Unit 1
Lesson-1

PROPERTIES OF THE ATOMIC NUCLEUS

The objectives of the lesson are to explain the following:

1.1 Introduction

1.2 Nuclear size and its determinations

1.3 Theories of nuclear composition

1.4 Packing fraction

1.5 Mass Defect

1.6 Binding energy and its variations with the mass number

1.7 Magnetic dipole moment

1.8 Classical multipole moments for point charges

1.9 Electric Quadrupole moment

1.10 Summary.

1.1 Introduction: Since the atom is electrically neutral under normal conditions and the atoms of radioactive element are transformed into atoms of another element by emitting negatively or positively charged particles, hence it can be said that atoms are made up of equal number of positive and negative charges. The important questions then arose: 1. How many electrons were there in an atom ? and 2. How were the electrons and positive charges arranged in it ?. The scattering of X-rays shown that the number of electrons in an atom of the higher elements was equal to about half the atomic weight, except that in the atom of hydrogen. Thomson assumed that an atom consisted of a sphere of positively electricity of uniform density throughout of which was distributed an equal and opposite charge in the form of electrons. Thomson’s theory came into conflict with the experiments of Rutherford and his collaborators on the scattering of α particles.. Rutherford had noticed that when alpha particles from a radioactive source fell on a photographic plate after penetrating a thin sheet of metal, the resulting trace was diffused sending fading off at the edges instead of being sharp. This spreading out of the particles on passing through thin layers of matter was called scattering . It was as a result of interaction with the atoms of the material through which they had passed. Rutherford and Geiger carried out experiments to count alpha particles with Geiger's gas counter. Geiger showed the small angle of alpha scattering and found nothing very unexpected. In view of J.Thomson model of the atom of appeared

possible that alpha particle scattering might be due to encounters with electrons. But Rutherford said Remembering that the mass, momentum and K.E of alpha particles are very large compared with the corresponding values of the electron. It does not seem possible that an alpha particle can be deflected through a large angle by a closed approach to an electron. Therefore, he concluded that the atom did not consist of a uniform sphere of positive electrification as supposed by Thomson, but that the positive charge was concentrated in a small region called the nucleus of the centre of the atom.

1.2 Nuclear size and its determination: In 1919 Rutherford observed that deviation from pure coulombs scattering anamalous scattering, was observable when alpha rays were scattered by the lightest elements, In these light elements, the closest distance of approach was of the order of $5\times10^{-15}m$. The distance of closest approach at which anomalous scattering begins was modified as the first measure of the nuclear radius. The shape of the nucleus is taken spherical because for a given volume this shape possesses the least surface and hence therefore provoke maximum short range binding forces between the nucleons(protons and neutrons) in the nucleus. Small asymmetries of the distributions of -ve charge are present in some metal as these nuclei exhibit high electric quadrupole moments. In most nuclei the ellipticity is only of the order of one percent. Thus we may suppose the protons are uniformly distributed inside the spherical nucleus.

There is an evidence that nuclear density ρ remains approximately constant over most of the nuclear volume and then decreases rapidly to zero. Thus means that nuclear volume is approximately proportional to the number of nucleons i.e. mass number 'A' . Hence radius of the nucleons $R \infty A^{\frac{1}{3}} \quad or \quad R = R_0 A^{\frac{1}{3}}$

The methods of measuring nuclear radius are divided in to two main categories . One group of method is based on the study of the range of nuclear forces in which the nucleus is probed by a nucleon of light nucleus. Other group of methods studies the electric field and charge distributions of the nucleus in which the nucleus is probed by electron or muon(μ -meson).

1.3 Theories of nuclear composition: Rutherford's nuclear theory based on the scattering of alpha particles suggest the nucleus to be of compact structure. Natural radioactivity suggested that though the nucleus is compact,, it is capable of emitting several particles e.g. α, β, γ particles. The study of alpha and gamma ray spectra suggests discrete levels in the nucleus while beta ray spectra suggests a new particle neutrino. Researches in artificial transmutation of elements show that alpha particles , p, n, e^{-} *and* e^{+} should be present in the nucleus some how of other cosmic ray studies predict us another particle like 'meson' inside it. Some of the well established properties of atomic nuclei are:

1.All nuclei are +vely charged and the magnitude of the electronic charge is an integral multiple (z) of the proton charge e.

2. More than 99.9% of the mass of an atom is concentrated inside the tiny volume of the nucleus .

3.We assume that nuclei are spherical or nearly spherical in shape having radius 'R' is given by

$$R = R_0 A^{\frac{1}{3}}$$

4.The important correlation between R and A suggests that there is a universal density for nucleon matter density

$$\rho = \frac{mass}{volume} = \frac{A \times 1.66 \times 10^{-27} Kg}{\frac{4}{3}\pi\left(1.2 \times 10^{-15}\right)^3 Am^3} = 10^{17} Kg/m^3$$

$$Number\ \ of\ \ \ nucleons/c.c. = \frac{Density}{Mass\ of\ \ a\ nucleon}$$

$$= \frac{10^{17}}{1.66 \times 10^{-27}} \approx 10^{44} nucleons/m^3$$

5.The nucleus is lightly bound system of the nucleons with a large potential energy. Several theories of nuclear compositions were put forward.

1.Proton-Electron theory: Prout suggested that all atomic weights were whole numbers and hence could be assumed as the integral multiple of the atomic weight of hydrogen.The slight change in the whole number was explained by the presence of two or more isotopes. This hydrogen theory confirms the presence of protons inside the atom. Since the electrons are

known to be emitted from some nuclei, it was natural to believe in the beginning that the electrons were the constituents of all nuclei. To account for the mass number of the nucleus whose atomic weight is nearly equal to the integer A, it was necessary to assume that nucleus would consist 'A' .But if this were the case the charge on the nucleus would be 'A', not equal to the atomic number'Z'. To remove this difficulty, it was assumed that in addition to 'A' protons the atomic nuclei would contain (A-Z) electrons. These would contribute a negligible amount to the mass of nucleus but would make the charge +z as required.

But this theory led to a number of contradictions with experiments and few of them are presented here

1. finite size
2. spin consideration
3. statistics
4. magnetic moment considerations
5. wave mechanical considerations
6. Compton wavelength
7. Beta decay
8. Electron neutrino pairs

The above points ruled out the existence of electron as semi permanent nuclei particles

2.Proton Neutron theory: The experimental discovery of the neutron led Heisenberg in 1932 to suggest that the nuclei might be composed of proton and neutrons rather than of protons and electrons. Thus for an atom $_{z}X^{A}$,the nucleus contains Z protons and (A-Z) neutrons. The total no. of particles inside the nucleus = A, the mass number. This nucleus is surrounded by Z electrons to make the atom electrically neutral . This theory avoids the failure of proton-electron theory.

1.4 Packing Fraction:-

The precision development in mass spectroscopy has shown that masses of isotopes are not whole numbers but they are very close to the whole number. Aston defined a new physical quantity known as packing fraction is expressed as

$$f = \frac{M-A}{A}$$

$$M = A(1+f)....................1.1$$

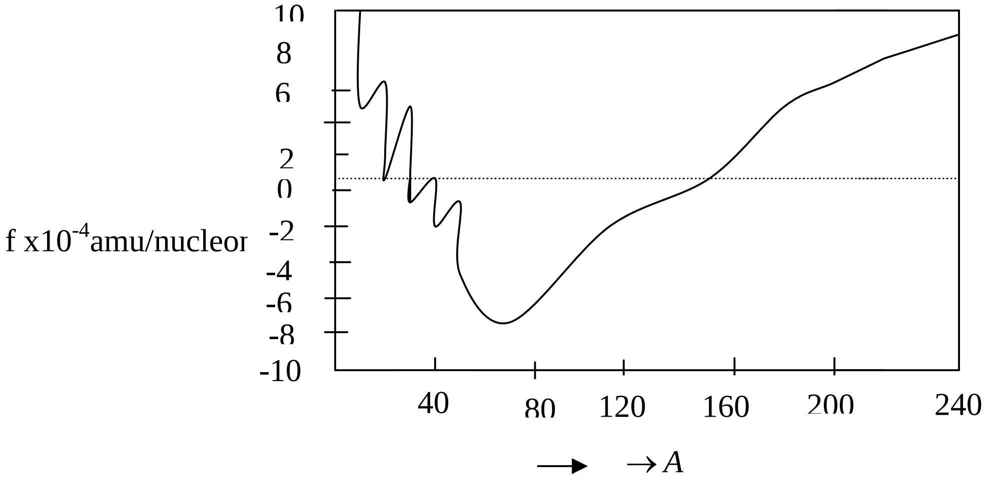


Fig:1. Packing fraction versus mass number

Where M is mass of the isotope and A is nearest whole number. The variation of packing fraction with mass number for large number of nuclides is shown in the fig(1). The curve is approximately smooth, f has high positive values for light elements.

It is zero for o^{16}. Now as A increases, packing fraction becomes negative pass through a flat minimum and finally becomes positive for A values for 180. It will be discussed that packing fraction is a useful quantity while explaining the stability of nuclides.

1.5 Mass Defect:-

Packing fraction is written as

$$f=\frac{\Delta M}{A}=\frac{\exp erimental\ \ mass\ \ -\ \ whole\ \ number}{whole\ \ number}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.2$$

In the beginning ΔM was termed as mass defect . This means that packing fraction is mass defect per nucleon. Some spectroscopists defined mass defect as (A-M) in place of (M-A).This introduces negative sign in the old definition i.e.

$$f=-\frac{mass\ defect}{A}$$

to avoid this confusion the expression for packing fraction relating the mass defect may be written as

$$f=\frac{mass\ \ difference}{A}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.3$$

It might, at first, be supposed that the mass of an atom should be the sum of the masses of its constituent particles i.e. protons and neutrons, electrons .But the experimentally measured mass of any stable atom is found to be less than the sum of the mass as of its constituents. The decrease in the mass is known as mass defect.

It is always true that actual mass never exceeds the added mass of its constituents. For a nuclide ${}_{z}X^{A}$, we write ${}_{Z}M^{A}$ for its actual atomic mass and $ZM_H\ \ and\ NM_n$ for the total mass of its constituents . The difference may be written as

$$\left\{ZM_H+(A-Z)M_n\right\}-{}_{Z}M^{A}=\Delta_Z M^{A}\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.4$$

This difference $\Delta_Z M^{A}$ is known as mass defect.

Example:1 Take ${}_{2}He^{4}$

It consists of 2 protons and 2 electrons and 2 neutrons. Therefore its expected mass should be

$$M_{He}=2(M_H+M_n)\qquad(\because M_H=M_P+M_e)$$

Here all masses are expressed in atomic mass units . It is given that

Mass of hydrogen atom M_H =1.008145 amu

Mass of neutron M_n = 1.008986amu

Mass of Helium atom $M_{He} = 2(M_H + M_n)$

$= 2(1.008145 + 1.008986)$

$M_{He} =$ 4.034262amu

But the experimentally measured mass value is 4.003873.

It is less by an amount 0.034amu

$$\Delta_z M^A = \{ZM_H + (A-Z)M_n\} -_z M^A$$

$$=4.03426 - 4.003873$$

$$\Delta_z M^A \approx 0.0304$$

Example:2 Argon ${}_{18}Ar^{40}$ No.of protons =18,No. of electrons = 18,

No. of Neutrons = 22

$$\Delta_z M^A = \{ZM_H + (A-Z)M_n\} -_z M^A$$

M_H = 1.008145amu

M_n = 1.008986amu

Experimental mass of Argon M_{Ar} =39.97505amu

$$\Delta m = \{18(1.008145) + (40-18)(1.008986)\} - 39.97505$$

$$= 40.344302 - 39.97505$$

$$\Delta m \approx 0.37 amu$$

1.6 BINDING ENERGY:

It is known that nucleus consists of large number of particles,namely neutrons and protons. Now the question is “what is the external agency that keeps these particles in a tightly bound structure inspite of the fact protons are positively charged and repel other protons ?” It turns out that particles should be held together by strong attractive forces. This idea is confirmed by the fact that when it is desired to break up a nucleus, i.e., work is done against the attractive forces, leaving aside, at present, the nature of the attracting forces we wish to discuss the origin of the attractive forces. When large amount of energy is supplied to a nucleus the constituents of nucleus are held apart. It means that total energy of the constituents (when they are at large distance) is greater than when they form nucleus. Conversely when the nucleons are brought together their total energy is less than the sum of the energies of its constituents when they are held apart. Now the natural question is what happens to the excess energy? Does it form the origin of attracting forces ?

It has been also seen that actual mass of nucleus is always less than the mass of its constituents. Where does the mass go?

The answers of the above questions become abundantly clear when all the questions are coordinated and we recall the famous Einstein relation

$$E = mc^2$$

where 'c' is the velocity of light in vacuum, m is any mass, and E is corresponding energy. The equation states that mass and energy are the manifestations of one same thing and one can be converted into other. Thus, we can say that mass defect $\Delta_z M^A$ appears as an equivalent amount of energy ΔE on forming a nucleus. ΔE is the energy released, due to the decrease of mass, when nucleus is formed by fusing together the requisite number of nucleons; alternately it is the energy required to separate the nucleons of nucleus. It is referred as the binding energy of the nucleus, B.E.

The binding energy of a nuclide ${}_Z X^A$ may be expressed as:

$$\begin{aligned} B.E &= \left(\Delta_z M^A\right)c^2 \\ &= \left\{ZM_H + (A-Z)M_n - {}_Z M^A\right\}c^2 \end{aligned}$$

The binding energy per nucleon will be

$$\frac{B.E}{A} = \frac{c^2}{A}\left\{ZM_H + (A-Z)M_n - {}_Z M^A\right\} \text{......................1.5}$$

The variation of binding energy per nucleon with mass number is shown in fig.1.2

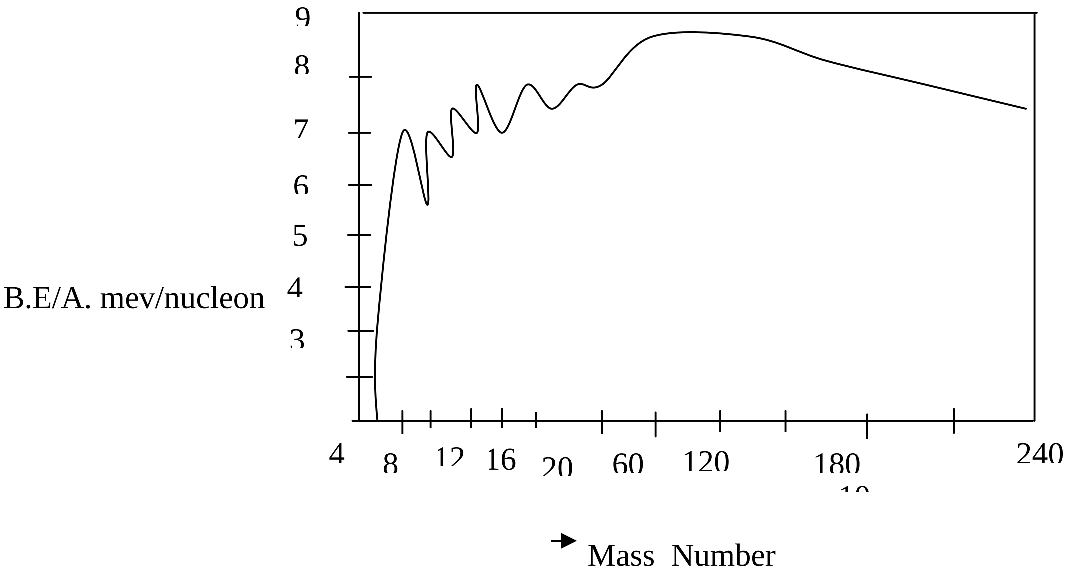


Fig:1.2. Binding Energy Curve

The variation of binding energyy per nucleon with mass number is shown in fig.2. The curve indicates that $\overline{B}$ is small for very light nuclides. It increases as A increases, reaches a maximum value of about 8.8Mev in the neighbourhood of A (= 50 ~ 60). The maximum is quite flat and $\overline{B}$ is 8.4Mev at about A = 156. For higher mass number $\overline{B}$ decreases to about 7.6Mev for uranium . The curve also shows peaks for the nuclides of mass number 4,8,12,16,20. It is now desired to explain the above noted features in brief.

(a)Small binding energy in case of light nuclei:-

In the case of light nuclei, there are few nucleons and as a result, most of them are at the surface of the nucleus. This surface effect try to distrupt the nucleus and thereby reduces the binding energy of the nucleus.

(b)Occurrence of peaks in binding energy curve:-

The peaks occur at mass number 4,8,12,16,20.Let us take the example of ${}_2He^4 . {}_2He^4$ contains the maximum possible number of 1s nucleons, the four particles differing only with respect to their two possible spin orientations and two possible values of charge. This

brings out zero angular momentum for helium nucleus. It means that there is no centrifugal force to reduce the strength of binding forces and hence helium shows a tightly bound configuration associated with maximum value of B.E. The similar arguments hold good for other highly stable nuclei showing peaks.

(c) A constant binding energy per nucleon:-

If the energy is expressed in mass units, then binding energy expression is written as

$$B.E = ZM_H + (A-Z)M_n - {}_Z M^A$$

$$= AM_n + (M_H - M_n)Z - {}_Z M^A$$

$$\overline{B} = (M_n - 1) + \frac{Z}{A}(M_H - M_n) - \left(\frac{{}_Z M^A - A}{A}\right)$$

$$\overline{B} = (M_n - 1) + \frac{Z}{A}(M_H - M_n) - f \ldots\ldots\ldots\ldots\ldots\ldots 1.5(a)$$

where f is packing fraction in atomic mass unit per nucleon. For the nuclide from A = 40 to 140, $\frac{Z}{A}$ has an average value of 0.46 in the same region

$$f = -6 \times 10^{-4}\, amu / nucleon.$$

Hence B = 0.008982 –(0.46)(0.000840) - f

= 0.0086 - f

= 8.5Mev/nucleon.

The average binding energy remain constant. Because(M_n-1) is the only predominating sterm and other terms are only correction terms.

(d) The decrease of binding energy per nucleon for high mass number:-

As the value of A further increases the coulomb repulsion increases. Furthermore, when A is sufficiently large nuclear forces are saturated and nuclear binding behaves like homopolar binding in chemical system. These two reasons are sufficient to account fall in binding energy per nucleon.

1.7 NUCLEAR MAGNETIC DIPOLE MOMENT:

Any charged particle moving in a closed path produces a magnetic field, which at large distances acts as due to magnetic dipole located at the current loop. The protons inside the nucleus are in orbital motion and therefore produce electric currents which produce extra nuclear magnetic fields. Each nucleon possesses an intrinsic magnetic moment which is parallel to its spin and is probably caused by the spinning of the nucleon. A spinning positive charge a magnetic field whose N-pole direction is parallel to the direction of spin. The magnetic moment is defined as positive in this case.

If a particle having a charge ‘q’ and mass ‘m’ circulates about a force center with a frequency ‘ν’. The equivalent current i = qν. From Kepler’s law of areas area swept $d\hat{A}$ in time dt by the particle is related with its angular momentum l as

$$\frac{d\hat{A}}{dt} = \frac{l}{2m} = \text{constant}$$

on integration over one period T, we get

$$\int d\hat{A} = \int_0^T \frac{\hat{l}}{2m} dt$$

$$\hat{A} = \frac{TI}{2m} \longrightarrow 1.6$$

Hence magnetic moment of a ring of current around an area of magnitude A is given by

$$\vec{\mu}_l = \mu_0 i\hat{A} = \mu_0 (q\upsilon)\left(\frac{T\vec{l}}{2m}\right) = \frac{q}{2m}\mu_0\vec{l} \longrightarrow 1.7$$

Thus $\vec{\mu}_l$ and $\vec{l}$ are proportional. This relation is also valid in quantum mechanics. However, since the particles (electron, proton and neutron) possess a spin in addition to orbital angular momentum, experimentally it is found that the spin is also the source of a magnetic moment . Using q = e and a dimensionless correction factor g_s , we can write equation (1.7) as

$$\vec{\mu}_s = g_s\left(\frac{\mu_0 e}{2m}\right)\vec{s} \rightarrow 1.8$$

The factor g_s is different for the electron, proton and neutron. Similarly, we introduce a factor g_l and have

$$\vec{\mu}_l = g_l\left(\frac{\mu_0 e}{2m}\right)\vec{l} \longrightarrow 1.9$$

The total magnetic dipole moment ' $\hat{\mu}$ ' is given as

$$\vec{\mu} = \vec{\mu}_s + \vec{\mu}_l = \left(\frac{\mu_0 e}{2m}\right)\left(g_s\vec{s} + g_l\vec{l}\right) \longrightarrow 1.10$$

For the nucleus of mass number A , magnetic dipole moment

$$\vec{\mu} = \frac{\mu_0 e}{2m}\left(\sum_{k=1}^{A} g_s\vec{s}_k + \sum_{k=1}^{Z} g_l\vec{l}_k\right) \longrightarrow 1.11$$

Since total angular momentum of the nucleus.

$$\vec{I} = \sum_{k=1}^{Z}\vec{l}_k + \sum_{k=1}^{A}\vec{s}_k \longrightarrow 1.12$$

$$\vec{\mu} = g\left(\frac{\mu_o e}{2m}\right)\vec{I} = g\left(\frac{\mu_o e\hbar}{2m}\right)\frac{\vec{I}}{\hbar} \longrightarrow 1.13$$

Where 'g' is the gyromagnetic ratio (g – factor) of the nucleus. It is the dimensionless ratio of the magnetic moment 'μ' in terms of μ_0 eħ/2m to the angular momentum in terms of ħ .

The magnetic dipole moment is measured in terms of nuclear magneton, defined as

$$\mu_N = \frac{\mu_o e\hbar}{2m_p} = \frac{\mu_0 e\hbar}{2m_n} \text{.............................} 1.14$$

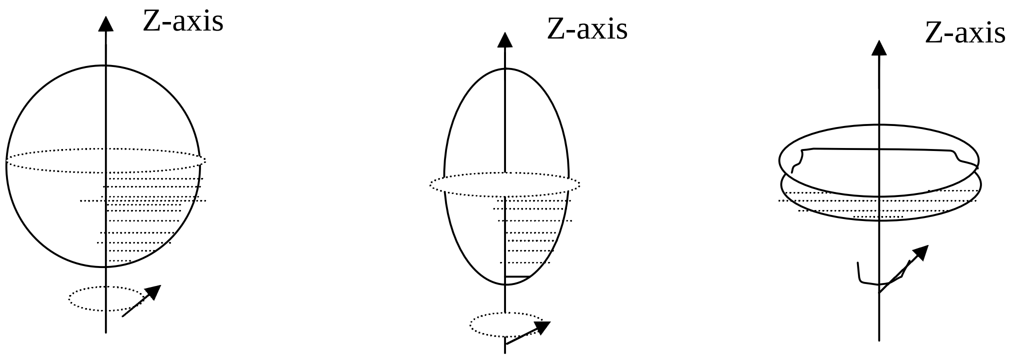
$$= 3.152 \text{ X } 10^{-8} \text{ ev} - \text{m}^2 {}_{/\text{ weber.}}$$

The magnetic moment of even- odd and odd – even nuclei is due to only a single (unpaired) nucleon. If the odd nucleon is a proton $g_l = 1$, $g_s = g_p$ and if it is a neutron $g_l = 0$, $g_s = g_n$ .In this case S = ½ and $I = l + \frac{1}{2}$ or $l - \frac{1}{2}$

1.8 CLASSICAL MULTIPOLE MOMENTS FOR POINT CHARGES:-

In addition to its magnetic moment a nucleus may have an electric quadrupole moment. The property may be thought of as arising from an elliptic charge distribution in the nucleus. We will show that a nucleus can have a quadruple moment only if its angular momentum $I \geq 1$.

1. The quadrupole moment would be zero if the +ve charge on a nucleus was distributed in a completely symmetrical spherical manner.
2. If the quadrupole moment would be +ve if the charge distribution, instead of being spherical, is drawn out in the direction of the spin axis in the form of prolate shape.
3. The quadrupole moment is -ve when the charge distribution is flattened about the spin axis in the form of oblate shape.



Spherical shape
Q = 0

Prolate shape
Q = +ve

Oblate shape
Q = -ve

Fig.1.3 Illustration of quadrupole moment

As nucleus in a stationary state does not possess a dipole moment because the center of mass and center of charge can be assumed to coincide with each other. If the charge is not concentrated at the origin, then the potential at any point P, situated outside the nucleus

along the Z- axis and a distance ‘ R’ from the center of the nucleus, due to a charge ‘e’ located at a point A(x,y,z) as shown in fig. is given by

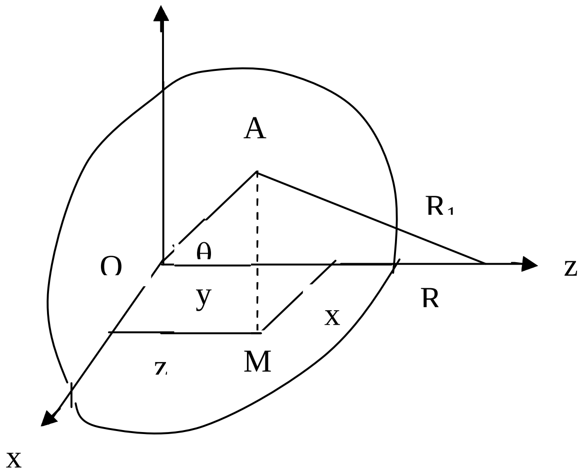


Fig. 1.4.Classicial picture for multipole moments

$$\phi_p = \frac{e}{4\pi\varepsilon_0 R_0} = \frac{e}{4\pi\varepsilon_0 \left(R^2 + r^2 - 2RrCos\theta\right)^{1/2}}$$

$$= \frac{e}{4\pi\varepsilon_0 R\left(1 + \frac{r^2}{R^2} - \frac{2r}{R}Cos\theta\right)^{1/2}}$$

$$= \frac{e}{4\pi\varepsilon_0 R}\left(1 + \frac{r^2}{R^2} - \frac{2r}{R}Cos\theta\right)^{-1/2} \longrightarrow 1.15$$

In the Legendre polynomial we define the generating function

$$(1-2zx+z^2)^{-1/2} = \sum_{n=0}^{\infty} z^n P_n(x) \ldots\ldots\ldots\ldots\ldots\ldots 1.16$$

In the present case $\frac{r}{R} = z, \quad \cos\theta = x$

$$\left(1 + \frac{r^2}{R^2} - \frac{2r}{R} Cos\ \theta\right)^{-1/2} = 1 + \frac{r}{R} P_1 (Cos\ \theta) + \frac{r^2}{R^2} P_2 (Cos\ \theta) + \ldots\ldots\ldots \longrightarrow 1.17$$

From eqn 1.17 therefore, in the Legendre polynomial

we know that

$$P_1 (\cos\theta) = \cos\theta$$

$$P_2 (\cos\theta) = \frac{3\cos^2\theta - 1}{2}$$

$$P_3(\cos\theta) = \frac{5Cos^3\theta - 3Cos\theta}{2} \qquad \text{-------------}1.18$$

Substituting eqn (1.18) in eqn (1.17)

$$\left(1 + \frac{r^2}{R^2} - \frac{2r}{R} Cos\theta\right)^{-1/2} = 1 + \frac{r}{R} Cos\theta + \frac{r^2}{R^2}\left(\frac{3Cos^2\theta - 1}{2}\right) + \frac{r^3}{R^3}\left(\frac{5Cos^3\theta - 3Cos\theta}{2}\right) + \ldots\ldots \longrightarrow 1.19$$

Substituting eqn (1.19) in eqn (1.15)

$$\phi_p = \frac{e}{4\pi\varepsilon_0 R}\left(1 + \frac{r}{R} Cos\theta + \frac{r^2}{R^2}\left(\frac{3Cos^2\theta - 1}{2}\right) + \frac{r^3}{R^3}\left(\frac{5Cos^3\theta - 3Cos\theta}{2}\right) + \ldots\ldots\right)$$

$$\phi_p = \frac{e}{4\pi\varepsilon_0 R} + \frac{er}{4\pi\varepsilon_0 R^2} Cos\theta + \frac{er^2}{4\pi\varepsilon_0 R^3}\left(\frac{3}{2} Cos^2\theta - \frac{1}{2}\right) + \ldots\ldots\ldots\ldots \longrightarrow 1.20$$

Here ‘θ’ is the angle between the r–direction and the z- axis. The term ‘er’ the product of charge and length, is referred to as the electric dipole moment. The term er^2 , the product of charge and a surface area (r^2), is the electric quadrupole moment. The next term is called the octupole moment. Thus in the above equation the coefficients of 1/R, $1/R^2$,$1/R^3$, and so on are the monopole, z- component of the dipole moment, z- component of the quadrupole moment and z- component of octupole moment respectively exhibited at a point P(0,0,R).Thus even a single isolated charge exhibits a quadrupole and other moments if it is not located at the origin of co-ordinates.

Substituting Cos θ = z/r in the above equation for the coefficient of $1/R^{3,}$ the effective classical quadrupole moment in the direction z exhibited at point P(0,0,R) is given by

$$q = \frac{1}{2} e\left(3z^2 - r^2\right) \ldots\ldots\ldots\ldots\ldots 1.21$$

The classical quadrupole moment would be eR^2 for a single proton situated at the nuclear radius R along the body axis. It would be -1/2 eR^2, for a single proton situated at the nuclear equator (z= 0 and r = R). Thus we can prove easily that the net quadrupole moment is zero for any spherically symmetric distribution of +ve charge in the nucleus. The nucleus will possess a net electric quadrupole moment, if there is one or more protons in addition to a symmetric distribution. It may have +ve or -ve value depending upon the position of the proton.

1.9 ELECTRIC QUADRUPOLE MOMENT:-

We now consider how the internal distribution of nuclear charge contributes to the effective moments. We place a nucleus having a charge density ρ(x y z) with its charge center at the origin. As the nucleus is surrounded by its orbital electrons hence an electrostatic potential Φ which originates from these electrons produces an electrostatic interaction energy, resulting from the interaction between φ and ρ. This energy is defined as

$$U = \int_v \rho(x,y,z)\phi(x,y,z)dv \longrightarrow 1.22$$

Taylor's series expansion of $f(x,y)$ is the neighbourhood of (a,b) is given

$$f(x,y) = f(a,b) + \frac{1}{1!}\left[(x-a)\frac{\partial}{\partial x} + (y-b)\frac{\partial}{\partial y}\right]_{\substack{x=a\\y=b}} f(a,b) + \frac{1}{2!}\left[(x-a)\frac{\partial}{\partial x} + (y-b)\frac{\partial}{\partial y}\right]^2_{\substack{x=a\\y=b}} f(a,b) + \dots\dots\dots$$

$$+\frac{1}{n!}\left[(x-a)\frac{\partial}{\partial x} + (y-b)\frac{\partial}{\partial y}\right]^n_{\substack{x=a\\y=b}} f(a,b) + \dots\dots\dots\dots\dots\dots 1.23$$

To express this energy in terms of the electric moments of the distribution, we expand the potential in a Taylor's series about the origin as

$$\phi(x,y,z) = \phi_0 + \left[\left(\frac{\partial\phi}{\partial x}\right)_0 x + \left(\frac{\partial\phi}{\partial y}\right)_0 y + \left(\frac{\partial\phi}{\partial z}\right)_0 z\right] + \left[\frac{1}{2}\left(\frac{\partial^2\phi}{\partial x^2}\right)_0 x^2 + \frac{1}{2}\left(\frac{\partial^2\phi}{\partial y^2}\right)_0 y^2 + \frac{1}{2}\left(\frac{\partial^2\phi}{\partial z^2}\right)_0 z^2\right] +$$

$$\left[\left(\frac{\partial^2\phi}{\partial x\partial y}\right)_0 xy + \left(\frac{\partial^2\phi}{\partial x\partial z}\right)_0 xz + \left(\frac{\partial^2\phi}{\partial y\partial z}\right)_0 yz\right] + \dots\dots\dots\dots\dots\dots\dots\dots \longrightarrow 1..24$$

Where the subscript ‘0’ means that the quantity is evaluated at the origin. Inserting this value in eqn (1) with the idea that each of the derivatives in constant with respect to the variable of integration, we get

$$U = \phi_0 \int \rho dv + \left[\left(\frac{\partial \phi}{\partial x} \right)_0 \int x\rho dv + \left(\frac{\partial \phi}{\partial y} \right)_0 \int y\rho dv + \left(\frac{\partial \phi}{\partial z} \right)_0 \int z\rho dv \right] +$$

$$\left[\begin{array}{l} \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial x^2} \right)_0 \int x^2 \rho dv + \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial y^2} \right)_0 \int y^2 \rho dv + \\ \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial z^2} \right)_0 \int z^2 \rho dv + \left(\frac{\partial^2 \phi}{\partial x \partial y} \right)_0 \int xy\rho dv + \left(\frac{\partial^2 \phi}{\partial x \partial z} \right)_0 \int xz\rho dv + \left(\frac{\partial^2 \phi}{\partial z \partial y} \right)_0 \int zy\rho dv + \ldots\ldots\ldots \end{array} \right] +$$

+ higher order terms ………..(1.25)

The first term gives simply the interaction energy of a point charge (mono pole). The three terms in the first bracket give the energy of a dipole. The six terms in the second bracket are the quadrupole energy terms. The above relation can be written in tensor form as

$$U = \phi_0 \int \rho dv + \left(\frac{\partial \phi}{\partial x_i} \right)_0 \int x_i \rho dv + \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial x_i \partial x_j} \right)_0 \int x_i x_j \rho dv + \ldots\ldots\ldots\ldots\ldots\ldots\ldots \longrightarrow 1.26$$

Here integrals are the various moments of the distribution.

Let us now discuss quadrupole energy terms. For an ellipsoid of rotations, because of symmetry, the three integrals involving the cross products xy, yz and xz vanish. When the z-axis is the symmetry axis the integral over y^2 gives the same result as the integral over x^2.

i.e. $x^2 = y^2$

Thefore, quadrupole interaction energy is

$$\Delta U_2 = \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial z^2} \right)_0 \int z^2 \rho dv + \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) \int \frac{x^2 + y^2}{2} \rho dv \ldots\ldots\ldots\ldots\ldots\ldots \longrightarrow 1.27$$

From Laplace’s equation, we have $\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$

By substituting this and equation of sphere $r^2 = x^2 + y^2 + z^2$, we get

$$\Delta U_2 = \frac{1}{4}\left(\frac{\partial^2\phi}{\partial z^2}\right)_0 \int \left(3z^2 - r^2\right)\rho dv$$

$$= \frac{1}{4} eQ \left(\frac{\partial^2\phi}{\partial z^2}\right)^0 \longrightarrow 1.28$$

where the quadrupole moment Q is defined as

$$Q = 1/e\int(3z^2 - r^2)\,\rho dv\text{--------}(1.29)$$

This relation shows that

1. Q = 0 for a spherically symmetric charge distribution $\{\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \frac{1}{3} r^2\}$
2. Q is +ve when $3z^2 > r^2$ and the charge distribution is stretched in the z-direction (prolate)
3. In an oblate distribution when $3z^2 < r^2$ and Q is –ve. Since the expression is divided by the electric charge, the dimension of the quadrupole moment is that of an area. As it is very small , hence it is measured in 'barns' in nuclear physics.

(1 barn = 10^{-28} m^2)

1.10 .Summary.

The methods of measuring nuclear radius are divided in to two main categories . One group of method is based on the study of the range of nuclear forces in which the nucleus is probed by a nucleon of light nucleus. Other group of methods studies the electric field and charge distributions of the nucleus in which the nucleus is probed by electron or muon(μ -meson). Prout suggested that all atomic weights were whole numbers and hence could be assumed as the integral multiple of the atomic weight of hydrogen.The slight change in the whole number was explained by the presence of two or more isotopes. The experimental discovery of the neutron led Heisenberg in 1932 to suggest that the nuclei might be composed of proton and neutrons rather than of protons and electrons. Thus for an atom $_zX^A$,the nucleus contains Z protons and (A-Z) neutrons.

For a nuclide $_zX^A$, we write $_ZM^A$ for its actual atomic mass and ZM_H *and* NM_n for the total mass of its constituents . The difference may be written as

$$\{ZM_H + (A - Z)M_n\} -_Z M^A = \Delta_Z M^A$$

This difference $\Delta_Z M^A$ is known as mass defect.

we can say that mass defect $\Delta_z M^A$ appears as an equivalent amount of energy ΔE on forming a nucleus. ΔE is the energy released, due to the decrease of mass, when nucleus is formed by fusing together the requisite number of nucleons; alternately it is the energy required to separate the nucleons of nucleus. It is referred as the binding energy of the nucleus, B.E.

Keywords:

Packing fraction, Mass defect, dipole moment, point charge, Quadrupole moment

Self assessment questions:

1. Define massdefect. Explain the binding energy of nuclei. Analyse the important features of binding energy per nucleon.
2. Derive an expression for magnetic dipole moment of nuclei.
3. Obtain an expression for electric quadrupole moment of nuclei.

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel.

Unit 1

Lesson 2

NUCLEAR FORCES

The objectives of the lesson are to explain the following:

2.1 Introduction

2.2 Properties of nuclear forces

2.3 Inferences drawn from the experimental data of Deuteron

2.4 Ground state of Deuteron

2.5 Summary

2.1 Introduction:

Earlier we considered the curve of binding energy per nucleon against the mass number (B/A against A curve). The value of B/A is approximately constant and it is about 8Mev/nucleon. This is about a million time higher than the binding energy of an electron in the hydrogen atom (which is 13.6eV). In other words, the force that keeps the nucleus together is much stronger than the electrical force which keeps the atom together. Also , this nuclear force must be stronger than the electrical force between the protons since protons are bound in the nuclei.

What holds the nucleus together? Bound systems are held together by forces. The earth is bound to the sun because of the gravitational force between them. The electron in a hydrogen atom is bound to the nucleus (which is just a proton) because of the account for the existence of nuclei. The gravitational attractive force between two protons is smaller by a factor of about 10^{39} than t he electrical repulsive force between them. In fact, it is customary to neglect the effects of gravity when one consider atoms or nuclei. Thus, one must recognize the existence of a third force in nature, the nuclear force. Further this nuclear force must be much stronger than the electric force; otherwise protons cannot live in close proximity as they do inside a nucleus. This is also expected from the B/A against A curve. When we discussed the size of the nucleus we saw that in a Rutherford α-scattering experiment, a departure from Coulomb law was observed with light elements as targets, only with the most energetic α-particles. This clearly showed that the effect or range of the nuclear force must be of the order of the nuclear radius. In other words the nuclear force is a short-range force. It falls off more rapidly with distance than $1/r^2$.

In general the force between nucleons of a nucleus are of four types.

1. Coulomb's electrostatic forces
2. Nuclear forces.
3. Tensor forces
4. Hard core repulsive forces

2.2. Properties of Nuclear forces:

1. The nuclear forces are short range forces
2. Nuclear forces are saturated forces
3. Nuclear forces are charge independent
4. Nuclear forces are spin dependent

2.2.1.Very short range forces:-

Nuclear forces are very short range of 10^{-15}m. The short range property has been defined from the deuteron problem. At greater distance these forces are negligible.

2.2.2.Saturation Property:-

Nuclear forces are saturated forces. It means that each nucleons attracts only those nucleons which are immediate neighbours. It does not interact with all other nucleons.

2.2.3.Charge independent :-

We know that the mass number 'A' is approximately equal to twice the atomic number 'Z' for the light and intermediate nuclei. It shows that the light nuclei prefer to odd nucleons in N –P pairs i.e. there is a strong interaction between neutron and protons.

For example ${}_2He^4$ has a more stability, this has mass number A = 4 there are 6 bonds , among these six bonds 4 associated with (n –p) forces and one each with (p –p) & (n –n) forces.

In spectral representation

(a) 1 s singlet configuration 1(np), 1(pp), 1(nn).

(b) 3 s triplet configuration 3(np)

the evidence of the light nuclei is that the corresponding nuclear forces are attractive in each of these states. The neutron excess in heavy nuclei, which is required to balance the coulomb repulsion of the protons, confirms that the 1(nn) (force) is attractive but it is insufficiently attractive to lead a stable di neutron.

The attractive nature of (n-p) (p-p) &(n-n) forces can be easily proved by considering a few simple nuclei. The relative stability of the deutron shows that (n –p) forces is attractive in nature and has appreciable magnitude. The addition of an extra neutron to form T^3 nucleus or of an extra proton to yield $_2He^3$ nucleus is accompanied by a marked increasing of binding energy, partly due to (n-n) and (p-p) forces respectively. In T^3 there a re two (n-p) & one (n-n) forces, while in $_2He^3$ there exist two (n-p) and one (p-p) forces. Their interaction can be represented as

$$T^3 \longrightarrow 3(np) + 1(np) + 1(nn)$$

$$He^3 \longrightarrow 3(np) + 1(np) + 1(pp)$$

The binding energies of T^3 and He^3 are 8.48 Mev and 7.72Mev, respectively. The binding energy difference is 0.76Mev.If (n-n) & (p-p) forces are identical them this difference of energy should be attributed to coulomb energy difference which is

$$E_c = \frac{3}{5}\frac{e^2}{4\pi\varepsilon_0 R^2}\left(Z(Z-1)\right)$$

And r = 2f this gives 0.76Mev, confirming there by (n-n) and (p-p) forces are charge symmetric.

2.2.4.Spin dependent of Nuclear forces:

The coherent scattering is obtained when slow energy neutrons strike the molecular hydrogen. It is known that molecular hydrogen at room temperature consists of 3 parts of ortho hydrogen (two proton with parallel spin) and one part of para hydrogen (spin are antiparallel) and the conversion rate of one into the other is very slow in the absence of a suitable catalyst. The molecular study of hydrogen reveals that ortho –hydrogen ever (0,2, 4 …..) rotational states, indicating there by that para-hydrogen possesses the minimum energy (spin is also zero). Thus, at low temperatures ($\approx 20^0$K) in presence of charcoal (catalyst) almost all hydrogen is in para –form. At low temperature de Broglie wavelength of incident neutron is 7 x 10^{-8} cm which is about nine times the separation of two protons (0.74 x10^{-8} cm) in hydrogen molecule.

Under these conditions (two protons may be assumed at the same place from the point of view of incident and scattered waves) the scattered waves from two protons will interfere appreciably and coherent scattering will take place. The scattering of unpolarised neutrons from para – hydrogen will be a coherent mixture of singlet and triplet scattering for in para-hydrogen spins are antiparallel and hence one of the proton spin will be parallel to and other one antiparallel to the spin of incident neutron. On the other hand the scattering from orthohydrogen either will be singlet or triplet one for the spins of incident neutron. On the other hand the scattering from orthohydrogen either will be singlet or triplet one for the spins of two protons are parallel.

The first theoretical investigation of coherent scattering has been provided by schrodinger and Teller.

The total nuclear spin of neutron and proton is writ ten as.

$$\hat{S} = \hat{S}_n + \hat{S}_p \ldots\ldots\ldots\ldots\ldots\ldots \rightarrow 2.1$$

In the operator form we write

$$\hat{S} \cdot \hat{S} = (\hat{S}n + \hat{S}_p) \ \cdot (\hat{S}n + \hat{S}_p) \ldots\ldots\ldots\ldots \rightarrow 2.2$$

$$\hat{S} \cdot \hat{S} = \hat{S}n \cdot \hat{S}n + \hat{S}n \cdot \hat{S}p + \hat{S}p \cdot \hat{S}n + \hat{S}p \cdot \hat{S}_P$$

$$\hat{S} \cdot \hat{S} = \hat{S}n \cdot \hat{S}n + 2\, \hat{S}n \cdot \hat{S}p + \hat{S}p \cdot \hat{S}p$$

$$2\, \hat{S}n \cdot \hat{S}p = \hat{S} \cdot \hat{S} - \hat{S}n \cdot \hat{S}n - \hat{S}p \cdot \hat{S}p$$

$$\hat{S}n \cdot \hat{S}p = \tfrac{1}{2} \{ \hat{S} \cdot \hat{S} - \hat{S}n \cdot \hat{S}n - \hat{S}p \cdot \hat{S}p\}$$

$$\hat{S}n \cdot \hat{S}p = \tfrac{1}{2} \{ S(S+1) - S_n(S_n+1) - S_p(S_p+1) \} \ldots\ldots\ldots\ldots \rightarrow 2.3$$

As $S_n = Sp = ½$.; Neutron and proton are ½ spin particles.

Equation (2.3) becomes

$$\hat{S}n \cdot \hat{S}p = \tfrac{1}{2} S(S+1) - 3/4 \ldots\ldots\ldots\ldots \rightarrow 2.4$$

Introducing now Pauli spin oplerator $\hat{S} = \frac{1}{2} \hat{\sigma} \ldots\ldots\ldots \rightarrow 2.5$

We write $\hat{\sigma}_n \cdot \hat{\sigma}_p = 4 \hat{S}n \cdot \hat{S}p$

$$= 2 S(S+1) - 3 \ldots\ldots\ldots\ldots \rightarrow 2.6$$

$$\hat{\sigma}_n \cdot \hat{\sigma}_p = -3 \text{ for singlet state ; } S = 0 \ldots\ldots\ldots\ldots \rightarrow 2.7$$

$$\hat{\sigma}_n \cdot \hat{\sigma}_p = 1 \text{ for triplet state; } S = 1 \ldots\ldots\ldots\ldots \rightarrow 2.8$$

with these conventions, a single expression can represent scattering, lengths for singlet state and triplet state i.e.

$$a_{t,s} = \tfrac{1}{4} (3a_t + a_s) + \tfrac{1}{4} (a_t - a_s) \hat{\sigma}_n \cdot \hat{\sigma}_p \ldots\ldots\ldots\ldots \rightarrow 2.9$$

To calculate the amplitude of the scattered of the scattered wave f_{Hy} the amplitude should be added directly

$$- f_{H_z} = a^1_{t,s} + a^{11}_{t,s} = \tfrac{1}{2} (3a_t + a_s) + \tfrac{1}{4} (a_t - a_s) \hat{\sigma}_n (\hat{\sigma}_{p1} + \hat{\sigma}p2)$$

$$= 1/2 (3a_t + a_s) + (a_t - a_s) \hat{S}n \cdot \hat{S}_H \ldots\ldots\ldots\ldots \rightarrow 2.10$$

where $\hat{\sigma}_{p1}$ & $\hat{\sigma}p2$ refers to the two protons and

$(\hat{\sigma}_{p1} + \hat{\sigma}p2) = 2 \hat{S}_{H.}$ total spin operator of hydrogen molecule.

Now the scattering cross-section are given by

$\sigma_{para} = 4\Pi\,(-\,f_{H_z})p2 = \Pi\,(3a_t + a_s)^2$ ……………….→2.11

and $\sigma_{ortho} = 4\Pi\,\{\,½\,(3a_t + a_s) + (a_t - a_s)\,\hat{S}_n.\hat{S}_H\}^2$ …………..→2.12

$\hat{S}_n.\hat{S}_H = 4\Pi\{\,¼\,(3a_t + a_s)^2 + (3a_t + a_s)\,(a_t - a_s)\,\hat{S}_n.\hat{S}_H + (a_t - a_s)^2\,\hat{S}_n{}^2.\hat{S}_H{}^2\,\}$ …….→2.13

The terms in equation (2.13) should be averaged for all originations of spin of neutrons and for this we write

$$<\{\hat{S}_n.\hat{S}_H\}^2> \;=\; <\{\,\hat{S}_{nx}\,\hat{S}_{Hx} + \hat{S}_{ny}\,\hat{S}_{Hy} + \hat{S}_{nz}\,\hat{S}_{Hz}\}^2\;>$$

$$= <\hat{S}_{nx}{}^2\,\hat{S}_{Hx}{}^2 + \hat{S}_{ny}{}^2\,\hat{S}_{Hy}{}^2 + \hat{S}_{nz}{}^2\,\hat{S}_{Hz}{}^2 + 2\,\hat{S}_{nx}\,\hat{S}_{Hx}\,\hat{S}_{ny}\,\hat{S}_{Hy} + 2\,\hat{S}_{ny}\,\hat{S}_{Hy}\,\hat{S}_{nz}\,\hat{S}_{Hz} + 2\,\hat{S}_{nx}\,\hat{S}_{Hx}\,\hat{S}_{nz}\,\hat{S}_{Hz}\;>$$ ……………→2.14

This gives $<\{\hat{S}_n.\hat{S}_H\}> = 0$

$$<\{\hat{S}_n.\hat{S}_H\}^2> \;=\; <\hat{S}_{nx}{}^2\,\hat{S}_{Hx}{}^2 + \hat{S}_{ny}{}^2\,\hat{S}_{Hy}{}^2 + \hat{S}_{nz}{}^2\,\hat{S}_{Hz}{}^2\;>$$

$$\hat{S}_{nx}{}^2 = \hat{S}_{ny}{}^2 = \hat{S}_{nz}{}^2 = ¼$$

$$\hat{S}_{Hx}{}^2 + \hat{S}_{Hy}{}^2 + \hat{S}_{Hz}{}^2 = \hat{S}_H{}^2$$

$$<\{\hat{S}_n.\hat{S}_H\}^2> \;=\; ¼\,\hat{S}_H{}^2 = ¼\,S_H(S_H + 1)$$

$$= 1/4\;1(1+1) = ½$$

For expression for cross-section can now be written as

$$\sigma_{para} = \Pi\,(3a_t + a_s)^2$$

$$\sigma_{ortho} = 4\Pi\,\{\,¼\,(3a_t + a_s)^2 + 1/2\,(a_t - a_s)^2\}$$

$\sigma_{ortho} = \sigma_{para} + 2\Pi(a_t - a_s)^2$ ………………→2.16

If n-p forces is spin – independent, $a_t = a_s$ and $\sigma_{ortho} = \sigma_{para}$. But the experimental values.

$$\sigma_{para} = 4 \text{ barns} \ \& \ \sigma_{ortho} = 125 \text{ barns.}$$

The large difference between two cross-section clearly suggests that n-p force is spin-dependent..

2.3 Inferences drawn from the experimental data of Deuteron:

The deuteron is the only two nucleon bound system and consists of one neutron and one proton. The experimentally measured data together with the inference drawn from them are outlined below.

1. charge = +e
2. Mass = 2.014735 amu
3. Radius of the deuteron: the radius of deuteron has been measured with the help of high energy electron scattering experiment. 2.1Fermi(1Fermi = 10^{-15} m).
4. Binding Energy: The binding energy of the deuteron is measured with high accuracy either by photo disintegration of deuteron or by (n-p) capture. The value is (2.225±0.002)Mev.
5. Angular Momentum(spin) : 1ħ
6. The result implies that in the deuteron ground state the intrinsic spin of neutron and proton have parallel alignment and no contribution from orbital motion of the two nucleons results. It further mean that in the ground state two nucleons lie in L = 0 i.e in spherically symmetric state.
7. Statistics: Bose – Einstein
8. Parity: Even
9. The magnetic moment:

It is measured with the help of magnetic resonance absorption method in which quantum energy needed to flip over a nucleus with its magnetic moment in the magnetic field is measured. Its value is 0.8754nm. The magnetic moment of deuteron is the addition of magnetic moments of proton and neutron but not difference of

μ_p =(2.7925±0.0001)nm μ_n = (- 1.9128 ±0.0001)nm

$$\mu_d = \mu_p + \mu_n = 0.8797\text{nm}$$

using the result of point (5), we say that deuteron is in the ground state and is spherically symmetric(L=0) and hence the magnetic moment of deuteron is due to the addition of proton and neutron magnetic moments and it cannot be due to the subtraction of the two. However, μ_d is not equal to the exact sum of μ_p and μ_n and difference (about 3%) is well outside the experimental error. But since the difference is small, we can infer the following points on the basis of above results.

(a) The ground state of deuteron is a triplet ($3s_1$) state i.e the spins of two nucleons are parallel.

(b) The orbital angular momentum in the ground state is zero. Because the other combination (L = 1, S =1) and L= 2 ,S =1) give the value of μ_d as0.677 nm and 0.323 nm which are very different from the experimental value.

(c) The neutron spin is ½

(d) Quadrupole moment: The quadrupole moment of deuteron has been measured by Rabi and his co-workers using radio frequency techniques and the result gives Q_d = 0.00202 barns (1 barn = 10^{-24} cm^2).It implies that charge distribution in the ground state is not spherically symmetric because a spherical charge distribution leads a value for Q_d = 0 or for the $\frac{z^2}{r^2} = \frac{1}{3}$.The result also indicate that charge distribution is of prolate shape,i.e., elongated along the z axis. This in turn emphasizes that spins of the particles are more found lined up one after the other rather than side by side.

Now the problem is how to account for the discrepancy in magnetic moment (of the order of 3%) and a non-zero quadrupole moment. The explanation was furnished by Schwinger and Rarita who suggested that ground state wave function is not strictly spherically symmetric(no strictly spherical charge distribution) but it is the combination of one spherically symmetric function and one non-spherically symmetric function.

The existence of spherically symmetric state 3_{S_1} is proved reasonable due to the very close resemblance of the μ_d with the sum $(\mu_n + \mu_p)$. The possible asymmetric states which are consistent with observed deuteron total angular momentum of unity, I =L+S = 1, three possible values of L which satisfy this relation are ${}^3P_1$, ${}^{1`}P_{1,}$ ${}^3D_1$. The two P states, however, give opposite parity for the system and these are excluded on the ground of conservation of parity which does not permit a bound system to have sometime the even parity and sometime the odd parity. Thus, the only alternative left is that ground state wave function is combination of ${}^3S_1$ and ${}^3D_1$ states. The function may be written as

$$\psi \ = a_s\psi_s + a_D\psi_D \text{.......................} 2.17$$

where ψ_s *and* ψ_D are the normalized wave functions in S and D states with total angular momentum I = 1 and ψ is normalized by writing

$$a_s^2 + a_D^2 \ = \ 1 \text{..................} 2.18$$

Now if it is assumed that deuteron spends part of its time is D-state then it will give some orbital magnetic moment which in turn explains the lack additivity of deuteron magnetic moment. The ${}^3D_1$ state also gives a charge distribution which is not spherically symmetric and explain the non-zero quadrupole moment. The observed values of magnetic moment and quadrupole moment are such that they demand 3.9% probability of existence of deuteron in ${}^3D_1$ and 96.1% in ${}^3S_1$ states. The probability in

${}^3D_1$ state is given by

$$\frac{a_D^2}{a_s^2 + a_D^2} = 0.039$$

$$= 3.9\%$$

Alternately, the above discussion may be summarized by saying that deuteron spends 96.1% time in ${}^3S_1$ and 3.9% time in ${}^3D_1$ and therefore, ground state of deuteron is mixture of ${}^3S_1$ and ${}^3D_1$ states.

GROUND STATE OF DEUTERON:

It has been said that deuteron is the simplest of two nucleon system and consists of one neutron and one proton. It is also mentioned that in most of the time deuteron is in the spherically symmetric state. Therefore, the following assumptions are

i) Deuteron consists of two particles of roughly equal ($M_n \cong M_p = M$) mass M., making there by the reduced mass

$$\mu = \frac{MM}{M+M} = \frac{M}{2} \text{.......................} 2.19$$

ii) The force between the two particles is short range and attractive and acts along the line joining the two particles and does not depend upon the orientations. It is a central force. However, this assumption appears to be in correct because, it can not account for the quadrupole moment of deuteron. But it is assumed here for the sake of mathematical simplicity.

iii)Since central force is conservative force and can be written as the gradient of some potential V(r)

$$\nabla V(r) = gradV(r)$$

$$\hat{F} = \left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z} \right) V(x, y, z)$$

$$\hat{F} = \hat{i}F_x + \hat{j}F_y + \hat{k}F_z$$

The Schrodinger equation for deuteron in the centre of mass system may be written as

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}(E - V)\psi = 0 \longrightarrow 2.20$$

where μ is reduced mass

∇^2 is laplacian operator $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

V is the potential energy describe the force between two nucleons.

E is the total energy of the system which is equal to B.E. of the deuteron.

Ψ is wave function.

In terms of spherical polar coordinates the schrodinger equation (2.20) is translated.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial\psi}{\partial r} \right) + \frac{1}{r^2 Sin\theta}\frac{\partial}{\partial\theta}\left(Sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{r^2 Sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E - V)\psi = 0 \longrightarrow 2.21$$

In the central force assumptions the wave function $\Psi(r,\theta,\Phi)$ is expressed as

$$\psi(r,\theta,\phi) = U_l^1(r) Y_{l,m}(\theta,\phi) \longrightarrow 2.22$$

substitute (2.22) in (2.21)

Multiplying through out by r^2 and then write radial and angular part terms separately

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\left(U_l^{1}(r)Y_{l,m}(\theta,\phi)\right)\right)\right]+\frac{1}{r^2Sin\theta}\left[\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial}{\partial\theta}\left(U_l^{1}(r)Y_{l,m}(\theta,\phi)\right)\right)\right]+$$

$$\frac{1}{r^2Sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2}\left(U_l^{1}(r)Y_{l,m}(\theta,\phi)\right)\right]+\frac{2\mu}{\hbar^2}(E-V)\left(U_l^{1}(r)Y_{l,m}(\theta,\phi)\right)=0$$

$$\Rightarrow\frac{1}{U_l^{1}(r)}\left[\frac{d}{dr}\left(r^2\frac{\partial U_l^{1}(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)\left(U_l^{1}(r)\right)\right]$$

$$=-\frac{1}{Y_{l,m}(\theta,\phi)}\left[\frac{1}{Sin\theta}\left[\frac{\partial}{\partial\theta}\left(Sin\theta\frac{\partial}{\partial\theta}Y_{l,m}(\theta,\phi)\right)\right]+\frac{1}{Sin^2\theta}\frac{\partial^2}{\partial\phi^2}\left(Y_{l,m}(\theta,\phi)\right)\right]\longrightarrow 2.23$$

Now equate the radial part term to some constant $l(l+1)$, *we have*

$$\Rightarrow\frac{1}{U_l^{1}(r)}\left[\frac{d}{dr}\left(r^2\frac{dU_l^{1}(r)}{dr}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)\left(U_l^{1}(r)\right)\right]=l(l+1)\longrightarrow 2.24$$

multiplying eqn(5) *bothsides by* $\frac{U_l^{1}(r)}{r^2}$

$$\Rightarrow\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dU_l^{1}(r)}{dr}\right)+\frac{2\mu}{\hbar^2}(E-V)\left(U_l^{1}(r)\right)=l(l+1)\frac{U_l^{1}(r)}{r^2}\longrightarrow 2.25$$

$$\Rightarrow\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dU_l^{1}(r)}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V(r)-\frac{l(l+1)\hbar^2}{2\mu r^2}\right]U_l^{1}(r)=0\longrightarrow 2.26$$

It is clear that the last term in the bracket, i.e., $\frac{l(l+1)\hbar^2}{2\mu r^2}$ is an addition to the actual potential V(r) and is known as centrifugal force, because its derivative with respect to 'r' is equal to classical centrifugal force when angular momentum is $\sqrt{l(l+1)}\hbar$. Thus , l represents orbital angular momentum quantum number. The function of centrifugal force is to disrupt the nucleus and therefore, the potential V(r) compensates the effect of centrifugal force at least over certain range of 'r'. The effect of centrifugal force will be minimum in the ground state (l=0) and the V(r) will be fully utilized in the binding the nucleons together.

In the groundstate $U_l^1(r)$ *is spherically symmetric and we can write*

$$U_l^1(r) = \frac{U(r)}{r} \longrightarrow 2.27$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\left(\frac{U(r)}{r}\right)\right) + \frac{2\mu}{\hbar^2}[E - V(r)]\frac{U(r)}{r} = 0$$

$$\Rightarrow \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{1}{r}\frac{dU(r)}{dr} - U(r)\right) + \frac{2\mu}{\hbar^2}[E - V(r)]\frac{U(r)}{r} = 0$$

$$\Rightarrow \frac{d^2U(r)}{dr^2} + \frac{2\mu}{\hbar^2}[E - V(r)]U(r) = 0$$

$$\frac{d^2U}{dr^2} + \frac{2\mu}{\hbar^2}[E - V(r)]U(r) = 0 \longrightarrow 2.28$$

Since force is every where attractive, the V(r) is negative and decreases with decreasing value of ‘r’. The following shapes have been proposed for potential V(r)

1. Exponential potential $V(r) = -V_0 e^{-\frac{r}{b}}$
2. The Gausian potential $V(r) = -V_0 e^{-\frac{r^2}{b^2}}$
3. Yukawa Potential $V(r) = -V_0 \frac{e^{-\frac{r}{b}}}{r/b}$
4. Potential with hard repulsive core

$V(r) = -V_0 e^{-r/b}$ for $r > b^1$

$V(r) = \alpha$ for $r < b^1 < b$

5.Square well potential $V(r) = 0$ for $0 < r < b^1$ Region (1)

$V(r) = -V_0$ for $b^1 < r < b$ Region (2)

$V(r) = 0$ for $r > b+b^1$ Region (3)

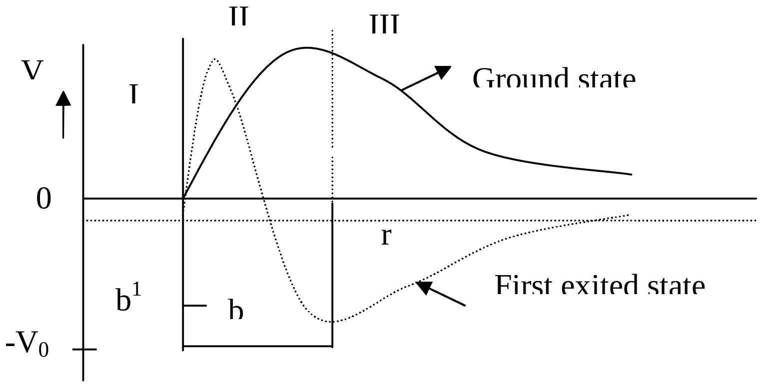


Fig: 2.1 The shapes of V(r) and u(r)

In all above representation 'b' is the range of the potential V(r) and V_0 is the depth of the potential well. The existence of hard repulsive core prevents the particles to come more closer than the distance b^1 and its presence is verified by scattering studies. Since the wave function is zero in the region I, we have only to solve it for the region II and III. The wave equation takes the following forms in region II and III

$$\frac{d^2U}{dr^2}+\frac{M}{\hbar^2}(-B+V_0)U(r)=0 \quad \text{……… Region (2)…………….2.29}$$

$$\frac{d^2U}{dr^2}+\frac{M}{\hbar^2}(-B)U(r)=0 \text{……………….. Region (3)…………..2.30}$$

Where 'B' is Binding energy of deuteron.

In eqn (2.29) & (2.30) V_0 & B are +ve numbers and B value is 2.225Mev

Put $\frac{M}{\hbar^2}(V_0-B)=k^2$ in eqn (2.29)

$\frac{M}{\hbar^2}B=\alpha^2$ in equation (2.30)

$$\frac{d^2U}{dr^2} + k^2U = 0 \longrightarrow 2.31$$

$$\frac{d^2U}{dr^2} - \alpha^2U = 0 \longrightarrow 2.32$$

General solution of eqn (2.31) & (2.32) are

$$U(r) = A \text{ Sin } kr + B \text{ Cos } kr \longrightarrow 2.34$$

$$U(r) = ce^{-\alpha r} + De^{\alpha r} \longrightarrow 2.35$$

The following boundary condition must be imposed

By using the boundary conditions

For well behaved function $\psi(r) = \dfrac{u(r)}{r}$ *as* $r \to 0,$ *the* ψ *is finite and* $r \to \infty,\ \psi$ *vanishes*

$$\psi(r) = \frac{u(r)}{r} = Ak \quad \underset{r\to 0}{Lt} \frac{Sinkr}{kr} + B\frac{Coskr}{r}$$

As $r \to 0 \quad finite = finite + B \quad Infinite(If \ there \ is \ no \ restriction \ on \ B$

In order to make LHS =RHS, B should be zero.

For well behaved function the solutions of eqn (2.34) becomes

$$\Rightarrow U(r) = ASinkr \longrightarrow 2.36$$

For well behaved function the solution (2.35) also becomes

$$\Rightarrow U(r) = ce^{-\alpha r} \longrightarrow 2.37$$

Further the wave function U(r) is also zero at r = b^1

There fore, the solution of equation can be written as

U(r) = Sin (r –b^1)

At boundary of the two regions i.e. r = b + b^1

The function u(r) and its derivative are continuous i.e., at r = b + b^1

This gives ASinkb $= ce^{-\alpha\left(b+b^1\right)}$

$$ASinkb = ce^{-\alpha\left(b+b^1\right)} \longrightarrow (2.38)$$

$$AkCoskb = -c\alpha c^{-\alpha\left(b+b^1\right)} \longrightarrow (2.39)$$

Divide (2.39) by (2.38)

$$KCotkb = -\alpha \longrightarrow (2.40)$$

$$\Rightarrow Cotkb = -\frac{\alpha}{k}$$

From eqn (2.29) & (2.30) $K = \frac{\sqrt{m(V_0 - B)}}{\hbar}, \alpha = \frac{\sqrt{mB}}{\hbar}$

$$Cotkb = -\frac{\alpha}{k} = \frac{\sqrt{mB}}{\hbar} \Big/ \frac{\sqrt{m(V_0 - B)}}{\hbar} = -\sqrt{\frac{B}{V_0 - B}} \longrightarrow 2.41$$

As B is much smaller than V_0 it implies that Cotkb is negative and small, which means that kb should be slightly larger $(2n+1)\frac{\pi}{2}$ where n = 0,1,2,3,…………..

$$kb = \frac{\pi}{2}$$

$$k^2 b^2 \approx \frac{\pi^4}{4} \longrightarrow (2.42)$$

Substitute ‘k’ value in eqn (2.42)

$$\Rightarrow \frac{m(V_0 - B)b^2}{\hbar^2} = \frac{\pi^2}{4}$$

neglecting B,

$$\Rightarrow \frac{m(V_0)b^2}{\hbar^2} = \frac{\pi^2}{4} \Rightarrow V_0 = \frac{\pi^2 \hbar^2}{4mb^2}$$

$$V_0 = \frac{\pi^2 \hbar^2}{16\pi^2 mb^2} = \frac{h^2}{16b^2 m}$$

If we take range b = 2 fermi, then

$$= \frac{\left(6.67 \times 10^{-34}\right)^2}{16\left(2 \times 10^{-15}\right)^2 \left(1.674 \times 10^{-27}\right)\left(1.6 \times 10^{-15}\right)}$$

$$= 25.5Mev$$

In the figure(2.1), the plot of U(r) versus 'r' shows that beyond r = b, the function U(r) decreases exponentially with 'r'. The radial distance at which the amplitude of function $U(r) = ce^{-\alpha r}$ is 1/e of its maximum amplitude is often called the radius of the deuteron.

$$\text{Radius} \qquad R_d = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{mB}} = 4.31 \times 10^{-15}$$

The ground state total wave function in the two regions can be written as

$$\psi(r,\theta,\phi) = U_l^{\,1}(r) Y_{l,m}(\theta,\phi)$$

$$U(r) = ASink\left(r - b^1\right)$$

$$U(r) = ce^{-\alpha r}$$

$$U_l^{\,1}(r) = \frac{U(r)}{r}$$

$$\psi_{II} = \frac{U(r)}{r} Y_{0,0} = \frac{1}{\sqrt{4\pi}} \frac{U(r)}{r} = \frac{1}{\sqrt{4\pi}} \frac{ASink(r - b^1)}{r} \text{ .... Region (2)}$$

$$\psi_{III} = \frac{1}{\sqrt{4\pi}} \frac{ce^{-\alpha r}}{r} \text{ .... Region (3)}$$

2.5.Summary:

The value of B/A is approximately constant and it is about 8Mev/nucleon. This is about a million time higher than the binding energy of an electron in the hydrogen atom (which is 13.6eV). In other words, the force that keeps the nucleus together is much stronger than the electrical force which keeps the atom together. Also , this nuclear force must be stronger than the electrical force between the protons since protons are bound in the nuclei.

This is also expected from the B/A against A curve. When we discussed the size of the nucleus we saw that in a Rutherford α-scattering experiment, a departure from Coulomb law was observed with light elements as targets, only with the most energetic α- particles. This clearly showed that the effect or range of the nuclear force must be of the order of the nuclear radius. In other words the nuclear force is a short-range force. It falls off more rapidly with distance than $1/r^2$.

The nuclear forces are short range forces, saturated forces, charge independent and spin dependent.

The observed values of magnetic moment and quadrupole moment are such that they demand 3.9% probability of existence of deuteron in ${}^3D_1$ and 96.1% in ${}^3S_1$ states.

Keywords:

Nuclear forces, Deuteron , Spin

Self assessment questions:

1. What are the characteristics of nuclear forces?
2. How do you determine the binding energy, magnetic moment and quadrupole moment of deuteron?
3. Obtain an expression for the total wave function for the ground state of deuteron on the basis of central force assumption..

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel

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Unit 1

Lesson 3

NUCLEON –NUCLEON SCATTERING

The objectives of the lesson are to explain the following:

3.1. Introduction

3.2. Proton – Proton scattering at low Energies:

3.3. Neutron – Proton scattering at low Energies:

3.4. Meson Theory of Nuclear Forces(Yukawa Potential)

3.5. Summary

3.1.Introduction: Since we use the principles of wave mechanics on nuclear problems and then by comparison with experimental data, find a consistent description of the nuclear forces acting between two nucleons (two body problem). We have seen the study of deuteron (only bound state of two nucleons) in previous chapter. There are two general methods of investigation, the study of n-p and p-p scattering events over a wide range of energy.

3.2.Proton – Proton scattering at low Energies:

The P-P scattering is the only way to get direct evidence on proton-proton force. There are two essential differences between p-p and n-n scattering. First, the p-p scattering is caused not only by nuclear force but also by the coulomb force. Second, the scattering and scattered particles are identical and obey the pauli exclusion principle and therefore, the wave function describing the two protons must change sign on the interchange of the two particles Hence a symmetric space wave function (s, d states etc) can only be associated with an anti-symmetric spin wave function. Where as a symmetric (triplet) spin wave function is required for an anti-symmetric space wave function.

Experimentally the study of p-p scattering, is capable much higher accuracy than n-p scattering, for the following reasons.

1. Protons are easily available over a wide range of energies
2. Protons can be made mono energetic
3. protons can be produced in well collimated beam.
4. Protons can be easily detected by their ionizing properties.
5. Protons undergo coulomb scattering. This increases the sensitivity in case one of the scattering probabilities is small and also gives sign of the phase shifts resulting from nuclear scattering
6. The proton combination obeys Fermi statistics. This simplifies the analysis of p-p scattering.

We are now interested in obtaining a theoretical expression for the different elastic scattering cross-section of protons by protons. The theory is more complicated than that of n-p scattering because the coulomb potential appreciably distorts the incident wave even at finite distance.

The radial wave equation for the proton-proton system is

$$\frac{d^2U}{dr^2}+\frac{2m}{\hbar^2}\left[E-V(r)-\frac{e^2}{4\pi\varepsilon_0 r}-\frac{l(l+1)\hbar^2}{2mr^2}\right]\mu=0 \longrightarrow 3.1$$

where V(r) is the square well nuclear potential.

The Rutherford cross-section for coulomb scattering, of particle of charge z_1, e by a particle of charge z_2e the center of mass system is

$$d\sigma=\left[\frac{(z_1e)^2(z_2e)^2}{4(4\pi\varepsilon_0)^2m^2v^4}Co\sec^4\frac{\theta}{2}\right]2\pi Sin\theta d\theta \longrightarrow 3.2$$

where ‘ v ’ is the velocity of the incident particle, ‘ m’ is the reduced mass of the system and ‘θ’ is the angle of scattering in the center of mass system. For P-P scattering $z_1 = z_2 = 1$ $m = M/2$, ‘θ’ = $2\theta_1$ and $Sin\theta\, d\theta = 4Sin\theta_1\, Cos\theta_1\, d\theta$ (where θ_1 is in laboratory system.)

Thus in laboratory system, the cross-section becomes

$$d\sigma = \frac{e^4}{(4\pi\varepsilon_0)^2 E_0{}^2}\left[\frac{1}{Sin^4\theta_1} + \frac{1}{Cos^4\theta_1}\right] Cos\theta_1\, 2\pi Sin\theta_1 d\theta_1 \longrightarrow 3.3$$

Where $E_0 = \frac{1}{2} mV^2$ (Kinetic energy of incident proton in the laboratory system). The term containing $Cos^4\theta_1$ is added because each proton at angle θ_1 in the L – system is accompanied by a recoil proton at an angle(90- θ_1)

Eqn (3.3) does not agree with experiment even at low energies where nuclear scattering is negligible. Mott introduced a third term from wave mechanical consideration

Thus eqn (3.3) becomes

$$d\sigma = \frac{e^4}{(4\pi\varepsilon_0)^2 E_0{}^2}\left[\frac{1}{Sin^4\theta_1} + \frac{1}{Cos^4\theta_1} - \frac{Cos\left\{\frac{e^2}{4\pi\varepsilon_0 \hbar v}\log\tan^2\theta_1\right\}}{Sin^2\theta_1 Cos^2\theta_1}\right] Cos\theta_1\, 2\pi Sin\theta_1 d\theta_1 \longrightarrow 3.4$$

The -ve sign is because the proton obey Fermi Statistics. Second and third terms drop out for unlike charged particles. For proton energies, above 1Mev, $\frac{e^2}{4\pi\varepsilon_0 \hbar v} \succ \frac{1}{7}$ and cosine term is nearly unity. The third term is called Mott term. For, $\theta_1 = 0 \ or \ \frac{\pi}{2},\ for \ E_0 \succ 1Mev,$ the Mott term is simplified and the above equation reduces to

$$d\sigma = \frac{e^4}{(4\pi\varepsilon_0)^2 E_0{}^2}\left[\frac{1}{Sin^4\theta_1} + \frac{1}{Cos^4\theta_1} - \frac{1}{Sin^2\theta_1 Cos^2\theta_1}\right] Cos\theta_1\, 2\pi Sin\theta_1 d\theta_1 \longrightarrow 3.5$$

The main difference between proton and neutron seems to be of electric charge and the nuclear force apparently does not arise from charge. Therefore, in P-P scattering at low energies it is expected that only the l= 0 scattering processes will be affected by the nuclear potential, just as in n-p scattering. For s wave, nuclear scattering the complete differential scattering cross-section in laboratory system is given by

$$\frac{d\sigma}{d\Omega}=\frac{e^4}{(4\pi\varepsilon_0)^2 E_0{}^2}\left[\begin{array}{l}\dfrac{1}{Sin^4\theta_1}+\dfrac{1}{Cos^4\theta_1}-\dfrac{1}{Sin^2\theta_1 Cos^2\theta_1}-\dfrac{8\pi\varepsilon_0\hbar v Sin\delta}{e^2}\\ \left\{\dfrac{Cos\left[\delta_0+\dfrac{e^2}{4\pi\varepsilon_0\hbar v}\log Sin^2\dfrac{\theta}{2}\right]}{Sin^2\dfrac{\theta}{2}}+\dfrac{Cos\left[\delta_0+\dfrac{e^2}{4\pi\varepsilon_0\hbar v}\log Cos^2\dfrac{\theta}{2}\right]}{Cos^2\dfrac{\theta}{2}}\right\}\\ +\left(\dfrac{8\pi\varepsilon_0\hbar v}{e^2}\right)^2 Sin^2\delta_0\end{array}\right]Cos\theta_1 \longrightarrow 3.6$$

In this equation 1^{st} , 2^{nd} and 3^{rd} terms are due to coulomb repulsion, the 5^{th} term due to nuclear scattering and 4^{th} due to interference between the coulomb and nuclear scattering effects. This relation reduces to eq(3.5) for a pure coulomb field when nuclear phase shift δ_0 is zero, i.e. when there is no nuclear scattering. The 4^{th} term is useful in determining δ_0 when δ_0 is small , because it is linear in Sin δ_0 and it is large compared to the last term which involves $Sin^2\delta_0$ .The differential cross section is a complicated function of energy E_0, the angle of scattering and the phase shift δ_0. Differential cross section for P-P elastic scattering for 2.4 Mev protons is shown in fig. At small scattering angles the scattering is essentially pure coulomb scattering. The nuclear scattering predominates in the central region of angles, near a c.m angle of 90^0. At forward and backward angles, the dips are caused by interference between nuclear and coulomb scattering.

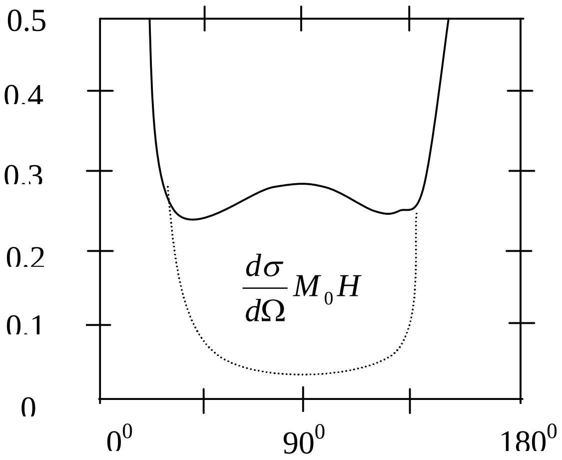


Fig. 3.1 Differential Scattering cross section for P-P scattering.

3.3.NEUTRON –PROTON SCATTERING AT LOW ENERGIES:

The fact that the deuteron is a bound system, shows that attractive forces exist between neutrons and protons. Further information on the inter-nucleon forces a can be obtained from a study of the scattering of free neutrons by protons. In such experiments a parallel bean of neutrons is allowed to impinge upon a target containing hydrogen atom and the number of neutrons deflected through various angles is determined as a function of neutron energy. Since neutrons have no charge, they are unaffected by the electrostatic field and their scattering will directly reflect the operation of the nuclear forces.

Two kinds of the reactions can be involved in neutron proton interaction .One scattering and other radiative capture .The latter has low probability and cross section for high energy neutrons ,as the cross section for the competing radiative capture reaction decreases with (1/V) ,where V is the neutron velocity. In practice protons are bound in molecules. The chemical binding energy of the proton in a molecule is about 0.1eV.Thus for neutron energies >1eV the proton can be assumed as free. This sets a lower limit to the neutron energy . If the neutron energy is less than 10MeV,only the S wave overlaps with the nuclear potential and scattered.

In the center of mass system, the Schrodinger equation for the two body(n-p system) problem is

$$\nabla^2\psi + \frac{M}{\hbar^2}\left(E - V(r)\right)\psi = 0 \longrightarrow 3.7$$

where M = proton or neutron mass = 2 × reduced mass of the system(m).

E= Incident K. E in c.m system

= ½ (incident K.E in L- co-ordinates)

and V(r) = Inter – nucleon potential energy.

At large distance from the center of scattering the solution of this equation is expected to be of the form

$$\psi = e^{ikz} + \frac{e^{ikr}}{r} f(\theta) \longrightarrow 3.8$$

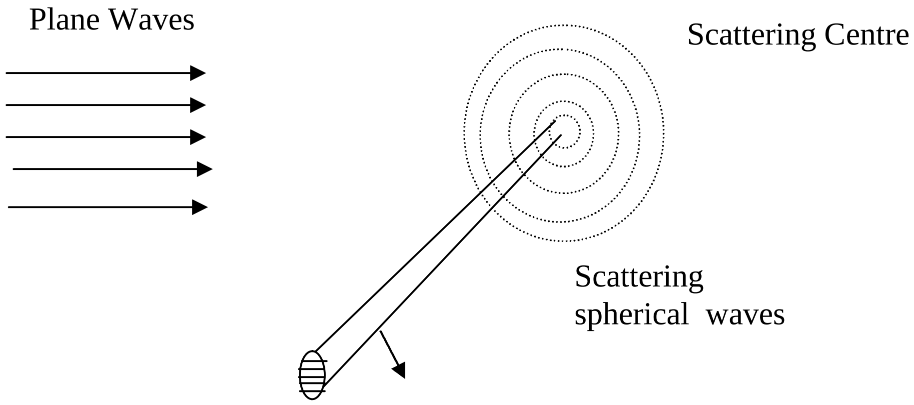


Fig.3.2. Scattering Process

The term represents a plane wave describing a beam of particles moving in the

z-direction towards the origin. The second term represents the scattered wave. The complex quantity f(θ) is the scattering amplitude in the direction θ and is to be evaluated in terms of K. In the case of a spherically symmetric potential the entire arrangement is axially symmetric about the incident direction and hence does not depend on the azimutal angle Φ the 1/r dependence is necessary for the conservation of particles in the outgoing wave. The volume of a spherical shell, between r and r + dr is and hence the density of particles in it or the probability of finding one particle in the spherical shell must vary with $1/r^2$ which is proportional to the square of the amplitude of the scattered wave in the shell. Hence the amplitude of the scattered wave must vary with 1/r.

To compute the differential scattering cross section, we must find the number of particles dN scattered in unit time by one target nucleus in to a solid angle d and the incident flux F. If V is the speed of an incoming particle with respect to the scattered , then

Incoming flux of particles F = $\psi_{in}{}^*\psi_{in}v = v$

Similarly dN is equal to the flux of scattered particle $\psi_{sc}{}^*\psi_{sc}v$ multiplied by the area r^2 dΩ on a spherical surface of radius r and is given by

$$dN = \psi_{sc}{}^*\psi_{sc}vr^2 d\Omega = \left|f(\theta)\right|^2 v d\Omega$$

The differential cross section $d\sigma = \left|f(\theta)\right|^2 v d\Omega = \left|f(\theta)\right|^2 d\Omega$

$$\text{or}\, \sigma = \int \left|f(\theta)\right|^2 d\Omega = 2\pi \int \left|f(\theta)\right|^2 Sin\theta d\theta \longrightarrow 3.9$$

First of all let us consider the wave equation (3.7) in the absence of a scattering center (v(r) = 0 for all values of r)

$$\nabla^2\psi + \left(\frac{mE}{\hbar^2}\right)\psi = 0 \longrightarrow 3.10$$

This has the solution $\psi = e^{ikz}$

$$\text{Where } \frac{1}{\lambda} = \sqrt{\frac{mE}{\hbar^2}} \longrightarrow 3.11$$

Lord Rayleigh proposed that this type of wave function can be expanded in to a series in terms of spherical harmonic functions Thus equation (3.11) can be written as an infinite series.

$$\psi = e^{ikz} = e^{ikrCos\theta} = \sum_{l=0}^{\alpha} R_l(r) Y_{l,0}(\theta) \longrightarrow 3.12$$

the radial function R_l (r) is the solution of the radial part of equation (3.10)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(K^2-\frac{l(l+1)}{r^2}\right)R=0\longrightarrow 3.13$$

This equation has two solutions, one is not finite at the origin and cannot represent the plane wave. The other is finite at origin and can be represented in terms of spherical Bessel functions as

$$R_l(r)=i^l\sqrt{4\pi(2l+1)}\,j_l(kr)\longrightarrow 3.14$$

Thus square of this gives the r- dependence of the probability density for each partial wave in expression (3.12). The values of first few spherical Bessel functions are.

$$j_0(kr)=\frac{Sinkr}{kr},\ j_1(kr)=\frac{Sinkr}{(kr)^2}-\frac{Coskr}{kr},$$
$$j_3(kr)=\left(\frac{3}{(kr)^3}-\frac{1}{kr}\right)Sinkr-\frac{3Coskr}{(kr)^2}$$

The spherical harmonic function.

$$Y_{l,0}(\theta\ )\ =\ \frac{(2l+1)^{1/2}}{(4\pi)^{1/2}}(Cos\theta)\longrightarrow 3.15$$

where $P_l(Cos\theta)$ is the Legendre polynomial of order l. The square of the spherical harmonic function gives the angular dependence of the probability density. The values of the first few Legendre polynomials are

$$P_0(Cos\theta)=1,\qquad P_1(Cos\theta)=Cos\theta\qquad P_2(Cos\theta)=\frac{3Cos^2\theta-1}{2}$$

For incident neutron kinetic energy les than 10 Mev the only partial wave involved in scattering is the l = 0 or S – wave.

