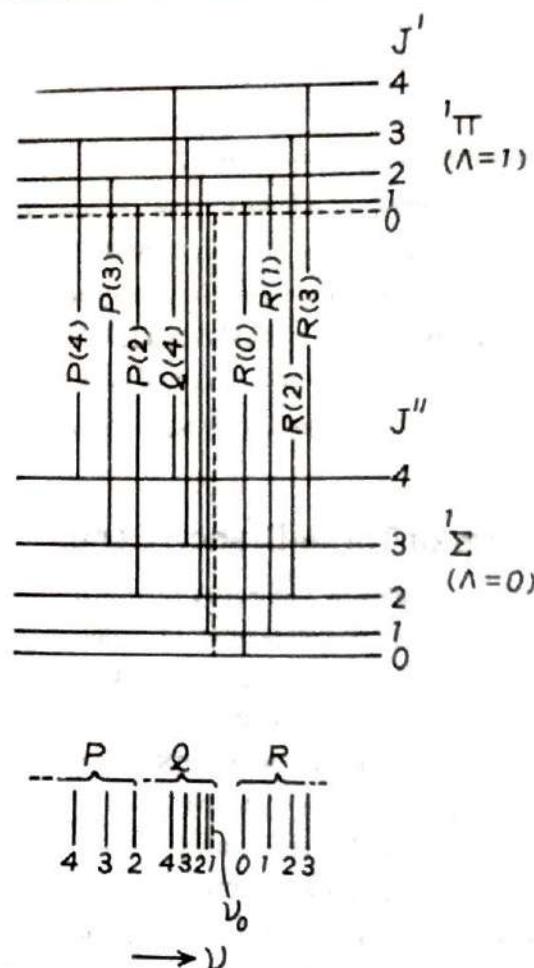
$$\nu = \nu_0 + B_v' J' (J' + 1) - B_v'' J'' (J'' + 1), \quad \dots(i)$$

where  $B_v'$  and  $B_v''$  are the rotational constants for the upper and lower vibrational and electronic states involved. Let us consider the electronic transition  ${}^1\Pi - {}^1\Sigma$ . For the upper electronic state  ${}^1\Pi$ , the electronic angular momentum along the internuclear axis corresponds to  $\Lambda = 1$ ; while for the lower state  ${}^1\Sigma$  we have  $\Lambda = 0$ . For this transition, the selection rule for  $J$  is

$$\Delta J = 0, \pm 1; \text{ but } J = 0 \leftrightarrow J = 0.$$

The rotational levels corresponding to the state  ${}^1\Pi$  are  $J' = 1, 2, 3, \dots$  ( $J' = 0$  is missing), while for the state  ${}^1\Sigma$  are  $J'' = 0, 1, 2, 3, \dots$ . The transitions and the resulting band-structure are shown in Fig. 8.

\*  $B_e = B_v - \alpha_e \left( v + \frac{1}{2} \right)$



(Fig. 8)

The transitions  $\Delta J = \pm 1$  give  $R$ - and  $P$ -branches as usual, while the additional transitions  $\Delta J = 0$  give the additional  $Q$ -branch.

**R-branch :**

$$\Delta J = J' - J'' = +1$$

so that

$$J' = J'' + 1.$$

Making this substitution in eq. (i), the wave-numbers of the lines of  $R$ -branch are given by

$$v_R = v_0 + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2, \quad \dots (ii)$$

where  $J'' = 0, 1, 2, \dots$ , giving lines  $R(0), R(1), R(2), \dots$ . If  $(B_v' - B_v'')$  is negative, the spacing between the lines of this branch decreases with increasing  $J''$ , and a head is formed.

**P-branch :**

$$\Delta J = J' - J'' = -1$$

so that

$$J' = J'' - 1.$$

Making this substitution in eq. (i), the wave numbers of the lines of  $P$ -branch are given by

$$v_P = v_0 - (B_v' + B_v'')J'' + (B_v' - B_v'')J''^2, \quad \dots (iii)$$

where  $J'' = 2, 3, 4, \dots$ , giving lines  $P(2), P(3), P(4), \dots$ .  $J''$  cannot be 1 because case.

**Q-branch :**

so that

$$\Delta J = J' - J'' = 0$$

Making this substitution in eq. (i), the wave numbers of the lines of  $Q$ -branch are given by

$$v_Q = v_0 + (B_v' - B_v'')J'' + (B_v' - B_v'')J''^2, \quad \dots (iv)$$

where  $J'' = 1, 2, 3, 4, \dots$ , giving lines  $Q(1), Q(2), Q(3), \dots$ . If  $(B_v' - B_v'')$  is negative, the branch spreads toward decreasing wave numbers, and the line-spacing increases with increasing  $J''$ . That is, the branch is degraded toward red, as shown. If  $(B_v' - B_v'')$  is positive, the branch would be degraded toward violet.

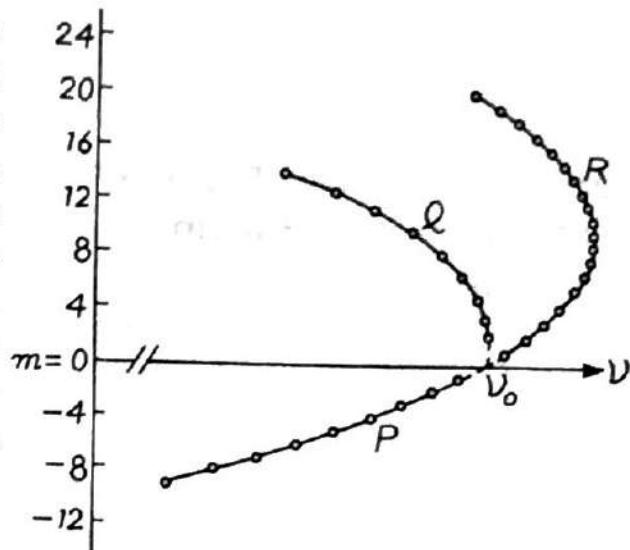
We know that the  $R$ - and  $P$ -branches can be represented by a common parabolic equation,

$$v_{R,P} = v_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2,$$

where  $m = J'' + 1$  and  $m = -J''$  for  $R$ - and  $P$ -branches respectively. Correspondingly, the  $Q$ -branch may be represented by

$$v_Q = v_0 + (B_v' - B_v'')m + (B_v' - B_v'')m^2,$$

where  $m = +J''$ . A comparison of these two equations shows that the Forrat parabola for the  $Q$ -branch would be different from that for the  $R$ - and  $P$  branches. Since, however, the term in  $m^2$  is the same in both equations, the vertices of the  $Q$ -parabola and  $R$ - $P$  parabola point in the same direction (Fig. 9). If  $B_v'$  and  $B_v''$  are not very different, the  $Q$ -parabola intersects the  $v$ -axis almost at right angles. This means that a head is formed at the beginning of the  $Q$ -branch. Thus, bands having a  $Q$ -branch very often show *two heads* either in the  $R$  and  $Q$  branches (if  $B_v' < B_v''$ ) as shown, or in the  $P$  and  $Q$  branches (if  $B_v' > B_v''$ ).



(Fig. 9)

The value of  $J''$  at which the vertex of the  $Q$ -parabola (band-head) lies is obtained by differentiating eq. (iv) and equating  $\frac{dv_Q}{dJ''}$  to zero. That is,

$$\frac{dv_Q}{dJ''} = (B_v' - B_v'') + 2(B_v' - B_v'')J'' = 0$$

or

$$J'' = -\frac{1}{2},$$

whatever be the values of  $B_v'$  and  $B_v''$ . Thus,  $Q$ -head always lies corresponding to  $J'' = -\frac{1}{2}$ , whereas  $P$  and  $R$  heads may lie anywhere depending upon the values of  $B_v'$  and  $B_v''$ . The position of the  $Q$ -head is obtained by putting  $J'' = -\frac{1}{2}$  in eq. (iv), which gives

$$v_{Q\text{-head}} = v_0 - \frac{1}{4}(B_v' - B_v''),$$

which is very close to the band-origin. The first  $Q$ -line ( $J'' = 1$ ) lies at

$$\nu_Q = \nu_0 + 2(B_v' - B_v'').$$

This means that no lines very close to the vertex occur and there is no returning limb of the  $Q$ -parabola. If, however, the difference  $(B_v' - B_v'')$  is large, the spacing between the  $Q$ -lines increases rapidly and so the  $Q$ -head is not pronounced.

The  $Q$ -head, if observed, is, however very important. In the vibrational analysis of a band-system, the wave numbers of the band-origins are required which are very difficult to be found. Hence, for routine work, the band-heads are used in place of band-origins. Since  $Q$ -head lies very close to the band-origin, therefore in a band-system whose bands have  $Q$ -branches, the  $Q$ -heads (and not the  $R$ - or  $P$ -heads) should be used to determine the vibrational constants.

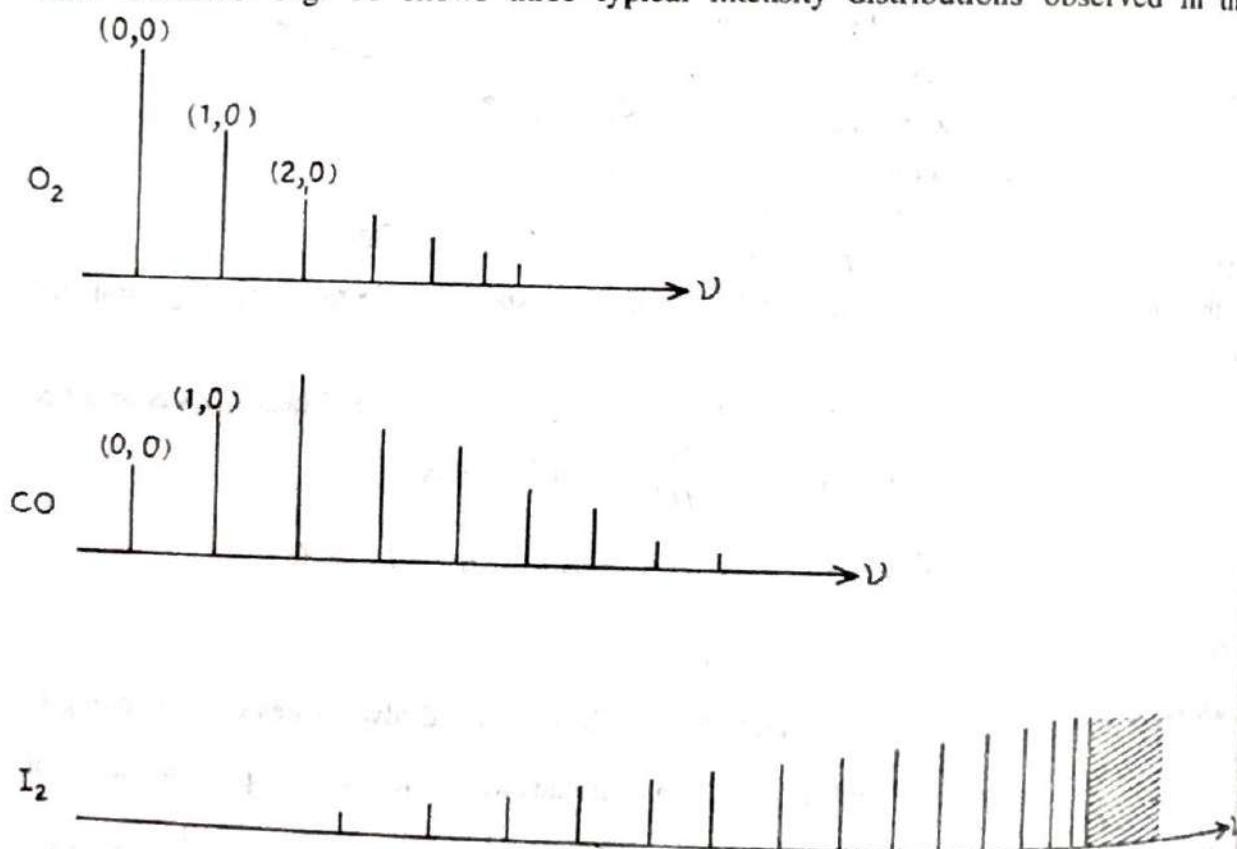
Moreover, it is very easy to use the  $Q$ -branch in determining  $\nu_0$  itself. We have

$$\nu_Q = \nu_0 + (B_v' - B_v'') J''(J'' + 1).$$

A plot of  $\nu_Q$  against  $J''(J'' + 1)$  gives a straight line whose intersection with the  $\nu$ -axis gives  $\nu_0$  and whose slope gives  $(B_v' - B_v'')$ .

## 7. Observed Intensity Distribution (Vibrational) in Band-Systems : Franck-Condon Principle

The distribution of intensity among the bands of an electronic band-system varies greatly from one molecule to another, and also from one band-system to another of the same molecule. Fig. 10 shows three typical intensity distributions observed in the



(Fig. 10)

absorption bands of  $O_2$ ,  $CO$  and  $I_2$  molecules. In case of  $O_2$ , the  $(0, 0)$  band is maximum intense while the successive bands of the  $v'$ -progression ( $v'' = 0$ ) appear with rapidly decreasing intensity. In the spectrum of  $CO$ , the intensity of bands along the progression first increases rapidly to a maximum and then gradually decreases. In the case

of  $I_2$  molecule, a long progression is observed. The intensity rises gradually, and the maximum reaches at very high  $v'$ -value, sometimes in the continuum.

The different types of intensity distributions are explained by Franck-Condon principle whose basic semi-classical idea is as follows :

*An electronic transition in a molecule takes place so rapidly compared to the vibrational motion of the nuclei that the instantaneous internuclear distance and the velocity of the nuclei can be considered remaining unchanged during the electronic transition.*

This means that in diagrams showing the potential energy curves of the two electronic states, the transitions must be represented by 'vertical' lines.

Another important factor to be considered is the distributions of the probability density  $|\psi_v|^2$  in various vibrational levels of each electronic state. Fig. 11 shows graphs of  $|\psi_v|^2$  along the various vibrational levels of the ground electronic state of a typical diatomic molecule. The greater the value of  $|\psi_v|^2$  at a particular value of internuclear distance  $r$  in a vibrational level, the greater is the likelihood of the nuclei to be found at that distance apart. Evidently,  $|\psi_v|^2$  is a maximum at the mid-point of the  $v = 0$  level, and near the turning points of the higher vibrational levels. Hence those transitions are more probable which begin from, or end at, the mid-point of  $v = 0$  level and either turning point of the  $v = 1, 2, 3, \dots$  levels. This idea can be incorporated in the Franck-Condon idea in the form of the following statement :

*The most probable vibrational transitions are those in which one of the two turning points of a vibrational level of one electronic state lies at approximately the same internuclear distance as one of the two turning points of a level of the other electronic state, except in case of  $v = 0$  level for which the mid-point rather than the turning point must be substituted.*

## 8. Quantum-Mechanical Formulation of Franck-Condon Principle

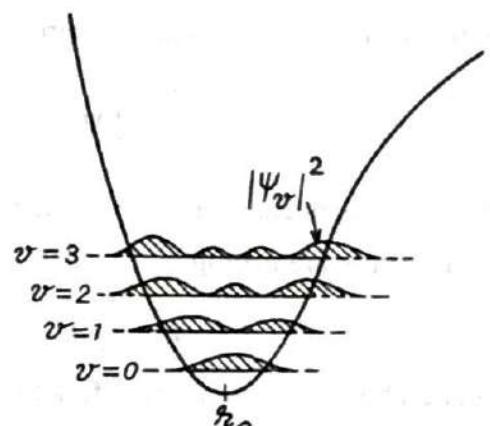
In quantum mechanics, the intensity of a spectroscopic transition between two states of total wavefunctions  $\psi'$  and  $\psi''$  is dependent on the square of the corresponding transition moment (matrix element)  $R$ , given by

$$R = \int \psi'^* M \psi'' d\tau, \quad \dots(i)$$

where  $M$  is electric dipole moment having components  $\sum e_i x_i$ , etc. Ignoring molecular rotation, let us apply the Born-Oppenheimer separation of electronic and vibrational (nuclear) coordinates by putting

$$\Psi = \Psi_e \Psi_v,$$

where  $\Psi_e$  and  $\Psi_v$  are the electronic and vibrational wave functions. Further, the dipole moment  $M$  can be separated into an electronic component  $M_e$  and a nuclear component  $M_n$ , that is,



(Fig. 11)

$$M = M_e + M_n.$$

Making these substitutions in eq. (i), the transition moment for the two vibronic (vibrational-electronic) states is given by

$$R = \int \Psi_e' * \Psi_v' * (M_e + M_n) \Psi_e'' \Psi_v'' d\tau_e d\tau_n,$$

where  $d\tau_e$  and  $d\tau_n$  are respectively the elements of volume of the space of the electronic coordinates and of the nuclear coordinates. The last expression may be re-written as

$$R = \int \Psi_e' * \Psi_v' * M_e \Psi_e'' \Psi_v'' d\tau_e dr + \int \Psi_e' * \Psi_v' * M_n \Psi_e'' \Psi_v'' d\tau_e dr, \dots \text{(ii)}$$

where  $d\tau_n$  has been replaced by  $dr$  because the vibrational (nuclear) wave functions  $\Psi_v$  depend on the internuclear distance  $r$  only.

Now, the nuclear dipole moment  $M_n$  is independent of the coordinates of the electrons (depends on  $r$  only). Therefore, the second integral in eq. (ii) can be written as

$$\int \left[ \int \Psi_e' * \Psi_e'' d\tau_e \right] \Psi_v' * M_n \Psi_v'' dr,$$

which is zero, because the electronic wavefunctions belonging to different electronic states of a molecule are orthogonal  $\left[ \int \Psi_e' * \Psi_e'' d\tau_e = 0 \right]^{\dagger}$ . Hence eq. (ii) remains as

$$R = \int \Psi_e' * \Psi_v' * M_e \Psi_e'' \Psi_v'' d\tau_e dr.$$

In general, the electronic wavefunction  $\Psi_e$  varies with internuclear distance  $r$ . However, it may be assumed that  $\Psi_e$  varies slowly with  $r$ , so that the last expression may be factorised to give

$$R = \int \Psi_e' * M_e \Psi_e'' d\tau_e \int \Psi_v' * \Psi_v'' dr.$$

But  $\int \Psi_e' * M_e \Psi_e'' d\tau_e$  is the electronic transition moment  $R_e$ . Therefore, we may write the last expression as

$$R^{v', v''} = R_e \int \Psi_v' * \Psi_v'' dr.$$

Actually  $\Psi_e$ , and hence  $R_e$ , depends to some extent on  $r$ . The wave-mechanical formulation of the Franck-Condon Principle rests on the assumption that the variation of  $R_e$  with  $r$  is slow and that  $R_e$  may be approximated by an average value  $\bar{R}_e$ . Hence we must write

$$R^{v', v''} = \bar{R}_e \int \Psi_v' \Psi_v'' dr.$$

The asterisk has been dropped from  $\Psi_v'$  because for vibrational wave functions  $\Psi_v^* = \Psi_v$ .

The average electronic transition moment,  $\bar{R}_e$ , governs the intensity of the band-system as a whole. The relative intensities of the various bands of the system (which correspond to various vibrational transitions) mainly depend on the square of the 'overlap' integral  $\int \Psi_v' \Psi_v'' dr$ , which is the integral over the product of the vibrational wavefunctions of the two combining electronic states. It is known as "Frank-Condon factor"  $q^{v', v''}$ ; that is,

$\dagger \int \Psi_v' * \Psi_v'' dr \neq 0$ , that is, the vibrational wave functions are not orthogonal because they belong to different electronic states.

$$q^{v', v''} = \left[ \int \psi_{v'} \psi_{v''} dr \right]^2.$$

The amount of overlap, and hence the value of the Franck-Condon factor, depends on the relative positions of the maxima and the nodes of the vibrational wavefunction  $\psi_v$  in each of the two combining electronic states, and consequently upon the relative shapes and positions of the corresponding potential energy curves. As shown in Fig. 12, for the level  $v = 0$ ,  $\psi_v$  has one central maximum, whereas for levels  $v > 0$  it has one prominent maximum slightly inside each turning point, and smaller maxima in between. In the diagram, the relative shapes and positions of the potential energy curves are such that the 'best' overlapping of the eigenfunctions (that is, maximum value of  $q^{v', v''}$ ) occurs for  $v' = 2$  and  $v'' = 0$  levels. Thus,  $v' = 2 \leftrightarrow v'' = 0$  transition is most probable, that is, the (2, 0) band of the system will have the maximum intensity. In general, we conclude that a vibrational transition will have a large Franck-Condon factor only if one of the two turning points of a level of one electronic state lies at approximately the same internuclear distance as one of the two turning points of a level of the other electronic state, except in case of  $v = 0$  level for which the middle-point of the level rather than the turning point must be substituted.

This is exactly the same as the semi-classical ideas of Franck. It is not that only the strongest transition would occur but also the weaker transitions would occur due to the overlap of the smaller peaks in the vibrational wavefunctions. This explains why instead of only one band, a number of bands in a certain progression appear with a more or less broad intensity maximum.

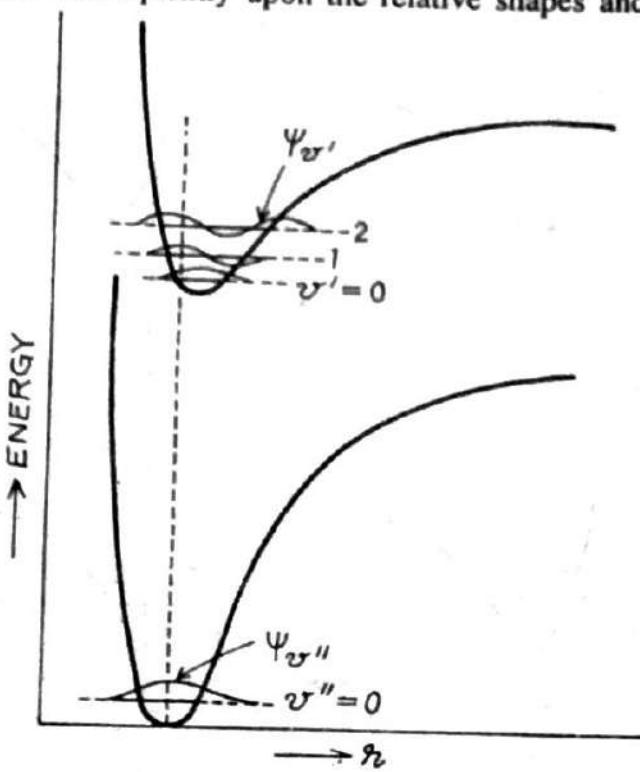
The expression for the intensity of a  $(v', v'')$  band in emission is

$$I_{emi}^{v', v''} = \frac{64}{3} \pi^4 c N_{v'} v^4 \overline{R_e^2} q^{v', v''},$$

where  $N_{v'}$  is the number of molecules in the vibration level  $v'$  and  $v$  is the wave number for the band ; and that for a band in absorption is

$$I_{abs}^{v', v''} = \frac{8 \pi^3}{3 h c} I_0 \Delta x N_{v''} v \overline{R_e^2} q^{v', v''},$$

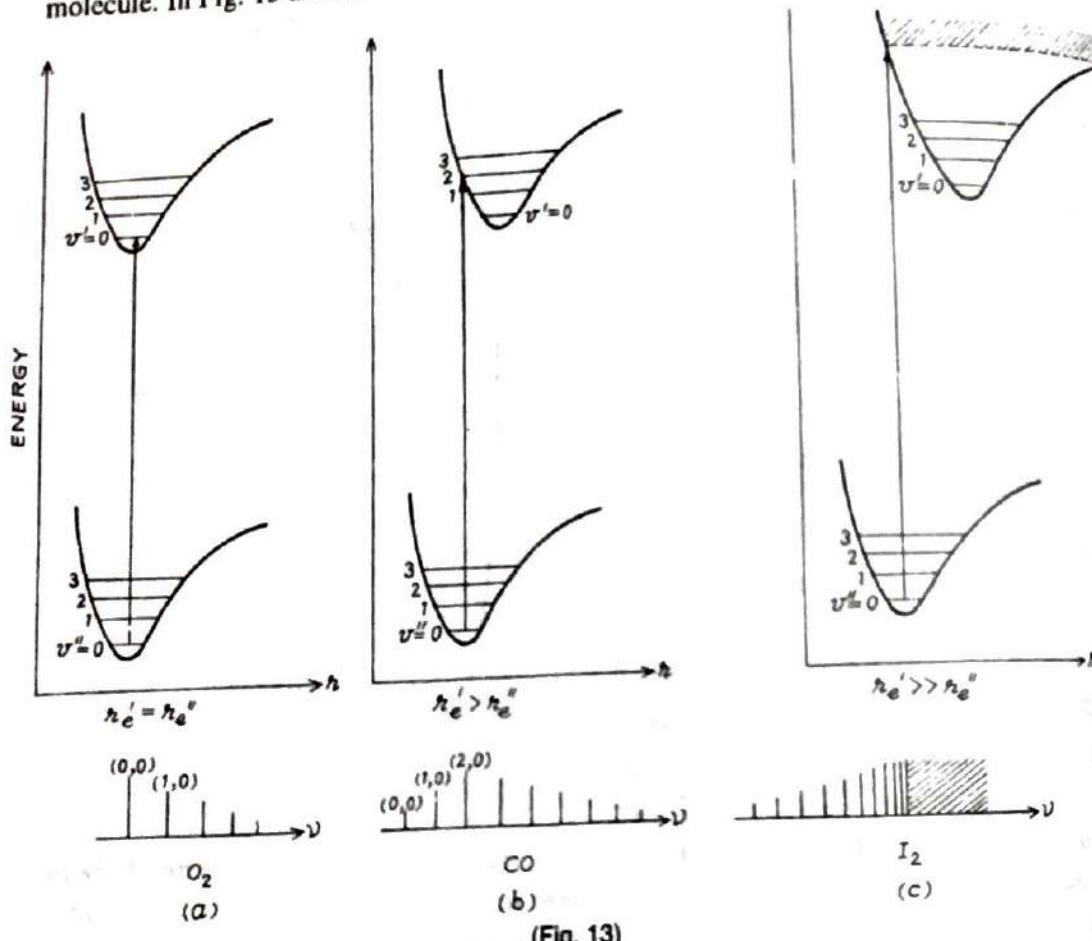
where  $I_0$  is the intensity of incident radiation,  $\Delta x$  is the thickness of the absorbing layer and  $N_{v''}$  is the number of molecules in the vibrational level  $v''$ .



(Fig. 12)

## 9. Explanation of Intensity Distribution in Absorption Bands from Franck-Condon Principle

Let us examine absorption transitions between two electronic states in a diatomic molecule. In Fig. 13 are shown three typical situations. In (a) the equilibrium internuclear



(Fig. 13)

distances are almost equal in both electronic states, in (b) the internuclear distance is slightly greater in the upper state, and in (c) it is much greater in the upper state. All (absorption) transitions start from the lowest  $v'' = 0$  level of the ground electronic state. In (a), the transition  $v'' = 0 \rightarrow v' = 0$  is most probable because it connects configurations of high probability and also appears as a 'vertical' line as required by the Franck-Condon Principle ( $r$  does not change during electronic transition). Transitions to higher levels  $v' = 1, 2, \dots$  also occur, but less often because they involve a change in  $r$  and thus deviate from the F.C. principle. Hence they lead to weak absorption bands. Thus in the band-system, the  $(0, 0)$  band appears with maximum intensity, and the intensity decreases rapidly for the higher bands. This is the intensity distribution observed in  $O_2$  absorption bands.

In (b), the most favoured transition is  $v'' = 0 \rightarrow v' = 2$  which now connects configurations of maximum probability and also satisfies the F.C. principle. Transitions to higher levels  $v' = 0, 1, 3, 4, \dots$  take place as well, but again lead to weak bands. Thus starting from the  $(0, 0)$  band, the intensity first rises to a maximum and then decreases. This distribution is observed in the absorption band-system of  $CO$  molecule.

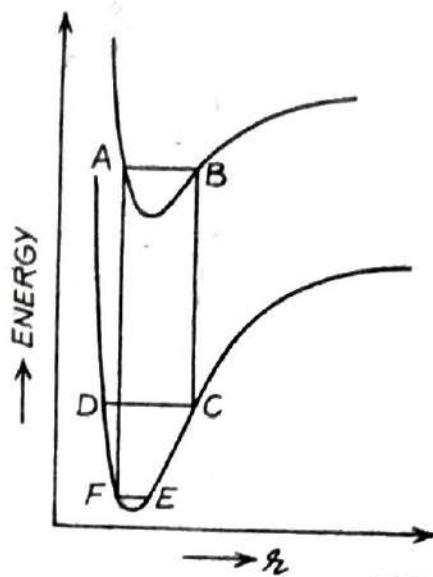
In (c), a vertical electronic transition from the mid-point of  $v'' = 0$  level is most likely to terminate in the continuum of the upper electronic state, thus dissociating the molecule. Thus, in this case, the spectrum is expected to consist of a progression of weak bands joined by a continuum of maximum absorption intensity. This is the case with the absorption spectrum of  $I_2$  molecule.

## 10. Explanation of Intensity Distribution in Emission Bands : Condon Parabola

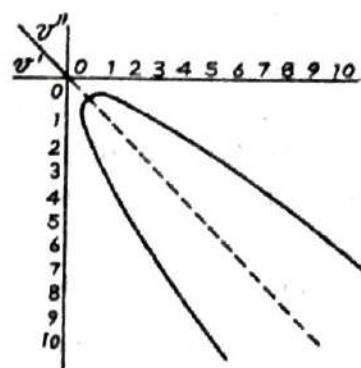
According to the Franck-Condon principle, the distribution of intensity in a band progression with  $v' = 0$  in emission corresponds exactly to that of a progression with  $v'' = 0$  in absorption. There is an intensity maximum at a  $v''$  value depending on relative position of the minima of the two potential curves. The greater the difference  $r_e' - r_e''$ , the larger is the  $v''$  value for the intensity maximum.

In emission, however, the initial level is a  $v'$  level and quite a good number of them are well populated depending upon the means of excitation. Hence a number of band-progressions are seen in emission (whereas only one progression with  $v'' = 0$  is usually seen in absorption). The intensity distribution for band-progressions in emission with  $v' > 0$  is different from that for the progression with  $v' = 0$ <sup>\*</sup>. In order to understand this, let us consider Fig. 14. Suppose, after excitation, a molecule occupies the level  $AB$  of the upper electronic state. During the vibration, the molecule spends more time at the turning points  $A$  and  $B$  from which the transitions are most probable. According to the Franck-Condon principle, immediately after the transition, the molecule will be either at  $F$  (vertically below  $A$ ) or at  $C$  (vertically below  $B$ ), having  $FE$  or  $CD$  its new vibrational level. Thus, there are two  $v''$ -levels to which probability of transition from a given  $v'$ -level is a maximum. In other words, there will be two intensity maxima in a  $v''$ -progression ( $v' = \text{constant}$ ), one at smaller  $v''$  and the other at larger  $v''$ . With increasing  $v'$ , the point  $C$  moves up more rapidly than the point  $F$ , that is, the two intensity maxima would separate more and more from each other and also would go to higher  $v''$  values. This is in agreement with observation.

If we plot the intensities of the bands of a system in a  $v' - v''$  array similar to a Deslandres table and joint up the most intense bands, we obtain a parabolic curve whose axis is the principal diagonal. It is called the 'Condon parabola'\*\* (Fig. 15). It represents the



(Fig. 14)



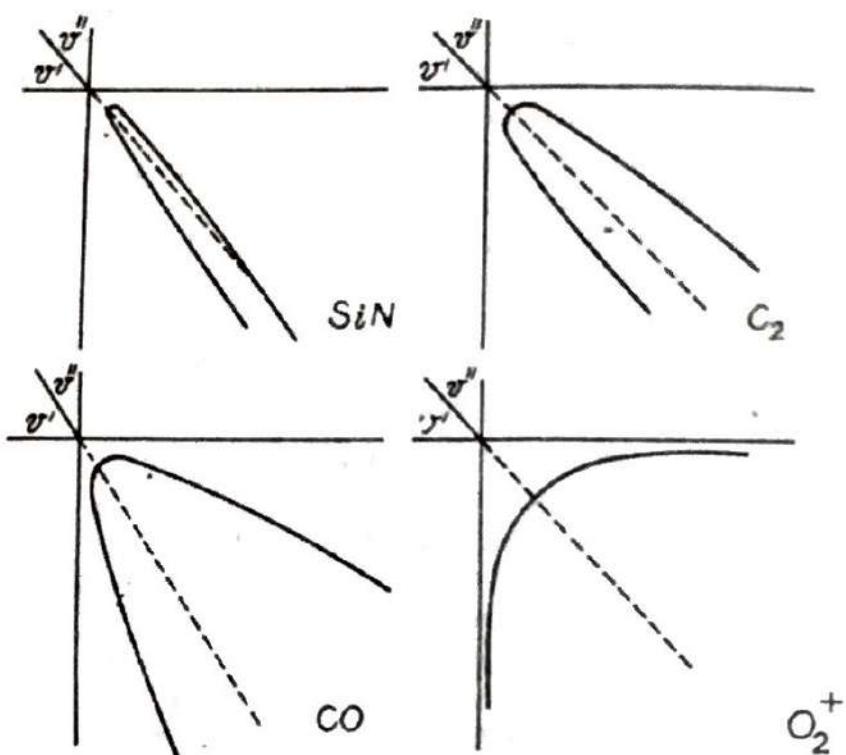
(Fig. 15)

\* The same is true for the absorption band progressions with  $v'' > 0$  whenever they appear, for example, in case of heavy molecules or at high temperatures.

\*\* The Condon parabola may be defined as the locus of the most intense bands in a  $v' - v''$  array.

distribution characteristics deduced above. There are two intensity maxima in all the horizontal rows with the exception of that with  $v' = 0$  which has only one maximum. As we move to higher  $v'$  values, the two maxima (limbs of parabola) separate further.

It can also be concluded from Fig. 14 that for a given progression  $v' = \text{constant}$ , the separation of the two intensity maxima, and therefore the width of the Condon parabola, increases with increasing difference  $r_e' - r_e''$  (minima of the potential curves). This is why that whereas the Condon parabola for SiN is almost a straight line, that for  $O_2^+$  is so much open as to have its limbs almost at right angles to each other (Fig. 16).



(Fig. 16)

In cases like SiN ( $r_e' = r_e''$ ), where the two maxima in each progression  $v' = \text{constant}$  coincide, the  $\Delta v = 0$  sequence (principal diagonal of the Deslandres table) is the strongest and traceable to quite high values of  $v'$ , whereas  $\Delta v = \pm 1$  sequences are either much weaker or not observed at all.

In cases like  $C_2$  and  $CO$ , the  $\Delta v = 0$  sequence appears quite strong but with only first few bands detectable, while in the neighbouring sequences  $\Delta v = \pm 1, \pm 2, \dots$  a larger number of bands are detectable. Whereas in the  $\Delta v = 0$  sequence the first band  $(0, 0)$  is the strongest, in the higher sequences the maximum intensity shifts to higher bands. Since  $CO$  has a wider parabola than  $C_2$ , a larger number of bands appear for  $CO$ .

For  $O_2^+$ , the difference  $r_e' - r_e''$  is appreciably large. The Condon parabola is so much widened that its two limbs follow the low  $v'$ - and  $v''$ -progressions.

There is one general feature of intensity distribution in all the cases. We know that the potential curves become increasingly asymmetrical with increasing  $r$ . This means that the nuclei spend more time in the extended phase ( $r > r_e$ ) than in the contracted phase ( $r < r_e$ ). Hence, according to Franck-Condon principle, transitions will be more probable

from (or to) the one side than from the other. Therefore, for a system degraded to red ( $r' > r''$ ) the right limb of the Condon parabola will be the stronger ; whereas for the systems degraded to the violet ( $r' < r''$ ) the left limb will be stronger. Thus, we can obtain many informations about a molecule from a study of its Condon parabola.

### 11. Line Intensities in a Band : Rotational Intensity Distribution

The intensity of a line in an electronic band depends upon the population of the appropriate rotational level of the initial electronic state, and upon the transition probability for the emission or absorption of that line. If the sample is in thermal equilibrium at an absolute temperature  $T$ , the line intensities in emission and in absorption are given by

$$I_{emi} = \frac{C_{emi} v^4}{Q_r} i e^{-B_v' J'(J'+1) \hbar c/kT}$$

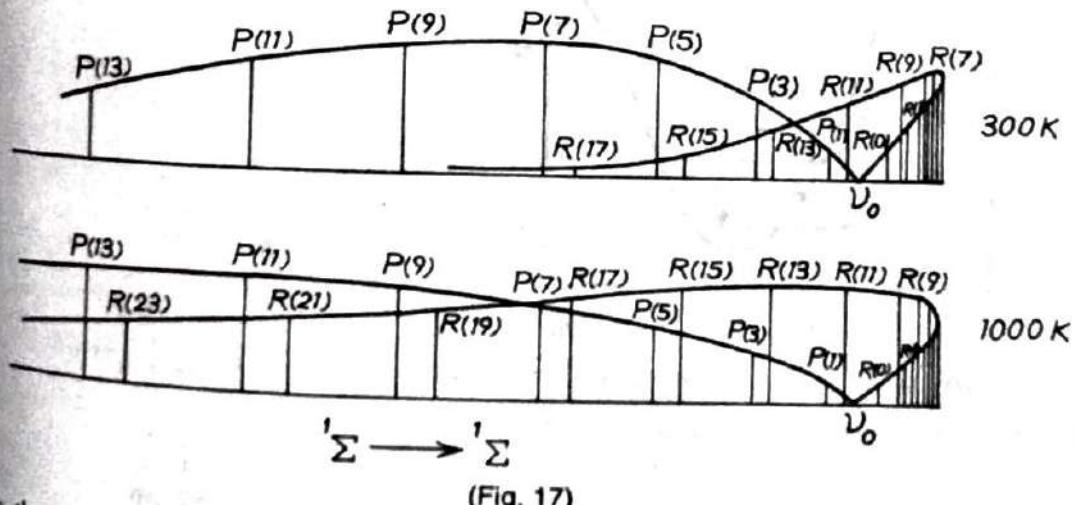
and

$$I_{abs} = \frac{C_{abs} v}{Q_r} i e^{-B_v'' J''(J''+1) \hbar c/kT},$$

where  $C_{emi}$  or  $C_{abs}$  is constant for a given band,  $Q_r$  ( $\approx \frac{kT}{\hbar c B}$ ) is the rotational partition function and  $i$  is the 'intensity factor' which is proportional to the transition probability and the statistical weight  $(2J+1)$  of the initial level. The actual form of  $i$  depends upon the type of electronic transition. For the simplest transition  ${}^1\Sigma - {}^1\Sigma$ , the value of  $i$  for the lines of  $R$ - and  $P$ -branches is given by

$$i_{R(J)} = i_{P(J)} = J' + J'' + 1.$$

With this value of  $i$ , the intensity equation are the same as for vibration-rotation bands. Plotting intensity against  $J$ , we find that in an electronic band of the type  ${}^1\Sigma - {}^1\Sigma$ , there is an intensity maximum in each of the  $R$ - and  $P$ -branches (Fig. 17). As temperature



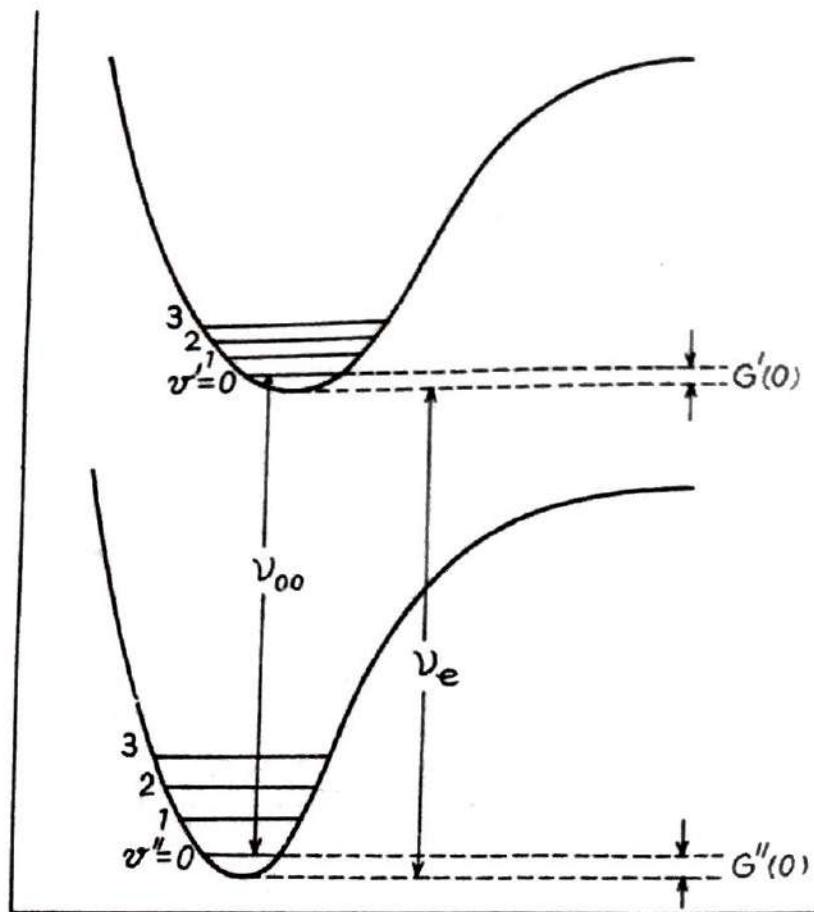
(Fig. 17)

rises, the maxima shift to higher  $J$  values and become flatter while the branches become richer in lines. The two branches are of comparable intensities but, on the whole, the  $P$ -branch is stronger in emission, while the  $R$ -branch is stronger in absorption.

## SOLVED PROBLEMS

1. The zero-point energy of the ground state of  $N_2$  molecule is  $1176 \text{ cm}^{-1}$ , and that of its lowest excited state is  $727 \text{ cm}^{-1}$ . The energy difference between the minima of the two potential energy curves is  $50,206 \text{ cm}^{-1}$ . What is the energy of the  $v' = 0 \rightarrow v'' = 0$  transition in  $\text{cm}^{-1}$ ? What is the corresponding wavelength? (Meerut 2006, sp. paper 89)

**Solution.** Let  $G''(0)$  be the zero-point energy of the ground electronic state, and  $G'(0)$  that of the first excited state. These energies together with energy difference  $v_e$  between the minima of the potential curves, and the energy  $v_{00}$  corresponding to the  $0, 0$  transition are shown in Fig. 18. The given data are :



(Fig. 18)

$$G''(0) = 1176 \text{ cm}^{-1}, G'(0) = 727 \text{ cm}^{-1} \text{ and } v_e = 50206 \text{ cm}^{-1}.$$

The energy of the  $0 \rightarrow 0$  transition is given by

$$\begin{aligned} v_{00} &= v_e + G'(0) - G''(0) \\ &= 50206 \text{ cm}^{-1} + 727 \text{ cm}^{-1} - 1176 \text{ cm}^{-1} = 49,757 \text{ cm}^{-1}. \end{aligned}$$

The corresponding wavelength (of the  $0 - 0$  band) is

$$\lambda_{00} = \frac{1}{v_{00}} = \frac{1}{49,757 \text{ cm}^{-1}} = \frac{10^8}{49757} \text{ Å} = 2010 \text{ Å}.$$

2. The values of  $\omega_e$  and  $\omega_e x_e$  for upper and lower states of CO molecule are  $1515\cdot61$ ,  $17\cdot25$ ,  $2170\cdot21$ ,  $13\cdot46 \text{ cm}^{-1}$  respectively. The  $0 - 0$  transition is observed at  $64746\cdot55 \text{ cm}^{-1}$ . Calculate the energy difference between the minima of the two curves.

(Meerut sp. paper 2002 S, 94)

**Solution.** The general expression for the vibrational energy of a diatomic molecule is

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2,$$

where  $\omega_e$  is the vibrational constant, and  $\omega_e x_e$  is the anharmonicity constant of the molecule. The zero-point energies of the upper and the lower electronic states are given by

$$G'(0) = \frac{1}{2} \omega_e' - \frac{1}{4} \omega_e' x_e'$$

and

$$G''(0) = \frac{1}{2} \omega_e'' - \frac{1}{4} \omega_e'' x_e''.$$

Here,  $\omega_e' = 1515\cdot61 \text{ cm}^{-1}$ ;  $\omega_e' x_e' = 17\cdot25 \text{ cm}^{-1}$ ,  $\omega_e'' = 2170\cdot21 \text{ cm}^{-1}$  and  $\omega_e'' x_e'' = 13\cdot46 \text{ cm}^{-1}$ .

$$\begin{aligned} \therefore G'(0) &= \frac{1}{2} \times 1515\cdot61 \text{ cm}^{-1} - \frac{1}{4} \times 17\cdot25 \text{ cm}^{-1} \\ &= 757\cdot805 \text{ cm}^{-1} - 4\cdot3125 \text{ cm}^{-1} = 753\cdot4925 \text{ cm}^{-1} \end{aligned}$$

and

$$\begin{aligned} G''(0) &= \frac{1}{2} \times 2170\cdot21 \text{ cm}^{-1} - \frac{1}{4} \times 13\cdot46 \text{ cm}^{-1} \\ &= 1085\cdot105 \text{ cm}^{-1} - 3\cdot365 \text{ cm}^{-1} = 1081\cdot740 \text{ cm}^{-1}. \end{aligned}$$

Also,

$$v_{00} = 64746\cdot55 \text{ cm}^{-1}.$$

Therefore, from Fig. 18, we have

$$\begin{aligned} v_e &= v_{00} - G'(0) + G''(0) \\ &= 64746\cdot55 \text{ cm}^{-1} - 753\cdot4925 \text{ cm}^{-1} + 1081\cdot740 \text{ cm}^{-1} = 65074\cdot80 \text{ cm}^{-1}. \end{aligned}$$

3. From the  $v''$ -progression of PN molecule, the successive values of upper electronic state vibrational quanta are obtained as  $1088\cdot3 \text{ cm}^{-1}$ ,  $1071\cdot3 \text{ cm}^{-1}$  and  $1060\cdot1 \text{ cm}^{-1}$ . Find the values of the molecular constants  $\omega_e' x_e'$  and  $\omega_e'$ .

(Meerut 97 sp. paper)

**Solution.** The first three vibrational quanta of the upper electronic state are given as

$$\begin{aligned} \Delta G'_{\frac{1}{2}} &= G'(1) - G'(0) = \omega_e' - 2\omega_e' x_e' = 1088\cdot3 \text{ cm}^{-1} \\ \Delta G'_{\frac{3}{2}} &= G'(2) - G'(1) = \omega_e' - 4\omega_e' x_e' = 1071\cdot3 \text{ cm}^{-1} \\ \text{and } \Delta G'_{\frac{5}{2}} &= G'(3) - G'(2) = \omega_e' - 6\omega_e' x_e' = 1060\cdot1 \text{ cm}^{-1} \end{aligned} \left. \begin{array}{l} \\ \\ \end{array} \right\} 17\cdot0 \text{ cm}^{-1} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} 11\cdot2 \text{ cm}^{-1}$$

The mean second difference of successive vibrational quanta is

$$\Delta^2 G' = 2\omega_e' x_e' = \frac{17\cdot0 \text{ cm}^{-1} + 11\cdot2 \text{ cm}^{-1}}{2} = 14\cdot1 \text{ cm}^{-1}.$$

$$\therefore \omega_e' x_e' = \frac{14\cdot1 \text{ cm}^{-1}}{2} = 7\cdot05 \text{ cm}^{-1}.$$

Now, from the first of the above three equations, we have

$$\begin{aligned} \omega_e' &= 2\omega_e' x_e' + 1088\cdot3 \text{ cm}^{-1} \\ &= 14\cdot1 \text{ cm}^{-1} + 1088\cdot3 \text{ cm}^{-1} = 1102\cdot4 \text{ cm}^{-1}. \end{aligned}$$

4. In the analysis of an electronic band system the following values were obtained :

$$\omega_e = 37206 \text{ cm}^{-1}, \quad \omega_e' = 439 \text{ cm}^{-1}, \quad \omega_e' x_e' = 28 \text{ cm}^{-1},$$

$$\omega_e'' = 563 \text{ cm}^{-1}, \quad \omega_e'' x_e'' = 18 \text{ cm}^{-1}.$$

Compute the  $v$  values of the first two bands in each of the progressions  $v' = 0$  and  $v'' = 1$ . Draw the corresponding energy level diagram. (Meerut sp. paper 95)

**Solution.** The  $v$ -values (wave numbers) for the bands (band-origins) of a system are given by

$$v_0 = v_e + \left\{ \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e' x_e' \left( v' + \frac{1}{2} \right)^2 \right\} - \left\{ \omega_e'' \left( v'' + \frac{1}{2} \right) - \omega_e'' x_e'' \left( v'' + \frac{1}{2} \right)^2 \right\}.$$

Substituting the given values for the constants :

$$v_0 = 37206 \text{ cm}^{-1} + \left\{ 439 \text{ cm}^{-1} \left( v' + \frac{1}{2} \right) - 28 \text{ cm}^{-1} \left( v' + \frac{1}{2} \right)^2 \right\}$$

$$- \left\{ 563 \text{ cm}^{-1} \left( v'' + \frac{1}{2} \right) - 18 \text{ cm}^{-1} \left( v'' + \frac{1}{2} \right)^2 \right\}.$$

The first two bands in the progression  $v' = 0$  are  $(0, 0)$  and  $(0, 1)$ ; and those in the progression  $v'' = 1$  are  $(0, 1)$  and  $(1, 1)$ . Thus, from the above expression, we get

$$v_{0,0} = 37206 \text{ cm}^{-1} + \left[ 439 \text{ cm}^{-1} \times \frac{1}{2} - 28 \text{ cm}^{-1} \times \frac{1}{4} \right]$$

$$- \left[ 563 \text{ cm}^{-1} \times \frac{1}{2} - 18 \text{ cm}^{-1} \times \frac{1}{4} \right]$$

$$= 37206 \text{ cm}^{-1} + 212.5 \text{ cm}^{-1} - 277 \text{ cm}^{-1}$$

$$= 37141.5 \text{ cm}^{-1}.$$

$$v_{0,1} = 37206 \text{ cm}^{-1} + \left[ 439 \text{ cm}^{-1} \times \frac{1}{2} - 28 \text{ cm}^{-1} \times \frac{1}{4} \right]$$

$$- \left[ 563 \text{ cm}^{-1} \times \frac{3}{2} - 18 \text{ cm}^{-1} \times \frac{9}{4} \right]$$

$$= 37206 \text{ cm}^{-1} + 212.5 \text{ cm}^{-1} - 804.0 \text{ cm}^{-1}$$

$$= 36614.5 \text{ cm}^{-1}.$$

$$v_{1,1} = 37206 \text{ cm}^{-1} + \left[ 439 \text{ cm}^{-1} \times \frac{3}{2} - 28 \text{ cm}^{-1} \times \frac{9}{4} \right]$$

$$- \left[ 563 \text{ cm}^{-1} \times \frac{3}{2} - 18 \text{ cm}^{-1} \times \frac{9}{4} \right]$$

$$= 37206 \text{ cm}^{-1} + 595.5 \text{ cm}^{-1} - 804.0 \text{ cm}^{-1}$$

$$= 36997.5 \text{ cm}^{-1}.$$

The general expression for the vibrational energy is

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2.$$

The energy difference between  $v'' = 1$  and  $v'' = 0$  levels is

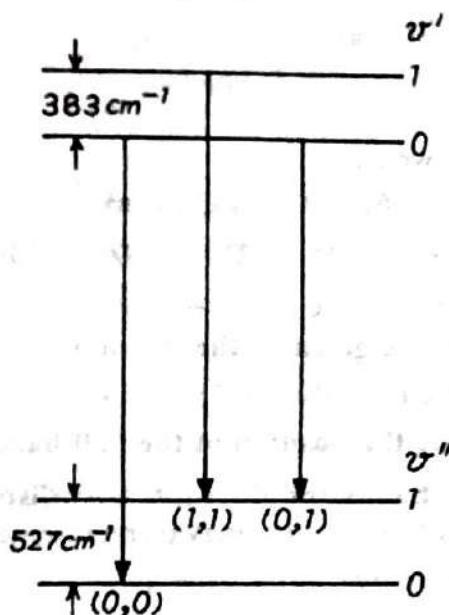
$$\Delta G''_{1/2} = G''(1) - G''(0) = \omega_e'' - 2 \omega_e'' x_e''$$

$$= 563 \text{ cm}^{-1} - 2(18 \text{ cm}^{-1}) = 527 \text{ cm}^{-1}$$

Similarly, the energy difference between  $v' = 1$  and  $v' = 0$  levels is

$$\Delta G'_{1/2} = \omega_e' - 2\omega_e' x_e' = 439 \text{ cm}^{-1} - 2(28 \text{ cm}^{-1}) = 383 \text{ cm}^{-1}.$$

The energy-level diagram is drawn in Fig. 19.



(Fig. 19)

### 5. The vibrational analysis of a band-system is given by

$$\nu = 20350 + (800 v' - 16 v'^2) - (600 v'' - 20 v''^2) \text{ cm}^{-1}.$$

Deduce the positions of four members of the  $v''$ -progression with  $v' = 1$ , and of three members of the  $\Delta v = + 1$  sequence. Calculate also the wavelength of the  $(0,0)$  band.

**Solution.** The band-origins of a system may be represented as

$$\begin{aligned} v_0 &= \nu_e + \left[ \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e' x_e' \left( v' + \frac{1}{2} \right)^2 \right] \\ &\quad - \left[ \omega_e'' \left( v'' + \frac{1}{2} \right) - \omega_e'' x_e'' \left( v'' + \frac{1}{2} \right)^2 \right]. \end{aligned}$$

When the vibrational levels are measured relative to the  $v = 0$  level in each electronic state, we can write

$$v_0 = v_{00} + (\omega_0' v' - \omega_0' x_0' v'^2) - (\omega_0'' v'' - \omega_0'' x_0'' v''^2),$$

where  $v_{00}$  is the wave number of the origin of the  $(0,0)$  band. The given equation is

$$\nu = 20350 + (800 v' - 16 v'^2) - (600 v'' - 20 v''^2) \text{ cm}^{-1}. \quad \dots(i)$$

Here  $\nu$  represents the wave numbers of the band-origins. Clearly

$$v_{(0,0)} = 20350 \text{ cm}^{-1}.$$

The wavelength of the  $(0,0)$  band is

$$\lambda_{(0,0)} = \frac{1}{v_{(0,0)}} = \frac{1 \text{ cm}}{20350} = \frac{10^8 \text{ Å}}{20350} = 4914 \text{ Å}.$$

The first four members of the  $v''$ -progression (with  $v' = 1$ ) are

$$(1,0); (1,1); (1,2); (1,3).$$

From the given eq. (i), we have

$$v_{(1,0)} = 20350 + (800 - 16) - 0 = 21134 \text{ cm}^{-1}$$

$$v_{(1,1)} = 20350 + (800 - 16) - (600 - 20) = 20554 \text{ cm}^{-1}$$

$$v_{(1,2)} = 20350 + (800 - 16) - (600 \times 2 - 20 \times 2^2) = 20014 \text{ cm}^{-1}$$

$$v_{(1,3)} = 20350 + (800 - 16) - (600 \times 3 - 20 \times 3^2) = 19514 \text{ cm}^{-1}$$

Now, the three members of the  $\Delta v = +1$  sequence are  
 $(1,0); (2,1); (3,2)$ .

Again, from the given eq. (i), we have

$$v_{(1,0)} = 20350 + (800 - 16) - 0 = 21134 \text{ cm}^{-1}$$

$$v_{(2,1)} = 20350 + (800 \times 2 - 16 \times 2^2) - (600 - 20) = 21306 \text{ cm}^{-1}$$

$$v_{(3,2)} = 20350 + (800 \times 3 - 16 \times 3^2) - (600 \times 2 - 20 \times 2^2) = 21486 \text{ cm}^{-1}$$

6. The bands of a system are given by the relation

$$v = 19221.2 + (1611.3 u' - 40.7 u'^2) - (1495.7 u'' - 31.5 u''^2) \text{ cm}^{-1}$$

where  $u = v + \frac{1}{2}$ . Calculate the position of the 0, 0 band and give your comments about the degradation of the bands and their intensity distribution.

**Solution.** The band-origins of a system may be represented by

$$v_0 = v_e + (\omega_e' u' - \omega_e' x_e' u'^2) - (\omega_e'' u'' - \omega_e'' x_e'' u''^2), \quad \dots(i)$$

where  $u = v + \frac{1}{2}$ . The given equation is

$$v = 19221.2 + (1611.3 u' - 40.7 u'^2) - (1495.7 u'' - 31.5 u''^2) \text{ cm}^{-1}$$

in which  $v$  represents the wave-numbers of the band-origins. On comparing, we have

$$\omega_e = 19221.2 \text{ cm}^{-1}, \omega_e' = 1611.3 \text{ cm}^{-1}, \omega_e' x_e' = 40.7 \text{ cm}^{-1}$$

$$\omega_e'' = 1495.7 \text{ cm}^{-1} \text{ and } \omega_e'' x_e'' = 31.5 \text{ cm}^{-1}.$$

Now, for the (0, 0) band, we have  $v' = 0, v'' = 0$ , so that  $u' = \frac{1}{2}, u'' = \frac{1}{2}$ . Then, by eq. (i), we have

$$\begin{aligned} v_{00} &= v_e + \left( \frac{1}{2} \omega_e' - \frac{1}{4} \omega_e' x_e' \right) - \left( \frac{1}{2} \omega_e'' - \frac{1}{4} \omega_e'' x_e'' \right) \\ &= 19221.2 \text{ cm}^{-1} + \left( \frac{1}{2} \times 1611.3 \text{ cm}^{-1} - \frac{1}{4} \times 40.7 \text{ cm}^{-1} \right) \\ &\quad - \left( \frac{1}{2} \times 1495.7 \text{ cm}^{-1} - \frac{1}{4} \times 31.5 \text{ cm}^{-1} \right) \\ &= 19221.2 \text{ cm}^{-1} + (805.65 \text{ cm}^{-1} - 10.175 \text{ cm}^{-1}) \\ &\quad - (747.85 \text{ cm}^{-1} - 7.875 \text{ cm}^{-1}) \\ &= 19221.2 \text{ cm}^{-1} + 795.475 \text{ cm}^{-1} - 739.975 \text{ cm}^{-1} \\ &= 19276.7 \text{ cm}^{-1}. \end{aligned}$$

**Degradation of Bands :** The  $B_v$  values of the different electronic states of a molecule run fairly parallel to the  $\omega_e$  values, that is,  $\frac{B_v}{\omega_e}$  is nearly constant. Here

$$\omega_e' > \omega_e''$$

$$\therefore B_v' > B_v''$$

or

$$(B_v' - B_v'') \text{ is positive.}$$

Hence the bands are degraded to the violet.

**Intensity Distribution :** Here

$$\omega_e' > \omega_e''$$

so that

$$B_v' > B_v''$$

and

$$r_e' < r_e''.$$

In this case, on applying the Franck-Condon principle, we obtain a Condon parabola with moderately separated limbs and having its vertex very near the  $(0, 0)$  band and its axis along the main diagonal of the  $v', v''$  table (Fig. 20). Thus, we expect a fairly strong  $\Delta v = 0$  sequence but only first few bands detectable, and stronger neighbouring sequences  $\Delta v = \pm 1, \pm 2, \dots$  with a greater number of bands detectable. In the  $\Delta v = 0$  sequence the first band  $(0, 0)$  is the strongest but in the higher sequences the maximum intensity shifts to higher bands of the sequence.

**7. Calculate the wavelength of the  $(0, 0)$  band from the following equation representing the bands of a system :**

$$v = 56008 + (500.4 u' - 6.0 u'^2) - (1400.0 u'' - 14.2 u''^2) \text{ cm}^{-1},$$

$$\text{where } u = v + \frac{1}{2}.$$

Write your comments regarding degradation of the bands and intensity distribution in the system.

(Meerut sp. paper 90)

**Solution.** The bands of a system are represented by

$$v = v_e + (\omega_e' u' - \omega_e' x_e' u'^2) - (\omega_e'' u'' - \omega_e'' x_e'' u''^2),$$

$$\text{where } u = v + \frac{1}{2}. \text{ Comparing it with the given equation, we have}$$

$$v_e = 56008 \text{ cm}^{-1}, \omega_e' = 500.4 \text{ cm}^{-1}, \omega_e' x_e' = 6.0 \text{ cm}^{-1}$$

$$\omega_e'' = 1400.0 \text{ cm}^{-1}, \omega_e'' x_e'' = 14.2 \text{ cm}^{-1}.$$

The wave number corresponding to the  $v' = 0, v'' = 0$  band would be given by

$$\begin{aligned} v_{00} &= v_e + \left( \frac{1}{2} \omega_e' - \frac{1}{4} \omega_e' x_e' \right) - \left( \frac{1}{2} \omega_e'' - \frac{1}{4} \omega_e'' x_e'' \right) \\ &= 56008 \text{ cm}^{-1} + \left( \frac{1}{2} \times 500.4 \text{ cm}^{-1} - \frac{1}{4} \times 6.0 \text{ cm}^{-1} \right) \\ &\quad - \left( \frac{1}{2} \times 1400.0 \text{ cm}^{-1} - \frac{1}{4} \times 14.2 \text{ cm}^{-1} \right) \\ &= 56008 \text{ cm}^{-1} + (250.2 \text{ cm}^{-1} - 1.5 \text{ cm}^{-1}) - (700.0 \text{ cm}^{-1} - 3.55 \text{ cm}^{-1}) \\ &= 56008 \text{ cm}^{-1} + 248.7 \text{ cm}^{-1} - 696.45 \text{ cm}^{-1} = 55560.25 \text{ cm}^{-1}. \end{aligned}$$

The corresponding wavelength is

$$\lambda_{00} = \frac{1}{v_{00}} = \frac{1}{55560.25 \text{ cm}^{-1}} = 1.8 \times 10^{-5} \text{ cm} = 1800 \text{ Å}.$$

**Degradation of Bands :** We know that  $\frac{B_v}{\omega_e}$  is nearly constant.

Here

so that

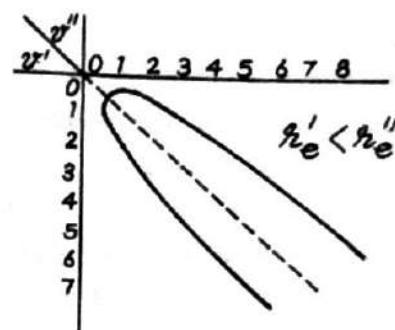
or

$$\omega_e' < \omega_e''$$

$$B_v' < B_v''$$

$$(B_v' - B_v'') \text{ is negative.}$$

Hence the bands are degraded to the red.



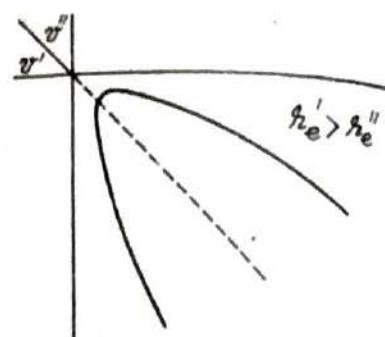
(Fig. 20)

## Intensity Distribution : Here

so that

and

In this case, on applying the F.C. principle we obtain a Condon parabola with widely separated limbs, having its vertex not lying on the main diagonal of the  $v', v''$  table (Fig. 21). Therefore, in the emission band system, a number of progressions are seen. In each progression there are two intensity maxima.



(Fig. 21)

8. Comparing the potential curves of the ground state and an excited state of a diatomic molecule, it was found that the latter curve had a sharper bottom and its minimum occurred at smaller  $r$ . Deduce conclusions from these about  $\omega$  and  $B$  values for the two states and about the degradation of the band-heads of the spectrum arising from a transition between these electronic states.

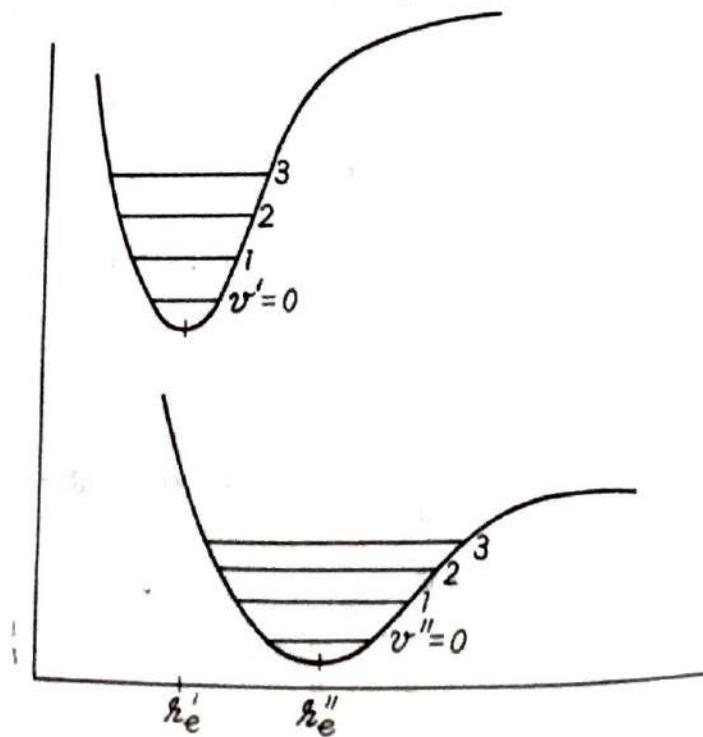
**Solution.** The potential curve of a diatomic molecule is parabolic near its minimum and may be described by

$$V(r) = \frac{1}{2} k x^2 = 2 \pi^2 m v_{osc}^2 (r - r_e)^2,$$

where  $v_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$ ;  $k$  is the force-constant, and  $v_{osc} = c\omega$  is the classical frequency of oscillation of the molecule. Thus,

$$V(r) = 2 \pi^2 m c^2 \omega^2 (r - r_e)^2.$$

The above equation of the parabola shows that smaller the  $\omega$  is, the flatter will be the potential curve in the neighbourhood of the minimum (Fig. 22). From the given potential



(Fig. 22)

curves we conclude, therefore, that the (upper) curve corresponding to the excited state has a large  $\omega$  value, that is, the spacings between its vibrational levels are larger:

$$\omega' > \omega''.$$

Further, the upper curve has a smaller  $r_e$  value; that is,

$$r_e' < r_e''.$$

We know that the rotational constant  $B_v = \frac{\hbar}{8\pi^2 c \mu r_e^2}$ . Therefore

$$B_v' > B_v''.$$

For a given vibrational state  $v$  we have  $B_v = B_v - \alpha_v \left( v + \frac{1}{2} \right)$ , so that

$$B_v' > B_v''.$$

That is,  $(B_v' - B_v'')$  is positive. Hence the bands are degraded toward the violet.

### 9. Rotational analysis of one band-system is given by

$$v = 24762 + 25m - 2.1m^2 \text{ cm}^{-1}.$$

Determine the position of the band-head, the values of  $B_v'$  and  $B_v''$ , and the degradation of the band.

**Solution.**  $v = 24762 + 25m - 2.1m^2 \text{ cm}^{-1}$  ... (i)

We know that the lines of  $P$  and  $R$  branches of a band are represented by a single formula

$$v = v_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2.$$

Here  $v_0$  is the band-origin. Comparing it with the given equation, we have

$$v_0 = 24762 \text{ cm}^{-1}.$$

$$B_v' + B_v'' = 25 \text{ cm}^{-1}$$

$$B_v' - B_v'' = -2.1 \text{ cm}^{-1}$$

Solving the last two equations, we get

$$B_v' = 11.45 \text{ cm}^{-1} \text{ and } B_v'' = 13.55 \text{ cm}^{-1}.$$

Now, the  $m$ -value corresponding to the vertex of the Förfat parabola (band-head) is given by

$$\begin{aligned} m_{\text{vertex}} &= -\frac{B_v' + B_v''}{2(B_v' - B_v'')} \\ &= -\frac{25 \text{ cm}^{-1}}{2 \times (-2.1 \text{ cm}^{-1})} = 5.9. \end{aligned}$$

The actual head lies at the nearest whole-number value of  $m_{\text{vertex}}$ , that is, at 6. Hence putting  $m = 6$  in eq. (i), we get

$$v_{\text{head}} = 24762 + (25 \times 6) - (2.1 \times 6^2) = 24836.4 \text{ cm}^{-1}.$$

The band-head ( $24836.4 \text{ cm}^{-1}$ ) lies toward the high-frequency side of the band-origin ( $24762 \text{ cm}^{-1}$ ). This means that the band is degraded toward the low-frequency side, that is, toward the red.

**10. The fine-structure lines of CN band at  $3883.4 \text{ \AA}$  can be represented by the following equation :**

$$v = 25798 + 3.85m + 0.068m^2 \text{ cm}^{-1}.$$

Calculate the separation between the null-line and the band-head and state the direction of degradation of the band. (Meerut 97, 89)

**Solution.** The fine-structure lines of a band are represented by

$$\nu = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2,$$

where  $\nu_0$  is the wave number of the band-origin (null-line), and  $B_v'$  and  $B_v''$  are the rotational constants in the two states involved in the transition.

Comparing it with the given equation, we get

$$\nu_0 = 25798 \text{ cm}^{-1}$$

$$B_v' + B_v'' = 3.85 \text{ cm}^{-1}$$

and

$$B_v' - B_v'' = 0.068 \text{ cm}^{-1}.$$

The separation between the null-line and the band-head is given by

$$\begin{aligned}\nu_{\text{head}} - \nu_0 &= - \frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')} \\ &= - \frac{(3.85 \text{ cm}^{-1})^2}{4 \times 0.068 \text{ cm}^{-1}} = - 54.5 \text{ cm}^{-1}.\end{aligned}$$

The negative sign means that the band-head  $\nu_{\text{head}}$  lies on the low-wave number side of the null-line, that is, the band is degraded toward the high-wave number side, that is, toward the violet.

## QUESTIONS

1. Describe the principal features of the electronic band spectrum of a diatomic molecule. Discuss the vibrational analysis of such a spectrum.  
*(Meerut sp. paper 2000, 92, Kanpur 2004, 02, 99)*
2. Discuss the observation of progressions and sequences in the spectra of diatomic molecules. Show how from the observation of  $v''$ -progressions and  $v'$ -progressions respectively, the vibrational quanta in the upper and the lower electronic states of the molecule are determined.  
*(Meerut sp. paper 97)*
3. Describe an experimental arrangement to record absorption spectrum of  $I_2$  molecule.  
*(Meerut 2002 S, sp. paper 2000)*
4. In what way the absorption spectra of diatomic molecules differ from the emission spectra ? What is the importance of the study of absorption spectra over that of emission spectra ?
5. In the fourth positive system of CO molecule a large number of  $v''$ -progressions is observed in emission while only one progression, namely  $v'' = 0$ , appears with appreciable intensity in absorption. Explain this.
6. At room temperature and moderate path-lengths the absorption spectrum of the  $I_2$  molecule shows progressions with  $v'' = 0, 1$  and even higher ; but under similar circumstances the absorption spectrum of CO generally shows only the progression  $v'' = 0$ . Explain this.
7. Discuss rotational fine structure of electronic vibrational transitions. What is fortat diagram ?  
*(Meerut 90, sp. paper 2002 S)*
8. Give an account of the salient features observed in the electronic spectrum of a diatomic molecule. Discuss the conditions under which the band-heads are degraded toward violet or red in the electronic spectrum. Why no such heads are generally observed in the infrared spectrum of a diatomic molecule ?  
*(Meerut 2004, 02 S, sp. paper 2005, 02, 99)*

9. Band heads are generally formed in the electronic spectrum of a diatomic molecule, while no such feature is observed in the infra-red spectrum. Explain.  
 (Meerut sp. paper 78)
10. Both red and violet degraded bands have been observed in electronic band systems, but rotation-vibration spectra show bands degraded to red only. Explain this.  
 (Meerut 2006, 98, sp. paper 89)
11. Explain the band-head formation in the vibronic spectrum of a diatomic molecule. When are the bands in the same band-system shaded towards red and violet both.  
 (Meerut sp. paper 88)
12. The frequency of a rotational line associated with a vibrational component of a transition between two electronic states can be approximated by  $v = v_0 + B'J'(J' + 1) - BJ(J + 1)$  where primes indicate the higher of the two electronic states and  $v_0$  is the frequency associated with the given vibrational component. Obtain expressions for the  $P$ ,  $Q$  and  $R$  branches of the  $v_0$  band group and show that if  $B > B'$ , the  $R$  branch will form the head.
13. The band-head of the  $Q$  branch is always at  $J = -\frac{1}{2}$ , while that of the  $P$ - or  $R$ -branch may be anywhere. Explain.
14. Explain why  $Q$ -head should be used to determine the vibrational constants if they appear along with  $P$  or  $R$  heads in the electronic spectrum of a diatomic molecule.
15. Describe Franck-Condon principle in emission and absorption. Discuss its importance.  
 (Meerut 2002 S, 2001, 98 S, sp. paper 2005)
16. State Franck-Condon principle and give its wave-mechanical interpretation. How does it help in understanding the intensity distribution in the vibrational structure of the electronic transitions of a diatomic molecule ?  
 (Meerut sp. paper 2006, 04, 03, 02, 01, 00 S, 99, 96, Kanpur 99)
17. Give a brief account of Franck-Condon principle. Discuss its use in explaining the intensity distribution in absorption bands, taking cases  $O_2$ , CO and  $I_2$  molecules.  
 (Meerut 99)
18. The wave mechanical formulation of the Franck-Condon principle rests on the assumption that the variation of the electronic transition moment  $R_e$  with the internuclear distance  $r$  is slow and  $R_e$  may be replaced by an average value  $\bar{R}_e$ . Discuss the implications of this statement. Hence explain the intensity patterns observed in the electronic transitions in emission.
19. You are given a Franck-Condon parabola. What informations could be deduced from it about the molecule ?
20. The bands of a system are given by the relation  

$$v = 49802.1 + (700.4 u' - 8.0 u'^2) - (1580.0 u'' - 12.1 u''^2),$$
 where  $u = v + \frac{1}{2}$ . Calculate the wavelength of the  $0,0$  band. Give your comments regarding the degradation of the bands and their intensity distribution in the system.  
 Ans.  $2026 \text{ \AA}$ , degraded to the red.

