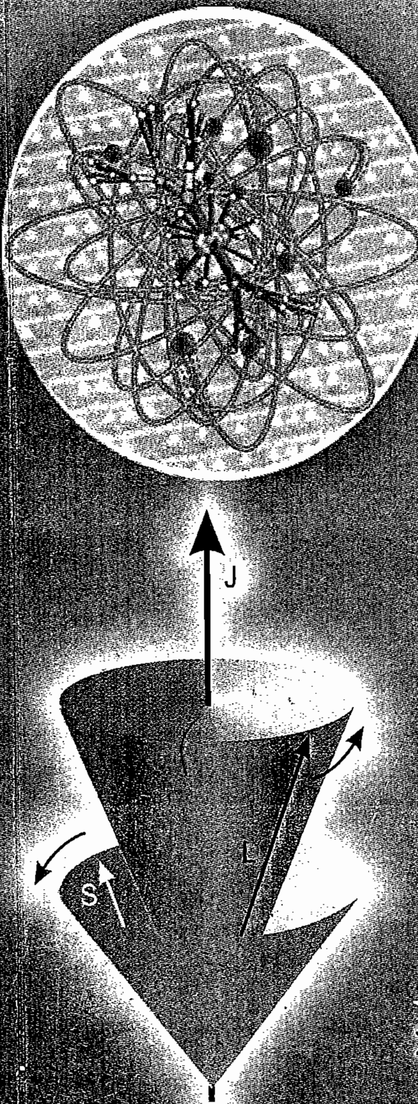
A Text Book of

ATOMIC AND MOLECULAR PHYSICS

T.Y. B.Sc. : Semester IV - Paper-II
(PH-342)



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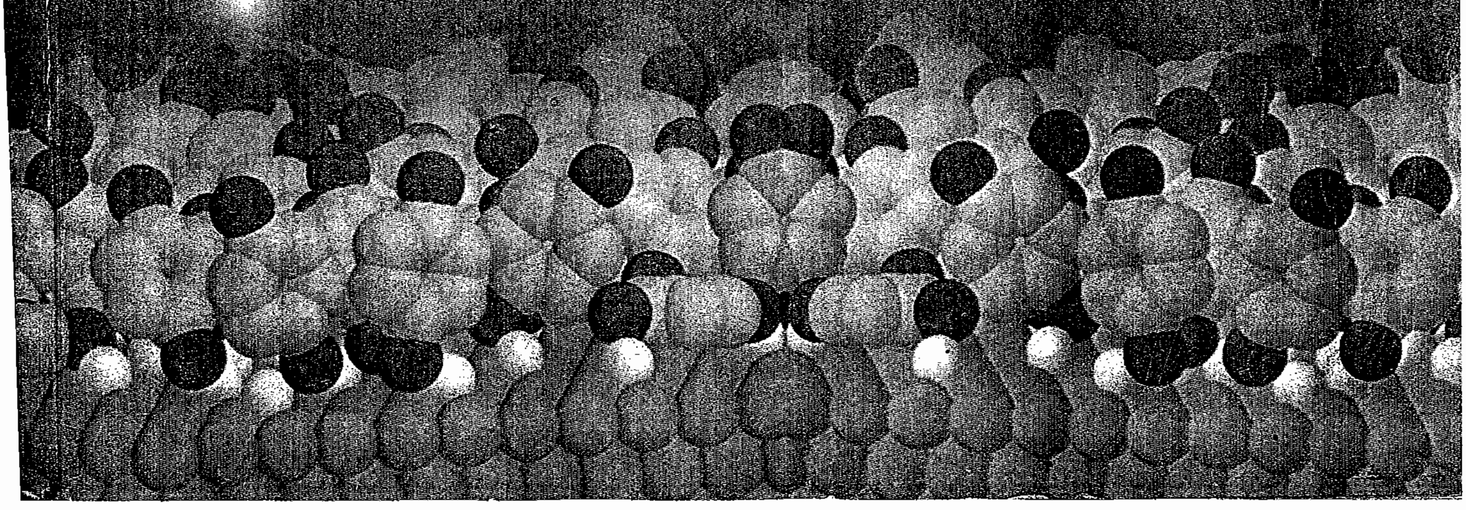

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A TEXT BOOK OF

ATOMIC AND MOLECULAR PHYSICS

For

T.Y.B.Sc. PHYSICS
Paper - II (SEMESTER - IV)

(PH - 342)

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Dr. C. V. RAMAN

The genius who won the Nobel Prize for Physics, with simple equipment barely worth Rs. 300. He was the first Asian scientist to win the Nobel Prize. He was a man of boundless curiosity and a lively sense of humor. His spirit of inquiry and devotion to science laid the foundations for scientific research in India. And he won honor as a scientist and affection as a teacher and a man.

PREFACE

This book has been written for the use of T.Y.B.Sc. Physics students of Pune University and other Universities who are specializing in physics. There are excellent books on this subject, like the classic by Beiser and White, the most informative by Gupta, Banwell, Eisberg and Hertberg. We gratefully acknowledge frequent reference to these books in course of writing this one.

The students find it very difficult to collect the matter for preparing this subject and they have to refer so many books. The students also get confused as to what depth they have to study the particular topics of the subject. Out book is sincere effort in this direction.

We have taken all the efforts to see that the all the topics included in the syllabus have been explained in detail, in a very simple and lucid manner. The subject matter has been arranged systematically and methodically. A large number of solved problems of all types have been included in the book. At the end of every chapter a set of short, long, multiple choice questions and a set of unsolved problem with answer has been given for practice.

Care has been taken to avoid mistakes and misprints in the book. In spite of this, any mistakes, errors or suggestions brought to our notice by students, teachers and readers, are most welcome.

The authors wish to express sincere thanks to **Mr. Dineshbhai Furia, Mr. Jignesh Furia, Mr. M. P. Munde** and entire staff of **Nirali Prakashan**, Pune for their kind co-operation for bringing this book in time.

December 2004 **Authors**

Popularisers.

Deepak Kr. Sharma. To be Dr. Devendra Kuntal

Syllabus

ATOMIC AND MOLECULAR PHYSICS

1. Vector atom mode, Space quantization and spinning electron, Physical interpretation of quantum numbers, Magnetic moments, Larmour Theorem, Stern-Gerlack experiment and problems. (8 L)

2. Pauli exclusion principle and electron configuration. Quantum states. Spectral notations of quantum states and problems. (5 L)

3 Spin-orbit interaction (single valence electron atom)

Energy levels of the Na atom, selection rules, spectra of sodium atom, sodium doublet, problems, based on these topics. (4 L)

4. Spectral terms of two electron atoms, terms of equivalent electrons, L-S and J-J coupling schemes, Singlet-Triplet separation for interaction energy of L-S coupling. Lande interval rule, spectra of Helium atom and problems. (8 L)

5. Atom in magnetic field, Normal Zeeman effect for single valence electron systems and problems. (4 L)

6. X-rays spectra, origin of characteristic and continuous X-ray emission spectra, Daune and Hunt law K, L, M, N series. Comparison of X-ray and optical spectra, Mosley law and its application and problems. (4 L)

7. Types of molecular spectra (Rotational, vibrational and electronic) rotational spectra of diatomic molecules, Rotational energy levels of rigid and non-rigid diatomic molecules. Isotope effect and problems. (7 L)

8. Vibrational energy levels for diatomic molecules, Energy levels of harmonic oscillator, rotation - vibration spectra of diatomic molecules, P, Q, R branches and problems based on these topics. (5 L)

9. Raman effect, Experimental arrangement to observe Raman spectra, quantum theory of Raman effect. (3 L)

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CONTENTS

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1

Vector Atom Model

The discovery of radioactivity, around 1900 and J. J. Thomson's discovery of the electron, provided a starting point for theories of atomic structure. The fact that atoms of a radioactive element are transformed into atoms of another element by emission of negative or positive charged particles led to the understanding that atoms are made up of positive and negative charged particles. On the basis of this, J. J. Thomson proposed a simple model for atom. He assumed that an atom consisted of electrons distributed in the positively charged sphere of radius 10^{-10} m. This model could not explain all features of optical spectra of hydrogen and other elements, thus discarded. In 1911, Rutherford proposed a new model based on scattering of α-particles by matter. According to this model, the positive charge of atom, instead of being distributed uniformly throughout the region of the size of the atom, is concentrated in small spherical region at the centre of dimension of the order of 10^{-15} m, and the negative charge is distributed over a sphere. Small region of positive charge is called the nucleus of the atom. Whole mass of atom lies in this region.

This model could not explain the stability of the atom and discrete atomic spectra. The scientist Neils Bohr modified the Rutherford's model in 1913 to overcome its limitations. He developed a theory of the constitution of atoms which accounted for many of the properties of atomic spectra and laid the basic foundation for later development of the atomic physics. Bohr used the quantum theory of radiation as developed by Planck and Einstein (1900). This model could not give complete picture of atom. Further, Sommerfeld modified the Bohr's model by assuming the concept of elliptical orbits for electrons and spinning motion of electron and the nucleus. This model is called Bohr-Sommefeld model. Though this model could explain the fine structure of spectral line, but it could not explain the fine structure lines and the justification for the relative intensities of the lines. To overcome the limitations of this model, a new model called vector atom model was proposed.

In this chapter, we take a review of the Bohr's atomic model, energy spectrum of hydrogen atom, Bohr-Sommerfeld model in introduction (section 1.1). Later on we will study vector atom model, concept of space quantization and electron spin, physical interpretation of quantum numbers, Stern-Gerlach experiment in details.

1.1 INTRODUCTION

Bohr's Atomic Model :

The hydrogen atom theory proposed by Neil Bohr in 1913, marked the beginning of a new era in atomic structure and spectroscopy. Bohr's theory provided the satisfactory explanation of the Balmer, Lyman, and Paschen series of hydrogen atom and the pickering series of ionized helium. In addition, he calculated the Rydberg constant on the basis of purely theoretical considerations. In short, this theory gave a physical meaning to the experimental discovery that the frequency of spectral line is given by the difference between two terms.

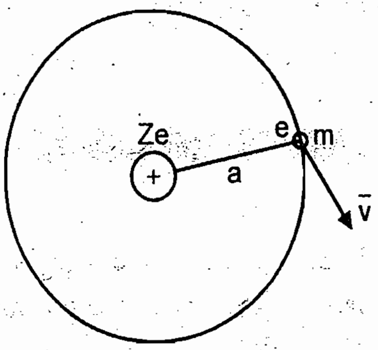


Fig. 1.1 : Bohr's circular orbit

Bohr modified the Rutherford's model by using the Planck's quantum theory of radiation. He assumed that the hydrogen atom consists of a stationary nucleus (proton) at the centre of atom whose mass is 1836 times mass of electron. A single electron revolves around the stationary nucleus. According to the Planck's quantum theory (1900), energy is radiated and absorbed in whole multiples of an elementary quantum of energy,

$$E = h\upsilon \quad \ldots (1.1)$$

where, υ is the frequency of the emitted or absorbed radiation and h is Planck's constant of action ($h = 6.64 \times 10^{-34}$ J.s). This quantum of energy is called photon.

Bohr's theory is based on the following three postulates.

First Postulate :

Bohr's first assumption was that an electron revolves in certain allowed circular orbits about the nucleus under the action of a Coulomb force. The force of attraction between the electron of charge e and the nucleus of charge Ze is given by

$$F = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a^2} \quad \ldots (1.2)$$

where a is the electron-nuclear distance, Z is the atomic number (Z = 1 for hydrogen), ε_0 is the permittivity of free space. The force given by equation (1.2) is equal to the centripetal force mv^2/a, where v is the velocity and m is the mass of the electron. For equilibrium condition,

$$\frac{mv^2}{a} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a^2} \quad \ldots (1.3)$$

which gives

$$v^2 = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{m\,a} \quad \ldots (1.4)$$

Second Postulate :

Bohr's second assumption for the hydrogen atom may be stated as "only those circular orbits for electrons are permitted for which the angular momentum ($\bar{L}$) is equal to the integral multiple of $\frac{h}{2\pi}$.

Thus,
$$L = n\left(\frac{h}{2\pi}\right) \qquad \text{... (1.5)}$$

where, n = 1, 2, 3, ...

Orbital angular momentum of an electron is given by
$$L = mva \qquad \text{... (1.6)}$$

where v is the linear velocity of electron in an orbit.

Equations (1.5) and (1.6) give
$$mva = n\left(\frac{h}{2\pi}\right) \qquad \text{... (1.7)}$$

Orbits permitted by the condition shown by equation (1.7) are called allowed orbits for electrons. These orbits are called non-radiating orbits.

Third Postulate :

A quantum of energy is radiated only when an electron jumps from higher energy orbit to the lower energy orbit and the frequency of emitted radiation is proportional to the difference between two energy states.

Thus,
$$h\upsilon = E_1 - E_2 \qquad \text{... (1.8)}$$

where υ is the frequency, E_1 and E_2 are the energies of initial and final states.

From equation (1.3), we get
$$mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a}$$
$$m^2v^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2m}{a} \qquad \text{... (1.9)}$$

Equation (1.7) gives
$$mv = \frac{n}{a}\frac{h}{2\pi}$$
$$m^2v^2 = \frac{n^2}{a^2}\frac{h^2}{4\pi^2} \qquad \text{... (1.10)}$$

From equations (1.9) and (1.10), we get
$$a = \frac{\varepsilon_0 n^2 h^2}{\pi me^2Z} \qquad \text{... (1.11)}$$

For hydrogen atom, Z = 1, the radius of nth orbit is given by
$$a_n = \frac{\varepsilon_0 n^2 h^2}{\pi me^2} \qquad \text{... (1.12)}$$

where n is called principal quantum number.

Equation (1.12) indicates that

$$a_n \propto n^2, \quad n = 1, 2, 3, \ldots\ldots$$

Thus radii of Bohr's orbit are proportional to the square of natural numbers.

Radius of first orbit, n = 1 is

$$a_1 = 0.53 \times 10^{-10} \text{ m}$$

$$a_1 = 0.53 \text{ A}^{\circ}$$

From equations (1.7) and (1.12), the velocity of an electron in n^{th} orbit is given by

$$v_n = \frac{e^2}{2\varepsilon_0 nh} \quad \ldots (1.13)$$

The kinetic energy of an electron in n^{th} orbit will be

$$T = \frac{1}{2} m v_n^2 \quad \ldots (1.14)$$

$$T = \frac{me^4}{8\varepsilon_0^2 n^2 h^2} \quad \ldots (1.15)$$

The potential energy, (U) of the electron when it is at a distance 'a' from the nucleus is given as

$$U = \int_a^{\infty} F \, dr \quad \ldots (1.16)$$

where F is the Coulomb's electrostatic force given by equation (1.2). Thus equation (1.16) gives

$$U = -\frac{me^2}{4\varepsilon_0^2 n^2 h^2} \quad \ldots (1.17)$$

The total energy of an electron in n^{th} orbit is sum of kinetic and potential energies.

Thus equations (1.15) and (1.17) give,

$$E_n = T + U$$

$$E_n = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2} \quad \ldots (1.18)$$

where E_n is the total energy of an electron in n^{th} orbit.

Equation (1.18) shows that

$$E_n \propto \left(\frac{1}{n^2}\right)$$

For the first orbit, n = 1, we get

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

Thus 13.6 eV energy is required to remove the electron completely from the first orbit of hydrogen atom. This is called the binding energy of an electron in first orbit. This is the minimum energy state of an electron. This state is called the ground state. The energy of an electron in the subsequent states is given by,

$$E_n = -\frac{13.6}{n^2}\ \text{eV} \qquad \text{...(1.19)}$$

Equation (1.19) indicates that the total energy of an electron increases as it goes away from the nucleus. This also indicates that energy difference of electron in consecutive orbits decreases with increase in the value of n.

Emission of Spectral Radiation :

According to the third postulate, when there is transition of an electron from higher energy orbit to the lower energy orbit, a photon of energy $h\upsilon$ is emitted. Let us consider the transition of electron from higher energy n^{th} orbit to lower energy m^{th} orbit, then the energy quanta emitted is given by,

$$h\upsilon = E_n - E_m \qquad \text{...(1.20)}$$

where E_n is the energy of electron in n^{th} orbit and E_m is the energy of an electron in m^{th} orbit.

From equations (1.18) and (1.20), we get

$$h\upsilon = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2} - \left[-\frac{me^4}{8\varepsilon_0^2 h^2 m^2}\right]$$

$$\upsilon = \frac{me^4}{8\varepsilon_0^2 h^3}\left[\frac{1}{m^2} - \frac{1}{n^2}\right] \qquad \text{...(1.21}$$

But $c = \upsilon\lambda$

where λ is wavelength of spectral line, c is the velocity of light.

Thus from equation (1.21), we get

$$\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0^2 ch^3}\left[\frac{1}{m^2} - \frac{1}{n^2}\right] \qquad \text{...(1.22}$$

The quantity $\frac{1}{\lambda} = \bar{\upsilon}$ is called wave number

$$\therefore \quad \bar{\upsilon} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right] \qquad \text{...(1.23)}$$

where R is the Rydberg's constant and it is given by

$$R = \frac{me^4}{8\varepsilon_0^2 ch^3} = 1.097 \times 10^7\ \text{m}^{-1} \qquad \text{...(1.24)}$$

Hydrogen spectrum consists of the following five series of spectral lines.

(1) **Lyman series :** This series exists when there is transition of an electron initial orbit n = 2, 3, 4 ... to final lower orbit m = 1. Wavelength of spectral lines of this series lies in the ultra-violet region.

(2) **Balmer series :** Spectral lines of Balmer series are observed when an electron transition is from initial orbit n = 3, 4, 5 ... to final lower orbit m = 2. This gives the visible region.

H_α line : transition of electron is from n = 3 to m = 2

H_β line : transition of electron is from n = 4 to m = 2.

H_γ line : transition of electron is from n = 5 to m = 2.

H_δ line : transition of electron is from n = 6 to m = 2

and so on ....

(3) **Paschen series :** For this series, electron transition is from n = 4, 5, 6 ... to m = 3. Spectral lines lie in the near infrared region.

(4) **Bracket series :** For this, electron transition is from n = 5, 6, 7 ... to m = 4. Spectral lines lie in the infrared region.

(5) **Pfund series :** For this series, electron transition is from n = 6, 7, 8 .... to m = 5. It lies in the far infrared region.

The spectral wavelengths calculated using the Bohr's relation (1.23) are in good agreement with the experimentally observed wavelengths for hydrogen atom. This is the good success of Bohr's theory.

Limitations of Bohr's Theory :

Following are few limitations of Bohr's theory.

1. It cannot explain the relative intensities of the spectral lines.
2. It cannot explain the spectra of two or more electron atom.
3. It cannot give details of fine structure of spectral line. According to the Bohr's theory, H_α line is single line of wavelength 6563 A°. But experimentally it is observed that H_α line consists of two spectral lines of small wavelength difference 1.4 A°. Bohr's theory could not explain this fine structure of spectral line.

Energy Levels and Series transitions of Hydrogen :

Fig. 1.2 shows the energy levels and different series transitions of hydrogen atom. In an energy level diagram each Bohr orbit or stationary state is represented by a horizontal line. Vertical scale is taken in terms of wave number ($\bar{\upsilon}$). Equation (1.18) shows that the energy values of quantized states are negative and approaches zero as the principal quantum number n increases.

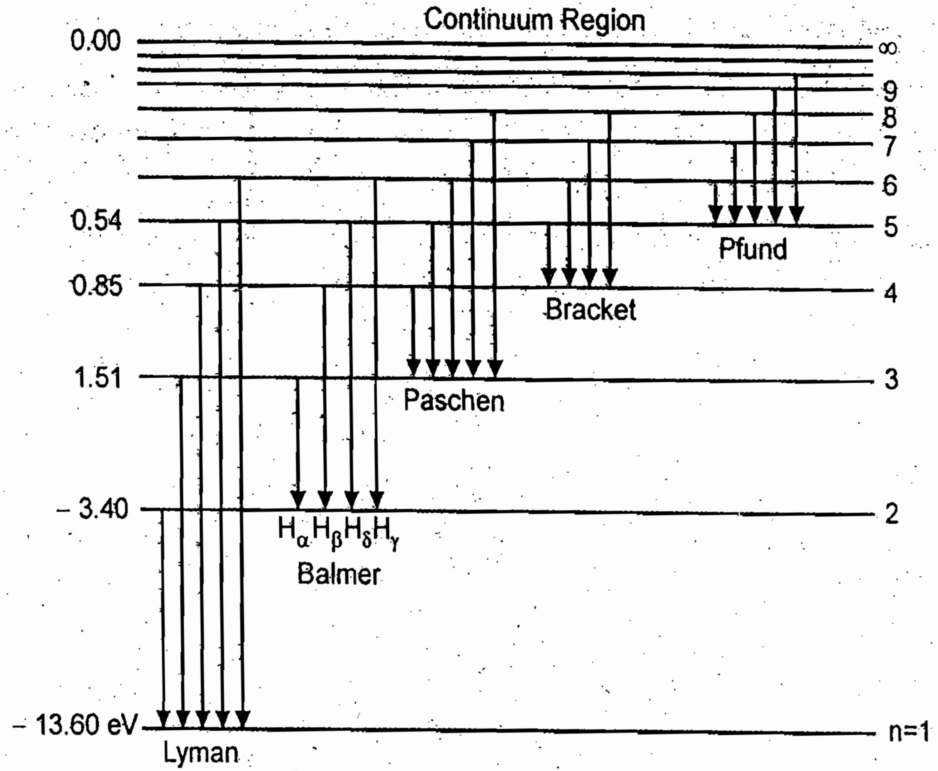


Fig. 1.2 : Energy levels and series transitions of hydrogen atom (Not to the scale)

Bohr-Sommerfeld Theory for hydrogen like atom :

Bohr's theory of hydrogen atom gives the satisfactory explanation for the existence of different spectral lines. Results of Bohr's theory are in good agreement with the experimental observations for the hydrogen atom. But this theory fails to explain the fine structure of atom and the different relative intensities of spectral lines. This may be due to Bohr's assumptions. He assumed that the nucleus is stationary and an electron moves in the circular orbit around the nucleus. Mass of an electron is considered to be negligible in comparison with nucleus.

Sommerfeld considered the motion of an electron and the nucleus such that both moves around their common centre of mass. This gives the concept of reduced mass of an electron-nucleus system as a whole. According to Sommerfeld, motion of an electron in an elliptical orbit, with nucleus at one of the focus, gives a system with two degrees of freedom.

Each degree of freedom must be quantized separately. In the polar coordinates, the position of an electron in an elliptical orbit, is specified with position coordinate r and the azimuthal angle θ. Fig. 1.3 shows the motion of an electron in an elliptical orbit.

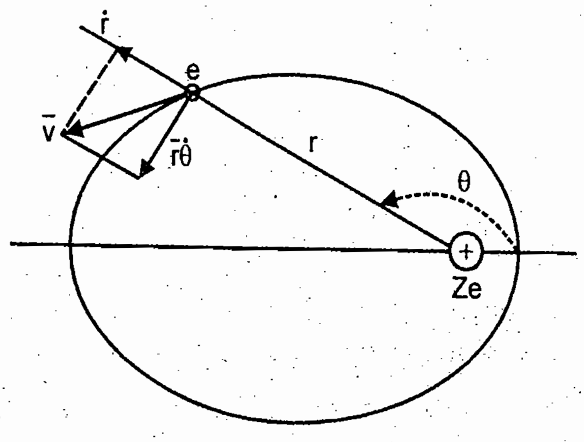


Fig. 1.3 : Sommerfeld's elliptical orbit

Both the coordinates r and θ change with time t. If m and v represent mass and linear velocity of an electron respectively, then kinetic energy of an electron is given by

$$T = \frac{1}{2} mv^2$$

Here, v has two components : (i) radial velocity $\frac{dr}{dt}$, (ii) angular velocity $r\frac{d\theta}{dt}$.

$$T = \frac{1}{2} m\left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\theta}{dt}\right)^2\right]$$

$$T = \frac{1}{2} m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2} mr^2\left(\frac{d\theta}{dt}\right)^2 \quad \text{... (1.25)}$$

Equation (1.25) involves two displacement coordinates r and θ and two momentum coordinates P_r and P_θ which are given as

$$P_r = m\left(\frac{dr}{dt}\right) \quad \text{... (1.26)}$$

$$P_\theta = mr^2\left(\frac{d\theta}{dt}\right) \quad \text{... (1.27)}$$

The potential energy is given by,

$$U = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} \quad \text{... (1.28)}$$

Two quantum conditions corresponding to two degrees of freedom are given by

$$\oint P_r \, dr = rh \quad \text{... (1.29)}$$

$$\oint P_\theta \, d\theta = kh \quad \text{... (1.30)}$$

where r and k are radial and azimuthal quantum numbers respectively. Both r and k takes integral values. P_r and P_θ are radial and angular momenta of an electron which are given by equations (1.26) and (1.27).

The detail analysis of Sommerfeld theory gives the principal quantum number as

$$n = r + k \quad \text{... (1.31)}$$

where

$$r = 0, 1, 2, 3 \ldots\ldots$$

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

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

Introduction of elliptical orbits do not generate new energy states for the hydrogen atom, but an electron may move in different orbits. For example, for given principal quantum number n, the energy value is fixed, but there are n different quantized orbits available for electron.

For n = 1 : k = 1, r = 0, only one circular orbit is possible.

For n = 2 : k = 1, 2, and r = 0, 1.

Thus there are two possible orbits, these are

k = 2 and r = 0	circular orbit
k = 1 and r = 1	elliptical orbit.

For n = 3 : We get k = 1, 2, 3 and r = 0, 1, 2.

Thus there are three obits possible.

k = 3 and r = 0	circular orbit
k = 2 and r = 1	elliptical orbit
k = 1 and r = 2	elliptical orbit

For n = 4 : We get k = 1, 2, 3, 4 and r = 0, 1, 2, 3.

There exist four possible orbits.

k = 4 and r = 0	circular orbit
k = 3 and r = 1	elliptical orbit
k = 2 and r = 2	elliptical orbit
k = 1 and r = 3	elliptical orbit

In general, if there are n number of orbits, then one is circular and remaining (n − 1) orbits are elliptical orbits. Fig. 1.4 shows the Sommerfeld elliptical orbits for n = 1, 2 and 3.

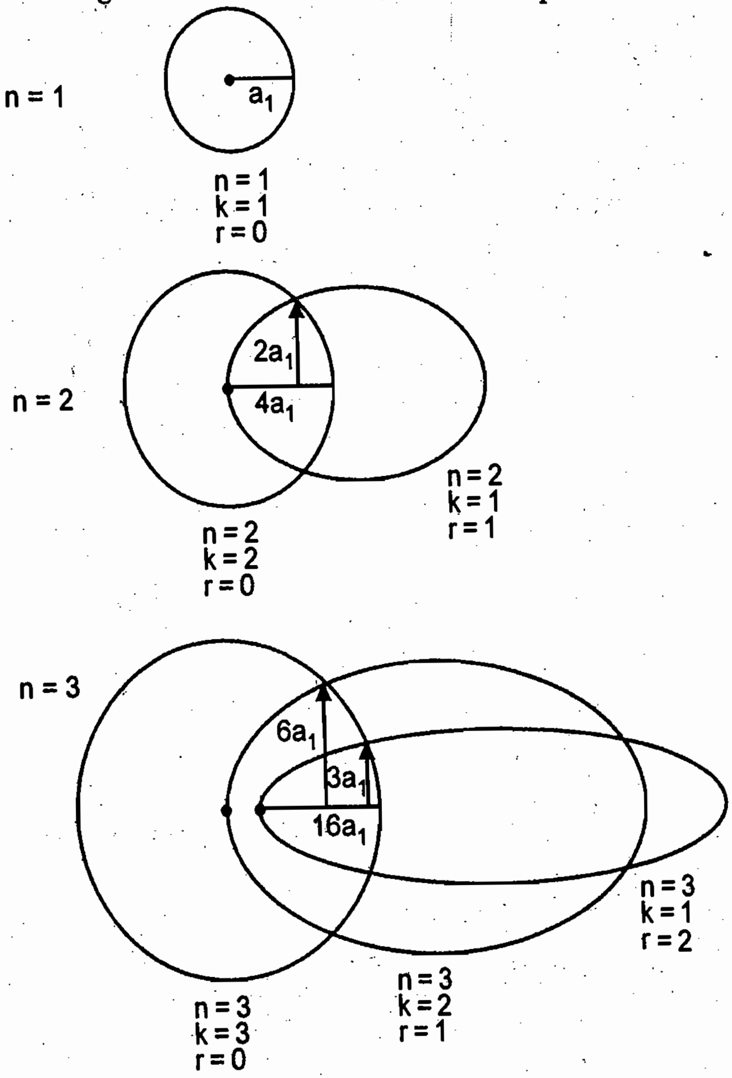


Fig. 1.4

Each quantized orbit is determined by two out of the three quantum numbers n, k and r given by equation (1.31). Normally, total or principal quantum number n and azimuthal quantum number θ are used to specify the quantized state.

According to this model, a given spectral line is produced by a number of different but equivalent transitions. For example, for n = 4, there are four possible orbits. All these orbits have same energy value as determined by total quantum number n. Such atomic states that can be described by more than one set of quantum numbers, which corresponds the same energy, are called ***degenerate levels***. If the special theory of relativity is applied to the motion of electron, then in case of single electron system, degeneracy can be removed. The velocity of electron in an elliptical orbit is not constant. It is more when an electron is near the nucleus and less when it is far away from the nucleus.

The mass of an electron varies with the velocity. According to the Sommerfeld, path of an electron is a precessing ellipse. The rate of precession is different for different orbits for the same ***n value***. This gives n different states with slight difference in energies. This may remove the degeneracy and leads to the fine structure.

Effect of Finite Motion of Nucleus :

According to Sommerfeld, the nucleus is not stationary but it has finite motion. Thus the system of electron and nucleus revolves about its common centre of mass. The mass of hydrogen nucleus is 1836 times greater than the electron mass. The Fig. 1.5 shows the motion of an electron and the nucleus about an axis passing through their centre of mass. d_N and d_e are the distances of the nucleus and electron from the centre of mass (C.M.) respectively. m_N and m_e are the masses of the nucleus and electron respectively. v_N and v_e are the velocities of the nucleus and electron respectively. ω is the angular velocity of the nucleus and an electron.

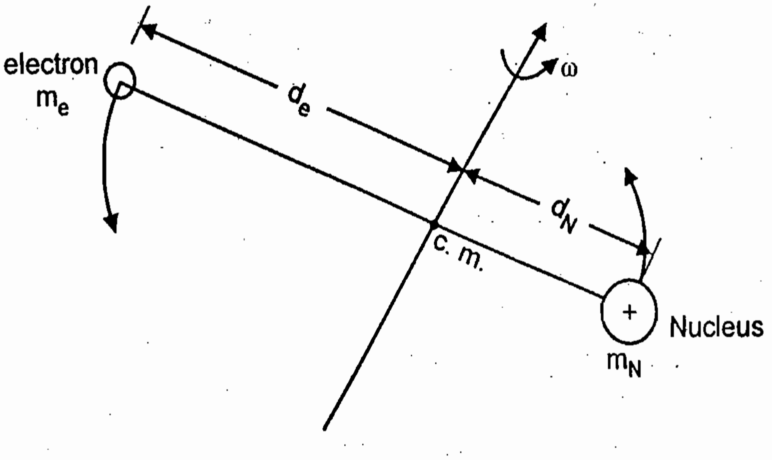


Fig. 1.5 : Motion of the nucleus and electron about their centre of mass

According to the conservation of momentum of atom we get,

$$m_N v_N = m_e v_e = p \quad \text{... (1.32)}$$

where p is the momentum of the system.

The total kinetic energy, T of the system is given by,

$$T = T_N + T_e \quad \text{... (1.33)}$$

where T_N and T_e are kinetic energies of the nucleus and an electron. These are given by,

$$T_N = \frac{p^2}{2m_N}$$

and

$$T_e = \frac{p^2}{2m_e}$$

Thus, we get

$$T = \frac{p^2}{2}\left[\frac{m_N + m_e}{m_N\, m_e}\right]$$

$$T = \frac{p^2}{2\mu} \qquad \text{... (1.34)}$$

where $\mu = \left(\frac{m_N\, m_e}{m_N + m_e}\right)$ is the reduced mass of the system.

With this value of reduced mass μ, the Rydberg constant given by equation (1.24) becomes,

$$R_S' = \frac{\mu e^4}{8\varepsilon_0^2\, ch^3} = 1.0967758 \times 10^7\ m^{-1} \qquad \text{... (1.35)}$$

This value is slightly smaller than the given equation (1.24).

Sommerfeld's Fine Structure Constant :

The velocity of an electron in its orbit is given by equation (1.4)

$$v^2 = \frac{Ze^2}{m\,a} \qquad \text{... (1.36)}$$

The quantity $\frac{1}{4\pi\varepsilon_0}$ is normalised to unity for simplicity. The expression for the radius of the orbit in the normalised unit is given by

$$a = \frac{n^2 h^2}{4\pi^2 me^2 Z} \qquad \text{... (1.37)}$$

Equations (1.36) and (1.37) give,

$$v = \frac{2\pi e^2 Z}{h \cdot n} \qquad \text{... (1.38)}$$

Comparing this with the velocity of light c,

$$\frac{v}{c} = \frac{2\pi\, e^2 Z}{ch \cdot n} \qquad \text{... (1.39)}$$

The quantity $\left(\frac{v}{c}\right)$ is called *Sommerfeld's fine structure constant, α.*

For the first Bohr orbit of hydrogen, (i.e. Z = 1, n = 1), we get,

$$\frac{v}{c} = \alpha = \frac{2\pi e^2}{ch} \qquad \text{... (1.40)}$$

$$\alpha \cong \frac{1}{137} \qquad \text{... (1.41)}$$

This fine structure constant is important in the study of the fine structure of hydrogen spectrum.

If the relativistic effect and the finite motion of nucleus is considered, the energy of an electron is found to depend on both total and azimuthal quantum numbers. The Sommerfeld's expression for the energy of an electron in the (n, k) state can be written directly as

$$E_{n,k} = -\frac{2\pi^2 \mu e^4 Z^2}{n^2 h^2}\left[1 + \frac{\alpha^2 Z^2}{n}\left(\frac{1}{k} - \frac{3}{4n}\right)\right] \qquad \dots(1.42)$$

where μ is the reduced mass of the system, α is fine structure constant given by equation (1.41).

Since the value of α is very small, the contribution to the energy $E_{n,\,k}$, is small due to the azimuthal quantum number k. The effect of the relativistic consideration is to replace the single energy level by several levels with slight difference in energies. Therefore, the frequency of the radiation emitted in the transition of an electron from n_2 to n_1 levels is slightly different according to the different values of k. As a result, a group of slightly separated spectral lines appears rather than the single line in case of hydrogen spectrum. Sommerfeld theory predicts many spectral lines for the fine structure. But all these spectral lines are not observed experimentally. The agreement between theory and experiment was obtained by putting some restrictions on the transitions. These restrictions are called *selection rules*. Allowed transitions are given by the selection rule on azimuthal quantum number k.

$$\Delta k = \pm 1 \qquad \dots(1.43)$$

Fig. 1.6 represents the energy levels of hydrogen given by Sommerfeld. (Not to the scale).

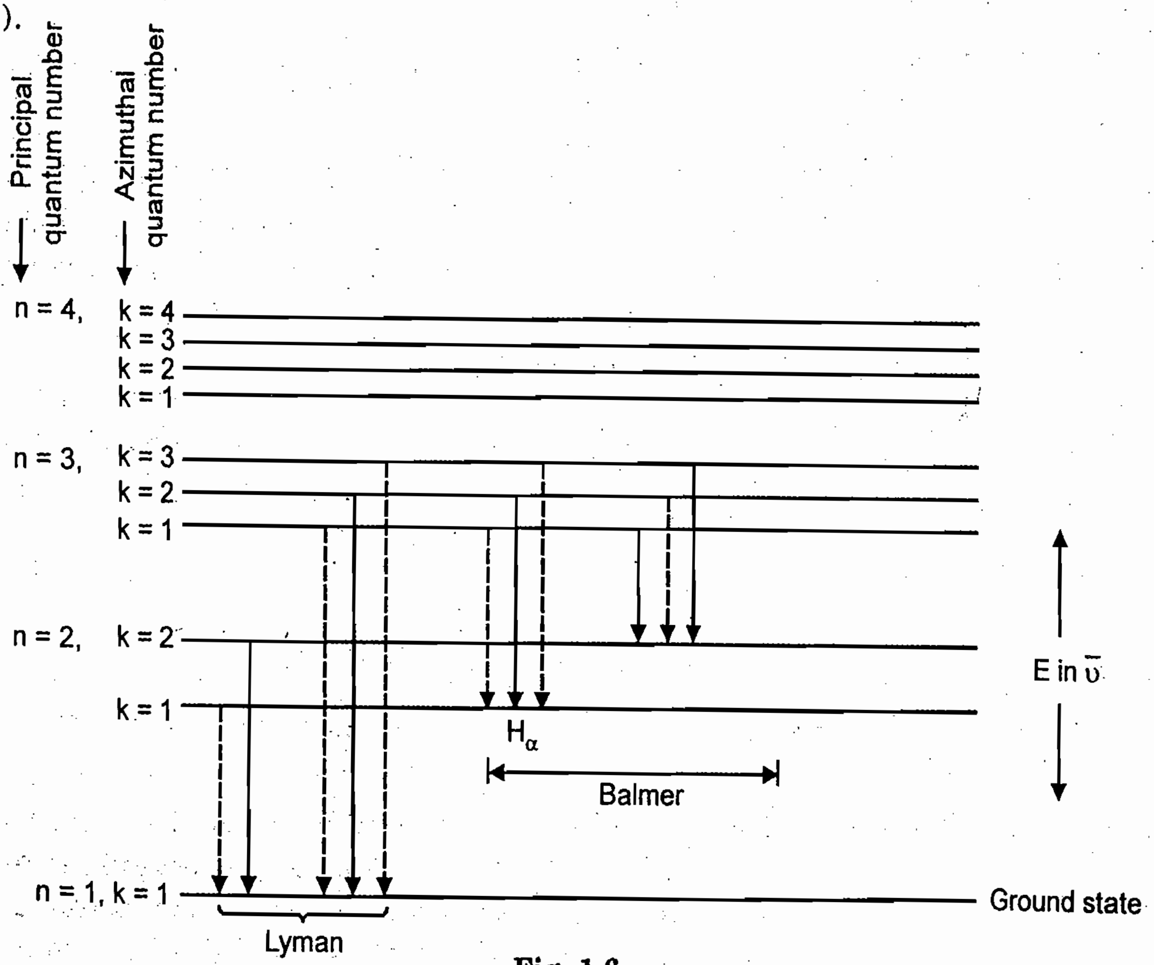


Fig. 1.6

1.2 VECTOR ATOM MODEL

Application of theory of relativity and the concept of elliptical orbits by Sommerfeld to the Bohr's theory, helped to explain the fine structure of spectra of hydrogen. For more than one-electron atoms, there was much disagreement between theory and experimental results. Bohr-Sommerfeld model fails to explain Zeeman effect and Stark effect. It could not give any information about the relative intensities of spectral lines. This may be due to the fact that Bohr's theory is based on the mixture of classical mechanics and the concept of quantum theory. Laws of classical mechanics are applied for orbital motion of electron while the concept of quantum theory is used for existance of stationary orbits and emission of radiation in a discrete form. In order to overcome all these difficulties, efforts were being taken by the scientists. The solution to the problem came in 1923, with De'Broglie's new theory of quantum dynamics and association of waves to the particles in motion.

The wavelength of such particles in motion is given by,

$$\lambda = \frac{h}{mv} \qquad \ldots (1.44)$$

where m is the mass of moving particle, v is the velocity and h is Planck's constant. This led to the concept of wave mechanics or quantum mechanics. Later on, this quantum theory was greatly improved and extended by Schrodinger. He successfully applied the quantum mechanics to the hydrogen atom and obtained the discrete energy states.

$$E_n = -\frac{2\pi^2 me^4 Z^2}{n^2 h} = -\frac{13.6}{n^2} \text{ eV} \qquad \ldots (1.45)$$

where m is mass of electron, h is Planck's constant and n is the principal quantum number which it takes only whole integral values i.e. $n = 1, 2, 3 \ldots\ldots \infty$

This n is same as given by Bohr-Sommerfeld theory, but its origin is natural.

This nature of the discrete energy states was the natural outcome of solution of Schrodinger's equation. While in case of the Bohr-Sommerfield theory, the discreteness of energy states was introduced quite artificially. Moreover, quantum mechanics solves many of the problems which could not be solved by the Bohr-Summerfeld theory. One of the most important outcome of the quantum mechanics was concept of quantum numbers. Thus through the continuous effects of the scientists Bohr, Sommerfeld, Uhlenbeck, Schrodinger, Goudsmit, Pauli, Stern and Gerlach, a new model of atom was suggested. This model is called vector atom model.

Vector atom model is based on :

(i) The concept of space quantization.

(ii) The concept of spinning electron.

The vector atom model is based on the concept of space quantisation and electron spin.

1.3 SPACE QUANTIZATION

As mentioned earlier, the motion of single electron of hydrogen like atom has been confined to two degrees of freedom. An electron orbit or energy state is determined by two of the three quantum numbers n, k and r. When the motion of an electron is considered in three dimensional space, then this gives three degrees of freedom. This leads to necessity of three quantum numbers to specify each energy state, instead of two. Addition of third quantum number does not affect size and shape of the Bohr-Sommerfeld orbits, but it specifies orientation of orbits with reference to some direction in space. When an atom is placed in uniform magnetic field $\bar{H}$, then the fixed axis in space is considered along the direction of the magnetic field. Due to the magnetic field $\bar{H}$, the plane of the orbit precesses about $\bar{H}$, just like the top precesses in a gravitational field. The orbital angular momentum vector generates the cone about the field direction, $\bar{H}$. Fig. 1.7 shows the motion of electron with three degrees of freedom. The position of an electron in the polar coordinates is given by r, θ and φ. Reference axis is considered along $\bar{H}$. The angle δ is the angle between $\bar{H}$ and orbital angular moment $\bar{L}$ of an electron. The vector $\bar{L}$ is normal to the orbit of an electron. Due to the quantum condition, the angle α takes certain discrete values. This gives rise to certain discrete orientations of orbits with respect to the $\bar{H}$. Thus the electron orbits are quantized in space. This is called **space quantization**. Consideration of three degree of freedom leads to the three quantum numbers n, k and m. The quantum number m is called **magnetic quantum number** and takes the values

$$\left.\begin{aligned} m &= \pm 1, \pm 2, \pm 3 \ldots\ldots \pm k \\ \text{where} \qquad k &= 1, 2, 3, \ldots\ldots n \\ n &= 1, 2, 3 \ldots\ldots \infty \end{aligned}\right\} \qquad \ldots (1.46)$$

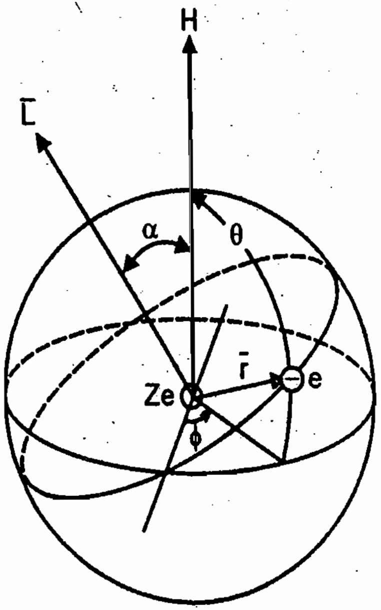


Fig. 1.7 : An electron motion in orbit with three degrees of freedom (r, θ and φ)

In vector atom model, quantum numbers n, k and m given by Bohr-Sommerfeld theory are replaced by new quantum numbers n, l and m_l as per the quantum mechanics. These are the principal quantum number (n), the orbital quantum number (l) and the orbital magnetic quantum number m_l. The values of these quantum numbers are

$$\left.\begin{aligned} n &= 1, 2, 3 \ldots\ldots\ldots \infty \\ l &= 0, 1, 2, 3 \ldots\ldots (n-1) \\ m_l &= -l, (-l+1), \ldots, 0, 1, \ldots (l-1), l \end{aligned}\right\} \qquad \ldots (1.47)$$

According to the quantum mechanics, the orbital angular momentum of an electron is given by,

$$\bar{L} = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right) \qquad \text{...(1.48)}$$

The projection of $\bar{L}$ on the direction of magnetic field $\bar{H}$ (i.e. along the Z-axis) has magnitudes which are given by,

$$L_z = m_l\left(\frac{h}{2\pi}\right) \qquad \text{...(1.49)}$$

where m_l is the orbital magnetic quantum number. Fig. 1.8 represents the space quantization of the orbital angular momentum for $l = 2$ and 3.

For $l = 2$, the number of orientations of $\bar{L}$ in space are $(2l + 1) = 5$. The magnitude of $\bar{L}$ is given by,

$$l^* = \sqrt{l(l+1)} \qquad \text{...(1.50)}$$

$$\therefore \quad l^* = \sqrt{2(2+1)} = \sqrt{6}$$

For $l = 3$, the number of orientations of $\bar{L}$ in space are

$$(2l+1) = (2 \times 3 + 1) = 7$$

The magnitude of $\bar{L}$ is given by,

$$l^* = \sqrt{3(3+1)} = \sqrt{12}$$

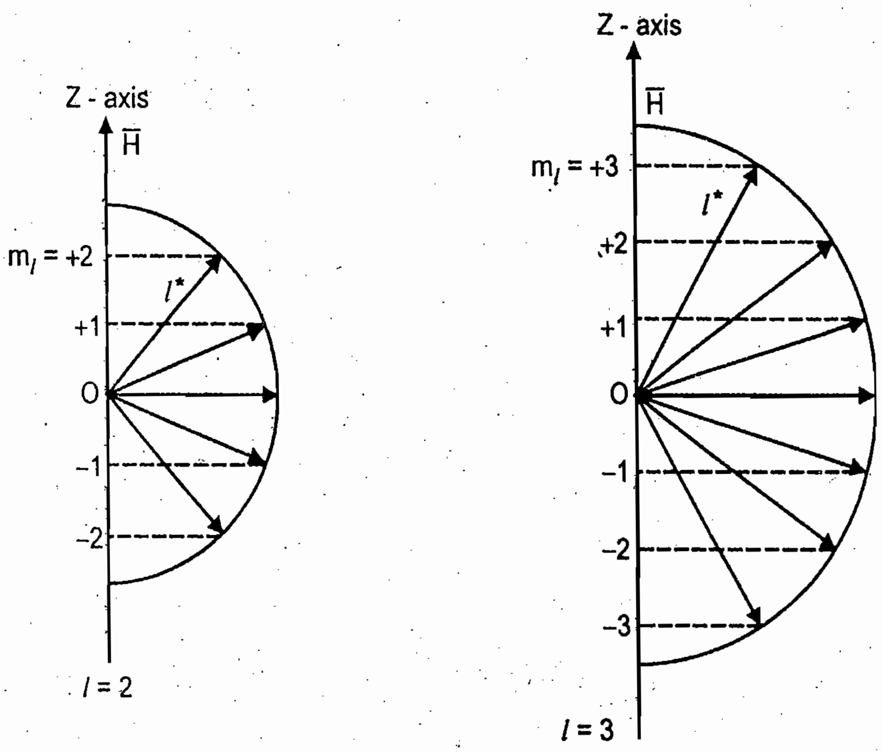


Fig. 1.8 : Space quantization of orbital angular momentum for $l = 2$ and $l = 3$

The quantization of the direction of $\bar{L}$ with respect to the external magnetic field $\bar{H}$, is called space quantization.

1.4 ELECTRON SPIN

According to the quantum mechanics, the Schrodinger's equation, when applied to the hydrogen atom, results into the three quantum numbers n, l and m_l for the specification of energy state of an electron. These three quantum numbers could not explain unusual feature noted in the spectra of certain gases, such as sodium vapour. Close examination of one prominent line in the emission spectrum of sodium is a doublet. The wavelengths of two lines of doublet are 5890 A° and 5896 A°. In order to solve this difficulty, S. Goudsmit and G. Uhlenbeck proposed the new concept of electron spin. According to this, electron has spinning motion about an axis passing through its centre. Two states, spin up and spin down are proposed. Corresponding to the spin motion, an electron has spin angular momentum $\bar{S}$ which given by

$$\bar{S} = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$

where s is spin quantum number. It's value is $s = \frac{1}{2}$.