In the absence of a scattering potential eqn(3.12) can be written

$$\psi = R_0(r)Y_{0,0}(\theta) + \sum_{l=1}^{\alpha} R_l(r)Y_{l,0}(\theta) = \frac{Sinkr}{kr} + \left(e^{ikz} - \frac{Sinkr}{kr}\right) \longrightarrow 3.16$$

The average value of the quantity with in the brackets over all directions in space is zero. The first term corresponds to the spherically symmetric partial wave (s – wave).For S-wave scattering, only the first term is affected and can therefore be written as in the presence of scattering potential V(r) . We can write it as $\psi_S = \frac{U(r)}{r}$

Thus as r $\longrightarrow \alpha$, the solution u(r) assumes the form $cSin(kr + \delta_0)$, where c is an arbitrary constant and δ_0 is some phase angle. Thus the complete wave function outside the scattering potential is

$$\psi = \frac{cSin(kr + \delta_0)}{r} + \left(e^{ikz} - \frac{Sinkr}{kr}\right)$$

$$= e^{ikz} + \frac{c}{r}\left(\frac{e^{ikr}e^{i\delta_0} - e^{-ikr}e^{-i\delta_0}}{2i}\right) - \frac{1}{kr}\left(\frac{e^{ikr} - e^{-ikr}}{2i}\right)$$

$$\psi \quad = e^{ikz} + \frac{e^{ikr}}{r}\left(\frac{ce^{i\delta_0} - 1/k}{2i}\right) - \frac{e^{-ikr}}{r}\left(\frac{ce^{-i\delta_0} - 1/k}{2i}\right) \longrightarrow 3.17$$

This scattering wave must contain no incoming wave therefore we can write the coefficient of e^{-ikr} as zero.

$$ce^{-i\delta_0} - 1/k = 0$$

$$\Rightarrow c = \frac{1}{k}e^{i\delta_0}$$

substitute above values in eq(3.17) then

$$\psi = e^{ikz} + \frac{e^{ikr}}{r}\frac{e^{2i\delta_0} - 1}{2ik} \longrightarrow 3.18$$

comparing this with the standard solution (3.9) we have

$$f(\theta)=\frac{e^{2i\delta_0}-1}{2ik}=\frac{e^{i\delta_0}}{k}\frac{e^{i\delta_0}-e^{-i\delta_0}}{2i}=\frac{e^{i\delta_0}}{k}Sin\delta_0 \longrightarrow 3.19$$

The total elastic scattering cross section is

$$\sigma_0 \;=\; 2\pi\int_0^{\pi}\frac{Sin^2\delta_0}{k^2}Sin\theta d\theta \;=\frac{4\pi}{k^2}Sin^2\delta_0 \;=\; 4\pi\lambda^2 Sin^2\delta_0 ....3.20$$

This analysis here is carried through only for $l = 0$ scattering

Higher orbital angular momentum waves also have to be considered at higher energies. The total cross-section can be written as a sum of partial cross-section , one for each l-wave. The partial cross-section

$$\sigma_l = 4\pi\bar{\lambda}^2(2l+1)Sin^2\delta_l \longrightarrow 3.21$$

Scattering length:

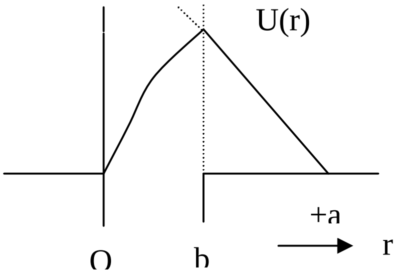
For neutrons of very low energy scattered by free protons, ƛ is very large and hence K is very small. It can be seen from eqn(3.19) that as K ⟶ 0 must also approach zero. Otherwise $f(\theta)$ would become infinite. Thus for low energy neutrons $f(\theta)$ can be written as

$$f_0 = \lim_{\delta_0\to 0}\frac{e^{i\delta_0}Sin\delta_0}{k}=\frac{\delta_0}{k}=-a \longrightarrow 3.22$$

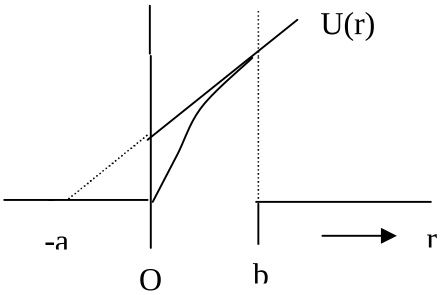
where the quantity + a is called the scattering length in the convention of Fermi and Marshall. Hence for low energy neutrons.

$$U(r)=c(kr+\delta_0)=ck(r-a)\longrightarrow 3.23$$

this is the equation of a straight line intersecting the r-axis at r = a, and is obtained by extrapolating the radial wave function u(r) from the point just beyond the range of the nuclear forces.



3.3.a Positive scattering length



3.3.b.Negative scattering length (unbound state)

Scattering from a potential giving a bound state produces a positive ‘a’. If the potential gives only a virtual state, the slope of the inner wave function at r = b is positive and ‘a’ is negative.

From eqn(3.20) & (3.22) the zero energy scattering cross section becomes

$$\sigma_0 = 4\pi a^2 \longrightarrow 3.24$$

This is identical with the scattering cross-section of an impenetrable sphere of radius ‘a’, in the limit of zero energy. The measurement of σ_0 determines the magnitude of the scattering length ‘a’ but not its sign.

Determination of the phase shift δ_0:

We shall now attempt to determine the phase shift δ_0 for low energy neutron - proton scattering by solving also the schrodinger’s equation in the region where the interaction between the two particles takes place. For this we make the simple assumption of a square well for the nuclear potential. Inside the well of depth V_0 and radius ‘b’ the radial wave equation for particles whose total energy has the positive value E is

$$\frac{d^2u}{dr^2}+\frac{M}{\hbar^2}(E+V_0)u(r)=0 \longrightarrow 3.25$$

Inside the square well this equation has the simple solution

$$u(r)=ASink_1r, where \quad k_1=\frac{\sqrt{M(E+V_0)}}{\hbar} \longrightarrow 3.26$$

Outside the square well, the solution can be written as

$$u(r)=B\,Sin(kr+\delta_0) \longrightarrow 3.27$$

At the edge of the rectangular well(r = b), the two solutions and their derivatives with respect to r must be continuous.

$$\therefore A\,Sink_1b=B\,Sin(kb+\delta_0)$$
$$k_1ACosk_1b=BkCos(kb+\delta_0)$$
$$Hence \quad k_1Cotk_1b=KCot(kb+\delta_0) \longrightarrow 3.28$$

From Deuteron problems

$$K \quad Cotkb=-\alpha$$

Which describes the binding energy B of the deuteron in terms of the same rectangular well (v_o ,b)

Here $K=\frac{\sqrt{M(V_0-B)}}{\hbar}$ and $\alpha = \frac{\sqrt{MB}}{\hbar}$

For low energy neutrons (E << V_o), we may assume K = k_1 (as V_o >> B), hence the wave function u(r) inside the well is nearly the same for the deuteron and the n-p scattering system. Thus for approximation can be written as

$$\frac{\sqrt{ME}}{\hbar}Cot\left(\frac{\sqrt{ME}}{\hbar}b+\delta_0\right)= -\frac{\sqrt{MB}}{\hbar}$$

As the scattering length ‘a’ is much larger than the range ‘b’ of the potential , thus for very low energy neutrons kb can be neglected in comparison to δ_0

$$\therefore \quad Cot\delta_0 = -\sqrt{\frac{B}{E}}$$

$$or \qquad Sin\delta_0 = \frac{\sqrt{E}}{E+|B|} \longrightarrow 3.29$$

substituting this value of $\sin^2\delta_0$ in equation (3.20) We obtain the approximate value of total scattering cross-section as

$$\sigma = 4\pi\hbar^2 \frac{E}{\left(E+|B|\right)^2}$$

$$= 4\pi\hbar^2\left(\frac{E}{E+|B|}\right)\frac{1}{E+|B|}$$

$$= \frac{4\pi\hbar^2}{M}\frac{1}{E+|B|} \longrightarrow 3.30$$

3.4.MESON THEORY OF NUCLEAR FORCES(Yukawa Potential):-

Any attractive force between two particles is regarded as the exchange of an attractive property. In molecular bonds, the valence electrons are exchanged. Now the natural question is “what is exchanged in nuclear bonds?” Is it electron , No it can not be ; because it leads to a very weak interaction. Yukawa, in 1935, proposed that nuclear forces are due to an exchange of particles of intermediate mass, known as mesons (Yukawa particle). Yukawa took the analogy from the quantum field theories of electromagnetic field in which photon exchange takes place and gravitational field in which exchange of graviton is assumed. Both these field particles have zero rest mass, but the nuclear field particles has finite rest mass. This is because of the difference that nuclear force is short range force while others are not. The rest mass m_π of the field particle may be computed as follows.

When one nucleon exerts force on the other, meson is created and the creation of meson violates the conservation of energy by amount ΔE corresponding to meson rest mass i.e.

$$\Delta E = m_\pi c^2 \longrightarrow 3.31$$

The duration of excursion of meson, Δt is given by uncertainty principle,

$$\Delta t \approx \frac{\hbar}{\Delta E} \longrightarrow 3.32$$

In this time meson can cover a distance R_0, given by

$$R_0 = c\Delta t = \frac{c\hbar}{\Delta E} \ldots\ldots\ldots\ldots\ldots 3.33$$

$$R_0 = \frac{c\hbar}{m_\pi c^2} = \frac{\hbar}{m_\pi c}$$

R_0 is the range of nuclear force and if we put $R_0 = 1.4$fermi

$$m_\pi = \frac{\hbar}{R_0 c} = \frac{0.045\times 10^{-34}}{1.4\times 10^{-15}\times 3\times 10^{8}.} \ldots\ldots\ldots\ldots\ldots\ldots 3.34$$

$$m_\pi = 270 m_e$$

$$\textit{where} \quad m_e \quad \textit{is the rest} \text{ mass of the electron}$$

$$= 9.109\times 10^{-31}\,Kg$$

A search for Yukawa particle started soon after its hypothesis and in 1947, Powell discovered Π – meson in cosmic radiation and has a mass 273 m_e This particle, Π – meson (pion), is exact Yukawa particle. The pions are of three kinds positive (Π^+) ,negative(Π^-) and neutral(Π^0) all with intrinsic spin S = 0 . The force field between two proton or two neutrons is carried by a neutral pion while between a neutron and proton by a charged pion. In the latter case conversion of one nucleon to the other takes place. The situation is illustrated as

$$P \longleftrightarrow P + \pi$$

$$n \longleftrightarrow n + \pi$$

$$P \longleftrightarrow n + \pi^+$$

$$n \longleftrightarrow P + \pi^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.35$$

To interpret the nucleon – nucleon scattering data interms of a potential function, let us compare the meson theory with the quantum theory of electro-magnetic interactions. To obtain a pion wave equation we express the total energy E of a pion in terms of the pion rest mass energy $m_\Pi c^2$ and momentum 'P' as

$$E^2 = P^2 C^2 + m_\Pi^2 c^4 \longrightarrow 3.36$$

The energy E and momentum component P are represented by the operator form

$$E = i\hbar\, \partial/\partial t, \qquad P_x = -i\hbar\, \partial/\partial x, \qquad P_y = -i\hbar\, \partial/\partial y, \qquad P_z = -i\hbar\, \partial/\partial z$$

Now eqn(3.36) can be written as

$$-\hbar^2 \frac{\partial^2}{\partial t^2} = -\hbar^2 \nabla^2 c^2 + m_\pi{}^2 c^4 \longrightarrow 3.37$$

It Φ is pion wave function, then wave equation for pion takes the form

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m_\pi{}^2 c^2}{\hbar^2}\right)\phi = 0$$

This is Klein Gordon equation for a free particle of spin 0 if we set $m_\Pi = 0$, we get

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\phi = 0 \longrightarrow 3.38$$

This is the wave equation for electromagnetic field. Now the simplest form of electromagnetic field is electrostatic field. The corresponding equation is obtained by putting

$$\frac{\partial \phi}{\partial t} = 0, i.e., \nabla^2 \phi = 0, Laplace \;\; equation$$

The identical equation for the meson field is

$$\left(\nabla^2 - \frac{m_\pi{}^2 c^2}{\hbar^2}\right)\phi = 0$$

This is in absence of any source of mesons, but in the presence of source, the equation should resemble with poisson's equation i.e. it should have the form

$$\left(\nabla^2 - \frac{m_\pi{}^2 c^2}{\hbar^2}\right)\phi = 4\pi g\delta(r)$$

$$\left(\nabla^2 - \mu^2\right)\phi = 4\pi g\delta(r) \text{............................} 3.39$$

Where $\mu = \frac{m_\pi c}{\hbar} = 1/R_0$. The factor 'g' plays the same role as the charge 'e' plays in the case of electrostatic field, and is a measured of nuclear field and known as mesonic charge. $\delta(r)$ is Dirac delta function $\{\delta(r)=1 \; at \; r = 0 \quad , \delta(r) = 0 \; at \; finite \quad r\}$. The solution of equation (3.39) comes out to be

$$\phi = -g\frac{e^{-\mu r}}{r} \longrightarrow 3.40$$

Therefore, the meson potential will be

$$V(r) = g\phi = -g^2\frac{e^{-\mu r}}{r}$$

The shape of the potential is shown in fig.3.4

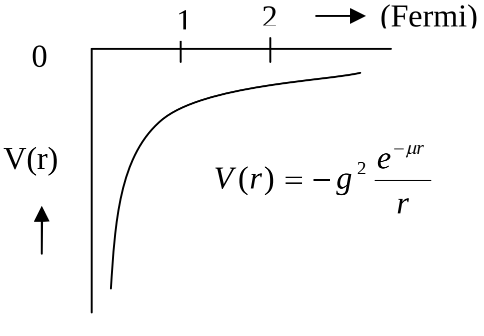


Fig . 3.4. Shape of the Potential

3.5.Summary: The P-P scattering is the only way to get direct evidence on proton-proton force. There are two essential differences between p-p and n-n scattering. First, the p-p scattering is caused not only by nuclear force but also by the coulomb force. Second, the scattering and scattered particles are identical and obey the pauli exclusion principle and therefore, the wave function describing the two protons must change sign on the interchange of the two particles. Yukawa, in 1935, proposed that nuclear forces are due to an exchange of particles of intermediate mass, known as mesons (Yukawa particle). Yukawa took the analogy from the quantum field theories of electromagnetic field in which photon exchange takes place and gravitational field in which exchange of graviton is assumed. Both these field particles have zero rest mass, but the nuclear field particles has finite rest mass.

Keywords:

Scattering, Phase shift, radial wave

Self assessment questions:

1. Explain proton-proton scattering at low energies
2. Discuss neutron-proton scattering at low energies
3. Explain the meson theory of nuclear forces.

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel

Unit 1

Lesson 4

NUCLEAR REACTIONS

The objectives of the lesson are to explain the following:

4.1 Introduction

4.2 Types of Reactions

4.3 Conservation laws

4.4 Nuclear Kinematics

4.5 Nuclear Energy

4.6.Summary

4.1 Introduction : A considerable part of our present knowledge of the nuclear structure comes from experiments in which a chosen nucleus is bombarded with different projectiles, such as protons, neutrons, deuterons or α - particles. When these particles come close enough to interact with the target nuclei, either elastic or inelastic scattering may take place or one or more particles which are altogether different may be knocked out of the nucleus, or the incident particle may perhaps be captured and a gamma ray emitted. When the mass number and/ or atomic number of the target nuclei changes after the bombardment, we say that a nuclear reaction has taken place.

Nuclear Reaction: Nuclear reaction is the process of strong interaction of an atomic nucleus with an elementary particle resulting in the formation of a new nucleus and one or more new particles.

A nuclear reaction can be represented as follows

$$X + x \longrightarrow Y + y$$

Where X is the target nucleus, 'x' the incident or projectile particle, Y the product nucleus and 'y' the out going or detected particle.

Nuclear reaction was discovered by Rutherford, this reaction an be represented as follows.

$$_7N^{14} + {}_2He^4 \longrightarrow {}_9O^{17} + {}_1H^1$$

In case of a nuclear reaction

1. The total atomic number of incident particle and target nucleus before the reaction must be equal to the total atomic number of the products after reaction.
2. The total sum of atomic mass numbers on both sides of the equation must be equal

Importance of Nuclear Reaction Equations:

The nuclear equations have many practical applications. Few of them are

1. We calculate the different elements atomic masses accurately
2. They help to discover and identify the new isotopes
3. They provide the experimental verification of Einstein's mass-energy relation ($E = mc^2$)
4. They provide the information to predict other possible reactions.

4.2 Types of Nuclear Reactions:

1. Elastic scattering
2. Inelastic scattering
3. Disintegration
4. Photo disentegration
5. Radiative capture
6. Direct Reaction
7. Heavy ion reactions

8. Spontaneous decay
9. Spallation Reactions
10. High energy Reactions

(1)Elastic scattering: In this the incident particle strikes the target and leaves without energy loss. But here direction of motion is altered. Scattering of alpha particles in gold is a good example of this process

$$\text{Ex. } {}_2He^4 + {}_{79}Au^{197} \longrightarrow {}_{79}Au^{197} + {}_2He^4$$

(2)Inelastic scattering: whenever scattered particle has excess energy to form elastic collision with nucleus then scattered particle may loss K.E.. This energy is being corresponding increase in the internal energy of the nucleus as which is excited to a higher quantum state. This excess energy is later radiated away in the form of a quantum

$$\text{Ex. } {}_3Li^7 + {}_1H^1 \longrightarrow ({}_3Li^7)^* + {}_1H^1$$

* is used to indicate that after scattering the nucleus is left in an excited state.

(3) Disintegration: On striking the target nucleus the incident particle is absorbed and a different particle is ejected. The product nucleus differs from target nucleus. The incident particle may be alpha particle, proton, neutron etc.The product particle may be a charged particle or a neutron

$$\text{Ex. } {}_7N^{14} + {}_2He^4 \longrightarrow {}_8O^{17} + {}_1H^1$$

(4)Photodisintegration: In this γ –rays are absorbed by the target nucleus, exciting it to a higher quantum state. If the energy is high enough, one or more particles may be liberated.An example is

$${}_1H^2 + \gamma \longrightarrow {}_1H^1 + {}_0n^1$$

(5) Radiative Capture: A particle may combine with a nucleus to produce a new nucleus or a compound nucleus which is in an excited state. The excess energy is emitted in the form of γ – ray photons. Ex. ${}_{12}Mg^{26} + {}_1H^1 \longrightarrow ({}_{13}Al^{27})^* \longrightarrow {}_{13}Al^{27} + \gamma$

(6)Direct Reactions: In this we have two categories

a)Pick up reactions

b)Stripping reactions

a)Pick up reaction: A collision of an incident particle with the nucleus may immediately pull one of the nucleons out of the target nucleus.

Ex. ${}_8O^{16} + {}_1H^1 \longrightarrow {}_8O^{15} + {}_1H^3$

b)Stripping reaction: In this a bombarding particle which is composed of more than one nucleon may loss one of them to the target.

Ex. ${}_{29}Cu^{63} + {}_1H^2 \longrightarrow {}_{29}Cu^{64} + {}_1H^1$

(7) Heavy ion Reactions: Nuclear reactions induced by heavy ions exhibit the characteristics both of compound nucleus and of the stripping and pickup mechanisms

Ex. ${}_7N^{14} + {}_{82}Pb^{207} \longrightarrow {}_7N^{13} + {}_{82}Pb^{208}$

(8)Spontaneous decay: Beta decay , alpha decay processes may be regarded as this type of nuclear reactions. In these reactions, the total energy of the system is not under the experimental's control. Here incident particle is not necessary.

${}_{84}Po^{212} \longrightarrow {}_{82}Pb^{208} + {}_2He^4$ (α decay)

this reaction takes place due to instability.

${}_1H^3 \longrightarrow {}_2He^3 + {}_{-1}e^0$ (β – decay)

(9)Spallation Reaction: On capture of a incident particle, a heavy nucleus has sufficient energy for the ejection of several particles Such a reaction is known as spallation reaction eg. The nuclear fission.

Ex. ${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{40}Zr^{98} + {}_{52}Te^{136} + 2\ {}_0n^1$

(10)High energy reaction: Energy range is about 150Mev then spallation process merges in to new kind of reaction in which new particles (mesons, strange particles) are produced along with neutrons and protons.

4.3 CONSERVATON LAWS: Certain quantities must be conserved in any nuclear reaction.

Various conservation laws which valid in ordinary nuclear interactions are given below.

1. Conservation of Energy
2. Conservation of momentum
3. conservation of Angular momentum
4. Conservation of Charge
5. Conservation of Nucleons
6. Conservation of Spin
7. Conservation of Parity
8. Conservation of Isotopic spin

1. **Conservation of Energy:** The total energy of the products, including both mass energy and kinetic energy of the particles plus the energy involved must be equal to the mass energy of the initial ingredients plus the kinetic energy of the bombarding particle.

2. **Conservation of Momentum:** The total linear momentum of the products must be equal to the linear momentum of the bombarding particle.(the target nucleus in ordinarily takes to be rest)

3. **Conservation of Angular momentum:** The total angular momentum j comprising the vector sum of the intrinsic spin angular momentum 's' and relative orbital angular momentum 'l' of the products must be equal to the total angular momentum of the initial particles.

4. **Conservation of Charge:** The total electric charge of the products must be equal to the total electric charge of initial particles.

5. **Conservation of Nucleons:** The law of conservation of nucleons states that the nucleons can neither be created nor be destroyed so that the number of nucleons minus the number of anti nucleons in the universe remains constant.

6. **Conservation of Spin:** The spin character of a closed system can not change i.e. the statistics remains same as that existed before reaction.

7. **Conservation of Parity:** The parity of the system determined by the target nucleons and bombarding particle must be conserved throughout the reaction.The total parity of the system is the product of intrinsic particles of the target nucleus and bombarding nucleus. No violation of parity has been observed in a nuclear reaction(Strong nuclear forces). Although parity does not appear to be conserved in weak interactions.

8. **Conservation of Isotopic spin:** The invariance of the nuclear Hamiltonian function towards the charge character of the nucleons can be expressed analytically as an invariance towards rotational shifts of the axes in isotopic spin space, and there should correspondingly exist a conservation law for the isotopic spin of a nuclear system.

4.4 NUCLEAR KINEMATICS:

At any energy, the conservation of energy and momentum imposes certain restrictions on the reactions. These restrictions are called kinematic reactions and this mathematical method is known as kinematics. Consider a nuclear reaction.

$$X + x \longrightarrow Y + y$$

Where X - target nucleus

x - bombarding particle

Y – Product nucleus

y - product particle

In this reaction we assumed that target nucleus is at rest so it has no kinetic energy.

Since the total energy is conserved in nuclear reaction, we get

$$M_Xc^2 + (E_x + m_x c^2) = (E_Y + M_Y c^2) + (E_y + m_yc^2) \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$

Where m_x = mass of incident particle

M_X = Mass of target nucleus

m_y = mass of product particle

M_Y = mass of product nucleus

From (4.1),

$$(M_X + m_x - M_Y - m_y)c^2 = E_Y + E_y - E_x = Q \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

Here we introduced a quantity Q which represents the difference between the kinetic energy of the products of reaction and that of the incident particle.

The quantity Q is called the energy balance of the reaction or more commonly Q- value of the reaction depending upon Q we have two types of reactions.

1. Exoergic reactions
2. Endoergic reactions

1.Exoergic reactions: If Q is +ve then that type of reaction is known as exoergic reaction. This takes place only if sum of the masses of incident particle and target nucleus is greater than that of masses of the product nuclei. K.E of the product nuclei being greater than that of the incident particle.

2.Endoergic reaction: If Q is -ve the reaction is said to be endoergic reaction. i.e. energy must be supplied usually as a K.E. of the incident particle.

Q-Equation:

$$Q = E_Y + E_y - E_x \longrightarrow 4.3$$

To measure a Q – value in an experiment we first measure the bombarding energy E_x and the energy of the ejected particle E_y at some specified angle θ. In eqn (4.3) E_Y – recoil energy of the product nucleus. It's value is small and hard to measure.

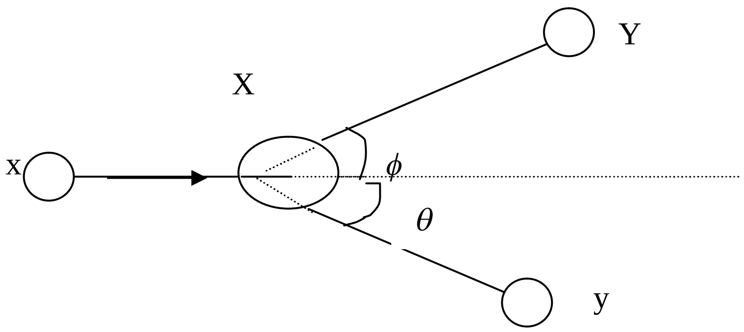


Fig: 4.1 Schematic diagram of a nuclear reaction

Thus applying the law of conservation of momentum we have.

$$m_x v_x = M_Y V_Y \cos\Phi + m_y v_y \cos\theta \longrightarrow (4.4)$$

and $$M_Y V_Y \sin\Phi = m_y v_y \sin\theta$$

Here v_x = velocity of incident particle

V_y = velocity of ejected particle

V_Y = velocity of product nucleus

From eqn(4.4), $M_Y V_Y \cos\Phi = m_x v_x - m_y v_y \cos\theta$

$$M_Y V_Y \sin\Phi = m_y v_y \sin\theta \qquad \ldots\ldots\ldots\ldots 4.4(a)$$

From eqn 4.4(a), we get

$$M_Y{}^2 V_Y{}^2 = m_x{}^2 v_x{}^2 + m_y{}^2 v_y{}^2 - 2 m_x v_x m_y v_y \cos\theta \ldots\ldots\ldots 4.4(b)$$

Since $E_x = \frac{1}{2} m_x v_x{}^2$, $E_y = \frac{1}{2} m_y v_y{}^2$, $E_Y = \frac{1}{2} M_Y v_Y{}^2$

Substituting the values of V_Y^2, v_x^2, v_y^2 from the above eqns, into eqn 4.4(b) we get the resultant equation as shown below

$$2E_Y M_Y = 2E_x m_x + 2E_y m_y - 4(m_x m_y E_x E_y)^{1/2} Cos\theta$$

$$or \qquad E_Y = E_x \frac{m_x}{M_Y} + E_y \frac{m_y}{M_Y} - \frac{2}{M_Y}(m_x m_y E_x E_y)^{1/2} Cos\theta$$

$$Q = E_Y + E_y - E_x$$

$$= E_x \frac{m_x}{M_Y} + E_y \frac{m_y}{M_Y} - \frac{2}{M_Y}(m_x m_y E_x E_y)^{1/2} Cos\theta + E_y - E_x$$

$$Q = E_x \frac{(m_x - M_Y)}{M_Y} + E_y \frac{(m_y + M_Y)}{M_Y} - \frac{2}{M_Y}(m_x m_y E_x E_y)^{1/2} Cos\theta \text{............................}(4.5)$$

Equation (4.5), represents the Q-value reaction. It gives the desired relation between the energy released and the measured quantities E_x, E_y and θ for a special case, when we are observing the out going particle if at 90^0 to a collimated beam of projectile the above eqn (4.5) reduces to

$$Q = E_Y \frac{(m_y + M_Y)}{M_Y} + E_x \frac{(m_x - M_Y)}{M_Y}$$

$$= E_Y\left(1 + \frac{m_y}{M_Y}\right) - E_x\left(1 - \frac{m_x}{M_Y}\right) \text{......................} 4.5(a)$$

By using modern techniques, we measure Q values for nuclear reaction producing charged particles, to an accuracy of 1 part in a thousand or better.

We now find the general solution of the Q – equation

From eqn(4.5)

$$Q = E_x \frac{(m_x - M_Y)}{M_Y} + E_y \frac{(m_y + M_Y)}{M_Y} - \frac{2}{M_Y}(m_x m_y E_x E_y)^{1/2} Cos\theta$$

$$QM_Y = E_x(m_x - M_Y) + E_y(m_y + M_Y) - 2(m_x m_y E_x E_y)^{1/2} Cos\theta$$

$$QM_Y + E_x(M_Y - m_x) = E_y(m_y + M_Y) - 2(m_x m_y E_x E_y)^{1/2} Cos\theta$$

$$\frac{QM_Y + E_x(M_Y - m_x)}{(m_y + M_Y)} = E_y - \frac{2(m_x m_y E_x E_y)^{1/2}}{(m_y + M_Y)} Cos\theta \text{..........................(4.6)}$$

$$\frac{QM_Y - E_x(m_x - M_Y)}{(m_y + M_Y)(E_Y)^{1/2}} = (E_Y)^{1/2} - \frac{2(m_x m_y E_x)^{1/2}}{(m_y + M_Y)} Cos\theta \text{.......................(4.7)}$$

Now

$$\left[(E_y)^{1/2} - \frac{(m_x m_y E_x)^{1/2}}{(m_y + M_Y)} Cos\theta\right]^2 = E_Y - \frac{2(m_x m_y E_x E_y)^{1/2}}{(m_y + M_Y)} Cos\theta + \frac{(m_x m_y E_x)}{(m_y + M_Y)^2} Cos^2\theta$$

$$E_y - \frac{2(m_x m_y E_x E_y)^{1/2}}{(m_y + M_Y)} Cos\theta = \left[(E_Y)^{1/2} - \frac{2(m_x m_y E_x)^{1/2}}{(m_y + M_Y)} Cos\theta\right]^2 - \frac{(m_x m_y E_x)}{(m_y + M_Y)^2} Cos^2\theta$$

From (4.7)

$$.\frac{QM_Y + E_x(M_Y - m_x)}{(m_y + M_Y)} = \left[(E_y)^{1/2} - \frac{2(m_x m_y E_x)^{1/2}}{(m_y + M_Y)} Cos\theta\right]^2 - \frac{(m_x m_y E_x)}{(m_y + M_Y)^2} Cos^2\theta$$

$$\left[(E_y)^{1/2} - \frac{2(m_x m_y E_x)^{1/2}}{(m_y + M_Y)} Cos\theta\right]^2 = \frac{QM_Y + E_x(M_Y - m_x)}{(m_y + M_Y)} + \frac{(m_x m_y E_x)}{(m_y + M_Y)^2} Cos^2\theta$$

$$\left(\sqrt{E_y} - u\right)^2 = v + u^2 \Rightarrow \left(\sqrt{E_y} - u\right) = \pm\sqrt{v + u^2}$$

$$\sqrt{E_y} = u \pm \sqrt{u^2 + v} \text{..........................(4.8)}$$

$$where \quad u = \frac{\sqrt{m_x m_y E_x} Cos\theta}{m_y + M_Y}, \qquad v = \frac{QM_Y + E_x(M_Y - m_x)}{m_y + M_Y} \text{...........(4.9)}$$

Exoergic reaction: (Q > 0) these reactions are possible even for $E_x = 0$. Thus for $E_x \rightarrow 0$.

From eqns (4.8) and (4.9) $E_y = \frac{QM_Y}{m_y + M_Y}(Q > 0)$ …………..4.10

The kinetic energy E_Y is the same for all angles θ. From this we observe the total momentum is effectively zero when $E_x \rightarrow 0$

In this case $Q = E_Y + E_y$ and $\theta + \Phi = 180^0$

Eqn (4.7) has two solutions. One is positive and another is negative. Hence 'E_y' to be single valued $Q > 0$ and $M_Y > m_x$ generally projectile 'x' is lighter than the product nucleus Y. Thus υ is +ve for all values of the bombarding energy and 'E_y' depends on cosθ and it has smallest value in the backward direction. $\theta = 180^0$

2)Endoergic Reactions: Q value is -ve then this reaction takes place. Generally these reactions are not possible because when $E_x \rightarrow 0$, eqn(4.7) gives $u^2 + v$ = -ve. Then $\sqrt{E_Y}$ is imaginary.

Threshold energy: The threshold energy is defined as the minimum kinetic energy of the incident particle which will initiate an endoergic reaction. This is expressed by E_{th}

This reaction is possible when E_x is large enough to make $u^2 + v = 0$

Then

$$E_x = -Q\left[\frac{m_y + M_Y}{m_y + M_Y - m_x - \left(\frac{m_x m_y}{M_Y}\right)Sin^2\theta}\right] \text{...........4.11}$$

E_x is minimum at θ = 0 and this is called threshold energy.

Therefore, By using relations

$$(E_x)_{th} = -\frac{Q(m_y + M_Y)}{m_y + M_Y - m_x}$$

$$Q = (M_X + m_x - M_Y - m_y)c^2$$

$$\text{In this case } M_X \succ\succ \frac{Q}{c^2} \quad \text{then}$$

$$(E_x)_{th} = -Q\frac{(m_x + M_X)}{M_X}$$

Thus we see that of threshold of the reaction particles first appear in θ = 0 direction with the K.E.

$$E_y = u^2 = (E_x)_{th}\left(\frac{m_x m_y}{(m_y + M_Y)^2}\right)$$

As the bombarding energy is raised, particle 'y' begins to appear at $\theta \succ 0$

4.5. Nuclear Energy

A Nuclear reactor is a device or apparatus in which nuclear fission is produced under a self sustaining controlled nuclear chain reaction.

Essential components of a nuclear reactor are given below.

1. Fuel
2. Reactor core
3. Reactor reflector
4. Reactor moderator
5. Reactor coolant
6. Reactor control materials
7. Reactor Sheilding

1) Fuel: The material containing the fissible isotope is called the reactor fuel. Generally U^{235} is used as fuel in many reactions.

2) Reactor core: This is the main part of the reactor. Reactor cores generally have a shape approximately a right circular cylinder with a diameter of few metres. In general reactor core have fuel elements, moderator control rods and cooling material housed in a pressure vessel.

3) Reactor reflector: The region surrounding the reactor core is known as reflector. It reflect back some of the neutrons which are leak out from the surface of the core.The material of the reflector is the same as that of moderator.

4) Reactor moderator: Reactor moderator is used to slow down the fast neutrons. Commonly used moderators are a)Ordinary water b) heavy water c) graphite (carbon) and d) Beryllium oxide. Heavy water is the best moderator.

5)Reactor Coolant: The material used to remove heat produced by fission as fast as it is liberated is known as reactor coolant.

Ex. Ordinary and heavy water, organic liquids(hydrocarbons), liquid metals and gases.

6) Reactor control materials: In a reactor it is very essential to control the fission process otherwise the chain may become explosive and consequently the reactor will be damaged.

7) Reactor Sheilding: In a nuclear reactor various types of rays are emitted. These rays may harm the persons working near the reactor. Hence thick walls of cement and concrete are constructed around the reactor which are known as shields.

Working: Some neutrons are remain in the reactor. To operate the reactor, all the controlling rods except one are taken out . Other controlling rods taken out slowly until the intensity of neutrons begins to increase. The reactor now works at a constant level by adjusting the single control rod.

Types of Reactors: Reactors are classified in to three types

1. Research Reactors
2. Production Reactors
3. Power Reactors

1) Research Reactors: Research reactors are used primarily to supply neutrons for physical research and radio isotope manufacture. In these reactors the total energy liberated is comparatively small, since they operate at a low level of reactivity.

We shall describe here five main types of research reactors.

1. Graphite – Moderated Research Reactors
2. Water – Boiler type Reactors
3. Swimming pool Reactors
4. Light – Water – Moderator, tank type Reactor
5. Heavy – Water – Moderator, tank type Reactor

1) Graphite – Moderated Research Reactors: This is the first reactor, which we built and operated it. This first reactor now called CP –1 (Chicago pile –1) was put into operation in 1942. This was operated without coolant flow at a power level of 200 watts. Similar assemblies with air as coolant, like the GLEEP (Graphite low energy experimental pile) and BEPO (British experimental pile), BNL (Brookhaven National Laboratory) are well known examples.

2) Water – Boiler type Reactors: The water boiler is usually a homogeneous mixture of a highly enriched uranium salt dissolved in ordinary water. The first reactor of this type was

LOPO (for low power operation)
HYPO (for high power operation)
SUPO (super power operation)
WBNS (Water Boiler neutron source)
ARR (Aromoue Research Reactor)
KEWB (kinetic Exponential water Boiler)

3) Swimming pool Reactors: It is light water moderated heterogeneous reactor which consists of a lattice of enriched uranium fuel immersed in a large pool of water. The water in the pool plays the role of moderator, coolant and shield BSR is the first swimming pool reactor which is completed in 1950. The Indian Reactor Apsara belongs to this type. It has maximum power level of 1 Mw. The other reactors are NRLR (Naval), Battel, (RR) swiss reactor etc.

4) Light – Water – Moderator, tank type Reactor: This reactor is similar to pool reactor in principle except that the core is suspended in a deep cylindrical tank of water and can not be moved. First reactor was built in 1952. and it was name d as MTR (Material Testing Reactor). In this reactor neutrons flux was increased . The other reactors are ETR, WTR, HFR (High flux reactor)

5) Heavy – Water – Moderator, tank type Reactor: The desirability of obtaining heavy water for use as a neutron moderator lies in the extremely small thermal absorption cross section deuterium. Because of this property the neutron economy in a heavy water system is greatly improved. The first reactor is CP-3 (Chicago pile –3) CIRUS or CIR is India’s second research reactor. CIR - Canadian Indian Reactor. Power is 40 MW Zerlina – India’s third Research reactor. It’s name stands for Zero energy lattice investigation nuclear assembly - In this natural uranium is used as fuel.

Purnima - It is India’s first experimental zero energy fast reactor. In this fuel is plutonium oxide.

R – 5 - Thermal research reactor with a nominal power of 100MW

II)Production Reactors: The purpose of a production reactor is sto convert fertile into fissible material. In these reactors uranium is used as fuel. Graphite as a moderator and water as coolant. The conversion efficiency of a production reactor is high when we use heavy water instead of graphite as a moderator.

III)Power Reactors: The primary purpose of a power reactor is the utilization of the fission energy produced in the reactor core and to convert it into useful power. During the chain reaction large amount of heat being generated in the reactors. Hence these reactors are used in power production and propulsion. Water moderator reactor could not be used if the tiny of the reactor core was high because water becomes highly corrosive fluid at high temperature. Alloy’s of some metals were develop which could resist higher temperatures. In order to keep the water coolant in contact with reactor core at low temperatures. Water is keep at sufficient pressure to prevent boiling. This water is circulated through the core through a heat exchanger and is brought back to the core in a cycle of operation. Steam is generated in the heat exchange in a secondary circuit. This stem is used to a tubine eneg.

1)Pressurised water reactors: This is a heterogeneous reactor(it means that fuel is concentrated in plates) rods or hollow cylinders which are distributed in a regular pattern with in the moderator.. Homogeneous means the fuel and moderator are mixed in the form of a solution . In heterogeneous reactor fuel is enriched uranium light water as a moderator and coolant.

2) Boiling Water Reactor: The boiling water reactor is a small nuclear power plant designed to allow stem to be generated directly in the reactor core. This uses light water as moderator coolant . Boiling Nuclear super heat (BONUS) is one of the Boiling water reactors.

3)Heavy water moderated reactor: The advantage of heavy water is the total cost of the core and cost of the consumed fuel are both less in the heavy water moderated reactor. Because natural uranium is used as a fuel and the conversion ration for the regeneration of fissile material can be close to unity. Both factors decrease the cost of the power produced. The first reactor is Nuclear power demonstration reactor (NPDR) In India we have this type of reactor at kota (430MW) Kalpakam (470MW), Narora (440MW)

4)Organic Moderated reactor: This is the another method to achieve the high temperatures at moderate pressures in a thermal reactor. In this we use organic liquid containing a high hydrogen content and of is high boiling point .The first reactor is MORE.(Organic moderated reactor testing experiment)
PNPF (Piqua Nuclear power facitity)

5)Gas cooled Reactor: In this the mean time air was employed as the coolant in the graphite moderated production reactors at wide scale. Helium, Beryllium , CO_2 are used as moderators.

6)Sodium Graphite Reactors: The high boiling point of liquid sodium makes it an excellent coolant for a high temperature reactor. High temperatures s can be achieved without high pressures. In this reactor graphite is used as moderator, sodium as coolant, and uranium as the fuel.

7)Liquid fuel Reactor: The homogeneous reactor experiment is to test the feasibility of maintaining a fission chain at high temperatures and pressures . The advantage of an aqueous homogeneous reactor are the high power density, low fuel inventory, continuous removal of fission products and radiation damage products, high degree of nuclear stability.

8)Fast reactor: The development of power reactor in which the bulk of fissions are produced by high energy neutrons is of importance in the civilian power reactor development programmes. Such reactors not only produce useful power. But also regenerate more fissile material than is consumed.

Cross – Section of a Nuclear Reaction: The nuclear cross- section gives an idea of the probability that a bombarding particle will interact with the target material.

Let N_t = target nuclei per unit area.

N_0 = number of incident particles sticking per second per unit area of target material

N = number of nuclei undergoing interaction per second

Now we define nuclear cross- section σ by

$$\sigma \quad = \frac{N}{N_0 N_t} m^2 / nucleus.$$

$$N_t = 1 \quad then \quad \sigma = \frac{N}{N_0}$$

Hence nuclear cross section may be defined as the ratio of number of nuclei undergoing interaction to the number of incident particles sticking per unit area when target nuclei per unit allows one.

It is a quantitative measure of the probability of a given nuclear reaction. fraction of incident particles are large than probability that the process will occur is greater.

The unit of nuclear reaction cross-section is barn.

$$1\text{barn} = 10^{-28}\ m^2$$

Determination of Cross-section: Consider a sheet of thickness t and area of cross section A containing n nuclei per unit volume. Let N_0 be the number of particles in the incident beam. Here we assume that each particle interacts only once. Further, due to scattering, absorption etc. Let dN particles be reduced from the beam in passing through a thickness dt. Let N be the number of particles which cross the sheet.

Now

$$-\frac{dN}{N}=\frac{Aggregate\,cross\text{–}\sec tion}{t\arg et\ \ area}$$

$$=\frac{nAdx\sigma}{A}=ndx\sigma$$

$$Integrating,\quad we\quad get$$

$$-\int_{N_0}^{N}\frac{dN}{N}=n\sigma\int_0^t dx$$

$$-\left(\log_e N\right)_{N_0}^{N}=n\sigma[x]_0^t$$

$$-\log_e\left(\frac{N}{N_0}\right)=n\sigma t$$

$$\log_e\left(\frac{N}{N_0}\right)=-n\sigma t$$

$$N=N_0e^{-n\sigma t}$$

From this relation, we can calculate σ. Thus $\sigma=\frac{1}{nt}\log_e\frac{N_0}{N}$.

4.6.Summary: Nuclear reaction is the process of strong interaction of an atomic nucleus with an elementary particle resulting in the formation of a new nucleus and one or more new particles.

A nuclear reaction can be represented as follows

$$X + x \longrightarrow Y + y$$

The nuclear equations have many practical applications. Few of them are

5. We calculate the different elements atomic masses accurately
6. They help to discover and identify the new isotopes
7. They provide the experimental verification of Einstein’s mass-energy relation ($E = mc^2$)
8. They provide the information to predict other possible reactions.

If Q is +ve then that type of reaction is known as exoergic reaction.

If Q is -ve the reaction is said to be endoergic reaction.

A Nuclear reactor is a device or apparatus in which nuclear fission is produced under a self sustaining controlled nuclear chain reaction.

Reactors are classified in to three types

4. Research Reactors
5. Production Reactors
6. Power Reactors

Keywords:
Elastic scattering, Radiative capture, Spallation reactions, stripping reactions, exo-ergic, endo-ergic reactions.

Self assessment questions:

1. Define nuclear reaction . Discuss various types of nuclear reactions.
2. Explain the conservation laws that are obeyed by nuclear reactions.
3. What do you mean by nuclear kinematics? Obtain an equation for Q-value of the nuclear reaction.Explain the threshold energy of nuclear reaction.
4. Explain the principle and working of a nuclear reactor.
5. Discuss about the general features of nuclear reactor.
6. What are the various types of reactors? Explain them briefly.

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel.

Unit 2

Lesson 5

NUCLEAR MODELS

The objectives of the lesson are to explain the following:

5.1 .Introduction

5.2.Shell model

5.3.Magic numbers

5.4.Extreme Single Particle Model

5.5.Semi Empirical Mass Formula

5.6.Liquid Drop Model

5.7.Summary

5.1. Introduction: It has been established that neutron and proton are the particles of which a nucleus is composed. The various properties, e.g., nuclear radius, nuclear mass, binding energy, packing fraction, magnetic moment, quadrupole moment etc. have also been dealt in detail in the same chapter. Now with the detailed study of nuclear forces it should be possible to interpret theoretically all the observed nuclear properties. Unfortunately, it has not been possible because two-body treatment can not be successfully applied to many body system because of much mathematical complexity . The total number of sub-nuclear particles is not very large, therefore, the statistical method to treat the problem becomes unsuitable and in the absence of any strong centre of force, the perturbation method can also not be applied. Thus, in the absence of suitable theoretical tool of investigation, physicists started a search for an alternative method of attack on the problem. This alternative method consists of looking round for a physical system - the model, the properties of which are known and they in turn are analogous to the properties of nucleus. In this way, on the basis of assumed models, physicists have tried to correlate various experimental data and to calculate some of properties.

A good model should describe

1. The properties of the ground nuclear states (spins, parities, magnetic dipole, magnetic dipole, electric quadrupole moment's etc.)

2.The properties of excited states especially the nuclear excitation spectrum.

3.The dynamical properties of the nucleus.

Ex. Probabilities of γ – quanta emission by individual nuclear excitation levels.

Physicists have restored to great number of nuclear models. No single model has provided a comprehensive description of the nucleus.

Nuclear models are various types and these are specified below.

1. Fermi gas model
1. Alpha particle model
2. Liquid drop model
3. Shell model
4. Collective model
5. Optical model

5.2.SHELL MODEL: Shell model can predict the magic numbers magnetic moment, quadrupole moment, ground state spin., and ground state energy. Evidences for the existence of shell model are given below.

5.3.Magic Numbers: The 1917, it was pointed out by Harkiins that nuclei with even numbers of protons or neutrons are more stable than those with odd numbers. Elasser, in 1934 observed that nuclides , which have either proton or neutron, number equal to 2,8,,20,50,82,126 shows pronounced stability. The numbers are called magic *numbers*, for the existence of such nuclides was not well understood for a long time. The name given is not scientific one but it serves the purpose of identifying the numbers conveniently. It was also observed that at these numbers nuclear properties show remarkable change. The nuclei such as O^{16} (Z = 8, N=8) and Pb^{208} (Z=82, N=126) are found exceptionally stable and are called doubly magic nuclei as both Z and N are magic numbers. It is further observed that as numbers 14,28 and 40, the stability is less than that for the above mentioned magic numbers and due to this reason the numbers are referred to as semi magic numbers.

Evidence for the existence of Magic numbers:

1. Mayer in 1948 suggested that nuclei with a magic number of nucleons are especially abundant in nature. Magic numbers are 2.,8,20,50,82, and126

2. ${}_2He^4$ and ${}_8O^{16}$ are particularly stable and it can be seen from the biding energy curve. The numbers 2 and 8 indicate stability because both are magic numbers. Further the stability of two nuclei is mainly due to consequence pairing of two protons and two neutrons align with opposite spins.

3. Above Z = 28 , the only nuclides of even Z which have isotopic abundances exceeding 60% are ${}_{38}St^{88}$ (N= 50) ${}_{56}Ba^{138}$ (N= 82) ${}_{58}Ce^{140}$ (N= 82)

4. No more than five isotones occur in nature for any neutron N except N = 50, where there are six and N = 82 where there are seven neutron numbers of 82, 50, there fore indicate particular stability.

5. Sn (Z = 50) has ten stable isotopes , more than any other element, while Ca (Z = 20) has six isotopes. This indicates that elements Z = 50 and Z = 20 are more stable than usually stable.

6. Alpha decay energies are rather smooth functions of A for a given Z but show striking discontinuities at N = 126 This represents the magic character of the number 126 for neutrons.

7. Very similar relations exist among the energies of beta ray emission. These energies are abnormally large when the neutron or proton of the final nucleus assumes a magic value.

8. The particularly weak binding of the first nucleon outside a closed shell is shown by unusually low probabilities for the capture of neutrons by nuclides having N = 50, 80 and 126

9. It is found that some isotones are spontaneous neutron emitters when excited above the nucleon binding energy by a preceding B- decay these are O (N= 9), Kr (N=51) Xe (N=83)

10. Nuclei with the magic proton numbers 50 (Sn) and 82 (Pb) have much smaller capture cross-sections than their neighbours.

11. The doubly magic nuclei (Z and N both magic numbers) ${}_2He^4$,${}_8O^{16}$, ${}_{20}Ca^{40}$, ${}_{82}Pb^{208}$ are particularly tightly bound.

12. The binding energy of the next neutron or proton after a magic number is very small.

13. The asymmetry of the fission of uranium could involve. The sub-structure of nuclei, which is expressed in the existence of the magic numbers.

14. The Schmidt theory of magnetic moments for odd A nuclides show the ground states of these nuclides change from even parity to odd parity or vice versa at the numbers A = 4, 16, 40 when the nucleon numbers are 2, 8 and 20 respectively.

15. The electric quadrupole moment of nuclei show sharp minima at the closed shell numbers indicating that such nuclei are nearly spherical.

5.4)EXTREME SINGLE PARTICLE MODEL:

1) In this model it is assumed that the nucleons in the nucleus move independently in a common potential, determined by the average motion of all other nucleons.

2). Most of the nucleons are paired so that a pair of nucleons contributes zero spin and zero magnetic moment . The paired nucleus thus form an inert core.

3). The properties of odd A nuclei are characterized by the unpaired nucleon and odd – odd nuclei by the unpaired proton and neutron.

4).In order to understand some of the properties of nuclei including the magic numbers two cases are given.

a) Infinite square well potential

b) Harmonic oscillator potential

The square well potential has an infinitely sharp edge where as the harmonic oscillator potential diminishes steadily at the edge. The addition of spin orbit potential eliminates some of the difficulties experienced with the above two potentials.

Schrodinger wave equation for a particle moving in a spherically symmetric al central field of force. The eigen states available to a nucleon of mass M moving in a spherically symmetric potential V(r) determined by the solutions of equation.

$$\left(\nabla^2 + \frac{2M}{\hbar^2}\left(E - V(r)\right)\right)\psi(r) = 0$$

where E is the energy eigen value. Here reduced mass 'μ' is replaced by M which is equal to nucleon mass. The general solution of this equation can be written as

$$\psi_{n,l,m}(r,\theta,\Phi) = u_{n,l}(r)\ Y_{l,m}(\theta,\Phi)$$

When $u_{n,l}(r)$ is the radial function. $Y_{l,m}(\theta,\Phi)$ are the spherical harmonics. The set of quantum numbers n,l,m determines an eigen state corresponding to an eigen value $E_{n,l}$. The radial wave function $u_{n,l}(r)$ is solution of the equation.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{du_{n,l}}{dr}\right)+\frac{2M}{\hbar^2}\left[E_{n,l}-V(r)-\frac{l(l+1)\hbar^2}{2Mr^2}\right]u_{n,l}=0$$

a) SQUARE WELL OF INFINITE DEPTH: Here we can calculate the position of various energy levels in an infinitely deep square well of radius 'R'. Let us assume that the potential is zero inside the well and infinite outside. Outside and at the boundary of well the radial wave function $u_{n,l}(r)$ vanishes. The radial wave functions are regular at the origin and inside the well are the spherical Bessel functions $J_l(K_{n,l}(r))$.

$$u_{n,l}(r)=j_l\left(k_{n,l}(r)\right)=\sqrt{\frac{k}{r}}\,j_{l+1/2}\left(k_{n,l}(r)\right)$$

where $j_{l+\frac{1}{2}}$ $(K_{n,l}(r))$ is a Bessel function and $K_{n,I}$ is the wave number can be defined by the equation.

$$K_{n,l}{}^2=\frac{2M}{\hbar}^2\left(E_{n,l}-V(r)\right)$$

Where $E_{n,l}$ is the total – ve energy is the well depth . Energies are to be measured from the bottom of the well and then we have

$$V(r)=-V_0$$

$$K_{n,l}{}^2=\frac{2M}{\hbar^2}\left(E_{n,l}+V_0\right)$$

$$K_{n,l}{}^2=\frac{2M}{\hbar^2}E^1{}_{n,l}\qquad(\because E^1{}_{n,l}=E_{n,l}+V_0)$$

where $E^1{}_{n,l}$ is +ve , measured from the bottom of the well.

With the helpl of boundary conditions the permitted values of $k_{n,l}$ are selected. In the sample case or well or infinite depth, the wave function has to vanish at the nuclear boundary i.e., at r = R

$$u_{n,l}(R) = j_l\left(k_{n,l}(R)\right) = 0$$

Each l value has set of zeros and each of them corresponds to a value of $k_{n,l}$ given by $k_{n,l} = x$.

Thus the eigen value $K_{n,l}R$ is the n^{th} zero of the l^{th} spherical Bessel function . The numbers n, giving the number of zeros of the radial part of the wave function is known as radial quantum number . It differs from the principle quantum number of atomic spectroscopy. A graph of spherical Bessel function for $l = 0,1$ *and* 2 is shown in fig 5.1 . The order of a level in a spherical square well of infinite depth is given by the order of increasing energy. The energy levels are, therefore,

$$E^1_{n,l} = \frac{k^2_{n,l}\hbar^2}{2M} = \frac{\hbar^2}{2MR^2}\left(k_{n,l}R\right)^2 = \frac{\hbar^2}{2MR^2}x^2 \qquad \text{(since } k_{n,l}R = x\text{)}$$

Each shell model actually consists of $2l+1$ sub states. Each level has $2(2l+1)$ protons and $2(2l+1)$ neutrons.

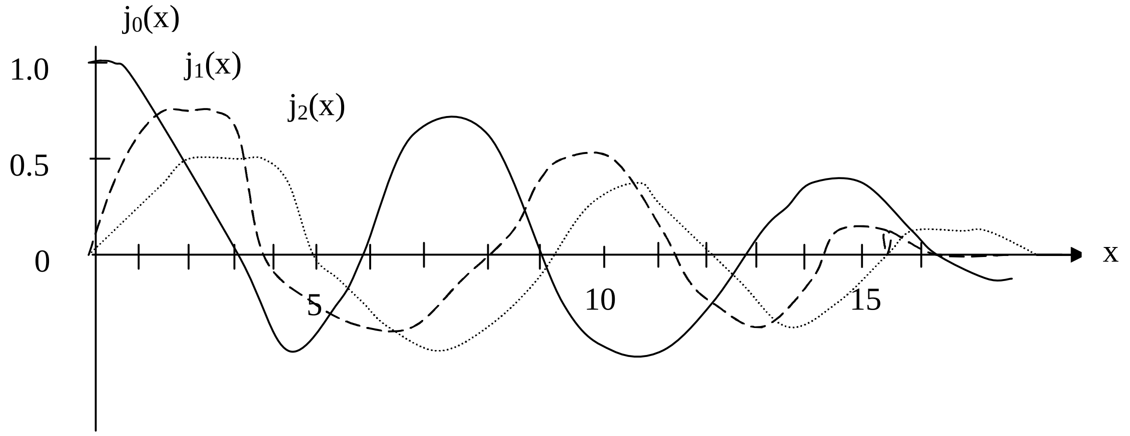


Fig.5.1 Spherical Bessel functions for $l = 0,1,2$

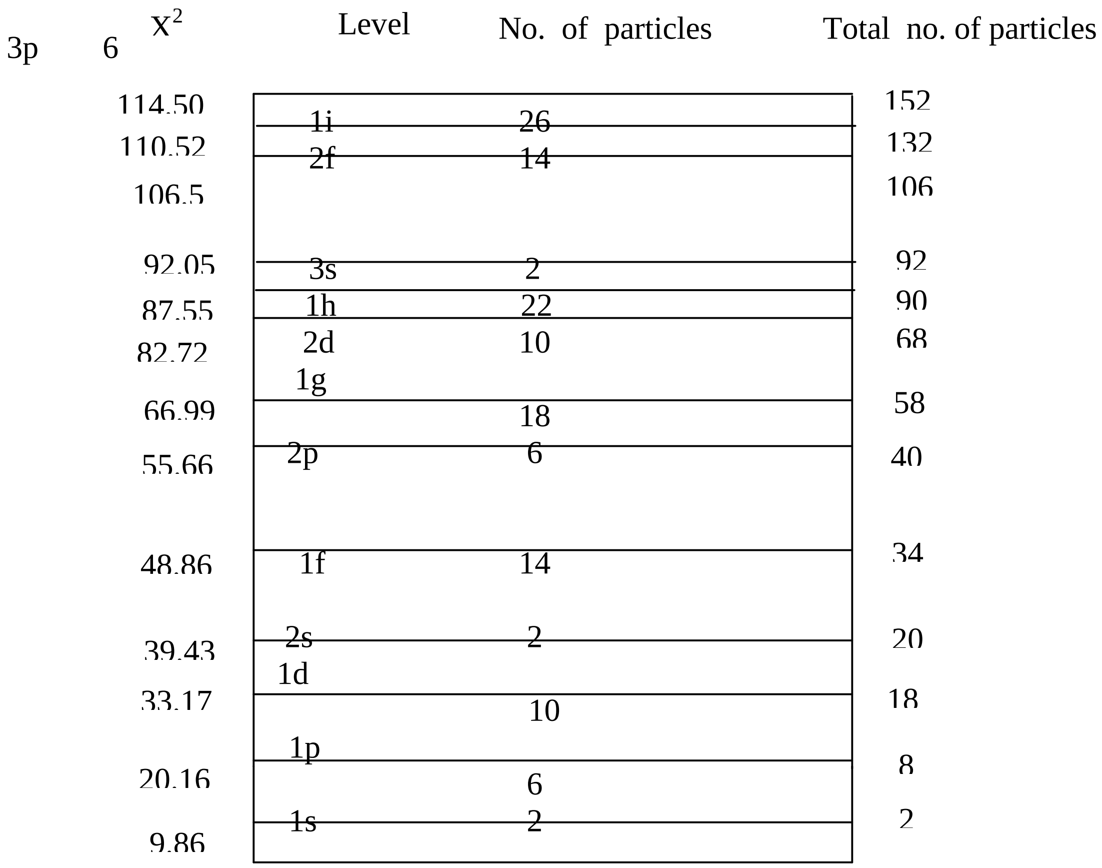


Fig:5.2 Levels and magic numbers predicted from infinitely deep square well.

Fig. 5.2 shows that the first energy level corresponds to $x = 3.14$ where $j_0(x) = 0$. *This* $l = 0$ state is written as 1s. It consists 2(2.0 +1) = 2 particles. The next level corresponds to x = 4.49, where $j_1(x) = 0$. This $l = 1$ state is written as 1p. It consists 2(2.1 +1) = 6 particles, thus giving altogether a total of eight other levels in

sequence are

$$1d(l = 2, x = 5.76, \quad no.\text{ of nucleons } 10), 2s(l = 0, \; x = 6.28, \; number \; 2),$$
$$1f(l = 3, \; x = 6.99, \; number \; 14), \ldots\ldots$$

These are listed in fig 5.2 . The left hand side represents the number of particles upto any particular level. Letter before terms s,p,d,f…. represents the order of zero in the Bessel function, e.g. 1s for first zero in Bessel function $j_l(x)$, 2s for second zero in this function .Here we see this shell closes at total particles 2,8,18,20,34,40,58,….. These are not the nuclear magic numbers.

b)Harmonic Oscillator potential: Consider a particle of mass 'M' moving with simple harmonic motion isotropically, bound in three dimensions held to a fixed point by a restoring force Kr, will vibrate about this fixed point with frequency

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{M}} \quad or \quad \text{angular} \quad \text{velocity} \quad \omega = \sqrt{\frac{k}{M}}$$

Hence the P.E function V(r) of the oscillating particle

$$V(r) = \int_0^r kr\ dr = \frac{1}{2}kr^2 = \frac{1}{2}M\omega^2 r^2$$

The energy eigen value corresponding to the eigen function

$\psi_{n,l,m}(r,\theta,\Phi) = u_{n,l}(r)\ Y_{l,m}(\theta,\Phi)$ is given by

$$E_{n,l} = \hbar\omega(2n + l - \frac{1}{2}) = \left(\Lambda + \frac{3}{2}\right)\hbar\omega$$

$$n = 1,2,3,................ \qquad l = 0,1,2,........... \qquad \Lambda = 2n + l - 2$$

When the angular dependence of the wave function is examined, it is found that for each Λ value , there is a degenerate group of levels with different l values such that $l \le \Lambda$ and even (odd) corresponds to even(odd) values of Λ. Thus the sequence of single degenerate levels, each band separated by energy $\hbar\omega$ from the next.. The degeneracy corresponding to each l value is $2(2l+1)$ as before.

However, the eigen states corresponding to the same value of Λ (=2n $+l$-2) are also degenerate . Since 2n = Λ - l + 2 is even for Λ even or odd, the degenerate eigen states are

$$(n,l)=\left[\frac{1}{2}(\Lambda+2),0\right],\left[\frac{\Lambda}{2},2\right]\ldots\ldots\ldots\ldots\ldots\ldots\ldots[2,\Lambda-2],[1,\Lambda]\quad for\quad \Lambda\quad even$$

$$=\left[\frac{1}{2}(\Lambda+1),1\right],\left[\frac{1}{2}(\Lambda-1),3\right],\ldots\ldots\ldots\ldots[2,\Lambda-2],[1,\Lambda]\quad for\quad \Lambda\quad odd$$

No. of neutrons or protons with the eigen value E_Λ

$$N_A=\sum_{k=0}^{\Lambda/2}2[2(2k)+1]\qquad for\ \ even\quad \Lambda$$

$$=\int_{k=0}^{\frac{\lambda-1}{2}}2[2(2k+1)+1]\qquad for\quad odd\quad \Lambda$$

$$=(\Lambda+1)(\Lambda+2)\ \text{in either case}$$

The total no. of particles for all levels up to Λ is

$$\sum_{\Lambda}N_\Lambda=\frac{1}{3}(\Lambda+1)(\Lambda+2)(\Lambda+3)$$

The single particle level scheme predicted by the infinite harmonic oscillator well is given below.

Λ	E_Λ	l values	Degenerate states	No. of particles $(\Lambda+1)(\Lambda+2)$	Total no. of particles $\frac{1}{3}(\Lambda+1)(\Lambda+2)(\Lambda+3)$
0	$\frac{3}{2}\hbar\omega$	0	1s	2	2
1	$\frac{5}{2}\hbar\omega$	1	1p	6	8
2	$\frac{7}{2}\hbar\omega$	0,2	2s,1d	12	20
3	$\frac{9}{2}\hbar\omega$	1,3	2p,2f	20	40
4	$\frac{11}{2}\hbar\omega$	0,2,4	3s,2d,1g	30	70

The result of harmonic oscillator potential indicates the shell closes at the numbers 2,8,20,40,70 etc, where as square well potential suggests the magic numbers at 2,8,20,34,40,58,68,70,92,106,112,138 and 156. Experimentally observed values are 2,8,20,50,82,126. There fore, the truth lies between these two potential.

C)Spin Orbit Coupling: Mayer and Hexel, Jensen and suess in 1949 suggested that a non-central component should be included in the force acting on a nucleon in a nucleus. Spin orbit coupling is corresponding to the interaction between the orbital angular momentum and the intrinsic angular moment (spin) of a particle. The magnetic moment is associated with the spin angular momentum and the magnetic field is induced due to the orbital angular momentum . This magnetic field has an effect on the magnetic moment.

The interaction energy

$$W = -\vec{\mu}_s . \vec{B}$$
$$= -f(r) \hat{s}.\hat{l}$$

Here μ_s is the magnetic moment, B is the magnetic field.

S and l are the spin and orbital angular momentum vectors respectively.

f (r) is the potential function. The potential describing the single particle wave function will be $V(r) - f(r)\hat{s}.\hat{l}$ V(r) is the central potential, f (r) is non-central potential component. They are dependent only on the radial distance and the size of the nucleus. Because of the strong coupling the two vectors combine to a total angular momentum j for this particle since s = ½ there are only two possible ways of s and l , resulting in the Stretch case j = l + s and Jacknife case j = l - s (see fig. 5.3)

$$s,l = \frac{1}{2}l \quad for \quad j = l + \frac{1}{2}$$
$$s,l = -\frac{1}{2}(l+1) \quad for \quad j = l - \frac{1}{2}$$

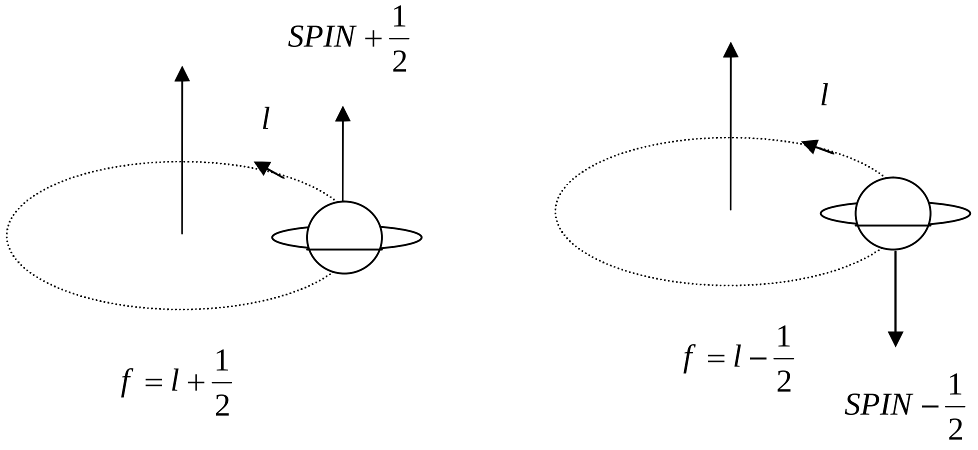


Fig.5.3.Coupling of orbital and spin angular momenta of a nucleon.

The spin orbit interaction splits each of the higher single particle levels. For a given l and they are characterized by total angular momentum quantum numbers $l+\frac{1}{2}, l-\frac{1}{2}$ and each sublevel can accommodate (2j+1) neutrons and protons.

Splitting of nucleon energy levels based on shell model.

The inherent assumptions of a single particle shell model are listed below.

1. The levels are gradually filled, the levels with higher j lies deepest.

2.The energy difference between $l+\frac{1}{2}$ level and $l-\frac{1}{2}$ level is quite large for a given l

and it increases with increasing l

3. An even no. of identical nucleon with same l and j couple to keep even parity (zero total

angular momentum and zero magnetic moment.)

4. An odd no. of identical nucleon with same l and j couple to give rise odd parity.

if l is odd and even parity if l is even and total angular momentum j and magnetic

moment is equal to that of single nucleon in that state.

5.If the state is occupied by two identical nucleons, there is additional paring energy associated with the states and the pairing energy increasing with j value.

On the basis of above assumption the existence of higher magic numbers can be deduced . As an example consider the 1d state. The state orbital angular momentum of 2 units and spin angular momentum of ½ unit; hence there are two possible values of total angular momentum 5/2 and 3/2 . the former is six fold degenerate and latter is four fold; on the whole 1d state, can accommodate 10 nucleons. When the value of l becomes large, the separation of $l-\frac{1}{2}$ level with $l+\frac{1}{2}$ level increases to such an extent that two belong to the different shells.

The situation is illustrated in figure5.4. for the levels 1g $_{9/2}$ (N=4), 1h$_{11/2}$ (N=5),etc. In figure 5.4, 2 digits on the right side give the magic numbers. The energy values are mentioned on the left side after subtracting zero point energy.

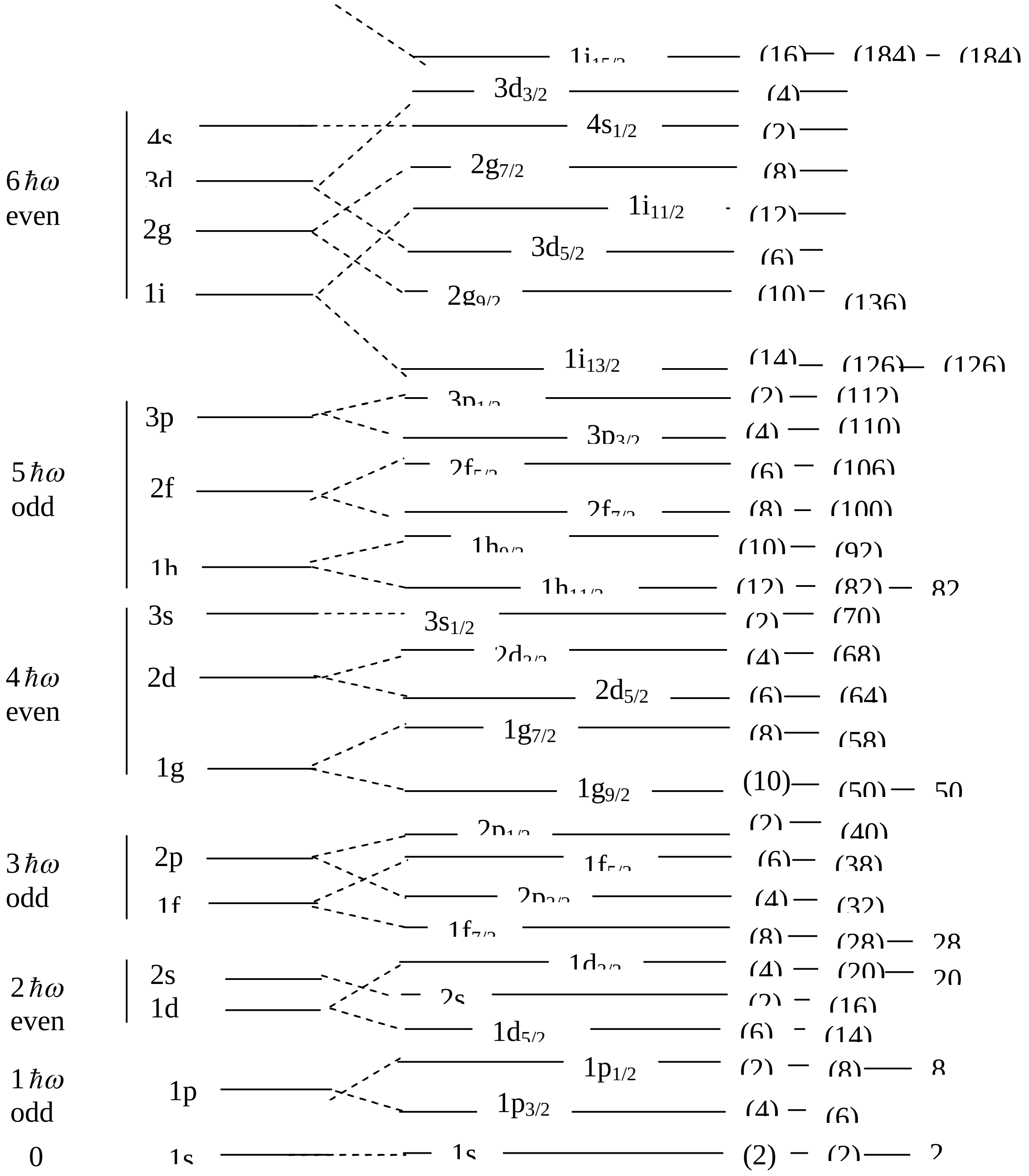


Fig. 5.4. splitting of energy levels in shell model

Examples of finding spin & parity of elements.

1) $_6C^{12}$ 6p & 6N I = 0 parity = $(-1)^0$ = +1 even

2) $_5B^{11}$ 5p & 6N $I = \frac{3}{2}$ parity = $(-1)^1$ = -1 odd

3) $_7N^{16}$ 7p & 9N $J_1 = \frac{1}{2}, l_1 = 1$ $J_1 + J_2 + l_1 + l_2 = 6$ *even*

$J_2 = \frac{5}{2}, l_2 = 1$ $I = \left(\frac{1}{2} - \frac{5}{2}\right) = 2$

$P = (-1)^{l_1 + l_2} = (-1)^3 = -1$ *odd*

4) $_{33}Ar^{73}$ 33p & 42N $I = \frac{3}{2}$ P = $(-1)^3$ = -1 odd

5) $_{28}Ni^{61}$ 28p & 33N $I = \frac{3}{2}$ P = $(-1)^3$ = -1 odd

4)Predictions of the shell model:

1)Stability of the closed shell nuclei: This scheme clearly reproduces all the magic numbers.

2)Spins and parities of nuclear ground states:

According to shell model the neutron and protons levels fill independently. There are following rules for the angular momenta and parities of nuclear ground state.

a)Even-even nuclei have total ground state angular momentum I = 0 there is no known exception to this rule.

b) With an odd number of nucleons i.e. a nucleus with odd z or odd N the nucleons pair off as far as possible so that the resulting orbital angular momentum and spin direction are just that of single odd particle. There are some exception to this rule and they will be discussed below.

c)An odd-odd nucleus will have total angular momentum which is the vector sum of the odd neutron and odd proton j values. The parity will be the product of the proton & neutron parity i.e..

Parity $=(-1)^{l_n+l_p}$

In the case of odd-odd nuclei the total angular momentum is due to the last proton and last neutron which are left as unpaired neutrons in the respective quantum state. The angular momentum of these two nucleons can combine in many ways. And resultant angular momentum is found by "Nordhiem" rule which states that if for two odd nucleons $j_1 + j_2 + l_1 + l_2$ is an even no. the resultant angular momentum I = $\left|J_1 - J_2\right|$

If $j_1 + j_2 + l_1 + l_2$ is an odd no., the spin I is large approaching I = $J_1 + J_2$

For the determination of resultant angular momentum of odd-odd nuclei we apply "Nordheim" rule

If $j_1 + j_2 + l_1 + l_2$ = even no., Spin I = $\left|J_1 - J_2\right|$

If $j_1 + j_2 + l_1 + l_2$ = odd no., Spin I = $J_1 + J_2$

5.5.SEMIEMPIRICAL MASS FORMULA:

The mass M of a neutral atom whose nucleus contains Z protons and A-Z neutrons is given by

$$ {}_ZM^A = ZM_P + (A-Z)M_N + ZM_e - E_B $$

$$ = ZM_H + (A-Z)M_N - E_B $$

Where E_B is the binding energy . may be made up of number of terms, each of which represents some general characteristics of nuclei

$$ E_B = E_v + E_s + E_c + E_a + E_p $$

Where E_v is volume binding energy, E_s is surface binding energy,E_c is coulomb binding energy. E_a is Asymmetric binding energy. E_p is pairing binding energy

Von weizsacker obtained the above formula in 1935. $_ZM^A$ is called semi-empirical mass formula.

The semi-empirical mass formula possesses following properties.

1.It explains the stability of the nuclide

2.it explains fission of heavy nuclide

3.it explains some of the regularities associated with alpha decay process

4.This formula is based upon the general structure of the nucleus and the nature of the binding forces i.e., it incorporate the following assumptions.

a) Nucleus is a droplet of incompressible matter (nuclear density is 10^{14} g/cc)

b)Nuclear forces are short range forces and possess saturation property.

c)There are electrostatic repulsion forces and surface tensional effects that will exists in nuclei.

1)Volume energy: The neutrons and protons are held together by short range attractive forces. These forces reduces the mass of the nucleus below that of its constituents by an amount proportional to the number of nucleons A since the volume of the nucleus is proportional to A hence this term may be regarded as a volume binding energy often called exchange energy and is given by E_v

$$E_v \ \alpha \ A \Rightarrow E_v = a_v A$$

Where a_v is proportionality constant and subscript v is volume energy.

2) Binding Energy: Since nulceus is finite, some nucleons are nearer to the surface so that they interact with few nucleons thus the binding energy E_v is reduced by an amount proportional to the surface area of the nucleus of radius R as the nucleons on the surface are less tightly bound than those in the interior. For light nuclei nearly all the nucleons are at the surface while for heavy nuclei about half the nucleons are at the surface. Thus the surface energy is analogous to the surface tension of nucleus.

$$E_s \ \alpha \ 4\Pi R^2$$

$$E_s \ \alpha \ 4\Pi(R_0 A^{1/3})^2 \quad \text{R is radius of spherical nucleus}$$

$$E_s = - a_s A^{2/3}$$

Where a_s is proportionality constant and subscript means surface energy.

3)Coulomb energy: Long range force in the nuclei is the coulomb repulsion between protons. The coulomb repulsion term is equal to potential energy of Z protons packed together in a spherically assembly of mean radius R= $R_0A^{1/3}$

$$\text{Uniform charge density } \rho_c = \frac{Ze}{\frac{4}{3}\pi R_0{}^3 A}$$

The electrostatic energy is simply the work done against electrostatic forces in assembling such a sphere. Let dq be the charge on the shell of thickness dr on the sphere of radius 'r'

$$dq = \rho_c \times 4\pi r^2 dr$$

The work done to bring the charge from infinity, to 'r' against the charge on the sphere.

$$dq = \frac{4\pi r^2 \rho_c \frac{4}{3}\pi r^3 \rho_c}{r}\frac{1}{4\pi\varepsilon_0}$$

$$E_c = -\int_0^R \frac{16\pi^2 r^5 \rho^2 dr}{3r}\frac{1}{4\pi\varepsilon_0}$$

$$= -\int_0^R \frac{16\pi^2 r^4 \rho^2 dr}{3}\frac{1}{4\pi\varepsilon_0}$$

$$= \frac{-16\pi^2 R^5 \rho^2}{15}\frac{1}{4\pi\varepsilon_0}$$

$$E_c = \frac{-3z^2e^2}{5R}\frac{1}{4\pi\varepsilon_0} \qquad (\sin ce \ \rho_c = \frac{Ze}{\frac{4}{3}\pi R^3})$$

$$E_c = \frac{-3z^2e^2}{5\pi R_0 A^{\frac{1}{3}}}\frac{1}{4\pi\varepsilon_0}$$

Coulomb repulsion binding energy $E_c = -\frac{3}{5}\frac{z^2e^2}{4\pi\varepsilon_0 R_0 A^{1/3}} = -a_c\frac{Z^2}{A^{1/3}}$

where a_c is a constant and the subscript c denotes coulomb energy.

4)Asymmetry energy: It has been observed that nuclei are most stable when nucleus consists of n equal number of protons and neutrons . As the value of A increases the number of protons increases and this transition to the asymmetric configuration from symmetric configuration reduces the stability of nuclei. Alternately, the binding energy decreases and this decrement is known as correction. (N –Z) excess of neutrons produces a deficit in binding energy because they are out of reach of other nucleon. The fraction of nuclear volume so affected is $\frac{N-Z}{A}$ and there fore, the total deficit should be proportional to

$$(N-Z)\frac{(N-Z)}{A} \quad or \quad \frac{(A-2Z)^2}{A}$$

$$hence \quad B_3 = -a_a\frac{(A-2Z)^2}{A}$$

In fact asymmetry energy is purely quantum mechanical effect in contrast with coulomb energy and surface energy. The presence of unbinding term $(N-Z)^2$ greatly favours Z =N, as stable configuration.

$$E_a \alpha \quad (N-Z)\left(\frac{N-Z}{A}\right)$$

$$E_a = - \quad a_a\frac{(N-Z)^2}{A}$$

$$E_a = - \quad a_a\frac{(A-2Z)^2}{A}$$

a_a is constant subscript represents ‘a ‘ is for asymmetry.

5) Pairing energy: The nuclides with even numbers of protons and neutrons are the most abundant and most stable. Nuclei with odd numbers of both neutrons and protons are the least stable. While nuclei for which either proton or neutron number is odd are intermediate in stability. To take account of this pairing effect an additional term is used. This term can be taken as zero for odd A, $-\delta$ for odd-odd and $+\delta$ for even-even nuclide.

$\delta = ap\,A^{-\frac{3}{4}}$ where a_p is the pairing energy constant.

$E_p = 0$ for A odd, Z even N odd or Z odd N even

$E_p = a_p/A^{3/4}$ for A even, Z even and N even

$E_p = -a_p/A^{3/4}$ f or A even, z odd and N odd.

By collecting together the different stability of mass correct terms, then semi empirical mass formula becomes.

$$_ZM^A = ZM_H + (A-Z)M_N - a_vA + a_sA^{2/3} + a_cZ^2 A^{-1/3} + a_a (A-2Z)^2 A^{-1} \pm a_pA^{-3/4}$$

This is called semi empirical mass formula.

Applications:

1) Fission of heavy nuclides
2) Behaviour of isobars in B –decay
3) Alpha decay , coulomb radius, radius of mirror etc, are excellent agreement with other methods.

Modifications:

$$_ZM^A = Z(M_H - M_N) + A(M_N - a_v) + a_sA^{2/3} + a_cZ^2 A^{-1/3} + a_a A - 4 a_a Z + 4 a_a Z^2/A \mp \delta$$

$$_ZM^A = a_1A + a_2Z + a_3Z^2 \mp \delta \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $a_1 = M_N - (a_v - a_a - a_sA^{-1/3})$

$a_2 = M_H - M_N - \psi a_a$

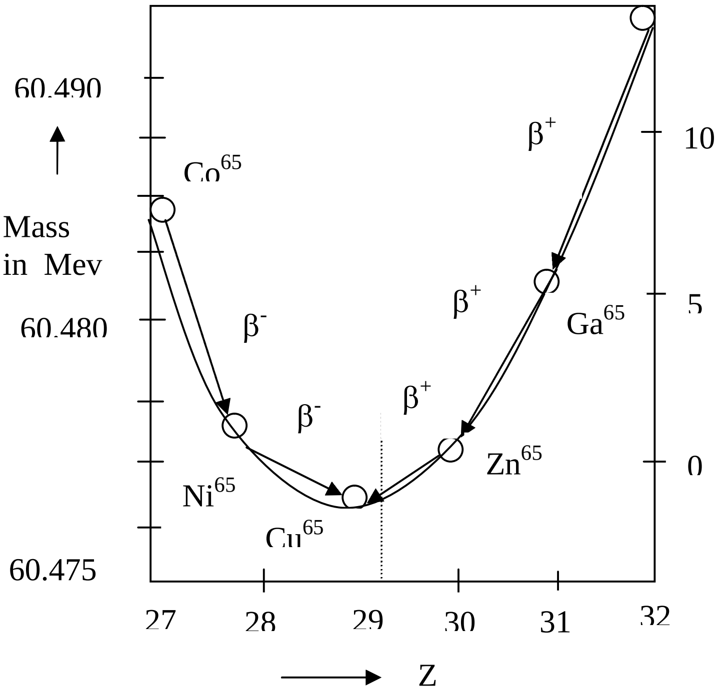
$$a_3 = 4\, a_a/A + a_c/A^{1/3}$$

eqn(1) gives the dependence of nuclear mass on nuclear charge for a constant mass number 'A'. This dependence gives parabola. Therefore it is very clear that most stable nuclide has the minimum mass corresponding value of 'Z' can be determined by finding the minimum of parabolic curve. Accordingly differentiate eqn(1) w.r.to 'Z' for constant A then we get

$$\frac{\partial\left({}_{z}M^{A}\right)}{\partial z} = a_2 + 2a_3 z = 0$$

$$\Rightarrow z_0 = -\frac{a_2}{2a_3}$$

This gives the value of 'z' for most stable isobar for given 'A'.