## Isotope Effect on Electronic Spectra

### 1. Spectroscopic Difference and Similarities between Isotopic Molecules

The isotopes of a given element have the same nuclear charge, but a different nuclear mass. Therefore, spectroscopically, isotopic molecules differ in two respects :

(i) **The vibrational frequencies, and hence the vibrational constants  $\omega_e$ , are different :** The classical vibrational frequency of a diatomic molecule is given by

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The force-constant  $k$  is determined by the electronic motion alone and is same for isotopic molecules. The reduced mass  $\mu$  is, however, different for them. If  $\omega_e^i$  is the vibrational constant for the heavier isotope (which is usually less abundant) and  $\omega_e$  for the lighter one, then we have

$$\frac{\omega_e^i}{\omega_e} = \frac{\nu_{osc}^i}{\nu_{osc}} = \sqrt{\frac{\mu}{\mu^i}} = \rho \text{ (say),}$$

where  $\rho < 1$ , because  $\mu^i > \mu$ . (The superscript  $i$  indicates the heavier isotope). Thus the heavier isotope has a smaller vibrational constant, that is, smaller spacings between vibrational levels. This causes different vibrational structures in the band-systems of isotopic molecules.

(ii) **The moments of inertia, and hence the rotational constants, are different**  
Again, this difference arises almost entirely due to a difference in the reduced masses of the isotopic molecules. The equilibrium internuclear distance  $r_e$ , which depends upon extranuclear electric field, is almost the same for them. The difference in moments of inertia, and hence in rotational constants, of isotopic molecules causes different rotational structures in their bands.

According to the Born-Oppenheimer approximation, the potential energy function of a molecule in a given electronic state depends upon the eigenvalues of the electronic wave equation of the molecule, and upon the coulombian repulsion between the nuclei. The first factor is almost independent and the second factor is entirely independent of the masses of the nuclei. Therefore, *the forms as well as the relative positions of the potential energy curves in different electronic states are the same for two isotopic molecules*. Thus isotopy affects only the vibrational and rotational energies of the molecule in each electronic state.

### 2. Effect on Electronic Spectra : Isotopic Displacement

The terms for an electronic state are :

$$T = T_e + G(v) + F(v, J).$$

The wave numbers corresponding to an electronic transition are given by

$$\begin{aligned}v &= T' - T'' \\&= (T_e' - T_e'') + (G' - G'') + (F' - F'') \\&= v_e + v_v + v_r,\end{aligned}$$

where  $v_e$  is the difference in energy of the minima of the potential energy curves of the two electronic states involved, and is the same for two isotopic molecules. It is the origin of the band-system.

The corresponding expression for the heavier, less abundant, molecule is

$$v^i = v_e + v_v^i + v_r^i.$$

Hence, in general, the isotopic displacement of a line in an electronic band is

$$v^i - v = (v_v^i - v_v) + (v_r^i - v_r).$$

$v_v^i - v_v$  is the vibrational contribution, and  $v_r^i - v_r$  is the rotational contribution to the total isotopic displacement.

We shall now consider them separately.

### 3. Vibrational Isotopic Displacement in Electronic Band-System

Treating the molecule as harmonic oscillator, the vibrational terms for two isotopic molecules are

$$G(v) = \omega_e \left( v + \frac{1}{2} \right)$$

$$G^i(v) = \omega_e^i \left( v + \frac{1}{2} \right),$$

where  $\omega_e^i$  is the vibrational constant for the heavier isotope.

Now,  $\omega_e^i = \rho \omega_e$ , where  $\rho = \sqrt{\mu/\mu^i}$  and is less than 1.

$$\therefore G^i(v) = \rho \omega_e \left( v + \frac{1}{2} \right)$$

$$G^i(v) - G(v) = (\rho - 1) \omega_e \left( v + \frac{1}{2} \right).$$

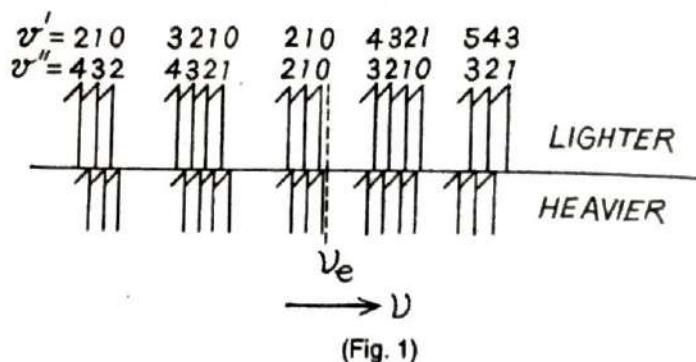
The isotopic displacement of a  $(v', v'')$  band would be

$$\begin{aligned}v_v^i - v_v &= (G'^i - G''^i) - (G' - G'') \\&= (G'^i - G') - (G''^i - G'') \\&= (\rho - 1) \omega_e' \left( v' + \frac{1}{2} \right) - (\rho - 1) \omega_e'' \left( v'' + \frac{1}{2} \right) \\&= (\rho - 1) \left\{ \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e'' \left( v'' + \frac{1}{2} \right) \right\} \\&= (\rho - 1) (G' - G'')\end{aligned}$$

$$v_v^i - v_v = (\rho - 1) v_v.$$

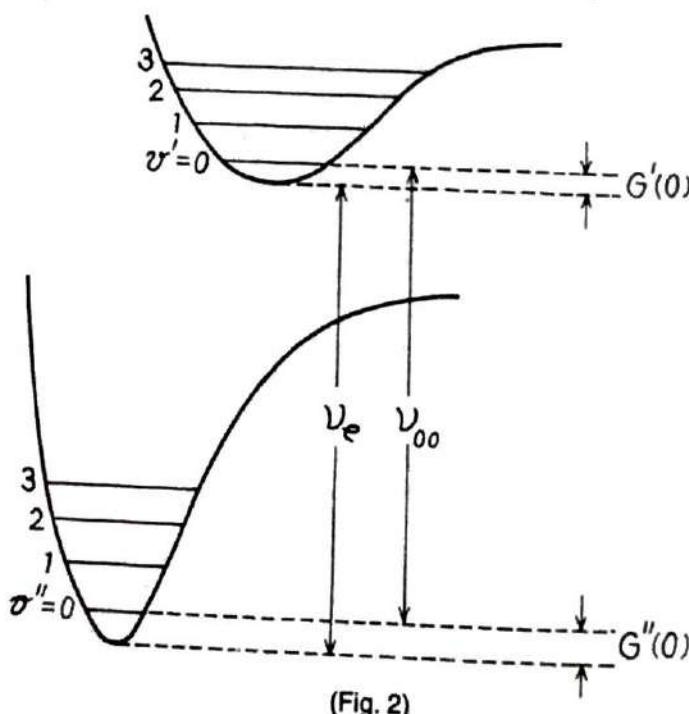
Thus, the vibrational displacement of a band is proportional to  $v_v$ , the wave-number distance of the band (band-origin) from the system-origin  $v_e$ . That is, the displacement increases linearly from band to band as we move away from the system-origin. Clearly, it would extrapolate to zero at the system-origin (where  $v' = v'' = -\frac{1}{2}$ ;  $v_v = 0$ ). Hence it would be zero for any band whose origin happens to coincide with the system-origin.

Since  $\rho < 1$  (less abundant molecule is the heavier),  $v_v' - v_v''$  is negative. That is corresponding bands (or band-heads) of the heavier isotope fall nearer to the system-origin. All the above features are shown in Fig. 1, which represents the vibrational isotopic displacement in a band-system. The band-heads of the less abundant (heavier) isotope are shown by lower (short) vertical lines.



The vibrational isotope effect has a number of applications :

(i) **Experimental Confirmation of Zero-point Energy :** If there were no zero-point energy, the  $(0, 0)$  band would have exactly coincided with the system origin ( $v_{00} = v_e$ ), as is evident from Fig. 2. As such there would be no isotopic displacement of the  $(0, 0)$  band.



Infact, experiment shows a small, but finite, displacement of the  $(0, 0)$  band. This means that the  $(0, 0)$  band does *not* exactly coincide with the system-origin. This, in turn, establishes that zero-point energy does exist and its magnitude is different in different electronic states of the molecule.

(ii) **Assignment of  $(v', v'')$  Values for the Bands of a System :** In the vibrational analysis of a band-system, the values  $v'$  and  $v''$  can be assigned to the bands with certainty if an isotopic displacement of bands is observable. This is because the displacement almost vanishes, though not completely, for the  $(0, 0)$  band which is therefore easily identified. The numbering of other bands then follows.

(iii) Identification of the Molecule emitting a given Band-system : In emission, band-systems often appear that belong to molecules which are chemically unstable but are formed in the discharge tube. These molecules are, therefore, not easily identified. In addition, band-systems of impurities also appear. If, however, an isotopic displacement is present, the emitter of the band-system is known with certainty because the isotopic displacement depends upon the masses of the two participating atoms. The bands due to  $\text{BO}$ ,  $\text{C}_2$  and  $\text{CN}$  were recognised in this way.

(iv) Determination of Relative Abundance of Isotopes : In the absorption spectrum of a mixture of isotopic molecules, the measured intensity ratio of the corresponding bands gives the abundance ratio of the molecules. In case of emission bands, however, the intensity ratio varies with the temperature of the source and so the determination of abundance ratio is complicated.

(v) Discovery of Rare Isotopes : The isotope effect (presence of weak bands very near to main bands) has led to the discovery of isotopes like  $\text{O}^{18}$ ,  $\text{O}^{17}$ ,  $\text{C}^{13}$ ,  $\text{N}^{13}$  which escaped detection in the mass spectrograph.

#### 4. Rotational Isotopic Displacement in Electronic Bands

Treating the diatomic molecule as a rigid rotator, the rotational terms for two isotopic molecules are

$$F(v, J) = B_v J(J + 1)$$

$$F^i(v, J) = B_v^i J(J + 1).$$

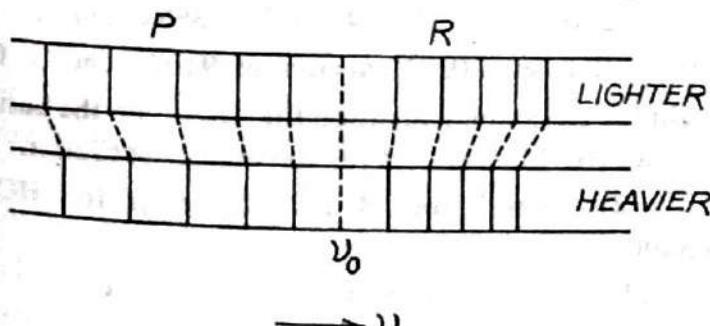
It can be shown that  $B_v^i = \approx \rho^2 B_v$ , so that

$$F^i(v, J) - F(v, J) \approx (\rho^2 - 1) B_v J(J + 1).$$

The rotational part of the isotopic displacement of a line in an electronic band would be

$$\begin{aligned} v_r' - v_r &= (F^{i'} - F^{i''}) - (F' - F'') \\ &= (F^{i'} - F') - (F^{i''} - F'') \\ &= (\rho^2 - 1) B_v' J'(J' + 1) - (\rho^2 - 1) B_v'' J''(J'' + 1) \\ &= (\rho^2 - 1) \{ B_v' J'(J' + 1) - B_v'' J'(J' + 1) \} \\ &\approx (\rho^2 - 1) v_r, \end{aligned}$$

where  $v_r$  is the rotational part of the wave number of a band line of the more abundant isotopic molecule. Thus, the rotational displacement of a line is roughly proportional to the wave-number interval  $v_r$  between that line and the band-origin  $v_0$ . The lines of the heavier isotope lie nearer the band-origin than the corresponding lines of the lighter isotope (Fig. 3). In the Fig. is shown only the rotational displacement. To this is to be



(Fig. 3)

added the vibrational displacement of the band as a whole. Hence the actual displacement of corresponding lines is greater than shown.

### SOLVED PROBLEMS

1. The origin of the  $v' = 0 \rightarrow v'' = 6$  band in an electronic transition observed in  $\text{N}^{14}\text{N}^{14}$  is located at  $35600 \text{ cm}^{-1}$ . Given that  $\omega_e' = 1460 \text{ cm}^{-1}$  and  $\omega_e'' = 2360 \text{ cm}^{-1}$  for  $\text{N}^{14}\text{N}^{14}$ , and based on the assumption that the harmonic approximation is adequate, calculate  $v_e$ , and the position of the corresponding band-origin for  $\text{N}^{14}\text{N}^{15}$ .

**Solution.** The band-origin wave number of an electronic band is given by

$$\begin{aligned}v_0 &= v_e + v_v \\&= v_e + G'(v) - G''(v) \\&= v_e + \omega_e' \left( v' + \frac{1}{2} \right) - \omega_e'' \left( v'' + \frac{1}{2} \right).\end{aligned}$$

For the (0, 6) band of  $\text{N}^{14}\text{N}^{14}$ , we have

$$\begin{aligned}v_0 &= v_e + 1460 \text{ cm}^{-1} \left( 0 + \frac{1}{2} \right) - 2360 \text{ cm}^{-1} \left( 6 + \frac{1}{2} \right) \\&= v_e + 730 \text{ cm}^{-1} - 15340 \text{ cm}^{-1} \\&= v_e - 14610 \text{ cm}^{-1}.\end{aligned}$$

But  $v_0 = 35600 \text{ cm}^{-1}$  (given).

$$\begin{aligned}\therefore v_e &= v_0 + 14610 \text{ cm}^{-1} \\&= 35600 \text{ cm}^{-1} + 14610 \text{ cm}^{-1} = 50210 \text{ cm}^{-1}.\end{aligned}$$

This is the wave number corresponding to the system-origin. Now, let  $v_0^i$  be the band-origin for  $\text{N}^{14}\text{N}^{15}$ . For this,  $v_e$  will remain unchanged. Thus

$$v_0^i = v_e + v_v^i.$$

But,  $v_v^i = \rho v_v$ .

$$\therefore v_0^i = v_e + \rho v_v.$$

For  $\text{N}^{14}\text{N}^{15}$ , we have

$$\rho = \sqrt{\mu/\mu'} = \sqrt{\frac{14 \times 14}{14 + 14}} / \sqrt{\frac{14 \times 15}{14 + 15}} = \sqrt{\frac{29}{30}} = 0.9832.$$

Also,  $v_v = v_0 - v_e = 35600 \text{ cm}^{-1} - 50210 \text{ cm}^{-1} = -14610 \text{ cm}^{-1}$ .

$$\begin{aligned}\therefore v_0^i &= 50210 \text{ cm}^{-1} + [0.9832 \times (-14610 \text{ cm}^{-1})] \\&= 50210 \text{ cm}^{-1} - 14364 \text{ cm}^{-1} = 35846 \text{ cm}^{-1}.\end{aligned}$$

2. The  $5' \leftarrow 0''$  transition in  $\text{HCl}^{35}$  occurs at  $91022 \text{ cm}^{-1}$ . Calculate the position of the band-origin for the same transition for  $\text{DCl}^{35}$  on the basis that in both electronic states the molecule behaves as a harmonic oscillator. Assume that  $\omega_e' = 2710 \text{ cm}^{-1}$ ,  $\omega_e'' = 2990 \text{ cm}^{-1}$  for  $\text{HCl}^{35}$ . Given  $\mu$  for  $\text{HCl} = 0.979889$  and  $\mu$  for  $\text{DCl} = 1.905000$ .

**Solution.** The wave number of an electronic band-origin is given by

$$\begin{aligned}
 v_0 &= v_e + v_g \\
 &= v_e + G'(v) - G''(v) \\
 &= v_e + \omega_e \left( v' + \frac{1}{2} \right) - \omega_e'' \left( v'' + \frac{1}{2} \right).
 \end{aligned}
 \quad (v_g \text{ is system-origin})$$

For (5, 0) band of HCl,  $v_0 = 91022 \text{ cm}^{-1}$ ,  $\omega_e' = 2710 \text{ cm}^{-1}$ ,  $\omega_e'' = 2990 \text{ cm}^{-1}$ ,  $v' = 5$ ,  $v'' = 0$ .

$$\begin{aligned}
 \therefore 91022 \text{ cm}^{-1} &= v_e + 2710 \text{ cm}^{-1} \left( 5 + \frac{1}{2} \right) - 2990 \text{ cm}^{-1} \left( \frac{1}{2} \right) \\
 &= v_e + 14905 \text{ cm}^{-1} - 1495 \text{ cm}^{-1}.
 \end{aligned}$$

This gives

$$\begin{aligned}
 v_e &= 91022 \text{ cm}^{-1} - 14905 \text{ cm}^{-1} + 1495 \text{ cm}^{-1} \\
 &= 77612 \text{ cm}^{-1}.
 \end{aligned}$$

$v_g$  (system-origin) is the energy difference between potential energy minima for the two electronic states, and remains unchanged on isotopic substitution.

Now, let  $v_0'$  be the band-origin for DCl. Then, we write

$$v_0' = v_e + v_g'.$$

But  $v_g' = \rho v_g$ , where  $\rho = \sqrt{\mu/\mu'}$ .

$$\therefore v_0' = v_e + \rho v_g = v_e + \rho (v_0 - v_e).$$

Now,  $\rho = \sqrt{\frac{0.979889}{1.905000}} = 0.7172$ .

$$\begin{aligned}
 \therefore v_0' &= 77612 \text{ cm}^{-1} + 0.7172 (91022 \text{ cm}^{-1} - 77612 \text{ cm}^{-1}) \\
 &= 77612 \text{ cm}^{-1} + 0.7172 (13410 \text{ cm}^{-1}) \\
 &= 77612 \text{ cm}^{-1} + 9618 \text{ cm}^{-1} = 87230 \text{ cm}^{-1}.
 \end{aligned}$$

3. The dissociation energy of the  $\text{H}_2$  molecule is 4.46 eV while that of the  $\text{D}_2$  molecule is 4.54 eV. Find the zero-point energy of the  $\text{H}_2$  molecule.

(Meerut 94, sp. paper 2005, 04, 03, 02 S, 00, 99, 98)

**Solution.** The form of the potential energy curve of any electronic state of a molecule is determined by the motions of the electrons and the Coulombian repulsion between the nuclei, and is not greatly influenced by the nuclear masses. Thus, the energy measured from the minimum of the potential curve to the dissociation limit,  $D_e$ , is very nearly the same for the isotopic molecules. The vibration of the molecule does, however, depend on the nuclear masses, and the vibrational frequency  $\omega_e$  is inversely proportional to the square-root of the reduced mass :

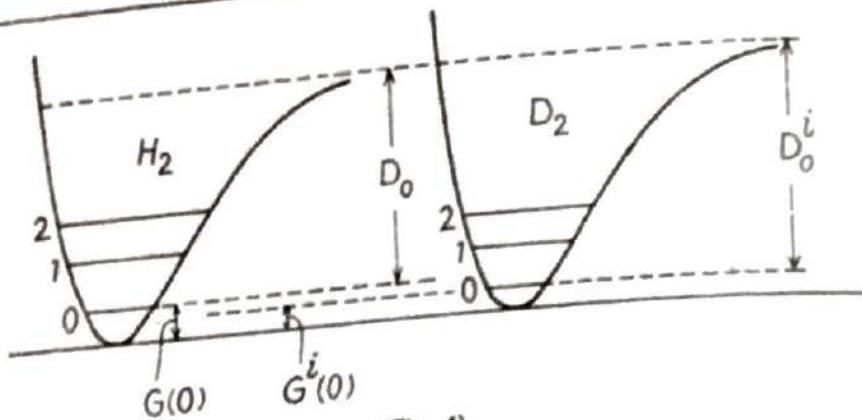
$$\omega_e \propto \sqrt{\frac{1}{\mu}}.$$

For two isotopic molecules with reduced masses  $\mu$  and  $\mu'$ , let us define  $\rho$  as

$$\rho = \sqrt{\frac{\mu}{\mu'}}.$$

$\rho$  is less than 1, if  $i$  stands for the heavier isotope.

It is clear from Fig. 4 that the difference in the dissociation energies is equal to the difference in the zero-point energies of the two isotopic molecules. That is,



(Fig. 4)

$$D_0' - D_0 = G(0) - G'(0).$$

But  $D_0' - D_0 = 4.54 \text{ eV} - 4.46 \text{ eV} = 0.08 \text{ eV}$  (given).  
 $\therefore G(0) - G'(0) = 0.08 \text{ eV}.$

Treating the molecules as harmonic oscillators, the vibrational energies are given by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right)$$

$$G'(v) = \omega_{e'} \left( v + \frac{1}{2} \right) = \rho \omega_e \left( v + \frac{1}{2} \right)$$

$$\therefore G(v) - G'(v) = (1 - \rho) \omega_e \left( v + \frac{1}{2} \right).$$

For  $v = 0$ , that is, the difference in zero-point energies is, therefore,

$$G(0) - G'(0) = \frac{1}{2} \omega_e (1 - \rho).$$

But this is 0.08 eV.

$$\therefore \frac{1}{2} \omega_e (1 - \rho) = 0.08 \text{ eV}$$

$$\frac{1}{2} \omega_e = \frac{0.08}{1 - \rho} \text{ eV.}$$

or

The zero-point energy of  $H_2$  is

$$G(0) = \frac{1}{2} \omega_e = \frac{0.08}{1 - \rho} \text{ eV.}$$

$$\text{Now, } \rho = \sqrt{\mu/\mu'} = \sqrt{\frac{1 \times 1}{1 + 1}} / \sqrt{\frac{2 \times 2}{2 + 2}} = \sqrt{\frac{1}{2}} = 0.707.$$

$$\therefore G(0) = \frac{0.08 \text{ eV}}{1 - 0.707} = 0.273 \text{ eV.}$$

But  $1 \text{ eV} = 8066 \text{ cm}^{-1}$ .

$$\therefore G(0) = 0.273 \text{ eV} \times 8066 \text{ cm}^{-1}/\text{eV} = 2202 \text{ cm}^{-1}.$$

### QUESTIONS

- What are vibrational and rotational isotope effects? How do they affect the electronic spectrum of a diatomic molecule? Discuss the importance of isotope effect in spectroscopic studies. (Meerut 2001 sp. paper)
- What is isotope effect. Mention briefly its applications. (Meerut 2000 S sp. paper)

3. Explain how the vibrational structure of a band-system in the electronic spectrum of a diatomic molecule is modified by the presence of an isotope. Illustrate by an example. Mention briefly the applications of isotope effect.
4. Explain how the rotational structure of a band is modified by the presence of an isotope. Illustrate by an example. Mention briefly the applications of isotope effect.  
*(Meerut sp. paper 92)*
5. What are the effects of nuclear isotopy on the band spectra of diatomic molecules ?

### PROBLEM

1. It is suspected that an observed sequence of electronic bands involves  $5' \leftarrow 4''$ ,  $4' \leftarrow 3''$ ,  $3' \leftarrow 2''$ ,  $2' \leftarrow 1''$  and  $1' \leftarrow 0''$  transitions in  $\text{C}^{12}\text{O}^{16}$ . Band-origins are located at 63399, 64118, 64829, 65532 and 66229  $\text{cm}^{-1}$  respectively. Predict the band-origins for  $\text{C}^{12}\text{O}^{18}$ . Assume that  $\omega_e' = 1516 \text{ cm}^{-1}$ ,  $\omega_e' x_e' = 17.25 \text{ cm}^{-1}$ ,  $\omega_e'' = 2170 \text{ cm}^{-1}$ , and  $\omega_e'' x_e'' = 13.46 \text{ cm}^{-1}$  for  $\text{C}^{12}\text{O}^{16}$ .

**Ans.** (5, 4) : 63445 ; (4, 3) : 64145 ; (3, 2) : 64838 ; (2, 1) : 65523 ; (1, 0) : 66202  $\text{cm}^{-1}$ .

---

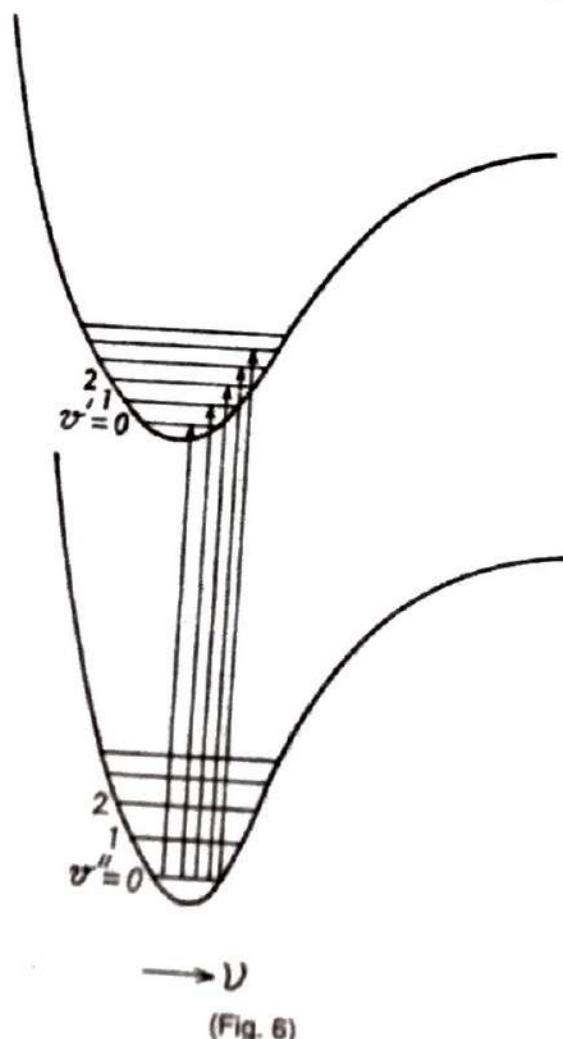
# Fluorescence and Phosphorescence

## 1. Luminescence

When the molecules of a gas (say) are raised to an excited electronic state by illuminating the gas with light of a definite frequency, they may revert to their initial state with the emission of discrete radiation of frequencies smaller than the frequency of the absorbed light. This phenomenon is known as 'luminescence'. The emission may vanish almost immediately after the removal of the exciting radiation, or it may persist for an appreciable time. The former is called 'fluorescence' and the latter 'phosphorescence'. Their combined name is luminescence.

## 2. Mechanism of Fluorescent Emission

Fluorescent emission is followed by electromagnetic absorption. In an absorption experiment, the temperature is often near room temperature, and the  $v'' = 0$  level of the ground electronic state of molecules is most populated. Therefore, on illuminating the molecules with continuous light, we would expect a single progression of bands in the electronic absorption spectrum due to transitions from  $v'' = 0 \rightarrow v'$  varying from  $v' = 0$  to large values (Fig. 1). For heavy molecules, like  $I_2$ , absorption transitions

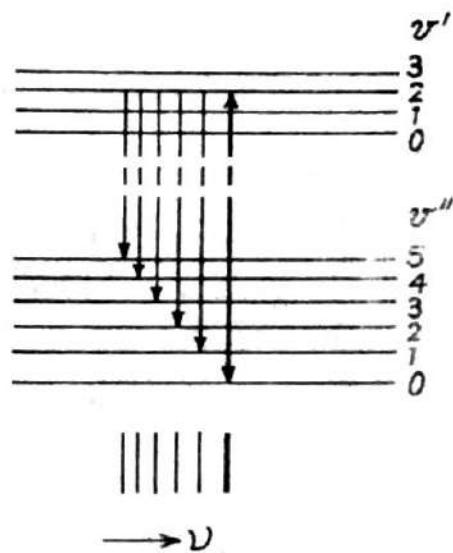


corresponding to  $v'' = 1, 2$ , may also be observed, though weakly. The intensity distribution in these bands depends upon the shapes and relative positions of the two potential energy curves and is governed by Franck-Condon principle. Such absorption spectra display the pattern of vibrational levels almost upto the limit of dissociation, and the dissociation energy of the molecule in the excited electronic state can be deduced by a suitable extrapolation.

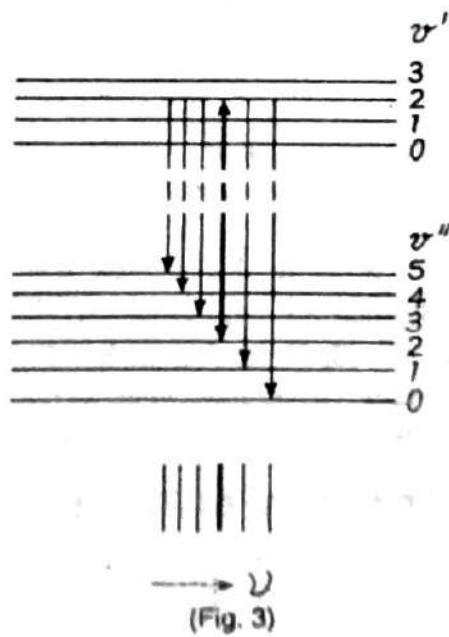
The fluorescent emission of radiation, on the other hand, is the process taking place after the molecules are raised to some high-energy electronic state by absorption of radiation. There are at least two different processes by which such an excited molecule can lose its excess energy and return to its ground state. In one, the excess energy may be lost as heat by repeated collisions with neighbouring molecules. No emission of radiation is observed in this process which is therefore known as 'non-radiative' process. Alternatively, the excited molecule may return directly to the level  $v'' = 0$  of the ground state with emission of the absorbed light, or, to other levels of the ground state with emission of light of lower frequencies. This process is fluorescence.

Let us first consider fluorescent radiation from diatomic gases at low pressure. Being at low pressure, there are little chances of molecular collisions. When such a gas is illuminated with light having the frequency of a single absorption band, the absorbing molecules are excited to the vibrational level of the upper electronic state of this particular absorption band only. The excited molecules then go over to the different vibrational levels of the ground electronic state with emission of radiation. Thus, in the fluorescence spectrum we expect a single progression ( $v' = \text{constant}$ ) of bands extending from the position of the absorption band toward lower frequencies with decreasing band separation (Fig. 2). This is a case of 'resonance fluorescence', having the characteristic that the molecules have not lost any energy in collisions before re-emission. The band coinciding with the exciting absorption band is called the 'resonance band' and the whole series of bands is called the 'resonance series'. Such series of bands have been observed in case of  $\text{Na}_2$ ,  $\text{I}_2$ , etc.

If the exciting radiation corresponds to an absorption band with  $v'' > 0$  (as is possible for heavy molecules), then some of the fluorescence bands may have  $v''$  smaller than that of the resonance (exciting) band (Fig. 3). Such bands lie on the high-frequency side of the resonance band and are called anti-Stokes members of the resonance series.



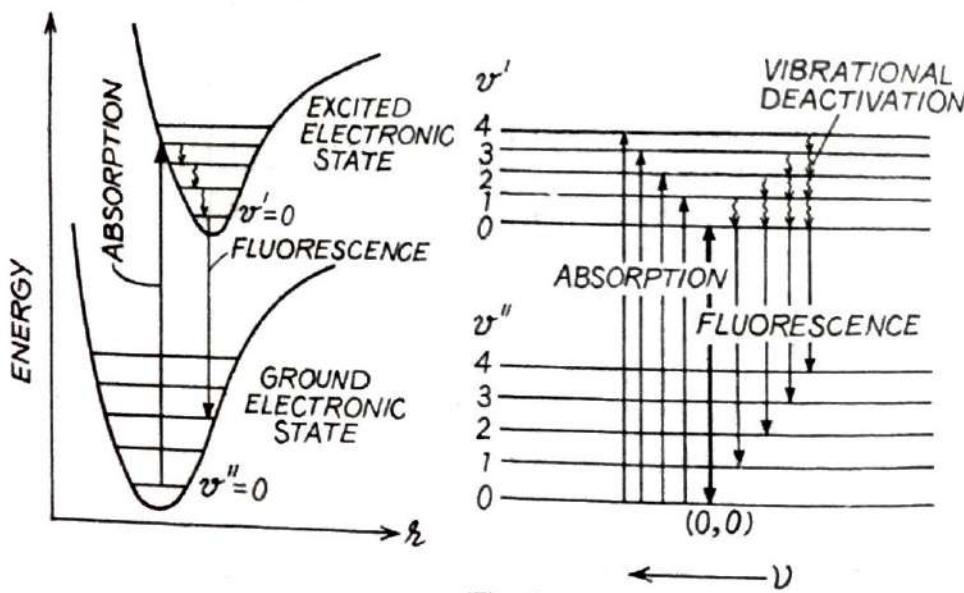
(Fig. 2)



(Fig. 3)

If the gas is kept at a high pressure, say by adding a foreign (rare) gas ; collisions become frequent. In this case, the molecules excited to a particular vibrational level of the upper electronic state collide with the neighbouring molecules of the fluorescing gas or with the atoms of the foreign gas, and lose or gain vibrational energy, thus switching over to other vibrational levels of the upper state. Transitions now take place from all these levels to the various levels of the ground electronic state. As a result, the fluorescence spectrum would consist of more  $v''$ -progressions corresponding to various  $v'$  values. Thus, with sufficient pressure of the foreign gas, the entire band-system can be obtained in the fluorescence spectrum. (In this case the fluorescence spectrum loses the characteristic of resonance). On the other hand, the absorption spectrum usually shows only one progression. Hence, in general, **fluorescence is a more powerful technique than absorption.**

Let us now consider the fluorescence in solutions, which is not characterised by resonance. Initially, the bulk of the molecules are in the lowest vibrational level  $v'' = 0$  of the ground electronic state. Absorption of radiation, say visible light, excites the molecules to various vibrational levels of the excited electronic state. In the absorption spectrum, therefore, the lowest-frequency band is the (0, 0) band, and the spectrum extends to higher frequencies (Fig 4). Now, before the fluorescent emission occurs, the



(Fig. 4)

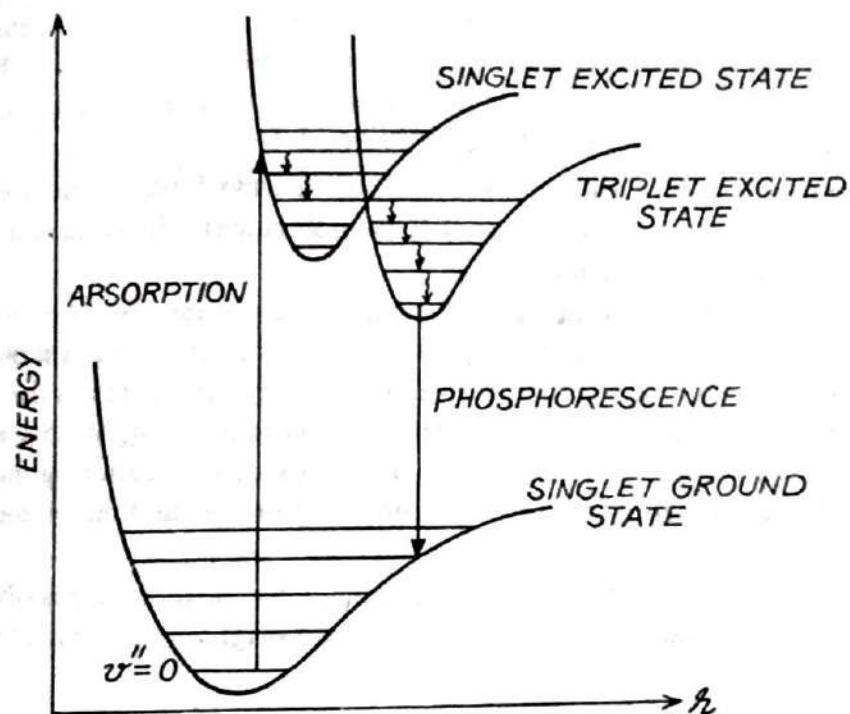
excited molecules lose vibrational energy due to collisions and most of them eventually come down to the lowest level  $v' = 0$  of the excited electronic state. This (non-radiative) process is called 'vibrational deactivation'. Fluorescent emission then takes place from  $v' = 0$  level to the various levels of the ground electronic state. These transitions generally occur within about  $10^{-4}$  second after excitation. In the fluorescence spectrum, clearly, the (0, 0) band is the band of highest frequency and the spectrum extends to lower frequencies. Obviously, whereas the absorption spectrum displays the vibrational levels of the excited electronic state, the fluorescence spectrum displays those of the ground state.

### 3. Mechanism of Phosphorescent Emission

Like fluorescence, phosphorescence is also emission of radiation by molecules excited as a result of absorption of radiation. It is, however, a delayed emission and

persists for periods upto seconds after the absorption process is ended. It has been explained as resulting from transitions that connect electronic states of *different* multiplicities.

Fig. 5 shows the mechanism of phosphorescent emission. Initially, at normal temperatures, the molecules of a sample are mostly in the lowest vibrational level



(Fig. 5)

$v'' = 0$  of the ground electronic state, which for almost all diatomic molecules (except  $O_2$ ) is a *singlet* state. Upon absorption of radiation they are excited to another *singlet* electronic state. Phosphorescence arises when a *triplet* excited state of the molecule exists between the singlet excited state and the ground state, and its potential energy curve crosses the curve of the excited singlet state. The excited molecules, by collisions, can undergo radiationless transitions to a lower vibrational level that may happen to have about the same energy as one of the levels of the crossing triplet state. Then there is a certain probability for the molecule to pass on to the triplet state. This is again a nonradiative process known as 'internal conversion'. Further vibrational deactivation by collisions in the triplet state carries the molecule stepwise down the vibrational levels until it reaches the lowest level of the triplet state. Transitions from this triplet state to the ground singlet state are responsible for the phosphorescent emission. Such transitions are in fact forbidden by the spin selection rule ( $\Delta S = 0$ ). This really means that such transitions have very long half-lives, and the resulting phosphorescent radiation may be emitted seconds or even minutes after the initial absorption.

If the intermediate (crossing) electronic state is also a singlet state then the above process occurs very quickly and leads to fluorescent emission.

Thus, both fluorescence and phosphorescence are the emissions due to the returning of the molecules from the excited electronic states, attained by absorption, to the ground state; but whereas fluorescence arises from transitions between electronic states of the same multiplicity, the phosphorescence arises from transitions between states of different multiplicities.

#### 4. Fluorescence Spectrum compared with Raman Spectrum

The mechanism of Raman scattering is quite different from that of fluorescence :

(i) In fluorescence, the incident photon is completely absorbed by the molecule which is raised to an excited state, from which it returns to a lower state after a finite life-time with the concurrent emission of a second photon. The molecule may return to various lower states in a number of ways, emitting photons of different energies which appear as fluorescent spectrum. In Raman effect, the incident photon is scattered, not absorbed, by the molecule, and only an exchange of energy takes place.

(ii) The frequencies of the fluorescence lines are always lower, or at most  $\sim$  to that of the incident light (except in case of very heavy molecules). The Raman lines are both of lower as well as of higher frequencies.

(iii) The fluorescence can occur only when the frequency of the incident light coincides with one of the absorption frequencies of the scattering gas molecules, that is corresponding to the energy difference between two stationary states of the molecule. The Raman effect can take place for any frequency of the incident light, that is, the incident frequency is not related to any characteristic frequency of the scattering molecule. Hence the structure of the Raman spectrum is quite different from that of the fluorescence spectrum.

(iv) In fluorescence, the amount of light radiated by the molecule is of the same order as the incident light so that the fluorescence lines are bright. The Raman lines are, on the other hand, very weak.

#### QUESTIONS

1. Distinguish between fluorescence and absorption spectroscopy of a diatomic molecule. *(Meerut sp. paper 2002 S. 99)*
2. Account for : Fluorescence is in general a more powerful technique than absorption.
3. Explain : Fluorescence is observed only for some suitable exciting wavelengths but Raman effect can be observed for any exciting wavelength.
4. Distinguish between Raman Spectra and fluorescence spectra of a diatomic molecule. *(Meerut sp. paper 2002, 95, 99)*
5. Write a short note on fluorescence spectra of gases.
6. Write a short note on phosphorescence.

## 24

# Classification of Molecular Electronic States

### 1. Molecular Electronic States

The atomic nuclei in a molecule are held together by electrons. Therefore, as for atoms, there are different electronic states of the molecule depending upon the electronic configuration in the molecule. The energy differences between these states are of the same order as for atoms (roughly from 1 to 10 eV).

In a diatomic molecule, the electrons move in an axially-symmetric electrostatic field produced by the two nuclei. Therefore, the *component* of the orbital angular momentum of the electrons along the internuclear axis is a constant of motion. The interaction of the electrons with the electrostatic field causes the electronic orbital angular momentum vector  $\vec{L}$  to precess about the field direction (internuclear axis) with quantised components  $M_L (h/2\pi)$ , where  $M_L$  can take only the values

$$M_L = L, L - 1, L - 2, \dots, -L.$$

In most molecules, the electrostatic field due to the nuclei is so strong that  $\vec{L}$  precesses very rapidly and loses its meaning as angular momentum; only its component  $M_L$  along the field remains well-defined. Further, in an electrostatic field, reversing the directions of motion of all electrons does not change the energy of the system, but changes simply  $M_L$  to  $-M_L$ . Therefore, in diatomic molecules, the states corresponding to  $+M_L$  and  $-M_L$  are degenerate (have the same energy). The absolute value of  $M_L$  is designated by a quantum number  $\Lambda$  (called 'lambda') so that

$$\Lambda = |M_L| = 0, 1, 2, \dots, L.$$

The corresponding angular momentum vector  $\vec{\Lambda}$  represents the component of the electronic orbital angular momentum along the internuclear axis, and its magnitude is  $\Lambda (h/2\pi)$ . The precession of  $\vec{L}$  in the molecule is illustrated in Fig. 1.

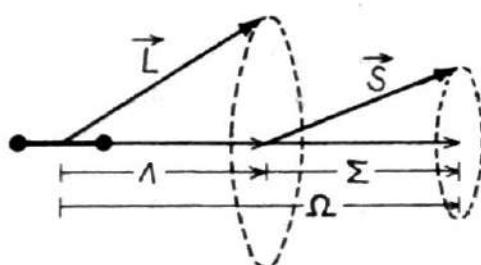
**The electronic states of the molecule are classified according to the value of  $\Lambda$ .** They are designated as

$$\Sigma, \Pi, \Delta, \Phi, \dots$$

$$\Lambda = 0, 1, 2, 3, \dots$$

$\Sigma$ -states are non-degenerate ( $M_L = 0$ ); whereas  $\Pi, \Delta, \Phi, \dots$  states are doubly-degenerate ( $\pm M_L$ ). The electronic states  $\Sigma, \Pi, \Delta, \Phi, \dots$ , often have widely different energies since the electric field which causes this splitting is very strong.

In molecules, the orbital motions of the electrons produce a (weak) internal magnetic field along the internuclear axis, except when the molecule is in a  $\Sigma$ -state in which the



(Fig. 1)

electron cloud is cylindrically symmetrical about the internuclear axis. This (magnetic) field causes the electronic spin angular momentum vector  $\vec{S}$  to precess about the internuclear axis (Fig. 1) with quantised components  $\Sigma (h/2\pi)$ , where the quantum number  $\Sigma$  can take only the values given by

$$\Sigma = S, S - 1, S - 2, \dots, -S.$$

That is,  $2S + 1$  different values are possible. In contrast to electronic angular momentum quantum number  $\Lambda$ , the spin magnetic quantum number\*  $\Sigma$  can be integral or half-integral, and also positive or negative. It is not defined for states with  $\Lambda = 0$ , that is,  $\Sigma$ -states which have no internal magnetic field.

The total electronic angular momentum about the internuclear axis, denoted by  $\vec{\Omega}$  and having a magnitude of  $\Omega (h/2\pi)$ , is obtained by adding  $\vec{\Lambda}$  and  $\vec{\Sigma}$ , that is

$$\vec{\Omega} = \vec{\Lambda} + \vec{\Sigma}.$$

Since  $\vec{\Lambda}$  and  $\vec{\Sigma}$  lie along the same line (internuclear axis), an algebraic addition is sufficient. Hence the quantum number corresponding to the total electronic angular momentum about the internuclear axis is given by

$$\Omega = |\Lambda + \Sigma|.$$

$\Omega$  can be integral or half-integral depending upon whether  $\Sigma$  is integral or half-integral.

**$\Lambda - \Sigma$  Interaction :** For a given value of  $\Lambda$  (when  $\Lambda \neq 0$ ), there are  $2S + 1$  different values of  $\Lambda + \Sigma$  which correspond to somewhat different energies of the resulting component electronic states. In other words, as a result of  $\Lambda - \Sigma$  (orbit-spin) interaction\*\*, an electronic state with a given  $\Lambda$  (when  $\Lambda \neq 0$ ) splits into a multiplet of  $2S + 1$  components. The number  $2S + 1$  is called the multiplicity of the state, and appears as a left superscript to the state symbol. Furthermore, the value of  $\Lambda + \Sigma$ , or  $\Omega$ , is added as a subscript.

As an example, let us consider the molecular electronic state  ${}^3\Delta$ . For this, we have

$$\Lambda = 2, 2S + 1 = 3 \text{ so that } S = 1.$$

$$\therefore \Sigma = S, S - 1, S - 2, \dots, -S \\ = 1, 0, -1.$$

The quantum number for the component of the total angular momentum about the internuclear axis has the values

$$\Omega = |\Lambda + \Sigma| = |2 + 1, 2 + 0, 2 - 1| \\ = 3, 2, 1.$$

Thus, the electronic state  ${}^3\Delta$  has three components

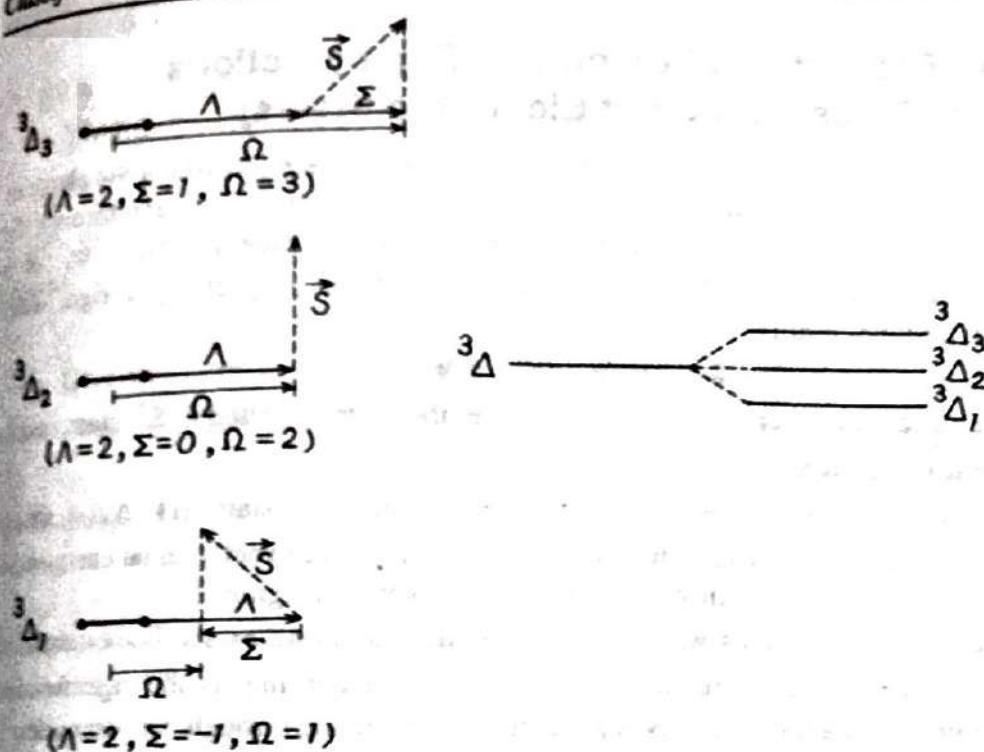
$${}^3\Delta_3, {}^3\Delta_2, {}^3\Delta_1$$

displayed in Fig. 2.

The *internal* magnetic field  $\vec{B}$  (say) that causes the precession of  $\vec{S}$  about the internuclear axis is proportional to  $\Lambda$ . The magnetic ( $\Lambda - \Sigma$ ) interaction energy of the spin in this field is  $\mu_B B$ , where  $\mu_B$  is the component of the spin magnetic moment along the

\* For molecules, the spin magnetic quantum number is denoted by  $\Sigma$ , and not by  $M_S$  (as is done in atoms). Further, this quantum number  $\Sigma$  must not be confused with the symbol  $\Sigma$  used for electronic state with  $\Lambda = 0$ .

\*\*This is the interaction of the magnetic field caused by the orbital motions of the electrons with the electron spin.



direction of  $\vec{B}$  and is proportional to  $\Sigma$ . The interaction energy of a multiplet term is, therefore, to a first approximation, given by

$$T = T_0 + A \Lambda \Sigma,$$

where  $T_0$  is the energy value when the spin is neglected, and  $A$  is a constant for a given multiplet term. This shows that the components of a molecular multiplet term are equispaced (unlike the components of an atomic multiplet term) with separation  $A \Lambda$ .

Moreover, the above relation shows that the number of multiplet components is always equal to the number of  $\Sigma$  values, that is  $2S + 1$ , irrespective of whether  $S$  is smaller or larger than  $\Lambda$ . On the other hand, in an atomic multiplet the number of components is  $2S + 1$  or  $2L + 1$  according as  $S < L$  or  $S > L$ .

The  $\Lambda - \Sigma$  interaction does not affect the two-fold degeneracy of the electronic states with  $\Lambda \neq 0$ . Each of the multiplet components of these state is doubly-degenerate. (This degeneracy is removed when electronic-rotational interaction is considered).

For multiplet components with  $\Omega = 0$ , however, the degeneracy exists only in a first approximation. Strictly speaking, for a  $^3\Pi_0$  component, for example, there are two sublevels of very slightly different energies which are designated  $^3\Pi_0^+$  and  $^3\Pi_0^-$ .

For  $\Sigma$ -states ( $\Lambda = 0$ ) the quantum number  $\Sigma$  is undefined, because in this case there is no internal magnetic field along the internuclear axis and hence no  $\Lambda - \Sigma$  interaction. Consequently  $\Omega$  is also undefined. Hence the symbol  $\Sigma$  designating the electronic state  $\Lambda = 0$  does not carry any subscript. However,  $\Sigma$ -states carry the multiplicity superscript irrespective of the fact that there is no actual splitting in these cases.

## 2. Symmetry Properties of Electronic Eigenfunctions (Symmetry Classification of Electronic States)

In a diatomic molecule, the electric field due to the two nuclei, in which the electrons move, is axially symmetric about the internuclear axis. Therefore, any plane through the internuclear axis is a plane of symmetry. The electronic eigenfunction  $\Psi_e$  of a non-degenerate state ( $\Sigma$  state) either remains unchanged, or only changes sign, when reflected at such a plane, that is,

$$\sigma \Psi_e = \Psi_e \text{ or } -\Psi_e,$$

where  $\sigma$  is the reflection operator. In the first case, the state is called a  $\Sigma^+$  state, and in the second case it is called a  $\Sigma^-$  state\*.

It is superfluous to make the  $+, -$  distinction for degenerate states ( $\Pi, \Delta, \dots$  states) because  $\Pi^+$  and  $\Pi^-$ , and correspondingly the other pairs, have exactly equal energies (so long the interaction of electronic motion with nuclear rotation is ignored).

In the case of  $\Lambda > 0$  states with  $\Omega = 0$ , a slight splitting exists. For example, in case of a  $^3\Pi_0$  state, we distinguish  $^3\Pi_0^+$  and  $^3\Pi_0^-$  according as the eigenfunction remains unchanged or changes sign upon reflection at any plane through the two nuclei.

If the two nuclei in the molecule have the *same charge* (such as  $O^{16}O^{16}$  and also  $O^{16}O^{18}$ ), the mid-point of the internuclear axis is a centre of symmetry\*\*. The electronic eigenfunctions remain either unchanged, or only change sign, when inverted at this centre of symmetry (that is, when the coordinates of all the *electrons*  $x_i, y_i, z_i$ , are changed to  $-x_i, -y_i, -z_i$ ), the coordinates of the nuclei remaining unchanged. The states to which the eigenfunctions of the former type belong are called "even" (*g*) states ( $\Sigma_g, \Pi_g, \dots$ ); while those to which the eigenfunctions of the latter type belong are called "odd" (*u*) states ( $\Sigma_u, \Pi_u, \dots$ ). In case of doubly-degenerate states ( $\Pi, \Delta, \dots$ ) the two components are either both even or both odd. The electron spin has no influence on the even-odd symmetry property and so the components of a multiplet term are either all even (*g*) or all odd (*u*)\*\*\*.

The behaviour of an eigenfunction toward an inversion operation is referred as "parity". The eigenfunction which remains unaltered on inversion at a centre of symmetry is said to have an 'even parity'; while that which changes only sign is said to have an 'odd parity.'

In practice, the ground electronic state of all diatomic molecules is  $^1\Sigma^+$  or  $^1\Sigma_g^+$  (if the nuclei have the same charge), except for molecules NO and O<sub>2</sub> whose ground electronic states are  $^2\Pi$  and  $^3\Sigma_g^-$  respectively.

The selection rules for the electronic transitions are as follows :

\*If  $\Lambda$  is not defined, as in Hunds' coupling case (c), the electronic states are designated  $0^+$  and  $0^-$  corresponding to  $\Sigma^+$  and  $\Sigma^-$ .

\*\* The electric field due to the two nuclei, in which the electrons move, remains unaltered by a reflection of the nuclei at this point.

\*\*\* If  $\Lambda$  is not defined as in Hund's coupling case (c), the even-odd symmetry is defined and we have  $0_g+, 0_u+, 0_g-, 0_u- \dots$  states.

- (i)  $\Delta \Lambda = 0, \pm 1$ ; thus  $\Sigma \leftrightarrow \Sigma$ ,  $\Sigma \leftrightarrow \Pi$ , but  $\Sigma \not\leftrightarrow \Delta$ .
- (ii)  $\Sigma^+ \leftrightarrow \Sigma^+$ ;  $\Sigma^- \leftrightarrow \Sigma^-$ ; but  $\Sigma^+ \not\leftrightarrow \Sigma^-$ .
- (iii)  $\Delta S = 0$ ; thus  ${}^1\Sigma \leftrightarrow {}^1\Sigma$ , but  ${}^1\Sigma \not\leftrightarrow {}^2\Sigma$ .
- (iv)  $g \leftrightarrow u$ ; but  $g \not\leftrightarrow g$  and  $u \not\leftrightarrow u$ .

In view of the above rules, the transition  ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$  is allowed but  ${}^1\Sigma_u^+ - {}^3\Sigma_g^-$  is not allowed.

## SOLVED PROBLEMS

1. Give the correct designations for the substates of (i)  ${}^1\Pi$ , (ii)  ${}^2\Pi$ , (iii)  ${}^3\Pi$ , (iv)  ${}^4\Pi$  and (v)  ${}^4\Delta$  states. Do such substates exist for, say,  ${}^3\Sigma$  state?

(Meerut sp. paper 2004, 03, 02, 01)

**Solution.** (i) For the electronic state  ${}^1\Pi$ , we have

$$\Lambda = 1, 2S + 1 = 1, \text{ so that } S = 0.$$

$$\therefore \Sigma = S, S - 1, S - 2, \dots, -S = 0.$$

The quantum number  $\Omega$  corresponding to the substates has the values

$$\Omega = |\Lambda + \Sigma| = 1.$$

There is only one component for the singlet state  ${}^1\Pi$ , which may be written as  ${}^1\Pi_1$ .

(ii) For the doublet electronic state  ${}^2\Pi$ , we have

$$\Lambda = 1, 2S + 1 = 2, \text{ so that } S = \frac{1}{2}.$$

$$\therefore \Sigma = \frac{1}{2}, -\frac{1}{2}$$

$$\Omega = |\Lambda + \Sigma| = \left| 1 + \frac{1}{2} \right|, \left| 1 - \frac{1}{2} \right| = \frac{3}{2}, \frac{1}{2}.$$

The substates (components) are

$${}^2\Pi_{3/2}, {}^2\Pi_{1/2}.$$

(iii) For the triplet electronic state  ${}^3\Pi$ , we have

$$\Lambda = 1, 2S + 1 = 3, \text{ so that } S = 1.$$

$$\therefore \Sigma = 1, 0, -1$$

$$\Omega = |\Lambda + \Sigma| = 2, 1, 0.$$

The substates are

$${}^3\Pi_2, {}^3\Pi_1, {}^3\Pi_0.$$

(iv) for the quartet electronic state  ${}^4\Pi$ , we have

$$\Lambda = 1, 2S + 1 = 4, \text{ so that } S = \frac{3}{2}.$$

$$\therefore \Sigma = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

$$\Lambda + \Sigma = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}.$$

Four  $\Sigma$  values correspond to four different equidistant energy levels, designated as

$${}^4\Pi_{5/2}, {}^4\Pi_{3/2}, {}^4\Pi_{1/2}, {}^4\Pi_{-1/2},$$

even though the last two of them have the same  $\Omega$  value ( $\Omega = |\Lambda + \Sigma| = \frac{1}{2}$ ). That is why  $\Lambda + \Sigma$ , rather than  $\Omega$ , is used to distinguish the multiplet components.

(v) For the  ${}^4\Delta$  state, we have

$$\Lambda = 2, 2S + 1 = 4, \text{ so that } S = \frac{3}{2}.$$

$$\therefore \Sigma = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}.$$

and

$$\Lambda + \Sigma = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}.$$

In this case  $\Lambda + \Sigma$  is positive throughout and therefore equal to  $\Omega$ . The substates are

$${}^4\Delta_{7/2}, {}^4\Delta_{5/2}, {}^4\Delta_{3/2}, {}^4\Delta_{1/2}.$$

Such substates do not exist for  ${}^3\Sigma$  state, because for a  $\Sigma$  state,  $\Lambda = 0$ .

**2. Explain the various symbols in the notation  ${}^2\Sigma_u^-$  which represents an electronic state of a molecule.**

**Explanation :** The given electronic state is designated as

$${}^2\Sigma_u^-.$$

(i)  $\Sigma$  is the name of the state. For this state, the electronic angular momentum quantum number is zero, that is,

$$\Lambda = 0.$$

This means that in this state the component of the electronic angular momentum along the internuclear axis is zero.

(ii) The superscript '2' represents the multiplicity of the state, that is,

$$2S + 1 = 2$$

so that

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

The resultant electronic spin of the molecule in this state is  $\frac{1}{2}$ .

(iii) The minus sign appearing as a superscript on the right-hand side indicates the symmetry property of the state. The eigenfunction  $\psi_e$  corresponding to this state changes sign on reflection at a plane through the internuclear axis.

(iv) The subscript  $u$  represents the parity of the eigenfunction of the state which, for the given state, is odd.

## QUESTIONS

- Give the scheme for classifying the electronic states of a diatomic molecule.  
*(Meerut 2006, sp. paper 98)*
- Explain the meaning of the various symbols in the notations  ${}^1\Sigma_g^+$ ,  ${}^4\Pi_u$ , and  ${}^3\Sigma_g^-$ .  
*(Meerut 88 sp. paper)*
- Explain the meaning of different terms mentioned below:  
 ${}^1\Sigma_g^+, {}^3\Pi_u, {}^1\Delta_u, {}^3\Sigma_u^-$

Indicate with reasons if  ${}^1\Sigma_u^+ \rightarrow {}^3\Sigma_g^-$  transition is allowed.

## PROBLEMS

1. A  ${}^3\Pi$ -state has components of slightly different energies. What quantum number is used to indicate these components and how are its allowed values deduced ? Give the correct designation of the components. Do comparable components exist for a  ${}^3\Sigma$ -state ?

(Meerut sp. paper 98)

**Ans.**  ${}^3\Pi_2$ ,  ${}^3\Pi_1$ ,  ${}^3\Pi_0$ ; no.

2. A  ${}^3\Delta$ -state has components of slightly different energies. What quantum number is used to indicate these components and how are its allowed values deduced ? Give the correct designation of the components. Do comparable components exist for a  ${}^3\Sigma$ -state ? Why ?

(Meerut sp. paper 93, 90)

**Ans.**  ${}^3\Delta_3$ ,  ${}^3\Delta_2$ ,  ${}^3\Delta_1$ ; no.

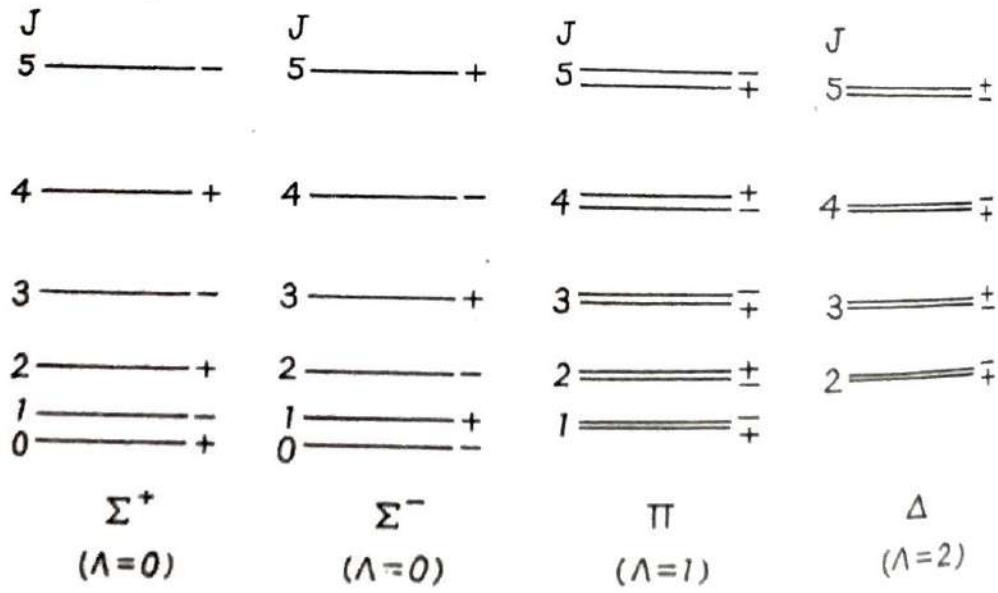
# Symmetry Properties of Rotational Levels : Nuclear Spin and Intensity Alternation

## 1. Symmetry Properties of Rotational Levels

The rotational levels of a given electronic state of a diatomic molecule are classified according to the behaviour of the *total* coordinate eigenfunction (not of the rotation eigenfunction alone) with respect to inversion at the origin of a space-fixed system of axes (not of a molecule-fixed system). A rotational level is called positive or negative according as the total coordinate eigenfunction  $\psi \left( = \psi_e \frac{1}{r} \psi_v \psi_r \right)$  remains unchanged or changes sign when inverted at such an origin (that is, when the signs of the coordinates of all electrons *and* the nuclei are reversed). By considering the symmetry properties of the functions  $\psi_e$ ,  $\psi_v$  and  $\psi_r$  separately, it may be seen that :

in a  $\Sigma^+$  state : even- $J$  levels are positive  
odd- $J$  levels are negative,  
and                            in a  $\Sigma^-$  state : even- $J$  levels are negative  
                                  odd- $J$  levels are positive,

as shown in Fig. 1.



(Fig. 1)

In  $\Pi$ ,  $\Delta$ , ..... states ( $\Lambda = 1, 2, \dots$ ), for each value of  $J$  there is a positive a negative rotational level of *equal* energy. For these states, levels with  $J < \Lambda$  do occur. Moreover, the degenerate levels are shown slightly splitted. Actually such a splitting appears when interaction of electronic motion with molecular rotation is taken into account.

The selection rule for transitions accompanied by dipole radiation is that **positive levels combine only with negative levels**, and vice versa. Symbolically :

$$+ \longleftrightarrow - , + \not\longleftrightarrow + , - \not\longleftrightarrow -$$

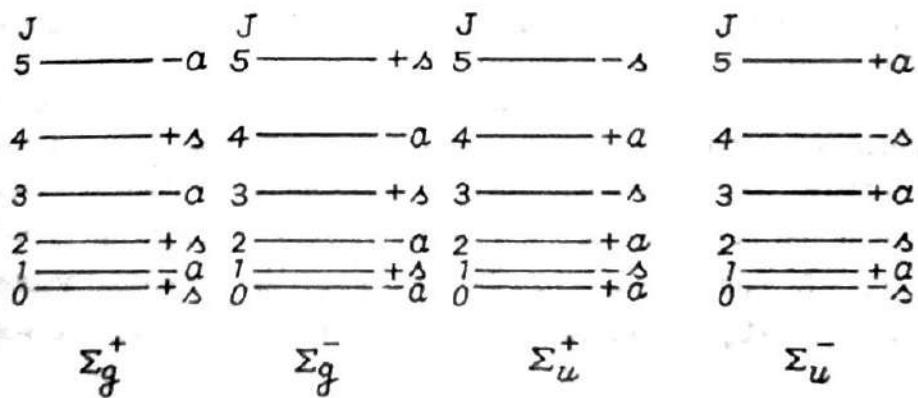
It can be seen from Fig. 1 that this selection rule supports the dipole-radiation selection rules for  $j$ , namely,  $\Delta J = \pm 1$  for  $\Lambda = 0$ ; and  $\Delta J = 0, \pm 1$  for  $\Lambda > 0$ .

The opposite selection rule holds for Raman transitions, that is, **positive levels combine with positive levels, and negative levels combine with negative levels**. Symbolically :

$$+ \longleftrightarrow + , - \longleftrightarrow - , + \not\longleftrightarrow -$$

Again, this rule supports the Raman selection rules for  $J$ , namely,  $\Delta J = 0, \pm 2$  for  $\Lambda = 0$ ; and  $\Delta J = 0, \pm 1, \pm 2$  for  $\Lambda > 0$ .

For (homonuclear) molecules having *identical* nuclei (such as  $O^{16}O^{16}$ , but not  $O^{16}O^{18}$ ) the wave equation remains unchanged if the two nuclei are mutually interchanged. This additional symmetry operation provides a further classification of the rotational levels. The levels are called symmetric (*s*) or antisymmetric (*a*) with respect to the nuclei according as the *total* coordinate eigenfunction  $\psi$  remains unchanged or only changes sign when the coordinates of the two nuclei are interchanged. It can be seen that the positive rotational levels are symmetric and the negative ones are antisymmetric for even electronic states ( $\Sigma_g^+$ ,  $\Sigma_g^-$ ); while the negative levels are symmetric and positive ones are antisymmetric for odd electronic states ( $\Sigma_u^+$ ,  $\Sigma_u^-$ ), as illustrated in Fig. 2.



(Fig. 2)

It can be noted that the even  $J$  levels are symmetric (*s*) and odd- $J$  levels are antisymmetric (*a*) when the electronic state is even and positive ( $\Sigma_g^+$ ) or odd and negative ( $\Sigma_u^-$ ). On the other hand, even- $J$  levels are antisymmetric (*a*) and odd- $J$  levels are symmetric (*s*) when the electronic state is even and negative ( $\Sigma_g^-$ ) or odd and positive ( $\Sigma_u^+$ ).

If the identical nuclei have zero nuclear spin, or if the interaction of the nuclear spin with the rest of the molecule is neglected, then a transition between a symmetric and an antisymmetric level is strictly prohibited. Symbolically,

$$a \not\longleftrightarrow s.$$

that is  $a \longleftrightarrow a$  and  $s \longleftrightarrow s$ . This rule holds not only for transitions with dipole radiation, but also for transitions with quadrupole radiation, Raman effect, collisions, etc.

The above rule supports the absence of infra-red rotation or vibration-rotation spectra of homonuclear molecules because the transitions  $\Delta J = \pm 1$  necessary for these spectra are in contradiction of the rule. However, Raman transitions  $\Delta J = 0, \pm 2$  do take place in homonuclear molecules because they are in accordance of the above rule.

## 2. Nuclear Spin and Intensity Alternation in Electronic Band Structure

The electronic bands of 'homonuclear' diatomic molecules ( $H_2, D_2, N_2, \dots$ ) show an alternation of intensities in their rotational structure; the rotational lines of each band are alternately weak and strong\*. The ratio of the intensities of successive lines is a characteristic of the (homonuclear) molecule. (The same intensity alternation is observed in the rotational Raman spectrum of these molecules). In case of certain molecules like  $O_2, C_2, \dots$  every second line is found totally missing. These observations are closely related with the spin of the nuclei of the molecule, and provide us an experimental method of determining nuclear spin.

The complete wavefunction  $\psi'$  for a molecule, including nuclear spin, may be written as the product

$$\psi' = \psi \beta,$$

where  $\psi$  is the coordinate wavefunction (including electron spin) and  $\beta$  is the nuclear spin wavefunction. In view of the exclusion principle, it is necessary that  $\psi'$  for a homonuclear diatomic molecule should either be symmetric or antisymmetric with respect to an exchange of the two nuclei according to whether the nuclei are bosons\*\* or fermions\*\* respectively.

Now, the symmetry of the co-ordinate wavefunction  $\psi$  is determined by the total orbital angular momentum of the rotating nuclei. It is symmetric ( $\psi_s$ ) for even- $J$  values and antisymmetric ( $\psi_a$ ) for odd- $J$  values when the electronic state is even and positive ( $\Sigma_g^+$ ) or odd and negative ( $\Sigma_u^-$ ). It is antisymmetric ( $\psi_a$ ) for even- $J$  values and symmetric ( $\psi_s$ ) for odd  $J$ -values when the electronic state is even and negative ( $\Sigma_g^-$ ) or odd and positive ( $\Sigma_u^+$ ). The rotational levels of a given electronic state are called symmetric ( $s$ ) or antisymmetric ( $a$ ) according as for them  $\psi$  is  $\psi_s$  or  $\psi_a$ .

\* This alternation of intensities of the rotational lines is superimposed on the usual Boltzmann intensity variation.

\*\* Nuclei having integral spins are bosons, while those having half-integral spins are fermions.

The spins of some of the nuclei are given in the following table :

	Spin $I$	Nuclei
bosons	{ 0	$He^4, C^{12}, O^{16}, S^{32}, Ca^{40}$
	1	$H^2, N^{14}$
fermions	{ $\frac{1}{2}$	$H^1, H^3, He^3, C^{13}, N^{15}, F^{19}, P^{31}$
	$\frac{3}{2}$	$Li^7, Na^{23}, Cl^{35, 37}, K^{39}, Br^{79, 81}$
	$\frac{5}{2}$	$O^{17}, I^{127}$
	$\frac{9}{2}$	$Bi^{209}$

Note that all nuclei whose mass number is an exact multiple of 4 have zero spin.

The nuclear spin wavefunction  $\beta$  for the molecule is constructed from the wavefunctions of the individual nuclei. If the spin quantum number for each nucleus is  $I$ , then each nucleus has  $2I + 1$  linearly independent spin wavefunctions (corresponding to  $M_I = I, I - 1, I - 2, \dots, -I$ ). They form  $(2I + 1)(2I + 1)$  spin wavefunctions for the molecule. Of these  $(2I + 1)I$  are symmetric ( $\beta_s$ ), and  $(2I + 1)I$  are antisymmetric ( $\beta_a$ ) with respect to exchange of nuclei. Thus, the ratio of the nuclear-spin statistical weights for the symmetric and antisymmetric spin states is

$$\frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{(2I + 1)(I + 1)}{(2I + 1)I} = \frac{I + 1}{I}.$$

This has important consequences regarding the relative population of the rotational levels of homonuclear molecules. The symmetric ( $s$ ) and antisymmetric ( $a$ ) levels do occur with different statistical weights. (Whether the even- $J$  levels, or the odd- $J$  levels, are the stronger depends upon the nature of the electronic state and that of the nuclei). This causes the rotational lines to alternate in intensity. In case of molecules with zero nuclear spin ( $I = 0$ ) the antisymmetric rotational levels, and hence alternate lines, are totally missing.

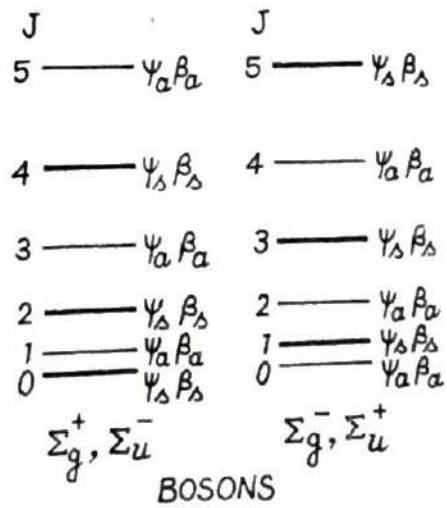
Let us treat the cases of bosons and fermions separately :

**Bosons :** When the nuclei of the homonuclear diatomic molecule are bosons, the complete wavefunction  $\psi'$  must be symmetric; so that states with following combinations of coordinate and nuclear-spin wavefunctions are possible :

$$\psi_s \beta_s \text{ and } \psi_a \beta_a.$$

Since symmetric nuclear-spin wavefunction ( $\beta_s$ ) corresponds to a higher statistical weight, and it is combined with symmetric coordinate wavefunction ( $\psi_s$ ), we conclude that in bosons, the symmetric rotational levels (belonging to  $\psi_s$ ) are the stronger. (In the extreme case of zero nuclear spin, like  $O_2$ , the antisymmetric rotational levels are totally missing).

In  $\Sigma_g^+$  and  $\Sigma_u^-$  states, even- $J$  levels are symmetric ( $\psi_s$ ), and hence stronger; while in  $\Sigma_g^-$  and  $\Sigma_u^+$  states, odd- $J$  levels are symmetric ( $\psi_s$ ) and hence they are stronger (Fig. 3). This conclusion holds for bosons.



(Fig. 3)

**Fermions :** When the nuclei of the molecule are fermions, the complete wavefunction  $\psi'$  must be antisymmetric; so that states with the following combinations are possible :

$$\psi_s \beta_a \text{ and } \psi_a \beta_s.$$

Now the symmetric nuclear-spin wavefunction ( $\beta_s$ ), which always corresponds to higher statistical weight, is combined with antisymmetric coordinate wavefunction ( $\psi_a$ ) and hence in fermions, the antisymmetric rotational levels (belonging to  $\psi_a$ ) are the stronger.

states with following combinations of coordinate wavefunction  $\psi$  and nuclear-spin wavefunction  $\beta$  are possible :

$$\psi' = \psi_s \beta_a, \psi_a \beta_s.$$

The ground electronic state of  $H_2$  is  ${}^1\Sigma_g^+$  (even and positive), and so even- $J$  levels are symmetric (belong to  $\psi_s$ ) and odd- $J$  levels are anti-symmetric (belong to  $\psi_a$ ). In view of the above combinations, the nuclear-spin wavefunctions corresponding to even- $J$  and odd- $J$  levels are  $\beta_a$  and  $\beta_s$ , respectively. Since  $\beta_s$  corresponds to a higher statistical weight, the odd- $J$  levels are stronger (Fig. 6).