The orbital angular momentum vector $\bar{L}$ can never be aligned parallel or antiparallel to the applied external magnetic field $\bar{H}$. This is because the L_z must be less than the total angular momentum L. If $L_z = 0$, then $\bar{L}$ is perpendicular to $\bar{H}$. According to the three-dimensional picture, the $\bar{L}$ lies on the surface of a cone which makes an angle α with the magnetic field direction i.e. Z-axis. Fig. 1.9 shows that the vector $\bar{L}$ lies on the surface of the cone for $l = 3$.

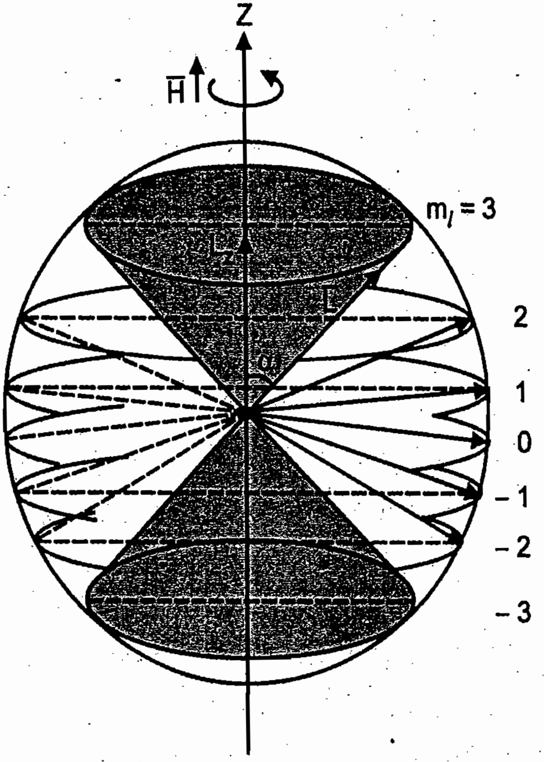


Fig. 1.9 : Vector $\bar{L}$ lies on the surface of cone

From Fig. 1.9, the angle α between $\bar{L}$ and $\bar{H}$ (i.e. L_z) is given by,

$$\cos\alpha = \frac{L_z}{|\bar{L}|} = \frac{m_l}{\sqrt{l(l+1)}} \qquad \text{... (1.51)}$$

Thus an angle α is quantized. The m_l cannot be greater l-value and thus the value of α cannot be equal to zero.

In the presence of the magnetic field $\bar{H}$, the energy of an electron is slightly different for the two spin directions. This energy difference accounts for the existence of the sodium doublet. The quantum numbers corresponding to the spin of electron are

$$\left.\begin{aligned} m_S &= +\frac{1}{2} \text{ for the spin up state} \\ m_S &= -\frac{1}{2} \text{ for the spin down state} \end{aligned}\right\} \qquad \text{... (1.52)}$$

This is known as spin magnetic quantum number. According to the quantum mechanics, the physical spinning of an electron is not correct because the electron is a point particle, without spatial size. To overcome this conceptual difficulty, all the experimental proofs support that the electron does have some intrinsic property. This is called *spin of an electron* which results into the spin magnetic quantum number (m_S), the fourth quantum number. Sommerfeld and Paul Dirac pointed out that this quantum number has origin in the relativistic properties of an electron.

1.5 QUANTUM NUMBERS

To describe the complete quantum state an electron in the atom, certain parameters are used. These sets of parameters are called quantum numbers. Schrodinger applied the quantum mechanics to the hydrogen atom and obtained the discrete energy states given by equation (1.45). The discrete nature of the energy states is the natural outcome of the Schrodinger's equation which is characterised by three quantum numbers- principal quantum number n, orbital angular momentum quantum number l, orbital magnetic quantum number m_l. The restrictions on these numbers are

$$\begin{aligned} n &= 1, 2, 3, 4, \ldots\ldots\ldots \infty \\ l &= 0, 1, 2, 3 \ldots\ldots (n-1) \\ m_l &= -l, (-l+1), \ldots\ldots 0, \ldots\ldots (l-1), l \end{aligned}$$

In addition to these three quantum numbers, the fourth quantum number called spin magnetic quantum number m_S is found to be necessary for the complete specification of the energy states. This spin magnetic quantum number came through the concept of electron spin which is intrinsic property of an electron as discussed in section (1.4).

(a) **Principal quantum number (n) :** The *principal quantum number (n) specifies the orbit number, size of the orbit and the energy* of the state as given by equations (1.12) and (1.45) respectively.

$$a_n = \left(\frac{\varepsilon_0 h^2}{\pi m e^2}\right)\frac{n^2}{Z}$$

$$E_n = -\left(\frac{m e^4}{8\varepsilon_0^2 h^2}\right)\frac{Z^2}{n^2}$$

The above relations indicate that the size of orbit and energy state depends on principal quantum number.

$$a_n \propto n^2$$

$$E_n \propto \frac{1}{n^2}$$

The values of n are

$$n = 1, 2, 3, 4 \ldots\ldots \infty$$

which represents the energy levels or shells K, L, M, N, O, P ...... respectively. The total number of electrons in a shell are $2n^2$.

(b) Orbital quantum number (l) : This quantum number arises due to the orbital motion of an electron in the orbit. This gives rise to the orbital angular momentum of electron. On the basis of classical mechanics, it is given by,

$$\vec{L} = m(\vec{v} \times \vec{a})$$

where m is mass of electron, $\vec{v}$ is velocity and $\vec{a}$ the radius vector. $\vec{L}$ is perpendicular to the plane of electron orbit.

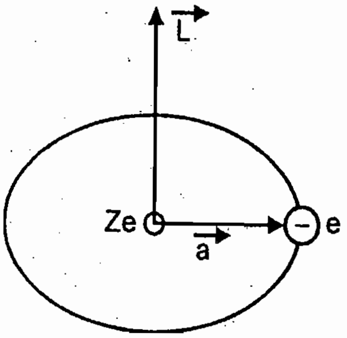


Fig. 1.10

According to the Bohr's second postulate, orbital angular momentum $\vec{L}$ of electron is given by,

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

If L = 0 in Bohr's model, then it indicates that the motion of electron is along the straight line through the nucleus. This is not physically acceptable solution.

The difficulties are resolved when the quantum mechanics is applied to the atomic system. According to the quantum mechanics, orbital angular momentum of an electron takes the discrete values as

$$\vec{L} = \sqrt{l(l+1)}\,\frac{h}{2\pi} \qquad \text{... (1.53)}$$

where l *is called orbital angular momentum quantum number*. The value of l is restricted to

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

n is the principal quantum number.

Equation (1.53) shows that for L = 0, (l = 0) is an acceptable value for $\vec{L}$. Quantum mechanically, L = 0 indicates the spherically symmetric electron cloud with no axis of revolution.

The values of l = 0, 1, 2, 3, 4, ... etc. represent the subshells s, p, d, f, g, ... etc. respectively.

For example,

n = 1,	K-shell,	l has only one value,	$l = 0$	s-subshell
n = 2,	L-shell,	l has two values,	$l = 0$	s-subshell
			$l = 1$	p-subshell
n = 3,	M-shell,	l has three values,	$l = 0$	s-subshell
			$l = 1$	p-subshell
			$l = 2$	d-subshell

And so on.

(c) **Orbital magnetic quantum number (m_l) :** If the atom is placed in weak magnetic field $\bar{H}$, then, the orbital angular momentum $\vec{L}$ of an electron interacts with the applied magnetic field $\bar{H}$. According to the quantum mechanics, the quantization of the direction of $\vec{L}$ takes place in discrete manner. The projection of $\vec{L}$ on the direction of external magnetic field along the Z-axis is given by

$$L_z = m_l \frac{h}{2\pi} \qquad \text{... (1.54)}$$

where m_l is called orbital magnetic angular momentum. The allowed values of m_l are

$$m_l = -l, (-l+1), \ldots\ldots 0, \ldots\ldots (l-1), l$$

This shows that, for the given l, there are $(2l + 1)$ possible orientations of electron orbit in space with respect to the magnetic field direction ((Z-axis). This is known as the space quantization which is discussed in detail in section (1.3).

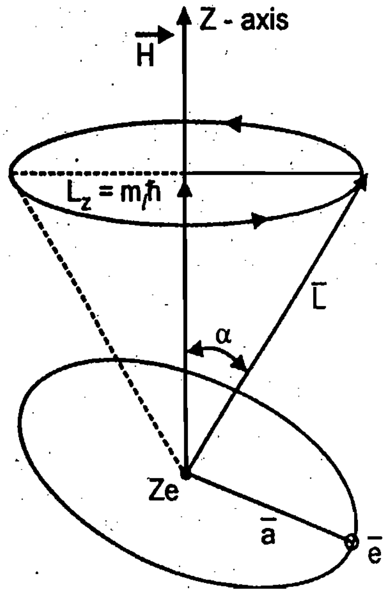


Fig. 1.11 : Vector $\vec{L}$ lies on the surface of a cone and precesses about $\vec{H}$

The angle between $\vec{L}$ and $\bar{L}_z$ is given by equation (1.51) as

$$\cos\alpha = \frac{L_z}{|\vec{L}|} = \frac{m_l}{\sqrt{l(l+1)}}$$

For $l = 0$; $m_l = 0$ and $L_z = 0$

$l = 1$, $m_l = -1, 0, +1$. This gives three discrete possible orientations of $\vec{L}$ in space.

$l = 2$, $m_l = -2, -1, 0, +1, +2$. This gives five possible orientations of $\vec{L}$ in space.

$l = 3$, $m_l = -3, -2, -1, 0, +1, +2, +3$.

This represent seven possible orientations of $\bar{L}$. The possible orientations of $\vec{L}$ are shown in Fig 1.8. for $l = 2$ and $l = 3$.

(d) Spin magnetic quantum number (m_s) : The spin magnetic quantum number (m_s) is due to the electron spin which is considered to be the intrinsic property of an electron. The detail discussion of concept of electron spin is given in section (1.4). The spin angular momentum of an electron is given by equation (1.52) as

$$\bar{S} = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$

where s is spin quantum number. It's value is $\frac{1}{2}$. The spin angular momentum $\bar{S}$ is also quantized, like $\bar{L}$, in space. It has two orientations with respect to the applied external magnetic field $\bar{H}$. The component of $\bar{S}$ along the field direction (Z-axis) is given by,

$$S_z = m_s \frac{h}{2\pi} \qquad \text{...(1.55)}$$

where m_s *is called spin magnetic quantum number*. It has only two possible values $m_s = \pm\frac{1}{2}$.

The value $m_s = +\frac{1}{2}$ corresponds to spin-up, while $m_s = -\frac{1}{2}$ corresponds to the spin-down.

Fig. 1.12 represents the vector diagram for two allowed orientations of spin $\bar{S}$ in space with respect to the magnetic field direction $\bar{H}$ along Z-axis.

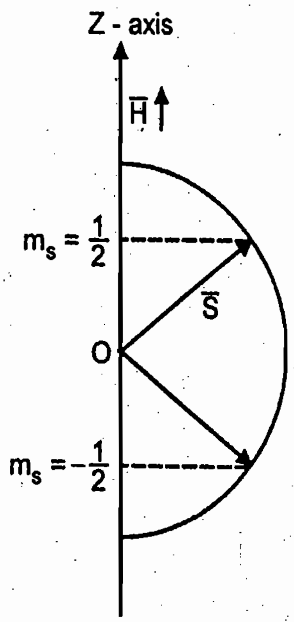


Fig. 1.12 : Two possible space orientations of $\bar{S}$

1.6 TOTAL ANGULAR MOMENTUM (J)

The *total angular momentum* of an electron is the vector sum of orbital angular momentum and spin angular momentum. Numerically it is expressed as

$$j = l \pm s \qquad \text{...(1.56)}$$

But $s = \frac{1}{2}$

$$j = l \pm \frac{1}{2} \qquad \text{...(1.57)}$$

According to the quantum mechanics, total angular momentum of an electron is given by,

$$\bar{J} = \sqrt{j(j+1)}\ \frac{h}{2\pi} \qquad \text{...(1.58)}$$

where j is called total angular momentum of an electron.

1.7 THE MAGNETIC MOMENT ($\bar{\mu}$)

Consider an electron moving with velocity $\bar{v}$ in a circular orbit of radius r about the nucleus. This electron generates small electric current i in the orbit. This current gives rise to the magnetic field. Thus an electron orbit is associated with tiny magnet. The magnetic moment associated with electron orbit is given by,

$$\bar{\mu}_l = \frac{A \cdot i}{c} \qquad \text{...(1.59)}$$

where c is the velocity of light, A is the area of the orbit.

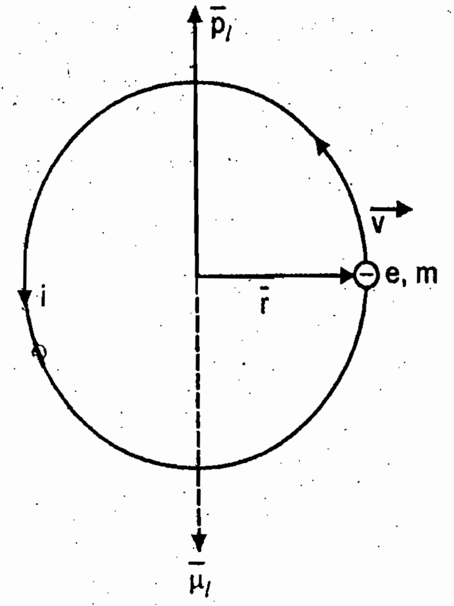


Fig. 1.13

The current i in an electron orbit is given by,

$$i = \frac{e}{T} \qquad \ldots (1.60)$$

where e is the charge of electron and T is the period of revolution. The area A of an electron orbit in terms of orbital angular momentum $\bar{p}_l$, the mass m of an electron and the period T can be expressed as

$$A = \frac{T}{2m} \bar{p}_l \qquad \ldots (1.61)$$

Equation (1.59) becomes,

$$\bar{\mu}_l = \frac{T}{2m} \cdot \bar{p}_l \cdot \frac{e}{T} \cdot \frac{1}{c}$$

$$\bar{\mu}_l = \frac{e}{2mc} \cdot \bar{p}_l \qquad \ldots (1.62)$$

The orbital angular momentum $\bar{P}_l$ is quantized and given by

$$\bar{p}_l = l \frac{h}{2\pi} \qquad \ldots (1.63)$$

where l is the orbital quantum number.

Equations (1.62) and (1.63) give,

$$\bar{\mu}_l = \frac{eh}{4\pi mc} l \qquad \ldots (1.64)$$

This result indicates that orbital magnetic moment $\bar{\mu}_l$ is proportional to the orbital angular moment. The quantity $\left(\frac{eh}{4\pi mc}\right)$ is called **Bohr magnetron** μ_B. Thus, we get,

$$\therefore \quad \mu_B = \frac{eh}{4\pi mc} \cdot \frac{ergs}{gauss} \qquad \ldots (1.65)$$

$$= \frac{e\hbar}{2\pi mc}$$

$$\mu_B = 0.927 \times 10^{-20} \text{ ergs/gauss}$$

$$\mu_B = 9.27 \times 10^{-24} \text{ joule/tesla}$$

The magnetic moments of atoms are expressed in the unit of Bohr magnetron.

[Note that 1 joule/tesla = 1 ampere – m^2]

Physical significance : The presence of the smallest unit of magnetic moment equal to one Bohr magnetron = $e\hbar/2mc$ shows that the magnetic moment of atom, like charge, mass, etc. is quantized. In addition to the orbital motion, an electron has an intrinsic property called spin. Corresponding to the spin motion, an electron has spin angular momentum given by equation (1.52) as

$$S = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$

where $s = \frac{1}{2}$ is the spin quantum number.

The magnetic moment associated with this spin is called *spin magnetic moment* ($\bar{\mu}_s$), which is given by,

$$\bar{\mu}_s = \frac{e}{mc} \cdot \vec{S}_z \qquad \ldots (1.66)$$

where m is the mass of electron, c is the velocity of light and $S_z = \pm \frac{1}{2}\left(\frac{h}{2\pi}\right)$ is the component of $\bar{S}$ along Z-axis (magnetic field direction).

$$\bar{\mu}_s = \pm \frac{eh}{4\pi mc} \qquad \ldots (1.67)$$

In case of many electron atom, the electrons usually pair up with their spins opposite to each other, so that spin magnetic momenta cancel. For unpaired electron, there exists some spin magnetic moment.

1.8 THE LARMOUR PRECESSION OF AN ELECTRON ORBIT

Consider the orbital motion of electron in the orbit. The orbital motion of an electron gives rise to the orbital angular momentum $\bar{p}_l$, which is the vector perpendicular to the orbit of an electron. When the atom is placed in the external magnetic field $\bar{H}$, then the orbital angular momentum vector $\bar{p}_l$ precess about the magnetic field direction. This precession of electron orbit is called Larmour precession. This is shown in Fig. 1.14.

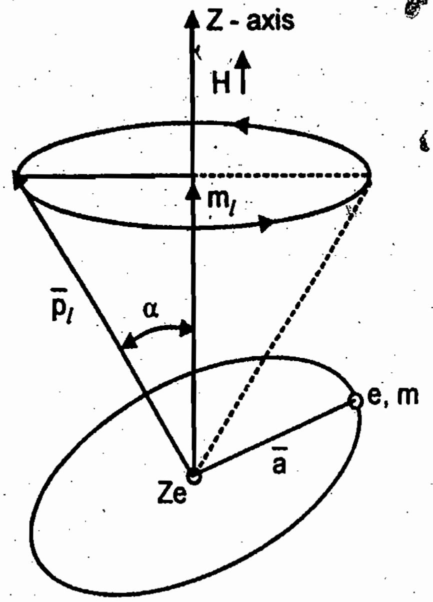


Fig. 1.14 : Larmour precession of electron orbit

The Larmour's Theorem, which is based on the classical theory of electrodynamics, states that the change in the motion of an electron in the orbit due to the external magnetic field $\bar{H}$ is the precession of orbit about the field direction with uniform angular velocity, ω_L.

$$\bar{\omega}_L = H \cdot \frac{e}{2mc} \qquad \text{...(1.68)}$$

and with uniform frequency υ_L.

$$\upsilon_L = H \cdot \frac{e}{4\pi mc} \qquad \text{...(1.69)}$$

where m is the mass of electron, c is the velocity of light and e is the charge of electron.

Larmour's theorem is very useful for calculating the energy levels of the atom in the presence of external magnetic field. In vector atom model, an electron orbit is vectorially represented with the orbital angular momentum $\bar{p}_l$. This is also known as **mechanical moment**. The angular velocity of precession of $\bar{p}_l$ about the magnetic field direction is given by,

$$\bar{\omega}_L = H \cdot \left(\frac{\bar{\mu}_l}{p_l}\right) \qquad \text{...(1.70)}$$

The ratio $\left(\frac{\bar{\mu}l}{\bar{p}_l}\right)$ is given by equation (1.62) as

$$\left(\frac{\bar{\mu}l}{\bar{p}_l}\right)_i = \frac{e}{2mc}$$

Thus equation (1.70) becomes

$$\bar{\omega}_L = H \cdot \frac{e}{2mc} \qquad \text{...(1.71)}$$

The frequency of precession is

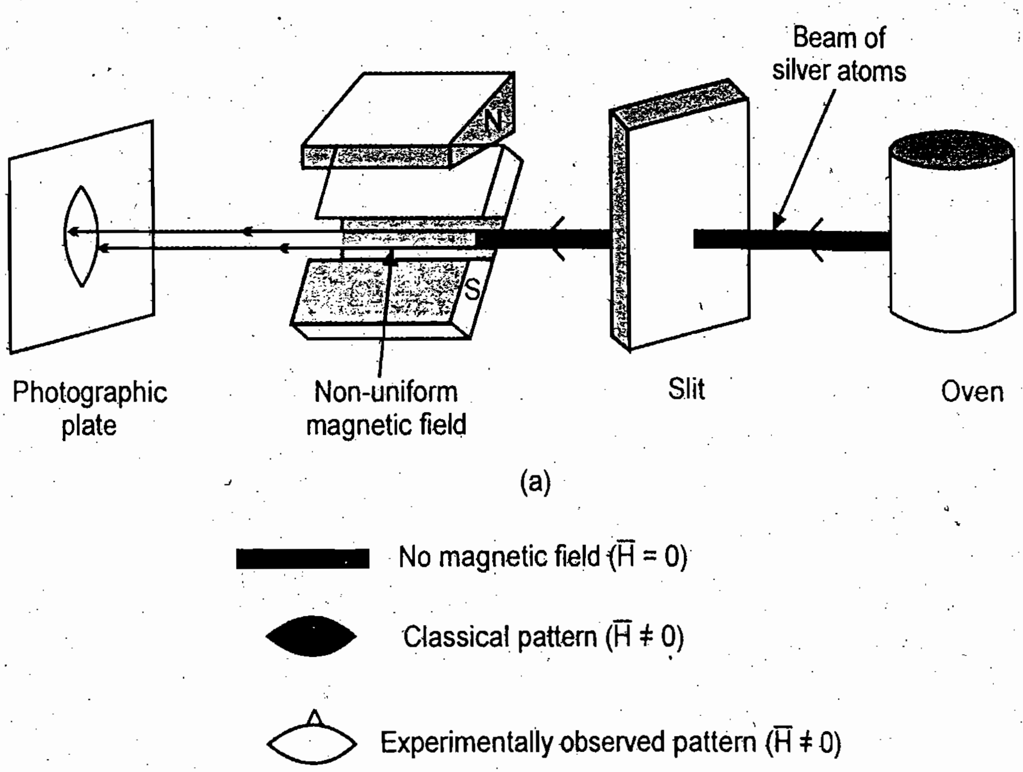
$$\upsilon_L = \frac{\bar{\omega}_L}{2\pi}$$

$$\upsilon_L = H \cdot \frac{e}{4\pi mc} \qquad \text{... (1.72)}$$

This result indicates that the frequency of precession does not depend on the orientation angle between $\bar{p}_l$ and $\bar{H}$.

1.9 STERN AND GERLACH EXPERIMENT

The vector atom model is based on the theory of quantum mechanics. The space quantization and the association of spin to an electron are two main features of this model. The experimental proof for both these features, is given in 1921 by two scientists Otto Stern and Walter Gerlach. A beam of silver atoms passed through the non-uniform magnetic field $\bar{H}$, was divided into two components. Similar results were obtained for the beams of other atoms. In the previous sections, we have seen that an atom has magnetic moment $\bar{\mu}$ due to the orbital and spin motion of an electron. Thus the atom is considered to be small tiny magnet. This atomic magnet experiences the magnetic force when kept in the magnetic field $\bar{H}$. If the magnetic field is non-uniform, then the forces on two poles of atomic magnet are not equal. This gives rise to the translatory displacement of the atom in the field direction and the rotation of its axis. The displacement of atom is directly proportional to field gradient. The experimental set-up used by Stern and Gerlach is shown in Fig. 1.15 (a).



(a)

(b)

Fig. 1.15 : (a) Experimental set-up of Stern and Gerlach experiment (b) Patterns on the photographic plate

The experimental set-up consists of two pole-pieces of electromagnets. Shape of one pole-piece is like knife-edge while other has flat face with rectangular groove. This special designing of pole pieces of magnets provides strong non-uniform magnetic field H. Electric oven, slit arrangement and photographic plate are important parts of the set-up.

A sample of silver is first heated in the oven so that heating gave a fine beam of silver with velocity equal to temperature of vaporisation. Slit produces a sharp and ribbon shaped beam of neutral silver atom from an oven. This silver beam passes through the non-uniform magnetic field between two pole-pieces. Lines of magnetic field are normal to beam. When such beam passes through pole-pieces, they are recorded on photographic plate as shown in Fig. 1.15 (b).

Stern and Gerlach observed that when the magnetic field is zero, trace of line as shown in Fig. 1.15 (b) was recorded on the photographic plate. In the presence of non-uniform magnetic field, a double trace was recorded on the plate as shown in Fig. 1.15 (b).

Discussion and interpretation of the results :

According to the theory of classical mechanics, the magnetic moment μ of the atom can have any orientation in space, as a result, the deflected beam should be spread out continuously as shown in Fig. 1.14 (c). The double trace recorded on the photographic plate can be understood on the basis of theory of quantum mechanics. The silver atom ($_{47}$Ag) has 47 electrons. The last 47th electron is unpaired which enters into the 5S sublevel of O shell. This unpaired electron decides the ground state of silver. The 46 core electrons of silver atom do not contribute to the magnetic moment of atom because of pairing. The last unpaired electron decides the magnetic moment of silver atom. The ground state of silver atom is represented by $S_{1/2}$. This shows that $l = L = 0$, $S = \frac{1}{2}$ which gives $J = L + S = 0 + \frac{1}{2} = \frac{1}{2}$. This is the total angular momentum.

For $l = 0$, $m_l = 0$, which gives the magnetic moment due to orbital motion of an electron equal to zero.

$$\mu_l = 0 \qquad \dots (1.73)$$

If we consider only the orbital motion of an electron, then the above result i.e. $\bar{\mu}_l = 0$, could not give the deflection of beam due to the magnetic field. This is contradictory with the experimental results. The deflection and splitting of silver atom beam under the application of non-uniform magnetic field can be explained if we consider the spinning motion of electron. The total magnetic moment $\bar{\mu}$ of atom is the vector sum of magnetic moment due to orbital motion, $\bar{\mu}_l$ and magnetic moment due to spin motion, $(\bar{\mu}_S)$. Thus we get,

$$\bar{\mu} = \bar{\mu}_l + \bar{\mu}_S \qquad \dots (1.74)$$

$$\text{But } \mu_l = 0 \quad \therefore \quad \bar{\mu} = \bar{\mu}_S \qquad \dots (1.75)$$

The spin magnetic moment $\bar{\mu}_S$ is given by equation (1.66) as

$$\bar{\mu}_S = \frac{e}{mc} S_z$$

where, $S_z = m_S\left(\frac{h}{2\pi}\right)$ is the component of $\bar{S}$ along the field direction (Z-direction).

$m_S = \pm\frac{1}{2}$ is the spin magnetic quantum number as given by equation (1.55).

Thus the magnetic moment of silver atom will be

$$\bar{\mu} = \pm\frac{1}{2}\left(\frac{eh}{2\pi mc}\right) \qquad \text{... (1.76)}$$

This indicates that atoms with magnetic moment

$$\bar{\mu} = +\frac{1}{2}\left(\frac{eh}{2\pi mc}\right) \left(\text{i.e. } m_S = +\frac{1}{2}\right) \qquad \text{... (1.77)}$$

are deflected downward while the atoms with magnetic moment

$$\bar{\mu} = -\frac{1}{2}\left(\frac{eh}{2\pi mc}\right) \qquad \text{... (1.78)}$$

are deflected upward which correspond to $m_S = -\frac{1}{2}$.

This provides the explanation for the splitting of beam of silver atoms.

Thus the Stern and Gerlach experiment provides two important results. The first, it verified the concept of space quantization, and the second existance of spin angular momentum of an electron.

SOLVED EXAMPLES

Example 1.1 : Calculate the linear velocity of an electron in the first, second and third orbit of hydrogen atom.

Solution : The velocity of an electron in nth orbit is given by,

$$v_n = \left(\frac{e^2 Z}{2\varepsilon_0 h}\right) \cdot \frac{1}{n}$$

For first orbit, we have n = 1, Z = 1.

$$v_1 = \frac{(1.6 \times 10^{-19})^2 \times 1}{2 \times (8.85 \times 10^{-12}) \times 6.64 \times 10^{-34}} \cdot \frac{1}{1}$$

$$v_1 = 2.17 \times 10^{-2} \times 10^{-38} \times 10^{46}$$

$$v_1 = 2.17 \times 10^{6} \text{ m/s}$$

For second orbit : n = 2.

$$\therefore \quad v_2 = 2.17 \times 10^{6} \times \frac{1}{2}$$

$$\therefore \quad v_2 = 1.08 \times 10^{6} \text{ m/s}$$

For third orbit : n = 3.

$$\therefore \quad v_3 = 1.36 \times 10^6 \times \frac{1}{3}$$

$$\therefore \quad v_3 = 0.72 \times 10^6 \text{ m/s}$$

Example 1.2 : Calculate the frequency of revolution of an electron in first and second orbit of hydrogen atom.

Solution : The frequency of revolution of an electron in the n^{th} orbit is given by

$$f_n = \left[\frac{me^4Z^2}{4\pi \varepsilon_0^2 h^3}\right] \cdot \frac{1}{n^3}$$

For first orbit, n = 1; for hydrogen, Z = 1.

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$$

$$h = 6.64 \times 10^{-34} \text{ Js}$$

$$\therefore \quad f_1 = \frac{9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^4 \times (1)^2}{4 \times 3.142 \times (8.85 \times 10^{-12})^2 \times (6.64 \times 10^{-34})^3} \times \frac{1}{(1)^3}$$

$$f_1 = \frac{59.6377 \times 10^{-107}}{2.8817 \times 10^5 \times 10^{-126}}$$

$$f_1 = 2.06 \times 10^{-4} \times 10^{14}$$

$$f_1 = 2.06 \times 10^{10} \text{ revolutions/s}$$

For the second orbit, n = 2.

$$f_2 = f_1 \times \frac{1}{(2)^3}$$

$$f_2 = 2.06 \times 10^{10} \times \frac{1}{8}$$

$$f_2 = 0.257 \times 10^{10} \text{ revolutions/s}$$

Example 1.3 : Determine the magnitude of orbital angular momentum $\bar{L}$ and the allowed values of L_z and θ for the hydrogen atom in $l = 3$ states.

Solution : The magnitude of orbital angular momentum $\bar{L}$ is given by,

$$|\bar{L}| = \sqrt{l(l+1)}\ \hbar$$

Since $l = 3$, $\therefore$

$$|\bar{L}| = \sqrt{3(3+1)}\ \hbar$$

$$|\bar{L}| = \sqrt{12}\ \hbar$$

The allowed values of L_z are given by,

$$L_z = m_l\, \hbar = m_e \left(\frac{h}{2\pi}\right)$$

For given l, m_e can have the following allowed values

$$m_l = -l, (-l+1), 0, (l+1), l$$

$$m_l = -3, -2, -1, 0, 1, 2, 3$$

$$\therefore \quad L_z = -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar$$

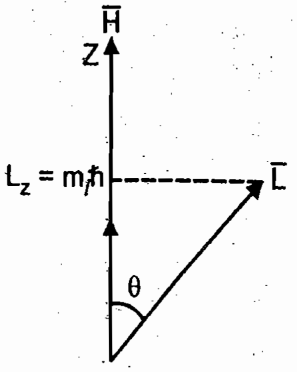


Fig 1.16

The allowed values of θ are

$$\cos\theta = \frac{L_z}{|\bar{L}|}$$

$$\cos\theta = \frac{m_l\hbar}{\sqrt{12}\hbar}$$

$$\theta = \cos^{-1}\left(\frac{m_l}{\sqrt{12}}\right)$$

θ = 30.0°, 54.8°, 73.2°, 90.0°, 107°, 125° and 150°.

Example 1.4 : Determine the possible allowed states for the principal quantum number $n = 3$, of hydrogen atom. Calculate the energies of these states.

Solution: For $n = 3$, the values of l are, $l = 0, 1, 2$

For $l = 0$, the value of m_l is $m_l = 0$

For $l = 1$, the values of m_l are $m_l = -1, 0, 1$.

For $l = 2$, the values of m_l are $m_l = -2, -1, 0, 1, 2$.

Thus, for $l = 0$, we have one state designated as 3S state associated with quantum numbers $n = 3$, $l = 0$, $m_l = 0$.

For $l = 1$, we have three 3P states associated with quantum number.

$n = 3$	$l = 1$	$m_l = -1$
$n = 3$	$l = 1$	$m_l = 0$
$n = 3$	$l = 1$	$m_l = -1$

Now for $l = 2$, we have five 3d states associated with quantum numbers.

$n = 3$	$l = 2$	$m_l = -2$
$n = 3$	$l = 2$	$m_l = -1$
$n = 3$	$l = 2$	$m_l = 0$
$n = 3$	$l = 2$	$m_l = 1$
$n = 3$	$l = 2$	$m_l = -2$

Thus there are 9 states for $n = 3$ [i.e. $N = 2n^2$].

All these $N = 9$ states have same principle quantum number $n = 3$, therefore, all these states have same energy which is given by,

$$E_3 = \frac{13.6}{3^2} \text{ eV}$$

$$\text{i.e.} \qquad E_3 = 1.51 \text{ eV}$$

QUESTIONS AND PROBLEMS

(A) Multiple choice questions :

1. The vector atom model is based on ....
   - (a) concept of spatial quantization.
   - (b) concept of electron spin.
   - (c) all of above.
   - (d) none of above.
2. The orbital angular momentum of the electron (L) as per wave mechanics is given by ....
   - (a) $\sqrt{l(l+1)}$ (b) $\sqrt{l(l+1)}\,\frac{h}{2\pi}$
   - (c) $\sqrt{s(s+1)}\,\frac{h}{2\pi}$ (d) $\sqrt{j(j+1)}\,\frac{h}{2\pi}$
3. Magnetic spin quantum number (m_s) has two values ....
   - (a) ± 1 (b) ± 0
   - (c) $\pm\frac{1}{2}$ (d) $\pm\frac{3}{2}$
4. In Stern Gerlach experiment, when there is no field, the trace obtained was ....
   - (a) a fairly sharp line trace.
   - (b) double trace on one side.
   - (c) double trace on either side.
   - (d) doublet.
5. Frequency of precession of orbit does not depend on
   - (a) electronic charge.
   - (b) magnetic field.
   - (c) velocity.
   - (d) orientation angle between momentum vector and magnetic field.

Ans. (1) c, (2) b, 3 (c), 4 (a), 5 (d).

(B) Answer in short :

1. Mention different quantum numbers associated with electron.
2. What are allowed values of m_s and m_l ?
3. What are two important results obtained from Stern and Gerlach experiment ?
4. What is Bohr magnetron ?
5. What is Larmour precession ?
6. Define magnetic moment associated with spin.
7. Define magnetic moment associated with electron orbit.

(C) Answer in detail (Long answer type questions) :

1. What are the basic features of the vector atom model ? Explain them.
2. What is the space quantization ? Explain it.
3. Explain the spin concept of an electron.
4. State the different quantum numbers. Give their physical significance.
5. What is the magnetic moment ? Obtain an expression for orbital and spin magnetic moments.
6. What is Bohr magnetron ?
7. Discuss in details, the Stern-Gerlach experiment.
8. What are the conclusions of the Stern-Gerlach experiment ?

(D) Numerical problems :

1. Calculate the linear velocity of electron in the third Bohr orbit using

   $h = 6.64 \times 10^{-34}$ Js, $c = 3 \times 10^{8}$ m/s and $e = 1.6 \times 10^{-19}$ c.
2. Determine the possible allowed states for principal quantum number $n = 2$. Calculate energies of these states.
3. If mass of electron is 9.3×10^{-31}, calculate value of Bohr magnetron.

   [Use values of constants as given in problem No.1)

   Ans. 9.27×10^{-24} J/T.

❒❒❒

2

Pauli's Exclusion Principle

2.1 INTRODUCTION

In the earlier chapter, we have seen that the state of an electron in atom is specified by the four quantum numbers - principal quantum number n, orbital quantum number l, orbital magnetic quantum number m_l, and spin magnetic quantum number m_s. These four quantum numbers are used to describe all possible electronic states regardless of the number of electrons in the atom. In order to understand the structure of atom, it is necessary to know the distribution of electrons into different shells and subshells. There was a basic question that how many electrons can be in a particular state ? In principle, every electron in an atom prefers to enter into the lowest possible energy state of the atom. If this is true, then all electrons will enter in lowest possible energy state. As we know, such situation do not exist in nature. Answer to above question was given by the scientist W. Pauli in 1925; which is referred as the famous exclusion principle. In the present chapter, we will discuss the Pauli's exclusion principle, electron configuration, spectral notations of quantum states.

2.2 THE EXCLUSION PRINCIPLE

It is necessary to know the Pauli's exclusion principle before doing the electron distribution in shells and sub-shells of the atom. The Pauli's exclusion principle states that "*No two electrons in the same atom can have same four quantum numbers.*" The principle may be stated as "*Every completely specified quantum state in an atom can be occupied by only one electron.*" Thus, exclusion principle puts certain restrictions on the values of four quantum numbers. When this principle is applied to the atom, the following two conclusions can be made. The first, for the given principle quantum number n, there can be no more than $2n^2$ electrons. Second, there can be only $2(2l + 1)$ electrons with the given value of l.

For example, consider n = 1.

Possible value of l is $l = 0$ (as $l = (n-1), (n-2), \ldots 0$)

$\therefore$ Possible value of m_l is $m_l = 0$ (as $m_l = \pm l, \pm l - 0), \ldots 0$

The quantum number m_s may be either $+\frac{1}{2}$ or $-\frac{1}{2}$,

For first electron, we get $n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$

For second electron, we get $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$.

According to the Pauli's principle, the third distinct set of quantum numbers is not possible for the third electron. Therefore for n = 1, only two electrons are possible. [i.e. $2n^2$].

2.3 ELECTRONIC CONFIGURATION

The electronic configuration of an atom is the distribution of electrons in various shells or subshells around the nucleus of the atom. An electron orbits or shells in an atom are represented by the letters K, L, M, N, O, P, ... etc. corresponding to the principal or total quantum number n = 1, 2, 3, 4, 5, 6, 7, ... etc. respectively. The K-shell is the innermost one, which corresponds to n = 1. The electrons with same n value forms the shell. The electrons in the given shell have same energy. The shells are divided into subshells. The electrons with same orbital quantum number l, form the subshell. The subshells are represented by small letters s, p, d, f, g, h, ... etc. corresponding to the orbital angular momentum quantum number $l = 0, 1, 2, 3, 4, 5, 6, \ldots$ etc. respectively. Table 2.1 shows the shells and subshells upto n = 4. The K-shell (n = 1) has only one s-subshell ($l = 0$); Electrons with n = 1 and $l = 0$, are called 2s electrons.

For K-shell, $n = 1 \therefore l = 0$

The possible values of $m_l = 0$

The values of m_s are $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$.

With these values of n, l, m_l and m_s, we can have only two non-identical sets of quantum numbers as :

$$(n = 1,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2})$$

$$(n = 1,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2})$$

No third set is possible. Therefore, according to the Pauli's exclusion principle, the K-shell can have at the most only two electrons, ($2n^2 = 2$) corresponding to two distinct sets of quantum numbers.

Consider the L-shell, n = 2.

The possible values of $l = 0, 1$

Thus there are two subshells, s - subshell, $l = 0$

p - subshell, $l = 1$

For 2s-subshell, $l = 0$, $\therefore$ $m_l = 0$ and $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$

Thus only two distinct sets of quantum numbers are possible for s-subshell.

$$(n=2,\ l=0,\ m_l=0,\ m_s=+\frac{1}{2})$$

$$(n=2,\ l=0,\ m_l=0,\ m_s=-\frac{1}{2})$$

Table 2.1 : Electron shells and subshells [n = 4 only]

Shell	**K**	**L**		**M**			**N**			
n	1	2		3			4			
Max. number of electrons ($2n^2$)	2	8		18			32			
Subshell	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
l	0	0	1	0	1	2	0	1	2	3
Max. number of electrons in subshell $2(2l+1)$	2	2	6	2	6	10	2	6	10	14

Thus 2s-subshell can have only 2 electrons.

For 2p-subshell :

We have $n = 2$ $\therefore$ $l = 1$

$\therefore$ $m_l = -1, 0, +1$

For $m_l = -1$, the possible values of m_s are $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$

For $m_l = 0$, the possible values of m_s are $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$

For $m_l = +1$, the possible values of m_s are $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$

Thus for 2p-subshell, we can have only following six non-identical sets of quantum numbers.

$$(n=2,\quad l=1,\quad m_l=-1,\quad m_s=+\frac{1}{2})$$

$$(n=2,\quad l=1,\quad m_l=-1,\quad m_s=-\frac{1}{2})$$

$$(n=2,\quad l=1,\quad m_l=0,\quad m_s=+\frac{1}{2})$$

$$(n=2,\quad l=1,\quad m_l=0,\quad m_s=-\frac{1}{2})$$

$$(n=2,\quad l=1,\quad m_l=1,\quad m_s=+\frac{1}{2})$$

$$(n=2,\quad l=1,\quad m_l=1,\quad m_s=-\frac{1}{2})$$

Thus, no other combination of quantum numbers is possible which is non-identical. Therefore, 2p-subshell can have at the most only 6 electrons corresponding to the above six distinct sets of quantum numbers. Finally, the L-shell can have only $(2 + 6) = 8$ maximum number of electrons, which is equal to $2n^2$.

In the similar manner, we can proceed for the M, N, O, P, ... etc. shells. In practice, we can understand the electronic structure of the complex atoms as succession of filled levels increasing in energy. In general, the order of filling of subshells in the atom is as follows : When a subshell is filled, the next electron goes into the lowest energy vacant sub-shell. Each subshell has particular number of orbitals. Each orbital has the capacity of only maximum two electrons. The state of electron in the given orbital is specified by three quantum numbers n, l and m_l. Out of two electrons in a orbital, one electron has a spin magnetic quantum number $m_s = +\frac{1}{2}$ and other electron has spin magnetic quantum number $m_s = -\frac{1}{2}$. The value $m_s = +\frac{1}{2}$ indicates that the spin vector of electron is pointed in upward direction, while $m_s = -\frac{1}{2}$ indicates that the spin vector is pointed in downward direction. The number of orbitals in given subshell are $(2l + 1)$. Thus, s-subshell $l = 0$, has one orbital; p-subshell $l = 1$, has three orbitals; d-subshell, $l = 2$, has five orbitals and so on. For the filling of electrons into the subshells, Hunds rule is also obeyed in addition to the exclusion principle.

The Hund's rule states that "*when an atom has orbital of equal energy, the order in which they are filled with electrons is such that a maximum number of electrons have unpaired spins.*" Both, exclusion principle and Hund's rule can be illustrated through the electronic configuration of the following atoms.

Let us consider the hydrogen atom, Z = 1.

It has only one electron. This electron enters into 1s-subshell of K-shell. Electronic configuration is : $1\,s^1$

The superscript 1 indicates that one electron is present in the 1s-subshell.

Let us consider neutral helium atom, Z = 2.

It has two electrons which enter into 1s-subshell of K-shell (n = 1). The electron configuration is $1s^2$.

For neutral lithium, Z = 3, there are 3 electrons.

Electronic configuration : $1s^2\ 2s^1$

For Beryllium atom, Z = 4, it has 4 electrons.

Electronic configuration : $1s^2\ 2s^2$

For Boron atom, Z = 5, it has 5 electrons

Electronic configuration : $1s^2$, $2s^2$, $2p^1$

For carbon atom, Z = 6, it has 6 electrons.

In this case, electronic configuration is $1s^2$, $2s^2$, $2p^2$.

Here two 2p-electrons cannot enter into the only one orbital with paired spin (↑↓), but they enter into two separate orbitals with unpaired spins (↑↑). This is according to the Hund's rule. The electronic configuration of the above elements is shown in the Fig. 2.1.

Shell →	K	L				Electronic configuration
Subshells →	1s	2s	2p			
Atom ↓						↓
Z = 4, Be	↑↓	↑↓				$1s^2$, $2s^2$
Z = 5, B	↑↓	↑↓	↑			$1s^2$, $2s^2$, $2p^1$
Z = 6, C	↑↓	↑↓	↑	↑		$1s^2$, $2s^2$, $2p^2$
Z = 7, N	↑↓	↑↓	↑	↑	↑	$1s^2$, $2s^2$, $2p^3$
Z = 8, O	↑↓	↑↓	↑↓	↑	↑	$1s^2$, $2s^2$, $2p^4$
Z = 9, F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2$, $2s^2$, $2p^5$

Fig. 2.1 : Electronic configuration for some lighter atoms

2.4 THE QUANTUM STATE OF AN ELECTRON

Every electron in an atom has its own unique set of four quantum numbers, n, l, m_l and m_s. This set of quantum numbers specifies the state of an electron in an atom which is called *quantum state of an electron.* The total number of quantum states for the given l can be calculated as follows :

For given l, there are $(2l + 1)$ allowed values of m_l ranging from $-l$ to $+l$ including zero. For each value of m_l, there exist two possible values of $m_s = \pm \frac{1}{2}$. Therefore, there are $2(2l + 1)$ non-identical sets of the four quantum numbers, (n, l, m_l and m_s) for the given l value.

Every set of these distinct quantum numbers, gives rise to one quantum state of an electron.

Thus, s-subshell, $l = 0$, has two quantum states,

p-subshell, $l = 1$, has six quantum states,

d-subshell, $l = 2$, has ten quantum states,

f-subshell, $l = 3$, has fourteen quantum states,

and so on.

For the given n, there are n possible values of l i.e. $l = 0, 1, 2, \ldots (n-1)$. The total number of states, for the given n (i.e. for shell) are

$$N = \sum_{l=0}^{n-1} 2(2l+1) \quad \ldots (2.1)$$

$$2[1+3+5+\ldots(2n-1)] = 2\left[n\left\{\frac{1+(2n-1)}{2}\right\}\right]$$

$$N = 2n^2 \quad \ldots (2.2)$$

This is equal to the total number electrons in the given shell.

Let us illustrate concept of quantum states by considering the example of **oxygen** atom.

In oxygen atom, Z = 8, therefore, there are 8 electrons.

First two electrons enter in s-subshell of K-shell (n = 1)

1st electron : $n = 1,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$

2nd electron : $n = 1,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2}$

Thus there are two non-identical quantum states for 1s-subshell.

Next two electrons enters in s-subshell of K-shell (n = 2).

3rd electron : $n = 2, l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$

4th electron : $n = 2, l = 0, m_l = 0, m_s = -\frac{1}{2}$

Thus there exist two quantum states for 2s-subshell.

The remaining four electrons enter into the 2p-subshell of L-shell.

For $l = 1$, m_l can have the values $-1, 0, +1$ and

For each m_l, m_s has two values $+\frac{1}{2}$ and $-\frac{1}{2}$.

5th electron : $n = 2,\ l = 1,\ m_l = -1,\ m_s = +\frac{1}{2}$

6th electron : $n = 2,\ l = 1, m_l = -1, m_s = -\frac{1}{2}$

7th electron : $n = 2,\ l = 1,\ m_l = +1,\ m_s = +\frac{1}{2}$

8th electron : $n = 2, l = 1, m_l = +1,\ m_s = -\frac{1}{2}$

Though there are six allowed quantum states for 2p-subshell, but in case of oxygen, only 4-electrons are left after filling the 1s and 2s subshells, therefore only four quantum states exist. Thus, 2p-subshell is not completely filled with electrons. In oxygen atom, there exists 8 quantum states. This example also shows that for the completely filled subshell, orbital magnetic moment and spin magnetic moment becomes zero.

2.5 SPECTRAL NOTATIONS OF QUANTUM STATE

Electron States :

The electron states are denoted by the small letters, s, p, d, f, g, h, ... corresponding to the orbital angular momentum quantum number $l = 0, 1, 2, 3, 4, ...$ respectively. For $l = 0$, we get s-subshell; for $l = 1$, p-subshell; $l = 2$, d-subshell; for $l = 3$, f-subshell and so on. The letters s, p, d, f have historical reference. The letter 's' indicates sharp series, p for principal series, d for diffuse and f for fundamental series. The state of electron is denoted by writing the value of principal quantum number n, before the correct letters which corresponds to the l - values.

For example,

1s state : $n = 1$ and $l = 0$

2s state : $n = 2$ and $l = 0$

2p state : $n = 2$ and $l = 1$

3s state : $n = 3$ and $l = 0$

The number of electrons are denoted by writing the superscript after the letters, s, p, d, ...

Consider the example of oxygen : The electron states are $1s^2$, $2s^2$, $2p^4$

The state $1s^2$ indicates that, there are two 1s electrons; $2s^2$ state indicates that there are two 2s electrons and $2p^4$ state shows that there are four 2p electrons in an oxygen atom.

Atomic States :

For writing the atomic states, it is necessary to know the orbital angular momentum L, spin angular momentum S and the total angular momentum J of the atom. The total angular momentum J of an atom is the vector sum of orbital and spin angular momentum of an atom.

$$\overline{J} = \overline{L} + \overline{S} \qquad \text{... (2.3)}$$

where $\overline{L} = \Sigma l_i$ is the orbital angular momentum of atom. It is the vector addition of orbital angular momentum vector l_i of all the electrons.