Schematic plote of M versus Z for odd A

5.6.LIQUID DROP MODEL:

In 1937, N. Bohr proposed the liquid drop model for the nucleus associated with semi empirical mass formula . In this model the finer features of nuclear forces are ignored but the strong inter nucleon attraction is stressed. The essential assumptions are

1) The nucleus consists of incompressible matter so that $R = R_0A^{1/3}$

2) The nuclear force is identical for every nucleon.

3) The nuclear force saturates.

The individual nucleons must be able to move about with in the nucleus much as does an atom of a liquid, therefore think of nucleus as being like a small drop of liquid such a model is known as liquid drop model.

The idea that the molecules in the drop of a liquid corresponding to the nucleons in the nucleus is confirmed due to the following similarities.

1) The nuclear forces are analogous to the surface tension force of a liquid.

2) The nucleons behave in a manner similar to that of molecules in a liquid.

3) The density of nuclear matter is almost independent of mass number ‘A’ which is analogous to the liquid drop where the density of liquid is independent of the size of drop.

4) The constant binding energy per nucleon is analogous to the latent heat of vapourisation

5) The disentegration of nuclei by the emission of particles is analogous to the evaporisation of molecules from the surface of liquid.

6) The energy of nuclei corresponds to international thermal vibrations of drop molecules.

7) The formation of compound nucleus and absorption of bombarding particles are correspond to the condensation of drops.

Inspite of these similarities we see some of the following differences.

1) Molecules attract one another at distances larger than the dimensions of the electron shells and repel strongly when the distance is smaller than the size of the electron orbits. Nuclear forces are attractive within the smaller range, the range of nuclear forces.

2) The average K.E. of molecule in the liquid is of the order of 0.1ev., the corresponding de Broglie wave length is 5×10^{-11}m. which is very much smaller than the inter nuclear distances The average K.E. of nucleons in a nuclei is of the order of 10Mev corresponding to wavelength is 6×10^{-15}m, which is the order of inter – nucleon distances. Hence the motion of molecules in the liquid is of classical character where as in nuclei the motion of the nucleons is of quantum character.

The success of this model has been beautifully demonstrated in explaining the following

1) Constant binding energy per nucleon
2) Behaviour of isobars
3) Constant density of nucleons with radius $R = R_0A^{1/3}$
4) Fission heavy nuclei
5) Nuclear reaction
6) Cross-section for resonance reaction
7) Stability limit of heavy nuclei.

The condition for fission: Let us consider the case of symmetrical fission in order to simplify the calculation. The fission energy E_f or Q - value for the nuclear fission relation will be written as

$$E_f = B_A - 2B_{\frac{A}{2}}$$

In the spontaneous fission

$$E_f = {}_z M^A - 2\,{}_{\frac{z}{2}}M^{\frac{A}{2}}$$

Semi empirical mass formula is

$${}_z M^A = ZM_H + (A-Z)M_n - a_v A + a_c\frac{Z^2}{A^{1/3}} + a_s A^{2/3} + a_a\frac{(A-2Z)^2}{A}$$

$${}_{\frac{z}{2}}M^{\frac{A}{2}} = \frac{Z}{2}M_H + \left(\frac{A}{2}-\frac{Z}{2}\right)M_n - a_v\frac{A}{2} + a_c\frac{\left(\frac{Z}{2}\right)^2}{\left(\frac{A}{2}\right)^{1/3}} + a_s\left(\frac{A}{2}\right)^{2/3} + a_a\frac{\left(\frac{A}{2}-2\frac{Z}{2}\right)^2}{\frac{A}{2}}$$

$$E_f = {}_z M^A - 2\,{}_{\frac{z}{2}}M^{\frac{A}{2}}$$

$$E_f = ZM_H + (A-Z)M_n - a_v A + a_c\frac{Z^2}{A^{1/3}} + a_s A^{\frac{2}{3}} + a_a\frac{(A-2Z)^2}{A} -$$

$$2\left[\frac{Z}{2}M_H + \left(\frac{A}{2}-\frac{Z}{2}\right)M_n - a_v\frac{A}{2} + a_c\frac{\left(\frac{z}{2}\right)^2}{\left(\frac{A}{2}\right)^{1/3}} + a_s\left(\frac{A}{2}\right)^{2/3} + a_a\frac{\left(\frac{A}{2}-\frac{2Z}{2}\right)^2}{\frac{A}{2}}\right]$$

$$E_f = \underbrace{a_s\left[A^{\frac{2}{3}} - 2\left(\frac{A}{2}\right)^{2/3}\right]}_{Surface\ \ energy} + \underbrace{a_c\left[\frac{Z^2}{A^{1/3}} - 2\frac{(Z/2)^2}{(A/2)^{1/3}}\right]}_{Coulomb\ \ energy}$$

$$a_s = 13.1 Mev$$
$$a_c = 0.609 Mev$$

Spontaneous fission is energetically possible only if $E_f \geq 0,$ *then*

$$-3.42A^{2/3} + 0.22\frac{Z^2}{A^{1/3}} \geq 0$$

$$\frac{Z^2}{A} \geq \frac{342}{22}$$
$$\frac{Z^2}{A} \geq 15$$

This condition is satisfied with mass number A > 85

The fission process affects these two energies in opposite ways. The tendency of one is to annual partly other. It is expected in the fission process because in the division of the nucleus, the separation between the proton groups increases reducing the coulomb energy while the total nuclear surface increases, increasing the surface energy.

BOHR WHEELER'S THEORY OF NUCLEAR FISSION:

Nuclear distortion explained on the basis of liquid drop .

The nuclear distribution have an appreciable influence on the surface energy and coulomb energy. The nuclear distribution can be stated by assuming that the shape of the nucleus is not sphere. The small distribution of liquid drop is given by

$$r_\theta = R\ f(\theta)$$

r_θ is the radius of deformed drop

where f(θ) can be expressed as an expression in the Legendre's polynomial.

$$f(\theta) = 1 + a_0 p_0(Cos\theta) + a_1 p_1(Cos\theta) + a_2 p_2(Cos\theta) + \ldots\ldots\ldots\ldots + a_n p_n(Cos\theta)$$

$$r_\theta = R + R\sum_{n=0}^{\alpha} a_n p_n(Cos\theta) \qquad for \quad n = 0,1,2,3\ldots\ldots\ldots\ldots$$

In f(θ) where $a_0, a_1, a_2\ldots..$ are the distortion parameters and p's are the Legendre's polynomial

$$p_0(\cos\theta) = 1 \qquad p_1(\cos\theta) = Cos\theta,$$
$$p_2(\cos\theta) = \frac{3Cos^2\theta - 1}{2}, \qquad p_3(\cos\theta) = \frac{5Cos^3\theta - 3Cos\theta}{2}$$

Here, the requirement of constant volume specifies that $a_0 = a_1 = 0$

Because the centre of mass of the drop is assumed to remain unchanged for these two cases.

$$f(\theta)=1+\sum_{l=0}^{\alpha} a_l\, p_l(Cos\theta)\text{.............(1)}$$

$$f(\theta)=1+\sum_{r=2}^{\alpha} a_r\, p_r(Cos\theta)$$

From orthogonality property of Legendre's polynomial the distortion parameter for f(θ) can be written as

$$a_n = \frac{\int_0^{\pi} f(\theta)p_n(Cos\theta)Sin\theta d\theta}{\int_0^{\pi} p_n{}^2(\cos\theta)Sin\theta d\theta}\text{...................(2)}$$

proof:

we know that

$$\int_{-1}^{+1} p_n{}^2(n)dn = \frac{2}{2n+1}$$

$$\int_{-1}^{+1} p_m(n)p_n(n)dn = 0 \qquad m \neq n$$

Multiplying (1) by $p_n(\cos\theta)Sin\theta d\theta$ and integrate between the limits 0 to π

$$\int_0^{\pi} f(\theta)p_n(\cos\theta)Sin\theta d\theta = \int_0^{\pi} 1\, p_n(Cos\theta)Sin\theta d\theta + \sum_{l=0}^{\alpha} a_l \int_0^{\pi} p_l(\cos\theta)p_n(Cos\theta)Sin\theta d\theta$$

$$\int_0^{\pi} P_0(\cos\theta)p_n(Cos\theta)Sin\theta d\theta + \sum_{l=0}^{\alpha} a_l \int_0^{\pi} p_l(\cos\theta)p_n(Cos\theta)Sin\theta d\theta$$

In the above equation l = n is the only non vanishing term hence we get i.e., $\int_0^{\pi} a_n\, p_n{}^2(Cos\theta)Sin\theta d\theta = \int_0^{\pi} f(\theta)p_n(Cos\theta)Sin\theta d\theta$

$$a_n = \frac{\int_0^{\pi} f(\theta) p_n(Cos\theta) Sin\theta d\theta}{\int_0^{\pi} p_n{}^2(\cos\theta) Sin\theta d\theta}$$

The small distribution of a liquid can be written as

$$r_\theta = Rf(\theta)$$

$$r_\theta = R[1 + a_2 p_2(\cos\theta) + a_3 p_3(Cos\theta) + ... + a_n p_n(Cos\theta)]$$

For a's which are identical with one another and equal to zeros nucleus is an undistorted sphere of radius $r_\theta = R$.

Surface energy of undistorted sphere is

$E_s{}^0 =$ surface area x surface tension coefficient

$$= 4\pi R^2 \times T$$

$$E_s{}^o = 4\pi R_0{}^2 T A^{2/3} = a_s A^{2/3}$$

Total surface energy of the distorted nucleons is given by

$$E_s{}^o = 4\pi r_\theta{}^2 T = 4\pi R^2 T[f(\theta)]^2$$

$$E_s{}^o = 4\pi R^2 T[1 + a_2 p_2(Cos\theta) + a_3 p_3(\cos\theta) + ...]^2$$

$$= 4\pi R_0{}^2 A^{2/3} T\left[1 + a_2\left(\frac{3Cos^2\theta - 1}{2}\right) + a_3\left(\frac{5Cos^3\theta - 3Cos\theta}{2}\right) + ...\right]^2$$

$$E_s{}^o = 4\pi R_0{}^2 A^{2/3} T\left[1 + a_2{}^2\frac{2}{5} + a_3{}^3\frac{5}{7} + ...\right]$$

By neglecting higher order terms

Surface energy of deformed nucleus is

$$E_s{}^o = 4\pi R_0{}^2 T A^{2/3}\left[1 + \frac{2}{5}a_2{}^2\right]...........................(3)$$

$$E_s{}^o = a_s A^{2/3}\left[1 + \frac{2}{5}a_2{}^2\right] \qquad \left[\because a_s = 4\pi R_0{}^2 T\right]$$

Electrostatic energy or coulomb energy of undistorted spherical shape is

$$E_c{}^o = \frac{3}{5}\frac{Z^2e^2}{R} = \frac{3}{5}\frac{Z^2e^2}{R_0A^{1/3}} = a_c\,\frac{Z^2}{A^{1/3}} \qquad where \qquad a_c = \frac{3}{5}\frac{e^2}{R_0}$$

similarly, the coulomb energy of deformed nucleus as

$$\begin{aligned} E_c{}^o &= \frac{3}{5}\frac{Z^2e^2}{r_\theta} = \frac{3}{5}\frac{Z^2e^2}{Rf(\theta)} \\ &= \frac{3}{5}\frac{Z^2e^2}{R_0A^{1/3}}\left[1+a_2\left(\frac{3Cos^2\theta-1}{2}\right)+a_3\left(\frac{5Cos^3\theta-3Cos\theta}{2}\right)+\ldots\ldots\ldots\ldots\ldots\right]^{-1} \\ &= \frac{3}{5}\frac{Z^2e^2}{R_0A^{1/3}}\left[1-\frac{1}{5}a_2{}^2+\frac{10}{49}a_3{}^2+\ldots..\right] \\ &= \frac{3}{5}\frac{Z^2e^2}{R_0A^{1/3}}\left[1-\frac{1}{5}a_2{}^2\right] \qquad (By\ \text{neglecting the higher order terms}) \\ &= a_c\,\frac{Z^2}{A^{1/3}}\left[1-\frac{1}{5}a_2{}^2\right] \end{aligned}$$

Total energy of undistorted nucleus

$$\begin{aligned} E_s{}^0 + E_c{}^o &= 4\pi R_0{}^2TA^{2/3} + \frac{3}{5}\frac{Z^2e^2}{R_0A^{1/3}} \\ &= a_sA^{2/3} + a_c\,\frac{Z^2}{A^{1/3}} \end{aligned}$$

Total energy of distorted nucleus

$$\begin{aligned} E_s{}^0 + E_c{}^o &= 4\pi R_0{}^2TA^{2/3}\left(1+\frac{2}{5}a_2{}^2\right) + \frac{3}{5}\frac{Z^2e^2}{R_0A^{1/3}}\left(1-\frac{1}{5}a_2{}^2\right) \\ &= a_sA^{2/3}\left(1+\frac{2}{5}a_2{}^2\right) + a_c\,\frac{Z^2}{A^{1/3}}\left(1-\frac{1}{5}a_2{}^2\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7) \end{aligned}$$

The total energy of distorted spherical shape which differ from former case because of the increase of surface energy due to increase in surface area and decrease of coulomb energy because of the centre of binary parts being further apart.

Now, distortion is given by

$$\Delta E_{s,c}{}^{0} = \left(E_s + E_c\right)^{o} - \left(E_s{}^{o} + E_c{}^{o}\right)$$

$$= a_s A^{2/3}\left(1 + \frac{2}{5}a_2{}^{2}\right) + a_c \frac{Z^2}{A^{1/3}}\left(1 - \frac{1}{5}a_2{}^{2}\right) - \left(a_s A^{2/3} + a_c A^{-1/3}\right)$$

$$= a_s A^{2/3}\frac{2}{5}a_2{}^{2} - a_c \frac{Z^2}{A^{1/3}}\frac{1}{5}a_2{}^{2}$$

$$= \frac{1}{5}a_2{}^{2}\left(2a_s A^{2/3} - a_c \frac{Z^2}{A^{1/3}}\right)$$

$$= \frac{1}{5}a_2{}^{2}\left(2E_s{}^{o} - E_c{}^{0}\right) \text{.....................(8)}$$

For the above expression it is obvious that if $2E_s{}^{0} \succ E_c{}^{0}$ then $\Delta E_{s,c}{}^{0}$ is +ve, the nucleus is metastable.

If $2E_s{}^{0} \prec E_c{}^{0}$ then $\Delta E_{s,c}{}^{0}$ is -ve, then the nucleus is completely unstable

If $2E_s{}^{0} = E_c{}^{0}$ then $\Delta E_{s,c}{}^{0} = 0$ which design a critical value for $\frac{Z^2}{A}$.

From (8)

$$\Delta E_{s,c}{}^{0} = \frac{1}{5}a_2{}^{2}\left(2E_s{}^{0} - E_c{}^{0}\right)$$

$$= \frac{1}{5}a_2{}^{2}\left[2\left(4\pi R_0{}^{2} T A^{2/3}\right) - \frac{3}{5}\frac{Z^2 e^2}{R_0 A^{1/3}}\right]$$

If $2E_s{}^{0} = E_c{}^{0}$ so that

$$2\left(4\pi R_0{}^2 T A^{2/3}\right) = \frac{3}{5}\frac{Z\ e^2}{R_0 A^{1/3}}\frac{1}{4\pi\varepsilon_0}\frac{Z^2}{A} = \frac{24\pi R_0{}^2 T 5 R_0 4\pi\varepsilon_0}{3e^2}$$

$$\left(\frac{Z^2}{A}\right)_{critical} = \frac{4\pi\varepsilon_0 40\pi R_0{}^3 T}{3e^2}$$

$$put \qquad R_0 = 1.6F \quad = 1.6\times 10^{-15}\, m$$

$$e = 4.8\times 10^{-10}\, esu$$

$$T = 0.057\times 10^{7}$$

$$\varepsilon_0 = 8.85\times 10^{-12}\ farad/m$$

$$\therefore \left(\frac{Z^2}{A}\right)_{critical} = 47.86$$

Let us express the fissionable parameters interms of critical value.

$$\chi = \frac{\left(\frac{Z^2}{A}\right)}{\left(\frac{Z^2}{A}\right)_{critical}}$$

where χ <1 , the nucleus is metastable against the spontaneous fission (stable)

When χ >1 , the nucleus is unstable, against spontaneous fission (unstable)

When χ =1 $\quad \frac{Z^2}{A} = \left(\frac{Z^2}{A}\right)_{critical}$

5.7.Summary: A good model should describe

1. The properties of the ground nuclear states (spins, parities, magnetic dipole, magnetic dipole, electric quadrupole moments etc.)

2.The properties of excited states especially the nuclear excitation spectrum.

3.The dynamical properties of the nucleus.

EXTREME SINGLE PARTICLE MODEL:

1) In this model it is assumed that the nucleons in the nucleus move independently in a common potential, determined by the average motion of all other nucleons.

2). Most of the nucleons are paired so that a pair of nucleons contributes zero spin and zero magnetic moment . The paired nucleus thus form an inert core.

3). The properties of odd A nuclei are characterized by the unpaired nucleon and odd – odd nuclei by the unpaired proton and neutron.

Spin orbit coupling is corresponding to the interaction between the orbital angular momentum and the intrinsic angular moment (spin) of a particle.

Predictions of the shell model:

1)Stability of the closed shell nuclei: This scheme clearly reproduces all the magic numbers.

2)Spins and parities of nuclear ground states:

The semi-empirical mass formula possesses following properties.

1.It explains the stability of the nuclide

2.it explains fission of heavy nuclide

3.it explains some of the regularities associated with alpha decay process

In 1937, N. Bohr proposed the liquid drop model for the nucleus associated with semi empirical mass formula . In this model the finer features of nuclear forces are ignored but the strong inter nucleon attraction is stressed. The essential assumptions are

1) The nucleus consists of incompressible matter so that $R = R_0A^{1/3}$

2) The nuclear force is identical for every nucleon.

3)The nuclear force saturates.

The individual nucleons must be able to move about with in the nucleus much as does an atom of a liquid, therefore think of nucleus as being like a small drop of liquid such a model is known as liquid drop model.

Keywords:
Magic numbers, Shell model, Spin-orbit coupling, Emperical mass formula, Liquid drop model.

Self assessment questions:

1. Explain the need of model for physical system.
2. What are magic numbers? Give some evidences for the existence of magic numbers.
3. Discuss about the nuclear shell model (extreme single particle model). How the shell model predicts the magic numbers.
4. What are the other predictions of shell model?
5. Derive weitz-sacker semi empirical mass formula. How this formula explains the behaviour of nuclear isobars.
6. How does the Bohr-wheeler theory explains the nuclear fission.

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel

Unit 2

Lesson 6

RADIO ACTIVITY-I

The objectives of the lesson are to explain the following:

6.1. Introduction

6.2 Alpha-Instability

6.3. Theory of Alpha Decay

6.4. Gamma Emission

6.5. Internal Conversion

6.6. Nuclear Isomerism

6.7. Summary.

6.1.Introduction: The phenomenon of radioactive disintegration is the result of instability of nuclei and their tendency to change into more simple species. In terms of binding energy, we can state that a nuclide will be energetically stable towards decay by some specified mode (α-emission, β-emission or spontaneous fission). If its binding energy is greater than the total binding energy of fragments into which it can disintegrate (i.e., if its atomic mass is smaller than the sum of the masses of the products that are formed as a result of decay process.) Such nuclides can of course be disintegrated if energy is supplied to them: the energy supplied appears in the form of kinetic energies of the fragments.

It has been observed that nuclei with $A \geq 140$ are unstable with respect to α- particle emission. This is because the emission of α- particle lowers the coulomb energy -- the principle negative energy contribution to the binding energy of heavy nuclei, but does not change the binding energy appreciably, for α- particle itself is a tightly bound structure.

6.2.Alpha – Instability:

The alpha particle is spontaneously ejected from a nucleus. In the process parent loses an aggregate of two protons and two neutrons.

The process may be expressed as

$$_ZX^A \longrightarrow {}_2He^4 + {}_{Z-2}Y^{A-4}$$

Where $_ZX^A$ represents the parent nuclei

$_{Z-2}Y^{A-4}$ represents the daughter nuclei

The process is energetically possible if the sum of the binding energies of last two protons and last two neutrons in the nucleus is less than the alpha binding energy of the value 28.3 Mev.

$$_ZX^A \longrightarrow {}_2He^4 + {}_{Z-2}Y^{A-4}$$

$$M_p^1C^2 = m_D^1 + T_D + m_\alpha^1 C^2 + T_\alpha \text{ ……………………….(1)}$$

M_p^1 is mass of parent nucleus

m_D^1 is mass of daughter nucleus

m_α^1 is mass of α – particle

T_D is kinetic energy of daughter nuclei

T_α is kinetic energy of alpha particle

$$Q = \hat{p}_D + \hat{p}_\alpha \text{..............(2)}$$

Conservation of energy diagram:

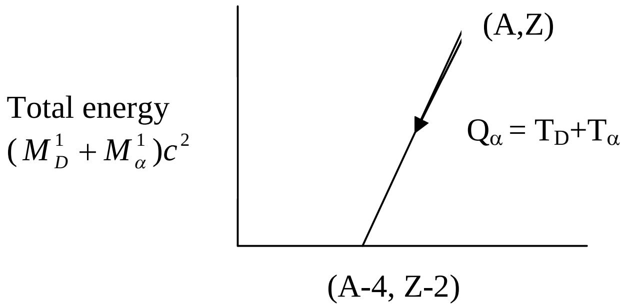


Fig.6.1. Conservation of energy

Conservation of momentum diagram:

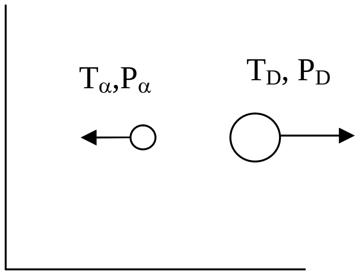


Fig.6.2. Conservation of momentum

$$M_pC^2 = (m_D + m_\alpha) C^2 + T_D + T_\alpha \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

This is conservation of mass energy eqn in terms of atomic mass energy

$$Q_\alpha = T_D + T_\alpha \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$Q_\alpha = (M_p - (m_D + m_\alpha)) C^2$$

The α particle decay can be measured in two ways

1. Particle spectroscopy 2. mass spectroscopy

$$T_D = \frac{P_D{}^2}{2m_D}, \qquad T_\alpha = \frac{P_\alpha{}^2}{2m_\alpha}$$

$$P_i = P_d + P_\alpha$$

Since in all problems of interest P_i is essentially taken as zero, i.e. it is assumed at rest. Hence $|P_d| = |P_\alpha$

$$T_D{}^2 = \frac{P_\alpha{}^2}{2m_D}$$

$$T_D = \frac{2T_\alpha m_\alpha}{2m_D} = \frac{m_\alpha}{m_D}T_\alpha$$

$$Q_\alpha = T_D + T_\alpha$$

$$= \left(\frac{m_\alpha}{m_D} + 1\right)T_\alpha = \left(\frac{m_D + m_\alpha}{m_D}\right)T_\alpha$$

$$\Rightarrow Q_\alpha = \frac{A}{A-4}T_\alpha \text{..................}(5)$$

$$\Rightarrow T_\alpha = \left(1 - \frac{4}{A}\right)Q_\alpha \text{................}(6)$$

The eqn(6) implies that most of the K.E. liberated in alpha decay is taken away by the α - particle while a small fraction by the daughter nucleus.

$$_{84}Po^{212} \longrightarrow {}_2He^4 + {}_{82}Pb^{208} + 8.6\text{Mev}$$

$$_{92}U^{238} \longrightarrow {}_2He^4 + {}_{90}Th^{234} + 4.2\text{Mev}$$

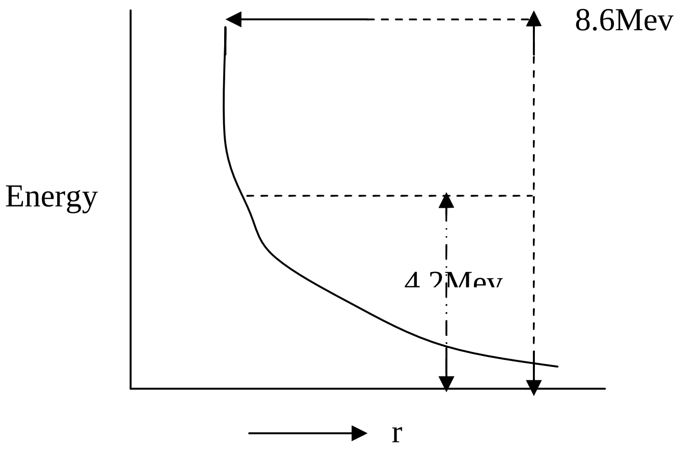


Fig. 6.3.Coulomb energy barrier for Z = 90 and Z = 92

6.3.THEORY OF ALPHA DECAY:

Rutherford in 1927 established that when α - particles of energy of the values 8.8Mev from Po^{213} source are bombarded on a thin U^{238} film, the particles are scattered in accordance with his theory or large angle scattering. Alternately, we can say that they have insufficient kinetic energy to surmount the potential energy barrier arising from the coulomb field round the uranium nucleus. The situation may be illustrated by considering the interaction of α – particle with radioactive nucleus U^{238}, in terms of potential energy curve (fig 1)

As α – particle approaches the nucleus the repulsion between the particle and nucleus increases and at a distance $r = r_1$ it is maximum,

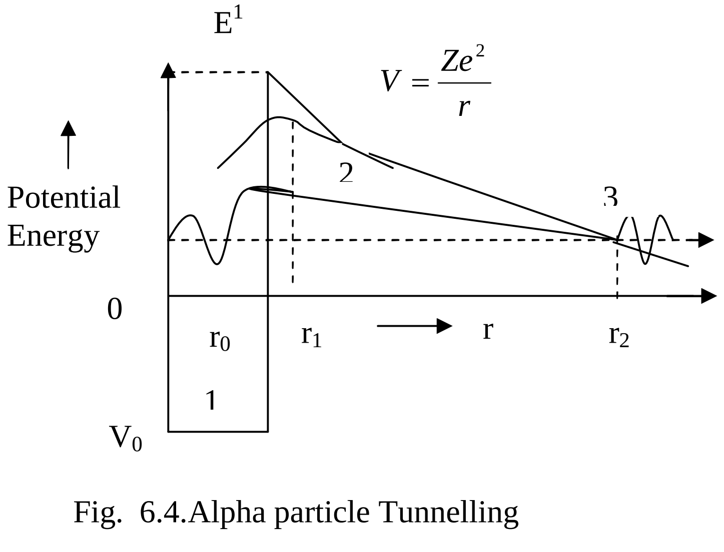


Fig. 6.4.Alpha particle Tunnelling

Near the nucleus and inside the nucleus the shape of the wave is not exactly know, but it is such that in this region we have a constant attraction potential. This is shown by V_0 up to distance r_0 from the nucleus. Classically, the α – particle rests inside the nucleus with kinetic energy equal to $(E + V_0)$ where E is the α – disintegration energy when the particle is far from the nucleus. From fig (1) it turns out that if the particle wants s to escape out of the nucleus it should have maximum energy represented by the curve. Similarly, if an α –particle wants to penetrate the nucleus from outside, again it should have an energy equal to the maximum (E^1) of the curve. Alternately, both way the particle will have to cross an energy barrier of hight E^1. The region between r_2 to r_0 forms the potential barrier because here the potential energy is more than total available energy. As the result of Rutherford experiment we can state the maximum value of potential energy should be greater than 8.8Mev, since α – particle from Po^{214} were scattered by nucleus. However, it is observed that U^{238} spontaneously emits α – particle of energy 4.18Mev.

According to classical ideas, in order to escape from the nucleus of U^{238} .But the energies carried out by alpha particle, emitted by radio-active nuclei, are much lower than the heights of the potential barriers of the respective nuclei. Thus it is very difficult to understand how the particles contained inside the nucleus can go over a potential barrier which is more than twice as high as their total energy. Classical mechanics, provided no explanation of this state. This s can be explain according quantum mechanical theory of barrier penetration. According , to which a particle can leak through a barrier even if its energy is less than the height of barrier. The leakage of the α – particle is termed as α – particle tunneling. The theory of α – particle tunneling was developed by Gamow and Gurney and Condon.

It is assumed that α – particle in the nucleus moves in the spherically symmetric ($l = 0$) field and the wave function is independent of the angle. Then the wave function in the three regions can be written as

$$\frac{d^2\psi}{dr^2} + \frac{2\mu}{\hbar^2}(E - V)\psi = 0$$

with $V = -V_0$ in the region (1)

$$V=\frac{2Ze^2}{r},\quad with\quad \frac{2Ze^2}{r}\succ E\quad in\ region\quad (2)\quad and$$
$$V=\frac{2Ze^2}{r},\quad the\quad E\succ\frac{2Ze^2}{r}\quad in\quad region\,(3)$$

In the above expression μ is the reduced mass of the α – particle and is given by $\frac{4}{1+4/A}$

The solution of eqn(1) can be written in form

$$\psi\ =Ae^{\frac{is}{\hbar}}\ \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

where S is variable characteristic of the point to which 'Ψ' belongs and is a function of r. Now

$$\frac{d\psi}{dr}=\frac{Ai}{\hbar}e^{\frac{is}{\hbar}}\frac{\partial s}{\partial r}$$
$$\frac{d^2\psi}{dr^2}=\frac{Ai^2}{\hbar^2}e^{\frac{is}{\hbar}}\left(\frac{\partial s}{\partial r}\right)^2+\frac{Ai}{\hbar}e^{\frac{is}{\hbar}}\frac{\partial^2 s}{\partial r^2}$$

Putting the values of above derivatives in eqn neglecting the second derivates of S for approximation purpose, we have

$$\frac{Ai^2}{\hbar^2}e^{\frac{is}{\hbar}}\left(\frac{\partial s}{\partial r}\right)^2+\frac{2\mu}{\hbar^2}(E-V)Ae^{\frac{is}{\hbar}}=0$$
$$\left(\frac{\partial s}{\partial r}\right)^2=2\mu(E-V)$$
$$\frac{\partial s}{\partial r}=\pm\left\{\sqrt{2\mu(E-V)}\right\}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

The plus sign is retained because we are interested in outgoing wave. Now

$$\int_{r=r_0}^{r=r_2}\frac{\partial s}{\partial r}=\int_{r_0}^{r_2}iPdr\ldots\ldots\ldots\ldots\ldots\ldots..(4)\quad because\qquad P=\sqrt{2\mu(V-E)}\quad \sin ce\quad V=\frac{2Ze^2}{r}\succ E$$

$$S_2 - S_0 = \int_{r_0}^{r_2} iPdr \text{.....................}(5)$$

Therefore, the values of the function at r =r$_0$ and r = r$_2$ are given by

$$\psi_0 = e^{\frac{is_0}{\hbar}}$$

$$\psi_2 = e^{\frac{is_2}{\hbar}} \text{....................}(6)$$

Decay probability:

The probability of finding the particle at the extreme of the potential barrier will be given by

$$P = \frac{|\psi_2|^2}{|\psi_0|^2}$$

$$= e^{2i/\hbar(S_2 - S_0)}$$

$$= e^{2i/\hbar \int_{r_0}^{r_2} iPdr}$$

$$= e^{-2\int_{r_0}^{r_2} \frac{P}{\hbar}dr}$$

$$= e^{-2\int_{r_0}^{r_2} \frac{1}{\hbar}\sqrt{2\mu\left(\frac{2Ze^2}{r} - E\right)}dr} \text{...................}(7)$$

$$= e^{-2G} \text{.......................}(8)$$

$$where \qquad G = \sqrt{\frac{2\mu}{\hbar^2}\left(\frac{2Ze^2}{r} - E\right)} \text{..........................}(9)$$

The eqn (8) gives the probability of α – particle tunneling

Geiger Nuttal Rule: At r = r$_2$ the potential energy and kinetic energy of α – particle are equal,

hence $\frac{2Ze^2}{r_2} = E$ therefore

$$G = \int_{r_0}^{r_2} \sqrt{\frac{2\mu}{\hbar^2}\left(\frac{2Ze^2}{r} - \frac{2Ze^2}{r_2}\right)} dr$$

……………………….(10)

$$G = \int_{r_0}^{r_2} \sqrt{\frac{2\mu E}{\hbar^2}\left(\frac{r_2}{r} - 1\right)} dr$$

The dependence of 'G' over 'E' implies that probability of α – emission depends upon the disintegration energy. The eqn (10) can be written as

$$G = \int_{r_0}^{r_2} \sqrt{\frac{4Ze^2\mu}{\hbar^2}\left(\frac{1}{r} - \frac{1}{r_2}\right)} dr \text{..........................}(10(a))$$

Taking only $$g = \int_{r_0}^{r_2} \left(\frac{1}{r} - \frac{1}{r_2}\right)^{1/2} dr$$

Put

$$r = r_2 Cos^2\theta \Rightarrow \theta = Cos^{-1}\sqrt{\frac{r}{r_2}}$$

$$dr = -2r_2 Cos\theta \sin\theta d\theta$$

$$\int\left(\frac{1}{r} - \frac{1}{r_2}\right)^{1/2} dr = \int\left(\frac{1}{r_2 Cos^2\theta} - \frac{1}{r_2}\right)^{1/2} \left(-2r_2 Cos\theta Sin\theta d\theta\right)$$

$$= -2\sqrt{r_2}\int \frac{\left(1 - Cos^2\theta\right)^{1/2}}{Cos\theta} \cos\theta \; Sin\theta \;\; d\theta$$

$$= -2\sqrt{r_2}\int \sin^2\theta \ d\theta$$

$$= -2\sqrt{r_2}\int \frac{1-Cos2\theta}{2}d\theta$$

$$= -2\sqrt{r_2}\left[\frac{1}{2}\left(\theta - \frac{1}{2}Sin2\theta\right)\right]_{\theta=Cos^{-1}\sqrt{\frac{r_0}{r_2}}}^{0}$$

Hence

$$\int_{r_0}^{r_2}\left(\frac{1}{r}-\frac{1}{r_2}\right)^{1/2}dr = -\sqrt{r_2}\left[Cos^{-1}\sqrt{\frac{r}{r_2}} - \sqrt{\left(1-\frac{r}{r_2}\right)}\sqrt{\frac{r}{r_2}}\right]_{r_0}^{r_2}$$

$$= -\sqrt{r_2}\left[Cos^{-1}1 - Cos^{-1}\sqrt{\frac{r_0}{r_2}} + \sqrt{\left(1-\frac{r_0}{r_2}\right)}\sqrt{\frac{r_0}{r_2}}\right]$$

$$Taking \qquad Cos^{-1}1 = 0$$

$$g = -\sqrt{r_2}\left[-\left(Cos^{-1}\sqrt{\frac{r_0}{r_2}} - \sqrt{\left(1-\frac{r_0}{r_2}\right)}\sqrt{\frac{r_0}{r_2}}\right)\right]$$

$$= \sqrt{r_2}\left[Cos^{-1}\sqrt{\frac{r_0}{r_2}} - \sqrt{\left(1-\frac{r_0}{r_2}\right)}\sqrt{\frac{r_0}{r_2}}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Substituting this value in eqn (10(a))

$$G = \sqrt{\frac{4\mu Ze^2 r_2}{\hbar^2}}\left[Cos^{-1}\sqrt{\frac{r_0}{r_2}} - \sqrt{\frac{r_0}{r_2} - \frac{r_o{}^2}{r_2{}^2}}\right]$$

$$Let\sqrt{\frac{r_0}{r_2}} = x$$

$$G = \sqrt{\frac{4\mu Ze^2 r_2}{\hbar^2}}\left(Cos^{-1}x - x\sqrt{1-x^2}\right)$$

$$For \quad small \quad values \quad of \;\; x \qquad Cos^{-1}x = \frac{\pi}{2} - x$$

$$G = \sqrt{\frac{4\mu Ze^2 r_2}{\hbar^2}}\left(\left(\frac{\pi}{2} - x\right) - x\right)$$

$$G = \sqrt{\frac{4\mu Ze^2 r_2}{\hbar^2}}\,\frac{\pi}{2}\left(1 - \frac{4x}{\pi}\right)$$

The Kinetic energy of the α - particle is given by

$$E = \frac{1}{2}\mu_\alpha v_\alpha{}^2 = \frac{2Ze^2}{r_2}$$

$$r_2 = \frac{4Ze^2}{\mu_\alpha v_\alpha{}^2}; \qquad v_\alpha = Velocity\ of \quad the\ \alpha \quad - particle$$

$$G = \sqrt{\frac{4\mu ze^2}{\hbar^2}\left(\frac{4Ze^2}{\mu V_\alpha^2}\right)}\frac{\pi}{2}\left(1 - \frac{4}{\pi}\sqrt{\frac{r_0\mu_\alpha V_\alpha^2}{2Ze^2}}\right)$$

$$G = \frac{4Ze^2\pi^2}{h\ v_\alpha}\left[1 - \frac{2}{\pi}\sqrt{\left(\frac{\mu_\alpha v_\alpha{}^2}{Ze^2}\right)}\right]$$

$$G = \frac{4Ze^2\pi^2}{h\ v_\alpha} - \frac{8\pi e}{h}\sqrt{\mu Zr_0} \text{.........................(12)}$$

$$\therefore P = e^{-2\left[\frac{4\pi^2 Ze^2}{hv_\alpha} - \frac{8\pi e}{h}\sqrt{\mu Zr_0}\right]} \text{..........................(13)}$$

Frequency of striking the barrier:

Now ‘n’ the frequency of α – particle with which it presents itself as the barrier is written as

$$n = \frac{v_\alpha}{2r_0} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

The theorictical value of this expression comes out to be $\frac{\hbar}{4m_\alpha {r_0}^2}$ and it is numerically equal to 10^{21} collisions counts. This makes the decay constant λ to be written in the form

$$\lambda = nP$$

$$= e^{-2\left[\frac{4\pi^2 Ze^2}{hv_\alpha} - \frac{8\pi e}{h}\sqrt{\mu Z r_0}\right]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(15)$$

$$\log_e^\lambda = \log_e^{\frac{v_\alpha}{2r_0}} - 2\left[\frac{4\pi Ze^2}{hv_\alpha} - \frac{8\pi e}{h}\sqrt{\mu Z r_0} \ldots\ldots\ldots\ldots\ldots(16)\right]$$

Now if a graph is plotted between the logarithm of decay constant and reciprocal of α – particle velocity, the graph is straight line and eqn is regarded as the theoretical form of Geiger Nuttal law It is to be noted that when α – particle is emitted, the interaction is between daughter nucleus and α – particle and therefore in the above expression Z should be replaced by (Z –2) and we write

$$\log_e^\lambda = \log_e^{\frac{v_\alpha}{2r_0}} - 2\left[\frac{4\pi(Z-2)e^2}{hv_\alpha} - \frac{8\pi e}{h}\sqrt{\mu(Z-2)r_0}\right] \ldots\ldots\ldots\ldots\ldots\ldots(17)$$

The expression for the average period is

$$\tau = \frac{1}{\lambda} = \frac{2r_0}{v_\alpha}\exp\left[2\left\{\frac{4\pi(Z-2)e^2}{hv_0} - \frac{8\pi e}{h}\sqrt{\mu(Z-2)r_0}\right\}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(18)$$

Some Remarks About Alpha Decay:

1)If ‘Q’ the energy of the α – particle and λ are known for the given nucleus, and the values of r_0 is calculated then it is found that the results are in good agreement with the formula $r = r_0 A^{1/3}$

In addition to this graph between - and reciprocal of $V_\alpha j$ is straight line. These two results confirm experimentally, Gamow theory of α – decay.

6.4.Gamma Emission:

The term gamma – rays is used to include all electromagnetic radiations emitted by radioactive substance. The spectral region which gamma rays occupy ranges from soft X – ray region to very short wavelength of the order of few x units.$(1x^0 = 10^{-11} cm)$

Properties of Gamma Rays:

1. The energy of gamma – rays is characterized by 'hν' , which may be expressed in ergs, 'ev' or in the unit of m_0c^2
2. The gamma – rays do not bend in electric and magnetic fields.
3. They travel with the velocity of light and made to diffract and interfere just as X –rays.
4. The gamma – rays are having very high penetrating power.
5. They produce less ionization per unit length of the path.

To find the energy of gamma – rays , generally we can use the following three methods They are

a) Demond crystal spectrometer

b) Measurement of moderate energies.

c) Pair spectrometer.

Multipole Radiations: Gamma radiations can be divided in to two general categories, namely electric and magnetic radiations. Electric radiations a rise from changes in the distribution of the electric changes in the nucleus, where as magnetic radiation arise from change sin the distribution of the magnetic poles or in the current distribution in the nuclei

For complete description of this radiation, requires the quantum theory of radiation. In this, we shall make the assumptios, as follows,

a)The wavelength of the emitted radiation is much larger than the nuclear radius.

b)The radiating system consists of individual nucleons which contribute to the radiation due to the motion of their charges and magnetic moments.

Let us consider the electromagnetic field in a uniform isotropic loss less medium i.e. the free space region free of sources of radiation. The maxwell's equation for E and B vectors are,

$$\begin{aligned} &\nabla . E = 0 \\ &\nabla . B = 0 \\ &\nabla \times E = -\frac{\partial B}{\partial t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1) \\ &\nabla \times B = \mu_0 \varepsilon_0 \frac{\partial E}{\partial t} \end{aligned}$$

There electric and magnetic fields are continuous vector functions of position and time. Thus time dependence is sinusoidal and fields can be written as

$$\left.\begin{aligned} E(r,t) &= E(r)\, e^{-i\omega t} + E^*(r)\, e^{i\omega t} \\ B(r,t) &= B(r)\, e^{-i\omega t} + B^*(r)\, e^{i\omega t} \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

On substitution of eqn(2) in eqn (1), we get,

$$\nabla \times E = -\frac{\partial B}{\partial t} = i\omega B \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$and \qquad \nabla \times B = \mu_0 \varepsilon_0 \frac{\partial E}{\partial t} = -i\omega \mu_0 \varepsilon_0 E \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

From (3) &(4),

$$\begin{aligned} B &= \frac{1}{i\omega}\left(\nabla \times E\right) \\ E &= \frac{1}{-i\omega\mu_0\varepsilon_0}\left(\nabla \times B\right) \end{aligned} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Using eqn(5), we can write eqn (3) & (4) as follows.

$$\nabla \times \left(\frac{1}{-i\omega\mu_0\varepsilon_0} \nabla \times B\right) = i\omega B$$

$$\nabla \times \nabla \times B = \omega^2 \mu_0 \varepsilon_0 B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

and

$$\nabla \times \left(\frac{1}{i\omega} \nabla \times E\right) = -i\omega\mu_0\varepsilon_0 E$$

$$\nabla \times \nabla \times E = \omega^2 \mu_0 \varepsilon_0 E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

From (6) & (7),

$$\begin{aligned} (\nabla \times \nabla \times -k^2)B = 0 \\ (\nabla \times \nabla \times -k^2)E = 0 \end{aligned} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

where $k^2 = \omega^2 \mu_0 \varepsilon_0$ *and* $(\nabla \times \nabla \times -k^2)$ *is an operator*

Therefore the vector eigen functions of the operator $(\nabla \times \nabla \times -k^2)$ have the form

$cLj(kr)\, Y(\theta,\phi)$ where c is a constant.

If we thus set $B_e(L,M) = c^{(e)} Lj(kr)\, Y(\theta,\phi)$.......................(9)

Then 'B' has now radial component , such fields are called electric multipole fields, hence the index (e) is used.

Therefore from eqn(5), the electric field strength given by

$$E_e(L,M) = -\frac{1}{i\omega\mu_0\varepsilon_0} c^{(e)} \nabla \times Lj(kr)Y(\theta,\phi) \text{.......................(10)}$$

If on the other hand from eqn(8) , we get,

$$E_m(L,M) = c^{(m)} Lj(kr)Y(\theta,\phi) \text{.........................(11)}$$

Then 'E' has no radial component such fields are called magnetic multipole fields. The corresponding magnetic field by using eqns(5) &(11).is

$$B_m(L,M) = \frac{1}{i\omega} c^{(m)} \nabla \times Lj(kr)Y(\theta,\phi) \text{......................(12)}$$

In the above eqns, the values of constants $c^{(e)}, c^{(m)}$ can be determined by using the normalization of fields. Since an electromagnetic wave contains on the average half of its energy in the magnetic field and half in the electric field, hence,

$$\varepsilon_0 \int |E|^2 dv = \frac{1}{\mu_0} \int |B|^2 dv = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar ck \text{.....................(13)}$$

For electric multipole radiation, eqn(9) can be inserted in eqn(13).

$$\frac{1}{\mu_0} \int_0^{R_0} \left[c^{(e)}\right]^2 |j(kr)|^2 r^2 dr \int (LY(\theta,\phi))^* (LY(\theta,\phi)) d\Omega = \frac{1}{2}\hbar ck \text{...........(14)}$$

Where R_0 is the radius of sphere (nucleus).

Since 'L' is a Hamiltonian operator, we obtain that the angular part of the integral is

$$\int (LY(\theta,\phi))^* (LY(\theta,\phi)) d\Omega = \int Y^* L^2 Y d\Omega = L(L+1)\hbar^2 \text{..................(15)}$$

For

$$r \to \alpha, \qquad j(kr) = \frac{1}{kr}\cos\left[kr - \frac{1}{2}\pi(L+1)\right]$$

$$\therefore \int_0^{R_0} \left|j(kr)\right|^2 r^2 dr = \frac{1}{k^2}\int_0^{R_0} \cos^2(kr - \frac{1}{2}\pi(L+1)dr$$

$$\approx \frac{R_0}{2k^2} \text{.............................(16)}$$

substitute eqns (15),(16) in eqn (14), we get,

$$\frac{1}{\mu_0}\left[c^{(e)}\right]^2 \frac{R_0}{2k^2} L(L+1)\hbar^2 = \frac{1}{2}\hbar ck$$

$$\left[c^{(e)}\right]^2 = \frac{1}{2}\hbar ck \times \frac{\mu_0 2k^2}{R_0 L(L+1)\hbar^2}$$

$$\left[c^{(e)}\right]^2 = \frac{ck^3\mu_0}{\hbar R_0 L(L+1)} \text{.....................(17)}$$

Similarly, we obtain for magnetic multipole radiation , by using eqn (11),(13),we get

$$\left[c^{(m)}\right]^2 = \frac{ck^3\varepsilon_0}{\hbar R_0 L(L+1)} \text{...................(18)}$$

These two constants values are substituting in equns (9),(10),(11) & (12) these are the multipole expansions for electric and magnetic field are

$$B_e(L,M)=\left[\frac{ck^3\mu_0}{\hbar R_0 L(L+1)\hbar}\right]^{1/2} Lj(kr)Y(\theta,\phi)$$

$$E_e(L,M)=-\frac{1}{i\omega\mu_0\varepsilon_0}\left[\frac{ck^3\mu_0}{\hbar R_0 L(L+1)\hbar}\right]^{1/2}\nabla\times Lj(kr)Y(\theta,\phi)$$

$$E_m(L,M)=\left[\frac{ck^3\mu_0}{\hbar R_0 L(L+1)}\right]^{1/2} Lj(kr)Y(\theta,\phi)$$

$$B_m(L,M)=\frac{1}{i\omega}\left[\frac{ck^3\mu_0}{\hbar R_0 L(L+1)\hbar}\right]^{1/2}\nabla\times Lj(kr)Y(\theta,\phi)$$

For L = 0 , the mltlipole fields are vanish identically, this is a consequence of the transverse nature of a light wave in free space.

Therefore, any arbitary field E(r) and B(r) can be expanded in terms of multipoles

$$E(r)=\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\left[a_e(L,M)E_e(L,M;r)+a_m(L,M)E_m(L,M;r)\right]$$

$$B(r)=\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\left[a_e(L,M)B_e(L,M;r)+a_m(L,M)B_m(L,M;r)\right]$$

where the coefficients $a_e(L,M)$ *and* $a_m(L,M)$ are the amplitude of the electric and the magnetic $2^l -$ poles respectively.

SELECTION RULES: The selection rules for emission of electric or magnetic multipole radiation may be obtained from the angular momentum and parity of the field.

1. The conservation of energy implies that the difference of energy in initial and final should be given by ħώ
2. The conservation of charge requires that initial and final states should have the same charge, since none is carried off by photons.
3. The conservation of angular momentum requires the difference of angular momentum I_i of initial and I_f of final state should be equal to $l\hbar$. The difference between two

momenta ranges from | I_i - I_f | to | I_i + I_f | , Hence the selection rule for angular momentum for both electric and magnetic radiation can be written as | I_i + I_f | ≥ l ≤ | I_i - I_f |. For example if transition is between $I_i(4^+) to\ I_f(2^+)$ then l can have values | 4 - 2 | to | 4 + 2 | i.e. l values from 2 to 6.

4. Now if initial and final states have the same parity electric multipoles of even l and magnetic multipoles of odd l are allowed.

If initial and final states have opposite parities, electric multipoles of odd l and magnetic multipoles of even are allowed.

6.5.INTERNAL CONVERSION: The internal conversion results due to electromagnetic interaction between excited nucleus and an orbital electron. In internal conversion the energy of interaction ejects one of the orbital electron.

The excited nucleus surrenders its energy to the orbital electron and hence the kinetic energy of the conversion electron, T_e will given by

$$T_e = (E_i - E_f) - I_i \text{ ………………}(1)$$

Where E_i and E_f are the energies of initial and final levels and I_i is the binding energy of electron in its orbit.

The internal conversion electrons produce a series of mono energetic lines and not a continuous spectrum as in β^- emission

The line with lowest energy is

$$T_{ek} = (E_i - E_f) - I_k \text{………………}(2)$$

The next line is $T_{el} = (E_i - E_f) - I_l$………………(3)

And so on.

Conversion coefficient: The two processes γ – emission and internal conversion often complete with one another. The relationship between the two de excitation processes is expressed by the internal conversion coefficient α . which is equal to ratio of the probability of conversion electron (P_e) to the probability of γ – emission (P_g) i.e.

$$\alpha = \frac{P_e}{P_g} \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$or \quad \alpha = \frac{\lambda_e}{\lambda_g} \ldots\ldots\ldots\ldots.(5)$$

eqns (4) & (5) also measures the total no of conversion electrons emitted over a given time divided by the total no. of gamma photons emitted in the same transition in the same time.

The conversion coefficient α can be expressed as

$$\alpha = \alpha_k + \alpha_L + \alpha_M + \ldots\ldots\ldots.. \qquad \ldots\ldots\ldots\ldots\ldots.(6)$$

Where α_k , $\alpha_{L,}$ α_M are partial conversion coefficients of k,L, ….electrons, respectively

The measurement of conversion coefficient provides information about ($E_i – E_f$), for the energy of conversion electrons is also expressed as

$$T_e = E_g = (E_i – E_f) - I_i \ldots\ldots\ldots\ldots\ldots\ldots..(7)$$

6.6.NUCLEAR ISOMERISM: Theoritical estimates indicate that normally the life time of γ – transition is of the order of 10^{-13} second. But there are about 250 known cases, in which life-time ranges from 10^{-10} sec to several years. In such cases nucleus remain is the excited state for measurable time and then decay. These delayed transitions are called isomeric transitions and the states from which they originate are called isomeric states or isomeric levels. Nuclear species which have the same atomic and mass numbers, but have different radioactive properties, are called nuclear isomers and their existence is referred to as nuclear isomerism.

The first example of nuclear isomerism and is shown in fig.

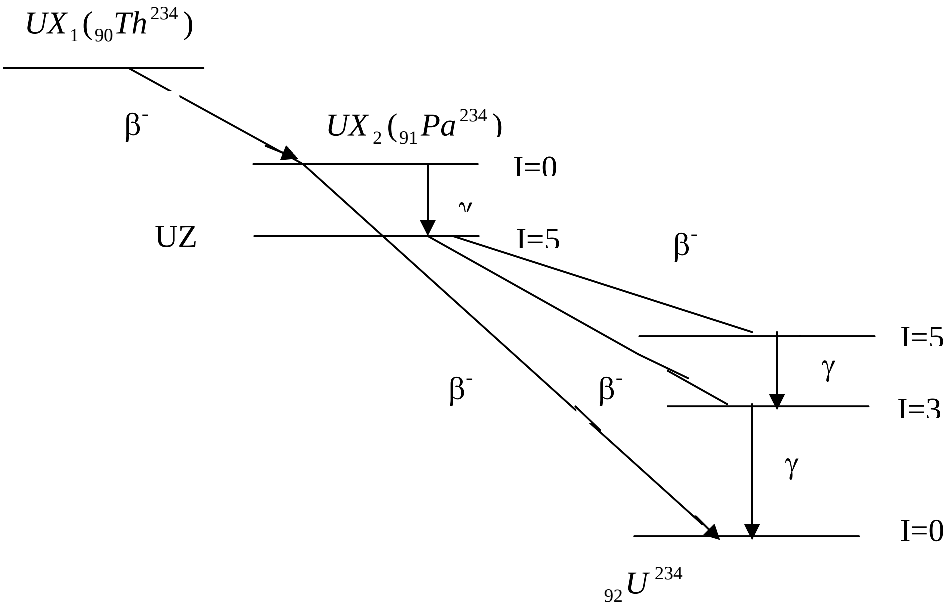


Fig. 6.5.Nuclear Isomerism of UX_2 and UZ

The beta emission of $UX_1({}_{90}{}^{Th234})$ gives an isomeric pair UX_2 and UZ of $({}_{91}Pa^{234})$. The transition of UX_2 to UZ by gamma emission is highly for bidden, since $\Delta I = 5$. Therefore, the usual decay process for UX_2 is beta decay giving rise to ${}_{92}U^{234}$.How ever a small percentage (0.12%) of UX_2 goes to UZ by gamma emission. UZ nucleus transforms to ${}_{92}U^{234}$ beta decay which leaves the nucleus in excited states. The de-excitation takes place by the emission of γ-rays.

Classification of Nuclear Isomer: Nuclear Isomers may be classified as

a) isomer with independent decay

b) Genetically related Isomers

c) Isomers of stable nuclei.

a)Isomers with independent decay: In this type , each isomer decays independently of the other with its own particular half life. The transition from the metastable to the ground state is highly forbidden. In figure T_1 and T_2 are the transition with the different half lives.

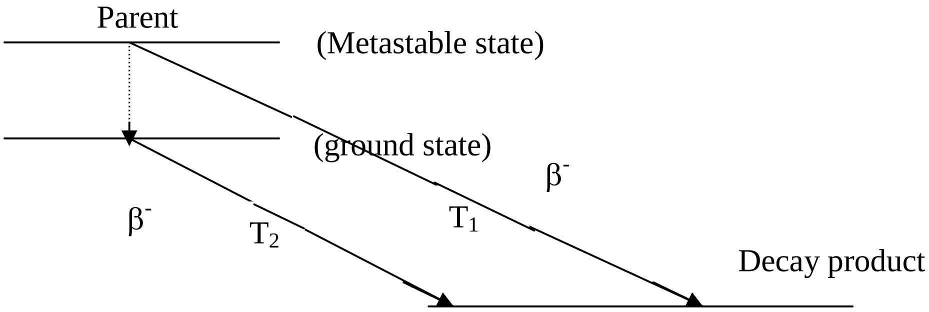


Fig. 6.6.Nuclear isomerism with independent Decay

b)Genetically related Isomers: In this type, the metastable state decays to the ground state with a definite half-life T_i

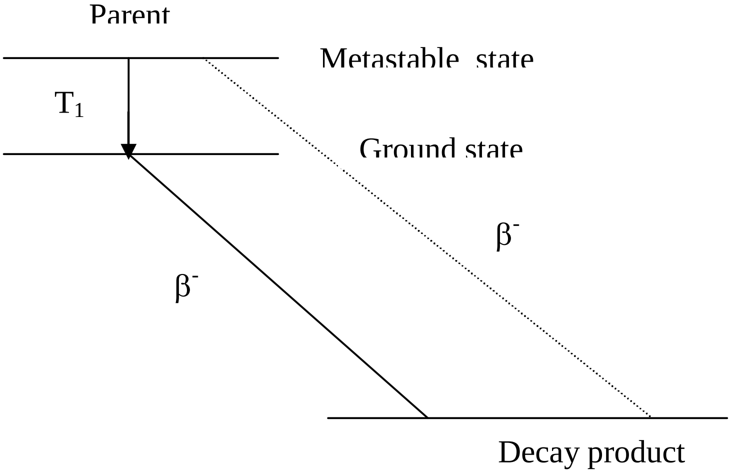


Fig. 6.7.Genetically related Isomers

Mostly, the gamma radiation is internally converted and produces line spectrum of electrons together with characteristic X- rays. The ground state decays to form the product with a half-life of T_2 different from T_1

c)Isomers of stable nuclei: In this type of isomers, the decay process involves an isomeric transitions from the metastable state to the ground state of a stable nuclide , accompanied by the emission of gamma radiation. More than 30 stable species are found in nature.

6.7.Summary:

It has been observed that nuclei with $A \geq 140$ are unstable with respect to α- particle emission. This is because the emission of α- particle lowers the coulomb energy -- the principle negative energy contribution to the binding energy of heavy nuclei, but does not change the binding energy appreciably, for α- particle itself is a tightly bound structure.

Rutherford in 1927 established that when α - particles of energy of the values 8.8Mev from Po^{213} source are bombarded on a thin U^{238} film, the particles are scattered in accordance with his theory or large angle scattering. Alternately, we can say that they have insufficient kinetic energy to surmount the potential energy barrier arising from the coulomb field round the uranium nucleus. The term gamma – rays is used to include all electromagnetic radiations emitted by radioactive substance. The spectral region which gamma rays occupy ranges from soft X – ray region to very short wavelength of the order of few x units.$(1x^0 = 10^{-11} cm)$

Gamma radiations can be divided in to two general categories, namely electric and magnetic radiations. Electric radiations a rise from changes in the distribution of the electric changes in the nucleus, where as magnetic radiation arise from change sin the distribution of the magnetic poles or in the current distribution in the nuclei

The internal conversion results due to electromagnetic interaction between excited nucleus and an orbital electron. In internal conversion the energy of interaction ejects one of the orbital electron.

Theoritical estimates indicate that normally the life time of γ – transition is of the order of 10^{-13} second. But there are about 250 known cases, in which life-time ranges from 10^{-10} sec to several years. In such cases nucleus remain is the excited state for measurable time and then decay. These delayed transitions are called isomeric transitions and the states from which they originate are called isomeric states or isomeric levels.

Keywords:
Spontaneous fission, barrier penetration, alpha decay, nuclear isomerism

Self assessment questions:

1. Give an account of alpha decay on the basis of quantum mechanical theory of barrier penetration.
2. What are the properties of gamma rays?
3. Explain in detail about the "nuclear isomerism" and "nuclear conversion"..

Text books

4. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
5. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
6. Nuclear physics by S.B.Patel

Unit 2

Lesson 7

RADIO ACTIVITY II

The objectives of the lesson are to explain the following:

7.1 Introduction

7.2. Beta Decay
7.3. The Neutrino Hypothesis
7.4. Fermi Theory of Beta Decay
7.5. Selection Rules
7.6. Summary

7.1.Introduction: The portion of the radiation, emitted from a radioactive source, that was strongly deflected by perpendicular magnetic field was termed beta-radiation. There are three modes of beta radiation : negatron (β^-) emission, orbital electron capture and positron (β^+) emission. Negatron emission is much more common than t he other decay processes. Beta rays are easily distinguished from α- particles by their considerably greater range in matter. When a radio-element emits a β^- particle , the product has the same mass number as the parent, but its atomic number increases by one unit. Similarly when a positron is emitted the mass number is still unchanged but the atomic number of the product is now one unit less than that of the parent. When the ratio of neutrons to protons is low , another type of decay known as orbital electron capture process has been found to occur. In this process instead of a proton being converted into a neutron with an emission of a positron, electrons are captured by the nucleus from the first (usually) or any other quantum level, which combines immediately with a proton to form a neutron. The product of this type would have the same mass number as its parent but its atomic number would be one unit lower as in the case of positron emission.

7.2.BETA DECAY: The spontaneous decay process in which mass number of nucleus remain unchanged, but atomic number changes, is termed as β – decay. The change in atomic number is accomplished by the emission of an electron, emission of a position or by the capture of an orbital electron. Thus , depending upon the three modes of decay, the β – decay are known asβ^- decay, β^+ decay and electron capture (k- capture). The half lives of β – active nuclei range between 0.06sec to 10^{18} years. The energy of emitted particle goes up to few Mev.

THREE FORMS OF BETA DECAY: when a nucleus has an excess of neutrons it is, in general, unstable with respect to nucleus which has got the same mass number but a greater number of proton. This occurs by emission of nuclear origin is termed as β^- particle. The β^- decay is energetically possible according to the binding energy concept when

$${}_ZM^{1A} > {}_{Z+1}M^{1A} + m_e \text{......................}(1a)$$

$$\text{or } {}_ZM^A > {}_{Z+1}M^A \text{........................}(2a)$$

Where ${}_ZM^{1A}$ and ${}_{Z+1}M^{1A}$ are the masses of parent and daughter nuclei, m_e is mass of electron and ${}_ZM^A$ and ${}_{Z+1}M^A$ are the masses of parent and daughter atoms.

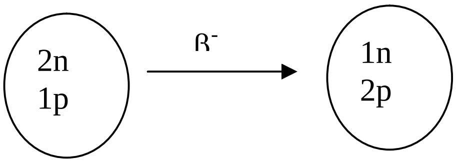
simple example is

$${}_1H^3 \xrightarrow{\beta^-} {}_2He^3$$

$$n \longrightarrow p + e^- \text{................}(3a)$$

$$P \longrightarrow n + e^+ \text{................}(4a)$$

There fore, we can say that in β^- decay a neutron is changed in to proton with subsequent emission of an electron. The example of eqn(3) is shown in figure.



Positron Emission: The atomic number is decreased either by the emission of positive electron by the capture of an orbital electron . The positron emission takes place when an excess proton is changed in to neutron according to

$P \longrightarrow n + e^{+}$……………(1b)

The process is energetically possible when

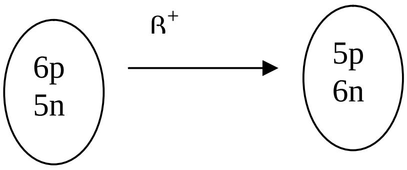
${}_{Z+1}M^{1A} > {}_{Z}M^{1A} + m_e$ …………..(2b)

${}_{Z+1}M^{A} > {}_{Z}M^{A} + 2\,m_e$…………..(3b)

The β^+ decay was discovered later than β^- decay because all naturally occurring nuclides have an excess of neutrons.

For example ${}_{6}C^{11} \xrightarrow{\beta^+} {}_{5}B^{11}$…………..(4b)

The above example is shown in the following figure.



Electron capture:-

When unstable nuclides are proton rich, the coulomb barrier tends to prevent the emission of a positron. The only alternative left for an unstable nucleus to transform in to a stable nucleus by the capture of an orbital electrons. There by, transforming proton in to neutron and decreasing the atomic number. This process is known as electron capture. This mode of decay was discovered in 1938 by Alvarez. The electron capture is important in heavy nuclei in which K subshell lies near to the nucleus and there fore K capture is more probable than ‘L’ capture and M capture.

The K-capture is energetically possible when

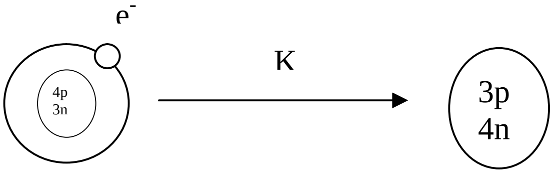
$_ZM^{1A} < \ _{Z+1}M^{1A} + m_e$ ……………..(1c)

$_ZM^A < \ _{Z+1}M^A$…………….(2c)

The simple example of K-capture is

$$_4Be^7 \xrightarrow{k} \ _3Li^7 \text{…………(3c)}$$

and is illustrated in figure.

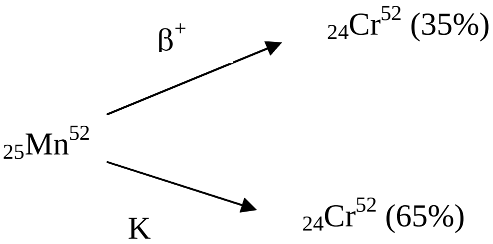


Some remarks about three forms of decay:

The close examination of the inequalities (2a, 3b, 3c) reveals the following points.

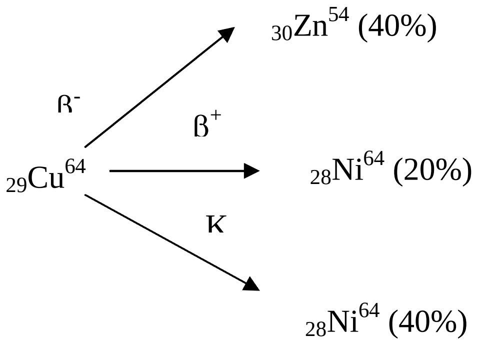
if $_ZM^A > \ _{Z+1}M^A$; the nucleus is β^- active and for $_ZM^A < \ _{Z+1}M^A$ the nucleus is β^+ active. It means that no stable isobars with charges differing by unity are possible.

When inequality (3b) is satisfied, the condition (2c) is automatically fulfilled . It implies t hat two processes (β^+ decay and K – capture) may run simultaneously. The example is



It is observed that ratio of running two process depends on atomic number ‘Z’. The ratio increases with increasing ‘Z’ for given decay energy. There fore, β^+ emission in heaviest element is very rare.

The isobars ${}_{z+1}R^A$ and ${}_{z+1}S^A$ may satisfy the inequalities (2a, 3b) for some given nuclei, then all the three forms of disintegrations will be observed. As for example



7.3.THE NEUTRINO HYPOTHESIS: The continuous energy distribution of electrons in β - decay proved to be a great puzzle, although the maximum energy of the distribution corresponds to that expected from the mass difference of the parent and the daughter. There is also an apparent failure to conserve linear and angular momentum in β - decay. The emitted electron does not travel in a direction opposite to that of product nucleus. The angular momentum and statistics are not conserved.

All these difficulties were eliminated by Pauli in 1933 by assuming the existence of an additional particle. This hypothetical particle is called neutrino. To preserve not only the principle of energy conservation but also the principle of conservation of electric charge and angular momentum and the rules governing statistics we must ascribe Certain properties to the neutrino. Charge is already conserved by the disintergarion electron in β - decay hence the neutrino has zero charge. In β - decay the parent and daughter nuclei always have the same mass number. This require that both have the same mass number. This require that both have the same statistics and that their nuclear angular momenta may differ only by zero or an integer multiple of $h/2\pi$. As the beta ray electron has Fermi-dirac statistics and spin $\hbar/2$, the neutrino must also have Fermi –Dirac statistics and an intrinsic spin $\hbar/2$ in order to conserve statistics and angular momentum. In addition to a neutrino. An antiparticle called anti-neutrino. Should also exist. The neutrino and antineutrino are represented as υ and $\ddot{\upsilon}$. The antineutrino has the same mass, spin, charge and magnitude of magnetic moment as those of neutrino. In all processes where a neutrino is emitted an antineutrino can be absorbed with the same result and vice versa. IN the neutrino the spin and angular momentum vector are oppositely directed and in the antineutrino these vectors are aligned together.

Neutrino is emitted with β^+ emission. Antineutrino is emitted with β^- emission. Neutrino is emitted with orbital electron capture.

$$n \longrightarrow P + e^- + \ddot{\upsilon}$$

$$P \longrightarrow n + e^+ + \upsilon$$

$$P + e^+ \longrightarrow n + \upsilon$$

The electron , neutrino and product nucleus share among them the energy, momentum and angular momentum available from the nuclear transitions. The β – particle gets maximum energy when the neutrino is emitted with zero momentum.

7.4.FERMI THEORY OF BETA DECAY: In 1934, Fermi made a successful theory of beta decay based on Pauli's neutrino hypothesis. This theory is based on the following assumptions.

a) The light particles the electron and neutrino are created by the transformation of neutron into a proton in a nucleus or vice versa.

b) The energy remains conserved in the decay process, the available energy being shared among the electron and the neutrino. Due to larger mass product nucleus does not receive K.E.

c) The neutrino has rest mass zero, or very small compared to that of the electron.

d) The β – decay process is analogous to the emission of electromagnetic radiation by an atom with the electron neutrino field acting in place of electromagnetic field.

e) Electron – neutrino field is weak in contrast to the short range strong interaction which exist between the nucleons bound in the nucleus.

f) Time dependent perturbation theory is very good approximation because of the smallness of coupling constants.

g) No nuclear parity change occurs

h) Ass nucleons move with velocities of only ~ c/10 in nuclei. Calculations can be made with non-relativistic nuclear wave functions.

Using Dirac's expression for the transition probability per unit time of an atomic system to emit photon, using time dependent perturbation theory, the probability that an electron of momentum between P_e and P_e +d P_e is emitted per unit time may be written as

$$P(P_e)dP_e = \frac{2\pi}{\hbar}\left|H_{if}\right|^2 \frac{dN}{dE_0} \text{...................(1)}$$

where $\frac{dN}{dE_0}$ is the number of quantum mechanical states of final system per unit energy interval. H_{if} the matrix element of the interaction for the initial & final states.

Interaction matrix element. It is defined as

$$H_{if} = \int \psi_f^* H \psi_i \, d\tau \text{....................(2)}$$

Where Ψ_f and Ψ_i respectively are the wavefunctions of the system in its final state and in its initial state. H is Hamiltonian operator that describes the weak interaction between the two states and $d\tau$ is the volume element

For the negatron decay $n \longrightarrow P + {}_{-1}e^0 + \ddot{\upsilon}$

We have $\Psi_i = \Psi$ (parent nucleus) $= \Psi_i$

$\Psi_f = \Psi$ (daugther nucleus) Ψ (electrton) Ψ (antineutrino)

$= \Psi_f \Psi_e \Psi_{\ddot{\upsilon}}$

we do not know the form of interaction operator H, but Fermi suggested a new constant called as Fermi coupling constant denoted by g.

The emission of neutrino and the absorption of an anti-neutrino of opposite momentum are equivalent we may replace $\psi_{\bar{v}}^{*}$ *and* ψ_v to make equation more symmetrical

$$H_{if} = g\int\left[\psi_f^{*}\psi_e^{*}\psi_v\right]M\psi_i\,d\tau \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

M is dimension less matrix element, which is an operator. Neutrino interact weakly with nucleons, so we use time independent wave function. The free particle propagation constant $K = \frac{P_v}{\hbar}$ as

$$\psi_v = V^{-1/2}\exp\left[-\left(\frac{i}{\hbar}\right)p_v r\right]\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

For ejected electron

$$\psi_e^{*} = V^{-1/2}\exp\left[-\left(\frac{i}{\hbar}\right)p_e r\right]\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

here V is the volume in which the system for normalization purposes.

P_v and P_e are the momenta of the neutrino and electron respectively, r is the position coordinate.

By assuming the plane waveform for the wave function of the electron and neutrino, we have neglected their possible interactions with the nucleus.

The matrix element becomes

$$H_{if} = g\int \psi_f^* \left\{\frac{1}{v}\exp\left[-\frac{i}{\hbar}(p_e + p_v)r\right]\right\} M\psi_i d\tau ....(6)$$

The exponential factor can be written as

$$\exp\left[-\frac{i}{\hbar}(p_e + p_v)r\right] = 1 - \frac{i}{\hbar}(p_e + p_v)r - \frac{1}{2\hbar^2}[(p_e + p_v)r]^2 + ...(7)$$

Be neglecting higher order terms

$$H_{if} = \frac{g}{v}\int \psi_f^* M\psi_i d\tau = \frac{g}{v}\left|M_{if}\right| ....(8)$$

where $\left|M_{if}\right|$ is the overlap integral or the nuclear matrix element of the final and initial wave functions of the nucleus.

STATISTICAL FACTOR; The position and momentum of electron or neutrino can be represented by a point in phase space, the space containing three spatial and three momentum dimensions. The uncertainity principle prevents us from representing a moving particle by a single vector. This is because such a representation would amount to specifying both the position and momentum exactly . Thus phase space must be divided into cells of volume

$$\Delta x\ \Delta y\ \Delta z\ \Delta P_x\ \Delta P_y\ \Delta P_z$$

The number of states of a particle restricted to a volume V in actual space and whose momentum lies between the limits P and P+dP is given by

$$dN = V \times 4\pi P^2 \frac{dP}{h^3} ....(9)$$

The number of states corresponding to the appearance in volume V of the electron with the momentum in the range P_e to $P_e + dP_e$ is

$$dN_e = 4\pi V P_e^2 \frac{dP_e}{h^3} \text{........................(10)}$$

$$\text{Similarly} \quad dN_v = 4\pi P_v^2 \frac{dP_v}{h^3} \text{...............................(11)}$$

An electron and neutrino are independent of one another and Hence the number of states available to them jointly given by

$$dN = \left(4\pi V P_e^2 \frac{dP_e}{h^3} \right)\left(4\pi P_v^2 \frac{dP_v}{h^3} \right) \text{.......................(12)}$$

The number of states per unit energy of the electron is

$$\frac{dN}{dE_0} = \frac{\frac{16\pi^2 V^2}{h^6} P_e^2 P_v^2 dP_e dP_v}{dE_0} \text{...........................(13)}$$

Total available energy

$$E_0 = E_v + E_e \text{.....................(14)}$$

For fixed electron energy E_e , we have

$$d E_0 = dE_v \text{ ....(15)}$$

The momenta P_e and P_v are related to the electron and neutrino energy respectively by the eqn

$$E_0^2 = P_e^2 C^2 + m^2 C^4 \text{.....................(16)}$$
$$E_v = CP_v \text{.....................(17)} \quad (assuming \quad zero \quad rest \quad mass)$$
$$dE_v = CdP_v \text{.....................(18)}$$

Using (15) ,(16), (17), (18) and (13) we have,

$$\frac{dN}{dE_0} = \frac{\frac{16\pi^2 V^2}{h^6} P_e^2 P_v^2 dP_e dP_v}{dE_0}$$

$$P_v = \frac{E_v}{c}$$

$$P_v = \frac{E_0 - E_e}{c}$$

$$P_v^2 = \frac{(E_0 - E_e)^2}{c^2}$$

Assuming zero rest mass , for fixed electron

Energy

$$dE_v = dE_0$$

$$dP_v = \frac{dE_v}{c} = \frac{dE_0}{c}$$

$$\frac{dP_v}{dE_0} = \frac{1}{c}$$

$$\therefore \frac{dN}{dE_0} = \frac{16\pi^2 V^2}{h^6} P_e^2 \left(\frac{E_0 - E_e}{c}\right)^2 dP_e \frac{1}{c} \text{.........................(19)}$$

H_{if} *and* $\frac{dN}{dE_0}$ values are substitute in (1)

$$P(P_e)dP_e = \frac{2\pi}{\hbar} \left|H_{if}\right|^2 \frac{dN}{dE_0}$$

$$= \frac{2\pi}{\hbar} \frac{g^2}{V^2} \left|M_{if}\right|^2 \frac{16\pi^2 V^2}{h^6} P_e^2 \left(\frac{E_0 - E_e}{c}\right)^2 dP_e \frac{1}{c}$$

$$P(P_e)dP_e = \frac{g^2 \left|M_{if}\right|^2}{2\pi^3 c^3 \hbar^7} (E_0 - E_e)^2 P_e^2 dP_e \text{.........................(20)}$$

Coulomb Correction: In the derivation of above relation no account has been taken of the coulomb interaction which can be neglected only for the lightest nuclei(Z<10) and sufficiently high electron energies. The plane wave for the emitted electron must be replaced by distorted coulomb wave function. This can be taken in to account by multiplying $|\psi_e|^2$ with a factor some time called coulomb factor $F(Z, E_0)$ also called Fermi function. It is the ratio of electron density at the daughter nucleus to the density at infinity i.e.

$$F(Z, E_e) = \frac{|\psi_e(0)|^2_{Coulomb}}{|\psi_e(0)|^2_{Free}} \text{...........................(21)}$$

In non-relativistic approximation, it has the value

$$F(Z, E_e) = \frac{2\pi\eta}{(1 - e^{-2\pi\eta})} \text{.....................(22)}$$

where $\eta = \frac{Ze^2}{4\pi\varepsilon_0}\text{h}\upsilon$ for electrons, $\eta = -\frac{Ze^2}{4\pi\varepsilon_0}\text{h}\upsilon$ for positrons

'Z' the atomic number of the product nucleus and V being velocity of electron at a great distance from the nucleus. When consideration is given to this affect equation 20 becomes

$$\begin{aligned} P(P_e)\,dP_e &= \frac{g^2|M_{if}|^2}{2\pi^3c^3\hbar^7} F(Z, E_0)(E_0 - E_e)^2 P_e^2 dP_e \\ &= c^2 F(Z, E_0)(E_0 - E_e)^2 P_e^2 dP_e \text{.........................(23)} \end{aligned}$$

$$c \quad = g|M_{if}|\left[2\pi^3c^3\hbar^7\right]^{-1/2} \text{...........................(24)}$$

The coulomb correction enhances the probability of electron emission and decreases the probability of positron emission . At low energies, the coulomb force loses its effect at high energies.

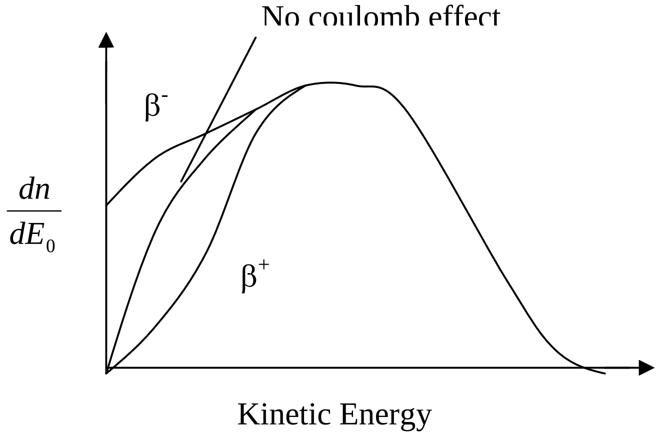


Fig. 7.1. Theoretical β - energy spectrum (Fermi theory)

7.5.SELECTION RULES: If electron and neutrino are emitted with their intrinsic spins antiparallel (singlet state), the change in nuclear spin must be strictly zero, if these are emitted with their spins parallel (triplet state) ΔI may be +1, 0 –1 . The former selection rule was proposed by Fermi and the latter was suggested by Gamow and Teller. Both types of allowed transitions orbital angular momentum and parity unchanged electron and neutrino carry away no orbital angular momentum.

The allowed transitions of the type ΔI = 1 obeying G – T selection rule and forbidden for F-selection rule.

The allowed transitions of the $0 \to 0$ type that are allowed by F- selection rule. But forbidden by G-T selection rule.

Thee allowed transitions are further classified as favoured (super allowed) unfavoured transitions . The allowed transitions is favoured if the nucleon which changes its chare remains in the same level, it is unfavoured if the nucleons changes its level, most of the allowed β - transitions are unfavoured.

FIRST FORBIDDEN; For these transitions $I_\beta = 1$ and parity changes

Fermi selection rule: ΔI = ±1,0 (except $0 \to 0$)

Gamow Teller rules: $\Delta I = \pm 2, \pm 1, 0$ (except $0 \rightarrow 0, 1/2 \rightarrow 1/2, 0 \leftrightarrow 1$)

Example: $Kr^{87} \longrightarrow Rb^{87} + \beta^{-}$ $(5/2 \rightarrow 3/2)$

$Ag^{111} \longrightarrow Cd^{111} + \beta^{-}$ $(1/2 \rightarrow 1/2)$

$Ce^{141} \longrightarrow Pr^{141} + \beta^{-}$ $(7/2 \rightarrow 3/2)$

SECOND FORBIDDEN; For these transitions $I_{\beta} = 2$ and no change in parity.

Example:

$Cs^{135} \longrightarrow Ba^{135} + \beta^{-}$ $(7/2 \rightarrow 3/2)$

$Be^{10} \longrightarrow B^{10} + \beta^{-}$ $(0 \rightarrow 3)$

$Na^{22} \longrightarrow Ne^{22} + \beta^{+}$ $(3 \rightarrow 0)$

Fermi selection rules: $\Delta I = \pm 2, \pm 1,$ (except $0 \leftrightarrow 1$)

Gamow Teller rules: $\Delta I = \pm 3, \pm 2, 0 \rightarrow 0$ (except $0 \leftrightarrow 2$)

nth forbidden:

Fermi selection rule $\Delta I = \pm n, \pm (n-1)$ parity changes for n odd

G-T selection rule $\Delta I = \pm n, \pm (n+1)$ parity does not change for n even.

Keywords:
Neutrino hypothesis, electron capture, over lap integral

Self assessment questions:

1. What are the three forms of beta decay.
2. How does the neutrino hypothesis over come the difficulties that are experienced with beta ray spectrum.
3. Explain in detail about the Fermi theory of beta decay.
4. Explain the selection rules of beta decay.

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel

Unit 2

Lesson 8

CLASSIFICATION OF ELEMENTARY PARTICLES

The objectives of the lesson are to explain the following:

8.1 Introduction

8.2. Classification of Elementary Particles

8.3 Interaction between the elementary Particles

8.4 Conservation Laws

8.5.Charge Conjugation

8.6.Space-Inversion Invariance (Parity)

8.7.Combined Inversion (CP)

8.8.Time Reversal Symmetry and CPT Invariance

8.9.Summary

8.1. Introduction: Extensively researches, have been carried out by the scientists to conclude about the ultimate representatives of the matter that may be the basic building blocks-nowadays called as elementary particles. A summary of such works is given below:

a) In the beginning of nineteenth century, it was established that matter is composed of atoms and molecules. But soon it was found that atom has also a rich structures and in 1897, J.J. Thomson established the existence of a particle-the electron that still is classified as an elementary particle.

b) At the start of twentieth century experiment and ideas of Rutherford and Bohr established that atom consisted of a positively charged nucleus with electrons revolving around it.

c) In 1932, J.Chadwick identified neutron and W. Heisenberg suggested that atomic nuclei consist of neutrons and protons. Thus atomic picture becomes somewhat clear with electron, neutron, proton and photon as the basic building blocks, photon has been added as a field particle for electromagnetic forces such as exist between the nucleus and electrons in the atom, i.e., it is a quantum unit of radiation. It has zero rest mass and is uncharged.

In the some year, C.D. Anderson found the positive electron or the positron while studying cosmic-ray showers. The discovery of this particle, being the antiparticle of electron, predicted the existence of antimatter. With this discovery it was thought that the atomic picture could be completed, apart from four afore-said particles with three possible antiparticles—antielectrons, antiprotons, and antineutrons;

8.2. Classification of Elementary Particles:

The elementary particles are separated in to two general groups called bosons and Fermions . These two groups have different types of spin and their behaviour is controlled respectively by a different kind of statistics

a) Bose Statistics

b) Fermi Statistics

Bosons are particles with intrinsic angular momentum equal to an integral multiple of $\hbar$. Fermions are all those particles in which the spin is half integral. The most important difference between the two classes of particles is that there is no conservation law controlling the total number of bosons in the Universe, where as the total number of fermions is strictly conserved.