The population ratio of rotational levels (= statistical weight ratio) is

$$\frac{\text{odd-}J}{\text{even-}J} = \frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{(1/2)+1}{1/2} = \frac{3}{1}.$$

The rotational Raman transitions corresponding to Stokes lines and the resulting spectrum are shown in Fig. 6. (The numbers written at the top of the spectral lines represent  $J$  value of the lower level involved). The odd- $J$  lines must be three times as strong as the even- $J$  lines, ignoring Boltzmann intensity variation. This is found in agreement with experiment. Conversely, from the observed intensity ratio we can determine the nuclear spin  $I$  of hydrogen, and conclude that it follows Fermi-Dirac statistics.

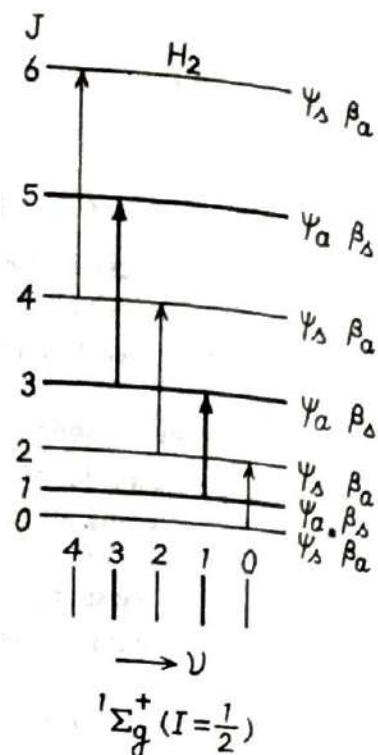
**D<sub>2</sub> and N<sub>2</sub>** : A heavy-hydrogen or nitrogen nucleus has a spin given by

$$I = 1.$$

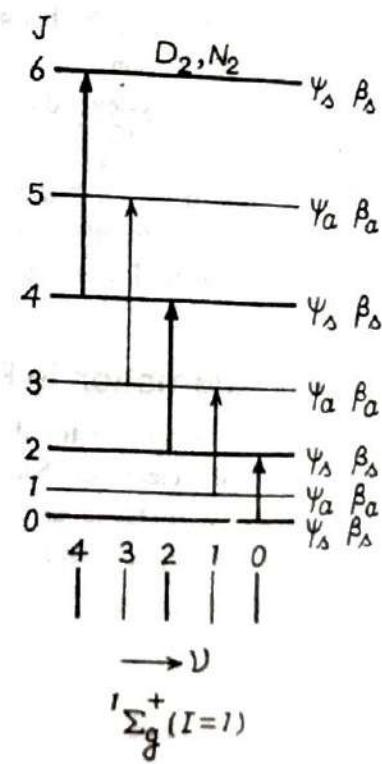
The nuclei of the D<sub>2</sub> and N<sub>2</sub> molecules are bosons and so the complete molecular wavefunction  $\psi'$  must be symmetric, having following combinations :

$$\psi' = \psi_s \beta_s, \psi_a \beta_a.$$

Again, the ground electronic state is  ${}^1\Sigma_g^+$  (even and positive), and so even- $J$  levels belong to  $\psi_s$ , and odd- $J$  levels belong to  $\psi_a$ . But now, in view of the above combinations, the even- $J$  and odd- $J$  levels have nuclear spin wavefunctions  $\beta_s$  and  $\beta_a$  respectively. As such, in molecules D<sub>2</sub> and N<sub>2</sub>, the even- $J$  levels (belonging to  $\beta_s$ ) are stronger (Fig. 7).



(Fig. 6)



(Fig. 7)

The population ratio of the rotational levels is

$$\frac{\text{even-}J}{\text{odd-}J} = \frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{1+1}{1} = \frac{2}{1}.$$

In the rotational Raman spectrum, therefore, the even- $J$  lines must be twice as strong as odd- $J$  lines (Fig. 7). This is actually found to be the case which confirms that the nuclei of  $D_2$  and  $N_2$  have a spin  $I = 1$  and follow Bose-Einstein statistics.

$O_2$ : The oxygen nucleus has a spin

$$I = 0,$$

and is a boson. Hence the  $O_2$  molecule has only one nuclear-spin wavefunction, namely\*,

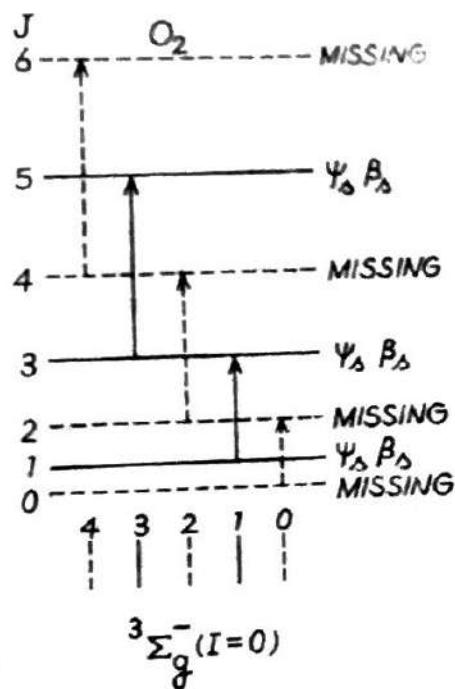
$$\beta_s = \beta^*(1) \beta^*(2),$$

which is symmetric with respect to the two nuclei. The complete molecular wavefunction  $\psi'$ , which must be symmetric (because the nuclei are bosons) is formed with the only possible combination,

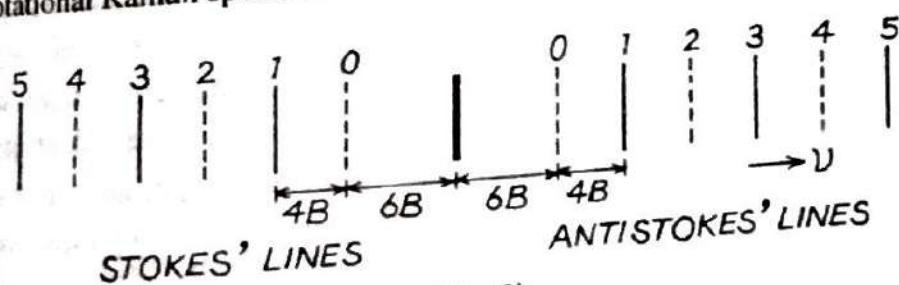
$$\psi' = \psi_s \beta_s.$$

The ground state of  $O_2$  molecule is  ${}^3\Sigma_g^-$  (even and negative), and so even- $J$  levels belong to  $\psi_a$  and odd- $J$  levels belong to  $\psi_s$ . Since in view of the above combination, the antisymmetric coordinate wavefunction  $\psi_a$  is not possible, the even- $J$  levels are missing (Fig. 8). Hence alternate lines, the even- $J$  lines, are missing from the rotational Raman spectrum. (Only odd- $J$  lines appear). Conversely, the absence of alternate rotational lines shows that the spin for each of the nuclei of the molecule is zero.

It appears difficult to decide whether every second line is missing or the rotational lines could be represented by a suitable choice of the rotational constant  $B$ , without assumption of missing lines. In fact, an unambiguous decision is always possible. Let us consider Fig. 9, which shows a rotational Raman spectrum.



(Fig. 8)



(Fig. 9)

\*For each nucleus,

$$I = 0.$$

The quantum number corresponding to the possible spin component in a field direction is

$$M_I = 0.$$

Hence the possible spin functions for the nuclei, labelled (1) and (2), are  $\beta^*(1)$  and  $\beta^*(2)$ .

There are three possibilities :

(i) if no line is missing, then the ratio

$$\frac{\text{separation between first Stokes and first anti-Stokes lines}}{\text{separation between successive lines in either branch}} = \frac{12B}{4B} = \frac{6}{2},$$

(ii) if even- $J$  lines are missing, then the above ratio is  $20B/8B = 5:2$ ,  
and (iii) if odd- $J$  lines are missing then the ratio is  $12B/8B = 3:2$ .

Therefore, without knowing  $B$ , we can decide with which case we are dealing. In case of Raman spectrum of  $O_2$ , this ratio is experimentally found to be  $5:2$ . Hence we can conclude that even- $J$  lines are missing.

#### 4. Ortho and Para Modifications

In a molecule, the spins of the nuclei can be considered, to a very good approximation, to have no interaction with one another or with the electrons of the molecule. This means that the nuclear-spin wavefunction is almost a constant of motion, remaining unchanged during a radiative transition of the molecule. Obviously, in a homonuclear diatomic molecule the nuclear-spin symmetry remains unchanged during a transition. Since, for a given type of (homonuclear) molecule, the space-symmetry of the molecular wavefunction is uniquely related with the nuclear-spin symmetry; the space-symmetry also does not change during a molecular transition. In other words, the selection rule regarding the space-symmetry of rotational levels is

$$\text{symmetric} \leftrightarrow \text{antisymmetric}.$$

This rule holds for collisions as well. For a given (homonuclear) molecule, the space-symmetry is directly connected with the evenness or oddness of  $J$ . Therefore, in a given electronic state, the even- $J$  level can combine only with the even- $J$  level, and odd- $J$  level with odd- $J$  level. This means that, once a molecule finds itself in a state of even- $J$ , it will tend always to remain in a state of even- $J$ , and similarly for odd  $J$ . In fact, the selection rule  $\text{sym} \leftrightarrow \text{antisym}$  holds absolutely for molecules having zero nuclear spin. For molecules with non-zero nuclear spin, the rule does not hold absolutely, though holds sufficiently strictly; and a molecule may go from an even- $J$  to an odd- $J$  level (or vice-versa) but the time required for such a transition is often quite long (depending upon the magnitude of nuclear-spin interactions)-sometimes days, weeks or months.

Dennison pointed out that in view of the sufficient strictness of the rule  $\text{sym} \leftrightarrow \text{antisym}$ , we can think of the separate physical existence of two distinct modifications of a given homonuclear diatomic molecule with non-zero nuclear spin (such as  $H_2$ ,  $D_2$ ,  $N_2$ ) one occupying the even- $J$  levels and the other the odd- $J$  levels. The modification corresponding to a symmetric nuclear-spin state (larger statistical weight) is called the 'ortho modification', and that corresponding to an antisymmetric nuclear-spin state is called the 'para modification'.

Let us consider the case of hydrogen molecule. The spin of each of its nuclei is  $I = \frac{1}{2}$ . This relative nuclear-spin statistical weights for the symmetric and antisymmetric nuclear-spin states are

$$\frac{N_s}{N_a} = \frac{I+1}{I} = \frac{(1/2)+1}{1/2} = \frac{3}{1}.$$

At ordinary temperatures, when many rotational states of the molecule are excited, the ortho-hydrogen is three times as abundant as the para-hydrogen, that is, ordinary hydrogen gas is three-fourth ortho-hydrogen and one-fourth para-hydrogen. In this case of  $I = \frac{1}{2}$ , the ortho modification has parallel nuclear spins ( $\uparrow\uparrow$ ) and the para modification has antiparallel nuclear spins ( $\uparrow\downarrow$ ). In the ground electronic state ( ${}^1\Sigma_g^+$ ) of  $H_2$ , the ortho modification occupies the odd- $J$  levels, and the para modification occupies the even- $J$  levels (Fig. 10).

We can, however, demonstrate the existence of these two modifications. If we maintain the hydrogen gas at very low temperature (under catalyzing effect of charcoal) for several days, all the molecules eventually settle into the lowest rotational state  $J = 0$ , which occurs only for the para hydrogen. That is, the gas is all para-hydrogen. If the gas is now allowed to warm up to ordinary temperature, the molecules at first can only go from  $J = 0$  to the higher even- $J$  levels due to the sufficiently strict rule sym  $\leftrightarrow$  antisym. Hence for some time, the gas remains in the pure 'para' state. During this period, the alternate odd- $J$  lines, which are stronger in the spectrum of ordinary hydrogen, remain absent from the rotational Raman spectrum. After this period, when normal equilibrium is established between the two forms of hydrogen, these lines reappear and with a greater intensity than those already present.

Various physical phenomena other than spectral transitions are different for ortho- and para-hydrogen (for example, the heat capacity and heat conductivity) which can help to distinguish between the two modifications.

When this method is applied for  $D_2$ , ortho-form is produced because in this case the lowest level  $J = 0$  belongs to the ortho-deuterium. Moreover for  $D_2$  ( $I = 1$ ), in contrast to  $H_2$ , the strong (ortho) and weak (para) levels are not differentiated by the parallel and antiparallel orientation of the nuclear spins, but by the fact that for the weak levels the nuclear spins are at  $60^\circ$  to each other, while for the strong levels the nuclear spins may be parallel as well as antiparallel.

Homonuclear molecules having zero nuclear spin, like  $O_2$ , occur only in one modification, the "ortho".

## 5. Isotopic Molecules

In the case of isotopic molecules like  $O^{16}O^{18}$ ,  $Cl^{35}Cl^{37}$ ,  $N^{14}N^{15}$ , the exchange of nuclei produces a configuration which is different from the original one. That is, the exchange of nuclei is *not* a symmetry operation. Therefore, the rotational levels of these molecules are not classified as symmetric and antisymmetric. As a result, there should be no alternation of intensities or no missing of alternate lines in isotopic molecules. This is actually found to be the case. The electronic bands of the  $O^{16}O^{18}$  molecule have all the

$J$	$H_2$	$\gamma_a \beta_s$	$\uparrow\uparrow$	ORTHO
5				
4		$\gamma_s \beta_a$	$\uparrow\downarrow$	PARA
3		$\gamma_a \beta_s$	$\uparrow\uparrow$	ORTHO
2		$\gamma_s \beta_a$	$\uparrow\downarrow$	PARA
1		$\gamma_a \beta_s$	$\uparrow\uparrow$	ORTHO
0		$\gamma_s \beta_a$	$\uparrow\downarrow$	PARA
		${}^1\Sigma_g^+ (I = \frac{1}{2})$		

(Fig. 10)

rotational lines, whereas every second line is missing in the bands of  $O_2(O^{16}O^{16})$ . Similarly, there are no ortho and para modifications for the isotopic molecule HD, as they are for  $H_2$  and  $D_2$ . An HD molecule can go over without restriction from an even- $J$  level to an odd- $J$  level, for example, by collision.

### SOLVED PROBLEMS

1. What do you understand by symmetric and antisymmetric nuclear-spin wavefunctions of a homonuclear diatomic molecule? Construct spin wavefunctions for the  $H_2$  and  $D_2$  molecules.

**Solution.** For a homonuclear diatomic molecule, the wavefunctions which remain unchanged with respect to an exchange of the nuclei are symmetric, while those which change sign are antisymmetric.

The nuclear-spin wavefunction  $\beta$  for the molecule is constructed from the wavefunctions of the individual nuclei. If the spin quantum number for each nucleus is  $I$ , there are  $(2I + 1)$  linearly independent wavefunctions corresponding to the values of the  $z$ -component of  $I$ , that is

$$M_I = I, I - 1, I - 2, \dots, -I,$$

a total of  $(2I + 1)$  values.

Let us consider the case of  $H_2$  molecule. For H nucleus,  $I = \frac{1}{2}$ , so that

$$M_I = \frac{1}{2}, -\frac{1}{2}.$$

The possible spin wavefunctions for each of the two nuclei say, 1 and 2, are

$$\beta^{1/2}(1), \beta^{-1/2}(1)$$

and

$$\beta^{1/2}(2), \beta^{-1/2}(2).$$

The nuclear spin wavefunctions for the  $H_2$  molecule would be the symmetric and antisymmetric combinations of the above. There are four possibilities :

$$\left. \begin{array}{l} \beta^{1/2}(1), \beta^{1/2}(2) \\ \beta^{-1/2}(1), \beta^{-1/2}(2) \end{array} \right\} \text{symmetric}$$

$$\left. \begin{array}{l} \beta^{1/2}(1), \beta^{-1/2}(2) \\ \beta^{-1/2}(1), \beta^{1/2}(2) \end{array} \right\} \text{no definite symmetry property}$$

We can make linearly independent combination of the last two, which are

$$\frac{1}{\sqrt{2}} [\beta^{1/2}(1)\beta^{-1/2}(2) + \beta^{-1/2}(1)\beta^{1/2}(2)] \text{symmetric}$$

$$\frac{1}{\sqrt{2}} [\beta^{1/2}(1)\beta^{-1/2}(2) - \beta^{-1/2}(1)\beta^{1/2}(2)] \text{antisymmetric}$$

Thus, we have three symmetric and one antisymmetric nuclear spin wavefunctions for  $H_2$ .

Let us now take up  $D_2$  molecule. For D nucleus,  $I = 1$ .

$$\therefore M_I = 1, 0, -1,$$

The possible spin wavefunctions of the two nuclei 1, 2, are

$$\beta^+ (1), \beta^0 (1), \beta^- (1)$$

and

$$\beta^+ (2), \beta^0 (2), \beta^- (2).$$

The spin function for the molecule would be the symmetric and antisymmetric combinations of any two of the above. There are 9 possibilities

$$\begin{array}{l}
 \beta^+(1) \beta^+(2) \\
 \beta^0(1) \beta^0(2) \\
 \beta^-(1) \beta^-(2) \\
 \frac{1}{\sqrt{2}} [\beta^+(1) \beta^0(2) + \beta^+(2) \beta^0(1)] \\
 \frac{1}{\sqrt{2}} [\beta^+(1) \beta^-(2) + \beta^+(2) \beta^-(1)] \\
 \frac{1}{\sqrt{2}} [\beta^-(1) \beta^0(2) + \beta^-(2) \beta^0(1)] \\
 \frac{1}{\sqrt{2}} [\beta^+(1) \beta^0(2) - \beta^+(2) \beta^0(1)] \\
 \frac{1}{\sqrt{2}} [\beta^+(1) \beta^-(2) - \beta^+(2) \beta^-(1)] \\
 \frac{1}{\sqrt{2}} [\beta^-(1) \beta^0(2) - \beta^-(2) \beta^0(1)]
 \end{array} \left. \begin{array}{l} \\ \\ \\ \text{symmetric} \\ \\ \\ \\ \\ \text{antisymmetric} \\ \\ \end{array} \right\}$$

Thus, for  $I = 1$  we have 6 symmetric spin wavefunctions, and 3 antisymmetric ones for the molecule.

**2. Show that the ratio of the number of symmetric spin states to the number of antisymmetric spin states in a molecule is  $(I + 1)/I$ , where  $I$  is the nuclear-spin quantum number.**

(Meerut sp. paper 2004, 03, 02, 01)

**Solution.** The number of possible spin states for a nucleus of a given spin quantum number  $I$  is  $(2I + 1)$ , equal to the number of possible values of its  $z$ -component quantum number  $M_I$ , where

$$M_I = I, I - 1, I - 2, \dots, -I.$$

Since the values of  $M_I$  differ by integers and range from  $I$  to  $-I$ , this number is  $(2I + 1)$ . So the total number of possible independent combinations of spin states for the two (identical) nuclei of a diatomic molecule is

$$(2I + 1)(2I + 1) = (2I + 1)^2$$

In  $(2I + 1)$  of these states both nuclei will have the same  $M_I$ , and so are in identical spin states. For these the nuclear-spin wavefunction of the molecule is symmetric with respect to an exchange of the nuclei.

Of the remaining

$$(2I + 1)^2 - (2I + 1) = 2I(2I + 1)$$

states, half will be symmetric and half antisymmetric, because half will involve the sums of products of individual spin wavefunctions and the other half will involve the differences of the same products. So the total number of symmetric wavefunctions is

$$(2I + 1) + \left(\frac{1}{2}\right)2I(2I + 1) = (2I + 1)(I + 1)$$

and the total number of antisymmetric wavefunctions is

$$\left(\frac{1}{2}\right)2I(2I + 1) = (2I + 1)I.$$

Thus, the ratio of symmetric and antisymmetric wavefunctions or spin states, is

$$\frac{(2I+1)(I+1)}{(2I+1)I} = \frac{I+1}{I}$$

3. What are the relative populations of alternate rotational levels of  ${}^1\Sigma_g^+$  states for  $B_2$ ,  $O^{17}O^{17}$  and  $O^{16}O^{17}$  molecules? Ignore Boltzmann factors. Nuclear spins of  $B$  and  $O^{17}$  and 3 and  $\frac{5}{2}$  respectively.

**Solution.** The spin of each nucleus of  $B_2$  is

$$I = 3.$$

Therefore, the ratio of the nuclear-spin statistical weights of the symmetric and antisymmetric spin states is

$$\frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{4}{3}.$$

The nuclei are bosons ( $I$  integral), and so the symmetric nuclear-spin states ( $\beta_s$ ) are associated with symmetric rotational states ( $\psi_s$ ), and  $\beta_a$  states are associated with  $\psi_a$  states, so that the complete molecular wavefunction is symmetric.

For the state  ${}^1\Sigma_g^+$  (even and positive), the even- $J$  levels are symmetric ( $\psi_s$ ) and the odd- $J$  levels are antisymmetric ( $\psi_a$ ). Hence the population ratio of even-numbered to odd-numbered rotational levels is

$$\frac{\text{even-}J(\psi_s \beta_s)}{\text{odd-}J(\psi_a \beta_a)} = \frac{N_s}{N_a} = \frac{4}{3}.$$

The spin of each nucleus of  $O^{17}O^{17}$  is

$$I = \frac{5}{2}.$$

In this case, we have

$$\frac{N_s(\beta_s)}{N_a(\beta_a)} = \frac{I+1}{I} = \frac{7}{5}.$$

The nuclei are now fermions ( $I$  half-integral), and so the complete molecular wavefunction must be antisymmetric with respect to the nuclei. Hence the possible combinations of coordinate and nuclear-spin wavefunctions are  $\psi_s \beta_a$  and  $\psi_a \beta_s$ .

Again, for the state  ${}^1\Sigma_g^+$ , the even- $J$  levels are symmetric ( $\psi_s$ ) and the odd- $J$  levels are antisymmetric ( $\psi_a$ ). Therefore,

$$\frac{\text{even-}J(\psi_s \beta_a)}{\text{odd-}J(\psi_a \beta_s)} = \frac{N_a}{N_s} = \frac{5}{7}.$$

In case of isotopic molecule  $O^{16}O^{17}$ , the population is not affected by nuclear spin. It is governed by Boltzmann factor only.

4. What is the total degeneracy of the  $J = 0, 1$  and  $2$  levels of the ground electronic state of (i)  $H_2$ , (ii)  $D_2$ , (iii)  $HD$  and (iv)  $C_2$  molecules?

**Solution.** The rotational levels of all diatomic molecules have a  $(2J+1)$  space-degeneracy.

The nuclear-spin statistical weight has the value  $(2I_A + 1)(2I_B + 1)$  for all rotational levels of a heteronuclear or isotopic molecule, where  $I_A$  and  $I_B$  are the spins of the (different) nuclei of the molecule. In case of homonuclear molecules, however, the

(Meerut sp. paper 96, 93)

nuclear statistical weight takes different values for the symmetric and antisymmetric nuclear-spin states. If  $I$  is the spin of each of the two (identical) nuclei, then

$$N_s = (2I + 1)(I + 1)$$

$$N_a = (2I + 1)I.$$

Hence the total degeneracy of the rotational levels of a heteronuclear molecule is  $(2I_A + 1)(2I_B + 1)(2J + 1)$ ; while for a homonuclear molecule it is  $(2I + 1)(I + 1)(2J + 1)$  for levels belonging to symmetric nuclear-spin states, and  $(2I + 1)I(2J + 1)$  for levels belonging to antisymmetric spin states.

Let us now consider the given molecules.

$$I = \frac{1}{2} \text{ (fermion).}$$

(i)  $\text{H}_2$  : In the ground state  ${}^1\Sigma_g^+$ , even- $J$  levels are space-symmetric and odd- $J$  levels are space-antisymmetric and are the stronger ones (because nuclei are fermions,  $\psi' = \psi_s \beta_a, \psi_a \beta_s$ ). Hence the total degeneracies are :

$$\text{for } J = 0; (2I + 1)I \times (2J + 1) = 1 \times 1 = 1,$$

$$\text{for } J = 1; (2I + 1)(I + 1) \times (2J + 1) = 3 \times 3 = 9,$$

$$\text{for } J = 2; (2I + 1)I \times (2J + 1) = 1 \times 5 = 5.$$

(ii)  $\text{D}_2$  :  $I = 1$  (boson).

In this case even- $J$  levels are the stronger. Therefore,

$$\text{for } J = 0; (2I + 1)(I + 1) \times (2J + 1) = 6 \times 1 = 6,$$

$$\text{for } J = 1; (2I + 1)I \times (2J + 1) = 3 \times 3 = 9,$$

$$\text{for } J = 2; (2I + 1)(I + 1) \times (2J + 1) = 6 \times 5 = 30.$$

(iii)  $\text{HD}$  : It is an isotopic molecule and so all rotational levels have the same nuclear-spin degeneracy  $(2I_A + 1)(2I_B + 1)$ .

$$I_A = \frac{1}{2}, I_B = 1,$$

Thus, we have

$$\text{for } J = 0; (2I_A + 1)(2I_B + 1) \times (2J + 1) = 6 \times 1 = 6,$$

$$\text{for } J = 1; (2I_A + 1)(2I_B + 1) \times (2J + 1) = 6 \times 3 = 18,$$

$$\text{for } J = 2; (2I_A + 1)(2I_B + 1) \times (2J + 1) = 6 \times 5 = 30.$$

(iv)  $\text{C}_2$  :  $I = 0$  (boson).

For  $\text{C}_2$ , the ground electronic state is  ${}^3\Pi_u (\Lambda = 1)$ . In this state the level  $J = 0$  does not exist.

All other levels  $J = 1, 2$  have  $\Lambda$ -doubling, but for  $\text{C}_2 (I = 0)$  one of these components is missing. Thus, the degeneracy of the appearing components is given by :

$$\text{for } J = 1; (2I + 1)(I + 1)(2J + 1) = 3$$

$$\text{for } J = 2; (2I + 1)(I + 1)(2J + 1) = 5.$$

## QUESTIONS

1. Describe the symmetry properties of the rotational levels for the homonuclear diatomic molecule. (Meerut 98 S)

Based on these properties, obtain the general features of the rotational structure for the  ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$  electronic transition. (Meerut sp. paper 2000, 96 93)

2. Explain the intensity alternation in the rotational structure of the  ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$  transition for the  $H_2$  molecule. State the relative intensities of lines, ignoring Boltzmann factors.

3. The Lyman bands of  $H_2$  arise due to the  ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$  transition. In these bands odd-numbered rotationl lines are found to be stronger. Predict the statistics of the hydrogen nuclei.

**Ans.** The odd-numbered rotational lines are those involving the odd- $J$  levels in the lower state  ${}^1\Sigma_g^+$ . In the even and positive electronic state, the odd- $J$  levels are antisymmetric (belong to  $\psi_a$ ). Since these levels are observed to be stronger, they correspond to symmetric nuclear-spin wavefunction  $\beta_s$ . The complete wavefunction for the molecule  $H_2$  is thus  $\psi' = \psi_u \beta_s$  which is antisymmetric with respect to the exchange of nuclei. Hence we conclude that the H nuclei (protons) follow Fermi-Dirac statistics.

4. Explain intensity alternations observed in the electronic spectra of homonuclear molecules with special reference to nuclear statistics. Discuss the changes produced in the spectrum by the presence of isotopic molecules. (Meerut 97, 89)

5. Explain the intensity alternation in the rotational Raman spectrum of  $H_2$  molecule. (Meerut sp. paper 2002 S, 98, 95 S, 90)

6. Explain the intensity alternation in the rotational Raman spectrum of  $H_2$  and  $O_2$  molecules. (Meerut 98 S)

7. Discuss the intensity alternation in the rotational Raman lines in the spectrum of a homonuclear diatomic molecule. Consider  $H_2$  and  $N_2$  molecules. (Meerut 99 S)

8. Discuss intensity alternation in the rotational Raman spectrum of a homonuclear diatomic molecule. How can this be used to find the nuclear spin of the molecule. (Meerut sp. paper 97)

9. Describe how one can conclude from the alternation of intensities observed in the rotational Raman spectrum of  $N_2$  molecule that the nitrogen nuclei obey Bose-Einstein statistics and further, that the nitrogen nuclei contain an even number of particles.

**Ans.** In  $N_2$ , the rotational Raman lines involving the even- $J$  levels are observed to be stronger. Hence these levels correspond to symmetric nuclear-spin state ( $\beta_s$ ). Since the ground electronic state of  $N_2$  is even and positive ( ${}^1\Sigma_g^+$ ), the even- $J$  levels are space-symmetric, that is, belong to symmetric coordinate wavefunction ( $\psi_s$ ). Thus, the symmetric nuclear-spin states are associated with the symmetric rotational states, that is, the complete molecular wavefunction  $\psi' = \psi_s \beta_s$  is symmetric. Therefore, the  $N$  nuclei must be bosons. This means that for  $N$  the nuclear spin  $I$  is integral. Since both the proton and the neutron have a spin of  $\frac{1}{2}$ , an even number of particles would yield an integral value of  $I$ .

10. Indicate briefly how nuclear spins can be determined by studying atomic and molecular spectra. Discuss the relative merits of the two methods when the spins to be determined are (i) 0, (ii) 1 and (iii) 9/2.

**Hint.** For (i) and (ii), the molecular spectra method based on intensity alternation are better. For (iii), the intensity ratio of  $(I + 1)/I = 11/9$  is difficult to measure.

but the counting of the  $2I + 1 = 10$  components in Back-Goudsmit effect is very easy. Hence atomic spectra method is better.

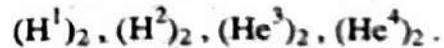
11. How is the existence of the ortho and the para forms of hydrogen molecule explained?

12. Account for : "The hydrogen molecule exists in ortho and para forms in the ground electronic state, unlike the helium atom which exists only in para form in the ground state."

Hint. The helium atom in its *ground state*  $1s^2$  has antiparallel spins of its two electrons. Hence it may be said to occur only in 'para' form.

### PROBLEMS

1. Find the ratio of intensities of adjacent lines in an electronic band spectrum of the following homonuclear diatomic molecules which are assumed to be in perfect thermal equilibrium. Assume  $kT$  so large that one may ignore the variation of intensity due to Boltzmann factor.



Ans. 3 : 1, 2 : 1, 3 : 1, 1 : 0 (alternate lines are missing).

2. Determine the values of the nuclear spin quantum number  $I$  for the nuclei in  $\text{N}_2$  and  $\text{C}_2$ , by using the measured intensity ratio 2/1 and 1/0. Ans. 1, 0.

3. Band spectrum measurements of diatomic molecules containing  $\text{Cl}^{35}$  nuclei yield an alternating intensity ratio of 3/5. What is the spin of the  $\text{Cl}^{35}$  nucleus.

Ans. 3/2.

## Coupling of Rotational and Electronic Motions : Types of Electronic Transitions

### 1. Rotational and Electronic Interactions

In an actual molecule, the nuclei vibrate relative to each other and also rotate as a whole about the centre of mass of the molecule. These nuclear motions and the electronic motion occur simultaneously and interact with each other. The total energy of the molecule is, therefore, not merely made up of three independent components, corresponding to the equation,

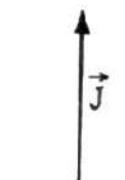
$$E = E_e + E_v + E_r,$$

but small interaction energies are to be included. The electronic-vibrational interaction is automatically taken into account when the vibrational levels are chosen so as to fit the potential curve of the electronic state. We have now to consider the electronic-rotational interaction and its influence on the rotational levels in different types of electronic states.

In general, the total angular momentum of a diatomic molecule is the resultant of three angular momenta : the electronic orbital angular momentum, the electronic spin angular momentum and the nuclear rotational angular momentum (it does not include nuclear spin) ; and is represented by vector  $\vec{J}$ , which has a magnitude of  $\sqrt{J(J+1)} \hbar/2\pi$ .

If the molecule is in a  ${}^1\Sigma$  state, that is, the electronic orbital angular momentum as well as the electronic spin angular momentum is zero ( $\Lambda = 0, S = 0$ ) ; the nuclear rotational angular momentum is identical with the total angular momentum  $\vec{J}$ . This corresponds to the 'vibrating-rotator' model (Fig. 1) whose rotational energy is expressed by

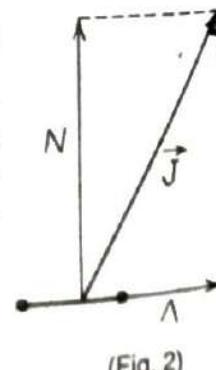
$$F(v, J) = B_v J(J+1),$$



(Fig. 1)

neglecting the term for the non-rigidity of the molecule.

If the molecule is in a singlet ( $S = 0$ ) state corresponding to  $\Lambda > 0$ , that is, in one of the  ${}^1\Pi, {}^1\Delta, \dots$  states, it then corresponds to the 'symmetric top' model (Fig. 2). In this case, the nuclear rotational angular momentum component  $N^\dagger$  perpendicular to the internuclear axis and the electronic orbital angular momentum component  $\Lambda$  along the internuclear axis form the total angular momentum  $\vec{J}$ . The rotational energy of the molecule is expressed by



(Fig. 2)

<sup>†</sup> The magnitude of the nuclear rotational angular momentum is  $N \frac{\hbar}{2\pi}$ , but  $N$  is not a quantum number. Its value is determined by the values of the quantum numbers  $J$  and  $\Lambda$ .

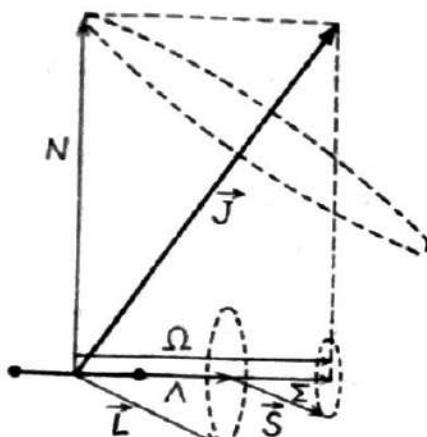
$$F(v, J) = B_v J(J + 1) + (A - B_v) \Lambda^2.$$

neglecting the centrifugal term.

In all other electronic states, the rotational energy depends upon the modes of the coupling between the various angular momenta. F. Hund, in 1926, described four types of couplings depending upon which of the different interactions predominate. These molecular models are called Hund's cases (a), (b), (c) and (d). They, however, represent limiting situations and most molecular states show an intermediate type of behaviour in practice.

## 2. Hund's Coupling Case (a)

This case occurs only for states corresponding to  $\Lambda > 0$ , and is illustrated in Fig. 3. In this case, the interaction of the nuclear rotation with electronic orbital and spin motions is weak. Instead, the electronic orbital angular momentum vector  $\vec{L}$  precesses rapidly about the internuclear axis with quantised component  $\Lambda$ . Further, in case (a), the magnetic field generated by the orbiting electrons is sufficiently strong to couple the spin vector  $\vec{S}$  to the internuclear axis, that is,  $\vec{S}$  also precesses rapidly about this axis with quantised component  $\Sigma^\dagger$ . The total component of electronic angular momentum about the axis has a magnitude  $\Omega$  ( $h/2\pi$ ), where the quantum number  $\Omega$  is the algebraic sum  $|\Lambda + \Sigma|$ , and takes  $2S + 1$  values ranging from  $\Lambda + S$  to  $\Lambda - S$ .



(Fig. 3)

The electronic angular momentum component  $\Omega$  along the internuclear axis and the nuclear rotational angular momentum component  $N$  perpendicular to the internuclear axis form, for the whole molecule, the total angular momentum  $\vec{J}$ . [Hund's case (a) is thus identical to the symmetric-top model except that now we have  $\Omega$  in place of  $\Lambda$ ]. The vector  $\vec{J}$  is constant in magnitude and direction. Both  $\Omega$  and  $N$  rotate about this vector (nutation). This molecular rotation is, however, much slower than the precession of  $\vec{L}$  and  $\vec{S}$  about the internuclear axis.

Since  $\Omega$  is the component of  $\vec{J}$  along the internuclear axis, ( $\vec{J}$  cannot be smaller than  $\Omega$ ), the quantum number  $J$  has the possible values

$$J = \Omega, \Omega + 1, \Omega + 2, \dots$$

$\Omega$ , and hence  $J$ , is integral or half-integral according as  $\Sigma$  is integral or half-integral. Thus, associated with each electronic sub-state (with a given  $\Omega$ ) there is a set of rotational levels with  $J = \Omega, \Omega + 1, \dots$ . Levels with  $J < \Omega$  do not occur.

In order to calculate these rotational energy levels we must find the nuclear rotational angular momentum  $N \frac{h}{2\pi}$ . Here  $N$  is not a quantum number, its value is fixed by the values of the quantum numbers  $J$  and  $\Omega$ , by (see vector diagram)

$$N^2 = J(J + 1) - \Omega^2.$$

<sup>†</sup> The magnitude is  $\Sigma \frac{h}{2\pi}$ , where the quantum number  $\Sigma$  has  $2S + 1$  values ranging from  $+S$  to  $-S$ .

This is, however, an approximate relation because the value of  $N$  will be affected by the components of  $\vec{L}$  and  $\vec{S}$  perpendicular to the internuclear axis. When these effects are included, the expression for  $N$  becomes

$$N^2 = J(J+1) - \Omega^2 + L_p^2 + S(S+1) - \Sigma^2 + \phi(J),$$

where  $L_p$  is the perpendicular component of  $\vec{L}$  and  $\phi(J)$  is a small interaction term.

The rotational energy term is given by

$$F(v, J) = B_v N^2 \\ = B_v [J(J+1) - \Omega^2 + L_p^2 + S(S+1) - \Sigma^2] + B_v \phi(J).$$

The term  $B_v [-\Omega^2 + L_p^2 + S(S+1) - \Sigma^2]$  is constant for a given vibrational level of a given electronic sub-state (for given values of  $v$  and  $\Omega$ ). Hence it may be regarded as part of the vibronic energy, and the purely rotational terms may be written as

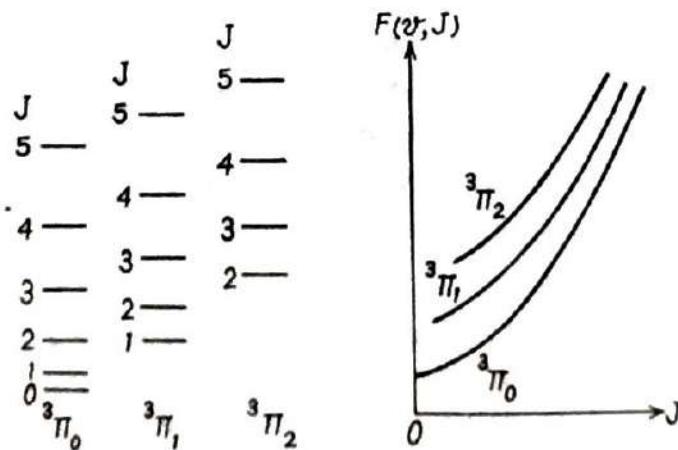
$$F(v, J) = B_v J(J+1) + \phi_i(J),$$

where we have put  $B_v \phi(J) = \phi_i(J)$ .

As an example, let us construct the rotational levels of a  ${}^3\Pi$  state in case (a). For this state, we have

$$\Lambda = 1, S = 1.$$

As a result of spin-orbit ( $\Sigma-\Lambda$ ) interaction, the given state is split up into  $(2S+1) = 3$  sub-states (multiplet component)  ${}^3\Pi_0$ ,  ${}^3\Pi_1$  and  ${}^3\Pi_2$  distinguished by  $\Omega = |\Lambda + \Sigma| = 0, 1, 2$ . Associated with each of these electronic sub-states is a pile of rotational levels, each having a characteristic  $J$ -value ( $J = \Omega, \Omega + 1, \Omega + 2, \dots$ ) and an energy  $F(v, J)$  given by the last expression (Fig. 4).



(Fig. 4)

Since the minimum value of  $J$  is  $\Omega$ , there is one missing level ( $J = 0$ ) in the pile associated with  ${}^3\Pi_1$  and two missing levels ( $J = 0, 1$ ) in the pile associated with  ${}^3\Pi_2$ . The small interaction term  $\phi_i$  differs for the multiplet components. Since  $B_v$  is almost independent of  $\Omega$ , the separations between levels with the same values of  $J$  in each pile are the same. If case (a) holds strictly, the three curves representing rotational energies can be brought into coincidence simply by a vertical shift.

When  $\Lambda = 0$ , and  $S \neq 0$ , the spin vector  $\vec{S}$  cannot be coupled to the internuclear axis which is a necessity for case (a). Hence Hund's case (a) cannot be applied to  $\Sigma$ -states.

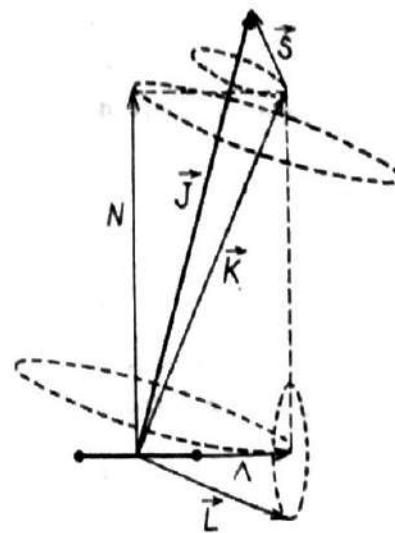
### 3. Hund's Coupling Case (b)

In this case, the vector  $\vec{L}$  is in rapid precession round the internuclear axis with quantised component  $\Lambda$ , but, in contrast to case (a), the magnetic field generated by orbiting electrons is so weak that the spin vector  $\vec{S}$  is no longer coupled to the internuclear axis, and hence the quantum number  $\Sigma$  is undefined. Consequently, case (b) always applies to  $\Sigma$ -states ( $\Lambda = 0$ ), and may also apply to other electronic states particularly when the molecule contains relatively few electrons.

The case (b) is illustrated in Fig. 5. The electronic orbital angular momentum component  $\Lambda$  along the internuclear axis, and the nuclear rotational angular momentum component  $N$  perpendicular to the internuclear axis form a resultant angular momentum  $\vec{K}$  (without spin) of the molecule about which  $N$  and  $\Lambda$  precess rapidly. The angular momentum  $\vec{K}$ , having a magnitude of  $\sqrt{K(K+1)} h/2\pi$ , is conserved and the quantum number  $K$  can have the integral values

$$K = \Lambda, \Lambda + 1, \Lambda + 2, \dots$$

Thus, associated with each electronic state there is a set of  $K$ -levels with  $K = \Lambda, \Lambda + 1, \dots$ . Levels with  $K < \Lambda$  do not occur.



(Fig. 5)

Now, because of a magnetic field generated in the direction of  $\vec{K}$  by the rotating molecule, the angular momenta  $\vec{K}$  and  $\vec{S}$  form the total angular momentum  $\vec{J}$  (including spin) of the molecule in a fixed direction about which both  $\vec{K}$  and  $\vec{S}$  precess slowly. The total quantum number  $J$ , according to the rules of vector addition, takes values given by

$$J = (K + S), (K + S - 1), \dots, |K - S|.$$

Thus, each  $K$ -level of a given electronic state is composed of  $2S + 1$  (when  $K > S$ ) or  $2K + 1$  component levels (when  $K < S$ ). These are called 'spin multiplet components', differing in  $J$ -values which may be integral or half-integral depending upon  $S$ . The slight splitting of the levels with different  $J$  but same  $K$  is due to the relatively weak magnetic spin-rotation ( $\vec{S} - \vec{K}$ ) coupling ; and increases with increasing  $K$ . This splitting is called case (b) spin-splitting.

Mulliken designated the component levels as  $F_1, F_2, F_3, \dots$ , those for which  $J = K + S$  being called  $F_1$ . Thus, doublet ( $S = \frac{1}{2}$ ) electronic states have  $F_1$  and  $F_2$  rotational levels with  $J = K + \frac{1}{2}$  and  $K - \frac{1}{2}$  respectively. The triplet ( $S = 1$ ) electronic states have  $F_1, F_2, F_3$  rotational levels with  $J = K + 1, K, K - 1$  respectively.

Let us now calculate these rotational levels. The value of  $N$  (not a quantum number)

$$N^2 = K(K+1) - \Lambda^2 + L_p^2 + \phi(K),$$

where  $\phi(K)$  is a small rotational-electronic interaction term. Thus, the rotational terms are given by

$$\begin{aligned} F(v, K) &= B_v N^2 \\ &= B_v [K(K+1) - \Lambda^2 + L_p^2] + \phi_i(K), \end{aligned}$$

where we have put  $B_v \phi(K) = \phi_i(K)$ .

The part  $B_v(-\Lambda^2 + L_p^2)$  may be included in the vibronic part of the energy. Hence the rotational terms become simply

$$F(v, K) = B_v K(K+1) + \phi_i(K). \quad \dots(i)$$

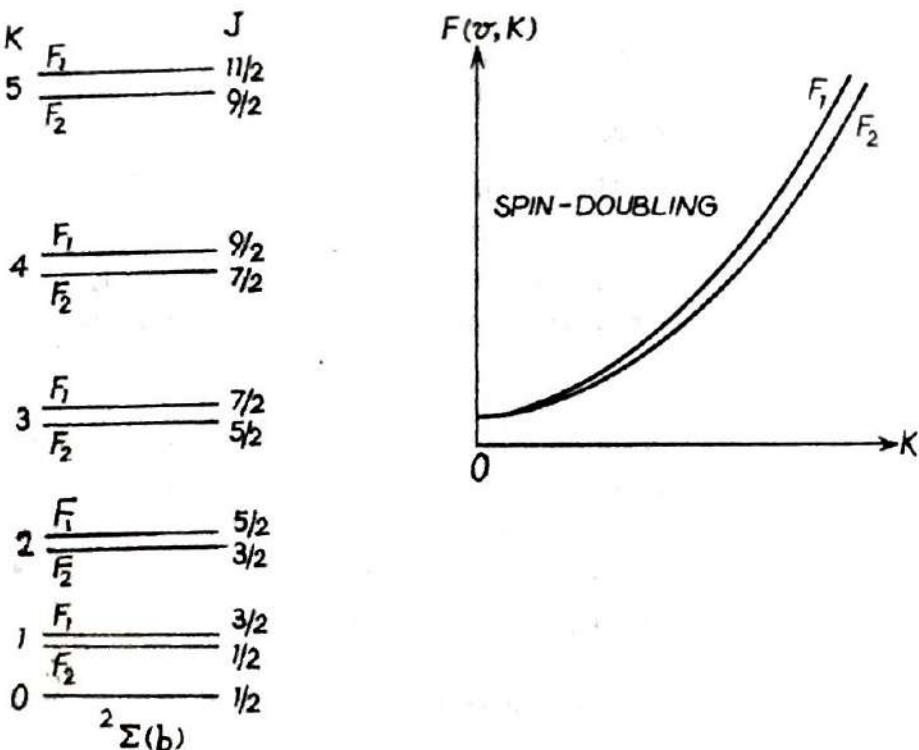
As an example, let us consider the rotational levels of a  ${}^2\Sigma$ -state. For this, we have

$$\Lambda = 0, \quad S = \frac{1}{2}.$$

Therefore,

$$\text{and } J = \frac{1}{2}; \left(\frac{3}{2}, \frac{1}{2}\right); \left(\frac{5}{2}, \frac{3}{2}\right); \left(\frac{7}{2}, \frac{5}{2}\right); \dots$$

Thus, the rotational levels of a  ${}^2\Sigma$ -state are doubled (spin-doubling), with the exception of the  $K = 0$  level, as shown in Fig. 6.



(Fig. 6)

Hund and Van Vleck calculated the values of  $\phi_i(K)$  in eq. (i) for the  ${}^2\Sigma$ -states, and showed that the rotational term values are given by

$$F_1(v, K) = B_v K(K+1) + \frac{1}{2} \gamma K,$$

and

$$F_2(v, K) = B_v K(K+1) - \frac{1}{2} \gamma(K+1).$$

where the splitting-constant  $\gamma \ll B_v$ . The splitting  $F_1(v, K) - F_2(v, K)$  is  $\gamma(K + \frac{1}{2})$  which increases linearly with  $K$ .

#### 4. Hund's Coupling Case (c)

This case is (rarely) found among the less stable excited states of heavier molecules, particularly the halogens. It occurs when the interaction between  $\vec{L}$  and  $\vec{S}$  is stronger than the interaction with the internuclear axis. That is,  $\Lambda$  and  $\Sigma$  are not defined. In this case, as illustrated in Fig. 7,  $\vec{L}$  and  $\vec{S}$  first form a resultant  $\vec{J}_a$  about which they precess. The vector  $\vec{J}_a$  is coupled to, and precesses round the internuclear axis with quantised component  $\Omega$ . The quantum number  $\Omega$ , can take the possible values

$$J_a, J_a - 1, \dots, \frac{1}{2} \text{ or } 0.$$

The electronic angular momentum component  $\Omega$  along the internuclear axis and the nuclear rotational angular momentum component  $N$  perpendicular to the internuclear axis then combine vectorially to give a resultant  $\vec{J}$  in a fixed direction, about which both  $\Omega$  and  $N$  precess.

It is clear that in case (c), an electronic state cannot be denoted by the symbols  $\Sigma, \Pi, \Delta, \dots$  because the quantum number  $\Lambda$  is not defined in this case. It can only be denoted by its  $\Omega$ -value  $0, \frac{1}{2}, 1, \dots$

The rotational energy values are roughly represented as

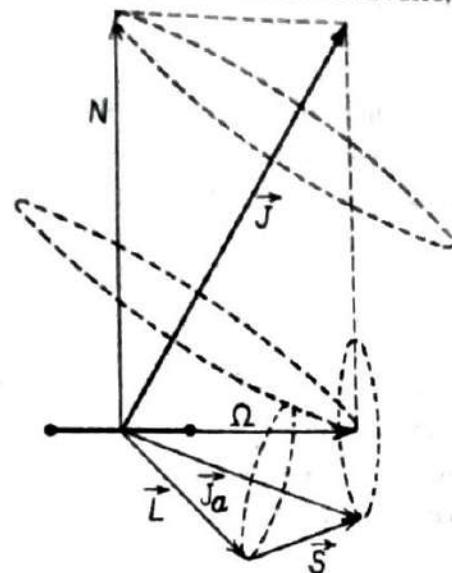
$$F(v, J) = B_v [J(J + 1) - \Omega^2];$$

where  $J = \Omega, \Omega + 1, \Omega + 2, \dots$

#### 5. Hund's Coupling Case (d)

This coupling case occurs in some very highly excited states of  $H_2$  and  $He_2$  molecules when the outer electron generating the orbital angular momentum  $\vec{L}$  is far removed from the nuclei and the inner electrons. Then, the nuclei plus inner electrons act like a point-charge so that the orbiting electron is not influenced by the electric field along the internuclear axis. That is, the vector  $\vec{L}$  is not coupled to the internuclear axis. In this case, the angular momentum of nuclear rotation, called  $\vec{R}$ , is separately quantised with magnitude  $\sqrt{R(R + 1)} \frac{\hbar}{2\pi}$ , where the quantum number  $R$  takes the values

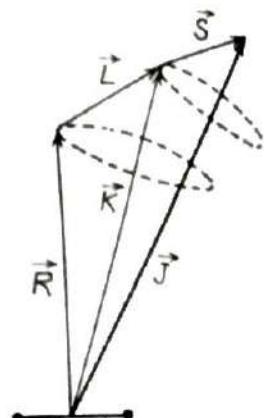
$$R = 0, 1, 2, \dots$$



(Fig. 7)

The angular momenta  $\vec{R}$  and  $\vec{L}$  combine vectorially to give a resultant  $\vec{K}$ , about which both  $\vec{R}$  and  $\vec{L}$  precess (Fig. 8). The quantum number  $K$ , for a given  $R$ , can have the values  $K = (R + L), (R + L - 1), (R + L - 2), \dots, |R - L|$ .

Thus, there are  $(2L + 1)$  different  $K$  values for each  $R$ , except when  $R < L$ . The rotational energy terms are given by



(Fig. 8)

$F(v, R) = B_v R(R + 1) +$  small interaction terms causing splitting into  $2L + 1$  components.

Thus, each main rotational level, fixed by the value of  $R$ , is splitted into  $2L + 1$  sublevels, each characterised by a value of  $K$ .

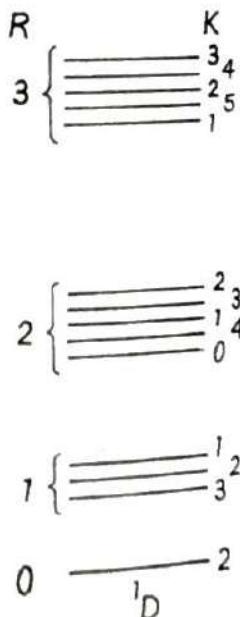
Finally, when  $S > 0$ , the vectors  $\vec{K}$  and  $\vec{S}$  couple to give  $\vec{J}$ , where  $J$  takes  $2S + 1$  values between  $K + S$  and  $K - S$ . Due to this coupling, each sub-level of a given  $K$ -value is further splitted into  $2S + 1$  still closer components, each characterised by a  $J$ -value. This splitting is, however, negligibly small and is usually disregarded.

In this case the molecular quantum numbers  $\Lambda$  and  $\Sigma$  are not defined. Hence each electronic state is identified as  $S, P, D$ , according to the value of  $L$ , as in atoms.

As an example, let us consider the electronic state  $^1D(L = 2, S = 0)$ . With this state, are associated a number of rotational levels,  $R = 0, 1, 2, \dots$ . Each of these has a pile of  $(2L + 1) = 5$  sublevels, each characterised by  $K$ . For  $R < L$ , however, the number of sublevels is  $2R + 1$ . This is shown in Fig. 9. It is seen that the levels with different  $K$  of a given  $R$  do not lie in the order of the  $K$  values, but the levels with equal  $|K - R|$  lie near one another. This is because the coupling between  $\vec{L}$  and  $\vec{R}$  is due mainly to gyroscopic forces, and not to the magnetic forces.

## 6. Uncoupling Phenomena

In practice, most molecular states deviate from Hund's coupling cases, which are infact limiting cases, and belong to some intermediate cases. The reason is that interactions which are ignored or given little weight in Hund's cases have an appreciable magnitude. Also the relative magnitudes of various interactions change with increasing rotation. For example, angular momentum vectors  $\vec{L}$  and  $\vec{S}$  coupled to the internuclear axis for small rotation are uncoupled from it with increasing rotation. Hence there are cases when, with increasing rotation, a transition takes place from one Hund's coupling case to another.



(Fig. 9)

There are two particularly important uncoupling phenomena which give rise to coupling transitions :

(i) **Orbital Uncoupling** : When  $\vec{L}$  is uncoupled from the internuclear axis, a transition from case (a) or (b) to case (d) takes place. This phenomenon is associated with  $\Lambda$ -type doubling.

(ii) **Spin Uncoupling** : When  $\vec{S}$  is uncoupled from the internuclear axis, a transition takes place from case (a) to case (b).

Both types of uncoupling may be present together in actual molecular states.

### 7. $\Lambda$ -Type Doubling

All molecular electronic states with  $\Lambda > 0$  and belonging to Hund's cases (a) and (b) are doubly-degenerate *so long the molecular rotation is ignored*. Correspondingly, each rotational level associated with these states is doubly-degenerate. For larger speeds of molecular rotation, however, the magnetic field set up by nuclear rotation is sufficiently strong to remove the degeneracy and split each  $J$ -level into two components with slightly different energies. The splitting, which is zero for  $J = 0$ , increases with increasing  $J$ . The component-levels of a given  $J$ , which are distinguished by letters *c* and *d*, differ in their symmetry properties. This type of doubling of the rotational levels is independent of electron spin, and occurs for all electronic states with  $\Lambda > 0$ . It is known as  $\Lambda$ -type doubling.

There is necessarily no  $\Lambda$ -type doubling for  $\Sigma$ -states, while it is too small to be observed in  $\Delta, \Phi, \dots$  states, as a rule. It is important in practice only in  $\Pi$ -states.

**$\Lambda$ -Doubling in  $^1\Pi$ -state** : For this electronic state, the Hund's cases (a) and (b) are identical (symmetric top). The state is associated with a pile of rotational levels, each characterised by a number  $J (= 1, 2, 3, \dots)$ . The electronic-rotational interaction splits each  $J$ -level into two, *c* and *d*, levels (Fig. 10) having term values given by

$$F_c(J) = B_v J(J + 1) + \phi_c(J)$$

$$F_d(J) = B_v J(J + 1) + \phi_d(J).$$

and

$$\begin{array}{c} J=K \\ d = \underline{\hspace{1cm}} \quad 5 \\ c = \underline{\hspace{1cm}} \quad 5 \end{array}$$

$$\begin{array}{c} d = \underline{\hspace{1cm}} \quad 4 \\ c = \underline{\hspace{1cm}} \quad 4 \end{array}$$

$$\begin{array}{c} d = \underline{\hspace{1cm}} \quad 3 \\ c = \underline{\hspace{1cm}} \quad 3 \end{array}$$

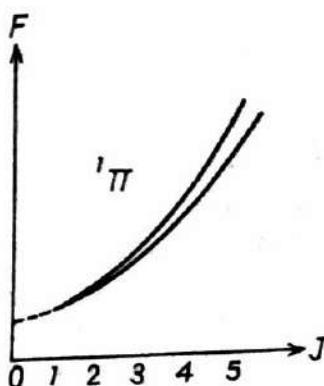
$$\begin{array}{c} d = \underline{\hspace{1cm}} \quad 2 \\ c = \underline{\hspace{1cm}} \quad 2 \end{array}$$

$$\begin{array}{c} d = \underline{\hspace{1cm}} \quad 1 \\ c = \underline{\hspace{1cm}} \quad 1 \end{array}$$

$^1\Pi$

( $\Lambda$ -doubling greatly exaggerated)

(Fig. 10)



Therefore, the  $\Lambda$ -doubling is

$$\Delta F(J) = \phi_c(J) - \phi_d(J).$$

It has been shown to a first approximation that

$$\phi_c(J) - \phi_d(J) = q J(J + 1),$$

where  $q$  is of the order of  $\frac{B^2}{h\nu}$ ,  $B$  being the rotational constant, and  $\nu$  is of the order of an electronic frequency. Thus

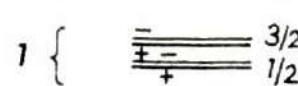
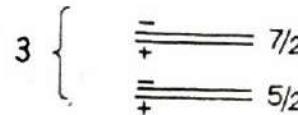
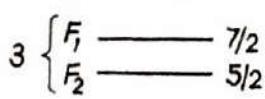
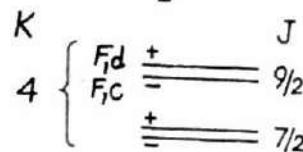
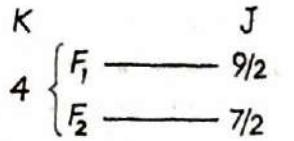
$$\Delta F(J) \approx \frac{B^2}{h\nu} J(J + 1).$$

That is,  $\Lambda$ -doubling increases quadratically with  $J$  and is pronounced only in molecules of hydrides (Al H) for which  $B$  is comparatively large.

**$\Lambda$ -Doubling in  ${}^2\Pi$ -State :** Here the  $\Lambda$ -doubling is different according as the state belongs to Hund's case (a) or (b) or some intermediate case. In case (b), there exists a pile of levels, each characterised by  $K$  ( $= \Lambda, \Lambda + 1, \dots$ ) ; and each of these  $K$ -levels is spin-split into  $(2S + 1)$  components when  $K > S$ , or in  $(2K + 1)$  components when  $K < S$ , differing in  $J$ -values;

$$J = (K + S), \dots, |K - S|.$$

Thus, in the  ${}^2\Pi$  state ( $\Lambda = 1; S = \frac{1}{2}$ ) ; we have  $K$ -levels ( $K = 1, 2, 3, \dots$ ), each being splitted into 2 components with  $J = K + \frac{1}{2}$  and  $J = K - \frac{1}{2}$  (Fig. 11).



${}^2\Pi(b)$

(Spin-splitting only  
greatly exaggerated)

${}^2\Pi(b)$

(spin-doubling +  $\Lambda$ -type doubling  
greatly exaggerated)

(Fig. 11)

Now, as a result of  $\Lambda$ -type doubling, each sub-level given by a  $J$ -value is splitted into two components  $c$  and  $d$ , the separation being given by a relation similar to above :

$$\Delta F(K) = \frac{B^2}{h\nu} K(K + 1).$$

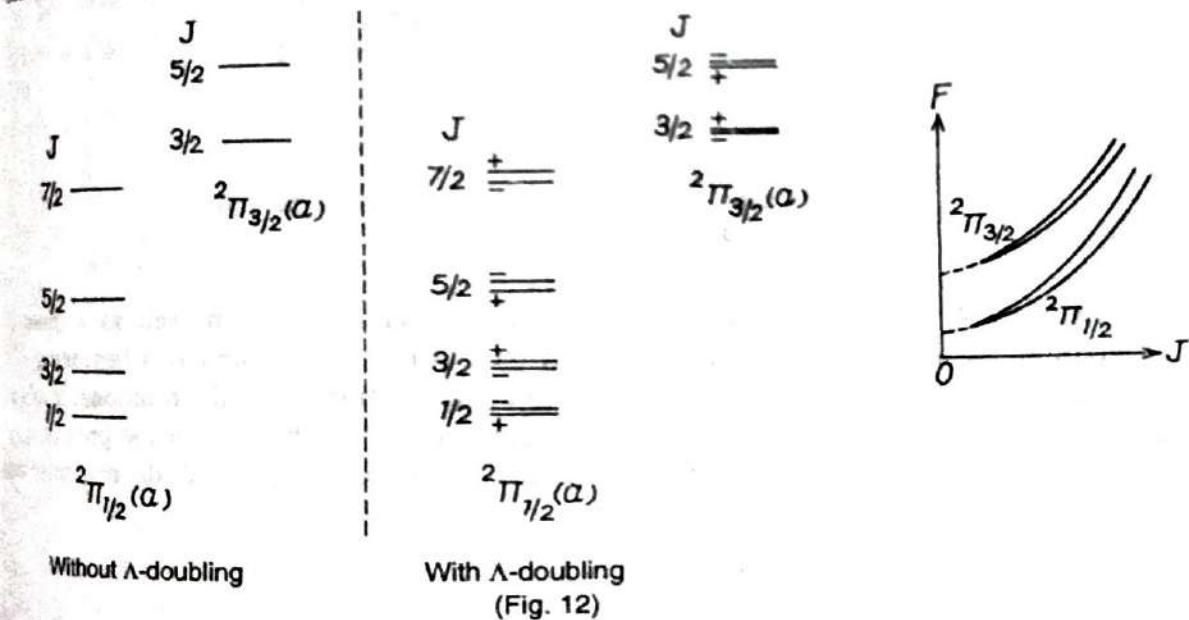
Thus, the  $\Lambda$ -type splitting increases quadratically with  $K$ . Owing to the loose coupling of the spin, the  $\Lambda$ -type doubling is almost entirely independent of spin, that is, it is same in both sub-levels  $J = K + S$  and  $J = K - S$  of a given  $K$ -level.

In Hund's case (a), however, the effect of spin is very marked, so that the  $\Lambda$ -type doubling differs greatly from one sub-state to another. In case of  $^2\Pi$  state ( $\Lambda = 1; S = \frac{1}{2}$ ), there are two electronic-substates  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  (corresponding to  $\Omega = \Lambda + S$  and  $\Lambda - S$ ) and each sub-state has a set of rotational levels characterised by a  $J$  value ( $J = \Omega, \Omega + 1, \dots$ ). Now, as a result of  $\Lambda$ -type doubling, each level in each electronic sub-state is splitted into two components, with separations given

$$\text{For } ^2\Pi_{1/2} \text{ sub-state : } \Delta F(J) = a \left( J + \frac{1}{2} \right)$$

$$\text{For } ^2\Pi_{3/2} \text{ sub-state : } \Delta F(J) = b \left( J^2 - \frac{1}{4} \right) \left( J + \frac{3}{2} \right),$$

where  $a$  and  $b$  are small constants ( $b \ll a$ ). It is thus clear that the  $\Lambda$ -type doubling is much larger in  $^2\Pi_{1/2}$  sub-state than in  $^2\Pi_{3/2}$ . That is, it is larger for smaller  $\Omega$ . This is shown in Fig. 12.



### $\vec{L}$ -uncoupling : Transition from case (b) to case (d)

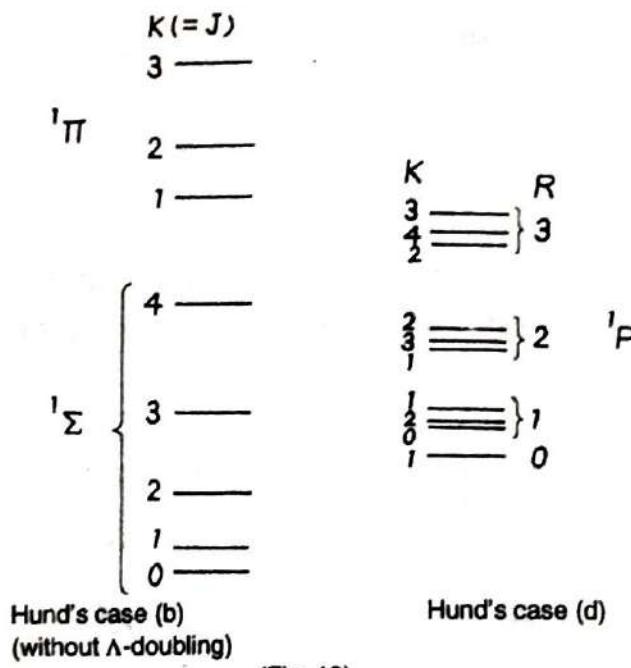
For some electronic states of  $H_2$  and  $He_2$ , the interaction between  $\vec{L}$  and the internuclear axis is so small that for higher rotational levels it is outweighed by the interaction with the rotational axis [case (d)]. That is, with increasing rotation,  $\vec{L}$  starts becoming uncoupled from the internuclear axis. In the limiting case of complete decoupling, case (d) is reached in which  $\vec{L}$  is coupled to the nuclear rotation angular momentum  $\vec{R}$  to give a resultant  $\vec{K}$ , where

$$K = (R + L), \dots, |R - L|.$$

Thus, there are  $(2L + 1)$  levels ( $K$ -levels) for each  $R$  (except when  $R < L$ ).

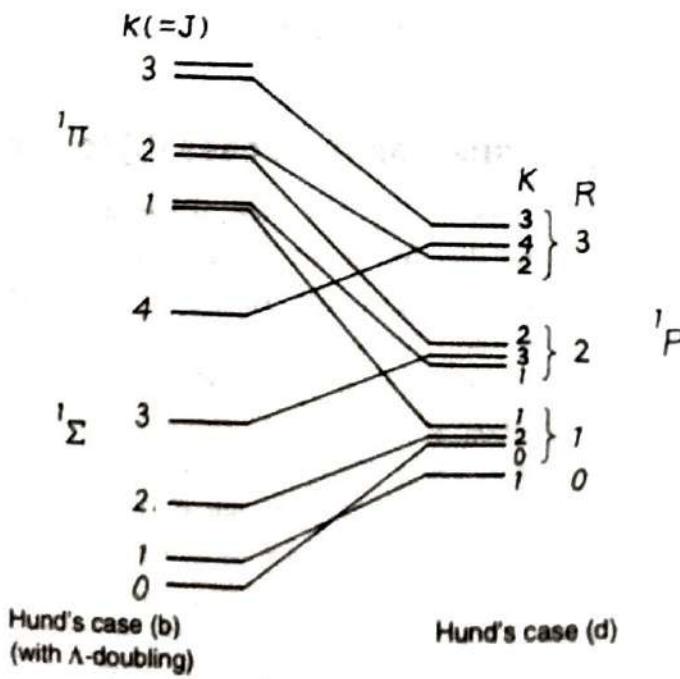
As an example of complete transition, let us consider the case  $L = 1, S = 0$ . In Hund's case (b) when  $\vec{L}$  is strongly coupled to the internuclear axis, we obtain  $(L + 1)$  electronic states with different  $\Lambda$  for a given value of  $L$ , of which those with  $\Lambda > 0$  are doubly-degenerate. Thus, here we have two separate electronic states,  $\Lambda = 0, 1$ , namely

$^1\Sigma$  and  $^1\Pi$ , each having a pile of  $K$ -levels ( $K = \Lambda, \Lambda + 1, \dots$ ). On the other hand, in case (d), we obtain only one electronic state (defined by the value of  $L$ )  $^1P$  having a number of rotational levels  $R = 0, 1, 2, \dots$ ; each with a pile of  $(2L + 1) = 3$   $K$ -levels. For  $R < L$  (that is, for  $R = 0$ ), the number of  $K$ -levels is  $2R + 1 = 1$ . The display of levels in the two cases is shown in Fig. 13.



(Fig. 13)

In Fig. 14, the degeneracy of levels of the  $^1\Pi$ -state is removed as a result of  $\Lambda$ -doubling which becomes important with increasing rotation and is a beginning of a gradual transition from case (b) to case (d). In complete transition, the rotational levels on the left eventually go over to those on the right such that  $K (= J$  in the present case) remains unchanged for a given level and that levels with equal  $K$  do not cross one another.



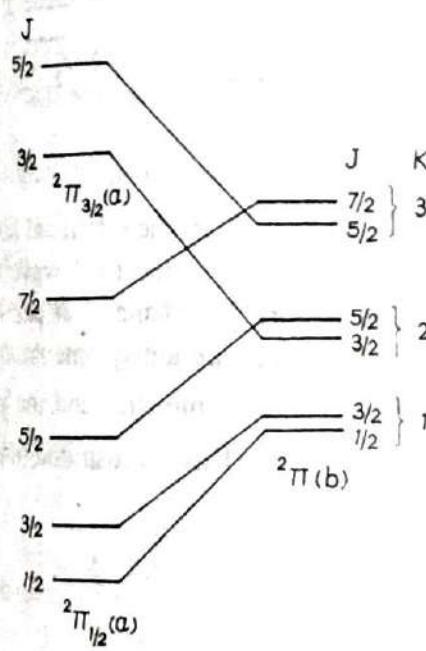
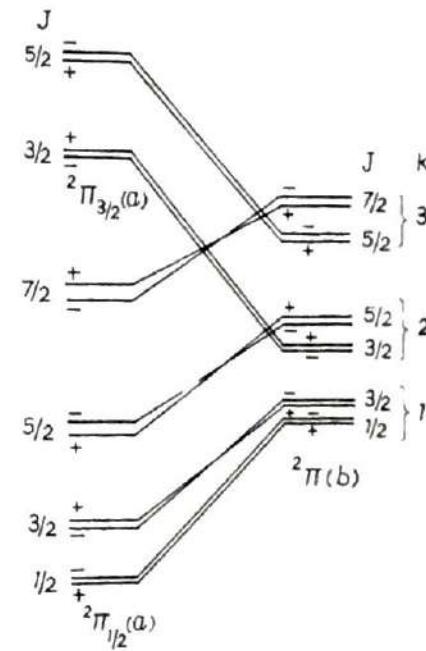
(Fig. 14)

## 9. Spin Uncoupling : Transition from case (a) to case (b)

In Hund's case (a),  $\vec{S}$  is strongly coupled to the internuclear axis, and the states (with same  $J$ ) differing in  $\Omega$  (that is, differing in orientation of  $\vec{S}$  to the axis) have relatively large energy differences. In case (b), on the other hand,  $\vec{S}$  is weakly coupled to  $\vec{K}$ , and the states (with same  $K$ ) differing in just the values of  $J$  (that is, differing in orientation of  $\vec{S}$ ) show only a small energy difference.

In certain multiplet electronic states, the rotational velocity of the molecule, which increases with increasing  $J$ , becomes comparable with the precessional velocity of  $\vec{S}$  about the internuclear axis. Finally, the influence of the molecular rotation predominates. Then  $\vec{S}$  is uncoupled from the internuclear axis and combines with  $\vec{K}$  to form the resultant  $\vec{J}$ , as in case (b). This process is called 'spin uncoupling', which results in transition of the state from case (a) to case (b).

The transition from case (a) to case (b) for the rotational levels of a regular  $^2\Pi$ -state is shown in Fig. 15, both while ignoring  $\Lambda$ -type doubling and also while considering  $\Lambda$ -type

(Ignoring  $\Lambda$ -doubling)(with  $\Lambda$ -doubling)

(Fig. 15)

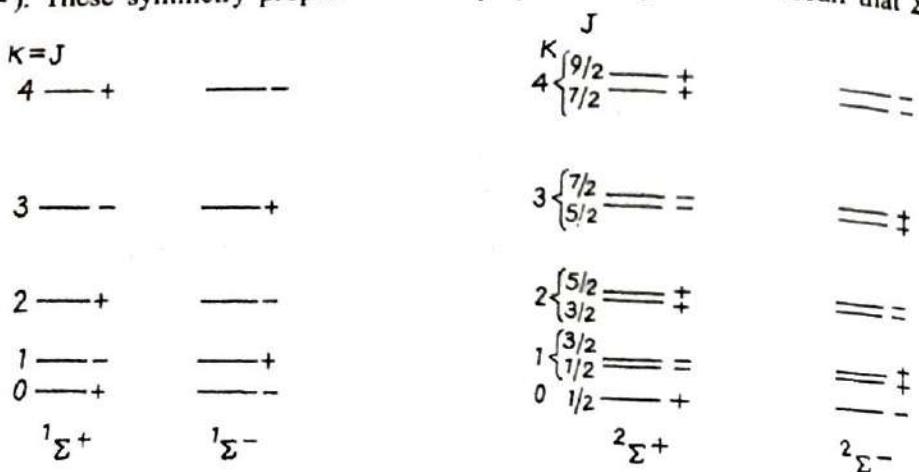
doubling. The value of  $J$  remains unchanged for each level because the total angular momentum is always conserved. Levels with equal  $K$  draw together with increasing spin-uncoupling. On the other hand, levels with equal  $J$  go over into levels with different  $K$ . Therefore, their separation increases with increasing  $J$  and increasing uncoupling.