$\overline{S} = \Sigma s_i$ is the spin angular momentum of an atom. It is the vector sum of spin angular momentum s_i of all the electrons in the atom. The addition of the total orbital momentum of electron in atom $\overline{L}$ and total spin $\overline{S}$ gives total momentum $\overline{J}$. This type of coupling of $\overline{L}$ and $\overline{S}$ for determination of $\overline{J}$ is called L – S or Russell-Saunder's coupling.

The total angular momentum vector $\overline{J}$ is characterised by the total angular momentum quantum number j. The total angular momentum $\overline{J}$ is also quantised. As per the quantum condition, $\overline{J}$ is as

$$\overline{J} = \sqrt{j(j+1)}\,\frac{h}{2\pi} \qquad \text{... (2.4)}$$

The total angular momentum of an atom is decided by the last unpaired electrons in an atom. The core of electrons in an atom, do not contribute to the total angular momentum $\overline{J}$ of an atom. The total number of allowed values of $\overline{J}$ for the given $\overline{L}$ and $\overline{S}$ are

$$\overline{J} = (L+S), (L+S-1)\ldots |L-S| \qquad \ldots (2.5)$$

For example, let $L = 3$, and $S = \frac{3}{2}$ then $J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$

Thus there are four values of $\overline{J}$. In general, there are (2S + 1) different values of $\overline{J}$. Each value of $\overline{J}$ gives a separate atomic state. This shows that there are (2S + 1) different energy states for the atom.

The quantity (2S + 1) is called the multiplicity of the of atomic state. The multiplicity

$(2S + 1) = 1$ represents the singlet energy level ($S = 0$)

$(2S + 1) = 2$ represents the doublet energy levels ($S = \frac{1}{2}$).

$(2S + 1) = 3$ gives the triplet energy levels ($S = 1$).

It should be noted that, if $L \leq S$, then the number of values of J are $(2L + 1)$.

The atomic states are denoted by the capital letters S, P, D, F, G, ... etc. which corresponds to the L = 0, 1, 2, 3, 4, ... respectively. The atomic state is denoted using the term symbol as $^{(2S+1)}L_J$ ... (2.6)

where (2S + 1) is the multiplicity, $S = \Sigma s_i$ is the resultant spin momentum of atom, L is the resultant orbital angular momentum of atom.

$L = 0,$	S - state
$L = 1,$	P - state
$L = 2,$	D - state
$L = 3,$	F - state and so on.

Let us consider some examples.

Hydrogen atom in ground state :

$$n = 1,\ l = 0,\ m_l = 0 \text{ and } m_s = \frac{1}{2}$$

$\therefore$ State of atom $^{(2S+1)}L_J$ will be $^2S_{1/2}$

and read as doublet S half. In this notation, superscript 2 gives multiplicity symbol S for L = 0 and subscript 1/2 stands for J.

Similarly, L = 3, and S = 1/2

$$\text{The values of } J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2} \text{ and } \frac{1}{2}$$

$$\text{The multiplicity } \Rightarrow (2S+1) = \left(2\times\frac{1}{2}+1\right) = 2$$

∴ L = 3 indicates F state as ${}^2F_{7/2,\ 5/2,\ 3/2,\ 1/2}$

The atomic states : ${}^2F_{7/2}$, ${}^2F_{5/2}$, ${}^2F_{3/2}$ and ${}^2F_{1/2}$. All these states are doublets. The atomic state ${}^2F_{7/2}$ can be read as doublet F seven halves and so on.

SOLVED EXAMPLES

Example 2.1 : Write the electronic configuration of fluorine and neon.

Solution : For fluorine F, Z = 9

∴ There are 9 electrons in fluorine atom.

The electronic configuration will be $1s^2, 2s^2, 2p^5$

For Ne atom, Z = 10

∴ There are 10 electrons in Ne atom

The electronic configuration will be $1s^2, 2s^2, 2p^6$

Example 2.2 : Determine the ground state of aluminium atom. Represent it using the spectral notations.

Solution : Consider the aluminium atom Al, Z = 13.

There are 13 electrons in Al atom. The shells and subshells are filled as follows :

$$1s^2, 2s^2\, 2p^6, 3s^2\, 3p^1$$

The electrons in 1s, 2s, 2p and 3s subshells are paired and are completely filled. The last 13th electron enters into 3p - subshell. This electron is unpaired. The paired electrons in the inner subshells do not contribute to the orbital and spin angular momentum of the atom. Therefore, the last unpaired electron in 3p-subshell decides the ground state and the total angular momentum $\overline{J}$ of the whole atom. Thus last unpaired electron : 3p-electron state.

∴ $n = 3, l = 1, m_l = -1, 0, +1$ and for each value of m_l, there are two values of $m_s = \pm\frac{1}{2}$.

Since only one electron is available in 3p-subshell, its state is specified by the quantum numbers $n = 3, l = 1, m_l = -1$ and $m_s = +\frac{1}{2}$

∴ Thus

$$L = l = 1$$

$$S = s = \frac{1}{2}$$

∴

$$\text{Multiplicity} = (2S+1) = 2$$

$$\text{Values of } J = \frac{3}{2}, \frac{1}{2}$$

Thus, the ground state of Al atom can be expressed as ${}^2P_{3/2,\ 1/2}$

Example 2.3 : If $L = 2, S = \frac{1}{2}$, then write the atomic states.

Solution : Given : $L = 2, S = \frac{1}{2}$

$$\text{The values of } J = \frac{5}{2}, \frac{3}{2}$$

$$\text{Multiplicity} = (2S + 1) = \left(2 \times \frac{1}{2} + 1\right) = 2$$

$\therefore$ L = 2 represents D-state.

Thus, the atomic states can be expressed as $^2D_{5/2}$ and $^2D_{3/2}$

Example 2.4 : Determine the total number quantum states of electrons in carbon atom.

Solution : For carbon atom, Z = 6, therefore, there are six electrons.

First two electrons enter in 1s-subshell of K-shell (n = 1).

1st electron : $(n = 1,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2})$

2nd electron : $(n = 1,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2})$

Next two electrons enter in 2s-subshell of L-shell (n = 2).

3rd electron : $(n = 2,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2})$

4th electron : $(n = 2,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2})$

Last two electrons enter in 2p-subshell of L-shell (n = 2).

5th electron : $(n = 2,\ l = 1,\ m_l = -1,\ m_s = +\frac{1}{2})$

6th electron : $(n = 2,\ l = 1,\ m_l = -1,\ m_s = -\frac{1}{2})$

Thus there are six quantum states of electrons in carbon atom.

Example 2.5 : Find the S, L and J value that corresponds to each of the following :

$$^1S_0,\ ^3P_2,\ ^3D_{3/2}\ ^2P_2$$

Solution : For $^1S_0$:

$L = 0,\ (2S + 1) = 1$

$\therefore$ $S = 0$ and Hence $J = 0$

For $^3P_2$:

$L = 1, (2S + 1) = 3$

$\therefore$ $S = 1$ Hence $J = 2$ or zero

[As J = 2 is admissible value with L = 1 and S = 1, $^3P_2$ represents an allowed state with J = 2]

For $^2D_{3/2}$:

$$L = 2,\ (2S+1) = 2$$

$$S = \frac{1}{2} \quad \text{Hence } J = \frac{5}{2} \text{ and } \frac{3}{2}$$

[As $J = \frac{3}{2}$ is an admissible value with $L = \frac{1}{2}$ and $S = \frac{1}{2}$

$^2D_{3/2}$ represents value with allowed term]

For $^2P_2$:

$$L = 1, (2S+1) = 2 \ \therefore\ S = \frac{1}{2} \quad \text{Hence } J = \frac{3}{2} \text{ and } \frac{1}{2}$$

As $J = 2$ is not admissible value with $L = \frac{1}{2}$ and $S = \frac{1}{2}$, $^2P_2$ does not represent an allowed state.

QUESTIONS AND PROBLEMS

(A) Multiple choice questions :

1. According to Pauli's exclusion principle, no two electrons in the same atom can have same .... quantum number.

(a) one
(b) two
(c) three
(d) four

2. For d-subshell, $l = 2$ has .... quantum states

(a) ten
(b) six
(c) two
(d) fourteen

3. Find the value of S, L and J for state $^2S_{1/2}$.

(a) $L = 2, S = \frac{1}{2}, J = \frac{5}{2}$
(b) $L = 0,\ S = \frac{1}{2},\ J = \frac{1}{2}$
(c) $S = 0, L = 1, J = 1$
(d) none of above

4. If $S = \frac{1}{2}$, $L = 2$, then the term symbols are ....

(a) $^2D_{5/2}$ and $^2D_{3/2}$,
(b) $^2D_{5/2}$ and $^2D_{1/2}$
(c) $^2D_{3/2}$ and $^2D_{1/2}$
(d) $^2S_{5/2}$ and $^2S_{3/2}$

5. 32 electrons in the Germanium are expressed in the form ....

(a) $1s^2\ 2s^8\ 3p^{18}\ 4d^{14}$
(b) $1s^2\ 2s^2\ 3s^2\ 4s^2\ 2p^6\ 3p^6\ 4p^2\ 3d^{10}$
(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^2$
(d) none of above

Ans. : (1) d, (2) a, (3) b, (4) a, (5) c.

(B) Answer in short :

1. State the Pauli's exclusion principle.
2. What is an electronic configuration of sodium ?
3. What is the orbital angular and spin angular momentum of completely filled subshells ?

4. What is the limit for the number of subshells in a shell ?
5. What is the quantum state of an electron ?
6. What is the multiplicity of the state ?
7. How do you calculate the values of $\overline{J}$?

(C) Answer in detail :

1. State and explain the Pauli's exclusion principle.
2. Explain the electronic configuration with suitable examples.
3. Discuss the quantum states of an electron.
4. Explain the representation of an electron state and the atomic state using the spectral notations.
5. What is the multiplicity ? Explain its importance in spectroscopy.
6. Show that the total number of quantum states for the given n are $2n^2$.

(D) Numerical Problems :

1. Determine the ground state of sodium atom. Represent it using the spectral notations.
2. Determine the total number of quantum states of electrons in magnesium atom.
3. Calculate the atomic states for
   (a) $L = 4$ and $S = \frac{1}{2}$
   (b) $L = 3$ and $S = 1$
   (c) $L = 2$ and $S = \frac{3}{2}$
   (d) $L = 5$ and $S = \frac{3}{2}$.
4. Determine the ground state of cadmium (Cd) atom ($Z = 48$). Represent it using the spectroscopic notations.

❑❑❑

3

Spectra of Single Valence Electron Systems

3.1 INTRODUCTION

In the preceding chapters, the development of vector atom model with necessary concepts of orbital angular momentum, Stern-Gerlach experiment and quantum numbers associated with it has been discussed. Also, you are made familiar with the Pauli's exclusion principle, electron configuration and term symbols.

In this chapter, we deal with the semiclassical calculations of the interaction energies by the use of vector atom model. It is experimentally found that all the possible combinations of permitted energy states of an atom do not actually appear as spectral lines. It is because of certain restrictions in transitions called as selection rules, which are also included in this chapter.

Lastly, we discuss the broad diversity of optical spectrum of sodium atom – which is one valence electron atom and the details of its energy levels. This chapter mainly deals with one-valence electron systems.

3.2 SPIN-ORBIT INTERACTION

The lines of the optical spectra emitted by alkali elements show a fine structure splitting which indicates that all energy levels such as P, D, F, G, etc. are doublet, except those for $l = 0$ [s level. This is due to spin-orbit interaction acting on the optically active electron, i.e. due to the coupling between the magnetic dipole moment of the electron and the internal magnetic field it feels because it moves through the electric field of the atom.

Experimentally, it has been observed that any expression for doublet term separations will involve the atomic number Z, the quantum number l and total quantum number n. Calculation of the interaction energy due to the addition of an electron spin to the vector atom model, was carried out by Pauly, Darwin, Dirac, Gordon and others on the basis of quantum mechanics.

'The interaction energy' is nothing but the change in kinetic energy of the system due to the precession of the electron around the field.

In the present section, we shall study the interaction between an electron's spin magnetic dipole moment and the internal magnetic field of a one-electron atom. 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 which is responsible, in part, for the fine structure of the excited stages of one-electron atoms. A semiclassical calculation of the interaction energy may also be made.

Classically, the spinning electron in the orbit, similar to mechanical top in gravitational field, was expected to precess in a magnetic field. The motion of the magnetic moment of a particle, atom or molecule about the axis of an applied magnetic field is known as '*Larmour Precession*'. The magnetic moment sweeps out a cone about the direction of the magnetic field at a constant angular frequency as shown in Fig. 3.1.

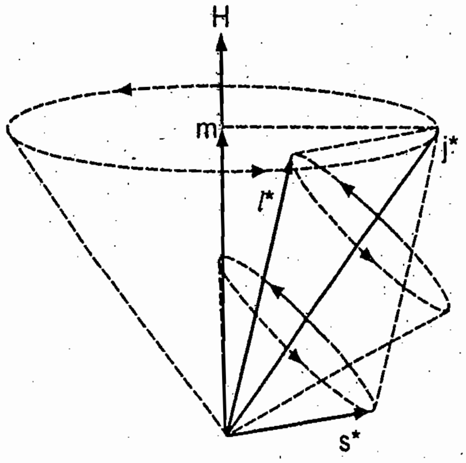


Fig. 3.1 : Classical precession of a single valence electron around the field direction H (Larmour precession)

For an atom, the angular frequency of precession, known as Larmour's frequency, is given by

$$\omega_L = H \cdot \frac{e}{2mc} \qquad \dots (3.1)$$

where $\frac{e}{m}$ is the charge to mass ratio of the electron, 'c' is the speed of light and 'H' is the intensity of magnetic field. In vector atom model, the orbit vectorially represents orbital angular momentum 'p_l'. So its projection on direction of $\vec{H}$ will give magnetic orbital quantum number m_l.

We know that

$$\frac{\mu_l}{p_l} = \frac{e}{2mc} \qquad \dots (3.2)$$

$$\therefore \quad \mu_l = p_l \cdot \frac{e}{2mc} = l \frac{eh}{4\pi mc} \qquad \dots (3.3)$$

$$\left(\because \; p_l = l \cdot \frac{h}{2\pi} \right)$$

where,
μ_l – magnetic moment
p_l – orbital angular momentum

The quantity $\frac{eh}{4\pi mc}$ in emu represents the smallest constant value of 'μ_l'. In terms of this smallest value, the magnitude of atomic and sub-atomic magnetic moments are measured. It is known as **Bohr magneton.** Its value is 9.21×10^{-21} erg-oersted^{-1} in emu. or 9.27×10^{-24} joule (wb/m^2)$^{-1}$ in MKS units.

∴ Therefore, the angular velocity of the Larmour precession can be written as

$$\omega_L = \frac{H \cdot \mu_l}{p_l} \quad \text{... (3.4)}$$

Similarly, the precession frequency is

$$\upsilon_L = \frac{H}{2\pi} \cdot \frac{\mu_l}{p_l} = H \cdot \frac{e}{4\pi mc} \quad \text{... (3.5)}$$

An electron behaves as if it possesses an intrinsic angular momentum $\frac{h}{2\pi}$ and magnetic moment. This electron moves in the electrical field $\vec{E}$ of the nucleus with velocity v. The magnetic field acts on this moving electron. The amount of magnetic field is given by,

$$\vec{H} = \frac{\vec{E} \times \vec{v}}{c} \quad \text{... (3.6)}$$

According to the electromagnetic theory, the electric field is

$$\vec{E} = \frac{Ze}{r^3} \vec{r} \quad \text{... (3.7)}$$

where 'Ze' is charge on the nucleus and 'r' is radial distance. From above two equations,

$$\vec{H} = \frac{Ze}{cr^3} \vec{r} \times \vec{v} \quad \text{... (3.8)}$$

According to Bohr's quantum condition,

$$m \vec{r} \times \vec{v} = l^* \frac{h}{2\pi} \quad \text{... (3.9)}$$

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

Therefore, the field becomes

$$H = l^* \frac{h}{2\pi} \frac{Ze}{mc} \cdot \frac{1}{r^3} \quad \text{... (3.10)}$$

In this field the spinning electron undergoes Larmour's precession around the field direction.

According to Larmour's theorem, angular velocity is the product of field strength (H) and the ratio between the magnetic and mechanical moment given by $\frac{e}{2mc}$.

$$\therefore \quad \omega_L = H \cdot 2 \cdot \frac{e}{2mc} \quad \text{... (3.11)}$$

The factor '2' is due to the fact that the ratio for spin motion is double than that for orbital motion. Substituting value of $\vec{H}$ from equation (3.10), the angular velocity ω_L becomes,

$$\omega_L = l^* \frac{h}{2\pi} \frac{Ze}{mc} \cdot \frac{1}{r^3} \cdot 2 \frac{e}{2mc}$$

$$\therefore \quad \omega_L = l^* \frac{h}{2\pi} \frac{Ze^2}{m^2c^2} \cdot \frac{1}{r^3} \qquad \dots (3.12)$$

If relativistic effect is considered, then there exists a relativistic precession of the electron in the opposite direction of the Larmour precession, the angular velocity of which is half that of Larmour type. Hence, the resultant precession is just half of that given by ω_L.

Therefore, the resultant angular velocity,

$$\omega = \frac{1}{2} \omega_L = \frac{1}{2} l^* \frac{h}{2\pi} \frac{Ze^2}{m^2c^2} \cdot \frac{1}{r^3} \qquad \dots (3.13)$$

$$\text{Now,} \quad \text{Interaction energy} = \begin{pmatrix} \text{Angular} \\ \text{velocity} \end{pmatrix} \times \begin{pmatrix} \text{Projection of spin} \\ \text{angular momentum} \\ \text{on } l^* \end{pmatrix}$$

$$\therefore \quad \Delta W_{ls} = \omega \times s^* \frac{h}{2\pi} \cos(l^* s^*) \qquad \dots (3.14)$$

$$\therefore \quad \Delta W_{ls} = \frac{1}{2} l^* \hbar \frac{Ze^2}{m^2c^2} \cdot \frac{1}{r^3} s^* \hbar \cos(l^* s^*) \qquad \left(\because \hbar = \frac{h}{2\pi}\right) \qquad \dots (3.15)$$

$$\therefore \quad \Delta W_{ls} = \frac{Ze^2}{2m^2c^2} \hbar^2 \cdot \frac{1}{r^3} \cdot l^* s^* \cos(l^* s^*) \qquad \dots (3.16)$$

$$\therefore \quad \Delta W_{ls} = \frac{Ze^2}{2m^2c^2} \frac{h^2}{4\pi^2} \cdot \frac{1}{r^3} \cdot l^* s^* \cos(l^* s^*) \qquad \dots (3.17)$$

The radial distance 'r' is the function of Z, n and l and it changes continuously in any given state.

Since the interaction energy is very small as compared to total energy, we need only to consider the average value of ΔW_{ls} and therefore of $\frac{1}{r^3}$.

From perturbation theory and quantum mechanics,

$$\left\langle \overline{\frac{1}{r^3}} \right\rangle = \frac{Z^3}{a_1^3 n^3 l \left(l + \frac{1}{2}\right)(l + 1)} \qquad \dots (3.18)$$

where 'a_1' is the radius of first Bohr orbit which is $\hbar^2/mc^2$.

So, the interaction energy, ΔW_{ls} becomes

$$\Delta W_{ls} = \frac{Ze^2}{2m^2c^2} \hbar^2 \cdot \frac{Z^2}{a_1^3 n^3 l \left(l + \frac{1}{2}\right)(l + 1)} \cdot l^* s^* (\cos l^* s^*) \qquad \dots (3.19)$$

For the factor $l^* s^* \cos(l^* s^*)$, we turn to the vector atom model.

In a field free space, both l^* and s^* precess around their resultant j^*. According to law of conservation of momentum, the resultant j^* and hence the angle between l^* and s^* always remain invariant. It is illustrated in Fig. 3.2.

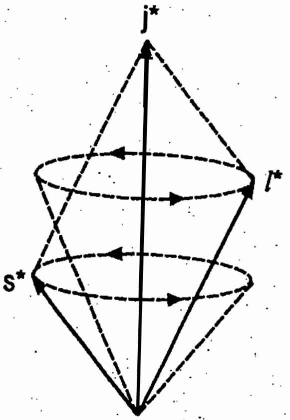


Fig. 3.2 : Precession of l^* and s^* around j^*

Using the Cosine law,

$$j^{*2} = l^{*2} + s^{*2} + 2l^* s^* \cos(l^* s^*) \qquad \dots (3.20)$$

Therefore ,

$$l^* s^* \cos(l^* s^*) = \frac{j^{*2} - l^{*2} - s^{*2}}{2} \qquad \dots (3.21)$$

Using the equations (3.18) and (3.21), the equation (3.17) becomes,

$$\overline{\Delta W_{ls}} = \frac{Ze^2}{2m^2c^2} \hbar^2 \cdot \frac{Z^3}{a_1^3 n^3 l \left(l + \frac{1}{2}\right)(l+1)} \cdot \frac{j^{*2} - l^{*2} - s^{*2}}{2} \qquad \dots (3.22)$$

$$\therefore \quad \overline{\Delta W_{ls}} = \frac{R\alpha^2 chZ^4}{n^3 l \left(l + \frac{1}{2}\right)(l+1)} \cdot \frac{j^{*2} - l^{*2} - s^{*2}}{2} \qquad \dots (3.23)$$

where, $R = \frac{2\pi^2 me^4}{ch^3}$ is Rydberg constant

and $\alpha^2 = \frac{4\pi^2 me^4}{c^2 h^2}$ is the square of the fine structure constant.

This interaction energy is also called *term shift.*

Dividing equation (3.23) by hc, we get *term-shift in wave numbers* as,

$$\Delta\Gamma_{l,s} = \frac{-R\alpha^2 Z^4}{n^3 l \left(l + \frac{1}{2}\right)(l+1)} \cdot \frac{j^{*2} - l^{*2} - s^{*2}}{2}$$

$$= -\Gamma \qquad \dots (3.24)$$

Negative sign indicates the convention that the term values are measured from series limit downwards.

This 'Γ' factor indicates spin-orbit interaction energy.

In short,

$$\Gamma = a\, l^* s^* \cos(l^* s^*)$$

$$\Gamma = a\frac{(j^{*2} - l^{*2} - s^{*2})}{2} \qquad \text{...(3.25)}$$

where,

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

3.3 ENERGY LEVELS OF SODIUM

In order to incorporate the features like orbits with large 'n' values, higher series members and series limits into the same atomic picture, energy level diagrams are frequently drawn. In *energy level diagrams*, the vertical axis is an energy axis and the energy levels or terms are shown as horizontal lines. The difference between any two levels gives directly the frequency of the radiation in wave numbers in cm^{-1}.

In atomic spectroscopy, the energy levels in the atom are described with a special name viz., '*terms*'. The energy value can be easily derived from the term value and also the representation by terms is much simpler. The zero of the energy is drawn at the top of the figure and other states below.

The deepest line with $n = 1$, represents the term value of the ground states and $n = \infty$ represents the zero of the energy, indicating the complete separation of electron. The term value increases in the downward direction. In energy level diagrams, the separation of the levels decreases towards the top of the diagram and converges to a value zero for $n \to \infty$. Few members each of various series like sharp series when initial level is S, similarly principal, diffuse, fundamental series are also indicated in the diagram.

Next to hydrogen, the alkali metals Li, Na, K, Rb and Cs have the simplest of the known spectra. Each alkali atom contains one single electron in an outermost shell in addition to the completed subshells of electron. It is this single unbalanced electron [so called optical electrons] which is responsible for the positive valence and simple spectrum of the alkali metals.

Sodium has eleven electrons. The electron configuration of the normal sodium atom is represented by $1s^2\, 2s^2\, 2p^6\, 3s$. The lowest level is a sharp or S level, followed by a principal or P level, then another sharp level S, a diffuse level D etc. Thus the energy level diagram of sodium consists of a series of sharp, principal, diffuse, fundamental energy levels approaching a common limit.

The normal or ground state 3^2s of sodium arises from the electron configuration $1s^2\, 2s^2\, 2p^6\, 3s$. In case of sodium, K and L shells are completely filled and if now the atom is to be excited, the different possible excited states for the outermost 3s electron are 3p, 3d, 4s, 4p, etc. depending upon the amount of excitation energy. The lower states 2p, 3s are designated as 2^2p and 3^2s. Also the stationary states are designated as 3^2P, 3^2D ... etc. All substates belonging to a given n in sodium have not same value of energy because of shield of nuclear charge and penetration of atomic core. The '*l* dependence' of energy is very important here, to the extent that 4S level lies lower than 3D orbit of the same orbit, similarly, 5S lies lower than 4D and 4F levels. For example, if now the excited electron is in 3p state then the complete electron configuration of the atom is represented as $1s^2\ 2s^2\ 2p^6\ 3p$ and the energy level 3^2P.

Similarly, if now the electron is in the 3d state, the electron configuration becomes as $1s^2\ 3d$ (2s electron shifted to higher 3d level) and the energy level 3^2D.

This same designation scheme is used for the level assignments shown for sodium in the Fig. 3.3. The electron configuration of each level is given by the excited electron only. Term values for sodium are given in table 3.1 which are shown in the left side of the figure.

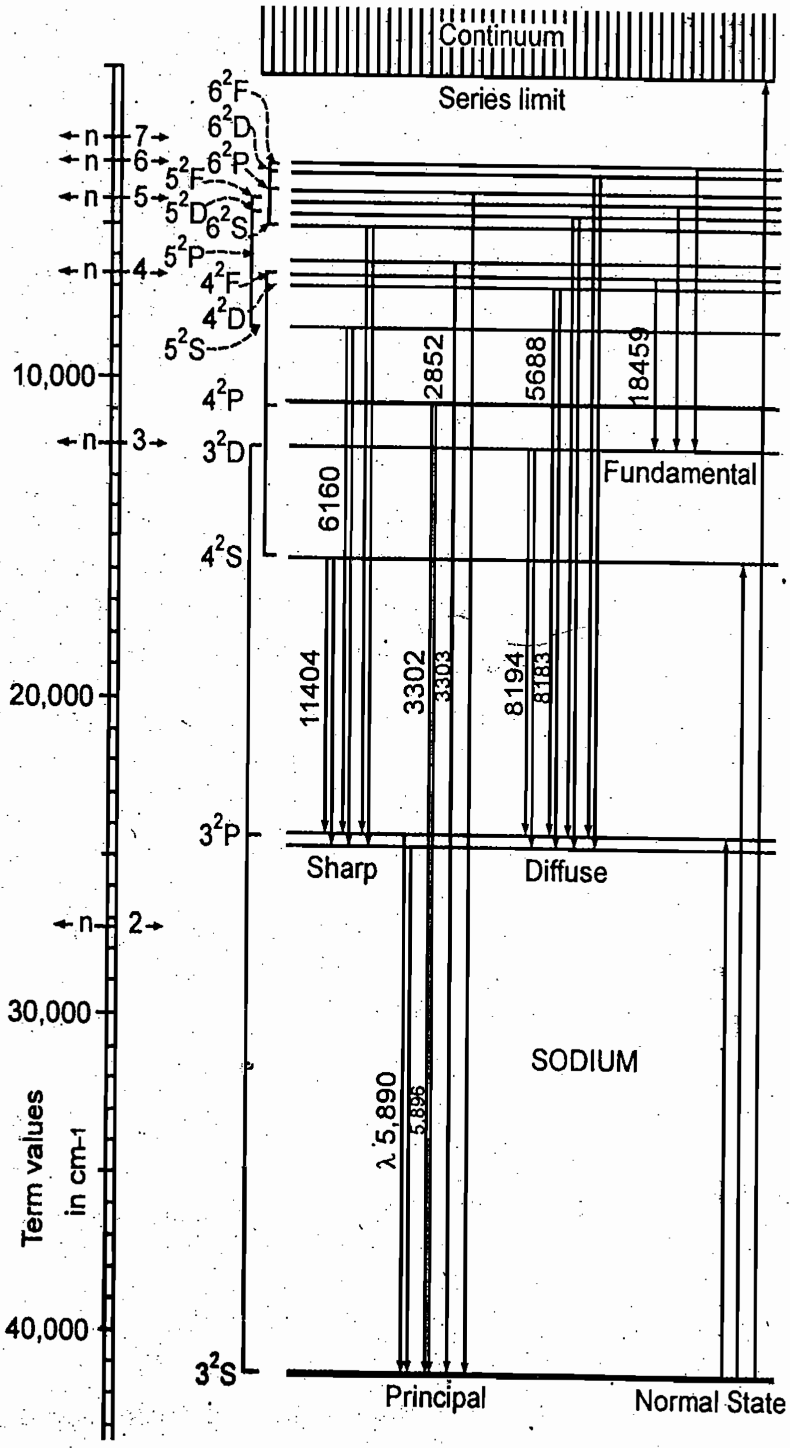


Fig. 3.3 : Energy levels of normal sodium atom

This diagram also shows the doublets (fine structure) and different lines of some components of the series.

Table 3.1 : Term values of sodium

Term	Electron	n = 3	n = 4	n = 5	n = 6	n = 7	n = 8
^{2}S	s, l = 0	41444.9	15706.5	8245.8	5073.7	3434.9	2481.9
^{2}P	p, l = 1	24492.7	11181.9	6408.9	4152.9	2908.9	2150.7
^{2}D	d, l = 2	12274.4	6897.5	4411.6	3059.8	2245.0	1720.1
^{2}F	f, l = 3		6858.6	4388.6	3039.7	2231.0	1708.2

These values are shown on the left side of the Fig. 3.3.

3.4 SELECTION RULES

General rules concerning the transitions which may occur between the states of a quantum-mechanical, physical system are known as *selection rules*. In other words, the transition rules in spectroscopy are known as selection rules. Physically, the selection rules arise because of symmetry properties of the oscillating charge distribution of the atom. It is experimentally found that all the possible combinations of permitted energy states of an atom don't actually appear as spectral lines.

We have seen that transitions can take place between 'S' and 'P' states, 'P' and 'D' states, 'D' and 'F' states, but under normal conditions no transitions can take place between 'S' and 'D' states, 'S' and 'F' states or 'P' and 'F' states. It is because of certain restrictions in transitions. These restrictions are called 'Selection Rules'.

On the basis of Selection Rules, transitions are called 'allowed' or 'forbidden'. These rules were first introduced on a purely empirical basis, but they were obtained by a rigorously deductive method in wave mechanics and hence they now rest on a permanent theoretical basis. These selection rules have been devised for L, for J and for S etc.

The selection rules are as follows :

(a) The selection rule for L : For this quantum number, the rule is $\Delta L = \pm 1$, i.e., transitions take place only between levels whose L quantum number differs by one i.e. only these lines are observed for which the value of L changes by ± 1.

(b) The selection rule for J : It is $\Delta J = \pm 1$ or 0. ($0 \leftrightarrow 0$ excluded). $\Delta J = 0$ is also permissible because the direction of spin of an electron in an orbit can have only two possible values ± 1/2, so that a change in 'S' of ± 1, when added vectorially to $\Delta L = \pm 1$ can lead to $\Delta J = 0$.

(c) The selection rule for S : For this quantum number, the rule is $\Delta S = 0$ which means that states that different 'S' (hence different multiplicities) do not combine with one another. Theory and experiment, however, show that this selection rule is only an approximate rule holding good in the case of light atoms.

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

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

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

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

In consequence,

$$\Delta m_j = 0 \text{ or } \pm 1.$$

These selection rules are statements of transition probabilities that are based on quantum mechanical calculations. These rules are useful in alloting proper quantum numbers to observe spectral lines in the series. With their aid, energy level diagrams can be constructed for natural complex multiplet lines and Zeeman effect lines.

3.5 SPECTRA OF SODIUM ATOM

Let us consider the optical excitations of **multi electron** atoms with the simplest case, alkali atoms. In their ground states, these atoms contain a set of completely filled subshells, the highest energy one being a p-subshell, plus a single additional electron in the next subshell.

In the optical line spectrum of an alkali atom, the excited states can be described completely by describing the single, so called optically active electron and the core of filled subshells can be ignored. The total energy of the atom is equal to that of the optically active electron.

Sodium is one of the alkali metals. The optical spectrum of sodium is typical spectrum of all the alkali atoms. Sodium atoms have 11 electrons. It consists of a nucleus, the core of 10 electrons which is an inert core of electrons in states $1s^2\ 2s^2\ 2p^6$ and contributes nothing to the angular momentum of the atom. Thus, first two shells are completed. The eleventh free electron or optical electron alone is responsible for the spectrum.

This 3s electron when excited, jumps to higher energy states, such as 3p, 4s, 3d, 4s, 5s, 5d, etc. depending upon the amount of excitation energy. When the atom returns back to its lower energy state, radiation is emitted in the form of a photon of definite frequency given by Bohr's frequency conditions. These electron transitions from higher energy orbit to lower energy orbit are responsible for different lines observed in sodium spectrum.

Actually the spectrum of sodium reveals that some lines consist of doublets. It is well known that the first member of the principal series is the sodium yellow line, (sodium D lines doublet) which is seen to consist of two lines very close to each other and separated by about 6A° with the help of a spectrograph with a high resolving power. These lines are due to transitions from a P state to the lowest (ground) S state. All lines in the principal, sharp and diffuse series, are doublet and are said to have 'fine structure'.

Since there is only one value J, the ground state of sodium is called singlet, though actually we get, multiplicity

$$2S+1 = 2.$$

As for the lowest state 3S, $l = 0$, $s = 1/2$ and $L = 0$, $S = \frac{1}{2}$, $2S + 1 = 2$, $J = \frac{1}{2}$. In terms of term-symbol, this state is written as $3^2S_{1/2}$.

For the P state, $l = 1, \; s = 1/2$

$$L = 1, \quad s = 1/2$$

$$\therefore \quad 2s+1 = 2$$

$$\therefore \quad J = L - 1/2 \text{ and } L + 1/2$$

$$\therefore \quad J = \frac{1}{2}, \frac{3}{2}.$$

Thus P state is a doublet state and is designated as $2P_{1/2}$ and $2P_{3/2}$.

Similarly, D state is also doublet state, written as $2D_{3/2}$ and $2D_{5/2}$.

In the same way, we get doublet everywhere except ground state. The lines of the optical spectrum emitted by alkali elements show a fine structure splitting which indicates that all energy levels are double except those for $l = 0$. This is due to a spin-orbit interaction acting on the optically active electron.

The energy level diagram of sodium is shown in Fig. 3.4. It shows the different lines in the different series and their transitions in the spectrum of sodium. These transitions of lines can be represented in four main series as follows

(1) Sharp series:

Transitions – $n^2 S_{1/2} \rightarrow 3^2 P_{3/2,\,1/2}$, doublet

$n = 4, 5, 6 \ldots$

(2) Principal series:

Transitions – $n^2 P_{3/2,\,1/2} \rightarrow 3^2 S_{1/2}$, doublet

$n = 3, 4, 5 \ldots$

(3) Diffuse series:

Transitions – $n^2 D_{5/2,\,3/2} \rightarrow 3^2 P_{3/2,\,1/2}$, triplets

$n = 3, 4, 5 \ldots$

(4) Fundamental series:

Transitions – $n^2 F_{7/2,\,5/2} \rightarrow 3^2 D_{5/2,\,3/2}$, triplets

$n = 4, 5, 6 \ldots$

As sodium source contains a large number of atoms, all possible excited states are available for transition, hence all the series are simultaneously observed. Note that in Fig. 3.4, the $2P_{3/2}$ level is actually slightly above the $2P_{1/2}$ level as j value is greater. The separation of levels decreases as the value of n (total quantum number) increases. Thus, the 3P double is wider than 3D and 3D is wider than 3F and so on. The spectral lines are emitted in transitions between energy levels whose quantum numbers satisfy the selection rules

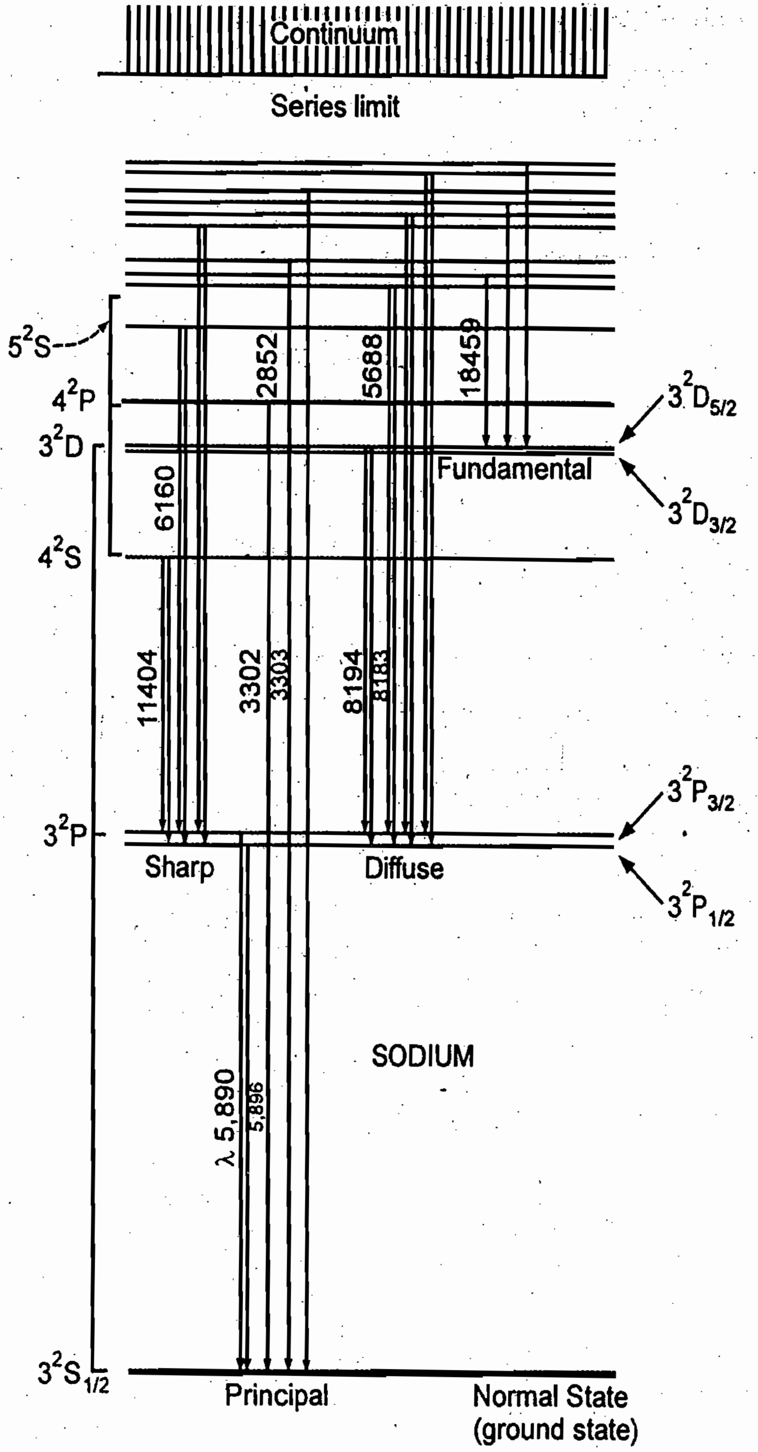


Fig. 3.4 : Transitions of spectral lines in energy level diagram of sodium atom

$$\Delta l = \pm 1$$
$$\Delta j = 0, \pm 1.$$

The transitions of diffuse series are

$3^2 D_{5/2,\,1/2} \rightarrow 3^2 P_{3/2,\,1/2}$ and give triplets as shown in Fig. 3.5.

(The transition $3^2D_{5/2} \rightarrow 3^2 P_{1/2}$ is forbidden as $\Delta J = +2$).

Similarly, we get triplets for the transitions of fundamental series.

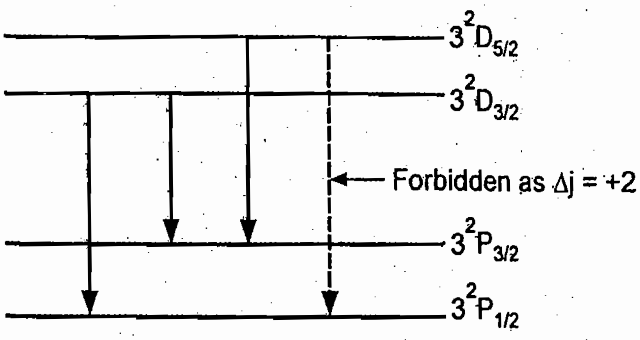


Fig. 3.5 : Triplet transitions of diffuse series

The resulting triplet of lines is known as a *compound doublet*. Thus the chief spectrum of sodium consists of spectral doublets and compound doublets.

3.6 The Sodium Doublet

As mentioned earlier, ten electrons of the normal sodium atom are interlocked in closed shells, so that the eleventh free electron alone is responsible for the spectrum. All the states of the sodium reveal that many lines are double.

In the multielectron system, the energy depends not only on the values of 'n' and 'L' but also on the value of J. Thus the $^2S_{1/2}$ terms are not splitted, since there is only one possible value of J namely $J = \frac{1}{2}$. On the other hand, the ^2P terms have J = 3/2 and J = 1/2 so that the energy of $^2P_{3/2}$ is slightly higher than that of $^2P_{1/2}$.

The upper terms ^2D, ^2F ... are also splitted, but the magnitude of the separation is too small to be noticeable.

Effectively only the ^2P level is splitted and any transition to or from this level results in two closely spaced lines. The classical example is the yellow sodium doublet lines which are also known as sodium 'D' lines at 589.592 nm and 588.995 nm. The D_1 component (5896 A°) is due to the transition $P_{1/2} \rightarrow S_{1/2}$ and the 'D_2' component (5890 A°) to $P_{3/2} \rightarrow S_{1/2}$ as shown in the Fig. 3.6. This well known bright doublet which is responsible

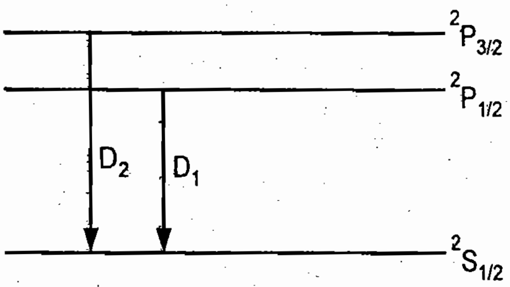


Fig. 3.6 : Principal series doublet

for the bright yellow light from a sodium lamp may be used to demonstrate several of the influences which cause splitting of the emission lines of atomic spectra.

Applying the selection rules $\Delta L = \pm 1$ and $\Delta J = 0$ or ± 1 (excluding $0 \rightarrow 0$), both the transitions are allowed, which explains the doublet fine structure of the sodium 'D' line. The diffuse and fundamental series start from doublet levels and end on doublet levels but the selection rules only permit triplets.

The doublet character of Na-spectrum is shown in Fig. 3.7.

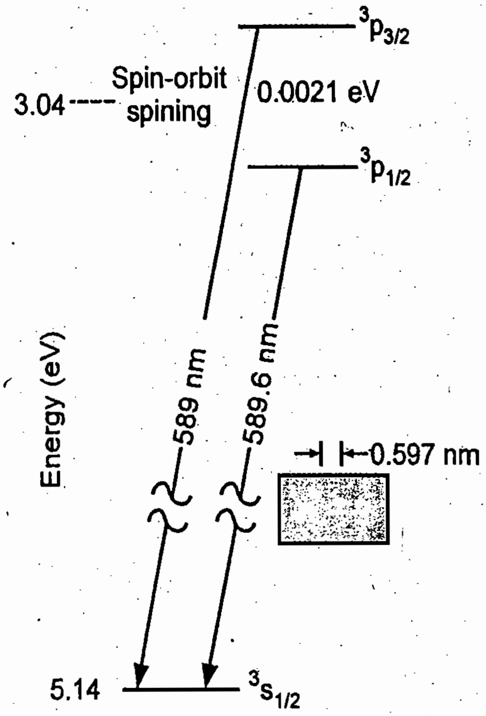


Fig. 3.7 : Sodium doublet

Some points are also noted in regarded to alkali spectra.

(1) Corresponding doublet separation increases with atomic number.

(2) Doublet separations in the ionised alkaline earths are larger than the corresponding doublets in the alkali metals.

(3) Within each element, doublet separations decrease in going to higher members of a series.

(4) Within each element 'P' doublets are wider than 'D' doublets of the same 'n' and 'D' are wide than 'F' of the same 'n'. Above figure explains these facts. Hence, in alkali spectra every component level is double excluding 'S' level because for 'S' state $l = 0$, so the possible value of j is only one i.e. 1/2.

SOLVED EXAMPLES

Example 3.1 : The frequency of strong yellow line in the spectrum of sodium is 5.09×10^{14} sec^{-1}. Calculate the wavelength of the light in nanometers.

Solution : We have the relation,

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

Here, in this case,

$$c = 3.0 \times 10^8 \text{ m sec}^{-1}$$
$$\upsilon = 5.09 \times 10^{14} \text{ sec}^{-1}$$

$\therefore$ The wavelength of light,

$$\lambda = \frac{3 \times 10^8}{5.09 \times 10^{14}} = 589 \times 10^{-9}$$

$$\therefore \quad \lambda = 589 \text{ nm}$$

Thus the wavelength of sodium light is 589 nm.

Example 3.2 : Find the orbital angular momentum of 'd' electron.

Solution : For 'd' electron, $l = 2$.

As, the orbital angular momentum is given as,

$$l^* = \sqrt{l(l+1)}\ \hbar$$

$$\therefore \quad l^* = \sqrt{l(l+1)}\ \frac{h}{2\pi}$$

$$l^* = \frac{\sqrt{2(2+1)} \times 6.63 \times 10^{-34}}{2 \times 3.14}$$

$$\therefore \quad l^* = 2.58 \times 10^{-34} \text{ Js.}$$

Thus, the orbital angular momentum for 'd' electron is 2.58×10^{-34} Js.

Example 3.3 : Calculate the value of electronic angular momentum of a one-electron atom in the state $^2D_{5/2}$.

Solution : The given term is $^2D_{5/2}$.

For this term,

$$\text{Multiplicity m} = 2S+1 = 2,\ S = \frac{1}{2} \text{ and } L = 2.$$

$$\therefore \quad J = L + S = 2 + \frac{1}{2} = \frac{5}{2}$$

The total electronic angular momentum is given by,

$$J^* = \sqrt{J(J+1)}\ \frac{h}{2\pi}$$

$$\therefore \quad J^* = \sqrt{\frac{5}{2}\left(\frac{5}{2}+1\right)} \times \frac{6.63 \times 10^{-34}}{2 \times 3.14}$$

$$\therefore \quad J^* = 3.123 \times 10^{-34} = 3.123 \times 10^{-34} \text{ Js}$$

Example 3.4 : The mean position of the first pair of lines of the principle series of sodium is 16960 cm^{-1}. If the convergence limit of the sharp series lines is at 24490 cm^{-1}, calculate the ionisation potential of sodium.

Solution : The first line (ignoring doublet structure) of the principal series corresponds to 3s – 3p and the convergence limit of the sharp series corresponds to $3p \rightarrow \infty$.

The sum of these two wave numbers

$$16960 + 24490 = 41450 \text{ cm}^{-1}$$

corresponds to $3s \rightarrow \infty$. i.e. the ionisation of the atom.

This wave number converted to electron-volt (eV) gives the ionisation energy which is,

$$\frac{41450}{8066} = 5.14 \text{ eV} \qquad [\because 1 \text{ eV} = 8066 \text{ cm}^{-1}]$$

Hence, the ionisation potential of sodium atom is 5.14 volts.

Example 3.5 : The ionisation energy of sodium is 494.7 kJ mol^{-1}. Calculate the wavelength of the electromagnetic radiation which is just sufficient to ionise the sodium atom. (Given : $c = 3 \times 10^8$ ms^{-1}; $h = 6.6 \times 10^{-34}$ Js; $N_A = 6.02 \times 10^{23}$).