Bosons is a term, which not only includes material particles but also includes those quanta and Photons which arise from interactions. Thus in the case of the simple electromagnetic field the bosons are merely the light photons or the X-ray photons. The photon has a mass of zero and a spin of unity and consequently described as a massless boson. A massless boson, called a graviton with a probable spin of two units has been postulated as a field particle for gravity. These bosons, created by the electromagnetic field, are essentially of one kind, while the bosons formed in the strong interaction are of two distinct kinds. First there are those which are known as pions or π-mesons (π^+, π^-, π^0). The second group of bosons are much heavier than that of pions, and are known as kaons or K-mesons (K^+,K^-,K^0).

The fermions fall in two main classes, according to whether they are lighter than mesons, or heavier. Those in the heavier group are called baryons. The leptons are the electrons, muons and neutrinos and their anti-particles. There are all with mass less than the pions and with spin half. Leptons interact weakly with other particles. The total number of leptons minus the total number of anti-leptons remains unchanged in all reactions and decay processes involving leptons and anti-leptons and decay process involving leptons and anti-leptons. The baryons consist of the two nucleons with their anti-particles ($n^0, \bar{n}^0 : p^+, p^-$) and the hyperons. Hyperons are the extremely unstable some what heavier particles and can be divided in to four sub-groups - particles (a neutral particle of mass about $180m_e$) The Σ - particles (Σ^- , Σ^0 & Σ^+ with masses in the range 2320 to $2340m_e$) the Ξ – particles (Ξ^-, and Ξ^0 with masses near 2580 m_e) and the $\overline{\Omega}$ particle (of mass about 3284 m_e). There is no reason to doubt the existence of the anti-particles of these fermions. The total number of baryons minus the total number of anti-baryons is absolutely conserved in all interactions. The kaons and pions together with the barons are placed in to group of strongly interacting particles, called hardons.

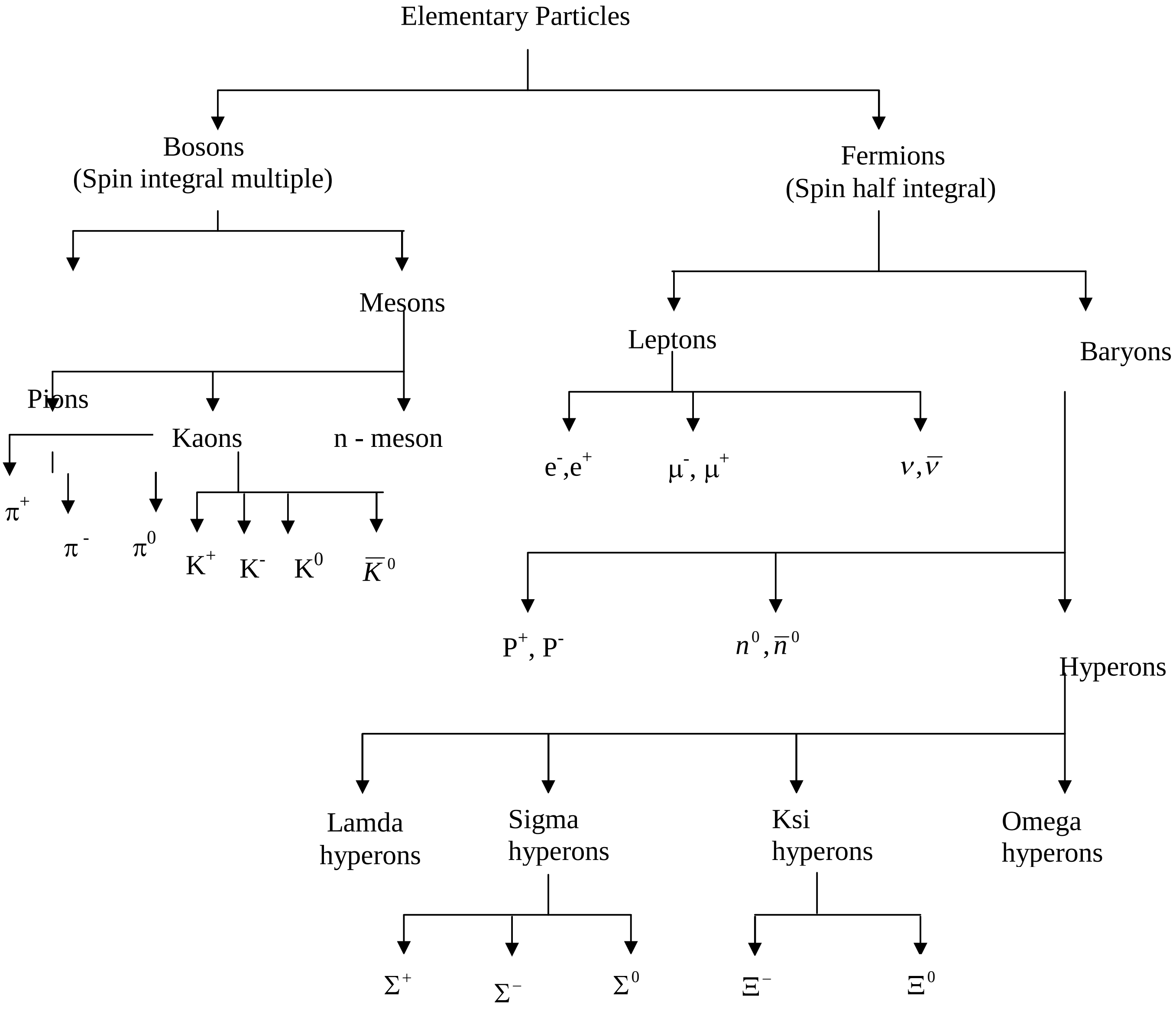


Fig. 8.1.Classification of elementary particles

8.3. INTERACTION BETWEEN THE ELEMENTARY PARTICLES:

The interactions among elementary particles can be classified in to following four types.

1.The gravitational Interaction

2.Electromagnetic Interaction

3.Strong Interaction

4.Weak Interaction

1.The gravitational Interaction: The first force that any of us discover is gravity. It holds the moon and earth together, keeping the planets in their solar orbits and binds stars to form our galaxy. Newton gave a formula $F = G\frac{m_1 m_2}{r^2}$ for the interaction between two masses. The gravitational effect does not depend on the colour, size , charge, velocities, spin and angular orientation but depends on the magnitude of the inertia. The gravitational force between two nucleons separated by a nucleon diameter is $F = G\frac{m_1 m_2}{r^2}$ = 6.7 x $10^{-11}\frac{(1.7\times10^{-27})^2}{(10^{-15})^2}$ ≈ 2 × 10^{-34} newton. And the gravitational attraction is only about 2 x 10^{-49} joule. Hence we see that it plays no role in particle reactions. Gravitation can thus be explained in terms of the interactions of gravitons. Their mass must be zero and therefore . Their velocity must be that of light. As the gravitational field is extremely weak. The gravitons can not be detected in laboratory.

2.Electromagnetic Interaction: The term electromagnetism is because the electricity and magnetism are both part of the same phenomenon. According to coulomb's law $F = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$ For two protons 10^{-15} meters apart.The repulsion force will be $9\times10^{9}\times\frac{(1.6\times10^{-19})^2}{(10^{-15})^2}$ ≈ 30 newtons. It is about 10^{-35} times greater than the gravitational attraction caused by the mass. The energy released by the complete seperation of these protons would be 3 x 10^{-14}Joules.

If the particles are not at rest but are moving, the field will not only be an electric field but would be new one depending on the velocity and magnitude of the charge. When the charge is accelerated, the energy is radiated out in the form of an electric and magnetic pulses. The pulse is called a photon and travels with the velocity of light. The interaction between two charged particles consists of an exchange of these photons.

The electromagnetic interaction is charge. Dependent. The electromagnetic interaction violate the law of isospin conservation. All other quantities such as charge parity, baryon number, lepton number, hypercharge, strangeness number are conserved.

Other examples of such type of interaction are the pair formation from photon and vice versa and the decay of neutral pion in to two gamma ray photons.

$$\pi^0 \longrightarrow r + r$$
$$\eta^0 \longrightarrow r + r$$

3.STRONG INTERACTION: The strong nuclear interaction is independent of the electric charge. The force is same between p- p & n-n . For this purpose the proton and neutron are one but in different electric charge states. Strong interactions involves mesons and baryons, The range is very much shorter than that of gravitational or electromagnetic interaction. Strong interaction falls off rapidly when the distance between two particles increases. Yukawa predicted that the new particles called mesons, should have a mass of the order of 200 to 300 electron masses.

The strong interaction between elementary particles are responsible for the total cross section as a function of energy. The strong interaction is a short range force ($\approx 10^{-15}$ m) and it conserves baryon number b, charge Q, hypercharge Y, parity Π, isospin T and its component T_z. It is responsible for kaon production, however the decay of mesons, nucleons and hyperons proceeds by an electromagnetic or weak interaction.

4.WEAK INTERACTION: The weak interaction is responsible for the decay of strange and non-strange particles and for non-leptonic decays of strange particles. The numerical constant which is characterstic of the weak interaction is obtained from Fermi's theory of β- decay. Its value is $g_F = 1.41 \times 10^{-62}$ Jm^2. In analogy with the expression for the other interactions the dimensionless weak interaction coupling constant is of magnitude $\frac{g_F^2}{(\hbar c)^2}\left(\frac{m_\Pi c}{\hbar}\right)^4 = 5 \times 10^{-14}$

Consider the reaction which do not involve a change of strangeness and yet which must be due to weak interaction. The neutron decay is the proto-type of all the β- decay.

$$n \longrightarrow P + e^- + \bar{\upsilon}_e$$

comparison of the four basic interactions

Field	Relative magnitude	Associated particles	Characteristic time
Strong interaction	1	Pion, kaon	10^{-23} sec
Electromagnetic Interaction	10^{-3}	Photon	10^{-20}sec
Weak interaction	10^{-13}	Intermediate boson	10^{-10}sec
Gravitational	10^{-39}	Graviton	10^{6}sec

8.4. CONSERVATION LAWS: The behaviour of the elementary particles is restricted by a number of conservation laws or invariance principles. That is to say, certain properties of representative physical quantities must remain unchanged in any process. The most familiar quantities in large scale experiments that are conserved in all interactions.

1.Conservation of Linear momentum: The linear momentum of a body is defined as product of its mass and velocity P = mv. When the net external force acting on the system is zero. The total Linear momentum of a system remains constant. i.e. $\frac{dP}{dt} = 0$, P = Constant

2.Conservation of Angular momentum: The conservation of angular momentum includes both orbital and spin angular momentum together. The first is given by the motion of the object as a whole about any chosen external axis of rotation. The second is the intrinsic angular momentum of each about an axis through its own centre of mass.

3.Conservation of Energy: Conservation of energy on other hand seems more complicated with elementary particles because a large fraction of the total energy is oftenly interchanged between rest energy associated with mass and kinetic or potential energy. The sum of these three, the total energy is always conserved in any reaction.

Ex:- $K^0 \longrightarrow \pi^+ + \pi^- + \pi^0$

The rest energy K^0 particles enough to produce π^+, π^-, π^0 particles.

4. Conservation of Charge: The most familiar of the conservation laws is the conservation of electric charge. The Charge is conserved in all process i.e. the total charge remains unchanged.

5. Conservation of Lepton number: The leptons are the fundamental particles that interact only through weak and electromagnetic interaction. The number of Leptons minus the number of anti-Leptons is conserved. The ordinary electron. Negative muon and neutrinos all have a lepton number +1. the corresponding anti leptons have a lepton number is –1.

Ex:- $\mu^+ \longrightarrow e^+ + \nu +$ ΰ

$$-1 = -1 + (-1) + 1$$

$$-1 = -1$$

This reaction is allowed

6.Conservation of Baryon number: The number of baryons minus the number of anti-baryons is conserved. In other words the net baryon number in any process always remain unchanged

In other word the net baryon number in any process always remains unchanged. All normal baryons such as P^+, n^0,π^0 Σ^+, Σ^0, Ξ^-, Ξ^0 and Ώ have baryon number is +1. Anti barons have –1.

$$\text{Ex:-}\quad \pi^0 \longrightarrow \pi^+ + P^-$$

$$1 = 0 + 1$$

$\Delta B = 0$ so this process is allowed.

7. CONSERVATION OF ISOSPIN: According to the ordinary idea of isotopic spin, each nuclear particle possess a certain total isotopic spin T and each possible projection of this isotopic spin along a certain axis T_3 appears to us as a different charge state of the corresponding particle.

In the case of nucleons, T = ½ and the 2T +1 i.e. $2\frac{1}{2}+1=2$, the possible values of T_3 are +1/2 (for proton state), -1/2 (for neutron state)

The Isospin of nucleons is ½.

For pions T = 1 and 2T + 1 = 2(1) + ! = 3

The possible values of T_3 are +1 (for π^+)

0 (for π^0)

-1 (for π^-)

The Isospin of pions is 1.

Relation between the quantities T_z, B and Q are

$$Q = T_z + B/2$$

Here B is the baryon number. T is the isotopic spin quantum number, T_z the component of T and Q is charge. B is+1 for proton, neutron & hyperon

B is zero for pion.

$Q_p = +1/2 + ½ = 1$

$Q_n = -1/2 +1/2 = 0$

$Q_{\pi^+} = +1 +0 = 1$

$Q\ \pi^0 = 0 + 0 = 0$

$Q_{\pi^-} = -1 + 0 = -1$

Isospin numbers are associated with hardrons (particles that exhibit strong interactions) but not with leptons. The isospin component T_z is conserved in both strong and electromagnetic interaction but not in weak interaction.

8.CONSERVATION OF HYPERCHARGE: A quantity called hypercharge is also conserved in strong and electromagnetic interaction. For example, for the triplet π^+, π^-, π^0. average charge is zero and hence all these three mesons have a hypercharge of zero.The hyper charge of the pair particles K^+ and K^0 is +1 and that of the pair of antiparticles K^- and K^0 is -1. Thus the alternative definition is that it is twice the difference between the actual charge Q and the isospin component T_z of a particle. Thus hyper charge

$$Y = 2(Q – T_z)$$

9.CONSERVATION OF STRANGENESS: The concept of strangeness has found wide application in particle physics. It is an additional quantum number which describes the interactions of elementary particles. It has been chosen in such a manner that it becomes zero for all the well know particles(non-strange particles)

One of the most common V-particles (π^0) was neutral and decayed ($\pi^0 \longrightarrow P + \pi^-$) in times 2.5×10^{-10} seconds. The V-particles can interact strongly and therefore, are produced only in pairs, once separated each number can decay in to ordinary particles only through the weak interaction. A typical example is

$$\begin{aligned}\pi^- + p^+ \longrightarrow \Lambda^0 + k^0 &\longrightarrow \pi^+ + \pi^- \\ \downarrow &\longrightarrow p^+ + \pi^-\end{aligned}$$

Both the associated creation of the strange particles and their individual stability against immediately decay were the features that earned than the title strange. Both features can be explained by insisting that the total strangeness must remain constant in fast particle reaction.

If the baryons are arranged in columns according to their electric charge. The electric charge centre of the nucleon is at +1/2 half way between P and n. The charge centre of π^0 is at 0. The triplet sigma is centred at 0 , but the doublet X$_i$ is centred at -1/2. The -- singlet is at charge -1. If we take charge centre of the nucleon doublet arbitrarily too be reference origin. Then we have

$$\text{For } \Lambda^0 \ldots \Delta Q = Q_\Lambda - Q_N = -\frac{1}{2}; \ \ for \ \Sigma - hyperon \ldots \Delta Q = Q_\Sigma - Q_N = -\frac{1}{2}$$

$$\text{For } \Xi \text{ doublet} \ldots \Delta Q = -1 \ \ for \ \overline{\Omega} \ldots \Delta Q = -\frac{3}{2}$$

By defining strangeness Quantum number as

$$S = 2\Delta Q$$

we obtain S = 0 for the nucleons and non-zero for hyperons.

Ex:-

$$\begin{aligned}&\Sigma^+ \longrightarrow \Lambda^0 + e^+ + v_e \\ &\Delta S = 0 \\ &\Sigma^- \longrightarrow n + e^- + \overline{v}_e \Rightarrow \Delta S = 1 \\ &\Lambda^0 \longrightarrow P + e^- + \overline{v}_e \Rightarrow \Delta S = 1\end{aligned}$$

Baryons:

Table

Particle	Symbol	Anti-Particle	Strangeness
Proton	P	$\overline{p}$	0
Neutron	N	$\overline{n}$	0
Lambda	Λ^0	$\overline{\Lambda}^0$	-1
Sigma	Σ^+ Σ^0 Σ^-	$\overline{\Sigma}^-$ $\overline{\Sigma}^0$ $\overline{\Sigma}^+$	-1 -1 -1

8.5. CHARGE CONJUGATION: Charge conjugation is defined as the interchange of particles and anti particles. It does not simply mean a change over the opposite electric charge or magnetic moment, the sign of other charge quantum numbers (hypercharge Y, baryon number B, lepton number (l_e, l_μ) is also reversed with out charging mass m and spin s Thus a unitary operator, also known as charge conjugation operator C satisfies the following relation.

$$CQC^{-1} = -Q, \quad CYC^{-1} = Y, \quad CBC^{-1} = -B$$
$$Cl_eC^{-1} = -l_e, \quad Cl_\mu C^{-1} = l_\mu$$

Some elementary particles e.g., r, π^0 - mesons and the positronium atom $\left(e^+ + e^-\right)$ are transformed in to themselves by charge conjugation. They are their own anti-particles. These are known as self conjugate or true neutral particles. The neutron (B= 1, Y = 1) and K^0 – mesons (Y =1 , B = 0) are not invariant under C.

8.6.SPACE – INVERSION INVARIANCE (PARITY):- The parity principle says that there is a symmetry between the world and its mirror image. This may be defined as reflection of every point in space through the origin of a co-ordinate systems x → -x, y → -y , z → -z. If a system or process is such that its mirror image is impossible to obtain in nature. The system of process is said to violate the law of parity conservation.

All phenomena involving strong and electromagnetic interactions alone do conserve parity. In these cases the systems can be classified by the eigen values of the parity operator P. For a single particle schrodinger wave function Ψ , the result of the parity operator is

$$P|\psi(x)\rangle = e^{i\alpha}|\psi(+x)\rangle$$

As α is an arbitrary real phase, hence can be set equal to zero.

$$P|\psi(x)\rangle = |\psi(-x)\rangle$$
$$P^2|\psi(x)\rangle = |\psi(x)\rangle$$

It shows eigen values of P as +1 or -1

The parity of the photon depends upon the mode of transition, it is due to the charge of the sign of electromagnetic current under the parity operation. The nucleons and electrons are assigned positive or even intrinsic parity. The pions have negative or odd parity as they involve in strong interactions with nucleons. K – mesons and n^0- mesons have negative parity. $\Lambda^0, \Xi^-, \Sigma, \Omega$ hyperon have positive intrinsic spin.

The consnervation of parity is applicable only to strong and electromagnetic interaction but not weak interaction.

8.7.COMBINED INVERSION(CP): Landu (1956) advanced a hypothesis to the effect that any physical interaction must be invariant under simultaneous reversal of position coordinates and change over from particle to anti-particle. For example a neutrino has a definite helicity and its parity conjugate has opposite helicity. The charge conjugate of the neutrino also has opposite helicity. Thus under the combined operation CP (or pc) the neutrino changes to anti-neutrino. The combined operation also known as combined parity (charge and space) is conserved in most of physical processes. Let us consider the decay of the positive pion

$$\pi^+ \longrightarrow \mu_L^+ + v_\mu L$$

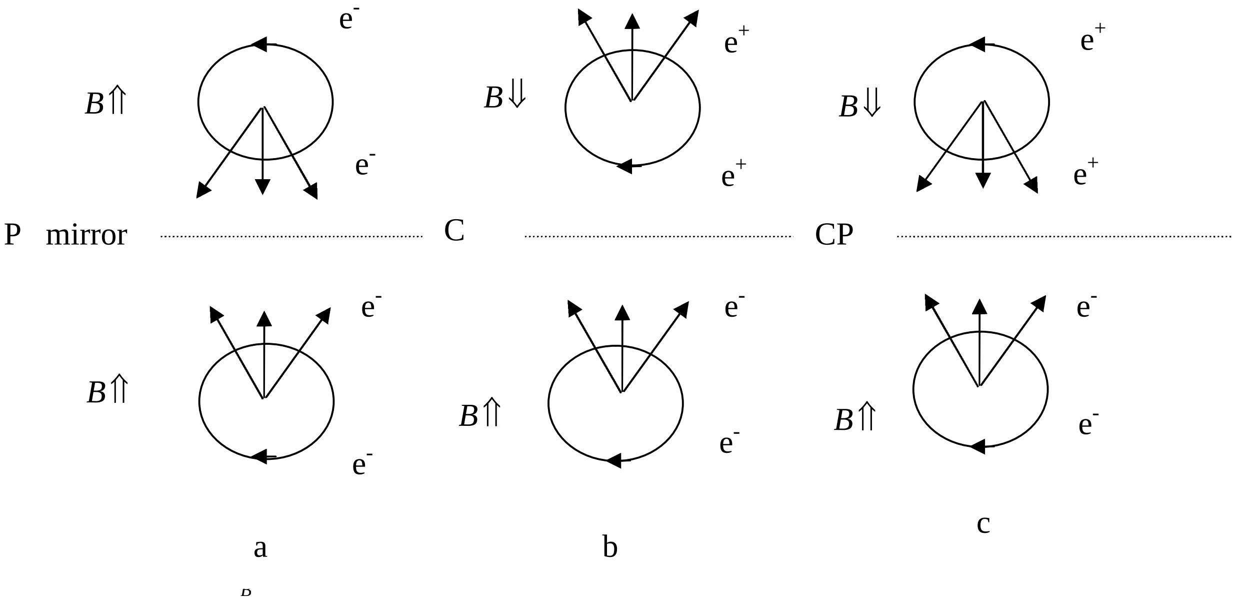
Here subscript L indicates that neutrino and +ve meon fly apartr with left handed spin. S the C-inversion changes particles in to anti-particles and vice-versa, where as P-inversion converts left handed motion to right handed motion. Hence

$$C-inversion: \quad \pi^- \longrightarrow \mu_L^- + v_\mu L \quad impossible \quad process$$

$$P-inversion: \quad \pi^+ \longrightarrow \mu_R^+ + v_\mu R \quad impossible \quad process$$

$$CP-inversion: \quad \pi^- \longrightarrow \mu_R^- + v_\mu R \quad possible \quad process$$

Let us consider the case of the Beta decay of polarized nuclei. The interpretation of the parity non-conversation, charge non-conversation and conservation under combined operation is shown in fig.8.2.In this figure B shows the direction of a magnetic field due to current loop, used for polarizing the nuclei. It represents the nuclear spin and thus known as polarization vector.



a) Parity mirror b) Charge Conjugation mirror c) CP mirror

Fig. 8.2

The upper diagrams represent the result of the reflection of process shown in the lower diagram of fig:

8.8.TIME REVERSAL SYMMETRY AND CPT INVARIANCE: Time reversal symmetry, denoted by T, means that events an atomic or subatomic, or in general, on a particle scale should be exactly reversible. Basic postulates of quantum field theory combined with relativity require that all interaction should be invariant under at the combination of three operation C,P and T i.e. the CPT operation. Lee and Yang realised that in weak interactions of the type of Beta decay, P and C invariance are violated but CPT invariance is valid.

8.9.Summary: The elementary particles are separated in to two general groups called bosons and Fermions . These two groups have different types of spin and their behaviour is controlled respectively by a different kind of statistics

b) Bose Statistics

b) Fermi Statistics

Bosons are particles with intrinsic angular momentum equal to an integral multiple of ħ . Fermions are all those particles in which the spin is half integral. The most important difference between the two classes of particles is that there is no conservation law controlling the total number of bosons in the Universe, where as the total number of fermions is strictly conserved.

The interactions among elementary particles can be classified in to following four types.

1.The gravitational Interaction

2.Electromagnetic Interaction

3.Strong Interaction

4.Weak Interaction

The behaviour of the elementary particles is restricted by a number of conservation laws or invariance principles. That is to say, certain properties of representative physical quantities must remain unchanged in any process. The most familiar quantities in large scale experiments that are conserved in all interactions.

Keywords:
Elementary particles, boson, fermion, meson, graviton

Self assessment questions:

1. Explain in detail about the classification and properties of elementary particles
2. What are various interactions that exist among the elementary particles.
3. Explain various conservation laws that are obeyed by elementary particles.
4. Explain the terms namely charge conjugation, space inversion invariance and combined inversion.

Text books

1. Nuclear physics by D.C.Tayal , Himalaya publishing company,Bombay.
2. Nuclear physics by R.C.Sharma, K.Nath&co, Merut
3. Nuclear physics by S.B.Patel

Unit - III

Lesson - 9

NMR : BASIC PRINCIPLES

Aim : To know about the basic principles of NMR and also to know about relaxation phenomena.

Objectives of the lesson :

1. Introduction : Nuclear properties, Spin and Magnetic moment etc.
2. To know about the Resonance condition
3. To know about Boltzmann distribution and the population of different levels.
4. Concept of Spin - Lattice Relaxation time.
5. To know about spin - spin interaction and also spin - spin relaxation mechanism.
6. Measurement of spin - lattice and spin spin relaxation times T_1, T_2 by pulse methods.
7. Summary of the Lesson

Structure of the lesson :

9.1 Introduction

NMR means Nuclear Magnetic Resonance. Two properties of nuclear particles pertinent to an understanding of NMR spectroscopy are net spin associated with protons and neutrons and the distribution of positive charge.

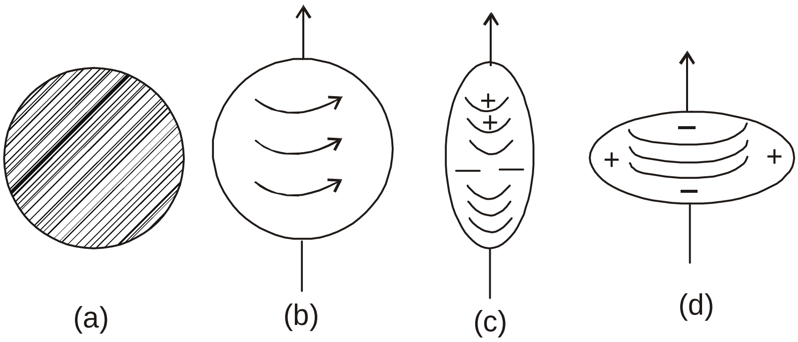


Fig 9.1 : Various representations of nuclei

(a) $I = 0, eQ = 0$ (b) $I = \frac{1}{2}, eQ = 0$ (c) $I \geq 1, eQ > 0$ and (d) $I \geq 1, eQ < 0$

If the spins of all the particles are paired there will be no net spin and the nuclear spin quantum number $I = 0$. The distribution of positive charge is spherical, so the nucleus is said to possess a zero quadrapole moment eQ where e is the unit of electro static charge and Q is the measure of the deviation of the charge distribution from spherical summetry. Fig. 9.1(a) is the representation of nuclei where I and eQ is zero. (Ex. ${}^{4}_{2}He,\ {}^{12}_{6}C,\ {}^{16}_{8}O$ and ${}^{32}_{16}S$). Fig. 9.1(b) is the represantation of $I = \frac{1}{2}$ and the charge distribution is spherical, $eQ = 0$ (Ex. ${}^{1}_{1}H$). In cases where $I \geq 1$, not only the nucleus have spin associated with, but the distribution of protonic charge will be non-spherical. A positive value of Q indicates that the protonic charge is oriented along the direction of the applied field vector. Fig. 9.1(c), while negative charge of Q indicates charge accumulation is perpendicular to the principle axis Fig. 9.1(d). Nuclei with even number of both protons and neutrons, belong to the type represented in Fig. 9.1(a).

NMR spectroscopy is often concerned with Nucleus $I = \frac{1}{2}$, example which include $H^1,\ P^{31}$, and F^{19}, but spectra cannot be obtained with nuclei $I = 0$.

For a nucleus with $I = \frac{1}{2}$ two values for the nuclear spin angular momentum quantum number $m_I = +\frac{1}{2}$ or $m_I = -\frac{1}{2}$ indicate allowed orientations of the nuclear magnetic moment vector in an external field. The value $+\frac{1}{2}$ corresponds to alignment of the vector with the applied field and $-\frac{1}{2}$ opposed to the magnetic field. The quantum number m_I has the values.

$$m_I = -I,\ (-I+1),\ ....(I-2),\ (I-1),\ I \text{ ----------------- (9.1)}$$

They are $(2I+1)$ in number.

For $I=1$, m has the values $+1,\ 0,\ -1$, corresponding to alignment, perpendicular and opposed to the field. In the absense of the magnetic field all orientation of nuclear moment are degenerate. This degeneracy is lifted on by the external field.

The magnetic moment μ associated with spin angular momentum is given by

$$\overline{\mu} = \gamma\ \overline{I}\ \hbar \text{ ---------------- (9.2)}$$

where γ is a scalar, called the gyromagnetic ratio and may take positive or negative value.

An alternate expression for the magnetic moment is given as

$$\overline{\mu} = g_N\ \mu_N\ \overline{I} \text{ ------------------------ (9.3)}$$

where g_N, the nuclear g factor and is a small dimensionless algebraic number and that takes different values for different nuclei, μ_N is the nuclear magneton and is defined by $\mu_N = \frac{e\hbar}{2m_P}$, where m_P is the proton mass. The value of μ_N is $5.051\times10^{-27}\ JT^{-1}\left(Nm^2\right)$.

9.2 Resonance Condition

First of all let us consider an isolated nucleus in a steady magnetic field $\overline{B_0}$. We supose that nuclear spin $\overline{I}$ is greater than zero so that the nucleas may possess a magnetic moment. From the theory of quantum mechanics, we know that length of the nuclear angular momentum vector is $\left[I(I+1)\right]^{1/2}\ \hbar$ but that the only measurable components of this vector are given by $m\hbar$, where m is the magnetic quantum number, which may take any of the $(2I+1)$ values in the series $I,\ I-1,\ I-2,\ ....,-(I-1),\ -I$. This is illustrated in the case of $I=\frac{3}{2}$ in Fig 9.2, where the angular momentum has just four measurable values along the direction of the applied field $\overline{B_0}$.

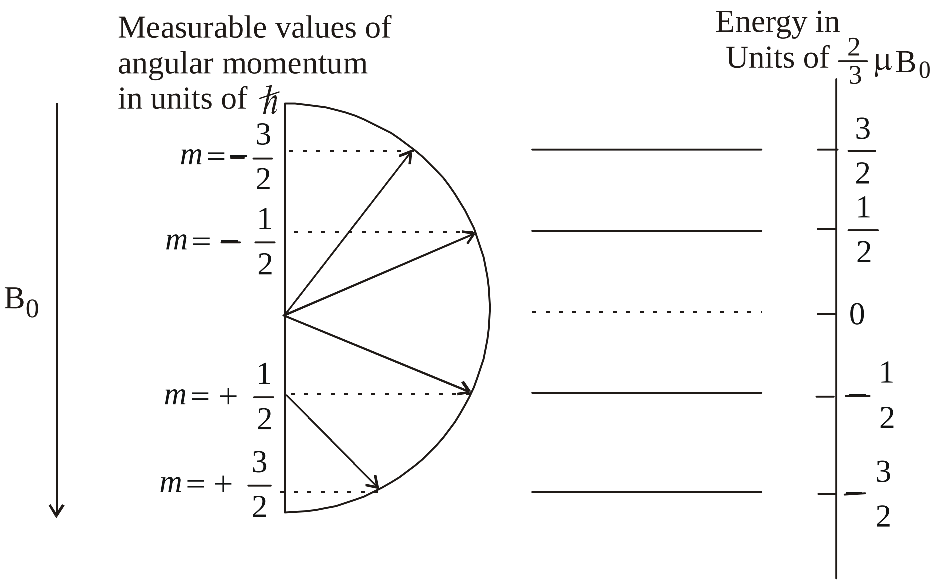


Fig. 9.2 Diagrams showing schematically the four measurable values of angular momentum for a nucleas having a spin number $\frac{3}{2}$ shown. When placed in a magnetic field $\overline{B_0}$.

The corresponding four energy levels are corresponding to this quantization of the angular momentum components, the nuclear magnetic moment has also $(2I+1)$ components in proportion. μ is the defined as the maximum measurable component of magnetic moment. Therefore the length of the magnetic moment vector is actually $\left[(I+1)/I\right]^{1/2}\mu$. However μ is the quantity which is of physical interest. The components of magnetic moment are given by the $(2I+1)$ values of $\frac{m\mu}{I}$, forming the series $\mu, \frac{(I-1)}{I}\mu,$ ....$-\frac{(I-1)}{I}\mu, -\mu$. The energy levels of the nuclear magnet in the magnetic field $\overline{B_0}$ are therefore given by $(2I+1)$ values of $-m\mu B_0/I$. These levels are illustrated in fig 9.2 for the case of $I=\frac{3}{2}$ and in the general case show a set of equally spaced levels with separation $\frac{\mu B_0}{I}$ between successive levels. This energy separation is often written as $g_N \mu_N B_0$ where μ_N is the nuclear magneton and $g_N = \frac{\mu}{\mu_0 I}$ is called the splitting factor or $g-$ factor. This g factor is infact the counter part of the Lande' splitting factor in atomic spectroscopy. It will be noticed that gI is the magnetic moment measured in units of the nuclear magneton.

The selection rule governing transitions between energy levels is the same as for the closely related Zeeman effect; transitions are allowed whic cause m to change by ± 1. A quantum of energy can therefore exite transitions between the energy levels if it has the same magnitude as the level spacing.

Thus we have

$$H = -\overline{\mu} \cdot \overline{B_0} = -\gamma \overline{J} \cdot \overline{B_0} = -\gamma \hbar \overline{I} \cdot \overline{B_0} = -\gamma \hbar B_0 \left| I \right\rangle_{\mp \frac{1}{2}}$$

$$= \frac{\gamma \hbar B_0}{2} - \left(\frac{-\gamma \hbar B_0}{2} \right) = \gamma \hbar \; B_0 \text{ ------------------ (9.4)}$$

$$\text{or} \quad H = -\overline{\mu} . \overline{B_0} = g_N \mu_N \overline{I} \cdot \overline{B_0} = \pm \left| \frac{g_N \mu_N B_0}{2} \right\rangle = g_N \mu_N B_0 \text{ -------------- (9.5)}$$

Thus for the simplest case of proton, $I = \frac{1}{2}$, the splitting of every clouds

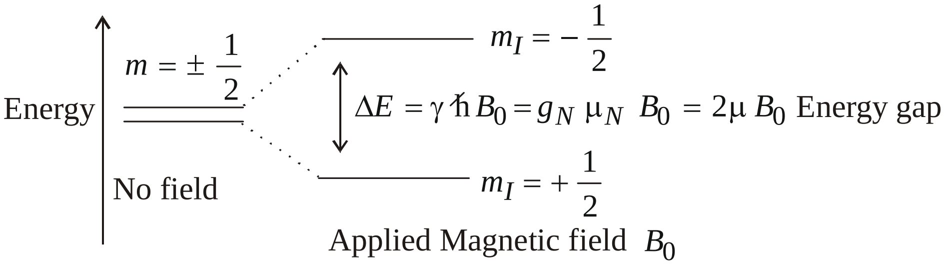


Fig. 9.3 Splitting of $m_I = \pm\frac{1}{2}$ state in steady magnetic field $\overline{B_0}$.

Thus a proton with $I = \frac{1}{2}$ and $m_I \pm \frac{1}{2}$, in the absense of magnetic field, possesses two energy levels which are degenerate and on the application of magnetic field $\overline{B_0}$, energy separation or gap is created in other words, the degeneracy is lifted on creating energy gap $\Delta E = \gamma \hbar B_0 = g_N \mu_N \overline{B_0}$ $= 2\mu B_0$.

For protons the value of $g = 5.58$, in a typical field of 1 Tesla, the resonance frequency required to cause transition would be 42.6 MHz. All the resonance frequencies of any nuclei fall in the radio frequency range, thus this NMR spectroscopy is also otherwise called RF spectroscopy.

Thus we have seen above the energy of interaction between the magnetic moment of the nucleus and the applied magnetic field $\overline{B_0}$. Let us look into the physical aspect of the interaction of magnetic moment $\overline{\mu}$ in the presence of applied magnetic field $\overline{B_0}$. We may find the necessary condition for observation of the magnetic resonance transitions from the properties of emission spectrum of the analogous atomic Zeeman effect. Zeeman effect transitions which involve a change in m of ± 1, produce radiation which is circularly polarised in the plane perpendicular to the applied steady magnetic field $\overline{B_0}$. In order to excite such transitions in the magnetic resonance experiment, it is threfore necessary to supply $r\,f$ radiation with the magnetic vector circularly polarised in a plane perpendicular to the steady magnetic field $\overline{B_0}$.

This requirement of circularly polarized radiation is just the one what would expect rom classical argument. If a magnetic dipole $\overline{\mu}$ is placed in a steady magnetic field $\overline{B_0}$ as shown in fig. 9.4.

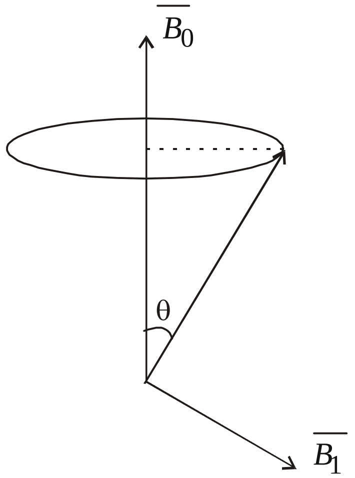


Fig. 9.4 Diagram illustrating the classical Larmor

precession of a magnetic moment $\overline{\mu}$ in a magnetic field $\overline{B_0}$

The magnetic dipole precesses about the direction of the magnetic field $\overline{B_0}$. This can be visualised as follows. The magnetic dipole $\overline{\mu}$ in the presence of magnetic field $\overline{B_0}$ experiences a couple $\left(\overline{\mu} \times \overline{B_0}\right)$, the resultant of the couple at a particular instant is to move the tip of the magnetic dipole into the plane perpendicular to μ and H_0 containing plane. Thus in the successive instances if the loci of the tip of the vector is seen it is circularly polarised perpendicular to the direction of the magneticfield $\overline{B_0}$.

This can be written as that the couple $\overline{\mu} \times \overline{B_0}$ may be equated to the rate of change of angular momentum since the angular momentum is $\frac{\mu}{\gamma}$, thus we have

$$\frac{1}{\gamma}\frac{d\overline{\mu}}{dt} = \overline{\mu} \times \overline{B_0} \text{ ------------------------ (9.6)}$$

The rate of precession is given as follows

$$\gamma\hbar B_0 = h\mathrm{v}_0 \text{ -------------------- (9.7)}$$

or $\gamma\ B_0 = 2\pi\,\mathrm{v}_0 = \omega_0$ angular frequency (9.8)

or $\overline{\omega_0} = \gamma\ \overline{B_0}$ is called fundamental equation of NMR / EPR, which relates the frequency with applied field $\overline{B_0}$ since γ is only a constant.

Here ω_0 is specifically termed as Larmor angular frequency, and γ is called gyro magnetic ratio of the dipole.

Suppose now that an additional small magnetic field $\overline{B_1}$ is at right angles to $\overline{B_0}$ in the plane containing $\overline{\mu}$ and $\overline{B_0}$. The dipole will explains a couple $\left(\overline{\mu} \times \overline{B_1}\right)$ tending to increase the angle θ between $\overline{\mu}$ and $\overline{B_0}$. If the small field $\overline{B_1}$ is made to rotate about $\overline{B_0}$ as axis in synchronism with the precession of the dipole, thus couple will cause the angle θ to increase steadily. If on the other hand $\overline{B_1}$ rotates with an angular frequency different from the Larmor prcessional frequency or in opposite sense (phase) the couple $\overline{\mu} \times \overline{B_1}$ will vary in magnitude and direction according to the relative phases of the phases and will merely produce small perturbations of the precessional motion with no net effect. A resonance therefore occurs when the angular frequency $2\pi\upsilon$ of the rotating field is equal to the angular frequency of Larmor precession namely. When

$$2\pi\upsilon = 2\pi\upsilon = \omega_0 = \gamma\ B_0 \text{ ------------- (9.9)}$$

When it is remembered that the nuclear gyromagnetic ratio γ is given by $\mu/I\hbar$, it is seen that classical resonance conduition agrees exactly with that derived from quantum theory 9.4 or 9.5.

Secondly we have also seen with the quantum theory or classical theory a condition for the observation of the resonance is that electromagnetic radiation be circularly polarized with the magnetic vector rotating in a plane perpendicular to the steady magnetic field. The agreement between the results of the classical and the quantum theory view points allows a number of features of the nuclear magnetic resonance phenomenon to be discussed rather simply interms of classical vector model of the nucleus.

Although the generation of high frequency rotating magnetic field is quite practicable is is usually much simpler to provide a linear oscillating field, for most purposes, linear polarization is quite adequate since as in the theory of rotating polarization in optically active crystals, a linearly oscillating field may be regarded as the superimposition of two rotating fields. Then as shown in fig. 9.5 if the linearly oscillating field has amplitude $2B_1$ it may be decomposed into two circularly polarized fields each of amplitude B_1, but rotating in opposite sense in a plane perpendicular to $\overline{B_0}$. Resonance will be obtained with the component which has correct sense, the other component having negligible effect.

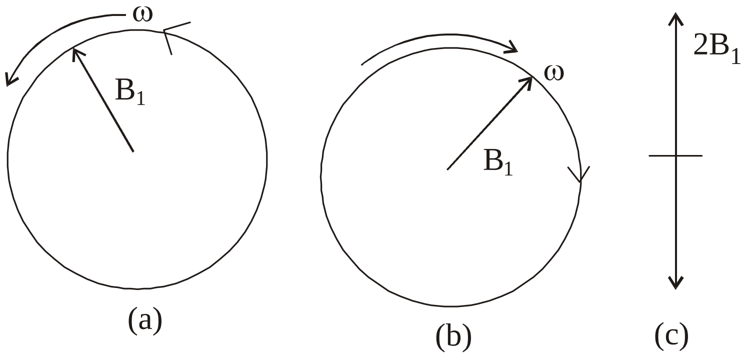


Fig. 9.5 If two equal vectors B_1 shown in (a) and (b) rotating in opposite senses, the resultant (c) is a linear vibration of amplitude $2B_1$ The steady field $\overline{B_0}$ is taken normal to the diagram

9.3 Boltzmann Distribution and the Population of different levels :

For $I=\frac{1}{2}$, each nucleus has two possible energy levels separated by a gap of $2\mu B_0$, if we now apply radiation of the resonance frequency polarized in a direction perpendicular to $\overline{B_0}$, transition between the two levels takes place. From the simple theory of the Einstein coefficients (Einstein 1917), the probability of transitions upwards by absorption is equal to the probability of transitions downwards by stimulated emission. In comparison with these probabilities the probability of transitions downwards by spontaneous emission is negligible. If the number of the nuclei in each energy level were equal, the average rate of transitions up and down would there fore be equal and there would be no net effect on the system. However since the nuclear spins are in equilibrium at temperature T_s, the population of lower level exceeds that of the upper level by Boltzmann factor $\exp\left(\frac{2\mu H_0}{kT_s}\right)$ where k is Boltzmann's constant. At room temperature for protons of 1 Tesla, this factor has the value

$$\exp\left[\frac{2\mu H_0}{kT_S}\right]^2 \simeq 1+\frac{2\mu H_0}{kT_S} = 1+8\times10^{-6} \text{ ------------------------ (9.10)}$$

On account of this typically small, but finite, excess of population in the lower energy state, there is a net absorption from the radio frequency field. In other words the difference of populations in different levels is responsible for the system to possess a net spin, followed by tiny net magnetic moment and there by the system to participate in the NMR phenomena (NMR absorption to occur).

Table 9. 1

Magnetic Resnonace Parameters for Certain Important Nuclei

Nucleus	Nuclear Spin units of $\hbar$)	Magnetic Moment (on units μ_N)	$\upsilon(\text{MHz})$ $B_0 = 1T$	$B_0 \equiv 3T$
1_H	$\frac{1}{2}$	2.7927	42.577	127.728
13_C	$\frac{1}{2}$	0.7022	10.705	32.115
19_F	$\frac{1}{2}$	2.6273	40.055	120.165
31_P	$\frac{1}{2}$	1.1305	17.236	51.708
2_H	1	0.8574	6.536	19.608
14_N	1	0.4036	3.076	9.228
11_B	$\frac{3}{2}$	2.6880	13.660	40.980
35_{Cl}	$\frac{3}{2}$	0.6833	3.472	10.416
79_{Br}	$\frac{3}{2}$	2.099	10.667	32.001

9.4 Spin - Lattice Relaxation Time

Let us now consider an assembly of identical atomic nuclei in the presence of a steady magnetic field $\overline{B_0}$. For simplicity we will at first suppose that the nuclear spin number is $\frac{1}{2}$. It will further be assumed that there is only a weak coupling between the nuclear magnets. At the same time some coupling between the nuclei has to be assumed so that the assembly may be considered to be in thermal equilibrium at temperature T_S. We shall however, suppose that the interaction of nuclear magnets wtih the remainder of the system is even smaller. The material is which the nuclear magnets are embedded is generally referred to as the lattice whether it be solid, liquid or gas. During resonance, the absorption of energy takes place and it corresponds to the transfer of some of the excess population from the lower level to the upper level. If there is no interaction between the system of nuclear spins and the lattice, the fractional excess of population $2\mu H_0 \,/kT_S$ steadily dwindles. The ratio of the populations may still formally be described by a Boltzmann factor with the temperature T_s of the spin system seadily rising. The spin system is in fact being subjected to a process of radio frequency heating. The temperature of the lattice is not affected since we have assumed negligible interaction between the spin system and the lattice. The interaction within the spin system and with in the lattice are greater than the interaction between the two systems and we are justified in speaking separately of a spin temperature and a lattice temperature. Such interaction tends to bring both into thermal equilibrium at the same temperature. In practice this common temperature is identical with that of lattice. Thus the radio frequency radiation is reducing the excess of population in the lower energy state, the interactions with the lattice are tending to restore the excess to its original value.

The spin temperature is initially equal to that of lattice and by the application of radio frequency field we raise the spin temperature to a value of greater than lattice temperature. If the field is now removed we may ask how rapidly with the temperture of the spin system return to that of lattice.

The same question arises also in another way. The spin system and the lattice system are in thermal equilibrium at a common temperature in the absense of rf field and in a vanishingly small steady magnetic field. The two energy levels are scarcely separated and their populations are practically identical. Now we apply a steady magnetic field of several Tesla. In this field identical populations correspond to a very high spin temperatre and we ask how rapidly will the population adjust them selves by interaction with the lattice to the values required by thermal equilibrium of spins with the lattice.

In order that the spin system may cool down to the temperature of the lattice, there must be a net downward transfer of nuclei to the lower energy level.

Since the population of the uppper level does not exceed that of the lower level, only possibility is probability of downwards transitiions exceeds that for upward transition.

Indeed we can show that the probability W_- per unit time for downward transitians must exceed the probability W_+ for upward transitions.

Let the number of nuclei per cm^3 in the upper energy state $\left(m=-\frac{1}{2}\right)$ be N_- and the lower state $\left(m=+\frac{1}{2}\right)$ be N_+. If the whole system of the spins and lattice were in thermal equilibrium at a temperature T, then by the principle of detailed balancing the number of transitions upwards and downwards must be equal which is given by

$$W_+ \; N_+ \; = W_- \; N_- \text{ --------------------- } (9.11)$$

In equilibrium N_+ and N_- are related by the Boltzmann factor so that

$$\frac{N_+}{N_-} = \frac{W_-}{W_+} = \exp\left[\frac{2\mu B_0}{kT}\right] \cong 1+2\frac{\mu B_0}{kT} \text{ -------------------- } (9.12)$$

We can write

$$1+\frac{W_-}{W_+} = 1+1+\frac{2\mu B_0}{kT}$$

or
$$\frac{W_+ + W_-}{W_+} = 2+\frac{2\mu B_0}{kT} = 2\left(1+\frac{\mu B_0}{kT}\right)$$

or
$$\frac{W_+ + W_-}{2} = W \; = \; W_+\left(1+\frac{\mu B_0}{kT}\right)$$

Let us note $\frac{W_+ + W_-}{2} = W$, average transition probability

or $W_+ = W\left(1-\frac{\mu B_0}{kT}\right)$

and similarly $W_- = W\left(1+\frac{\mu B_0}{kT}\right)$

$$\left.\begin{aligned} W_+ &= W\left(1-\frac{\mu B_0}{kT}\right) \\ W_- &= W\left(1+\frac{\mu B_0}{kT}\right) \end{aligned}\right\} \text{ ------- } (9.13)$$

Let us consider spin system at a temperature T_S different from the lattice temeprature T, the excess number 'n' per cm^3 in the lower state where $n = N_+ - N_-$, changes by <u>two</u> with each transition, then the rate of change of n is given by

$$\frac{dn}{dt} = 2N_- W_- - 2N_+ W_+ \text{ --------------------- (9.14)}$$

Using (9.13), this becomes

$$\frac{dn}{dt} = 2W\left(n_0 - n\right) \text{ ------------------- (9.15)}$$

where $n_0 = \frac{N\mu B_0}{kT}$ - ------------------- (9.16)

and $N = N_+ + N_-$ the total number of nuclei per cm^3. Thus n_0 is the value of n when the spin system is in thermal equilibrium with the lattice. Integrating (9.15) gives

$$n_0 - n = \left(n_0 - n_a\right) e^{-2wt} \text{ ------------------------ (9.17)}$$

Where n_a is the initial value n. Equation (9.17) shows that the equilibrium is approached exponentially with a characteristic time

$$T_1 = \frac{1}{2W} \text{ ----------------------- (9.18)}$$

The approach of the spin and lattice systems to equilibrium may be termed as thermal relaxation process and for this reason T_1 is called the spin lattice relaxation time or the thermal relaxation time Bloch has given T_1 the alternative name of longitudinal relaxation time.

The nature of spin lattice interaction and the theoritical evaluation of the relaxation time T_1 will be discussed later.

The values of T_1 which are encountered experimentally usually lie in the range of 10^{-4} to 10^4 seconds. The value is usually longer for solids than for liquids and gases.

For solids it is rarely shorter than 10^{-2} sec while at low temperatures it may be very long.

For liquids T_1 may be as short as 10^{-2} or 10^{-3} sec and rarely exceeds 10 sec, in general the value of T_1 also depends on the strength of the magnetic field B_0.

9.5 Spin - Spin interaction / Spin - Spin Relaxation Mechanism

Hitherto we have discussed about the interaction between spins and the lattice. Let us now probe the interaction between spins themselves. Since each nucleus possesses a small magnetic dipole moment there will be a magnetic dipole-dipole interaction between each pair of nuclei. Classically it may be viewed as follows. Each nuclear magnet finds itself not only in the applied field $\overline{B_0}$ but also in a small local magnetic field $\overline{H}_{\text{local}}$ produced by neighbouring nuclear magnets. The direction of the local field differs from nucleus to nucleus depending on the relative disposition of the neighbouring nuclei in the lattice and on their magnetic quantum number m.

The magnetic field of a magnetic dipole moment μ at a distance r is of the order of μ / r^3 so that only the nearest neighbours make important contribution to $\overline{H}_{local}$. Taking r for a value of $1\,\overset{0}{\text{A}}$ and for μ one nuclear magneton we find

$$B_{\text{local}} \sim \mu_0\, r^{-3} \sim 5 \text{ oeresteds ------------------ (9.19)}$$

The steady magnetic field will not therefore be the same for each nucleus but will vary over a range of several oeresteds from one nucleus to another. Thereby the resonance condition will not be perfectly sharp. Instead the energy levels are broadened by an amount of $g\mu_0\, B_{\text{local}}$. If we have fixed radio frequency υ_0 and traverse the steady magnetic field, the resonance will be found to be spread about B_0 over a range of the order of B_{local}. Since the steady field differs from nucleus to nucleus there will be distribution of the frequencies of the Larmor precession covering a range $\delta\omega_0$ which is found from (9.19) and (9.8).

$$\delta\omega_0 \sim r\, B_{\text{local}} \sim \mu_0{}^2 / \hbar\, r^3 \sim 10^4 \sec^{-1} \text{ ------------- (9.20)}$$

If the two spins have precession frequencies differing by $\delta\omega_0$ and are initially inphase they will be out of phase in a time $\sim \dfrac{1}{\delta\,\omega_0} \sim 10^{-4}\sec$.

This is not the only way in which the relative phases of two pressing spins j and k may be disturbed. Nucleus j produces at nucleus k a magnetic field oscillating at its Larmor frequency and as a result may induce transition in k. The energy for the transition of nucleus k comes of course from nucleus j; there is infact a mutual exchange of energy in the process. Since the rlative phases of nuclei change in a time of the order of $\dfrac{1}{\delta\omega_0}$ the correct phasing for this spin exchange process should occur after a time interval of this order and this inturn should determine the life time of a spin state. It is well known that a life time of $\dfrac{1}{\delta\omega_0}$ produces a broadening of the energy levels of $\sim \hbar\ \delta\omega_0$. From (9.20) and also from the definition of γ, this energy breadth is

$$\hbar\,\delta\omega_0 \simeq \hbar\gamma\, B_{\text{local}} = g\,\mu\, B_{\text{local}} \text{ ------------------- (9.21)}$$

It therefore follows that the resonance condition, that this process results in further broadening of the resonance line at a fixed radio frequency by an amount of the order of B_{local}.

These two namely, phase disturbing and line broadening processes are present only when identical nuclei are concerned. For a system of non-identical nuclei, the local field is still present but the spin exchange process is absent.

It is convenient to introduce a spin-spin interaction time T_2 to describe the life time or phase memory time of nuclear spin state where $T_2 \sim \frac{1}{\delta\omega_0} \sim 10^{-4}\,\text{sec}$.

Bloch has called T_2, the transverse relaxation time.

The shape of the absorption line as a function of frequency in a fixed magnetic field B_0 by mean of a normalized function $g(\upsilon)$ where υ is the frequency is given by

$$\int_0^{\infty} g(\upsilon)\,d\upsilon = 1 \text{ ------------------- (9.22)}$$

For absorption lines of similar shpae, the maximum value of the shape further $g_{(\upsilon)\max}$ will be large for narrow lines and small for broad lines. Then the quantity $1/g_{(\upsilon)\max}$ is a rough guide to the width of the line. Thus it follows T_2 is of the order of $g_{(\upsilon)\max}$. In this connection to form a precise definition of T_2, we put $T_2 = \frac{1}{2} g_{(\upsilon)\max}$ ---------------- (9.23).

The coefficient $\frac{1}{2}$ is inserted to make this definition consistent with that of Bloch (1946). From (9.23) T_2 is connected only with the peak value of the normalized line-shape curve.

9.6 Spin - Lattice (T_1) and spin - spin (T_2) Relaxation Time meaments by Pulse methods

Here we consider the behaviour of spin system subjected to one or more rf pulses. We assume that the rf from the transmitter to the probe is turned off and on so fast that the envelope of the rf during the pulse has the shape of square wave. We also assume that the length of the pulse t_p is short relative to T_1 and T_2 so that no relaxations occurs during the time t_p.

We evaluate the angle through which a given pulse causes $\overline{M}$ to proces and we commonly identify the pulses as $90^0\left(\frac{\pi}{2}\right)$, $180^0(\pi)$ pulses etc., we consider at present only the rf signal arising after the pulse has been turned off.

9.6.1 Free Induction Decay :

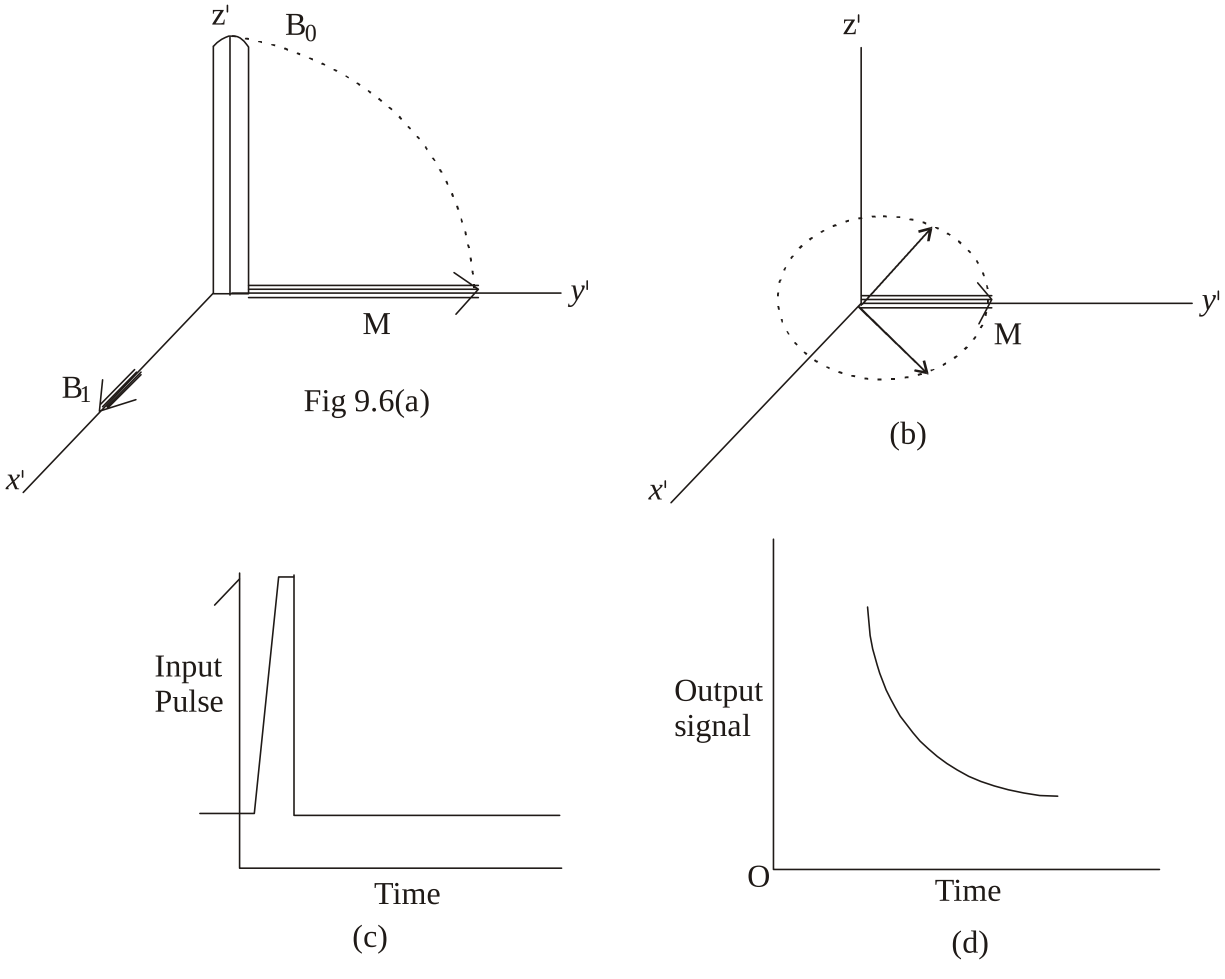


Fig 9.6(a) A 90^0 pulse along x' rotates $\overline{M}$ from the equilibrium position to the y' axis **(b)** $\overline{M}$ decreases as the magnetic moment dephases **(c)** input signal a 90^0 pulse corresponding to (a) **(d)** Exponential free induction decay corresponding to (b).

Suppose a 90^0 pulse is applied along the x' axis in the frame rotating at the rf . $\overline{M}$ lies entirely along the y' axis as indicated in Fig. 9.6(a). Since the apparatus is normally arranged to detect signals induced in a coil along the fixed x or y axis, the magnitude of M_{xy} determines the strength of the observed signal called <u>Free induction signal</u> since the nuclei precesses freely without applied rf. As Transverse relaxation $\left(T_2\right)$ occurs the signal decays. In a perfect homogeneous field the time constant of the decay would be T_2, but infact the free induction Signal decays in a time T_2^*, that often is determined by the field inhomogenuity. Since the nuclei in different parts of field precess at slightly different frequencies, hence quickly get out of phase with each other, the signal decays with a characteristic time T_2 as defined by

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \left(\frac{r\,\Delta B_0}{2}\right) \text{ ------------------ } (9.24)$$

Fig 9.6(b) specifies $\overline{M}$ decreases as magnetic moment dephase Fig. 9.6(c) shows an input signal a 90^0 pulse corresponding to Fig. 9.6(a) Fig 9.6(d) shows the exponential free induction decay corresponding to Fig. 9.6(b). This decay directly measures the decrease in M_{xy}. Thus even though detection of the signal occurs when no rf is applied to the nuclear spin system (i.e. after the pulse) the rf reference is applied to the detecter continueously. The detector responds to the magnetization which has a fixed phase relation to B_1, hence which occurs along a fixed axis in the rotating frame (in this case the positive y' axis). Suppose now that the rf is slightly different from the Larmor frequency of the nuclei. If we again consider the frame rotating at the radio frequency then immediately after the 90^0 pulse $\overline{M}$ lies the y' axis. The detector now displays not only the exponential decaying value of M_{xy} but also the interference effects as M_{xy} and the reference frequency alternately come in and out of phase with each other.

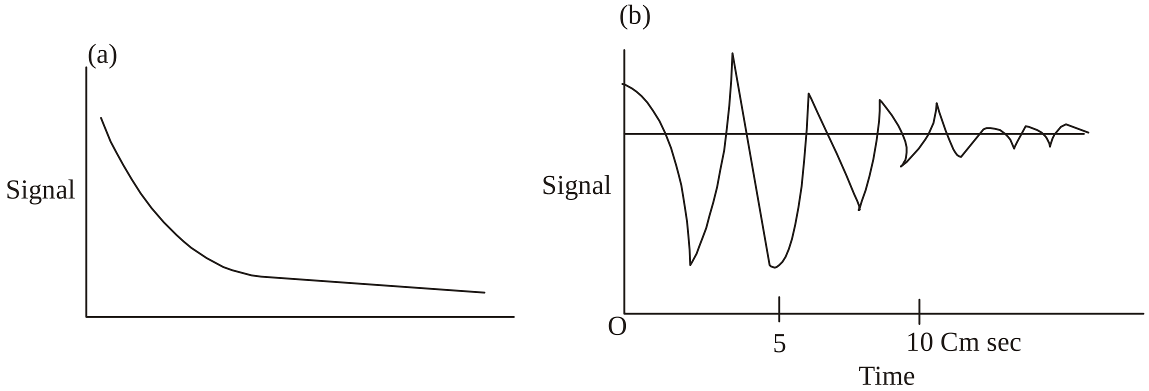


Fig 9.7(a) Free Induction Decay (FID) for rf for precisely at Larmor frequency

(b) FID for rf off resonance

We can extend the discussion by considering a system that has several nuclei of the same species (Ex. protons) that differ in Larmor frequency because of chemical shift and spin-spin coupling. Clearly some nucli are then precessing at a frequency different from that of rotating frame and interference effect can occur like that of Fig. 9.7 but often much more complex.

Measurement of FID is the basic way in which the magnitude and other characteristics of $\overline{M}$ are determined. The FID following a 90^0 pulse provides the spectral information needed in the Fourier Transform NMR and the FID resulting from sequences of two or more pulses is used in the determination of relaxation times.

9.6.2 Measurement of T_1 : Pulse methods provide the most versatile method of measuring T_1 over a wide range of values. The most commonly used procedure is the 180^0 , τ , 90^0 sequence as illustrated below.

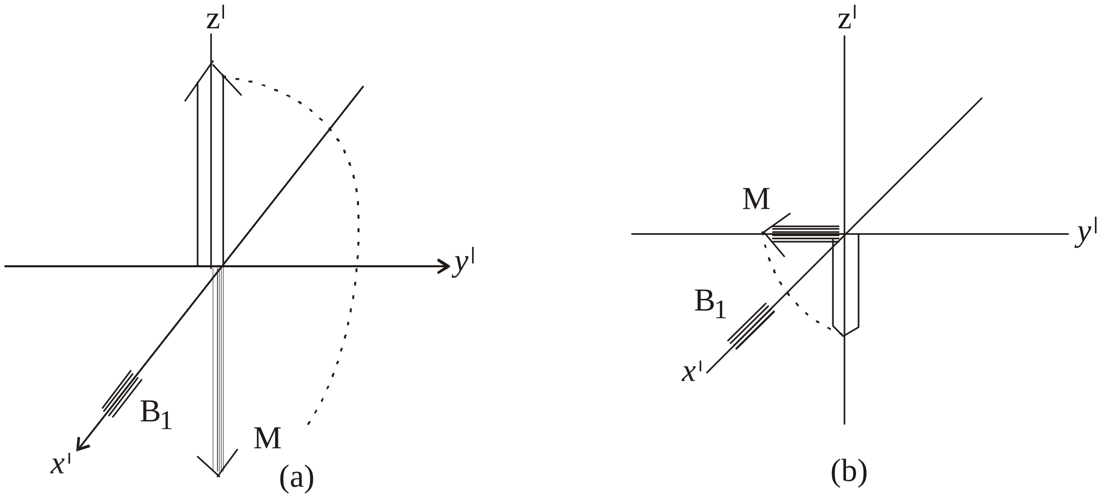
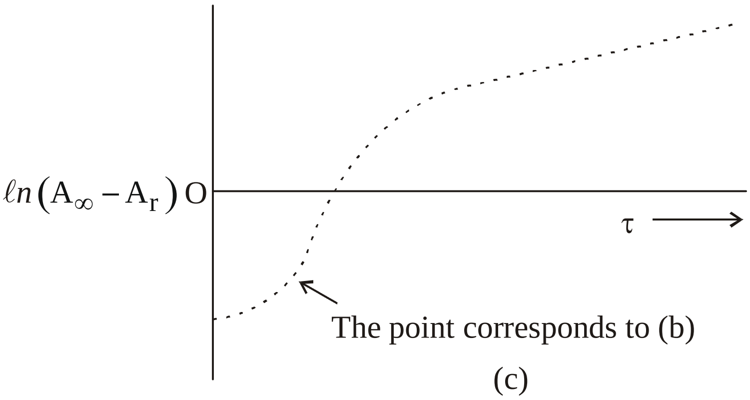


Fig. 9.8 Determination of T_1 by 180^0 , τ , 90^0 sequences (a) $\overline{M}$ is inverted by 180^0 pulse, at time 0 (b) after a time τ a 90^0 pulse rotates $\overline{M}$ to the y' (or - y') axis.



(c) The initial amplitude of the FID after the 90^0 pulse which is proportional to the value of $\overline{M}$ at time T is plotted as function of τ . Note that each point results from a separate 180^0 , τ , 90^0 sequence. The point corresponding to (b) is indicated by arrow.

First a 180^0 pulse inverts the magnetization along the z' axis. Longitudinal relaxations now occurs causing $M_{z'}$ to go from the values of $-M_0$ through zero to its equilibrium value M_0. If at a time τ after the 180^0 pulse, a 90^0 pulse is applied also along the x' axis. $\overline{M}$ rotated to y' axis (in the fig - y' axis). A free induction signal results, the height of which is proportional to the magnitude of M, hence to the value of $M_{z'}$ at time τ. If the system is now allowed to return to equilibrium by waiting atleast five times T_1 and the 180^0, τ, 90^0 sequence repeated for different values of τ the decay rate of M_z can be established as indicated in the fig. 9.8. The range over whcich τ is varied depends of course on T_1 and generally must go as high as 3 - 4 times T_1.

Quantitatively the decay of M_z is given by Bloch equations with $M_x = M_y = 0$

$$\frac{dM_z}{dt} = -\left(M_z - M_0\right)/T_1 \text{ ------------------ (9.25)}$$

integrating this equation with $M_z = -M_0$ at $t = 0$, gives

$$\left.\begin{aligned} M_z &= M_0\left(1-2\exp.\left(-\tfrac{t}{T_1}\right)\right) \\ M_z &= M_0 - 2M_0 \exp - \tfrac{t}{T_1} \end{aligned}\right\} \text{--------(9.26)}$$

This is the function plotted in the fig. 9.8
In practice equation (9.26) is written in the form

$$\ln\left(A_\infty - A_r\right) = \ln\left(2A_\infty - \tfrac{\tau}{T_1}\right) \text{ ------------------ (9.27)}$$

Where $A_r =$ initial amplitude of the FID following the 90^0 pulse at a time τ

$A_\infty =$ Limiting volume of A_r for a very long interval between the 180^0 and 90^0 pulses. π is determined from the slope of the plot $\ln\left(A_\infty - A_r\right)$ Vs τ.

It can be seen from (9.27) that $A = 0$ for $\tau = T_1$.

$\ln 2 = 0.69T_1$. Thus T_1 can be found from the pulse spacing τ that results in no free induction signal following the 90^0 pulse. While useful for rough measurement this procedure is inadequate for accurate determinations of T_1.

T_1 can also be found from 90^0 τ 90^0 sequence provided $T_1 >> T_2$. In this case the free induction following first 90^0 pulse decays to zero much more rapidly than M_z reaches equlibrium at time τ as in the 180^0 τ 90^0 sequence. If a series of 90^0 pulse is repeated several times with comon interval τ, $\overline{M}$ rapidly decreases to a steady state value depending on τ and T_1. The steady state value of the signal is noted and the 90^0 τ 90^0 .... sequence repeated for different values of τ. Since M is rotated 90^0 rather than 180^0, the initial condition for integration of equation (9.7) is $M=0$ at $t=0$. Thus there is a plot of $\ln\left(A_\infty - A_N\right)$ Vs τ gives a straight line from which T_1 can be measured. The 90^0 τ 90^0 sequence is often saves time when T_1 is long. This procedure is limited to the case $T_2 << T_1$ otherwise magnetization remaining along the y' at time τ would be rotated by z' axis and invalidate the equation used to determine T_1. In general 180^0 τ 90^0 method is for most accurate work.

9.6.3 Measurement of T_2 by the spin echo method : Unless $T_2 << \left(\frac{2}{r\,A B_0}\right)$, the contribution of inhomogenity in B_0 to the free induction decay preclude the use of this decay time T_2^* as a measure of T_2. An ingenious method for over coming the inhomogenity problem was proposed by Hahn who called it as the spin echo method. The method consists of the application of a 90^0, τ, 180^0 sequence and observation at a time 2τ of free induction echo. The rationale of the method is shown in fig. 9.9 which depicts the behaviour of the magnetization in the rotating frame.

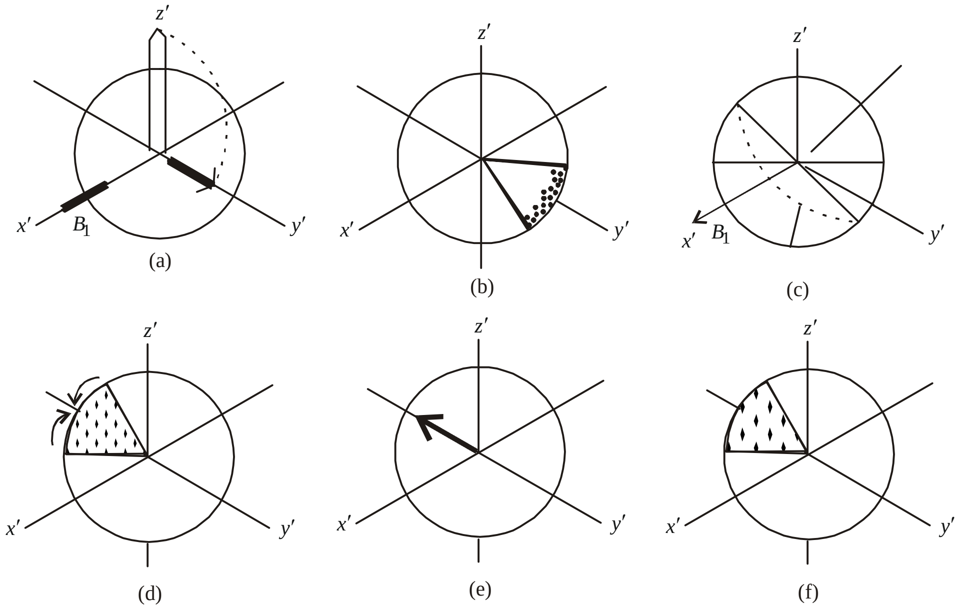


Fig. 9.9 The Hahn spin echo experiment (a) a 90^0 pulse applied along x' at time 0 causes

$\overline{M}$ to trip to the positive y' axis (b) The macroscopic magnetisation m_i of nuclei in different parts of the sample dephase as a result of the inhomogenity of B_0. Those nuclei precessing faster than the average (the rotation rate of the frame) appear in the rotating frame to more faster towards the observer. Looking down from the z' axis they appear to move clock wise while the slower than average move counter clock wise. (c) A 180^0 pulse along x' axis at time τ cause all mi to rotate 180^0 about the x' axis. (d) The faster nuclei, still moving clock wise in the rotating frame appear to move away from the observer. (e) At time 2τ the m_i rephase along the negative y' axis. (f) The continuing movement of the m_i causes then again to lose phase coherence.

In (a) $\overline{M}$ is shown being tipped through 90^0 by the application of B_1 along the positive x' axis. The total magnetization $\overline{M}$ can be thought of as the vector sum of individual macroscopic magnetization m_i arising from nuclei in different parts of sample and hence experiencing slightly different values of the applied field which is never perfectly homogeneous.

There is thus a range of precession frequencies centered about υ_0 which we have taken as the rotation frequency of the rotating frame.

In Fig. 9.9(b) then m_i begins to fan out as some nuclei precess faster and slower than the frame. At a time τ after the 90^0 pulse a 180^0 pulse is applied along the positive x' axis as shown in Fig. 9.9(c).

The effect of this pulse is to rotate each m_i by 180^0 about the x' axis. Thus those m_i that are moving faster than the frame naturally continue to move faster but in Fig. 9.9(d) their motion is away from the observer. At time 2τ all m_i came into phase along the negative y' axis as shown in Fig. 9.9(e). The continuing movement of the m_i causes then again to lose phase coherence shown in fig. 9.9(f).

The rephasing of the mi causes a free induclion signal to build to a maximum at 2τ but the signal is of course negative relative to the initial free induction decay since rephasing of the m_i occurs along the negative y' axis.

If the transeverse relaxation does not occur the echo amplitude might just as large as the initial value of the free induction following 90^0 pulse. However, each mi decreases during the time 2τ because of natural processes responsible for transeverse relaxation in the time T_2. Thus the echo amplitude depends on T_2 and this quantity may in principle be determined from a plot of peak echo amplitude as a function of τ and shown in the fig. 9.10.

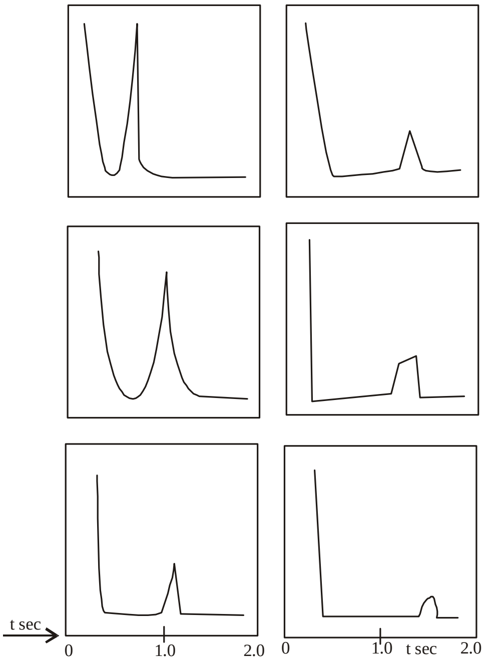


Fig. 9.10 : A typical Hahn spin echo experiment

Consisiting of six $90^0 \ \tau \ 180^0$ sequences with τ varying from 0.1 to 1.0 sec. Note that amplitude of the echo decreases as τ increases. In this experiment the echoes are positive rather than negative since a diode detectors are used which measures only amplitude and not phase of the signal.

The spin echo technique as we have described is limited in its range of applicability because of the effect of molecular diffusion. The precise focussing of all m is dependent upon each nucleus remaining in a constant magnetic field during the time of the experiment 2τ. If diffusion causes nuclei to move from one part of inhomogeneous field to another the amplited is reduced. For the present it is sufficient to note the effect of diffusion in the spin - echo experiment is dependent upon the spatial magnetic field gradients (G), the diffusion coefficient (D) and the time during which diffusion can occur. It has been shown that amplitude of echo for a pulse separation τ is

$$A(\text{echo at } 2\tau) \propto \exp\left[{}^{-2\tau}\!\Big/_{T_2}\Big) - \frac{2}{3} r^2 \ G^2 \ DT^3\right] \text{ ---- (9.28)}$$

equation (9.28) shows that the echo amplitude does not decay in a simple exponential fashion. Because of the τ^3 dependence the effect of diffusion is particularly pronounced for large values of τ and thus effects most measurement of long T_2's. For example Carr and purcell showed that in a measurement of T_2 for water at $25^0 C$ the application of a field gradient caused a decrease in the time constant or echo decay from about 2 to 0.2 sec.

9.7 Summary

1. Even number of protons and neutron number containing nuclei do not possess nuclear spin number I and also do not possess magnetic moment, hence they do not participate in NMR.
2. Boltzmann distribution dictates that at RT, the population of lower energy spin states are slightly little greater than population of higher energy spin states. This causes nuclei to possess a tiny net nuclear spin angular momentum and consequently net magnetic moment.
3. The energy of interaction between magnetic moment $\overline{\mu}$ and magnetic field $\overline{B_0}$ cause a separation of energy gap from the lowest to the highest by $2\mu B_0$ and number of energy levels are given by $\frac{\mu B_0}{\mathrm{I}}$ which are equidistant.
4. The nucleus possessing magnetic moment $\overline{\mu}$ ineracts with $\overline{B_0}$ cause a couple $\left(\overline{\mu} \times \overline{B_0}\right)$, the resultant of which is the magnetic dipole moment $\overline{\mu}$ precesses about the direction of the magnetic field $\overline{B_0}$ with a constant angle θ. This procession is known as Larmor precession and in the form of expression given by $\omega_0 = \gamma H_0$, where γ is called gyromagnetic ratio, may be positive or negative.
5. Nuclear magnetic resonance absorption falls in the radio frequency region, transitions are caused by the application radio frequency oscillator giving precisely the quantum of energy gap equal to energy gap caused due to the application of steady field.
6. As nuclear magnetic resonance absorption takes place the population difference dwindles and this is restored back due tot he spin-lattice interaction and by this spin lattice relaxation T_1 can be measured by Pulse methods.
7. There is spin - spin interaction and consequently spin - spin relaxation T_2 which tells about life memory time of state and T_2 can be measured by pulse methods.

9.8 Key Words

Nuclear spin, Nuclear magnetic moment, Quadrapole moment, Resonance, Larmor preessional frequency, Nuclear resonance absorption of energy, Boltzmann distribution, Lattice, spin-lattice relaxation tme T_1, spin - spin relaxation time T_2, pulse methods, linear oscillating field, circularly polarized field, Free induction decay.

9.9 Review Questions

1. Explain the principle of NMR and obtain the resonance condition.
2. Distinguish between spin - lattice and spin - spin relaxation, how do you measure T_1 and T_2 by pulse methods.
3. Explain Larmor precession and what is Larmor frequency.
4. What is Boltzmann distribution, explain how spin - lattice relaxation phenomena is helpful for recording NMR continueously.

9.10 Text and Reference Books

1. Molecular Structure and Spectroscopy by G. Arul dhas - (PHI)
2. Nuclear Magnetic Resonance by ER Andrew Cambridge Universy Press
3. Fundamentals of Molecular spectroscopy by C.B. Banwell.
4. Spectroscopy by BP Straughen and Walker

Unit - III

Lesson - 10

BLOCH EQUATIONS

Aim : To know about the Bloch Equations and solutions to Bloch equations for low B_1 and also to know about NMR spectrometer and structural properties from NMR experiment.

Objectives of the lesson :

1. Introduction to Bloch's approach about nuclear magnetic susceptibilities
2. To know about classical and quantum mechanical view of Bloch equation
3. To derive solutions to Bloch equation for low passage of B_1.
4. To know about NMR spectrometer details Bridge method, Rollins method, Nuclear Induction method and Pulse method.
5. To know about information from NMR and the measurement of nuclear properties and general physical applications of NMR.

Structure of the lesson :

10.1 Introduction

Hitherto our approach to the NMR phenomena is to know about the magnetic properties of nucleus and also certain macroscopic properties. In this regard, Bloem bergen, Purcell and Pound (1948) have done pioneering work in the field of NMR. On the other hand Bloch (1946) in developing the theory of nuclear induction argued in mainly macroscopic terms throughout. His more phenomenological approach is particularly well suited to the study of transient effects while at the same time for the systems in steady state it is broadly consistent with the quantum treatment. Here we use Bloch's approach to derive expressions for the real and imaginary parts of nuclear magnmetic susceptibility.

10.2 Classical and Quantum Mechanical View point of Bloch Equations

Let us consider from a classical view pont a nucleus of magnetic moment in a magnetic field $\overline{B}$. The nuclear magnet experiences a couple $\overline{\mu} \times \overline{B}$ which may be equated to the rate of change of angular momentum. Since the angular momentum of the nucleus is $\frac{\overline{\mu}}{\gamma}$, we have

therefore $\frac{1}{\gamma}\frac{d\overline{\mu}}{dt} = \overline{\mu} \times \overline{B}$ $\left(\text{since } \frac{d\overline{J}}{dt} = \overline{\mu} \times \overline{B} \text{ or } \frac{1}{\gamma}\frac{d\overline{\mu}}{dt} = \overline{\mu} \times \overline{B}\right)$ ------------------- (10.1)

If $\overline{B}$ is constant this equation of motion represents the precision of the vector $\overline{\mu}$ about the vector $\overline{B}$ with an angular frequency γB .

If we consider an assembly of weakly interacting nuclear spins, the magnetization vector $\overline{M}$ is the vector sum of the nuclear magnetic moments in unit volume.

Summing over unit volume, we have

$$\frac{d\overline{M}}{dt} = \gamma\, \overline{M} \times \overline{B} \quad \text{----------------- (10.2)}$$

This equation which has been obtained from classical point is nevertheless also valid in quantum mechanics. It is a well known principle, fully exploited by Bloch that the quantum mechanical expectation value of any quantity follows in its time dependence just as in the classical equation of motion.

The stedy state solution of equation (10.2) for constant $\overline{B}$ is of the same form as that of (10.1) and represent the precession of the vector $\overline{M}$ about $\overline{B}$ with an angular frequency γB.

We shall however be concerned with the case, where the three Cartesion components of $\overline{B}$ are all not constant, instead let us suppose their values are

$$B_x = B_1 \cos wt, \qquad B_y = -B_1 \sin wt, \qquad B_z = B_0 \text{ ------------------ (10.3)}$$

These components represent the actual situations in a nuclear magnetic resonance experiment. B_x, B_y together represent a magnetic field of amplitude B_1, rotating in a plane normal to the steady field B_0 in the same as the precession of nucleus having a positive value of γ. (If γ should be negative the sign of B_y must be changed). Equation (10.2) is not quite complete in an actual nuclear spin systems since the RHS does not express all the mechanisms by which $\overline{M}$ may change.