## 10. Symmetry Properties of Rotational Levels

In addition to the electronic types for molecular states, the symmetry properties of rotational energy levels associated with them are required for the interpretation of band structure. An energy level is classified as positive or negative according as the *total*

coordinate wavefunction for the state remains unchanged or changes sign by inversion at the origin of a space-fixed system of axes. Let us consider the different types of electronic states separately :

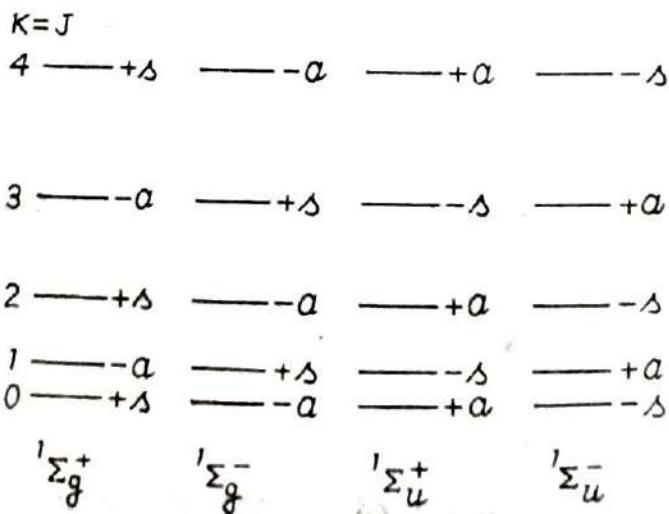
**$\Sigma$ -States :** For a  $\Sigma^+$ -state, the rotational levels with even values of  $K$  (not  $J$ , however for singlet states  $K = J$ ) are positive and those with odd values of  $K$  are negative; whereas for a  $\Sigma^-$  state the even  $K$  levels are negative and the odd- $K$  levels are positive. The spin part of the electronic wavefunction for a multiplet  $\Sigma$ -state is unchanged by inversion. Hence the  $J$ -components of each  $K$ -level all have the same symmetry (all +, or all -). These symmetry properties are displayed in Fig. 16. We recall that  $\Sigma$ -states



(Fig. 16)

always belong to Hund's coupling case (b).

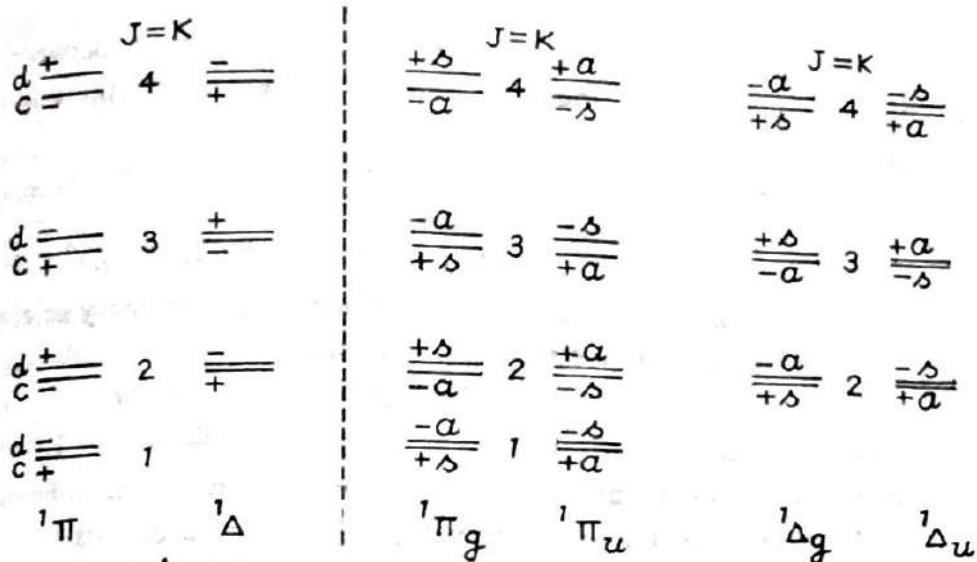
For (homonuclear) diatomic molecules having identical nuclei the rotational levels are classified as symmetric ( $s$ ) or antisymmetric ( $a$ ) according as the total wavefunction remains unaltered or changes sign when the two nuclei are interchanged. It can be seen that the positive levels are symmetric and the negative ones are antisymmetric for even electronic states ( $\Sigma_g^+, \Sigma_g^-$ ); while the negative levels are symmetric and the positive ones are antisymmetric for odd electronic states ( $\Sigma_u^+, \Sigma_u^-$ ). This is illustrated in Fig. 17.



(Fig. 17)

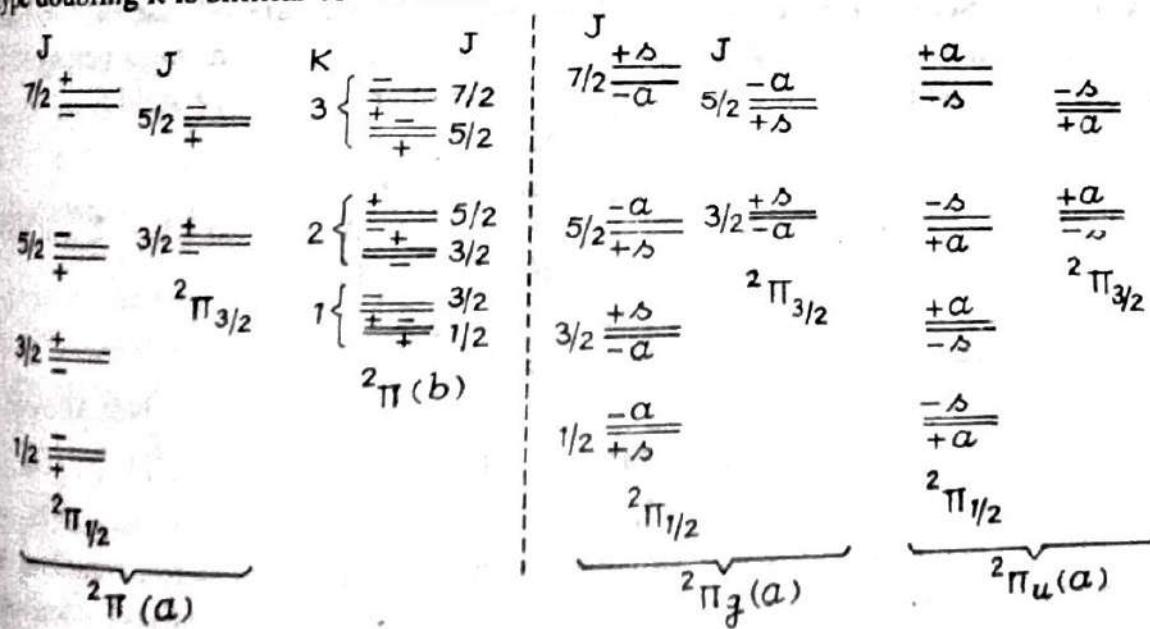
**$\Pi, \Delta$ -States :** For electronic states with  $\Lambda > 0$ , each of the  $\Lambda$ -type doublet components of the rotational levels has opposite symmetry, one being positive and the

other negative, and it is alternately the lower and the upper level that is positive. In case of identical nuclei there are even and odd electronic states, and the rotational levels are classified as symmetric or antisymmetric in the same manner as for  $\Sigma_g$  or  $\Sigma_u$ . That is, in even ( $g$ ) electronic states the positive levels are symmetric and the negative are antisymmetric; and conversely in odd electronic states ( $u$ ). The levels for  $^1\Pi$  and  $^1\Delta$  states are shown in Fig. 18.



(Fig. 18)

Multiplet electronic states with  $\Lambda > 0$  behave in a similar way. As examples, the symmetry properties of the rotational levels of  $^2\Pi$ -states belonging to case (a) are shown in Fig. 19. The symmetry properties do not change in going to Hund's case (b). For demonstration, a  $^2\Pi$ -state belonging to case (b) is also included in the diagram. Except for  $\Lambda$ -type doubling it is similar to  $^2\Sigma$ -state.



(Fig. 19)

## 1. Selection Rules for Electronic Transitions

For emission or absorption of dipole radiation, the selection rules depend on what quantum numbers can be rigidly assigned in the two states involved in the transition, and

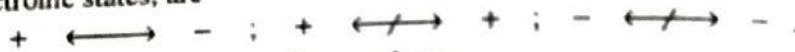
therefore on the coupling case. Still we can distinguish between selection rules that hold quite generally, independent of the coupling case of the electronic state, and those that hold only for a definite coupling case.

**General Selection Rules :** The selection rule for the total angular momentum quantum number  $J$  is

$$\Delta J = 0, \pm 1, \quad (\text{but } J = 0 \leftrightarrow J = 0),$$

whatever the coupling conditions are.

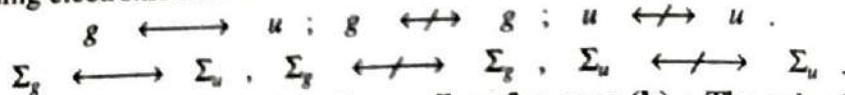
The symmetry selection rules for electric dipole transitions between individual rotational levels, whatever the coupling conditions and whether belonging to the same or different electronic states, are



In addition, for homonuclear molecules ; we have



Finally, in case of a molecule with nuclei of equal charge, the symmetry selection rule for the combining electronic states for electric dipole transitions are

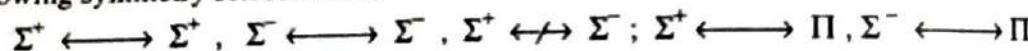


**Selection Rules for case (a) and as well as for case (b) :** The selection rules for molecular electronic transitions in Hund's cases (a)and (b) are as follows :

$$(i) \quad \Delta \Lambda = 0, \pm 1.$$

Thus,  $\Sigma \longleftrightarrow \Sigma, \Sigma \longleftrightarrow \Pi, \Pi \longleftrightarrow \Pi, \Pi \longleftrightarrow \Delta$ .

When both combining states have  $\Lambda = 0$ , the electronic wavefunctions have the following symmetry selection rule



$$(ii) \quad \Delta S = 0,$$

that is, only (electronic) states of the same multiplicity combine with one another.

**Additional Selection Rule when both combining states are of case (a) :** In Hund's case (a), the quantum number  $\Sigma$  and hence  $\Omega$  are defined. If both states belong to case (a), the following additional rule, for the quantum numbers  $\Sigma$  and  $\Omega$  hold :

$$(i) \quad \Delta \Sigma = 0$$

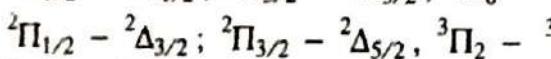
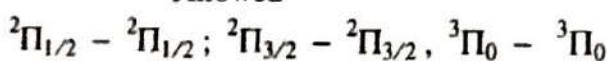
$$(ii) \quad \Delta \Omega = 0, \pm 1.$$

Since change of  $\Sigma$  is not allowed, and  $\Omega$  ranges from  $\Lambda + \Sigma$  to  $|\Lambda - \Sigma|$ , it follows that *the change in  $\Omega$  must be identical with that in  $\Lambda$* , that is,

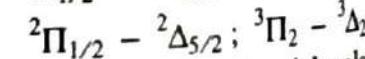
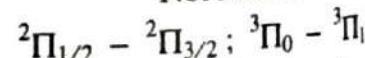
$$\Delta \Omega = \Delta \Lambda.$$

Thus, these rules allow or disallow as shown below :

Allowed



Not Allowed



If  $\Omega = 0$  for both electronic states then the transitions between rotational levels corresponding to  $\Delta J = 0$  are forbidden. That is, an additional (special) selection rule is

for  $\Omega = 0 \longleftrightarrow \Omega = 0; \Delta J \neq 0$ , only  $\Delta J = \pm 1$  would occur.

This means that no *Q*-branch appears in transitions  $^1\Sigma - ^1\Sigma, ^3\Pi_0 - ^3\Pi_0$  etc. For  $\Delta \Omega \neq 0$  (for example  $^2\Pi_{3/2} - ^2\Pi_{5/2}$ ), an intense *Q*-branch is present. For  $\Delta \Omega = 0$  (for

example  $^2\Pi_{3/2} - ^2\Pi_{3/2}$ ) a weak  $Q$ -branch is present whose intensity decreases rapidly with increasing  $J$ .

**Additional Selection Rules for case (b) only :** In Hund's case (b) the quantum number  $K$  (total angular momentum apart from spin) is defined. If both states belong to case (b), the following selection rule holds

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

with the added restriction

$$\text{for } \Sigma \longleftrightarrow \Sigma \text{ electronic transition, } \Delta K \neq 0.$$

The additional rules described above hold only if *both* the combining states belong to one and the same coupling case. If one electronic state belongs to case (a) and the other to case (b), then there remain only the selection rules common for both coupling cases.

## 12. Branch Notations

The selection rules for quantum numbers  $\Lambda, \Sigma$  and  $S$  determine the allowed electronic transitions to give band-systems and sub-systems. They say nothing about the line-structure of bands. To consider the latter, we must know the selection rules for transitions between rotational energy levels. These are

$$\Delta J = 0, \pm 1 \quad (\text{but } J' = 0 \leftrightarrow J'' = 0; \text{ and } \Delta J \neq 0 \text{ for } \Omega = 0 \rightarrow \Omega = 0)$$

$$\Delta K = 0, \pm 1 \quad (\text{for case b only; and } \Delta K \neq 0 \text{ for } \Sigma-\Sigma \text{ transition}).$$

In the absence of an external field the  $J$ -rule holds rigorously, but the  $K$ -rule is strict only in transitions between two case (b) states; changes of  $\Delta K = \pm 2$  and even  $\pm 3$  are known to occur when one of the electronic states is a case (a) or an intermediate state.

In a given band, the lines corresponding to the same change in  $J$  (that is, having same value of  $\Delta J = J' - J''$ ) constitute a 'branch'. Thus, the band consists of three different branches, labelled as below :

$$\Delta J = J' - J'' = -1 \quad (P\text{-branch}).$$

$$\Delta J = J' - J'' = 0 \quad (Q\text{-branch}).$$

$$\Delta J = J' - J'' = +1 \quad (R\text{-branch}).$$

An individual line of a branch is denoted by the value of the 'lower' rotational quantum number [ $J$  for case (a),  $K$  for case (b)] in parenthesis. Thus,  $P(5)$  indicates  $\Delta J = -1$  and  $J'' = 5$  so that  $J' = 4$  (for case b,  $\Delta K = -1$  and  $K'' = 5$  so that  $K' = 4$ ).

For singlet states ( $J \equiv K$ ) the above notation is sufficient. In dealing with the multiplet electronic states belonging to case (b), however, when the spin-splitting arises, the above mentioned  $K$ -rule is relaxed. Then we have more than one value of  $\Delta K$  for a given  $\Delta J$ . That is, there will be more than one branch with a given value of  $\Delta J$ . (A branch corresponds not merely to a constant  $\Delta J$  but also to a constant  $\Delta K$ ). In such bands, the lines resulting from transitions for which  $\Delta J = \Delta K$  are much stronger than those resulting from transitions for which  $\Delta J \neq \Delta K$ . The branches formed by the first set are called 'main branches', and those formed by the second set are called 'satellite branches'. Mulliken has suggested a notation for all possible branches of a band. In this notation, the letters  $P, Q, R$  indicate, as usual,  $\Delta J = -1, 0, +1$ ; and these letters are preceded by a superscript  $N, O, P, Q, R, S, T$  corresponding to  $\Delta K = -3, -2, -1, 0, 1, 2, 3$ .

Thus, a branch with  $\Delta K = 0$  and  $\Delta J = +1$  would be written as  ${}^Q R$ , which is read ' $Q$  form  $R$ '. For a main branch, the superscript, which is identical with the main letter, is omitted. The following table displays the various branches possible in a most complicated band:

$\Delta J$	$\Delta K$	-3	-2	-1	0	+1	+2	+3
-1	$N_P$	$O_P$		$P$ (main branch)	$Q_P$	$R_P$	$S_P$	$T_P$
0	$N_Q$	$O_Q$		$P_Q$ (main branch)	$Q$	$R_Q$	$S_Q$	$T_Q$
+1	$N_R$	$O_R$		$P_R$	$Q_R$ (main branch)	$R$	$S_R$	$T_R$

The spin-multiplet components with different  $J$ , for a given  $K$ -level of an electronic state (case b) are designated as  $F_1, F_2, \dots$  corresponding to  $J = K + S, \dots, K - S$ . This causes two  $R$ -branches, two  $P$ -branches and two  $Q$ -branches to appear in the spectrum. To distinguish between them, sub-scripts are added following the main symbol. The branches resulting from transitions between two  $F_1$ -type levels are written as  $R_1, Q_1, P_1$ ; while those from transitions between two  $F_2$ -type levels as  $R_2, Q_2, P_2$ . If one of the combining levels is  $F_1$  type and the other  $F_2$  type, then the branches are indicated as  $P_{12}, Q_{12}, R_{12}$  or as  $P_{21}, Q_{21}, R_{21}$ , the number for the upper state rotational level being written first.

When both electronic states have  $\Lambda$ -doubling, it is usual to denote the two levels of each pair by the letters  $c$  and  $d$ . When the  $\Lambda$ -doubling produces observable splitting of the lines of the branches then these symbols are also included in the notation. Thus, in the most complex case the notation may take a form such as  ${}^P Q_{1e2d}$ .

**Intensity Factors :** The intensity of any one line of a band depends on :

- (i) the probability of the electronic transition,
- (ii) the vibrational intensity distribution (F. C. Principle),
- (iii) the population of the molecules in the initial energy level,
- (iv) the intensity factor  $i$ , which depends on the branch type and  $J$  (or  $K$ ) value,
- (v) a factor depending upon emission or absorption.

Expressions for the  $i$ -factor have been worked out for the various coupling cases and the intensity distributions among the branch lines deduced. These may be summarised as below :

For electronic transitions  $\Delta\Lambda = 0$  (such as  $\Sigma - \Sigma, \Pi - \Pi, \Delta - \Delta$ ), the intensity of band lines of a  $P$  or  $R$  branch at first increases with increasing  $J$ , reaches a maximum, and then slowly falls off to zero. On the whole, the  $P$ -branch is stronger in emission and the  $R$ -branch in absorption. The  $Q$ -branch, if present (as in  $\Pi - \Pi$ ), is weak and the intensity of lines decreases very rapidly from the very beginning (no maximum). The satellite branches ( $\Delta J \neq \Delta K$ ) are much weaker compared to main branches ( $\Delta J = \Delta K$ ) and in them the intensity falls off very rapidly with increasing  $K$ .

For transitions  $\Delta\Lambda = \pm 1$  (such as  $\Sigma - \Pi$ ), the  $Q$ -branch is also of the same type (that is, with a maximum) as the  $P$  and  $R$  branches, but about twice as strong as either the  $P$  or the  $R$ -branch which, in this case, are roughly equal in intensity except for the low values where the  $R$ -branch is stronger.

### 13. Rotational Structure of Electronic Bands

In writing an electronic transition, the upper state is always written first. For example,  $^1\Sigma - ^1\Pi$  means a transition for which  $^1\Sigma$  is the upper state and  $^1\Pi$  is the lower state (not initial and final).

Further,  $^1\Sigma \rightarrow ^1\Pi$  means a transition (emission) from the upper  $^1\Sigma$  state to the lower  $^1\Pi$  state; and  $^1\Sigma \leftarrow ^1\Pi$  means a transition (absorption) from the lower  $^1\Pi$  state to the upper  $^1\Sigma$  state.

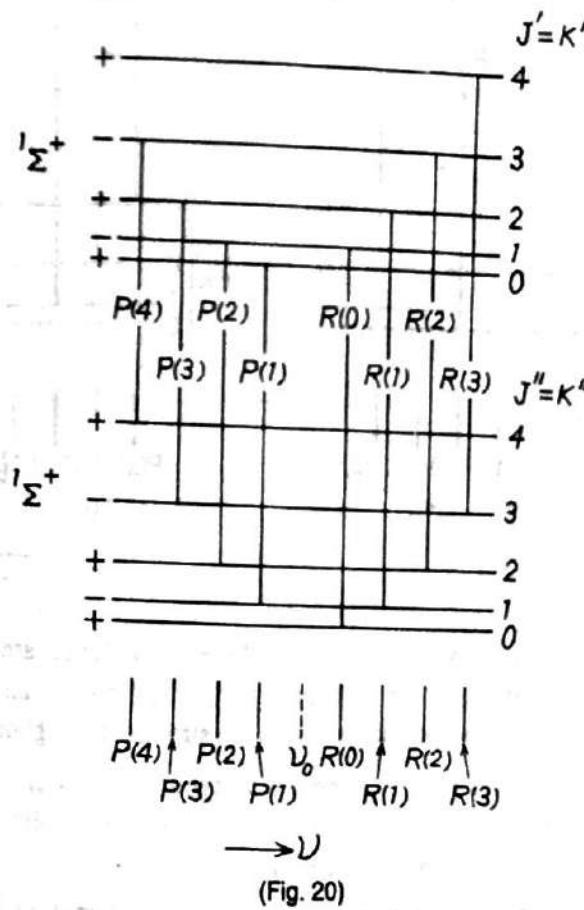
Let us now consider specific examples of electronic transitions :

(a)  $^1\Sigma - ^1\Sigma$  Transitions : Allowed electronic transitions between  $^1\Sigma$ -states are  $^1\Sigma^+ - ^1\Sigma^+$  and  $^1\Sigma^- - ^1\Sigma^-$  for heteronuclear molecules and  $^1\Sigma_g^+ - ^1\Sigma_u^+$ ,  $^1\Sigma_g^- - ^1\Sigma_u^-$  for homonuclear molecules. For  $^1\Sigma$ -states, Hund's cases (a) and (b) are identical. The symmetries of both sets of rotational levels for a  $^1\Sigma^+ - ^1\Sigma^+$  transition are shown in Fig. 20. The selection rules in operation are :

$$(i) \Delta J = 0, \pm 1; J = 0 \leftrightarrow J = 0$$

( $\Delta K \neq 0$  for  $\Sigma - \Sigma$  transition. Since here  $J = K$ , hence  $\Delta J \neq 0$ ).

$$(ii) + \longrightarrow - .$$



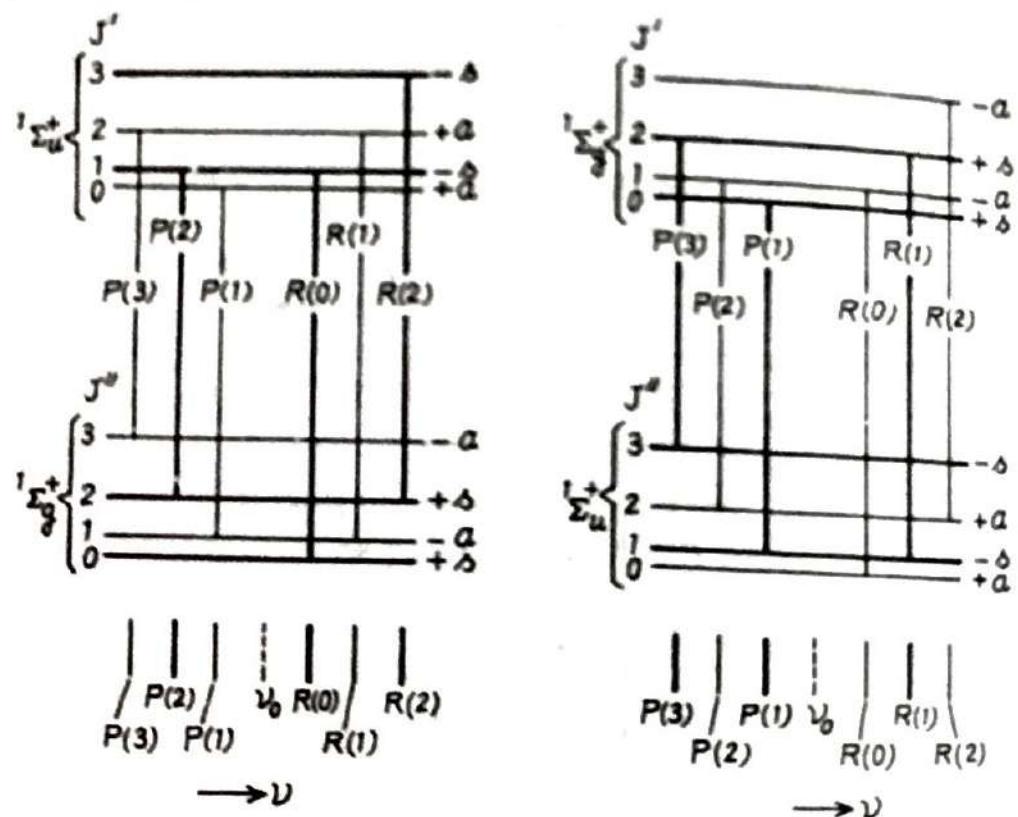
(Fig. 20)

On drawing transitions according to these rules, it is seen that the band consists of a single  $P(\Delta J = -1)$ , and a single  $R(\Delta J = +1)$  branch ; with one missing line  $P(0)$  at the origin. The  $Q$ -branch is forbidden by the rule  $+ \leftrightarrow -$ , and also by the rule  $\Delta K \neq 0$  for  $\Sigma - \Sigma$  transitions. The question of spin-splitting and of  $\Lambda$ -type doubling does not arise (because  $S = 0, \Lambda = 0$ ).

Exactly the same structure occurs for a  ${}^1\Sigma^+ - {}^1\Sigma^-$  transition, since the change in symmetry (+, -) of all levels would not affect the selection rules so that the same rotational levels would combine. It is therefore not possible to tell from a  ${}^1\Sigma^+ - {}^1\Sigma^-$  transition alone, whether both electronic states are (+) or both (-). The examples of  ${}^1\Sigma^+ - {}^1\Sigma^+$  transitions are found in BeO and CuH bands.  ${}^1\Sigma^+ - {}^1\Sigma^-$  transitions are rare.

Transitions between  ${}^1\Sigma^+$  and  ${}^1\Sigma^-$  electronic states would, in conformity with the  $+ \leftrightarrow -$  and  $J$ -rules give only a  $Q$ -branch without  $P$  and  $R$  branches. Theoretical intensity relations, however, show that the  $Q$ -branch must be of zero intensity. Hence no such band can ever appear. This is the explanation of the selection rule  $\Sigma^+ \leftrightarrow \Sigma^-$ .

For like nuclei, the observed transitions  ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$  and  ${}^1\Sigma_g^+ - {}^1\Sigma_u^+$  for bosons are represented in Fig. 21.



(Fig. 21)

In assigning the symmetry we remember that the positive levels are symmetric and the negative levels are antisymmetric for an even (*g*) electronic state, and vice-versa for an odd (*u*) electronic state. For bosons, the *s*-levels are stronger throughout.

We see that the patterns are of the same type as for  ${}^1\Sigma^+ - {}^1\Sigma^+$  in case of heteronuclear molecules because the selection rules  $\Delta J = \pm 1$  and  $+ \leftrightarrow -$  are not violated by the additional rule sym.  $\leftrightarrow$  antisym.

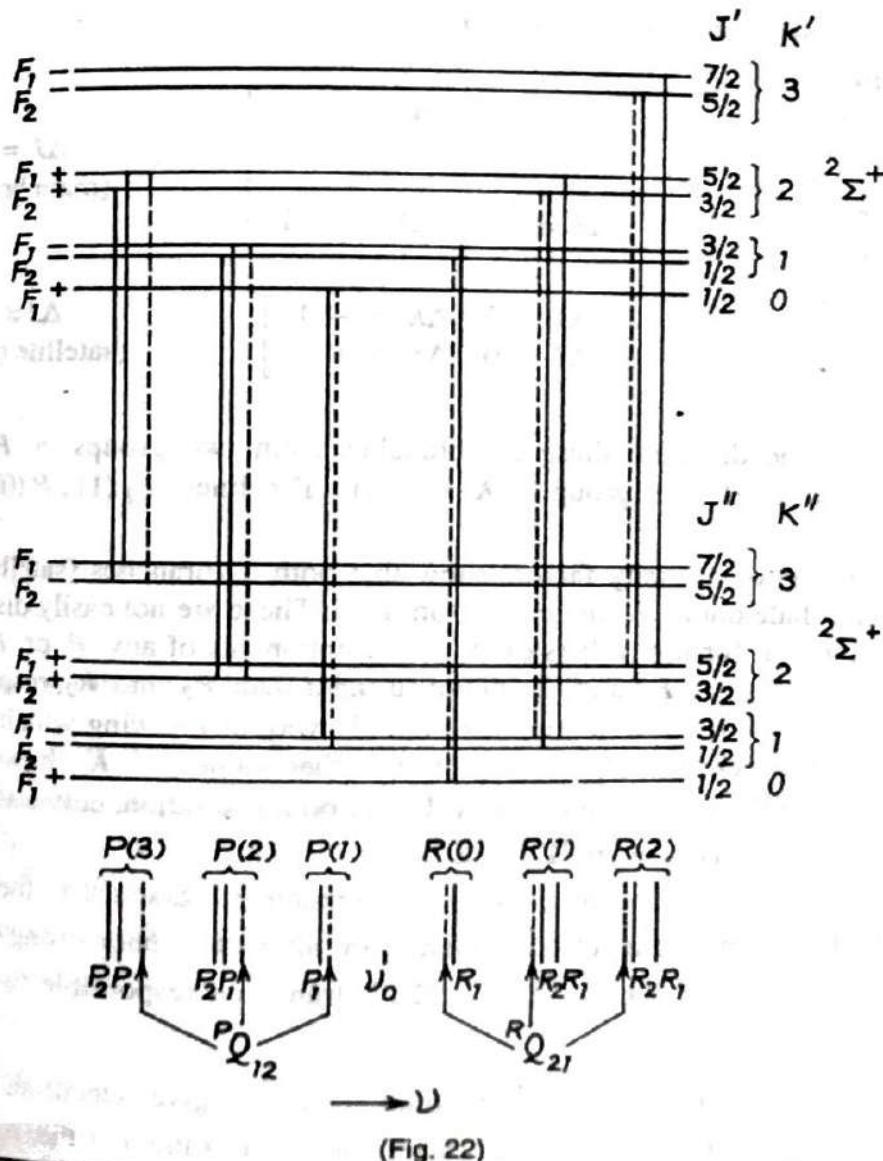
The additional feature of these transitions is intensity alternation. It is clear from the above figures that for one and the same molecule, the transition  ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$  is distinguished from  ${}^1\Sigma_g^+ - {}^1\Sigma_u^+$  by the fact that for the first the even-numbered rotational lines are stronger, while for the second the odd-numbered lines are the stronger throughout. This conclusion is for bosons for which the diagrams have been drawn.

Reverse would be the case if the molecule were fermion. Therefore, if the statistics of the nuclei is known, we can decide which one of the above two transitions is involved, on the basis of the observed alternation of intensities. Conversely, we can draw conclusions regarding the nuclear statistics if the type of the electronic states is known.

(b)  $^2\Sigma - ^2\Sigma$  Transitions : The observed transition is  $^2\Sigma^+ - ^2\Sigma^+$ , the best example of which is provided by the violet CN bands\*.

Each of these bands consists of a  $P$ -branch and a  $R$ -branch, each line being resolved into two strong components and one weak satellite. Thus, the  $R$ -branch consists of  $R_1, R_2$  and  $R_{Q21}$ , and the  $P$ -branch consists of  $P_1, P_2$  and  $P_{Q12}$ . The lines  $R_2(0), P_2(1)$  and all  $P(0)$  lines are missing.

The  $^2\Sigma$ -states ( $\Lambda = 0, S = \frac{1}{2}$ ) always belong strictly to Hund's case (b), so that there is a spin-doubling of each rotational level, but no  $\Lambda$ -type doubling. The state is



(Fig. 22)

\* The electronic configuration of CN is



and the ground state is  $^2\Sigma^+$ .

associated with a pile of rotational levels,  $K = 0, 1, 2, 3, \dots$  ( $K = \Lambda, \Lambda + 1, \dots$ ) ; and for each  $K$ -level there are two component levels  $F_1$  and  $F_2$ , with  $J = K + \frac{1}{2}$  and  $J = K - \frac{1}{2}$ , whose separation increases linearly with  $K$ . For  $K = 0$ , there is only one level  $J = \frac{1}{2}$ . These levels have been displayed in Fig. 22.

According to the symmetry rule, for a  $^2\Sigma^+$  state ; both  $F_1$  and  $F_2$  components of an even  $K$ -level are positive; while those of an odd  $K$ -level are negative.

The selection rules which will be operative are :

$$\Delta J = 0, \pm 1 \quad (\text{but } J = 0 \leftrightarrow J = 0)$$

$$+ \leftrightarrow -$$

$$\Delta K = \pm 1 \quad (\Delta K \neq 0 \text{ for } \Sigma-\Sigma \text{ transition})$$

As it is a case of multiplet state of case (b); the rule for  $K$  will be strict. These rules indicate that in all six branches are expected :

Branches	Rule	
$P_1(K)$	$\Delta J = -1, \Delta K = -1$	$\Delta J = \Delta K$ (main branches)
$P_2(K)$		
$R_1(K)$	$\Delta J = +1, \Delta K = +1$	
$R_2(K)$		
$P Q_{12}(K)$	$\Delta J = 0, \Delta K = -1$	$\Delta J \neq \Delta K$ (satellite branches)
$R Q_{21}(K)$	$\Delta J = 0, \Delta K = +1$	

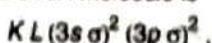
As is seen from the diagram, these six branches form two groups, a  $P$ -form group ( $\Delta K = -1$ ) and an  $R$ -form group ( $\Delta K = +1$ ). The lines  $P_2(1), P(0), R_2(0)$  are missing.

A consideration of intensity factors show that both  $Q$ -branches (satellites) are very weak and rapidly fade out as  $K$  increases from zero. These are not easily distinguished in the spectrum. Further, for low values of  $K$ , the components of any  $P$  or  $R$  doublet are quite unequal in intensity ;  $P_1$  and  $R_1$  being stronger than  $P_2$  and  $R_2$  respectively. This difference is important because it supplies the only way of knowing which branches are  $P_1$  and  $R_1$  and which are  $P_2$  and  $R_2$ . For higher values of  $K$ , however, the two components practically equalise in intensity. Under poor resolution, only a single  $P$  and a single  $R$  branch is observed as in  $^1\Sigma - ^1\Sigma$ .

The effect of additional symmetry for homonuclear  $^2\Sigma$ -states is the same as for  $^1\Sigma$ -states. The two components of the doublets are alternately *both* strong or *both* weak. The only case observed so far is  $^2\Sigma_u^+ - ^2\Sigma_g^+$  transition responsible for the negative nitrogen bands due to  $N_2^+$ .

(e)  $^1\Pi - ^1\Sigma$  Transitions : Several diatomic molecules give electronic band-systems corresponding to the transition  $^1\Pi - ^1\Sigma^+$ . One important example is the AlH molecule\*

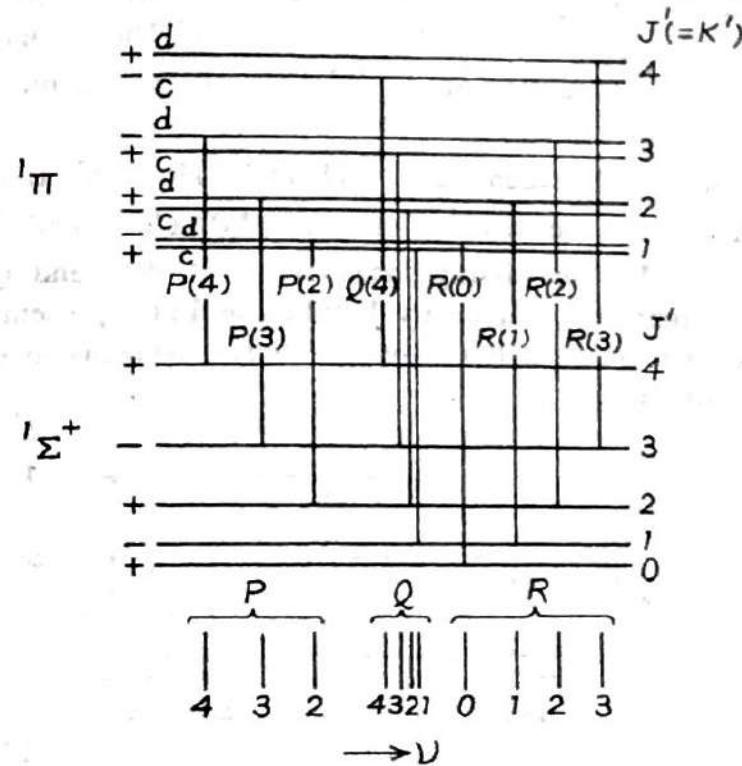
\* The electronic configuration of the AlH molecule is



and its ground state is  $^1\Sigma^+$ .

which gives a red-degraded band-system. Each band of the system shows a rotational structure consisting of a single *P*-branch, a single *Q*-branch and a single *R*-branch. The *P* and *R* branches are, on the average, of about equal intensity except for low *J*-values where the *R*-branch is stronger. The *Q*-branch is about twice as strong. Three lines *P(0)*, *P(1)* and *Q(0)* are missing.

For both  ${}^1\Pi$  and  ${}^1\Sigma^+$  states, the Hund's coupling cases (a) and (b) are identical. For the  ${}^1\Sigma^+$ -state, we have a set of single levels corresponding to  $J = K = 0, 1, 2, 3$ ; the even-*J* levels being positive and the odd-*J* levels negative. For the  ${}^1\Pi$ -state, we have a set of  $\Lambda$ -type doublet levels with  $J = K = 1, 2, 3, \dots$ ; the doublet components of each level being of opposite (+, -) symmetry. These levels have been shown in Fig. 23.



(Fig. 23)

The selection rules in operation are

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

$$+ \leftrightarrow - \quad (\text{symmetry rule})$$

$\Delta J = 0$  corresponds to the *Q*-branch,  $\Delta J = + 1$  to the *R*-branch and  $\Delta J = - 1$  to the *P*-branch. These branches commence with lines *Q(1)*, *R(0)* and *P(2)*. The head is formed in the *R*-branch.

The  $\Lambda$ -doubling of the  ${}^1\Pi$ -state does *not* break the rotational line into doublet components, because due to the rule  $+ \leftrightarrow -$ , a given level of the  ${}^1\Sigma^+$  state can combine only with the one or the other component of the level of the  ${}^1\Pi$ -state.

In the observed transition  ${}^1\Pi - {}^1\Sigma^+$ , the *P* and *R*-branches involve only the upper  $\Lambda$ -component levels of the  ${}^1\Pi$ -state whereas the *Q*-branch involves only the lower  $\Lambda$ -components. The reverse would be the case in the transition  ${}^1\Pi - {}^1\Sigma^-$ . This means that if the  $\Lambda$ -doubling of the  ${}^1\Pi$ -state were negligible, it would have been impossible to distinguish between the transitions  ${}^1\Pi - {}^1\Sigma^+$  and  ${}^1\Pi - {}^1\Sigma^-$ .

The wave numbers of the lines in the three branches are given as :

$$\nu_R = \nu_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2; J = J'' = 0, 1, 2, \dots$$

$$\nu_Q = \nu_0 + (B_v' - B_v'')J + (B_v' - B_v'')J^2; J = J'' = 1, 2, 3, \dots$$

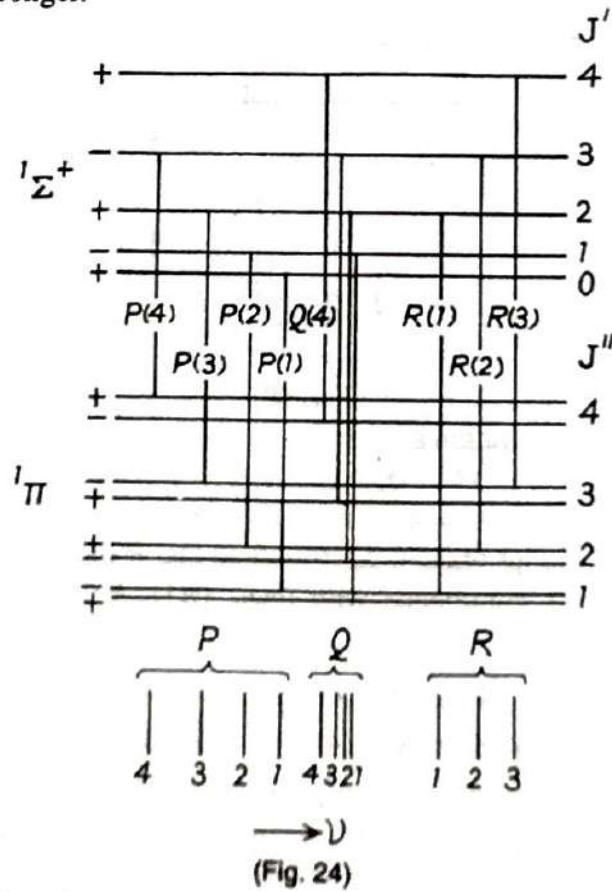
$$\nu_P = \nu_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2; J = J'' = 2, 3, 4, \dots$$

As  $(B_v' - B_v'')$  is small compared to  $(3B_v' - B_v'')$  or  $(B_v' + B_v'')$ , the spread of the  $Q$ -branch is smaller than that of  $R$  and  $P$ -branches

(d)  ${}^1\Sigma^+ - {}^1\Pi$  transitions : An important example of the transition  ${}^1\Sigma^+ - {}^1\Pi$  is found in the molecule CO.

The rotational structure of this transition is very similar to that  ${}^1\Pi - {}^1\Sigma^+$  transition. The branches  $P$ ,  $Q$  and  $R$  appear as before ; the  $P$  and  $R$  branches of about equal intensity and the  $Q$ -branch about twice as strong. The  $P$  and  $R$  branches involve one component of the  $\Lambda$ -doubling of the  ${}^1\Pi$ -state, and the  $Q$ -branch involves the other component.

The main difference between  ${}^1\Sigma^+ - {}^1\Pi$  and  ${}^1\Pi - {}^1\Sigma^+$  transitions is that in the present case ( ${}^1\Sigma^+ - {}^1\Pi$ ) the missing lines are  $P(0)$ ,  $Q(0)$ , and  $R(0)$  ; whereas in the previous case ( ${}^1\Pi - {}^1\Sigma^+$ ) the missing lines were  $P(0)$ ,  $P(1)$  and  $Q(0)$ . Apart from this, there is a slight difference in the intensity distribution. In the present case, the  $P$ -branch is stronger than the  $R$ -branch (at low  $J$ -values only), whereas in the previous case the  $R$ -branch was the stronger.

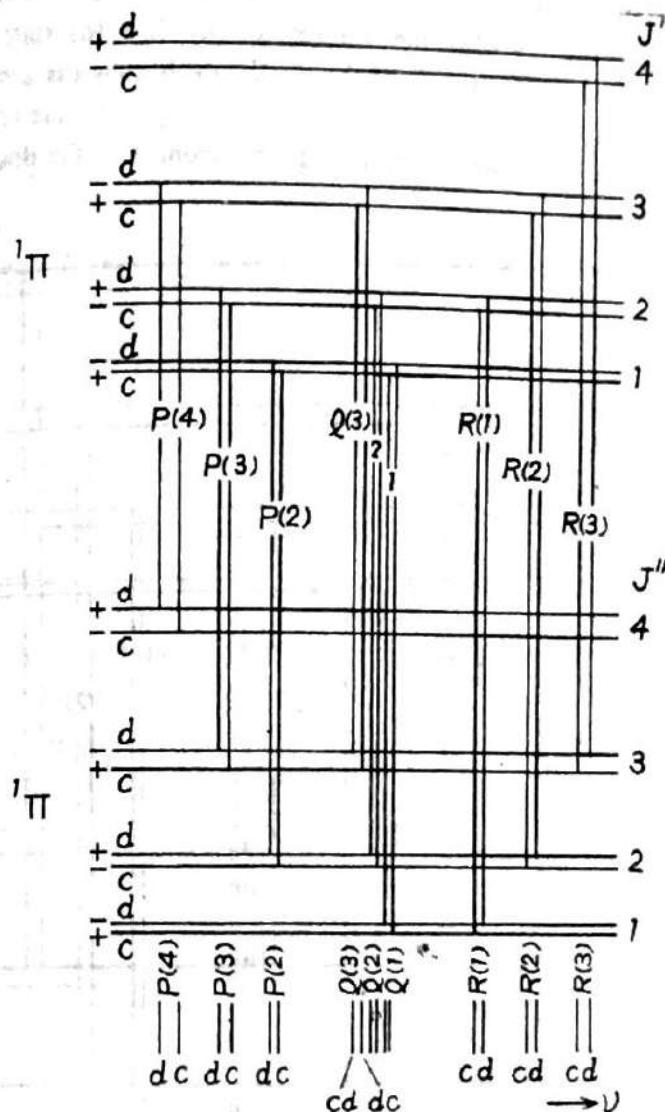


(Fig. 24)

The transition  ${}^1\Sigma^+ - {}^1\Pi$  is shown in Fig. 24. Comparing the band-structures in Fig. 24 and 23, we can decide whether the transition is  ${}^1\Sigma^+ - {}^1\Pi$  or  ${}^1\Pi - {}^1\Sigma^+$  if the region in the neighbourhood of zero line is resolved, just by seeing which of the two lines  $R(0)$  and  $P(1)$  is missing or which of the branches  $P$  and  $R$  is the stronger for low  $J$  values.

(e)  ${}^1\Pi - {}^1\Pi$  transitions : This transition gives a strong  $P$ -branch, a strong  $R$ -branch and a weak  $Q$ -branch ; each rotational line of the branches being splitted into two  $\Lambda$ -type components. The missing lines are  $P(0)$ ,  $Q(0)$ ,  $R(0)$  and  $P(1)$ .

Here for both of the electronic states  ${}^1\Pi - {}^1\Pi (\Lambda = 1, S = 0)$  the Hund's cases (a) and (b) are identical. Each state consists of a set of rotational levels  $J = 1, 2, 3, 4, \dots$ . Each level shows a  $\Lambda$ -type doubling ; the two components being of opposite  $+, -$  symmetry (Fig. 25).



(Fig. 25)

The selection rules are :

$$\Delta J = 0, \pm 1;$$

$$+ \leftrightarrow -.$$

We find that the branches start from the doublet lines  $P(2)$ ,  $Q(1)$  and  $R(1)$ . In all, there are six branches :  $P_c$ ,  $P_d$ ,  $R_c$ ,  $R_d$ ,  $Q_{cd}$ ,  $Q_{dc}$ . Since  $\Delta\Lambda = 0$ ; the  $Q$ -branch is very weak and its intensity decreases rapidly with increasing  $J$ .

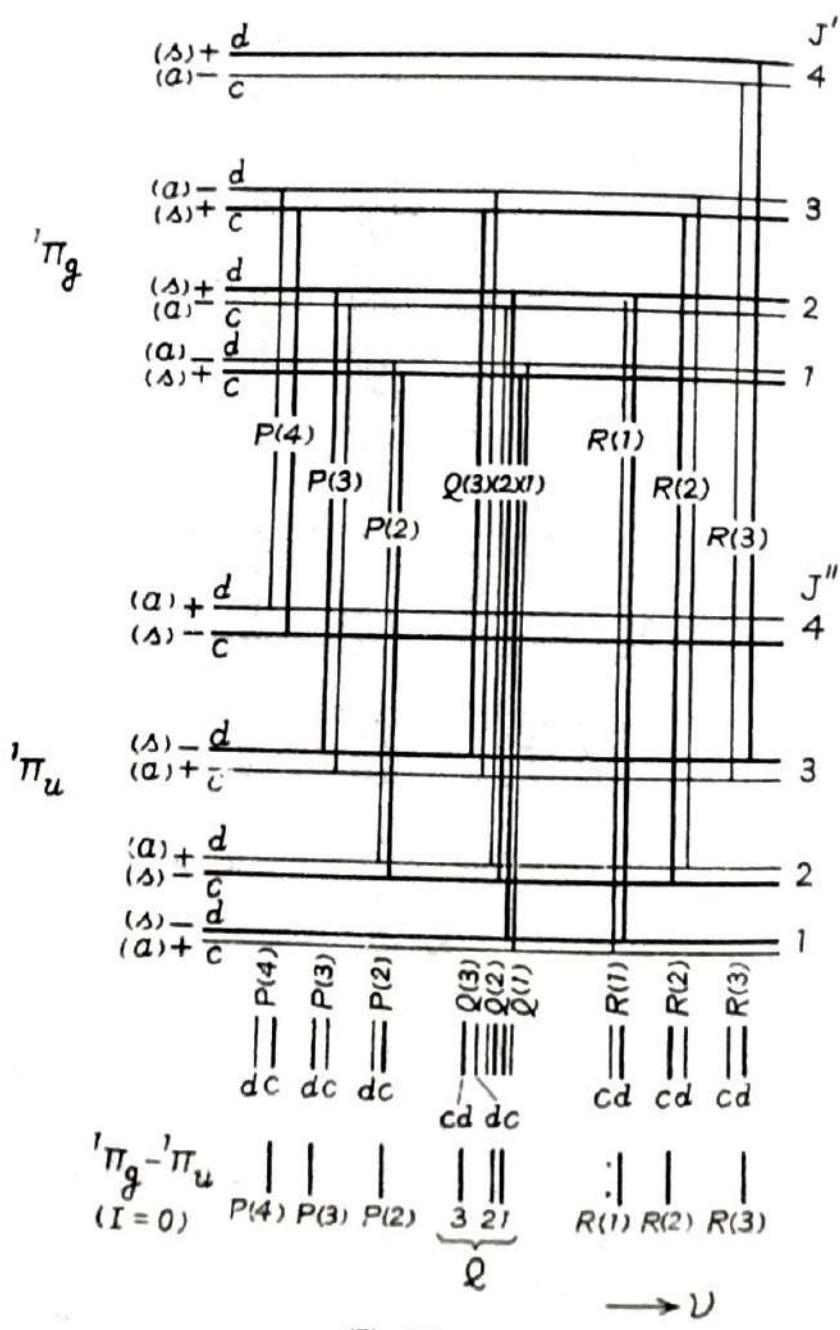
The magnitude of  $\Lambda$ -splitting in the  $P$  and  $R$ -branches is equal to the difference of the  $\Lambda$ -type doublet separations of the upper and the lower states, and that in the  $Q$ -branch

is equal to their sum. Therefore, for those levels for which  $Q$  as well as  $P$  and  $R$  doublets are observed, the magnitude of the  $\Lambda$ -type doubling can be determined directly.

The  $\Lambda$ -components of a doublet have equal intensities, unlike the spin-components of a multiplet.

The sole example of a  ${}^1\Pi - {}^1\Pi$  transition for unlike nuclei is the AlH band at  $3380 \text{ \AA}$ .

In the case of a homonuclear molecule with nuclear spin, the sub-levels of a given  $J$ -value will have unequal statistical weights, so that the two components of each doublet will be of unequal intensity. Fig. 26 shows a transition  ${}^1\Pi_g - {}^1\Pi_u$ . The criteria is that in a ( $g$ ) state the  $+$  levels are ( $s$ ) while the  $-$  levels are ( $a$ ). In a ( $u$ ) state, the  $+$  levels are ( $a$ ) and the  $-$  levels are ( $s$ ). Further, if the nuclei are bosons (as assumed here), the  $s$ -levels are the stronger throughout. Since the stronger components are all  $+$  in the upper state, and all  $-$  in the lower state ; the stronger component of the doublets in a given



(Fig. 26)

branch will be alternately the higher- $\nu$  and the lower- $\nu$  component as  $J$  increases. That is, a given sub-branch such as  $R_c$  will have opposite intensity alternation with the neighbouring sub-branch  $R_d$ . These features of the  ${}^1\Pi_u - {}^1\Pi_g$  transitions are indicated in the spectrogram shown below the energy-level diagram.

For a  ${}^1\Pi_u - {}^1\Pi_g$  transition,  $s$  and  $a$  would have to be exchanged throughout, so that in the spectrogram the stronger lines will be weaker, and vice-versa.

When the nuclear spin  $I$  is zero, one (weaker) component of every doublet vanishes, as shown in a separate spectrogram. A casual inspection of this spectrogram indicates as if the band consists of single branches (with no missing lines). Actually, a comparison of the two spectrograms shows that in the lower spectrogram the even-numbered lines in each branch are displaced to one side and the odd-numbered lines to the other side of a mean position. This effect is called 'staggering'. It is seen in the  ${}^1\Pi - {}^1\Pi$  violet system of  $C_2$  molecule.

#### 14. Forbidden Transitions in Molecular Spectra

Under certain conditions, electronic transitions occur that contradict the normally operative selection rules. They are called 'forbidden transitions'. They can be observed in absorption by using very long absorbing paths. In emission they appear only under special condition of excitation. Rotational transitions that are forbidden by the ordinary selection rules may also appear (weakly) in certain allowed bands.

Forbidden transitions usually occur because certain selection rules may hold only to a first approximation. For example, the rule

$$\Delta S = 0$$

holds less and less strictly with increasing spin-orbit interaction, that is, with increasing atomic number. Actually, triplet-singlet transition  ${}^3\Pi - {}^1\Sigma$  has been observed for molecules CO (Cameron bands) and the halogens, both in absorption and emission. Similarly, the Vegard-Kaplan emission bands of  $N_2$  are the result of the transition  ${}^1\Sigma^+ - {}^1\Sigma_g^+$ .

Two other examples of approximate selection rules are :

$$\Sigma^+ \leftrightarrow \Sigma^-$$

$$\Delta K \neq 0 \text{ for } \Sigma - \Sigma \text{ transition.}$$

These rules are strictly valid only when electronic and rotational motions can be separated under Born-Oppenheimer approximation. The rotational distortion of the electronic motion may cause the appearance of  $\Sigma^+ - \Sigma^-$  transitions, with  $\Delta K = 0$  which is now allowed by the symmetry rotational rule  $+ \leftrightarrow -$ , while  $\Delta K = \pm 1$  would be forbidden. The resulting bands would have  $Q$ -branches only. In fact, the near ultraviolet absorption bands of  $O_2$  arise from the transition  ${}^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$ .

Another cause of the appearance of forbidden transitions is that a selection rule may hold strictly for dipole radiation but not for quadrupole radiation or magnetic dipole radiation. For example, for quadrupole as well as for magnetic dipole radiation, the symmetry selection rule for the combining rotational levels is

$$+ \longleftrightarrow + ; - \longleftrightarrow -$$

which is just the opposite of the rule  $+ \longleftrightarrow -$  holding for dipole radiation. In fact, in the  $^3\Sigma - ^1\Pi$  bands of OH, weak satellite branches have been found which are forbidden by the rule  $+ \longleftrightarrow -$ , but allowed by the rule for magnetic dipole radiation.

In homonuclear molecules, the symmetry selection rule for quadrupole or magnetic dipole radiation yield forbidden band-systems, not just forbidden branches in allowed band-systems. For these molecules, the rule symmetry  $\longleftrightarrow$  antisymmetry remains unaltered. Therefore, according to  $+ \longleftrightarrow +$  and  $- \longleftrightarrow -$ , the (electronic) transitions  $g-g$  and  $u-u$  can appear as quadrupole or magnetic dipole radiation (which are forbidden in ordinary dipole radiation). An example is provided by the Lyman-Birge bands of N<sub>2</sub> which represent a  $^1\Pi_g - ^1\Sigma_g^+$  transition. Similarly, the red atmospheric oxygen bands are accounted for on the assumption that they represent a magnetic dipole transition  $^1\Sigma_g^+ - ^3\Sigma_u^-$ .

### SOLVED PROBLEMS

1. Which of the following electronic transitions are not allowed ? Which rules are violated ?

- (a)  $^1\Sigma^+ - ^1\Sigma^-$ , (b)  $^3\Sigma^+ - ^1\Sigma^-$ , (c)  $^3\Delta_u - ^1\Sigma_g$ , (d)  $^1\Pi_g - ^1\Sigma_g$ ,
- (e)  $^2\Pi_{3/2} - ^2\Pi_{1/2}$ .

(Meerut sp. paper 2002, 98, 92)

**Solution.** (a), (b), (c), (e) are not allowed.

- (a) It violates the rule  $\Sigma^+ \longleftrightarrow \Sigma^-$
- (b) It violates the rule  $\Delta S = 0$ .
- (c) It violates the rules  $\Delta S = 0$ ,  $\Delta \Lambda = 0, \pm 1$  and  $g \longleftrightarrow u$ .
- (e) It violates the rule  $\Delta \Lambda = \Delta \Omega$ .

2. Which of the following electronic transitions are allowed/not allowed ? Which rules are obeyed/violated.

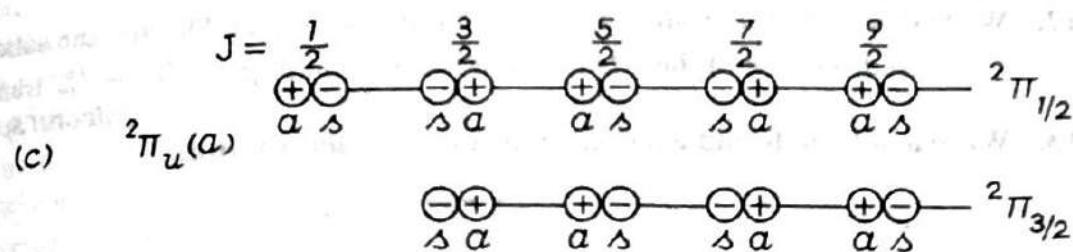
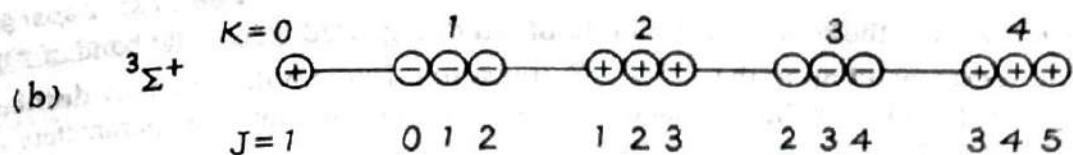
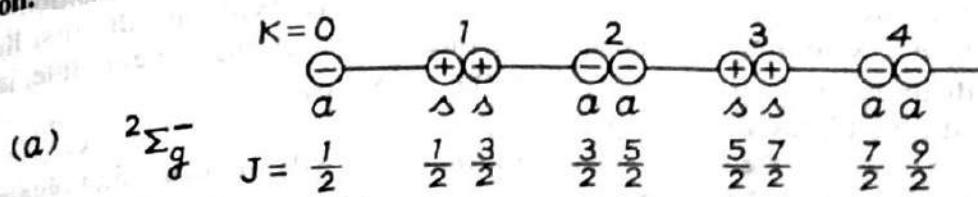
- (a)  $^1\Sigma_g^+ - ^1\Sigma_g^+$ , (b)  $^1\Sigma_g^- - ^1\Sigma_g^+$ , (c)  $^3\Delta_u - ^3\Pi_g$ , (d)  $^2\Sigma_g^+ - ^2\Sigma_g^+$ ,
- (e)  $^1\Sigma_u^+ - ^3\Sigma_g^-$ , (f)  $^3\Pi_g - ^3\Delta_u$ , (g)  $^2\Pi_{3/2} - ^2\Delta_{3/2}$ , (h)  $^3\Delta_1 - ^3\Pi_2$ .

- Solution.**
- (a) Allowed. (it obeys  $\Delta S = 0$ ,  $\Sigma^+ - \Sigma^+$ ,  $u \longleftrightarrow g$ )
  - (b) Not allowed. (It violates  $\Sigma^+ \longleftrightarrow \Sigma^-$  and  $g \longleftrightarrow u$ ).
  - (c) Allowed. (It obeys  $\Delta S = 0$ ,  $\Delta \Lambda = 0 \pm 1$  and  $u \longleftrightarrow g$ ).
  - (d) Allowed, as (a).
  - (e) Not allowed. (It violates  $\Delta S = 0$ ,  $\Sigma^+ \longleftrightarrow \Sigma^-$ ).
  - (f) Allowed, as (c).
  - (g) Not allowed. (It violates  $\Delta \Lambda = \Delta \Omega$ ).
  - (h) Not allowed. (It violates  $\Delta \Lambda = \Delta Q$ ).

3. Indicate the  $J$ -values, and where appropriate,  $K$ -values, and symmetries of the first few rotational levels of each of the following electronic states :

- (a)  $^2\Sigma_g^-$ ,
- (b)  $^3\Sigma^+$ ,
- (c)  $^2\Pi_u$  ( $a$ ).

Solution.



## QUESTIONS

1. Discuss Hund's cases (a) and (b) of coupling of rotation and electronic motion in diatomic molecules. Give examples.

(Meerut 99 S, 98, sp. paper 2004, 03, 00, 98, 89)

2. Discuss clearly the different Hund's cases of coupling of rotation and electronic motion in diatomic molecules. Give specific examples where case (c) type of coupling is valid.

3. Discuss the various coupling schemes for the angular momenta in a diatomic molecule. Explain the origin of  $\Lambda$ -doubling.

4. Discuss the symmetry properties of rotational levels of a homonuclear diatomic molecule in a  $^1\Sigma^+$  state. Explain how these symmetry properties modify the rotational structure in an electronic transition. (Meerut sp. paper 98)

5. What are the electronic quantum numbers of diatomic molecules ? State the selection rules for any two coupling cases. (Meerut sp. paper 96)

6. A transition is described as  $^2\Sigma_g^- \leftarrow ^2\Sigma_u$  for an uncharged, homonuclear diatomic molecule. What is wrong with this statement ?

Ans. The symmetry of the electronic eigenfunctions of the non-degenerate  $\Sigma$ -states has not been indicated. The  $\Sigma$ -states must be described as  $\Sigma^+$  or  $\Sigma^-$ .

7. Describe the symmetry properties of the rotational level for homonuclear diatomic molecule. Also discuss the rotational structure of a red-degraded electronic band of AlH molecule corresponding to the  $^1\Pi - ^1\Sigma$  transition.

(Meerut sp. paper 2002, 96)

8. Construct an energy-level diagram for a band of  ${}^1\Pi - {}^1\Sigma^+$  transition. Indicate the symmetries and  $J$ -values of all rotational levels. What are the first lines of each branch? Assuming that the splitting due to  $\Lambda$ -doubling is negligible, is it possible to distinguish this transition from a  ${}^1\Pi - {}^1\Sigma^-$  transition?

**Hint :** First lines are  $P(2)$ ,  $Q(1)$ ,  $R(0)$ .

9. Write down the electronic configuration of the AlH molecule and obtain its ground state. Also discuss the fine structure of the red-degraded electronic bands of AlH molecule corresponding to the  ${}^1\Pi - {}^1\Sigma$  transition.

(Meerut sp. paper 98 S, 98, 94)

10. Discuss the rotational structure of a red-degraded electronic band of AlH molecule corresponding to the  ${}^1\Pi - {}^1\Sigma$  transition. Explain the intensity distribution in the different branches of such a transition and elucidate the parameters on which it would depend.

11. Discuss the rotational structure of the violet CN bands corresponding to the  ${}^2\Sigma - {}^2\Sigma$  electronic transition.

12. Write down the electronic configuration of CN radical. Discuss the salient features of the 'red' system of the CN molecule corresponding to  ${}^2\Pi - {}^2\Sigma$  transition.

(Meerut sp. paper 93)

13. Write a note on forbidden transitions in molecular spectra.
-

## Co-relation between Atomic and Molecular States : Building-up Principle

### 1. Introduction

The theoretically possible number of electronic states of a diatomic molecule is as large as for atoms, yet for most molecules only two or three electronic states have been found on the basis of their observed band spectra. The latter question is, however, related with the stability of the electronic states. At present we shall discuss what electronic states are possible for a diatomic molecule. This can be done by the successive bringing together of the parts of the molecule. This is known as 'building-up principle'.

Whereas the building-up of an atom can be accomplished only in one way, for a molecule there are three different possibilities :

(i) The molecule may be built-up by bringing together the constituent atoms, complete with all their electrons, from an initial infinite separation. The vector model can be used to co-relate the states of the resultant molecule with the states of the separated atoms.

(ii) The nucleus of an atom, with an appropriate nuclear charge, and the necessary number of electrons, can be splitted into two nuclei drawn apart to a finite separation to give the required molecule. This (hypothetical) process enables us to co-relate the states of the molecule with those of the united atom.

(iii) The nuclei can be held at a fixed separation and the individual electrons can be added one after another to the nuclei and are assigned proper orbitals. The different possible electronic arrangements then give the possible states, just as for atoms.

### 2. Determination of Molecular (Electronic) States from the States of the Separated Atoms

**Unlike Atoms :** Suppose two *unlike* atoms with azimuthal and spin quantum numbers  $L_1, S_1$  and  $L_2, S_2$  respectively are brought up to each other adiabatically to form a molecule. In this process, the spherical symmetries of the potential fields in both (isolated) atoms are destroyed. Instead, a strong electric field is formed in the direction of the internuclear axis of the molecule formed. The vectors  $\vec{L}_1$  and  $\vec{L}_2$  precess about this axis with space-quantised components  $M_{L_1} (h/2\pi)$  and  $M_{L_2} (h/2\pi)$ , where the quantum numbers  $M_{L_1}$  and  $M_{L_2}$  take the values :

$$M_{L_1} = L_1, L_1 - 1, \dots, -L_1$$

$$M_{L_2} = L_2, L_2 - 1, \dots, -L_2.$$

The resultant electronic orbital angular momentum component along the internuclear axis is  $\Lambda (h/2\pi)$ , where the quantum number  $\Lambda$  of the molecule thus formed is

$$\Lambda = |M_{L_1} + M_{L_2}|.$$

The combinations of all possible  $M_{L_1}$  and  $M_{L_2}$  values give all possible  $\Lambda$  values. Thus, from a given combination of states of the separated atoms, there results a number of different states of the molecule. For  $\Lambda > 0$ , each molecular state is degenerate because states which differ only in the sign of both  $M_{L_1}$  and  $M_{L_2}$  have equal energies. For  $\Lambda = 0$  ( $\Sigma$ -states), however, this degeneracy does not exist; each combination corresponds to a different molecular state ( $\Sigma^+$  and  $\Sigma^-$ ).

As a first example, let us consider the case when an atom in  $S$ -state ( $L_1 = 0$ ) approaches another atom in  $D$ -state ( $L_2 = 2$ ). Then, we have

$$M_{L_1} = 0$$

$$M_{L_2} = 2, 1, 0, -1, -2$$

so that

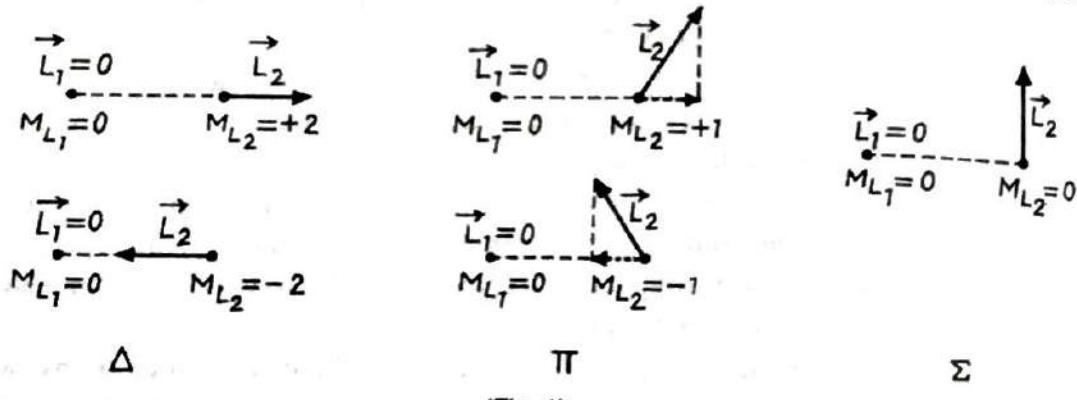
$$M_{L_1} + M_{L_2} = 2, 1, 0, -1, -2$$

and thus

$$\Lambda = |M_{L_1} + M_{L_2}| = 2, 1, 0, 1, 2.$$

The two values  $\Lambda = 2$  and the two values  $\Lambda = 1$  correspond to a doubly-degenerate  $\Delta$ -state and a doubly-degenerate  $\Pi$ -state respectively, while  $\Lambda = 0$  represents a  $\Sigma$ -state. These three molecular states have different energies.

The possible orientations of  $\vec{L}_1$  and  $\vec{L}_2$  giving rise to  $\Delta$ ,  $\Pi$  and  $\Sigma$  states are shown



(Fig. 1)

in Fig. 1. The symmetry of  $\Sigma$ -state which has arisen from  $M_{L_1} = 0$  and  $M_{L_2} = 0$  is determined from the following rule, given by Wigner and Witmer,

$\Sigma^+$  if  $L_1 + L_2 + \Sigma l_{11} + \Sigma l_{12}$  is even

$\Sigma^-$  if  $L_1 + L_2 + \Sigma l_{11} + \Sigma l_{12}$  is odd.

We know that  $\Sigma l_i$  determines the parity, even or odd, of an atomic state where the summation is over all the electrons in incomplete subshells of the atom. Thus, the symmetry of the  $\Sigma$ -state in question depends on the  $L$  values as well as on the parities of the atomic states from which it results. For the given example of the  $S$  and  $D$  atomic states, when parities are given, the resulting molecular states would be as follows :

$S_g + D_g$  or  $S_u + D_u$  :  $\Sigma^+, \Pi, \Delta$

$S_g + D_u$  or  $S_u + D_g$  :  $\Sigma^-, \Pi, \Delta$ .

As a second example, we take up the combination of two separated (unlike) atoms, each in an atomic  $P$ -state ( $L_1 = L_2 = 1$ ). For this case, we have

$$M_{L_1} = 1, 0, -1$$

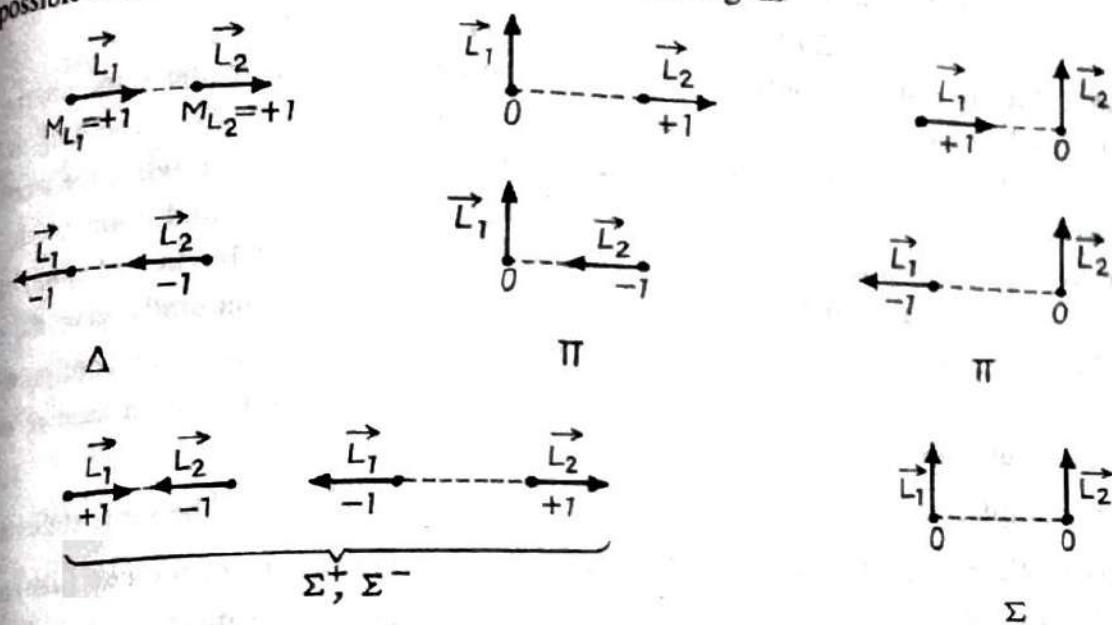
$$M_{L_2} = 1, 0, -1$$

so that,  
and thus

The two values  $\Lambda = 2$  give one (doubly-degenerate)  $\Delta$ -state, the four values  $\Lambda = 1$  give two (doubly-degenerate)  $\Pi$ -states, and the three  $\Lambda = 0$  values give three  $\Sigma$ -states.  
We write these states in the following way :

$$\Sigma(3), \Pi(2), \Delta.$$

The possible orientations of  $\vec{L}_1$  and  $\vec{L}_2$  are shown in Fig. 2.



(Fig. 2)

The number of  $\Sigma$ -states is three. Two of the configurations yielding  $\Sigma$ -states differ only in the sign of both  $M_L$  values (Fig. 2). One of these is  $\Sigma^+$  and the other is  $\Sigma^-$ . (These two states are *not* degenerate). The remaining  $\Sigma$ -state, which arises from  $M_{L_1} = M_{L_2} = 0$ , is  $\Sigma^+$  or  $\Sigma^-$  according as  $L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2}$  is even or odd\*. This can be decided only when the parities of the separated atomic states are given. For the given example of the  $P$  and  $P$  atomic states, when parities are given, the resulting molecular states would be as follows :

$$P_g + P_g \text{ or } P_u + P_u : \Sigma^+(2), \Sigma^-(2), \Pi(2), \Delta$$

$$P_g + P_u : \Sigma^+, \Sigma^-(2), \Pi(2), \Delta.$$

We have yet to determine the multiplicity of the resulting molecular states from the multiplicities of the atomic states of the separated atoms. The electron spin is not affected by the electrostatic field of the nuclei. Therefore, when two atoms with electron spins  $S_1$  and  $S_2$  combine to form a molecule, the resulting electron spin  $S$  of the molecule takes all possible values given by vector addition, that is,

$$S = (S_1 + S_2), (S_1 + S_2 - 1), (S_1 + S_2 - 2), \dots, |S_1 - S_2|.$$

Each electronic state of the molecule can have each of these multiplicities,  $(2S + 1)$ . For example, if in the above case the atomic states are  ${}^2P$  and  ${}^2P$ , then we have

\*In fact, the number of  $\Sigma$ -states that arise is always odd. Of these, one  $\Sigma$ -state always arises from  $M_{L_1} = M_{L_2} = 0$  and the symmetry of this single  $\Sigma$ -state is obtained by the above rule. All other  $\Sigma$ -states, even in number, form pairs of  $\Sigma^+$  and  $\Sigma^-$  states.

$$S_1 = \frac{1}{2}, S_2 = \frac{1}{2}$$

$$\therefore S = 1, 0$$

and

$$(2S + 1) = 3, 1;$$

that is, both triplet and singlet states are possible for each electronic state derived above. Thus, on combining two unlike atoms, each in a  $^2P$ -state, as much as twelve electronic states are possible for the resulting molecule. These are

$$^3\Sigma(3), ^1\Sigma(3), ^3\Pi(2), ^1\Pi(2), ^3\Delta, ^1\Delta.$$

**Like Atoms :** If the nuclei of the two separated atoms have the same charge, the resulting molecular states must be classified as even (*g*) or odd (*u*) according to their parity. When the combining atoms are in *different* atomic states, then, when the atoms are far apart, inversion of their electronic wavefunctions about the mid-point of the line joining the nuclei produces atomic configurations with nucleus 1 having quantum values  $(L_2, S_2)$  and nucleus 2 having values  $(L_1, S_1)$ . This would naturally give the same manifold of electronic states for the resulting molecule as the original configurations. Hence, in this case the resulting molecular states will be the same as in case of unlike atoms, but double in number.