Solution : The ionisation energy of sodium is

$$\Delta E = 494.7 \text{ kJ/mol}$$

$$= \frac{494.7 \times 10^3}{6.02 \times 10^{-23}} \text{ J/atom}$$

$$\therefore \quad \lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^{23}}{494.7 \times 10^3}$$

$$\lambda = 24.09 \times 10^{-7} \text{ m}$$

QUESTIONS AND PROBLEMS

(A) Multiple choice questions or objective problems :

1. The doublets observed in alkali spectra are due to ....
   (a) screening of k-electrons.
   (b) spin-orbit interaction of the electrons.
   (c) pressure of isotopes.
   (d) none of these.
2. The Bohr magneton is of the order of ....
   (a) 10^{-23} erg/gauss.
   (b) 10^{-20} erg/gauss.
   (c) 10^{-25} erg/gauss.
   (d) none of these.
3. The maximum change in energy of a 'p' electron due to the precessional motion of its orbit in a magnetic field of 3×10^4 gauss is of the order of
   (a) 2.8×10^{-8} ergs.
   (b) 2.8×10^{-12} ergs.
   (c) 2.8×10^{10} ergs.
   (d) 2.8×10^{-16} ergs.
4. Which of the interactions cause to the non-conservation of orbital angular momentum of the electrons in an atom ?
   (a) spin-orbit interaction.
   (b) spin-spin interaction.
   (c) electrostatic interaction between electrons.
   (d) electrostatic interaction between electrons and nucleus.
5. The selection rule for orbital quantum number for electric dipole transitions in single electron atom is...........
   (a) $\Delta l = 0, \pm 1$ (b) $\Delta l = \pm 1$
   (c) $\Delta l = 0$ (d) $\Delta l = 1$.

Ans. (1) b, (2) b, (3) d, (4) a, (5) c.

(B) Short answer questions :

1. Define spin-orbit interaction energy.
2. State Larmour theorem.
3. What is spin-orbit interaction ?
4. Why 4s level is filled first by electrons than 3d level in outer atomic shells of atom ?
5. What is the selection rule for the orbital quantum number for electric dipole transitions in a single electron atom ?
6. What is the S value for $^2D_{3/2}$?
7. What is the 'L' value for state $^2D_{3/2}$?
8. What are the values of total angular momentum of single 'f' electrons ?
9. What are selection rules ?
10. Why we get triplets for the transitions of fundamental series ?
11. What are the selection rules for quantum numbers 'm_s' and 'm_l' ?
12. What are the selection rules for quantum numbers 'L' and 'S' ?

(C) Answer in brief.

1. Derive spin-orbit interaction energy expression. What is the significance of negative sign ?
2. Draw energy level diagram and discuss the energy levels of sodium.
3. What are selection rules ? Describe selection rules in connection with different quantum numbers.
4. Mention uses of selection rules.
5. Discuss the spectrum of sodium, explaining fine structure of sodium D lines.
6. Explain the existence of doublets and triplets in the series of sodium spectrum.
7. Give the representation of spectral lines of different series in sodium spectrum in terms of term symbols.
8. Derive the expression for ω_L for spin orbit interaction. What is the change in ω_L due to relativistic treatment ?
9. Describe the main features of the doublet character of Na-spectrum.
10. Discuss the spectra of sodium atom and draw.
    (a) Energy level diagram.
    (b) Fine structure.

(D) Numerical Problems :

1. If one of the states of the configuration is $^6H_{6/2}$, what are the other possible states ?
2. Calculate the values of
   (a) l, s and j (b) L, S, and J
   For a 'd' electron in one-electromatic system.
3. Use the vector model of the atom to determine possible values of the total angular momentum for a sodium, when principal quantum number n = 3. Draw an energy level diagram and indicate the transitions you would expect to occur. Calculate the angles between $\vec{l}$ and $\vec{s}$ vectors in each case.

□□□

4

Spectra of Two Valence Electron System

4.1 INTRODUCTION

In the previous chapter, we have calculated interaction energy by the use of vector atom model. Further we have introduced the optical spectrum of sodium atom which is one valence electron atom and also studied related selection rules. The one-electron system gives rise to doublet energy levels and transitions between them give doublets.

In this chapter, we introduce the role of two valence electron system and study the spectra associated with it. It is observed that the atoms like beryllium, magnesium, zinc, cadmium, mercury, calcium, etc. contain two valence electrons and give rise to series of singlet and triplet energy levels and spectrum lines. In this chapter, we also discuss coupling schemes like L-S, j-j couplings, singlet-triplet separation.

Then we shall move on to the Lande's interval rule and spectra of He-atom which is two valence electron atom.

4.2 SPECTRAL TERMS OF TWO ELECTRON ATOM

We have already seen in the vector atom model that each component part is assigned a quantum number, the numerical value of which may conveniently the thought of as the length of the vector which represents the angular momentum of that component.

Each electron is assigned a spin angular momentum $s^* \frac{h}{2\pi}$ where $s^* = \sqrt{s\,(s+1)}$ and $s = \frac{1}{2}$ in addition to the orbital angular momentum $l^* \frac{h}{2\pi}$ where $l^* = \sqrt{l\,(l+1)}$ ($l = 0, 1, 2, 3, \ldots$). Two-electron system is one of the many-electron system and in these systems each electron has its 'l' and 's' or 'l^*' and 's^*' vectors. The vector addition of all angular momentum vectors would give the total angular momentum (J) of the atom.

There are several ways in which the different vectors of the electrons may combine to give the vectors representing the atom as a whole. The method of combination depends on the interaction (or coupling) between the component vectors.

Each spin may couple to its own orbit as in case of one-electron; other possibilities are orbit - other orbit, spin-spin and so on. Out of the possible ways, two couplings namely L-S and j-j are more prominent. The total angular momentum of the atom as a whole gives the energy state (or energy levels). Often the words-the term or term value-are used in place of energy level. The terms for two valence electron atom can be determined by using the coupling schemes.

Electron configurations commonly occuring in two-electron systems are s·s, pd, pf, d·d, df, etc.

Let us consider first the ll, ss, jj coupling schemes.

Orbit-Orbit or ll Coupling Scheme :

Consider the orbital motions of two electrons and let l_1 and l_2 represent their respective orbital quantum numbers. Their angular momenta are $l_1^* \frac{h}{2\pi}$ and $l_2^* \frac{h}{2\pi}$ or simply l_1^* and l_2^* respectively.

On quantum mechanical approach l_1^* and l_2^* are quantized with respect to each other in such a way that they form a resultant L^* where $L^* = \sqrt{L(L+1)}$ and L = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, ... for S, P, D, F, G, H, I, J, K, L, ... terms respectively.

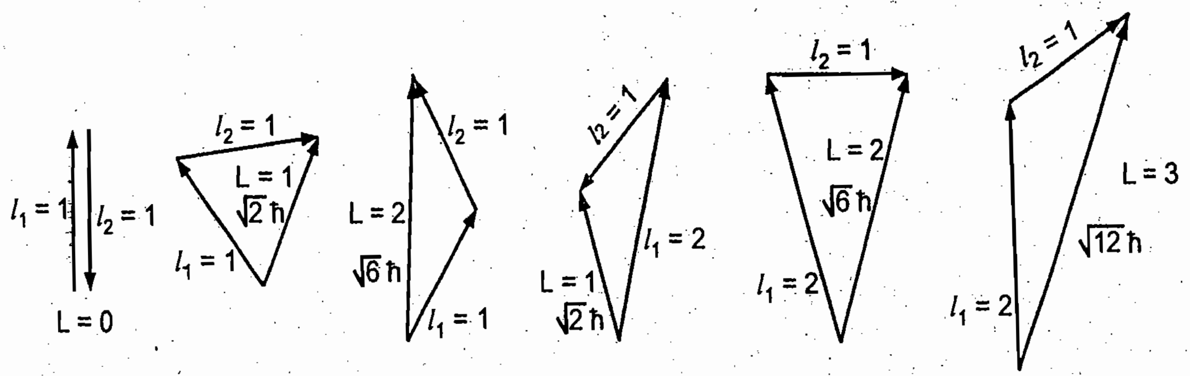


Fig. 4.1 : Schematic diagram suggesting how $l_1 \oplus l_2$ gives L = 0, 1 or 2 when $l_1 = 1$, $l_2 = 1$ and gives L = 1, 2 or 3 when $l_1 = 2$, $l_2 = 1$

Fig. 4.1 shows how $l_1 + l_2$ gives L = 0, 1, 2, ...

Consider, for example, one electron in a 'p' orbit and the other in a 'f' orbit. i.e. a 'pf' configuration.

For 'p' electron, $l_1 = 1$

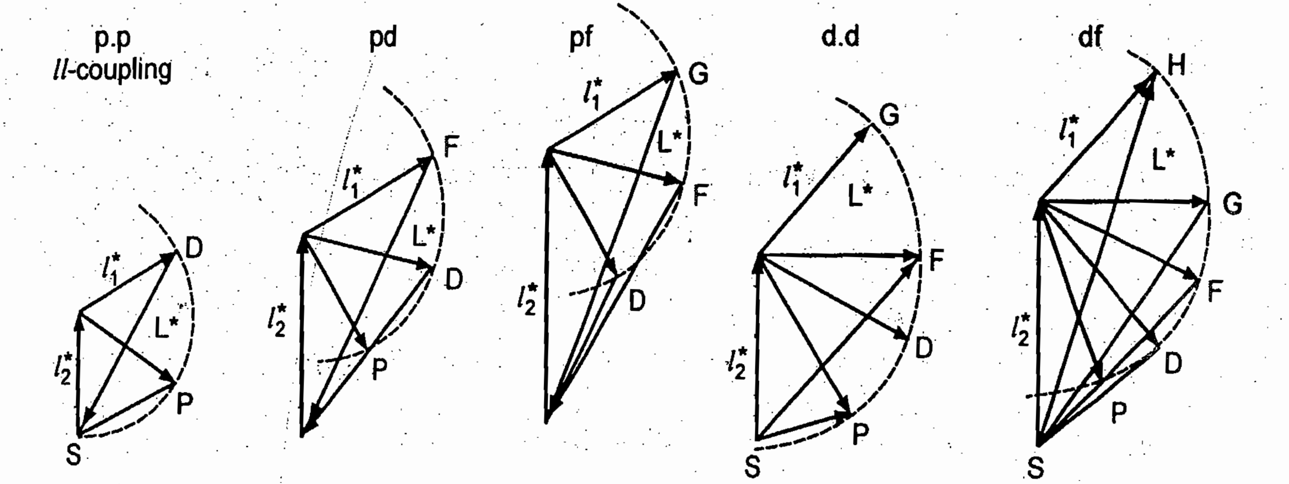
and for 'f' electron, $l_2 = 3$

The two vectors $l_1^* = \sqrt{l_1(l_1+1)}$ and $l_2^* = \sqrt{l_2(l_2+1)}$ are

$$l_1^* = \sqrt{1(1+1)} = \sqrt{2}$$

and
$$l_2^* = \sqrt{3(3+1)} = \sqrt{12}$$

These two vectors $l_1^* = \sqrt{2}$ and $l_2^* = \sqrt{12}$ may orient themselves in any one of three positions, $L^* = \sqrt{6}, \sqrt{12}$ and $\sqrt{20}$ corresponding to L = **2, 3, 4,** (**or** D, F, G terms) respectively. 'L' has integral values between '$l_2 - l_1$' to '$l_2 + l_1$' for $l_2 \geq l_1$. **Vector** diagrams of ll coupling for the 'pf' configuration and other electron **configurations commonly** occuring in two-electron systems are also shown in Fig. 4.2.



$l_1 = 1, l_2 = 1$
L = 0, 1, 2

$l_1 = 1, l_2 = 2$
L = 1, 2, 3

$l_1 = 1, l_2 = 3$
L = 2, 3, 4

$l_1 = 2, l_2 = 2$
L = 0, 1, 2, 3, 4

$l_1 = 2, l_2 = 3$
L = 0, 1, 2, 3, 4, 5

Fig. 4.2 : Vector diagrams of *ll* couplings in two valence electron systems

The different terms for the different electron configuration obtained are given in the following term table 4.1.

Table 4.1

s.s, S	ps, P	ds, D	fs, F
sp, P	p.p, SPD	dp, PDF	fp, DFG
sd, D	pd, PDF	d.d, SPDFG	fd, PDFGH
sf, F	pf, DFG	df, PDFGH	f.f, SPDFGHI

The dot between two electrons of the same type indicates that the electrons have different total quantum numbers. If they are alike, some of the terms are not allowed. When $l_2 < l_1$, the roles of the two electrons are interchanged. We observe from Table 4.2 that a 'p' term may arise from two electrons in 'd' orbits. It is also observed that the atom may be in a 3P, a 3D or a 3F state in case of two electrons when one in a 'p' orbit and other in a 'd' orbit.

ss Coupling :

With two electrons, each having a spin angular momentum of $S^* \frac{h}{2\pi}$ where $S^* = \sqrt{S(S+1)}$ and $S = \frac{1}{2}$, there are two ways in which a spin resultant $S^* \frac{h}{2\pi}$ may be formed. Let s_1^* and s_2^* represent the respective spin vectors of the two electrons.

$s_1 = 1/2, \; s_2 = 1/2$
S = 0

$s_1 = 1/2, \; s_2 = 1/2$
S = 1

Fig. 4.3 : Vector diagrams of ss coupling of two valence electrons

Quantizing these (as shown in Fig. 4.3) we get, $s_1^* = \frac{1}{2}\sqrt{3}$ and $s_2^* = \frac{1}{2}\sqrt{3}$. The two resultants are one with $S^* = 0$ and the other with $S^* = \sqrt{2}$. Thus, the resultant quantum values are $S = 0$ and $S = 1$. The resultant $S^* = 0$ will give rise to singlet terms while $S^* = \sqrt{2}$ gives rise to triplet terms.

We must have to consider the coupling between electron vectors and configuration for the spectral terms in case of two valence electrons. The LS coupling which occurs most frequently and hence is also known as normal coupling. In this type the several spin vectors 'S' of the electrons combine to form a resultant S^*; the several orbital vectors 'l' of the electrons likewise combine to form a resultant L^*; and then finally L^* and S^* after coupling form J^* which represents the total angular momentum of the atom $J^* \frac{h}{2\pi}$. The guiding principles in this type of coupling show that J must always be positive, never negative and $J^* = \sqrt{J(J+1)}$

Consider as a specific example, the case of one electron in a 'p' orbit and the other in a 'd' orbit. i.e. two electrons in a 'pd' configuration in LS coupling.

For 'p' electron,

$$l_1 = 1 \text{ and } s_1 = \frac{1}{2}$$

Similarly, for 'd' electron,

$$l_2 = 2 \text{ and } s_2 = \frac{1}{2}$$

∴ L values in this case are,

$$L = (2+1), \ldots (2-1) = 3, 2, 1$$

and S = '0' or '1'.

The multiplicity of the state is given by,

$$m = (2S+1).$$

Here $m = 1 \text{ or } 3$.

Therefore, the state is either singlet or triplet. Thus, two-electron system gives rise to singlets or triplets with L = 1, 2, 3 and corresponding 'P', 'D', 'F' terms.

Also, J has values lying between (L + S) and (L – S) ∴ The term symbols for S = 0 and J = L = 1, 2, 3 are $^1P_1$, $^1D_2$, $^1F_3$ which corresponds to three singlet terms.

With S = 1 there are three possibilities for each of the three L's.

When S = 1, L = 1 ('P' terms) then 'J' has values lying between (1 + 1) and (1 – 1) i.e. 0, 1, 2 values.

∴ The term symbols for S = 1 and L = 1 corresponding J = (1 + 1) ... (1 – 1) are $^3P_0$, $^3P_1$, $^3P_2$ or can be written as $^3P_{0,1,2}$.

Similarly, we get the term symbols for L = 2 and L = 3 i.e. 'D' and 'F' terms as $^3D_{1,2,3}$ and $^3F_{2,3,4}$.

The term S, P, D, F, ... gives the value of L, and the subscript gives the resultant value of J. The superscript to left expresses multiplicity.

Hence, 'pd' configuration of two electrons in LS coupling gives in all twelve terms, three singlet and nine triplet as shown in the vector diagram in Fig. 4.4.

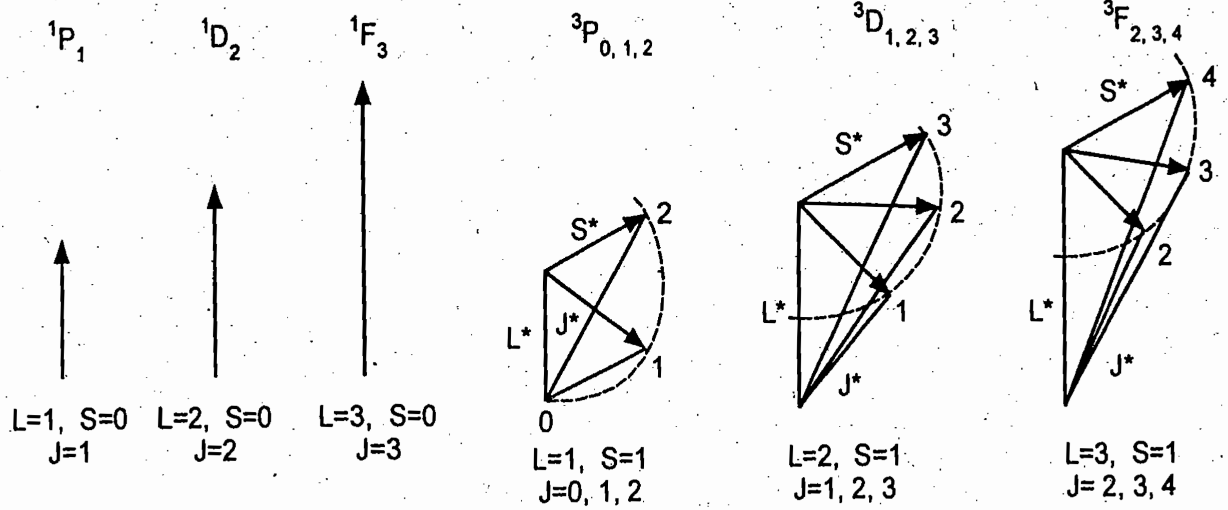


Fig. 4.4 : Vector diagrams of two pd valence electrons in LS coupling

All allowed terms arising from common two valence electron configurations are given in table 4.2.

Table 4.2

s·s, $^1S_0\ ^3S_1$	p·p, $^1S_0\ ^1P_1\ ^1D_2$	$^3S_1\ ^3P_{0,1,2}\ ^3D_{1,2,3}$
s p, $^1P_1^o\ ^3P_{0,1,2}$	p d, $^1P_1^o\ ^1D_2^o\ ^1F_3^o$	$^3P_{0,1,2}^o\ ^3D_{1,2,3}^o\ ^3F_{2,3,4}^o$
s d, $^1D_2\ ^3D_{1,2,3}$	p f, $^1D_2\ ^1F_3\ ^1G_4$	$^3D_{1,2,3}\ ^3F_{2,3,4}\ ^3G_{3,4,5}$
s f, $^1F_3^o\ ^3F_{2,3,4}^o$	d d, $^1S_0\ ^1P_1\ ^1D_2\ ^1F_3\ ^1G_4$	$^3S_1\ ^3P_{0,1,2}\ ^3D_{1,2,3}\ ^3F_{2,3,4}\ ^3G_{3,4,5}$

Terms, for which the sum '$l_1 + l_2$' is odd, are called 'odd' terms, all others are called even terms. Odd terms are distinguished by the small superscript "o" to the right of the term symbol S, P, D, ... etc.

jj Coupling :

In this type of coupling, the spin s_1^* of one electron is quantized with respect to its own l_1^* to form a resultant j_1^* such that j_1 takes half-integral values only.

Similarly, for second electron, s_2^* and l_2^* gives j_2^*, which also takes half-integral values. These j_1^* and j_2^* are in turn quantized with respect to each other to form a resultant J^*, such that J takes integral values only.

As an example, consider 'pd' configuration.

For the 'p' electron :

$$l_1 = 1,\ s_1 = \frac{1}{2} \quad \therefore\ j_1 = \frac{1}{2} \text{ and } \frac{3}{2}$$

For the 'd' electron :

$$l_2 = 2,\ s_2 = \frac{1}{2} \quad \therefore\ j_2 = \frac{3}{2} \text{ and } \frac{5}{2}$$

Combining these four values of j in all possible ways, we obtain,

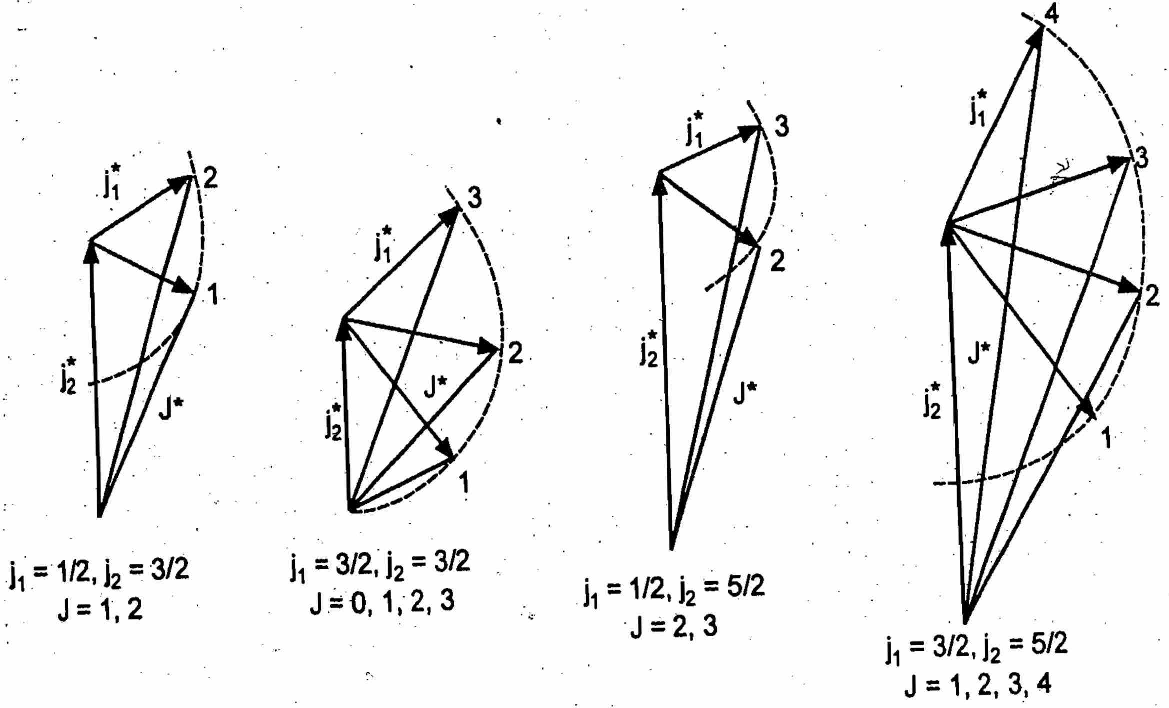
when $j_1 = \frac{1}{2}, j_2 = \frac{3}{2} \quad \therefore \; J = 1 \text{ and } 2$

$j_1 = \frac{1}{2}, j_2 = \frac{5}{2} \quad \therefore \; J = 2 \text{ and } 3$

$j_1 = \frac{3}{2}, j_2 = \frac{3}{2} \quad \therefore \; J = 0, 1, 2, 3$

$j_1 = \frac{3}{2}, j_2 = \frac{5}{2} \quad \therefore \; J = 1, 2, 3, 4, \text{etc.}$

Thus, in all 'J' values are twelve, giving the same number of terms arrived in the LS coupling scheme. The vector diagrams of 'pd' electrons in jj coupling are shown in Fig. 4.5.



$j_1 = 1/2, j_2 = 3/2$ $J = 1, 2$

$j_1 = 3/2, j_2 = 3/2$ $J = 0, 1, 2, 3$

$j_1 = 1/2, j_2 = 5/2$ $J = 2, 3$

$j_1 = 3/2, j_2 = 5/2$ $J = 1, 2, 3, 4$

Fig. 4.5 : Vector diagrams of two pd valence electrons in jj coupling

4.3 TERMS FOR EQUIVALENT ELECTRONS

If two electrons have the same total quantum number n, and the same azimuthal quantum number 'l', they are called *equivalent electrons*. All the equivalent electrons are not allowed to enter into the configuration. Some of them are excluded by the application of Pauli's Principle.

In the calculation of spectral terms arising from two or more equivalent electrons we must take the Pauli's exclusion principle into account and start with the very strong magnetic field quantum numbers n, l, m_l and m_s. This set of quantum numbers is used in the presence of a strong magnetic field where the coupling between the electrons is completely broken down for the calculation of the allowed spectral terms arising from two equivalent electrons.

Consider as an example, two equivalent 'p' electrons. We first write down the six possible states for a single 'p' electron in a very strong field. They are :

$m_s =$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$m_l =$	1	0	-1	1	0	-1
	(a)	(b)	(c)	(d)	(e)	(f)

as values for m_l are + 1, 0 and – 1 and $m_s = \pm\frac{1}{2}$. Since the exclusion principle requires that no two electrons have all quantum numbers alike, we collect all possible combinations of the above states two at a time, with no two alike. The possible combinations are :

ab ac ad ae af
bc bd be bf
cd ce cf
de df
ef

In each of these 15 combinations, we add the two values of m_s to obtain the strong field values of M_S and the two values of m_l to form M_L. The results are tabulated as follows :

	ab	ac	ad	ae	af	bc	bd	be	bf	cd	ce	cf	de	df	ef
$M_S =$	1	1	0	0	0	1	0	0	0	0	0	0	-1	-1	-1
$M_L =$	1	0	2	1	0	-1	1	0	-1	0	-1	-2	1	0	-1

The highest value of M_L is two indicating the presence of 'D' term (as $M_L = 2$ comes from L = 2) For L = 2, the other values of M_L are 2, 1, 0, – 1, – 2. Corresponding values of M_S show that there are strong - field quantum numbers to form a ^{1}D term. The ^{1}D terms are :

	ad	ae	af	bf	cf
$M_S =$	0	0	0	0	0
$M_L =$	2	1	0	-1	-2

} ^{1}D

Taking these five terms out, we find the numbers remaining to form 3P and ^{1}S terms which are :

	ab	ac	bc	bd	cd	ce	de	df	ef
$M_S =$	1	1	1	0	0	0	-1	-1	-1
$M_L =$	1	0	-1	1	0	-1	1	0	-1

} ^{3}P

and

	be
$M_S =$	0
$M_L =$	0

} ^{1}S

Two equivalent 'p' electrons therefore give rise to ^{1}S, ^{3}P and ^{1}D terms.

It is seen from the table 4.2 that two non-equivalent 'p' electrons give rise to ^{1}S, ^{1}P, ^{1}D ^{3}S, ^{3}S, ^{3}P and ^{3}D terms. The Pauli's exclusion principle excludes ^{1}P, ^{3}S and ^{3}D terms whe the two electrons have equal 'n' values.

Consider another example of two 'd' electrons in LS coupling. We first write down al possible combinations of m_{s_1} and m_{s_2} in one array and those of m_{l_1} and m_{l_2} in another a shown in Fig. 4.6. All possible combinations of the magnetic quantum numbers ar allowed if the total quantum numbers are different. The runnning values of M_L are 4 t – 4, 3 to – 3, 2 to – 2, 1 to – 1 and 0. These values give rise to G, F, D, P and S term

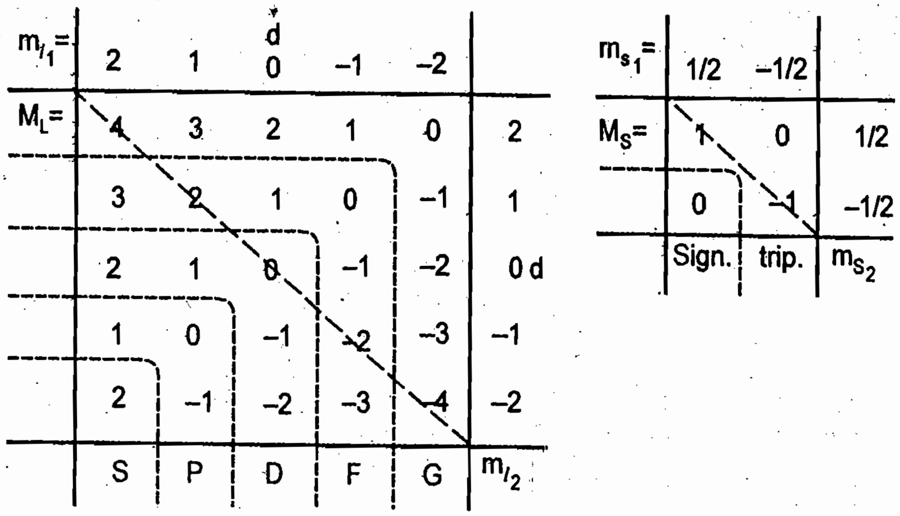


Fig. 4.6 : Magnetic quantum numbers for two similar d-electrons (L-S coupling)

respectively; and the two sets of M_S = 1, 0, –1 and 0 corresponding to triplets and singlet terms are given in table 4.2 for d·d. If the two 'd' electrons are equivalent, i.e. equal value of n, certain of these terms are forbidden. When M_S = + 1 or – 1, the values of M_L = 4, 2, 0, – 2 and – 4, along the diagonal line are forbidden. Since the values in the lower left of th array are identical with, and are a mirror image of those in the upper right half, one o these groups must also be eliminated from the calculations. Therefore the remaining values are seen to form two runs, M_L = 3 to – 3 and 1 to – 1 which are tabulated below -

M_S = 1, M_L = 3 2 1 0 – 1 – 2 – 3

M_S = –1, M_L = 3 2 1 0 – 1 – 2 – 3

M_S = 1, M_L = 1 0 – 1

M_S = –1, M_L = 1 0 – 1

If now M_L values are assumed alike, the values of M_S = 1 or – 1 are forbidden. Since the two M_S = 0 values are identical, one of these must also be excluded. The remaining combinations are as follows :

M_S = 0, M_L = 4 3 2 1 0 – 1 – 2 – 3 – 4

M_S = 0, M_L = 3 2 1 0 – 1 – 2 – 3

M_S = 0, M_L = 2 1 0 – 1 – 2

M_S = 0, M_L = 1 0 – 1

M_S = 0, M_L = 0

The second and fourth rows give the quantum numbers for ^{3}F and ^{3}P terms. The remaining rows correspond to ^{1}G, ^{1}D and ^{1}S terms.

4.4 L-S AND jj COUPLING SCHEMES

Since an atom consists of large number of electrons with different orbital and spin momenta, coupling scheme is necessary to obtain the resultant orbit and spin momenta of an atom as a whole. Coupling schemes are of two types. Out of the possible ways, two couplings namely LS and jj are more prominent.

(I) LS or Russel - Saunders Coupling :

Here, the 'l' vectors of all electrons combine to form a resultant $\vec{L}$ and 's' vectors of all these electrons combine to form a resultant $\vec{S}$. Then $\vec{L}$ and $\vec{S}$ give the resultant $\vec{J}$ by vector addition which represents the total angular momentum of the atom. The process may be symbolically represented as, $(l_1 + l_2 + l_3 + \ldots) + (s_1 + s_2 + s_3 + \ldots) = \vec{L} + \vec{S} = \vec{J}$. The guiding principles in this type of coupling are :

(a) All the three vectors $\vec{L}$, $\vec{S}$ and $\vec{J}$ must be quantized.

(b) $\vec{L}$ is always an integer including zero. i.e. $\vec{L}$ may be 0, 1, 2, 3 etc. depending upon the number of electrons in the atom and the directions of their orbital vectors.

(c) 'S' may assume values 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, ... depending upon the number of electrons in the atom and the directions of their spin vectors as shown in Fig. 4.7. Thus, S will have an integral value for even number of electrons and half integral for odd number of electrons.

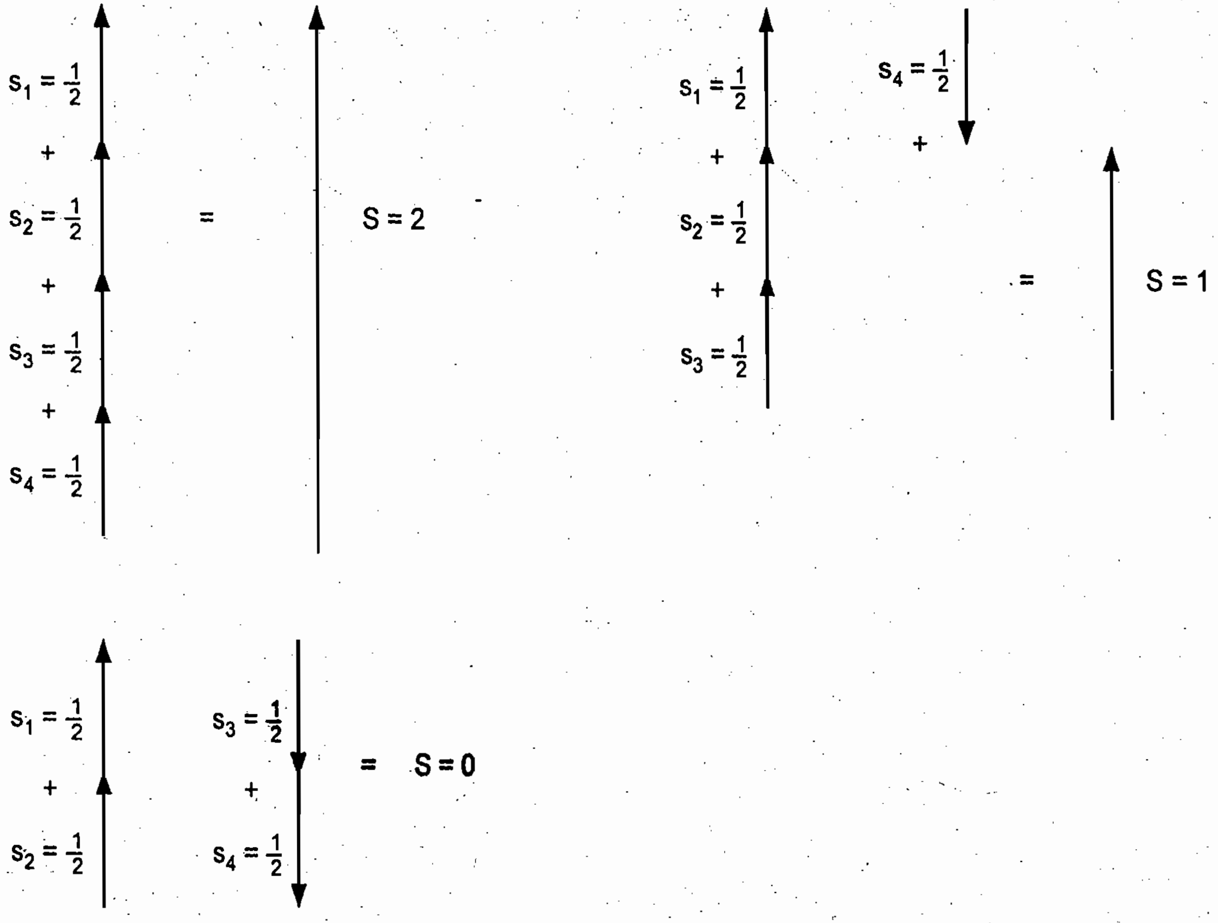


Fig. 4.7 : Vector addition of S vectors (four-electron system)

(d) Therefore, J, the vector sum of 'L' and 'S' must be an integer. (0, 1, 2, 3, ... etc.) J must always be positive, never negative.

This type of coupling is commonly used.

(II) jj Coupling :

In jj coupling, the spin motion of each electron gets coupled with its orbital motion to form a resultant motion represented by total angular momentum $\vec{J}$.

Thus, by taking vector addition of orbital and spin vectors of each electron, the total angular momentum of the atom is obtained. The vector addition of $\vec{j_1}$ and $\vec{j_2}$ (individual vectors) gives $\vec{J}$.

$$\text{Hence,} \qquad (\vec{l_1} + \vec{s_1}) + (\vec{l_2} + \vec{s_2}) + \ldots = \vec{j_1} + \vec{j_2} + \ldots = \vec{J}$$

$$\text{or,} \qquad \vec{j_1} + \vec{j_2} + \ldots = \vec{J}.$$

such that J takes integral values only. This type of coupling occurs rarely. Vector models for LS and jj coupling are shown in Fig. 4.8

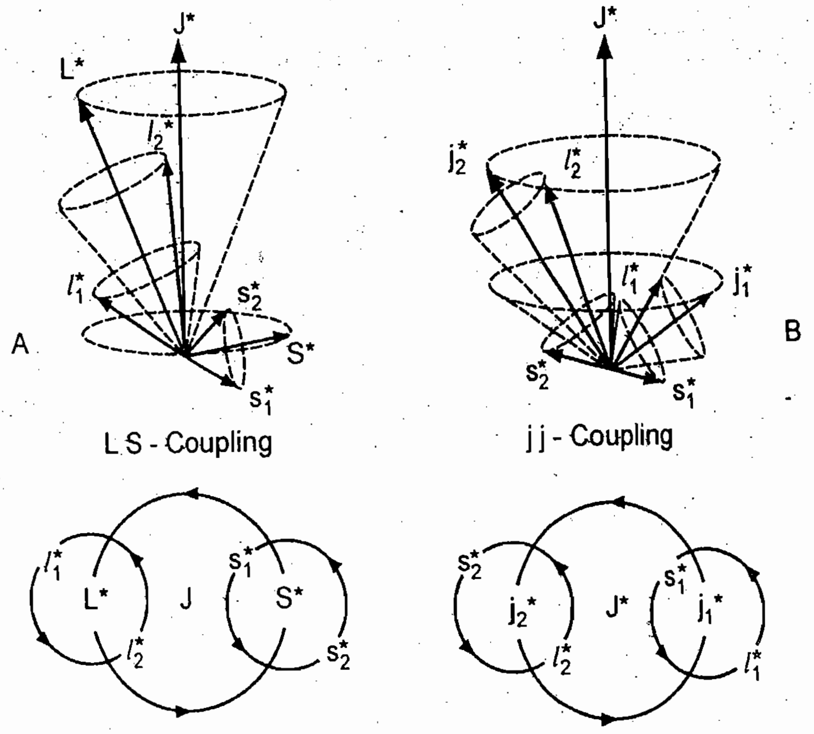


Fig. 4.8 : Ideal vector models for (A) LS coupling, and (B) jj-coupling, Examples, drawn with $l_1 = 1, l_2 = 2, J = 3$.

4.5 SINGLET-TRIPLET SEPARATIONS (Interaction energies of LS and jj couplings)

We have seen in the case of single valence electron that due to the interaction between orbital motion and spin motion of the electron, there is a change in the total energy of the system. This energy change gives rise to fine structure of spectral lines.

Now, in case of two valence electrons, there are four angular momenta l_1^*, l_2^*, s_1^* and s_2^*, with six possible interactions as -

$$\begin{array}{ll} s_1^* \text{ with } s_2^* & l_2^* \text{ with } s_2^*, \\ l_1^* \text{ with } l_2^* & l_1^* \text{ with } s_2^* \\ l_1^* \text{ with } s_1^* & l_2^* \text{ with } s_1^* \end{array}$$

We have seen that the shift of each fine structure level is given by,

$$\begin{aligned} -\Delta T_{l,s} &= a\, l^* s^* \cos \overline{(l^* s^*)} \\ &= a\left(\frac{j^{*2} - l^{*2} - s^{*2}}{2}\right) = \Gamma \qquad \ldots (4.1) \end{aligned}$$

Applying this equation to these six interactions, the six energy relations will be -

$$\left.\begin{aligned} \Gamma_1 &= a_1 s_1^* s_2^* \cos (s_1^* s_2^*) \\ \Gamma_2 &= a_2 l_1^* l_2^* \cos (l_1^* l_2^*) \\ \Gamma_3 &= a_3 l_1^* s_1^* \cos (l_1^* s_1^*) \\ \Gamma_4 &= a_4 l_2^* s_2^* \cos (l_2^* s_2^*) \\ \Gamma_5 &= a_5 l_1^* s_2^* \cos (l_1^* s_2^*) \\ \Gamma_6 &= a_6 l_2^* s_1^* \cos (l_2^* s_1^*) \end{aligned}\right\} \qquad \ldots (4.2)$$

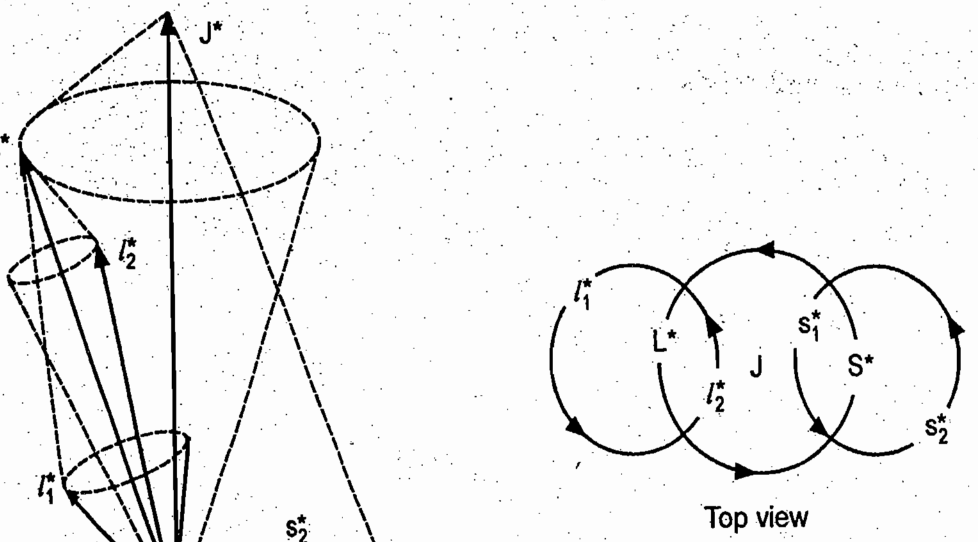
According to classical model of the precession of vectors, each spin s* and each orbit l^* produces a field. The other vectors tend to carry out 'Larmour precession' around this field. The rate of precession is different for different vectors. The vector precessing more rapidly has predominating interaction over other slowly precessing vectors. LS and jj coupling models give good agreement with experiments.

(a) LS Coupling:

In this coupling, the interaction energies Γ_1 and Γ_2 are assumed to predominate over Γ_3 and Γ_4 while Γ_5 and Γ_6 are assumed negligibly small. The vector diagram of this coupling scheme is shown in Fig. 4.9 with Γ_1 and Γ_2 predominant, s_1^* and s_2^* precess rapidly around their resultant S* and l_1^* and l_2^* precess rapidly around their resultant L*. Due to weaker interactions Γ_3 and Γ_4, L* and S* precess more slowly around their resultant J*. We consider the terms

$$\Gamma_1 = a_1 s_1^* s_2^* \cos (s_1^* s_2^*) ; \qquad \Gamma_3 = a_3 l_1^* s_1^* \cos (l_1^* s_1^*)$$

$$\Gamma_2 = a_2 l_1^* l_2^* \cos (l_1^* l_2^*) ; \qquad \Gamma_4 = a_4 l_2^* s_2^* \cos (l_2^* s_2^*)$$



Top view

Fig. 4.9 : Sketch of vector model for L - S coupling

By cosine law for triangles,

$$S^{*2} = s_1^{*2} + s_2^{*2} + 2 s_1^* s_2^* \cos (s_1^* s_2^*) \quad \ldots (4.3)$$

$$\therefore \quad s_1^* s_2^* \cos (s_1^* s_2^*) = \frac{S^{*2} - s_1^{*2} - s_2^{*2}}{2} \quad \ldots (4.4)$$

Hence,

$$\Gamma_1 = \frac{1}{2} a_1 (S^{*2} - s_1^{*2} - s_2^{*2}) \quad \ldots (4.5)$$

and

$$\Gamma_2 = \frac{1}{2} a_2 (L^{*2} - l_1^{*2} - l_2^{*2}) \quad \ldots (4.6)$$

The average value of the cosine must be evaluated as the angles between the vectors are continuously changing. Due to constancy of certain angles throughout the various precessions, the average value of cosine can be easily calculated. A well-known theorem in trigonometry gives the average value in terms of projections.

For example, the projection of l_1^* on L^* the L^* on S^* and finally S^* on s_1^* gives, for the average cosine.

This average value is -

$$\overline{\cos (l_1^* s_1^*)} = \cos (l_1^* L^*) \cos (L^* S^*) \cos (S^* s_1^*) \quad \ldots (4.7)$$

Similarly,

$$\overline{\cos (l_2^* s_2^*)} = \cos (l_2^* L^*) \cos (L^* S^*) \cos (S^* s_2^*) \quad \ldots (4.8)$$

It is assumed that s_1^*, l_1^* precess much more rapidly than L^* and S^*, so that their components normal to the respective axes of rotation will cancel out.

Using cosine law for vector triangle of L^*S^*, average values of cosines, taking common factor $\cos(L^*S^*)$ we get,

$$\Gamma_3 + \Gamma_4 = (a_3\alpha_3 + a_4\alpha_4) L^*S^* \cos(L^*S^*) \qquad \dots (4.9)$$

$$= \frac{1}{2}(a_3\alpha_3 + a_4\alpha_4)(J^{*2} - L^{*2} - S^{*2}) \qquad \dots (4.10)$$

Where

$$\alpha_3 = \frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2S^{*2}} \cdot \frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2L^{*2}} \qquad \dots (4.11)$$

and

$$\alpha_4 = \frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2S^{*2}} \cdot \frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2L^{*2}} \qquad \dots (4.12)$$

For any given triplet, s_1^*, s_2^*, l_1^*, l_2^*, S^* and L^* are fixed in magnitude, hence a_3, a_4, α_3 and α_4 are constants. Hence, writing

$$A = a_3\alpha_3 + a_4\alpha_4 + \dots \qquad \dots (4.13)$$

Equation (4.10) becomes

$$\Gamma_3 + \Gamma_4 = AL^*S^* \cos(L^*S^*) = \frac{1}{2} A(J^{*2} - L^{*2} - S^{*2}) \qquad \dots (4.14)$$

It is necessary to evaluate the 'A' coefficients to obtain complete expression of energies.

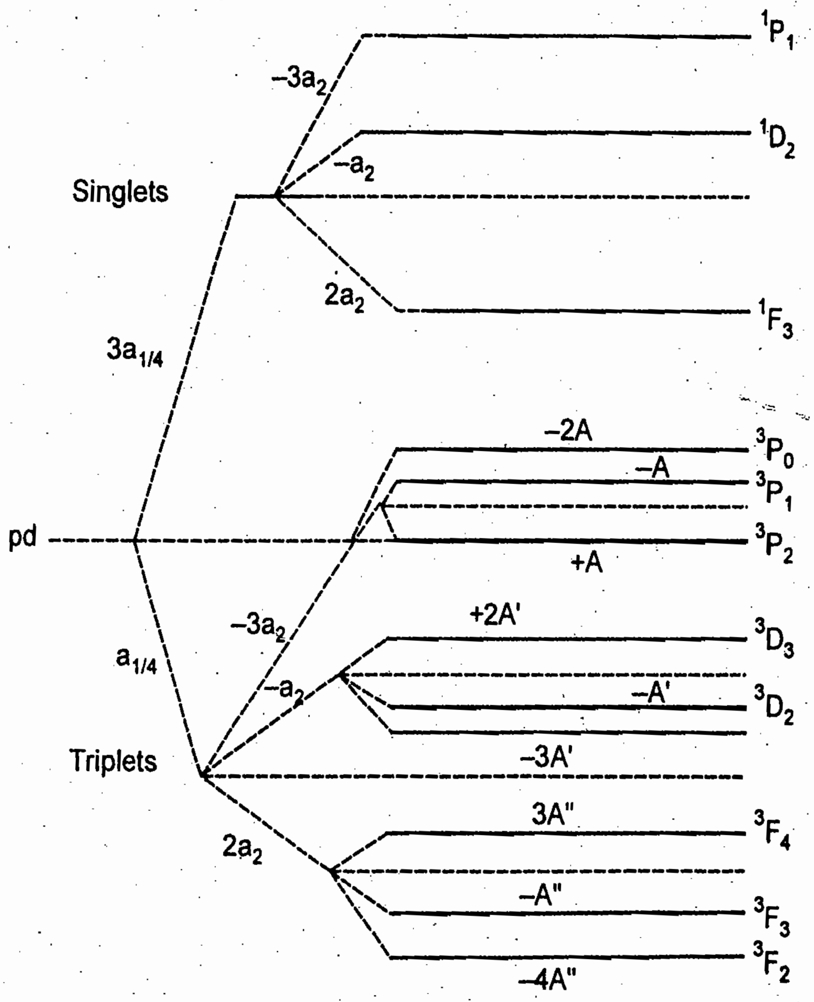


Fig. 4.10 : Fine structure separations of pd configuration in LS coupling

From the comparison of calculated energies and observed fine structure, it is found that spin-orbit interactions are due to electrostatic effects. It is the general observation that the singlet levels lie above the corresponding triplet levels of the same electron configuration. Hence, the coefficient 'a_1' of Γ_1 is negative. Now, we are in position to calculate the effect of each interaction $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$.