The component M_z represents the resultant magnetic moment per unit volume parallel to the steady field $\overline{B_0}$. In the absence of rotating Magnetic field and with the spin system and the lattice in thermal equilibrium this component is given by

$$M_0 = \chi_0 B_0 \text{ ------------------- (10.4)}$$

If the spin system and the lattice are not in thermal equilibrium, then in the absence of a radio frequency field Mz approaches M_0 exponentially with a characteristic time T_1. In this case 'z' component of the equation of motion is

$$\frac{d\,Mz}{dt} = \frac{M_0 - Mz}{T_1} \text{ ---------------------- (10.5)}$$

This equation is just rewriting the equation namely

$$\frac{dn}{dt} = 2W\left(n_0 - n\right) \text{ and } T_1 = \frac{1}{2W} \quad \text{(9.5 \& 9.18)}$$

and remembering that Mz is proportional to the excess number of nuclei in the lower energy state. It is because T_1 determines the approach to equilibrium of the component of M parallel to B_0, that Bloch has termed T_1 the longituawnal relaxation time.

We see therefore that to complete the z component of the equation of motion in the general case we must add RHS of (10.5) to the z component (10.2).

The transeverse components of M_x and M_y represent the rotating component of the processing Magnetization vector $\overline{M}$. We know that local irregularities of the magnetic field cause individual processing nuclei to get out of phase with each other in a time of the order of the spin -

spin interactions time T_2. In the absense of the radico frequency magnetic field any phase coherence of the nuclie would be destroyed in a time of the order of T_2, thus bringing M_x, M_y to zero. Bloch, therefore assumed for simplicity that the approach to zero is exponential with a characteristic time T_2 giving

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \text{ and } \frac{dM_y}{dt} = -\frac{M_y}{T_2} \text{ --------------- (10.6)}$$

Because T_2 enters these equations governing the time dependence of the transverse magnetization components M_x, M_y, Bloch has used the name transverse relaxation time for T_2.

Thus to complete x, y components of the equations of motion in the general case, we must add the RHS of (10.6) to the x, y componenets of (10.2).

On evaluating the vector product $\overrightarrow{M} \times \overline{B}$ and substituting for the components of $\overline{B}$ from (10.3) the three components equations now become

$$\frac{dM_x}{dt} = \gamma\left[M_y B_0 - \left(-M_z B_1 \sin\omega t\right)\right] - \frac{M_x}{T_2}$$

$$= \gamma\left[M_y B_0 + M_z B_1 \sin\omega t\right] - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = -\gamma\left[M_x B_0 - M_z B_1 \cos\omega t\right] - \frac{M_y}{T_2}$$

$$= \gamma\left[M_z B_1 \cos\omega t - M_x B_0\right] - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \gamma\left[-M_x B_1 \sin\omega t - M_y B_1 \cos\omega t\right] + \frac{M_0 - M_z}{T_1}$$

Thus

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \gamma\left[M_y B_0 + M_z B_1 \sin\omega t\right] - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \gamma\left[M_z B_1 \cos\omega t - M_x B_0\right] - \frac{M_y}{T_2} \\ \frac{dM_z}{dt} &= \gamma\left[-M_x B_1 \sin\omega t - M_y B_1 \cos\omega t\right] + \frac{M_0 - M_z}{T_1} \end{aligned}\right\} \text{(10.7)}$$

These three (10.7) are referred to as Bloch equations

10.3 Solutions to Bloch Equations

The steady state solutions of these (10.7) differential equations namely solutions to Bloch equations are given as here under :

It is convenient to introduce two new variables u and v, defined by

$$u = M_x \cos \omega t - M_y \sin \omega t \text{ ------------------ (10.8)}$$

$$\mathrm{v} = -\left(M_x \sin \omega t + M_y \cos \omega t\right) \text{ ------------- (10.9)}$$

which implies that

$$M_x = u \cos \omega t - \mathrm{v} \sin \omega t \text{ --------------- (10.10)}$$

$$M_y = -\left(u \sin \omega t + \mathrm{v} \cos \omega t\right) \text{ ------- (10.11)}$$

From (10.10)

$$\dot{M}_x = \dot{u} \cos \omega t - \omega u \sin \omega t - \dot{\mathrm{v}} \sin \omega t - \omega \mathrm{v} \cos \omega t \text{ ------------- (10.12)}$$

From (10.11)

$$\dot{M}_y = -\dot{u} \sin \omega t - \omega x \cos \omega t - \dot{\mathrm{v}} \cos \omega t + \omega \mathrm{v} \sin \omega t \text{ ----------- (10.13)}$$

Equating (10.12) with (10.7(i)), we have

$$\dot{u} \cos \omega t - \omega u \sin \omega t - \dot{\mathrm{v}} \sin \omega t - \omega \mathrm{v} \cos \omega t$$

$$- \gamma B_0 u \sin \omega t - \gamma B_0 \mathrm{v} \cos \omega t + \gamma B_1 \sin \omega t + \gamma B_1 \sin \omega t \, M_z$$

$$- \frac{u \cos \omega t}{T_2} + \frac{\mathrm{v} \sin \omega t}{T_2} \text{ ------------ (10.14)}$$

Similarly equating (10.13) with (10.7 ii)

$$-\dot{u} \sin \omega t - \omega u \cos \omega t - \dot{\mathrm{v}} \cos \omega t + \omega \mathrm{v} \sin \omega t =$$

$$\gamma B_1 \cos \omega t \, M_z - \gamma B_0 u \cos \omega t + \gamma B_0 \mathrm{v} \sin \omega t + u \frac{\sin \omega t}{T_2} + \frac{\mathrm{v} \cos \omega t}{T_2} \text{ -------- (10.15)}$$

By writing $\omega_0 - \omega = \Delta\omega$, the equations (10.14) and (10.15) are rewritten as

$$\dot{u}\cos\omega t - \dot{\mathrm{v}}\sin\omega t + \Delta\omega\, u\sin\omega t + \Delta\omega\, \mathrm{v}\cos\omega t$$

$$= \gamma B_1 \sin\omega t\, M_z - \frac{u\ \cos\omega t}{T_2} + \frac{\mathrm{v}\sin\omega t}{T_2} \text{ ---------- (10.14a)}$$

Similarly, $-\dot{u}\sin\omega t - \dot{\mathrm{v}}\cos\omega t + \Delta\omega\, u\cos\omega t - \Delta\omega\ \mathrm{v}\ \sin\omega t$

$$= \gamma B_1 \cos\omega t\ M_z + \frac{u\sin\omega t}{T_2} + \frac{\mathrm{v}\cos\omega t}{T_2} \text{ ----------- (10.15a)}$$

Equation (10.7 iii) reads

$$\dot{M}_z + \frac{M_z}{T_1} = -\gamma B_1\ u\ \cos\omega t\ \sin\ \omega t + \gamma B_1\ \mathrm{v}\ \sin^2 \omega t$$

$$+\gamma B_1\ u\cos\omega t\ \sin\omega t + \gamma B_1\ \mathrm{v}\ \cos^2\ \omega t + \frac{M_0}{T_1}$$

i.e. $\dot{M}_z + \dfrac{M_z}{T_1} = \gamma\ B_1\ \mathrm{v} + \dfrac{M_0}{T_1}$ ------------- (10.16)

Now, Multiplying (10.14a) by $\cos\omega t\,(-)$ Multiplying (10.15a) by $\sin\omega t$ we have

$$\dot{u} + \Delta\omega\, \mathrm{v} = -\frac{u}{T_2} \text{ ------------- (10.17)}$$

Similarly, Multiplying (10.14a) by $\sin\omega t$ (+) Multiplying (10.15a) by $\cos\omega t$, gives

$$\dot{\mathrm{v}} + \frac{\mathrm{v}}{T_2} - \Delta\omega u = -rB_1 M_z \text{ --------------- (10.18)}$$

Thus we have

$$\dot{M}_z + \frac{M_z}{T_1} - \gamma B_1 \mathrm{v} = \frac{M_0}{T_1} \text{ ------------ (10.16)}$$

$$\dot{u}+\frac{u}{T_2}+\Delta\omega\,\mathrm{v}=0 \text{ ----------------- } (10.17)$$

$$\dot{\mathrm{v}}+\frac{\mathrm{v}}{T_2}-\Delta\omega\,u=-\gamma\,B_1\,M_z \text{ ----------- } (10.18)$$

We seek a steady state solution of Bloch equations (called slow passage). In this case

$$\dot{u}=\dot{\mathrm{v}}=\dot{M}_z=0 \text{ ---------------- } (10.19)$$

Thus eliminating u from (10.17) and (10.18)

$$\dot{u}=0, \text{ and } \frac{u}{T_2}=-\Delta\omega\,\mathrm{v}$$

substituting this in (10.18)

$$\dot{\mathrm{v}}=0, \text{ and } \frac{\mathrm{v}}{T_2}-\Delta\omega\left(-\Delta\omega\,\mathrm{v}\,T_2\right)=-\gamma\,B_1\,M_z$$

$$\frac{\mathrm{v}}{T_2}+\left(\Delta\omega\right)^2\mathrm{v}T_2=-\gamma\,B_1\,M_z$$

$$\mathrm{v}\left[\frac{1+\left(\Delta\omega\right)^2T_2^2}{T_2}\right]=-\gamma\,B_1\,M_z$$

$$\mathrm{v}=-\gamma\,B_1\,M_z\,T_2\left[1+\left(\Delta\omega\right)^2\,T_2^2\right]^{-1} \text{ -------------- } (10.20)$$

Substituting for v from (10.20) into (10.16), we have

$$\dot{M}_z+\frac{M_z}{T_1}-\gamma\,B_1\,\mathrm{v}=\frac{M_0}{T_1}$$

Since $\dot{M}_z=0$,

$$\frac{M_z}{T_1}-\gamma\,B_1\,\mathrm{v}=\frac{M_0}{T_1} \text{ or } M_z-\gamma B_1\,\mathrm{v}T_1=M_0$$

or $M_z = M_0 + \gamma B_1 \text{ v } T_1$

$$M_z = M_0 + \gamma B_1 T_1 \left(-\gamma B_1 M_z T_2\right) \left[1+(\Delta\omega)^2 T_2^2\right]^{-1}$$

$$M_z = M_0 - \frac{\gamma^2 B_1^2 M_z T_1 T_2}{1+(\Delta\omega)^2 T_2^2}$$

$$M_z \left[1+\frac{\gamma^2 B_1^2 T_1 T_2}{1+(\Delta\omega)^2 T_2^2}\right] = M_0$$

i.e. $M_z \left[1+(\Delta\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2\right] = M_0 \left[1+(\Delta\omega)^2 T_2^2\right]$

$$M_z = \frac{M_0 \left[1+(\Delta\omega)^2 T_2^2\right]}{1+(\Delta\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \text{ ----------------- (10.21)}$$

substituting for M_z form (10.21) and inserting this in (10.20) we have

$$\text{v} = \frac{-\gamma B_1 T_2}{\left(1+(\Delta\omega)^2 T_2^2\right)} \left[\frac{M_0 \left(1+(\Delta\omega)^2 T_2^2\right)}{1+(\Delta\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}\right]$$

$$\text{v} = \left[\frac{-\gamma B_1 M_0 T_2}{1+(\Delta\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}\right] \text{ ------------- (10.22)}$$

Finally substituting for v from (10.22) into (10.17)

$$\dot{u} = 0, \text{ and } \frac{u}{T_2} + \Delta\omega \text{ v} = 0 \text{ -------------- (10.17)}$$

$$\frac{u}{T_2} = -\Delta\omega \text{ v or } u = -\Delta\omega \text{ v} T_2$$

$$u = \frac{-\Delta\omega\, T_2\left(-\gamma B_1 M_0 T_2\right)}{1+\left(\Delta\omega\right)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}$$

$$u = \frac{\left(\gamma B_1\right)\Delta\omega\; M_0\; T_2^2}{1+\left(\Delta\omega\right)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \quad \text{---------------- (10.23)}$$

Using (10.10) and (10.11) and remembering that $\Delta\omega = \omega_0 - \omega \;\; \omega_0 = r B_0$ and $M_0 = \chi_0 B_0$ we have $M_x = u\cos\omega t - \mathrm{v}\sin\omega t$

$$M_x = \frac{\gamma B_1\left(\omega_0 - \omega\right)T_2^2\;\chi_0 B_0\;\cos\omega t}{1+\left(\Delta\omega\right)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}\;(-)\;\frac{\left(-\gamma B_1\;\chi_0 B_0 T_2\right)\sin\omega t}{1+\left(\Delta\omega\right)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}$$

$$M_x = \chi_0\,\omega_0\; B_1\; T_2 \left[\frac{\left(\omega_0 - \omega\right)T_2\cos\omega t + \sin\omega t}{1+\left(\omega_0 - \omega\right)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}\right] \quad \text{---------------- (10.24)}$$

$$M_y = -\left[u\sin\omega t + \mathrm{v}\cos\omega t\right]$$

$$= -\left[\frac{\gamma B_1\left(\Delta\omega\right)T_2^2 M_0\;\sin\omega t}{1+\left(\Delta\omega\right)^2\; T_2^2 + \gamma^2 B_1^2\; T_1 T_2} + (-)\;\frac{\gamma B_1 M_0 T_2\;\cos\omega t}{1+\left(\Delta\omega\right)^2 T_2^2 + \gamma^2 B_1^2\; T_1 T_2}\right]$$

$$M_y = \omega_0\,\chi_0\, B_1 T_2 \left[\frac{\cos\omega t - T_2\left(\omega_0 - \omega\right)\sin\omega t}{1+\left(\omega_0 - \omega\right)^2\; T_2^2 + \gamma^2 B_1^2\; T_1 T_2}\right] \quad \text{------------- (10.25)}$$

Thus we have

$$M_x = \chi_0\,\omega_0\; B_1 T_2 \left[\frac{\left(\omega_0 - \omega\right)T_2\cos\omega t + \sin\omega t}{1+\left(\omega_0 - \omega\right)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}\right] \quad \text{----------------- (10.24)}$$

$$M_y = \chi_0\,\omega_0\, B_1 T_2 \left[-\frac{\left(\omega_0 - \omega\right)T_2\sin\omega t + \cos\omega t}{1+\left(\omega_0 - \omega\right)^2\; T_2^2 + \gamma^2 B_1^2 T_1 T_2}\right] \quad \text{----------- (10.25)}$$

$$M_z = \chi_0 B_0 \left[\frac{1+(\omega_0-\omega)^2 T_2^2}{1+(\omega_0-\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \right] \text{--------------- (10.21)}$$

Equation (10.24) is modified

$$M_x = \frac{1}{2}\chi_0 \omega_0 T_2 \left[\frac{2B_1 \cos\omega t \; (\omega_0 - \omega) T_2 + 2B_1 \sin\omega t}{1+(\omega_0-\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \right]$$

equation (10.25) is modified as

$$M_y = \frac{1}{2}\chi_0 \omega_0 T_2 \left[\frac{2B_1 \cos\omega t - 2B_1 (\omega_0 - \omega) T_2 \sin\omega t}{1+(\omega_0-\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \right]$$

and $$M_z = \chi_0 B_0 \left[\frac{1+(\omega_0-\omega)^2 T_2^2}{1+(\omega_0-\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \right].$$

In the actual experiment the oscillating field is linearly polarized of the form $B_x = 2 B_1 \cos wt$ rather than circularly polarized, we find from the above equations, the components χ' and χ'' of the nuclear magnetic susceptibility are

$$\chi' = \frac{1}{2}\chi_0 \omega_0 T_2 \left[\frac{(\omega_0-\omega) T_2}{1+(\omega_0-\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \right] \text{-------------- (10.26)}$$

$$\chi'' = \frac{1}{2}\chi_0 \omega_0 T_2 \left[\frac{1}{1+(\omega_0-\omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2} \right] \text{--------------- (10.27)}$$

We also recognize the term $\gamma^2 B_1^2 T_1 T_2$ in the denominator of the above equation as being dimensionless parameter determining the degree of saturation. Let us consider the Bloch susceptibilities when B_1 is small enough to avoid appreciable saturation namely when

$$\gamma^2 B_1^2 T_1 T_2 << 1 \text{ ------------------- (10.28)}$$

In this situations we see equation (10.21) as

$M_z \cong M_0 = \chi_0 B_0$ as expected at all frequencies, since the saturation is avoided.

The nuclear magnetic susceptibilities are now given by

$$\chi' = \frac{1}{2}\chi_0\,\omega_0\,T_2\left[\frac{(\omega_0-\omega)T_2}{1+(\omega_0-\omega)^2\,T_2^2}\right] \text{ ------------------- (10.29)}$$

This represents the real part of complex susceptibility which is responsible for the dispersion mode, which accompanies the absorption process in NMR experiment.

$$\chi'' = \frac{1}{2}\chi_0\,\omega_0\,T_2\left[\frac{1}{1+(\omega_0-\omega)^2\,T_2^2}\right] \text{ -------------------- (10.30)}$$

This represents the imaginary part of complex susceptibility which is responsible for the absorption mode in the NMR experiment. The susceptibilities are plotted in the following fig 10.1 as a function of dimension less product $(\omega_0-\omega)T_2$. The curve for χ'' shows the rresonant character of the absortption (imaginary part of complex susceptibility) and the curve for χ' shows the dispersion which accompanies the absorption (real part of complex susceptibility).

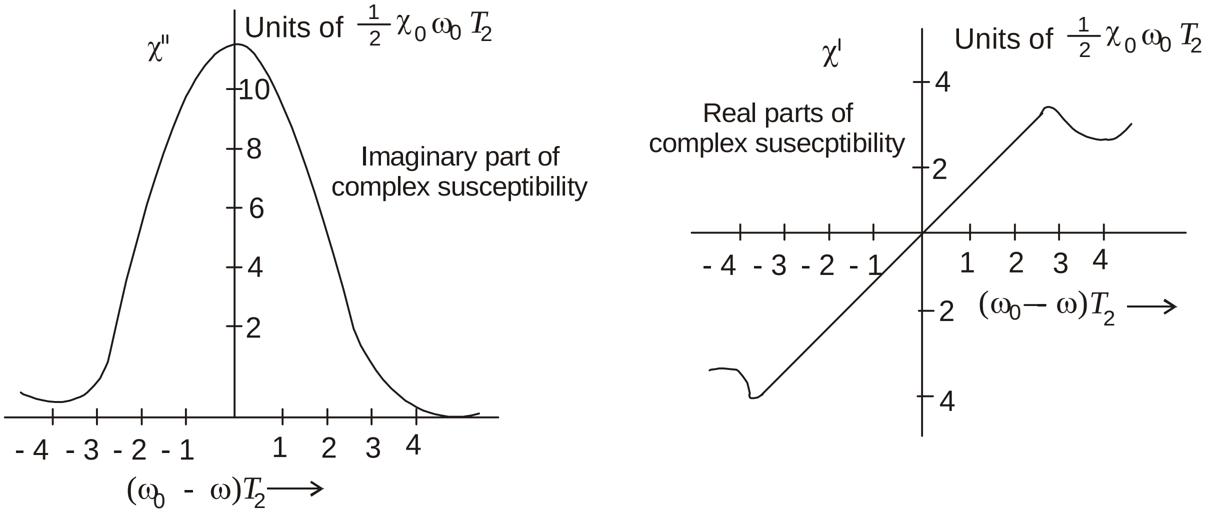


Fig 10.1 : The Bloch nuclear magnetic susceptobilities plotted against the dimensionless product $(\omega_0-\omega)T_2$. The graphs apply to the conditions of negligible saturation.

10.3 NMR Spectrometer details

The essential features of nuclear magnetic resonance absorption experiments which distinguishes then from nuclear induction experiments is that the resonance effects are detected by their reaction on the circuit supplying the radio frequency field. The arrangement used by Rollin (1946, 1949) in his pioneer experiments at low temperatures is probably the simplest.

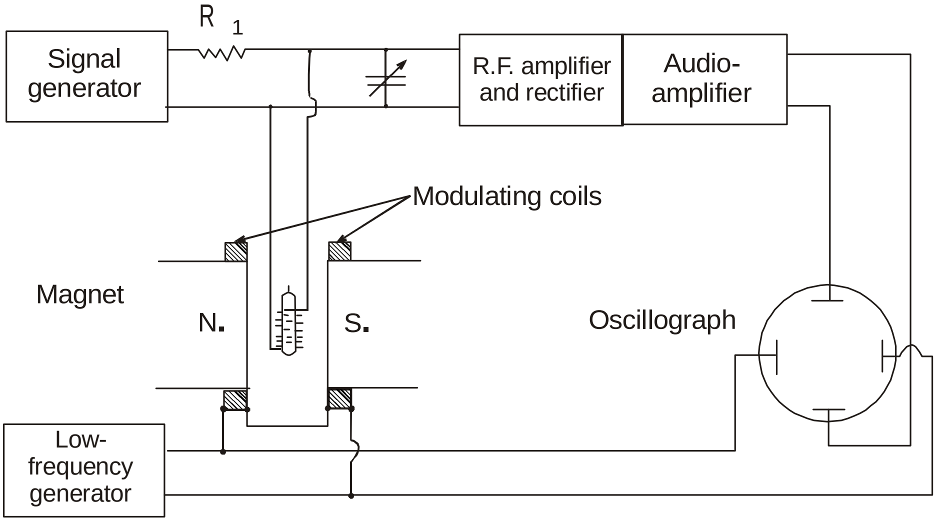


Fig. 10.2 : Schematic diagram of Rollin's arrangement for observing nuclear magnetic resonance

In order to detect the resonance of protons in water at room temperature, about $1cm^3$ of water is placed in a sealed glass as shown in fig. 10.2 and is put with in the coil of tuned circuit and held between the poles of a magnet supplying the steady field $\overline{B_0}$. Radio frequency current is supplied to the coil through a high impedence R_1 from a signal generator. Which thus acts effectively as constant current source. At resonance the rf power absorbed by proton causes a decrease in Q quality factor and in the parallel impedence circuit which in turn produces a drop in rf voltage across the circuit. This rf voltage is amplified and rectified. In order to display the resonance absorption clearly, it is common practice to modulate the steady magnetic field B_0 at a low frequency often about 25Hz with an amplitude of a few Oeresteds by means of auxilary magnet coils. When the mean value of the steady field is close to the resonant value, the field is swept twice through the resonanct each cycle producing an audio amplitude modulation of the radio frequency carrier. After recification the audio signal is further amplified and it is then displayed on a CRO, the time base of which runs in synchronism with the modulation. The oscilliograph trace then gives a visible indication of absorption line as shown in fig 10.3.

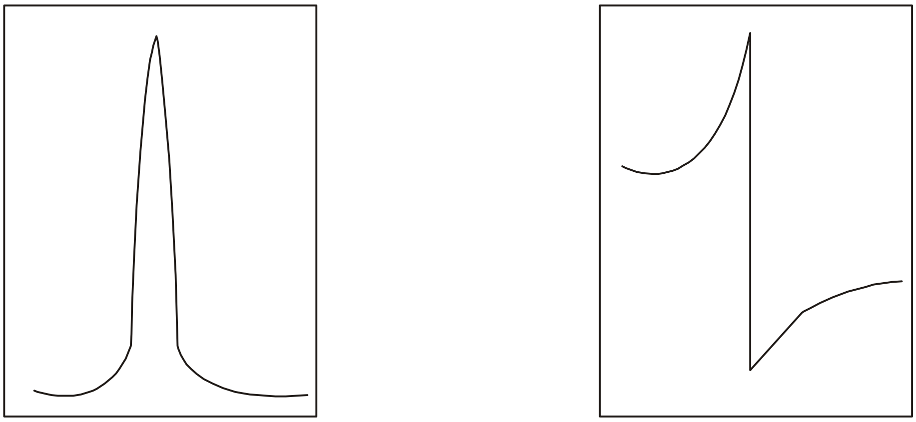
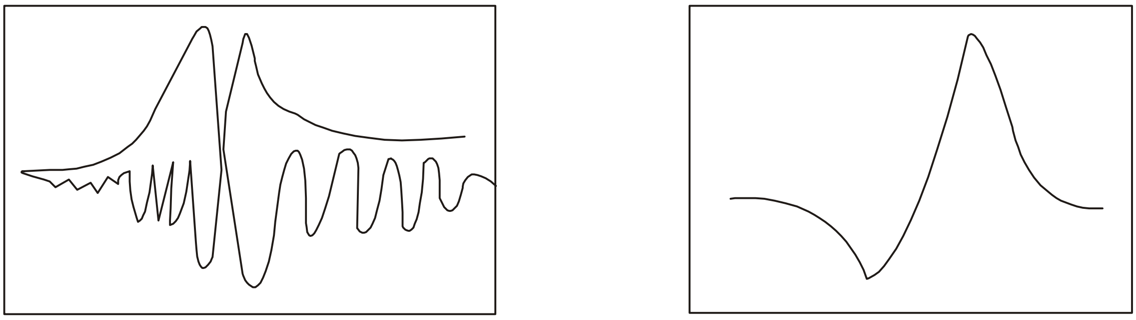


Fig : 10.3 **(a)** NMR absorption curve for protons in a solution of Ferric nitrate A CRO picture from early work of Bloemlergen Purcell and Pound (1948)

(b) NMR dispersion curve for the protons in a solution of ferric nitrate A CRO picture from the early working of Bloembergen purlell and pound (1948)



(c) An example of the transient effect (wiggles) observed in paraffin oil. The decaying oscillations always appear after passage through the resonance condition. Since the resonance condition is traversed from left to right and right to left once each per modulation cycle the oscillogram shows two super imposed sets of decaying oscillations.

(d) A mixed absorption and dispersion curve which results from the use of rf bridge which is not currently balanced.

It will be noticed that field be modulated while maintaining rf frequency constant is advantageous. Nevertheless, we could as well have the frequency modulated keeping the field constant. However, generally varying the magnetic field is simpler than to vary the frequency, since the latter entails a corresponding variation of the tuning of the rf amplifier. Moreover in the complicated circuits, there are many more frequency sensitive elements which would require simultaneous adjustments. If the oscilliograph trace is to give faithful reproduction of the variation of χ'' wtih magnetic field at fixed frequency two conditions are to be met.

1. Any residual inhomogenity in the magnetic field endows the absorption line with spurious breadth. Therefore steady magnetic field $\overline{B_0}$ should as homogeneous as possible throughout the volume of the sample.

2. The second condition for true reproduction of variation χ'' with field that condition shall approximate to those the steady-state absorption to which χ'' refers.

   The steady state conditions are approximated as follows

   (a) If the frequency is swept with fixed field, then on sweeping through resonance, the rate of cahnge of frequency υ must satisfy the requirement

   $$\frac{d\upsilon}{dt} << (\delta\,\upsilon)^2 \text{ --------------- } (10.31)$$

   where $\delta\upsilon$ is the line width expressed in frequency units.

   (b) If the steady field $\overline{B_0}$ is varied at fixed frequency then we should have

   $$\frac{d\,B_0}{dt} << |\gamma|\,(\delta\,B_0)^2 \text{ ---------------- } (10.32)$$

   where $\delta\,B_0$ is the line width expressed in field units which is related to $\delta\upsilon$ by

   $$2\pi\ \delta\upsilon = |\gamma|\delta\,B_0 \text{ -------------- } (10.33)$$

If (10.31) and (10.32) are not satisfied transient effects as shown in fig. 10.c would result, there fore the trace no longer represents the steady state absorptions curve. Rollin's circuit possesses the advantages of

(a) of simplicity (b) providing direct measure of χ'' while the bridge method gives a mixture of χ'' and χ' unless carefully adjusted.

Bridge Method : Possesses the advantage of

(a) more rf amplification before detection and thus a better noise factor may be obtained.

(b) Another advantage accrues from balancing out most the carrier voltage namely extraneous noise intoduced from the signal generator as a modulation of the carrier is balanced out to the same degree.

10.5 The Bridge Arrangement of Bloembergen, Purcell and Pound

In this fist successful NMR absorption experiment Purcell, Torrey and Pound (1946) used a bridge circuit the details of which have been given by Bloemberger (1948)

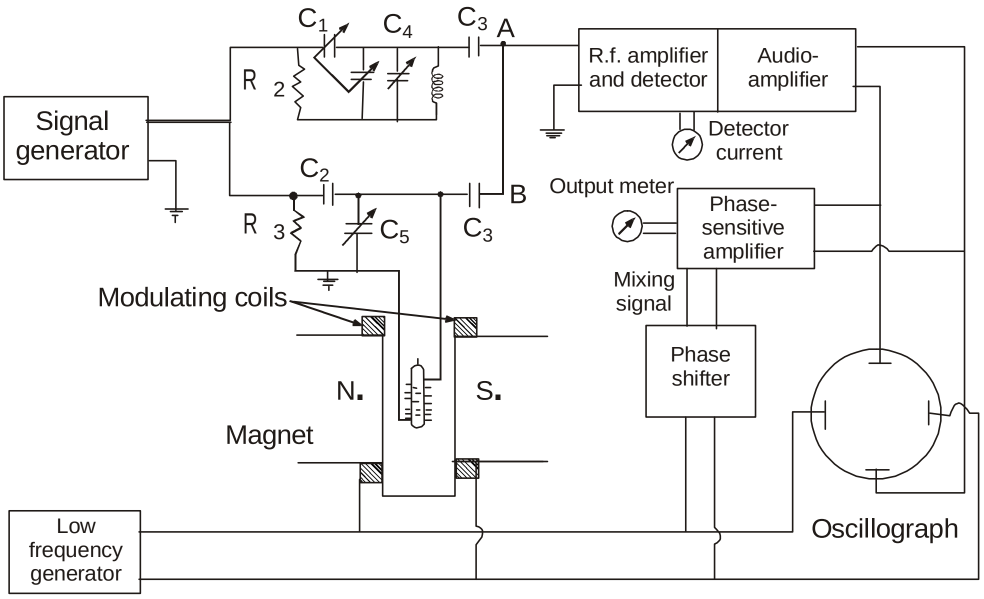


Fig. 10.4 : Schematic diagram of the apparatus of Bloembergen, Purcell and Pound (1948). In a typical arrangement for work at 30 Mc./s. the circuit components were : $R_2 = R_3$ = 50 ohms (the characteristic impedance of the coaxial cable used); $C_1 = C_6 = 5\text{pF}$, maximum; $C_2 = 3\text{pF}; C_4 = C_5 = 60\text{pF}.$ A typical coil consists of 12 turns r8 s.w.g. copper wire wound to give a coil 1.5 cm. long and 0.7 cm. inside diameter.

Two almost identical tuned circuits are fed in parallel with rf power through properly terminated cables and small coupling condensers C_1 and C_6. The coil of one circuit contains the material under investigations and is placed in between the poles of the magnet. By placing an additional electric half wave length of cable in one circuit at AB, the output of the two circuits may be subtracted at A and fed to an amplifier. If the two circuits were identical and if AB were an exact half wave length of loss free cable, the signal from the dummy circuit would exactly cancel that from the circuit containing the experimental material, when the nuclei are not at resonance. The half wave length of the cable could of course be placed in either arm of the bridge and could precede the tuned circuit instead of following it.

The small output coupling condensers C_3 are choosen to make the impedence seen when looking back from the amplifier approximately equal to the value for which the amplifier noise factor is best. The main part of the amplifier is often a communication receiver; a pre amplifier is then desirable to improve the noise factor at the particular frequency of operations. The bridge is balanced in phase and in amplitude by adjustment of the condenser C_4 and the coupling condenser C_1. The latter adjustment not only affects the amplitude balance but unfortunately also affects the phase balance since C_1 is effectively in parallel with the tuned circuit, the terminating resistance R_2 is small. The coupling condenser C_1 is therefore ganged in opposite sense with a similar condenser

C_6 so that total tuning capacity is unaltered during a change in coupling. In this the phase and amplitude controls are made almost orthogonal and the bridge may be balanced by a few successive adjustments. The purpose of the bridge is (i) to reduce the carrier level to a value low enough to permit considerable amplification before rectification and (ii) to cancel out most of the noise arising from spurious modulation of the output of the signal generator.

10.6 Nuclear Induction

The expermimental arrangmeents described upto now are termed as single arrangements. In the nuclear induction experiments, a combined transmiting and receiving methods have been employed. The received signal frequently produces only a very small amplitude modulation of the transmitted signal; the bridge and the oscillater methods were therefore devised to enhance this modulations. The double coil nuclear induction method devised by Bloch, Hansen and Packard (1946) and used in their independent discovery in ordinary matter of NMR phenomenon avoids the difficulty of single coil methods. The schematic diagram is shown in fig. 10.5.

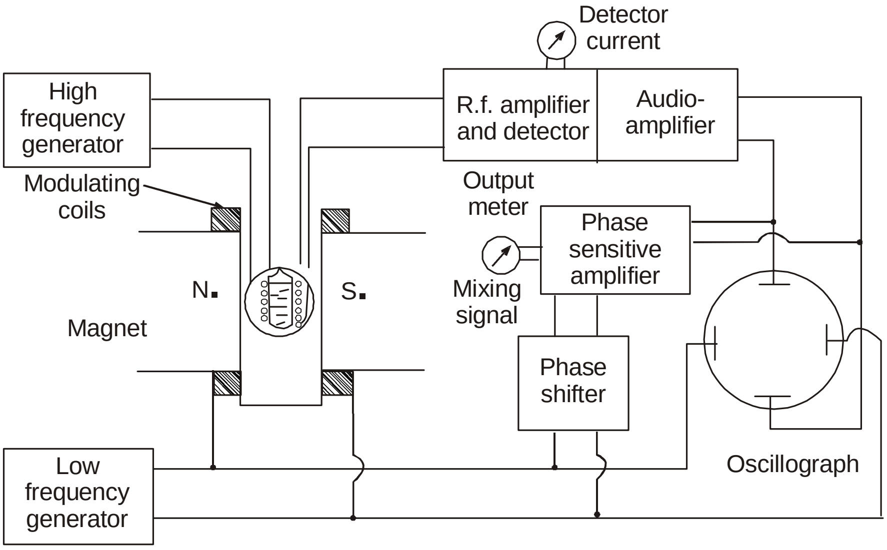


Fig. 10.5 : Schematic diagram of the apparatus for the nuclear induction method

The nuclear induction signal is received in the second coil places with its axis perpendicular to both the steady field and to the axis of the transmiter coil. Thus with a perfect geometric arrangement the only signal in the receive coil is induced by the precession of the resultant magnetic moment of the nuclei. This signal usually very small may be amplified considerably before rectification thus enabling a good noise factor to be obtained.

Thus the double coin specimen circuit achieves the same result by geometric means as do the bridge arragnements by electrical means. The specimen is placed within a receiving coil between the poles of a magnet. The transmitting coil with its axis in the third mutually perpendicular direction is supplied with current from a signal generator. The specimen is arranged to give as good a filling factor as possible for the receiving coil and the transmitting coil is wound outside it. The receiving coil is tuned by a parallel condenser and forms the input circuit of the first stage of a radio frequency amplifier. The signal may be fed after recification and audio amplification either to an oscillographs or if weak, to a phase sensitive amplifier and recording meter A low audio frequence source supplies current for modulation of the steady magnetic field and also provides a synchronus time base for the CRO display and a mixing signal for the phase sensitive amplifier. The essential diference between this arragnement and the bridge arrangmeent lies in the rf circuit.

It will be noticed that if receiver and transmitter coils are not perfectly orthogonal a signal is directly induced in the receiver coil from the transmitter. If the angular departure of the receiver coil from perfect setting is ε, the directly induced signal called the leakage is very roughly equal to a fraction $\sin\varepsilon \approxeq \varepsilon$ of the transmitted voltage. Nuclear induction voltage may be as low as a fraction of 10^{-5} of the transmitter voltage. If the leakage signal were to be made less than this it would be necessary for the angle ε to be one second of an arc. Fortunately, it is not necessary to attempt for such pefection.

The preessing resultant nuclear magnetic moment may be resolved into two parts : a dispersion part u proportional to χ' whose component along the axis of the transmitter coil in the phase with the radio frequency flux produced by that coil (primary flux) and an absorption part v proportional to χ'' whose component along the same axis is in quadrature with the primary flux X. On the other hand the leakage flux is a part of primary flux and there fore they have the same phase. The dispersion signal and the leakage signal are thus in quadrature and the former produces a phase modulation of the latter. On the other hand the absorption signal is in phase with the leakage signal and thus produces an amplitude modulations. The detecter which follows the rf amplifier responds only to the amplitude modulation and thus gives a measure of χ''. In order to control the leakage flux, Bloch, Hansen and Packard (1946) mounted a semicircular sheet of metal which they called a paddle at the end of the transmitter coil as shown in fig 10.6.

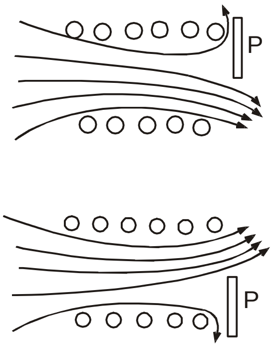


Fig. 10.6 : The steering effect of the paddle P on the lines of the radio frequency flux generated by the nuclear induction transmitter coil which is shown in sector

The paddle causes flux lines to deviate from an axially symmetrical disrtribution. By mounting the paddle in a spindle lying on the axis of the transmitter coil, the flux leakage with the receiver coil whose axis at right angles in the plane of the diagram may be varied continuously by rotating the paddle. The leakage flux may thus be reduced to any desired level. The condition of the balance is monitered by means of the detector current meter shown in fig. 10.5 in just the same way as with bridge circuits. One important piece of information with the nuclear induction method is it tells about the sign of nuclear magnetic moment which the single coil absorption methods do not yield.

10.7 Pulse Methods

The experimental arragnements desribed so far have been characterized by the continueous application to the nuclie of a rf magnetic field at or near Larmor frquency. Torrey (1949_ and Hahn (1950) have described expermiments in which the rf field is not applied continueously but in the form of pulses. Transient nuclear induction signals are obtained both during a pulse and after it. An examination of the transient behaviour enable experimental values of two relaxations times T_1 and T_2 to be derived. The apparatus used by both workers is shown schematically in fig 10.7.

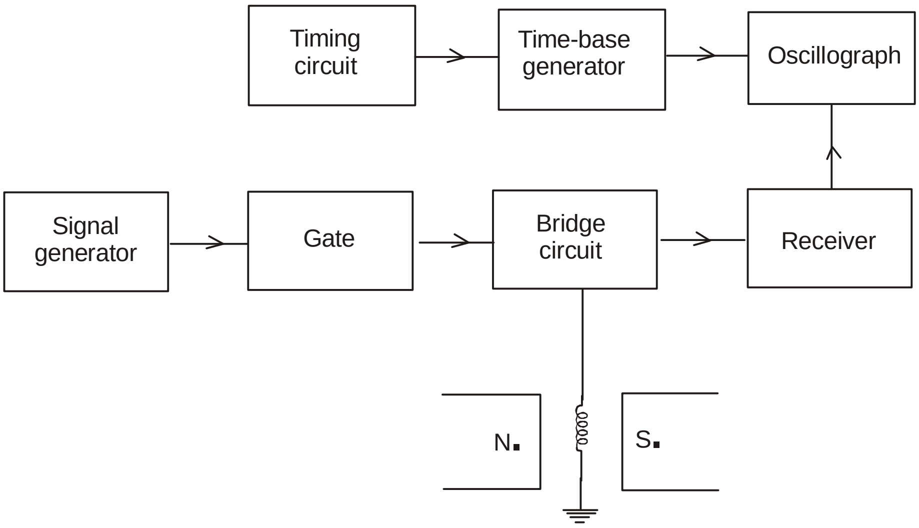


Fig. 10.7 : A schematic diagram of the apparatus for pulse methods

It is a straight forward modification for pulse working of the bridge methods described earlier. It will be noticed however, that it is not necessary to modulate that steady magnetic field. The radio frequency pulses may be obtained either by direct pulse modulation of the radio frequency oscillator or as indicated in fig 10.7 by gating the output of continueously oscillating generater. The latter method is preferred since then the frequency is then more stable. Moreover, if it is described to examine the phase of the transient signal after a pulse has been completed a source of coherent oscillations is still available for comparison purposes. It is of course necessary to take precautions to prevent any leakage of radio frequency power through the gate during the 'off' periods.

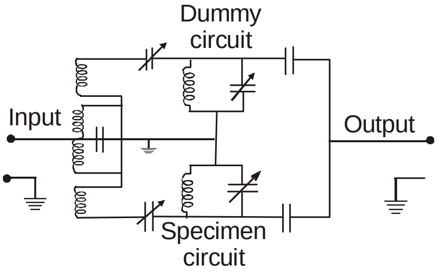


Fig. 10.8 : Radio frequency bridge circuit with the centre tapped transformer on the input side bridge (Torrey, 1949)

Torrey (1949), who was mainly interseted in the transient response while the pulse was being applied used the bridge circuit shown in fig. 10.8. Hahn (1950) on the other hand was more intersted in the response during the 'off' period after a pulse had ended. In the 'off' period the nuclear induction signal alone is present so that bridge circuit is not essential and the straight forward arrangement may be used. In fact for these experiments the single coil plays in turn the role of both the coils in double coil nuclear induction apparatus in the 'on' period the coil acts as transmitter and in the 'off' period it acts as receiver. Nevertheless when intense rf pulses are used a bridge is desirable to prevent undue over loading of the receiver in the 'on' period. Pulse methods have been mainly devised to study the transient effects and their sensitivity is equally cmpatable with the sensitivity of steady state methods.

10.8 Information from NMR, Measurement of Nuclear Properties and General Physical Applications

10.8.1 Determination of Nuclear Magnetic Moments

It was hsown for the nuclear magnetic resonance condition

$$h\upsilon_0 = \frac{\mu}{I} B_0 \text{ ---------------- (10.34)}$$

from this equation it is seen that one can determine the magnetic moment μ of a nucleus by measuring its magnetic resonance frequency υ_0 in known magnetic field B_0, provided of course that one knows nuclear spin number I and one had adequate value for Plank's Constant h. The measurement of nuclear magnetic moments has infact proved to be a most important application of the NMR phenomenon and the moments of more than seventy species of nuclei have been determined by this method.

10.8.2 Determination of the sign of nuclear moments

One special virtue of the nuclear induction technique is that it gives information concerning the sign of nuclear magnetic moment where as single coil methods do not. The sign determines the sense of precession of the nuclear magnetic moment in a magnetic field and hence also the phase of nuclear induction signal relative to the leakage signal. Strictly the method only compares the sign of the two nuclear magnetic moments finding whether they are like or unlike and ultimately relies on upon the knowledge that the sign of the proton moment is positive inorder to give actual sign.

10.8.3 Determination of Nuclear Spin number :

Before the advent of NMR methods, the spin numbers of the majority of the nuclie to which these methods could be applied had already been determined by other methods as for example from band spectra, from the hyperfine structure of line spectra and from atomic beam work.

Signal Strength Method : This method has been used more extensively than the others. Although it is frequently more convenient to find an unknown spin number by a comparison of the resonance signal strength with that of a nucleus of known spin number, a measurement may be made of the absolute signal strength and spin number is found using proper equations. For this purpose Pound includes a signal strength calibrator in his spectro graph circuit.

10.8.4 Determination of Nuclear Electric Quadrapole Moments : A nuclear spin number greater than $\frac{1}{2}$ possesses in general an electric quadrapole moment and that the interaction between two moment and its electric environment causes a displacement of the nuclear energy levels. The displacements of the energy levels are functions of the product of the electric quadrapole moment Q and the electric field gradient at the nucleus. From the measurements of this electric quadrapole splitting of the nuclear magnetic resonance spectrum for solid speciman the product of Q and the electric field gradient may be deduced. Absolute values of Q are there fore not obtainable and the method is limited in finding the ratio of the quadrapole moments of nuclei which are known to be subjected to the same electric environment.

10.8.5 Determination of the Proton Magnetic Moment in Absolute Units : Nuclear magnetic moments are usually measured in terms of the moment of the proton and may be converted into other units in which proton moment is known. The importance of these measurements is not limited merely to the conversion of nuclear magnetic moments into useful units. Their interrelation leads to more accurate values for some of the fundamental physical constants. Further more the measurement of proton moment in absolute units provides a practical basis for the alternate measurements of magnetic fields. The measurement of the proton moment is absolute units namely erg / oerested was carried out at the National Bureau of Standards in Washington by Thomas, Driscoll and Hipple (1949, 1950). Their main task was the accurate absolute measurement of a magnetic field B_0 in which proton resonance frequency ν_0 was determined. The resonance condition can be written as

$$\gamma = \frac{\mu}{I\hbar} = \frac{2\pi\,\nu_0}{B_0} \quad \text{------------ (10.35)}$$

the ratio of frequency to field thus yields a value for the gyro magnetic ratio γ. In order to convert this value into a value of magnetic moment μ, a value of Planck's constant has to be taken from other work. The spin number I is of course well known to be $\frac{1}{2}$ for the proton.

10.8.6 The Determination of Proton Magnetic Moment in Nuclear Magnetons : The material adopted for this determination consists in measuring in the same steady magnetic field B_0 both the proton magnetic resonance frequency υ_0 and also the frequency υ_c of orbital motion of the proton, some times called cyclotron resonance frequency. The latter frequency is well known to be

$$\upsilon_c = \frac{e\ B_0}{2\pi\ M_p\ c} \text{ ------------- } (10.36)$$

where 'e' is the charge of the proton in electro static units, M_p is mass of the proton, c is the velocity of light. For $I = \frac{1}{2}$ the proton magnetic resonance frequency is

$$\mathrm{v}_0 = \frac{2\mu_p\ B_0}{h} \text{ --------------- } (10.37)$$

where μ_p is the magnetic moment of the proton. By dividing equation (10.36) and (10.37)

$$\frac{\upsilon_0}{\upsilon_c} = \frac{\mu_p}{e\ \hbar/2M_p\ c} = \frac{\mu_P}{\mu_N} \text{ ------------ } (10.38)$$

and we see that the ratio of the two frequencies is a direct measure of the proton magnetic moment in terms of nuclear magneton μN.

10.8.7 Determination of the Proton Magnetic Moment in Bohr Magnetons : For this determination, measurements were made in the same steady magnetic field B_0 both for the proton magnetic rsonance frequency υ_0 and also cyclotron frequency υ_e, of the orbital motion of the electron.

The latter frequency is given by

$$\upsilon_e = \frac{e\ B_0}{2\pi\ M_e\ c} \text{ ------ } (10.39)$$

By dividing equations (10.37) and (10.39), we get

$$\frac{\upsilon_0}{\upsilon_e} = \frac{\mu_P}{e\hbar/2M_e c} = \frac{\mu_P}{\beta} \text{ ------------- } (10.40)$$

where β is the Bohr magneton. The ratio of two frequencies is thus a direct measurement of the proton magnetic moment in Bohr magnetons.

10.8.8 Impact on the Evaluation of the Fundamental Atomic Constants : First we notice that the experminets give $\frac{\mu_P}{\mu N}$ and $\frac{\mu_P}{\beta}$ from (10.38) and (10.40) thus

$$\left[\frac{\mu_P}{\mu N}\bigg/\frac{\mu_P}{\beta}\right] = \left(\frac{\beta}{\mu N}\right) = \left[\frac{e\hbar}{2M_e c}\bigg/\frac{e\hbar}{2M_p c}\right] = \frac{M_p}{M_e} \text{ -------- } (10.41)$$

Secondly we may combine the absolute measurement of the gyro magnetve ratio γ_p of the protons with μ_p/β from (10.40).

$$\frac{\gamma_p}{\mu_P/\beta} = \left(\frac{2\mu_P}{\hbar}\right)\left(\frac{e\hbar}{2\mu_p M_e c}\right) = \frac{e}{M_e c} \text{ -------------- } (10.42)$$

Since the electronic charge e is in electrostatic units thus gives the ratio e_{emu}/M_e , of the charge of the electron in electromagnetic units to its mass.

Similarly we may combine the value of γ_p with $\mu_p/\mu N$ to obtain the ratio of charge to mass for the proton

$$\frac{\gamma_p}{\left(\mu_P/\mu N\right)} = \left(\frac{2\mu_P}{\hbar}\right)\left(\frac{e\hbar}{2\mu_P M_p c}\right) = \frac{e}{M_p c} = \frac{e_{emu}}{M_p} \text{ ------------ } (10.43)$$

This value when multiplied by the accurately known value of the isotopic weight of the proton gives the value for Faraday. This value and also the values of $\left(M_p/M_e\right)$, e_{emu}/M_e , e_{emu}/M_p are obtained with an accuracy of about 30 parts per million.

10.8.8 Applications of Nuclear Magnetic Resonance : The pioneer experiments discussed have opened up a rich field of research and more then several hundreds of publications have taken place all these years. The most obvious application is to the determination of nuclear properties. From the resonance condition one may obtain wtih considerable accuracy, values of the nuclear gyromagnetic ratio for any stable nucleus of reasonable abundance. The nuclear spin number can be found if it is not known and hence the nuclear magnetic moment is obtained. The sign of the nuclear moment is also obtainable. Nuclie with spin number $I \geq 1$ have an electric quadrapole moment relative values of which may be determined from the fine structure of the nuclear magnetic resonance spectrum.

Once a nuclear gyromagnetic ratio is known it may be used for the calibration of magnetic fields and for related problems with magnets. The great prcision of measurement of the nuclear magnetic resonance frequency in a given magnetic field has led to the accurate determination of certain important physical quantities which in turn have necessiated a revaluation of the fundamental physical quantities. Which in turn have necessiated a revaluation of the fundamental physical constants. The nuclear magnetic resonance condition has been found in matter in all its forms : Liquids and gases ionic and molecular solids. In each case and particularly for the solid state valuable informatin has been obtained concerning the structure and other non nuclear properties of the material.

Nuclear magnetic resonance imaging (NMRI) is a new diagnostic technique which has revolutionized medical imaging and biomedical research. They are only very few restrictions for NMRI since it is considered risk free for all patients.

10.9 Summary

1. Classically or quantum mechanically Bloch equations tell about the growth and decay of Magnetization values M_x, M_y, M_z, which in turn involve T_1, T_2 and their measurements by pulse methods.
2. The steady state solutions of Bloch equations reveal nuclear magnetic susceptibilities χ'' and χ' namely absorption mode, dispersion mode and their shapes also.
3. NMR spectrometer used by early workers for the detected NMR signal using single coil (absorption) and double coil or crossed coil (Nuclear induction) have been elaborately explained to know about nuclear properties of several varieties etc.
4. Several applications of NMR have been highlighted including the latest NMR imaging technique for the diagnosis of any type of defect in the human body.

10.10 Key Words

Block equations, steady state solutions for low B_1, Relaxation times T_1, T_2, nuclear susceptibilities χ' and χ'' Rollin's NMR spectrometer Bridge technique, Nuclear Induction Technique, Pulse methods, Nuclear properties.

10.11 Review Questions

1. What are Bloch eqations, obtain solution for Bloch equations for the steady state conditions (low value of B_1).
2. Describe NMR spectrometers absorption type and highlight the NMR signal detections with the apparatus.
3. Describe NMR spectrometer using induction technique and show the merits and demerits of this induction technique.
4. Mention briefly about NMR pulse methods through a schematic diagram ? What type of information can be obtained from NMR phenomena, high light NMR applications.

10.12 Text and Reference Books

1. Nuclear Magnetic Resonance by E R Andrew Cambridge University Press
2. Molecular Structure and Spectroscopy by G. Aruldhas (PHI)
3. Spectroscopy by B.P. Straughen and Walker
4. Fundamentals of Molecular Spectroscopy by C.B. Banwell

Unit - III

Lesson - 11

ESR PRINCIPLE AND SPECTROMETER

Aim : To know the principle of ESR, ESR spectrometer, characteristics of A and g values, unpaired electron fine structure and hyperfine structure.

Objectives of the lesson :

1. To know the ESR principle and using simple ESR spectrometer, to know the phenomenon.
2. Using ESR spectrometer and to know the function of various parts of the spectrometer.
3. To know the characteristics of g and A values.
4. To know about the fine structure and Hyperfine structure of the unpaired electrons.

Structure of the lesson :

11.1 Introduction

Electron Spin Resonance (ESR) is a spectroscopic technique confined to the study of those species having one or more unpaired electrons. The method takes advantage of the spin of the electron and its magnetic moment to reveal a wealth of information. It has been possible in many cases, for example, to obtain detailed information on the unpaired electron (spin) density distribution. Obviously the necessity for at least one unpaired electron limits the number of applications of the technique. This technique has been applied to the study, of a large range of paramagnetic systems among the most important of which have been free radicals, triplet states and transition metal ions.

11.2 The ESR Experiment

The origin of ESR spectroscopy lies in the spin of the electrons and its associated magnetic moment and the technique is best introduced by considering the alignment of magnetic dipoles in the presence of an applied magnetic field. It should be noted that magnetic dipoles associated with electrons may arise from both spin and orbital angular momenta (or a combination of the two). Orbital angular momentum has its origin in the rotation of an electron about its own axis. In the majority of cases of immediate interest the magnetic dipole arises from spin angular momentum only, but cases where there is coupling between the two angular momenta will also be considered.

The energy E of a magnetic dipole moment μ in the presence of magnetic induction is given by

$$E = -\overline{\mu} \cdot \overline{B} \text{ --------------------- (11.1)}$$

From the point of view of classical mechanics any orientation of the magnetic dipole with respect to the magnetic field would be possible. One orientation that in which that the magnetic dipole is aligned parallel to the field corresponds to $E_{\min}$ and one orientation that in which the magnetic dipole is aligned anti-parallel to the field corresponds to $E_{\max}$. If the energy of interaction is large compared to kT, the alignment of the great majority of dipoles would correspond to $E_{\min}$. However, as electrons obey quantum and not classical merchanics only two orientations of electron magnetic moment are allowed and in addition, the energy of interaction in the ESR experiment is considerably smaller than kT. The spin and charge of the electron confer upon it a magnetic moment μ, the component of which along the direction of an applied magnetic induction is

$$\mu_z = -\text{ g } \mu_B M_S \text{ ------------- (11.2)}$$

where g is dimension less proportionality constant referred to as the g factor or spectroscopic splitting factor, μ_B is Bohr magneton $\left(= eh/4\pi m_e\right)$, where e and m_e are the charge and mass of the electron respectively and h is Plank's constant and M_S electron spin quantum number A combination of equations (4.1) and (4.2) gives $E = g\ \mu_B\ B M_S$, the electron spin quantum has two allowed states $+\frac{1}{2}$ and $-\frac{1}{2}$ and consequently the two energy states are

$$E_1 = +\frac{1}{2} g\ \mu_B\ B$$

and $$E_2 = -\frac{1}{2} g\ \mu_B\ B$$

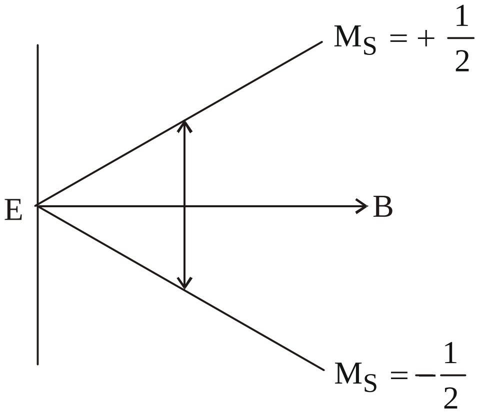


Fig. 11.1 Energy levels for a single unpaired electron as a function of magnetic field strength

The energy difference between the two staes as shown in Fig. 11.1 is $g\,\mu_B\,B$ and the application of electromagnetic radiation of a suitable frequency υ will induce transitions between the two states when the energy of radiation is equal to ΔE i.e.

when $h\upsilon = g\ \mu_B\ B$ -------------- (11.3).

It is the transition between two energy states which is studied by ESR.

Before discussing this important relationship in more detail it is useful to consider the nature of electro magnetic radiation. Electromagnetic radiation can be regarded as coupled electric and magnetic fields, oscillating perpendicular both to the direction of propagation and to each other. It is the magnetic compnent of this electro magnetic radiation which interacts with the magnetic dipole associated with the unpaired electron. Consequently transitions between the energy levels in Fig. 11.1 occur when the application of the electromagnetic radiation results in a reorientation of the electron magnetic moment. If the electro magnetic radiation is applied such that the oscillating magnetic field is parallel to the applied magnetic induction field $\left(\overline{B}\right)$ an oscillation of energy levels occurs but no reorientation of the electron magnetic moment. If follows that if the ESR absorption is to be observed, the oscillating magnetic field must be applied perpendicular to the applied magnetic field. The successful observation of the ESR spectrum requires suitable value for the frequency (υ) and the magnetic induction field (B) to satisfy the condition given in equation (11.3).

The choice of the frequency is governed by the magnitude of the magnetic field which itself is determined by instrumental and theoritical considerations.

The proportionality constant g in equation (11.3) has a value of 2.0023 for the free electron. Since magnetic fields in the range 0 - 1.2T are used in many commercial spectrometers a frequency in the microwave region is required. Magnetic fields of 0.35T are often selected for comercial spectrometers with a corresponding frequency requirement of ~ 9.5 GHz such spectrometers are reffered to as X-band spectrometers. Some commercial spectrometers (Q band) operate at higher magnetic field (1.25 T) with a corresponding higher microwave frequency 35GHz.

11.3 THERMAL EQUILIBRIUM AND RELAXATION

It is instructive at this stage to consider why a magnetic induction of ~0.35 T is commonly selected. The condition for ESR absorption would be equally well satisfied by a magnetic induction of (say) 1T and a frequency of 28GHz. The smaller magnetic induction would certainly be more convenient from some points of view. In order to appreciate the reason for this choice it is necessary to consider the difference between the populations of the two energy states which exists at thermal equilibrium. If the number of spins occupying the upper and lower energy states are n_1 and n_2 respectively then $\frac{n_1}{n_2} = e^{-\Delta E/kT}$, where k is Boltzmann constant and T is absolute temperature. Substitution of $g\mu_B B$ for ΔE in this expression reveals that the population difference between the two states is extremely small for a sample having the free electron g factor. Even with an applied field of 0.35T, the population of difference is only about 0.0014 for thermal equilibrium at room temperature and it follows that the magnetic induction in this order of magnitude are required if the sensitivity of the technique is to be reasonable.

A further complication appears to be present when an oscillating field is applied and transitions are stimulated between the two energy states. The rate of change in upper level is given by

$$\frac{d\,n_1}{dt} = -\,p_1 n_1 + p_2 n_2$$

wher p_1 is the transition probability of a transition from the upper to the lower level and p_2 is the reverse transition probability. Under conditions of stimulated transitions $p_1 = p_2 = p$. Where

p is the stimulated transition probability and

$\frac{dn_1}{dt} = p(n_2 - n_1) = pn,$ where n is the population difference $(n_2 - n_1)$.

Now if a total of N spins are present $N = n_1 + n_2$ and therefore

$2n_1 = N - n$ and

$\frac{dn_1}{dt} = -\frac{1}{2}\frac{dn}{dt},$ By substitution, therefore

$\frac{dn}{dt} = -2pn$ and

$n_t = n_0 e^{-2pt}$, where n_t is the population difference at time t and n_0 is the initial population difference at $t = 0$. According to this relationship, therefore the population difference between the two states decreases with time. By analogy with the above arguments, the rate at which energy is absorbed by the sample is given by

$$\frac{dE}{dt} = -n_1 p_1 (\Delta E) + n_2 p_2 \Delta E = p \Delta E n$$

It follows that if the population difference n is decreasing with time, the magnitude of the electromagnetic energy absorbed by the sample must also decrease with ultimately to zero.

Fortunately the intensity of an ESR spectrometer is normally independent of time and consequently there must be some process operating which maintains a population difference. That is there must be some mechanism operating which allows the spins occupying the upper level to lose energy and return to the lower level other than by means of radiative transitions. The non radiative process occurring is the transfer of energy from the spin system to the other degrees of freedom with in the environment (the lattice) and is termed relaxation.

It is useful to refer to the time scale for such process as the spin-lattice relaxation time. A short relaxation time (i.e. rapid loss of energy to the lattice) allows the population difference to be maintained at relatively high temperatures. However if the relaxation time is long the population difference may not be maintained leading to the condition referred to as saturation.

11.4 Experimental Methods

The condition to be satisfied to observe ESR absorption is

$$h\upsilon = g\mu_B B$$

There are therefore two quite distinct ways in which a spectrometer could be designed in order to observe the ESR aborption. The frequence (υ) could be varied at a fixed dc magnetic induction (B), alternately, the magnetic induction could be varied at a fixed frequency. However in the microwave region of the spectrum there are a number of experimental difficulties involved in the former approach.

Consequently ESR spectrometers operate with a fixed frequency (of ~ 9GHz) and a magnetic induction, which can be varied linearly over the range 0.35 $\pm$ (say) 0.30T.

Two further factors suppot the choice of 9GHz as a suitable frequency. First this frequency corresponds to a sample cavity with reasonable large dimensions (approx 2 cm x 1 cm x 4 cm) allowing a convenient sample size higher frequencies necessitate a smaller sample cavity with consequent restrictions on sample size. Secondly at higher frequencies larger magnetic inductions are required with an increasing risk that the magnetic induction experienced by sample may not be homogeneous to the required degree. A broadening of the absorption curve would result.

11.4.1 A simple ESR Spectrometer : It is now possible to summarize a few basic requirements necessary to construct an X band ESR spectrometer and to observe an ESR spectrum.

(a) a suitable electro magnet capable of supplying a homogeneous magnetic induction which can be varied linearly around 0 : 35T.

(b) a source of microwave radiation in the region of 9GHz.

(c) a suitable sample cavity.

(d) a crystal detector to measure variations in microwave power.

(e) a suitable recorder to display the output signal from the detector.

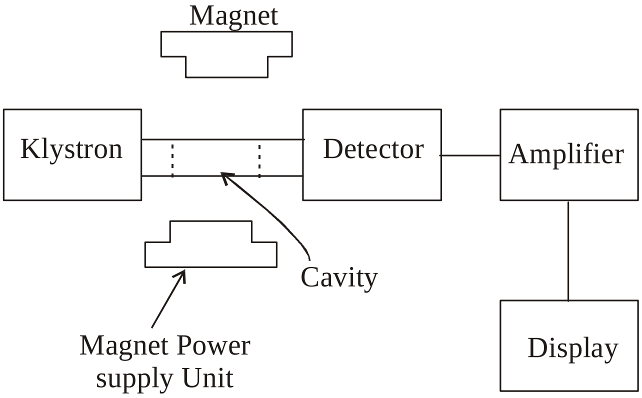


Fig. 11.2 Block diagram of a simple ESR spectrometer

On the basis a simple spectrometer such as illustrated in the block diagram in Fig. 11.2 could be constructed. A suitable source of electro magnetic radiation is a Klystron oscillator which produces mono chromatic radiation of the required frequency. (Fine adjustment of the frequency is achieved by variations of the d.c. voltage applied to one of the Klystron electrodes known as the reflecter).

Typically the Klystron is required to give approximately 30 mw of power, attenuation of wich allows a power as low as 0.25 mw to be used.

The monochromatic output from the Klystron is transmitted to the sample cavity by means of a wave guide consisting of a length of gold plated brass tubing rectangular in cross section with internal dimenssions appropriate to the Klystron frequency (2.29 × 1.02 cm) for X - band spectrometer. The 'transmission' type of sample cavity consists of a section of blanked off wave guide with two small holes in the end walls through which the microwave power is transmitted. The distance between the end walls is carefully choosen so as to concentrate the micro wave power with in the cavity by means of multiple reflections off the end waals. The cavity is situated between the poles of the electromagnet such that the sample is at the centre of the applied magnetic induction. The sample itself is usually contained in a thin walled quartz tube, free of paramagnetic impurities. The outside diameter of the tubing varies from X - band to Q band; in the former an outside diameter of between 4 and 5 mm would be fairly typical. The microwave power transmitted through the cavity is then detected (a semi conducting crystal detector is usually used for this purpose) amplified and fed to a suitable recorder.

The out put from a spectrometer such as that described would be in the form of a decrease in detector current at that magnetic induction where the absorption condition given in equation (11.3) is satisfied (Fig. 11.3).

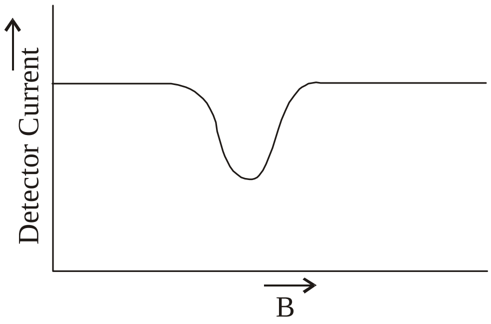


Fig. 11.3 Variation of detector current with magnetic induction obtained using a transmitter cavity

However the spectrometer would suffer from a number of disadvantages, perhaps the most serious of which is that its performance would be limited by the 'noise' associated with a crystal detector operating at high currents. This difficulty could be overcome by reducing the power reaching the crystal detector but this would not be compatible with a transmission cavity. However it is possible to reduce the power reaching the crystal detecter, while still maintaining a high microwave power in the sample cavity, if a microwave bridge is employed in conjunction with a reflection cavity.

11.4.2 The 'Reflection' Cavity and Microwave Bridge : The 'reflection' cavity is usually constructed from a section of the wave guide with a length corresponding to two wave lengths (approx 4.5 cm for X - band spectrometer) with a single aperture at the junction between the cavity and the wave guide. The internal dimensions of the cavity are such that multiple reflections of the microwave radiation from the end walls create a stationary wave as that shown in Fig. 11.4.

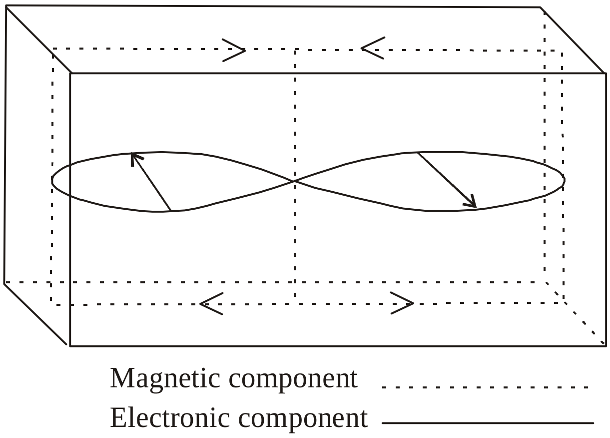


Fig. 11.4 A reflection cavity showing the microwave magnetic and electric field pattern

It will be noted that the position corresponding to the maximum intensity of the oscillating magnetic field lies on plane running through the centre of cavity and this is therefore the correct position to locate the sample tube. It should also be noted that this position corresponds to the node in the oscillating electric field. Interaction between the oscillating electric field and solvents are therefore at a minimum at this position. However, for solvents with a high dielectric constant a flat quartz sample tube of small path length (~ 1 mm) may be used. This design of the 'reflection' cavity is by no means unique. For example cylindrical cavities have found application particularly in the study of gaseous samples. A schematic reproduction of a microwave bridge used in conjunction the 'reflection' cavity is shown in Fig. 11.5 and incorporates a device known as a magic - T. At the magic T microwave power is prevented from passing directly from Klystorn to the crystal detector. Instead the power is equally divided between two arms, one leading to the sample cavity and the other to the 'matched load'. The impedence of the load can be varied so as to balance exactly that of the cavity so that no power reaches the detector. However when the applied magnetic field is such that equation (11.3) is satisfied the sample absorbs some of the microwave power so unbalancing the microwave bridge and allowing power to reach detector. This procedure has the advantage that the conditions can be selected such that the power reaching crystal detector does so at its minimum noise level. This is achieved by permanently offsetting the load on the microwave bridge to achieve the optimum conditions. The output would now have the form shown in Fig. 11.6(a).

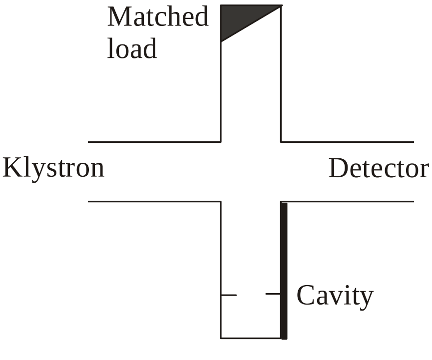


Fig. 11.5 A Magic T microware bridge.

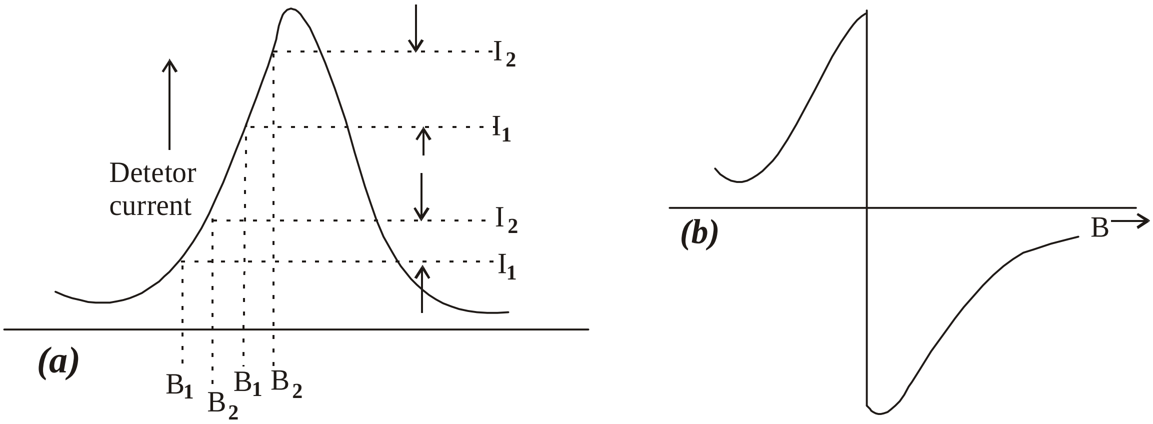


Fig. 11.6 The output obtained from an ESR spectrometer when employing
(a) a reflection cavity
(b) when also employing magnetic field modulation.

The effect of applying 100 kHz magnetic field modulation of small amplitude is illustrated in (a) where magnetic field modulation varying between B_1 and B_2 produces an output signal varying between I_1 and I_2.

11.4.3 Magnetic Field Modulation : Such a spectrometer would have a good signal to noise ratio but sensitivity and resolution would still be rather poor. This final problem is over come by modulation of the d.c. magnetic induction. In practice the most common modulation frequency selected for this purpose is 100 kHz and it is applied by means of small coils mounted with in the walls of the sample cavity. The efect of magnetic induction modulation is perhaps best understood through a discussion of features in fig. 11.6.

Consider the dc magnetic induction sweep to be moving steadily through the absorption and the amplitude of the 100 khz magnetic induction modulation to be relatively small; it is clear that the microwave power reaching the crystal detector is also modulated at the same frequency but that the amplitude of this latter modulation (the output signal) varies with the position of magnetic field sweep. A phase sensitive detector is now employed which compares the output signal from the microwave bridge with a reference signal of the same frequency (100 kHz) and is sensitive to both amplitude and phase of the output signal. As the dc magnetic field is swept linearly through the absorption, the detecter output a sine wave the amplitude of which starting from zero, and then with a 180^0 change in phase increases to a maximum again before returning finally to zero. The output from the detector is amplified rectified and then integrated to give a dc output to the recorder equal intensity to the amplitude of the modulated output signal. The final output to the recorder is proportional to the slope of the absorption curve and can be regarded as its derivative.

11.5 The ESR Spectrum

11.5.1 : Characteristics of the g factor

(1) The equation $h\upsilon = g\,\mu_B\,B$ ---------------- (11.3)

For an electron of spin $S=\frac{1}{2}$, the spin angular momentum quantum number can have values of $m_S = \pm\frac{1}{2}$ which in the absence of magnetic field leads to a doubly degenerate spin state. When the magnetic field is applied, the degneracy is lifted. In the above equation (11.3) where all other symbols have usual meanings and g is spectroscopic splitting factor, truely g is a tensor. For a free electron g has a value of 2.00 and precisely 2.0023 due to quantum electro dynamics correction. The value of g will be independent of magnetic field only in the isotropic systems such as organic radicals in low viscosity solutions. In many free radicals the g value of the odd electron system is close to that of a free electron value but in metal ion g values are greatly different from free electron value. In a large number of other systems the g factor is anisotropic, varying markedly with the oreintation of the sample. g factor for systems where the magnetic moment arises from spin angular momentum only will be 2, but for a system where the magnetic moment arises from orbital angular momentum only g will be 1.

(2) When there is an appreciable spin - orbit coupling in a molecule or ion which gives the splitting of the ground state that is large compared to kT there will be appreciable contribution to moment from the coupling. This situation prevails for atoms in the gas phase and most of the rare earth ions. The moment expected when spin orbit coupling is present is given by the

$$\mu_{S,O} = g\sqrt{J(J+1)}\;BM \text{ ----------- (11.4) (BM for Bohr Magneton)}$$

Recalling that J is the total angular momentum of the ground state and according to LS coupling given by $|L+S|,\ |L+S-1|,\ldots\ldots.|(L-S)|$. If the shell is less than half filled with electrons, the ground state is $|L-S|$ and if it is more than half filled it is $|L+S|$ and the g factor is given by

$$g = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \text{ ------------- (11.5)}$$

In the above equation for a free electron $S=\frac{1}{2}$, $L=0$, $J=\frac{1}{2}$ and the value of $g=2.00$ is easily calculated. Also halogen atoms have the same ground state term ${}^2P_{\frac{3}{2}}$, $L=1$, $S=\frac{1}{2}$, $J=\frac{3}{2}$ and this yields $g=\frac{4}{3}$ identical with the experimental value.

(3) No such agreement is found when unpaired electron is placed in a chemical environment either in a free radical or a transition metal ion complex crystal lattice. In such a chemical environment the orbital motion of the electrons is quenched, Jahn Teller distortion also serves to remove orbital degeneracy. On the other hand a certain amount of orbital motion generally is sustained as a result of spin orbit coupling. Consequently because of quenching and sustaining competetion, results giving rise to g vaues different from the value of 2.0023.

Only when there are significant deviations from the free electron value one can gain some useful information about the nature of excited states.

(4) The situation in transition metal ions is more complicated and interesting. The properties of transition metal are determined by the relative magnitudes of the crystal field and spin-orbit coupling. These two interactions have opposite effects and we can distinguish theree cases.

(a) The effect of spin orbit coupling is much larger than that of the crystal field. The rare earth ions fall in this class because the f electros are well sheilded from the crystal field effects so that LS coupling is not distrubed and J is a good quantum number; thus the rare earth ions are very much like free ions.

(b) The effect of crystal field is strong enough to break the coupling between L and S and hence J is no longer a good quantum number. The splitting of m_L levels is large. i.e. (the orbital dengeneracy is quenched) and the EPR transitions are described by the selection rule $\Delta ms = \pm 1$. The first row of the transition metal ions falls into this category. The magnetic moments cannot be calculated by equation (11.4) but correspond to more nearly to the "spin only" value where $g = 2$.

(c) In the strong field case the effect of crystal field is very large so that LS coupling is broken down completely. This corresponds to covalent bonding and is applicable to the complexes of the 4d, 5d transition metals and to the strong complexes of 3d transition metals such as cyanide. In many of these cases a molecular orbital description gives better results than the crystal field approximation.

(5) The magnitude of the g tensor gives considerable information about the ground and excited states in complexes. In general the magnitudes of g depends upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field. If the paramagnetic radical ion is located in a perfectly cubic crystal lattice (eg. octahedral or tetrahedral) the g value is independent of the orientation of the crystal and the g is said to be isotropic.

In a crystal site of lower symmetry, g value depends upon the orientation of the crystal and thus g is anisotropic. The Z direction is defined coincident with the highest fold rotation axis which can be determined by X ray methods. The g_z is equivalent to g_{11}, the value obtained when Z axis is parallel to the external magnetic induction. The g values along x

and y axis are g_x and g_y which in a tetragonal site are equal and referred to as $g_\perp$, the value obtained with external magnetic field perpendicular to Z axis. If θ is the angle between the magnetic field and the Z axis, the experminetal g value is given by the following equation for a system with axial symmetry.

$$g^2 = g_{11}^2 \cos^2\theta + g_\perp^2 \sin^2\theta \text{ -------------- (11.6)}$$

(6) Information from g tensor : The g tensor is a sensitive parameter and can give exact idea of the local symmetry of the paramagnetic ion. Often in the crystals if the paramagnetic ion occupies a substitutional site, then depending on whether charge compensensation is needed or not, it is possible to predict the orientation of the tensor from an ideal of the geometry of the environment.

Also in single crystals the number of geometrically inequivalent sites, whether the paramagnetic (ion) system occupies a lattice site or vacancy, depends mainly on the space group of the crystal. Thus the radical F_3^{2-} produced in $KASF_6$ by irradiation occupies 3 magnetically distinct sites related to each other by 120^0 rotation about the unique axis of the Hexagonal unit cell $KASF_6$.

(7) In cases where the paramagnetic impurity doped into a dia magnetically host lattice, the number of magnetically distinct sites as well as the magnitudes of the principal values of the g tensor depend strongly (a) the position of single or multiple charge compensating vacancies and (b) the distance between charge compensating valancies and the paramagnetic impurities.

Thus Cu(II) doped in K_2SO_4, it has been shown that there are as many as eight magnetically distinct sites as predicted from crystal structure, the g factor and g tensor dispositions quantitatively related to the various Cu-K valancy configurations.

Therefore a careful analysis of the g tensor apart from revealing the nature of electronic ground state of the paramagnetic system under observation, also throws considerable light in the understanding of charge compensation mechanism in the solid state.

(8) Since g tensors are highly sensitive to the geometry of the lattice, phase transitions in solids could be very accurately monitered using the EPR spectra as the probe. This has been especially true when high spin ions are introduced into the host lattices where the minute changes in the lattice parameters have a telling effect on the nature of EPR spectra.

11.6 Fine Structure :

It may be of interest to consider briefly all the interaction to which unpaired electron in a transition metal ion are subjected as well as their approximate magnitudes for first row transition metal complexes.

$$W = W_F + V + W_{LS} + W_{SS} + \beta B(L+2S) + W_N - \gamma \mu_N \bar{B} \bar{I} \text{ ----------------- (11.7)}$$

W is the energy of the ion in a complex.

W_F : includes the energy in the free ion in the gaseous state $\left(\sim 10^5\, cm^{-1}\right)$

V : is the electrostatic energy due to crystal field and also known as zero field splitting or fine structure splitting $\left(10^3 \text{ to } 10^4\, cm^{-1}\right)$.

W_{LS} : it refers to the energy associated with spin orbit coupling $\left(\sim 10^2\, cm^{-1}\right)$

W_{SS} : it is the magnetic interaction between electron spins $\left(\sim 1\, cm^{-1}\right)$

$\beta B(L+2S)$ is the effect of external magnetic field $\left(1 cm^{-1}\right)$.

W_N : It is the interaction of nuclear moment if $I \neq 0$ with the electron spin under going the transition $\left(\sim 10^{-2}\, cm^{-1}\right)$ and this is the hyperfine splitting.

$\gamma \cdot \beta_N \cdot \bar{B} \cdot \bar{I}$: is the effect of magnetic field on the nuclear magnetic moment $\left(\sim 10^{-3}\, cm^{-1}\right)$.

11.6.1 : Zero-Field Splitting and Kramer's Degeneracy :

When a metal ion is placed in a crystalline field, the degeneracy of the d orbitals will be resolved by the electro static interaction (V in equation (11.7)). The spin degeneracy will remain until a magnetic field is applied. When the species contains more than one unpaired electron, the spin degeneracy can also be resolved by the crystal field. Thus the spin levels may be split even in the absense of a magnetic field. This phenomenon is called zero field splitting. However when the species contains an odd number of unpaired electrons, the spin degeneracy of every level remains doubly degenerate and this is known as Kramer's degeneracy. For an even number of unpaired electrons the spin degeneracy may be removed entirely by the crystal field. These concepts and consequences of zero field splitting will be illustrated with a few examples.

Consider case of a molecule or ion with two unpaired electrons i.e. $S=1$ and $ms=-1,\ 0,\ +1$ (The total spin quantum number S is the sum of the spin quantum numbers of each of unpaired electrons). In the absense of the zero field splitting two possible transitions $0 \rightarrow +1$ and $-1 \rightarrow 0$

$(\Delta ms = \pm 1)$ are degenerate and only one signal is observed in the EPR spectrum in fig. 11.7(a).

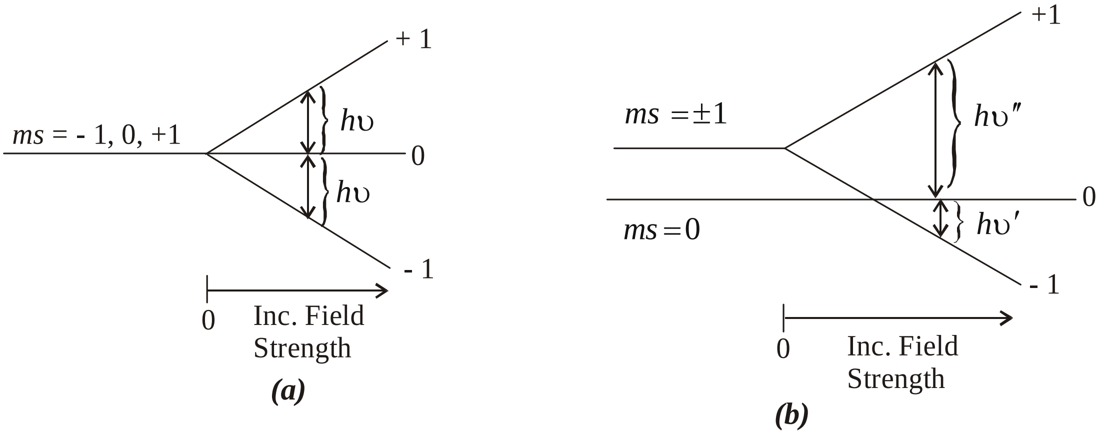


Fig. 11.7 The energy level diagram and spectrum for a molecule or Ion with $S = 1$

(a) in the absence of the of and (b) in the presence of zero field splitting.

Zero field splitting removes the degeneracy in m_S as indicated in Fig. 11.7(b) when subsequent splitting by the applied field occurs, the two resulting transistions are not degenerate. As a result two peaks are observed in the spectrum when zero field splitting exists, but only one when it is absent Fig. 11.7(b) is the energy level diagram for the splitting of the ground state ${}^3A_{2g}$ of $Ni^{(\text{II})}$ in an octahedral field when spin orbit coupling is large and zero field splitting occurs.

The energy level diagram for $Mn^{\text{II}}\left(d^5\right)$ is represented Fig. 11.8. This is an interesting example, because there are odd number electron and Kramer's degeneracy must exist. The term symbol for the free ion ground state is ${}^6S$. As indicated in Fig. 11.8 the zero field splitting produces three doubly degenerate spin states $\left(ms = \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}\right)$(Kramers degeneracy). Each of these split into two singlets by the applied field producing six levels. As a result of this five transitions $\left(-\frac{5}{2} \rightarrow \frac{-3}{2}, \frac{-3}{2} \rightarrow \frac{-1}{2}, \frac{-1}{2} \rightarrow \frac{1}{2}, \frac{1}{2} \rightarrow \frac{3}{2}, \frac{3}{2} \rightarrow \frac{5}{2}\right)$ are expected. The spectrum is further complicated by the hyperfine splitting due to the magnetic nucleus $\left(I = \frac{5}{2}\right)$. Thus five peaks each split into six hyperfine components as expected. In contrast to hyperfine splitting the term fine splitting is used when an absorption band is split because of non degeneracy arising from zero field splitting. Components of fine splittings have varying intensities; the intensity is greatest for the central lines and smallest for the outer most lines. In simple cases the separation between lines varies as $3\cos^2\theta - 1$ where θ is again the angle between the direction of the field and the Z axis.