For example, from  $^1S_g + ^1P_u$  we obtain,  $^1\Sigma^+$  and  $^1\Pi$  states. The same states would arise from  $^1P_u + ^1S_g$ , that is, when the electronic wavefunctions of the two (like) atoms are inverted (that is, the excitation energies of the two atoms are interchanged). Thus, in all, we shall obtain two  $^1\Sigma^+$  and two  $^1\Pi$  states. These have equal energies for large internuclear distance, but different energies for small internuclear distance on account of the interaction of the two atoms. The wavefunctions of each pair ( $^1\Sigma^+, ^1\Sigma^+$ ) and ( $^1\Pi, ^1\Pi$ ), can be reformed as linear combinations, one of which is always even (*g*) and the other odd (*u*), and which differ in energy. Thus, in the example  $^1S_g + ^1P_u$  for like atoms, the four separate states are

$$^1\Sigma_g^+, ^1\Sigma_u^+, ^1\Pi_g, ^1\Pi_u.$$

Thus, when two *like* atoms in *different* atomic states combine ; each of the states occurring for unlike atoms occurs twice, once as an even state and once as an odd state.

When the two like combining atoms are in identical atomic states, the parity of the resulting molecular states can only be decided by group theory.

### 3. Determination of Molecular States from the States of the United-atom

**Unlike Atoms :** When the nucleus of an atom is hypothetically splitted into two unlike nuclei to form a molecule with the same number of electrons, an (inhomogeneous) electric field is produced in the direction of internuclear axis. In most of the cases, this field is strong enough to break the coupling between  $\vec{L}$  and  $\vec{S}$ . Then,  $\vec{L}$  couples to the internuclear axis and precesses about it with quantised components of magnitude  $\Lambda(h/2\pi)$ , where the quantum number  $\Lambda$  takes values :

$$\Lambda = |M_L| = L, L - 1, L - 2, \dots, 0.$$

The spin  $S$ , and hence the multiplicity, of the molecule remains the same as in the united-atom.

As an example, let us consider the splitting of a Mg atom (12 electrons) in a  $^3D_g$ -state. For this, we have

$$L = 2$$

$$\Lambda = 2, 1, 0.$$

so that,  
Thus, we get the molecular states

$$^3\Delta, ^3\Pi \text{ and } ^3\Sigma,$$

provided we imagine the Mg atom to yield a BeO ( $4 + 8$  electrons) or a BN ( $5 + 7$  electrons) molecule (unlike nuclei). Whether the resulting  $\Sigma$ -state is a  $\Sigma^+$  or a  $\Sigma^-$  state depends upon whether

$$L + \Sigma l_i$$

for the united-atom is even or odd. Since  $L + \Sigma l_i$  is even for  $^3D_g$  state, the  $^3\Sigma$  state is  $^3\Sigma^+$ . Thus, the resulting molecular state can be finally written as :

$$^3\Delta, ^3\Pi \text{ and } ^3\Sigma^+.$$

**Like Atoms :** If the united-atom is splitted into a molecule with nuclei of equal charge, exactly the same states are obtained as for unlike atoms, except that the  $g-u$  parity has to be added. Wigner and Witmer have shown that the resulting molecular states are all even or all odd according as the state of the united-atom is even or odd. Suppose in the above example of Mg atom in  $^3D_g$  state the resulting molecule is C<sub>2</sub> ( $6 + 6$  electrons). Then, the resulting molecular states would be

$$^3\Delta_g, ^3\Pi_g \text{ and } ^3\Sigma_g^+.$$

#### 4. Determination of Molecular States from Electron Configuration

The molecular-orbital (MO) description of molecules is an extension of the description of atomic orbitals (AO). The orbitals of the atoms forming the molecule combine into a set of molecular orbitals covering the whole molecule. The inner electrons of the atoms stay in the unperturbed orbitals on their respective atoms, while the valence electrons are stripped out and occupy the molecular orbitals in accordance with the Aufbau principle<sup>1</sup>, Pauli principle<sup>2</sup> and the Hund's rule<sup>3</sup>.

As for atoms, the molecular states are described by a set of quantum numbers assigned to the electrons occupying the molecular orbitals. These orbitals are best described in terms of the (atomic) orbitals to which they would go in the limits of the united atom ( $r \rightarrow 0$ ) and of the separated atoms ( $r \rightarrow \infty$ ).

Let us first consider the motion of a single valence electron about a molecular core consisting of the two nuclei and the remaining inner electrons. The field in which the electron moves is, to a good approximation, axially symmetric with respect to the

1. The orbitals are filled up in the order of increasing energy.
2. It restricts the maximum number of electrons in a particular orbital.
3. One electron is assigned to each of the degenerate orbitals before a second electron is assigned to any one of them, and the electrons in the singly-occupied orbitals have parallel spins.

internuclear axis. The solution of the Schrödinger equation for the motion of an electron in such a field gives a discrete set of (negative) energy values which correspond to the stationary electronic states of the molecule. Each state is characterised by three quantum numbers  $n$ ,  $l$  and  $\lambda$ . Of these,  $n$  and  $l$  can only be defined in the limiting cases of the united-atom ( $r \rightarrow 0$ ) or the separated atoms ( $r \rightarrow \infty$ ) whereas  $\lambda$  can be precisely defined for all internuclear distances.  $\lambda$  is the quantum number of the electronic orbital angular momentum component along the internuclear axis which has a magnitude of  $\lambda (h/2\pi)$ . The possible values of  $\lambda$  are :

$$\lambda = 0, 1, 2, 3, \dots$$

and the electron is accordingly described as  $\sigma$ ,  $\pi$ ,  $\delta$ ,  $\phi$ , .....

Let us first consider the molecular orbitals which arise when a united-atom is imagined to be splitted into a molecule. In the united-atom, the electron states are defined by  $n$ ,  $l$  and  $m_l$ . On splitting, so long the internuclear distance is small, the possible electronic states are the same as those for the united-atom placed in an electric field (Stark effect). In this case,  $n$  and  $l$  are still approximately defined, but  $m_l$  is replaced by  $\lambda$  which is precisely defined.  $\lambda$  arises as a result of precession of the electronic orbital angular momentum vector  $\vec{\Gamma}$  about the internuclear axis with components  $m_l (h/2\pi)$ , where

$$\lambda = |m_l| = l, l - 1, l - 2, \dots, 1, 0.$$

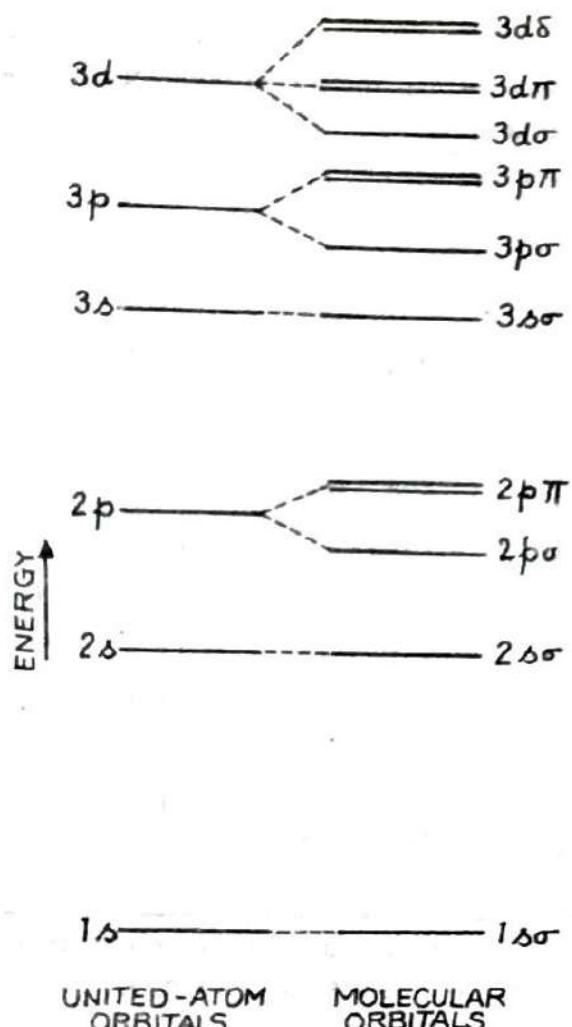
States with  $\lambda \neq 0$  are doubly-degenerate, because a positive and a negative  $m_l$  of the same magnitude correspond to one and the same  $\lambda$ . Thus, in the united-atom approximation (for small internuclear distances), the molecular orbitals are described by quantum numbers  $n$ ,  $l$  and  $\lambda$ , where  $n$  and  $l$  are the same as for the united-atom. The atomic orbitals and the corresponding molecular orbitals may be tabulated as under :

United-Atom Orbitals	$n$	$l$	$\lambda$	Resulting Molecular Orbitals
1s	1	0	0	1s $\sigma$
2s	2	0	0	2s $\sigma$
2p		1	0, 1	2p $\sigma$ , 2p $\pi$
3s	3	0	0	3s $\sigma$
3p		1	0, 1	3p $\sigma$ , 3p $\pi$
3d		2	0, 1, 2	3d $\sigma$ , 3d $\pi$ , 3d $\delta$

The molecular orbitals (for small internuclear distances) have been designated as 1s  $\sigma$ , 2s  $\sigma$ , 2p  $\sigma$ , 2p  $\pi$ , ..... In these designations the number denotes the  $n$  value, the Roman letter denotes the  $l$  value (s, p, d, ..... for  $l = 0, 1, 2, \dots$ ) and the Greek letter denotes the  $\lambda$  value ( $\sigma$ ,  $\pi$ ,  $\delta$ , ..... for  $\lambda = 0, 1, 2, \dots$ ). All orbitals, except the  $\sigma$ -orbitals, the doubly-degenerate.

The energy order of the molecular orbitals is shown in Fig. 3.

If the two nuclei of the resulting molecule have *equal* charges, the electron states are described as even states ( $\sigma_g, \pi_g, \dots$ ) or odd states ( $\sigma_u, \pi_u, \dots$ ) according as the wavefunction remains unaltered or changes sign by reflection at the origin. For an even  $l$  of the united-atom ( $s, d, \dots$  electrons) the wavefunctions are even, while for odd  $l$  ( $p, f, \dots$  electrons) they are odd. Thus,  $1s$  orbitals of the united-atom would give a  $1s\sigma_g$  orbital of the resulting homonuclear molecule, and similarly, the  $3d$  atomic orbital would give  $3d\sigma_g, 3d\pi_g$  and  $3d\delta_g$  molecular orbitals. On the other hand, the  $2p$  atomic orbitals would give  $2p\sigma_u$  and  $2p\pi_u$  molecular orbitals.



(Fig. 3)

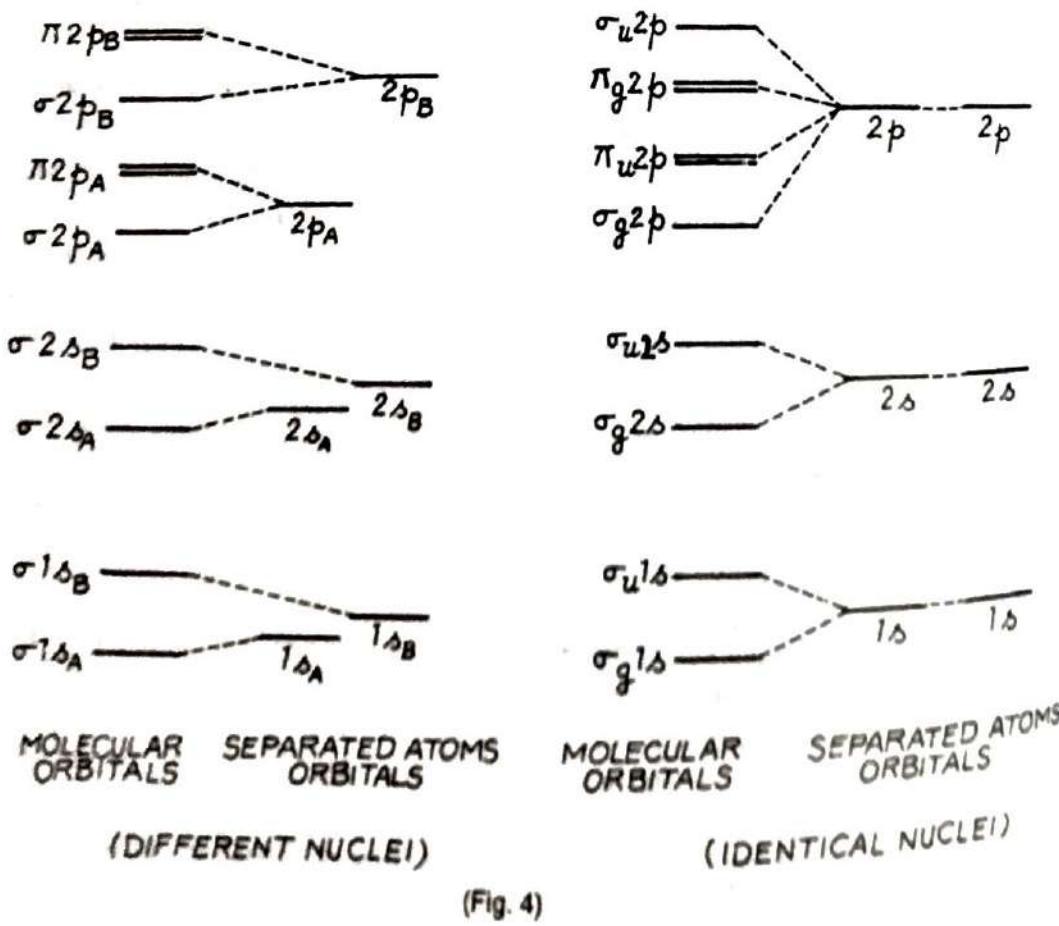
Let us now consider the molecular orbitals arising when two separated atoms, with nuclei *A* and *B*, approach each other to form a molecule. As an example, let us take the formation of the molecular ion  $H_2^+$  which consists of two hydrogen nuclei (protons) and one electron. When a hydrogen atom and a hydrogen nucleus (proton) are infinitely separated, there are two possibilities. Either the electron is with nucleus *A* (which forms the atom) and *B* remains as proton; or *B* forms the atom and *A* remains as proton. There is a degeneracy in these two cases. As *A* and *B* approach each other, an electric field is produced in which  $\vec{r}$  is again space-quantised with components  $m_l (h/2\pi)$ .  $|m_l| = \lambda$  is again the quantum number associated with electronic orbital angular momentum component along the internuclear axis. In this case, in designating an electron in a resulting molecular orbital, the  $n$  and  $l$  values that the electron had in the separated atom *A* (say) are added after the symbol indicating the  $\lambda$ -value, that is, as  $\sigma 1s_A$ , and so on.

If the two nuclei have *equal* charges, the states of the electron are called even (*g*) or odd (*u*) according as the wavefunction remains unaltered or changes sign by reflection at the origin and are written as  $\sigma_g, \sigma_u, \pi_g, \pi_u, \dots$ . In the separated atoms ( $r \rightarrow \infty$ ), the states  $1s, 2s, 2p, \dots$  have the same energy when the nuclei of the atoms are identical ( $A = B$ ). As the atoms approach each other, this degeneracy is removed and we obtain, for example, a  $\sigma_g 1s$  and a  $\sigma_u 1s$  states (that is, equal number of even and odd molecular states).

The molecular orbitals as derived from the separated-atoms approximation (for large internuclear distances) both for different nuclei and identical nuclei may be tabulated as below :

Separated-atoms (A and B) Orbitals	$n$	$l$	$\lambda$	Resulting Molecular Orbitals	
				Different nuclei	Identical nuclei
$1s_A, 1s_B$	1	0	0	$\sigma 1s_A, \sigma 1s_B$	$\sigma_g 1s, \sigma_u 1s$
$2s_A, 2s_B$	2	0	0	$\sigma 2s_A, \sigma 2s_B$	$\sigma_g 2s, \sigma_u 2s$
$2p_A, 2p_B$				$\{\sigma 2p_A, \sigma 2p_B\}$ $\{\pi 2p_A, \pi 2p_B\}$	$\{\sigma_g 2p, \sigma_u 2p\}$ $\{\pi_g 2p, \pi_u 2p\}$
$3s_A, 3s_B$	3	0	0	$\sigma 3s_A, \sigma 3s_B$	$\sigma_g 3s, \sigma_u 3s$
$3p_A, 3p_B$				$\{\sigma 3p_A, \sigma 3p_B\}$ $\{\pi 3p_A, \pi 3p_B\}$	$\{\sigma_g 3p, \sigma_u 3p\}$ $\{\pi_g 3p, \pi_u 3p\}$
$3d_A, 3d_B$				$\{\sigma 3d_A, \sigma 3d_B\}$ $\{\pi 3d_A, \pi 3d_B\}$ $\{\delta 3d_A, \delta 3d_B\}$	$\{\sigma_g 3d, \sigma_u 3d\}$ $\{\pi_g 3d, \pi_u 3d\}$ $\{\delta_g 3d, \delta_u 3d\}$

All molecular orbitals, except  $\sigma$ -orbitals, are doubly-degenerate. The energy order of these orbitals is shown in Fig. 4.



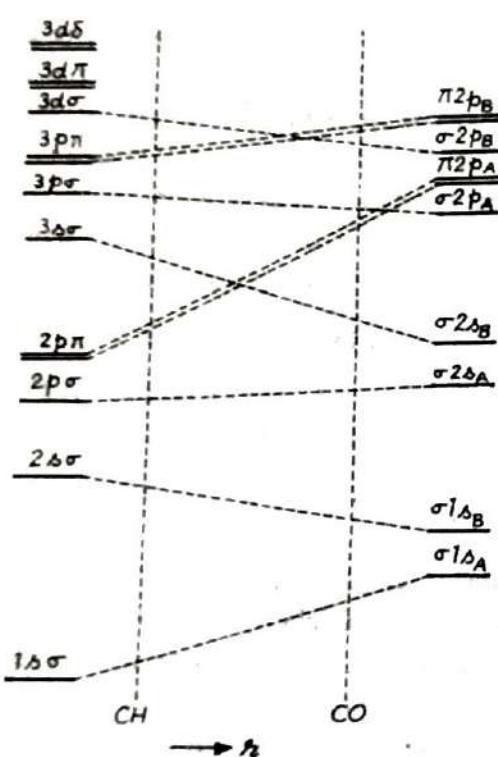
We have deduced above the molecular orbitals for the limiting cases of very small internuclear distances (united-atom approximation) and of very large internuclear distances (separated atoms approximation). These (limited) molecular orbitals are now to be correlated to obtain the desired orbitals appropriate to intermediate internuclear distances associated with actual molecules. As we move from the cases of very small and very large internuclear distances toward the intermediate internuclear distance, the quantum numbers  $n$  and  $l$  loose more and more their meanings as quantum numbers but the number of states remains unchanged (Ehrenfest adiabatic law). The quantum number  $\lambda$ , however, retains its meaning as quantum number for all internuclear distances.

The following rules are observed while co-relating the two limiting cases :

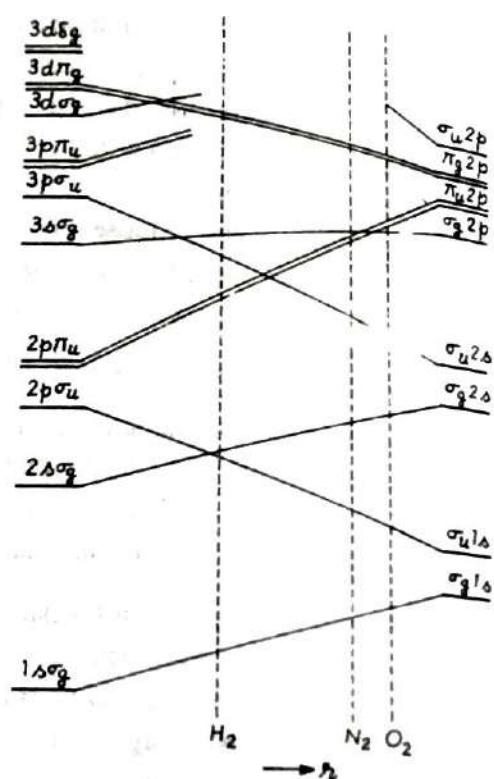
- (i) The electronic orbital angular momentum component  $\lambda (\hbar/2\pi)$  is conserved at all internuclear distances. This means that the quantum number  $\lambda$  remains unchanged for each orbital, although  $n$  and  $l$  may change. Thus, a  $\sigma$ -orbital can go over only to a  $\sigma$ -orbital, a  $\pi$ -orbital to a  $\pi$ -orbital, and so on.
- (ii) According to the non-crossing rule, the potential energy curves of molecular electronic states of the same species (same  $\Lambda$ , same multiplicity and same symmetry) never cross. This means that two  $\sigma$ -orbitals, for example, cannot intersect when the internuclear distance is changed. Thus, the lowest  $\sigma$ -orbital on the left goes over to the lowest  $\sigma$ -orbital on the right, the second lowest  $\sigma$ -orbital on the left to the second lowest  $\sigma$ -orbital on the right, and so on. The same holds for  $\pi$ ,  $\delta$ , ..... orbitals.
- (iii) The  $g-u$  parity is conserved at all internuclear distances. This is to be taken into account for the non-crossing rule to apply in the case of homonuclear molecules. Thus, the lowest  $\sigma_g$ -orbital on the left must be correlated to the lowest  $\sigma_g$ -orbital on the right, the second lowest  $\sigma_g$  on the left to the second lowest  $\sigma_g$  on the right, and so on. The same applies to the  $\sigma_u$ ,  $\pi_g$ ,  $\pi_u$ , ..... orbitals.

The correlation of molecular orbitals for diatomic molecules of different nuclei as well as of identical nuclei are shown in Fig. 5 and 6 respectively. To the extreme left and the extreme right are given the orbitals in the united-atom and in the separated-atoms approximations, that is, those in the molecule for very small and very large internuclear distances respectively. The region in between corresponds to intermediate internuclear distances. The approximate positions of the orbitals of some actual molecules are also shown by vertical broken lines. On account of the  $g-u$  parity conservation, the order of the orbitals for intermediate internuclear distances is somewhat altered for molecules of identical nuclei compared to those of different nuclei.

After deriving the electron orbitals for the diatomic molecules, we can determine the electron configurations of these molecules. A molecule can be built up by adding successive electrons to the various orbitals in accordance with the Pauli's principle which states that no two electrons can have the same set of the four quantum numbers  $n$ ,  $l$ ,  $m_l$  and  $m_s$ . Thus, a  $\sigma$ -orbital is closed with 2 electrons  $\left( m_l = \lambda = 0, m_s = \pm \frac{1}{2} \right)$ .



(Fig. 5)



(Fig. 6)

while all the other orbitals ( $\lambda > 0$ ) can have a maximum of 4 electrons ( $m_l = +\lambda, m_s = \pm \frac{1}{2}$  and  $m_l = -\lambda, m_s = \pm \frac{1}{2}$ ). Thus, for example, in a molecular system of 6 electrons, for small internuclear distance, 2 will go to the lowest orbital  $1s\sigma$ , 2 will go to the next higher orbital  $2s\sigma$ ; and the remaining 2 will go to the still next higher orbital  $2p\sigma$ , so that the electron configuration for the ground state would be  $(1s\sigma)^2 (2s\sigma)^2 (2p\sigma)^2$ . Similarly, for large internuclear distance, the ground-state configuration would be  $(\sigma 1s_A)^2 (\sigma 1s_B)^2 (\sigma 2s_A)^2$ ; or when the nuclei are identical,  $(\sigma_g 1s)^2 (\sigma_u 1s)^2 (\sigma_g 2s)^2$ .

From the electron configuration we can determine the term type of the corresponding molecular state. The term type depends, however, upon the couplings of the electronic motions. Most of the molecules obey  $L-S$  coupling, that is, the orbital angular momenta, and similarly the spin angular momenta, of the individual electrons are coupled more strongly with one another than each orbital angular momentum with the corresponding spin angular momentum. Therefore, for the whole molecule, the resultant electronic orbital angular momentum component ( $\Lambda$ ) along the internuclear axis is the 'algebraic' sum of the orbital angular momentum components ( $\lambda_i$ ) of all the electrons. That is,

$$\Lambda = \sum_i \lambda_i$$

In this addition we have to take into account the fact that two opposite directions are possible for each individual  $\lambda$  vector, corresponding to the positive and the negative values of  $m_l$ .

The resultant electronic spin angular momentum of the molecule is the 'vector' sum of the individual electron spins. That is,

$$S = \sum_i s_i.$$

$S$  is integral or half-integral according as the number of electrons is even or odd.

Closed orbitals (containing their full quota of electrons) do not contribute to the resultant  $\Lambda$  or  $S$ , and so they need not be considered in determining the term type.

Let us now derive the molecular terms for certain common electron configurations :

$\sigma$ :

$$\lambda = 0 \quad s = \frac{1}{2}.$$

$$\therefore \Lambda = \sum_i \lambda_i = 0$$

$$S = \sum_i s_i = \frac{1}{2}.$$

and

The multiplicity of the molecular state is  $2S + 1 = 2$ . Thus, the state is  $^2\Sigma$ . It can be seen from the display of wavefunctions that  $\sigma$ -orbitals always give a symmetric electronic state, so that the state is

$$^2\Sigma^+.$$

In a similar way, we can show that the electron configurations  $\pi$  and  $\delta$  give the molecular states  $^2\Pi$  and  $^2\Delta$  respectively.

$\sigma\sigma$ :

$$\lambda_1 = 0, \lambda_2 = 0; s_1 = \frac{1}{2}, s_2 = \frac{1}{2}.$$

$$\therefore \Lambda = \sum_i \lambda_i = 0$$

and

$$S = (s_1 + s_2), (s_1 + s_2 - 1), \dots, |s_1 - s_2| \\ = 1, 0$$

so that the multiplicities are

$$(2S + 1) = 3, 1.$$

Hence the molecular states are

$$^3\Sigma^+, ^1\Sigma^+.$$

$\sigma\pi$ :

$$\lambda_1 = 0, \lambda_2 = 1; s_1 = \frac{1}{2}, s_2 = \frac{1}{2}.$$

$$\therefore \Lambda = 1$$

$$S = 1, 0$$

$$(2S + 1) = 3, 1.$$

so that  
Hence the molecular states are

$$^3\Pi, ^1\Pi.$$

Similarly, we can show that the configuration  $\sigma\delta$  would give the molecular states  $^3\Delta$  and  $^1\Delta$ .

$$\underline{\pi\pi} : \quad \lambda_1 = 1, \lambda_2 = 1; s_1 = \frac{1}{2}, s_2 = \frac{1}{2}.$$

$$\therefore \Lambda = \sum_i \lambda_i = 2, 0.$$

Here we have taken note of the fact that two opposite directions are possible for each individual  $\lambda$  vector (Fig. 7).

The molecular states corresponding to  $\Lambda = 2$  and  $\Lambda = 0$  are  $\Delta$  and  $\Sigma$ , each arising in two ways. Hence, they must be degenerate. The degeneracy of the  $\Delta$  states  $\rightarrow\rightarrow$  or  $\leftarrow\leftarrow$  persists even when the finer interaction of the two electrons is taken into account. On the other hand,  $\Sigma$  states ( $\rightarrow\leftarrow$  or  $\leftarrow\rightarrow$ ) split into a  $\Sigma^+$  and a  $\Sigma^-$  state. Infact,  $\Sigma$  states are always non-degenerate. Hence, the derived states are

$$\Delta, \Sigma^+, \Sigma^-,$$

the  $\Delta$  state being doubly-degenerate.

The resultant spin  $S$  is 1 or 0 giving multiplicity 3 or 1. Therefore, the molecular terms for two non-equivalent  $\pi$  electrons are

$${}^3\Delta, {}^1\Delta, {}^3\Sigma^+, {}^1\Sigma^+, {}^3\Sigma^-, {}^1\Sigma^-.$$

Similarly, we can show that the configuration  $\delta\delta$  would give the molecular states

$${}^3\Gamma, {}^1\Gamma, {}^3\Sigma^+, {}^1\Sigma^+, {}^3\Sigma^-, {}^1\Sigma^-,$$

where  $\Gamma$  corresponds to  $\Lambda = 4$ .

$$\underline{\pi\delta} : \quad \lambda_1 = 1, \lambda_2 = 2; s_1 = \frac{1}{2}, s_2 = \frac{1}{2}.$$

$$\therefore \Lambda = \sum_i \lambda_i = 3, 1,$$

as illustrated in Fig. 8. The corresponding molecular states are  $\Phi$  and  $\Pi$ , both being doubly-degenerate.

$$\begin{array}{c} \lambda_1=1 \quad \lambda_2=2 \\ \longrightarrow \quad \longrightarrow \\ \Lambda=3 \end{array} \quad OR \quad \begin{array}{c} \lambda_1=1 \quad \lambda_2=2 \\ \longleftarrow \quad \longleftarrow \\ \Lambda=3 \end{array}$$

The resultant spin  $S$  is 1 or 0 giving multiplicity 3 or 1. Therefore, the total number of possible molecular states is four, namely,

$${}^3\Phi, {}^1\Phi, {}^3\Pi, {}^1\Pi.$$

(Fig. 8)

$$\begin{array}{c} \lambda_2=2 \\ \longleftarrow \quad \longrightarrow \\ \lambda_1=1 \quad \Lambda=1 \end{array} \quad OR \quad \begin{array}{c} \lambda_2=2 \\ \longrightarrow \quad \longleftarrow \\ \Lambda=1 \quad \lambda_1=1 \end{array}$$

If the electrons whose terms are to be determined are equivalent\*, we must take account of the Pauli principle in determining  $\Sigma \lambda_i$  and  $\Sigma s_i$ , that is, the electrons must differ either in  $m_l$  or in  $m_s$ . Let us consider some configurations of two or more equivalent electrons.

$\sigma^2$ : Two non-equivalent  $\sigma$  electrons ( $\sigma\sigma$ ) yield the following molecular states:

$${}^3\Sigma^+, {}^1\Sigma^+.$$

\* If two or more electrons in a molecule have the same quantum numbers  $n, l$  (apart from spin), same  $\lambda$  in the same direction, and the same symmetry  $g$  or  $u$ ; they are called 'equivalent' electrons.

For two equivalent  $\sigma$  electrons, since the  $m_l$  are equal,  $m_s$  must be different, that is, the spins must be antiparallel. This means that the triplet term  $^3\Sigma^+$  which corresponds to parallel spins ( $S = 1$ ) would not occur. The only term which would occur is  $^1\Sigma^+$ .

Alternatively, a closed orbital yields only the  $^1\Sigma^+$  state. Since  $\sigma$ -orbital is closed by 2 electrons, the configuration  $\sigma^2$  would give only the  $^1\Sigma^+$  state.

$\pi^2$ : Two non-equivalent  $\pi$  electrons ( $\pi\pi$ ) give the following molecular states :

$$^3\Delta, ^1\Delta, ^3\Sigma^+, ^1\Sigma^+, ^3\Sigma^-, ^1\Sigma^-.$$

In case of  $\Delta$  states ( $\lambda_i$  having same direction), for equivalent electrons, the spins must be antiparallel. Hence  $^3\Delta$  state can not occur, only  $^1\Delta$  would occur.

In case of  $\Sigma$ -states ( $\lambda_i$  having opposite directions), spins may be parallel as well as antiparallel. Therefore, both  $^3\Sigma$  and  $^1\Sigma$  states can result. It can, however, be shown from symmetry considerations of the positional and spin eigenfunctions of  $\Sigma$ -states that  $\Sigma^-$  occurs only as triplet, and  $\Sigma^+$  occurs only as singlet. Hence, for two equivalent  $\pi$  electrons, we have only the three states

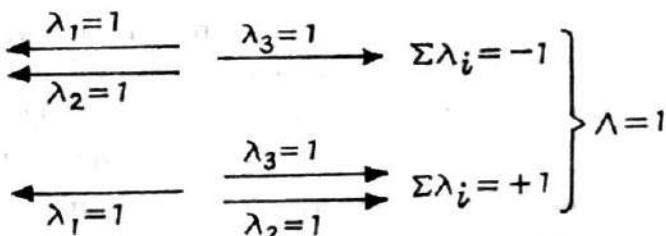
$$^1\Delta, ^1\Sigma^+, ^3\Sigma^-.$$

By Hund rule, the state with greatest multiplicity,  $^3\Sigma^-$ , lies lowest.

In the same way, we can show that the configuration  $\delta^2$  would yield  $^1\Gamma$ ,  $^1\Sigma^+$  and  $^3\Sigma^-$  states.

$\pi^3$ : For three equivalent  $\pi$  electrons, the three  $\lambda_i$  can have only two relative orientations shown in Fig. 9 with resultants  $-1$  and  $+1$  respectively. Hence, the only possible value for  $\Lambda$  is  $\Lambda = 1$ ,

which gives a  $\Pi$  term.



(Fig. 9)

In both cases, two of the electrons having  $\lambda$ 's in the same direction must have antiparallel spins in order to satisfy the Pauli's principle. Therefore, the total spin can be only  $S = \frac{1}{2}$ . Hence, the only state which would result is

$$^2\Pi.$$

In the same way, it can be shown that three equivalent  $\delta$  electrons ( $\delta^3$ ) would yield only one state, namely,  $^2\Delta$ .

Closed orbitals always give a single  $^1\Sigma^+$  state. Hence, the configurations  $\sigma^2, \pi^4, \delta^4, \dots$  all give the  $^1\Sigma^+$  molecular state alone\*.

\* For the configuration  $\pi^4$ , for example, due to Pauli principle, the  $\lambda_i$ 's must form antiparallel pairs, therefore,  $\Lambda = 0$ . Similarly, the  $s_i$ 's must form antiparallel pairs, therefore,  $S = 0$ . Hence, only  $^1\Sigma$  state.

If equivalent as well as non-equivalent electrons are present in an electron configuration, we must determine separately the values of  $\Lambda$  and  $S$  for the equivalent and non-equivalent electrons and then add them in the same manner as for the addition of  $\lambda_i$ 's and  $s_i$ 's. Some important configurations and the corresponding molecular states are as under :

$\pi^2 \sigma$	: ${}^2\Sigma^+, {}^2\Sigma^-, {}^2\Delta, {}^4\Sigma^-$
$\pi^2 \pi$	: ${}^2\Pi(3), {}^2\Phi, {}^4\Pi$
$\pi^2 \delta$	: ${}^2\Sigma^+, {}^2\Sigma^-, {}^2\Delta(2), {}^2\Gamma, {}^4\Delta$
$\pi^3 \sigma$	: ${}^1\Pi, {}^3\Pi$
$\pi^3 \pi$	: ${}^1\Sigma^+, {}^1\Sigma^-, {}^1\Delta, {}^3\Sigma^+, {}^3\Sigma^-, {}^3\Delta,$
$\pi^3 \delta$	: ${}^1\Pi, {}^1\Phi, {}^3\Pi, {}^3\Phi$ .

For molecules consisting of identical nuclei, the resulting states must also be labelled as even (*g*) or odd (*u*). *The molecular states are all even if in the electron configuration the number of "odd" electrons ( $\sigma_u, \pi_u, \dots$ ) is even, whereas they are all odd if the number of "odd" electrons is odd.* Electronic configurations for homonuclear molecules containing only completely filled orbitals always give a single  ${}^1\Sigma_g^+$  state which is totally symmetric.

## 5. Term Types of Molecules : Examples

In order to determine the possible term types for a given molecule, we must write down its electron configurations for the ground state and for the various excited states. For this, we start placing the electrons in the lowest possible orbitals as far as is allowed by the Pauli principle, thus obtaining the ground state. Then we transfer one or more of the outer electrons into higher orbitals and obtain all the excited electronic states of the given molecule. Finally, we can determine the resulting term types in each case.

In general, for molecules  $H_2^+$ ,  $H_2$ , and the hydrides, the orbitals of the united-atom approximation (Fig. 3) are adopted; while for most of the heavier diatomic molecules the orbitals of the separated-atoms approximation (Fig. 4) are adopted. The order of molecular orbitals, however, depends on the internuclear distance and on the nuclear charge; and also (in case of heteronuclear molecules) on the degree of dissimilarity of the two nuclei. It is therefore different for different molecules, and can only be obtained from the co-relation diagrams. For example, *for O<sub>2</sub> and other homonuclear molecules heavier than O<sub>2</sub>, the orbitals lie in the order shown in Fig. 6; while for molecules lighter than O<sub>2</sub> the orbital  $\pi_u$  2p lies lower than  $\sigma_z$  2p.*

For determining the electron configurations and the corresponding term types, we divide the molecules into three categories : (i)  $H_2^+$ ,  $H_2$  and the hydrides, (ii) homonuclear diatomic molecules other than  $H_2^+$  and  $H_2$ , (iii) heteronuclear diatomic molecules.

**H<sub>2</sub> and the Hydrides :** For the  $H_2$  molecule and the diatomic hydrides the internuclear distances are small (for  $H_2$ , 0.74 Å), and so they are assumed to approach the united atom. Hence, we must use the orbitals on the left sides of Fig. 5 and 6.

(i)  $H_2^+$  : The molecular ion  $H_2^+$  has a single electron which occupies the lowest  $1s \sigma_g$  orbital. Thus, its ground-state configuration is



and the corresponding molecular term is



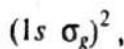
The term is even because the number of odd electrons is zero (even).

The first excited state results when the electron is raised from the lowest orbital to the next higher one which, for  $H_2^+$  and  $H_2$ , is  $2p\sigma_u$  (see Fig. 6). This corresponds to the molecular term



because now the number of odd electrons is odd (1).

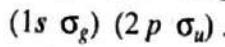
(ii)  $H_2$  : The ground state of  $H_2$  is the state in which both electrons are in the lowest  $1s\sigma_g$  orbital, giving the configuration



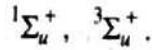
so that the ground state molecular term is



The lowest excited state results from one of the electrons going from the lowest orbital to the next higher one which, for  $H_2$ , is  $2p\sigma_u$  (see Fig. 6). This gives a configuration

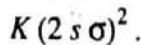
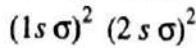


The molecular terms corresponding to the  $\sigma\sigma$  configuration are



The terms are odd because the number of odd electrons is 1 (odd).

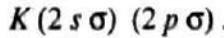
(iii)  $LiH$ ,  $BeH^+$  : Each of these molecules contains four electrons. According to Pauli principle and Fig. 5, the ground state configuration is



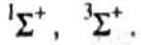
Because the two  $1s$  electrons form the  $K$ -shell of the Li or Be atom, which is only slightly influenced by the molecular formation, hence the symbol  $K$  is written for  $(1s\sigma)^2$ . The above configuration,  $\sigma^2$ , in which the  $\sigma$ -orbital is closed, gives a single



state. The excited states of  $LiH$  are obtained if one electron is raised from the  $2s\sigma$  orbital into higher orbitals. The lowest excited state configuration is

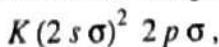


This configuration ( $\sigma\sigma$ ) gives the states



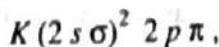
of which only the former has been experimentally observed.

(iv)  $BeH$ ,  $BH^+$  : There are five electrons. The ground-state configuration is



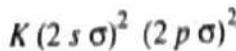
which gives a  $^2\Sigma^+$  state.

The first excited configuration is



which gives a  $^2\Pi$  state.

(v)  $BH$ ,  $CH^+$  : Each of these molecules has six electrons. The ground-state configuration is



which gives a  ${}^1\Sigma^+$  state ( $\sigma$ -orbital is closed).

The first excited configuration is (see Fig. 5)

$$K(2s\sigma)^2(2p\sigma)(2p\pi).$$

This configuration ( $\sigma\pi$ ) gives  ${}^3\Pi$  and  ${}^1\Pi$  states.

The second excited configuration is

$$K(2s\sigma)^2(2p\pi)^2,$$

which gives the states  ${}^1\Delta$ ,  ${}^1\Sigma^+$  and  ${}^3\Sigma^-$ .

(vi) CH : There are seven electrons. The ground-state electron configuration is

$$K(2s\sigma)^2(2p\sigma)^2(2p\pi)$$

which gives a  ${}^2\Pi$  state, which is the observed ground state of the molecule CH.

Since the energy difference between  $2p\sigma$  and  $2p\pi$  is small (see Fig. 5), the lowest excited states are obtained not by raising the  $2p\pi$  electron to higher orbitals but by transferring an electron from the  $2p\sigma$  to the  $2p\pi$  orbital. Thus, the first excited configuration is

$$K(2s\sigma)^2(2p\sigma)(2p\pi)^2.$$

This configuration ( $\pi^2\sigma$ ) gives the molecular terms  ${}^2\Sigma^+$ ,  ${}^2\Sigma^-$ ,  ${}^2\Delta$ ,  ${}^4\Sigma^-$ . The first three of these have been observed.

(vii) NH, OH<sup>+</sup> : These are eight-electron molecules. The lowest electron configuration and the corresponding terms are

$$K(2s\sigma)^2(2p\sigma)^2(2p\pi)^2, \quad {}^1\Sigma^+, {}^1\Delta, {}^3\Sigma^-$$

Of these,  ${}^3\Sigma^-$  is the ground-state term of NH, in agreement with experiment.

As in case of CH, the lowest excited states are obtained by transferring one or both electrons from the  $2p\sigma$  to the  $2p\pi$  orbital. Thus, the first two excited configurations and the corresponding terms are :

$$K(2s\sigma)^2(2p\sigma)(2p\pi)^3, \quad {}^1\Pi, {}^3\Pi$$

and

$$K(2s\sigma)^2(2p\pi)^4, \quad {}^1\Sigma^+$$

(viii) HF : There are ten electrons. The lowest configuration and the corresponding ground term are :

$$K(2s\sigma)^2(2p\sigma)^2(2p\pi)^4. \quad {}^1\Sigma^+$$

The next higher configuration and the molecular term are

$$K(2s\sigma)^2(2p\sigma)^2(2p\pi)^3(3s\sigma). \quad {}^1\Pi, {}^3\Pi$$

(ix) NaH, MgH<sup>+</sup> : These are 12-electron molecules. The ground-state configuration and the molecular term are :

$$\underbrace{K(2s\sigma)^2(2p\sigma)^2(2p\pi)^4}_{\text{or}}(3s\sigma)^2$$

$$KL(3s\sigma)^2. \quad {}^1\Sigma^+$$

The two 2s-electrons and the six 2p-electrons form the L-shell of Na or Mg atom which is only slightly disturbed in molecular formation. Hence, the symbol L is written for  $(2s\sigma)^2(2p\sigma)^2(2p\pi)^4$ .

The first excited configuration and terms would be

$$KL(3s\sigma)(3p\sigma) \quad {}^1\Sigma^+, {}^3\Sigma^+$$

Only  ${}^1\Sigma^+$  has been experimentally observed.

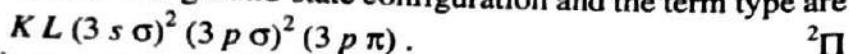
(x) AlH : There are 14 electrons. The ground-state configuration and the corresponding term are



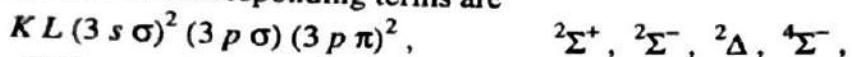
The lowest excited electron configuration and the corresponding term are



(xi) SiH : There are 15 electrons. The ground-state configuration and the term type are



The lowest excited configuration and the corresponding terms are



as in case of CH. However, for SiH, apart from the  $^2\Pi$  ground-state, only the excited  $^2\Delta$  state is known.

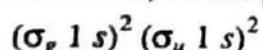
**Homonuclear Diatomic Molecules other than  $H_2^+$  and  $H_2$**  : When the nuclear charge is higher than two, the united-atom is not a good approximation because the  $K$  shells and possibly higher shells of both atoms are not affected by the molecule formation. Hence for the molecules now under consideration, the orbitals appropriate to the separated-atoms approximation must be used. The order of these orbitals is displayed on the right side of Fig. 6.

(i)  $He_2^+$  : This molecular ion has three electrons; two of them occupy the lowest  $\sigma_g 1s$  orbital and the third goes to the next higher  $\sigma_u 1s$  orbital. Thus, the ground-state electron configuration, and the corresponding term, are



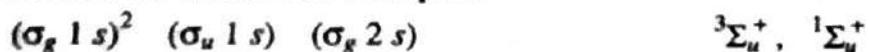
The state is odd because the number of odd electrons is odd (1).

(ii)  $He_2$  : This is a four-electron molecule, whose ground-state configuration would be



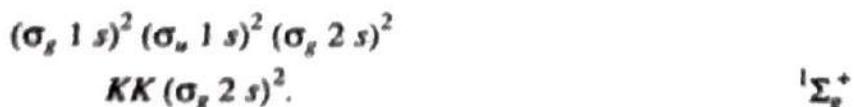
which corresponds to a  $^1\Sigma_g^+$  state ( $\sigma$ -orbital is closed). This is, experimentally, an *unstable* state.

However, for  $He_2$ , a large number of excited states, in which an electron goes from the  $\sigma_u 1s$  orbital into higher orbitals, are stable. For example :



These (excited) states have actually been observed.

(iii)  $Li_2$  : The ground-state configuration of the  $Li_2$  molecule with six electrons, and the corresponding term are



The lower excited configurations and the terms are



<sup>a)</sup> Let us remember that for molecules lighter than  $O_2$  the orbital  $\pi_u 2p$  ... or than  $\sigma_g 2p$  (See Fig. 6).

(iv)  $\text{Be}_2$  : This has eight electrons. The ground-state configuration and the term are expected to be as

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2.$$

This is, however, an unstable state. The molecule  $\text{Be}_2$  does *not* exist.

 $^1\Sigma_g^+$ 

(v)  $\text{B}_2$  : It has 10 electrons. The lowest configuration is

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^2.$$

This configuration ( $\pi^2$ ) gives rise to the following three even states, even because the number of odd electrons is even,

$$^1\Delta_g, ^1\Sigma_g^+, ^3\Sigma_g^-.$$

By Hunds multiplicity rule,  $^3\Sigma_g^-$  is the lowest and forms the ground state. The excited state results from the configuration

$$KK(\sigma_g 2s)^2 (\sigma_u 2s) (\pi_u 2p)^2 (\sigma_g 2p).$$

(vi)  $\text{C}_2$  : The ground-state configuration of the  $\text{C}_2$  molecule, with its 12 electrons, and the corresponding term are expected to be

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^4.$$

 $^1\Sigma_g^+$ 

This configuration places the electrons into the lowest possible orbitals. The observed spectrum of the  $\text{C}_2$  molecule (Swan bands), however, shows that the ground state of  $\text{C}_2$  is  $^3\Pi_u$  (not  $^1\Sigma_g^+$ ). Hence another possible configuration for the ground state is (See Fig. 6).

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^3 (\sigma_g 2p).$$

This configuration ( $\pi^3 \sigma$ ) yields two odd electronic states, odd because the number of odd electrons is odd, namely

$$^3\Pi_u, ^1\Pi_u.$$

One of these, the  $^3\Pi_u$  state, forms the ground state. The explanation of this contradiction between theory and experiment is that near the equilibrium internuclear distance of  $\text{C}_2$  the orbitals  $\pi_u 2p$  and  $\sigma_g 2p$  lie very near each other and it may happen due to electronic interaction that the  $^3\Pi_u$  state resulting from  $\pi_u^3 \sigma_g$  lies lower than the  $^1\Sigma_g^+$  state resulting from  $\pi_u^4$ . The other state  $^1\Pi_u$  resulting from  $\pi_u^3 \sigma_g$  has been observed as the lower state of the Deslandres bands of  $\text{C}_2$ . The upper states of the Swan bands and the Deslandres bands are  $^3\Pi_g$  and  $^1\Pi_g$  respectively which arise from the configuration

$$KK(\sigma_g 2s)^2 (\sigma_u 2s) (\pi_u 2p)^3 (\sigma_g 2p)^2.$$

(vii)  $\text{N}_2$  : This molecule has 14 electrons. The ground-state configuration, and the term are

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2.$$

 $^1\Sigma_g^+$ 

In this configuration all the orbitals are completely filled. The resulting ground state  $^1\Sigma_g^+$  is in agreement with observation.

The initial excited electron configuration and the corresponding terms are (see Fig. 6) :

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p) (\pi_g 2p). \quad ^3\Pi_g, ^1\Pi_g$$

and

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^3 (\sigma_g 2p)^2 (\pi_g 2p) . \left\{ \begin{array}{l} {}^3\Sigma_u^+, {}^3\Sigma_u^- \\ {}^1\Sigma_u^+, {}^1\Sigma_u^- \\ {}^3\Delta_u, {}^1\Delta_u \end{array} \right.$$

The first configuration ( $\sigma \pi$ ) gives two states, while the second one ( $\pi^3 \pi$ ) gives six states. They account for the lowest observed excited states  ${}^3\Sigma_u^+$ ,  ${}^3\Pi_g$  and  ${}^1\Pi_g$  respectively.

(viii)  $O_2$  : For  $O_2$  and onwards the order of molecular orbitals changes; now the orbital  $\sigma_g 2p$  is lower (and hence filled first) than the  $\pi_u 2p$  orbital (Fig. 6). The lowest electron configuration of  $O_2$ , with 16 electrons, is

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^2 .$$

This configuration ( $\pi^2$ ) yields three molecular states, namely,

$${}^3\Sigma_g^-, {}^1\Sigma_g^+, {}^1\Delta_g .$$

All these are even states because the number of odd electrons is even. Of these,  ${}^3\Sigma_g^-$  is the lowest (Hunds multiplicity rule) and is the ground state of  $O_2$ , in agreement with observation. The other two states have also been observed.

The first excited electron configuration of  $O_2$  is

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^3 (\pi_g 2p)^3$$

which gives rise to six states, of which  ${}^3\Sigma_u^+$  and  ${}^3\Sigma_u^-$  have been observed.

(ix)  $F_2$  : There are 18 electrons. The ground-state configuration is

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^4 .$$

Since all the orbitals are closed, it yields a  ${}^1\Sigma_g^+$  state which is the ground state of  $F_2$ , in agreement with experiment.

The first excited electron configuration is

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^3 (\sigma_u 2p)$$

which gives rise to the molecular states  ${}^3\Pi_u$  and  ${}^1\Pi_u$ .

(x)  $Na_2$  : There are 22 electrons. The ground-state configuration is

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^4 (\sigma_u 2p)^2 (\sigma_g 3s)^2$$

$$KKLL (\sigma_g 3s)^2 ,$$

which yields the ground state  ${}^1\Sigma_g^+$ .

(xi)  $Cl_2$  : There are 34 electrons. The ground-state configuration is

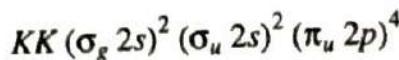
$$KKLL (\sigma_g 3s)^2 (\sigma_u 3s)^2 (\sigma_g 3p)^2 (\pi_u 3p)^4 (\pi_g 3p)^4 ,$$

which yields the ground state  ${}^1\Sigma_g^+$ .

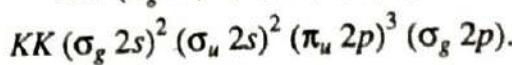
**Heteronuclear Diatomic Molecules :** These molecules have no centre of symmetry so that the  $g-u$  classification disappears. The separated-atoms orbitals can still be used to describe molecular configurations so long the charges on the two nuclei differ by a small amount only.

(i)  $BeO$ ,  $BN$  : Each of these molecules contains 12 electrons, as in  $C_2$ . Hence their lowest configuration can be written in the same way as of  $C_2$ ,  $\dots$  that  $g-u$  will be

omitted. For  $C_2$ , however, two different electron configurations are written for the ground-state. These are



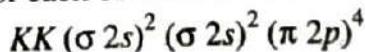
and



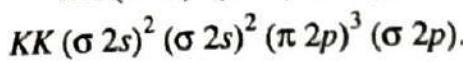
$^1\Sigma_g^+$

$^3\Pi_u, ^1\Pi_u$

It is the second configuration which gives the observed ground state ( $^3\Pi_u$ ) of  $C_2$ . The corresponding configurations for each of the BeO and BN molecules would be



and

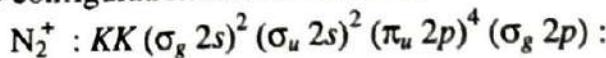


$^1\Sigma^+$

$^3\Pi, ^1\Pi$

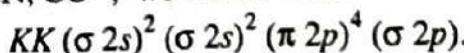
For BeO, the first configuration gives the observed ground state  $^1\Sigma^+$ , while for BN the lowest observed state is  $^3\Pi$ .

(ii) BO, CN,  $CO^+$  : These molecules contain 13 electrons each, as  $N_2^+$  does, for which the ground state configuration and the term are



$^2\Sigma_g^+$

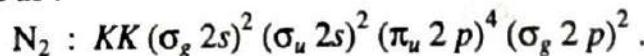
Correspondingly, for BO, CN,  $CO^+$ , we would write



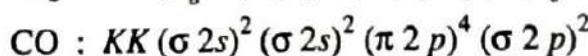
$^2\Sigma^+$

Not only the ground state, but also the first two excited states for BO, CN and  $CO^+$  are same as for  $N_2^+$ .

(iii) CO : It has 14 electrons as for  $N_2$ . Hence we may write the ground state configurations and terms as :



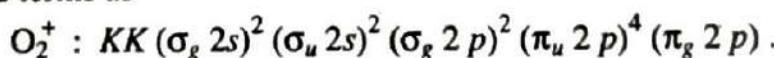
$^1\Sigma_g^+$



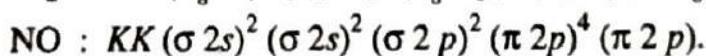
$^1\Sigma^+$

Though the ground states are same, the higher excited states of CO and  $N_2$  are different because a slight difference in the charge of the two nuclei of CO affects the relative order of the higher orbitals.

(iv) NO : It has 15 electrons as for  $O_2^+$ . Hence we may write the ground state configurations and terms as



$^2\Pi_g$



$^2\Pi$

The single unpaired electron in the  $\pi 2p$  orbital accounts for the doublet nature of this state, and also for the fact that the molecule NO is, like  $O_2$ , paramagnetic.

(v) CS : It has 22 electrons, like  $Na_2$ . Hence for the ground state, we may write



$^1\Sigma_g^+$



$^1\Sigma^+$

## SOLVED PROBLEMS

1. Two unlike atoms with  $^3P$  configurations combine to form a diatomic molecule. Deduce the spectroscopic designations of all possible molecular states. (We are not concerned here with +, - or g, u symmetry). (Meerut sp. paper 2002)

**Solution.** For  $^3P + ^3P$ , we have

$$L_1 = 1; L_2 = 1$$

$$\begin{aligned}M_{L_1} &= 1, 0, -1; M_{L_2} = 1, 0, -1 \\M_{L_1} + M_{L_2} &= 2, 1, 0; 1, 0, -1; 0, -1, -2 \\ \therefore \Lambda &= |M_{L_1} + M_{L_2}| = 2, 1, 0, 1, 0, 1, 0, 1, 2 \\&= 2, 2, 1, 1, 1, 1, 0, 0, 0.\end{aligned}$$

These values of  $\Lambda$  yield one (doubly-degenerate)  $\Delta$ -state, two (doubly-degenerate)  $\Pi$ -states and three  $\Sigma$ -states, that is,

$$\Sigma(3), \Pi(2), \Delta.$$

Now, the multiplicity of each atomic states is 3, that is,

$$2S_1 + 1 = 2S_2 + 1 = 3$$

so that

$$S_1 = 1; S_2 = 1.$$

The possible values for the spin  $S$  of the resulting molecule are

$$\begin{aligned}S &= (S_1 + S_2), (S_1 + S_2 - 1), \dots, |S_1 - S_2| \\&= 2, 1, 0.\end{aligned}$$

The corresponding multiplicities are :

$$(2S + 1) = 5, 3, 1.$$

Each of the states deduced above can occur with each of these multiplicities. Hence, the possible molecular states are

$$^5\Sigma(3), ^3\Sigma(3), ^1\Sigma(3), ^5\Pi(2), ^3\Pi(2), ^1\Pi(2), ^5\Delta, ^3\Delta, ^1\Delta.$$

**2. Considering NH molecule, obtain the resultant molecular electronic states, treating it from the view point of separated atoms.**

**Solution.** The electron configurations of a normal N atom and a normal H atom, and the corresponding atomic states are :

$$N : \boxed{1s^2 2s^2} 2p^3; ^4S, ^2P, ^2D \quad \Sigma l_i = 3$$

$$H : 1s; ^2S \quad \Sigma l_i = 0$$

We now derive the molecular states arising from the combinations

$$^2S + ^4S; ^2S + ^2P; ^2S + ^2D.$$

$$\underline{^2S + ^4S}: \quad L_1 = 0, L_2 = 0.$$

$$\therefore \Lambda = |M_{L_1} + M_{L_2}| = 0,$$

which gives a  $\Sigma$ -state. Since  $L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2} = 0 + 0 + 3 + 0 = 3$  (odd), the state is a  $\Sigma$ -state.

Again, for the given atomic states, we have

$$S_1 = \frac{1}{2}, S_2 = \frac{3}{2}.$$

The spin for the molecule NH is

$$\begin{aligned}S &= (S_1 + S_2), (S_1 + S_2 - 1), \dots, |S_1 - S_2| \\&= 2, 1.\end{aligned}$$

The corresponding multiplicities are

$$(2S + 1) = 5, 3.$$

Hence the possible molecular states are

$$^5\Sigma^+, ^3\Sigma^-.$$

$$\underline{^2S + ^2P}: \quad L_1 = 0, L_2 = 1.$$

$$M_{L_1} = 0; M_{L_2} = 1, 0, -1$$

$$\begin{aligned} M_{L_1} + M_{L_2} &= 1, 0, -1 \\ \Lambda = |M_{L_1} + M_{L_2}| &= 1, 0, 1 \\ &= 1, 1, 0. \end{aligned}$$

This yields a (doubly-degenerate)  $\Pi$ -state and a  $\Sigma$ -state. Since  $L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2} = 0 + 1 + 3 + 0 = 4$  (even), the  $\Sigma$ -state is  $\Sigma^+$ .

$$\begin{aligned} \text{Again } L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2} &= 0 + 1 + 3 + 0 = 4 \text{ (even)} \\ S_1 = \frac{1}{2}, S_2 = \frac{1}{2} \\ \therefore S &= 1, 0 \\ (2S + 1) &= 3, 1. \end{aligned}$$

and

The possible molecular states are

$$^3\Pi, ^1\Pi, ^3\Sigma^+, ^1\Sigma^+.$$

$$\begin{aligned} \underline{\mathbf{2S + 3D :}} \quad L_1 &= 0; L_2 = 2. \\ M_{L_1} = 0; M_{L_2} &= 2, 1, 0, -1, -2 \\ M_{L_1} + M_{L_2} &= 2, 1, 0, -1, -2 \\ \Lambda = |M_{L_1} + M_{L_2}| &= 2, 1, 0, 1, 2 \\ &= 2, 2, 1, 1, 0. \end{aligned}$$

This yields a (doubly-degenerate)  $\Delta$ -state as well as a  $\Pi$ -state and a  $\Sigma$ -state. Since  $L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2} = 0 + 2 + 3 + 0 = 5$  (odd), the  $\Sigma$ -state is  $\Sigma^-$ . The molecular multiplicities are again 3 and 1. Hence the molecular states are :

$$^3\Delta, ^1\Delta, ^3\Pi, ^1\Pi, ^3\Sigma^-, ^1\Sigma^-.$$

Thus, in all there are 12 possible states. However, only a few of them are stable.

**3. Obtain the molecular terms for diatomic  $N_2$  molecule formed by combining two nitrogen atoms each in a  $^4S$  state.** (Meerut sp. paper 2000 S, 99, 94)

**Solution.** The configuration of a normal nitrogen atom is

$$\boxed{1s^2 2s^2} 2p^3,$$

so that  $\Sigma l_i = 3$ . Its ground state is a  $^4S$  state.

Let us derive molecular terms arising from the combination  $^4S + ^4S$ , of two like (nitrogen) atoms. We have

$$L_1 = 0, L_2 = 0; S_1 = \frac{3}{2}, S_2 = \frac{3}{2}.$$

From this, we have

$$M_{L_1} = L_1, L_1 - 1, \dots - L_1 = 0,$$

$$\text{and } M_{L_2} = L_2, L_2 - 1, \dots - L_2 = 0.$$

$$\therefore \Lambda = |M_{L_1} + M_{L_2}| = 0.$$

Thus, the molecular state is  $\Sigma$ .

$$\text{Now; } L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2} = 0 + 0 + 3 + 3 = 6 \text{ (even).}$$

Hence the molecular state is  $\Sigma^+$ .

Let us now determine the molecular multiplicity.

$$\begin{aligned} S &= (S_1 + S_2), (S_1 + S_2 - 1), \dots, |S_1 - S_2| \\ &= 3, 2, 1, 0. \end{aligned}$$

$\therefore (2S + 1) = 7, 5, 3, 1.$   
The  $\Sigma^+$  states occur with each of these multiplicities, so that we have a septet, a quintet, a triplet and a single  $\Sigma$ -state. These are written as

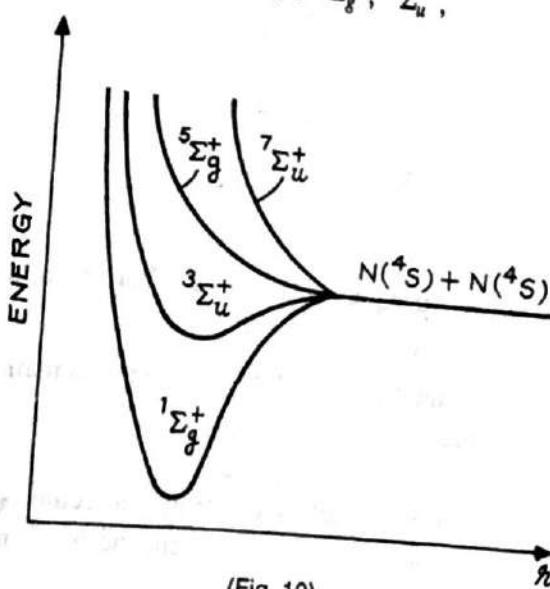
$$^7\Sigma^+, ^5\Sigma^+, ^3\Sigma^+, ^1\Sigma^+.$$

When the two like atoms forming the molecule are in *identical* states ( $S_1 = S_2, L_1 = L_2$ ), fewer molecular states are obtained. It can be concluded from group theory that when the resulting molecular spin is even (singlet, quintet, nonet) the molecular state  $\Sigma^+$  can only be even ( $g$ ); while when the resulting molecular spin is odd (triplet, septet) the molecular state  $\Sigma^+$  can only be odd ( $u$ ). Thus, the molecular terms are

$$^7\Sigma_u^+, ^5\Sigma_g^+, ^3\Sigma_u^+, ^1\Sigma_g^+.$$

Heitler and London have shown that in molecular states of different multiplicities resulting from two atoms in  $S$  states, the state with the lowest total spin  $S$  always lies lowest and the others lie in the order of their multiplicities. Hence, the molecular terms deduced above lie in the order

$$^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+, ^7\Sigma_u^+,$$



(Fig. 10)

as shown in Fig. 10. The states  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$  are stable, while the states  $^5\Sigma_g^+$  and  $^7\Sigma_u^+$  are unstable.  $^1\Sigma_g^+$  is the ground state of the  $N_2$  molecule, in agreement with experiment.

4. A magnesium atom in a  $^3P$  state is split to give a diatomic carbon molecule. What are the possible terms of the molecule ?

(Meerut sp. paper 90)

Solution. The first few electron configurations and the corresponding terms of the Mg atom are as follows :

Ground :  $1s^2 2s^2 2p^6 \quad 3s^2 \quad ^1S \quad \Sigma_l = 0$

Excited :  $1s^2 2s^2 2p^6 \quad 3s \ 3p \quad ^1P^*, ^3P^* \quad \Sigma_l = 1$

Excited :  $1s^2 2s^2 2p^6 \quad 3s \ 3d \quad ^1D, ^3D \quad \Sigma_l = 2$

The atom Mg ( $Z = 12$ ) is in  $^3P$  state which is an odd state ( $^3P^*$ ). For this state, we have

$$L = 1.$$

Therefore, the molecular quantum number  $\Lambda$  can take the values given by

$$\begin{aligned}\Lambda &= L, L - 1, \dots, 0 \\ &= 1, 0.\end{aligned}$$

Hence, the possible molecular states are  $\Pi$  and  $\Sigma$ . Now for the united-atom in  ${}^3P$  state,  $L + \Sigma l_i = 1 + 1 = 2$  (even), and so the  $\Sigma$ -state is  $\Sigma^+$ .

Now the spin, and hence the multiplicity, of the molecule remains the same as of the united-atom. Hence the terms are

$${}^3\Pi, {}^3\Sigma^+.$$

Since the united-atom has been splitted into a homonuclear diatomic molecule, the  $g-u$  parity is to be found out. Since the state of the united-atom is odd, the resulting molecular states are also odd. Thus, the molecular terms are

$${}^3\Pi_g, {}^3\Sigma_g^+.$$

**5. A Si atom in a  ${}^3P$  state is split to give a homonuclear diatomic molecule. What are the possible terms for the molecule ?** (Meerut sp. paper 89)

**Solution.** The ground-state configuration of Si atom (14 electrons) is

$$1s^2 2s^2 2p^6 3s^2 \quad 3p^2,$$

$$\Sigma l_i = 2$$

which gives  ${}^3P$ ,  ${}^1D$ ,  ${}^1S$  states. All these are even states.

Now, for the  ${}^3P$  state, we have

$$L = 1.$$

$$\therefore \Lambda = 1, 0.$$

Hence the possible molecular states are  $\Pi$  and  $\Sigma$ . For the united-atom in  ${}^3P$  state,  $L + \Sigma l_i = 1 + 2 = 3$  (odd), and so the  $\Sigma$ -state is  $\Sigma^-$ .

The spin and hence the multiplicity of the molecule remains the same as in the united-atom. Hence the molecular terms are

$${}^3\Pi \text{ and } {}^3\Sigma^-.$$

The Si atom is splitted into a homonuclear diatomic molecule, so  $g-u$  parity is to be mentioned. Since the state of the united-atom is even, the resulting molecular states are also even. Thus, the molecular terms are

$${}^3\Pi_g, {}^3\Sigma_g^-.$$

**6. A carbon atom has been splitted into a BH radical. Obtain the resulting molecular electronic states and show the co-relations of these states with the states of the united atom.**

**Solution.** The electron configuration of a normal carbon atom (6 electrons) is

$$1s^2 2s^2 2p^2.$$

$$(\Sigma l_i = 2)$$

This configuration gives rise to the following atomic states :

$${}^3P, {}^1D, {}^1S.$$

According to the Hund's rules,\* the state  ${}^3P$  is the lowest, then  ${}^1D$  and then  ${}^1S$ . On splitting the carbon atom into a BH radical, these states give the following molecular states :

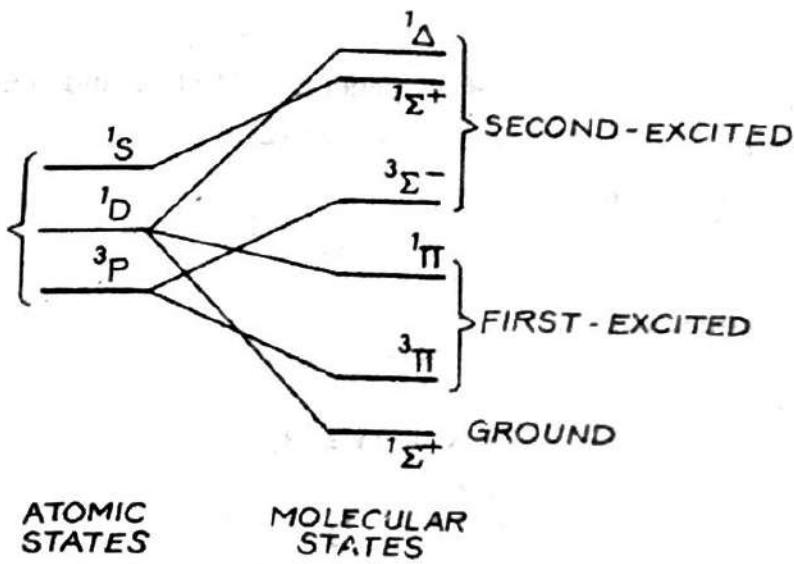
\*According to the Hund's multiplicity rule, for equivalent electrons the state with the largest multiplicity is of lowest energy. Further, according to Hund's angular momentum rule, for states with the same multiplicity the one with the largest orbital angular momentum is of lowest energy.

$^3P$	$^3\Sigma^-$ , $^3\Pi$	$(L + \Sigma l_i \text{ is odd})$
$^1D$	$^1\Sigma^+$ , $^1\Pi$ , $^1\Delta$	$(L + \Sigma l_i \text{ is even})$
$^1S$	$^1\Sigma^+$	$(L + \Sigma l_i \text{ is even})$

For finding the co-relation, let us write down the ground and the initial excited configurations, and the corresponding molecular states for the BH radical, with six electrons.

Lowest (ground)	$K(2s\sigma)^2(2p\sigma)^2$	$^1\Sigma^+$
First excited	$K(2s\sigma)^2(2p\sigma)(2p\pi)$	$^3\Pi$ , $^1\Pi$
Second excited	$K(2s\sigma)^2(2p\pi)^2$	$^3\Sigma^-, ^1\Sigma^+, ^1\Delta$

The co-relation of atomic and molecular state is shown in Fig. 11.



(Fig. 11)

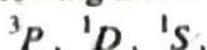
The ground  $^1\Sigma^+$  state is co-related with the atomic  $^1D$  state, because this is the lowest atomic state that can produce a  $^1\Sigma^+$  molecular state.

7. Consider BH molecule. Derive the resultant molecular electronic states, treating from the viewpoint of the separated-atoms and also of the united-atom. Hence draw the correlation diagram between the electronic states resulting from these two extreme cases.

**Solution.** Let us first find the states of the BH molecule from the states of the united atom. The BH molecule has 6 electrons. Therefore, the united atom which can be splitted into the BH molecule is carbon. The electron configuration of a normal C atom is

$$1s^2 \quad 2s^2 \quad 2p^2 \quad (\Sigma l_i = 2)$$

This configuration gives rise to the following atomic states



which are written in the order of increasing energy. These atomic states give rise to the following molecular states :

$^3P$	$L = 1, \Lambda = 0, 1$	$^3\Sigma^-, ^3\Pi$	$(L + \Sigma l_i \text{ is odd})$
$^1D$	$L = 2, \Lambda = 0, 1, 2$	$^1\Sigma^+, ^1\Pi, ^1\Delta$	$(L + \Sigma l_i \text{ is even})$
$^1S$	$L = 0, \Lambda = 0$	$^1\Sigma^+$	$(L + \Sigma l_i \text{ is even})$

Let us now derive the molecular states by combining a normal B atom and a normal H atom, which are initially well separated. The configurations and the states of these atoms are :

B :	$1s^2 \quad 2s^2$	$\boxed{2p} \quad ^2P$	$(\Sigma l_i = 1)$
H :	$1s$	$^2S$	$(\Sigma l_i = 0)$

For the combination  $^2P + ^2S$ , we have

$$\begin{aligned} L_1 &= 1, L_2 = 0 \\ M_{L_1} &= 1, 0, -1; M_{L_2} = 0 \\ M_{L_1} + M_{L_2} &= 1, 0, -1 \\ \therefore \Lambda &= |M_{L_1} + M_{L_2}| = 1, 0, 1 \\ &= 1, 1, 0. \end{aligned}$$

These values of  $\Lambda$  yield one (doubly-degenerate)  $\Pi$ -state and one  $\Sigma$ -state, which is a  $\Sigma^+$ -state because  $L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2}$  is even (2).

Again, for the atomic states, we have

$$S_1 = \frac{1}{2}, S_2 = \frac{1}{2}.$$

Therefore, for the molecule,

$$S = 1, 0.$$

The corresponding multiplicities are

$$(2S + 1) = 3, 1.$$

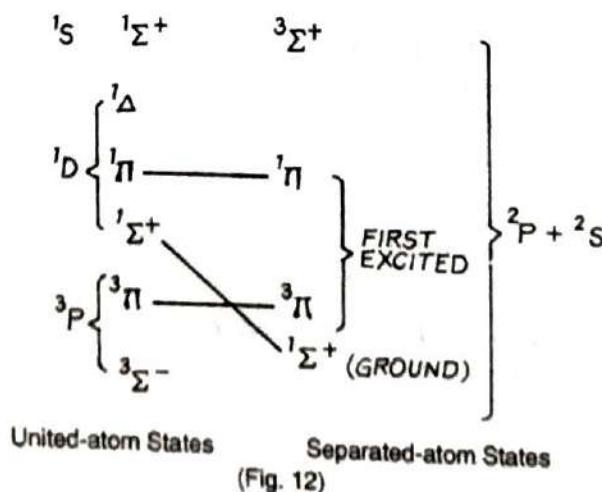
Thus, the resulting molecular states are

$$^3\Pi, ^1\Pi, ^3\Sigma^+, ^1\Sigma^+.$$

For determining the correlation between the united-atom and separated-atoms molecular states, let us write the electron configuration and corresponding terms for the ground and first two excited states of the BH molecule.