Let us consider the 'pd' electron configuration. The schematic representation of the fine structure of pd configuration is shown in Fig. 4.10.

In this figure, energy level attributed to n and l values of the two electrons is shown at the left.

The equation for Γ_1 is

$$\Gamma_1 = \frac{1}{2} a_1 (S^{*2} - s_1^{*2} - s_2^{*2}) \qquad \ldots (4.15)$$

Here, $s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$ $\therefore$ $S = 0$ or 1.

$S = 0$ gives singlets and $S = 1$ gives triplets.

$\therefore$ For $S = 0$,

$$\Gamma_1 = \frac{1}{2} a_1 \left[0 - \left(\sqrt{\frac{3}{4}}\right)^2 - \left(\sqrt{\frac{3}{4}}\right)^2\right]$$

$\therefore$

$$\Gamma_1 = \frac{1}{2} a_1 \left(-\frac{3}{2}\right) = -\frac{3a_1}{4}$$

For $S = 1$,

$$\Gamma_1 = \frac{1}{2} a_1 \left[(\sqrt{2})^2 - \left(\sqrt{\frac{3}{4}}\right)^2 - \left(\sqrt{\frac{3}{4}}\right)^2\right]$$

$$\Gamma_1 = \frac{1}{2} a_1 \left(2 - \frac{3}{2}\right) = \frac{a_1}{4}$$

Thus,

$$\Gamma_1 = -\frac{3a_1}{4} \text{ and } \frac{a_1}{4}$$

This is the first splitting shown in the Fig. 4.10. The equation for Γ_2 is

$$\Gamma_2 = \frac{1}{2} a_2 (L^{*2} - l_1^{*2} - l_2^{*2})$$

Here, $l_1 = 1, l_2 = 2$

$\therefore$ $L = 1, 2, 3$ i.e. P, D, F terms respectively.

For $L = 1$,

$$\Gamma_2 = \frac{1}{2} a_2 [(\sqrt{2})^2 - (\sqrt{2})^2 - (\sqrt{6})^2]$$

$\therefore$

$$\Gamma_2 = \frac{1}{2} a_2 (-6) = -3 a_2$$

For $L = 2$,

$$\Gamma_2 = \frac{1}{2} a_2 [(\sqrt{6})^2 - (\sqrt{2})^2 - (\sqrt{6})^2] = \frac{1}{2} a_2 (2)$$

$\therefore$

$$\Gamma_2 = -a_2$$

For $L = 3$,

$$\Gamma_2 = \frac{1}{2} a_2 [(\sqrt{12})^2 - (\sqrt{2})^2 - (\sqrt{6})^2]$$

$\therefore$

$$\Gamma_2 = \frac{1}{2} a_2 (12 - 2 - 6) = 2 a_2$$

Thus, the values of Γ_2 are $-3a_2$, $-a_2$ and $2a_2$. This is the second splitting shown in the above Fig. 4.10 for singlets and triplets.

The Hund's rule applied for LS coupling states that out of all terms with the same L value arising from any given electron configuration

(i) a term with the highest multiplicity i.e. the highest S value, will lie deepest.

(ii) of these the terms with the highest L value will lie deepest.

The separation of the terms from the centre of gravity terms can be calculated from $\Gamma_3 + \Gamma_4$.

$$\therefore \qquad \Gamma_3 + \Gamma_4 = \frac{1}{2} A\,(J^{*2} - L^* - S^{*2})$$

For the term $^3P_0$,
$$\Gamma_3 + \Gamma_4 = \frac{1}{2} A\,[0 - (\sqrt{2})^2 - (\sqrt{2})^2] = -2A$$

For the singlet terms with $S = 0$, the α's and hence A's vanish.

In the similar way, all the separations shown in the diagram (Fig. 4.10) can be calculated.

SP Configuration :

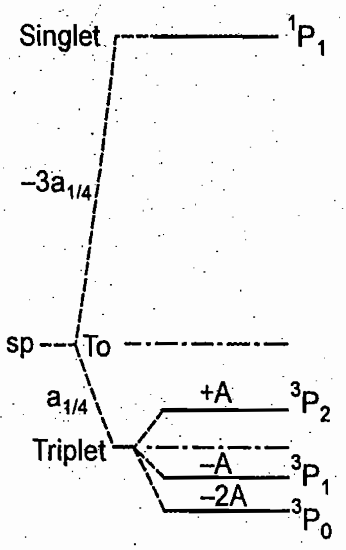


Fig. 4.11 : Schematic representation of the interaction energies between two valence electrons in LS coupling

For 'sp' configuration as shown in Fig. 4.11, the expression for tan factor, is,

$$\Gamma_1 = \frac{1}{2} a_1\,(S^{*2} - s_1^{*2} - s_2^{*2})$$

For $S = 0$,
$$\Gamma_1 = -\frac{3a_1}{4}$$

For $S = 1$,
$$\Gamma_1 = \frac{a_1}{4}$$

Thus, the values of Γ_1 are $-\frac{3a_1}{4}$ and $\frac{a_1}{4}$. This is the first splitting shown in the Fig. 4.11.

Now, as $l_1 = 0$, $l_2 = 1$

We have $L = 1$, i.e. only 'p' term

For L = 1,

$$\Gamma_2 = \frac{1}{2} a_2 [(\sqrt{2})^2 - 0 - (\sqrt{2})^2]$$

$$= \frac{1}{2} a_2 [2 - 0 - 2] = 0$$

$$\therefore \quad \Gamma_2 = 0$$

∴ This is the second splitting shown in the above Fig. 4.11 for singlets and triplets.

For $^3P_0$ term,

$$\Gamma_3 + \Gamma_4 = \frac{1}{2} A [0 - (\sqrt{2})^2 - (\sqrt{2})^2] = -2A$$

Similarly,

For $^3P_1$ term $\Gamma_3 + \Gamma_4 = -A$ and for $^3P_2$ term, $\Gamma_3 + \Gamma_4 = +A$.

All the separations shown in the diagram can be calculated in this way.

4.6 THE LANDE INTERVAL RULE

Statement : For a given triplet i.e. for given 'S' and 'L' each fine structure term difference is proportional to the larger of the two J values associated with it. i.e. the separation in the energy of adjacent levels of a multiplet is proportional to the total angular momentum quantum number of the level of higher energy. This prediction is called the Lande interval rule.

The rule is of great help in determining the values of J that are to be assigned to various observed levels. This rule is widely used in atomic physics.

In LS coupling, we have, already seen $\Gamma_3 + \Gamma_4$ gives the separation among the components of triplets and it is given by

$$\Gamma_3 + \Gamma_4 = \frac{1}{2} A [J(J+1) - L(L+1) - S(S+1)] \quad \ldots (4.16)$$

Let the adjacent terms in a given triplet have J values as J and (J + 1).

∴ Term difference

$$-\Delta T = \frac{1}{2} A [(J+1)(J+2) - L(L+1) - S(S+1)]$$

$$- \frac{1}{2} A [J(J+1) - L(L+1) - S(S+1)]$$

$$\therefore \quad \Delta T = \frac{1}{2} A [(J+1)(J+2) - J(J+1)]$$

$$\therefore \quad \Delta T = A(J+1) \quad \ldots (4.17)$$

The intervals are thus proportional to the larger J values. This is an excellent agreement between observed separations and the interval rule. This clearly justifies the use of the vector atom model and signifies the LS electron coupling. The rule also determines the separation of fine structure lines in LS coupling.

The same result can be obtained by considering pd configuration. Now, consider pd configuration.

Three triplets are : $^3P_0 \; ^3P_1 \; ^3P_2$, $^3D_1 \; ^3D_2 \; ^3D_3$, $^3F_2 \; ^3F_3 \; ^3F_4$

In this the ratios are : 1 : 2, 2 : 3, 3 : 4

The numerical ratios conclude that term difference is proportional to larger of the two J values.

A graphical representation of the Lande interval rule is shown in Fig. 4.12 for ^3D term.

For ^3D term : S = 1, L = 2, J = 1, 2, 3.

Thus, the components of given triplet ^3D are $^3D_1$ $^3D_2$ and $^3D_3$

Now for $^3D_1$,

$$\Gamma_3 + \Gamma_4 = \frac{A}{2}[J(J+1) - L(L+1) - S(S+1)]$$

$$= \frac{A}{2}[1(1+1) - 2(2+1) - 1(1+1)]$$

$$\therefore \quad \Gamma_3 + \Gamma_4 = -3A \qquad \text{... (4.18)}$$

Similarly, for $^3D_2$,

$$\Gamma_3 + \Gamma_4 = \frac{A}{2}[6 - 6 - 2] = -A \qquad \text{... (4.19)}$$

and for $^3D_3$ term,

$$\Gamma_3 + \Gamma_4 = \frac{A}{2}[12 - 6 - 2] = 2A \qquad \text{... (4.20)}$$

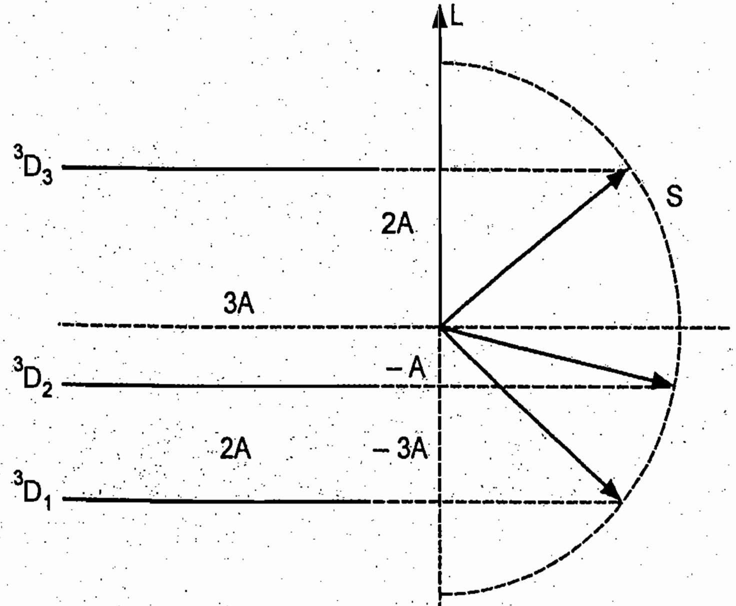


Fig. 4.12 : Graphical representation of Lande's interval rule for ^3D term

Thus, in Fig. 4.12, S^* is shown quantized with L^* in three allowed positions J = 1, 2 and 3. The resultant intervals have the ratio 2 : 3. The dotted line is at the centre of gravity. The J vectors are not shown in the representation.

4.7 SPECTRA OF HELIUM

Helium (Z = 2) has two electrons, both of which according to Pauli's principle, can occupy the first K shell. The two electrons complete the first period of the periodic system. The normal helium atom is therefore represented by $1s^2$. i.e. two electrons, for which n = 1 and $l = 0$. The total number being affixed at the top of s. A single electron is responsible for the energy levels of both hydrogen and sodium. However, there are two 1s electrons in the ground state of helium and coupling affects the properties and behaviour of the helium atom.

During the eclipse of 1868, Jansson detected helium lines in the solar spectrum. Lockyer suggested the name helium. (Helios is the Greek word for sun) for this element, spectral lines from which were observed many years before. Ramsey first isolated helium on the earth in 1895. Long before the helium spectrum was understood.

The excellent experimental work of Evan's, Fowler and Paschen has confirmed that Pickering series arises from ionized helium atom which has two electrons revolving round its nucleus in normal state. The pickering series was produced in pure helium. The ionized helium will give rise to this series of spectral lines represented by the relation

$$\bar{\upsilon} = 4R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{... (4.21)}$$

which represents all of the known series of ionized helium. When electron transition is from $n_2 = 5, 6, 7, \ldots$ to $n_1 = 4$, the group of lines is called Pickering series. Fourier series is represented by $n_1 = 3$ and $n_2 = 4, 5, 6, \ldots$. The lines of Lyman series lie in the ultra-violet region.

These two series are given accurately by $n_1 = 2$ and $n_1 = 1$, n_2 taking running values $3, 4, 5, \ldots$ and $2, 3, 4, \ldots$ etc.

Ionized Helium :

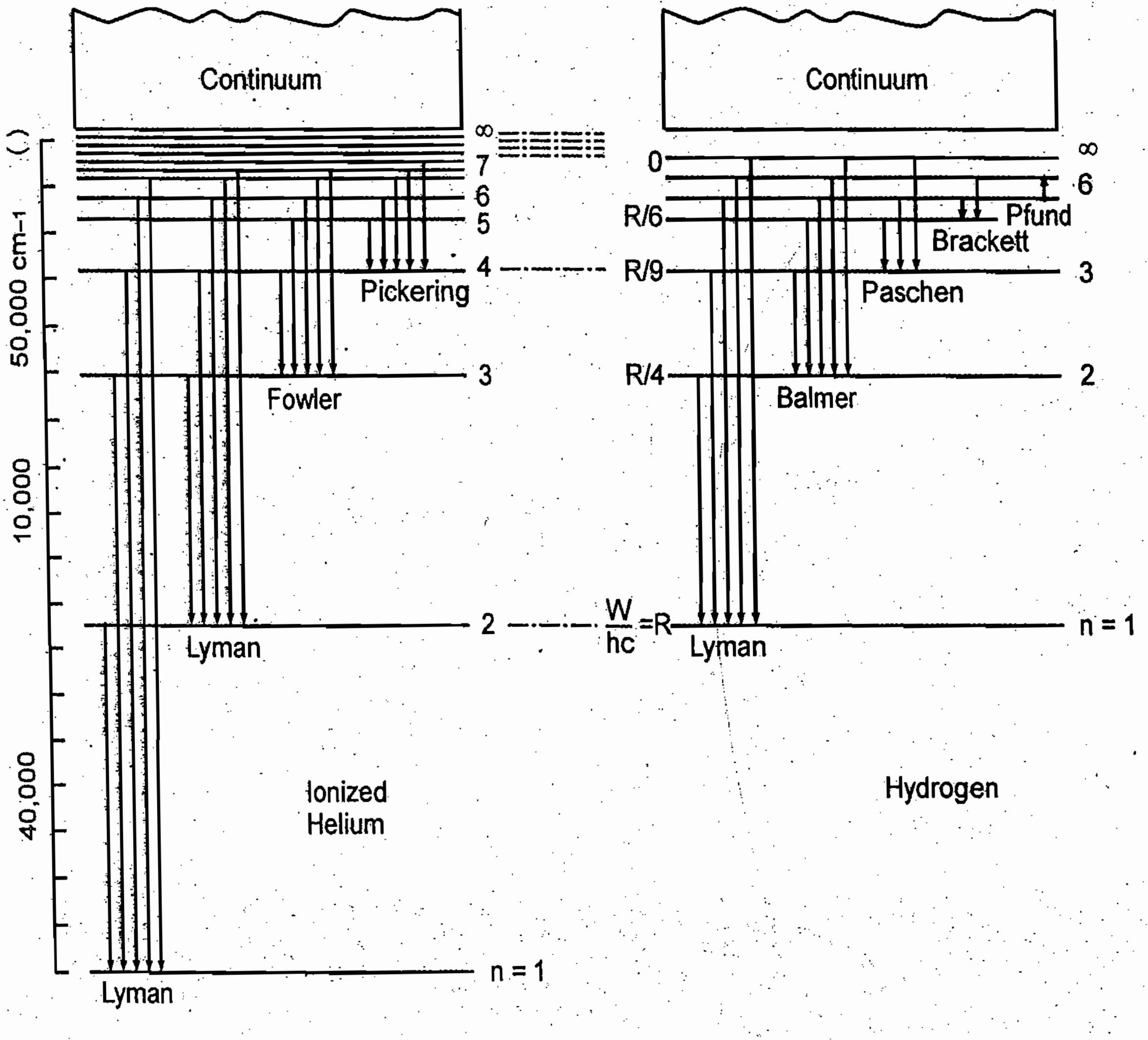


Fig. 4.13 : Energy level diagrams of hydrogen and ionized helium

Fig. 4.13 shows energy level diagrams for hydrogen and ionized helium to the same scale. It is observed in this diagram that each member of Balmer series and alternate member of the Pickering series apparently have the same transitions. The first few members of each of the different series are shown in the diagram. The line λ 4686 has predicted eight components in the fine structure. This predicted fine structure was for the first time given by Sommerfeld and Unsold. With **Z = 2** it was expected that the fine structure separation would be about 16 times more than that of hydrogen. This line from spectrum of ionized helium corresponds with the first member of the Paschen series in hydrogen spectrum Fig. 4.14 shows the fine structure of the ionized helium line λ 4686.

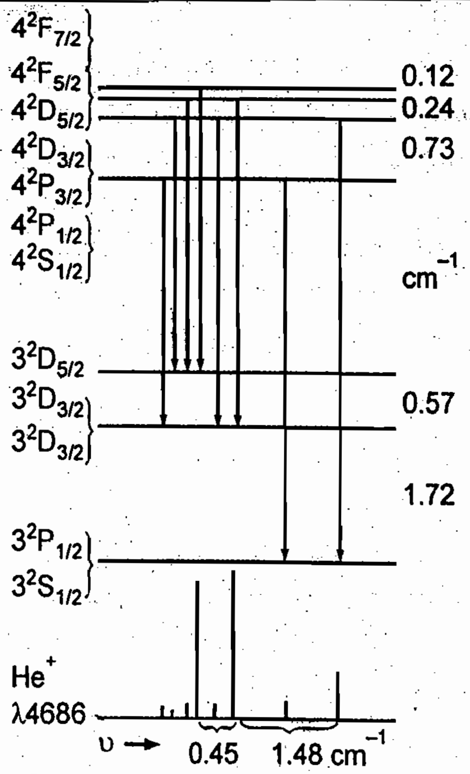


Fig. 4.14 : Diagram of the fine structure of the ionised helium line λ 4686

Energy Levels of Normal Helium Atom :

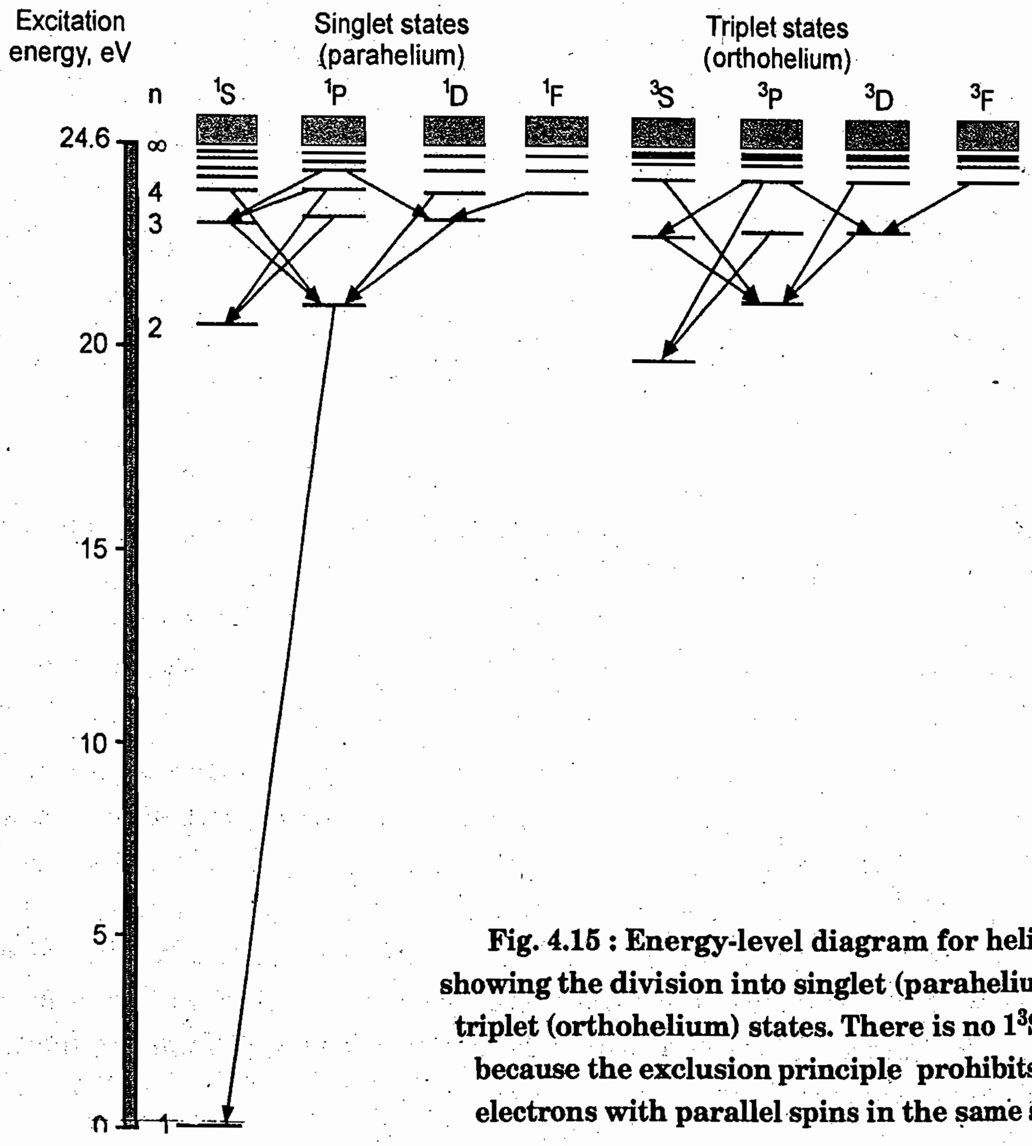


Fig. 4.15 : Energy-level diagram for helium showing the division into singlet (parahelium) and triplet (orthohelium) states. There is no 1^3S state because the exclusion principle prohibits two electrons with parallel spins in the same state

He atom contains two valence electrons. Therefore it emits, in general, same type of spectra as are given by alkaline earths. The spectrogram for helium shows two systems- one singlet system containing all the four chief series (sharp, principal, diffuse and fundamental), and one triplet system which also contains all the four chief series. The singlet system belongs to para-helium (spins antiparallel) because for singlets S = 0. The triplet system belongs to ortho-helium (spins parallel) because S = 1.

The energy level diagram of normal helium atom is as shown in the Fig. 4.15.

The various levels represent configurations in which one electron is in its ground state and the other is in an excited state. There is a division into singlet and triplet states. (i.e. parahelium and orthohelium) as shown in Fig. 4.16. An orthohelium atom can loose excitation energy in a collision and become one of parahelium, while a parahelium atom can gain excitation energy in a collision and become one of orthohelium. Ordinary liquid or gaseous helium is therefore a mixture of both. The lowest triplet states are metastable.

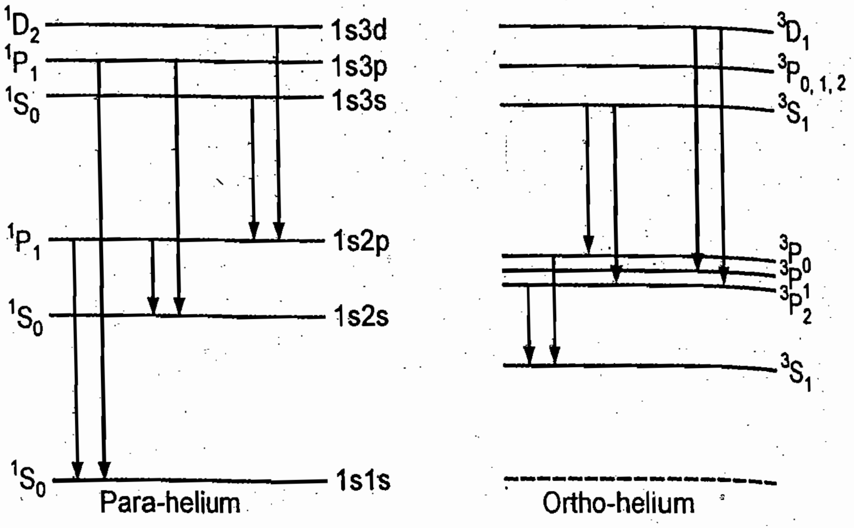


Fig. 4.16 : Terms and transitions in the spectrum of He

Orthohelium doesn't exist in the state defined by the principal quantum number n = 1 (1^3S_1) due to operation of Pauli's principle. In this state, the two electrons would have parallel spins and therefore identical sets of quantum numbers. The lowest state of ortho-helium is 2^3S_1. The state 3^2S_1 represents metastable state. The 2^1S_0 state is also metastable state, because of selection rule $\Delta l = \pm 1$ restricts any transition to 1^1S_0 state.

The diagram shows that there is enormous energy shift from the normal $1S^2\ ^1S_0$ state to the first excited states 1S 2S $^1S_0$ and $^3S_1$. It is the characteristic of helium and all inert gases. The fine structure of the very narrow orthohelium series triplets was predicted by slater and verified by Heisenberg. Heisenberg has shown that the enormous energy difference between the first two or three triplet levels and their associated singlet levels is due to an electrostatic resonance interaction. The normal state of helium, for example to be 24.470 volts below the series limit, a value differing only 0.003 volt from the spectroscopic value 24.467 volts.

SOLVED EXAMPLES

Example 4.1 : Using 'p-p' electron configuration and 'd-d' electron configuration find all possible values of the total angular momenta.

Solution : (1) For p-p electron configuration :

For first electron :

$$l_1 = 1,\ s_1 = \frac{1}{2}$$

For second electron :

$$l_2 = 1,\ s_2 = \frac{1}{2}$$

∴ Resultant orbital momentum is,

$$L = (l_1 + l_2) \text{ to } (l_1 - l_2) = 0, 1, 2$$

and resultant spin momentum is

$$S = (s_1 + s_2) \text{ to } (s_1 - s_2)$$

$$S = 0, 1$$

∴ Total angular momentum is

$$J = L + S \text{ to } L - S$$

∴ For $S = 0$, multiplicity $(2S + 1) = 1$

$$\therefore \quad J = L = 0, 1, 2$$

∴ The singlet terms are $^1S_0$, $^1P_1$, $^1D_2$

∴ For $S = 1$, multiplicity $(2S + 1) = 3$

For $L = 0$, $J = 1$; for $L = 1$, $J = 0, 1, 2$ and for $L = 2$, $J = 1, 2, 3$

∴ The singlet and triplet terms are $^3S_1$, $^3P_{0,1,2}$, $^3D_{1,2,3}$

(2) For d-d electron configuration :

For first electron :

$$l_1 = 2,\ s_1 = \frac{1}{2}$$

For second electron :

$$l_2 = 2,\ s_2 = \frac{1}{2}$$

∴ Resultant orbital momentum is,

$$L = (l_1 + l_2) \text{ to } (l_1 - l_2) = 0, 1, 2, 3, 4$$

and resultant spin momentum is

$$S = (s_1 + s_2) \text{ to } (s_1 - s_2)$$

$$\therefore \quad S = 0, 1$$

∴ Total angular momentum is

$$J = L + S \text{ to } L - S$$

For $S = 0$, $m = 2S+1 = 1$

$\therefore$ $J = L = 0, 1, 2, 3, 4$

$\therefore$ The singlet terms are ${}^1S_0$, ${}^1P_1$, ${}^1D_2$, ${}^1F_3$, ${}^1G_4$

For $S = 1$, $m = 2S+1 = 3$

When $L = 0$, $J = 1$

When $L = 1$, $J = 0, 1, 2$

$L = 2$, $J = 1, 2, 3$

$L = 3$, $J = 2, 3, 4$

$L = 4$, $J = 3, 4, 5$

$\therefore$ The singlet and triplet terms are ${}^3S_1$, ${}^3P_{0,1,2}$, ${}^3D_{1,2,3}$, ${}^3F_{2,3,4}$, ${}^3G_{3,4,5}$.

Example 4.2 : Determine the values of L, the quantum number describing the ll coupling of the angular momenta of two atomic orbitals, for two d electrons. What are the corresponding letter symbols ?

Solution : The permitted values of L are given by

$$L = (l_1 + l_2), l_1 + l_2 - 1, \dots |l_1 - l_2|$$

For two d electrons,

$l_1 = 2$, $l_2 = 2$

$$\therefore \quad L = 2+2=4$$
$$L = 2+2-1=3$$
$$L = 2+2-2 = 2$$
$$L = 2+2-3=1$$
$$L = 2+2-4 = |2-2| = 0$$

which correspond to the letters G, F, D, P and S respectively.

Example 4.3 : In an atom, the components of a normal triplet have separation of 19 and 38 cm^{-1} between adjacent levels in LS coupling. The next higher state in multiplet has separations 22 and 33 cm^{-1} respectively. Determine the terms for these two states and draw the corresponding energy level diagram showing the allowed transitions.

Solution : According to Lande interval rule, the separation between adjacent levels is proportional to the higher J value. Let first multiplet have J values J, J + 1 and J + 2.

$\therefore$ $A(J+1) = 19$

and $A(J+2) = 38$ where 'A' is constant.

This gives $J = 0$

$\therefore$ The states have J values 0, 1, 2.

Let the second multiplet have J values J', J' + 1 and J' + 2

$\therefore$ $A'(J'+1) = 22$

$A'(J'+2) = 33$

where A' is constant.

This gives J' = 1

∴ The states have J values 1, 2, 3.

Now, S = 1 ∴ L = 2

∴ Terms are $^3D_3$, $^3D_2$ and $^3D_1$

∴ According to selection rule,

$$\Delta J = 0, \pm 1 \quad (0 \rightarrow 0 \text{ excluded})$$

∴ The possible allowed transitions are 6 and shown in the following Fig. 4.17.

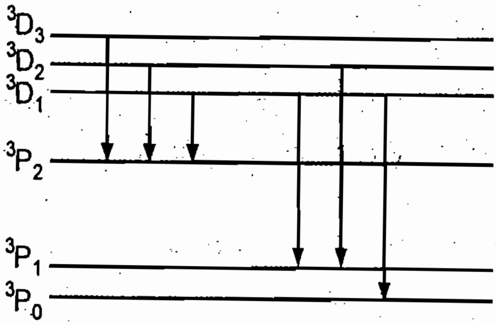


Fig. 4.17 : Triplet-triplet transitions

Example 4.4 : If the doublet splitting of the first excited state $2\ ^2P_{3/2} - 2\ ^2P_{1/2}$ of He^+ is 5.84 cm^{-1}, calculate the corresponding separations of H.

Solution : The doublet splitting of a one-electron atomic state arising due to spin-orbit interaction is given by,

$$\Delta T = \frac{R\,\alpha^2\,Z^4}{n^3 l \left(l + \frac{1}{2}\right)(l + 1)}\ cm^{-1}$$

where R is Rydberg constant,

α is fine structure constant and

Z is atomic number

∵ For a given state, (n, l constant), therefore we have,

$$\Delta T \propto Z^4$$

For He^+ and H, Z = 2 and 1 respectively.

$$\therefore \quad \frac{\Delta T_{He^+}}{\Delta T_H} = \frac{(2)^4}{(1)^4} = 16$$

$$\therefore \quad \Delta T_H = \frac{1}{16} \quad \therefore \quad \Delta T_{He}+ = \frac{1}{16} \times 5.84\ cm^{-1}$$

$$\Delta T_H = 0.365\ cm^{-1}$$

QUESTIONS AND PROBLEMS

(A) Multiple choice questions :

1. Multiplicity of the state '$^1F_3$' is given by ....

   (a) 1 (b) 2 (c) 3 (d) 4

2. 'J' value for state $^6H_{5/2}$ is given by ....

   (a) 1/2 (b) 3/2 (c) 5/2 (d) 7/2

3. Which of the following has the order of increasing energy ?

   (a) $^1D_2$ $^3D_2$ $^3F_2$ (b) $^3F_2$ $^3D_2$ $^1D_2$ (c) $^3D_2$ $^3F_2$ $^1D_2$ (d) $^1D_2$ $^3F_2$ $^3D_2$

4. For a 'd' electron the two possible states are ....

   (a) $^2D_{3/2}$ and $^2D_{5/2}$ (b) $^2D_{1/2}$ and $^2D_{3/2}$ (c) $^2D_{5/2}$ and $^2D_{1/2}$ (d) $^2D_{7/2}$ and $^2D_{5/2}$

5. The allowed terms arising from the interaction of s.d electrons configuration in LS coupling are as ....

   (a) $^1S_0$ $^3S_1$ (b) $^1P_1$ $^3P_{0,1,2}$ (c) $^1F_3$ $^3F_{2,3,4}$ (d) $^1D_2$ $^3D_{1,2,3}$

Answer: (1) a (2) c (3) b (4) a (5) d

(B) Answer in short :

1. What is a spectral term or terms symbol ?
2. Draw vector diagrams of LS and jj couplings.
3. What are Tau (Γ) factors ?
4. What are the odd terms and even terms ?
5. Define equivalent electrons.
6. Determine the different values for the total orbital quantum number of two-electrons system with $L_1 = 3$ and $L_2 = 2$.
7. What are the 'L' and 'S' quantum numbers corresponding to $^2D_{3/2}$?
8. Determine the values of J, the quantum number describing the Russel-Saunders coupling between 'L' and 'S' for two 'd' electrons.

(C) Answer in detail :

1. Explain LS coupling scheme for two valence electron system using neat vector diagram.
2. Explain jj coupling scheme for two valence electron system using neat vector diagram.
3. State and explain Lande's interval rule. Represent it graphically for ^3D term.
4. Discuss spectra of Helium. Mention the characteristics of this spectra.
5. Give an account of the spectral terms arising from two equivalent electrons.
6. Describe the broad features of the spectrum of Helium atom and show how the observations have been accounted for.

7. Write short notes on the following :
   (i) Coupling schemes,
   (ii) singlet and triplet series in two valence electron atom,
   (iii) Lande's interval rule,
   (iv) Spectra of He atom.
8. Explain the fine structure of He atom.

(D) Numerical problems :

1. Determine singlet-triplet separations in terms of interaction energies between two valence electrons in 'sp' configuration. (Use LS coupling).
2. Determine singlet-triplet separations in terms of interaction energies between two valence electron in 'pd' configuration. (Use LS coupling).
3. Derive all the terms arising from the electron configuration f-g using L-S coupling scheme.
4. Using vector diagrams, determine the possible values of the total angular momentum of a two-electron system for which $l_1 = 3$ and $l_2 = 2$.
5. Using vector diagrams, determine the possible values of the total angular momentum of an electron system for which (a) L = 2, S = 3, (b) L = 3, S = 2.

❐❐❐

5

Normal Zeeman Effect

5.1 INTRODUCTION

We know that every atom consists of a very small nucleus, which contains positively charged protons and neutral neutrons, with an equal number of electrons (equal to number of protons) revolves around the nucleus in circular path as planets do around the sun, but classical electromagnetic theory denies the possibility of such stable electron orbit.

To overcome this difficulty, Niels Bohr applied quantum ideas to atomic structure in 1913 and succeeded to obtain a model, which with great accuracy still describes a convenient picture of an atom.

As we are also familiar with the concept that the atomic electron has two motions as it revolves around the nucleus, namely orbital motion, forming orbital angular momentum vector and spin motion forming a spin angular momentum vector. These two motions contribute to the magnetic field (internal). So, it will be much interesting to see, what will happen when an atom is kept in an external magnetic field.

5.2 ATOM IN A MAGNETIC FIELD

When atom is kept in a magnetic field H, a magnetic dipole moment μ exists. This magnetic dipole moment has potential energy δE, that depends upon both the magnitude μ of its magnetic moment and orientation of this moment with respect to field as shown in Fig. 5.1.

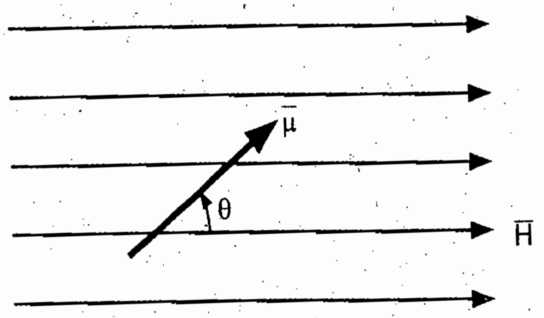


Fig. 5.1 : A magnetic dipole of moment $\bar{\mu}$ at angle θ relative to magnetic field $\bar{H}$

A torque τ acting on magnetic dipole in H is given by

$$\tau = \mu H \sin\theta \qquad \ldots (5.1)$$

where θ is angle between $\bar{\mu}$ and H.

τ is minimum when dipole is perpendicular to field. τ is zero when it is parallel or antiparallel to field. We have to calculate potential energy δE. To do this, we establish a reference configuration in which $\delta E = 0$.

P.E. at any other orientation of $\bar{\mu}$ is the external work that must be done to rotate the dipole from $\theta_0 = 90^\circ$ to the angle θ.

$$\therefore \quad \delta E = \int_{90^\circ}^{\theta} \tau \, d\theta = \mu H \int_{90^\circ}^{\theta} \sin\theta \, d\theta$$

$$\delta E = -\mu H \cos\theta \quad \text{... (5.2)}$$

When $\bar{\mu}$ points in the same direction of H, then

$$\delta E = -\mu H, \quad \text{(minimum value)}$$

Magnetic moment of current loop :

In the magnetic moment of a current loop of area $\vec{A}$ through which current I is flowing is given by

$$\bar{\mu} = I\vec{A} \quad \text{... (5.3)}$$

$$\mu = IA \quad \text{(considering only magnitude)}$$

We know that an electron revolving in a circular orbit of radius r and making n revolutions is equivalent to current (– ne) in a circular loop of area πr^2.

The magnetic moment of electron will be

$$\bar{\mu} = -ne\pi r^2 \quad \text{... (5.4)}$$

An electron of mass m, moving in a circular orbit of radius r with velocity v, has angular momentum

$$\vec{L} = m\vec{v} r$$

The velocity of electron will be

$$v = r\omega$$

$$\therefore \quad v = 2\pi n r$$

$\therefore$ The magnitude of angular momentum is

$$L = 2\pi m n r^2 \quad \text{... (5.5)}$$

From equations (5.4) and (5.5),

$$\mu = -\left(\frac{e}{2m}\right) L$$

where μ is magnetic moment of electron due to orbital motion.

Let it be denoted by μ_l.

$$\therefore \quad \bar{\mu}_l = -\left(\frac{e}{2m}\right) \vec{L} \quad \text{... (5.6)}$$

Substituting equation (5.6) in equation (5.2),

$$\delta E = \frac{e}{2m} LH \cos\theta \qquad \ldots (5.7)$$

But $$L = \sqrt{l(l+1)}\,\hbar = \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$$

where, l is the orbital quantum number, h is the Planck's constant and

$$\cos\theta = \frac{L_Z}{L} = \frac{m_l}{\sqrt{l(l+1)}}$$

where L_Z is component of angular momentum $\vec{L}$ in direction of magnetic field vector $\bar{H}$ and m_l is the magnetic quantum number which has $(2l + 1)$ values from $-l$ to $+l$ through zero.

Substituting value of L and cos θ in equation (5.7),

$$\delta E = m_l \left(\frac{eh}{4\pi m}\right) H$$

$$= m_l \left(\frac{e\hbar}{2\pi m}\right) H$$

The quantity $\left(\frac{eh}{4\pi m}\right) = \left(\frac{e\hbar}{2\pi m}\right)$ is called Bohr magnetron and has a value 9.27×10^{-24} joule per tesla. Bohr's magnetron is unit of magnetic moment.

Suppose an electron in atom goes from initial higher energy level E_{oi} to final lower energy level E_{of} when no magnetic field is supplied, then,

$$\upsilon_o = \frac{E_{oi} - E_{of}}{h}$$

When magnetic field H is applied, the energy of initial and final states are given by

$$E_i = E_{oi} + m_{li} \left(\frac{eh}{4\pi m}\right) H$$

$$E_f = E_{of} + m_{lf} \left(\frac{eh}{4\pi m}\right) H$$

The frequency of emitted photon (spectral line) is given by

$$\upsilon = \frac{E_i - E_f}{h} = \frac{E_{oi} - E_{of}}{h} + (m_{li} - m_{lf}) \left(\frac{e}{4\pi m}\right) H$$

$$= \upsilon_o + \Delta m_l \left(\frac{e}{4\pi m}\right) H \qquad \ldots (5.8)$$

Selection rule for $\Delta m_l = +1, 0,$ and -1.

Then we get three values of υ given by

$$\upsilon_1 = \upsilon_0 + \left(\frac{e}{4\pi m}\right)H = \upsilon_0 + \Delta\upsilon$$

$$\upsilon_2 = \upsilon_0 \qquad \dots (5.9)$$

and
$$\upsilon_3 = \upsilon_0 - \left(\frac{e}{4\pi m}\right)H = \upsilon_0 - \Delta\upsilon$$

where
$$\Delta\upsilon = \left(\frac{e}{4\pi m}\right)H$$

But,
$$\upsilon = \frac{c}{\lambda}$$

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

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

$\therefore$ Shift in wavelength is

$$d\lambda = \Delta\lambda = \pm\frac{\lambda^2}{c}\left(\frac{e}{4\pi m}\right)H \qquad \dots (5.10)$$

5.3 NORMAL ZEEMAN EFFECT FOR SINGLE VALENCE ELECTRON SYSTEM

The effect of magnetic field on the spectrum of an atom, was first studied by Prof. Zeeman in the year 1896, when he kept a sodium flame between the pole-pieces of a strong electromagnet. He found that primarily a single spectral line splits up into 3 components- one line having larger frequency, other having lower frequency than the frequency of original line and third one having *frequency* of original line. Such splitting effect is named as *normal Zeeman effect.*

Here as electron has two motions (orbital and spin), but due to application of strong magnetic field l-s coupling gets broken and splitting is due to $\bar{l}$ vector only.

If we neglect the spin of electron, then angular momentum possessed by electron is given as

$$p_l = l\frac{h}{2\pi}$$

Now as we know that orbital magnetic moment is given by

$$\mu_l = e\frac{lh}{4\pi m} = \frac{e}{2m}p_l$$

Now in presence of an external magnetic field, the l vector precesses around the field direction. Such precession is a Larmour precession.

The precessional frequency is given as,

$$\omega_l = H\frac{\mu_l}{p_l} = \frac{e}{2m}H \qquad \dots (5.11)$$

(H is taken as magnetic field and $\frac{\mu_l}{p_l}$ ratio is known as **gyromagnetic ratio.**)

The electron gains an additional energy due to this precession, which can be written as :

$$\begin{aligned}\Delta E &= \omega_l \times \text{projection of orbital angular momentum on the field direction}\\ &= \frac{e}{2m} H \cdot p_l \cos\theta\\ &= \frac{eH}{2m}\frac{lh}{2\pi}\cos\theta\\ &= \frac{eHh}{4\pi m} m_l \text{ where } m_l = l\cos\theta\end{aligned}$$

where m_l takes $(2l + 1)$ values from $-l, \ldots, 0, \ldots, +l$. Hence a magnetic field splits up each energy level into $(2l + 1)$ sublevels, separation being $\frac{eh}{4\pi m}$.

If E_{1H} and E_{2H} are the energies of two levels in presence of magnetic field and if E_1 and E_2 being energies in absence of magnetic field, with m_l values being m_{l1} and m_{l2} then

$$E_{1H} = E_1 + m_{l1}\frac{eHh}{4\pi m} \qquad \ldots (5.12)$$

and

$$E_{2H} = E_2 + m_{l2}\frac{eHh}{4\pi m} \qquad \ldots (5.13)$$

Hence a radiation will be emitted in presence of a magnetic field if

$$E_{1H} - E_{2H} = (E_1 - E_2) + \frac{eHh}{4\pi m}(m_{l1} - m_{l2})$$

or

$$h\upsilon = h\upsilon_0 + \frac{eHh}{4\pi m}\Delta m_l$$

or

$$\upsilon = \upsilon_0 + \frac{eH}{4\pi m}\Delta m_l$$

where υ_0 is the frequency of a line in absence of magnetic field. The splitting will be observed, which is based on selection rule, $\Delta m_l = 0$ or ± 1.

Hence we observe three possible lines.

(i) $\upsilon_1 = \upsilon_0$ for $\Delta m_l = 0$ ... (5.14 a)

(ii) $\upsilon_2 = \upsilon_0 + \frac{eH}{4\pi m}$ for $\Delta m_l = +1$ ... (5.14 b)

(iii) $\upsilon_3 = \upsilon_0 - \frac{eH}{4\pi m}$ for $\Delta m_l = -1$ ... (5.14 c)

In a magnetic field, the energy of a particular atomic state, depends on the value of m_l as well as on n.

Therefore, a state of total quantum number n breaks up into various substates, when an atom is kept in a magnetic field, and their energies are slightly more or less than energy of state in absence of magnetic field. This leads to splitting of individual spectral lines into separate lines when atoms radiate in a magnetic field.

The spacing between the lines will depend on magnitude of the field. Fig. 5.2 shows normal Zeeman effect.

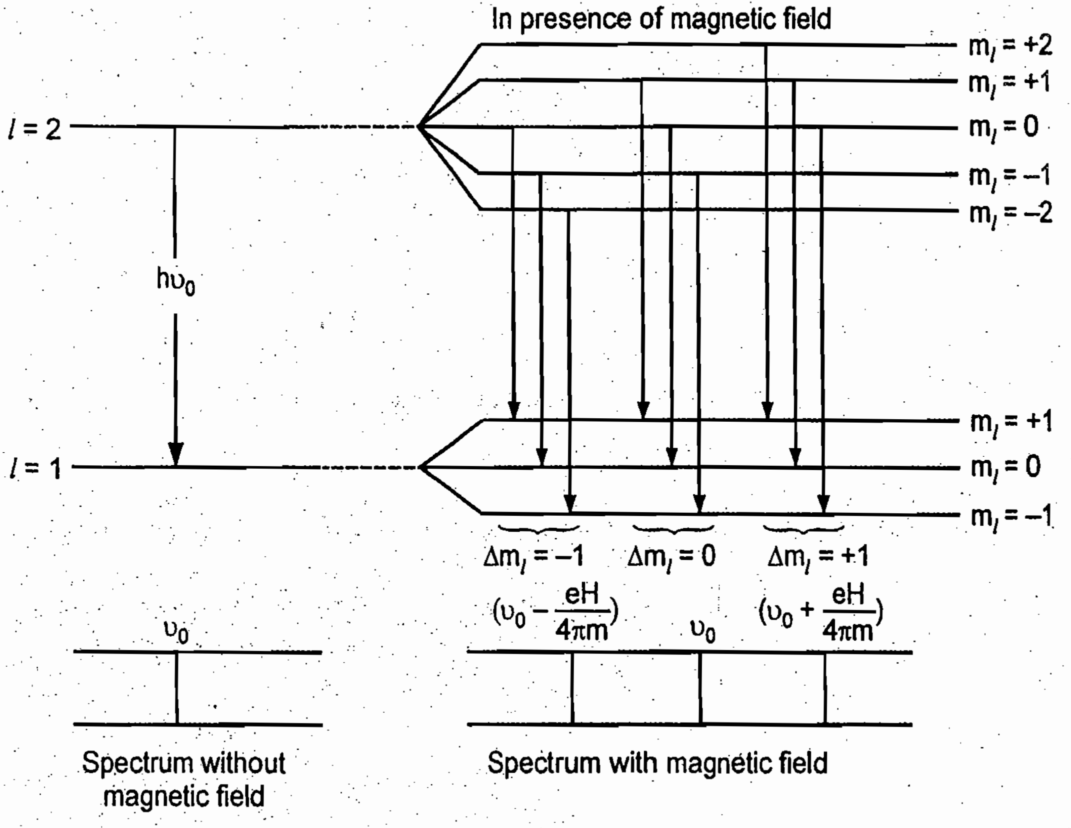


Fig. 5.2 : Normal Zeeman effect

In the diagram, the three transitions in a bracket represent the same change in the value of Δm_l, hence same energy change and hence a single spectral line.

It is to be remembered that Zeeman effect gives confirmation of space quantisation.

5.4 EXPERIMENTAL SET UP FOR ZEEMAN EFFECT

The splitting of spectral line into three components in a strong magnetic field is called normal Zeeman effect.

To study Zeeman effect experimentally, a gas discharge tube (as shown in Fig. 5.3) is placed in between pole-pieces of strong electromagnet (which produce field about 25 k gauss). Light from a source of light (i.e. sodium discharge tube) is observed with high resolving power spectrograph like Lummer Gerke plate with a constant deviation spectrometer. A camera may be used in place of eye piece of spectrometer to get photographic record on plate. From the photograph, the displacement of splitted component from original position can be measured.