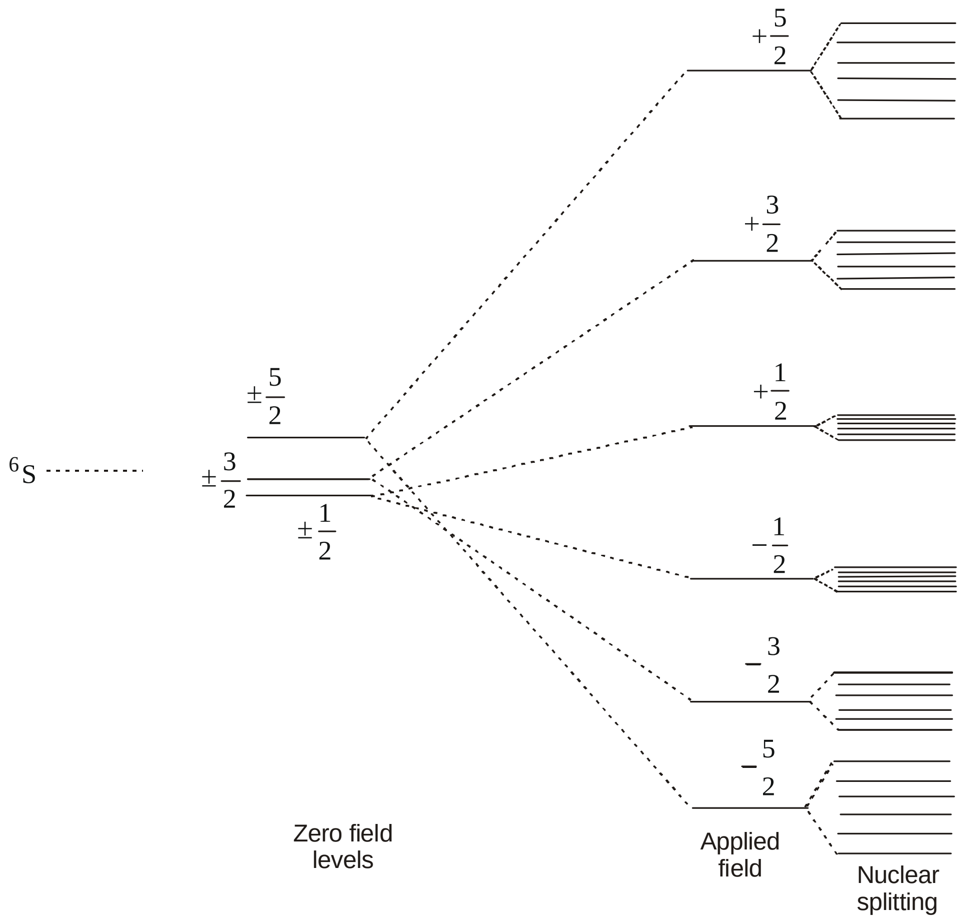


Fig. 11.8 : Splitting of the levels in the octahedral M_n^{II} complex

11.7 Information from Hyperfine Tenser A

The electron spin - nuclear spin interaction H_{SI} : This interaction is referred to as the hyperfine interaction consists of two parts, one purely isotropic involves only unpaired S-electron density at the nucleus and other conventional dipole - dipole type interaction involving the nucleus and p, d, f of unpaired electrons.

H_{SI} is given by

$$H_{SI} = -g\,\mu_B\,g_N\,\mu_N \sum_{ij}\left[\frac{r_{ij}^{2}\left(S_j\,r_{ij}\right)}{\left(S_j\,I_i\right)^3}\left(I_i\,r_{ij}\right)\right] r_{ij}^{-5}$$

$$+\frac{g\pi}{3}\, g\ \mu_B\ g_N\ \mu_N \sum_{ij} \delta\left(r_{ij}\right) I_i\ S_j \text{ --------------- } (11.8)$$

Where $\delta\left(r_{ij}\right)$ is Dirae delta function vanishes except at $r_{ij}=0$. It is a measure of the amplitude of the unpaired spin density at the nucleus and this is valid for s - type spin density. The first term which is valid for p, d type electrons and vanishes for s electrons since the magnetic field at the centre of a spherical charge cloud is zero.

From the nature of the hyperfine interaction given in equation (11.8) it follows that the experimental hyperfine fine constants can give rise to unpaired spin-density populations in the various atomic orbitals provided the free atom values of $|\psi_0|^2$ and $\left\langle r^{-3}\right\rangle$ are known. The ratio of the observed hyperfine constant to that of the theoritical value gives an idea of the square of the coefficient of the pertinent orbital in the ground state wave function. Thus if

$$\psi = C_s\ \psi_s + C_p \psi_p + C_s'\ \psi_s' + C_p'\ \psi_p' \text{ ------------------------ } (11.9)$$

where the non-primed wave function correspond to orbitals of the atom for which the isotropic and dipolar hyperfine constants are experminentally derived, then

$$C_s^2 = \frac{Aiso(\text{Exptl})}{Aiso\ (SCP)} \text{ and } C_p^2 = \frac{B \text{ dipolar } (\text{Exptl})}{B \text{ dipolar}(\text{SCP})}$$

If we now consider the hyperfine coupling (11.10) constants (isotropic and dipolar parts) to a central atom in a molecule of symmetry say C_{2V} or C_{3V} then hybridisation ratio λ is given by

$$\lambda = \left[\frac{C_p^2}{C_s^2}\right]^{\frac{1}{2}} \text{ ------------------------- } (11.11)$$

$$= \frac{\text{observed dipolar}}{\text{SCF dipolar}\left(n_p\right)} \div \frac{\text{observed isotropic}}{\text{SCF isotropic } \left(n_S\right)}$$

It can be shown that from the orthogonality of the wave functions the bond angles ϕ_{ij} between i^{th} and j^{th} is given by

$$\lambda_i\ \lambda_j\ \cos\phi_{ij} + 1 = 0 \text{ -------------------- } (11.12)$$

For an AB_n molecule with BAB angle of ϕ

$$\lambda\left(C_{2V}\right) = \sec\phi/2\sqrt{-\sec\phi}$$

or $\phi = 2\cos^{-1}\left(\lambda^2+2\right)^{1/2}$ ------------------------ (11.13)

For C_{3V} molecule $\phi = \cos^{-1}\left[\frac{1.5}{2\lambda^2+3} - \frac{1}{2}\right]$ ----------------------- (11.14)

If λ^2 is determined from orbit population which in turn are related to the hyperfine constants equation (11.13) and (11.14) lead directly to the determination of bond angles.

11.8 Hyperfine Structure

This structure arises from the interaction of the unpaired electron with the magnetic moments of nuclei within its orbital.

11.8.1 Origin of hyperfine Interaction : There are two quite distinct ways in which an unpaired electron may interact with magnetic nuclei to produce hyperfine structure. The first of these is the dipole - dipole interaction between the electron and the nuclear magnetic moments. This interactions is directional since it depends upon the angle made between the magnetic fieldand the line joining the dipoles. Its magnitude decreases rapidly $\left(\alpha\ r^{-3}\right)$ as the distance between the dipole increases. Since the interaction is directional it is referred to as the anisotropic interaction. For a system such as an organic free radical in solution, the orientation of the radical with respect to the magnetic field changes rapidly and the interaction averages to zero. The hyperfine interaction observed in solution must therefore result from an alternative mechanism.

The second mechanism by which interaction can occur is the 'Fermi' or contact interaction which is a result of a finite unpaired electron density at the nucleus. This condition is satisfied when the unpaired electron occupies an s orbital, but not when it occupies a p, d, or f orbitals where there will be an orbital node at the nucleus. This interaction is independent of orientation with respect to the magnetic induction and is therefore isotropic.

11.8.2 Energy Levels for a Radical : With $S=\frac{1}{2}$, $\mathrm{I}=\frac{1}{2}$

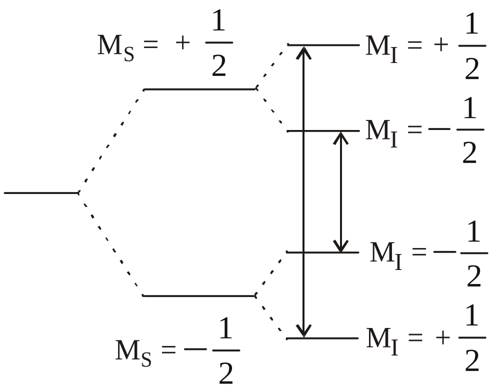


Fig. 11.9 : Energy levels (at constant magnetic induction) and allowed transition for the hydrogen atom

As already noted, the hyperfine structure observed in the ESR spectrum arises from interaction of the unpaired electron with any nuclear magnetic dipole in its vicinity. In other words, the total magnetic field experienced by an unpaired electrons is that due to the applied magnetic field plus that arising from any small local fields.

Consider the simplest possible free radical, the hydrogen atom, which has one unpaired electron $\left(S=\frac{1}{2}\right)$ and one proton $\left(\mathrm{I}=\frac{1}{2}\right)$. There are therefore two orientations of the nuclear magnetic moment for each orientation of the electron megnetic moment leading to the four energy levels illustrated in Fig. 11.9. Selection rule for an ESR transition, $\Delta M_S = \pm 1$. Since, total angular momentum must remain unchanged a second selection rule applies when interaction with nuclear magnetic moment are present i.e. $\Delta M_\mathrm{I} = 0$.

For the hydrogen atom two transitions are therefore allowed and are indeed observed. The spacing between the two absorptions corresponding to these two transitions is termed the hyperfine splitting constant (a) The fields at which the abosorption occur are there fore

$$\overline{B} = \overline{B}^1 \pm a/2 \text{ ------------- } (11.15)$$

Where $\overline{B}^1$ is the field where the absorption would occur if $a=0$. One further feature of the spectrum of the hydrogen atom is the relative intensity of the two absorptions. The population difference of the two nuclear spin states for a particular electron spin state is only 0.0000025 at room temperature and NMR spectroscopy depends on this small difference. However from the point of view of ESR spectroscopy the two states are effectively equally populated and the two absorptions will be of equal intensity with in experimental accuracy. The spectrum of the hydrogen atom therefore consists of two equally intense absorption.

It would be helpful at this stage to introduce a term which is useful when dealing with more complicated ESR spectra i.e. the spin hamiltonian operator. An operator represents an instruction to carry out a defined mathematical operation on a particular function. The spin Hamiltonian operator operates on the spin part of wave function describing a particular state to give energies of the system. In the absence any nuclear interaction, combination of the magnetic moment operator $\widehat{\mu_z}\left(= -\mu_N \widehat{S_Z}\right)$ with equation (11.1) gives the spin Hamiltonian operator H .

$$\mathrm{H} = g\,\mu_N\, B\, \widehat{S_Z} \text{ -------------- } (11.16)$$

from which the energy states $\pm g\,\mu_N\, B/2$ are obtained

This form of Hamiltonian is obviously inadequate in those situations where interaction with nuclear magnetic moment occurs. The additional term required, the Hamiltonia operater for isotropic hyperfine interaction, can be shown to have the form

$$\mathrm{H}_{iso} = b A \widehat{S_Z}\ \widehat{I_Z} \quad \text{-------------- (11.17)}$$

where 'A' is the isotropic hyperfine 'coupling' constant and has the unit of frequency. The complete Hamiltenion for the hydrogen atom is therefore :

$$\mathrm{H} \quad = g\,\mu_B\,\overline{B}\,\widehat{S_Z} + h\,A\widehat{S_Z}\,I_Z \quad \text{-------------- (11.18)}$$

Actually both (11.17) and (11.18) are incomplete since they do not include nuclear Zeermanterm $\left(=-g_N\,\mu_N\,\overline{B}\,\widehat{I_Z}\right)$. However this can be omitted from the Hamiltanian for the purpose of the present discussion since it does not affect the transition energies. Therefore spin states for the hydrogen atom and application of the spin Hamiltonian gives the energy of these states

$$E_1 = +\frac{1}{2}\,g\,\mu_B\,B + \frac{1}{4}h\,A, \quad E_2 = +\frac{1}{2}\,g\,\mu_B\,B - \frac{1}{4}h\,A$$

$$E_3 = -\frac{1}{2}\,g\,\mu_B\,B + \frac{1}{4}h\,A, \quad E_4 = -\frac{1}{2}\,g\,\mu_B\,B - \frac{1}{4}h\,A$$

Applying ESR selection rules the allowed transition are

$$\Delta E_{1,4} = g\,\mu_B\,B + \frac{1}{2}hA, \qquad \Delta E_{2,3} = g\mu_B - \frac{1}{2}h\,A$$

these equations are analogous to (11.15) i.e.

$$B_{1,4} = B' - {hA}/{2g\,\mu_B},\ B_{2,3} = B' + {h\,A}/{2g\,\mu_B}$$

and the relation between the hyperfine splitting constant (a) and the isotropic splitting constant (A) is therefore

$a = \dfrac{hA}{g\,\mu_B}$, it can be seen from this equation that a cannot be converted to A unless g factior is known. If g is known the

$$a(mT) = 0.0357\left(\frac{g_e}{g}\right)A \ \text{ MHz}$$

where g is the g factor for hydrogen atoms and g_e is the free electron g -factor (2.0023)

11.9 Summary

(1) ESR is like NMR, the interaction of electron magnetic moment interacting with external magnetic induction $\overline{B_0}$ which causes unpaired electron to precess around $\overline{B_0}$ with constant angular frequency $\omega_0 = \gamma B_0$. The energy of interaction is $h\upsilon = g\,\mu_B\,\overline{B_0}$. The required external frequency to cause transitions to take place falls in microwave region.

(2) Experimental methods involve simple ESR spectrometer using transmission type cavity, reflection type cavity along with microwave bridge. The absorption mode and in the recorder its derivative part are also shown. The necessity of magnetic field modulation is also explained.

(3) g values are explained, basically g is not a constant and actually it is a tensor, its dependence on various types of interaction have been presented. When g is an isotropic, it is necessary to rotate the crystal through mutually perpendicular direction and ultimately principal values of g tensor namely g_{xx}, g_{yy}, and g_{zz} are to be evaluated.

(4) Fine structure splitting means crystal field splittings and Kramer's doublets occur in the odd electron system whose degeneracy is only lifted by the application of magnetic field only.

(5) Information from A tensor yields information about bond angles indirectly in the molecules. The relationship between isotropic A value and anisotropic 'a' value has been presented.

11.10 Keywords

Unpaied electron, Fine structure, Hyperfine structure, g tensor, A tensor, anisotropy and isotropy of g and A values, reflection cavity, transmission cavity, thermal equilibrium, relaxation magic T micro wave bridge, Absorption mode and derivative mode, Zero field splitting.

11.11 Review Questions

(1) Explain the principle of ESR and using a schematic ESR spectrometer explain different parts involved in the phenomena.

(2) What are the characteristics of g tensor and hyperfine coupling constant A tensor.

(3) Explain with a neat ESR spectrometer, how the phenomena is helpful to know about bond angles in molecule or crystals.

11.12 Text and Referrence Books

(1) Molecular structure and spectro scopy by G. Aruldnas (PHI)

(2) Nuclear magnetic Resonance by ER Andrew (Cambridge University Press)

(3) Fundamentals of Molecular spectroscopy by C.B. Banwell

(4) Spectroscopy by BP Straughen and S. Walker

Unit - III

Lesson - 12

NUCLEAR QUADRUPOLE RESONANCE, PRINCIPLE AND NQR SPECTROMETER

Aim : To know the fundamental requirements of NQR, General Principles of integral spins and half integral spin, Block diagram of NQR spectrometer and their details and Applications of NQR spectroscopy.

Objectives of the lesson :

1. To know the principles of NQR
2. Basic requirements for the detection of NQR spectroscopy
3. General principles, definitions, parameters
4. Experimental detection of NQR frequencies
5. NQR spectrometers : super regenerative type, continuous wave type and pulse method type
6. Chemical applications and solid state applications of NQR spectroscopy

Structure of the lesson :

12.1 Introduction

Nuclear Quadrupole Resonance (NQR) is a branch of radio frequency spectroscopy which is closely related to nuclear magnetic resonance (NMR). Both techniques involve the coupling of radio frequency radiation with a nuclear magnetic moment to bring about the transitions between nuclear orientations of different energies. The difference between the two lies in the origin of external nuclear energy levels. In the case of NMR, the energy levels are governed by the interaction of the nuclear magnetic dipole moment with an externally applied magnetic induction. In the Nuclear Quadrupole Resonance the levels are governed by an interaction of the nuclear electric quadrupole moment with the electric field gradient produced at the site of the nucleus by the charge distribution to its environment.

The way in which the quadrupole interaction is observed depends upon the relative magnitudes of the nuclear magnetic and nuclear quadrupole interaction. When the magnetic interaction is large in comparison with the quadrupole the latter causes a splitting or broadening of the NMR lines. When the quadrupole interaction is dominant, the transition frequencies are largely determined by the electric field gradients at the nucleus and the magnetic interaction (in non zero field) is seen as splitting or broadening of NQR lines. In the absence of magnetic induction, there is no magnetic interaction and the unperturbed resonance lines are observed. Here we are concerned with zero field or pure quadrupole resonance or just NQR. With NMR the transition frequencies are proportional to the applied magnetic induction, so the transitions between the magnetic levels are possible using a fixed frequency oscillator while sweeping the magnetic field. With NQR the electric induction gradient is a fixed property of the molecule or crystal and is considerably larger than any practical externally applied field gradient. This means a variable frequency detection must be used. The range of NQR interaction is such that transition frequencies can occur any where between 100 kHz and 1 GHz (1000 MHz) making detection by a single spectrometer is not possible.

12.1.1 The Fundamental requirements of Nuclear Quadrupole Resonance Spectroscopy :

(1) The sample must contain a nucleus with a quadrupole moment in an asymmetrical environment. This necessarily implies that the nuclear spin quantum number I should be greater than $\frac{1}{2}$ and the site symmetry of the atom containing the quadrupolar nucleus should be less than cubic or tetrahedral.

(2) The effect is observed only in the solid state, where the field gradient axes are fixed in space. In a liquid the molecular vibrations are tumbling motions which occur at a rate much greater than the radio frequency scale cause the average field gradient experienced by the nucleus to be reduced to zero. The effect could be seen in principle in gases (if the collision rate is low) or in liquid crystals which have been oriented.

(3) To make the detection possible the chosen nuclear isotopic should be present in reasonably high natural abundance and in addition about 2 gram or more of poly crystalline material are usually required. The resonance lines in general are much broader by a factor of 10^3 or 10^4 than those observed in high resolution NMR and therefore are more difficult to detect.

(4) A sensitive radio frequency detection system is required the operating frequency of which is variable over the region of the spectrum of interest. For example ^{35}Cl NQR frequencies fall in the range of 0 - 60 MHz and most of this region covered by one spectrometer.

By remembering the above reasons, the most popular NQR nuclei are $^{14}N,\ ^{35}Cl\ ^{37}Cl,\ ^{79}Br,\ ^{81}Br$ and $^{127}\mathrm{I}$. Other suitable nuclear isotopes are $^{10,11}B,\ ^{27}Al,\ ^{33}S,\ ^{55}Mn,\ ^{59}Co,\ ^{63,65}Cu,\ ^{69,71}Ga,\ ^{75}As,\ ^{93}Nb,\ ^{115}In,\ ^{121,123}Sb,\ ^{135}Ba,\ ^{175}Lu,\ ^{185}\mathrm{Re},\ ^{157}Au,\ ^{201}Hg$.

12.2 General Principles

Let us consider the nature of nuclear quadrupole moment and see how this interacts with its electronic environment. The quadrupole moment of the nucleus is a consequence of its spin and spin degeneracy; it is unlike the quadrupole moment of the molecules. A nucleus for which $\mathrm{I} \geq 1$ behaves as if it does not have spherical symmetry but is distorted along the axis of the spin. In a simple modes in which the nuclear charge distribution is related to that of a molecule, we may imagine the charge to be compressed or extended along this axis according to the sign of its quadrupole moment. A positive moment has a prolate spheroidal shape (extension along the spin axis) and a negative moment has an oblate spheroidal shape (contradiction along the spin axis) shown in fig. 12.1. The magnitude of the quadrupole moment eQ corresponds to the deviation of the nucleus from spherical symmetry and is defined as

$$eQ = \int \rho r^3 \left(3\cos^2\theta - 1\right) d\tau \text{ --------------- (12.1)}$$

where e is the absolute value of the electronic charge, ρ is the charge density in a volume element $d\tau$ inside the nucleus at a distance r from the centre and θ is the angle which the radius vector r makes with the nuclear spin axis (nucleus in the spin state $\mathrm{M_I = I}$)

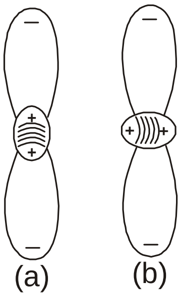


Fig. 12.1 The interaction of a quadrupole nucleus with a p - orbital charge distribution. Interaction energy of (a) is less than that of (b)

In many molecules, the electronic distribution around a nucleus is not spherically symmetric unless the atom containing the nucleus happens to be at a site of tetrahedral or cubic symmetry. If the atom in question has a nucleus with zero eQ, the potential energy associated with the nuclear - electronic interaction will be independent of nuclear orientation. If however the nuclear electronic quadrupole moment is non zero, the energy of the system will depend upon the nuclear orientation. Obviously there will be particular orientation in which the potential energy will have a minimum value. On a classical (non quantized) level consider the orientation in fig. 12.1. This shows two possible orientations of a quadrupolar nucleus with respect to an electronic charge distribution similar to that generated by a filled p - orbital. In the fig. 12.1(a) the energy of interaction will be lower because there is less separation between opposite charges. This could be equated with the ground state configurations and fig 12.1(b) with an excited state, since energy has to be expended to turn the nucleus which moves the opposite charges further apart. On the molecular level, of course the nuclear orientations will be quantised and the nucleus will precess, like a gyroscope about the direction of the maximum field gradient. (if this has axial symmetry) rather than as shown in fig. 12.1. Thus here there is another anology with NMR, where the nuclear magnetic dipole moment precesses about the direction of the applied induction.

For a quadrupolar nucleus, therefore different nuclear orientations give rise to a set of energy levels. Transitions between these levels may be brought about by the fact that the quadrupolar nucleus still possesses a magnetic dipole moment and if an oscillating magnetic induction is applied from a coil round the sample, coupling occurs between the magnetic moment of the nucleus and the magnetic components of radiation. In this way the nuclear orientation is altered with respect to the direction of the maximum field gradient. Note that the energy levels are set by an electric quadrupolar interaction but that the transitions are magnetic dipole in type.

When the electric field gradient is symmetrical about an axis, the expression for the energy level is

$$E = \frac{e^2 Qq}{4\mathrm{I}(2\mathrm{I}-1)}\left[3M_{\mathrm{I}}^2 - \mathrm{I}(\mathrm{I}+1)\right] \text{ ----------- } (12.2)$$

where eQ is the nuclear quadrupole moment defined in equation (12.1) eq is the magnitude of electric field gradient in the direction of the axis of symmetry, I is the nuclear spin quantum number and M_{I} is the nuclear magnetic quantum number which takes the values $+\mathrm{I},\ \mathrm{I}-1$ .... $(-\mathrm{I})$. Note that there is degeneracy in $+M_{\mathrm{I}}$ and $-M_{\mathrm{I}}$ states because of the M_{I}^2 term. The electric field gradient is a tensor quantity and this can be defined in a diagonal form so that all off - diagonal terms $e.g. \frac{\partial^2 V}{\partial x\, \partial y}$, are zero, when the three axis x, y, z are called the principal axis of the tensor. According to Laplace equations, the sum of the field gradients in these directions, which are second derivatives of the electro static potential V is equal to zero.

$$\frac{\partial^2 V}{\partial x^2}+\frac{\partial^2 V}{\partial y^2}+\frac{\partial^2 V}{\partial z^2}=0 \text{ ------------- (12.3)}$$

The convention to choose the principal axes in such a way that

$$\left|\frac{\partial^2 V}{\partial z^2}\right| \geq \left|\frac{\partial^2 V}{\partial y^2}\right| \geq \frac{\partial^2 V}{\partial x^2} \text{ and to define}$$

$$\frac{\partial^2 V}{\partial z^2}=eq \text{ -------------------- (12.4)}$$

and an Asymmetry parameter η is also defined :

$$\eta=\left(\frac{\partial^2 V}{\partial x^2}-\frac{\partial^2 V}{\partial y^2}\right)\Big/\frac{\partial^2 V}{\partial z^2} \text{ ----------- (12.5)}$$

η measures the departure of the field gradient from axial symmetry and can take values from 0 to when $\partial^2 V/\partial x^2$ equals to $\partial^2 V/\partial y^2$, the field gradient is symmetric about z axis and η equals to zero

12.2.1 Half Integral Spin : Firstly we shall consider the case of common quadrupolar nuclei ^{35}Cl ^{79}Br and ^{81}Br which have a spin $\mathrm{I}=3/2$ from equation (12.2) there will be only two levels of energies

$$\left.\begin{aligned} E_{\pm\frac{1}{2}} &= -\frac{1}{4}e^2 Qq \\ E_{\pm\frac{3}{2}} &= +\frac{1}{4}e^2 Qq \end{aligned}\right\} \text{ --------------- (12.6)}$$

The selection rule for magnetic dipole transition is

$$\Delta M_I = \pm 1 \text{ -------------- } (12.7)$$

only one frequency is therefore observed

$$\upsilon = \frac{1}{2}\frac{e^2 Qq}{n} \text{ -------------- } (12.8)$$

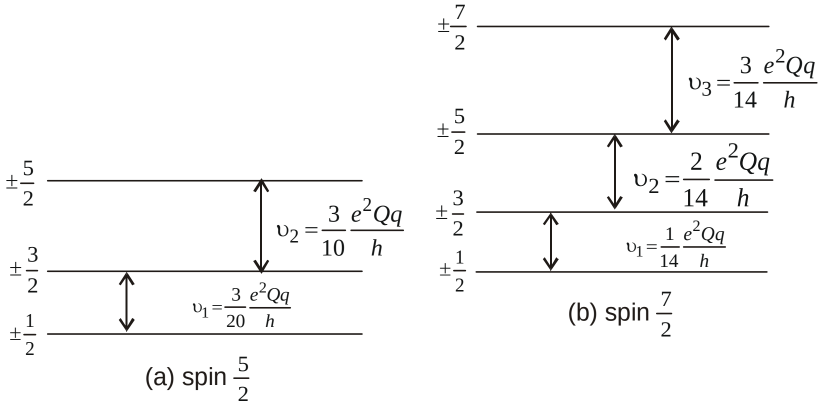
The expression e^2Qq/h is termed as the nuclear quadrupole coupling constant and has the units of frequency (MHz). It can be of either sign, according to the sign of eQ, or eq, but this is not found from a simple measurement of the transition frequency since a reversal of sign has the effect of inverting the order of levels, leaving the frequency unchanged.

For nuclei of spin $I = 5/2$ for example ^{127}I, ^{121}Sb transition between three levels are possible [see fig 12.2(a)]. The magnetic dipole selection rule (12.7) ensures that only two transitions frequencies are observed.

$$\left.\begin{aligned} \upsilon_{\frac{1}{2}\rightarrow\frac{3}{2}} &= \frac{3}{20}\frac{e^2 Qq}{h} \\ \upsilon_{\frac{3}{2}\rightarrow\frac{5}{2}} &= \frac{3}{10}\frac{e^2 Qq}{h} \end{aligned}\right\} \text{ --------------- } (12.9)$$

In this case of an axially symmetric field gradient the frequencies are in the ratio of 1:2, it will be seen later that the effect of a finite η term is to cause departure from this situation.

For the spin $7/2$ case e.g. ^{59}Co or ^{123}Sb, three transitions between four energy levels are possible [see Fig. 12.2(b)].



(a) spin $\frac{5}{2}$

(b) spin $\frac{7}{2}$

Fig. 12.2 Zero field quadrupolar energy levels and transitions for (a) $I = \frac{5}{2}$ and (b) $I = \frac{7}{2}(\eta = 0)$

when the asymmetry parameter is non zero, the degeneracy in $\pm M_I$ remains but the transition frequencies are modified. For spin $\frac{3}{2}$, the transition frequency is given by

$$\upsilon=\frac{1}{2}\frac{e^2Qq}{h}\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}} \text{ ---------------- } (12.10)$$

In this case the quadrupole coupling constant cannot derived from the NQR frequency υ unless η is known. However in practice η is often small for singly coordinated atoms (eg. Chlorine and the error in neglecting η values below 0.1 is less than 0.16% so in this instance the coupling constant may be taken as twice the resonance frequency. For spin $\frac{5}{2}$ and $\frac{7}{2}$, the transition frequencies for η values of < 0.25 are given in Table 12.1.

The main effect of non zero asymmetry parameter is to remove harmonic relationship between successive transitions. From a ratio of two resonance frequencies both $\frac{e^2Qq}{h}$ and the asymmetry parameter η can be determined.

Table - 12.1

Spin	Transition frequency $n \neq 0$
1	$\upsilon_0=\frac{1}{2}\left(\frac{e^2Qq}{h}\right)\eta$ $\upsilon_-=\frac{3}{4}\left(\frac{e^2Qq}{h}\right)\left(1-\frac{\eta}{3}\right)$ $\upsilon_+=\frac{3}{4}\left(\frac{e^2Qq}{h}\right)\left(1+\frac{\eta}{3}\right)$
$\frac{3}{2}$	$\upsilon_1=\frac{1}{2}\left(\frac{e^2Qq}{h}\right)\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}}$

$\frac{5}{2}$

$$\upsilon_1 = \frac{3}{20}\left(\frac{e^2 Qq}{h}\right)\left(1 + 0.09259\eta^2 - 0.63403\eta^4\right)$$

$$\upsilon_2 = \frac{3}{10}\left(\frac{e^2 Qq}{h}\right)\left(1 + 0.20370\eta^2 + 0.16215\eta^4\right)$$

$\frac{7}{2}$

$$\upsilon_1 = \frac{1}{14}\left(\frac{e^2 Qq}{h}\right)\left(1 + 3.6333\eta^2 - 7.2607\eta^4\right)$$

$$\upsilon_2 = \frac{2}{14}\left(\frac{e^2 Qq}{h}\right)\left(1 - 0.56667\eta^2 + 1.8595\eta^4\right)$$

$$\upsilon_3^3 = \frac{3}{14}\left(\frac{e^2 Qq}{h}\right)\left(1 - 0.1001\eta^2 - 0.01804\eta^4\right)$$

12.2.2 Integral Spins : For nuclei of spin $I = 1$, the most important example which is ^{14}N the resonance frequencies are given below.

$$\left.\begin{aligned} \upsilon_+ &= \frac{3}{4}\frac{e^2 Qq}{h}\left(1 + \frac{\eta}{3}\right) \\ \upsilon_- &= \frac{3}{4}\frac{e^2 Qq}{h}\left(1 - \frac{\eta}{3}\right) \\ \upsilon_0 &= \frac{1}{2}\frac{e^2 Qq}{h}\eta \end{aligned}\right] \text{------------------- (12.11)}$$

υ_0 is rarely observed since a large value of η is needed to bring into a frequency range where detection is possible when η is zero the single transition is observed.

$$\upsilon = \frac{3}{4}\frac{e^2 Qq}{h} \text{ --------------- (12.12)}$$

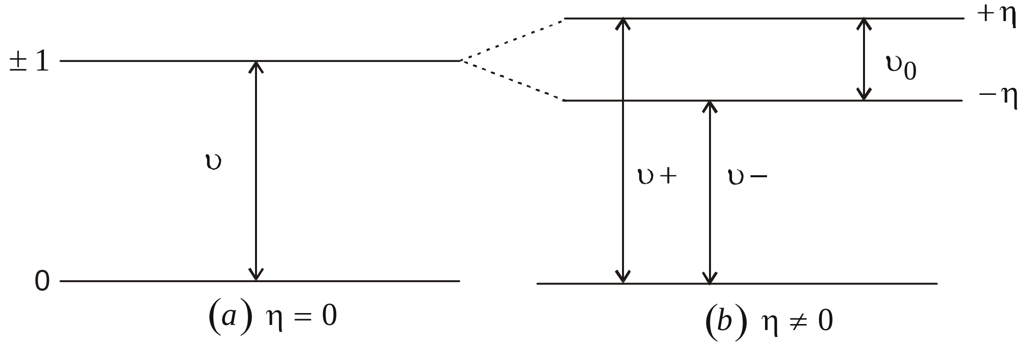


Fig. 12.3 zero field pure quadrupole energy levels and transitions for $I=1$, $(a)\ \eta = 0$ and $(b)\ \eta \neq 0$.

The transition frequencies which are measured from a nuclear quadrupole resonance spectrum of a poly crystalline sample can provide (with the exception of spin $\frac{3}{2}$ case) the values of the quadrupole coupling constant $\frac{e^2Qq}{h}$ and the asymmetry parameter η using the above equation. to determine η for spin $\frac{3}{2}$, it is necessary to resort to Zeeman splitting studies in which a weak magnetic field is applied to the sample.

12.3 Experimental Detections of NQR Frequencies

The detection of NQR signals is dependent upon the coupling of nuclear magnetic moment with a suitably applied rotating magnetic field $\overline{B_1}$. In this respect it resembles detection in nuclear magnetic resonance but the field following differences exist.

(1) As indicated earlier the NQR frequency is determined by the electric field gradient with in the crystal so a variable frequency detector is necessary. In the case of NMR the oscillator frequency used is determined largely by the magnitude of the applied field.

(2) Relaxation times of quadrupolar nuclei tend to be shorter than those of nuclei which possess only a magnetic moment, because of the greater efficiancy of quadrupolar relaxation processes in comparison with dipolar processes. This means that a high radio frequency (r.f.) power is required in order to observe resonance.

(3) The degeneracy of quadrupole spin states $(\pm M_I)$ causes a net cancellation of the nuclear induction perpendicular to the axis of the transimitting coil. Therefore crossed

coil detection is not possible in zero magnetic field and single coil systems are used. (A cross coil system could be used in the presence of a weak magnetic field since this removes the degneracy).

The variable frequency requirement rules out the bridge form of detection often used in NMR since this sytem requires complicated adjustments.

There are three usual methods for NQR detection (1) Super regenative method (2) Continuous wave oscillator (3) Palsed rf or spin - echo method. The first two methods both use an rf oscillator to act as detector as well as an exciter of the nuclei. In the third method these functions are carried out by a separate receiver and transmitter.

12.3.1 The Super - regenerative Oscillator : The super-regenerative oscillater (SRO) was the first circuit to be used in the detection of NQR in solids by Dehmelt and Kruger in (1950). Essentially it consists of an rf oscillator which is turned off periodically at a rate which is a small fraction $\left(\sim {}^{1}\!/_{1000}\right)$ of the rf frequency when turned on again the oscillations build up either from noise (this is termed as incoherent mode of operation) or from the tail of the preceeding pulse (coherent mode) until they reach their limiting value (see Fig. 12.4). The sample is situated in the inductance coil of the tank circuit of the oscillater (This is a parallel combination of an inductance and a variable which sets the running frequency of the oscillator) and the circuit parameters are adjusted for coherent mode operation. If an input signal due to the exchange of rf energy with sample appears

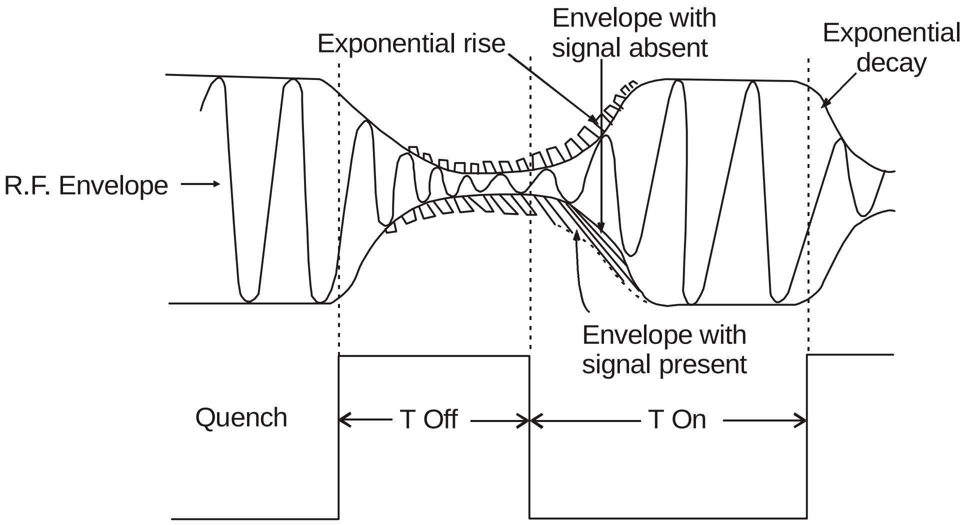


Fig. 12.4 Oscillation envelope of a super - regenerative oscillator

In the tank circuit of the oscillator at the tuned frequency, the oscillator build up sooner and the over alla rea of the rf envelope is increased. This increases the level of the oscillator valve anode current, which is detected, either directly on an oscilloscope or by other means. The rate at which the oscillator is quenched determines the phase relationship between successive bursts of

rf and also in extreme case determines whether the oscillator is operating in the linear or logarithmic mode. The former mode requires a rapid quench frequency so that oscillation never reach their limiting value. In this (the linear mode the output is a linear function of input when the oscillations are allowed to limit with a slower quench frequency and the relationship between the input and output is logarithmic and it is this mode of operation which is useful for NQR detection. When in this mode the SRO can be made to have variable coherence by changing the quench frequency. A change in coherence has a considerable effect on the power system (plot of amplitude versus frequency) of the oscillator. As the coherence decreases the line width of the radiation increases sharply. Since the quenching of the oscillator is an extreme form of amplitude modulation, the power spectrum of the radiation wil contain side bands separated from the carrier frequency by integral multiples of the quench frequency. The important feature of the SRO as an NQR detector is that width of the lines in the power spectrum can be adjusted to be comparable with the natural line width of the nuclear resonance. By NMR standards NQR lines are very broad, perhaps of the over of 1 - 30 kHz. The advantage of the SRO is that all the nuclei can be excited simultaneously, rather than a just a proportion of these, as with continuous wave oscillators. A disadvantage is that each NQR absorption can also be excited by the SRO side bands and hence a frequency - swept spectrum will contain multiple lines from a single NQR signal. However these side bands response can be supressed by varying the quench frequency at a rate which is much slower than the quench frequencies itself but faster than the recording time constant of the instrument. This has the effect of moving the side hands in and out from the fundamental signal and when a recording constant of about 10 seconds is used the side bands becomes smeared out and only the fundamental signal is recorded.

A block diagram of SRO NQR spectrometer is shown in fig. 12.5

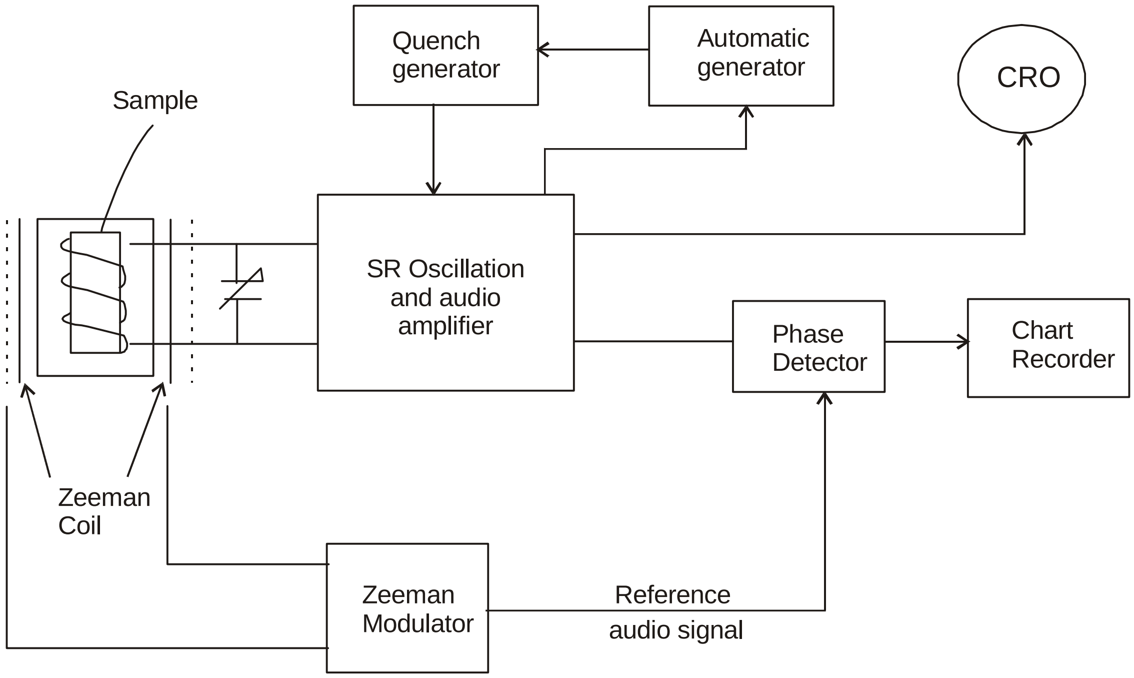


Fig. 12.5 Block diagram of a super regenerative NQR spectrometer using Zeeman modulator

This is based upon the Decca NQR spectrometer which is used for the detection resonances in the region 5 - 60 MHz. The sample usually 2 - 3 gm polyerstalline material is contained in a thin waled glass tube which fills the rf coil. The coils usually situated in a copper or brass can and the whole probe assembly is immersed in a Dewar vessel of coolent usually liquid Nitrogen. NQR measurements are often made at low tempertatures because line intensities are usually (but not always) greater than at room temperature. This follows from a more favourable Boltzmann distribution of energy level population, and in addition there is less broadening from molecular torsional vibrations or hindered rotation at low temperature. However large changes in the relaxation times with temperature can in some cases result in an increase of signal strength with temperature.

A frequency sweep is carried out by a motor drive to the variable capacitor in tank circuit. An optimum quench frequency is selected and during the run an automatic gain control maintains a constant coherence level (i.e. a constant sensitivity) while the rf frequency is swept. This is accomplished by changing the mark space ratio of the quench pulses while keeping the quench frequency constant. Signlas are detected by changes in the anode voltage level and can be observed on an oscillioscope or more usually using a phase sensitive detecter. This is a device for improving the signal to noise ratio of a signal which is in phase with a particular reference frequency. Usually this is an audio frequency with which the NQR signal is modulated. The easiest way accomplishing this is include a 'vari cap' diode (a voltae dependent capacitor) in the tank circuit. The phase detector then measures the component of the signal which is present at this audio frequency and the out put is fed to a chart recorder.

This frequency modulation method has the disadvantage that signals other than those due to NQR absorption may be detected (e.g. from radio transmitters piezo electric responses. For NQR observations a form of magnetic modulations is useful because only true NQR signals can respond it. With magnetic or Zeeman modulation a magnetic field up to 0.02 T periodically applied to the sample at a low audio frequency (< 200 Hz). The magnitude of line splitting caused by a magnetic field is a sensitive function of the orientation of the crystal with respect to the field. For a poly crystallene sample therefore application of the field causes the signal to be broadened and almost erased for the period during wich the magnetic field is applied. A large coil surrounding the samples supplied with bisymeetric wave form  to provide the modulating field. This wave form is used to ensure that no residual magnetide field is present in the coil during the 'off' period. The reference frequency supplied to the phase detector is infact at twice the frequency of this bisymmetric wave form since there will be two 'field off' 'fieldon' periods percycle. When an NQR signal is present the phase detecter then, detects the component of it which is in phase with the 'fileld off' period and this is recorded on a chart recorder in the normal way. Some calibration of the chart is necessary and this can be provided by a frequency marker unit.

Super - regenerative oscillators can operate successfully at several hundred MHz but in the low frequency range below 5 - 10 MHz their sensitivity is often reduced. It is in this region that continuous wave oscillators have been most commonly used.

12.3.2 Continueous Wave Oscillator : A continuous wave oscilalter is some what simpler than an SRO, there is no quenching of the oscillations. The sytem can be self - detecting in that the oscillater both excites and detects the rf absorption at the resonance condition. An oscillator may be regarded as an amplifier with positive feed back to supply its own input and thus maintains contineous oscillation. Only when there is enough feed back to sustain oscillations the current is very sensitive to changes in the shunt inpedence of the tank circuit. When the oscillator frequency equals that of the nuclear quadrupole resonance, the level of amplitude of the oscillator falls and this is detected usually by grid rectification and then by an audio frequency modulation technique. This type of oscillater (known as a marginal oscillator) is capable of rf levels some what lower than those of the SRO. Allow its sensitivity is greatest and its noise factor is also more favourable.

Another type of oscillator due to Robinson has a different feed back arrangement. This uses a second valve or (transister) which provides a limited output giving a constant amount of feed back. This system (the limited oscillator) has the advantage that sensitivity is maintained over a wider frequency range without the need for constant adjustment of the feed back. Both of these oscillator detecters give better line shapes than the SRO type of detector and have infact been well used in NMR application where low levels of rf are often needed. For NQR they are usually used, for nuclei whose resonances are more easily saturated for example ^{14}N . The frequency range for this nucleus is 1 - 5 MHz a difficult region for SRO detection.

A typical ^{14}N NQR spectrometer of this type has a simpler form to that shown in fig. 12.5. No quench generator is of course required and indeed an automatic gain control system is not absolutely necessary. The frequency sweep is made by a motar drive to the tank circuit capacitor. The output from the oscillator is usually passed on to a audio amplifier before phase detection. Both frequency modulation or Zeeman molecular can be used for detection when the asymmetry parameter is small but the latter form does not work well with ^{14}N signals when η is large since a high field strength is required to cause an appreciable splitting of such signals. For 12.6 shows the ^{14}N NQR signal from te 2gm of hexamethylene tetramine at room temperature obtained with a Robinson type oscillator detection.

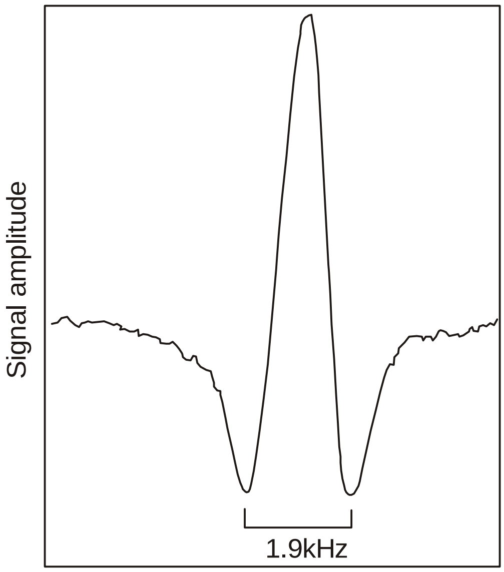


Fig. 12.6 ^{14}N NQR signal from hexamethyl tetra amine, $\upsilon = 3.308\,\mathrm{MHz}$ at $2.96\mathrm{K}$

Chlorine resonance is also possible witht his type of oscillator provided that the line width is small (< 5KHz);

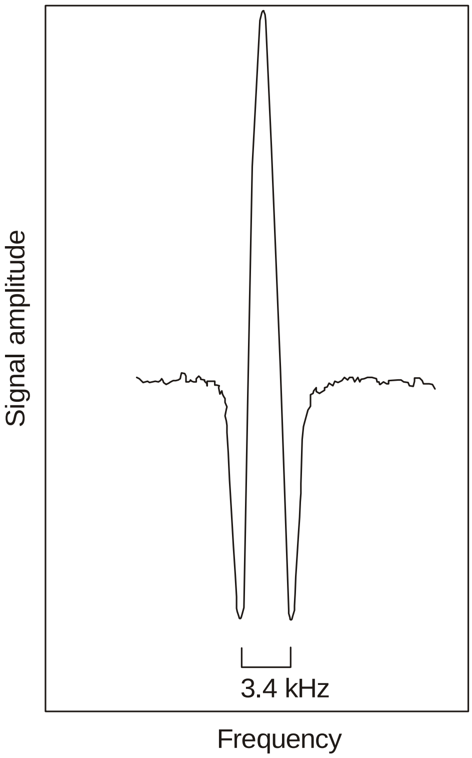


Fig. 12.7 One of the ^{35}Cl Quadrupole Resonance signals from gallium trichloride using a C.N. spectrometer, $\upsilon = 20.27$ MHz at 294 K

Fig. 12.7 shows a resonance signal from ^{35}Cl gallium trichlorate at room temperature. This compound exists as a dimer in which there are two bridging chlorines and four terminal ones. The molecule has a two fold symmetry so only three lines are observed at 20.22 and 19.08 MHz due to the terminal chlorine atoms and at 14.67 MHz due to the bridging chlorine atom (frequencies at 360K. Notice the large frequency difference between resonances of bridging and terminal chlorine atoms.

12.3.3 Pulsed RF detection : The use of pulsed methods for the detection of NQR has not been as widely adopted as those described in the two provisons sections, owing largely to the more complex circuitry and higy rf power required; How ever the amount of information obtainable is greater for example nuclear relaxation times can be studied by this method. The action of rf pulses on the nuclear spins is similar to both NQR and NMR. When in a magnetic field the nuclei will precess about the field direction at a rate of γB where γ is the gyro magnetic ratio of the nucleus and $\overline{B}$ is the magnetic induction. In zero field, the quadrupolar nuclei may be regarded as precessing about the direction of the principal axis of the electric field gradient in the crystal (the Z axis, at least if $\eta = 0$). The rate of precession is dependent upon their orientation, θ, in classical terms this is equal to $3e^2 \; Qq \; \cos\theta / 4\Omega$, where Ω is the nucleur angular momentum. In a poly crystalline sample this field gradient Z axes will be in all possible directions with respect to the rf coil, so there will always be a proportion of crystallites so arranged in the sample that their Z axis coincide with the field direction in the laboratory frame of reference to be compared with the field direction in NMR. When an intense radio frequency field $\overline{B_1}$ is applied to the sample via an rf coil, the nuclei (in both NMR and NQR cases) begin in addition to precess about $\overline{B_1}$ at a rate of $\gamma\overline{B_1}$. If this field is applied at right angles to $\overline{B}$ say anlong X axis in a rectangular cordinate system, XYZ (with $\overline{B}$ along the Z axis) the rotation will be in the YZ plane. For NQR of poly cryslalline samples there is no directional requirement of the rf field since the choice of a laboratory frame Z direction is arbitrary. The length of the time for which $\overline{B_1}$ is switched on controls the amount of rotation of the macroscopie nuclear magnetization vector. If the pulse is switched off when this rotation is 90^0, the magnetization is then in a position to induce rf voltage in the coil. A single coil or two coaxial coils may be used for NQR detection but otherwise the apparatus is similar to that used for NMR. The relaxation times T_1 and T_2 are also measured by the same techniques. The absence of magnetic induction requirement allows larger samples to be used than in usual NMR, which aids signal detection. Where a narrow band transmitter or receiver is used searching over a wide frequency range is tedious because constant returning is necessary to maintain sensitivity. Searching for NQR signal is more difficult than NMR, where the frequency range of any particular nucleus is relatively narrow and can be predicted from the value of $r\overline{B}$. Pulsed method are useful for detecting very broad resonances which may not be observable by any other technique.

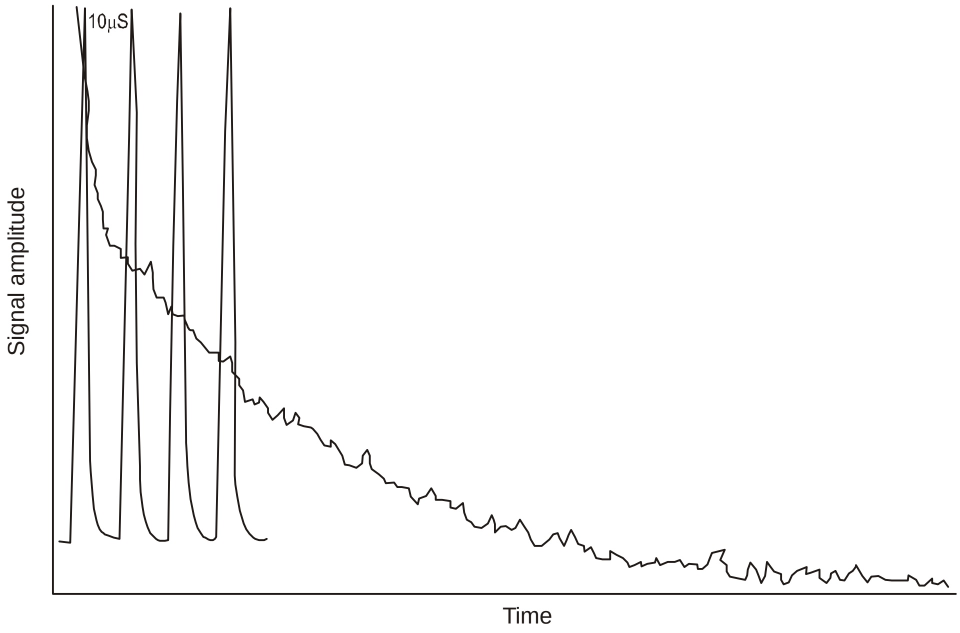


Fig. 12.8 Free induction delay signal for ^{35}Cl resonance in $CsDCl_2$ $\upsilon = 21.28\,\mathrm{MHz}$ at 290 K.

Figure 12.8 shows the free induction delay signal (following 90^0 pulse) from ^{35}Cl resonance in $CsDCl_2$ at 290 K using a pulsed rf spectrometer. The marker spacing in $10\,\mu s$ and the time constant of the delay T_2^* is $50\,\mu s$.

12.4 Chemical Appliations of Nuclear Quadrupole Resonance :

The main uses of Nuclear Quadrupole Resonances are summarized below :

(1) Information about chemical bonding in the solid state.

(2) Molecular structure information.

(3) Characterization of molecular or ionic species (i.e. as a finger print technique).

(4) Test for electronics wave functions used in calculating theoritical coupling constants.

(5) Crystallographic and molecular symmetry information.

(6) Detection of phase transitions.

(7) Solid state molecular motion studies.

12.4.1 Solid State application :

(1) Line splittings due to crystallographic in equivalence : In the solid state a molecule will be subjected to slight perturbations due to its environment by means of many intermolecular forces and this often has the effect of causing a distortion from ideal symmetry. Thus a molecule like $SiCl_4$ or $GeCl_4$ which has tetrahedral symmetry in the vapour phase loses this in the solid state and four chlorine atoms become crystallographically inequivalent. This results in a four line NQR spectrum. Here the solid state splittings of the order of 200 kHz but values 500 kHz are typically found. Atoms which are chemically different usually give rise to splittings greater than this. The number of lines which are observed for each transition in NQR spectrum is equal to the number of crystallographically in equivalent nuclear sites in the asymetric unit of unit cell. This means that a full NQR spectrum can decide a point symmetry of the molecule if the space group and the number of molecules in the unit cell are known. The latter can be found from the unit cell dimensions and the density.

12.4.2 Phase transitions : The ability of NQR to detect crystallographic inequivalence can be used as a means for studying the phase transitions in the solid state. A phase transition is indicated when there is a large change in the number of resonance lines or when there is an abrupt cahnge in the curve of NQR frequency versus temperature. These effects occur because of the sensitivity of the frequency to intermolecular forces and to low freuquency modes, so any change in these will be detected. The phase transitions in many molecules have been studied by this method.

12.4.3 Zeeman Studies : The resonance line splitting caused by the application of a magnetic field to a single crystal specimen enables η to be determined and the orientation of the principal axies of the electronic field gradient tensor to be found with respect to those of the crystal. If the molecular symmetry enables these axes to be related to the molecular axes, the orientation of the molecules in the crystal lattice can be found. However, large single crystals are not always available so the technique is not so easy to apply. The splitting of the zero field lines is dependent upon the orientation of the crystall with respect to magnetic field direction. By studying the nature of this dependence the orientation of the field gradient axes can be found. In the case of p-chlorophenol a single crystal ^{35}Cl NQR study was able to give almost a full crystal structure determination.

When a powder sample is used the crystallites are oriented in a random fashion so the application of a magnetic field causes the lines to be smeared out. However of the zero field resonance are of sufficient intensity the application of a weak magnetic field allow some residual splitting to be observed. The magnitude of this can be related to the value of η if the field strength is known. This technique is useful for spin $3/2$ nuclei (e.g. ^{35}Cl) where η is not obtainable directly from the NQR spectrum.

12.4.4 Molecular motion : The normally observed reduction in NQR frequency with increase in temperature is caused in the majority of cases by the increasing amplitudes of molecular thermal motion which have a partial averaging effect on the electric field gradient. Angular motion or librations are often responsible for the temperature depenence and the frequency of these can be calculated using an expression by Bayer. Some correlation with observed vibration frequencies is possible using infrared, Raman and neutron inelastic scattering spectroscopy. The temperature dependence of the spin - lattice relaxation time T_1 is also a powerful technique for the evaluation of energy barriers associated with solid state molecular motion.

12.4.5 Hydrogen bonding : The quadrupole coupling constants of nuclei in many hydrogen - containing molecules is often observed to be greater in the vapour state (as obtained by microwave measurements) than in the solid (NQR). For example the ^{35}Cl quadrupole coupling constatn for HCl is 21 percent smaller in the solid state than in the vapour. The ^{14}N quadrapole coupling constant in NH_3 is also smaller by 22.5 percent in the solid state. A reduction in quadrupole coupling constant on going from the gas to the solid state is often observed but these shifts are very much larger than the average and appear to be due to a reduction in the field gradient at the nucleus caused by strong intermolecular hydrogen bonding in the solid state.

Hydrogen bonds are also detectable by solid state measurements alone. For instance the ^{35}Cl NQR spectrum of Sodium Tetra Chloroaurate dihydrate observed by Fryer and Smith shows four resonances one of which is about 2.5MHz lower at 77K. The lower frequency signal is attributed to a chlorine atom which involved in two hydrogen bonds to adjacent water molecules. This resonance shows a shift in frequency upon deuteriation of the sample where as the upper resonance frequencies are unaffected. The anomalous temperature dependence of the lower frequency resonance is caused by the gradual break down of the hydrogen bonding because of larger thermal motion of the H_2O molecules as the temperature is increased. The NQR deuteriation shift is negative the substitution of D for H is expected the motional amplitude of the water molecule and increase the hydrogen bonding interaction.

The ^{35}Cl NQR spectrum of 4 chloropyridinium hexachlorostannate also shows an anomaly low frequency line due to $SnCl_6^{2-}$ ion. Brill and Welsen observed four lines at 14.97, 17.32, 17.52 and 35.92 MHz at (298K).

The latter high frequency line is due to $C - {}^{35}Cl$ from the cation. An Xray study infact showed a tetragonally distorted anion, the two long $Sn - Cl$ bonds of which were $N-H \cdots\cdots Cl$ hydrogen bonding with cation.

The simplest hydrogen bond which is open to investigation by NQR is that in the hydrogen chloride ion, HCl_2^- asymmetrical $\left(Cl-H\cdots Cl \quad \text{Type I}\right)$ and symmetrical $\left(Cl-H-Cl, \quad \text{Type II}\right)$ forms of the ion exist and their different structures are reflected in large shift (8 MHz) in their ^{35}Cl resonance frequencies type I icons were found to be ^{35}Cl frequencies of about 20 MHz (assigned to the more covalently bonded chlorine atom) while Type II ion exhibited a lower frequency 12 MHz. Type I ion showed a positive deuteriation shift of 0.7 MHz which is of opposite sign to that observed in $Na\ Au\ Cl_4\ \ 2H_2O$. This is because hydrogen bond is no longer intermolecular but is the major source of field gradient in the ion. Type II ions showed hardly any deuteriation shift but this is to be expected if the proton or deunteron is situated in a symmetrical potential well.

Table 12.2

NQR frequencies observed for molecules containing halogen bridges

Molecule	Nucleus	Terminal Halogen frequency MHz	Bridge Halogen frequency MHz	Temp(K)
$GaCl_3$	^{35}Cl	19.084, 20.225 $\eta = 8, 9, 3.4\%$	14.667 $\eta = 47.3\%$	306
$AuCl_3$	^{35}Cl	31.116, 33.340	23.285	77
$I\,Cl_3$	^{35}Cl	33.413, 34.918	13.740	297
$Al\,Br_3$	^{79}Br	113.790, 115.450	97.945	77

12.4.6 Molecular Structure : In many instances the NQR spectrum itself can provide direct structural information. Halogen quadrupole resonance frequencies respond predominantly to ionic character of the $M-Cl$ and on this basis frequency shift tables can be drawn up, Tables $M-Cl$ and $C-Cl$ group frequences have been published by Semin. In both tables there is a considerable spread of frequencies in a particular band which is not surprising in view the sensitivity of NQR frequencies to substituent effects and lattice effects. As an example of the use of group frequency table, consider the NQR spectrum of trichloro acetyl chloride $C\,Cl_3\,Co\,Cl$. Four resonances are observed at 33.72, 40.13, 40.47 and 40.46 MHz. The lower frequency line is described to the $Co\,Cl$ group and the upper three lines to CCl_3 group. This type of analysis can be used for many halogen containing organic compounds.

In ionic compounds the NQR frequencies of halide containing ions are often a useful 'finger print' for their identifications in compounds of unknown structure. Such as ions as $B\,Cl_4^-$, $Al\,Cl_4^-$, PCl_4^+, PCl_6^- and $Sb\,Cl_6^-$ have been identified this way.

Atoms of different chemical sites in a molecule will also exhibit a difference in their NQR frequency. For example the NQR spectrum of tetra chloro (phenyl) arsenic (V) $Pn\,AsCl_4$, shows that four ^{35}Cl resonances in the form of two doublets separated by almost 10 MHz. This spectrum is consistent with trigonal bipyramidal structure in which the pheyl group is equitorially located. As expected chemically the two axial chlorines are considerably more ionic than those in equatorial positions and therefore their resembles occur at a lower frequency. The two chlorine atoms are not crystallo graphically equivalent and consequently have slightly different resonance frequencies. The same is true for the equatorial chlorine atoms.

12.5 Summary :

(1) NQR spectroscopy resembles NMR spectroscopy in the sense energy levels are caused for the different orientations of nuclear dipole moment. The transitions are caused by the application of external radio frequency oscillator to cause absorption and change in the nuclear orientations. The difference in NQR and NMR lies in the creation of energy levels. In NMR energy levels are created by the interaction of the nuclear magnetic dipole moment with the application of steady magnetic induction $\overline{B_0}$. In NQR, energy levels are inherently available in the system it self due to the interaction of electric quadrapule moment in to the electricfield gradient tensor (nuclear / molecular property) at the site of the nucleus.

(2) Unlike NMR, NQR is carried out by varying the frequency to observe NQR signals.

(3) NQR spectrometers are of three types namely super Regenerative type, continuous wave type and pulse method type. Every spectrometer has its merits and demerits also.

(4) Nuclear Quadrupole resonance spectroscopy is also a powerful tool to know about molecular properties, type of bonding etc.

12.6 Keywords :

Nuclear Quadrupole moment, Electric field gradient tensor, axial symmetry, Quadrupole coupling constant, NQR resonance frequencies, Relaxation time T_1, continuous wave, Super Regenerative, Pulse method type spectrometer, Frequency modulation, Zeeman effect studies, Temperature Versus NQR frequencies.

12.7 Review Questions :

(1) Explain the principle of NQR ? What are the requirements of observing NQR phenomena. Explain NQR transitions with half integral spins and Integral spins.

(2) Explain various types of NQR spectrometers and high light the type of information to be obtained from there spectrometer.

(3) Explain NQR phenomenon, what are the applications of NQR spectroscopy.

12.8 Text and Reference Books :

1. Nuclear Magnetic Resonance by ER Andrew Cambridge University Press
2. Spectroscopy by BP Straughen and S Walker (John Wiley)
3. Physical Methods in Inorganic Chemistry by R.S. Drago (East - West Edition)
4. Molecular structure and Spectroscopy by Arul dhas (PHI)
5. Fundamentals of Molecular Spectroscopy by C.B. Banwell

Unit - III

Lesson - 13

PROBLEMS IN MAGNETIC RESONANCE
NMR, ESR & NQR

Aim : To work out different type of problems in Magnetic Resonance (NMR, ESR & NQR).

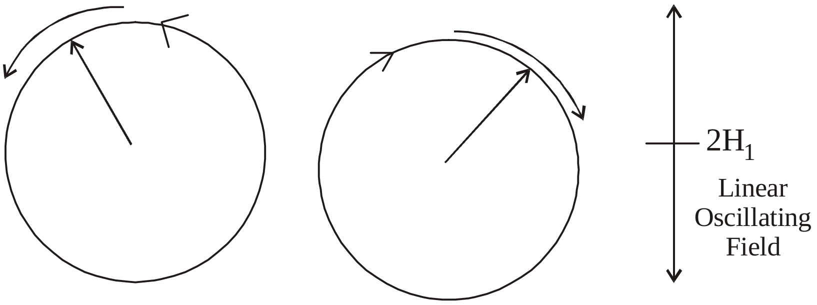
Objective of the lesson :

1. To chalk out various problems in Nuclear Magnetic Resonance and to know structural relation of the compound from problems worked out.
2. To identify the variety of problems in Electron spin Resonance and to know how the solutions are helpful in knowing molecular structure or crystal structure.
3. To scan the different concepts of nuclear quadrupole resonance and work out for the problems and to infer applications of Nuclear Quadrupole Resonance technique.

Structure of the lesson :

13.1 Problems in Nuclear Magnetic Resonance (NMR)

(1) Illustrate that a linear oscillating magnetic field of amplitude $2H_1$, is the combination of two rotating fields, moving in opposite direction with an amplitude of H_1



Rotating fields of amplitude H_1 moving in opposite senses

Let $H_1 e^{\pm i\omega t}$ is the rotating field moving in the opposite direction. i.e. $H_1 e^{i\omega t} + H_1 e^{-i\omega t}$

$$H_1\left[e^{i\omega t} + e^{-i\omega t}\right] = H_1[\cos\omega t + \sin\omega t] + H_1[\cos\omega t - i\ \sin\omega t]$$

$$= 2H_1 \cos\omega t$$

at $\omega t = 0$, $H_1 + H_1 = 2H_1$ --------------- (1)

at $\omega t = \frac{\pi}{2}$, $H_0(0) + H_1(0) = 0$ ------------(2)

at $\omega t = \pi$, $2H_1(-1) = -2H_1$ --------------- (3)

at $\omega t = \frac{3\pi}{2}$, $2H_1(0) = 0$ ------------------ (4)

and $\omega t = 2\pi$, $2H_1(1) = 2H_1$---------------- (5)

(1), (2), (3), (4) and (5) constitute a linear oscillating with an amplitude of $2H_1$.

(2) The magnetic moment of $CO^{59} = 4,6163\,NM$ (Nuclear Magneton), what would be the resonance frequency of Cobalt nuclei in a field of 1 Tesla. Given the proton magnetic moment is 2.7942 NM (Nuclear Magneton and I for cobalt = $\frac{7}{2}$) and Proton resonance frequency is 42.6 MHz is a field of 1 Tesla.

The successive energy levels in NMR experiment is given by

$h\upsilon = \frac{\mu B_0}{I}$, where μ is magnetic moment of the nucleus B_0 is the applied 1 Tesla. I is the Nuclear spin Number.

$$\upsilon = \frac{\mu B_0}{I h}$$

$$\upsilon_{CO} = \frac{\mu_{CO} B_O}{I_{CO} h} \text{ and } \upsilon_P = \frac{\mu_P B_0}{I_P h}$$

$$\frac{\upsilon_{CO}}{\upsilon_P} = \frac{\frac{\mu CO B_0}{ICO h}}{\frac{\mu_P B_0}{Ip h}} = \frac{\mu_{CO}}{I_{CO}} \frac{Ip}{\mu p} = \frac{4.6163 (NM) \times \left(\frac{1}{2}\right)}{2.7942 (NM) \times \left(\frac{7}{2}\right)}$$

$$\upsilon_{CO} = (\upsilon_p) \frac{\mu_{CO}}{I_{CO}} \frac{I_p}{\mu_p} = \frac{(42.6)\ 4.6163}{2.7942} \times \frac{1}{7}$$

$$= \frac{196.654}{19.559} = 10.05 \text{MHz}$$

(3) Find the gyro magnetic ratio of proton, the resonance frequency of proton is 42.6 MHz in a field of 1 Tesla.

We have $\omega_0 = \gamma B_0$ or $\gamma = \frac{\omega_0}{B_0}$

$$\gamma = \frac{2\pi \upsilon_0}{B_0} = \frac{2\pi(42.6) \times 10^6}{10^4 \text{ oerested}} = \frac{2(3.14)\ 42.6 \times 10^6}{10^4}$$

Gyro magnetic ratio of proton = 2.675×10^4

(4) Given the proton magnetic moment $= 2.7942 \times 5.051 \times 10^{-27}\ J/T^{-1}$ and Electro magnetic moment $= 9.274 \times 10^{-24}\ J/T^{-1}$. Resonance frequency for protons in a field of 1T is 42.6 MHz. Evaluate the resonance frequency electron in the same field of 1T.

$$\upsilon = \frac{\mu B_0}{I h}$$

or $\upsilon_p = \dfrac{\mu_p B_0}{\left(\frac{1}{2}\right) h}$ and $\upsilon_e = \dfrac{\mu_e B_0}{\left(\frac{1}{2}\right) h}$

$$\therefore \left(\frac{\upsilon_e}{\upsilon_p}\right) = \frac{\dfrac{\mu_e B_0}{\frac{1}{2}h}}{\dfrac{\mu_p B_0}{\frac{1}{2}h}} = \frac{\mu_e B_0}{\mu_p B_0} = \left(\frac{\mu_e}{\mu_p}\right)$$

$$\upsilon_e = \left(\upsilon_p\right)\frac{\mu_e}{\mu_p} = \frac{9.274\times10^{-24}}{2.7942(5.051)\times10^{-27}}(42.6)\times10^6$$

$$\upsilon_e = \frac{395.0724\times10^{-18}}{14.1135\times10^{-27}} \simeq 28\,\text{GHz}$$

(5). Find the nuclear g factor of proton given that proton magnetic moment is 2.7942 NM (Nuclear Magneton)

We have the nuclear g factor of any nucleus is given by

$g_N = \dfrac{\mu}{\mu_N I}$, where μ is the magnetic moment of the nucleus, μ_N is the nuclear magneton

$\therefore$ Nuclear g factor of proton is $g_p = \dfrac{\mu_p}{\mu_N I} = \dfrac{2.7942(\text{NM})}{\left(\frac{1}{2}\right)1.00(\text{NM})}$

$g_N = 5.5884$ (Nuclear g factor of proton).

(6) What is the nuclear g factor for CO^{59} given that & magnetic moment of Cobalt is 4.6163 nuclear magneton and I of $CO^{59} = 7/2$

$$g_{CO} = \frac{\mu_{CO}}{\mu_N I} = \frac{4.6163\mu_N}{\mu_N\left(\frac{7}{2}\right)} = \frac{4.6163\times2}{7} = 1.3189$$

(7) Calculate the strength of magnetic field to give a precessional frequency of 100 MHz for ^{17}O nucleus given

$$g_N = 0.757,\ \mu_N = 5.051\times10^{-27}\ \text{J/T},\ I = \frac{5}{2}$$

The resonance frequency of any two adjacent levels is given

$$h\upsilon = g_N \mu_N B_0 \text{ or } B_0 = \frac{h\upsilon}{g_N \mu_N}$$

$$B_0 = \frac{6.626\times10^{-34}\times100\times10^{6}}{0.757 \times 5.051\times10^{-27}} \simeq 17.33 \text{ Tesla}$$

(8). What is the nuclear resoance frequency of ^{19}F nucleus given that $g_F = 5.2546,$ and $\mu_N = 5.051\times10^{-27}$ J/T for a field of 1 Tesla,

Basic equation is $h\upsilon_F = g_N \mu_N B_0$

$$\upsilon_F = \frac{5.2546 \times 5.051 \times 1}{6.626\times10^{-34}} = 40.05 \text{ MHz}$$

(9). In the NMR spectrum of ^{14}N, with $I=1$, how many spectral lines will be observed ? Calculate the frequency required for the NMR line in an external field of 1 Tesla $(g_N = 0.403)$.

A nucleus with spin I, when placed in a magnetic field will have $(2I+1)$ levels equally spaced energy levels. The energy separation between any two adjacent levels is $g_N \mu_N B_0$. Hence only one line will be observed whose frequency is given by

$$\upsilon = \frac{g_N \mu_N B_0}{h} = \frac{0.403 \times 5.051 \times 10^{-27}\times1.00}{6.626\times10^{-37}} = 3.07 \text{ MHz}$$

(10). Calculate the difference in energies of protons oriented with and against of strength of 1.5 Tesla. What is the frequency of radiation the photons have with this energy ? $g_N = 5.5857$

We have the energy separation $g_N \mu_N B_0$

i.e. $\Delta E = g_N \mu_N B_0 = 5.5857 \times 5.05 \times 10^{-27} \times 1.5$

$$= 4.231\times10^{-26} \text{ Joules}$$

The frequency of radiation equivalent to this energy is

$$\upsilon = \frac{4.231\times 10^{-26}\,\mathrm{J}}{6.626\times 10^{-34}\,\mathrm{J\cdot S}} = 6.3854\times 10^{7}\,\mathrm{S}^{-1}$$

$$= 63.854\ \mathrm{MHz}\,.$$

(11). A system of protons at a temperature of $25^0\,\mathrm{C}$ in a magnetic field of 2T. What is the ratio of proton spins in the lower state to the number in the upper state. If N_0 is the number in the ground state and N_1 in the upper state according to Boltzmann distribution.

Boltzmann constant is 1.381×10^{-23} J/T

$$N_0 = N_1 \exp\frac{\Delta E}{kT}$$

$$\Delta E = g_N\ \mu_N\ B_0 = 5.585\times\left(5.051\times 10^{-27}\,\mathrm{JT}^{-1}\right)\times 2\mathrm{T}$$

$$= 56.42\times 10^{-27}\,\mathrm{J}$$

$$\frac{\Delta E}{kT} = \frac{56.42\times 10^{-27}}{1.381\times 10^{-23}\times 298} = 13.71\times 10^{-6}$$

$$\frac{N_0}{N_1} = e^{0.000014} = 1.000014$$

(12). A particular NMR instrument operates at 30.256MHz. What magnetic fields are required to bring a proton nucleus and a $^{13}\mathrm{C}$ nucleus to resonance at this frequency magnetic moment of proton = 2.7927 μ_N and magnetic moment of $^{13}\mathrm{C} = 0.7022\,\mu_N$, For $^{13}\mathrm{C}$, $I = \frac{1}{2}$.

We have $h\upsilon = \frac{\mu B_0}{I}$, $B_0 = \frac{h_\upsilon I}{\mu}$

For proton $$B_0 = \frac{\left(6.626\times 10^{-34}\times 30.256\times 10^{6}\right)\left(\frac{1}{2}\right)}{2.7927\times 5.051\times 10^{-27}}\ \mathrm{T}$$

$$B_0 = 0.710\ \mathrm{Tesla}$$

For ^{13}C $\quad B_0 = \dfrac{6.626\times10^{-34}\times30.256\times10^{6}\times\frac{1}{2}}{0.7022\times5.051\times10^{-27}} = 2.826 \text{ Tesla}$

(13) An NMR signal for a compound is found to be 180 Hz downward from TMS peak using a spectrometer operating at 60 MHz. Calculate the chemical shift in ppm.

Chemical shift in ppm $= \dfrac{\text{chemical shift in Hz}}{\text{operating frequency in MHz}} = \dfrac{180}{60} = 3\text{ppm}$

(14). Calculate the frequency for proton resonance at 1.5 T, compare this with vibrational frequency in Hz, $\bar{\upsilon}_{vib} = 4390 \text{ cm}^{-1}$ and rotational frequency for the $J=0\rightarrow1$ transition

Proton resonance frequency in a field of 1 Tesla is 42.5772 MHz.

Rotational constant $B = 60\,\text{cm}^{-1}$

$$\bar{\upsilon}_{J\rightarrow J+1} = 2B(J+1)\text{ cm}^{-1}$$

$$\bar{\upsilon}_{0\rightarrow1} = 2\times60\text{ cm}^{-1} = 120\,\text{cm}^{-1}.$$

$$\upsilon_{nmr} = \left(42.5772\times10^{6}\right)(1.5) = 63.8658\times10^{6}\text{ Hz}$$

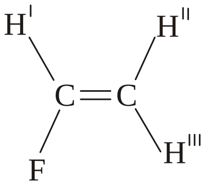
$$\bar{\upsilon}_{nmr} = \frac{\upsilon_{nmr}}{c} = \frac{63.8658\times10^{6}}{3\times10^{10}} = 21.2886\times10^{-4}\text{ cm}^{-1}.$$

$$\frac{\bar{\upsilon}_{vib}}{\bar{\upsilon}_{nmr}} = \frac{4390}{21.2880\times10^{-4}} = 206.21\times10^{4}$$

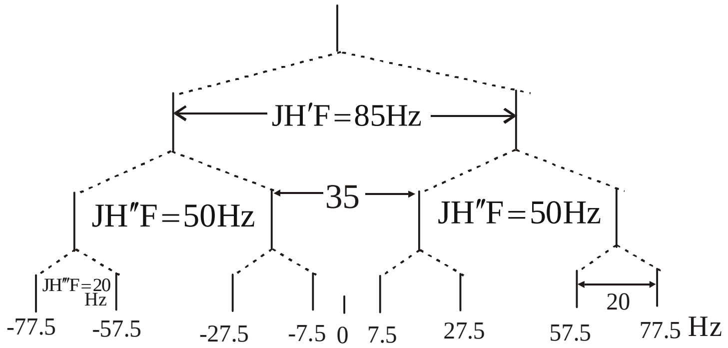
$$\frac{\bar{\upsilon}_{rot}}{\bar{\upsilon}_{nmr}} = \frac{120}{21.2886\times10^{-4}} = 5.64\times10^{4}$$

Thus $\bar{\upsilon}_{vib}$ is 206×10^{4} times larger than $\bar{\upsilon}_{nmr}$ and $\bar{\upsilon}_{rot}$ is 5.6×10^{4} times larger than $\bar{\upsilon}_{nmr}$

(15). Analysis of the NMR spectrum of Vinyl fluoride gives the following spin - spin coupling constant. Sketch the NMR diagram spectrum of fluorine nucleus.



$J_{H'F} = 85\text{ Hz},\ J_{H''F} = 50\text{ Hz},\ J_{H'''F} = 20\text{ Hz}$



Stick diagram of the first order flourine NMR spectrum of vinyl fluoride

(16). The nucleus ^{11}B has $I=\frac{3}{2}$ and $g_N = 1.792$ calculate its energy levels in a magnetic field1.5T.

A nucleus with spin $I=\frac{3}{2}$, placed in a magnetic field will have $2I+1 = 2\times\frac{3}{2}+1=4$ equally spaced energy levels. The energy separation between any two adjacent levels is $g_N\,\mu_N\,B_0$. Hence the energy separation between any two successive levels of the present problem is given by

$$g_N\,\mu_N\,B_0 = (1.792)5.051\times10^{-27}\times1.5$$

$$= 9.3685\times10^{-27}\text{ J}$$

The resonance frequency is given by

$$\upsilon=\frac{9.3685\times10^{-27}\text{ J}}{6.626\times10^{-36}} = 1.4139\times10^{7}\text{ Hz}$$

$$=14.139\,\text{MHz}$$

(17) Calculate the magnetic field strength required to get a transition frequency of 60 MHz for fluorine $g_N = 5.255$, we have the resonance condition given as

$h\upsilon = g_N \mu_N B_0$ or

$$B_0 = \frac{h\upsilon}{g_N \mu_N} = \frac{6.626\times10^{-34} \times 60\times10^6}{(5.255)(5.051)\times10^{-27}} = \frac{14.97}{10}$$

$$= 1.497\,\text{Tesla}$$

(18) Calculate the ratio of population of two nuclear spin states for protons in magnetic field of 4T and at 27^0C. $k = 1.381\times10^{-23}\,\text{J/T}$ (Boltzmann constant)

N_0 is the population in the lower energy state

N_1 is the population in the higher energy state

According to Boltzmann distribution

$$N_0 = N_1 \exp\frac{\Delta E}{kT}$$

$$\Delta E = g_N\ \mu_N\ B_0, \quad kT = 1.381\times10^{-23}(300)$$

$$\frac{N_0}{N_1} = \exp\frac{\Delta E}{kT} \text{ and } \Delta E = 5.585\times5.051\times10^{-27}\times 4\,\text{J}$$

$$= 112.839\times10^{-27}$$

$$\frac{\Delta E}{kT} = \frac{112.839\times10^{-27}}{1.381\times10^{-23}\times300} = 0.27236\times10^{-4}$$

$$\frac{N_0}{N_1} = e^{0.000027236} = 1.000027236$$

(19). Calculate the energy difference of two protons oriented with and against the magnetic field strengt 2 Tesla. What is the frequency of radiation of this energy $g_N = 5.5857$

Energy separation = $g_N \mu_N B_0 = 5.5857\times5.051\times10^{-27}\times2$

$$5.642\times10^{-26}\ \text{J}$$

The frequency of radiation equivalent to this energy is

$$\upsilon = \frac{5.642 \times 10^{-26}\,\mathrm{T}}{6.626 \times 10^{-34}} = 0.85149 \times 10^{8}\ \mathrm{Hz} \text{ or } 85.149\ \mathrm{MHz}.$$

(20). The frequency separation between protons in $C_6\ H_6$ and TMS is 510.5 Hz when the field is 1.65T, what is the chemical shift $g_N = 5.585$

$$\text{chemical shift } \delta = \frac{\upsilon_s(\text{sample}) - \upsilon_r(\text{Reference})}{\upsilon_0} \times 10^6\ \mathrm{PPm}.$$

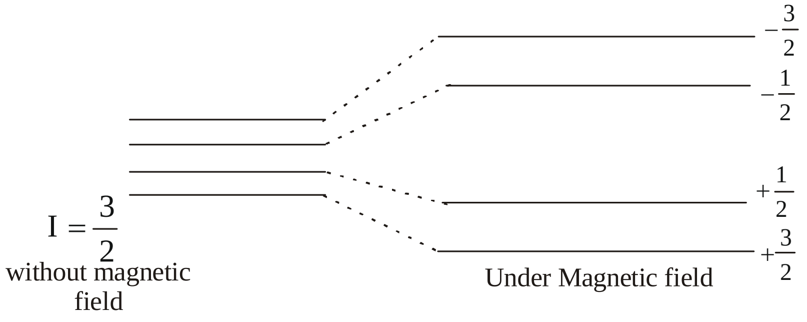
$$\upsilon_0 = \frac{g_N\ \mu_N\ B_0}{h} = \frac{5.585 \times 5.051 \times 10^{-27} \times 1.65}{6.626 \times 10^{-34}} = 70.2 \times 10^6\ \mathrm{MHz}$$

$= (\upsilon_s \text{ sample} - \upsilon_r \text{ reference})$ is given as 510.5 Hz.

$$\delta = \frac{510.5\,\mathrm{Hz}}{70.2 \times 10^6\ \mathrm{Hz}} \times 10^6\ \mathrm{ppm} = 7.272\,\mathrm{ppm}$$

(21). K^{39} has $I = \frac{3}{2}$ and nuclear g factor 0.2606 (a) Draw a diagram to show all possible orientations of magnetic moment of ${}^{39}K$ nucleus in magnetic field (b) calculate the transition frequency of one of these orientation to an adjacent one in a field of 0.1 T (Nuclear magneton $\mu_N = 5.0504 \times 10^{-27}\ \mathrm{JT}^{-1}$.