Ground	$K(2s\sigma)^2(2p\sigma)^2$	$^1\Sigma^+$
First excited	$K'2s\sigma)^2(2p\sigma)(2p\pi)$	$^3\Pi, ^1\Pi$
Second excited	$K(2s\sigma)^2(2p\pi)^2$	$^3\Sigma^-, ^1\Sigma^+, ^1\Delta$

The correlation is shown in Fig. 12.



8. Consider CH molecule. Derive the resultant molecular electronic states on the basis of united-atom as well as separated-atoms. Draw a correlation diagram.

**Solution.** Let us first derive the molecular states on the basis of united-atom. The CH molecule has 7 electrons. Therefore, the united-atom that can be splitted into CH molecule is nitrogen. The configuration of a normal N atom is

$$\boxed{1s^2 \ 2s^2} \quad 2p^3. \quad (\Sigma l_i = 3)$$

This configuration gives rise to the following odd atomic states :

$$^4S^*, \ ^2D^*, \ ^2P^*$$

From Hund's multiplicity rule the  $^4S^*$ -state is the ground-state; and from Hund's angular momentum rule the  $^2D^*$  state is of lower energy than the  $^2P^*$  state. These atomic states give rise to the following molecular states :

$$^4S^* : \quad ^4\Sigma^- \quad (L + \Sigma l_i \text{ is odd})$$

$$^2D^* : \quad ^2\Sigma^-, \ ^2\Pi, \ ^2\Delta \quad (L + \Sigma l_i \text{ is odd})$$

$$^2P^* : \quad ^2\Sigma^+, \ ^2\Pi \quad (L + \Sigma l_i \text{ is even})$$

Let us now derive the molecular states by combining a normal carbon atom and a hydrogen atom. The configurations and the states of these atoms are :

$$C : \quad \boxed{1s^2 \ 2s^2} \quad 2p^2 ; \quad ^1S, \ ^1D, \ ^3P \quad (\Sigma l_i = 2)$$

$$H : \quad 1s \quad ; \quad ^2S \quad (\Sigma l_i = 0)$$

For the combination  $^1S + ^2S$ , we have

$$L_1 = 0, L_2 = 0$$

$$M_{L_1} = 0, M_{L_2} = 0$$

$$M_{L_1} + M_{L_2} = 0$$

$$\therefore \Lambda = |M_{L_1} + M_{L_2}| = 0.$$

$\Lambda = 0$  corresponds to a  $\Sigma$ -state which is a  $\Sigma^+$ -state because  $L_1 + L_2 + \Sigma l_{i1} + \Sigma l_{i2}$  is even (2).

Again, for the atomic states, we have

$$S_1 = 0, S_2 = \frac{1}{2}.$$

Therefore, for the resulting molecule

$$S = \frac{1}{2} \text{ (doublet).}$$

Hence the resulting state is

$$^2\Sigma^+.$$

For the combination  $^1D + ^2S$ , we have

$$L_1 = 2; L_2 = 0$$

$$M_{L_1} = 2, 1, 0, -1, -2 \text{ and } M_{L_2} = 0$$

$$M_{L_1} + M_{L_2} = 2, 1, 0, -1, -2$$

$$\therefore \Lambda = |M_{L_1} + M_{L_2}| = 2, 1, 0, 1, 2 \\ = \underline{2}, \underline{2}, \underline{1}, \underline{1}, 0,$$

which correspond to a (doubly-degenerate)  $\Delta$ -state, a (doubly-degenerate)  $\Pi$ -state and a  $\Sigma$ -state. The  $\Sigma$ -state is  $\Sigma^+$  because

$L_1 + L_2 + \Sigma_{l_1} + \Sigma_{l_2}$  is even (4).

Taking the spin considerations into account, as above, the molecular states are

$$^2\Lambda \quad ^2\Pi \quad ^2\Sigma^+$$

For the combination  ${}^3P + {}^2S$ , we have

$$L_1 = 1, L_2 = 0$$

$$M_{L_1} = 1, 0, -1; M_{L_2} = 0$$

$$M_{I_1} + M_{I_2} = 1, 0, -1$$

$$\therefore \Delta \equiv |M_{L_1} + M_{L_2}| = 1, 0, -1$$

$$= 1, 1, 0.$$

These values of  $\Lambda$  yield one (doubly-degenerate)  $\Pi$ -state and a  $\Sigma$ -state. The  $\Sigma$ -state is  $\Sigma^-$  state because  $L_1 + L_2 + \Sigma l_1 + \Sigma l_2$  is odd (3).

Again, for the atomic states, we have

$$S_1 = 1, S_2 = \frac{1}{2}.$$

Therefore, for the resulting molecule,

$$S = \frac{3}{2}, \frac{1}{2} \text{ (quartet, doublet)}$$

Hence the resulting molecular states are

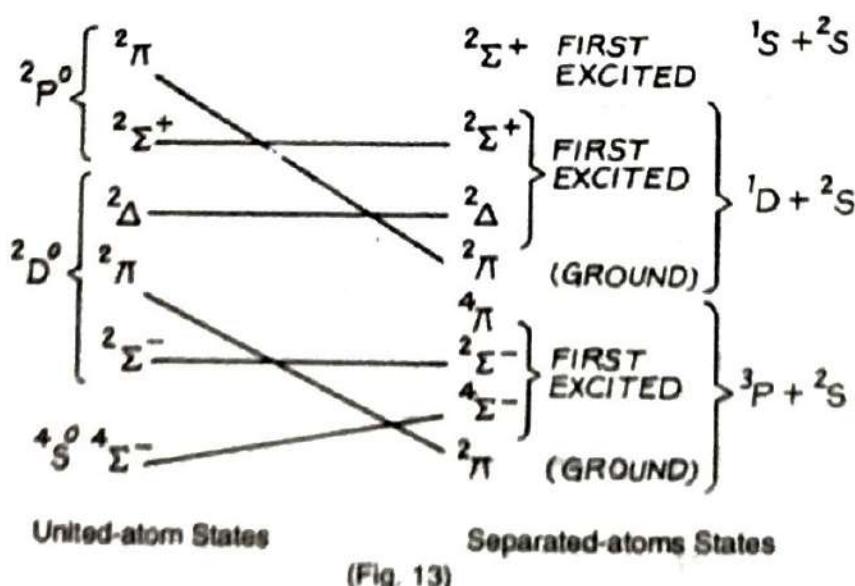
$$^4\Pi \quad ^2\Pi \quad ^4\Sigma^- \quad ^2\Sigma^-$$

Now, let us write down for CH, with seven electrons, the lowest and the first excited electronic configurations, and the corresponding molecular states :

Lowest:  $K(2s\sigma)^2(2p\sigma)^2(2p\pi)^2\Pi$  (ground state)

$$\text{First excited : } K(2s\sigma)^2(2p\sigma)(2p\pi)^2 \quad ^4\Sigma^+ \quad ^2A_1 \quad ^2\Sigma^+ \quad ^2\Sigma^-$$

The correlation is shown in Fig. 13.



## QUESTIONS

- Explain the difference between 'separated atoms' and 'united atom' models for determining the molecular states. *(Meerut sp. paper 88)*
- Discuss the method of determining term manifold of a diatomic molecule on the basis of united atom approximation. *(Meerut sp. paper 97)*
- Deduce all possible molecular terms arising from the following combinations of separated atoms :
  - $^1S$ - and  $^1P$ -atoms; (b)  $^1S$ - and  $^3P$ -atoms; (c)  $^2S$ - and  $^3P$ -atoms; (d)  $^2P$ - and  $^3D$ -atoms.

**Ans.** (a)  $^1\Sigma$ ,  $^1\Pi$ ; (b)  $^3\Sigma$ ,  $^3\Pi$ ; (c)  $^4\Sigma$ ,  $^2\Sigma$ ,  $^4\Pi$ ,  $^2\Pi$ ;  
 (d)  $^4\Sigma(3)$ ,  $^2\Sigma(3)$ ,  $^4\Pi(3)$ ,  $^2\Pi(3)$ ,  $^4\Delta(2)$ ,  $^2\Delta(2)$ ,  $^4\Phi$ ,  $^2\Phi$ .
- Determine the terms for the electron configurations  $\sigma \sigma$  and  $\pi^2$ . *(Meerut sp. paper 97)*
- Give the electronic configuration and the resulting states of the ground and the first excited state of  $H_2$  molecule. *(Meerut sp. paper 88)*
- Determine the electronic configurations and term types for the lowest and the first excited configurations of  $LiH$  and  $BeH$  molecules. *(Meerut sp. paper 97)*
- Write down the electronic configuration of  $AlH$  molecule and obtain its ground state. *(Meerut sp. paper 95, 94)*
- Write down the electronic configuration of the nitrogen molecule using relevant molecular orbitals and explain the various symbols used in it. Obtain the ground and first excited states of the nitrogen molecule. *(Meerut sp. paper 95, 94)*
- Write the molecular orbitals and spectroscopic designation for the ground state of  $O_2$  molecule. *(Meerut sp. paper 94)*
- Consider  $NH$  molecule. Derive the molecular states treating from the view point of united-atom and also of separated atoms. Draw a diagram showing the correlation of the states.

# Molecules and Chemical bonds : The Stability of Molecular States

## 1. Molecular Formation

We have seen in the last chapter that theoretically a large number of molecular electronic states are possible. However, all of these are not stable. Closely connected with the stability of the various molecular states is the stability of the molecule itself. A molecule is physically stable if external energy is required to break it up into its constituent atoms. The ground-state potential energy curve of a stable molecule has a minimum, indicating that the energy of the joint system is less than the energy of the separated constituent atoms.

When two atoms combine to form a diatomic molecule, they bring with them their peripheral electrons. In this process, the outermost loosely-bound electrons of the atoms are disturbed and their wavefunctions are significantly modified. It is this interaction which leads to binding, that is, to a lower total energy. Thus, the valence electrons play the central role in molecular binding.

There are two main situations which may occur in molecular bindings :

(i) An *ionic bond* is formed. One or more electrons from one atom may transfer to the other, and the resulting positive and negative ions attract each other. An example is NaCl molecule in which the bond exists between  $\text{Na}^+$  and  $\text{Cl}^-$  ions (not between Na and Cl atoms).

(ii) A *covalent bond* is formed. One or more pairs of electrons are shared by the two atoms. As these electrons move around and in between the atoms, they spend more time between the atoms than elsewhere, thus producing a net attractive force. Example are  $\text{H}_2^+$  molecular ion and  $\text{H}_2$  molecule in which one and two electrons respectively belong jointly to the two protons.

The above are the extreme cases of binding. There are molecules which have an intermediate type of bond in which the atoms share electrons unequally. An example is the HCl molecule in which the Cl atom attracts the shared electrons more strongly than the H atom.

## 2. Ionic Binding

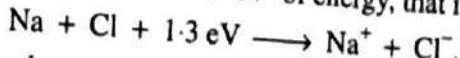
Ionic binding between two atoms occurs when one of them has a low ionisation energy\*, and hence a tendency to become a positive ion; while the other one has a high electron affinity†, and hence a tendency to become a negative ion. Sodium (Na) having an

\*The ionisation energy of an element is the energy needed to remove an electron from one of its atoms.

†The electron affinity of an element is the energy released when an electron is added to one of its atoms.

ionisation energy of 5.1 eV is an example of the former, and chlorine (Cl) having an electron affinity of 3.8 eV is an example of the latter. If a  $\text{Na}^+$  ion and a  $\text{Cl}^-$  ion be in the same vicinity, the electrostatic attraction between them would bring them together. The condition for a stable molecule of  $\text{NaCl}$  to be formed is that the total energy of the system of the two ions be less than the total energy of a system of two atoms of the same elements.

Let us consider the formation of  $\text{NaCl}$  molecule from an atom of Na and an atom of Cl which are initially far apart. A transference of an electron from Na to Cl atom would require a supply of  $5.1 \text{ eV} - 3.8 \text{ eV} = 1.3 \text{ eV}$  of energy, that is,

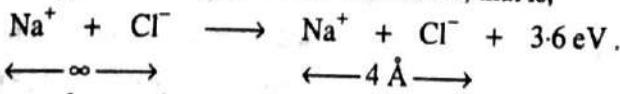


Thus, at large separation, the system  $\text{Na}^+ + \text{Cl}^-$  has an energy higher than the system  $\text{Na} + \text{Cl}$  by 1.3 eV.

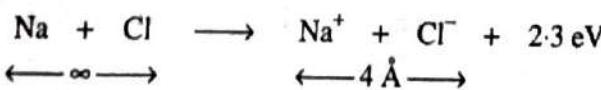
As the ions  $\text{Na}^+$  and  $\text{Cl}^-$  come closer under electrostatic attraction, the mutual potential energy of the system initially decreases (becomes more negative). For example, at a separation of 4 Å the energy is

$$\begin{aligned} V &= -\frac{1}{4\pi\epsilon_0} \frac{e^2}{R} \\ &= -(9.0 \times 10^9 \text{ N m}^2/\text{C}^2) \frac{(1.6 \times 10^{-19} \text{ C})^2}{4 \times 10^{-10} \text{ m}} \\ &= -5.8 \times 10^{-19} \text{ J} \\ &= -\frac{5.8 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J/eV}} \\ &= -3.6 \text{ eV}. \end{aligned}$$

This means that when the ions  $\text{Na}^+$  and  $\text{Cl}^-$  initially at infinite separation, come to a separation of 4 Å, energy amounting to 3.6 eV is released, that is,



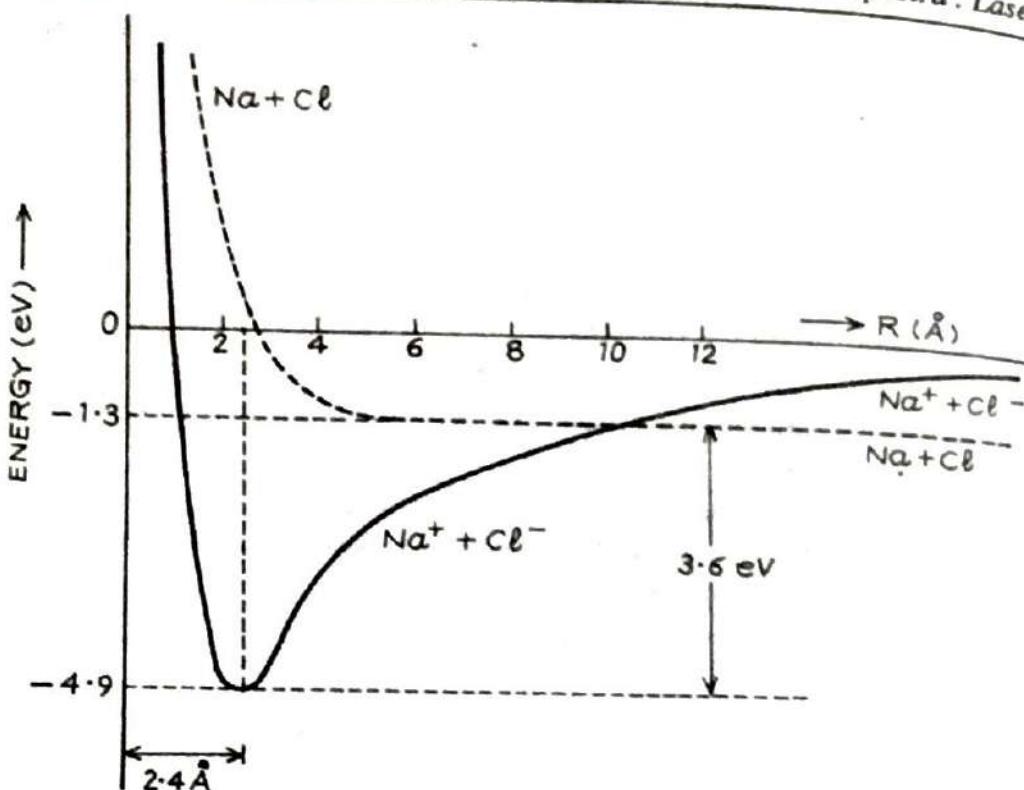
If we shift an electron from a Na atom to an infinitely distant Cl atom and allow the resulting ions to come closer to a distance of 4 Å, there is a net *release* of energy of  $5.6 \text{ eV} - 1.3 \text{ eV} = 2.3 \text{ eV}$ :



Thus, at small separation ( $< 10.5 \text{ \AA}$ ) the energy of the system  $\text{Na}^+ + \text{Cl}^-$  is *less* than that of the system  $\text{Na} + \text{Cl}$  (which remains unchanged with decreasing separation).

Evidently, the  $\text{NaCl}$  molecule formed by the electrostatic attraction of  $\text{Na}^+$  and  $\text{Cl}^-$  ions is *stable* (since energy would have to be given to the molecule in order to dissociate it into Na and Cl atoms).

The variation of energy of the system  $\text{Na}^+ + \text{Cl}^-$  and also of  $\text{Na} + \text{Cl}$ , with separation is shown in Fig. 1. It is seen that the energy of the system  $\text{Na}^+ + \text{Cl}^-$  does not go on decreasing indefinitely with decreasing separation. The reason is that when the two ions come so close that their electron clouds begin to overlap, then two effects take place each of which increases the potential energy :



(Fig. 1)

(i) the nuclei of the ions are no longer completely shielded by their surrounding electrons and so they begin to repel each other electrostatically ;

(ii) at very small internuclear separation, the electron clouds of  $\text{Na}^+$  and  $\text{Cl}^-$  constitute a single atomic system to which Pauli's exclusion principle applies, and some electrons go to higher energy states than before. Therefore, the potential energy of the  $\text{NaCl}$  molecule now decreases less rapidly, and ultimately increases rather sharply when the  $\text{Na}^+$  and  $\text{Cl}^-$  ions approach each other too closely. This means that the attractive force between the two ions ultimately turns into a repulsive force.

There is a separation at which the attractive and repulsive forces exactly balance and the energy of the molecule is a minimum. This is known as 'equilibrium internuclear separation' and is  $2.4 \text{ \AA}$  for  $\text{NaCl}$ . The energy at this separation is  $4.9 \text{ eV}$  lower than for distantly separated ions. Hence, compared to two neutral atoms  $\text{Na} + \text{Cl}$ , the combined system,  $\text{NaCl}$  molecule, is lower in energy by  $3.6 \text{ eV}$  ( $1.3 \text{ eV} - 4.9 \text{ eV} = -3.6 \text{ eV}$ ) To dissociate a  $\text{NaCl}$  molecule into  $\text{Na}$  and  $\text{Cl}$  atoms requires an energy of  $3.6 \text{ eV}$ .

As the  $\text{NaCl}$  molecule is held by ionic binding, it is called an ionic molecule. It has a permanent electric dipole moment because the regions of positive charge ( $\text{Na}^+$ ) and negative charge ( $\text{Cl}^-$ ) are separated. Hence an ionic molecule is said to be a "polar" molecule. Ionic binding is also called "heteropolar" binding. Ionic bonds are not directional, for each ion has a closed-shell configuration which is spherically symmetrical. Ionic bonds can also be formed with more than one valence electron, as in the case of the  $\text{MgCl}_2$  molecule.

### 3. Covalent Binding : Two Approaches

Molecules like  $H_2$  cannot be formed by bringing positive and negative hydrogen ions together. If we calculate the energy required to form  $H^+$  and  $H^-$  ions by shifting an electron from one H atom to the other and add to this the energy of the electrostatic attraction between the ions, we would find that there is no distance of separation at which the total energy is negative. That is, ionic binding does not result in a bound  $H_2$  molecule.

The fact that *neutral* atoms can attract one another strongly and form stable molecules like  $H_2^+$ ,  $H_2$ ,  $N_2$ , etc. is explained quantum mechanically by the behaviour of the electronic eigenfunction describing the charge distribution of the molecule. When two atoms approach each other, the resulting charge distribution leads to attraction and can be interpreted as a sharing of electrons by both atoms. This binding is called 'covalent'. It is also known as 'atomic' or 'homopolar' binding.

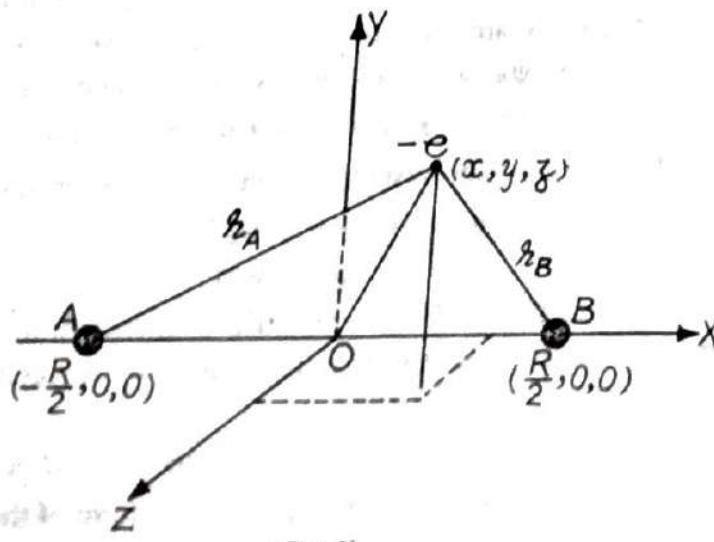
Two different theoretical approaches have been used to investigate covalent binding. One is the 'Heitler-London' or 'valence-bond' method which starts out from the separated atoms. The other is the 'Hund-Mulliken' or 'molecular orbital' method which starts out from the molecular orbitals that could be occupied by electrons. The former method has been extended by Slater and Pauling, and the latter by Herzberg and Lennard-Jones.

The simplest molecular systems to be treated are  $H_2^+$  and  $H_2$ .

### 4. Valence-bond Treatment of Hydrogen Molecular Ion ( $H_2^+$ )

The hydrogen molecular ion  $H_2^+$  is the simplest molecular system consisting of two protons (nuclei) and a single electron. The protons repel each other, and each of them attracts the electron electrostatically. The system will be stable if the total energy exhibits a minimum at some value of internuclear separation.

Let  $R$  be the separation between the two protons  $A$  and  $B$  (Fig. 2) situated on the X-axis, and  $r_A$  and  $r_B$  be the distances of the electron ( $x, y, z$ ) from  $A$  and  $B$  respectively. The total potential energy of the system is



(Fig. 2)

$$V = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r_A} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_B} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{K}$$

According to Born-Oppenheimer approximation, the protons, being much more massive than the electron, may be considered fixed at a separation  $R$ . The Schrödinger's equation for the electron is

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0,$$

which may be written as

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} \left[ E + \frac{1}{4\pi\epsilon_0} \left( \frac{e^2}{r_A} + \frac{e^2}{r_B} \right) \right] \psi = 0.$$

The term  $\frac{1}{4\pi\epsilon_0} \frac{e^2}{R}$  in  $V$  has been omitted because under the approximation it is a constant. From the geometry of the figure, we can write  $r_A$  and  $r_B$  in terms of  $R$ . Then, we get

$$\begin{aligned} \nabla^2 \psi + \frac{8\pi^2 m}{h^2} & \left[ E + \frac{1}{4\pi\epsilon_0} \frac{e^2}{\left\{ \left( x + \frac{R}{2} \right)^2 + y^2 + z^2 \right\}^{1/2}} \right. \\ & \left. + \frac{1}{4\pi\epsilon_0} \frac{e^2}{\left\{ \left( x - \frac{R}{2} \right)^2 + y^2 + z^2 \right\}^{1/2}} \right] \psi = 0. \end{aligned}$$

The solving of this equation is a complicated affair, but we can use an approximate approach to arrive at the electron wave function and bond energy of  $H_2^+$ .

When the two protons  $A$  and  $B$  are very far apart (that is,  $R$  is large compared to  $a_0$ , the radius of the smallest Bohr orbit), the electron remains either very near  $A$  or very near  $B$ . Let  $\psi_A$  and  $\psi_B$  be the wave functions describing the system in these two situations. In either situation, the system is equivalent to a neutral hydrogen atom, plus a non-interacting ionised hydrogen atom. Therefore, each of the wave functions  $\psi_A$  and  $\psi_B$  resembles very closely with the ground-state ( $1s$ ) wave function of the hydrogen atom. Since the two situations correspond to states of same energy, the wave functions  $\psi_A$  and  $\psi_B$  are degenerate. These wave functions have been pictured in Fig. 3 (a).

When the protons  $A$  and  $B$  are brought nearer ( $R$  decreases), the above degeneracy is removed and neither  $\psi_A$  nor  $\psi_B$  describes the system even approximately. An adequate description can, however, be obtained by taking a linear combination of  $\psi_A$  and  $\psi_B$ . The two normalised wave functions for the system  $H_2^+$  may now be written as

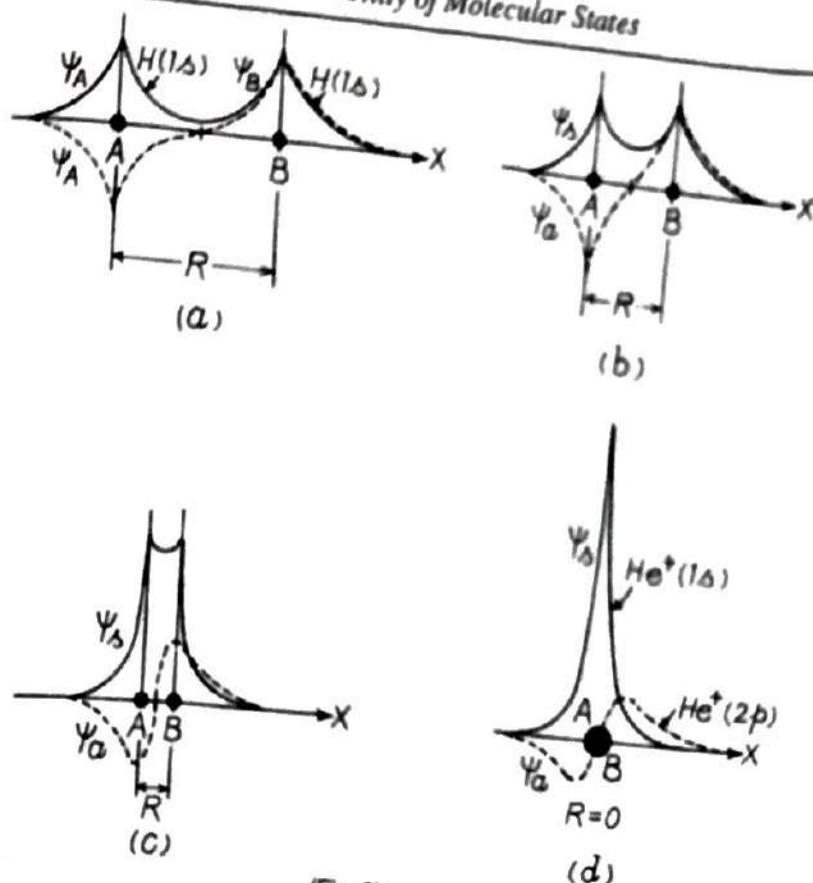
$$\psi_s = N_s (\psi_A + \psi_B)$$

and

$$\psi_a = N_a (\psi_A - \psi_B),$$

which are respectively symmetric and antisymmetric with respect to mutual exchange of  $A$  and  $B$ . These wave functions for two different values of  $R$ , comparable to  $a_0$ , are shown in Fig. 3 (b and c).

When the protons are imagined to be fused together ( $R = 0$ ), the system is equivalent to a  $He^+$  ion. The wave function  $\psi_s$  takes the form of the ground-state ( $1s$ ) wave function\* of  $He^+$ , and  $\psi_a$  approaches an excited-state ( $2p$ ) wave function of  $He^+$  which has a node at the origin (Fig. 3 d).



(Fig. 3)

Thus, we see that, for intermediate values of  $R$  (Fig. b and c), in the state corresponding to  $\psi_s$ , the electron is quite likely to be found in the region between the protons. This is spoken of as *sharing* of the electron by the two protons. There is, on the average, an excess of negative charge between the protons which results in an *attractive* force between them. This attraction is enough to overcome the mutual repulsion of the protons. Hence the system is stable in this state.

On the other hand, in the state corresponding to  $\psi_a$ , the electron is quite unlikely to be found between the protons and never in the plane mid-way between the protons where  $\psi_a = 0$ . Now there is, on the average, a deficiency of negative charge between the protons, and in consequence a repulsive force. With only repulsive forces acting, the system cannot remain stable.

Let us now see how the total energy of the  $H_2^+$  system varies with separation  $R$ . We first consider the symmetric state. When  $R$  is large, the electron energy of attraction,  $E_s$ , must be the 1 s-state energy of the hydrogen atom which is  $-13.6 \text{ eV}^\dagger$ ; while when  $R = 0$ , it must be equal to the 1 s-state energy of the  $He^+$  ion which is  $Z^2$  or 4 times that of the H atom, that is  $-54.4 \text{ eV}$ .

The electrostatic potential energy of repulsion of the protons is

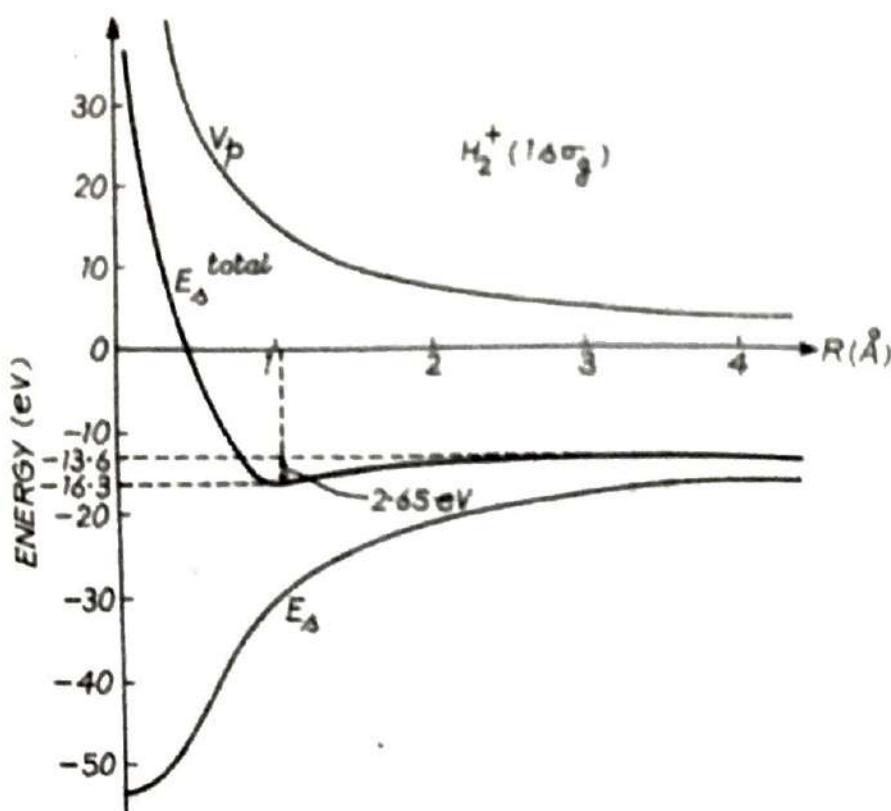
$$V_p = + \frac{1}{4\pi\epsilon_0} \frac{e^2}{R},$$

and so  $V_p \rightarrow 0$  as  $R \rightarrow \infty$ , and  $V_p \rightarrow \infty$  as  $R \rightarrow 0$ .

\*The 1 s wave function of  $He^+$  has the same form as that of H but with a greater amplitude at origin.

† For H atom or  $He^+$  ion, the energy expression is  $E_n = - \frac{R_\infty h c Z^2}{n^2}$ , where  $R_\infty$  is Rydberg constant.

Both  $E_s$  and  $V_p$  have been plotted as functions of  $R$  in Fig. 4.



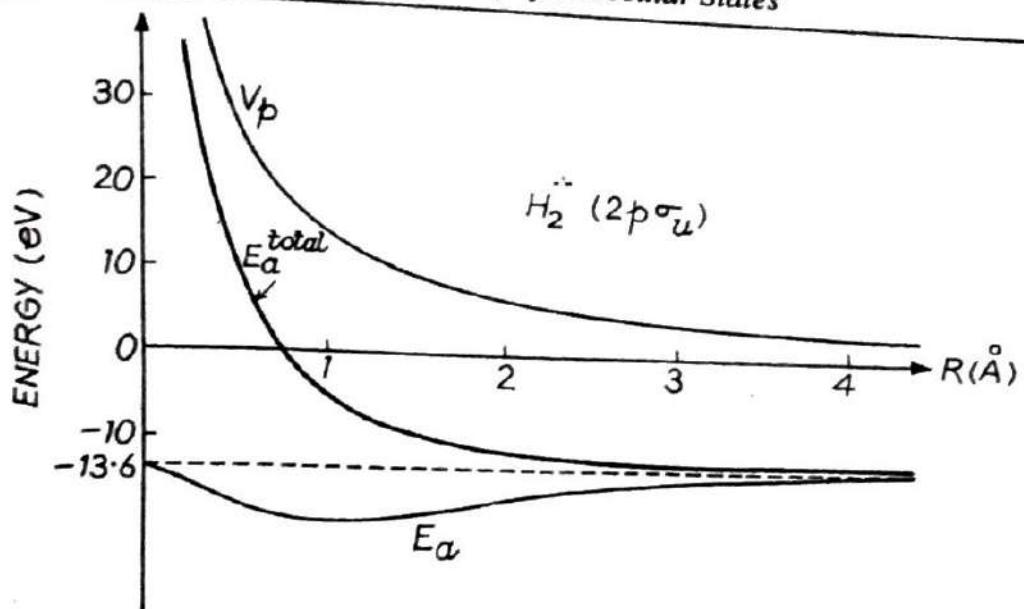
(Fig. 4)

The total energy  $E_s^{\text{total}}$  of the system  $\text{H}_2^+$  is the sum of the electron energy  $E_s$  and the potential energy  $V_p$  of the protons. It has also been plotted in Fig. 4. For large  $R$ , the total energy is constant at  $-13.6 \text{ eV}$ . As  $R$  decreases,  $E_s$  decreases faster than  $V_p$  increases. Hence there is a net decrease in the total energy. With further decrease in  $R$ , the total energy reaches a minimum and then increases rather sharply. The appearance of energy minimum corresponds to a stable molecular state. This result is confirmed by experiments on  $\text{H}_2^+$  which indicate a binding energy\* of  $2.65 \text{ eV}$  and an equilibrium separation of  $1.06 \text{ \AA}$ . The total energy of  $\text{H}_2^+$  is the  $-13.6 \text{ eV}$  of the hydrogen atom plus the  $-2.65 \text{ eV}$  binding energy, or  $-16.3 \text{ eV}$  in all.

In the case of the antisymmetric state (Fig. 5), at large  $R$ , the electron energy  $E_a$  is again the  $1s$ -state energy of  $\text{H}$  atom ( $-13.6 \text{ eV}$ ); but at  $R = 0$ , it is the energy of the  $2p$  state of  $\text{He}^+$  ion which is also  $-13.6 \text{ eV}$ . There is, however, a small dip at intermediate values of  $R$ , but not enough to yield a minimum in the total energy ( $V_p$  is same as before). Hence the total energy  $E_a^{\text{total}}$  continuously increases as  $R$  decreases. This corresponds to a repulsive force at all separations and the state is unstable.

The symmetric and antisymmetric states of  $\text{H}_2^+$  considered above corresponds to molecular orbitals  $1s\sigma_g$  and  $2p\sigma_u$  in the united-atom notation (or  $\sigma_g 1s$  and  $\sigma_u 1s$

\*The binding energy is the energy needed to break  $\text{H}_2^+$  into  $\text{H} + \text{H}^+$  atoms; it is the difference between the minimum energy and the energy at infinite separation.



(Fig. 5)

in separated-atoms notation), and the corresponding electronic states are  ${}^2\Sigma_g^+$  and  ${}^2\Sigma_u^+$  which are stable and unstable respectively.

## 5. The LCAO Method for $\text{H}_2^+$

In the previous section we graphically determined molecular wave functions by considering appropriate atomic wave functions. This section is a mathematical version of the same.

The LCAO method takes its name from the use of a Linear Combination of Atomic Orbitals (or wave functions) to obtain a molecular orbital (or wave function).

The atomic orbitals which can be combined to obtain  $\text{H}_2^+$  orbital are the ground-state ( $1s$ ) hydrogen wave functions. Let  $\psi_A$  and  $\psi_B$  be the hydrogen wave functions which describe hydrogen atoms at  $A$  and  $B$  (Fig. 2). They can be combined in two ways to give molecular wave functions, which are

$$\psi_s = N_s (\psi_A + \psi_B) \quad \dots(i)$$

and

$$\psi_a = N_a (\psi_A - \psi_B). \quad \dots(ii)$$

The normalisation constants  $N_s$  and  $N_a$  have values such that

$$\int_{-\infty}^{+\infty} |\psi_s|^2 dV = 1 \quad \dots(iii)$$

and

$$\int_{-\infty}^{+\infty} |\psi_a|^2 dV = 1 \quad \dots(iv)$$

which mean that the electron exists somewhere.

Now, for the symmetric molecular wave function, we have

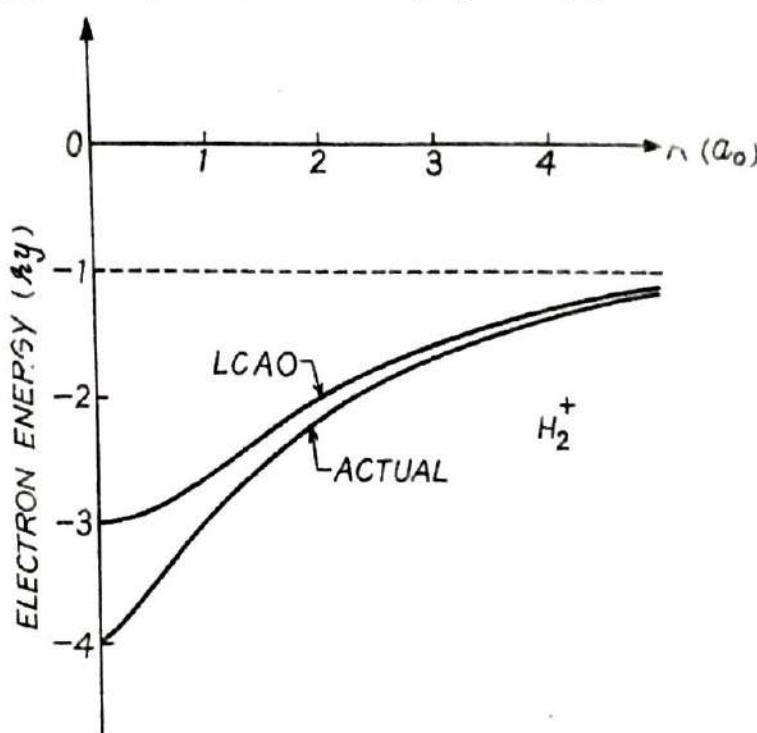
$$\begin{aligned} \int_{-\infty}^{+\infty} |\psi_s|^2 dV &= 1 = \int_{-\infty}^{+\infty} N_s^2 |\psi_A + \psi_B|^2 dV \\ &= N_s^2 \left[ \int_{-\infty}^{+\infty} |\psi_A|^2 dV + \int_{-\infty}^{+\infty} |\psi_B|^2 dV + 2 \int_{-\infty}^{+\infty} \psi_A \psi_B dV \right]. \end{aligned}$$

But  $\int_{-\infty}^{+\infty} |\psi_A|^2 dV = \int_{-\infty}^{+\infty} |\psi_B|^2 dV = 1$  because  $\psi_A$  and  $\psi_B$  are already normalised. Also, let us put

when  $R' \rightarrow \infty$ ,  $E_s' \rightarrow -1$  ry

and when  $R' = 0$ ,  $E_s' = -3$  ry.

A comparison between  $E_s'$  versus  $R'$  as given by LCAO method, and the actual one is given in Fig. 6. It is seen that the LCAO method is exact when  $R'$  is large, fairly accurate at intermediate (equilibrium) values, but becomes progressively poorer as  $R' \rightarrow 0$ .



(Fig. 6)

A calculation for the antisymmetric case gives

$$E_a' = -1 + \frac{K - J}{1 - S} . \quad \dots \text{(xii)}$$

To find the total energy of  $H_2^+$  molecular ion, we must add the mutual potential energy  $V_p'$  of the two protons to the electron energy  $E_s'$  or  $E_a'$ . Since, we have,

$$V_p' = + \frac{1}{4\pi\epsilon_0} \frac{e^2}{R} ,$$

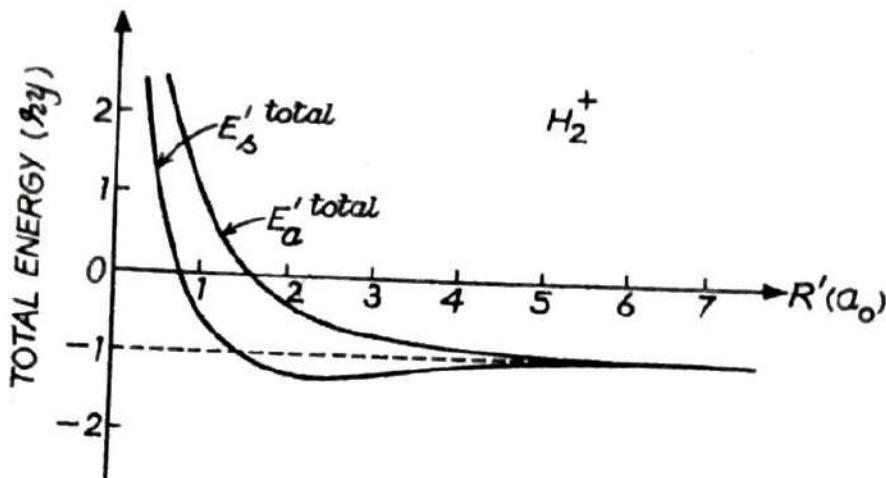
where  $R$  is in meter and  $V_p'$  in joule. In the "atomic units"  $a_0$  and rydberg, we would write

$$V_p' = + \frac{2}{R'} .$$

Hence  $E_s'^{\text{total}} = E_s' + V_p' = -1 + \frac{K + J}{1 + S} + \frac{2}{R'} ,$

and  $E_a'^{\text{total}} = E_a' + V_p' = -1 + \frac{K - J}{1 - S} + \frac{2}{R'} .$

The variation of the total energies with  $R'$  is given in Fig. 7. The curve for the symmetric state has a minimum at  $R' = 2.5 a_0$  with a binding energy of 0.13 ry ( $= 1.8$  eV). The correct values for  $H_2^+$  are  $2.0 a_0$  and  $0.195$  ry ( $= 2.65$  eV) respectively. The discrepancy indicates the approximate nature of the LCAO method, yet it provides a



(Fig. 7)

qualitative insight into the molecular binding. The curve for the antisymmetric state of  $H_2^+$  has no minimum, showing that this state is unstable.

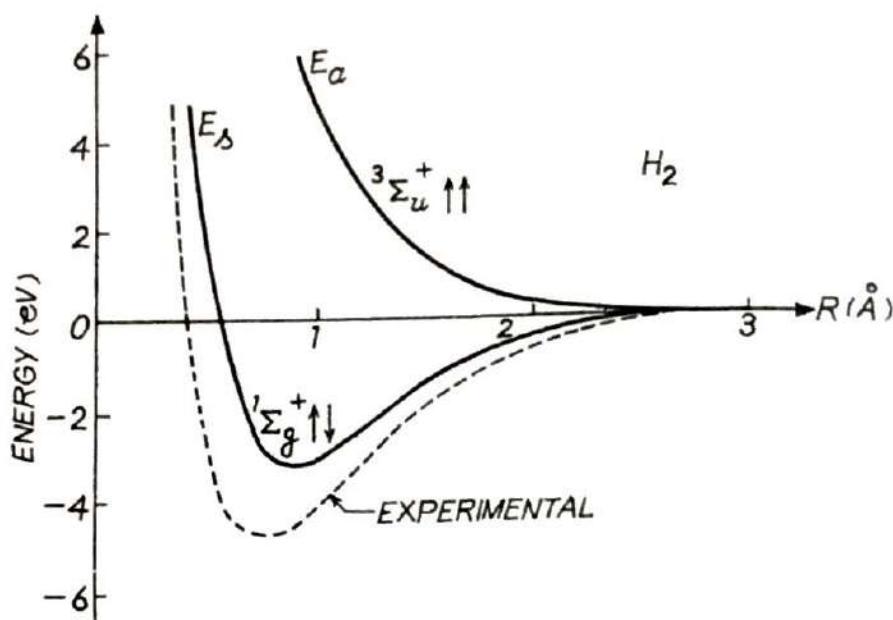
## 6. Valence-bond (Heitler-London) Treatment of $H_2$ Molecule

The  $H_2$  molecule is held by a covalent bond between two neutral H atoms. The bond is provided by a pair of electrons which are *shared* by the two atoms. Compared to  $H_2^+$  whose bond is provided by a single electron,  $H_2$  is more compact and more tightly bound. Its equilibrium internuclear separation is 0.74 Å with a binding energy of 4.74 eV. (The corresponding values for  $H_2^+$  are 1.06 Å and 2.65 eV). The wave functions of  $H_2$  are different than those of  $H_2^+$  because of the electrostatic repulsion between the two electrons in  $H_2$ , a factor absent in  $H_2^+$ .

Heitler and London treated the stability of  $H_2$  molecule by starting out from the state of two separated normal H atoms as zero approximation and then introducing the interaction of the two atoms as a perturbation. Two normal H atoms in the  $^2S$  state give rise to two molecular states  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$ . Heitler and London showed that  $^1\Sigma_g^+$ , which is the ground state of the molecule, is stable while the state  $^3\Sigma_u^+$  is unstable.

According to Heitler-London theory, the strong binding forces between two H atoms arise from "exchange degeneracy". Hence they are called 'exchange forces'. When the two atoms are very much far away from each other, then the mutual exchange of the two electrons results into a configuration which is indistinguishable from the original configuration. That is, the two configurations are degenerate. When the atoms approach each other, an interaction between them takes place which removes the degeneracy. The energy corresponding to one configuration is smaller than the energy of the system for large separation, while that corresponding to the other configuration is greater. The exchange forces between the two atoms are attractive for the configuration of smaller energy which is therefore a stable state; while they are repulsive for the configuration of greater energy which is therefore an unstable state.

Let us now consider an  $H_2$  molecule, a system consisting of two electrons 1 and 2 in the field of two protons A and B (Fig. 8). The various distances are as shown.



(Fig. 9)

the product of a spatial eigenfunction  $\psi_s$  or  $\psi_a$ , which describes the coordinates of the electrons, and a spin function  $\beta_s$  or  $\beta_a$  (say) which describes the orientations of their spins. For a system of two electrons, there are three symmetric spin functions  $\beta_s$  corresponding to parallel spins, and only one antisymmetric spin function  $\beta_a$  corresponding to antiparallel spins (see page 112). The acceptable (antisymmetric) total eigenfunction would be formed only as

$$\Psi_{total} = \psi_s \beta_a$$

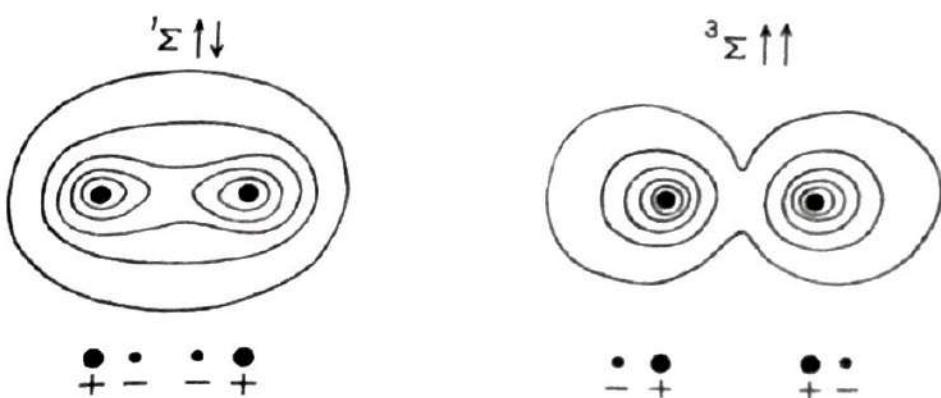
and

$$\Psi_{total} = \psi_a \beta_s.$$

Thus, the stable state  $E_s$  corresponding to  $\psi_s$  occurs with antiparallel spins ( $\beta_a$ ), that is, it is a  $^1\Sigma$ -state; while the unstable state  $E_a$  corresponding to  $\psi_a$  occurs with parallel spins ( $\beta_s$ ), that is, it a  $^3\Sigma$ -state. We can also say that **two hydrogen atoms attract each other when their electron spins are antiparallel, and repel each other when the electron spins are parallel.**

Since there is only one spin function corresponding to antiparallel spins while there are three spin functions corresponding to parallel spins, the chance of the formation of a stable  $H_2$  molecule by the interaction of two normal H atoms is only 25%.

The probability density distribution of the electrons in the  $H_2$  molecule, calculated for the  $^1\Sigma$  and  $^3\Sigma$  states, is shown graphically in Fig. 10. In the case of the  $^1\Sigma$  state (attraction) the electron clouds of the two atoms blend into each other, that is, the electrons are being shared by both the atoms. In sharing, the electrons spend, on the average, more time between the protons than on the outside, and the greater electron density between the protons produces strong binding between them. In the  $^3\Sigma$ -state (repulsion) the electron clouds remain almost completely separated, that is, the electrons tend to avoid the region between the protons. Thus, they spend, on the average, more time on the outside of the

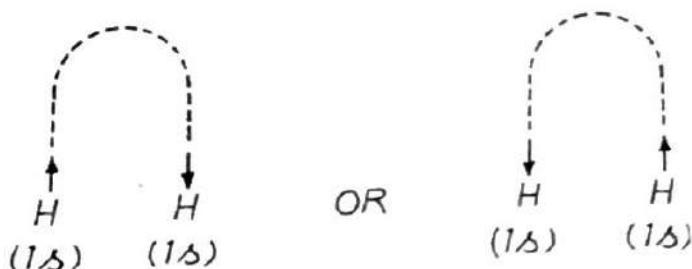


(Fig. 10)

protons where they act to pull the protons apart in addition to permitting them to repel each other. Thus, binding becomes impossible.

## 7. Generalisation of Heitler-London Theory for Molecules other than H<sub>2</sub>

According to Heitler-London (valence-bond) theory of H<sub>2</sub> molecule, the covalent bond between the two neutral H atoms is formed by a *shared* pair of electrons with "antiparallel spins". This means that H<sub>2</sub> molecule is formed when two H atoms, whose electrons have antiparallel spins, approach each other. These electrons are mutually exchangeable and give rise to an attractive exchange force (Fig. 11).



(Fig. 11)

If the exchanging (shared) electrons had parallel spins they would have resulted in a repulsive force and no molecule would be formed. It is on this basis that the  ${}^1\Sigma$  state of H<sub>2</sub> is stable while the  ${}^3\Sigma$  state is unstable.

Let us apply this theory to the formation of other molecules. The case next to H<sub>2</sub> in simplicity is that of the interaction of a normal He atom with a normal H atom. The He atom has two 1s electrons with antiparallel (paired) spins\*, while the H atom has only one 1s electron. The formation of HeH molecule is possible only if an electron from one atom is exchangeable with an electron of "antiparallel" spin from the other atom. Here this is not so. We can see that, due to Pauli's principle, the electron of the H atom is exchangeable only with that electron of He whose spin is parallel to its own† (Fig. 12). But this, according to Heitler and London, would produce a repulsive exchange force.

\*These electrons have 'antiparallel' spins due to Pauli's principle.

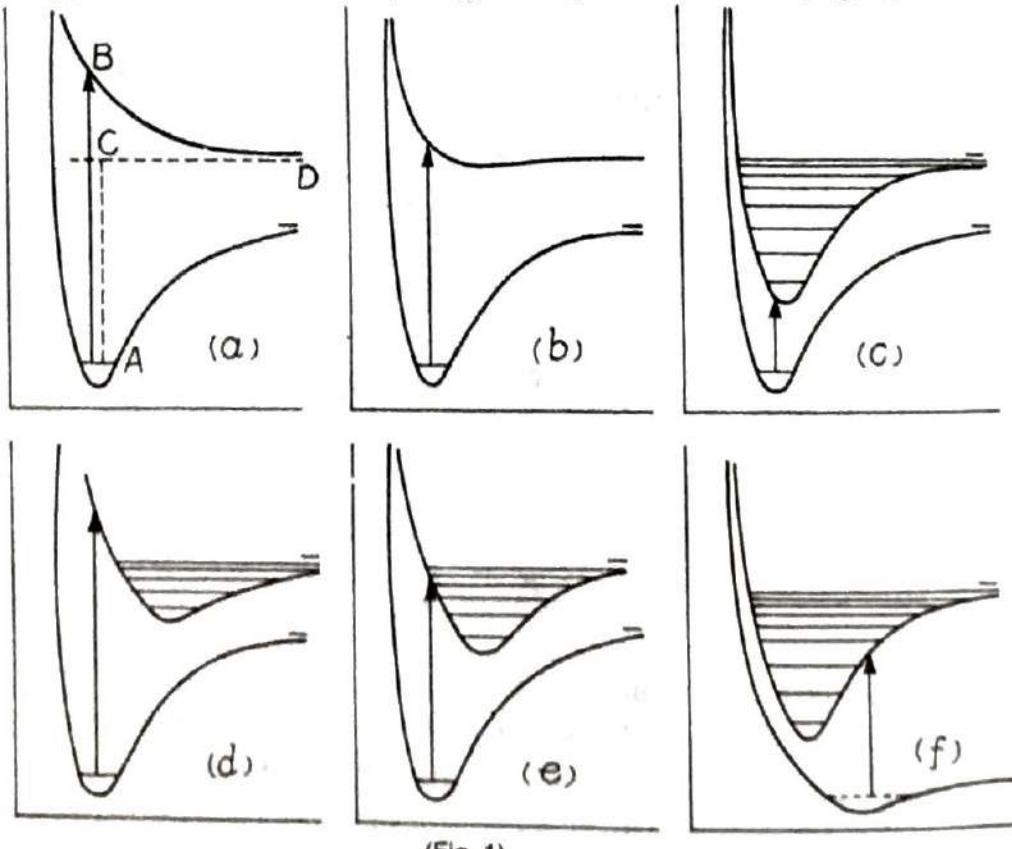
†If the electron of H atom be exchanged with the antiparallel-spin electron of He atom, then both electrons of the He atom would have parallel spins which is not allowed by Pauli's principle.

# Continuous and Diffuse Molecular Spectra : Dissociation and Predissociation

## 1. Continuous Spectra

In addition to discrete molecular spectra, the continuous molecular spectra frequently appear, both in absorption and in emission. The continuous spectra usually arise from transitions between two states, one of which has a continuous range of energy levels. The continuous nature of the energy state is the result of free kinetic energy in some part of the molecular system, and thus corresponds to either ionisation or to dissociation of the molecule into atoms. For molecules, the continua corresponding to ionisation lie well down in the ultraviolet and are rarely observed. Infact, the absorption of a continuum in the visible or near ultraviolet by a molecule can nearly always be assigned to molecular dissociation.

The various possibilities for absorption are illustrated by the potential energy curves in Fig. 1. An important case of dissociation continua in absorption is that in which a transition takes place from the lowest vibrational level of the (stable) ground state to a continuous upper state characterised by a repulsive potential curve\* (Fig. a). The most



\*A repulsive potential curve is one that has no minimum.

favoured transitions are those for which Franck-Condon principle is satisfied. That is, the strongest absorption corresponds to a transition  $AB$  going vertically upward from the minimum of the lower curve. Thus, the absorption spectrum in this case shows a broad patch of continuum in which the maximum absorption corresponds to an energy ( $AB$ ) which is appreciably greater than the energy ( $AC$ ) required just to produce dissociation. (The excess energy goes into the kinetic energy of the free atoms resulting from the dissociation process). The (longest) wavelength corresponding to the (smallest) energy  $AC$  which can be absorbed, is the long-wave limit of the continuum. In practice, however, is reached. This is because a transition in the neighbourhood of this limit would correspond to a large change ( $= AD$ ) in the internuclear distance which is practically not allowed by Franck-Condon principle. Such an absorption continuum is observed for halogen hydrides.

When the upper curve runs quite flat up to the region above the ground-state minimum (Fig. b), the absorption continuum is narrower and the long-wave limit is more clearly defined. Although the continuum does not possess a sharp edge, yet a fairly good estimate may be made for the energy of the dissociation limit. In some cases, flat upper curves of this type lead to continua showing diffuse banded structure.

When both the upper and the lower potential curves are quite stable (Fig. c), the absorption spectrum consists of a sharp banded structure, without any continuum. If, however, the upper state is much less stable than the lower state, so that its minimum is at a much greater internuclear distance (Fig. d), then the most probable (vertical) transitions occur from the minimum of the ground state to points on the upper curve which are above the dissociation limit. Thus, it is a case of absorption continuum when the upper is *not* unstable.

In the intermediate case between (c) and (d), when the potential curves are positioned as in Fig. (e); the most favoured absorption transitions go to a part of the upper curve which has about the same energy as the dissociation limit. The absorption spectrum consists of a series of converging bands at the long-wave end which merges into a continuum at shorter wavelengths. The convergence limit of the bands (the beginning of the continuum) gives the exact position of the asymptote of the potential curve of the upper state, that is, the position of the dissociation limit. This case occurs for  $O_2$  and the halogens and provides us a method of determining the dissociation energies of these molecules.

Certain metal vapours like  $Hg_2$ ,  $Cd_2$  have a ground state of very low stability (Fig. f). For these molecules, only very weak van der waals forces act between the atoms in their ground states. At low pressure practically all the molecules are thermally dissociated, giving only atomic lines in the absorption spectrum. With increasing pressure, however, the number of transient molecules due to atomic collisions increases and the atomic lines become broader to give *diffuse bands\** and patches of continuum. These spectra yield information about the theory of pressure-broadening of atomic lines and the nature of van der waals forces.

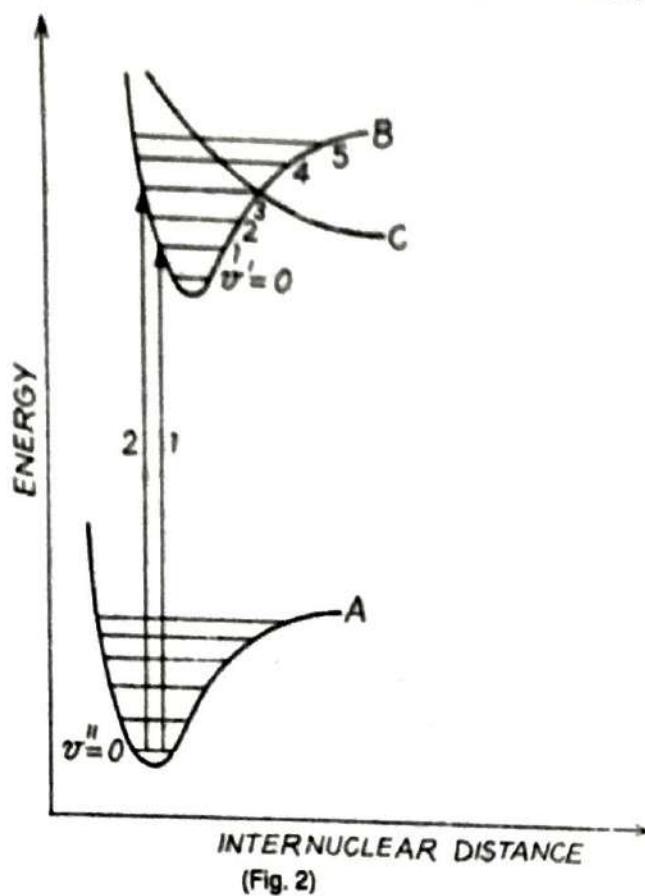
We thus see that the study of continuous spectra leads to an understanding of dissociation process, determination of dissociation energies, pressure-broadening, etc.

\*The diffuse bands referred to here are quite distinct from the diffuse bands resulting from predissociation.

Hence electronic states with repulsive potential curves are of great importance in molecular spectra.

## 2. Predissociation

Whenever the potential curves of two different excited electronic states of a molecule intersect such that the discrete energy levels of one curve overlap the continuous range of levels of the other (Fig. 2), then there is a possibility of a *radiationless* transition from the



discrete state to the continuous state, followed by spontaneous dissociation of the molecule. This process is called 'predissociation'. It is responsible for two characteristic phenomena observed in molecular spectra, namely, 'diffuseness of bands' and 'breaking-off of band-structure'.

(i) **Diffuseness of Bands** : In some molecular absorption spectra, such as of  $S_2$ , it has been observed in passing along a given  $v'$ -progression ( $v'' = \text{constant}$ ) that the first few bands of the progression show a normal type of rotational fine structure consisting of sharp lines; but beyond a certain value of  $v'$  the rotational lines of the bands become diffuse.

Those bands which have diffuse structure in absorption do not occur in emission. For example, in case of  $S_2$ , only those bands appear in emission that correspond to the sharp absorption bands, whereas the diffuse bands of the same system can in no way be obtained in emission. Thus, in emission, the band-system breaks off at a definite value of  $v'$ . This is known as 'breaking-off of band-system' (not to be confused with 'breaking-off of band-structure').

(ii) **Breaking-off of Band-structure :** In some emission bands there is found a sudden breaking-off of the band-structure at a certain point. For example, in the (0, 0) band of the  $C^2\Sigma \rightarrow X^2\Sigma$  system of CaH, the R-branch lines run smoothly upto  $R(9)$  and then terminate abruptly, the last line  $R(9)$  showing a slight perturbation. The P-branch behaves similarly, ending abruptly at  $P(11)$ , the last line again being slightly perturbed. The breaking-off is clearly due to the failure of rotational levels of the upper electronic state with  $K' > 10$ . Other examples of this sudden termination of band-structure in emission are found in  $A^1\Pi \rightarrow X^1\Sigma$  system of AlH, the second and the fourth positive systems of  $N_2$ , the third positive system of CO, etc. Such band-systems do not occur in absorption.

These two phenomena have in many cases the same origin, that is, predissociation.

In Fig. 2, two excited states  $B$  and  $C$  of a molecule intersect. The state  $B$  has a minimum and the usual set of vibrational levels, while the state  $C$  has no minimum and accordingly is unstable. The transition 1 from the ground state  $A$  to the excited state  $B$  would give a normal absorption band with sharp rotational structure. Transition 2 is however quite different. The energy absorbed by the molecule in transition 2 is not large enough to dissociate it in the state  $B$ , but the molecule can "cross-over", *without radiation*, to the state  $C$  and then (pre) dissociate. This radiationless transition takes place in a time which is long compared with that required for molecular vibration but shorter than that required for rotation. This is, the molecule finds enough time to vibrate, but not to rotate, before it dissociates in state  $C$ . Thus, in transition 2, the vibrational energy remains quantised but the rotational energy is no longer strictly quantised. Therefore, the vibrational structure of the band-system is not influenced by the radiationless decomposition (predissociation), but the rotational structure of the bands becomes diffuse. Thus, the diffuseness of the bands in absorption indicates predissociation if the bands are preceded by sharp bands in the same progression.

The radiationless transition probability is governed by selection rules and Franck-Condon principle, and determines the degree of diffuseness. Sometimes there is only a slight broadening of the rotational lines, while in some cases the rotational structure may be completely washed out.

The abrupt termination of band-structure in emission may similarly be explained. If the molecule is excited to a *rotational* level of a stable electronic state above the dissociation limit\* and a radiationless transition to another excited electronic state is possible, then the molecule may either return back with radiation or cross-over to the other state without radiation and then (pre) dissociate. If the mean-life for radiationless transition is less than that for radiation, then most of the molecules will pre-dissociate. Therefore, the rotational lines in emission involving transitions from rotational levels above the dissociation limit will be extremely weak in intensity or entirely missing.

Thus, in general, a *predissociation is established either by the absorption bands becoming diffuse, or by the emission bands breaking-off at a certain point.*

**The breaking-off of emission bands is a much more sensitive test for the predissociation than the diffuseness of absorption bands :** The diffuseness of the

\*There are cases in which sharp rotational levels are observed upto quite above the dissociation limit.

rotational lines is noticeable only when the line-width becomes greater than the Doppler width which is between 0.01 to 0.1 Å. The natural line-width is of the order of 0.001 to 0.01 Å. Therefore, in order that the line-width shall be greater than the Doppler width, the radiationless transition probability must be at least 10 to 100 times greater than the radiative transition probability.<sup>†</sup>

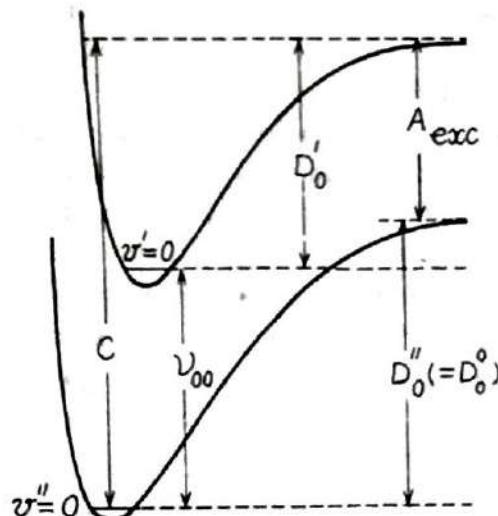
On the other hand, the weakening in the intensity of band structure arising from transitions from predissociated levels becomes appreciable as soon as the radiationless transition probability is of the same magnitude as that of the radiative transition. Thus, usually the observation of predissociation in an emission spectrum is a much more sensitive test than in absorption.

The study of predissociation has led to important conclusions about molecular structure, to an explanation of some photochemical processes, and to a determination of dissociation energy.

### 3. Determination of Dissociation Energy

The dissociation energy (or heat of dissociation)  $D_0^0$  of a diatomic molecule  $A B$  is defined as the work required to dissociate the molecule from the lowest level ( $v = 0, J = \Omega$ ) of the electronic ground state into *normal* atoms,  $A + B$ .

In each of its stable electronic states, the molecule has a certain dissociation energy  $D_0$  which corresponds to a dissociation from the lowest level of that state. When two electronic states are under consideration, the dissociation energies are denoted by  $D_0'$  and  $D_0''$  for the upper and the lower states respectively (Fig. 3). One or both of the atoms



(Fig. 3)

produced by dissociation may be in an excited state. If the lower is the ground state, then  $D_0''$  is the energy of dissociation as ordinarily defined ( $D_0'' = D_0^0$ ), provided the ground state dissociates into normal atoms. However, there are a few cases such as the BeO molecule in which the ground state does not dissociate into normal atoms. Then  $D_0^0$  is smaller than  $D_0''$ .

<sup>†</sup> Half-width  $\propto \frac{1}{\text{mean life}} \propto \text{probability.}$

The spectroscopic determination of the dissociation energy  $D_0^0$  of a molecule always involves two steps : (1) determination of the energy of a dissociation limit,  $C$ , above the ground state, and (2) determination of the products of dissociation at this limit, that is, atomic excitation energy  $A_{exc}$ . When these two are known, the dissociation energy is immediately obtained by the simple expression,

$$D_0^0 = D_0'' = C - A_{exc}.$$

### (I) Determination of Dissociation Limit :

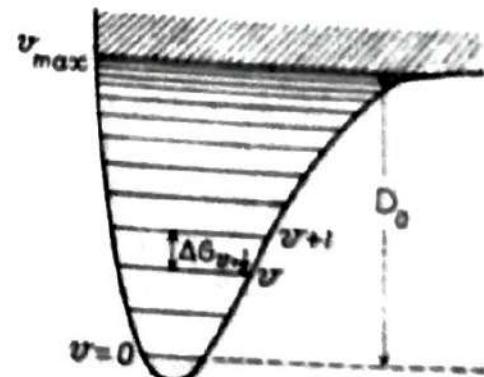
The methods of determination of dissociation limit are the following :

(i) **Band Convergence** : A very accurate value for the dissociation limit is obtained when a  $v'$ -progression ( $v'' = \text{constant}$ ) of bands is observed up to the convergence point, with its adjoining continuum, in absorption. The position of the convergence point, that is, the beginning of the continuum, corresponds to the energy of the dissociation limit  $C$  of the excited electronic state. This can be obtained by direct measurement. The dissociation energy  $D_0^0$  can be evaluated by the above expression after  $A_{exc}$  is known.

If the wave number of the (0, 0) band,  $\nu_{00}$ , of the observed progression is known, then the dissociation energy for the excited state can be evaluated :

$$D_0' = C - \nu_{00}.$$

(ii) **Extrapolation to Convergence Limit** : Birge-Sponer Method : For those cases in which no band convergence is observed, Birge and Sponer have suggested an extrapolation to the convergence limit from the observed bands. We know that in a vibrational energy-level diagram for a given electronic state, the dissociation energy for the state is the distance from the  $v = 0$  level to the (unobserved) limiting level  $v = v_{\max}$  at which the intervals between successive levels would vanish (Fig. 4). That is,  $D_0$  is equal to the sum of all the vibrational levels ;



(Fig. 4)

$$D_0 = \sum_v \Delta G_v + \frac{1}{2}.$$

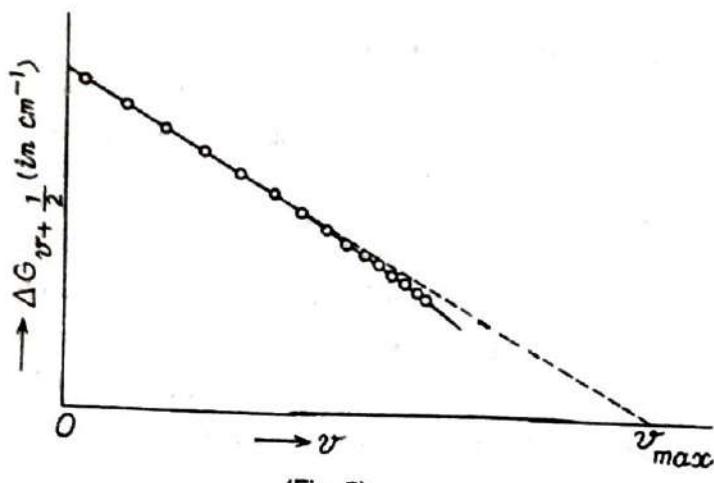
Now, the vibrational energy levels can be expressed as a power series in terms of the vibrational quantum number  $v$  :

$$G(v) = \omega_r \left( v + \frac{1}{2} \right) - \omega_r x_r \left( v + \frac{1}{2} \right)^2 + \dots$$

In higher terms being neglected as the series is rapidly convergent. The separation between successive levels  $v$  and  $v + 1$  is thus

$$\begin{aligned} \Delta G_{v+1} &= G(v+1) - G(v) \\ &= \left\{ \omega_r \left( v + \frac{3}{2} \right) - \omega_r x_r \left( v + \frac{3}{2} \right)^2 \right\} - \left\{ \omega_r \left( v + \frac{1}{2} \right) - \omega_r x_r \left( v + \frac{1}{2} \right)^2 \right\} \\ &= \omega_r - 2\omega_r x_r - 2\omega_r x_r v \\ &= -2\omega_r x_r v + (\omega_r - 2\omega_r x_r) \end{aligned} \quad \dots (i)$$

This equation is of the same form as the general equation of a straight line. Hence a graphical plot of the observed  $\Delta G_v + \frac{1}{2}$  (spacing between successive bands of a progression) against  $v$  will be a straight line with a negative slope of  $-2\omega_e x_e$  (Fig. 5). The area under this straight line extrapolated to  $v_{max}$  (where  $\Delta G = 0$ ) is the sum of all the  $\Delta G_v + \frac{1}{2}$ 's and gives the dissociation energy  $D_0$ .



(Fig. 5)

Analytically, the linearly extrapolated dissociation energy is given by

$$\begin{aligned}
 D_0 &= \sum_{v=0}^{v_{max}} \Delta G_v + \frac{1}{2} \\
 &= (\omega_e - 2\omega_e x_e) + (\omega_e - 4\omega_e x_e) + (\omega_e - 6\omega_e x_e) + \dots \text{to zero} \\
 &= \frac{\omega_e^2}{4\omega_e x_e} - \frac{1}{2}\omega_e \\
 &= \frac{1}{2}\omega_e \left( \frac{\omega_e}{2\omega_e x_e} - 1 \right) \\
 &= \frac{1}{2}\omega_e v_{max} * .
 \end{aligned}$$

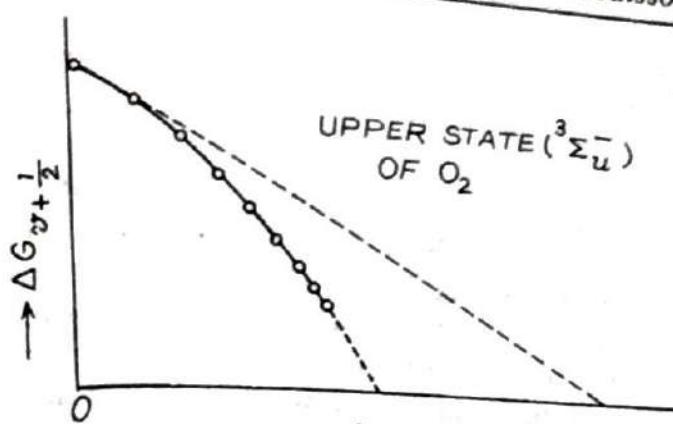
Thus, on determining  $\omega_e$  (by vibrational analysis of bands) and  $v_{max}$  (by extrapolation), the dissociation energy  $D_0$  can be calculated.

In most cases, however,  $\Delta G$  is not a linear function of  $v$ . For the ground state of  $H_2$ , for example, the plot of  $\Delta G$  against  $v$  is in fact a curve and the area under the straight line is larger than that under the actual curve. Hence the dissociation energy obtained by linear extrapolation is higher than the actual value.