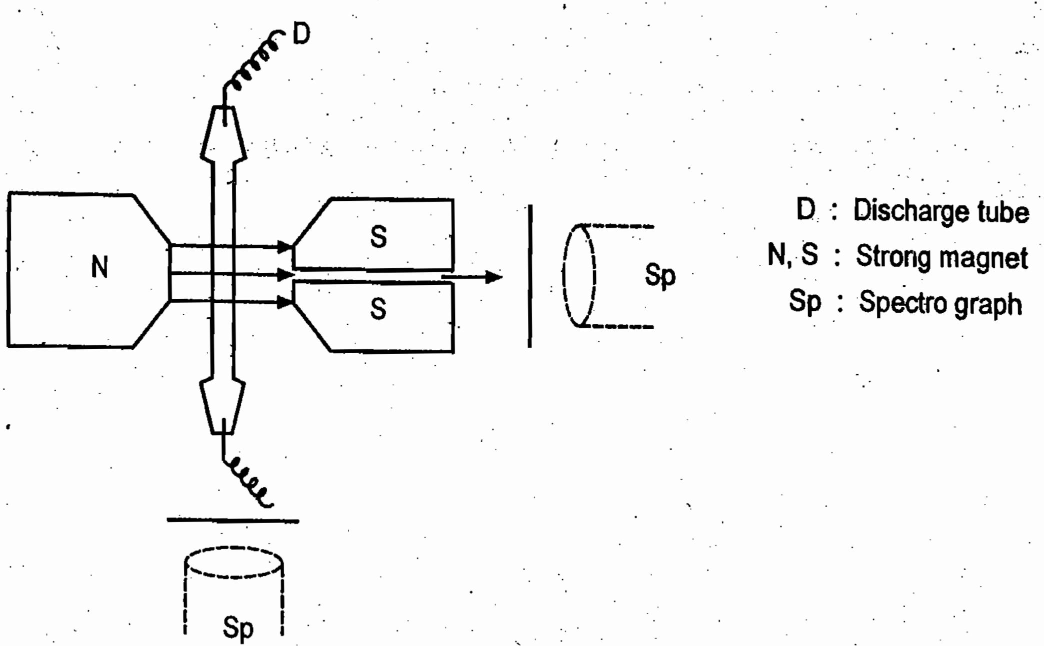


Fig. 5.3 : Experimental set up for Zeeman effect

The Zeeman effect may be observed in two ways :

1. **Perpendicular to the direction of magnetic field :** In this case, a single spectral line observed (when no field is applied) is splitted into three components when magnetic field is applied. i.e. triplet is observed. Central line is undisturbed line and is plane polarized with vibration parallel to the field. The outer two lines are also plane polarized having vibration in direction perpendicular to field. This is known as normal transverse Zeeman effect.

2. **Parallel to the direction of magnetic field :** To observe the effect, a hole is bored through one of the pole pieces. The light coming through the hole is observed with spectrograph (with camera also). It is observed that a single spectral line is split up into two components when the magnetic field is applied i.e. doublet consisting of two spectral lines is observed. Both the lines are displaced from the original position and are circularly polarized in opposite directions. This is known as normal longitudinal Zeeman effect.

The displacements in both the cases are proportional to strength of magnetic field.

Normal Zeeman effect is obtained from sources of element like Ca, Cu, Zn, Cd, etc.

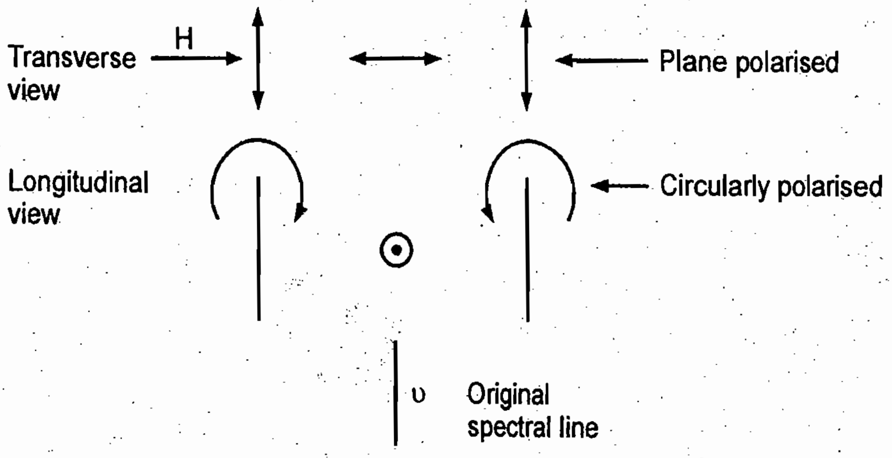


Fig. 5.4 : Zeeman pattern in transverse and longitudinal view

Note : When a single spectral line is split into four or more lines, when observed in direction perpendicular to that of the magnetic field, it is known as anomalous Zeeman effect.

SOLVED EXAMPLES

Example 5.1 : Find the minimum magnetic field needed for Zeeman effect to be observed, in a spectral line of 400 nm wavelength, when a spectrometer whose resolution is 0.010 nm is used.

Solution : Given : $\lambda = 400 \text{ nm} = 400 \times 10^{-9} \text{ m}$

Here $d\lambda = 0.010 \text{ nm} = 0.010 \times 10^{-9} \text{ m}$

Now, as $\upsilon = \frac{c}{\lambda}$

$$\therefore \quad d\upsilon = -\frac{c}{\lambda^2} d\lambda$$

Ignoring the negative sign,

$$\therefore \quad d\upsilon = \Delta\upsilon = \frac{c}{\lambda^2} \Delta\lambda$$

$$= \frac{3 \times 10^8}{(400 \times 10^{-9})^2} \times (0.01 \times 10^{-9})$$

$$= \frac{30}{16} \times 10^{10} = 1.87 \times 10^{10} \text{ cycles/sec}$$

As the separation of Zeeman component is

$$\Delta\upsilon = \frac{eH}{4\pi m}$$

$$\therefore \quad H = \frac{4\pi m \, \Delta\upsilon}{e}$$

$$= \frac{4 \times 3.14 \times 9.11 \times 10^{-31} \times 1.87 \times 10^{10}}{1.6 \times 10^{-19}}$$

$$= 133.7 \times 10^{-2}$$

$$= 1.337 \text{ wb/m}^2$$

Example 5.2 : A sample of a certain element is placed in a 1 Tesla magnetic field and suitably excited. How far apart are the Zeeman components of the 5000 A° spectral line of this element ?

Solution : Given : H = 1 Tesla, $\lambda = 5000 \text{ A}^\circ = 5000 \times 10^{-10} \text{ m}$, $\Delta\lambda = ?$

The separation of the Zeeman components is

$$\Delta\upsilon = \frac{eH}{4\pi m}$$

Since, $\upsilon = \frac{c}{\lambda}$

$$\therefore \quad \Delta\upsilon = -\frac{c}{\lambda^2} \Delta\lambda$$

(Here ignoring the negative sign.)

$$\therefore \quad \Delta\lambda = \frac{\lambda^2}{c} \Delta\upsilon = \frac{\lambda^2}{c} \cdot \frac{eH}{4\pi m}$$

$$= \frac{(5000 \times 10^{-10})^2 \times 1.6 \times 10^{-19} \times 1}{3 \times 10^8 \times 4 \times 3.14 \times 9.11 \times 10^{-31}}$$

$$= 0.1165 \times 10^{-10} \text{ m}$$

$$= 0.1165 \text{ A}^\circ$$

Example 5.3 : The Zeeman components of a 500 nm spectral line are 0.0106 nm apart when the magnetic field is 0.40 Tesla. Find the ratio $\frac{e}{m}$ for the electron from this data.

Solution : Given : $\lambda = 500 \text{ nm} = 500 \times 10^{-9}$ m, $\Delta\lambda = 0.0106 \text{ nm} = 0.0106 \times 10^{-9}$ m.

H = 0.40 Tesla.

Now, as
$$\upsilon = \frac{c}{\lambda}$$

$$\therefore \quad d\upsilon = \Delta\upsilon = -\frac{c}{\lambda^2}\Delta\lambda$$

(Ignoring the negative sign.)

$$\therefore \quad \Delta\upsilon = \frac{c}{\lambda^2}\Delta\lambda$$
$$= \frac{3 \times 10^8 \times (0.0106 \times 10^{-9})}{(500 \times 10^{-9})^2}$$
$$= 1 \times 10^{-7} \times 10^{17}$$
$$= 1 \times 10^{10} \text{ cycles/sec.}$$

As separation of Zeeman components is

$$\Delta\upsilon = \frac{eH}{4\pi m}$$

$$\therefore \quad \frac{e}{m} = \frac{4\pi\,\Delta\upsilon}{H}$$
$$= \frac{4 \times 3.14 \times 1 \times 10^{10}}{0.40}$$
$$= 31.4 \times 10^{10} \text{ Hz/Tesla}$$

QUESTIONS AND PROBLEMS

(A) Fill in the blanks :

1. When a single spectral line is splitted into four or more spectral lines when viewed through perpendicular direction to magnetic field is called ......
2. Bohr magnetron has value ......
3. The magnetic moment of electron in orbital motion depends upon ......
4. Zeeman shift depends upon ......

(B) Answer in short :

1. What is Zeeman effect ?
2. Define Bohr magnetron.
3. What is Larmour precession ?
4. What is anomalous Zeeman effect ?
5. Write formula for Zeeman shift.

(C) Answer in detail :

1. What is Zeeman effect ? Distinguish between normal Zeeman effect and anomalous Zeeman effect.
2. Explain in detail what happens to an atom in magnetic field.
3. With neat diagram explain experimental set up to produce and observe Zeeman effect.
4. In Zeeman effect, show that

$$\upsilon = \upsilon_0 + \frac{eH}{4\pi m} \Delta m_l$$

   Hence discuss three cases.
5. Draw energy level diagram showing transitions in Zeeman effect. Hence write formulae for frequency for a spectrum with magnetic field.

(D) Numerical problems :

1. The Zeeman components of a 650 nm spectral line are 0.014 nm apart, when magnetic field is 1.25 Tesla. Find the ratio e/m for the electron from this given data.

   Ans : $\frac{e}{m} = 9.95 \times 10^{10}$ Hz/Tesla.

2. The calcium line of wavelength $\lambda = 4226.73$ A° (P → S) exhibits normal Zeeman splitting when placed in uniform magnetic field of 2.5 wb/m^2. Calculate the wavelength of three components of normal Zeeman pattern and separation between them.

   Ans. : $\lambda_1 = 4226.5216$ A°, $\lambda_2 = 4226.73$ A°, $\lambda_3 = 4226.9384$ A° and $\Delta\lambda = 0.2084$ A°

3. A sample of certain element is placed in 0.30 T magnetic field and suitably excited. How far apart the Zeeman component of the 450 nm spectral line of this element ?

   Ans. : 0.00283 nm.

4. The Zeeman components of a 500 nm spectral lines are 0.0116 nm apart when the magnetic field is one Tesla. Find the e/m for electron.

❐❐❐

6

X-ray Spectra

6.1 INTRODUCTION

The discovery of X-rays is one of the milestone in the history of Physics. In 1895, Roentgen, a German Physicist invented X-rays while working on discharge of electricity through gases. His simple observation opened up a series of discoveries in atomic physics, photo chemistry and structure of material.

X-rays are widely used in medicine (i.e. surgery and radiotherapy), engineering, industry and scientific research because of their special properties. In year 1912, M. Laue performed diffraction experiments and confirmed wave nature of X-rays. Now-a-days X-ray diffraction technique is an important tool in scientific research and Biotechnology.

In this chapter we discuss characteristic and continuous spectra, K, L, M, N series, comparison of X-ray with optical spectra and Moseley law in detail. Fig. 6.1 is a diagram of an X-ray tube (Coolidge tube). A cathode, heated by a filament through which an electric current is passed, supplies electron by thermionic emission. A high potential difference V is maintained between the cathode and a metallic target. The electrons are attracted towards cathode. The face of the target is at an angle relative to the electron beam. The X-rays that leave the target pass through side of tube. The tube is evacuated to permit the electrons to get to the target unimpeded.

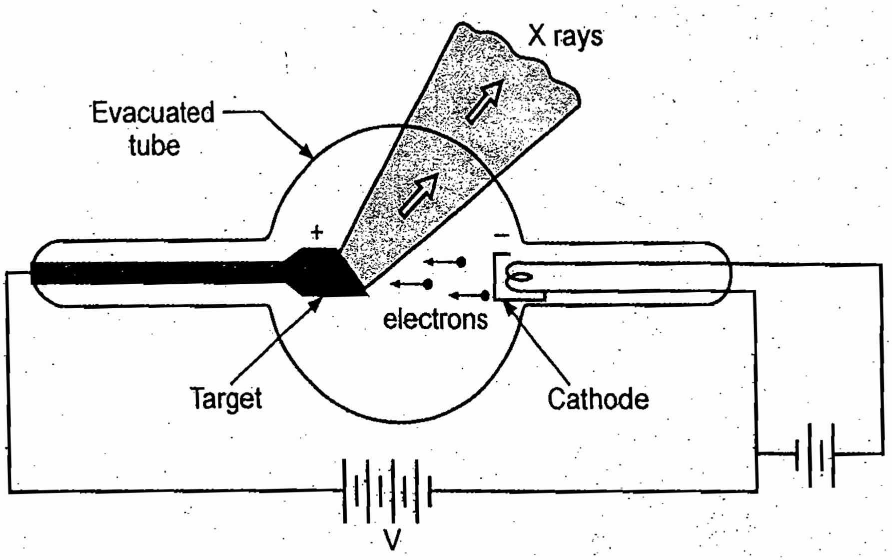


Fig. 6.1 : An X-ray tube

Fig. 6.2 shows a spectra when tungsten and molybdenum targets which are bombarded by electrons at several different accelerating potentials. The curve exhibits two features :

1. In the case of molybdenum, intensity peaks occured indicate the enhanced production of X-rays at certain wavelength. These peaks occur at specific wavelength for each target material. These peaks are originated in rearrangement of electron structure of the target atom having been disturbed by bombarding electrons.

2. The X-rays produced at a given accelerating potential V vary in wavelength but none has wavelength shorter than particular value of λ_{min}. As V increases, λ_{min} decreases.

3. At a particular accelerating voltage, λ_{min} is same for tungsten and molybdenum targets.

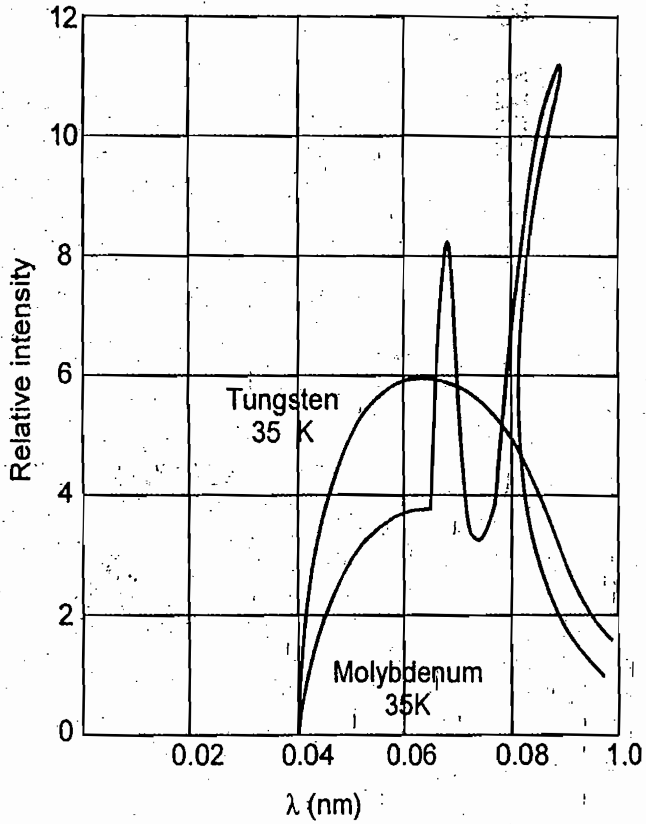


Fig. 6.2 : X-ray spectra of tungsten and molybdenum at 35 kV

6.2 DUANE AND HUNT LAW

Duane and Hunt found experimentally that "short wavelength limit varies inversely as accelerating voltage".

$$\lambda_{min} \propto \frac{1}{V}$$

Their precise relation is

$$\lambda_{min} = \frac{hc}{eV}$$

$$= \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^{8}}{1.6 \times 10^{-19} \text{ V}}$$

or $$\lambda_{min} = \frac{12400}{V} A^{0} \qquad \text{... (6.1)}$$

This is called as *Duane and Hunt relation.*

The second observation i.e. shorter wavelength limit depends on accelerating voltag fits in quantum theory of radiation. Most of the electrons striking the targets underg number of collisions, with their energy going into heat. (That is why the targets of X-ra tubes are made of materials having high melting point such as tungsten.)

Few electrons, though loose most or all of their energy in single collision with the targe atom, this is the energy that is evoked as X-rays.

X-ray production, except for peaks mentioned above, represents inverse photoelectri effect. Instead of photon energy being transformed into electron kinetic energy, (as i photoelectric effect), electron kinetic energy is transferred into photon energy. Since wor functions are of order few eV, whereas the accelerating potentials in X-ray tube ar typically of the order of kilovolt. We can ignore work function and interprete shorte wavelength limit as

$$eV = h\upsilon_{max}$$

$$= \frac{hc}{\lambda_{min}}$$

$$\lambda_{min} = \frac{hc}{eV} = \frac{1.24 \times 10^{-6}}{V} \text{ volt-meters} \qquad \ldots (6.2)$$

which is known as the Duane-Hunt formula.

6.3 ORIGIN OF CONTINUOUS AND CHARACTERISTIC X-RAY SPECTRA

We have seen that X-ray spectra of target bombarded by fast electrons show narrow spikes at wavelength characteristics of the target material.

These are in addition to a continuous distribution of wavelengths down to a minimum wavelength inversely proportional to electron energy. Continuous X-ray spectrum is the result of the inverse photoelectric effect.

Continuous X-ray Spectrum:

The X-rays emitted by target material have a continuous distribution of intensity above a certain minimum wavelength given by,

$$\lambda_m = \frac{1.242 \times 10^{6}}{V} = \frac{12420}{V} \text{ A}^{\circ}$$

where V is applied voltage.

The minimum wavelength is known as Duane-Hunt limit or continuous spectrum boundary. It is independent of nature of target.

Continuous X-rays are produced by the phenomenon of Bremsstrahlung, which is a German word meaning 'braking' or 'slowing down' radiation. Electrons emitted from the cathode in the X-rays are accelerated towards the target, strike it, penetrate deep into the interior of its atoms and are attracted by the nuclei due to strong electrostatic interaction. The electron, therefore, deviates from its original path, as shown in Fig. 6.3.

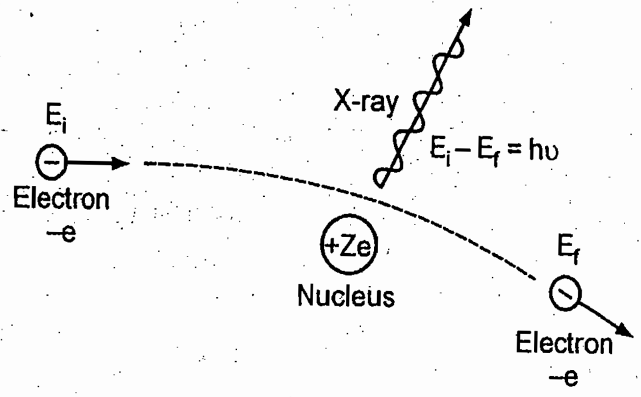


Fig. 6.3

The deviation of the electron from its straight line path is equivalent to it collision with the nucleus. The electron loses more of its energy due to the collision. This energy appears as an X-ray photon. If E_i is the initial kinetic energy of the electron and E_f is the final kinetic energy, then the energy of the X-ray photon = $E_i - E_f$. If υ is the frequency of the X-ray photon emitted, then,

$$h\upsilon = E_i - E_f$$

The electron may suffer several collisions with various nuclei before coming to rest and each collision is accompanied by the emission of an X-ray photon. Hence, a number of photons of different frequencies are emitted. As there are a large number of electrons in the beam and each electron suffers collision in a different way, we get photons of almost all frequencies or wavelengths, thus producing a continuous X-ray spectrum.

The production of continuous spectrum is the result of inverse photo-electric effect with electron kinetic energy $E_i - E_f$ being transformed into a photon energy $h\upsilon$.

According to classical theory, the continuous X-ray spectrum should consist of all frequencies between zero and infinity. But according to quantum theory, there is a minimum wavelength upto which the continuous X-ray spectrum extends. To find the value of λ_{min}, let the velocity of the incident electron decreases from v_i to v_f due to interaction with the nucleus. Then frequency of X-ray photon is given by

$$h\upsilon = \frac{1}{2}mv_i^2 - \frac{1}{2}mv_f^2$$

When electron is brought to rest by electrostatic interaction, $v_f = 0$ and photon has maximum frequency or minimum λ.

$$h\upsilon_{max} = \frac{1}{2}mv_i^2$$

V is P.D. between **cathode and target** then

$$\frac{1}{2}mv_i^2 = eV$$

$$\therefore h\upsilon_{max} = eV$$

$$\therefore \quad \lambda_{min} = \frac{c}{\upsilon_{max}} = \frac{ch}{eV}$$

$$= \frac{1.242 \times 10^{-6}}{V} \text{ m}$$

The plot of relative intensity of X-ray spectra versus wavelength at various potentia differences applied to an X-ray tube between the cathode and the target (Tungsten) is showı in Fig. 6.4.

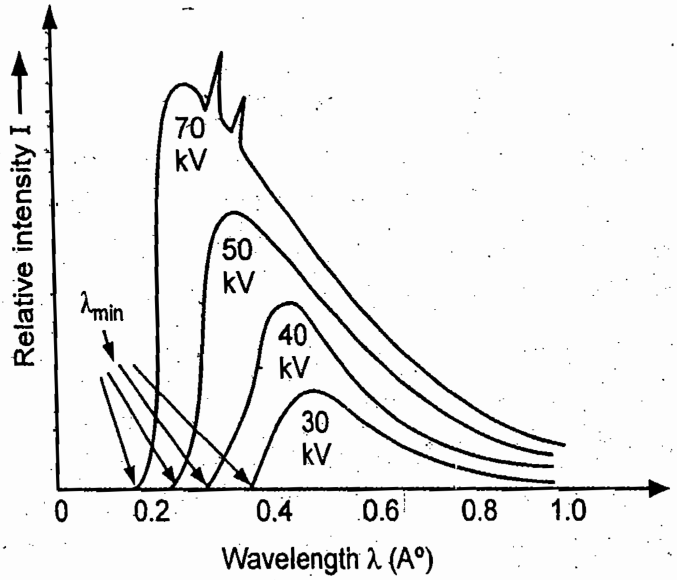


Fig. 6.4

The special features are :

(a) Change of target material : As $\lambda_{min} = \frac{ch}{eV}$ where c, h and e are constants, the cut-off wavelength is, therefore, the same for all target materials.

(b) Change in accelerating voltage :

(i) The continuous spectrum ends abruptly at a minimum wavelength λ_{min}. The value of λ_{min} decreases with increasing accelerating potential.

(ii) The intensity rises to a maximum at a certain wavelength, after which it gradually falls off. The intensity never reaches zero, showing that the radiation contains all possible wavelengths, above a certain minimum.

(iii) The wavelength corresponding to maximum intensity λ_m shifts gradually to lower wavelength side, as the accelerating potential is increased in such a way that $(\lambda_m V^{1/2})$ is almost a constant.

(iv) For a particular target material, the intensity of continuous X-ray spectrum, corresponding to all wavelengths as well as the maximum intensity, increase with accelerating potential.

(v) For applied potential difference 70 kV, two sharp peaks are seen. The sharp peaks are due to characteristic radiation. The line spectra is absent till the potential difference is greater than a particular value. The smoothly varying curves represent the continuous spectrum and the superimposed lines on the continuous background constitute the characteristic spectrum.

6.4 CHARACTERISTIC X-RAY SPECTRUM

The characteristic X-ray spectrum consists of sharp peaks superimposed on the continuous spectrum. Wavelength is characteristic of the target element. It is highly monochromatic and independent of the applied voltage. The intensity of the characteristic spectrum lines is very large - sometimes 10^4 times that of the continuous spectrum in that region.

The characteristic wavelength is given by Moseley's law

$$\lambda (Z-b)^2 = a \text{ (constant)}$$

where b is different for different materials.

Every substance gives rise to a particular set of characteristic X-rays, consisting of one or more series, known as K, L, M, etc. series. The X-rays in K series of a particular element have smaller wavelength than in the L or M series, whereas the wavelength of the X-rays in the same series say K, produced from an element of higher atomic weight is less than that produced from an element of lower atomic weight.

Production of characteristic X-rays : An atom consists of a central nucleus having a positive charge and revolving round it, in more or less circular orbits, a suitable number of electrons. The electron in the innermost orbit is attracted by the nucleus with the greatest force and to detach it from the atom maximum energy is required. The innermost orbit is given the name K level or shell and the outer orbits L, M, etc. levels respectively. Thus more energy is required to detach an electron from an inner level than from an outer level.

When an atom is bombarded by fast moving electrons, an electron coming with a high velocity penetrates through the outer shell containing electrons and removes an electron from one of the inner shells. An incoming electron knocking out an electron from K shell of an atom is shown in Fig. 6.5 (b). The incident and the dislodged electrons both rush out of the atom, causing a vacancy in the K shell or level.

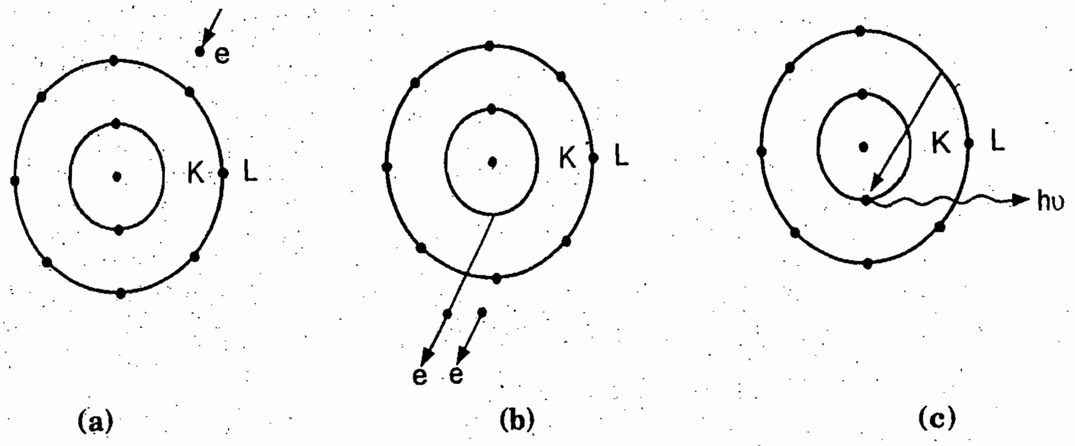


Fig. 6.5

Immediately, one of the electrons from the higher levels (e.g. L level) jumps into the K level. A radiation of frequency υ is emitted at the same time. The frequency of the radiation, is given by the relation,

$$E_K - E_L = h\upsilon$$

or

$$\upsilon = \frac{E_K - E_L}{h}$$

where E_K is the energy required to extract an electron from the K level and E_L is the energy required to extract an electron from the L level and h is Planck's constant having a value equal to 6.62×10^{-34} joule-sec. The frequency of the radiation is very high and is of the order of 10^{18} per second.

The wavelength of the corresponding X-rays is given by,

$$\lambda = \frac{c}{\upsilon} = \frac{hc}{E_K - E_L}$$

If an electron from the M level falls into the K level, X-rays of still higher frequency (shorter wavelength) will be produced. The frequencies of X-rays produced by the fall of an electron from an outer level to the K level can be arranged into a series, called K series, consisting of K_α, K_β, K_γ etc. lines, as shown in Fig. 6.6.

A jump from L level to K level gives rise to K_α line and from M level to K level K_β line and so on, till we get limiting line, known as K-series limit.

Similarly, when the incident electrons carry a lesser amount of energy, an electron is displaced from the L level and an electron from M or other outer level takes its place, so that a radiation of a lower frequency than that of K series is emitted. This corresponds to the L series of the X-ray spectrum. For the same element, the L lines of the X-ray spectrum have smaller frequency (larger wavelength) than the K lines. A jump from M shell to L shell gives rise to L_α line and from N shell to L shell gives rise to L_β line and so on, till we get the limiting line, known as L-series limit.

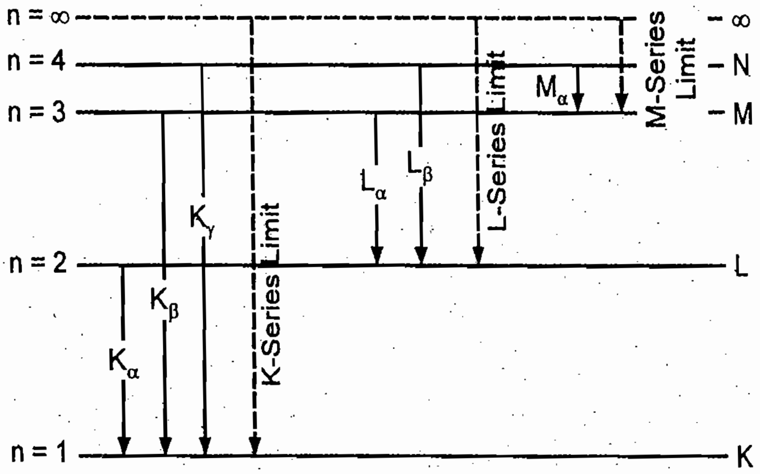


Fig. 6.6 : Spectral lines in different series and their transition

The wavelengths of these lines in the K, L, or M series depend upon the atomic weight of the anti-cathode and these wavelengths are known as *characteristic X-rays* for the material of the given target.

6.5 MOSELEY'S LAW

In 1913-14, Moseley carried out a systematic study of the characteristic X-ray spectra of various elements used as targets in an X-ray tube. For this purpose, he used Bragg's spectrometer to find that the characteristic X-ray spectra of different elements. They are remarkably similar to each other in the sense that each consists of K, L, and M series. However, he found one very important difference. The frequency of lines in every series, produced from an element of higher atomic number is greater than that produced by an element of lower atomic number. This is because the binding energy of electrons increases as we go towards the elements of higher atomic number. Since there is a greater positive charge on the nucleus of higher atomic number, large amount of energy is required to liberate an electron from the K, L and M shells of that element.

Consider K_α line of the characteristic X-ray spectrum of any element. It is found that higher the atomic number of the target material, higher is the frequency of the K_α line produced by it. The exact mathematical equation between frequency and atomic number is given by,

$$\upsilon \propto (Z - b)^2$$

$$\sqrt{\upsilon} \propto (Z - b)$$

or

$$\sqrt{\upsilon} = a(Z - b)$$

where Z is the atomic number of the element and a and b are constants for a particular series but vary from one series to another. The constant b is known as 'nuclear screening constant'. For lines in K series, b = 1; for lines in L series, it's value is more. The relation is known as Moseley's Law for the characteristic or line X-ray spectrum.

Statement : The frequency of a spectral line in the characteristic X-ray spectrum varies directly as the square of the atomic number of the element emitting it.

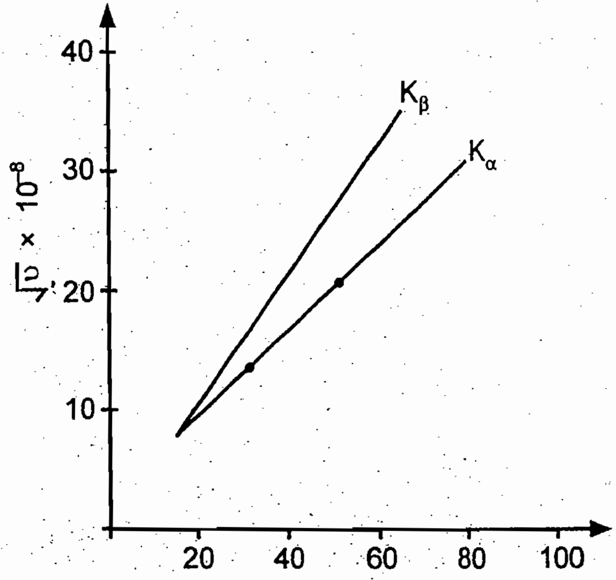


Fig. 6.7

Above Fig. 6.7 shows Moseley's diagram for K_α and K_β lines, which is obtained by plotting $\sqrt{\upsilon}$ versus atomic number of different elements of the periodic table. The graph is linear as expected.

The exact form of Moseley's law is

$$\bar{\upsilon} = \frac{1}{\lambda} = R(Z-\sigma^2)\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

where R is Rydberg's constant, Z is atomic number, σ is correction factor and n_1 and n_2 are the principal quantum numbers of the energy levels between which the transition occurs.

Importance of Moseley's Law :

The great importance of Moseley's law lies in the fact that it proves for the first time that it is the atomic number and not the atomic weight of an element, which determines its characteristic properties (both physical and chemical). It gives the indication that the elements in the periodic table must be arranged according to their atomic numbers and not by their atomic weights. This fact is further supported by the chemical properties of the elements.

Moseley's law has led to the discovery of new elements like hafnium (72), promethium (61), technetium (43) and rhenium (75) etc., by the indication of gaps in Moseley's diagram. The law has also helped in determining the atomic number of rare earth elements, thereby fixing their positions in the periodic table.

Moseley's law is in accordance with Bohr's theory. When an electron jumps from an orbit n_2 to the orbit n_1, the frequency of radiation is given by,

$$\upsilon = \frac{me^4}{8\varepsilon_0^2 h^3} \cdot Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$= \left[\left(\frac{me^4}{8\varepsilon_0^2 h^3}\right)\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\right]Z^2$$

$$\therefore \qquad \upsilon \propto Z^2 \quad \text{or} \quad \sqrt{\upsilon} \propto Z.$$

Moseley took into account the screening effect of electrons, which Bohr did not. Thus the expression becomes $\sqrt{\upsilon} \propto (Z-b)$.

6.6 FINE STRUCTURE OF X-RAY SPECTRA

Moseley's observations about characteristic X-ray spectra were made in 1913. He observed that, most of the lines in the X-ray spectrum were found to consist of two or more lines. For example, K_α line was found to be a doublet i.e. two very close lines for all elements beyond. Sodium (At. No. 11). Similarly, K_β line also showed a complex structure.

Thus each X-ray line is found to consist of two or more lines very close together. This is known as *fine structure of X-ray lines.*

To explain the emission of characteristic X-ray spectra, we considered the total energy difference only due to change of principal quantum number n. But to have a complete picture, the effect of changes in other quantum numbers have also to be taken into account. To a first approximation, the energy of an electron is determined by its configuration, which depends upon the principal as well as the orbital quantum number. Further, to take into account the sufficient large influence of spin quantum number, we take the vector sum of the orbital and spin quantum number, j – the total angular momentum quantum number.

In the K-shell (n = 1, l = 0) the orbital is spherically symmetrical and only one value of j is possible i.e. $j = l + s = +\frac{1}{2}$. The number of levels in K-shell $(2l + 1) = 1$ i.e. there is only one level. In spectroscopic notation, it is denoted as $1s_{1/2}$.

For the L-shell (n = 2, l = 1, 0) two values of j are possible, $j = \frac{3}{2}$ and $j = \frac{1}{2}$ corresponding to $l = 1$ i.e. $(l + s) = \left(1 + \frac{1}{2}\right) = \frac{3}{2}$ and $(l - s) = \left(1 - \frac{1}{2}\right) = \frac{1}{2}$ and one value $j = \frac{1}{2}$ corresponding to $l = 0$ i.e. $(l + s) = +\frac{1}{2}$. Thus there are three subshells L_I $(n = 2, l = 0, j = +\frac{1}{2})$ L_{II} $(n = 2, l = 1\ j = \frac{1}{2})$ and L_{III} $(n = 2, l = 1, j = \frac{3}{2})$. In spectroscopic notation, these are denoted as $L_I = 2s_{1/2}$, $L_{II} = 2p_{1/2}$, and $L_{III} = 2p_{3/2}$.

For the M-shell (n = 3, l = 2, 1, 0) there are five subshells, M_I $(n = 3, l = 0,\ j = \frac{1}{2}) = 3s_{1/2}$, M_{II} $(n = 3, l = 1, j = \frac{1}{2})$, $= 3p_{1/2}$, M_{III} $(n = 3, l = 1, j = \frac{3}{2}) = 3p_{3/2}$, M_{IV} $(n = 3, l = 2, j = \frac{3}{2}) = 3d_{3/2}$ and M_V $(n = 3, l = 2, J = \frac{5}{2}) = 3d_{5/2}$.

Similarly, for N-shell there are seven subshells denoted as $N_I = 4s_{1/2}$, $N_{II} = 4p_{1/2}$, $N_{III} = 4p_{3/2}$, $N_{IV} = 4d_{3/2}$, $N_V = 4d_{5/2}$, $N_{VI} = 4f_{5/2}$, $N_{VII} = 4f_{7/2}$. It should be noted that each subshell can have a maximum of (2j + 1) electrons.

This is known as the multiplicity of the shell and arises from the fact that the total angular momentum vector can be oriented in (2j + 1) directions, according to the rule of spatial quantisation. Thus, the multiplicity of the K-shell $\left(j = \frac{1}{2}\right) = 2$ for L_I $\left(j = \frac{1}{2}\right) = 2$, $L_{II}\left(j = \frac{1}{2}\right) = 2$, $L_{III}\left(j = \frac{3}{2}\right) = 4$, $M_I\left(j = \frac{1}{2}\right) = 2$, $M_{II}\left(j = \frac{1}{2}\right) = 2$, $M_{III}\left(j = \frac{3}{2}\right) = 4$, $M_{IV}\left(j = \frac{3}{2}\right) = 4$, $M_V = \left(j = \frac{5}{2}\right) = 6$ and so on for N subshells.

An energy level diagram, based on the above data, is shown in Fig. 6.8, in which each level represents an allowed electron state. If an electron is removed from a sub-shell, the atom gets ionised. The vacancy thus created may be filled by an electron from an outer shell, according to selection rules, giving rise to fine-structure of the lines. These selection rules are

$$\Delta l = \pm l; \quad \Delta j = 0, \pm 1, \quad \Delta n = \text{any value}$$

K_α line which is produced by the transition of an electron from L-level to K-level, will now consist of two lines K_α (1) and K_α(2) for transitions from L_{III} or $2P_{3/2}$ to K or $1s_{1/2}$ and from L_{II} or $2p_{1/2}$ to K or $1s_{1/2}$, level according to $l = 1 \rightarrow l = 0$ or $\Delta l = +1$ and $j = \frac{3}{2} \rightarrow j = \frac{1}{2}$ or $\Delta j = +1$ and $l = 1 \rightarrow l = 0$ or $\Delta l = +1$ and $j = \frac{1}{2} \rightarrow j = \frac{1}{2}$ or $\Delta j = 0$.

The transition from L_I to K (or $2s_{1/2}$ to $1s_{1/2}$) involving $l = 0 \rightarrow l = 0$ or $\Delta l = 0$ is not allowed. Thus K_α line is a doublet. K_α and K_γ lines also consist of two very close lines each. Some allowed transitions giving rise to fine structure in K_α, K_β and L_α lines is shown in Fig. 6.8.

There are other weak lines observed in X-ray spectra which cannot be expressed as difference of any two levels given in the figure. These lines are called non-diagram lines and generally lie close to one of diagram lines. These are known as satellite lines and are produced due to transitions in atoms from which two or more electrons have been removed.

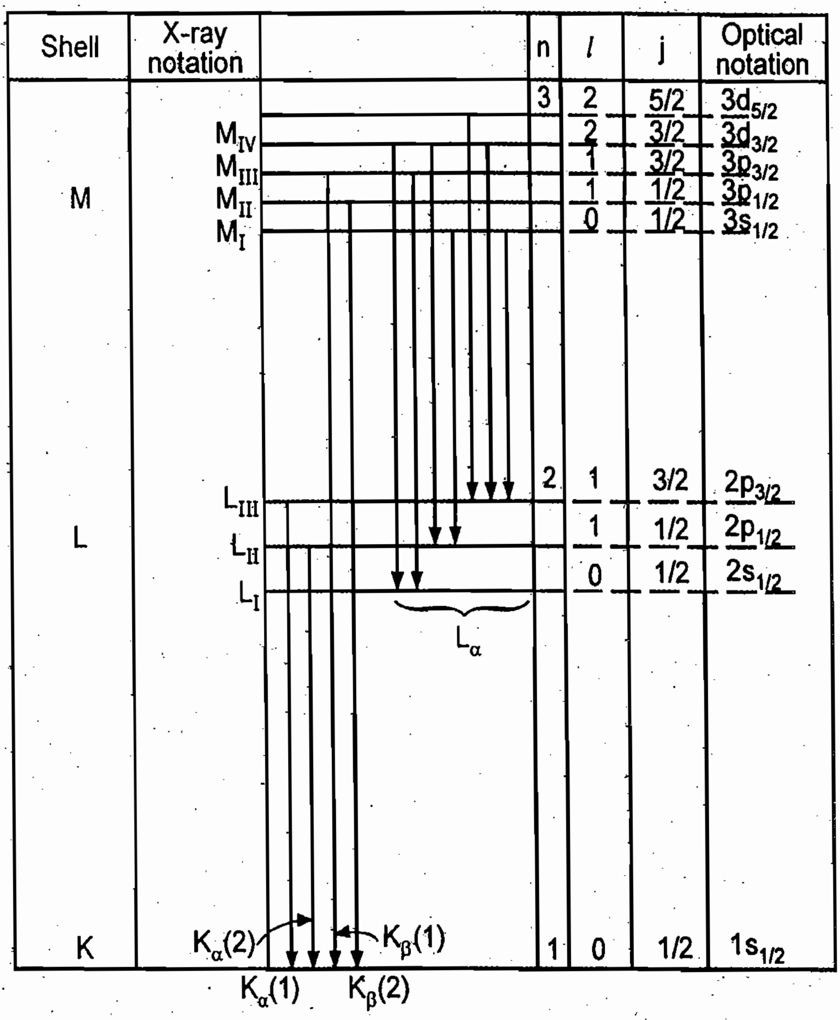


Fig. 6.8 : Fine structure of X-ray spectra

6.7 COMPARISON OF X-RAY AND OPTICAL SPECTRA

The X-ray spectra emitted by different elements are like one another and simpler than corresponding optical spectra. The main differences between the two spectra are as follows :

Optical Spectra	X-ray spectra
1. This spectra is observed when there is a transition of electron located in the outermost shell of an atom. Such electron is also known as optical electron.	1. X-ray spectra is observed when there is a transition of electron from inner shells (such as K, L, M ... shells) of an atom.
2. Optical photon has less energy (or small frequency)	2. As energies of inner shells are much large, X-ray photon emitted has high energy (or high frequency)
3. Optical radiation has less penetrating power.	3. The X-ray radiation has very high penetrating power. (X-ray photon is 10^4 times more penetrating than an optical photon).
4. The optical radiation lies in the visible range of the electromagnetic spectrum (wavelength range being 400 nm to 700 nm).	4. The X-ray radiation lies in between gamma ray to ultra-violet region of electromagnetic spectrum. (wavelength being 0.01 nm to 10 nm)
5. Optical spectra show abrupt periodic changes from element to element. This is because the electronic structure at the surface of atom changes periodically from element to element.	5. X-ray spectra vary smoothly from element to element because X-ray spectra depends on B.E. of electron in inner shells.
6. Optical radiation does not produce ionization and fluorescence.	6. X-ray radiation can produce ionization and fluorescence.
7. Optical radiation is not harmful to human body.	7. Repeated exposure to X-rays are hazardous to human body.

SOLVED EXAMPLES

Example 6.1 : Find the nuclear screening constant for L series of X rays if it is known that X-rays with a wavelength of $\lambda = 1.43$ A° are emitted when an electron in a tungsten atom (z = 74) is transferred from M level to L level. (Take $R = 10.97 \times 10^6$ m^{-1}).

Solution : When electron jumps from M to L level, the first member of the L series i.e. L_α line is given out. Its wavelength by Moseley's law is

$$\frac{1}{\lambda} = R\,(Z-b)^2\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = \frac{5R}{36}\,(Z-b)^2$$

Substituting,

$$\therefore \quad \frac{10^{10}}{1.43} = 10.97 \times 10^{6} \times \frac{5}{36}(74 - b)^2$$

$$\therefore \quad b = 6.25$$

Example 6.2 : Find the shortest wavelength present in the radiation from an X-ray machine whose accelerating potential is 100 K.

Solution : Minimum wavelength is given by,

$$\begin{aligned} \lambda_{\text{min}} &= \frac{ch}{eV} \\ &= \frac{3 \times 10^{8} \times 6.64 \times 10^{-34}}{1.6 \times 10^{-19} \times 100 \times 10^{3}} \\ &= \frac{1.242 \times 10^{-6}}{100 \times 10^{3}} \\ &= 1.242 \times 10^{-11} \\ &= 0.0124 \text{ nm} \end{aligned}$$

Example 6.3 : Electrons are accelerated in a television tube through potential difference of 10 kV. Find the highest frequency and minimum wavelength of the electromagnetic waves emitted, when these strike the screen of the tube. In which region of the spectrum will these waves lie.

Solution : Minimum wavelength,

$$\lambda_{\text{min}} = \frac{ch}{eV} = 1.242 \times 10^{-6} \text{ m}$$

Here, $V = 10 \text{ kV}$

$$\therefore \quad \lambda_{\text{min}} = \frac{1.242 \times 10^{-6}}{10 \times 10^{3}} = 1.242 \text{ A}^{\circ}$$

$$\upsilon_{\text{max}} = \frac{c}{\lambda_{\text{min}}} = \frac{3 \times 10^{8}}{1.242 \times 10^{-10}} = 2.42 \times 10^{18} \text{ Hz}$$

The waves lie in X-ray region of electromagnetic radiation (X-rays lie in wavelength region 0.3 A° – 100 A°).

Example 6.4 : If the K, L and M energy levels of platinum are 80000, 14000 and 5000 eV respectively. Calculate wavelength of K_{α} and K_{β} lines from platinum.

Given : $1 \text{ eV} = 1.6 \times 10^{-19}$ J, $h = 6.6 \times 10^{-34}$ Js.

Solution : Energy of K level region,

$$\begin{aligned} E_K &= 80000 \text{ eV} \\ &= 80000 \times 1.6 \times 10^{-19} \text{ J} \end{aligned}$$

Energy of L-level, $E_L = 14000 \times 1.6 \times 10^{-19}$ J

Energy of M level, $E_M = 5000 \times 1.6 \times 10^{-19}$ J

Wavelength for K_{α} line,

$$\begin{aligned} \lambda_1 &= \frac{hc}{E_K - E_L} \\ &= \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{(80000 - 14000) \times 1.6 \times 10^{-19}} \\ &= \frac{19.8 \times 10^{-26}}{66 \times 1.6 \times 10^{-16}} \end{aligned}$$

$$\lambda_1 = 0.1875 \text{ A}^{\circ}$$

Similarly,

$$\text{Wavelength for } K_\beta \text{ line} = \frac{hc}{E_M - E_K}$$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{(80000 - 5000) \times 1.6 \times 10^{-19}}$$

$$= 0.165 \text{ A}^\circ$$

QUESTIONS AND PROBLEMS

(A) Objective type questions :

1. **State true or false.**
   - (i) X-ray spectra arise from transitions to outer shell.
   - (ii) Intensity peak of X-ray is independent of target material.
   - (iii) The frequency of optical spectral line is small.
   - (iv) Frequency of X-ray is proportional to atomic mass of target element.
   - (v) In characteristic X-ray spectrum, there are sharp lines which depend on target material.

(B) Answer in short :

1. What are different types of spectra ?
2. State Duane and Hunt law.
3. What is importance of Moseley's law ?
4. How X-ray production is inverse of photoelectric effect ?

(C) Answer in detail :

1. What are X-rays ? How they are produced ?
2. State and explain Duane and Hunt law.
3. Discuss origin of continuous X-ray spectrum.
4. What is characteristic X-ray spectrum ? Discuss its origin.
5. State and explain Moseley's law. Discuss applications of Moseley's law.
6. Using energy level diagram obtain the electron transition for K_{α_1}, K_{α_2} and K_{β_1}, K_{β_2} lines.
7. Compare X-ray spectra with optical spectra.