(a) For ${}^{39}K$, $I = \frac{3}{2}$ possible M_I values $+\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. The possible will be



(b) The energy is given as $E = \mu_N\ g_N\ B\, m_I$

$$\text{and } \Delta E\left[m_I = \frac{3}{2} \rightarrow m_I \frac{1}{2}\right] = \mu_N\, g_N\, B$$

$$0.2606 \times 5.054 \times 10^{-27}\,\mathrm{J\,T^{-1}} \times 0.1\,\mathrm{T} = 1.3 \times 10^{-28}\,\mathrm{J}$$

Transition frequency $= \dfrac{\Delta E}{h} = \dfrac{1.3 \times 10^{-28}\,\mathrm{J}}{6.626 \times 10^{-34}\,\mathrm{JS^{-1}}} = 0.2 \times 10^{6}\,\mathrm{S^{-1}}$

$$= 0.2\ \mathrm{MHz}$$

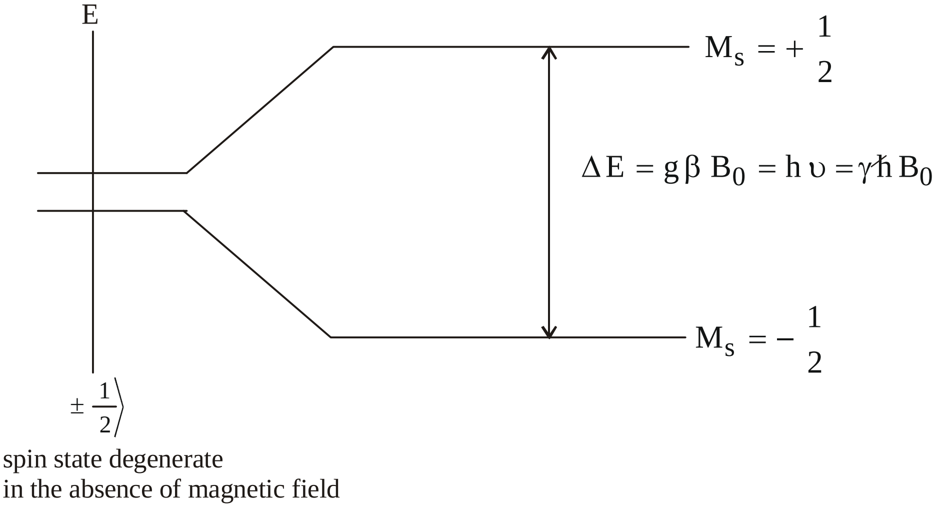
(22) A NMR spectrometer operating at 60 MHz frequency gives proton spectra at a field of 1.4092T. At what field would $^{11}\mathrm{B}$, be observed $I=\frac{3}{2}$ and $g=1.7920$, operating frequency $= 60\times10^{6}\ \mathrm{Hz}$ and

$$\upsilon = 60\,\mathrm{MHz} = \frac{\Delta E}{h} = \frac{g_N\,\mu_N\,B}{h} = \frac{1.7920 \times 5.504\times10^{-27}\ \mathrm{J\ T^{-1}}}{6.626\times10^{-34}\ \mathrm{JS}} \times B$$

$$B = \frac{60\times10^{6} \times 6.626 \times 10^{-34}\,\mathrm{JS^{-1}}}{1.7920\times5.504\times10^{-27}} = 43.93\times10^{-1} = 4.393\,\mathrm{T}$$

13.2 Problems in Electron spin Resonance (ESR)

(1) Sketch the electron energy levels in the field of magnetic induction and obtain the relation of $\omega_0 = \gamma H_0$ and what is the relationship between γ and g of electron what are selection rules for EPR transitions. We have the splitting of energy levels of an electron with $S=\frac{1}{2}$ in the preseence of a magnetic induction B_0 as follows.



$$H = -\overline{\mu_e}\cdot\overline{B_0} = +g_e\mu_B\ B_0\ \left|S_z\right\rangle_{\pm\frac{1}{2}}$$

$$= g_e\ \mu_B B_0\left(\frac{1}{2}\right) - g_e\mu_B\ B_0\left(-\frac{1}{2}\right)$$

$$= g_e\mu_B B_0$$

We have $\gamma\hbar B_0 = g_e\mu_B B_0$ or $\gamma_e = \frac{g_e\mu_B}{\hbar}$

gyro magnetic ratio of fine electron is given by

$$\gamma_e = \frac{g_e\mu_B}{\hbar} = \frac{(2.0023)\ (9.274)\times 10^{-24}}{1.0545\times 10^{-34}\ \text{Joule sec}}\ \text{Joule/Tesla}$$

$$= 17.60\times 10^{10}\ \text{Rad/sec/Tesla}\cdot$$

We have $h\upsilon_0 = g_e\mu_B B_0$

$$\upsilon_0 = \frac{g_e\mu_B B_0}{h},\ 2\pi\upsilon_0 = \frac{g_e\mu_B B_0}{\frac{h}{2\pi}}$$

$$\omega_0 = \left(\frac{g_e\mu_B}{\hbar}\right)B_0\ \text{ or }\ \omega_0 = \gamma_e B_0$$

This is the Larmor precessional frequency.

(2) Write down the general expression for g in molecules / atoms / crystals and deduce the value of g for free electron and show for free electron precise value of $g=2.0023$. The general expression for g factor of electrons in molecules 1 atom / crystals is given by

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

For a free electron $L = 0,\ S = J$

$$\therefore g = 1+\frac{S(S+1)+S(S+1)}{2S(S+1)} = 2.000$$

$\overline{\mu_e} = -\, g_e \, \mu_B \, \overline{S}$ (Negative sign indicates that magnetic moment and spin are in opposite direction)

Spin of the electron $= \frac{1}{2}$, $\therefore 2\overline{\mu}_e = g_e \, \mu_B$

or $$g_e = \frac{2\mu_e}{\mu_B} = \frac{2\left(9.2838 \times 10^{-24} \text{ JT}^{-1}\right)}{\left(9.274 \times 10^{-24} \text{ JT}^{-1}\right)} = 2.0021$$

(3) Electron spin resonance is observed for atomic hydrogen with an instrument operating at 9.5 GHz. If the g value of the electron in the hydrogen atom is 2.0026, what is the magnetic field needed to observe ESR signal.

$$\mu_B = 9.274 \times 10^{-24} \text{ JT}^{1}$$

$$E = h\upsilon_e = g_e \, \mu_B \, B \text{ or } B = \frac{h\upsilon_e}{g_e \, \mu_B}$$

$$B = \frac{6.626 \times 10^{-34} \times 9.5 \times 10^{9}}{2.0026 \times 9.274 \times 10^{-24}} = 0.339 \text{ Tesla}$$

(4) A free electron is placed in a magnetic field strength of 1.3T. Calculate the resonance frequency if $g = 2.0023$.

Resonance frequency of the electron is

$$\upsilon_e = \frac{g_e \, \mu_B \, B}{h} = \frac{2.0023 \times 9.274 \times 10^{-24} \, 1.3}{6.626 \times 10^{-34}}$$

$$= 3.643 \times 10^{10} \text{ Hz} = 36.43 \text{ GHz}$$

(5) A sodium atom $\left(I = \frac{3}{2}, S = \frac{1}{2}\right)$ in the zero field has the Hamiltonian $H = a \, \overline{I} \cdot \overline{S}$. Find the energy levels and transitions.

Sodium has one valance electron, the Hamiltonian is

$$H = a \, \overline{I} \cdot \overline{S}$$

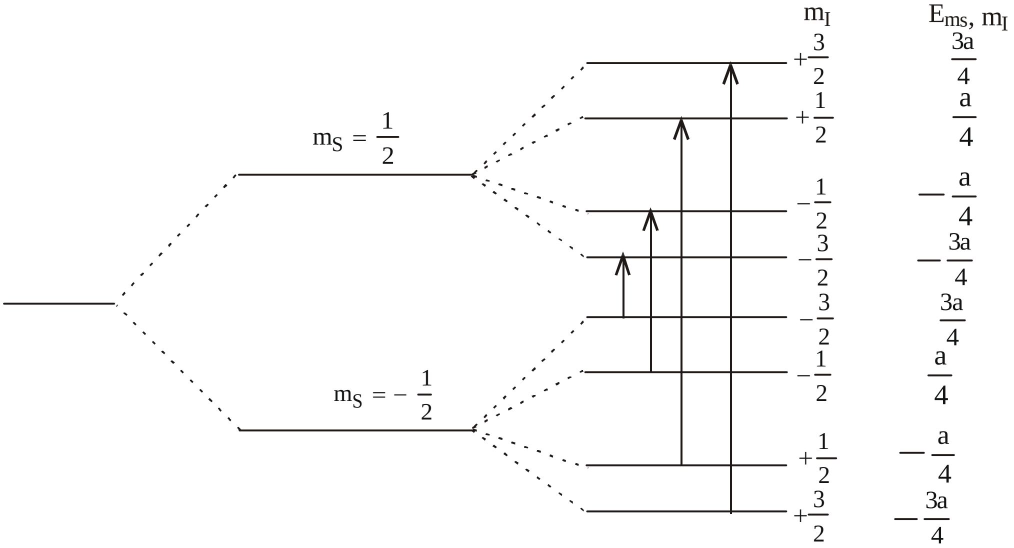
Energy $E_{m_s, m_I} = a_{m_s} \, m_I$, $m_s = \pm \frac{1}{2}$, $m_I = \pm \frac{3}{2}, \pm \frac{1}{2}$

For a given m_s, m_I will have 4 orientations.

For $m_S = \frac{1}{2}$, the $(m_S,\, m_I)$ combinations will be $\left(\frac{1}{2}, \frac{3}{2}\right), \left(\frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, -\frac{1}{2}\right)$ and $\left(\frac{1}{2}, -\frac{3}{2}\right)$

similarly for $m_S = -\frac{1}{2}$ there will be four combinations.

The selection rules are $\Delta m_S = \pm 1$ and $\Delta m_I = 0$. Four transition of equal intensity will result transitions are illustrated in the following



Energy levels and transitions of a free electron coupling with a sodium nucleus $I = \frac{3}{2}$ (energies are with respect to $m_S = \frac{1}{2}$ and $m_S = -\frac{1}{2}$ respectively).

(6) The electron in atomic hydrogen has $g = 2.0032$ in a spectrometre 9.250 GHz, two lines from H appeared at 357.3 and 306.6 mT. Calculate the hyperfine coupling constant.

$$E = h\upsilon = g\mu_B B + h_a\ M_I \quad \text{or} \quad g\mu_B B = h\upsilon - h a M_I$$

$$B = \frac{h}{g\mu_B}\left[\upsilon - a M_I\right] = \frac{6.626 \times 10^{-34}\,\text{JS}\left[9.25 \times 10^9 - a M_I\right]}{(2.0032)\ 9.2732 \times 10^{-24}}$$

$$= 0.3567 \times 10^{-10}\left[9.25 \times 10^9 - a M_I\right]$$

For $M_I = -\frac{1}{2}$ and for $B = 357.3\,mT$

$$0.3573T = 3.567\times10^{-11}\left[9.25\times10^9 + \frac{a}{2}\right] \text{------------ (1)}$$

and For $M_I = \frac{1}{2}$, $B = 306.6\,mT$

$$0.3066T = 3.567\times10^{-11}\left[9.25\times10^9 - \frac{a}{2}\right] \text{----------- (2)}$$

Subtracting (2) from (1), we get

$$0.0507 = 3.567\times10^{-11}\ a\ \cdot$$

$$a = \frac{0.0507}{3.567\times10^{-11}} = 1.42\times10^9\ Hz$$

(7) An unpaired electron interacts with n_1 nuclei of spin I_1 and n_2 nuclei of spin I_2. Show that the number of hyperfine components is given by $N = (2n_1 I_1 + 1)(2n_2 I_2 + 1)$.

Hence generalise the result

The effective spin of n_1 nuclei of spin $I_1 = n_1 I_1$.

Spin $n_1 I_1$ splits a level into $(2n_1 I_1 + 1)$ components. Similarly n_2 nuclei of spin I_2 will split a level into $(2n_2 I_2 + 1)$ components

Therefore the number of hyperfine components

$$N = (2n_1 I_1 + 1)(2n_2 I_2 + 1)$$

Generalising, if an unpaired electron interacts with n_1 nuclei of spin I_1, n_2 nuclei of spin I_2, n_3 nuclei of spin I_3 and so on, the number of hyperfine component N will be given by $N = (2n_1 I_1 + 1)(2n_2 I_2 + 1)(2n_3 I_3 + 1)\cdots\cdots$

(8) Evaluate the method of solving anisotropic g factors and anisotropic hyperfine coupling constants.

Anisotropic g factors :

First let us assume that there is no hyperfine interaction in the spectrum and that the hamiltonian H $= \mu_N \, g \cdot \overline{B} \cdot \widehat{S}$ can therefore be taken to represent such a system. The simplest case to examine is that in which unpaired electron occupied a site about which there is cubic or spherical symmetry. In such a case g remains isotropic and the Hamiltonian has the form

$$H = g\,\mu_N \left(B_x \widehat{S_x} + B_y \widehat{S_y} + B_z \widehat{S_z}\right)$$

The isotropy is lost in crystals with axial, tetragonal or tetrahedral symmetry. There is now one axis which is unique and it is used to label this as the Z axis. The terms g_{11} and $g_\perp$ are introduced to represent the values of g measured when the magnetic induction is applied parallel and perpendicular respectively to the Z axis. Consequently $g_x = g_y = g_\perp$ and $g_z = g_{11}$ and the spin Hamiltonian.

$$H = \mu_N \left[g_{11}\, B_z \widehat{S_z} + g_\perp \left(B_x \widehat{S_x} + B_y \widehat{S_y}\right)\right]$$

In the case of lower symmetry each axis is unique and the spin Hamiltonian becomes

$$H = \mu_N \left[g_{xx}\, B_x \widehat{S_x} + g_{yy}\, B_y \widehat{S_y} + g_{zz}\, B_z \widehat{S_z}\right]$$

Suppose that in a particular crystal, symmetry axis of the paramagnetic unit coincides with the crystal axis. If such a crystal is mounted in the spectro meter cavity such that the symmetry (c) axis is horizontal, it is possible to determine g_{11} and $g_\perp$ by variation of the crystal about a vertical [a (or b)] axis. As the crystal is rotated the value of g varies between g_{11} and $g_\perp$. Rotation of the crystal about the b(or a) axis will result in the same behaviour, while rotation about C axis will give a constant value of $g_\perp$.

If however the symmetry axis of the paramagnetic unit does not coincide with the crystal axes, it is necessary to resort to the methods of matrix algebra in order to determine the g factors. Suppose the crystal is mounted such that it can be rotated in turn about these mutually perpendicular axes x, y and z. It can be shown the rotation about the x axis, the measured value of g^2 varies as $g^2 = g_{yy}^2 \cos^2\theta + 2g_{yz}^2 \cos\theta \sin\theta + g_{zz}^2 \sin^2\theta$. For rotation about y axis g^2 varies

$$g^2 = g_{zz}^2 \cos^2\theta + 2g^2\,zx \cos\theta \sin\theta + g_{xx}^2 \sin^2\theta$$

and for rotation about the z axis, g^2 varies

$$g^2 = g_{xx}^2 \cos^2\theta + 2g_{xy}^2 \cos\theta\sin\theta + g_{yy}^2 \sin^2\theta$$

At appears that the rotation about each axis leads to the determination of three values of g^2. For example, rotation about x axis gives the g_{yy}^2 when $\theta=0$, g_{zz}^2, when $\theta=90^0$ and g_{yz}^2 when $\theta=45^0$ or 135^0. Six independent components of g^2 tensor can be found in this way. The tenser is symmetric and hence the remaining three components are also known. Diagonalization of the tensor using standard procedure should reveal the three principal values of g^2 from which the principal g factors g_{xx}, g_{yy} and g_{zz} are readily found.

Antisotropy of hyperfine coupling : In a large number of oriented system anisotropy of the nuclear hyperfine coupling constant is formed and is often quite large. The appearence of the ESR spectrum can therefore change rapidly as the crystal is rotated.

The origin of the anisotropic hyperfine interaction have already been discussed assuming as a result of the interaction between the electron and the nuclear dipoles. Suppose the hyperfine coupling constant for a particular nucleus is measured by rotation of the crystal about the x, y, and z axis as before. The measured value of A^2 is related to θ by the equations

$$A^2 = A_{yy}^2 \cos^2\theta + 2A_{yz}^2 \cos\theta \sin\theta + A_{zz}^2 \sin^2\theta$$

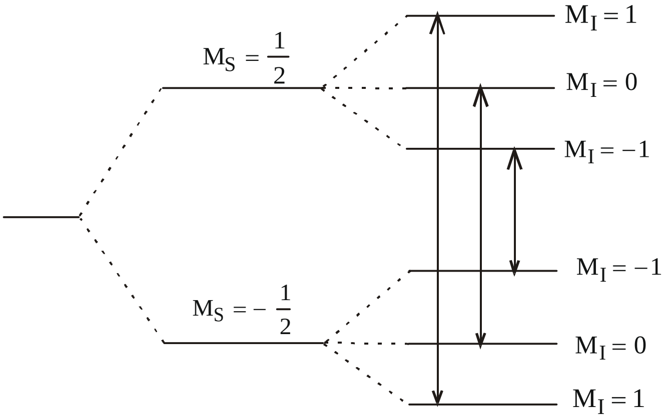
$$A^2 = A_{zz}^2 \cos^2\theta + 2A_{xz}^2 \cos\theta \sin\theta + A_{xx}^2 \sin^2\theta$$

$$A^2 = A_{xx}^2 \cos^2\theta + 2A_{xy}^2 \cos\theta \sin\theta + A_{yy}^2 \sin^2\theta$$

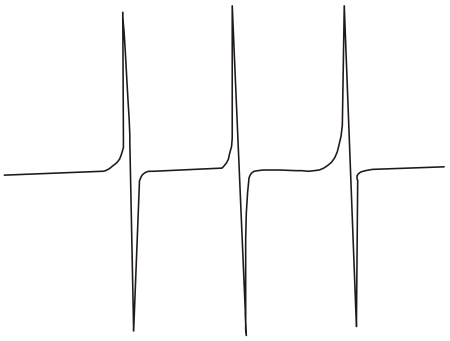
for rotation about the x, y and z axis respectively. Again the tensor is symmetric and hence the six independent components determined from the above equation are sufficient to establish the tensor. Diagonalizing of the resulting tensor should then establish principal values of A^2 and hence A_{xx}, A_{yy} and A_{zz} as before be determined.

(9) Evaluate hyperfine interaction from nuclei with $I>\frac{1}{2}$ nuclei with spin $I=1$, are often present in organic free radicals e.g. ^{14}N and ^{1}D. The natural abundance of the latter nucleus is again very small but the study of spectra of free radicals which have been deuterated at one or more Carbon atoms can be informative. The hyperfine splitting pattern obtained from nuclei with spin

$I=1$ differ significantly from those discussed so far. Three orientations of the nuclear spin (corresponding to $M_I = +1, 0 -1$) are now allowed for each orientation of electrons spin. Fig. given below gives the energy level diagram for a single nucleus of spin $I=1$.



(a)



(b)

(a) Energy levels and allowed transitions for the interaction of an unpaired electron with a single nucleus with $I = 1$.

(b) The ESR spectrum of the peroxylamine disulphonate ion.

The allowed transitions are three equally spaced, equally intense absorptions are expected. The spectrum of Nitrogen atoms show this pattern. (In the above figure (b)). The energy level diagram for two equivalent nuclei of spin I can be readily constructed predicting five equally spaced absorption with relative intensities 1 : 2 : 3 : 2 : 1.

A number of nuclei with spin $I=\frac{3}{2}$ may be uncountered in organic free radicals namely ^{7}Li, ^{23}Na, ^{33}S, ^{35}Cl, ^{37}Cl and ^{39}K. The three alkali metals are included here because one very common means of preparing radical anions of aromatic molecules is by reaction with an alkali metal. The transfer of an electron from the metal to the lowest occupied π molecular orbital of the molecule produces the radical anion together with alkali metal counterion. Four orientations of nuclear spin are now allowed for each orientation of the electron spin and consequently $I=\frac{3}{2}$, produces four equally spaced equally intense lines.

(10) Energy levels of a radical with a single set of equivalent protons

Let us discuss an unpaired electron interacts with a single set of equivalent proton.

Consider a free radical in which an unpaired electron is able to interact with two equivalent protons. For each arrangement of the electron magnetic moment, there are four arrangements of the nuclear magnetic moments i.e.

	Proton A	Proton B
I	$+\frac{1}{2}$	$+\frac{1}{2}$
II	$+\frac{1}{2}$	$-\frac{1}{2}$
III	$-\frac{1}{2}$	$+\frac{1}{2}$
IV	$-\frac{1}{2}$	$-\frac{1}{2}$

Arrangements I and IV have a net nuclear spin of +1 and -1 respectively. On the other hand arrangements II and III have a net nuclear spin of zero and are clearly indistinguishable.

This situation is summarized in the following figure (a)

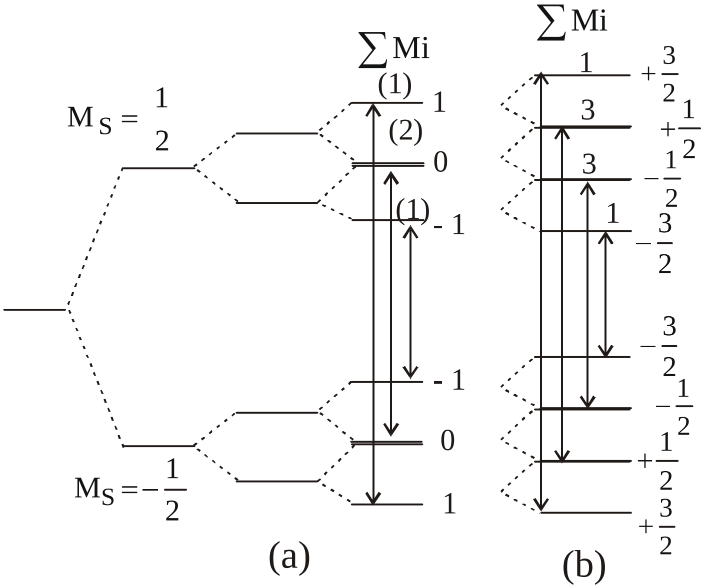


Fig. Caption : Energy levels and allowed transition for the interaction of an unpaired electron with (a) with two equivalent nuclei $I=\frac{1}{2}$. (b) Three equivalent nuclei $I=\frac{1}{2}$ (The relative intensities of the transitions are given in picture).

It should be noted that three transitions are allowed but since $\sum M_I = 0$ state is doubly degenerate this transition will have double the intensity of the other two transitions. The energy levels for the $\sum M_I = +1$ and $\sum M_I = -1$ states are equally spaced from the $\sum M_I = 0$ state and the ESR spectrum consists of three equally spaced absorptions with 1 : 2 : 1 relative intensities.

The situation of an unpaired electron with three equivalent protons also follows the same arguments. There will now be one arrangement where all three nuclei have their magnetic moments parallel to the applied inductions $\left(\sum M_I = +\frac{3}{2}\right)$ and are arrangement where all the magnetic moments are anti parallel to the applied induction $\left(\sum M_I = -\frac{3}{2}\right)$. There will be three arrangements where one magnetic moment is parallel and two are anti parallel to the applied induction $\left(\sum M_I = -\frac{1}{2}\right)$ and finally three arrangements where are magnetic applied induction $\left(\sum M_I = +\frac{1}{2}\right)$. Four transitions are now allowed (fig (b) above) leading to four equally spaced absorption in the ESR spectrum. The central two absorption are now triply degenerate and have intensity three times that of outer absorptions. The informations may be summarized in the form of the general rules.

(1) n equivalent protons give $(n+1)$ equally spaced absorptions in ESR spectrum.

(2) The relative intensities of these absorptions will be proportional to the coefficients of a binomial expansion of order n.

n	Relative intensity of absorption (ESR spectrum)	Number of levels for each value of M_S
0	1	1
1	1 1	2
2	1 2 1	4
3	1 3 3 1	8
4	1 4 6 4 1	16
5	1 5 10 5 1	32
6	1 6 15 20 15 16 1	64

(11) Energy levels for a radical with multiple set of equivalent protons. The general procedure can be illustrated with two examples :

The simplest example is an unpaired electron interacts with two magnetically nonequivalent protons.

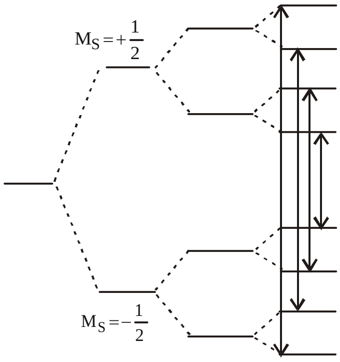


Fig. : Energy levels and allowed transitions of the interaction of an unpaired electron with two non equivalent nucleus with $I = \frac{1}{2}$

The energy level diagram is shown, four equally intense transitions are allowed. The spacing between component pairs being a_1 and a_2. As a second example consider the interaction of the unpaired electron with one pair of equivalent protons splitting constant a_1) and with single protons (splitting constant a_2) Assuming $a_2 > a_1$, consider first the interaction a_2.

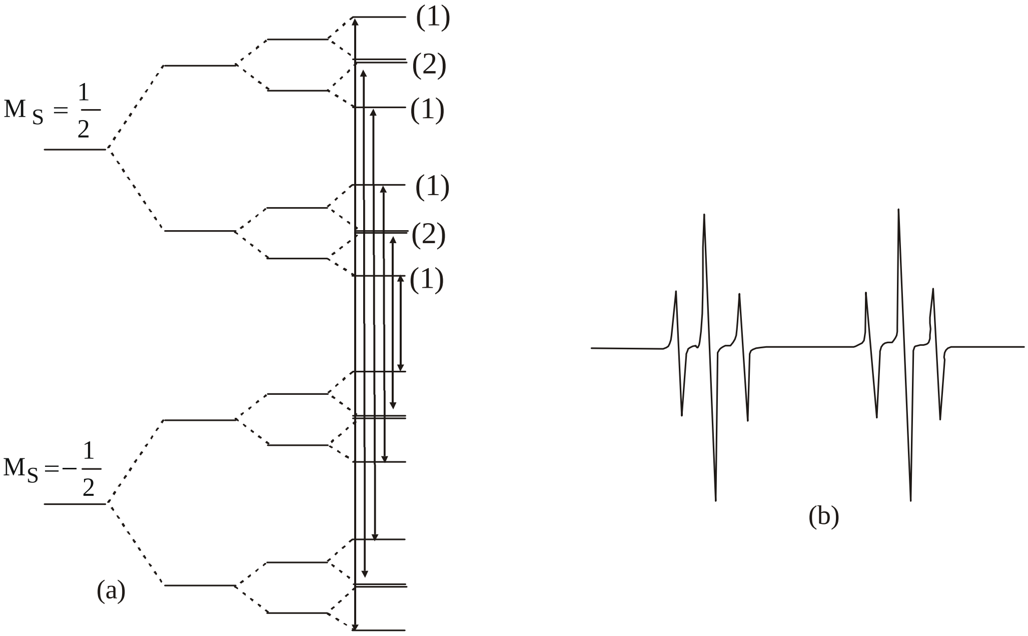


Fig. Caption : (a) Energy levels and allowed transitions for the interaction of an unpaired electrons with a single nucleus $I = \frac{1}{2}$ and also with two equivalent nucleus $I = \frac{1}{2}$. (b) ESR spectrum of pyrogallol radical dianion (compute simulation).

13.3 Problems in Nuclear Quadrupole Resonance

(1) Obtain the NQR energy levels for $I = \frac{3}{2}$ and show the possible transitions for $I = \frac{3}{2}$ nucleus, assume $\eta = 0$.

For $I = \frac{3}{2}$, $m_I = \pm\frac{3}{2}$ and $m_I = \pm\frac{1}{2}$

$$E_{\pm\frac{3}{2}} = \frac{e^2 Q q}{4I(2I-1)}\left[3M_I^2 - I(I+1)\right]$$

Substituting for $m_I = \frac{3}{2}$ and $I = \frac{3}{2}$, we have

$$E_{\pm\frac{3}{2}} = \frac{e^2Qq}{4\left(\frac{3}{2}\right)(3-1)}\left[3\left(\frac{9}{4}\right) - \frac{3}{2}\left(\frac{5}{2}\right)\right] = \frac{e^2Qq}{12}\left[\frac{27}{4} - \frac{15}{4}\right]$$

$$E_{\pm\frac{3}{2}} = \frac{e^2Qq}{4}$$

again next orientation $I = \frac{3}{2}$, $m_I = \pm\frac{1}{2}$, then

$$E_{\pm\frac{1}{2}} = \frac{e^2Qq}{4\left(\frac{1}{2}\right)(3-1)}\left[3\left(\frac{1}{4}\right) - \frac{3}{2}\left(\frac{5}{2}\right)\right] = \frac{e^2Qq}{12}[-3]$$

$$E_{\pm\frac{1}{2}} = -\frac{e^2Qq}{4}$$

Selection rule is $\Delta m_I = \pm 1$, Transitions takes place $E_{\pm\frac{3}{2} \to \pm\frac{1}{2}}$

i.e. $\frac{e^2Qq}{4} - \left(\frac{-e^2Qq}{4}\right) = \frac{e^2Qq}{2}$

The corresponding transition frequency is $\frac{\Delta E}{h} = \frac{e^2Qq}{2h}$

The term $\frac{e^2Qq}{h}$ is termed as nuclear Quadrupole coupling constant and has the dimension of frequency (MHz). It can be +Ve or - Ve according to the sign, but not simply found from a simple measurement of the transition frequency.

A single NQR line is observed.

(2) Obtain the NQR energy levels for $I=\frac{5}{2}$ and show the possible transition for $I=\frac{5}{2}$ nucleus, assume $\eta=0$. For $I=\frac{5}{2}$, the possible m_I values are $\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$

$$I=\frac{5}{2},\ m_I=\pm\ \frac{5}{2},$$

$$E_{\pm\frac{5}{2}}=\frac{e^2\,Q\,q}{4\left(\frac{5}{2}\right)\left[2\left(\frac{5}{2}\right)-1\right]}\left[3\left(\frac{5}{2}\right)^2-\frac{5}{2}\left(\frac{7}{2}\right)\right]$$

$$E=\frac{e^2\,Q\,q}{4I(2I-1)}\left[3M_I{}^2-I(I+1)\right],\ E_{\pm\frac{5}{2}}=\frac{e^2\,Q\,q}{40}\left[\frac{75}{4}-\frac{35}{4}\right]$$

$$E_{\pm\frac{5}{2}}=\frac{e^2\,Qq}{4}$$ ----------- (1)

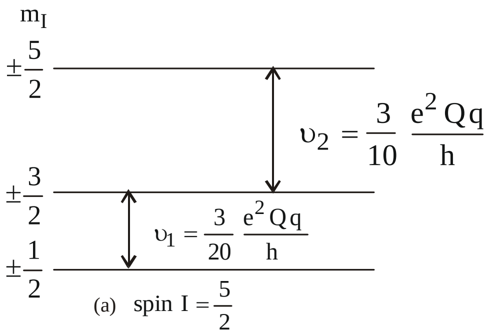
$$I=\frac{5}{2},\ m_I=\pm\frac{1}{2},\ E_{\pm\frac{1}{2}}=\frac{e^2\,Q\,q}{4\left(\frac{5}{2}\right)\left(2\left(\frac{5}{2}\right)-1\right)}\left[3\left(\frac{1}{4}\right)-\frac{5}{2}\left(\frac{7}{2}\right)\right]$$

$$E_{\pm\frac{1}{2}}=\frac{e^2\,Q\,q}{40}\left[\frac{3}{4}-\frac{35}{4}\right]=-\frac{e^2\,Q\,q}{5}$$ -------------- (3)

Selection rule is $\Delta m_I=\pm 1$ therefore

$$E_{\pm\frac{5}{2}}\rightarrow E_{\pm\frac{3}{2}}=\frac{e^2\,Q\,q}{h}-\frac{\left(-e^2\,Q\,q\right)}{20}=\frac{6e^2\,Qq}{20}=\frac{3e^2\,Q\,q}{10}$$ ---------- (I)

$$E_{\pm\frac{3}{2}}\rightarrow\frac{1}{2},\ \frac{-e^2\,Qq}{20}-\frac{\left(-e^2\,Qq\right)}{5}=\frac{-e^2\,Q\,q+4e^2\,Qq}{20}=\frac{3e^2\,Q\,q}{20}$$ ---------- (II)



(a) spin $I = \frac{5}{2}$

The corresponding frequencies are $\upsilon_1 = \frac{3}{20}\frac{e^2 Q q}{h}$; $\upsilon_2 = \frac{3}{10}\frac{e^2 Qq}{h}$

Frequencies are in the ratio of $1:2$.

(3) Obtain the NQR energy levels for $I=\frac{7}{2}$ and show the possible transitions for $I=\frac{7}{2}$ nucleus, assume $\eta=0$.

For $I=\frac{7}{2},\ m_I = \pm\frac{7}{2},\ E_{\pm\frac{7}{2}} = \frac{e^2 Q q}{4I(2I-1)}\left[3M_I^2 - I(I+1)\right]$

$$E_{\pm\frac{7}{2}} = \frac{e^2 Qq}{4\left(\frac{7}{2}\right)2\left(\frac{7}{2}\right)-1}\left[3\left(\frac{7}{2}\right)^2 - \frac{7}{2}\left(\frac{9}{2}\right)\right] = \frac{e^2 Q q}{84}\left[3\left(\frac{49}{4}\right) - \frac{63}{4}\right]$$

$$E_{\pm\frac{7}{2}} = \frac{e^2 Q q}{84}\left[\frac{147}{4} - \frac{63}{4}\right] = \frac{e^2 Q q}{84}\left[\frac{84}{4}\right] = \frac{e^2 Qq}{4} \text{ ---------- (1)}$$

For $I=\frac{7}{2},\ m_I = \frac{5}{2},\ E_{\pm\frac{5}{2}} = \frac{e^2 Q q}{84}\left[3\left(\frac{5}{2}\right)^2 - \left(\frac{63}{4}\right)\right]$

$$E_{\pm\frac{5}{2}} = \frac{e^2\ Q\ q}{84}\left[\frac{75-63}{4}\right] = \frac{e^2\ Q\ q}{28} \text{ --------- (2)}$$

Thus the transition according to selection rule $\Delta m_I = \pm 1$ yields

$$E_{\pm\frac{7}{2}\to\frac{5}{2}} = (1) - (2) = \frac{e^2 Qq}{4} - \frac{e^2 Qq}{28} = \frac{3}{14} e^2 Qq \text{ ------------- } (I)$$

For $I = \frac{7}{2},\ m_I = \frac{3}{2},\ E_{\pm\frac{3}{2}} = \frac{e^2 Q q}{84}\left[3\left(\frac{3}{2}\right)^2 - \frac{63}{4}\right] = \frac{e^2 Qq}{84}\left[\frac{27}{4} - \frac{63}{4}\right]$

$$E_{\pm\frac{3}{2}} = \frac{e^2 Q q}{84}\left[-\frac{36}{4}\right] = \frac{-3e^2 Qq}{28} \text{ ------------- } (3)$$

Then the transition according to selection rule $\Delta m_I = \pm 1$

$$E_{\pm\frac{5}{2}} \to E_{\pm\frac{3}{2}} \quad (2) - (3) = \frac{e^2 Q q}{28} - \left(\frac{-3e^2 Q q}{28}\right) = \frac{e^2 Q q}{7} = \frac{2e^2 Qq}{14} \text{ --------- } (II)$$

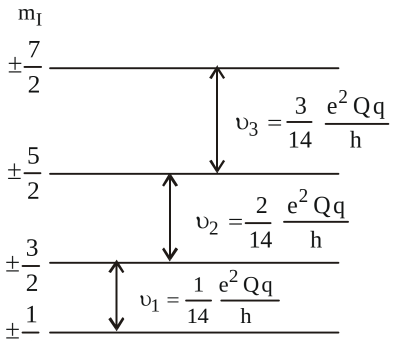
For $I = \frac{7}{2},\ mI = \frac{1}{2},\ E_{\pm\frac{1}{2}} = \frac{e^2 Q q}{84}\left[3\left(\frac{1}{4}\right) - \frac{63}{4}\right] = \frac{e^2 Q q}{84}\left[-\frac{15}{4}\right] = -\frac{5e^2 Qq}{28}$

Thus the transition according to the selection rule $\Delta m_I = \pm 1$

$$E_{\pm\frac{3}{2}} \to E_{\pm\frac{1}{2}} = -\frac{3}{28}\left(e^2 Qq\right) - \left(-\frac{5e^2 Qq}{28}\right) = \frac{1}{14} e^2 Q q \text{ ------------ } (III)$$

Thus there are 3 transitions whose frequencies are

$$\frac{3}{14}\frac{e^2 Q q}{h},\ \frac{2}{14}\frac{e^2 Qq}{h},\ \text{and}\ \frac{1}{14}\frac{e^2 Qq}{h}$$



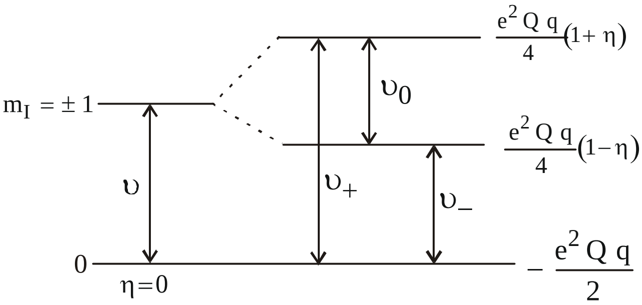
(a) spin $I = \frac{7}{2}$

These three transition frequencies are in the ratio of 1 : 2 : 3 respectively.

(4) The ^{14}N NQR resonance of a compound shows 3 lines at 5.997, 3.501 and 2.496 MHz.

Calculate the quadrupole coupling constant $\frac{e^2 Q q}{h}$ and η.

The energy levels and allowed transitions are shown in the adjacent figure $I=1$, $\eta=0$ case is also included.



Every levels and transitions for $I=1$ system

The frequencies of the three transitions are given by $\upsilon_0 = \frac{1}{2}\frac{e^2 qQ}{h}\eta$

$$\upsilon_{\pm} = \frac{3}{4}\frac{e^2 Qq}{h}\left[1 \pm \frac{\eta}{3}\right]$$

$$\upsilon_{+} = \frac{3}{4}\frac{e^2 Qq}{h}\left[1 + \frac{\eta}{3}\right] = 5.997 \text{ MHz --------- (1)}$$

$$\upsilon_{-} = \frac{3}{4}\frac{e^2 Qq}{h}\left[1 - \frac{\eta}{3}\right] = 3.501 \text{ MHz ---------- (2)}$$

$$\upsilon_0 = \frac{1}{2}\frac{e^2 Qq}{h}\eta = 2.496\,\text{MHz ---------------- (3)}$$

Adding (1) and (2), we have $\frac{3}{2}\frac{e^2 Q q}{h} = 9.498\,\text{MHz}$

$$\frac{e^2 Qq}{h} = \frac{2(9.498)}{3} = 6.332\,\text{MHz}$$

from (3) $\eta = 2(2.496) \Big/ \frac{e^2 Qq}{h} = \frac{2(2.496)}{6.332}$

$\eta = 0.788$

(5) The spin ^{59}CO nucleus is $\frac{7}{2}$. Assuming axial field gradient, $(\eta = 0)$, obtain expressions for frequencies of the quadrupole transitions.

For axially symmetric system,

$$E_{m_I} = \frac{e^2 Q\, q\left[3m_I^2 - I(I+1)\right]}{4I(2I-1)}$$

The m_I values are $\pm\frac{7}{2}, \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$

$$E_{\pm\frac{1}{2}} = -\frac{5}{28} e^2 q\, Q, \qquad E_{\pm\frac{3}{2}} = -\frac{3}{28} e^2 q\, Q$$

$$E_{\pm\frac{5}{2}} = \frac{1}{28} e^2 q\, Q, \qquad E_{\pm\frac{7}{2}} = \frac{1}{4} e^2 q\, Q$$

$$\upsilon_1 = \frac{E\pm\frac{3}{2} - E\pm\frac{1}{2}}{h} = \frac{1}{14}\frac{e^2 Qq}{h}$$

$$\upsilon_2 = \frac{E\pm\frac{5}{2} - E\pm\frac{3}{2}}{h} = \frac{2}{14}\frac{e^2 Qq}{h}$$

$$\upsilon_3 = \frac{E\pm\frac{7}{2} - E\pm\frac{5}{2}}{h} = \frac{3}{14}\frac{e^2 Qq}{h}$$

Thus for system of $I = \frac{7}{2}$, gives three transitions of frequencies υ_1, υ_2 and υ_3 in the ratio of 1 : 2 : 3.

(6) The $^{35}\mathrm{Cl}$ resonance tetra chlorophenyl arsenic (V) $(\mathrm{ph\,As\,Cl_4})$ occur at 24.0, 25.0, 34.18 and 34.68 MHz. Assuming a trigonal bipyramidal structure with the phenyl group in an equitorial position assign the observed frequencies. The axial chlorines are more ionic than the equational chlorines.

As axial chlorines are more ionic by the equation.

$$\left(e^2\,Q\,q\right)_{\mathrm{mol}} = (1-s+d)(1-i)e^2\,Qq \text{ atoms}$$

their resonances are expected at a lower frequency. Again the two axial chlorine atoms are expected to be crystallo graphically in equivalent. Hence the lines at 24.00 MHz and 25.00 MHz are assigned to axial chlorine atom and those at 34.18 and 34.68 MHz are assigned to the equatorial chlories.

(7) Making use of the data of the above problem evaluate the positions of the $^{37}\mathrm{Cl}$ resonances in the same compound.

The ratio of quadrupole moment of the two isotopes are given by

$$\frac{(eQ)^{35}\,\mathrm{Cl}}{(eQ)\,^{37}\mathrm{Cl}} = \frac{-8.5}{-6.7} = 1.2686\,.$$

The frequencies of $^{37}\mathrm{Cl}$ resonances are obtained by dividing those of $^{37}\mathrm{Cl}$ by 1.2686.

The resonance frequencies are obtained as follows 18.92, 19.71, 26.94 and 27.34 MHz.

(8) Briefly out line the application of NQR spectroscopy :

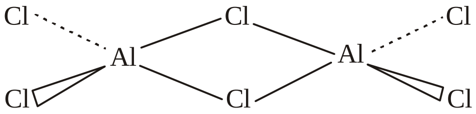
In atom or molecules, the EFG at a particular nucleus, is due to valence electrons. The closed shell and s electrons do not contribute to EFG. Only p and d electrons in valance shell contribute to EFG. The quadrupole coupling constant, q at a particular nucleus is given by

$$q = e\int \psi^* \left[\frac{3\cos^2\theta - 1}{r^3}\right] \psi\, d\tau\,,$$ where ψ is the wave function of the valance electron

and θ is the angle between the fixed Z axis in space and the radius vector r (from nucleus to electron). In molecules ψ is the LCAO wave function. Thus the dominant contribution of EFG at the nucleus is due to p - electron, and p type loan pairs. Thus the nuclear quadrupole constant for atom. q atom or for molecule q_{mol} can be calculated the following are the applications of NQR.

(a) Nature of Chemical bond : A comparison of NQR coupling constant in the atomic and molecular state of the same nucleus provide information about the extent of hybridization and ionic character of chemical bond. For example consider the case of H_2S. The electronic configuration of S is the $Ne\ 3s^2\,3p^4$ and because HSH angle is nearly 90^0 it has been assumed that p orbitals of s are involved in bonding. However NQR experiments showed large asymmetric parameter for sulphur. It is clear that $q_{xx} \neq q_{yy}$ and therefore pure p orbitals are not involved in bonding. A possible explanation is the p - d hybridization.

(b) Structural information : A large number of group III halides of the type $AlCl_3\left(MX_3\right)$ have been structured by NQR. The basic halogen spectrum consists of three resonance lines, two are closely spaced together and are far above the third. The fact that different resonance frequencies are observed for the same nucleus indicate that they are not chemically identical. In these compounds, there are two types of halogen atoms corresponding



to bridge and end positions ^{35}Cl line width has been correlated with NQR coupling constant in various compounds and shows that it is due to distribution of p - electrons. Some of the line widths together with NQR coupling constants are listed in the following table.

Table : Correlation of ^{35}Cl line width and NQR coupling constant in liquid

Liquid	Line width (G)	Quadrupole coupling constant MHz
$TiCl_4$	2.2	12
$VoCl_3$	5.5	22
$CrO_2\,Cl_2$	8.3	32
$SiCl_4$	14.7	40

The NQR spectra of $TiCl_4$ is different from VCl_4. The spectra is very complex. In VCl_4 'Cl' nucleus exposed to a large magnetic field because it is paramagnetic. If it did not vary with time it will give very large shif to ^{35}Cl resonance, however there are local fluctuation due to off electrons in VCl_4 NQR coupling constants ^{35}Cl, ^{79}Br and ^{127}I and some of their compounds are given in the following table.

Table NQR coupling constant of ^{35}Cl, ^{79}Br, ^{127}I and some of their compounds

molecule	NQR coupling constant eqQ mol.	Molecule	NQR coupling constant eQq mole
Cl(atmoic)	- 109.7	Br (atomic)	769.7
Br Cl	- 103.6	Br Cl	876.8
I Cl	- 82.5	Li Br	37.2
F Cl	- 145.9	Na Br	58.0
K Cl	0.04	CH_3Br	528.9
Rb Cl	0.77	I(atomic)	- 2292.8
CS Cl	3.00	Na I	259.9
CH_3Cl	- 74.7	KI	- 60.0

It can be noticed from the above table, that quadrupole constant for KCl is almost zero hence the bonding essentially ionic in KCl.

(c) Charge transfer compounds : It is believed that when molar CCl_4 and p xylene as well as Br and benzene or CBr_4 and p xylene are brought togehter a charge transfer compound is formed. The frozen solution of these mixtures were studied and it is found that the resonance frequencies of the halogens are not appropriately different from those in the pure molecular state. The conclusion is therefore is, that there is a lack of charge transfer of these compounds in the ground state.

13.4 Summary

Magnetic Resonance Phenomena contain Nuclear Magnetic Resonance, Electron Spin Resonance and Nuclear Quadrupole Resonance NMR & NQR have some similarities. NMR & ESR too have same identical features in principles. All these three NMR, NQR and ESR do not fall in the same frequency region. NMR, NQR come under radio frequency region, ESR falls into microwave region. Under these different phenomena all sorts of problems have been worked. Application aspect inference about molecular structure of various types compounds have been elaborately studied.

13.5 Keywords

Nucleus, Electron, Quadrupole moment, Magnetic moment, Spin, Charge distribution, Relaxation times T_1, T_2, Resonance, Larmor precessional frequency, symmetry parameter Quadrupole coupling constant.

13.6 Review Questions

The individual problems themselves are review questions in this lesson

13.7 Text and Reference Books

(1) Nuclear Magnetic Resonance by ER Andrw Cambridge University Press.

(2) Fundamentals of Molecular spectroscopy by CN Banwell (Tata McGra-Hill)

(3) Spectroscopy by SP Shranghen and Walker

(4) Atomic and Molecular spectroscopy by Moolchand Gupta (New Age International)

(5) Molecular Structure and Spectroscopy by G Aruldhas (PHI).

Unit - IV

Lesson - 14

INTRODUCTION : MOLECULAR SPECTROSCOPY

Aim : To know the types of spectra, Regions of the electromagnetic spectrum, types of molecules Rigid rotator, rotational energy levels, selection rules and transitions.

Objectives of the lesson :

1. To know about the brief description of molecular spectroscopy
2. To know about types of spectra and region of the spectrum
3. To know about the types and shapes of molecules
4. To know about molecule as rigid rotator and transitions, energy levels etc.,
5. To know about the salient featurs of Rotational spectra.

Structure of the lesson :

14.1 Introduction

(i) A molecule has a number of discrete electronic levels with electronic level A and electron level B exists. A transition between two electronic level results in a radiation that falls in the visible or ultra violet region.

(ii) With each electronic level are associated a number of vibrational energy levels whose spacing decreases with increasing quantum number v. A transition between two vibrational levels results in a radiation that falls in the near infra-red region.

(iii) With each vibrational level are associated a number of rotational levels. Whose spacing increases with increasing quantum number J. A transition between two rotational energy levels results in a radiation that fall in far infrared or microwave region.

(iv) It is obvious that all the lines that arise from transitions between rotational levels J' and J'' associated with a given pair of vibrational levels v' and v'' of a given pair of electronic levels A and B from a band. Therefore each line in each band of the system arises due to change in all the three energies E_e, E_v and E_r. Thus

$$\upsilon = \frac{E' - E''}{hc} = \frac{E'_e - E''_e}{hc} + \frac{Ev' - Ev''}{hc} + \frac{E_{J'} - E_{J''}}{hc}.$$

$$\upsilon = \upsilon_e + \upsilon_v + \upsilon_r \text{ ------------ } (14.1)$$

with $\upsilon_e > \upsilon_v > \upsilon_r$

(v) Further we note that, for a given band υ_e and υ_v are constants, while υ_r changes from line to line. This position in the system where $\upsilon_r = 0$ is called the band origin; its wave number is $(\upsilon_e + \upsilon_v)$.

For a given system of bands (band system) υ_e is constant υ_v changes from band to band. The position in the system where $\upsilon_v = 0$ (and $\upsilon_r = 0$) is called he system origin; its wave number is υ_e.

(vi) The electronic band system lies in the visible or ultra violet region. Apart from electronic bands, we also have non-electronic bands. They involve transitions in the same electronic level. Such bands are of two types.

(vii) **Vibrational - Rotational bands :** A vibration - rotation band arises due to transitions between two vibration levels of the same electronic level. The lines of the band result from the transitions between rotational levels of one vibrational level to the vibrational levels of other vibrational level. The wave number of a line is $\upsilon_v + \upsilon_e$. Such bands occur in the near infrared region.

(viii) **Pure Rotational Bands :** In this case, electronic level is the same and vibrational level is also the same. Transitions between two rotational levels associated with one and the same vibrational level of a given electronic level give rise to pure rotation lines. The wave number of a line is υ_r. These lines fall in the far infrared or in the microwave regions.

14.2 Types of Spectra

The spectra which are emitted by molecules (when the emitting substance is in molecular state) containing two or more atoms. Molecular spectra under low dispersion appears as continuous bands and for this reigon they are often called band spectra. Usually a band has a sharp intense edge on one side called 'band head' gradually decreases in intensity towards the other side. With high resolving power instruments band spectra are bound to have three fold structure.

(i) Each band is seen to be composed of a large number of lines which are crowded together at the long wave length side called band head, and they recede from band head, the lines (become) more widely separated and also weaker, the lines however being so close together as to appear under low resolution like a continueous spectrum.

(ii) There is a regular sequence in which the several bands follow one another and thus constitute a group of bands.

(iii) These different groups of bands are quite close and thus because of their regular arrangement form a band system.

14.2.1 Regions of the spectrum :

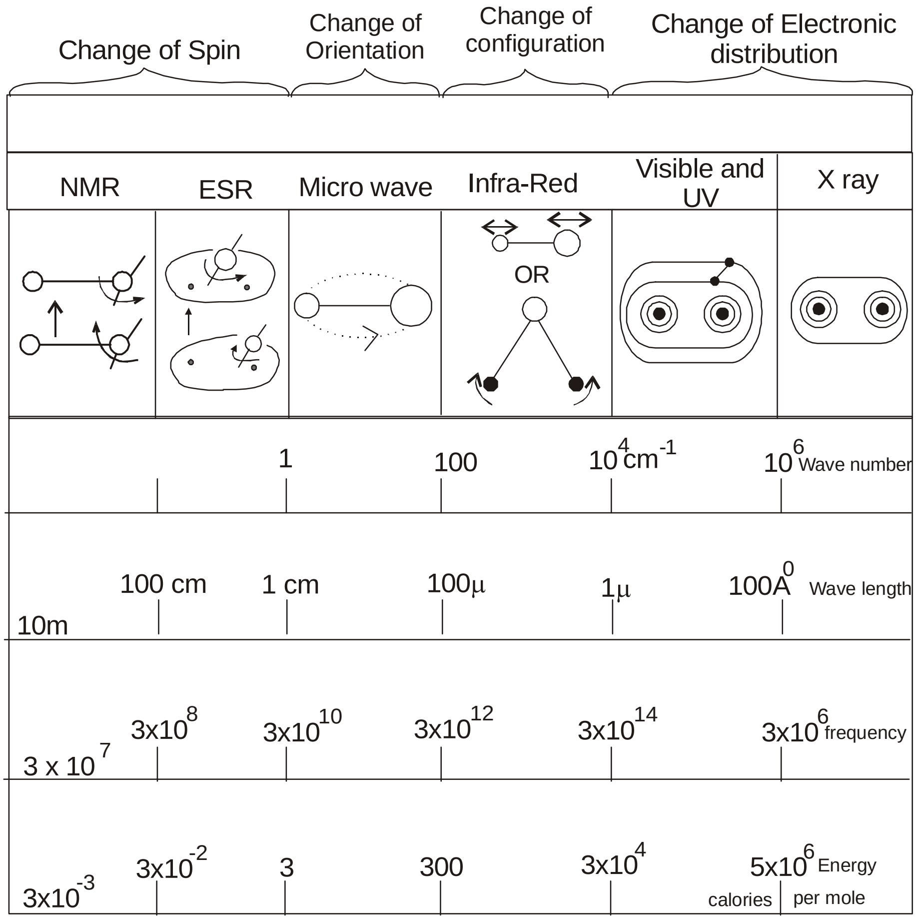


Fig 14.1 The Regions of Electromagnetic spectrum

In Fig. 14.1 we have sketched the region into which electromagnetic radiations have been divided in an arbitrary manner and boundaries are not precise. The molecular processes associated with each region are quite different and are noted along with the corresponding regions. We give a brief description in the following few lines.

(1) Radio frequency region (2) Microwave region (3) Infrared Region (4) Visible and UV region

and (5) X - ray region.

SNo.	Name of the Region	Range of frequency	Range of wave length	Phenomena to occur
1.	Radio frequency region	3×10^{6} to 3×10^{10} MHz	10 cm - 1 cm	NMR&ESR spectroscopy
2.	Microwave region	3×10^{10} to 3×10^{12} MHz	$1\text{cm}-100\mu$	The rotational spectroscopy
3.	Near Infrared region	3×10^{12} to 3×10^{14} MHz	$100\mu-1\mu$	Vibrational spectroscopy
4.	Visible and UV region (Electron spectroscopy)	3×10^{14} to 3×10^{16} MHz	$1\mu-100\overset{0}{\text{A}}$	Electron spectroscopy
5.	X - ray region	3×10^{16} and above	$100\overset{0}{\text{A}}$ or less	X-ray region energy changes involve the inner electrons of atoms or molecule

From the view point of experimental methods and theoritical significance, molecular spectra fall in the three groups according as they lie in :

(a) the far (long wave length $20-150\mu$) infrared region. This we see under the head Far Infrared spectroscopy.

(b) the near (short wave length) infrared region : We discuss under the head. Infrared spectroscopy.

(c) Visible or UV region : This we discuss under the head visible and UV spectroscopy.

This explanation for three types of band spectra demands that internal energy of a molecule i.e. the energy other than translational is essentially of three kinds namely electronic, vibrational and rotational which are all quantised and thus the molecule possesses only certain discrete energy states. Suppose energy difference of two states is $E'-E''$, then the wave number (frequency in cm^{-1}) corresponds to this line.

υ (wave number) $=\dfrac{E'-E''}{hc}\,\mathrm{cm}^{-1}$, c is the velocity of light.

The three types of bands discussed above are correlated respectively with (i) changes in rotational energy (ii) simultaneous changes of the rotational and vibrational energies (iii) simultaneous changes in the rotational, vibrational and electronic energies.

14.2.2 Electronic spectra (UV or visible) : From various considerations that a potential 5 to 10 V is required to change the energy level of an electron in a molecule or in other words, two electron states of an electron have an energy difference of about 5 to 10 eV. The frequency (wave number) of an electronic transition of 5eV which is equivalent to $8\times10^{-19}\ \mathrm{erg/mole}$ will be

$$\upsilon = \frac{8\times10^{-19}}{6.6\times10^{-34}\times 3\times10^{8}} = 4\times10^{6}\ \mathrm{m}^{-1}$$

or $$\lambda=\frac{1}{\upsilon} = \frac{1}{4\times10^{6}}\,\mathrm{m} = 25\times10^{-6}\mathrm{m} = 2500\,\overset{0}{A}$$

In each electronic state there are a possible vibrational states corresponding to different value of the vibrational energy of the molecule. Two successive vibrational levels of the same electronic state have an energy difference of 0.1 eV.

Further the energy corresponding to rotation of the molecules about two (for a linear molecule) or three axes is quantised and thus we conclude that each vibrational level has a set of rotational set levels. Two rotational levels in one and the same vibrational and electronic state have an energy difference of 0.005 eV.

Electronic		Vibrational		Rotational	
Charge in energy	5eV	Change in Energy	0.1 eV	Change in energy	0.005eV

Near Infrared Spectra : In the absense of any electronic transition"(no charge in electronic state) vibrational transition can occur i.e. there is a possibility of a transistion from one vibrational energy level to another with the same electronic ground state of the molecule involving an energy of $0.1\mathrm{eV}\left(1.6\times10^{-20}\ \mathrm{erg/mole}\right)$ the frequency of radiation will be

$$\upsilon=\frac{1.6\times10^{-20}}{6.6\times10^{-34}+3\times10^{8}} = 8\times10^{4}\ \mathrm{m}^{-1}$$

or $\lambda=125000\,A^{0} = 12.5\mu$ (Near infrared portion of the spectrum)

Far Infra spectra : In the far infra region transitions occur that are purely rotational in character unaccompanied by changes in electronic and vibrational energies. Such a transitions involves an energy change of 0.005eV and frequency of radiation is

$$\upsilon = \frac{0.005 \times 1.6 \times 10^{-19}}{6.6 \times 10^{-34} \times 3 \times 10^{8}} = \frac{8 \times 10^{4}}{19.8} m^{-1}$$

$$\text{or} \quad \lambda = \frac{19.8}{800} cm = 2.47 \times 10^{-2} = 2,47,000 \overset{0}{A} = 247 \mu$$

This shows that these radiation will lie in the far infrared region. The bands in the far infrared are therefore called rotational spectra.

14.3 Types and Shapes of Molecules :

Principle of Moment of Inertia :

Out of 3N degrees of freedom of an assembly of N particles three belong to the rotation of whole assembly about three mutually perpendicular axis. We assume that there is no interaction between rotation and vibration i.e. molecule is rigid. We know that moments of intertia of assembly of N particle about any axis of rotation is given by

$$I = m_1 r_1^2 + m_2 r_2^2 + \cdots\cdots\cdots\cdots\cdots$$

Where m_i is the mass of the i^{th} particle whose perpendicular distance from the axis is r_i. Out of 3 directions, one orientation in a direction corresponds to have moment of inertia maximum or minimum and the origin of these axes is the centre of mass. The maximum and minimum values are called the principle moment of inertia and their axes are called principal axes. The three principal moments of inertia are conventionally denoted by I_a, I_b, I_c with $I_a < I_b \le I_c$.

Angular momentum interms of Principal moment of Inertia : The general expression for angular momentum if the principal axis transformation is not considered is given by

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \begin{bmatrix} \omega_x \\ \omega_y \\ \omega_z \end{bmatrix}$$

Where P, ω, and I refer to angular momentum, angular velocity and moment of inertia of the assembly of N particles with the principal axis transformation, nine components of I are reduced to three only. I_{xx}, I_{yy}, I_{zz} designated as I_a, I_b and I_c. Let the corresponding angular velocities along the three principal axis be ω_a, ω_b and ω_c.

$$\begin{bmatrix} P_a \\ P_b \\ P_c \end{bmatrix} = \begin{bmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{bmatrix} \begin{bmatrix} \omega_a \\ \omega_b \\ \omega_c \end{bmatrix}$$

or $P = I_a\ \omega_a + I_b\,\omega_b + I_c\ \omega_c$

Kinetic Energy interms of Principal moments of Inertia :

$$T = \frac{1}{2}\left(\bar{\omega} \cdot \bar{P}\right) = \frac{1}{2}\left(P_a\,\omega_a + P_b\,\omega_b + P_c\,\omega_c\right)$$

$$= \frac{1}{2}\left(I_a\,\omega_a{}^2 + I_b\,\omega_b{}^2 + I_c\,\omega_c{}^2\right)$$

$$= \frac{P_a{}^2}{2I_a} + \frac{P_b{}^2}{2I_b} + \frac{P_c{}^2}{2I_c}.$$

Analysis of Spectra : In the discussion of rotational energies and rotational spectra of molecules, we have to specify the relative values of the trhee principal moments of inertia of the molecule. On the basis, description will involve three structures namely linear, symmetric top and asymmetric top molecules. We can distinguish these cases as follows :

(i) asymmetric tops : three distinct moments of Ineria

$$I_a \neq I_b \neq I_c$$

(ii) Symmetric tops : two moments of inertia are equal

if $I_a = I_b < I_c$ called oblate symmetric top (DISC)

if $I_a < I_b = I_c$ called prolate symmetric top (rugby football)

(iii) Spherical top : all moments of inertia are equal.

$I_a = I_b = I_c = I$.

(iv) Linear diatomic molecules : two equal moments of inertia and third one zero.

$I_a = 0$

$I_b = I_c$

(A) Linear and Diatomic molecules

$I_a = 0,\ I_b = I_c = I$

(B) Spherical Top molecules :

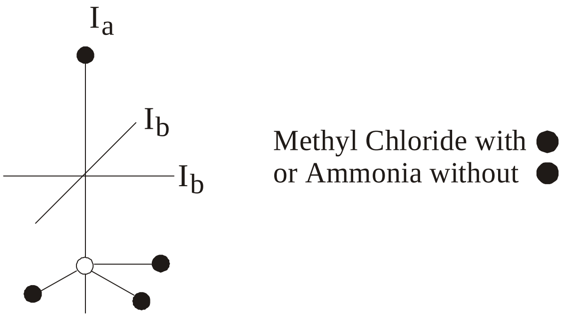
The moment of inertia of spherical top molecule is independent of the orientation of the rotational axis in the molecule i.e. $I_a = I_b = I_c = I$ and thus there is again only one value of the moment of inertia in spherical top molecules and energy levels are therefore given by the equation

$$F(J) = BJ(J+1); \quad J = 0,1,2$$

Thus energy level pattern is identical with that a linear molecule. Since a spherical top molecule is by symmetry nonpolar, its rotation produces no change in moment and no dipole transitions occur rotational states can however be observed in combination with vibration.

(c) Symmetric Top molecules : Two moment of inertia are equal in symmetric top molecules and are labelled as I_b. The other is not zero and differs from I_b. It is labelled as I_a. By symmetry considerations, one can show that any molecule with a three fold rotation axis must be asymmetric top and the I_a axis (the top axis) coincides with the symmetry axis.

The I_b axis, would lie in a plane perpendicular to the top axis. The examples are CH_3Cl and NH_3 and shown in Fig. 14.2



Principal axis of Methyl Chloride or Ammonia

Energy levels and selection rules :

The rotational energy in general is written as

$$E_r = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

Prolate type : If we consider a prolate symmetric top,

$$I_a = I_c \text{ then } E_r = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_a} \text{ ------------ (14.2)}$$

As for linear molecules, it is assumed that the total angular momentum is quantised and in terms of quantum number J is given by

$$P=\sqrt{\{J(J+1)\}}\,\frac{h}{2\pi},\ J=0,1,2, \text{ ---------- } (14.3)$$

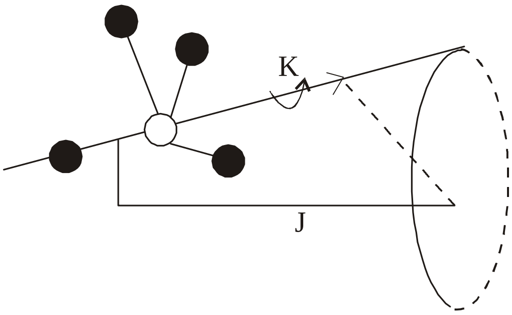


Fig. 14.3 : Classical motion of symmetric top comprising rotation about the top axis and precession of that axis about the total angular momentum

The rotational energy in such type of molecules depends upon two quantum number J and K owing to the fact that here $\bar{J}$, the classical total angular momentum vector is not necessarily directed perpendicular to the top axis. The magnitude and direction of $\bar{J}$ is preserved in classical motion by the rotation of molecule about I_a axis and a precession or rotation of that axis about the direction of $\bar{J}$. (Fig. 14.3) component K of angular momentum vector $\bar{J}$ in the direction of the top axis (I_a axis or called unique principal intertial axis) is also quantised. This condition of equation is represented as

$$P_a=K\left(\frac{h}{2\pi}\right),\ K=0,\ \pm 1,\ \pm 2 \text{ ------------- } (14.4)$$

or $$P^2 = P_a{}^2 + P_b{}^2 + P_c{}^2 \text{ or } P_b{}^2 + P_c{}^2 = P^2 - P_a{}^2$$

$$=J(J+1)\left[\frac{h}{2\pi}\right]^2 - K^2\left(\frac{h}{2\pi}\right)^2$$

Therefore equation (14.2) becomes

$$E_r(JK) = K^2\frac{h^2}{8\pi^2 I_a} + J(J+1)\ \frac{h^2}{8\pi^2 I_b} - \frac{K^2 h^2}{8\pi^2 I_b}$$

$$=J(J+1)\frac{h^2}{8\pi^2 I_b}+\left[\frac{h^2}{8\pi^2 I_a}-\frac{h^2}{8\pi^2 I_b}\right]K^2\text{ergs}\cdot$$

or the term value is $F_{JR}=\frac{E_rJK}{hc}$

$$=\frac{h}{8\pi^2 I_b c}J(J+1)+\left[\frac{h}{8\pi^2 I_a c}-\frac{h}{8\pi^2 I_b c}\right]K^2\ \text{cm}^{-1}$$

$$=BJ(J-H)+(A-B)K^2\,\text{cm}^{-1}\text{ ----------- (14.5)}$$

in which $B=\frac{h}{8\pi^2 I_b c}\text{cm}^{-1}$ and $A=\frac{h}{8\pi^2 I_a c}\ \text{cm}^{-1}$

The quantum numbers may take values

$$\left.\begin{matrix}J=0,1,2\\K=0,\pm1,\pm2......\end{matrix}\right\}\text{ ------------- (14.6)}$$

and all the states with $K>0$ are doubly degerate.

The selection rules are :

Diploe transition $\Delta J=0,\ \pm1,\ \Delta K=0$

For an absorption experimment, pertinent rule is

$$\Delta J=+1,\ \Delta K=0\text{ ------------ (14.7)}$$

Oblate Type : For this type of molecule $I_a=I_b<I_c$ and unique axis or top axis of the figure will be I_c and not I_a. For an oblate symmetric top, there is a constant angular momentum component equal to $\pm K\left[\frac{h}{2\pi}\right]$ along the top axis (I_c axis). Proceeding exactly in a similar way like prolate type with $I_a=I_b$ and I_c different, we have

$$F(J,K)=BJ(J+1)-(B-C)K^2\ \text{cm}^{-1}\text{ ----------- (14.8)}$$

where $C = \dfrac{h}{8\pi^2 I_c c} \mathrm{cm}^{-1}$ and $(B - C)$ is positive.

Since $I_b < I_c$.

Spectra : Symmetric top molecules with a centre of symmetry $(C_2H_6,\ C_6H_6,\ BF_3)$ do not have dipole moment and therefore no pure rotation spectrum is observed in their case. But most of the symmetric molecules have a dipole moment that is directed along the top axis. Since their dipole moment lies in that direction of the top axis, no rotation molecule about their axis can change any component of dipole moment. Consequent in such cases, selection rules for a symmetric top are $\Delta J = \pm 1,\ \Delta K = 0$.

As these molecules give rise to pure rotation absorption spectrum the frequencies of spectral lines will be given by

$$\upsilon = F(J+1,\ K) - F(J,\ K)$$

$$\upsilon = B(J+1)(J+2) + (A-B)K^2 - \left[BJ(J+1) + A - BK^2\right]$$

$$= 2B(J+1)\mathrm{cm}^{-1} \text{ --------------- (14.9)}$$

and thus independent of the rotational constant A.

We can find out the term values $F(J,\ K)$ in the case of prolate and oblate type of symmetric top molecules on substitution of the values of rotation constant. For example, for

Prolate type : CH_3F molecule $A = 5.10\,\mathrm{cm}^{-1},\ B = 0.85\,\mathrm{cm}^{-1}$

Oblate type : NH_3 molecule $B = 9.94\ \mathrm{cm}^{-1},\ C = 6.31\,\mathrm{cm}^{-1}$

Results obtained from the analysis of spectra : The value of B from (14.9) is insufficient for the determination of bond lengths and bond angles of a polyatomic molecule, since the molecule must have atleast two structural parameters in order to satisfy the condition of non zero dipole moments. This value of B must be contained from a value of A or C.

(D) Asymmetric molecules : A molecule with three different moments of inertial is called asymmetric top molecule.

The rotational energy expression is

$$E_r = \frac{P_a{}^2}{2I_a} + \frac{P_b{}^2}{2I_b} + \frac{P_c{}^2}{2I_c} \text{ --------------- (14.10)}$$

But unlike the symmetric top case, no component of total angular momentum vector $\bar{J}$ is quantised, no quantum number other then $\bar{J}$ is available to characterise the rotational energy state. It is therefore impossible to give one simple expression for all the energy levels. The problem is treated in quantum mechanies by using symmetric top wave functions with B and C replaced by $\frac{1}{2}(B+C)$ or A and B replaced by $\frac{1}{2}(A+B)$.

Equation (14.10) leads to a polynomial equation of $(2J+1)^{th}$ degree involving rotational constants A, B, C for each J value. For the first few levels, energy levels may be given.

14.4 The molecule as a Rigid Rotator : Explanation of Rotational Spectra

If there are two mass points in a molecules, the line joining the two is an axis of symmetry and rotation about an axis perpendicular to this line has signficance; also the moment of inertia about all such perpendicular axis will be the same. As a first approxmation rotating diatomic molecules whose nuclei are considered as being separated by a definite mean distance may be treated as a rigid rotator with free axis. Suppose masses m_1, m_2 are joined by a rigid bar (the bond) whose length is $r_0 = r_1 + r_2$ Fig. 14.4. This molecule rotates about centre of gravity C.

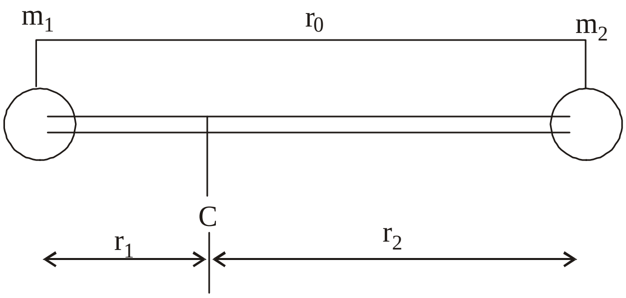


Fig. 14. 4 : A rigid diatomic molecule treated as two masses m_1 and m_2 joined by a rigid base of length $r_0 = r_1 + r_2$

We shall calculate the rotational energy levels, frequency of spectral lines arising due to transition between two energy levels, selection rules for the transitions for the case of diatomic molecules. In this analysis we shall assume that the bond between the atoms is stiff and does not change in length (rigid rotator)

Rotational Energy Levels : The diatomic molecule has an internuclear distance r_0. The molecule has a natural rotation about the axis through its centre of gravity C as shown in Fig. 14.4. The moment of inertia of an assembly of i particles such as the atoms of a molecule is expressed as

$$I = m_1 r_1^2 + m_2 r_2^2 + m_3 r_3^2 + \cdots\cdots$$

$\sum_i m_i r_i^2$ where r_i refers to the distance of particles from the axis of rotation. In the present case

$$I = m_1 r_1^2 + m_2 r_2^2 \text{ -------------- (14.11)}$$

where r_1 and r_2 are the distances of m_1 and m_2 from the axis of rotation through C. As the system is balanced about its centre of gravity, we can have

$$m_1 r_1 = m_2 r_2 \text{ ------------------- (14.12)}$$

Further $r_0 = r_1 + r_2$ --------------------- (14.13)

From equation (14.12) and (14.13) we find that

$$r_1 = \frac{m_2}{m_1 + m_2} r_0 \ \& \ r_2 = \frac{m_1}{m_1 + m_2} r_0$$

Putting r_1 and r_2 in equation (14.11) we have

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = m' r_0^2 \text{ --------- (14.14)}$$

where $\frac{m_1 m_2}{m_1 + m_2}$ is reduced mass and given the symbol m'. If the molecule is rotating with an angular velocity ω, then classically it would have an energy $\frac{1}{2} I\omega^2$. As we have discussed in atomic spectra an electron rotating with angula velocity ω about the nucleus has an angular momentum $I\omega$, which can assume the values that are integral multiplies of $\frac{h}{2\pi}$ (Bohr quantum condition); it is easy to write that

$$I\omega = J \frac{h}{2\pi} \text{ where } J = 0, 1, 2, \ldots\ldots.$$

Therefore allowed rotational energies will be given by

$$E_r = \frac{1}{2} I\omega^2 = \frac{1}{2I} I^2 \omega^2 = \frac{J^2 h^2}{8\pi^2 I} \text{ ----------- (14.15)}$$

where $J = 0, 1, 2, ...$ termed as rotational quantum number.

Energy levels of Rigid rotator on applying Schrodinger equation :

The schrodinger equation in three dimentions as

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

Which where converted into spherical coordinates become

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial \psi}{\partial r}\right] + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta \frac{d\psi}{d\theta}\right] + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \text{ --------- (14.16)}$$

In order to apply the above equation to the problem of rigid rotator, we have to arrive at some conclusions for m, r and V as discussed below

In Cartesian coordinates the Kinetic energy T of a single particle of mass m can be expressed as

$$T = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) \text{ which in spherical coordinates is}$$

$$T^* = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2 \sin^2\theta\right)$$

If the distance r of the particle from the origin is fixed, the derivation $\dot{r}$ will be zero so that

$$T = \frac{1}{2}m r^2\left(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta\right) \text{ ------------ (14.17)}$$

Since two particles form a rigid rotator, the total Kinetic energy will be

$$T = T_1 + T_2 = \frac{1}{2}m_1 r_1^2\left(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta\right) + \frac{1}{2}m_2 r_2^2\left(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta\right)$$

As this is the case of rigid rotator, the inter particle distance is fixed, potential energy will come out to be zero. Therefore V is zero and T represents the total energy of the rigid rotator.

Therefore $E = T = \frac{1}{2}\left(m_1 r_1^2 + m_2 r_2^2\right)\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta$

From equation (14.11) the RHS of the above equation represents moment of Inertia I placed at a fixed distance equal to unity (linear = 1) from the origin (centre of mass). Consequently for the rigid rotator we must put $V = 0,\ r = 1,$ and I inplace of m and equation (14.16) becomes

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial\psi}{\partial\theta}\right]+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2 IE}{h^2}\psi=0 \text{ ---------- (14.18)}$$

From the above equation it is obvious that ψ is a function of θ and ϕ i.e. $\psi=\psi(\theta,\phi)$

We shall apply the method of separation of variables for the solution of (14.18) for this let us express ψ is a product of two functions namely $\Theta(\theta)$ and $\Phi(\phi)$, even involving one variable only i.e.

$$\psi(\theta,\phi)=\Theta\,\theta\,\Phi\,\phi$$

so that $\dfrac{\partial\psi}{\partial\theta}=\Phi\dfrac{\partial\Theta}{\partial\theta}$

and $\dfrac{\partial^2\psi}{\partial\phi^2}=\Theta\,\dfrac{\partial^2\Phi}{\partial\phi^2}$

Putting the values of above differentials and ψ in equation (14.18) and multiplying the whole equation by $\dfrac{\sin^2\theta}{\Theta\Phi}$ we get

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta}{\partial\theta}\right]+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{8\pi^2 IE}{h^2}\sin^2\theta=0$$

On separating the variables

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta}{\partial\theta}\right]+\beta\sin^2\theta=-\frac{1}{\Phi}\,\frac{\partial^2\Phi}{\partial\phi^2}$$

where $\beta=\dfrac{8\pi^2 IE}{h^2}$

In the above equation, left hand side involves the variables θ only where as on RHS involves ϕ only. As the two variables θ and ϕ are independent, the two terms can be equated only when each is equal to a constant, say m^2, so that

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right]+\beta\sin^2\theta=m^2 \text{ ------------ (14.19)}$$

and $$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m^2 \text{ ---------------- (14.20)}$$

The solution of (14.20) is $\Phi = Ce^{\pm im\phi}$

For Φ to be a single valued function, it should have the same value for $\phi=0$ and 2π i.e.

$$\Phi = Ce^{\pm imo}=C,\text{ and }\Phi = Ce^{\pm i2\pi m}$$

should be the same or $\cos 2\pi m \pm i\sin 2\pi m = 1$

which can be true only if m is zero or an integer.

Now we can take up the solution of (14.19) we can write (14.19) on multiplying by $\frac{\Theta}{\sin^2\theta}$ as

$$\frac{1}{\sin^2\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right]+\left[\beta-\frac{m^2}{\sin^2\Theta}\right]\Theta\ =0\,.$$

Putting $x=\cos\theta$ so that $\frac{\partial\Theta}{\partial\theta}=\frac{\partial\Theta}{\partial x}\frac{\partial x}{\partial\theta}=-\sin\theta\,\frac{\partial\Theta}{\partial x}$.

or $\frac{\partial}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$.

Thus in the above equation, we get

$$\frac{1}{\sin\theta}x-\sin\theta\,\frac{\partial}{\partial x}\left[-\sin^2\theta\,\frac{\partial\Theta}{\partial x}\right]+\left[\beta-\frac{m^2}{\sin^2\theta}\right]\Theta=0\,.$$

or $$\frac{\partial}{\partial x}\left\{\left(1-x^2\right)\frac{\partial\Theta}{dx}\right\}+\left\{\beta-\frac{m^2}{1-x^2}\right\}\Theta=0 \text{ ---------- (14.21)}$$

It is a Legendre's differential equation; x can assume values from $\cos 0$ or (+1) to $\cos\pi(-1)$. To solve the above equation, let us write

$$\Theta=\left(1-x^2\right)^{m/2} G .$$

So $$\frac{\partial\Theta}{\partial x}=-mx\left(1-x^2\right)^{\frac{m}{2}-1}G+\left(1-x^2\right)^{\frac{m}{2}}\cdot\frac{\partial G}{\partial x}$$

$$\therefore\left(1-x^2\right)\frac{\partial\Theta}{\partial x}=-mx\left(1-x^2\right)^{\frac{m}{2}}G+\left(1-x^2\right)^{\frac{m}{2}+1}\cdot\frac{\partial G}{\partial x}$$

Hence the first term of equation (14.21) is

$$\frac{\partial}{\partial x}\left\{\left(1-x^2\right)\frac{\partial\Theta}{\partial x}\right\}=\left\{-m\left(1-x^2\right)^{m/2}G+\left(1-x^2\right)^{\frac{m}{2}+1}\right\}\frac{\partial G}{\partial x}$$

$$-\left\{2x(m+1)\left(1-x^2\right)^{m/2}\right\}G'+\left(1-x^2\right)^{\frac{m}{2}+1}G''$$

where $G'=\dfrac{\partial G}{\partial x}$ and $G''=\dfrac{\partial^2 G}{\partial x^2}$

Putting this value of the first term in (14.21) and dividing through out by $\left(1-x^2\right)^{m/2}$, we get

$$\left(1-x^2\right)G''-2(m+1)x\,G'+\{\beta-m(m+1)\}G=0\,,$$

or $\left(1-x^2\right)G''-2ax\,G'+b\,G=0$ ----------- (14.22)

Where $a=m+1$ and $b=\beta-m(m+1)$.

Let us express $G(x)$ as power series i.e

$$G(x)=\alpha_0+\alpha_1x+\alpha_2x^2+\alpha_3x^3+........$$

and $$G'(x)=\alpha_1+2\alpha_2x+3\alpha_3x^2+4\alpha_4x^4+........$$

and $$G''(x)=2\alpha_2+6\alpha_3x+12\alpha_4x^2+........$$

Putting these values in equation (14.22), we get on arranging the terms in ascending powers of x, so that

$$\left(2\alpha_2+b\alpha_0\right)x^0+\left\{6\alpha_3+\left(b-2a\right)\alpha_1\right\}x+\left\{12\alpha_4+\left(b-4a-2\right)\alpha_2\right\}x^2=0$$

Equating the coefficients of every power of $x=0,$ we get

$$2\alpha_2+b\alpha_0=0$$

$$6\alpha_3+\left(b-2a\right)\alpha_1=0$$

$12\alpha_4+\left(b-4a-2\right)\alpha_2=0$ or in general

$$\left(n+1\right)\left(n+2\right)\alpha_{n+2}+\left\{b-2na-n\left(n-1\right)\right\}\alpha_n=0$$

where $n=0$ or an integer. Putting the values of a and b in the above relation, we get the recursion formula

$$\frac{\alpha_{n+2}}{\alpha_n}=\frac{\left(n+m\right)\left(n+m-1\right)-\beta}{\left(n+1\right)\left(n+2\right)}$$

for the coefficients in the power series for $G\left(x\right)$.

For $G\left(x\right)$ to be a polynomial, the series $G\left(x\right)$ must terminate after a finite number of terms which is possible only if

$$\left(n+m\right)\left(n+m+1\right)-\beta=0$$

or $\beta=\left(n+m\right)\left(n+m+1\right)=\ell\left(\ell+1\right)$ $\left[\ell=n+m \text{ say}\right]$

We have seen that m must be zero or an integer and since the same condition applies to n, the sum $\left(n+m\right)$ i.e. ℓ should be zero or integer i.e.