The plot for the upper state  ${}^3\Sigma_u^-$  of  $O_2$  shows a negative curvature throughout its whole course (Fig. 6), and a linear extrapolation would give a value about 35% too high. When only the first few vibration quanta are experimentally known, we can only adopt linear extrapolation and the dissociation energy so obtained will be only approximate. If, however, sufficient vibrational quanta are observed so that a curvature of the  $\Delta G$  curve

\*We can see by putting  $\Delta G_v + \frac{1}{2} = 0$  and  $v = v_{max}$  in eq. (i) that

$$v_{max} = \frac{\omega_e}{2\omega_e x_e} - 1.$$

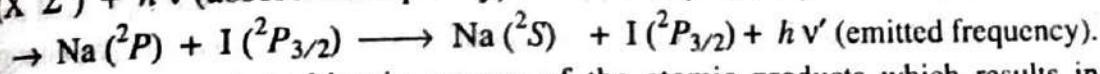
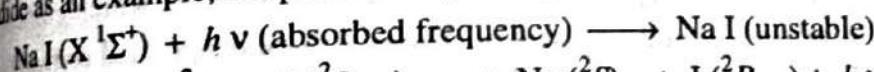


(Fig. 6)

can be detected, then quadratic or higher terms are included in the formula for  $\Delta G$  and graphical extrapolations other than linear are used to obtain  $D_0$ .

By this method we obtain the dissociation energy of the electronic state whose vibrational quanta are used. The advantage of the extrapolation method is that it can be applied to any electronic state for which a few vibrational levels are known. It enables us to estimate  $v$  at the dissociation limit and emphasises the importance of the anharmonicity of molecular vibrations near the dissociation limit.

(iii) **Excitation of Atomic Fluorescence :** When continuous or diffuse absorption raises a molecule to an unstable electronic state which dissociates into a normal atom and an excited atom, then the absorption process may be followed by the emission of an atomic line in fluorescence (provided the excited atomic state is not metastable). Taking sodium iodide as an example, the process may be represented as :



Any excess energy goes into kinetic energy of the atomic products which results in Doppler broadening of the atomic lines. If the frequency of the absorbed light is sufficiently high, excitation to other molecular states dissociating into other products may take place. Thus, the long-wave limit at which the atomic fluorescence can just be excited gives an upper limiting value for the dissociation limit. The advantage of this method is that it yields correct information about the nature of the dissociation products produced at the limit, and thus an upper limiting value for the heat of dissociation of the molecule. This method has been applied to the alkali halides.

(iv) **Predissociation Limits :** Whenever predissociation (including the induced predissociation and accidental predissociation) is observed, the predissociated energy level must lie above the dissociation energy. Thus, the energy of predissociation gives an upper limiting value for the dissociation energy of the state causing the predissociation. However, only in special cases, predissociation can lead to an exact numerical value for a dissociation limit.

#### 2. Determination of Dissociation Products :

The products of dissociation and their state of excitation is also required to be known in order to find the dissociation energy of the molecule in its ground state into normal atoms. There are several ways for it :

(i) **Energy Differences of Dissociation Limits :** If two or more different dissociation limits of a molecule have been determined, their differences must be equal to possible energy differences of the separate atoms.

(ii) **Application of Wigner-Witmer Correlation Rules :** By applying these rules we can find out from which atomic states (of the dissociated atoms) the molecular state in question (whose dissociation limit is being considered) can actually result.

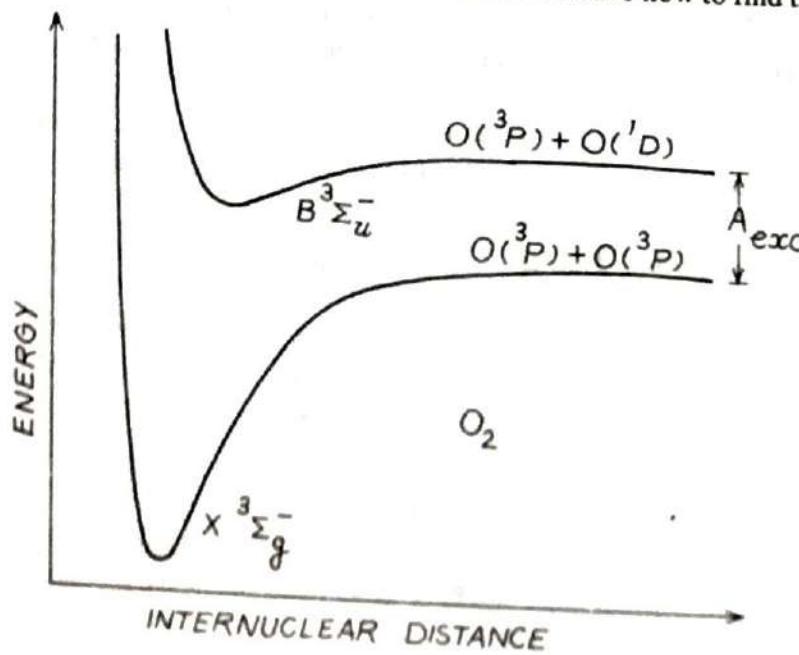
(iii) **Application of Non-crossing Rule :** Except in rare circumstances (case of BeO), according to non-crossing rule, the electronic ground state must always dissociate into *normal* atoms. Therefore, of the various possible dissociation products at a given dissociation limit, those may be excluded that would lead to a dissociation of the ground state into excited atoms. (This applies for determining the products at the ground state).

(iv) **Observation of Atomic Fluorescence :** When a molecular gas is irradiated with light of frequency higher than the dissociation limit, it shows an atomic fluorescence spectrum indicating that the molecules have actually been dissociated into atoms. The atomic lines so obtained can lead to the determination of the state of excitation of atoms.

(v) **Use of Thermo-chemical Data :** An approximate value of the dissociation energy can be obtained from thermochemical measurements. Such values always refer to dissociation into normal atoms. Thus, if an accurate spectroscopic dissociation limit is known, the dissociation products at this limit are obtained.

#### 4. Dissociation Energy of O<sub>2</sub> Molecule

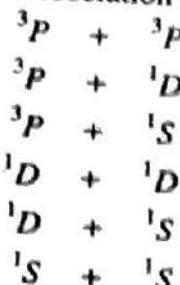
O<sub>2</sub> is one of the molecules for which spectroscopic data gives the most certain and accurate value for the dissociation energy. The strongest system of O<sub>2</sub> is the Schumann-Runge progression of absorption bands ( $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ ) which converges to a well defined limit, at which a continuum sets in. The slightly extrapolated *convergence limit* is found to be at 1759 Å, which corresponds to 7.047 eV. This is the energy required to go from the lowest vibrational level of the ground electronic state ( $X^3\Sigma_g^-$ ) to a pair of oxygen atoms at least one of which is in an excited state. We have now to find the products



(Fig. 7)

of dissociation at the convergence limit in the  $B^3\Sigma_u^-$  state, before the energy of dissociation to normal atoms can be obtained.

Now, oxygen atom has three low-lying states : the  $^3P$  ground state, and the metastable states  $^1D$  (1.967 eV higher than  $^3P$ ) and  $^1S$  (4.188 eV higher than  $^3P$ ). The following combinations are therefore possible as dissociation products :



The last three combinations can be eliminated immediately because two singlet atoms ( $S = 0$ ) cannot combine to give a triplet molecule ( $S = 1$ ).

The first combination  $^3P + ^3P$  cannot give a  $^3\Sigma_u^-$  state, according to Wigner-Witmer rules, and so it is also to be eliminated. (Two normal atoms,  $^3P + ^3P$ , can however give a  $^3\Sigma_g^-$  state, and the ground state of the molecule is infact dissociated in two normal atoms). Thus, there remains only two possibilities,  $^3P + ^1D$  and  $^3P + ^1S$  for the dissociation products, which have energies of 1.967 eV and 4.188 eV respectively, above the  $^3P + ^3P$  ground state. Thus, the dissociation energy ( $D_0^0$ ) for the ground state  $X^3\Sigma_g^-$  of  $O_2$  assuming the above two possibilities, are

$$7.047 - 1.967 = 5.080 \text{ eV} \quad (\text{for } ^3P + ^1D)$$

$$7.047 - 4.188 = 2.859 \text{ eV} \quad (\text{for } ^3P + ^1S)$$

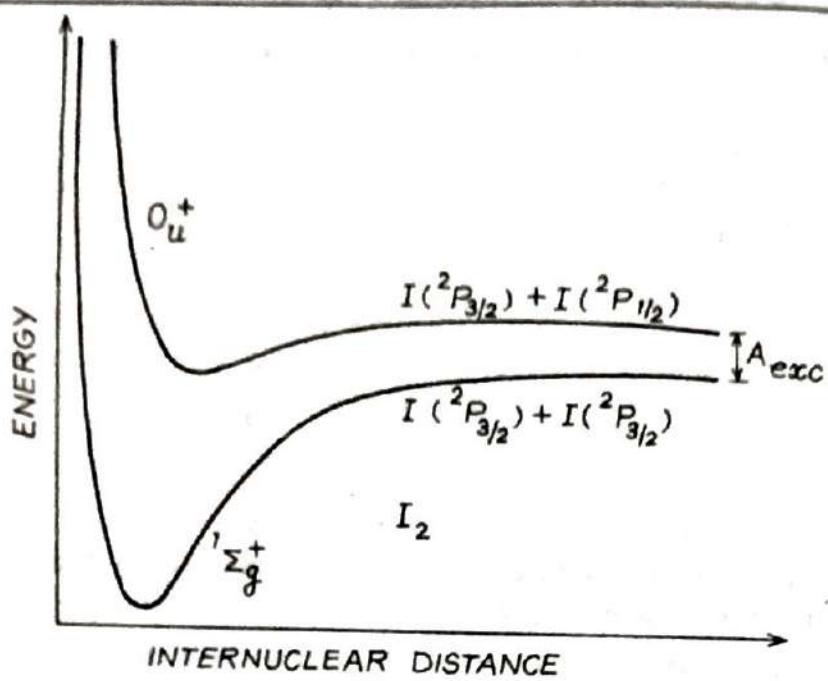
The latter value is smaller than the energy of the highest observed vibrational level in the ground state, which lies 3.4 eV above the lowest level  $v'' = 0$ . Since  $D_0^0$  must be greater than this, the combination  $^3P + ^1S$  is ruled out. Thus, we are left with the combination  $^3P + ^1D$ , giving a dissociation energy of 5.080 eV for  $O_2$ .

## 5. Dissociation Energy of $I_2$ Molecule

The dissociation energy of  $I_2$  molecule is determined from its most readily observed band-system in absorption. The spectrum shows a well-marked convergence of bands to a continuum. The extrapolated limit,  $C$ , of this convergence is found to be at 4995 Å, which corresponds to 2.484 eV.

The electronic states of  $I_2$  approach Hund's coupling case (c), and the absorption transition is from a ground state  $^1\Sigma_g^+$  to an excited state  $0_u^+$  (Fig. 8). The ground state can be derived from normal iodine atoms  $^2P_{3/2} + ^2P_{3/2}$ , while the upper state must arise from one normal and one excited atom  $^2P_{3/2} + ^2P_{1/2}$ , as derived from correlation rules. The atomic excitation energy of  $^2P_{1/2}$  is 0.942 eV as obtained from an analysis of atomic spectra. The dissociation energy to normal atoms would be given by the energy of the convergence limit less this amount, that is,

$$D_0^0 = C - A_{exc} = 2.484 \text{ eV} - 0.942 \text{ eV} = 1.542 \text{ eV.}$$



(Fig. 8)

## 6. Dissociation Energy of N<sub>2</sub> Molecule : Use of Predissociation Limits

The heat of dissociation of nitrogen molecule has been determined mainly from predissociation limits. The N<sub>2</sub> molecule has a ground state  $X^1\Sigma_g^+$ , and various excited states  $A^3\Sigma_u^+$ ,  $B^3\Pi_g$ ,  $C^3\Pi_u$ ,  $a^1\Pi_g$ , ..... In the  $C^3\Pi_u$  state, a breaking-off was observed in the vibrational levels  $v' = 2, 3$  and  $4$ ; which led to the determination of a dissociation limit at 12.139 eV above the ground state.

The nitrogen atom has three low-lying states : the  $^4S$  ground state and the metastable states  $^2D$  and  $^2P$ , lying at 2.383 eV and 3.574 eV respectively above  $^4S$ . The following combinations are thus possible as dissociation products at the limit 12.139 eV. The corresponding heats of dissociation  $D_0^0$  are written before them.

$^4S + ^4S$	12.139 eV
$^4S + ^2D$	9.756 eV
$^4S + ^2P$	8.565 eV
$^2D + ^2D$	7.373 eV
$^2D + ^2P$	6.182 eV
$^2P + ^2P$	4.991 eV

The combination  $^4S + ^4S$  is eliminated because it can give only  $\Sigma$  states, whereas the band spectrum indicates that the (unstable) state causing the predissociation is a  $\Pi$  or a  $\Delta$  state. The combinations  $^2D + ^2P$  and  $^2P + ^2P$  drop out because the corresponding  $D_0^0$  values are smaller than the sum of the observed vibrational quanta in the ground state which is 6.6 eV. Thus remains the combinations  $^4S + ^2D$ ,  $^4S + ^2P$  and  $^2D + ^2D$ .

However, another predissociation has been observed in the  $B^3\Pi_g$  state with a limit at 9.839 eV. The  $D_0^0$  values corresponding to the remaining combinations of the dissociation products at the predissociation limit 9.839 eV are as follows :

$^4S + ^2D$	7.46 eV
$^4S + ^2P$	6.27 eV
$^2D + ^2D$	5.07 eV

But, since the last observed vibrational level of the ground state lies at 6.6 eV, only the first of these (7.46 eV) can be a possible value of  $D_0^0$  ( $N_2$ ).

Therefore, using the more accurate value resulting from the predissociation at 12.139 eV, we find for the heat of dissociation of molecule, the value

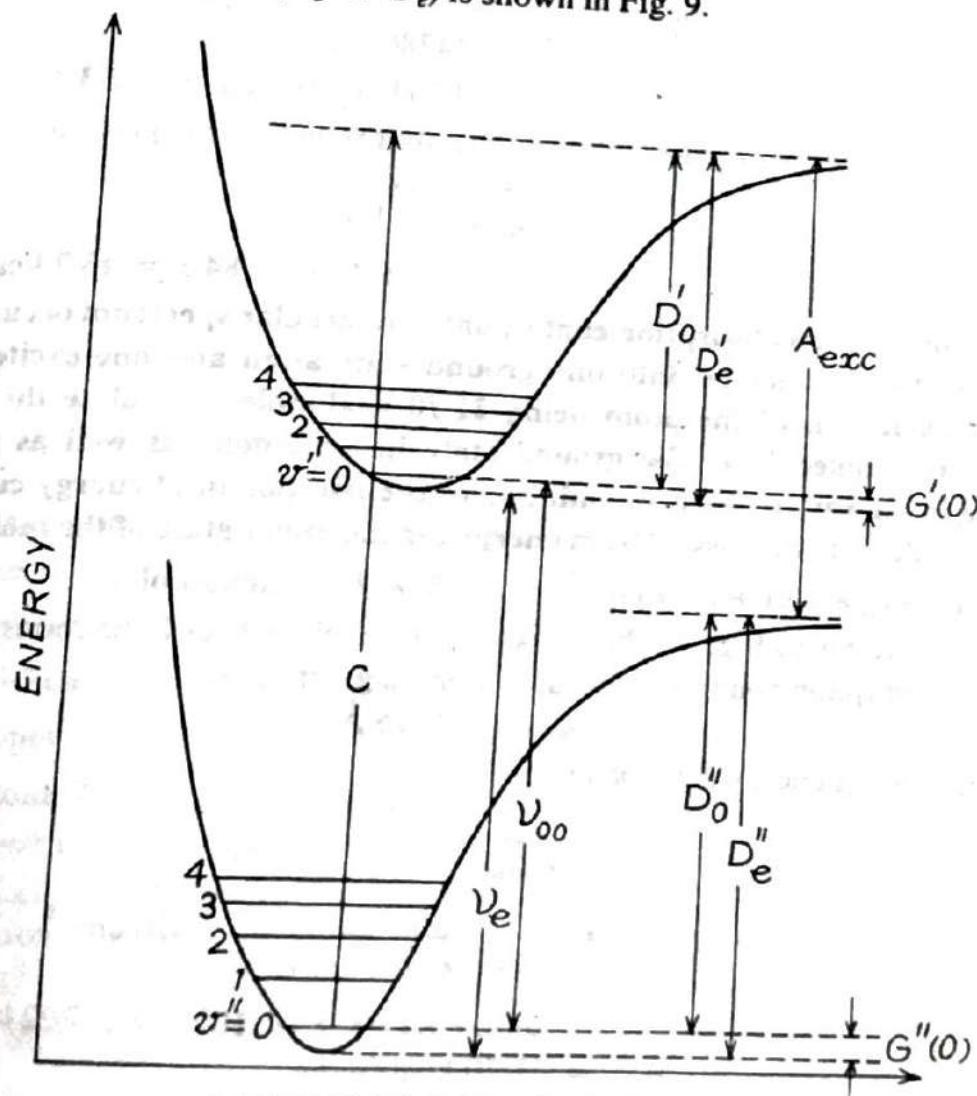
$$D_0^0 = 7.373 \text{ eV.}$$

Gaydon has, however, given an alternative explanation of the predissociation leading to a value  $D_0^0 = 9.756 \text{ eV.}$

### SOLVED PROBLEMS

1. The ground-state dissociation energy of a molecule is 78.0 kcal/mole. Its first electronically-excited state dissociates into one ground-state atom and one excited atom, the energy of excitation of the excited atom being 50.0 kcal/mole. What is the maximum wavelength of light causing dissociation? Ignore zero-point energies. If the calculate the bond dissociation energy of the excited state in kcal/mole.

**Solution.** The complete illustration of data pertinent to the determination of bond-dissociation energies ( $D_0$  or  $D_e$ ) is shown in Fig. 9.



INTERNUCLEAR DISTANCE

(Fig. 9)

In the given problem, the difference between  $D_0$  and  $D_e$  (zero-point energy) is to be ignored. Then, we have

$$\begin{aligned}D'' &= 78.0 \text{ kcal/mole}, \\A_{exc} &= 50.0 \text{ kcal/mole}, \\v_e &= 29500 \text{ cm}^{-1}.\end{aligned}$$

We know that  $1 \text{ cm}^{-1} = 2.858 \times 10^{-3} \text{ kcal/mole}$ .

$$\therefore v_e = 29500 \times (2.858 \times 10^{-3}) = 84.3 \text{ kcal/mole.}$$

Initially, the molecule may be assumed to be in the  $v'' = 0$  level of the ground electronic state. On absorption of light, it may be excited to any vibrational level of the upper electronic state including  $v' = \infty$  level (dissociation). The energy corresponding to the dissociation (onset of an absorption continuum) is, from the figure, given by

$$\begin{aligned}C &= D'' + A_{exc} \\&= 78.0 + 50.0 = 128.0 \text{ kcal/mole} \\&= \frac{128.0}{2.858 \times 10^{-3}} = 44786 \text{ cm}^{-1}.\end{aligned}$$

This is the minimum wave-number energy required for dissociation.

The corresponding (maximum) wavelength of light causing dissociation would, therefore, be

$$\begin{aligned}\lambda_{diss} &= \frac{1}{C} = \frac{1}{44786 \text{ cm}^{-1}} \\&= 2.233 \times 10^{-5} \text{ cm} = 2233 \text{ Å}.\end{aligned}$$

The bond-dissociation energy for the electronically-excited state is given by

$$\begin{aligned}D' &= C - v_e \\&= D'' + A_{exc} - v_e \\&= 78.0 + 50.0 - 84.3 = 43.7 \text{ kcal/mole.}\end{aligned}$$

**2. The onset of an absorption continuum in molecular spectrum occurs at 4995 Å. The upper state dissociates into one ground state atom and one excited atom, the energy of excitation of the atom being 21.70 kcal/mole. Calculate the dissociation energy of the molecule in the ground state in kcal/mole, as well as in eV. If the difference in energy between the minima of the two potential energy curves is 43.13 kcal/mole, calculate the dissociation energy for the upper state of the molecule. Ignore zero-point energies. Given :  $1 \text{ cm}^{-1} = 2.858 \times 10^{-3} \text{ kcal/mole}$ .**

**Solution.** Refer to Fig. 9. The (maximum) wavelength of light corresponding to the onset of an absorption continuum (dissociation) is given to be

$$\lambda_{diss} = 4995 \text{ Å}.$$

The corresponding energy absorbed is

$$\begin{aligned}C &= \frac{1}{\lambda_{diss}} \\&= \frac{1}{4995 \times 10^{-8} \text{ cm}} = 20020 \text{ cm}^{-1} \\&= 20020 \times (2.858 \times 10^{-3}) = 57.22 \text{ kcal/mole.}\end{aligned}$$

Also,

$$A_{exc} = 21.70 \text{ kcal/mole}$$

and

Then, from the figure, we have (ignoring difference between  $D_0''$  and  $D_e''$ ).

$$v_e = 43.13 \text{ kcal/mole.}$$

$$D'' = C - A_{exc}$$

$$= 57.22 - 21.70 = 35.52 \text{ kcal/mole.}$$

Now, 1 eV = 23.06 kcal/mole.

Also,

$$\therefore D'' = \frac{35.52}{23.06} = 1.540 \text{ eV.}$$

$$D' = C - v_e$$

$$= 57.22 - 43.13 = 14.09 \text{ kcal/mole}$$

$$= \frac{14.09}{23.06} = 0.611 \text{ eV.}$$

3. The schumann-Runge bands of  $O_2$  in the ultraviolet converge to a limit followed by a continuum. The convergence limit is 1750 Å and the (0, 0) band of the system corresponds to  $v_{00} = 49410 \text{ cm}^{-1}$ . Calculate the heat of dissociation of the upper state in eV.

Solution. Refer to Fig. 9. The maximum wavelength of light corresponding to the onset of absorption continuum (dissociation) is given to be

(Meerut special paper 91)

$$\lambda_{disso} = 1750 \text{ Å.}$$

The corresponding energy absorbed is

$$C = \frac{1}{\lambda_{disso}}$$

$$= \frac{1}{1750 \times 10^{-8} \text{ cm}} = 57143 \text{ cm}^{-1}.$$

Also,

$$v_{00} = 49410 \text{ cm}^{-1}.$$

$$\therefore D_0' = C - v_{00}$$

$$= 57143 \text{ cm}^{-1} - 49410 \text{ cm}^{-1} = 7733 \text{ cm}^{-1}.$$

Now 1 eV = 8066 cm<sup>-1</sup>.

$$\therefore D_0' = \frac{7733 \text{ cm}^{-1}}{8066 \text{ cm}^{-1}/\text{eV}} = 0.96 \text{ eV.}$$

4. From the analysis of an absorption spectrum of  $Cl_2$ , the following constants are determined :

$\omega_e' = 239.4 \text{ cm}^{-1}$ ,  $\omega_e' x_e' = 5.4 \text{ cm}^{-1}$ ,  $v_e = 18310 \text{ cm}^{-1}$ ,  $\omega_e'' = 564.9 \text{ cm}^{-1}$ ,  $x_e'' = 4.0 \text{ cm}^{-1}$ . The convergence limit (onset of a continuum) occurs at 20890  $\text{cm}^{-1}$ . The upper electronic state of  $Cl_2$  correlates with one ground-state atom and excited atom. The excitation energy of the latter is  $881 \text{ cm}^{-1}$ . Determine  $D_0$  and for the lower and the upper states.

Solution. Let  $G'(0)$  and  $G''(0)$  represent the zero-point energies in the upper and lower electronic states respectively. These energies, the convergence limit  $C$ , the excitation energy  $A_{exc}$ , and the dissociation energies in the upper and the lower states are presented in Fig. 9. Now, we have

$$D_0'' = C - A_{exc}$$

$$= 20890 \text{ cm}^{-1} - 881 \text{ cm}^{-1} = 20,009 \text{ cm}^{-1}.$$

$$\begin{aligned}
 D_e'' &= D_0'' + G''(0) \\
 &= D_0'' + \left( \frac{1}{2} \omega_e'' - \frac{1}{4} \omega_e'' x_e'' \right) \\
 &= 20,009 \text{ cm}^{-1} + \left( \frac{1}{2} \times 564.9 \text{ cm}^{-1} - \frac{1}{4} \times 4.0 \text{ cm}^{-1} \right) \\
 &= 20,009 \text{ cm}^{-1} + (282.45 \text{ cm}^{-1} - 1.0 \text{ cm}^{-1}) = 20,290 \text{ cm}^{-1} \\
 D_e' &= C - \{v_e - G''(0)\} \\
 &= C - \left[ v_e - \left( \frac{1}{2} \omega_e'' - \frac{1}{4} \omega_e'' x_e'' \right) \right] \\
 &= 20890 \text{ cm}^{-1} - 18310 \text{ cm}^{-1} + 281.45 \text{ cm}^{-1} = 2861 \text{ cm}^{-1} \\
 D_0' &= D_e' - G'(0) \\
 &= D_e' - \left( \frac{1}{2} \omega_e' - \frac{1}{4} \omega_e' x_e' \right) \\
 &= 2861 \text{ cm}^{-1} - \left( \frac{1}{2} \times 239.4 \text{ cm}^{-1} - \frac{1}{4} \times 5.4 \text{ cm}^{-1} \right) \\
 &= 2861 \text{ cm}^{-1} - (119.7 \text{ cm}^{-1} - 1.35 \text{ cm}^{-1}) \\
 &= 2742 \text{ cm}^{-1}.
 \end{aligned}$$

5. The bands of the visible absorption system of the  $I_2$  molecule are represented by

$$v = 15641.6 + (128.0 u' - 0.83 u'^2) - (214.6 u'' - 0.61 u''^2),$$

where  $u = v + \frac{1}{2}$ . Calculate the heat of dissociation of  $I_2$ . Given that the upper electronic state dissociates into one normal iodine atom and the other an excited atom with its excitation energy equal to  $7598 \text{ cm}^{-1}$ .

**Solution.** The given equation yields the values of the vibrational constants as under :

$$\omega_e' = 128.0 \text{ cm}^{-1}, \omega_e' x_e' = 0.83 \text{ cm}^{-1},$$

$$\omega_e'' = 214.6 \text{ cm}^{-1}, \omega_e'' x_e'' = 0.61 \text{ cm}^{-1}.$$

The band-convergence,  $C$ , corresponds to  $v' = v_{\max}$  and  $v'' = 0$ . Now

$$\begin{aligned}
 v_{\max} &= \frac{\omega_e}{2 \omega_e x_e} - 1 \\
 &= \frac{128.0 \text{ cm}^{-1}}{2 \times 0.83 \text{ cm}^{-1}} - 1 = 76.
 \end{aligned}$$

Thus, for band convergence  $C$ , we have

$$u' = v' + \frac{1}{2} = 76.5 \text{ and } u'' = v'' + \frac{1}{2} = 0.5.$$

$$\begin{aligned}
 \therefore C &= 15641.6 + (128.0 \times 76.5 - 0.83 \times 76.5^2) - (214.6 \times 0.5 - 0.61 \times 0.5^2) \\
 &= 15641.6 + (9792 - 4857) - (107.3 - 0.15) \\
 &= 15641.6 + 4935 - 107 \\
 &= 20469 \text{ cm}^{-1}.
 \end{aligned}$$

With this energy the molecule dissociates into one normal and one excited atom. The dissociation energy to normal atoms is therefore

$$\begin{aligned}
 D_0^0 &= D_0'' = C - A_{exc} \\
 &= 20469 \text{ cm}^{-1} - 7598 \text{ cm}^{-1} = 12871 \text{ cm}^{-1} \\
 &= \frac{12871 \text{ cm}^{-1}}{8066 \text{ cm}^{-1}/\text{eV}} = 1.59 \text{ eV}.
 \end{aligned}$$

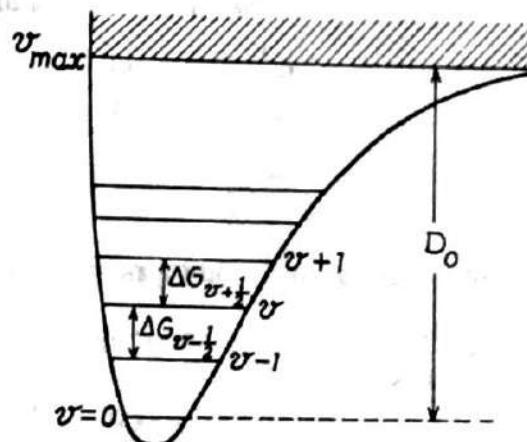
**6. Vibrational energy of a molecule in a particular electronic state can be represented by**

$$G = \omega_0 v - \omega_0 x_0 v^2.$$

Calculate the dissociation energy  $D_0$  if  $\omega_0 = 2000 \text{ cm}^{-1}$  and  $\omega_0 x_0 = 20 \text{ cm}^{-1}$ .

(Meerut sp. paper 94)

**Solution.** When the molecule receives energy just corresponding to the horizontal asymptote, the molecule dissociates into atoms. If the energy is greater, the excess appears as (unquantised) kinetic energy of the dissociated atoms. Hence, above the asymptote, a continuum joins the discrete vibrational term series. The height of the asymptote above the lowest vibrational level is equal to the work required to dissociate the molecule. This is called the dissociation energy  $D_0$ . It is seen that  $D_0$  is equal to the sum of all the vibrational quanta (Fig. 10), that is,



(Fig. 10)

$$D_0 = \sum_v \Delta G_v + \frac{1}{2}.$$

$D_0$  can be calculated when  $\Delta G$  is a linear function of  $v$ , that is, when the vibrational terms are represented by

$$G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2,$$

the cubic and higher terms being ignored. If the vibrational terms are referred to the lowest term  $G(0)$  as zero, we obtain

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2,$$

where  $\omega_0 = \omega_e - \omega_e x_e$  and  $\omega_0 x_0 = \omega_e x_e$ . The separation between successive levels  $v$  and  $v + 1$ , in terms of  $\omega_0$  and  $\omega_0 x_0$ , is

$$\begin{aligned}
 \Delta G_{v+\frac{1}{2}} &= G_0(v+1) - G_0(v) \\
 &= \{\omega_0(v+1) - \omega_0 x_0(v+1)^2\} - \{\omega_0 v - \omega_0 x_0 v^2\} \\
 &= \omega_0 - \omega_0 x_0 - 2\omega_0 x_0 v.
 \end{aligned}$$

Similarly, the separation between successive levels  $v - 1$  and  $v$  is

$$\begin{aligned}\Delta G_{v-\frac{1}{2}} &= G_0(v) - G_0(v-1) \\ &= \{\omega_0 v - \omega_0 x_0 v^2\} - \{\omega_0(v-1) - \omega_0 x_0(v-1)^2\} \\ &= \omega_0 + \omega_0 x_0 - 2\omega_0 x_0 v.\end{aligned}$$

The mean vibrational quanta in the state  $v$  is therefore

$$\begin{aligned}\Delta G_v &= \frac{1}{2} \left[ \Delta G_{v+\frac{1}{2}} + \Delta G_{v-\frac{1}{2}} \right] \\ &= \omega_0 - 2\omega_0 x_0 v.\end{aligned}$$

The dissociation corresponds to that value of  $v$  for which the mean vibrational quanta just becomes zero. Let it be  $v_{\max}$ . Thus

$$0 = \omega_0 - 2\omega_0 x_0 v_{\max}.$$

$$\therefore v_{\max} = \frac{\omega_0}{2\omega_0 x_0}.$$

The dissociation energy is just the term value corresponding to  $v_{\max}$ . Thus

$$\begin{aligned}D_0 &= G_0(v_{\max}) = \omega_0 v_{\max} - \omega_0 x_0 v_{\max}^2 \\ &= \omega_0 \frac{\omega_0}{2\omega_0 x_0} - \omega_0 x_0 \frac{\omega_0^2}{4\omega_0^2 x_0^2} \\ &= \frac{\omega_0^2}{2\omega_0 x_0} - \frac{\omega_0^2}{4\omega_0 x_0} \\ &= \frac{\omega_0^2}{4\omega_0 x_0}.\end{aligned}$$

Substituting the given values  $\omega_0 = 2000 \text{ cm}^{-1}$  and  $\omega_0 x_0 = 20 \text{ cm}^{-1}$ , we get

$$\begin{aligned}D_0 &= \frac{(2000 \text{ cm}^{-1})^2}{4 \times 20 \text{ cm}^{-1}} = 50000 \text{ cm}^{-1} \\ &= \frac{50000 \text{ cm}^{-1}}{8066 \text{ cm}^{-1}/\text{eV}} = 6.2 \text{ eV}.\end{aligned}$$

7. The value of  $\omega_e$  and  $\omega_e x_e$  are  $691.75$  and  $4.720 \text{ cm}^{-1}$  respectively for the molecule  $\text{NBr}^{79}$ . From the Birge-Sponer method, estimate the dissociation energy and also the highest value of  $v$  before dissociation occurs.

(Meerut sp. paper 92, 89)

**Solution.** The dissociation energy in a given electronic state is the sum of all the vibrational quanta :

$$D_0 = \sum_{v=0}^{v_{\max}} \Delta G_v + \frac{1}{2}.$$

Now,  $\Delta G_{v+\frac{1}{2}} = G(v+1) - G(v)$

$$\begin{aligned}&= \left\{ \omega_e \left( v + \frac{3}{2} \right) - \omega_e x_e \left( v + \frac{3}{2} \right)^2 \right\} - \left\{ \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \right\} \\ &= \omega_e - 2\omega_e x_e (v+1).\end{aligned}$$

$$\therefore D_0 = \sum_{v=0}^{v_{\max}} \Delta G_{v+\frac{1}{2}}$$

$$= (\omega_e - 2\omega_e x_e) + (\omega_e - 4\omega_e x_e) + (\omega_e - 6\omega_e x_e) + \dots 0.$$

$$= \frac{\omega_e^2}{4\omega_e x_e} - \frac{1}{2}\omega_e.$$

Substituting the given values :

$$D_0 = \frac{(691.75 \text{ cm}^{-1})^2}{4 \times 4.720 \text{ cm}^{-1}} - \frac{1}{2} \times 691.75 \text{ cm}^{-1}$$

$$= 24345.1 \text{ cm}^{-1} - 345.875 \text{ cm}^{-1}$$

$$= 24999 \text{ cm}^{-1}.$$

$$1 \text{ cm}^{-1} = 2.858 \times 10^{-3} \text{ kcal/mole.}$$

$$\therefore D_0 = 24999 \times (2.858 \times 10^{-3}) = 71.5 \text{ kcal/mole.}$$

The highest value of  $v$  before dissociation occurs is finite and corresponds to  $\Delta G_g + \frac{1}{2} = 0$ , that is,

$$\omega_e - 2\omega_e x_e (v_{\max} + 1) = 0.$$

$$\therefore v_{\max} = \frac{\omega_e}{2\omega_e x_e} - 1$$

$$= \frac{691.75 \text{ cm}^{-1}}{2 \times 4.720 \text{ cm}^{-1}} - 1$$

$$= 73 - 1$$

$$= 72.$$

## QUESTIONS

- Write a short note on continuous and diffuse molecular spectra.
- Explain with brief arguments : Electronic states with repulsive potential curves are of great importance in molecular spectra.
- What is predissociation ? Explain it in terms of potential diagram.
- What is predissociation ? Discuss its use in the evaluation of dissociation energy of a diatomic molecule. (Meerut sp. paper 90)
- "Generally predissociation is regarded to be established either by the absorption bands becoming diffuse or by the emission bands breaking off at a certain point in a series." Elucidate this statement giving suitable examples. (Meerut sp. paper 2002)
- Discuss the appearance of the electronic emission spectrum resulting from a transition between a stable upper electronic state of a diatomic molecule and a lower state which is stable but predissociated at a large internuclear distance.
- Give a critical account of the different methods for the determination of dissociation energies of diatomic molecules.
- Discuss (i) band convergence method and (ii) atomic fluorescence method of evaluation of dissociation energy of a diatomic molecule.
- Describe the Birge-Sponer method of determining the dissociation energy of a diatomic molecule. (Meerut sp. paper 96, 94, 89)
- What do you understand by the dissociation energy of a diatomic molecule ? Describe an experimental method for determining the dissociation energy of a diatomic molecule. Illustrate your answer with the example of  $N_2$  molecule. (Meerut sp. paper 88)

11. Describe how the dissociation energy of  $O_2$  molecule has been determined.  
 12. Describe how the dissociation energy of  $I_2$  is determined from its absorption spectrum. Discuss the limitations of Birge-Sponer method of extrapolation.  
 (Meerut sp. paper 95)
13. What is heat of dissociation of a diatomic molecule ? Show that the vibrational quantum number corresponding to dissociation energy is given by

$$v_D = \frac{\omega_0}{2 \omega_0 x_0}.$$

where symbols have their usual meanings.

(Meerut sp. paper 97)

### PROBLEMS

1. The absorption bands of the  $I_2$  molecule show a convergence at  $20,037\text{ cm}^{-1}$ . Assuming that the upper state of the molecule is due to one normal atom in the  $^2P_{3/2}$  state and another atom in the excited state  $^3P_{1/2}$ , calculate the heat of dissociation of the molecule. The  $^3P_{1/2}$  state of the I atom is  $7598\text{ cm}^{-1}$  above the ground state  $^2P_{3/2}$ . Given :  $1\text{ eV} = 8066\text{ cm}^{-1}$ . Ans.  $1.542\text{ eV}$ .
2. A banded structure is observed in the absorption spectrum of  $O_2$  which changes to a continuum at a wavelength corresponding to  $7.047\text{ eV}$ . The upper state of the molecule  $O_2$  dissociates into one ground state and one excited state ( $^1D$ ) atom, the excitation energy being  $1.967\text{ eV}$ . Determine  $D_0''$  for  $O_2$  in kcal/mole.  
 (1 eV =  $23.063\text{ kcal/mole}$ ).  
 (Meerut sp. paper 93)  
 Ans.  $117.16\text{ kcal/mole}$ .
3. The zero-point energy of the ground state of  $O_2$  is  $793\text{ cm}^{-1}$  and the difference between the potential minima of the two electronic states referred in the last problem is  $49800\text{ cm}^{-1}$ . Determine  $D_e''$  and  $D_e'$  for  $O_2$  in  $\text{cm}^{-1}$ .  
 (1 eV =  $8066\text{ cm}^{-1}$ ).  
 Ans.  $41768\text{ cm}^{-1}, 7834\text{ cm}^{-1}$ .

# Temporal and Spatial Coherences

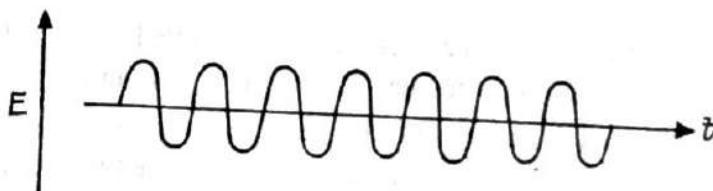
## 1. Coherence

A wave which appears to be a pure sine wave for an infinitely long period of time, or in an infinitely extended space, is said to be a perfectly coherent wave. In such a wave there is a definite relationship between the phase of the wave at a given time and at a certain time later, or at a given point and at a certain distance away. No actual light source, however, emits a perfectly coherent wave. Light waves which are pure sine waves only for a limited period of time or in a limited space are partially coherent waves.

There are two different criteria of coherence; the criteria of time and the criteria of space. This gives rise to temporal coherence and spatial coherence.

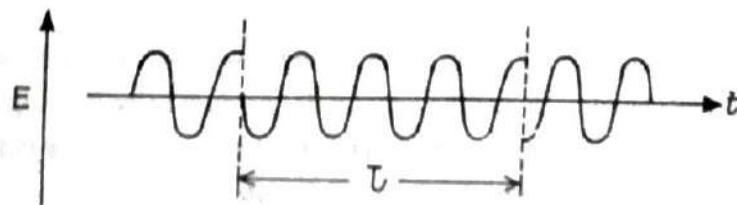
## 2. Temporal Coherence

The oscillating electric field  $E$  of a perfectly coherent light wave would have a constant amplitude of vibration at any point, while its phase would vary linearly with time. As a function of time the field would appear as shown in Fig. 1. It is an ideal sinusoidal function of time.



(Fig. 1)

However, no light emitted by an actual source produces an ideal sinusoidal field for all values of time. This is because when an excited atom returns to the initial state, it emits light "pulse" of short duration such as of the order of  $10^{-10}$  second for sodium atom. Thus, the field remains sinusoidal for time-intervals of the order of  $10^{-10}$  second, after which the phase changes abruptly. Hence the field due to an actual light source will be as shown in Fig. 2.



(Fig. 2)

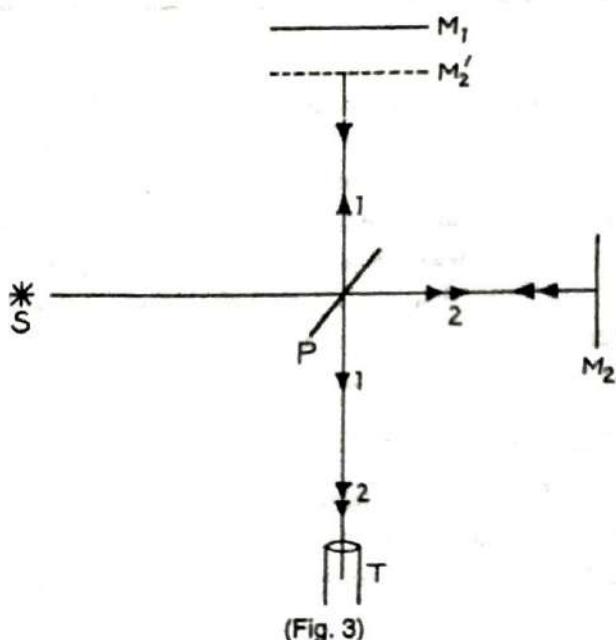
**Coherence Time and Coherence Length :** The average time-interval for which the field remains sinusoidal (that is, definite phase relationship exists) is known as "coherence

time" of the light beam, and is denoted by  $\tau$ . The distance  $L$  for which the field is sinusoidal is given by.

$$L = \tau c,$$

where  $c$  is the speed of light.  $L$  is called the "coherence length" of the light beam.

The coherence time (or the coherence length) can be measured by means of Michelson's interferometer (Fig. 3). A light beam from the source  $S$  falls on a semi-silvered



(Fig. 3)

plate  $P$  at which it is partly reflected and partly transmitted. The reflected and the transmitted beams, 1 and 2, are reflected back from mirrors  $M_1$  and  $M_2$  respectively and enter the telescope  $T$  in which interference fringes are observed. We know that two beams can produce a stationary interference pattern only if there is a definite phase relationship between them.

Let  $M'_2$  be the image of  $M_2$  formed by the plate  $P$ . The arrangement is then equivalent to an air-film enclosed between two reflecting surfaces  $M_1$  and  $M'_2$ . If  $d$  be the separation between  $M_1$  and  $M'_2$ , then  $2d$  will be the path difference between the interfering beams. Now, if

$$2d \ll L,$$

then there will be a definite phase relationship between the two beams and interference fringes will be observed. If, on the other hand,

$$2d \gg L,$$

there will be no definite phase relationship and the fringes will not be observed. Therefore, starting with equal path-lengths, as the distance  $d$  is increased (by moving one mirror), the fringes become gradually poorer in contrast and finally disappear. ***The path difference at disappearance gives an estimation of coherence length.***

As an example, for the neon 6328-Å line, the interference fringes disappear when the path difference between the light beams is about 3 cm, so that the coherence time is

$$\tau \approx \frac{L}{c} \approx \frac{3 \text{ cm}}{3 \times 10^{10} \text{ cm/s}} \approx 10^{-10} \text{ s}.$$

On the other hand, for the red cadmium line,  $\lambda = 6438 \text{ Å}$ , coherence length is about 30 cm which gives  $\tau = 10^{-9} \text{ s}$ .

The coherence time for a laser beam is much larger than that for an ordinary source of light. For a well-controlled laser, the coherence time is as large as 2 ms, giving a coherence length of 600 km\*. Such large coherence lengths imply that, using laser beams, high-contrast interference fringes can be obtained for very large path differences.

### 3. Temporal Coherence as related with Monochromaticity of Spectral Line

Every spectral line has a finite width which means that it corresponds to a continuous distribution of wavelengths in some narrow interval between  $\lambda$  and  $\lambda + \Delta\lambda$ . This is obvious from the fact that for every spectral line the interference pattern in the Michelson interferometer experiment eventually disappears when the path difference between the interfering beams is gradually increased. We also know that the pattern disappears when the path difference exceeds the coherence length. Thus, the concept of temporal coherence is directly related to the width (or spectral purity or monochromaticity) of the spectral line.

**Frequency Spread (or Width) of a Spectral Line :** Let us adopt the criterion that when the path difference between the interfering beams becomes equal to the coherence length  $L$ , the rings due to two closely-spaced wavelengths  $\lambda_1$  and  $\lambda_2$  are completely out of step at the centre (that is, a bright ring of  $\lambda_1$  coincides with a dark ring of  $\lambda_2$ ). Then, we can write

$$L = n \lambda_1 = (n + \frac{1}{2}) \lambda_2.$$

Eliminating  $n$ , we get

$$L = \left( \frac{L}{\lambda_1} + \frac{1}{2} \right) \lambda_2$$

$$\frac{L}{\lambda_2} - \frac{L}{\lambda_1} = \frac{1}{2}$$

$$L \frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} = \frac{1}{2}$$

$$L = \frac{\lambda_1 \lambda_2}{2(\lambda_1 - \lambda_2)} = \frac{\lambda^2}{2(\lambda_1 - \lambda_2)}$$

If instead of two discrete wavelengths  $\lambda_1$  and  $\lambda_2$ , the beam consists of all wavelengths lying between  $\lambda$  and  $\lambda + \Delta\lambda$ , then the interference pattern produced by wavelengths  $\lambda$  and  $\lambda + \frac{1}{2} \Delta\lambda$  would disappear, if

$$L = \frac{\lambda^2}{2\left(\frac{1}{2} \Delta\lambda\right)} = \frac{\lambda^2}{\Delta\lambda}$$

Now, for each wavelength lying between  $\lambda$  and  $\lambda + \frac{1}{2} \Delta\lambda$ , there is a corresponding

wavelength (lying between  $\lambda + \frac{1}{2} \Delta\lambda$  and  $\lambda + \Delta\lambda$ ) such that the minima of one fall on the maxima of the other, causing the fringes to disappear. In other words, the fringes will

\*  $L = \tau c = (2 \times 10^{-9} \text{ s}) \times (3 \times 10^8 \text{ m s}^{-1}) = 6 \times 10^5 \text{ m} = 600 \text{ km}$ .

have a very poor contrast for

$$L \geq \frac{\lambda^2}{\Delta\lambda}$$

or

$$\Delta\lambda \geq \frac{\lambda^2}{L}.$$

Thus, if the fringes become indistinct when the path difference exceeds  $L$ , we can conclude that the spectral line (of mean wave-length  $\lambda$ ) has a wavelength-spread (width) given by

$$\Delta\lambda = \frac{\lambda^2}{L}.$$

For the cadmium red line ( $\lambda = 6438 \text{ \AA}$ )  $L$  is as large as about 30 cm. This corresponds to a wavelength-spread given by

$$\Delta\lambda = \frac{\lambda^2}{L} \approx \frac{(6438 \text{ \AA})^2}{30 \times 10^8 \text{ \AA}} \approx 0.01 \text{ \AA}.$$

For the sodium yellow line ( $\lambda = 5893 \text{ \AA}$ ),  $L$  is about 3 cm, and

$$\Delta\lambda = \frac{(5893 \text{ \AA})^2}{3 \times 10^8 \text{ \AA}} \approx 0.1 \text{ \AA}.$$

Further, since  $v = \frac{c}{\lambda}$ , the frequency-spread  $\Delta v$  of a line would be

$$\Delta v = \frac{c}{\lambda^2} \Delta\lambda \approx \frac{c}{L}.$$

We know that  $\tau = \frac{L}{c}$ , where  $\tau$  is coherence time.

$$\therefore \Delta v \approx \frac{1}{\tau}.$$

Thus, the frequency-spread of a spectral line is of the order of the inverse of the coherence time, that is, ***longer the coherence time, the smaller is the frequency-spread.*** (A perfectly sharp monochromatic line,  $\Delta v = 0$ , would correspond to an infinite interval of coherence time,  $\tau = \infty$ ).

For an ordinary source,  $\tau \approx 10^{-10} \text{ s}$ , and so the frequency spread is

$$\Delta v \approx 10^{10} \text{ Hz.}$$

For sodium yellow line ( $\lambda = 5893 \text{ \AA}$ ), we have

$$v = \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm s}^{-1}}{5893 \times 10^{-8} \text{ cm}} = 5 \times 10^{14} \text{ Hz}$$

and thus

$$\frac{\Delta v}{v} \approx \frac{10^{10} \text{ Hz}}{5 \times 10^{14} \text{ Hz}} \approx 2 \times 10^{-5}.$$

The quantity  $\Delta v/v$  represents the monochromaticity (spectral purity) of the source. Clearly, even for an ordinary light source, the monochromaticity is quite small. For a laser beam,  $\Delta v/v = 4 \times 10^{-8}$ .

## 4. Spatial Coherence

The spatial coherence is the phase relationship between the radiation fields at different points in space. Let us consider light waves emitting from a source  $S$  (Fig. 4). Let  $A$  and  $B$  be two points lying on a line joining them with  $S$ . The phase relationship between the points  $A$  and  $B$  depends on the distance  $AB$  and on the temporal coherence of the beam. If

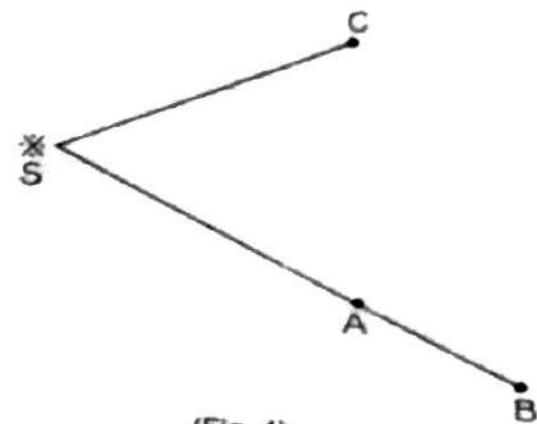
$AB \ll L$  (coherence length), there will be a definite phase relationship between the points  $A$  and  $B$ , that is, there will be high coherence between the points  $A$  and  $B$ . On the other hand, if

$$AB > > L,$$

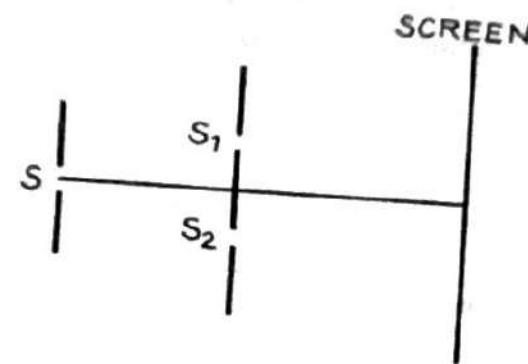
there will be no coherence between the points  $A$  and  $B$ .

Let us now consider points  $A$  and  $C$  which are *equidistant* from  $S$ . If the source  $S$  is a true *point* source, then the waves shall reach the points  $A$  and  $C$  in exactly the same phase, that is, the two points will have perfect (spatial) coherence. If, however, the source  $S$  is extended, the points  $A$  and  $C$  will no longer remain in coherence.

This may be demonstrated by Young's double-slit experiment illustrated in Fig. 5. Light emitting from a narrow slit  $S$  falls on two slits  $S_1$  and  $S_2$  placed symmetrically with respect to  $S$ . The beams emerging from  $S_1$  and  $S_2$ , having been derived from the same original beam, maintains a *constant* phase difference at all points on the screen. Hence a stationary interference pattern is observed on the screen.



(Fig. 4)

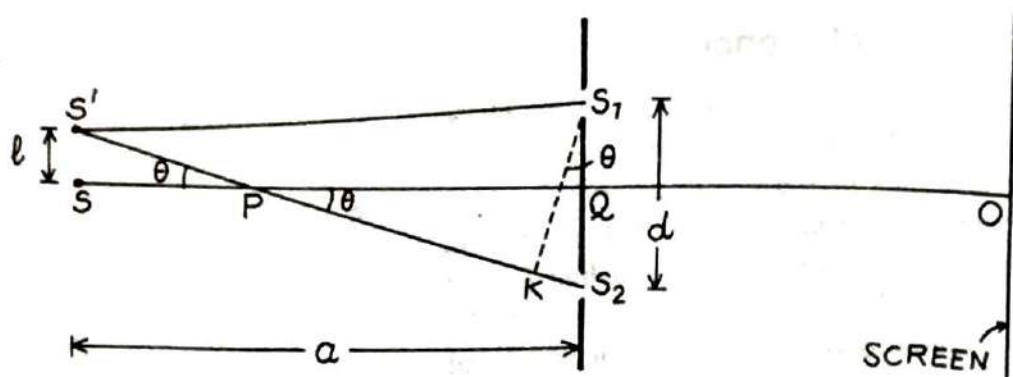


(Fig. 5)

If, however, the width of the slit  $S$  is gradually increased, the pattern becomes poorer and poorer in contrast and finally disappears. This means that as the size of the source is increased, the situation of spatial coherence on the screen changes into a situation of incoherence. This happens because when the slit  $S$  is wide, the slits  $S_1$  and  $S_2$  receive waves from different independent parts of  $S$  and hence do not remain coherent with respect to each other.

## 5. Spatial Coherence as related to the size of the Source

We may derive a relationship between the spatial coherence and the size of source. An extended source is made up of a large number of point-sources. Let us first consider the case when the Young's double-slit is illuminated by two independent point-sources  $S$  and  $S'$  at a distance  $l$  apart (Fig. 6). We shall find that minimum value of  $l$  at which pattern on the screen would disappear. The waves from  $S$  which reach the point  $O$  on the screen via Young's slits  $S_1$  and  $S_2$  have zero path difference. Hence there is a bright fringe



(Fig. 6)

at  $O$  due to  $S$ . Now, the waves from  $S'$  reaching the point  $O$  via  $S_1$  and  $S_2$  have a path difference  $S'S_2 - S'S_1 = KS_2$ . Clearly, we shall obtain a dark fringe at  $O$  due to  $S'$  when

$$KS_2 = \frac{\lambda}{2}, \quad \dots(i)$$

where  $\lambda$  is the wavelength of light. When this is the case, the maxima of the interference pattern due to  $S$  will fall on the minima due to  $S'$  so that the fringes would disappear. Now, from the figure,

$$KS_2 \approx \theta d,$$

where  $d$  is the separation between  $S_1$  and  $S_2$ . Let  $a$  be the distance between  $S$  and  $Q$ . Now, again from the figure

$$\theta \approx \frac{QS_2}{PQ} = \frac{SS'}{SP}.$$

$$\therefore a = SP + PQ \approx \frac{SS'}{\theta} + \frac{QS_2}{\theta} = \frac{l}{\theta} + \frac{d/2}{\theta}$$

$$\text{or } \theta \approx \frac{l + (d/2)}{a}.$$

$$\therefore KS_2 \approx \theta d = \frac{(l + d/2) d}{a}.$$

Assuming that  $l > > \frac{d}{2}$ ; we can write\*

$$KS_2 \approx \frac{ld}{a}.$$

Thus, in view of eq. (i), the interference pattern would disappear if

$$\frac{ld}{a} \approx \frac{\lambda}{2}$$

$$\text{or } l \approx \frac{\lambda a}{2d}. \quad \dots(ii)$$

From this it is clear that if we illuminate the double-slit with an extended source whose linear dimension exceeds  $\lambda a/2 d$ , then no interference pattern will appear on the screen.

Now, if we have an extended incoherent source having linear dimension roughly  $\lambda a/d$  then for every point on the source, there is a point at a distance  $\lambda a/2 d$  which

\* In fact the distance  $d$  is very small compared to  $l$ , but this fact has been ignored in Fig. 6 for the sake of clarity.

produces fringes shifted by half a fringe-width. Hence the interference pattern will not be observed. Thus, for an extended (incoherent) source made up of independent point-sources, interference fringes of good contrast will be observed only when

$$l \ll \frac{\lambda a}{d}.$$

or, when

$$d \ll \frac{\lambda a}{l}.$$

If the extended source  $SS'$  subtends an angle  $\alpha$  at the slits, that is, at point  $Q$ , then

$$\alpha \approx l/a,$$

and the above condition for obtaining fringes of good contrast takes the form

$$d \ll \frac{\lambda}{\alpha}.$$

The distance  $l_w$  given by

$$l_w = \frac{\lambda}{\alpha}$$

is termed as "lateral spatial coherence width". It is the distance over which the beam is spatially coherent. We conclude that to obtain a good interference pattern with Young's double-slit, the separation between the slits ( $S_1$  and  $S_2$ ) should be kept much less than the coherence width.

Using ordinary extended light sources, we must pass the light through a pinhole in order to obtain a spatially coherent beam of light. However, a laser beam is itself highly spatially coherent.

## SOLVED PROBLEMS

**1. The orange krypton line ( $\lambda = 6058 \text{ \AA}$ ) has a coherence length of  $\sim 20 \text{ cm}$ . Calculate the line width in terms of wavelength.**

**Solution.** The wavelength spread of a spectral line of wavelength  $\lambda$  is given by

$$\Delta\lambda \approx \lambda^2/L,$$

where  $L$  is coherence length. Thus

$$\Delta\lambda \approx \frac{(6058 \text{ \AA})^2}{20 \times 10^8 \text{ \AA}} \approx 0.018 \text{ \AA}.$$

**2. Laser linewidths as low as  $20 \text{ Hz}$  occur. Calculate the coherence length. Given :  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ .**

**Solution.** As above,

$$\Delta\lambda \approx \lambda^2/L.$$

Now,  $v = c/\lambda$  and so the frequency spread of a line is

$$\Delta v = \frac{c}{\lambda^2} \Delta\lambda \approx \frac{c}{L}$$

or

$$L \approx \frac{c}{\Delta v} \approx \frac{3.0 \times 10^8 \text{ m s}^{-1}}{20 \text{ s}^{-1}} = 1.5 \times 10^7 \text{ m} = 15000 \text{ km}.$$

**3. The coherence time for the red cadmium line ( $\lambda = 6438 \text{ \AA}$ ) is about  $10^{-9} \text{ s}$ . Estimate the monochromaticity of the line.**

**Solution.** The frequency spread of a spectral line is related to coherence time as

$$\Delta v = 1/\tau.$$

Here  $\tau = 10^{-9}$  s.

$$\therefore \Delta v = 10^9 \text{ s}^{-1}.$$

The frequency of the red cadmium line is

$$v = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{6438 \times 10^{-10} \text{ m}} = 4.66 \times 10^{14} \text{ s}^{-1}.$$

$\therefore$  monochromaticity of the line is

$$\frac{\Delta v}{v} \approx \frac{10^9 \text{ s}^{-1}}{4.66 \times 10^{14} \text{ s}^{-1}} \approx 2 \times 10^{-6}.$$

**4. The sun subtends an angle of about  $32'$  on earth. Suppose sunlight is falling normally on Young's double-slit arrangement having a filter which allows only light of wavelength  $5000 \text{ \AA}$  through it. What should be the separation between the two slits in order to obtain good- contrast fringes on the screen ?**

**Solution.** The angle subtended by the extended source (sun) at the double-slit is

$$\alpha = 32' = \left( \frac{32}{60} \right)^{\circ} = \frac{\pi}{180^{\circ}} \times \left( \frac{32}{60} \right) \text{ rad} = 0.009 \text{ rad} \approx 0.01 \text{ rad.}$$

Thus, the lateral spatial coherence width is

$$l_w = \frac{\lambda}{\alpha} \approx \frac{5000 \times 10^{-8} \text{ cm}}{0.01} \approx 0.005 \text{ cm.}$$

Thus, if the separation between the two slits is small compared to  $0.005 \text{ cm}$ , interference fringes of good contrast are obtained on the screen.

## QUESTIONS

1. Explain the concept of coherence. Discuss temporal coherence and spatial coherence, illustrating them with the help of suitable experiments.
  2. Distinguish between spatial and temporal coherences in laser emission.
- (Meerut sp. paper 2001, 99)*
3. Explain how the purity of a spectral line is related with the concept of temporal coherence. Show that the frequency-spread of a spectral line is of the order of the inverse of the coherence time.
  4. Discuss spatial coherence as related to the size of the source. Obtain expression for the lateral spatial coherence width and give its significance.
-

# LASER : Einstein's Coefficients and Light Amplification

## 1. LASER : An Introduction

The word 'LASER' is an acronym for Light Amplification by Stimulated Emission of Radiation. It is a source which emits an intense, almost perfectly monochromatic, directional, and highly coherent beam of light. Its working depends on the phenomenon of "stimulated emission", first predicted by Einstein in 1916.

Einstein considered the equilibrium between matter and electromagnetic radiation in a black-body chamber at a constant temperature in which exchange of energy takes place due to absorption and spontaneous emission of radiation by the atoms. He found that the usual absorption and emission processes alone are not sufficient to explain the equilibrium. He then predicted that there must be a third process also, now called "stimulated emission". This prediction was paid little attention until 1954, when Townes and Gordon developed a microwave amplifier (MASER) using ammonia,  $\text{NH}_3$ . In 1958, Schawlow and Townes showed that the maser principle could be extended into the visible region and in 1960, Maiman built the first laser using ruby as the active medium. Soon after, Javan constructed the first gas laser, namely, the He-Ne laser. Since then, laser action has been obtained in a large variety of materials including liquids, ionised gases, plastics, dyes, semiconductors etc. at wavelengths from ultraviolet to radio-frequency regions, with power ranging from a few milliwatts to megawatts. Some lasers emit only in pulses, while others emit a continuous wave.

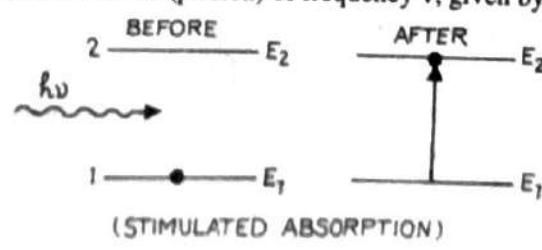
## 2. Interaction of Radiation with Matter

An atomic system is characterised by discrete energy states, and usually the atoms occupy the lowest energy state, known as the ground state. An atom in a lower energy state may be excited to a higher energy state through a number of processes, one process being absorption of electromagnetic radiation of proper frequency. On the other hand, an atom in an excited state can transit to a lower energy state through the emission of electromagnetic radiation. The emission may be spontaneous or stimulated, as predicted by Einstein. Let us consider these processes separately.

**(Stimulated) Absorption of Radiation :** An atom, initially in a lower state 1, rises to a higher state 2 by absorbing a quantum of radiation (photon) of frequency  $\nu$ , given by

$$\nu = \frac{E_2 - E_1}{h},$$

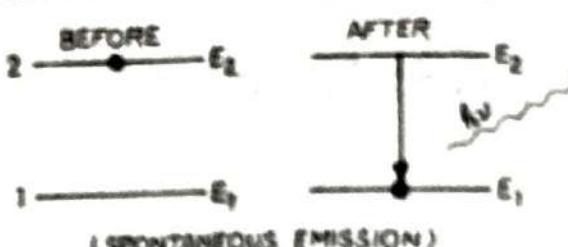
where  $E_1$  and  $E_2$  are the energies of the atom in the states 1 and 2 respectively (Fig. 1). This is stimulated (or induced) absorption of radiation, the absorbed photon



(Fig. 1)

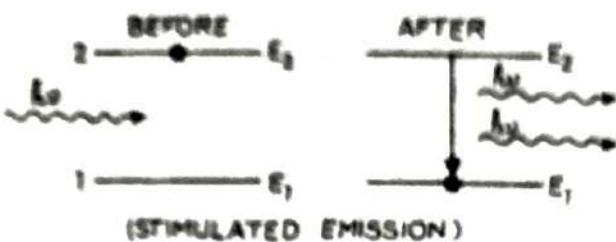
being the stimulating photon. (The absorption is necessarily stimulated).

**Spontaneous Emission of Radiation :** Let us now consider an atom initially in the higher (excited) energy state 2 (Fig. 2). Observations show that its life-time in higher state is usually very small ( $\sim 10^{-8}$  second) and it, of its own accord, decays to the lower energy state 1, emitting a photon of frequency  $v = (E_2 - E_1)/\hbar$ . This is 'spontaneous' emission of radiation. If there is an assembly of atoms, then the radiation emitted spontaneously by each atom has a random direction and a random phase, and is therefore incoherent from one atom to another.



(Fig. 2)

**Stimulated Emission of Radiation :** According to Einstein, an atom in an excited energy state, under the influence of the electromagnetic field of a photon of frequency  $v$  incident upon it, decays to a lower energy state, emitting an additional photon of same frequency  $v$  (Fig. 3). Thus, two photons of same frequency, one incident and the other emitted, move on. This is 'stimulated' (or induced) emission of radiation. The direction of propagation, energy, phase and state of polarisation of the emitted photon is exactly the same as that of the incident stimulating photon. In other words, the stimulated radiation is completely coherent with the stimulating radiation. As a result of this process, radiation passing through an assembly of atoms is amplified.



(Fig. 3)

### 3. Einstein Coefficients

Let us consider an assembly of atoms (sample of matter) which is in thermal equilibrium with radiation of frequency  $v$  and spectral energy density  $u(v)^*$  at temperature  $T$ . Let  $N_1$  and  $N_2$  be the number of atoms per unit volume in energy states 1 and 2 with energies  $E_1$  and  $E_2$  respectively at any instant. An atom in the lower energy state  $E_1$  can absorb radiation and get excited to the state  $E_2$ . The probability rate of occurrence of the absorption transition  $1 \rightarrow 2$  would be proportional to  $N_1$  and also to  $u(v)$ . Thus, the number of absorption transitions per unit time per unit volume can be written as

$$N_1 B_{12} u(v).$$

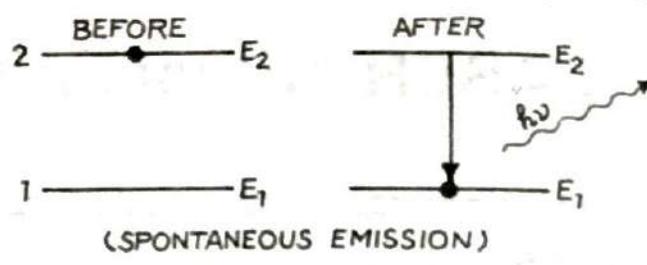
The proportionality constant  $B_{12}$  is a characteristic of energy states 1 and 2, and is known as 'Einstein's 'B' coefficient of absorption of radiation'.

Let us now consider the emission transitions at frequency  $v$  (both spontaneous and stimulated) when an atom de-excites from energy state  $E_2$  to  $E_1$ .

\* The energy density  $u(v)$  is defined such that  $u(v) dv$  is radiation energy per unit volume within the frequency interval  $v$  and  $v + dv$ .

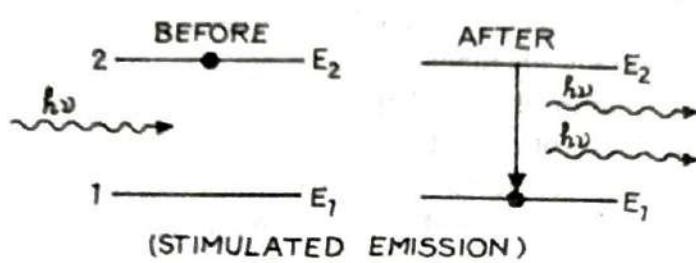
being the stimulating photon. (The absorption is necessarily stimulated).

**Spontaneous Emission of Radiation :** Let us now consider an atom initially in the higher (excited) energy state 2 (Fig. 2). Observations show that its life-time in higher state is usually very small ( $\approx 10^{-8}$  second) and it, of *its own accord*, decays to the lower energy state 1, emitting a photon of frequency  $\nu = (E_2 - E_1)/\hbar$ . This is 'spontaneous' emission of radiation. If there is an assembly of atoms, then the radiation emitted spontaneously by each atom has a random direction and a random phase, and is therefore incoherent from one atom to another.



(Fig. 2)

**Stimulated Emission of Radiation :** According to Einstein, an atom in an excited energy state, *under the influence of the electromagnetic field of a photon of frequency  $\nu$  incident upon it*, decays to a lower energy state, emitting an additional photon of same frequency  $\nu$  (Fig. 3). Thus, two photons of same frequency, one incident and the other emitted, move on. This is 'stimulated' (or induced) emission of radiation. *The direction of propagation, energy, phase and state of polarisation of the emitted photon is exactly the same as that of the incident stimulating photon.* In other words, the stimulated radiation is completely coherent with the stimulating radiation. *As a result of this process, radiation passing through an assembly of atoms is amplified.*



(Fig. 3)

### 3. Einstein Coefficients

Let us consider an assembly of atoms (sample of matter) which is in thermal equilibrium with radiation of frequency  $\nu$  and spectral energy density  $u(\nu)^*$  at temperature  $T$ . Let  $N_1$  and  $N_2$  be the number of atoms per unit volume in energy states 1 and 2 with energies  $E_1$  and  $E_2$  respectively at any instant. An atom in the lower energy state  $E_1$  can absorb radiation and get excited to the state  $E_2$ . The probability rate of occurrence of the absorption transition  $1 \rightarrow 2$  would be proportional to  $N_1$  and also to  $u(\nu)$ . Thus, the number of absorption transitions per unit time per unit volume can be written as

$$N_1 B_{12} u(\nu).$$

The proportionality constant  $B_{12}$  is a characteristic of energy states 1 and 2, and is known as 'Einstein's 'B' coefficient of absorption of radiation'.

Let us now consider the emission transitions at frequency  $\nu$  (both spontaneous and stimulated) when an atom de-excites from energy state  $E_2$  to  $E_1$ .

\* The energy density  $u(\nu)$  is defined such that  $u(\nu) d\nu$  is radiation energy per unit volume within the frequency interval  $\nu$  and  $\nu + d\nu$ .

The probability rate of spontaneous emission  $2 \rightarrow 1$  is determined only by the properties of the states 2 and 1, and is proportional to the number of atoms  $N_2$  in the energy state 2. Thus, the number of spontaneous emission transitions per unit time per unit volume can be written as

$$N_2 A_{21} .$$

Again, the proportionality constant  $A_{21}$ , depends on the properties of energy states 2 and 1, and is known as 'Einstein's 'A' coefficient of spontaneous emission of radiation'.

Finally, the probability rate of stimulated emission transition  $2 \rightarrow 1$  is proportional to the energy density  $u(v)$  of the stimulating radiation. Thus, the number of stimulated emission transitions per unit time per unit volume can be written as

$$N_2 B_{21} u(v) ,$$

where  $B_{21}$  is 'Einstein's 'B' coefficient of stimulated emission of radiation'.

At thermal equilibrium, the number of upward transitions  $1 \rightarrow 2$  should be equal to the number of downward transitions  $2 \rightarrow 1$ , that is,

$$N_1 B_{12} u(v) = N_2 [A_{21} + B_{21} u(v)] \quad \dots(i)$$

or 
$$u(v) = \frac{N_2 A_{21}}{N_1 B_{12} - N_2 B_{21}} = \frac{A_{21}}{B_{21}} \frac{1}{\frac{N_1}{N_2} \left( \frac{B_{12}}{B_{21}} \right) - 1} .$$

The equilibrium distribution of atoms among different energy states at temperature  $T$  is given by Boltzmann's law according to which

$$\frac{N_2}{N_1} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}}$$

or 
$$\frac{N_1}{N_2} = e^{(E_2 - E_1)/kT} = e^{hv/kT} ,$$

because  $v = \frac{E_2 - E_1}{h}$ .  $k$  is Boltzmann's constant. Consequently

$$u(v) = \frac{A_{21}}{B_{21}} \frac{1}{e^{hv/kT} \left( \frac{B_{12}}{B_{21}} \right) - 1} . \quad \dots(ii)$$

This is a formula for the spectral energy density of radiation of frequency  $v$  in thermal equilibrium with atoms in energy states 1 and 2, at temperature  $T$ . It must be consistent with black body radiation. Hence comparing it with Planck radiation formula

$$u(v) = \frac{8\pi h v^3}{c^3} \frac{1}{e^{hv/kT} - 1} ,$$

we get

$$\frac{B_{12}}{B_{21}} = 1$$

$\dots(iii)$

and

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h v^3}{c^3} .$$

$\dots(iv)$

These results were obtained by Einstein in 1917, and that is why the coefficients  $A_{21}$ ,  $B_{12}$  and  $B_{21}$  are called Einstein's *A* and *B* coefficients.

From eq. (iii), we conclude that the coefficient of stimulated absorption ( $B_{12}$ ) is equal to the coefficient of stimulated emission ( $B_{21}$ ). It means that *in presence of electromagnetic radiation, the probabilities of stimulated absorption and stimulated emission in atom are equal*.

From eq. (iv) we see that the ratio of spontaneous emission coefficient to stimulated emission coefficient varies with frequency as  $v^3$ . It means that *larger the energy difference between the two states ( $E_2 - E_1 = hv$ ), the much more likely is spontaneous emission compared to stimulated emission*.

#### 4. Possibility of Amplification

Spontaneous emission gives out radiation at random moments and in random directions. Stimulated emission, on the other hand, has a very important property. If a narrow beam of radiation passes through a region containing *only excited atoms*, then the emitted (stimulated) radiation has the same direction, frequency and phase as the incoming (stimulating) radiation. Hence the stimulating radiation and stimulated (emitted) radiation are strictly coherent and the resultant beam is amplified. Clearly, for the amplification of the beam, stimulated emission should predominate over spontaneous emission.