(D) Numerical Problems :

1. X-ray tube operating at 44 kV emits X-rays of wavelength 0.284 A°. Calculate Planck's constant. **[Ans.** 6.62×10^{-34} Js]
2. What voltage must be applied to an X-ray tube for it to emit X-rays with minimum wavelength 5000 A° ? **[Ans.** 24.85 kV]
3. Determine wavelength of K_α X-rays emitted by an element having z = 79, $a = 2.468 \times 10^{15}$ s^{-1} and $b = 1$. **[Ans.** 0.1977 A°]
4. The effective charge experienced by an M (n = 3) electron in an atom of atomic number Z is about (Z – 7.4) e. Show that frequency of L_α, x-rays of such element is given by $\frac{5CR(Z-7.4)^2}{36}$.

□□□

7

Introduction to Molecular Spectra

7.1 INTRODUCTION

Molecular spectroscopy is the study of the interaction of electromagnetic waves and matter which gives us more information related to the structure of matter. Electromagnetic radiations can be considered as a simple harmonic waves propagated from source. These electromagnetic waves are the characteristics of the respective source. Any matter consists of atoms and molecules. The atoms are bounded together to form molecule. In 1961, G.W. Lewis presented his theory of valency and explained the bonding. According to Pauding, a chemical bond exists between two atoms if the bonding force is stronger enough to have stability to consider these number of atoms as an independent molecular species. The electromagnetic radiations given by the molecule depend on the types of the atoms and the types of the bonding between them.

In this chapter, we discuss types of molecular spectra, spectra of diatomic molecule and rotational energy levels of rigid and non-rigid diatomic molecules.

Molecular Spectra

There are many ways of classifying electromagnetic radiations given out by atoms and molecules. These can be classified by the frequency range. The regions does not have any fixed boundaries as such which can give us the precise wave length. However, the molecular processes associated with each region are quite different, still we can have the classification depending on the different regions as follows :

	Region		Frequency	Wavelength
1.	Radiofrequency region	-	$3 \times 10^6 - 3 \times 10^{10}$ Hz	10 m – 1 cm
2.	Microwave region	-	$3 \times 10^{10} - 3 \times 10^{12}$ Hz	1 cm – 100 μm
3.	Infrared region	-	$3 \times 10^{12} - 3 \times 10^{14}$ Hz	100 μm – 1 μm
4.	Visible & Ultraviolet region	-	$3 \times 10^{14} - 3 \times 10^{16}$ Hz	1 μm – 10 nm
5.	X-ray region	-	$3 \times 10^{16} - 3 \times 10^{18}$ Hz	10 nm – 100 pm
6.	γ-ray region	-	$3 \times 10^{18} - 3 \times 10^{20}$ Hz	100 pm – 1 pm

7.2 TYPES OF MOLECULAR SPECTRA

We know that molecules can remain in the ground state as well as excited states. The transition between the allowed energy states of a molecule with the emission or absorption of radiation give rise to molecular spectra. The frequency of emitted or absorbed photon is given by

$$\upsilon = \frac{E_2 - E_1}{h} \quad \text{if } E_2 > E_1 \text{ (i.e. absorption)}$$

or

$$\upsilon = \frac{E_1 - E_2}{h} \quad \text{if } E_1 > E_2 \text{ (i.e. emission)}$$

The energy levels of molecule are more complex than atom. In case of molecule, various types of motion of individual nuclei can take place.

The excited energy level of a diatomic molecule for a fixed electronic configuration arise from :

(i) rotation of molecule about an axis passing through the centre of mass of molecule and perpendicular to the line joining atoms.

(ii) the vibrations of atoms about their equilibrium position in molecule.

Therefore, total energy consists of :

(i) Energy due to excitation of electron in the molecule i.e. Electronic energy, E_e.

(ii) Energy due to rotation of molecule i.e. Rotational energy, E_r.

(iii) Energy due to vibration of molecule i.e. Vibrational energy, E_v.

$$\therefore \quad \text{Total energy, } E = E_e + E_r + E_v$$

The magnitudes of these energies are sufficiently different and

$$E_e > E_v > E_r$$

Hence, we can classify molecular spectra into **three distinct regions.**

1. **Pure Rotational Spectrum :**

The transitions between the rotational energy states of a molecule with the emission or absorption of a photon give rise to pure rotational spectrum.

In this case electronic configuration of the atom and vibrational state of molecule remains the same.

Rotational levels are separated by small energy interval of order of 10^{-3} eV. Pure rotational spectra lie in microwave or far infrared region.

2. **Rotational - Vibrational Spectrum :**

The transitions between vibrational energy states of a molecule with the emission or absorption of a photon, when electronic configuration of an atom remains the same, giving rise to rotational-vibrational spectrum.

If the rotational state of molecule do not change, we get a pure vibrational spectrum. Vibrational spectra lie in near IR region. Vibrational states are separated by energy interval of about 0.1 eV.

3. Electronic Spectrum :

The transitions between two electronic energy states of an atom in a molecule with emission or absorption of photon give rise to electronic spectrum. The energy separation between different electronic states is in between 1 eV - 10 eV. The electronic spectra lie in visible and ultravisible part of spectrum.

7.3 ROTATIONAL SPECTRA

Microwave spectroscopy deals with the study of rotations of molecules. The molecules have different shapes and with different atoms bonded together. The rotational motion naturally will involve the moment of inertia of a molecule. Hence the study of the rotational spectra can be used for the analysis in many scientific and industrial applications. We can use the rotational spectra to distinguish the presence of isotope in a sample. It can even detect different isomers provided, they have different moment of inertia. Rotational spectra can also be used in the chemical examination of interstellar space. It has been used to determine some stable molecules in the space like water, ammonia, etc. which helps in predicting the presence or origin of the biological molecule. By comparing the intensities of the rotational transitions, temperature of the interstellar material can be estimated.

Like any energy levels of electrons in atoms, the rotational energy levels are quantized. One can mathematically calculate the energy of the levels due to the rotation of the molecule. The system becomes more complicated with more number of molecules and the type of bonding between the atoms. Hence for simplicity, we consider a diatomic molecule as a rigid rotator.

Only the molecules, having permanent electric dipole moment, can give rise to pure rotational spectra. Hence molecules like HCl, HBr, HI, H_2O, etc. show the rotational spectra in far infrared region. Homonuclear molecules such as H_2, O_2, N_2 also show rotational Raman spectra because of the polarisability of the molecule.

7.4 THE RIGID DIATOMIC MOLECULE

Consider the simplest linear diatomic molecule as shown in Fig. 7.1. Let m_1 and m_2 be

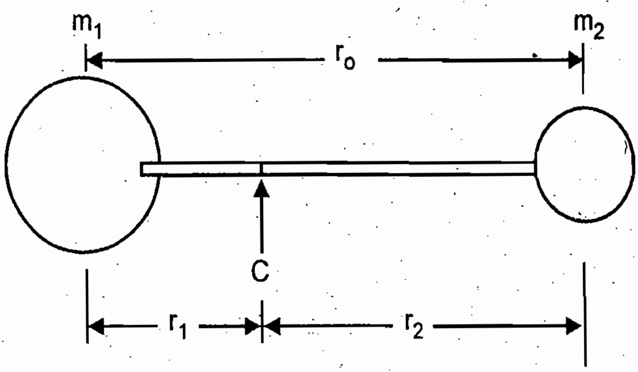


Fig. 7.1 : A rigid diatomic molecule treated as two masses, m_1 and m_2 joined by a rigid bar of length $r_0 = r_1 + r_2$

the mass of each atom. Let the molecules are joined by a bond such that the distance between them remains constant. The bond length is given by

$$r_0 = r_1 + r_2 \qquad \dots (7.1)$$

The molecule rotates around an axis passing through center of gravity C or centre of mass of system and perpendicular to line joining m_1 and m_2 respectively from centre of mass, then

$$m_1 r_1 = m_2 r_2 \qquad \dots (7.2)$$

The moment of inertia of the diatomic molecule about a point C is given by

$$I = m_1 r_1^2 + m_2 r_2^2$$

By using equation (7.2) in the above equation we have

$$\begin{aligned} I &= m_2 r_2 r_1 + m_1 r_1 r_2 \\ &= r_1 r_2 (m_1 + m_2) \qquad \dots (7.3) \end{aligned}$$

From equations (7.1) and (7.2), we have

$$\begin{aligned} m_1 r_1 &= m_2 r_2 \\ &= m_2 (r_0 - r_1) \\ \therefore \quad (m_1 + m_2) r_1 &= m_2 r_0 \\ \therefore \quad r_1 &= \frac{m_2}{m_1 + m_2} r_0 \qquad \dots (7.4) \end{aligned}$$

Similarly,

$$r_2 = \frac{m_1}{m_1 + m_2} r_0 \qquad \dots (7.5)$$

Substituting equations (7.4) and (7.5) in equation (7.3), we get

$$\begin{aligned} I &= \frac{m_1 m_2}{m_1 + m_2} r_0^2 \\ &= \mu r_0^2 \qquad \dots (7.6) \end{aligned}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is known as *reduced mass of the system.* Here we have converted two body problem into a single body. Hence we can say that the rotation of diatomic molecule is equivalent to the rotation of single particle.

If the molecule is rotating with angular velocity ω, then classically it has energy equal to $\frac{1}{2} I\omega^2$. The angular momentum $L = I\omega$.

$$\therefore \quad E = \frac{L^2}{2I} \qquad \dots (7.7)$$

According to quantum mechanics, the angular momentum is quantized and given by

$$L = \sqrt{J(J+1)}\,\hbar \quad \text{where } \hbar = \frac{h}{2\pi}$$

Equation (7.7) becomes

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules where } J = 0, 1, 2, \dots \qquad \dots (7.8)$$

where h is Planck's constant and J is known as *rotational quantum number*. J takes only integral values from zero upwards.

Equation (7.7) and (7.8) shows that

(i) Diatomic molecule cannot have any arbitrary value of rotational energy. The energy is quantised and is limited by rotational quantum number J.

(ii) The rotational energy depends upon moment of inertia i.e. on mass, shape and size of molecule.

7.5 ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE

When we deal with the spectra due to the transitions from one energy level to other energy level, the differences between these energies are important. If ΔE is the difference between the energy levels, then the corresponding frequency of radiation emitted or absorbed is given by

$$\upsilon = \frac{\Delta E}{h} \text{ in Hz}$$

It can be expressed in terms of wave number as

$$\overline{\upsilon} = \frac{\Delta E}{ch} \text{ cm}^{-1}$$

where c is the velocity of light.

In general, the rotational spectra are discussed in terms of wave number, hence let us consider energies expressed in these units. By using equation (7.8) we get,

$$\varepsilon_J = \frac{E_J}{ch} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ in cm}^{-1} \qquad \text{... (7.9)}$$

$$\therefore \quad \varepsilon_J = BJ(J+1) \text{ cm}^{-1} \text{ where } J = 0, 1, 2, \ldots \qquad \text{... (7.10)}$$

where B is known as *rotational constant* which is given ($\overline{\upsilon}$) as

$$B = \frac{h}{8\pi^2 Ic} \text{ cm}^{-1} \qquad \text{... (7.11)}$$

By using equation (7.11) we can show the energy levels diagrammatically as shown in Fig. 7.2. For $J = 0$, $\varepsilon_J = 0$, hence the molecule is not rotating at all. For $J = 1$, the rotational energy level is 2B and rotating molecule has its lowest angular momentum. In this manner we may continue to calculate ε_J with increasing J values. With the increase in the value of J, value of ε_J increases. At normal temperatures, the centrifugal force of rapidly rotating molecule is always less than the strength of the bond, hence the molecular bond is stable.

Now, consider difference between the levels to discuss the spectrum. Imagine that the molecule is raised from energy level $J = 0$ to $J = 1$ state by absorption of energy.

Energy absorbed will be :

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

$$\therefore \quad \overline{\upsilon}_{J=0 \to J=1} = 2B \text{ cm}^{-1}$$

The absorption line will appear at $2B^{-1}$.

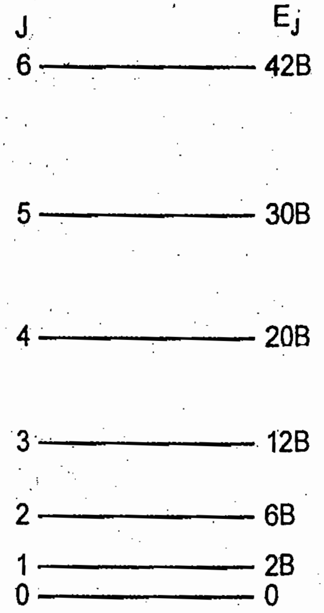
If the molecule is raised from J = 1 to the J = 2 level by absorption of more energies, then;

$$\begin{aligned}\bar{\upsilon}_{J=1\rightarrow J=2} &= \varepsilon_{J=2}-\varepsilon_{J=1}\\ &= 6B-2B\\ &= 4B\ \text{cm}^{-1}\end{aligned}$$

In general,

$$\begin{aligned}\bar{\upsilon}_{J\rightarrow J+1} &= \varepsilon_{J+1}-\varepsilon_{J}\\ &= B(J+1)(J+2)-BJ(J+1)\\ &= B[J^2+3J+2-J^2-J]\\ &= B(2J+2)\end{aligned}$$

$$\therefore \quad \bar{\upsilon}_{J\rightarrow J+1} = 2B(J+1)\ \text{cm}^{-1} \qquad \text{... (7.12)}$$



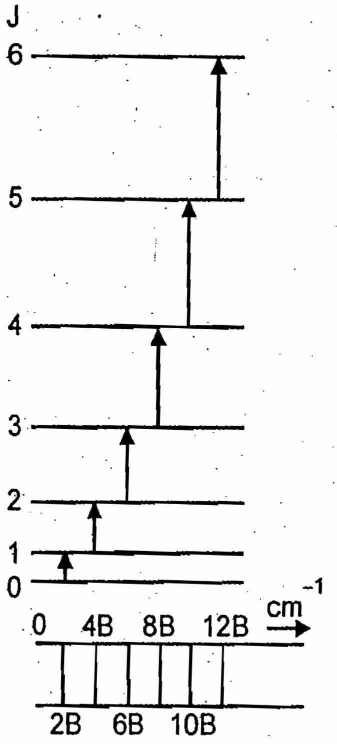


Fig. 7.2 : The allowed rotational energy levels of a rigid diatomic molecule

Fig. 7.3 : Allowed transition between the energy levels of a rigid diatomic molecule

The energy level transitions result in an absorption spectra having lines at 2B, 4B, 6B, 8B, ... cm^{-1}. We can also get an identical emission spectra having lines at 2B, 4B, 6B, 8B, ... cm^{-1}. It is shown at the bottom of the Fig. 7.3. It is clear that in the case of rotational spectra we get the lines which are equally spaced from each other.

The Schrödinger's wave equation shows that for rigid molecule transitions are such that J changes by unity only, other transitions are forbidden. Hence the selection rules for the rigid diatomic rotator are

$$\Delta J = \pm 1$$

This type of spectrum will be observed only in the case of heteronuclear molecule i.e. HCl, CO, etc. as they have changing dipole moment. If molecule is homonuclear, there will be no dipole component change during the rotation hence no interaction with radiation and molecule like N_2 and O_2 will not show a rotational spectrum.

7.6 NON-RIGID DIATOMIC MOLECULE

It is possible to calculate inter-nuclear distances from microwave spectra. Consider th hydrogen fluoride molecule, the inter-nuclear distance for $J = 1$ is 0.931 A°; for $J = 4$, it i 0.938 A°; for $J = 6$, it is 0.946 A° and for $J = 10$, it is 0.969 A°. It means that the separatio between successive lines (hence B) decreases steadily with increasing J. In the same wa B is no longer constant, but it also decreases with increase in the J value. Hence bon length increases with increase in J value and the bond between the molecule is not a rigi but elastic. It is quite obvious that with increase in the frequency of rotation, the centrifugal force tends to increase, hence the atoms are more apart from each other.

As a matter of fact, all bonds are elastic in nature. When the molecules rotate with elastic bond between them, they may have vibrational energy also. As the bond stretches and compresses with change in the frequency of rotation, we can consider the motion of the molecule as a simple harmonic motion. The force constant k is given by

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \qquad \dots (7.13)$$

where $\bar{\omega}$ is vibrational frequency, c is velocity of light and μ is the reduced mass of the system. Hence the variation in B with J is determined by the force constant.

Because of the elasticity, r and B changes during vibration. If we measure these quantities by microwave techniques, we observe many vibrations during rotation. However, the rotational constant is given by

$$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 \mu r^2 c}$$

$$\therefore \qquad B \propto \frac{1}{r^2}$$

since all the quantities are independent of vibration.

In simple harmonic motion molecular bond is compressed and extended on equal distance from equilibrium hence the average distance remains constant but the avarage value of $1/r^2$ is not constant.

Spectrum of non-rigid diatomic molecule :

We can set up the Schrödinger's equation for rotational energy. Then we will get,

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2 (J+1)^2 \text{ in joule} \qquad \dots (7.14)$$

or

$$\varepsilon_J = \frac{E_J}{hc} = BJ(J+1) - DJ^2 (J+1)^2 \text{ cm}^{-1} \, * \qquad \dots (7.15)$$

where D is the *centrifugal distortion* constant given by :

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1} \text{ which is positive quantity} \qquad \dots (7.16)$$

From the values of B and D we can prove that

$$D = \frac{16B^3 \pi^2 \mu c^2}{k} \qquad (\text{i.e. } \bar{\omega}^2 = k/4\pi^2 c^2 \mu)$$

By using equation (7.13),

$$D = \frac{4B^3}{\bar{\omega}^2} \quad \text{where } \bar{\omega} \text{ is vibrational frequency of bond.} \qquad \dots (7.17)$$

---

* If force field is unharmonic, then

$$\varepsilon_J = BJ(J+1) - DJ^2 (J+1)^2 + HJ^3 (J+1)^3 + KJ^4 (J+1)^4 \dots \text{ cm}^{-1}$$

where H, K are small constants depending upon geometry of the molecule. They are negligible as compared with D.

Equations (7.13) and (7.14) indicate that if we go from rigid to non-rigid diatomic molecule, the energy level is lowered. The selection rule for non-rigid diatomic molecular spectra is still

$$\Delta J = \pm 1$$

Now consider the expression for the transition as

$$\begin{aligned}
\varepsilon_{J+1} - \varepsilon_J &= \bar{\upsilon}_J = [B\,(J+1)(J+2) - D\,(J+1)^2\,(J+1)^2\,(J+2)^2] \\
&\quad - [B\,J\,(J+1) - D\,J^2\,(J+1)^2] \\
&= B\,[\,(J+1)\,(J+2) - J\,(J+1)] - D\,[(J+1)^2\,(J+2)^2 - J^2\,(J+1)^2] \\
&= B\,(J+1)\,(J+2-J) - D\,(J+1)^2\,[(J+2)^2 - J^2] \\
&= 2B\,J\,(J+1) - 4D\,(J+1)^3\ \text{cm}^{-1} \qquad \text{... (7.18)}
\end{aligned}$$

The above equation (7.15) represents transitions from J to J + 1 or J + 1 to J. The energy level diagram for the rigid and non-rigid diatomic molecules is shown in Fig. 7.4. The spectrum of non-rigid diatomic molecule is similar to that of rigid diatomic molecule except that each line is displaced slightly to low frequency, the displacement increases with $(J + 1)^3$.

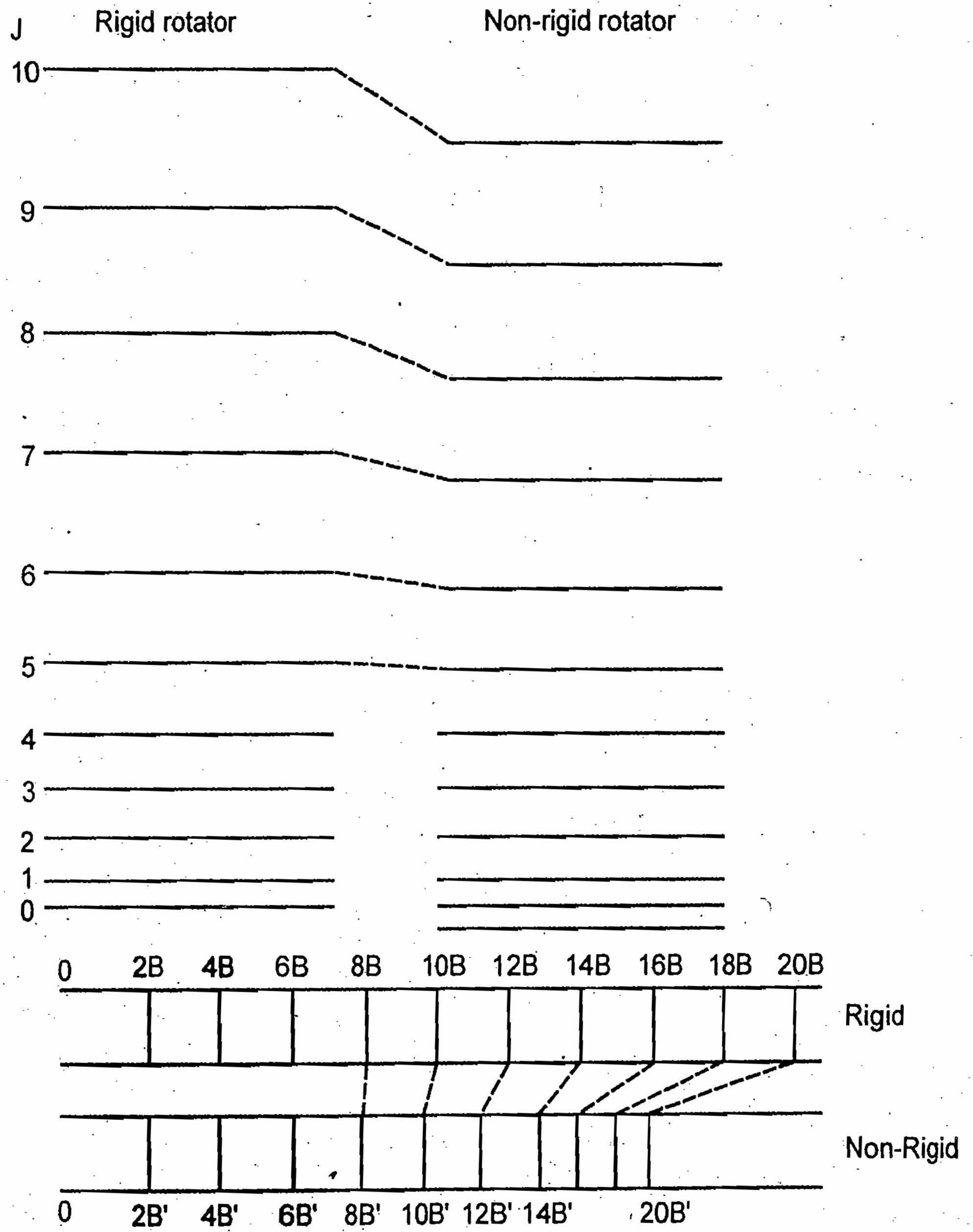


Fig. 7.4 : The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D = 10^{-3}$ B

If we know the value of D, then we can determine the value of J of lines observed in a spectrum. Similarly it can also be used to find the approximate value of vibrational frequency of diatomic molecule by using equation :

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16.33 \times 10^6 \, (\text{cm}^{-1})^2$$

$$\therefore \qquad \bar{\omega} \approx 4050 \text{ cm}^{-1}$$

More accurate value of $\bar{\omega}$ is 4138.3. Present value is 2% inaccurate. This is partly to the assumption of simple harmonic motion and partly due to inaccuracy in D.

7.7 ISOTOPIC EFFECT

In the rotational spectra of diatomic molecule, if we substitute the atom by its isotope, then there is a change in the spectral lines. As a matter of fact, there is no change in internuclear distance as well as the chemical properties of the molecule. However, there is change in the total mass and hence in the moment of inertia of the molecule and changing B value. Consider the carbon monoxide molecule as $^{12}C\,^{16}O$ and with the isotope as $^{13}C\,^{16}O$. Let the primed quantities are represented for isotopes.

$$B = \frac{h}{8\pi^2 Ic}$$

and

$$B' = \frac{h}{8\pi^2 I'c}$$

where prime refers to heavier molecule.

The calculated values are $B = 1.92118 \text{ cm}^{-1}$ and $B' = 1.83669 \text{ cm}^{-1}$.

Hence,

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I'c}{h}$$

$$= \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is reduced mass and internuclear distance is considered unchanged by isotopic substitution.

Taking mass of oxygen = 15.9994 and that of carbon 12 to be 12.00 we have :

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994 \, m'}{15.9994 + m'} \times \frac{12 + 15.9994}{12 \ast 15.9994}$$

Solving, we get $m' = 13.0007$. This value is within 0.02 % of best value obtained by another method.

The change in the rotational energy levels of the molecule such as CO is shown in the Fig. 7.5.

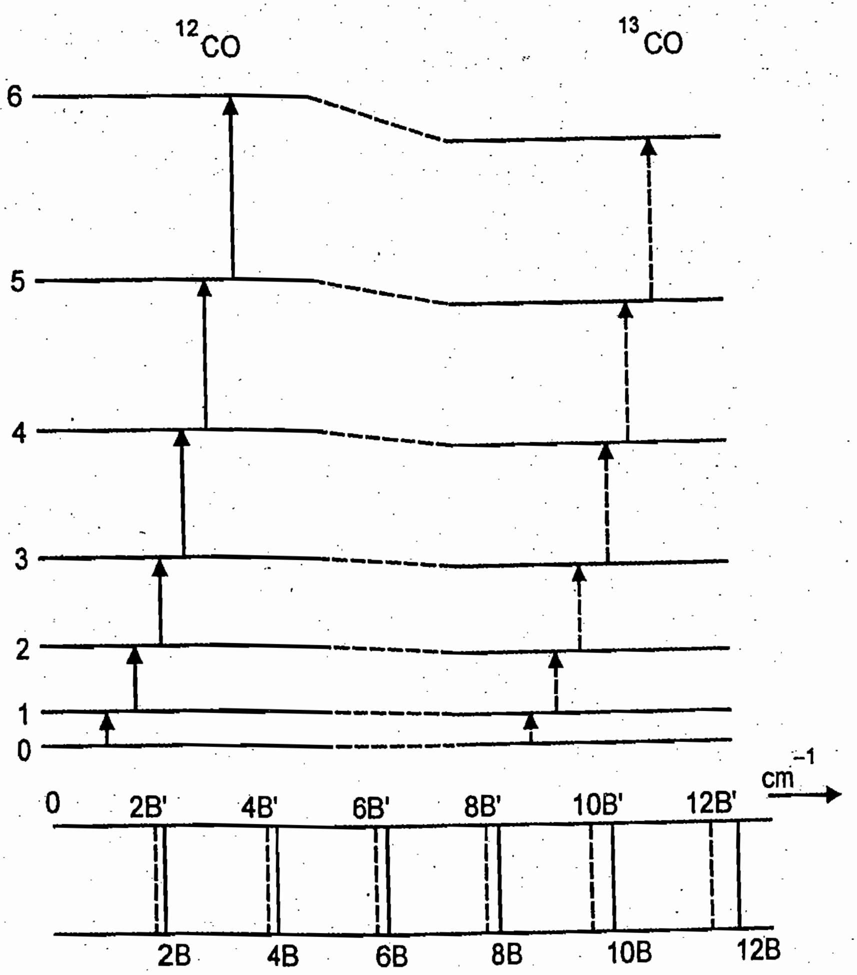


Fig. 7.5 : The effect is isotopic substitution on the energy levels and hence rotational spectrum of a diatomic molecule such as carbon monoxide

The transitions in the heavier molecule are shown by dotted lines. Due to this shift in the spectral lines we can determine the atomic weights with extreme precision. It can also help us to estimate the abundance of isotopes by comparison of absorption intensities.

SOLVED EXAMPLES

Example 7.1 : The moment of inertia of the carbon monoxide molecule is 1.46×10^{-46} kg·m^2. Calculate the lowest rotational energy of the molecule and the angular velocity. (Given $h = 6.62 \times 10^{34}$ joule-sec, $\mu_{CO} = 1.14 \times 10^{-26}$ kg)

Solution : The energy of the rotating diatomic molecule is given by

$$E_J = \frac{h^2 J (J+1)}{8\pi^2 I}$$

The lowest rotational energy level corresponds to J = 1.

$$\therefore \qquad E_1 = \frac{h^2}{8\pi^2 I} \times 1(2)$$

$$= \frac{h^2}{4\pi^2 I}$$

Substituting the values of h and I we have,

$$E_1 = \frac{(6.62 \times 10^{-34})^2}{4 \times \pi^2 \times (1.46 \times 10^{-46})}$$

$$= 7.61 \times 10^{-23} \text{ joule}$$

$$= \frac{7.61 \times 10^{-23}}{1.6 \times 10^{-19}} \qquad (1\text{eV} = 1.6 \times 10^{-19} \text{ joule})$$

$$= 4.76 \times 10^{-4} \text{ eV}$$

For J = 1, the angular velocity is given by

$$\omega = \frac{\sqrt{2E}}{I} \qquad \left(\text{where } E = \frac{1}{2} I\omega^2\right)$$

Hence the intermolecular distance is given by

$$r = \sqrt{\frac{I}{\mu_{CO}}}$$

$$= \sqrt{\frac{1.46 \times 10^{-46}}{1.14 \times 10^{-26}}} \frac{\text{kg.m}^2}{\text{kg}}$$

$$= 1.13 \times 10^{-10} \text{ m}$$

$$= 1.13 \text{ A}^\circ$$

Example 7.2 : For the rotational absorption spectra, a line is observed for the transition J = 0 to J = 1. It occurs at 1.153×10^{11} Hz in $^{12}C\ ^{16}O$ and at 1.102×10^{11} cycles/sec. In $^{n}C\ ^{16}O$ for the isotope of carbon, calculate the mass numbers of the unknown carbon isotope.

Solution : The absorbed frequency of the molecule and the moment of inertia are related as

$$\upsilon \propto \frac{1}{I}$$

Let I be the M.I. of $^{12}C\ ^{16}O$ molecule and I' be the M.I. of $^{n}C\ ^{16}O$ molecule. The relation of the M.I. and the reduced mass is

$$\frac{I}{I'} = \frac{\mu'}{\mu}$$

$$\therefore \quad \frac{\mu'}{\mu} = \frac{\upsilon}{\upsilon'}$$

$$\text{or} \quad \frac{\mu}{\mu'} = \frac{\upsilon'}{\upsilon}$$

$$\therefore \quad = \frac{1.102 \times 10^{11}}{1.153 \times 10^{11}}$$

$$\therefore \quad \frac{(12 \times 16)/28}{(n \times 16)/(n + 16)} = \frac{1.102}{1.153}$$

$$\therefore \quad \frac{12}{n} = \frac{n+1}{28} = \frac{1.102}{1.153}$$

$$\therefore \quad n = \frac{16}{1.23} = 13$$

Hence the isotope is $^{13}C\ ^{16}O$.

Example 7.3 : Absorption line in CO occurs at a frequency 1.153×10^{11} Hz due to the transition J = 0 to J = 1. Calculate the moment of inertia and internuclear separation of the molecule. ($h = 6.62 \times 10^{-27}$ erg-sec, The Avogadro's number $N_A = 6.023 \times 10^{23}$).

Solution : The energy of the rotating diatomic molecule is given by

$$E_J = \frac{h^2 J(J+1)}{8\pi^2 I}$$

The energy separation between J = 0 and J = 1 is

$$\Delta E = E_{J=1} - E_{J=0} = \frac{h^2}{4\pi^2 I}$$

$$\overline{\upsilon} = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I}$$

$$\therefore \quad I = \frac{h}{4\pi^2 I \overline{\upsilon}}$$

$$= \frac{6.62 \times 10^{-27} \text{ erg-sec}}{4 \times \pi^2 \times 1.153 \times 10^{11}}$$

$$= 1.46 \times 10^{-39} \text{ gm.cm}^2$$

The reduced mass of the CO molecule is given by

$$\mu_{CO} = \frac{M_C M_O}{M_C + M_O}$$

$$= \frac{(12 \times 16)/(6.023 \times 10^{23})^2}{(12 + 16) \times 7.023 \times 10^{23}}$$

$$= \frac{12 \times 16}{28 \times 6.023 \times 10^{23}}$$

$$= 1.14 \times 10^{23} \text{ gm}$$

But,

$$I = \mu r^2$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.46 \times 10^{-39}}{1.14 \times 10^{23}}} = 1.135 \times 10^{-8} \text{ cm}$$

$$\therefore \quad r = 1.135 \text{ A}^{\circ}$$

Example 7.4 : Determine the rotational energy of CO on the quantum level J = 2 if the equilibrium nuclear distance of CO is 1.131 A°. (1 a.m.u. = 1.66×10^{-27} kg)

Solution :

Reduced mass,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$= \frac{16 \times 12}{16 + 12} = 6.857 \text{ a.m.u.}$$

$$= 6.857 \times 1.66 \times 10^{-27} \text{ kg}$$

$$= 1.14 \times 10^{-26} \text{ kg}$$

$$I = \mu r^2 = 1.14 \times 10^{-26} \times (1.131 \times 10^{-10})^2$$

$$= 1.46 \times 10^{-46} \text{ kg m}^2$$

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$= \frac{(6.63 \times 10^{-34})^2}{8 \times 3.14 \times 3.14 \times 1.46 \times 10^{-46}}$$

$$= 0.763 \times 10^{-22} \text{ J}$$

QUESTIONS AND PROBLEMS

(A) Multiple choice questions :

1. Pure rotational spectrum lie in ...... region.
   (a) infrared (b) microwave (c) visible (d) X-ray
2. The vibrational states are separated by ......
   (a) 0.1 eV (b) 10 eV (c) 10^{-3} eV (d) 1.1 eV
3. The spacing between two consecutive absorption rotational spectra is ......
   (a) 4B (b) 8B (c) Nil (d) 2B
4. For non-rigid molecule, rotational constant is proportional to ......
   (a) r^2 (b) r (c) $\frac{1}{r^2}$ (d) $\frac{1}{r}$

Ans. : (1) b, (2) a, (3) d, (4) c

(B) Answer in short :

1. What is selection rule for J ?
2. What is pure rotational spectra ?
3. What is rotational constant ?
4. What is centrifugal distortion constant ?
5. What information we get from isotopic effect ?

(C) Answer in detail :

1. Describe various types of molecular spectra.
2. What is diatomic molecule ? Obtain an expression for rotational energy spectra of diatomic molecule.
3. What is rigid diatomic molecule ? Discuss the rotational spectra of rigid molecule.
4. What is non-rigid diatomic molecule ? Discuss the rotational spectra of non-rigid molecule.
5. Explain isotopic effect.

(D) Numerical problems :

1. The J = 0 to J = 1 absorption line in carbon monoxide (CO) occurs at frequency 1.153×10^{11} Hz. Calculate :
   (a) moment of inertia,
   (b) bond length,
   (c) lowest energy level of molecule corresponding to J = 1.
   (Given : 1 a.m.u. = 1.66×10^{-27} kg)
   Ans. : (a) 1.46×10^{-46} kg.m^2, (b) 1.14 A°, (c) $E_{J=1} = 4.76 \times 10^{-4}$ eV
2. The $J = 0 \rightarrow J = 1$ rotational absorption lines occur at 1.153×10^{11} Hz in $^{12}C\ ^{16}O$ and at 1.102×10^{11} in $^{x}C\ ^{16}O$. Find mass number of unknown isotope of carbon.
   Ans. : 13

❑❑❑

8

Molecular Vibrational Spectra

8.1 INTRODUCTION

Energy levels and the corresponding absorption and emission spectra of molecules are complicated as compared to the atoms due to following reasons :

1. Nuclear motion in molecules cannot be neglected as compared to atoms; this nuclear motion gives many more energy levels.
2. Molecular energy states cannot be classified only according to it's angular momentum.
3. The motion of electrons has considerable effect on the energy levels.
4. The nuclear-nuclear potential repulsion affect the effective potential for the motion of electron.

However, in diatomic molecule, the component of angular momentum along the internuclear axis is conserved because of the symmetrical charge distribution about the axis. We can solve the wave equation of motion of nuclei alone neglecting the motion of the electrons, to get the energy eigen values of the potential energy. It is quite clear that when two atoms are brought nearer to form a stable molecule, electronic energy decreases rapidly while energy of repulsion increases. For certain value of internuclear distances, the total nuclear potential energy becomes minimum, this is the equilibrium internuclear separation. These nuclei vibrate about their respective equilibrium positions along the internuclear axis, and the molecule rotates about the centre of mass.

In the previous chapter we have considered the rotational motion of atoms in a molecule. The elasticity of chemical bond results in anomalous results due to the stretching of the bond with increase in the rotational quantum number. Now let us consider the vibration of the atoms about their mean position.

8.2 DIATOMIC MOLECULE AND VIBRATIONAL ENERGY LEVELS

In the case of diatomic molecule, atoms are vibrating as if they are connected by a spring as shown in the Fig. 8.1. The external force acting on the system is zero. The atoms are vibrating back and forth as shown in the figure. Let m_1 and m_2 be the masses of the atom which form molecule. Let r_0 be the equilibrium distance between them (length of the bond). Here we consider the bond as a spring. From Fig. 8.1 it is clear that the displacement of the spring at any time is given by,

$$x = a + b \qquad \text{... (8.1)}$$

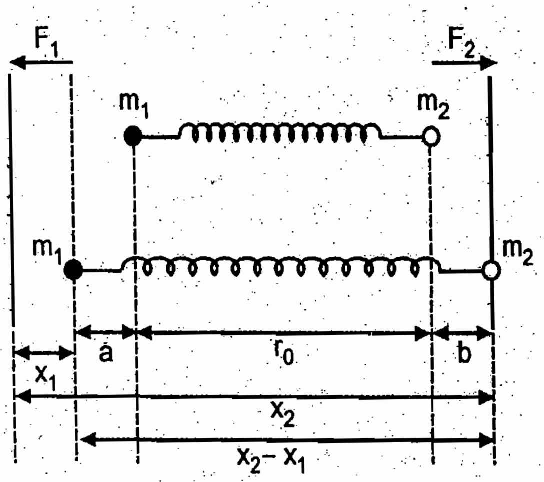


Fig. 8.1 : Vibrating atoms in a diatomic molecule.

Hence, the length of the spring at any time is given by,

$$r_0 + x = x_2 - x_1$$

$$\therefore \quad x = x_2 - x_1 - r_0 \qquad \text{... (8.2)}$$

If k is the force constant of the spring representing bond between the two atoms, and F_1 and F_2 are the restoring forces acting on m_1 and m_2 respectively then,

$$F_1 = kx \quad \text{and} \quad F_2 = -kx$$

Let a_1 and a_2 be the acceleration of mass m_1 and m_2. The Newton's second law gives us

$$F_1 = m_1 a_1 = m_1 \frac{d^2 x_1}{dt^2} = kx \qquad \text{... (8.3)}$$

Similarly,

$$F_2 = m_2 a_2 = m_2 \frac{d^2 x_2}{dt^2} = -kx \qquad \text{... (8.4)}$$

Multiplying equation (8.3) by m_2 and equation (8.4) by m_1 and then subtracting equation (8.3) from equation (8.4), we have

$$m_1 m_2 \frac{d^2 x_2}{dt^2} - m_1 m_2 \frac{d^2 x_1}{dt^2} = -m_2 kx - m_1 kx$$

$$\therefore \quad m_1 m_2 \left(\frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} \right) = -kx\,(m_1 + m_2)$$

$$\therefore \quad \frac{m_1 m_2}{m_1 + m_2} \left(\frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} \right) = -kx \qquad \text{... (8.5)}$$

Differentiating equation (8.2) twice w.r.t. t we have,

$$\frac{d^2 x}{dt^2} = \frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2}$$

Substituting the R.H.S. of above equation in equation (8.5) we may write,

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2x}{dt^2} = -kx$$

or $$\mu \frac{d^2x}{dt^2} + kx = 0 \quad \text{...(8.6)}$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the system. Above equation (8.6) represents a simple harmonic oscillator with force constant k and having frequency of oscillation

$$\omega_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{..., (8.7)}$$

8.3 VIBRATIONAL ENERGY LEVELS FOR DIATOMIC MOLECULE

Non-rigid diatomic molecule can be considered as a simple harmonic oscillator. When the energy of the molecule is increased, then the atoms vibrate more vigorously back and forth i.e. the compression and extension in the bond will be more. From equation (8.7) it is clear that the frequency of oscillation is independent of the bond length but it depends only on the force constant of the bond and the masses of the atom.

Vibrational energies like any other atomic and molecular energies are quantized. These vibrational energies can be calculated by solving Shcrodinger's equation of the system. Hence, the vibrational energies are given by

$$E_v = \left(v + \frac{1}{2}\right) h\omega_0 \text{ joule} \quad \text{... (8.8)}$$

where v is known as *vibrational quantum number*. v = 0, 1, 2, 3, ... Converting the energies in terms of the spectroscopic units, cm^{-1}, we have

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \frac{\omega_0}{c} \text{ cm}^{-1} \quad \text{... (8.9)}$$

Let, $\bar{\omega}_0 = \dfrac{\omega_0}{c}$ cm^{-1} i.e. frequency in terms of wave number.

$$\therefore \quad \varepsilon_v = \left(v + \frac{1}{2}\right) \bar{\omega}_0 \quad \text{... (8.10)}$$

The lowest vibrational energy can be obtained by having v = 0.

$$\therefore \quad E_v = \frac{1}{2} h\omega_0 \text{ in joules } (\omega_0 \text{ in Hz})$$

or $$\varepsilon_v = \frac{1}{2} \bar{\omega}_0 \text{ in cm}^{-1} \ (\bar{\omega}_0 \text{ in cm}^{-1})$$

It indicates that the diatomic molecules do not have zero vibrational energy. i.e. the atoms in the molecule can never be completely at rest relative to each other. The quantity $\frac{1}{2} h\omega_0$ in joule or $\frac{1}{2} \bar{\omega}_0$ in cm^{-1} is the lowest possible energy say zero point energy. It depends only on the strength of the chemical bond and the atomic masses.

Consider the Schrodinger's equation. The solution leads to the selection rule given by,

$$\Delta v = \pm 1$$

The vibrational energy changes will give rise to observable spectrum. The vibrational spectra will be observed only in heteronuclear diatomic molecules as they only have dipole moment.

The vibrational energy levels given by equation (8.10) for v = 0, 1, 2, ... are $\frac{1}{2}\bar{\omega}_0, \frac{3}{2}\bar{\omega}_0, \frac{5}{2}\bar{\omega}_0$ ...... in cm^{-1} or $\frac{1}{2}h\omega_0, \frac{3}{2}h\omega_0, \frac{5}{2}h\omega_0$ ...... in joules.

The energy levels are equispaced and are as shown in the Fig. 8.2. The energy level at ground state is not zero (as in case of rotational energy level).

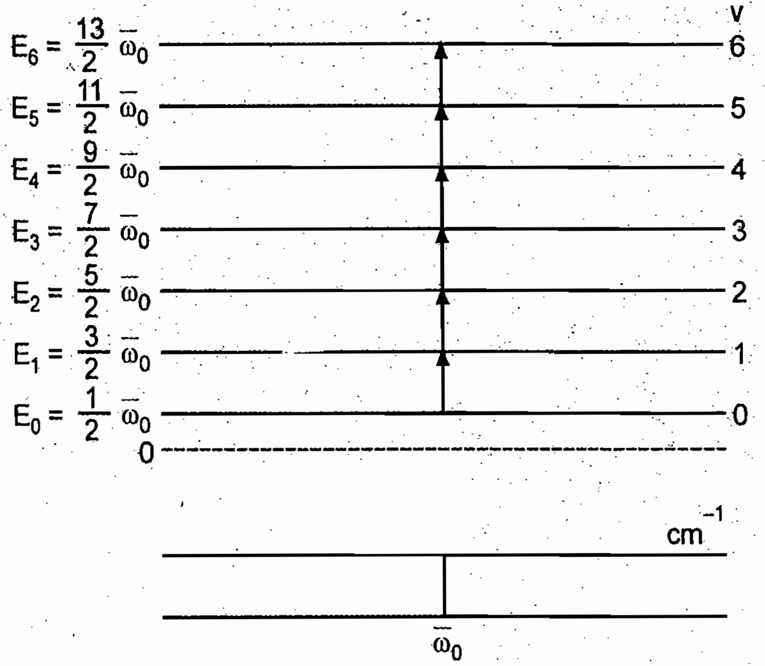


Fig. 8.2 : Vibrational energy levels of diatomic molecule with allowed transitions

Now, consider the transition for absorption v + 1 and v, using equation (8.10) we have,

$$\varepsilon_{v+1} - \varepsilon_v = \left(v + 1 + \frac{1}{2}\right)\bar{\omega}_0 - \left(v + \frac{1}{2}\right)\bar{\omega}_0$$

$$= \bar{\omega}_0 \ cm^{-1}$$

And for emission, we have,

$$\varepsilon_v - \varepsilon_{v+1} = \bar{\omega}_0 \ cm^{-1}$$

or

$$E_v - E_{v+1} = h\omega_0$$

$$\therefore \quad h\omega = h\omega_0$$

This gives frequency of spectral line in vibrational emission spectra. Similarly, frequency of spectral line in vibrational spectra is also ω_0.

As the vibrational energy levels are equally spaced, transitions between any two neighbouring states will give same energy change, hence we will get only one line as shown in Fig. 8.2. Naturally, the radiation absorbed or emitted must be equal to radiation of it's own oscillatory frequency.

8.4 SIMPLE HARMONIC OSCILLATOR

The compression and extension of bond in a molecule may be linked with the behaviour of spring, hence we can write,

$$F = -k(r - r_{eq})$$

where, F is restoring force

r is internuclear distance

k is force constant

r_{eq} is minimum equilibrium distance

In this case the energy curve is parabolic as shown in Fig. 8.3.

$$E = \frac{1}{2} k (r - r_{eq})^2 \qquad \text{... (8.11)}$$

Energy is zero at r_{eq} and ε_1 arises because of compression and extension of bond.

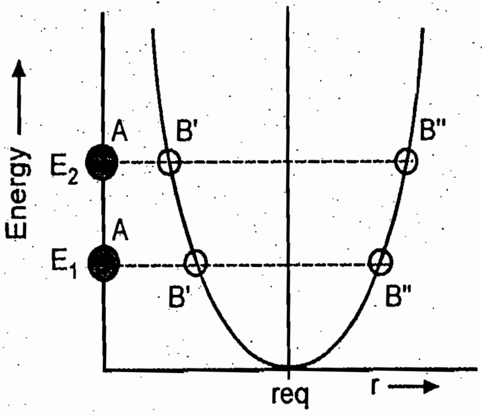


Fig. 8.3

Fig. 8.3 shows that if one atom (A) is considered to be stationary on the r = 0 axis, the other will oscillate between B' and B". If the energy is increased to ε_2, the oscillation will become more vigorous, but the vibrational frequency will not change. An elastic bond, like a spring, has a certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion. Classically, oscillation frequency is

$$\omega_{osc.} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz}$$

where μ is the reduced mass of the system. To convert this frequency to wavenumbers, the unit most usually employed in vibrational spectroscopy, we must divide by the velocity of light, c, expressed in cm s^{-1}.

$$\bar{\omega}_{osc.} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \qquad \text{... (8.12)}$$

Vibrational energies, like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system may be calculated from the Schrodinger's equation. For the simple harmonic oscillator,

$$E_v = \left(v + \frac{1}{2}\right) h\omega_{osc.} \text{ joules } (v = 0, 1, 2, \dots) \qquad (8.13)$$

where v is called the vibrational quantum number. Converting to the spectroscopic units, cm^{-1}, we have :

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \bar{\omega}_{osc.} \text{ cm}^{-1} \qquad \dots (8.14)$$

as the only energies allowed to a simple harmonic vibrator. Some of these are shown in Fig. 8.3.

In particular, we should notice that the *lowest* vibrational energy, obtained by putting v = 0 in equation (8.13) or (8.14) become

$$E_0 = \frac{1}{2} h\omega_{osc.} \text{ joules } [\omega_{osc.} \text{ in Hz}]$$

or

$$\varepsilon_0 = \frac{1}{2} \bar{\omega}_{osc.} \text{ cm}^{-1} \quad [\bar{\omega}_{osc.} \text{ in cm}^{-1}] \qquad \dots (8.15)$$

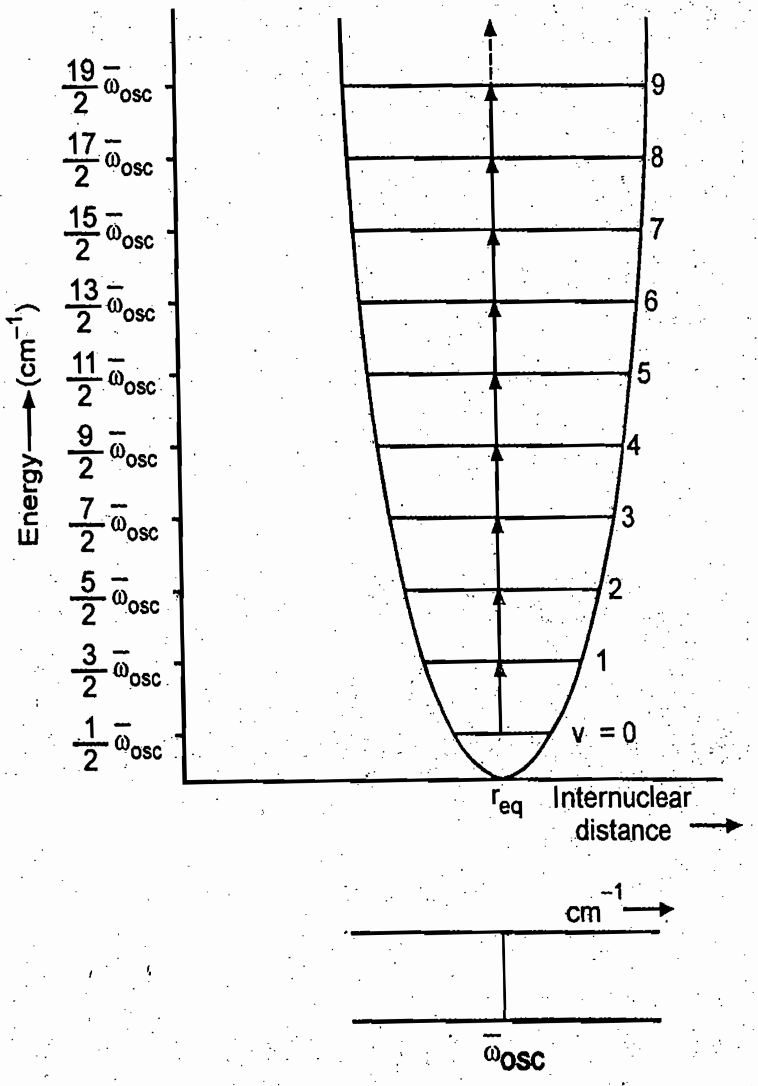


Fig. 8.4 : The allowed vibrational energy levels for a diatomic molecule undergoing simple harmonic motion

The quantity $\frac{1}{2}\, h\bar{\omega}_{osc.}$ joules or $\frac{1}{2}\, \bar{\omega}_{osc.}\ cm^{-1}$ is known as the *zero-point energy*; it depends only on the classical vibration frequency.

The selection rule for the harmonic oscillator undergoing vibrational changes :

$$\Delta v = \pm 1$$

It should be noted that vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation, if the vibration involves a change in the dipole moment of the molecule. Thus vibrational spectra will be observable only in heteronuclear diatomic molecules since homonuclear molecules have no dipole moment.

Applying the selection rule we have,

$$\varepsilon_{v+1 \to v} = \left(v + 1 + \frac{1}{2}\right)\bar{\omega}_{osc.} - \left(v + \frac{1}{2}\right)\bar{\omega}_{osc.}$$

$$\therefore \quad \varepsilon_{v+1 \to v} = \bar{\omega}_{osc.}\ cm^{-1} \text{ for emission}$$

$$\text{and} \quad \varepsilon_{v \to v+1} = \bar{\omega}_{osc.}\ cm^{-1} \text{ for absorption} \qquad \dots (8.16)$$

whatever the initial value of v.

Such result is also obvious from Fig. 8.4 since the vibrational levels are equally spaced, transitions between any two neighbouring states will give rise to the same energy change. Further, since the difference between energy levels expressed in cm^{-1} gives directly the wave number of the spectral line absorbed or emitted.

$$\bar{\upsilon}_{spectroscopic} = \varepsilon = \bar{\omega}_{osc.}\ cm^{-1} \qquad \dots (8.17)$$

This, again, is obvious if one considers the mechanism of absorption or emission in classical terms. In absorption, for instance, the vibrating molecule will absorb energy only from radiation with which it can coherently interact and this must be radiation of its own oscillation frequency.

8.5 ROTATION-VIBRATIONAL SPECTRA OF DIATOMIC MOLECULE

If we observe the near infra-red spectra of diatomic molecule, it consists of bonds. These bonds are having close lines arranged in a particular manner. This fine structure suggests that in a vibrational transition, the molecule also changes rotational energy states. Hence we can consider that the diatomic molecule can execute rotations and vibrations quite independently. There is no any type of interaction between rotational and vibrational energy. We can assume that the combined rotational-vibrational energy is simply the sum of the separate energies like

$$E_{total} = E_{rot.} + E_{vib.} \text{ in joules.}$$

$$E_{total} \text{ or } E_{J,v} = \frac{J(J+1)}{2I}\hbar^2 + \left(v + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}}$$

$$= \frac{J(J+1)\hbar^2}{2I} + \left(v + \frac{1}{2}\right)\hbar\upsilon_0$$

$$\varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib.}$$

We know that,

$$\varepsilon_{rot} = \varepsilon_J = B[J(J+1)]$$

$$\therefore \quad \varepsilon_{rot} = BJ(J+1)$$

The rotational energy levels for two different vibrational states are shown in Fig. 8.5. By using equation (8.10) for $E_v = E_{vib}$, we get

$$\varepsilon_{total} = BJ(J+1) + \left(v + \frac{1}{2}\right)\bar{\omega}_0 \qquad \ldots (8.18)$$

In the case of liquid, pure vibrational spectra is more prominant because the interactions between adjacent molecules are responsible for emission of radiation. In case of gas or vapour molecule, rotational spectra is more prominant. The rotational levels for the two lowest vibrational levels v = 0 and v = 2 is shown in the Fig. 8.5. The rotational constant B in equation (8.18) is taken to be same for all J and v; the separation between two levels of given J is the same in the v = 0 and v = 1 states. It can be shown that the selection rules for the combined motions are same as those for each one separately as

$$\Delta v = \pm 1, \pm 2 \ldots\ldots\ldots$$

$$\Delta J = \pm 1.$$

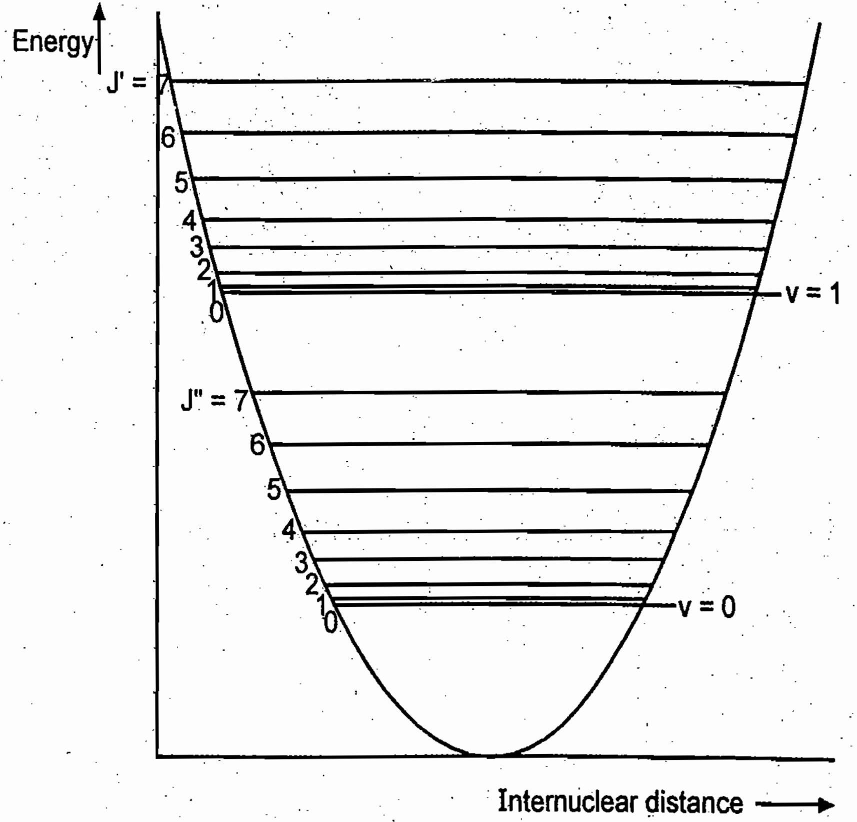


Fig. 8.5 : The rotational energy levels for two different vibrational states

8.6 TRANSITIONS IN ROTATIONAL-VIBRATIONAL ENERGY LEVELS

P, Q, R branches : Let J' represents the rotational energy levels for vibrational quantum number v = 1 and J" for v = 0. If ΔJ = + 1 then we get R branch and if ΔJ = –1 then we get, P branch. The energy level diagram is shown in Fig. 8.6 along with the transitions. At the bottom, the spectrum arising due to it is shown.

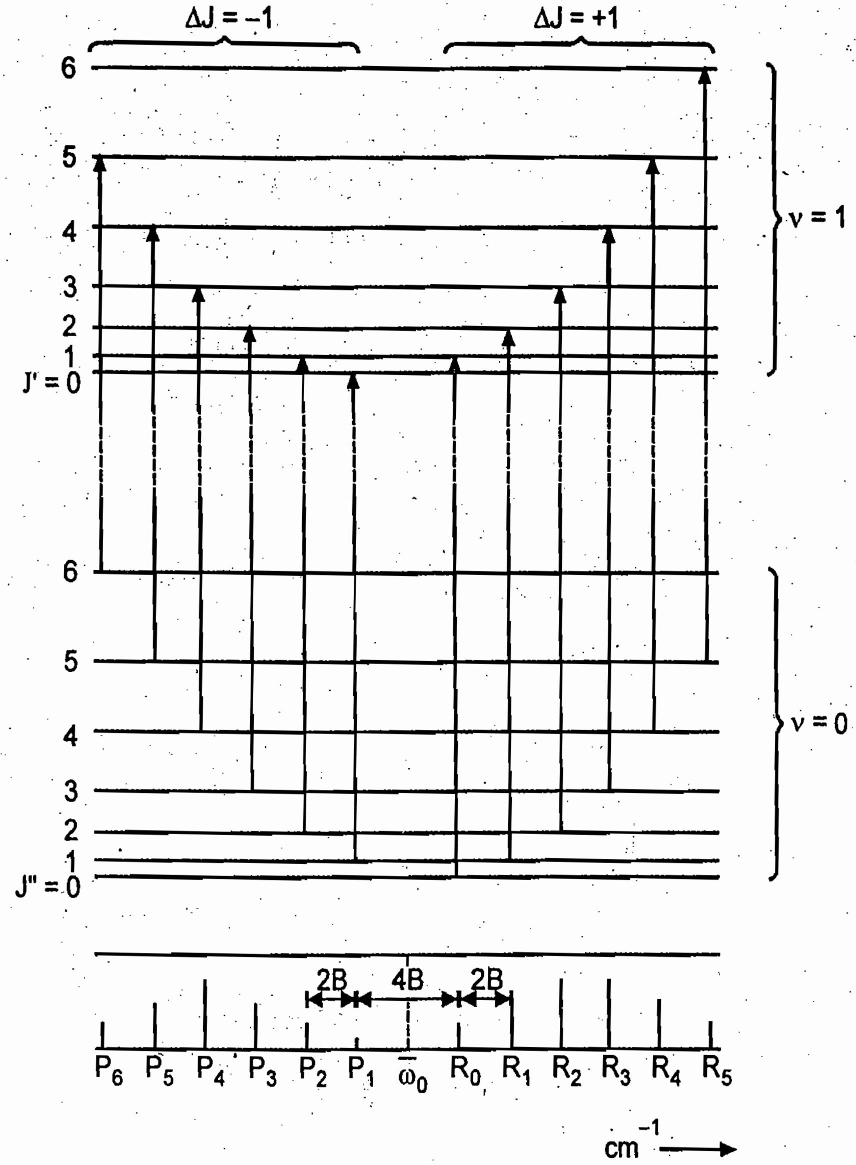


Fig. 8.6 : Transitions between rotational-vibrational energy levels of diatomic molecules along with the spectrum arising due to them

We can get the analytical expression for the spectrum, by applying the selection rules. Now consider only the transition v = 0 to v = 1 and by using equation 8.18, we get,

$$\therefore \quad \Delta\varepsilon_{J,\,v} = \varepsilon_{J',\,v=1} - \varepsilon_{J'',\,v=0}$$

$$= BJ'(J'+1) + \frac{3}{2}\bar{\omega}_0 - \left[BJ''(J''+1) + \frac{1}{2}\bar{\omega}_0\right]$$

$$= \bar{\omega}_0 + B\,[J'(J'+1) - J''(J''+1)] \qquad \dots (8.19)$$

(i) For R branch we have,

$$\Delta J = +1 \text{ i.e. } J' = J'' + 1$$

Hence, by using the **value of J' in equation** (8.19), we get the equations for the R branch of the spectrum.

$$\therefore \quad \Delta\varepsilon_{J,\,v} = \bar{\omega}_0 + B\,[(J''+1)(J''+2) - J''(J''+1)]$$

$$= \bar{\omega}_0 + B\,(J''+1)\,[J''+2-J'']$$

$$\therefore \quad \Delta\varepsilon_P = \Delta\varepsilon_{J,v} = \bar{\omega}_0 + 2B(J''+1)\ \text{cm}^{-1} \qquad \text{...(8.20)}$$

where $J'' = 0, 1, 2, \ldots\ldots\ldots$

(ii) For P branch, we have,

$$\Delta J = -1 \quad \text{i.e.} \quad J'' = J' + 1 \quad \text{or} \quad J' - J'' = -1$$

Using the value of J" in equation (8.19) we get the equation for the P branch of the spectrum.

$$\therefore \quad \Delta\varepsilon_{J,v} = \bar{\omega}_0 + B[J'(J'+1) - (J'+1)(J'+2)]$$

$$= \bar{\omega}_0 + B(J'+1)[J' - J' - 2]$$

$$\Delta\varepsilon_P = \Delta\varepsilon_{J,v} = \bar{\omega}_0 - 2B(J'+1) \qquad \text{...(8.21)}$$

where $J' = 0, 1, 2, \ldots\ldots$

(iii) Q branch : Here $\Delta J = 0$ i.e. transitions are

$$J' \rightarrow J'$$

The frequency in Q branch is given by,

$$\omega_0 = \varepsilon_{1,J} - \varepsilon_{0,J}$$

$$\omega_0 = \omega_0$$

or $\upsilon_0 = \upsilon_0$

As transition for which $\Delta J = 0$ is not allowed, there is no line as $\upsilon_0 = \upsilon_0$ i.e. Q branch is missing.

Equations (8.20) and (8.21) can be combined together as

$$\Delta\varepsilon_{J,v} = \bar{\upsilon}_{\text{spect}} = \bar{\omega} + 2Bm\ \text{cm}^{-1} \qquad \text{...(8.22)}$$

where, $m = \pm 1, \pm 2, \ldots\ldots\ldots$

Note that m cannot be zero as it gives the values of J' or J" to be –1. The frequency $\bar{\omega}_0$ is usually known as the *band origin or band centre.*

Equation (8.22) represents combined vibrational-rotational spectrum.

From Fig. 8.5 the P branches or R branches are equally spaced (i.e. 2B).

If $m = -1$ i.e. $\Delta J = -1$, we get P branch; for $m = -1$, $\Delta J = +1$, we get R branch. If we have $\Delta J = 0$ and ± 2 for consistency in the lebelling of the lines then we have,

$$\Delta J = -2 \quad -1 \quad 0 \quad +1 \quad +2$$

$$\text{branches} = O \quad P \quad Q \quad R \quad S$$

The P and R branches are shown in the Fig. 8.5.

The equation 8.22 is in agreement with the experimentally observed values. For rotation-vibration bands of diatomic molecule are found to consist of a number of lines with constant separation of approximately equal to 2B cm^{-1}. Similarly, the gap at the centre of the band on each side of the lines is 4B cm^{-1}.

SOLVED EXAMPLES

Example 8.1 : The force constant of the bond in CO molecule is 1956 N/m. Calculate the frequency of vibration of the molecule and the spacing between its vibrational energy levels in eV. Given : reduced mass of CO is 1.16×10^{-26} kg, $h = 6.63 \times 10^{-27}$ erg-sec. and $1 \text{ eV} = 1.6 \times 10^{-12}$ erg., $c = 3 \times 10^{8}$ m/s.

Solution : The frequency of vibration is given by,

$$\begin{aligned}\omega_0 &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\\ &= \frac{1}{2\pi}\sqrt{\frac{1956 \text{ N/m}}{1.16 \times 10^{-26} \text{ kg}}}\\ &= 6.535 \times 10^{13} \text{ Hz}\end{aligned}$$

The separation between two successive vibrational energy levels is

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{v+1} - \varepsilon_v = h\omega_0\\ &= 6.63 \times 10^{-27} \times 6.535 \times 10^{13}\\ &= 4.333 \times 10^{-13} \text{ erg.}\end{aligned}$$

The spacing between vibrational energy levels in eV is given by

$$\begin{aligned}\Delta E &= \frac{4.333 \times 10^{-13}}{1.6 \times 10^{-12}}\\ &= 0.271 \text{ eV}\end{aligned}$$

Example 8.2 : In the near infrared spectrum of HCl molecule, a single band at 2856 cm^{-1} is observed, due to the transition between the vibrational level. Show that the force constant K is 4.79×10^{5} dyne/cm if mass of hydrogen is 1.7×10^{-24} gm.

Solution : The force constant is given by,

$$K = 4\pi^2 \mu c^2 \omega_e^2$$

Here,

$$\begin{aligned}\omega_e &= 2856 \text{ cm}^{-1}\\ \mu &= \frac{M_H M_{Cl}}{M_H + M_{Cl}}\\ &= \frac{1 \times 35}{1 + 35} M_H\\ &= \frac{35}{36} \times 1.7 \times 10^{-24}\\ &= 1.653 \times 10^{-24} \text{gm}\end{aligned}$$

$$\begin{aligned}\therefore \quad K &= 4\pi^2 \times 1.653 \times 10^{-24} \times (3 \times 10^{10})^2 \times 2856)^2\\ &= 4.791 \times 10^{5} \text{ dyne/cm}\end{aligned}$$

Example 8.3 : The mean of the intermolecular distances for HCl^{35} in the v = 0 and v = 1 levels is 1.293 A°. Calculate the difference in cm^{-1} between P and R branches of the fundamental band for HCl^{35}.

Given : $h = 6.62 \times 10^{-27}$ erg- sec., $c = 3 \times 10^{10}$ cm/s.

Solution : The reduced mass of HCl molecule is

$$\mu = \frac{(1 \times 35)/(6.023 \times 10^{23})^2}{(1+35)/(6.023 \times 10^{23})}$$

$$= \frac{35}{36 \times (6.023 \times 10^{23})}$$

$$= 1.614 \times 10^{-24} \text{ gm}$$

The rotational constant for the molecule is

$$B = \frac{h}{8\pi^2 Ic}$$

$$= \frac{h}{8\pi^2 \mu r^2 c}$$

$$= \frac{6.62 \times 10^{-27} \text{ erg- sec.}}{8 \times \pi^2 \times (1.61 \times 10^{-24}) \times (1.293 \times 10^{-8} \text{ cm})^2 \times (3 \times 10^{10})}$$

$$= 10.383 \text{ cm}^{-1}$$

We know that when the interactions between vibration and rotation are ignored, then the line in P, Q, R branches in terms of wave number is given by,

$$\bar{\upsilon}_{\text{spect}} = \bar{\omega}_0 + 2Bm$$

For P branch, m = – 1 and for R branch m = + 1

$$\therefore \quad \bar{\upsilon}_{\text{P-branch}} = \bar{\omega}_0 - 2B$$

$$\bar{\upsilon}_{\text{R-branch}} = \bar{\omega}_0 + 2B$$

Hence, the difference in the P and R branches of the fundamental band is given by,

$$\bar{\upsilon}_{\text{R-branch}} - \bar{\upsilon}_{\text{P-branch}} = 4B$$

$$= 4 \times 10.383$$

$$= 41.532 \text{ cm}^{-1}$$

QUESTIONS AND PROBLEMS

(A) Multiple choice questions :

1. The spacing between P and Q branch is ....

   (a) $\frac{k}{m}$ (b) $\frac{b^2}{2I}$ (c) $\frac{h}{4\pi I}$ (d) 4B

2. Lowest vibrational state ($\upsilon = 0$) has .... energy.

   (a) zero (b) $h\upsilon_0$ (c) $\frac{1}{2} h\upsilon_0$ (d) mc^2

3. The spacing between successive P bands is ....

   (a) B (b) 2B (c) 4B (d) 8B

4. For diatomic molecule following transition is not allowed.

   (a) $\Delta J = 0$ (b) $\Delta J = +1$ (c) $\Delta J = -1$ (d) none of above.

Ans. (1) d, (2) c, (3) b, (4) a.

(B) Answer in short :

1. What is reduced mass ?
2. What is vibrational quantum number ?
3. Write selection rule for P, Q and R branches in rotational-vibrational energy level.
4. Why all molecules do not show rotational spectra ?
5. What is zero point energy ?

(C) Answer in detail :

1. Obtain an expression for rotational energy level of non-rigid diatomic molecule.
2. Show that the vibrations of atoms of diatomic molecule are simple harmonic.
3. Discuss energy level of harmonic oscillator.
4. Discuss rotational-vibrational spectra.
5. Draw transition in energy level diagram of rotational-vibrational spectra. Hence explain P, Q, R branches.

(D) Numerical Problems :

1. The force constant of CO band is 187 Nm^{-1}. Find the frequency of vibration of CO molecule and spacing between vibrational energy levels.

   [Given : Mass of ^{12}C atom = 1.99×10^{-26} kg and of ^{16}O atom = 2.66×10^{-26} kg]

   Ans. : $\upsilon = \upsilon_0 = 2.04 \times 10^{13}$ Hz, $\Delta E = 8.44 \times 10^{-2}$ eV

2. The spacing between vibrational levels of carbon monoxide molecule is 0.08 eV. Calculate value of force constant. Take mass of carbon 12 and that of oxygen 16 times mass of proton = 1.67×10^{-27} kg.

   Ans. : k = 167.8 Nm^{-1}

3. Assume that the H_2 molecule behaves exactly like a harmonic oscillator with force constant of 573 N/m. Find the rotational quantum number corresponding to it's 4.5 dissociative energy.

   Ans. : 8.

❑❑❑

9

Raman Effect

9.1 INTRODUCTION

Raman effect was discovered by Sir C. V. Raman of India in 1928 while studying the scattering of light by liquid. Later, he was awarded the Nobel Prize in 1930 for discovery of Raman effect which led to number of experiments for elucidation of molecular structure, location of various functional groups or chemical bond and quantitative analysis of complex mixture.

In this chapter, we discuss Raman effect, quantum theory and experimental arrangement to observe Raman spectra.

9.2 RAMAN EFFECT

When electromagnetic radiation passes through pure transparent substance (i.e. solid, liquid or gas), it may undergo scattering in addition to absorption and transmission.

If I_o is intensity of incident radiation and I_s, I_t and I_a are intensities of the scattered, transmitted and absorbed radiation respectively then,

$$I_o = I_a + I_s + I_t \qquad \dots (9.1)$$

The scattered radiations consist of :

1. Central line called as Rayleigh line, frequency of such line is same as frequency of source (υ_o).
2. A series of displaced lines with frequency υ_R on both sides of central line. This phenomenon of scattering with modified frequency is called as *Raman scattering*.

Raman scattering is weak scattering and is about 1 % of the incident radiation or less than 0.01 per cent of Rayleigh scattering. Raman scattering does not involve absorption of radiation and scattering occurs in 10^{-12} sec after excitation. Raman spectroscopy deals with the measurement of scattered radiation as a function of wavelength. Raman spectra is a graph of scattered intensity verses wavelength.

There are other types of scattering named as Tyndall scattering (which is due to collids and emulsions) and Rayleigh scattering (which is due to ordinary liquid, crystals and glasses). Rayleigh scattering is valid for particle size not more than 0.1 of the light of 40 - 70 nm, while Tyndall scattering is valid for particle size between 1 – 100 nm. In Rayleigh scattering, the final state of atom or molecule is same as initial state, the frequency of photon is unchanged giving unshifted line.

When white light is used in Rayleigh scattering, there is enhancement of different colours present in incident beam. The blue colour of sky is due to Rayleigh scattering of sunlight by particle of air with dimension less than one-tenth of the wavelength of light. The scattering intensity of Rayleigh scattering is proportional to fourth power of frequency.

If the final state of atom or molecule is different from initial state, the process is inelastic scattering. i.e. Raman scattering.

The lines in Raman scattering are frequently arranged symmetrically on both sides of the Rayleigh line. The lines of frequency less than that of Rayleigh line ($\upsilon < \upsilon_0$) are called as *Stoke's lines*. The lines with frequency greater than Rayleigh line ($\upsilon > \upsilon_0$) are called as *anti- Stoke's lines*. The difference between the frequencies of Raman (υ_R) and Rayleigh line matches with the fundamental vibrational frequency ($\upsilon_{vib.}$) or the rotational frequency ($\upsilon_{rot.}$) of the molecule of the scattered material. It means that the frequency shift is (also called as *Raman shift*) is the difference between frequency of Rayleigh line and a particular Raman line.

$$\Delta \upsilon_R = \upsilon_0 - \upsilon_R \qquad \text{... (9.2)}$$

If υ^s and υ^a are the frequencies of the Stoke's and anti-Stoke's Raman lines respectively, then we may write,

$$\left.\begin{aligned} \upsilon^s &= \upsilon_0 - \upsilon_{vib.} \\ \upsilon^a &= \upsilon_0 + \upsilon_{vib.} \end{aligned}\right\} \qquad \text{... (9.3)}$$

and

$$\left.\begin{aligned} \upsilon^s &= \upsilon_0 - \upsilon_{rot.} \\ \upsilon^a &= \upsilon_0 + \upsilon_{rot.} \end{aligned}\right\} \qquad \text{... (9.4)}$$

The Raman scattering is shown in Fig. 9.1

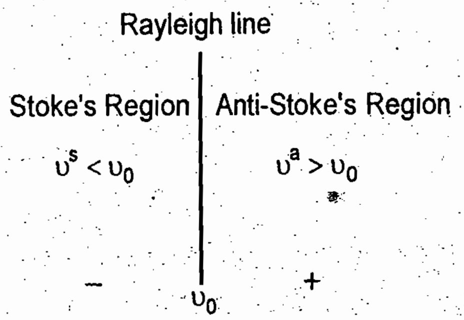


Fig. 9.1 : A sketch showing Raman effect

9.3 QUANTUM THEORY OF RAMAN EFFECT

Quantum mechanical picture is based on Kramer-Heisenberg theory of light. According to this theory, when a photon of frequency υ_0 interacts with molecule of substance, it will jump from any of its initial vibration or rotational level $E'_{V'/J'}$ (where $V'/J' = 0, 1, 2, 3, \ldots$) to any higher vibrational or rotational level $E''_{V''/J''}$. The higher energy level is unstable level for photon and molecule also and its life time is of the order of 10^{-17} sec. The molecule in the virtual level subsequently returns to any one of the initial vibrational and rotational level $E'_{V'/J'}$ with emission of photon. The process of release of photon may be divided into the following three cases :

Case I :

The molecule may return from virtual state to any of its initial state such that the frequency of released photon is that of incident photon.

i.e. $$E''_{V''/J''} - E'_{V'/J'} = h\upsilon_0 \qquad \ldots (9.5)$$

or $$\upsilon_0 = \frac{E''_{V''/J''} - E'_{V'/J'}}{h}$$

This is true for 0 → 0, 1 → 1, 2 → 2, etc. transitions. This phenomenon of emission of photon is called as Rayleigh scattering and is due to the interaction of photon with nucleus. The energy level diagram of Rayleigh scattering is shown in Fig. 9.2 (a). This indicates presence of unmodified Rayleigh line in the scattered light Raman scattering.

Case II :

The molecule in state $V'/J' = 0$ absorbs incident photon and jumps to virtual level and then subsequently returns to any one of the initial states with the release of photon with lower frequency (υ^s) than the incident photon. i.e.

$$E''_{V''/J''} - E'_{V'/J'} = h\upsilon^s \qquad \ldots (9.6)$$

This is true for 0 → 1, 0 → 2, 0 → 3, etc. transitions.

This is known as Stoke's Raman scattering. The diagram for Stoke's Raman scattering or effect is as shown in Fig. 9.2 (b).

Case III :

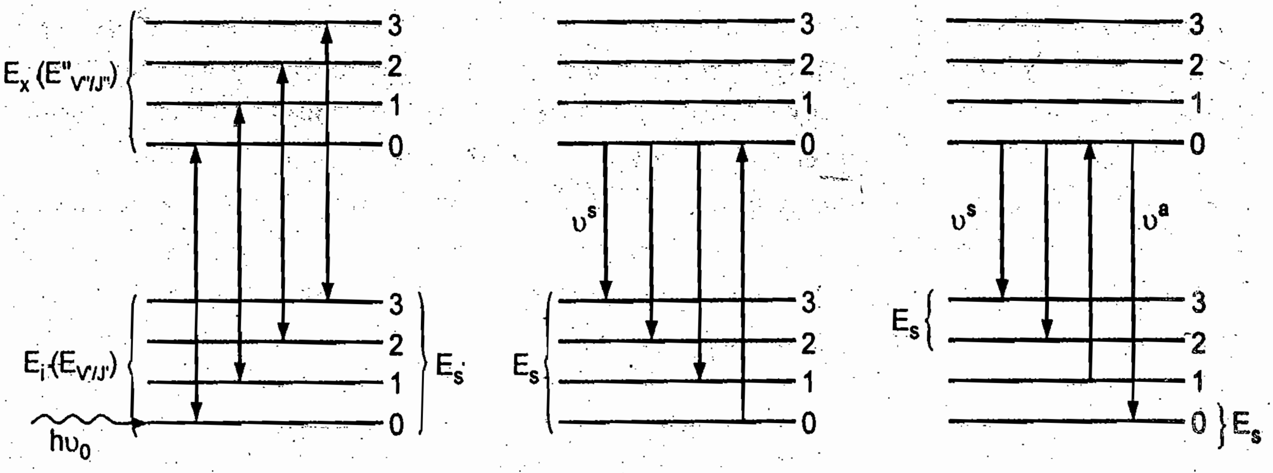
The molecule in higher initial level $V'/J' = 1$ gains energy from incident photon and jumps to any one of the virtual levels. The molecule subsequently returns to any of the initial level with the release of the photon :

(i) With frequency υ^a higher than that of incident photon i.e.

$$E''_{V''/J''} - E'_{V'/J'} = h\upsilon^a \qquad \ldots (9.7)$$

This is true for 1 → 0, 2 → 0, etc. transitions. This process of release of photon is called anti-Stoke's Raman effect.

(ii) With lower frequency (υ^s) by mechanism of case II. This will be true for 1 → 2, 1 → 3, etc. transitions and shown in Fig. 9.2 (c).



(a) Rayleigh scattering

(b) Stoke's Raman scattering

(c) Anti-Stoke's Raman scattering

Fig. 9.2 : Energy level diagram of Raman effect

According to quantum theory, a wave of frequency υ_0 consists of photon of each of energy $h\upsilon_0$. When this light falls on molecules of solid, it undergoes a collision with molecule.

1. If collision is elastic, there is no transfer of energy from the photon to molecule and vice versa. Hence photon is scattered without change in energy and frequency of photon is same as incident photon. This explains presence of Rayleigh line.

2. If the collision is ~~elastic~~ Inelastic, there is exchange of energy between photon and molecule.

Let the incident photon with energy $h\upsilon$ collide with a molecule of K.E. $\frac{1}{2}mv^2$ and intrinsic energy E'. Let υ^s is frequency of scattered photon, v_1 is velocity of molecule and E'' is intrinsic energy, then according to conservation of energy,

$$h\upsilon_0 + \frac{1}{2}mv^2 + E' = h\upsilon_1 + \frac{1}{2}mv_1^2 + E''$$

As there is no change in temperature, there is no change in K. E.

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_1^2$$

Hence,

$$\mathbf{h\upsilon_0} + E' = h\upsilon^s + E''$$

$$\mathbf{h\upsilon_0} = h\upsilon^s + (E'' - E')$$

$$\mathbf{h\upsilon_0} = h\upsilon^s + \Delta E$$

$$\mathbf{\upsilon_0} = \upsilon^s + \frac{\Delta E}{h}$$

There are two cases :

Case I :

Molecule gains energy from the photon and goes from a lower energy E' to a higher energy state E".

$$\therefore \qquad E'' - E' = \Delta E \text{ is positive}$$

$$\nu_0 = \nu^s + \frac{\Delta E}{h}$$

Or

$$\nu^s = \nu - \frac{\Delta E}{h}$$

$$\nu^s = \nu - \Delta \nu$$

The frequency of scattered photon is less than the incident photon. This explains presence of modified Stoke's line on lower frequency or longer wavelength side of Raman spectrum.

Case II :

The molecule may be at excited state initially. It may lose energy to the photon, which may now have frequency ν^a. The molecule now goes to initial higher energy level E' to lower energy level E", so that E" – E' is negative.

Hence

$$\nu_0 = \nu^a - \frac{\Delta E}{h}$$

$$\nu^a = \nu_0 + \frac{\Delta E}{h}$$

or

$$\nu^a = \nu_0 + \Delta \nu$$

The frequency of scattered photon is higher than that of incident photon. This explains presence of anti-Stoke's lines on the higher frequency or shorter wavelength side of the Raman spectrum.

9.4 CHARACTERISTICS OF RAMAN LINES

The important parameters of Raman lines are :

1. **Intensity :**

   Intensity of Raman line varies directly as $(\nu_0 - \nu_{vib.})^4$ except in vicinity of Raman Resonance Scattering i.e. Intensity depends on frequency of radiation.

   Stoke's lines are invariably stronger than anti-Stoke's lines i.e. anti-Stoke's lines are generally fainter than Stoke's lines.

   Intensity of anti-Stoke's lines grows with temperature.

2. **Width and shape :**

   Raman lines are narrow in gases, **liquids and crystals**; while in amorphous substance, lines are broad and diffuse. **Width of Raman** line increases with increase in temperature. The shape **of Raman line** is independent of incident radiation.

3. **Frequency shift:**

Frequency shift of Raman line from Rayleigh line varies from 4000 to few wave number and independent of frequency of incident radiation.

4. **Polarisation:**

Raman scattered radiation is at least partially polarised irrespective of the polarisation of the incident radiation. Polarisation depends on structure of molecule as well as symmetry of vibrational motion. The scattered radiation may be polarised in a plane parallel and perpendicular to the plane of polarisation.

Let if $I_{||}$ and $I_{\perp}$ be intensity of scattered radiation polarised in parallel and perpendicular planes respectively.

The ratio $I_{||}$ to $I_{\perp}$ is called as degree of depolarisation and denoted by

$$P = \frac{I_{||}}{I_{\perp}}$$

Depolarisation plays important role in determining the symmetry of a vibrational mode.

Theoretically, ρ is less than 3/4 for totally symmetric modes.

If $\rho = 3/4$, modes are not totally symmetrical.

If $\rho < 6/7$, then vibrations are asymmetric and capable of polarisation of radiation.

When $\rho > 6/7$, depolarisation of radiation occurs.

9.5 EXPERIMENTAL ARRANGEMENT TO OBSERVE RAMAN SPECTRA

The Raman effect has been studied by a large number of workers. The general technique used by these researchers is to illuminate the substance under investigation with high monochromatic source of light, and photograph of scattered radiation is taken by arranging spectrograph in transverse direction.

The original simple arrangement of Raman was not quite efficient and required very long exposure of about 100 hours and more to obtain good records of the Raman spectrum. Hence, improvement were made as regards the container of the substance, the source of radiation, filter and spectrograph, etc.

The first apparatus used was developed by Wood and ordinarily used to study Raman effect in liquid. Certain modifications in the experimental arrangement were done for study of Raman effect in solid and liquid.

To obtain a good Raman spectra, the incident beam should be strong as Raman scattering is weak. Secondly, the beam should be highly monochromatic as Raman lines are observed on both sides of central line (Rayleigh line). This purpose is served by using Laser. The complete flow sheet diagram of basic Raman spectrometer is shown in Fig. 9.3.

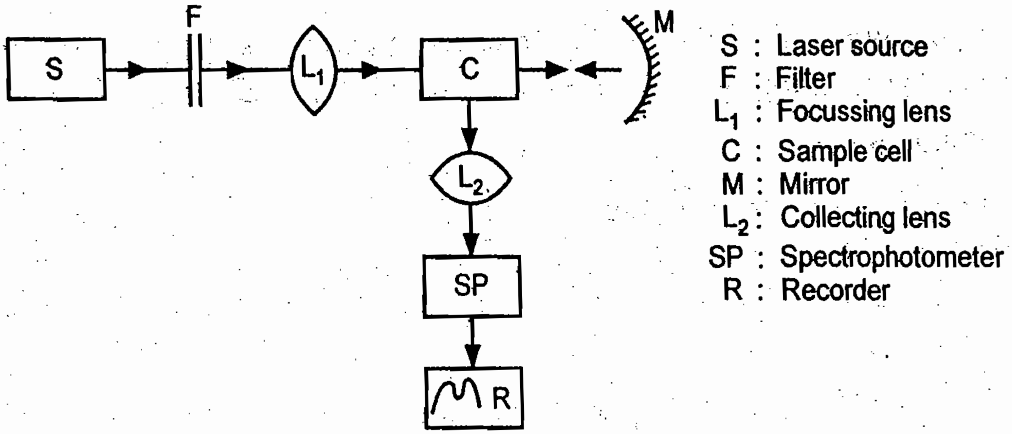


Fig. 9.3 : Flow sheet of a simple Raman spectrometer

Raman Spectrometer consist of

(i) a suitable gas laser source S and

(ii) an optical system comprising filter F, focusing lens L_1 and mirror M to focus the beam on or into sample. There is a collecting lens L_2 to feed the scattered radiation to spectrophotometer SP. Spectrophotometer counts the photons as a function of frequencies. This analysis is displayed as a plot of scattering intensity verses frequency by the recorder R. Typical hypothetical spectra is presented in Fig. 9.4.

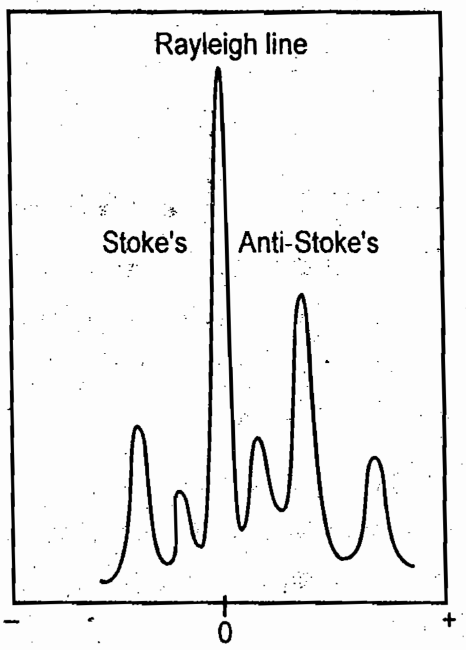


Fig. 9.4 : Hypothetical Raman spectrum using laser

1. Laser Source :

Before discovery of laser, mercury arcs were used as a source of radiation.

The advent of accessible and relatively inexpensive laser sources during the past few years has caused major revolution in Raman scattering by displacing the traditional mercury source (discharge tube) as an exciting source. Now-a-days, a laser is ideal Raman source. It gives narrow, highly monochromatic beam of radiation which can be focussed into sample through filter.

The commonly used laser sources are :

1. Continuously operating He - Ne (633 nm), Ar^+ ion (488 nm) and Hg - Cd (441, 325 nm) gas lasers;
2. Pulsed and continuously operating forms of Ruby (694 nm) and Nd - YAG (1.06 micron) solid lasers;
3. Tunnable dye laser in visible range (0.43 – 0.65 μm);
4. UV laser (184 – 260 nm)

The power of laser is of the order of 50 mW – 2 W. The type of laser to be used depends upon type of study. i.e. He - Ne (100 mW, 633 nm) laser is frequently used due to narrow wavelength.

The advantages of using laser are as follows :

1. We do not need to cool the sample and need not use filter to get monochromatic beam of radiation.
2. Raman spectra can be recorded by using small amount of analyte.
3. Second order Raman spectra can be recorded.
4. The polarisation of laser beam is well defined and may be controlled within 0.1 %.
5. Broadening due to Doppler effect can be minimized.
6. As width of laser line is of the order of 0.005 cm^{-1} or less, a precise information could be obtained.

2. Sample Cell :

The sample cell is made up of non-fluorescent fused quartz having well polished flat bottom. The top of cell is sealed with a transparent cap to avoid dust and designed to permit deoxygenation of the sample. The cell is completely filled to avoid reflections. The spectra of liquid (coloured or colourless) is completely recorded by focussing the beam vertically through bottom window into the sample and then the scattered radiation perpendicular to incident beam is collected. The spectra of solid are recorded by using capillary. The thin capillary tube, filled with sample and sealed at one end, with the laser beam directed along its length. Radiation scattered from the sample is directed, via mirror, into a spectrometer operating in visible region. The spectrometer has monochromatic either a quartz or grating and detected by photoelectric detector. The output of detector is supplied to an amplifier and recorder (R). It is observed that solid gives more Rayleigh background. The spectra of sample which are sensitive to laser wavelength are recorded using by rotating cell technique to avoid degradation of sample (like CCl_3 COCl etc.)

In case of biological substance, local heating may degrade some biological molecule (i.e. its absorbs the energy at laser wavelength). In these type of biological systems. (e.g. cytochrome - C, hemoglobin) the resonance Raman scattering of laser radiation from vibrational mode of biological molecules are recorded. The hypothetic Raman spectrum is shown in Fig. 9.4.

9.6 APPLICATIONS OF RAMAN SPECTROSCOPY

Due to simplicity of this technique, Raman effect has many advantages over IR spectra. Hence they are used in following purposes :

1. To study the structure of molecule, the structural changes occurring in molecule due to association, dissociation and solvation, etc.
2. In study of chemical equilibria.
3. For analysing complex mixture of molecules.
4. For identifying compounds.
5. For studying kinetics of fast reaction.
6. For determination of the rotational and vibrational levels.
7. To study molecular vibrations and to elucidate the stereochemical features of molecules.
8. In study of crystals which are complementary to X-ray diffraction technique.
9. In study of certain aspect in Nuclear Physics like spin.
10. Biological applications :
    - Provides information on peptide backbone disulphide bridges and environment of some of side chains (tyrosine, hystidine, etc.)
    - Study of structural and conformational changes and denaturation of macromolecule (like proteins, carbohydrates).
    - Study the conformation of nucleic acid.
    - Study of structural and conformational aspect of lipids, biological membrane and lipid protein complex.

ILLUSTRATIVE EXAMPLES

Example 9.1 : A compound is irradiated by 4358 A° line of mercury. Raman lines are observed at wavelengths 4420 and 4620 A°. Compute the value of Raman shift for each line in terms of wave number.

Solution:

$$\upsilon_0 - \upsilon_R = \Delta \upsilon_R$$

$$\frac{c}{\lambda_0} - \frac{c}{\lambda_R} = \frac{c}{\Delta \lambda_R}$$

or

$$\frac{1}{\lambda_0} - \frac{1}{\lambda_R} = \frac{1}{\Delta \lambda_R}$$

For λ = 4420 A°,

$$\frac{1}{4358 \times 10^{-8}} - \frac{1}{4420 \times 10^{-8}} = \Delta \overline{\upsilon}$$

$$\therefore \quad \Delta \overline{\upsilon} = 320 \text{ cm}$$

For λ = 4620 A°,

$$\Delta \overline{\upsilon} = \frac{1}{4358} - \frac{1}{4620} = 1300 \text{ cm}^{-1}$$

Example 9.2 : A sample was excited by the 4358 A° line of mercury. A Raman line was observed at 4447 A°. Calculate Raman shift.

Solution : Since Raman line is observed at longer wavelength (shorter frequency) than exciting line, it is a Stoke's line in Raman spectroscopy.

Raman shift :
$$\Delta \upsilon \ (\text{cm}^{-1}) = \frac{10^8}{\lambda_{\text{exc}} \ (\text{in A}^\circ)} - \frac{10^8}{\lambda_{\text{Raman}} \ \text{in} \ (\text{A}^\circ)}$$

$$\Delta \upsilon = \frac{10^8}{4.358 \times 10^3} - \frac{10^8}{4.447 \times 10^3}$$

$$= (2.295 - 2.249) \times 10^4$$

$$= 0.046 \times 10^4$$

$$= 460 \text{ cm}^{-1}$$

Example 9.3 : At what wavelength in A° would the anti-Stoke's line appear in the Raman spectrum of the above example 9.2.

Solution : From previous example, Raman shift $\Delta \upsilon = 460 \text{ cm}^{-1}$

Anti-Stoke's line will appear at frequency 460 cm^{-1} higher than the frequency (in cm^{-1}) associated with 4358 A° Hg line (used as source of excitation)

$$\upsilon_{\text{exc}} \ (\text{cm}^{-1}) = \frac{10^8}{\lambda_{\text{exc}}} = \frac{10^8}{4.358 \times 10^3}$$

$$= 2.295 \times 10^4 \text{ cm}^{-1}$$

$$\therefore \quad \upsilon_{\text{anti-Stoke}} = (2.295 \times 10^4 \text{ cm}^{-1}) + (460 \text{ cm}^{-1})$$

$$= 2.341 \times 10^4 \text{ cm}^{-1}$$

$$\upsilon = \frac{c}{\lambda} = \frac{10^8}{\lambda}$$

$$\upsilon (\text{in A}^\circ) = \frac{10^8}{\upsilon \ \text{cm}^{-1}} = \frac{10^8}{2.341 \times 10^4}$$

$$= 4272 \text{ A}^\circ$$

QUESTIONS AND PROBLEMS

(A) Multiple choice questions : Select the correct answer.

1. The lines of frequency less than frequency of Rayleigh line are called as .....
   (a) Stoke's lines (b) anti-Stoke's lines
   (c) sodium lines (d) none of above
2. Anti-Stoke's lines are .... than Stoke's lines.
   (a) intense (b) fainter
   (c) of same intensity (d) none of above
3. Raman scattering is useful for study of ....
   (a) structure of molecule (b) molecular vibrations
   (c) complex mixture of molecule (d) of all of above

4. In Raman spectrophotometer, the sample cell used for study of solid is ....
   (a) glass flask (b) quartz flask
   (c) capillary tube open at both ends
   (d) capillary tube filled with sample and open at both ends

5. If the final state of atom or molecule is same as initial state, then the scattering is ....
   (a) Raman scattering (b) Rutherford scattering
   (c) Rayleigh scattering (d) none of above

Ans.: (1) - a, (2) - b, (3) - d, (4) - d, (5) - c.

(B) Answer in short:

1. What is Raman effect ?
2. What are Stoke's lines ?
3. What are anti-Stoke's lines ?
4. What is Rayleigh line ?
5. What is Raman shift ?
6. What are the biological applications of Raman effect ?

(C) Answer in detail:

1. What is Raman effect ? With proper sketch explain occurrence of Stoke's lines and anti-Stoke's lines.
2. Explain Raman effect on the basis of quantum theory.
3. Describe the experimental arrangement to observe Raman spectra.
4. What are the applications of Raman spectra ?

(D) Numerical problems:

1. The Rayleigh line in Raman experiment is 4358 A° and the spectrum shows the Stoke's line at 6433 A°. Find the wavelength of anti-Stoke's line.

   Ans.: 3295 A°

2. A substance shows Raman line at 4567 A° when exciting line 4358 A° is used. At what position Stoke's and anti-Stoke's lines for the same substance will be observed when the position of Rayleigh line is at 4047 A°.

   Ans. : 4227 A° (Stoke's line), 3882 A° (anti-Stoke's line)

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