Now, the ratio of the probability  $A_{21}$  of spontaneous emission to the probability  $B_{21} u(v)$  of stimulated emission is given by

$$\frac{A_{21}}{B_{21} u(v)} = e^{hv/kT} - 1. \quad [\text{by eq. (ii) and (iii) above}]$$

In the visible region with ordinary optical sources,  $hv >> kT$ , and so, for atoms in thermal equilibrium with radiation, spontaneous emission is far more probable than stimulated emission. As an example, for an ordinary optical source,  $T = 10^3$  K and  $v = 5 \times 10^{14} \text{ s}^{-1}$  (corresponding to  $\lambda = 6000 \text{ \AA}$ ). Then, we have

$$\frac{hv}{kT} \approx \frac{(6.63 \times 10^{-34} \text{ Js})(5 \times 10^{14} \text{ s}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(10^3 \text{ K})} \approx 24.$$

This gives

$$\frac{A_{21}}{B_{21} u(v)} = e^{hv/kT} - 1 = e^{24} - 1 \approx 10^{10}.$$

Thus, *from ordinary light sources, the emission is predominantly due to spontaneous transitions and hence the emitted light is incoherent*.

On the other hand, if  $hv << kT$ , the number of stimulated emissions far exceeds the number of spontaneous emissions. This condition applies to atomic transitions at room temperature in the microwave region. As an example, for  $\lambda = 10 \text{ cm}$  ( $v = 3 \times 10^9 \text{ s}^{-1}$ ) at room temperature 300 K, we have

$$\frac{hv}{kT} = \frac{(6.63 \times 10^{-34} \text{ Js})(3 \times 10^9 \text{ s}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \approx 5 \times 10^{-4}.$$

This gives

$$\frac{A_{21}}{B_{21} u(v)} = e^{hv/kT} - 1 = e^{5 \times 10^{-4}} - 1 \approx 5 \times 10^{-4}.$$

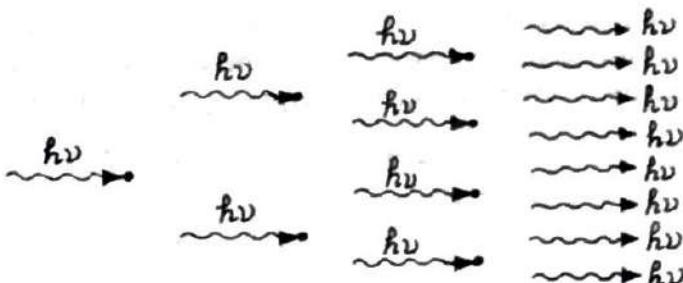
This means that the stimulated emission rate is much higher than the spontaneous emission rate. Hence amplification in this region is possible and has been obtained in MASERS.

## 5. Population Inversion : A Necessary Condition for Light Amplification

Let us consider an assembly of atoms (an active medium) distributed over different energy states. Suppose, a light beam of frequency  $\nu$ , which coincides with one of the characteristic frequencies of the atoms, is passing through the medium. Now, one of the following two processes takes place :

(i) A light photon (of frequency  $\nu$ ) is *absorbed* by an atom in an energy state  $E_1$  and the atom is excited\* to a higher energy state  $E_2$ , such that  $\nu = (E_2 - E_1)/h$ . In this case, the intensity of the beam passing through the medium gradually decreases, until the beam is totally attenuated.

(ii) A light photon (of frequency  $\nu$ ) is incident on an atom which is already in an excited energy state  $E_2$ . This atom decays to a lower energy state  $E_1$ , emitting a photon of same frequency  $\nu$ . The emitted photon is in perfect coherence with the incident photon. (This is stimulated emission of radiation). If these two photons are incident on two other atoms in the state  $E_2$ , they give rise to the emission of two more photons, thus resulting in four coherent photons. This process continues (Fig. 4) and the intensity of the light beam increases exponentially. This increase in light intensity is known as 'light amplification'.



(Fig. 4)

**Necessary Condition for Light Amplification (Laser Action) : Population Inversion** : Under ordinary conditions of thermal equilibrium, the number of atoms in higher energy state  $E_2$  is considerably smaller than the number in lower energy state  $E_1$  ( $N_2 < N_1$ ), so that there is very little stimulated emission compared with absorption. If, however, by some means, the number of atoms in the higher energy state be made sufficiently larger than the number in the lower energy state, then stimulated emission is promoted. *The situation in which the number of atoms in the higher energy state exceeds that in the lower energy state ( $N_2 > N_1$ ) is known as "population inversion".* In this situation, the assembly of atoms would lase.

Stimulated emissions are further encouraged by increasing the radiation density  $u(\nu)$  of the stimulating radiation. This is achieved by enclosing the emitted radiation in a "cavity" between two parallel reflectors. The radiation repeatedly travels back and forth, and the photons passing through the atoms go on multiplying by repeated stimulated emission. Hence a strong coherent beam of light emerges from the system.

**Mathematical Treatment** : Let us consider a collection of atoms (an active medium) and let a *nearly monochromatic* light beam of frequency  $\nu$  be propagating through the medium along the  $x$  direction. The intensity  $I_\nu$  of a light beam of frequency  $\nu$  is related

\*Atoms excited to higher energy state due to absorption give up their energies by spontaneous (incoherent) emission and by collisions with other atoms.

to the energy density  $u(v)$  of the light. If the light beam in question has frequencies in the range  $v$  and  $v + \Delta v$ , then the relation between the intensity and the energy density can be written as

$$I_v \Delta v = c u(v) \Delta v,$$

where  $c$  is the speed of light in the medium.

Let  $N_1$  and  $N_2$  be the number of atoms per unit volume of the medium in energy states  $E_1$  and  $E_2$  respectively at any instant. In practice, the energy levels are not absolutely sharp, but have a finite energy spread due to Doppler effect and certain other causes. Therefore, during the passage of the light beam of frequency  $v$  through the medium, only certain number of atoms, say  $\Delta N_1$  out of  $N_1$  atoms in the state  $E_1$  undergo absorption transitions. The rate of such upward transitions per unit volume is

$$\Delta N_1 B_{12} u(v) = \Delta N_1 B_{12} (I_v/c),$$

where  $B_{12}$  is Einstein's  $B$  coefficient. Similarly, the rate of downward induced transitions is

$$\Delta N_2 B_{21} u(v) = \Delta N_2 B_{21} (I_v/c).$$

During each upward transition, a quantity of radiation energy  $h\nu$  is absorbed from the propagating light beam. Similarly, during each downward induced transition, an equal amount of energy is added to the light beam. So, the rate of change of spectral energy density of the beam in the frequency interval  $\Delta v$  is

$$\begin{aligned} \frac{d}{dt} \{u(v) \Delta v\} &= \{\Delta N_2 B_{21} (I_v/c)\} h\nu - \{\Delta N_1 B_{12} (I_v/c)\} h\nu \\ &= \frac{h\nu}{c} (\Delta N_2 - \Delta N_1) B_{12} I_v, \end{aligned} \quad \dots(i)$$

because  $B_{21} = B_{12}$ . Here we have neglected the radiation arising out of spontaneous emission because such radiations propagate in random directions and are, in general, lost from the beam.

Suppose, the light beam covers a distance  $dx$  in time  $dt$  in the medium. Then  $dx = c dt$ , or  $dt = dx/c$ . Now, we have

$$\frac{d}{dt} \{u(v) \Delta v\} = \frac{d}{dx} \{c u(v) \Delta v\} = \frac{d}{dx} (I_v \Delta v).$$

Therefore, eq. (i) can be written as

$$\frac{d}{dx} (I_v \Delta v) = \frac{h\nu}{c} (\Delta N_2 - \Delta N_1) B_{12} I_v$$

or

$$\frac{dI_v}{dx} = \frac{h\nu}{c} \left( \frac{\Delta N_2 - \Delta N_1}{\Delta v} \right) B_{12} I_v.$$

Let us put

$$\frac{h\nu}{c} \left( \frac{\Delta N_2 - \Delta N_1}{\Delta v} \right) B_{12} = \alpha_v, \quad \dots(ii)$$

where  $\alpha_v$  is 'gain constant' at frequency  $v$ . Then, we have

$$\frac{dI_v}{dx} = \alpha_v I_v$$

$$\frac{dI_v}{I_v} = \alpha_v dx.$$

Integrating, we get

$$I_v = (I_v)_0 e^{\alpha_v x} \quad \dots \text{(iii)}$$

where  $(I_v)_0$  is a constant term.

Now, since the levels  $E_1$  and  $E_2$  have finite widths, the spectral line due to transition between these levels has a finite frequency-spread, say  $\Delta\nu$ , about a mean frequency  $\nu_0$ . We can estimate the value of gain constant  $\alpha_v$  at this mean frequency  $\nu_0$  by putting  $\Delta\nu = N$  in eq. (ii). That is,

$$(\alpha_v)_0 = \frac{h\nu_0}{c} \left( \frac{N_2 - N_1}{\Delta\nu} \right) B_{12}.$$

Using the relation  $\frac{A_{21}}{B_{21}} = \frac{8\pi h \nu^3}{c^3}$ , and remembering that  $B_{21} = B_{12}$ , we get

$$(\alpha_v)_0 = \frac{h\nu_0}{c} \left( \frac{N_2 - N_1}{\Delta\nu} \right) \frac{A_{21} c^3}{8\pi h \nu_0^3}$$

$$\text{or } (\alpha_v)_0 = \frac{c^2}{8\pi \nu_0^2 \Delta\nu} (N_2 - N_1) A_{21}. \quad \dots \text{(iv)}$$

Now, there may be two cases :

If  $N_2 > N_1$  (as a result of population inversion), then  $(\alpha_v)_0$  is positive, and from eq. (iii),  $I_v$  increases as  $x$  increases. This means that as the light beam progresses through the medium, its intensity  $I_v$  increases exponentially, that is, there is an amplification of the intensity of the light beam. Thus, ***population inversion is necessary for light amplification.***

If, on the other hand,  $N_2 < N_1$  as ordinarily happens,  $(\alpha_v)_0$  is negative and  $I_v$  decreases exponentially as  $x$  increases.

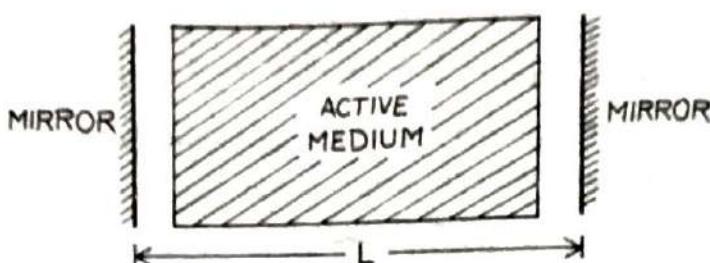
## 6. Achievement of Population Inversion : Pumping

For any laser device to operate, the achievement of population inversion in the active medium is necessary. That is, a larger number of atoms of the medium should be excited to higher energy states. ***The process by which atoms are raised from a lower to a higher energy state is called "pumping" of atoms.*** The pumping process in lasers involves a number of energy levels with complex excitation processes. Different methods of atomic excitations are adopted in different types of lasers. Some of the methods are :

- (i) excitation by a strong source of light, say flash lamp or arc lamp (optical pumping).
  - (ii) excitation by electron impact (electrical pumping).
  - (iii) excitation by chemical reaction (chemical pumping).
  - (iv) excitation by supersonic gas expansion (gas-dynamic pumping).
- and so on.

## 7. Optical Resonator

A medium with population inversion is capable of amplifying a light beam passing through it. However, if the medium is to act as an oscillator which can supply light energy and act as a source of light, a part of the output energy must be fed back into the medium. Such a feedback can be achieved by placing the active medium between two mirrors



(Fig. 5)

facing each other (Fig. 5). The mirrors reflect most of the output energy back to the medium. Such a system formed by two mirrors represents a resonant cavity, and is referred to as an optical resonator. To obtain an output light beam, one of the mirrors is made *partially reflecting*.

Let us consider a wave which starts from one of the mirrors and travels towards the other. In passing through the active medium, the wave is amplified. If the second mirror is partially reflecting, then the wave is partially transmitted and the rest is reflected back towards the first mirror. In travelling to the first mirror, the wave is again amplified and returns to its starting position. Thus, in between the two mirrors, there are waves propagating along both directions. These waves interfere, and for a stable standing wave pattern to be formed in the cavity, the total phase change suffered by the wave in one complete round trip must be an integral multiple of  $2\pi$ . Thus, if  $L$  is the length of the cavity, then

$$\frac{2\pi}{\lambda}(2L) = 2m\pi; \quad m = 1, 2, 3, \dots \quad \dots(i)$$

where  $\lambda$  is the wavelength of the radiation in the medium enclosed by the cavity.

Now,  $\lambda = c/v$ , where  $v$  is frequency of the radiation. Then, eq. (i) gives

$$v = m \frac{c}{2L}, \quad \dots(ii)$$

which gives the discrete frequencies of oscillation. Different values of  $m$  lead to different oscillation frequencies which constitute the longitudinal modes of the cavity. The frequency difference between adjacent longitudinal modes is

$$\Delta v = \frac{c}{2L}.$$

We can see from eq. (ii) that for an actual optical resonator,  $m$  is very large. For example, for an optical resonator of length  $L \approx 60$  cm operating at an optical frequency of  $v \approx 5 \times 10^{14}$  Hz (corresponding to  $\lambda \approx 6000 \text{ \AA}$ ), we obtain

$$m = \frac{v \times 2L}{c} = \frac{(5 \times 10^{14} \text{ s}^{-1}) \times (2 \times 0.6) \text{ m}}{3.0 \times 10^8 \text{ m s}^{-1}} = 2 \times 10^6.$$

In obtaining eq. (ii) for the various oscillating frequencies, we have assumed that a wave can propagate to and fro unmodified inside the resonator. This is, however, not true in practice since the mirrors of any practical resonator have finite transverse dimensions and hence only that portion of the wave which strikes the mirror would be reflected (the portion of the wave lying outside the transverse dimension of the mirror would be lost from the resonator). Now, the wave travelling back to the first mirror has finite transverse dimensions, depending on the transverse dimensions of the mirror. Now, a beam with a finite transverse dimension diffracts as it propagates. Thus, when the beam comes back to

the first mirror, it would have a larger transverse dimension than the mirror. Further, since only the portion of the wave intercepted by the mirror would be reflected, the remaining portion lying outside the mirror would be lost. This loss is referred to as diffraction loss.

If we consider a resonator made of mirrors of transverse dimension  $a$  and separated by a distance  $L$ , then the wave after reflection at one of the mirrors undergoes diffraction divergence at an angle roughly  $\lambda/a$ . The angle subtended by one of the mirrors at the other mirror is roughly  $a/L$ . Hence for diffraction losses to be low, we must have

$$\frac{\lambda}{a} \ll \frac{a}{L}$$

$$\frac{a^2}{L\lambda} \gg 1.$$

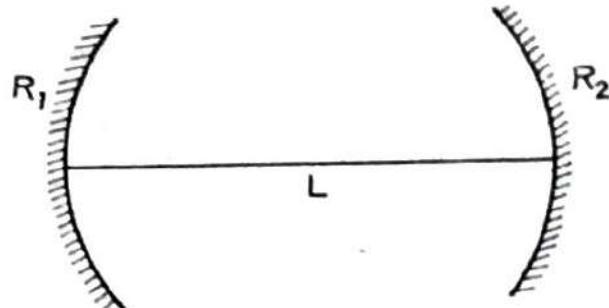
or

The quantity  $a^2/L\lambda$  is known as the Fresnel number. As an example, if the resonator mirrors have transverse dimension of 1 cm and are separated by 60 cm, then for a wavelength of 5000 Å ( $= 5 \times 10^{-5}$  cm) we have

$$\frac{a^2}{L\lambda} \approx 330 \gg 1$$

and hence the diffraction loss will be extremely small.

The loss can be reduced by using spherical mirrors to form the resonant cavity (Fig. 6). The spherical mirrors help in focusing; hence causing much less loss due to diffraction. However, only certain combinations of curvatures and mirror separations can give low diffraction loss. These resonators are referred to as stable resonators. The stability condition can be expressed as :



(Fig. 6)

$$0 \leq \left(1 - \frac{L}{R_1}\right) \left(1 - \frac{L}{R_2}\right) \leq 1,$$

where  $R_1$  and  $R_2$  are the radii of curvatures of the mirrors.

## QUESTIONS

- What is a laser ? Explain the terms 'absorption', 'spontaneous emission' and 'stimulated emission' of radiation. (Meerut 99 S, sp. paper 2006, 02, 00)
- Explain stimulated absorption, spontaneous emission, and stimulated emission of radiation. Obtain a relation between transition probabilities for the two emissions. (Meerut 2005 sp. paper)
- What are transition probabilities ? Explain spontaneous emission and induced emission. Prove ! 
$$\frac{A_{21}}{B_{21}} = \frac{8\pi h v^3}{c^3}.$$
 (Meerut 2003 sp. paper)
- Obtain a relation between transition probabilities of spontaneous and stimulated emissions. What are Einstein's A and B coefficients ? (Meerut 2006 sp. paper)
- What is a laser ? What are the important features of stimulated emission ? Discuss the essential requirements for producing laser action. (Meerut 2000 sp. paper)

6. What is meant by Einstein's  $A$  and  $B$  coefficients ? What is stimulated emission ? Under what condition there is a possibility of radiation growing in intensity as it passes through matter ? (Meerut 2006, 93 sp. paper)
7. Explain the meaning of amplification of the intensity of light. Show mathematically that population inversion is necessary for the amplification of light intensity (laser action).
8. What is pumping process ? Explain optical pumping. (Meerut 2006 sp. paper)  
Hint : Take example of ruby laser to explain optical pumping.
9. What is optical resonator ? Explain its role in maintaining laser oscillations.

### PROBLEM

1. What is the frequency difference between two adjacent modes in an optical resonator having a cavity of length 1.0 m. Ans. 150 MHz.
-

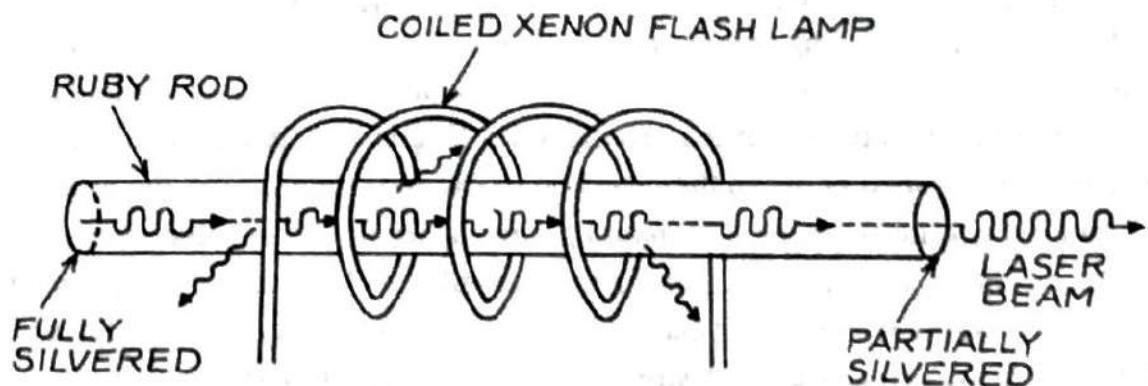
# Types of Lasers : Characteristics and Applications of Lasers

## 1. Introduction

Any laser device consists of three main components : the active medium, the pumping source, and the optical resonator. The active medium is an assembly of atoms, molecules, or ions (in solid, liquid, or gaseous form), which acts as an amplifier for light beams. As such, there are different types of lasers depending upon the active medium. However, to amplify a light beam, the medium has to be maintained in a state of population inversion, that is, a state in which the number of atoms in an upper energy level is larger than the number of atoms in a lower energy level. The pumping source provides a state of population inversion between a pair of energy levels of the atomic system. When the active medium is placed inside an optical resonator, the system acts as an oscillator.

## 2. The Ruby Laser : A Three-level System

The ruby laser was the first laser developed in 1960. It is a solid-state laser. It consists of a pink ruby cylindrical rod whose ends are optically flat and parallel (Fig. 1). One end is

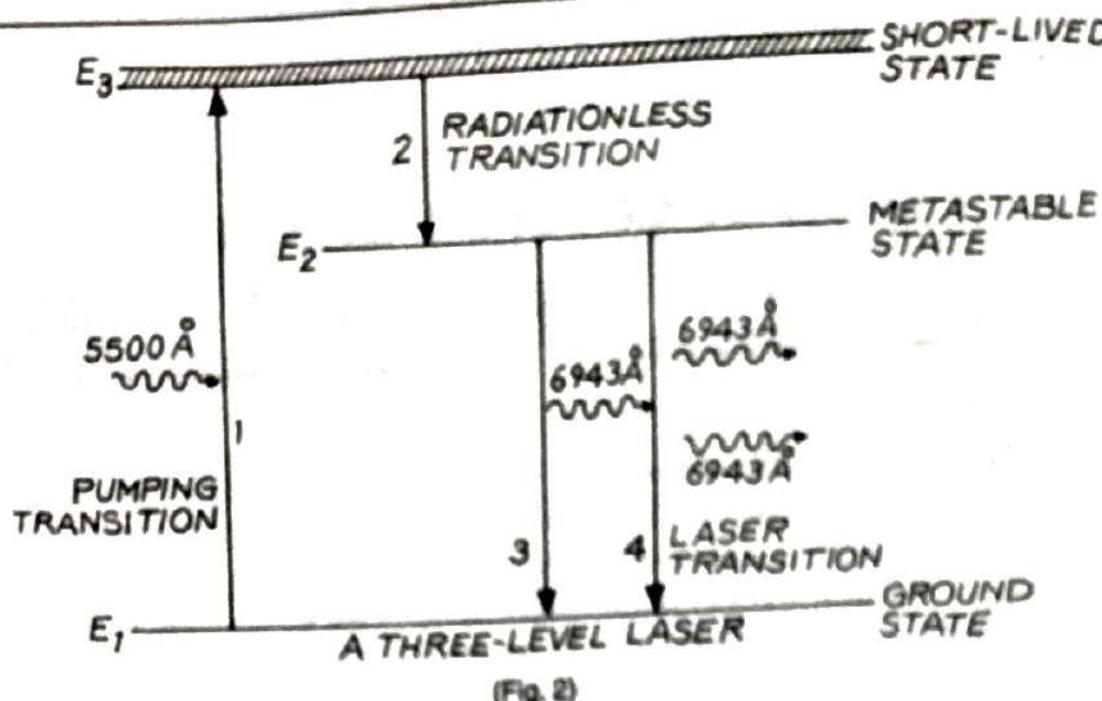


(Fig. 1)

fully silvered and the other is partially silvered. The two ends thus form a resonant cavity. The ruby rod is placed inside a coiled xenon flash lamp. The flash lamp is connected to a capacitor (not shown) which discharges a few thousand joules of energy in a few milliseconds, resulting in a power output of a few megawatts from the flash lamp.

**Working :** The ruby rod is a crystal of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) doped with 0.05% chromium oxide ( $\text{Cr}_2\text{O}_3$ ), so that some of the  $\text{Al}^{+++}$  ions are replaced by  $\text{Cr}^{+++}$  ions. These "impurity" chromium ions give pink colour to the ruby and give rise to the laser action.

A simplified version of the energy-level diagram of chromium ion is shown in Fig. 2. It consists of an upper short-lived energy level (rather energy band)  $E_3$  above its ground-state energy level  $E_1$ , the energy difference  $E_3 - E_1$  corresponding to a wavelength of about 5500 Å. There is an intermediate excited-state level  $E_2$  which is



metastable\* having a life-time of  $3 \times 10^{-3}$  s (about  $10^5$  times greater than the life-time of  $E_3$  which is  $\approx 10^{-8}$  s).

Normally, most of the chromium ions are in the ground state  $E_1$ . When a flash of light (which lasts only for about a millisecond) falls upon the ruby rod, the 5500-Å radiation photons are absorbed by the chromium ions which are "pumped" (raised) to the excited state  $E_3$ . The transition 1 is the (optical) pumping transition. The excited ions rapidly give up, by collision, part of their energy to the crystal lattice and decay to the "metastable" state  $E_2$ . The corresponding transition 2 is thus a *radiationless* transition. Since the state  $E_2$  has a much longer life-time, the number of ions in this state goes on increasing while, due to pumping, the number in the ground state  $E_1$  goes on decreasing. Thus, population inversion is established between the metastable (excited) state  $E_2$  and the ground state  $E_1$ .

When an (excited) ion passes *spontaneously* from the metastable state to the ground state (transition 3), it emits a photon of wavelength 6943 Å. This photon travels through the ruby rod and, if it is moving parallel to the axis of the crystal, is reflected back and forth by the silvered ends until it stimulates an excited ion and causes it to emit a fresh photon *in phase with the stimulating photon*. This "stimulated" transition 4 is the laser transition. (The photons emitted spontaneously which do not move axially escape through the sides of the crystal). The process is repeated again and again because the photons repeatedly move along the crystal, being reflected from its ends. The photons thus multiply. When the photon-beam becomes sufficiently intense, part of it emerges through the partially-silvered end of the crystal.

**Drawback :** There is a drawback in the three-level laser such as ruby. The laser requires very high pumping power because the laser transition terminates at the ground state, and more than one-half of the ground-state atoms must be pumped up to the higher state to achieve population inversion. Moreover, ions which happen to be in their ground state absorb the 6943-Å photons from the beam as it builds up.

\*A metastable state is relatively long-lived state whose life-time may be  $10^{-3}$  s, or more, instead of the usual life-time of  $10^{-8}$  s.

The ruby laser is a "pulsed" laser, that is, it emits laser light in pulses. The duration of an individual pulse is of the order of  $0.1 - 1 \mu\text{s}$ ; the time interval between two successive pulses is about  $1 - 10 \mu\text{s}$ ; the power of each pulse is as high as  $10^4 - 10^5 \text{ W}$ . The phenomenon is known as 'spiking' in ruby laser and can be explained as follows:

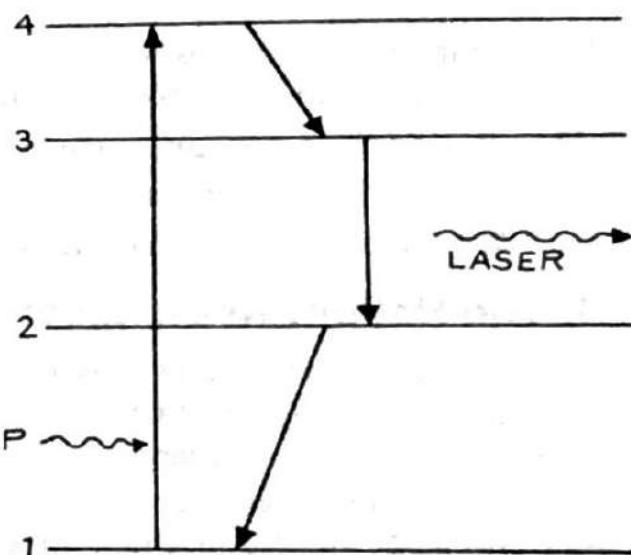
The duration of the exciting flash of light is of the order of a millisecond, but it is intense enough to build up population inversion very rapidly. As soon as a larger population is produced in the upper level, the laser action starts producing a pulse. This (that is, the stimulated transitions) depletes the upper level population more rapidly than it is restored by the flash light. The laser action then stops for a few microseconds. In the mean time, the flash lamp again builds up population inversion producing another pulse. This sequence is repeated. Hence a series of pulses is produced until the intensity of the flash light falls to such a level that it can no longer rebuild the required population inversion.

### 3. Four-Level Solid State Lasers

The ruby laser is a three-level laser and hence not very efficient. There are more efficient solid state lasers based on the four-level system shown in Fig. 3. Level 1 is the ground level and levels 2, 3, and 4 are the excited levels of the system. Atoms from level 1 are lifted by a pump right to level 4, from where they rapidly decay to level 3 through some non-radiative transition. Level 3 is a metastable level with a (long) life-time of the order of  $10^{-3} \text{ s}$ . This level becomes the upper laser level and level 2 becomes the lower laser level. Level 2 must have a very short life-time so that the incoming atoms from level 3 decay at once from level 2 to level 1 from where they are again pumped to level 4. If the rate of decay of atoms from level 2 to level 1 is faster than the rate of arrival of atoms into level 2, population inversion is established between levels 3 and 2, and laser action is initiated.

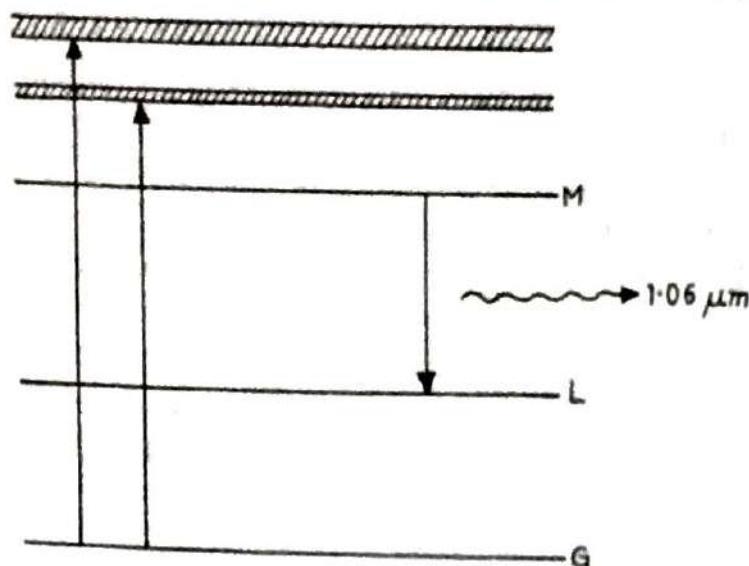
The level 4 could be a *broad* level. Then, an optical pump emitting radiation over a band of frequencies can efficiently lift atoms from level 1 to level 4. Now, the level 4 cannot be the upper laser level because the upper laser level must be narrow. Further, the lower laser level 2 must be sufficiently above the ground level 1 so that at ordinary temperatures the population of level 2 is negligible (otherwise the pumping power needed for population inversion would be much more).

The so-called Nd : YAG laser is an example of lasers using various energy levels of the neodymium ion  $\text{Nd}^{+++}$ . These ions are known to be situated into a number of lattices, like  $\text{Y}_3\text{Al}_5\text{O}_{12}$  lattice, abbreviated as YAG.



(Fig. 3)

A simplified energy-level diagram of  $\text{Nd}^{+++}$  ions is shown in Fig. 4. The ions are raised to energy levels (rather energy bands) above the metastable level  $M$  by means of a



(Fig. 4)

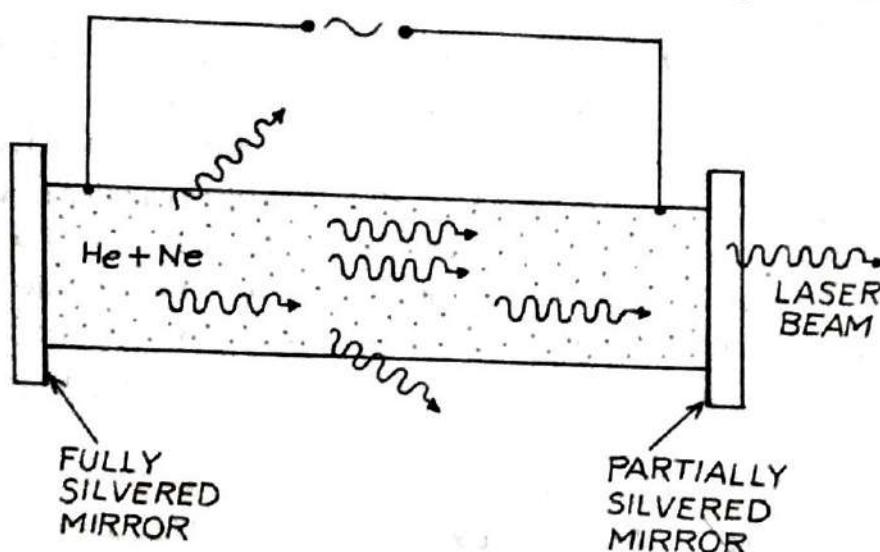
flash lamp or a continuous wave lamp. The excited ions decay to the metastable level  $M$  which has a life-time of about 0.25 ms. Laser action is now obtained between the levels  $M$  and  $L$  at  $\lambda = 1.06 \mu\text{m}$  in the infra-red region.

The Nd : YAG lasers can give pulses of 100 ps duration having intensities as high as  $10^{11} \text{ W/cm}^2$ . They are used to study laser-induced fusion reactions.

#### 4. The Helium-Neon Laser

The helium-neon laser was the first gas laser to be operated successfully. It was fabricated by Javan in 1961. It is a four-level laser in which population inversion is achieved by electric discharge.

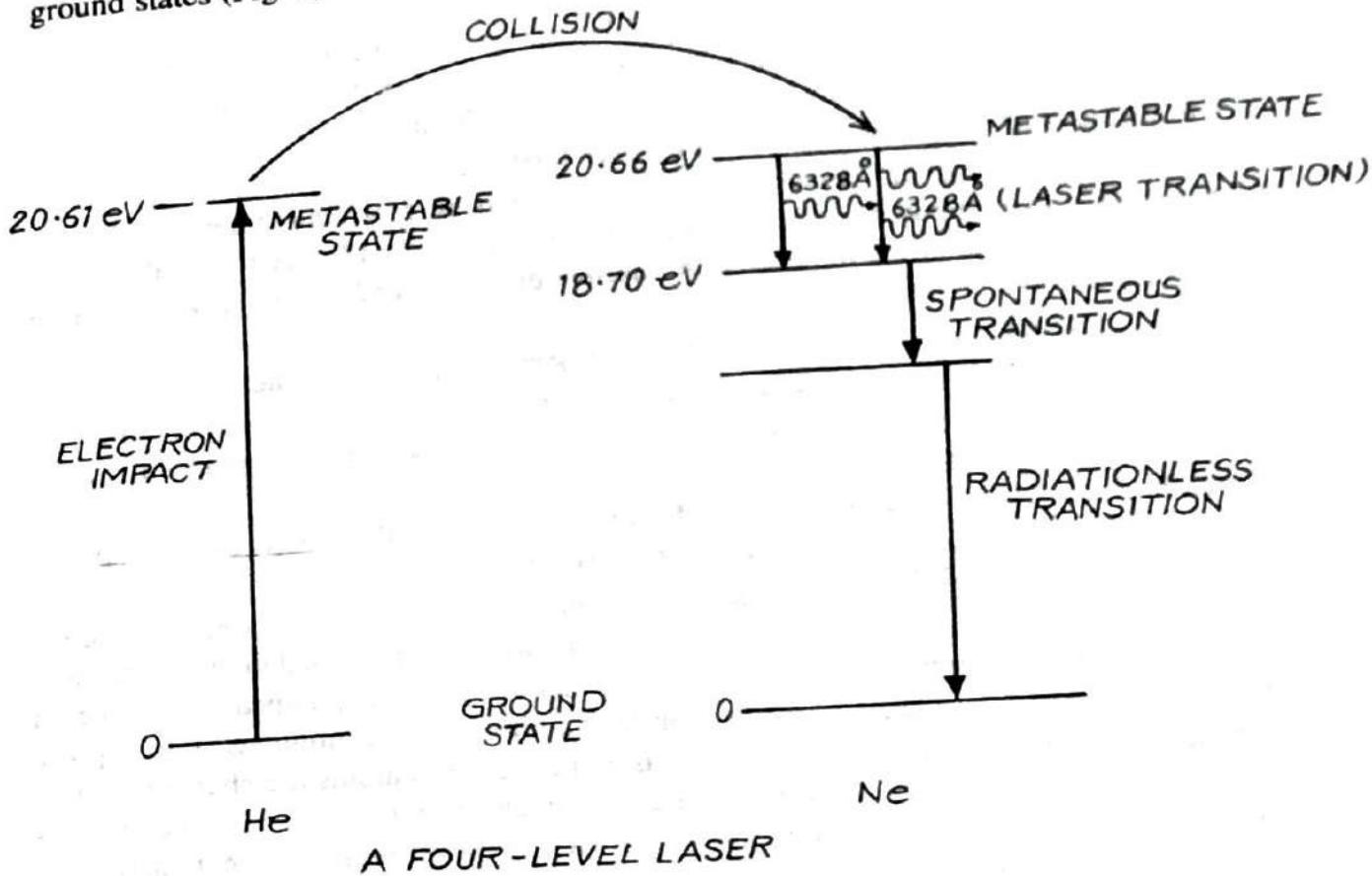
The helium-neon laser consists of a long and narrow discharge tube filled with a mixture of He and Ne in a ratio of about 10 : 1 at a pressure of about 1 mm of mercury (Fig. 5). The gas mixture (He + Ne) forms the lasing medium. It is placed between a pair



(Fig. 5)

of optically plane and parallel mirrors which form a resonant cavity. One of the mirrors is fully silvered and the other is partially silvered. The spacing of the mirrors is equal to an integral number of half-wavelengths of the laser light. An electric discharge may be produced in the gas-mixture by electrodes connected to a high-frequency electric source.

**Working :** When a discharge is passed through the gas mixture, electrons are accelerated down the tube. These accelerated electrons collide with, and "pump" (excite) the He and Ne atoms to *metastable* states 20.61 eV and 20.66 eV respectively above their ground states (Fig. 6). Some of the excited He atoms transfer their energy to ground-state



(Fig. 6)

Ne atoms by collisions, with the 0.05 eV of additional energy being provided by the kinetic energy of atoms\*. Thus, He atoms help in achieving a population inversion in the Ne atoms.

When an excited Ne atom passes *spontaneously* from the metastable state at 20.66 eV to the state at 18.70 eV, it emits a 6328-Å photon. This photon travels through the gas-mixture, and if it is moving parallel to the axis of the tube, is reflected back and forth by the mirror-ends unit it stimulates an excited Ne atom and causes it to emit a fresh 6328-Å photon in phase with the stimulating photon. This stimulated transition from 20.66-eV level to 18.70-eV level is the laser transition. This process is continued and a beam of coherent radiation builds up in the tube. When this red-light beam becomes sufficiently intense, a portion of it escapes through the partially-silvered end.

\*The advantage of this collision process is that the lighter He atoms can be easily pumped up to their excited states; the much heavier Ne atoms could not be raised efficiently without them.

From the 18.70-eV level the Ne atom passes down spontaneously to a lower metastable state emitting incoherent light, and finally to the ground state through collision with the tube walls. The final transition is thus radiationless.

Actually, there are other energy levels between the 20.66-eV and 18.70-eV levels in Ne atom; and transitions between them result in the emission of radiation having wavelengths 3.39  $\mu\text{m}$ , 1.15  $\mu\text{m}$  besides the visible radiation of wavelength 0.6328  $\mu\text{m}$  (6328 Å).

Typical power outputs of He-Ne lasers lie between 1 and 50 mW of continuous wave for inputs of about 5 - 10 W.

He-Ne gas laser is a 'tunable' laser. The He-Ne laser can be tuned (adjusted) to give radiation in any desired wavelength range. This can be done by choosing end mirrors having high reflectivity over only the required wavelength range.

#### Advantages of Gas Lasers over Solid-state Lasers :

(i) The gas lasers, in general, emit light which is more directional and more monochromatic as compared to that from solid-state lasers. This is due to the absence of certain effects like crystalline imperfection, thermal distortion and scattering which appear in solid-state lasers.

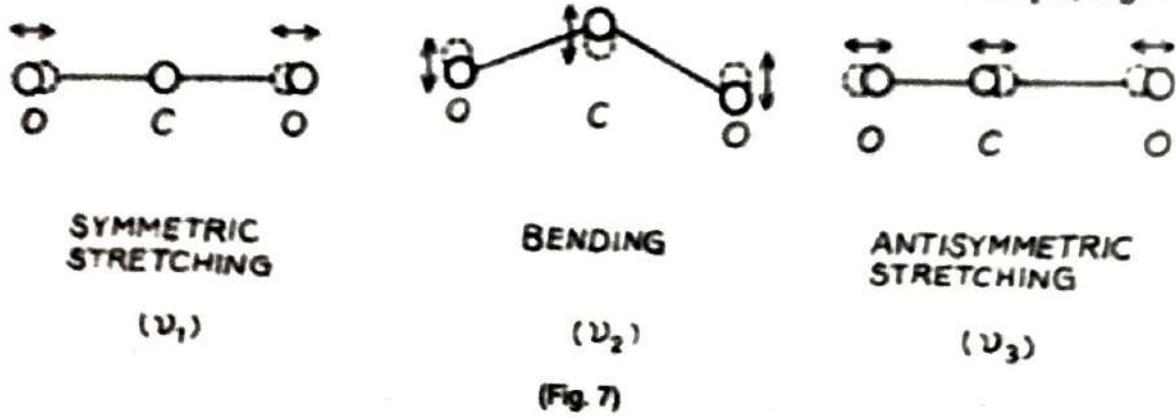
(ii) Gas lasers can be operated continuously because electron impacts that excite the He and Ne atoms occur all the time (unlike the pulsed excitation from the xenon flash lamp in the ruby laser). Hence, they are capable of supplying a continuous laser beam without any cooling arrangement.

(iii) Further, since the laser transition does not terminate at the ground state, the power needed for excitation is less than that in a three-level ruby laser.

The technique of obtaining population inversion in four-level gas lasers is different than that in three-level solid-state lasers. In solid-state lasers, population inversion is obtained by optical pumping in which the lasing medium is pumped to a state of population inversion by means of a flash lamp or a high-power continuous lamp. Optical pumping would be very inefficient for gas lasers because gas atoms are characterised by sharp energy levels, whereas solid atoms are usually characterised by energy bands. This is why for gaseous laser medium, the electrical discharge is an efficient method of producing population inversion.

## 5. The Carbon Dioxide ( $\text{CO}_2$ ) Laser

The  $\text{CO}_2$  laser is a molecular gas laser. A molecule is made up of two or more atoms. Hence, in addition to the electronic motions; atoms in the molecule may vibrate in different modes, and the molecule as a whole may rotate about some axis. For example, Fig. 7



(Fig. 7)

From the 18.70-eV level the Ne atom passes down spontaneously to a lower metastable state emitting incoherent light, and finally to the ground state through collision with the tube walls. The final transition is thus radiationless.

Actually, there are other energy levels between the 20.66-eV and 18.70-eV levels in Ne atom; and transitions between them result in the emission of radiation having wavelengths 3.39  $\mu\text{m}$ , 1.15  $\mu\text{m}$  besides the visible radiation of wavelength 0.6328  $\mu\text{m}$  (6328 Å).

Typical power outputs of He-Ne lasers lie between 1 and 50 mW of continuous wave for inputs of about 5 – 10 W.

**He-Ne gas laser** is a 'tunable' laser. The He-Ne laser can be tuned (adjusted) to give radiation in any desired wavelength range. This can be done by choosing end mirrors having high reflectivity over only the required wavelength range.

#### Advantages of Gas Lasers over Solid-state Lasers :

(i) The gas lasers, in general, emit light which is more directional and more monochromatic as compared to that from solid-state lasers. This is due to the absence of certain effects like crystalline imperfection, thermal distortion and scattering which appear in solid-state lasers.

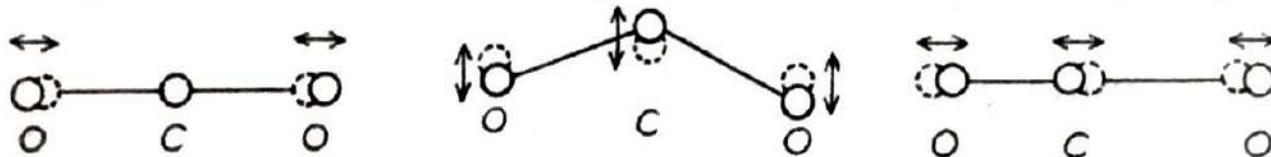
(ii) Gas lasers can be operated continuously because electron impacts that excite the He and Ne atoms occur all the time (unlike the pulsed excitation from the xenon flash lamp in the ruby laser). Hence, they are capable of supplying a continuous laser beam without any cooling arrangement.

(iii) Further, since the laser transition does *not* terminate at the ground state, the power needed for excitation is less than that in a three-level ruby laser.

The technique of obtaining population inversion in four-level gas lasers is different than that in three-level solid-state lasers. In solid-state lasers, population inversion is obtained by optical pumping in which the lasing medium is pumped to a state of population inversion by means of a flash lamp or a high-power continuous lamp. Optical pumping would be very inefficient for gas lasers because gas atoms are characterised by sharp energy levels, whereas solid atoms are usually characterised by energy bands. This is why for gaseous laser medium, the electrical discharge is an efficient method of producing population inversion.

## 5. The Carbon Dioxide ( $\text{CO}_2$ ) Laser

The  $\text{CO}_2$  laser is a molecular gas laser. A molecule is made up of two or more atoms. Hence, in addition to the electronic motions; atoms in the molecule may vibrate in different modes, and the molecule as a whole may rotate about some axis. For example, Fig. 7



SYMMETRIC  
STRETCHING

( $v_1$ )

BENDING

( $v_2$ )

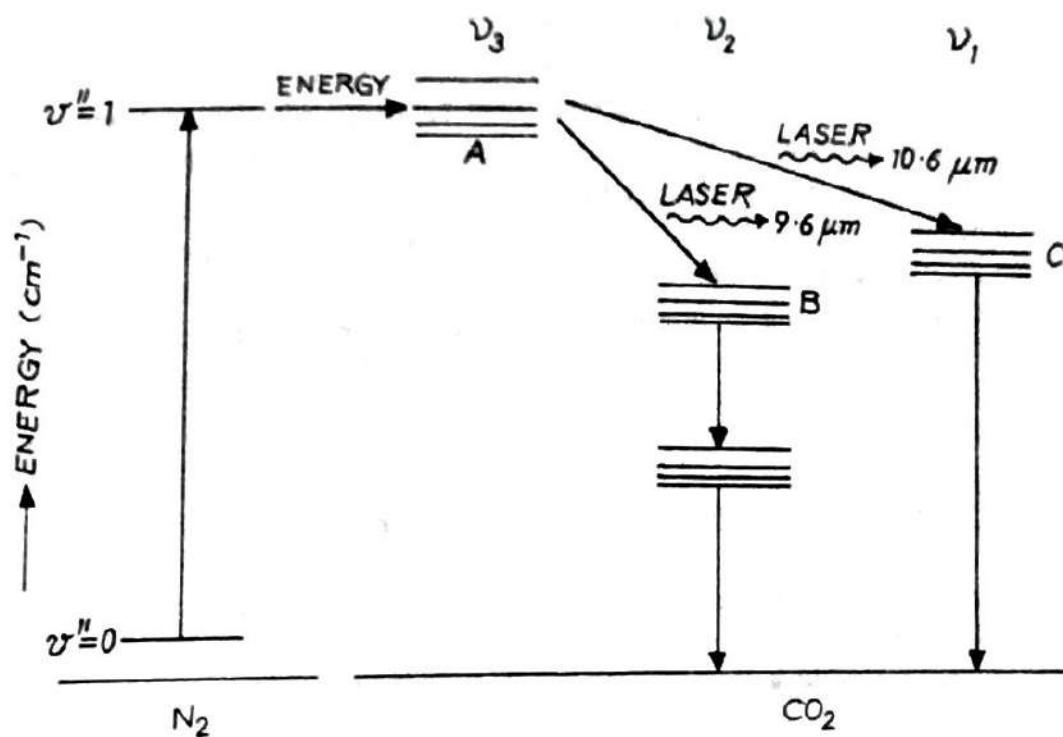
ANTISYMMETRIC  
STRETCHING

( $v_3$ )

(Fig. 7)

shows the three modes of vibration of a  $\text{CO}_2$  molecule. These are : (i) symmetric stretching mode (frequency  $v_1 = 1337 \text{ cm}^{-1}$ ), (ii) bending mode ( $v_2 = 667 \text{ cm}^{-1}$ ) and asymmetric stretching mode ( $v_3 = 2349 \text{ cm}^{-1}$ ). As such, a molecule has discrete electronic levels (like atoms), each electronic level has a number of vibrational levels associated with it, and each vibrational level has a number of rotational levels associated with it. A transition between two electronic levels gives radiation in the visible or ultraviolet; a transition between vibrational levels of the same electronic level gives radiation in the near infra-red region, while a transition between rotational levels of the same vibrational level gives radiation in the far infra-red or microwave region.

**Working :** The laser uses  $\text{CO}_2$  gas mixed with  $\text{N}_2$  gas. The active centres are the  $\text{CO}_2$  molecules which lase when transitions occur between a rotational level associated with a vibrational level, and a rotational level associated with a lower vibrational level of the electronic ground state. In Fig. 8 are shown vibrational (and rotational) levels of the electronic ground state of  $\text{CO}_2$ , and those of  $\text{N}_2$ .



(Fig. 8)

When a discharge is passed in a tube containing  $\text{CO}_2$ , the electron collisions excite the  $\text{N}_2$  and  $\text{CO}_2$  molecules to higher vibrational-rotational levels. The collision cross-section for excitation of  $\text{CO}_2$  to the level A (Fig. 8) is very large. This level is also populated by *radiationless* transitions from upper excited levels. Further, the level A of  $\text{CO}_2$  is nearly coincident with the highly populated  $v'' = 1$  level of  $\text{N}_2$ . Thus, there is a very efficient transfer of energy from a  $\text{N}_2$  molecule to a  $\text{CO}_2$  molecule, resulting in the excitation of  $\text{CO}_2$  molecule. This increases the pumping efficiency of the  $\text{CO}_2$  laser. (Here  $\text{N}_2$  plays the same role as He plays in He-Ne laser).

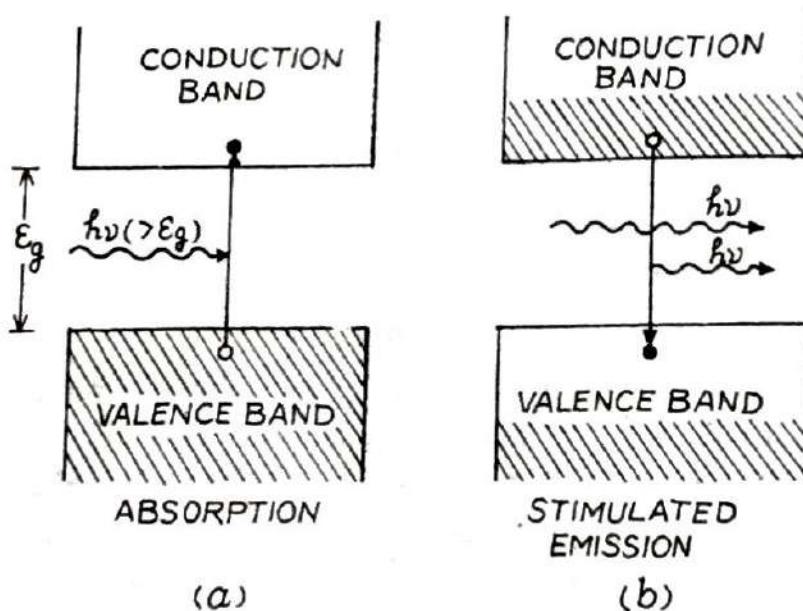
As a result of the above processes, population inversion is established between level A and the lower levels B and C. This initiates laser action producing laser beams at  $9.6 \mu\text{m}$  and  $10.6 \mu\text{m}$ .

**Applications :** Output powers of several watts to several hundred watts are obtained from CO<sub>2</sub> lasers. Hence CO<sub>2</sub> laser, because of its high output power, finds application in industry for welding, drilling, cutting etc. They are also used in open air communication systems and optical radar systems.

## 6. Semiconductor Injection Laser

An important class of broadly tunable lasers which have proved to be very useful particularly in optical communication and optical-computer design are the semiconductor injection lasers. This is the third historical development in lasers. In 1961, Bernard and Duraffourg for the first time put forward the idea that stimulated emission of photons is possible in semiconductors from transmission between conduction band and valence band. Since then, semiconductor lasers have been rapidly developed. The first semiconductor laser was made from gallium arsenide, GaAs.

**Principle :** A semiconductor has a small energy gap  $\epsilon_g$  ( $\approx 1$  eV) between its valence band having energy states occupied by electrons, and the empty conduction band (Fig. 9 a). At room temperature, however, some of the valence electrons acquire thermal energy greater than  $\epsilon_g$  and cross over into the conduction band, leaving behind holes in the valence band. If a light photon of energy greater than  $\epsilon_g$  happens to interact with the electrons, one of the two processes may occur : (i) the photon may be absorbed by a valence-band electron which would be excited to the conduction band leaving behind a hole in the valence band (Fig. a); (ii) the photon may stimulate an already excited conduction-band electron which would drop to the valence band, emitting a fresh photon in coherence with the stimulating photon (Fig. b). Which of the two processes is more probable depends upon whether most of the electrons are in the valence band or in the conduction band.



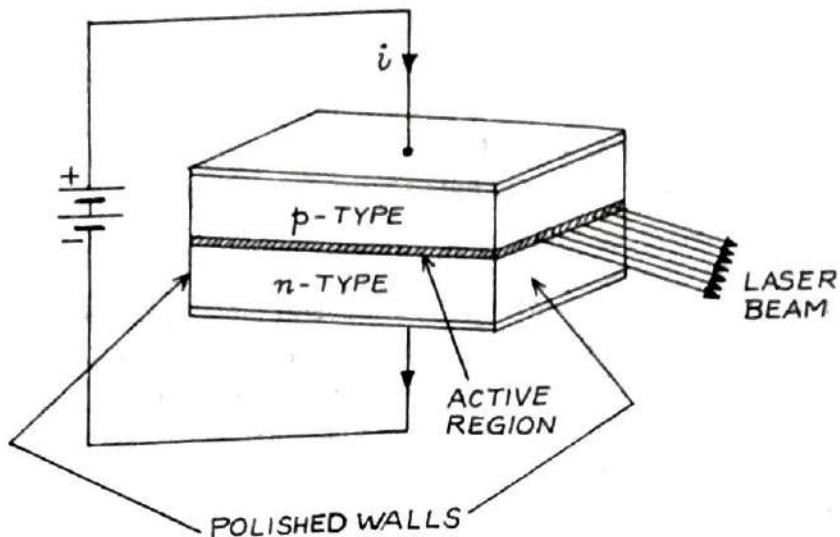
(Fig. 9)

Under ordinary conditions of thermal equilibrium, the number of electrons in higher-energy states (conduction band) is much smaller than in lower-energy states (valence band), so that there is little stimulated emission compared with absorption. If, however, by some means a large number of electrons are made available in high-energy states, stimulated emission is promoted. Once this situation called "population inversion"

is achieved, the photons go on multiplying by repeated stimulated emissions and a strong coherent beam of light emerges from the semiconductor.

**Achievement of Population Inversion :** Population inversion can be achieved near a *p-n* junction having high doping densities and forward currents. The large number of injected carriers creates a region near the junction where there is a very large number of electrons in the conduction band together with a very large number of holes in the valence band, that is, a population inversion (Fig. 9 b).

**Basic Structure :** The basic structure of a gallium arsenide *p-n* junction, used as an injection laser, is shown in Fig. 10. The pair of parallel planes perpendicular to the plane of



(Fig. 10)

the junction is polished, while the two remaining sides of the diode are roughened. When a *forward* bias is applied to the laser diode, a current flows. The injected electrons move from the *n*-side to the *p*-side and the holes from the *p*-side to the *n*-side. As the electrons and holes recombine, photons are emitted. These photons are reabsorbed or radiated away. This is the spontaneous emission which occurs in all directions at low current. As the current is increased, eventually a threshold current is reached at which the emitted photons stimulate the emission of more photons. These photons are internally reflected several times at the polished walls, stimulating more and more photons, all coherent with them. When the photon beam becomes sufficiently intense, it emerges out from the junction.

The main difficulty with this GaAs laser is the high threshold current density ( $\approx 10^5 \text{ A/cm}^2$ ) at room temperature. Hence this laser could be operated only at low temperatures at which the required current density is lower. Heterostructure lasers have now been built which operate at room temperature at moderate current densities.

**Comparison With Other Lasers :** Semiconductor lasers are similar to other lasers in that the emitted radiation is intense, monochromatic, directional and highly coherent, both spatially and temporally. However, in some respects, semiconductor lasers differ from other lasers :

- (i) In semiconductor lasers, the electron transitions are associated with the band structure of the materials, whereas in other lasers the transitions take place between discrete energy levels. Therefore, the radiation from a semiconductor laser is less monochromatic (has wavelength range of few angstroms) than that from other lasers (which have a range of only a fraction of an angstrom).

(ii) Because the active region in a semiconductor laser is very narrow ( $\approx 1 \mu\text{m}$  thickness), the divergence of the laser beam is considerably larger than in case of other lasers.

(iii) A semiconductor laser is very compact in size, less than 1 mm.

(iv) The spectral characteristics of a semiconductor laser are strongly influenced by the properties of the junction medium, such as the band gap and refractive index variations.

(v) In the  $p-n$  junction laser, the laser action is produced by passing a forward current through the junction. Hence the emitted laser light can be modulated into light pulses simply by modulating the current.

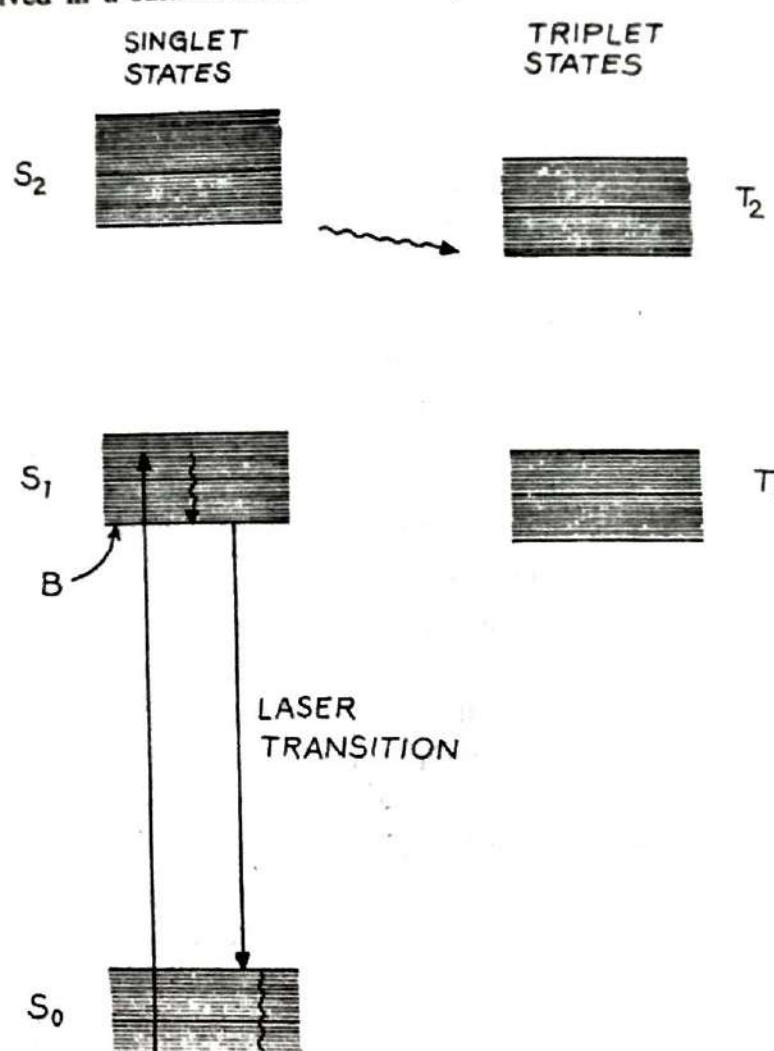
(vi) Semiconductor lasers have very short photon life times. Therefore, modulation at high frequencies can be achieved.

(vii) The semiconductor laser, because of its compact size and capability for high-frequency modulation, is the best light source for optical-fiber communication.

## 7. Dye Lasers

Dye lasers are *liquid lasers* which have several advantages over solid-state lasers. Besides having a very high optical cavity, liquid lasers are free from distortions caused by optical strain, imperfections and internal damages in crystals used in solid-state lasers. In dye laser, an organic dye dissolved in a suitable solvent like ethyl alcohol, methanol, toluene, benzene, water, etc. is used as the active medium. The lasing range covered by various dyes is from  $3000 \text{ \AA}$  to  $13,000 \text{ \AA}$ . The most widely used dye is rhodamine 6 G which emits in yellow-red region. For emission in blue-green region, coumarin dyes are used.

The levels involved in the laser transition are the different vibrational levels of the different electronic states of the dye molecule. A typical energy-level diagram of a dye molecule is shown in Fig. 11. The molecule has singlet as well as triplet electronic states.  $S_0$  represents the ground electronic level (a singlet);  $S_1, S_2, \dots$  represent excited singlet electronic levels; while  $T_1, T_2, \dots$  represent the triplet electronic levels. Each electronic level has a large



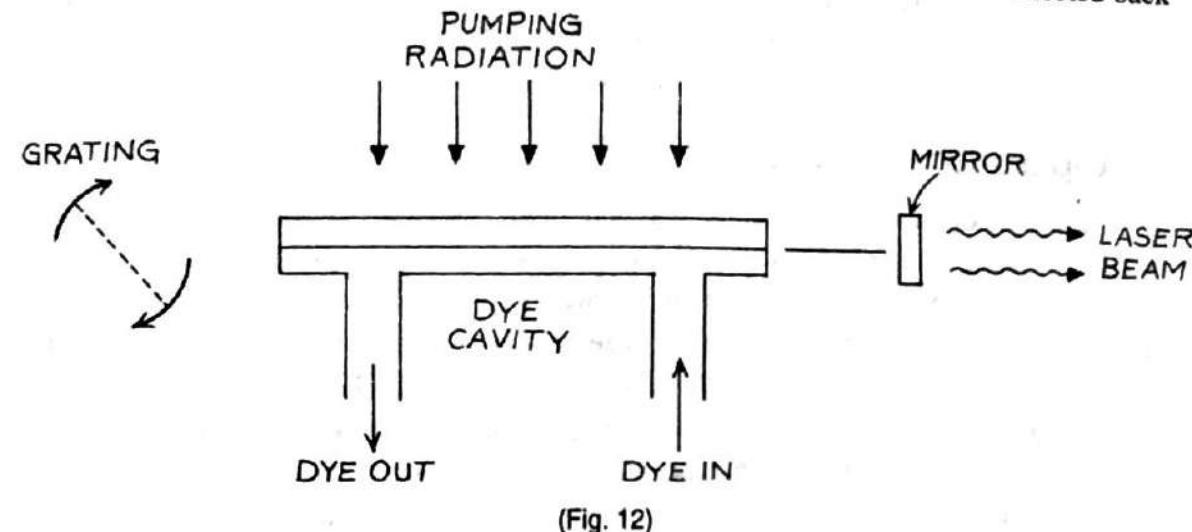
(Fig. 11)

number of vibrational levels and each of these, in turn, contains several rotational levels. In liquids, the rotational levels are so close that they give rise to a continuum of levels between the vibrational levels.

By optical pumping (absorption of light), the dye molecules rise from the ground state  $S_0$  to a higher vibrational-rotational level of the next electronic level  $S_1$ . Due to thermal distribution in the level  $S_1$ , most of the dye molecules decay to the lowest vibrational level  $B$  of  $S_1$  within a time of about  $10^{-12}$  s through a non-radiative process. Now, laser action takes place when the molecules decay from the level  $B$  to one of the higher-lying vibrational level of  $S_0$ , from which they return to the lowest level by another non-radiative process.

Molecules from the state  $S_1$  can also make a non-radiative transition to the triplet level  $T_1$  (a process known as 'intersystem crossing'). This reduces the population of level  $S_1$  which is the upper laser level, thus reducing the gain. This difficulty is overcome by passing oxygen through the solution which acts as a quenching agent of the triplet state.

For the tuning of laser wavelength, one mirror of the usual laser cavity is replaced by a diffraction grating, as shown in Fig. 12. In order that the laser radiation be reflected back



(Fig. 12)

along the cavity axis, the angle  $\theta$  between the normal to the grating and the cavity axis must satisfy the condition

$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots$$

where  $d$  is the grating element and  $\lambda$  is the radiation wavelength. Only for this wavelength, the radiation reflected back will travel along the cavity axis. The tuning of wavelength is done by rotating the grating which changes the angle  $\theta$ .

Dye lasers play an important role in atomic and molecular spectroscopy. This laser has led to a rapid growth in non-linear spectroscopy.

## 8. Characteristic Properties of Laser Beam

Basically, a laser beam and a beam derived from a normal source of light are both electromagnetic radiation, but they differ drastically in coherency, monochromaticity, directionality and intensity. Some characteristic properties of laser beams are as follows :

(i) **Laser beam is highly coherent, temporally as well as spatially.** The coherence time and coherence length for a laser beam are much larger than those for an ordinary source light. Typically, the coherence time for a laser beam is about 2 ms, giving a

coherence length of 600 km ; against the coherence time of  $10^{-9}$  s and coherence length of 30 cm for red cadmium light. As a result, high-contrast interference fringes can be obtained by two laser beams having a path difference of several hundred kilometers. The corresponding coherence length for light from a discharge lamp is much less than 1 m.

(ii) **Laser beam is almost perfectly monochromatic.** A large coherence time results in a small frequency spread ( $\tau = 1/\Delta\nu$ ) . Hence, whereas light from a fine spectral line in a gas discharge tube has a wavelength precise to about 1 part in  $10^6$  , the sharpness of a laser line is a thousand times greater, that is, 1 part in  $10^9$  .

(iii) **Laser beam is highly directional.** An ordinary source of light radiates in all possible directions. But, the output from a laser is an ideal uniform plane wave with almost zero divergence. This means that the laser rays are almost *perfectly parallel*. Hence a laser beam is very narrow and can travel to long distances without spreading.

Because of the high directionality of the laser beam, it can be brought to an extremely sharp focus. Flux densities of  $10^{15}$  W/cm<sup>2</sup> for focussed laser light are readily achieved. In contrast, an oxyacetylene flame has a flux density of only  $10^3$  W/cm<sup>2</sup>.

(iv) **Laser beam is extremely intense.** It can vaporise even the hardest metal. Because of its high energy density and directional property, a laser beam can produce temperatures of the order of  $10^4$ °C at a focussed point.

## 9. Applications of Lasers

The monochromacy, directionality and high intensity of laser beam have made possible a large range of investigations in various scientific fields; such as Physics, Chemistry, Biology, Medicine, etc., many of which would not have been possible without lasers. It has exciting applications in the realms of communication, industry and warfare. The following examples just illustrate the wide applicability of lasers.

(i) **Laser in Science and Research :** Laser beam has been used to perform an improved version of the Michelson-Morley experiment. The original experiment performed in 1881 had shown that the velocity of light is unaffected by earth's motion through space within an accuracy of about 150 mm/s. The apparatus using two He-Ne lasers improved the accuracy to about 3 mm/s.

Laser beams, being very much collimated, have been used in precision measurements of long distances. The distance to the moon, for example, has been determined to an accuracy of 15 cm.

Laser-torch is used to see objects at very long distances. Laser beam is also used in three-dimensional lensless photography (holography) and in nonlinear optics.

Laser rays have proved to be useful in detecting nuclear explosions and earthquakes, in vapourising solid fuel of rockets, in the study of the surfaces of distant planets and satellites.

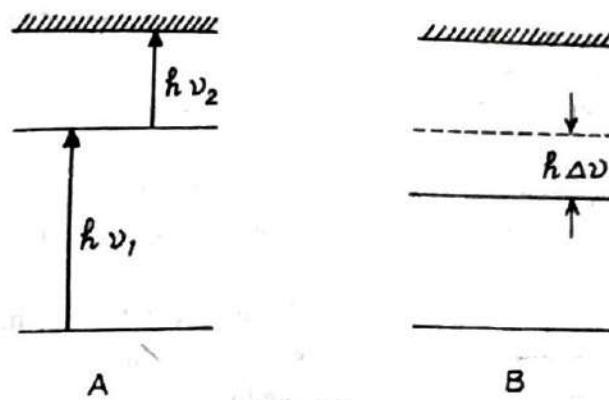
Laser are finding increasing applications in the study of Raman, ESR and NMR spectroscopy

(ii) **In Isotope Separation :** Lasers (particularly, tunable lasers) are successful in separating efficiently the isotopic species of an element present in an isotopic mixture. The laser isotope separation is very important in nuclear power generation. Natural uranium ore contains mainly the isotope U<sup>238</sup> and only 0.7% of U<sup>235</sup> which, infact, fuels nuclear plants and hence must be separated from the ore. Besides this, there are other

applications of *pure* isotopes in medicine, science and technology if they could be produced economically.

Laser isotope separation is based on the fact that atoms of different isotopes of the same element have slightly different energy levels due to difference in their nuclear masses. This difference is called isotopic shift. Therefore, light of a certain frequency may be absorbed by one isotope, but not by the other isotope. Thus, if extremely monochromatic light emerging from a properly tuned laser is made to fall on a mixture of two isotopes, then atoms of *only one* of the isotopes are (selectively) excited. The excited atoms may be separated from the mixture by one of the many methods available. One method is a two-step photoionisation method, described below :

Fig. 13 shows two isotopes A and B, their excitation levels, ionisation levels, and the isotopic shift,  $h\Delta\nu$ . The isotope A is *selectively* excited by absorption of a photon of



(Fig. 13)

energy  $h\nu_1$  from a tunable laser. The excited isotope is subsequently ionised by another photon of energy  $h\nu_2$  from the (tunable) laser. The ions are then separated from the mixture in a mass spectrometer by applying an electric field.

(iii) **Laser-Induced Fusion** : Fusion is a thermonuclear reaction in which atoms of two elements are compressed to an extent that their nuclei fuse together and a new element is formed, whose mass is less than the sum of the masses of the two elements. The lost mass appears as energy released in the process. In fact, 1 gram of mass lost produces  $9.0 \times 10^{13}$  J of energy. Thus, a controlled fusion reaction is almost an inexhaustible source of energy.

There are two major problems in initiating and sustaining a thermonuclear fusion reaction. (i) The fusing material should be heated to a high, of the order of  $10^7$  K temperature so that the nuclei have kinetic energies high enough to fuse together against their mutual electrostatic repulsion. (ii) Matter at such high temperature is in a fully ionised state, known as a plasma. It is necessary to confine the hot plasma for long enough to sustain fusion reactions.

A laser is capable of producing very high temperature and pressure required to initiate a fusion reaction, and confining the fusion material by inertial forces generated when an intense laser pulse interacts with the fusion material.

In a typical scheme, a very small solid pellet containing deuterium-tritium mixture (fusion material) is projected into a chamber where it is irradiated with intense, high-energy laser pulse of short duration ( $\approx 1$  ns). This results in the blasting away of pellet surface, and producing temperature and pressure in the interior of the pellet which are high enough for the nuclei to fuse, releasing a large amount of energy.

**(iv) Lasers in Chemistry :** Laser beam provides a precise and controlled means for studying the nature of chemical bonds in molecules. It is useful in microelectronic design and fabrication. Ultraviolet lasers can be used to deposit metallic films and add dopants in semiconductor substrates with a spatial resolution of about  $1 \mu$  (micron). Infra-red  $\text{CO}_2$  lasers can deposit metal structures about  $50 \mu$  wide by laser-induced chemical vapour deposition.

**(v) In Communication :** The field of communication technology has been revolutionised by the use of laser beam in conjunction with optical fibres. The frequency of light waves are very high ( $\sim 10^{15}$  Hz) as compared to radiowaves ( $\sim 10^6$  Hz) and microwaves ( $\sim 10^9$  Hz). Therefore, a light beam acting as a carrier wave is capable of transmitting far more information in comparison to radio waves and microwaves. A typical laser beam can transmit  $\sim 10^{12}$  speech signals over the same channel.

**(vi) In Ranging :** Lasers can be used to find the position, size and shape of a distant object. For this, a signal from a laser switches on a counting circuit and the signal reflected by the object terminates the count.

**(vii) In Atmospheric Study :** Laser is used for remote probing of the atmosphere, for detecting pollutant gases and for measuring water vapour concentration and temperatures at long ranges.

**(viii) In Biology :** The ability of laser beam to concentrate high power density of light at a point enables the study of biological samples available in very small quantities.

**(ix) In Medicine :** The laser beam is used in delicate eye surgery like cornea grafting. Using laser beam, the surgical operation is completed in a much shorter time. It is also used in the treatment of kidney stone, cancer, tumour and in cutting and sealing the small blood vessels in brain operation.

**(x) In Industry :** The laser beam is used for cutting fabric for clothing on one hand and steel sheets on the other. It can drill extremely fine holes in paper clips, single human hair and hard materials including teeth and diamond. Extremely thin wires used in cables are drawn through the diamond hole. Metallic rods can be melted and joined by means of a laser beam (laser welding). The surfaces of engine crank-shafts and the cylinder walls are hardened through heat-treatment by laser. The laser beam is used to vaporise unwanted material during the manufacture of electronic circuits on semiconductor chips.

**(xi) In War :** During war-time, lasers are used to detect and destroy enemy missiles. Now, laser-rifles, laser-pistols and laser bombs are also being made which can be aimed at the enemy in the night.

**(xii) In Space :** In space, laser has been used to control rockets and satellites and in directional radio-communication like fiber-optic telephony.

## QUESTIONS

1. Describe the construction and working of Ruby laser, a three-level laser system. What are the characteristics of a laser beam ? *(Meerut sp. paper 2005, 01)*
2. Explain the principle of laser and essential requirements to produce laser action. How is population inversion attained in a four energy level laser differ from that of a three level laser ? *(Meerut 2001, sp. paper 2005, 03, 00)*

3. Describe a He-Ne gas laser. How is population inversion achieved in this type of laser. Mention advantages of a gas laser over a solid state laser.  
*(Meerut 2000 S, 99 S, sp. paper 2006, 05, 02, 00)*
  4. Write a note on gas lasers.
  5. Explain the principle, construction and working of a CO<sub>2</sub> laser. Describe its use in experimental spectroscopy.  
*(Meerut 2006)*
  6. Explain how a semiconductor junction diode can be used as a laser. What are its merits over the other radiation-pumped lasers ?  
*(Meerut 95 S)*
  7. What is population inversion ? Explain with examples. Explain the principle and working of a semiconductor Ga-As laser. *(Meerut 2004, 02, 95, sp. paper 2004)*
  8. Discuss the condition of population inversion in a three-level laser system. Describe the working of a semiconductor laser.  
*(Meerut sp. paper 96, 93)*
  9. What are the characteristics of a laser beam ? Mention its uses.  
*(Meerut 99 S, sp. paper 2006, 05, 02, 01, 00)*
-