$\ell=0,1,2,3,.......$etc.,

We know that $\beta=\dfrac{8\pi^2 IE}{h^2}$

then $\dfrac{8\pi^2 IE}{h^2}=\ell\left(\ell+1\right)$

so that $E=\ell(\ell+1)\dfrac{h^2}{8\pi^2 I}$

Replacing ℓ by J, we get

$$E_r=\frac{h^2}{8\pi^2 I}J(J+1)\text{, where } J=0,1,2,.... \text{ ---------- (14.23)}$$

The above equaion obviously relates the allowed rotational energies to a molecular property I and quantum number $\bar{J}$. If this energy, E_r is converted to the units of rotational term values, it becomes

$$F(J)=\frac{E_r}{hc}=\frac{h}{8\pi^2 Ic}J(J+1) \text{ ------------- (14.24)}$$

Where $F(J)$ is called rotational term $\left(\text{unit } m^{-1}\right)$. This equation can further be written as

$$F(J) = BJ(J+1)m^{-1},\ J=0,2,.......$$

Where B is called rotational constant and is given by

$$B=\frac{h}{8\pi^2 Ic}m^{-1} \text{ ---------- (14.25)}$$

If we account for the multiplicity of rotational energy levels, the so called degeneracy, then the populations of the various rotational energy levels can be calculated from Boltzmann's distribution

$$N_J=N_0\,e^{-E_J/kT}$$

in which for the sake of representation as Avagadro's number of molecules has been considered. This equation states that out of molecules N_O the Avagadro's number, N_J molecules occupy J^{th} state of energy equal to E_J at absolute tempertature T^0K. The degeneracy (which implies the existence of more than one energy state with the same energy) of rotational level is found to be $(2J+1)$. Therefore Boltzmann distribution can be written as

$$N_J=(2J+1)N_0\,e^{-E_J/kT}.$$

and shows population maximum at a value other than $J=0$.

Frequency of Spectral line : If a rotational transition occurs from an upper level with quantum J' to the lower level of quantum number J'' then the frequency of spectral line expressed in wave numbers is given by

$$\upsilon_r = \frac{E'_r - E''_r}{h\,c} = \frac{h}{8\pi^2 Ic}\left[J'(J'+1) - J''(J''+1)\right]$$

$$= B\left[J'(J'+1) - J''(J''+1)\right]$$

If a rotating molecule possesses a dipole moment, then it can interact with oscillating electro magnetic radiation. That is the molecule can with draw from or give up energy to the radiation consequently transference of energy from radiation to the molecule or vice versa takes place. In other words a molecule must have a dipole moment in order to give rise to rotational spectra.

Spectral Transition and Selection Rules :

$$P_{mn}(x) = \int \psi^*{}_m \mu_x \ \psi_n \, d\tau \text{ ---------------- (14.26)}$$

If all the components of dipole moment in x, y, z directions (all the three components) goes to zero no transition can occur. Therefore for a particular transition to occur one of the components of P_{mn} must be non zero. One particular condition apart from others under which the integral $P_{mn}(x)$ vanishes is that the component μ_x of dipole moment be zero in the equilibrium condition. This condition leads to the conclusion that amolecule which is symmetrical in ground state and consequently does not possess resultant dipole moment will not interact with radiation. As a result the molecule will not yield a spectrum unless an electric moment is produced by disturbing the symmetry of the electrons or nuclei.

For a rigid rotator if we insert the appropriate eigenfunction for upper and lower states in equation (14.26) assuming that μ_x is not zero, it is found that $P_{mn}(x)$ will be zero unless $J' - J'' = \pm 1$. This means that only those rotational transitions which involve an increase or decrease of unity in the rotational quantum number are permitted. This is termed as the selection rule for rotational transistions i.e. the selection rule is

$$\Delta J = J' - J'' = \pm 1 \text{ ------------ (14.27)}$$

For the rotator $J' > J''$ (since J' refers to the upperstate) and therefore considering only $\Delta J = +1$, we have for the emitted or absorbed lines of the rigid rotator.

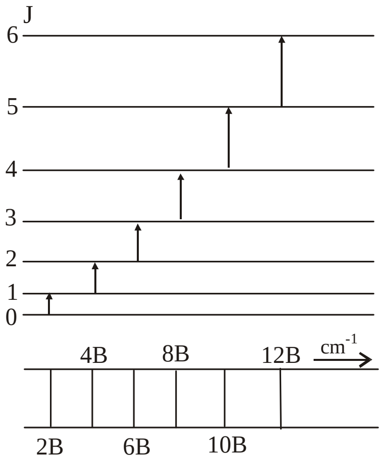


Fig. 14.5 Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from the absorption spectrum

$$\upsilon_r = F(J''+1) - FJ''$$

$$= B(J''+1)\,(J''+2) - BJ''(J+1)$$

$$= 2B(J''+1'), \quad J'' = 0,1,\, 2$$

Writing J instead of J'' for lower state we have

$$\upsilon_r = 2B(J+1), \quad J = 0,1,\, 2,\ldots.. \text{ ----------- (14.28)}$$

Spectrum : Putting these values for J, we find that the frequencies for consequtive lines in the pure rotation spectrum of a diatomic molecule are $2B,\ 4B,\ 6B, 10\,B$ etc. Therefore on the frequency (wave number) scale the lines are equidistant as seen in Fig. 14.5.

The rotational frequency is given by

$$\upsilon = c\,2B\sqrt{J(J+1)} = c\cdot 2B\,J$$

i.e. the rotation frequency in any given state of the rotator is approximately equals to the frequency of the spectral line that has this state as upper level.

14.5 Salient Features of Rotational Spectra :

(1) The bands which appear in far infrared region at wave length of $200\times10^4\,\overset{0}{A}$ or more are due to transitions involving very small energy changer of about 0.005eV. With such

a small quantum of energy electronic and vibrational energy states will not be excited or in other words only transitions that are purely rotational in character will appear. Only those molecules which have permanent electric dipole moment can give rise to pure rotational spectra. Thus homo nuclear diatomic molecules such as H_2, O_2, N_2 etc do not exhibit pure rotation spectra. While hetero nuclear diatomic molecules such as HF, HCl, HBr etc do exhibit rotational spectra. The far infrared spectra are known only in absorption. Molecules HCl, HBr, HI, H_2O and NH_3 have been studied in detail.

(2) In practice the rotational spectra are observed in abosrption for heteronuclear diatomic molecules such as HF, HCl, HBr, Co etc. the rotational spectra consists of a simple series of absorption maximum which are very nearly equidistant on a wave number scale. Measurements of the frequencies of these maxima help to determine the moment of inertia and the internuclear distance.

(3) For infrared radiations can be absorbed by a rotational molecule and there by increase rotation, only if a permanent dipole moment is present. Such a molecule interacts with the oscillating electronic field of the incident radiation to absorb rotational energy and to produce absorption spectra.

(4) The basic molecular requirement for the emission or absorption of rotation by a transition between rotational energy states is that molecule must have a permanent dipole moment. During the rotation of a heteronuclear diatomic molecule which have a permanent dipole moment, the component of this dipolemoment in a fixed direction changes periodically with the frequency of rotation of the molecule, emitting radiation of the same frequency. However homo nuclear molecules have no dipole moment and hence there is no emission of infrared radiation.

14.6 Summary

(1) Electronic transitions vibrational transitions, Rotational energy transitions have been discussed indicating the respective changes in energies, frequencies, wave length etc. The type of molecular level change in the transition has also been identified.

(2) Various types of molecules namely linear diatomic molecules, spherical top molecules, symmetric and asymmetric molecules have been elaborated.

(3) The different type of spectra, spacing of energy levels, have been explained.

(4) Pure rotational spectra, energy levels, frequency of the transitions, selection governing the transitions, and type of molecules which undergo rotational changes and other molecules which do not produce rotational spectra have been discussed.

(5) Finally the salient features of pure rotational spectroscopy has been presented

14.7 Keywords

Asymmetrical molecule, spherical top molecules, linear diatomic molecule, dipole moment, rotational energies, selection rules, rotational constant B, rotational quantum namber J, reduced mass, centre of mass, rigid rotator, bond length far infrared region, microwave region, homo nuclear molecules, heteronuclear molecules, rotational spectrum, term value, frequency (wave number), angular momentum, moment of inertia, angular frequency, Kinetic energy, Potential energy.

14.8 Rievew Questions :

(1) Describe the various regions of electromagnetic spectrum, various types of molecules, and briefly mention the type of spectra to obtain from various molecular changes.

(2) What do you mean by Rigid rotater. Obtain the energy levels, frequency (wave number involved in the transition)

(3) What are the salient features of pure rotational spectroscopy, Distinguish between types of molecules that give rise to rotational spectra and not.

14.9 Text and Reference Books :

(1) Elements of spectroscopy by Gupta, Kumar, Sharma Pragati Prakasham
(2) Molecular Structure and Spectroscopy by G Amldhas (PHI)
(3) Fundamentals of Molecular spectroscopy by CN Banwell (Tata Mc Graw Hill)

Unit - IV

Lesson - 15

DIATOMIC MOLECULES AS NON-RIGID ROTATOR

Aim :

1. To study the Diatomic molecule as a Non Rigid Rotator with some illustrated examples,
2. To study the intensity of spectral lines
3. To know about the effect of Isotropic substitution
4. To learn about the Quadrupole hyperfine interaction,
5. To know about Stark modulated microwave spectrometer
6. To learn about the applications of rotational spectroscopy

Objectives of the lesson :

To learn indetail about

1. Diatomic molecule as a Rigid Rotator with 3 illustrated examples
2. Rotational lines and intensity distribution
3. Usefulness in extracting information through isotopic substitution
4. Effect of nuclear quadrupole interaction on rotational lines
5. Brief sketch and information from the Stark modulated microwave spectrometer
6. About the Applications of rotational spectroscopy

Structure of the lesson :

15.1 Molecule as a Non rigid rotator
15.2 Valadity of theory, determination of inter nuclear distance and moment of Inertia
15.3 Intensity of Spectral lines
15.4 The effect of isotopic substitution
15.5 Vibrational Excitation effect
15.6 Quadrupole Hyperfine Interaction
15.7 Microwave Spectrometer

15.1 Molecule as a non-rigid rotator

Experimental investigation have shown that the successive lines in the far infrared spectrum are not evenlyspaced and that the frequency separation decreases slightly with increasing J values. The cause of this decrease becomes at once obvious if we calculate internuclear distance from the rotational constant, B values. It shows that bond legnth increases with J and that assumption under which a diatomic molecule is treated as rigid rotator is false and infact all bonds are elastic to some extent. We infer from the increase in length with J that more quickly a diatomic molecule rotates, the greater is the centrifugal force tending to move the atoms apart.

Now we discuss the consequences of the change in bond length with J. Firstly when a bond is elastic, it will stretch and compress periodically with a certain functional frequency dependent upon the masses of the atoms and the elasticity (or force constant) of the bond i.e. this means in other words that the molecul may have vibrational energy and if the motion is simple harmonic, force constant is given by

$K = 4\pi^2 \omega^2 c^2 m'$, where ω is the vibration frequency (in m^{-1}). The vibration of B with J determined by the free constant i.e. the Weaker the bond more readily will it distort under centrifugal forces.

The second consequence of elasticity is that the quantities r and B vary during vibration.

We thus see that three different set of values must be assigned to B and r i.e. B_e and r_e (separation between nuclei) at equilibrium, Bo and ro (average inter nuclear separation) in the vibrational ground state or B_n and r_n incase molecule possesses excess vibrational energy, where n is the vibrational quantum number.

Energy levels : For non-rigid rotator Schrodinger wave equation yields to the rotational energy levels as

$$E = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 K} J^2 (J+1)^2 \text{ or } F(J) = \frac{E}{hc}$$

$$= BJ(J+1) - DJ^2 (J+1)^2 \text{ cm}^{-1} \text{ ---------- (15.1)}$$

where D is called centrifugal distortion constant and is given by

$$D = \frac{h^3}{32\pi^4 I^2 r^2 K c} \text{cm}^{-1}$$ and is a positive quantity.

Equation (15.1) is true when force is simple harmonic. If force field is anharmonic, the expression becomes

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 + \cdots\cdots \text{cm}^{-1} \quad \text{--------} \ (15.2)$$

where H, K are small constants dependent upon the geometry of the molecule.

where $B = \frac{h}{8\pi^2 Ic}$, so we found that

$$D = \frac{16B^3\pi^2 m'c^2}{K} = \frac{16B^3\pi^2 m'c^2}{4\pi^2\omega^2 c^2 m'} = \frac{4B^3}{\omega^2} \quad \text{------------} \ (15.3)$$

where ω is the vibration frequency of the band in the normal state. Since B is generally about $10\,\text{cm}^{-1}$ where as ω is the order of $1000\,\text{cm}^{-1}$, it is evident that D will be small nearely $10^{-3}\,\text{cm}^{-1}$ or so.

Spectrum : Fig. 15.1 shows that lowering (not exact in extent) of rotational levels when passing from the rigid to non-rigid diatomic molecule. The spectra are also compared. Selection rule is still $\Delta J = \pm 1$.

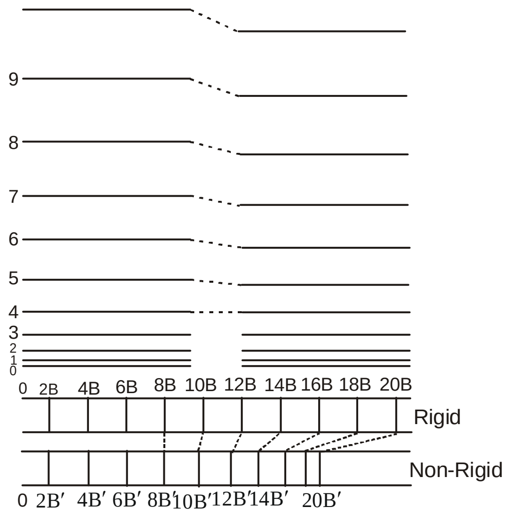


Fig. 15.1 The change in rotational energy levels and rotational spectrum when passing from a rigid to a non rigid diatomic molecule.

The analytical expression for transition can be written as

$$F(J+1)-F(J)=\upsilon_r=B\left[(J+1)(J+2)-J(J+1)\right]-D\left[(J+1)^2(J+2)^2-J^2(J+1)^2\right]$$

$$=2B(J+1)-4D(J+1)^3\,\mathrm{cm}^{-1} \text{ --------- (15.4)}$$

where υ_r represents both upward transition J to $(J+1)$ or downward $(J+1)$ to J. We note from (15.1) that the lines are no longer equidistant but their separations decreases slightly with increasing J. The effect, however is small owing to the smallness of D as compared to B.

Knowledge of D provides two informations. First the determination of J value of lines in an observed spectrum and second the determination of the vibrational frequency of diatomic molecule (though not precisely). For a hydrogen fluride equation (15.3) has the value

$$\omega^2=\frac{4B^3}{b}=16.33\times10^6\left(\mathrm{cm}^{-1}\right)^2$$

i.e. $\omega=4050\,\mathrm{cm}^{-1}$

The force constant then follows directly

$$K=4\pi^2c^2\omega^2 m'=960\,\mathrm{N\,m}^{-1}$$

Which indicates as expected H - F is relatively a strong band.

15.2 Valadity of the Theory

Determination of Internuclear distance (Bond length) and Moment of Inertia

(a) CO molecule : The first line $(J=0)$ in the rotation spectra of Carbon monoxide appears at

$$\upsilon_r=3.84235\,\mathrm{cm}^{-1}$$

so that from $\upsilon_r=2B(J+1)=2B$ since $J=0$.

We get $B=\frac{\upsilon_r}{2}=1.92118\,\mathrm{cm}^{-1}$

Further moment of Inertia is calculated from

$$I_{CO}=\frac{h}{8\pi^2 Bc}=\frac{6.62\times10^{-27}}{8(3.14)^2\times1.92118\times3\times10^{10}}$$

$$= 1.45673\times10^{-39}\ \text{gm}-\text{cm}^2$$

To calculate the bond length, we first find out the value of reduced mass of CO molecule given by

$$m' = \frac{m_1 m_2}{m_1+m_2}\cdot\frac{1}{N_O}$$ where N_O is Avagadro's number

$m' = 12\,\text{gm},\ m_2 = 15.9949\,\text{gm}$
Carbon Oxygen

The reduced mass of CO - molecule will be

$$m'_{CO} = \left(\frac{12\times15.9949}{12+15.9949}\right)\frac{1}{6.244\times10^{23}}\,\text{gm}$$

The bond length of the CO molecule will be

$$r^2_{CO} = \frac{I_{CO}}{m'_{CO}} = \frac{\left(1.45673\times10^{-39}\right)\left(6.244\times10^{23}\right)27.9949}{\left(12\times15.9949\right)}$$

$$\frac{254.6366307\times10^{-16}}{191.9388} = \left(1.326655323\right)\times10^{-16}$$

$$r_{CO} = 1.152\times10^{-8}\,\text{cm} = 1.152\ \overset{0}{A}\cdot$$

The value of bond length of CO molecule has been found in good agreement with the experimental results.

This separation between energy levels specified by J' and J'' is given by

$$(\Delta E)\ J',\ J'' = E'-E'' = \frac{h^2}{8\pi^2 I}\left[J'(J'+1)-J''(J''+1)\right]$$

Energy level separation between $J'=1$ (upper level) and $J''=0$ (lower level) is

$$(\Delta E)_{1,0} = \frac{h^2}{8\pi^2 I}[2-0] = \frac{2h^2}{8\pi^2 I}$$

$$(\Delta E)_{1,0} = \frac{2\cdot\left(6.62\times10^{-27}\right)^2}{8\times(3.14)^2\times1.456\times10^{-39}}$$

$$= \frac{(87.6488)10^{-54}}{(114.8446)10^{-39}} = 0.7632\times10^{-15}\,\text{Erg}$$

$$= 0.7632\times10^{-22}\,\text{Jouls}$$

which is quite small compared with the value of kT - being 4.14×10^{-4} Ergs at room temperature. Rotational energy levels usually have energy separation of less than kT. The factor $\frac{h^2}{8\pi^2 I}$ is termed as the energy level spacing factor.

(b) **HCl molecule :** From the frequencies of rotational absorption lines for HCl, it is obtained that

$$2\frac{h}{8\pi^2\,Ic} = 20.7\text{cm}^{-1}$$

or $$2B = 20.7\,\text{cm}^{-1},\ B = 10.35\,\text{cm}^{-1}$$

So, that the moment of inertia is

$$I_{HCl} = \frac{h}{8\pi^2 B\,c} = \frac{6.62\times10^{-27}}{8(3.14)^2\,10.35\times3\times10^{10}}$$

$$= 2.70\times10^{-40}\ \text{gm}-\text{cm}^2$$

Reduced mass of HCl is

$$m' = \frac{m_1\,m_2}{m_1+m_2}\cdot\frac{1}{NO} = \frac{(1.008)\,(35.46)}{(1.008+35.46)} = \frac{1}{6.024\times10^{23}}$$

$$= 1.627\times10^{-24}\,\text{gm}\cdot$$

Bond length of HCl molecule is

$$r^2{}_{HCl} = \frac{I_{HCl}}{m'} = \frac{2.70\times10^{-40}}{1.627\times10^{-24}} = 1.659496005\times10^{-16}$$

$$r_{HCl} = 1.2882\times10^{-8}\,\text{cm} = 1.2882\,\overset{0}{\text{A}}$$

The separation between energy levels $J=0$ to $J=1$ will be

$$(\Delta E)_{1,0} = \frac{2h^2}{8\pi^2 Ic} = 2Bhc$$

$$(\Delta E)_{1,0} = (20.7)\,(6.62)\,10^{-27} \times 3\times10^{10} = 0.411\times10^{-14} \text{ erg}$$

$$=0.411 \times 10^{-21} \text{ Joules.}$$

(c) HI molecule : The rotational spectrum in the far infrared of hydrogen iodide consists of a series of equidistant lines with a spacing of 12.8cm^{-1} or

$$2B=2\cdot \frac{h}{8\pi^2 I\,c} = 12.8\,\text{cm}^{-1},\ B=6.4\,\text{cm}^{-1}$$

Therefore, moment of Inertia $I_{HI} = \dfrac{h}{8\pi^2 Bc}$

$$= \frac{6.62 \times 10^{-27}}{8(3.14)^2\,(6.4)\,3\times10^{10}} = 4.3712 \times 10^{-40} \text{ gm cm}$$

<u>Reduced mass will be</u>

$$m' = \left(\frac{1\times 27}{1+127}\right)\left(\frac{1}{6.024\times10^{23}}\right) = 1.65\times10^{-24}\,\text{gm}$$

Bond length $r^2_{H-I} = \dfrac{I_{H-I}}{m'} = \dfrac{4.372\times10^{-40}}{1.65\times10^{-24}}$

$$r^2_{H-I} = 2.64 \times 10^{-16} = 1.625\,\overset{0}{A}$$

Table 15.1

Internuclear Distances from Rotational Spectra

Molecule	**Moment of Inertia** $1 \mathrm{gm}-\mathrm{cm}^2$	**Bond length** $(\mathrm{r}) \overset{0}{\mathrm{A}}$
Hydrogen Fluoride	1.34×10^{-40}	0.92
Hydrogen Chloride	2.66×10^{-40}	1.29
Hydrogen Bromide	3.31×10^{-40}	1.42
Hydrogen Iodide	4.37×10^{-40}	1.63

Examination of rotational spectra is thus a valuable and accurate means of calculating inter nuclear distances at least for smimple molecules.

One disadvantage of this method of structural investigation even for simple molecules is that in order to exhibit a rotational spectra, the molecule should possess a permanent dipole moment. Molecules like N_2, O_2, CO_2 do not therefore show rotational spectra in far infrared region.

15.3 Intensities of Spectral Lines

Let us consider briefly the relative intensities of spectral lines from the equation

$$\upsilon_{J \to J+1} = 2B(J+1)\ \mathrm{cm}^{-1}$$

For this the prime requirement is plainly a knowledge of the relative probabilities of transitions between various energy levels. For instance a molecule has more or less a chance of making the transition $J=0 \to J=1$ than the transition $J=1$ to $J=2$. We mentioned above calculation which show that a change of $\Delta J = \pm 2, \pm 3$ etc. was forbiddent in other words the transition probability for all these changes is zero. Precisely similar calculations show that the probabiltiy of all changes with $\Delta J = \pm 1$ is almost the same. all, to a good approximations are equally likely to occur.

This does not mean however that all spectral lines will be equally intense. Although the intrinsic probability that a single molecule in the $J=0$ states say will move to $J=1$ is the same as that of a single molecule moving from $J=1$ to $J=2$ in an assemblage of molecules such as in a normal gas sample, there will be different number of molecules in each level to begin with and therefore total numbers of molecules will carryout trnasition between the various levels. In fact since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial number of molecules in each level. The first factor governing the population of the levels is the Boltzmann distribution. Here we know that the rotational energy in the lowest level is zero, since $J=0$ so if we have N_O molecules in this state, the number in any higher state is given by

$$\frac{N_J}{N_O} = \exp\left(\frac{-E_J}{kT}\right) = \exp\left\{\frac{-BhcJ(J+1)}{kT}\right\} \text{ ---------------- (15.4)}$$

Where we must remember c is the velocity in $cm\,s^{-1}$ and B is in cm^{-1}. A very simple calculation shows N_J varies with J; for example taking a typical value of $B=2\ cm^{-1}$ and room temperature (say $T=300K$) the relative population in $J=1$ state is given by

$$\frac{N_1}{N_0} = \exp\left\{\frac{2\times 6.63\times 10^{-34}\times 1\times 2}{1.38\times 10^{-23}\times 300}\right\}$$

$$\frac{N_1}{N_0} = \exp(-0.019) \simeq 0.98$$

and we see that there are almost as many molecules in the $J=1$ state at equilibrium as in the $J=0$. In a similar way the two graphs of fig. 15.2 have been calculated showing the more rapid decrease of $\frac{N_t}{N_0}$ with increasing J and with larger B.

A second factor is also required the possibility of degeneracy in the energy states. Degeneracy is the existence of two or more nergy states which have exactly the same energy. In the case of diatomic rotator we may approach the problem in terms of its angular momentum. The defining equation for the energy and angular momentum of a rotator are

$$E = \frac{1}{2} I\omega^2, \ \overline{P} = I\omega$$

where I is the moment of inertia, ω is the rotational frequency (in radians per second) and $\overline{P}$ is the angular momentum.

Rearrangement of these give $\overline{P} = \sqrt{2EI}$

The energy level expression can be written

$$2EI = J(J+1)\frac{h^2}{4\pi^2} \text{ and hence}$$

$$P = \sqrt{J(J+1)}\,\frac{h}{2\pi} = \sqrt{J(J+1)} \text{ units ------------ (15.5)}$$

while following convention we take $\frac{h}{2\pi}$ as the fundamental unit of angular momentum. Thus we see that $\overline{P}$ like E is also quantized.

In the above discussed $\overline{P}$ is a vector i.e. it has the direction and magnitude. The direction of angular momentum vector vector is conventionally taken to be along the axis about which rotation occurs and it is usually drawn as an arrow of length proportional to the magnitude of momentum vector. The number of different directions which angular momentum vector may take up is limited by a quantum mechanical law which may be stated

"For integral values of rotational quantum number (in this case J) the angular momentum vector may only take up directions such that its component along a given reference direction is zero or an integral multiplies of momentum units.

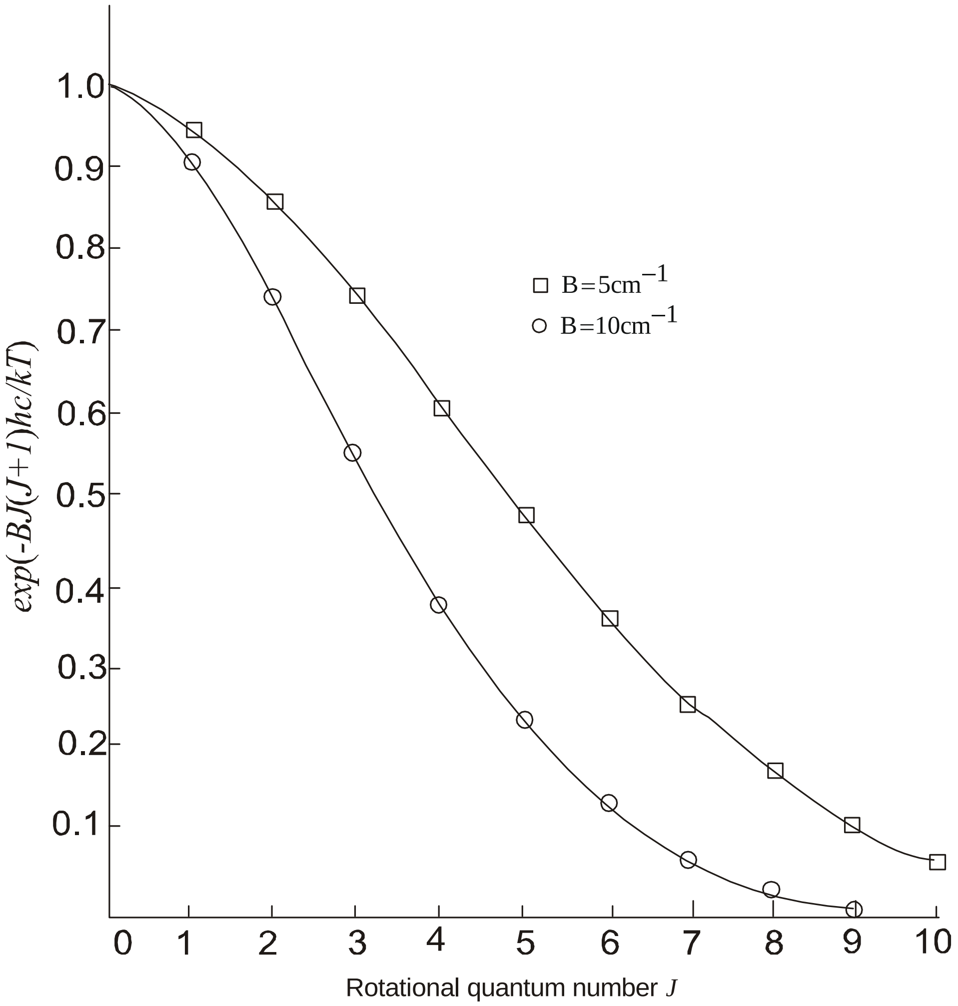


Fig. 15.2 The Boltzmann populations of rotational energy levels.;

The diagram has been drawn taking values of $B = 5\,\text{cm}^{-1}$ and $T = 300\,K$ in equation (15.4).

We can see the implication of this most easily by means of a diagram. In fig. 15.3, we show the case $J=1$. Here $\overline{P} = \sqrt{1\times 2} = \sqrt{2}$ and as fig. shown in Fig. 15.3@ shows a vector length of $\sqrt{2} = (1.41)$ can have only three integrals or zero components along a reference direction here assumed to be from top to the bottom in the plane of the paper : $+1,\ 0,\ -1$. Thus the angular momentum vector in this instance can be oriented in only fig. 15 - 3 (a - d) with respect to the reference direction.

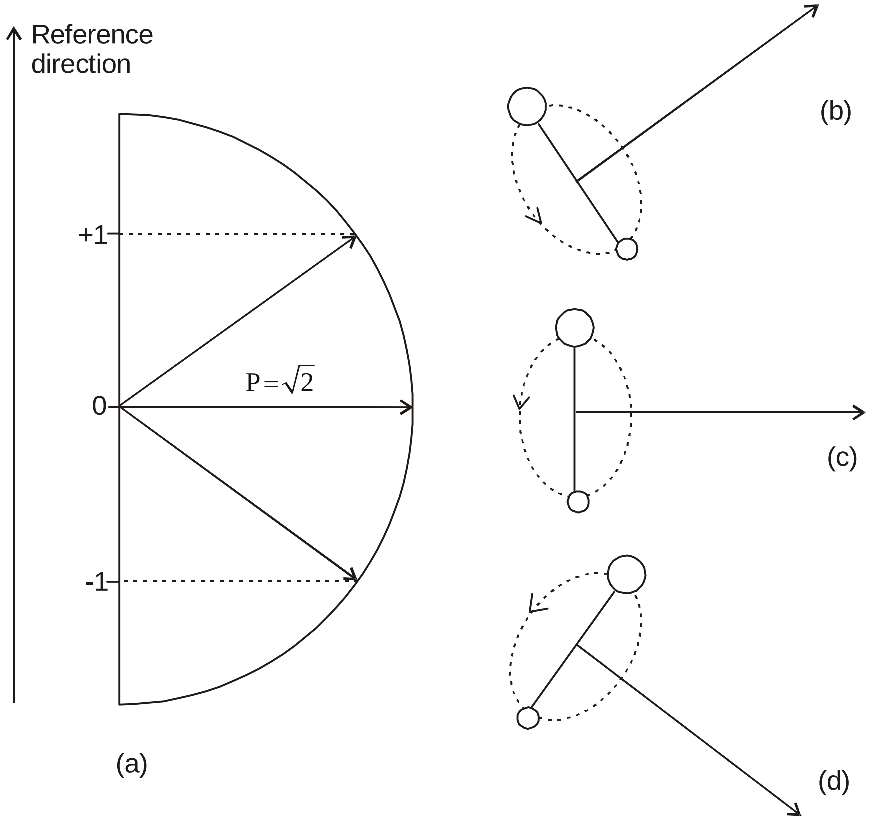


Fig. 15.3 The three degenerate orientation of the rotational angular momentum vector for a molecule with $J=1$

All three rotational directions are, of course associated with the same angular momentum and hence the same rotational energy : $J=1$ level is thus, three fold dengenerate.

Figure 15.4(a) and (b) shows the situation for $J=2$ ($\overline{P}=\sqrt{6}$ and $J=3,\ P=2\sqrt{3}$) with five fold, 7 fold degeneracy respectively. In general it may readily be seen that each energy level is $2J+1$ fold degenerate.

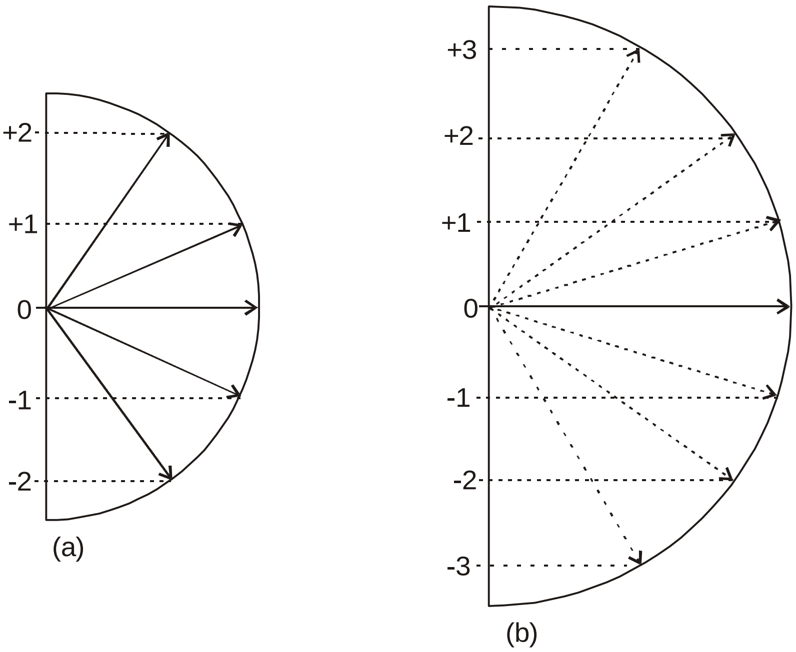


Fig. 15.4 The five and seven fold degenerate rotational orientations for a molecule with $J=2$ and 3 respectively

Thus we seet that, although the molecular population in each level decreases exponentially (equation 15.4) the number of degenerate levels available increase radiply with J. Total relative populations at an energy EJ.

will plainly be :

$$\text{Population} \propto (2J+1)\,\text{Exp}\left(\frac{-EJ}{kT}\right) \text{ ------ (15.6)}$$

when this is plotted against J, the points fall on a curve of the type shown in Fig. 15.5 indicating that the population rises to a maximum and then diminishes. Differentiation of equation (15.6) shows that the population is a maximum at the nearest integral J value to

$$\text{Maximum population } J=\sqrt{\frac{kT}{2hcB}}-\frac{1}{2} \text{ ---------- (15.7)}$$

We have seen that line intensities are directly proportional to the populations of the rotational levels, hence it is plain that transitions between levels with very low or very high J values will have small intensities while the intensity is maximum at or near the J value given by (15.7).

15.4 The Effect of Isotopic Substitution

When a particular atom is a molecule is replaced by its isotope an element identical in every way except for its atomic mass - the resulting substance is identical chemically with the original. In particular there is no appreaciable change inter nuclear distance on isotopic substiution. There is however a change in total mass and hence in the moment of inertia and B value of the molecule.

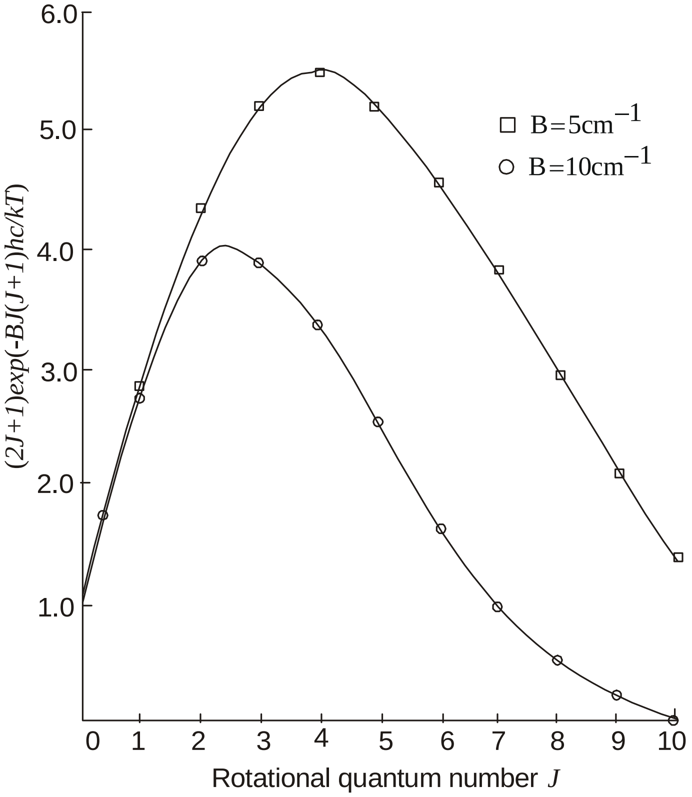


Fig. 15.5 The total relative populations including degeneracy of the rotational energy levels of a diatomic mole : The diagram has been drawn for the same condition as fig 15.2

Considering Carbon monoxide as an example, we see that on going from $^{12}C\ ^{16}O$ to $^{13}C\ ^{16}O$ there is mass increase and hence a decrease in the B value. If we designate ^{13}C molecule with a prime we have $B > B'$. This change will be reflected in the rotational energy levels of the molecule and Fig. 15.6 shows much exaggerated the relative lowering of the ^{13}C levels with respect to those of ^{12}C. Plainly as shown by the diagram at the foot of figure, the spectrum fo the heavier species will show a smaller separation between the lines $(2B')$ than that of the lighter on

$(2B)$. Again the effect has been much exaggerated for clarity and the transition due to the heavier molecule are shown dotted.

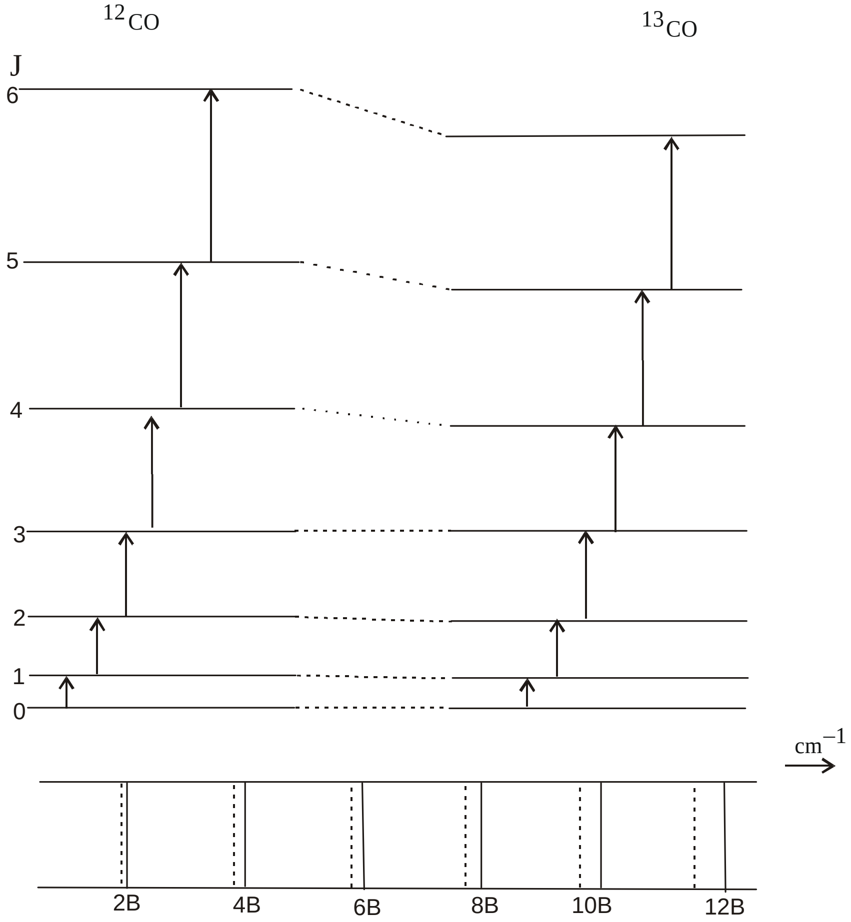


Fig. 15.6 The effect of isotopic substitution on the energy levels and hence rotational spectrum of diatomic molecule such as Carbon monoxide

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam etal as already stated found the first rotational absorption of $^{12}C\ ^{16}O$ to be at 3.84235 cm^{-1}, while that of $^{13}C\ ^{16}O$ was at $3.67337\,cm^{-1}$. The values of B determined from these figures are:

$B = 1.92118\,cm^{-1}$ and $B' = 1.83669\,cm^{-1}$ where the prime refers to the heavier molecule. We have immediately

$$\frac{B}{B'} = \left(\frac{h}{8\pi^2 Ic}\right) = \left(\frac{8\pi^2 I'c}{h}\right) = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is the reduced mass and the inter nuclear distance is considered unchanged by isotopic substituation. Taking the mass of Oxygen to be 15.9994 and that of Carbon 12 to be 12.00, we have :

$$\frac{\mu'}{\mu} = 1.046 = \left(\frac{15.994\,m'}{15.994 + m'}\right) \times \left(\frac{12 + 15.994}{12 \times 15.999}\right)$$

From which m', the atomic weight of Carbon 13 is found to be 13.0007. This is with in 0.02% of the best value obtained in other ways. It is note worthy that the data quoted above were obtained by Gilliam etal for $^{13}C\ ^{16}O$ molecules in natural abundance (i.e. about 1% of ordinary Carbon monoxide). Thus besides allowing an extremely precise determination of atomic weights, microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorptions intensities.

15.5 Vibrational Excitation Effect

In addition to rotational motion a molecule has vibrational motion which is an harmonic. Hence a further connection to the centrifugal distortion has to be made to account for the vibrational excitation of the molecule. The internuclear distance of the molecule varies as the vibrational excitation of the molecule changes. Then each vibrational state υ will have a slightly different rotational constant

$$B_v = \frac{h}{8\pi^2 I_\upsilon c} \quad \text{----------- (15.8)}$$

For a diatomic molecule it can be shown that

$$B_v = B_e - \alpha_e\left(\upsilon + \frac{1}{2}\right);\ \alpha e \simeq \frac{12\,Be^2}{\omega} \quad \text{------------ (15.9)}$$

Here is the rotational constant for the equilibrium hypothetical state of no vibration and α_e is a small positive constant whose approximate value is given above. This effect is very small for states having verly low values.

15.6 Quadrupole Hyperfine Interaction

Nuclei with spin $I \geq 1$ lack the spherical symmetry along the spin axis and possess an electric quadrupole moment eQ. Such nuclei are eihter elongated along the spin axis or shortened in that direction. The nuclear quadrupole moment eQ is a measure of the departure from spherical symmetry and has units of cm^2.

Consider a nucleus and let V be the electric potential at its site due to all electrons and other nuclei.

Then

$$V = \sum_{i} \frac{e}{r_i} + \sum_{j} \frac{\overline{Z}_j \cdot \overline{e}}{R_j} \text{ -------------- } (15.10)$$

where the i summation is over all electrons and j is overall nuclei except the one in question, r_i , R_j are the distances of electrons and nuclei from the nucleus of interest. Z_i is the charge on the j^{th} nucleus. Another quantity of interest is the electric field gradient eq along the Z molecular axis which is defined by

$$eq = \left\langle \frac{\partial^2 V}{\partial x^2} \right\rangle \text{ ---------- } (15.11)$$

where the average is over the electronic sates of the molecule. For symmetric rotor if the nucleus of interest lies on the molecular symmetry axis (chlorine atom in CH_3Cl) the first order perturbation theory gives the following connection to the rotational energy

$$EQ = E^{(1)}_{JK_m} = \frac{e^2 q Q\left[3K^2/J(J+1) - 1\right]}{2I(2I-1)\,(2J-1)(2J+3)} \left[\frac{3}{4}C(C+1) - I(I+1)(J)(J+1)\right] \text{ ---------- } (15.12)$$

where $C = F(F+1) - I(I+1) - J(J+1)$

$F = I + J$ is the total angular momentum quantum number, which takes the values

$(I+J), (I+J-1), ... |I-J|$ --------- (15.13)

The quantity e^2qQ is usually refered to as the quadrupole coupling constant, where K is set to zero in (15.12), the result applies to the linear molecule.

As an example consider a prolate symmetric rotor having a nucleus of spin $I = \frac{3}{2}$ on the molecular symmetry axis (chlorine atom is CH_3Cl). For $J = 0$, $K = 0$, F can have the only value $\frac{3}{2}$. For $J = 0$, $K = 0$, F can have the only value $\frac{3}{2}$. For $J = 1$, K can have the values $0, \pm 1$, and

$F=\frac{1}{2}, \frac{3}{2}$ and $\frac{5}{2}$. Figure 15.7 gives the possible values of J, K, F and the energy levels based on (15.12). The selectio rules

$$\Delta J = \pm 1,\ \Delta K=0 \text{ and } \Delta F=0,\ \pm 1 \text{ ---------- } (15.14)$$

allows three transitions. Without the quadrupole interaction the $J=0 \rightarrow J=1$ transition satisfying the condition $\Delta K=0$ gives a line $2B$. With quadrupole interaction in its place we will have three lines with frequencies

$$\left.\begin{aligned} \upsilon_1 &= 2B-0.25e^2qQ \\ \upsilon_2 &= 2B-0.05e^2qQ \\ \upsilon_3 &= 2B+0.20e^2qQ \end{aligned}\right\} \text{ ------------------------------- } (15.15)$$

The frequencies thus depend upon the field gradient along one principal axis

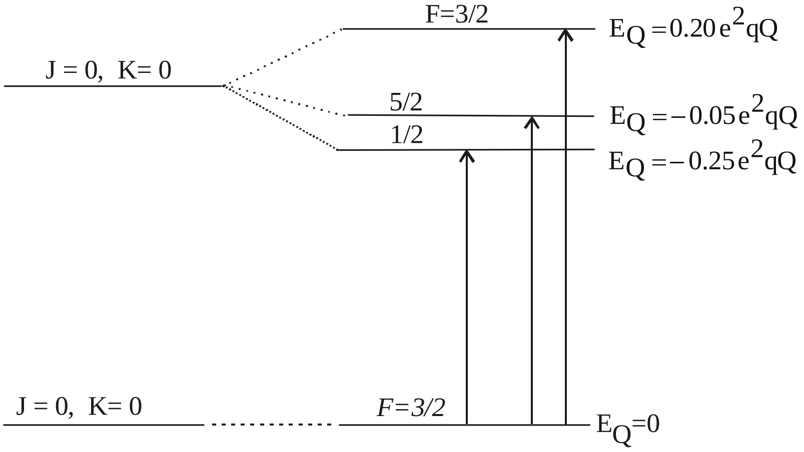


Fig. 15.7 First order conection to rotational energy due to quadrupole hyperfine interaction

Transition between higher J states are more complex and give rise to more components. Their frequencies can also be obtained using 15.12. The theory is much more complex for asymmetric top molecules and the energy EQ generally depends upon the field gradient along two principal axes. Theories describing the concepts of hybridization, ionic character, multiple bond character of the chemical bond in terms of nuclear quadrupole coupling constant e^2qQ have already been formulated. Therefore an analysis of the quadrupole hyperfine structure immediately gives very valuable information regarding electron distribution in molecules.

15.7 Microwave Spectrometer

The following components are needed for the spectrometer. (i) Source (ii) measurement of frequency (iii) guidance of the radiation to the absorbing substance (iv) sample cell (v) Detector A schematic representation of microwave spectrometer is shown in fig. 15.8.

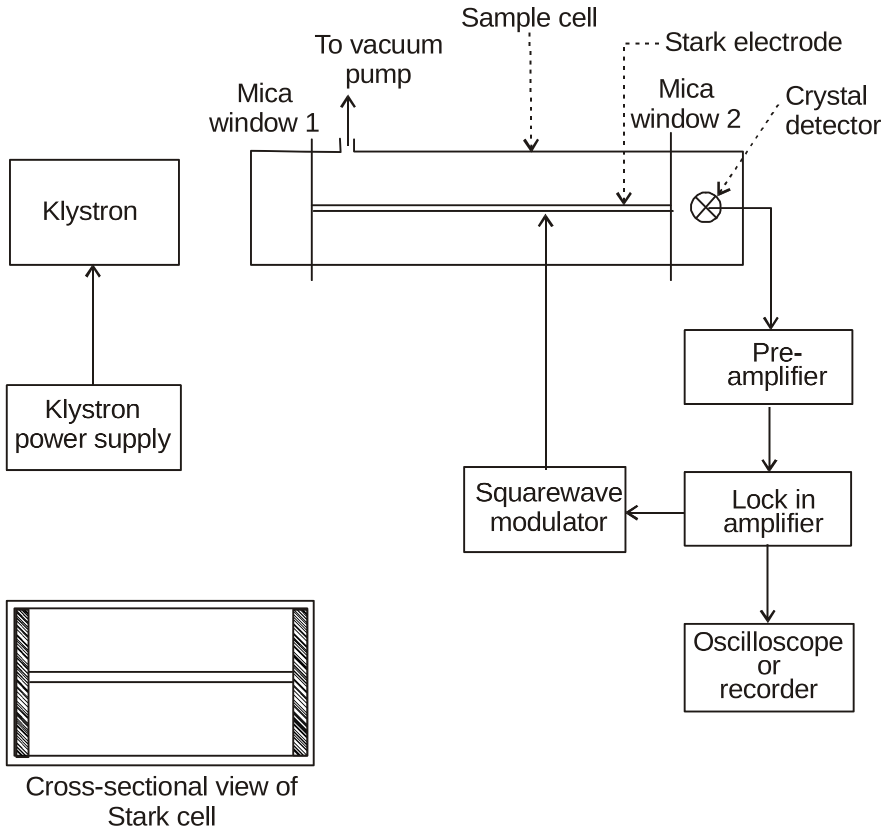


Fig. 15.8 Schematic representation of a microwave spectrometer

Source : Most of the spectrometers have in the past used Klystrons which exists monochromatic microwave radiation of very high stability. The frequency of the Klystron can be varied mechanically over a wide range or electrically over a small range. In place of Klystron backward wave oscillators which can be tuned electronically over a very wide range of frequencies can also be used. However, to avoid instability they have to be phase locked to a stable low frequency sweep oscillator. In recent times Gunn diodes are used extensively as they need only 20V input power compared to the 300 - 4000V required for Klysron and Backward oscillators. They can be turned mechanically over the whole range without voltage adjustments as in the case of Klyston. As these sources are fairly monochromatic dispersion of the radiation by means of prism or grating monochromator is not needed.

Frequency measuring device : Cavity wave meters, accuracy between ± 1 to $\pm 5\,\mathrm{Hz}$ are used to get rough estimate of the frequency of the microwave radiation. Accurate frequency measurements can be done directly by frequency counters or by the use of beat techniques.

Guidance of radiation to cell : Microwave radiation from the source can be transmitted to the sample cell through hollow metallic tube (usually copper) or rectangular cross section called wave guides. Wave guides of different dimensions are needed depending on the type of spectrometer used - X band $(8-12.4\,\mathrm{GHz})$. K band $(12.4-18\,\mathrm{GHz})$ etc., It is necessary to couple out a small fraction of power from the main transmission line for frequency measurment monitoring power etc.

A simple and efficient arrangement for their purpose is the Bethe hole directional coupler. Another useful device is the magic tee which is used as a power divider, as a bridge for balancing microwave power etc. In addition to these, one requires wave guide bends, connectors, tapers, impedance matching devices attenuators etc.

Sample Cell : Different types of cells have been developed depending on the nature of the experiments. Each has its own advantage and disadvantages. One of the comonly used cells is the Stark cell employing Stark modulation techniques. The sample cell consists of a long $\left(3 \text{ to } 4\text{m}\right)$ recangular wave guide, the ends of which are sealed off by means of thin mica windows. It has provision to evaluate and to admit the sample to be studied. The radiation is allowed to enter the cell through mica window 1 and that passes through - window 2 is detected. In Stark cell a flat metal strip is mouted halfway betweent the broad faces of the wave guide cell with a dielectric (teflan) insulating the plate from the metallic wave guide. By injecting a 0 - 2000V zero based square wave potential between the metallic plate and the wave guide, the resonance frequencies of the molecules can be modulated via the Stark effect. The modulation is followed by a phase lock detector which will respond only to molecular resonances. Hence cell back ground characteristics are eliminated in Stark modulated spectro graph.

Detector : A silicon crystal mounted in a coaxial cartridge is the most commonly used detector. The incoming radiation gives rise to a dc current. In Stark spectrographs the transmitted radiation is modulated only when a molecular resonance (absorption) occurs. On resonance, a small square wave is inprinted on the top of the dc signal. This ac component is amplified and detected by a phase sensitive detector which is connected to an oscilloscope or chart recorder. Improved signal to noise ratio is possible only when the modulation frequency is optimum $\left(30-100\text{kHz}\right)$.

15.8 Information Derived from Rotational Spectra and Molecular Structure

Perhaps the most important information that one can get from rotational spectra is details about molecular structure. Rotational constants can be obtained with very high accuracy. Information about the position of atoms in a molecule is obtained from the following three rotational constants from which three principal moments of inertia I_a, I_b and I_c of the molecule can be obtained

$$A = \frac{h}{8\pi^2 I_a},\ B = \frac{h}{8\pi^2 I_b},\ C = \frac{h}{8\pi^2 I_c}$$

In a diatomic molecule there is one observable principal moment of inertia which along with atomic masses gives the interatomic distance.

$$I = \mu r^2,\ r = \left[I\left(\frac{1}{m1} + \frac{1}{m2}\right)\right]^{1/2}$$

where m_1 and m_2 are the masses of the two atoms. A linear molecule of n atoms has in general $(n-1)$ bond distances to be determined. In this case also, only one of the bond distances can be obtained from rotational spectra. However the additional $(n-2)$ bond distances have to be obtained by isotopic substitution as interatomic distances are invariant under isotopic substitution. For symmetric tops also only one of the moments of inertia can be obtained from the rotational spectra. Therefore one requires the rotational constant of as many different isotropically substituted species as they are unknown structural parameters (bond lengths and bond angles). For symmetric top it is possible to get all the three principal moments of inertia from rotational spectra which can give only three molecular parameters. The additional necessary equations to determine all the parameters have to be obtained by determining the moments of inertia of isotopic species of the same molecule. When it is not possible to get sufficient isotopic combinations, combinations of microwave data with data from other sources is done for unambiguous determination of structure.

At this stage it is probably appropriate to distinguish between the hypothetical equilibrium distance r_e and average distance in the ground vibrational state r_0. The distance r_e corresponds to a hypothetical vibrationless state of the molecule where it rotates very slowely. However in the ground vibrational state the molecule has a vibrational energy of $\frac{1}{2}h\upsilon$ and the r_0 value obtained from B_0 is an average value of interatomic distance over the vibration. In the strict sense r_0 is not a simple average it can be represented as

$$\frac{1}{ro} = \left\langle \frac{1}{r^2} \right\rangle^{1/2} \text{------------------ (15.16)}$$

Even if the vibration of the diatomic molecule is harmonic r_0 and r_e would be different with $r_e > r_0$.

At room temperature as most of the molecules are in the $\upsilon = 0$ vibrational state, the experimental rotational constant we get is the B_0 value.

A limitation of structure determination by isotopic substitution is the effect of zero point vibrations. Since the shape of the potential function depends on the electron configuration only, the equilibrium distance r_e is expected to be the same for all isotopes. However, r_0 should not be the same since the constant α_e. Some of the molecular constants determined from rotational spectra are listed in Table 15.1.

Therefore constant of a bond can also be estimated from the values of rotational constant.

$$\bar{\upsilon}^2 = \frac{4B^3}{D}, \ \bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

The force constant K is then given by

$$K = \frac{16\pi^2 c^2 \mu B^3}{D} \text{ ------------- } (15.17)$$

Dipole moment : Precise determination of electric dipole moment is possible from microwave spectroscopy by measurement of the Stark effect. Arrangements exist to measure dipole moment values as low as 0.05 Debye. Moreover Stark effect data gives the value of dipole moment in the appropriate vibrational level. Dipole moments can also throw light on the nature of molecular bonds. Table 15.1 includes the dipole moment values of some of the molecules determined by microwave spectroscopy.

Table - 15.1
Molecular constants from Rotational Spectra

Molecule	Bond length $\left(A^0\right)$	Bond angle	Dipole moment (Debye)
FCl	1.6281	--	0.88
BrCl	2.138	--	0.57
OCS	1.164 $(C=0)$	--	0.71
	1.558 $(C=S)$	--	
HCN	1.064 $(C-H)$	--	3.00
	1.156 $(C\equiv N)$	--	
ClCN	1.629 $(C-Cl)$	--	2.802
	1.163 $(C-N)$		
NH_3	1.090	$107^0\ 21^1$	1.468
NF_3	1.371	103^0	0.234
CH_3Cl	1.095 $(C-H)$	109^0	1.8609
H_2O	0.958	$104^0\ 30'$	1.846

Atomic mass : The very high resolution possible in microwave spectroscopy allows its use for the determination of atomic masses. The rotational spectra of molecules and isotopes give B and B' where prime refers to the isotope molecule.

$$B = \frac{h^2}{8\pi^2 Ic}, \quad B' = \frac{h^2}{8\pi^2 I'c}$$

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

From the known value of μ, one can evaluate μ' from which the mass of the isotope may be estimated.

Nuclear Quadrupole moment : Measurement of quadrupole hyperfine structure in molecules gives the quantity e^2qQ the quadrupole coupling constant. For the evaluation of eQ a knowledge of the quantity q is necessary, which can be estimated by other studies. However, a knowledge of q is not necessary for the determination of the ratios of the quadrupole moment of different isotopes of the same element and those can be precisely evaluated from the microwave measurements. Some of the nuclear quadrupole moments determined from microwave spectra are listed in Table 15.2.

Table 15.2

Nuclear Quadrupole Moments

Nucleus	**Quadrupole moment**	**Nucleus**	**Quadrupole moment**
	10^{-24}cm^2		10^{-24}cm^2
^{10}B	0.06	^{37}Cl	- 0.052
^{11}B	0.03	^{79}Br	0.28
^{14}N	0.02	^{81}Br	0.31
^{17}N	- 0.005	^{127}I	- 0.75
^{35}Cl	- 0.066	^{129}I	- 0.47

15.9 Summary

We have seen the behaviour of two types of molecules discussed in detail the linear and the symmetric top. These give rise to the same basic pattern of spectral lines; a succesion of absorption maxima separated by a nearly constant difference. Their spectra may be distinguished under high resolution since the symmetric top molecules are multiplets with $J+1$ components, while lines from linear molecules have no fine structure. A symmetric top molecules on the other hand give rise to more complex spectra which cannot be analysed in simple terms. Thus we have immediately a method for determining the overall shape of a given molecule. However, we have seen that four parameters are very accurately measurable from microwave spectra

(1) The precise B values lead often judicious isotopic substitution to the bond lengths and angles of fairly simple molecules. Many accurate structural determinations have been made in this way.

(2) The departure of the molecule from the ideal rigid condition can be assessed by the evaluation of distortion constant such as D_J and D_{JK}. These lead to calculations of appropriate molecular force constants.

(3) Measurements on isotopically substituted molecules have led to some of the most accurate estimated precise values of molecular dipole moments.

All this leads to a large volume of useful structural information of great value to physicists and chemists too.

15.10 Key Words

Non Rigid Rotator, vibrational energy, force constant, distortion constant, Moment of Inertia, Bond length, Bond angle, internuclear distance, Intensity of spectral lines, Boltzmann distribution, Isotopic substitution, Vibrational excitation effect, Quadrupole hyperfine interaction, microwave spectrometer, molecular structure, atomic mass, dipole moment, nuclear quadrupole moment.

15.11 Review Questions :

(1) Treating the diatomic molecule as a non rigid rotator, obtain energy level diagram, successive energy levels separation of energy, frequency, determination of force constant, internuclear distance.

(2) Write in detail about the intensities of rotational spectral lines. Also explain the type of information available from isotopic substitution.

(3) Explain the effect quadrupole hyperfine interaction on rotational lines. Through a schematic diagram explain in detail the microwave spectrometer.

(4) Write down the applications of rotational spectroscopy in detail.

15.12 Text and Reference Books

(1) Elements of Spectroscopy by Gupta, Kumar, Sharma Pragati Prakasham

(2) Molecular structure and Spectroscopy by G Aruldhas (PHI)

(3) Fundamentals of Molecular spectroscopy by CN. Banwell (Tata Mc-Graw Hill)

Unit - IV

Lesson - 16

VIBRATING DIATOMIC MOLECULE

Aim :

1. To know and study the molecule as a vibrating diatomic molecule
2. To treat the diatomic molecule as a harmonic oscillator and also as anharmonic oscillator
3. To treat the diatomic molecule as a vibrating rotator like rigid rotator cum harmonic oscillator and like nonrigid rotator cum anharmonic oscillator.

Objectives of the lesson :

1. To study the diatomic molecule as a vibrating one, to deduce energy diagram, energy level, frequency (wave number)
2. To treat the diatomic molecule as a harmonic oscillator and also as anharmonic oscillator, to deduce energy curve, energy levels and expression for the frequency / (wave number)
3. To draw the inference by treating diatomic molecule as a vibrating rotator (Rigid rotator cum harmonic oscillator one way and non rigid rotator cum anharmonic oscillator as another way)

Structure of the lesson :

16.1 Vibrating diatomic molecule as a Harmonic oscillator

16.2 Vibrating diatomic molecule as anharmonic oscillator

16.3 Molecule as a vibrating rotator, Fine structure of Infrared bands by ignoring the interaction between vibrational and ro tational energies

16.4 Summary

16.5 Key words

16.6 Review Questions

16.7 Text and Reference Books

16.1 Vibrating Diatomic molecule as a Harmonic Oscillator Frequency of Vibration

A vibrating diatomic molecule can be approximated to a linear harmonic oscillator whose frequency of vibration can be calculated on the classical lines using Newton's equation of motion. Suppose the bond distorted from its equilibrium length r_e to a new length r, then restoring forces on each atom of a diatomic molecule are

$$m_1 \frac{d^2 r_1}{dt^2} = -K(r - r_e)^*$$

$*$ This relation is similar to $f = -Kx$, where K is a force constant. The relation is also called Hooke's law which states that restoring force on a system displaced by some external force to some distance is proportional to the displacement of the system from its equilibrium position and is directed always in opposite direction of deflecting force.

$$m_2 \frac{d^2 r_2}{dt^2} = -K(r - r_e)$$

Where K is known as a force constant and is measure of the stiffness of the bond r_1 and r_2 are the positions of atom 1 and 2 relative to the centre of mass of the molecule. We already know that

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

$$r_2 = \frac{m_1 r}{m_1 + m_2}$$

Putting the value of r_1 in first equation of motion, we got

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2 r}{dt^2} = -K(r - r_e) \text{ ----------------- (A)}$$

Since, r_e is constant, its differentiation with respect to 'E' will be zero so that we can write

$$\frac{d^2 r}{dt^2} = \frac{d^2(r - r_e)}{dt^2}$$

Putting in equation (A)

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2(r - r_e)}{dt^2} = -K(r - r_e) \text{ ---------------- (B)}$$

Let us put $r - r_e = x$, and $\frac{m_1 m_2}{m_1 + m_2} = m'$

where x would then represent the displacement of the bond length from its equilibrium position. Therefore equation (B) gives

$$m' \frac{d^2x}{dt^2} = -Kx \text{ or}$$

$$\frac{d^2x}{dt^2} + \frac{K}{m'} x = 0 \text{ or}$$

$\frac{d^2x}{dt^2} + \omega^2 x = 0$, which is the equation of simple harmonic motion with a frequency of vibration expressed in cm^{-1} unit (wave number)

$$= \frac{1}{c}\sqrt{\left(\frac{K}{m'}\right)}$$

$$= \frac{1}{2\pi c}\sqrt{\left(\frac{K}{m_1}\right)}\ cm^{-1}$$

Energy Levels : Vibrational energies like other molecular energies are quantised and the permitted vibrational energies for any particular system can be calculated from Schrodinger equation. The eigen values for the energy of a linear harmonic oscillators are of the type

$$E_v = \left(v + \frac{1}{2}\right) hc\omega \text{ ------------- (16.1)}$$

where v is the vibrational quantum number, equal to zero or an integer and ω is the vibrational frequency of the oscillator expressed in wave numbers. We shall now derive it using Schrodinger wave equation.

A vibrating diatomic molecule is appropriated as a harmonic oscillator. The potential energy of the function under the influence of which nuclei vibrate is then a parabolic and is of the form given by

$$V(r) = \frac{1}{2}K\left(r - r_e\right)^2 = \frac{1}{2}K x^2$$

where x is the displacement from the mean position or equilibrium position. Then Schrodinger wave equation can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m'}{h^2}\left(E_v - \frac{1}{2}Kx^2\right)\psi = 0$$

where m' is the reduced mass of the diatomic molecule. If we put

$$\alpha = \frac{8\pi^2 m' E_v}{h^2} \text{ and } \beta = \sqrt{\left[\frac{4\pi^2 m' K}{h^2}\right]} = 2\pi\sqrt{\frac{m'K}{h^2}} \text{ then } \frac{d^2\psi}{dx^2} + \left(\alpha - \beta^2 x^2\right)\psi = 0$$

Further we introduce a dimension less independent variable

$$\xi = \sqrt{\beta}\,x \text{ so that } \frac{d^2}{dx^2} = \beta\frac{d^2}{d\xi^2} \text{ in the above equation}$$

Thus $\beta\frac{d^2\psi}{d\xi^2} + \left(\alpha - \beta^2\frac{\xi^2}{\beta}\right)\psi = 0$ or

$$\xi = \frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0$$

If we try the solution of this equation in the form

$$\psi(\xi) = C\,U(\xi)e^{-\xi^2/2}$$

then equation on putting for the ψ and $\frac{d^2\psi}{d\xi^2}$ becomes

$$\frac{d^2U}{d\xi^2} - 2\xi\frac{dU}{d\xi} + \left[\frac{\alpha}{\beta} - 1\right]U = 0$$

which will become Hermite diffrential equation provided we put $\left(\frac{\alpha}{\beta} - 1\right) = 2v$ or $\frac{\alpha}{\beta} = 2v+1$

so that we can replace $U(\xi)$ by Hermite polynomial $H_v(\xi)$. Thus

$$\frac{d^2H_v(\xi)}{d\xi^2} - 2\xi\frac{dH_v(\xi)}{d\xi} + 2v\,H_v(\xi) = 0\,.$$

Therefore solution of Schrodinger equation becomes

$$\psi = C\,H_v(\xi)e^{-\xi^2/2}$$

and is valid only for $v=0,1,2,.....$. This restriction on v also restricts energy values E.

Finally writing $\frac{\alpha}{\beta} = 2v + 1$

or $$\frac{8\pi^2\,m'\,Ev/h^2}{2\pi\sqrt{m'K/h^2}} = 2v + 1 = 2\left(v+\frac{1}{2}\right)$$

or $$E_v = \frac{h}{2\pi}\sqrt{\left(\frac{K}{m'}\right)}\left[v+\frac{1}{2}\right]$$

$$= h\upsilon\left[v+\frac{1}{2}\right]$$

$$E_v = hc\omega\left[v+\frac{1}{2}\right]$$

where ω is the vibrational frequency of the vibratory diatomic molecule expressed in wave number. The above equation gives the allowed energies for the harmonic oscillator. Significance of the above equation lies in predicting the existence of zero point energy equal to $\frac{1}{2}hc\omega(v=0)$.

If we transform energy value to term value (on dividing by hc) we obtain for the vibrating terms

$$G(v) = \frac{Ev}{hc} = \omega\left(v+\frac{1}{2}\right) \text{ ------------ (16.2)}$$

Putting $v=0,1,2,....$ we get

$$G(v) = \frac{\omega}{2}, \frac{3\omega}{2}, \frac{5\omega}{2}, \frac{7\omega}{2}.......$$

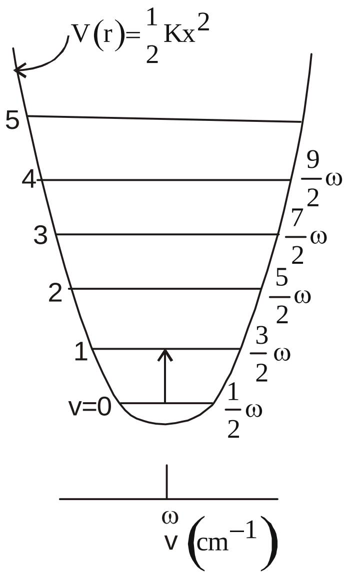


Fig. 16.1 : Equi spaced discrete vibrational levels

Thus we have a series of equispaced discrete vibrational levels (Fig. 16.1) the common separation being $\omega\left(cm^{-1}\right)$. The spacing between vibrational levels is considerably larger than the spacing between rotational levels of a molecule.

Spectrum : Suppose a transition occurs from an upper vibrational level in which the quantum number is v' to a lower state with quantum number v''. The change in vibrational energy will be

$$E'_v - E''_v = \left(v' - v''\right) h c \omega$$

The frequency υ_v of the radiation in wave numbers, accompanying the vibrational transition, would be

$$\upsilon_v = \frac{E'_v - E''_v}{hc} = \left(v' - v''\right)\omega$$

$$= G\left(v'\right) - G\left(v''\right) \text{ ----------- (16.3)}$$

Suppose a transition occurs between $v' = 1,$ and $v'' = 0,$ then

$$\left(\Delta E\right)_{1,\,0} = E'_1 - E''_0 = h c \omega$$

The frequency of this transition would be

$$\left(v_\upsilon\right)_{1,0} = \frac{\left(\Delta E\right)_{1,0}}{hc} = \omega \text{ cm}^{-1}$$

$$= \frac{1}{2\pi c}\sqrt{\left(\frac{K}{m'}\right)}\ \text{cm}^{-1}$$

Therefore we can write $(\Delta E)_{1,0} = hc(v_{\upsilon})_{1,0}$.

Thus vibrational spectrum is expected to consist of a single hand at $\omega\ \text{cm}^{-1}$. Thus an intense band in the infrared spectrum is to be concluded as vibrational spectrum, owing its origin to harmonic vibrations of the nuclei along inter nuclear axis. However infrared spectrum also consists of some weak bonds (called overtones) at frequencies slightly lesser than $2\omega, 3\omega, \ldots.\text{etc}$. Their appearance suggests that the vibration deviate from being harmonic and analysis should be made by treating the vibratory diatomic molecule as anharmonic oscillator.

The vibration spectra are known only in absorption. Electromagnetic radiation can induce transitions among the vibrational energy levels. For the transfer of energy between the radiation and the vibrating molecule an electrical coupling must be present. If the vibrating molecule produces an oscillating dipole moment then the desired coupling results due to the interaction of this dipole moment with the electric field of radiation. Consequently homo-nuclear diatomic molecules like H_2, N_2 and O_2 that possess a zero dipole moment for any bond length will not interact with the radiations. On the other hand molecules like HF, HCl, HBr, HCN have a dipole moment which is some function of internuclear distance (and consequently gives rise to an oscillating dipole moment) will exhibit vibrational spectra.

Population of Energy Levels : Let us take a specific case, say HCl molecule. For HCl molecule the frequency of spectral line arising due to transition between $v = 0$ and $v = 1$ states is $(\upsilon)_{1,0} = 2890\,\text{cm}^{-1}$,

so that $(\Delta E)_{1,0} = hc\upsilon_{10} = 6.62\times10^{-27}\times3\times10^{10}\times2890$

$$= 5.75\times10^{-1.3}\,\text{erg}\cdot$$

representing the energy of the molecule in $v=1$ state compared with one in $v=0$ state. The Boltzmann distribution at 25^0C gives the ratio of population of these two states as :

$$\frac{N_1}{N_0} = e^{-\Delta E/kT} = 8\times10^{-7}$$

which shows that the population N_0 in $v=0$ state the lowest state greater than the population

N_1, in $v=1$ state, or in other words, only a very small friction of the molecules populate in the higher vibrational levels at ordinary temperature. This means that most of the molecules are in the lowest vibrational state. In a spectroscopic study therefore one investigates the absorption of radiation by these $v=0$ states molecules.

Thus main vibrational transition in absorption is $v=1 \leftarrow v=0$.

Transition Rule : For the probability of any given transition it is essential to assume that the diatomic has a permanent dipole moment. For a linear harmonic oscillator the eigen unction are of the form

$$\psi_n = N_n e^{-q^2} H_n(q)$$

where $q = x\sqrt{b}$ (in which x is the displacement of the particle from the equilibrium position and $b = \frac{4\pi^2 \upsilon_m}{h}$ where υ is the frequency of oscillation of the particle of mass m. N_n is a normalizing factor and $H_n(q)$ represents a Hermite polynomial of degree n defined by

$$H_n(q) = (-1)^n e^{q^2} \frac{d^n e^{-q^2}}{dq^n}$$

By inserting appropriate eigen function in the equation

$$P_{mn}(x) = \int \psi^* m \mu_x \ \psi n \ d\tau$$

From this we find that the result differs from zero only, if the change in the vibrational quantum number in the two states, between which transition is to occur is equal to unity. Therefore for a harmonic oscillator the selection rule is $\Delta v = \pm 1$.

Putting two conditions in (16.3) we get $v_\upsilon = \omega$. Predicting that for a harmonic oscillator the frequency v_υ of the radiation emitted or absorbed should be equal to the mechanical frequency ω of the vibration of the system. Thus we find that like classical theory quantum theoritically the frequency of radiated light is equal to the frequency $\upsilon_{osc} (= \omega)$ of the oscillator no matter what the v value of the initial state is. In fig 16.2 the allowed transitions are indicated by vertical lines. It is obvious from the figure that they will give rise to the same frequency.

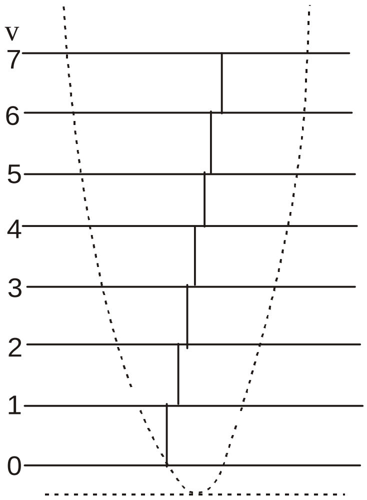


Fig. 16.2 : Potential energy curve, energy levels, and infrared transitions of the harmonic oscillator

16.2 Vibrating Diatomic Molecule as Anharmonic Oscillator

For a strictly harmonic oscillator change in vibrational quantum number is restricted to unit $(\Delta v = \pm 1)$ and hence each mode of vibration would yield one band only. But actual investigation of the vibration rotation spectrum shows that there is one strong band with one or two other bands called overtimes or harmonies. Appearance of these bands corresponds to the frequencies which are possible if the change in the vibrational quantum number is 2, 3, etc., Thus we infer that

(i) Over tones occur because selection rule $\Delta v = \pm 1$ is not strictly obeyed but transitions corresponding to $\Delta v > 1$ do take place. It means dipole moment of the molecule is not strictly linear with respect to the inter nuclear displacement $x = (r - r_e)$ and so points to anharmonicity of the molecule.

(ii) Further overtones (weak bonds) appear not exactly at 2ω, 3ω but at lesser and lesser values. It indicates that vibrational energy levels are not exactly equally spaced but converge slowely. This attributed to the fact that for an actual molecule, the potential energy curve is not strictly parabolic (except near the minimum). It means potential energy function is not merely quadratic but we have to inculde a cubic term at least i.e.

$$V(r)=\frac{1}{2!}\left.\frac{\partial^2 V(r)}{\partial r^2}\right|_{r=r_e}(r-r_e)^2+\frac{1}{3!}\left.\frac{\partial^3 V(r)}{\partial r^3}\right|_{r=r_e}(r-r_e)^3+\cdots\cdots$$

$$=f\left(r-r_e\right)^2-g\left(r-r_e\right)^3=fx^2-gx^3$$

where $g \ll f$. On putting this value of $V(r)$ in the schrodinger equation and solving by perturbations method, we arrive at the energy values given by forthcoming equation (16.5).

Thus real molecules do not obey exactly the laws of simple harmonic motion; real bands although elastic are not homogeneous as to obey Hooke's law. Fig. 16.3 shows the energy curve for a typical diatomic molecule under going an harmonic extensions and compressions together with (dotted) the ideal simple harmonic parabola.

To explain this curve P.M. Morse gave purely emperical expression called Morse function as

$$E=D_{eq}\left[1-\exp\left\{a\left(r_{eq}-r\right)\right\}\right]^2 \text{ --------------- (16.4)}$$

where D_{eq} is the dissociation energy, 'a' is a constant for a particular molecule.

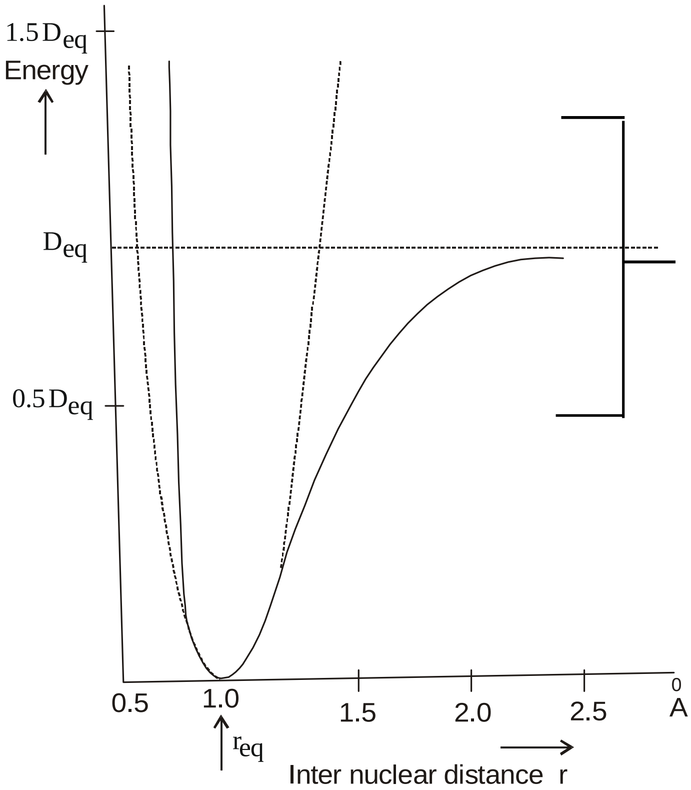


Fig. 16.3 : The Morse curve

r_{eq} is the value of internuclear distance r that corresponds to the minimum of Morse curve (potential energy curve).

Energy Levels : (Eigen values for energy) when equation (16.4) is substituted in the Schrodinger wave equation eigen values for the energy i.e. allowed vibrational energy levels are found to be

$$E_v = \left(v+\frac{1}{2}\right)hc\,\omega_e - \left(v+\frac{1}{2}\right)^2 hc\,x\,\omega_e + \left(v+\frac{1}{2}\right)^3 hcy\,\omega_e + \cdots\cdots \text{ ------ (16.5)}$$

Where x, y etc. are the anharmoniaty constants; ω_e is called equilibrium frequency of the molecule expressed in the wave number and is the value for small displacements. In term values, we obtain for vibrational terms

$$G(v) = \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)x\,\omega_e + \left(v+\frac{1}{2}\right)^3 y\,\omega_e + \cdots\cdots \text{ ------ (16.6)}$$

The quantity ω_e is the spacing (in cm^{-1}) of energy levels that would occur if the potential energy curve were a parabola, $\omega_e\,x$ is the anharmonicity constant' which is much small than ω_e and is always positive Eqn. (16.6) shows that the energy levels of an harmonic oscillator are not equidistant but their separation decreases slowly with increasing v (Fig. 16.4).

Transition Rules :

The use of eigen value equation (16.5) alters the corresponding eigen functions and the alteration in eigen functions when applied to the functions. $P_{mn}(x) \int \psi_m^* \mu_x \psi_n \, d\tau$ leads to the result thatt he matrix component, which determines the probability of transition is no loner zero for all transitions other than those for which the change in vibrational quantum number is unity. The selection rules fo rthe anharmonic oscillator are found to be

$\Delta v = \pm 1, \pm 2, \pm 3$ ------------ (16.7)

The transitions from

$v = 1, v = 0$ gives fundamental band

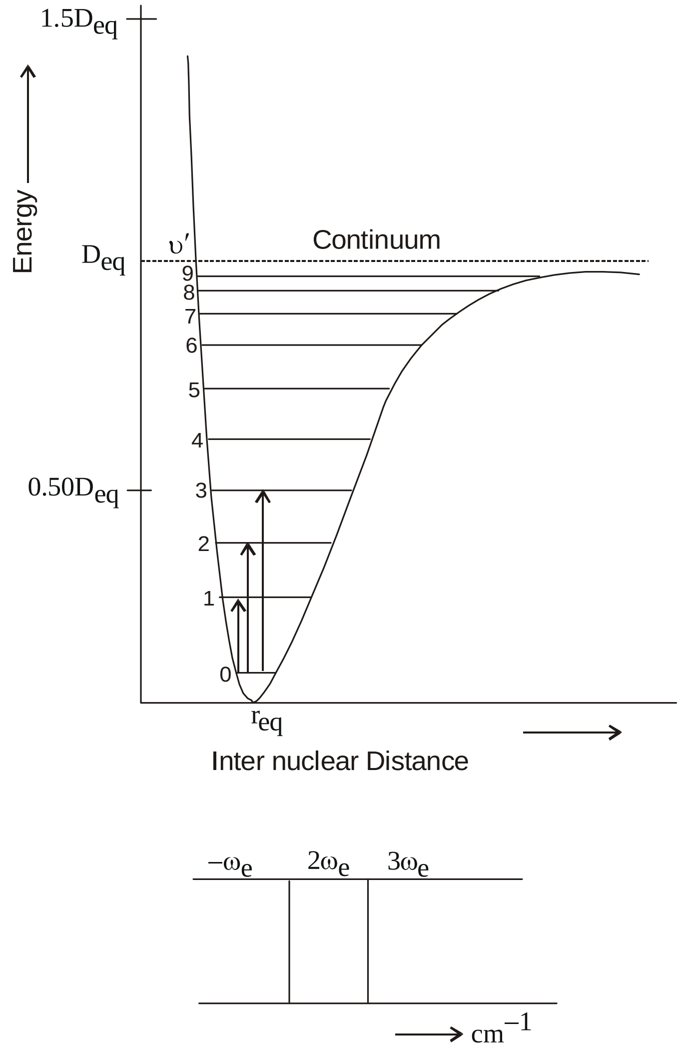


Fig. 16.4 : The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations

$v=2, v=0$ gives first over tone (second harmonic)

$v=3$ to $v=0$ gives second over tone (third harmonic)

Spectrum : Frequency of Vibration :

Now suppose a transition occurs from the upper state v' to the lower state v'', then the energy change will be

$$E\,v' - E\,v'' = (v' - v'')hc\omega_e - \{v'(v'+1) - v''(v''+1)\}hcx\,\omega_e$$

or the corresponding frequency of radiation resulting from the transition will be

$$v_{\upsilon} = \frac{E'_v - E''_v}{hc} = G(v') - G(v'') \text{ ----------- (16.8)}$$

$$= (v' - v'')\omega_e - \{v'(v'+1) - v''(v''+1)\} x\,\omega_e \text{ ------- (16.8)}$$

The vibrational quantum number in the final state is always zero it follows that

$$v_{\upsilon \to 0} = v\omega_e - \{v(v+1)\} x\,\omega_e$$

$$= \{1 - (v+1)x\}\upsilon\omega_e \text{ ----------------- (16.9)}$$

where v is the vibrational quantum number in the initial sate, Thus

for fundamental band : $v = 1,$ to $v = 0$

$$\upsilon_1 = (1 - 2x)\omega_e \text{ --------- (a)}$$

for first over tone band $v = 2$ to $v = 0$

$$\upsilon_2 = (1 - 3x)2\omega_e \text{ --------(b) ----------- (16.10)}$$

for second over tone band $v = 3$ to $v = 0$

$$\upsilon_3 = (1 - 4x)3\omega_e \text{ -------(c)}$$

where υ_1, υ_2 and υ_3 are frequencies of the origin (or centres) of the fundamental, first and second over tone bands respectively. Since the frequencies of first and second over tone bands are approximately 2 to 3 times the frequency of the fundamental band, they appear in regions of the shorter wave lengths than do the fundamental. The intensity of bands falls off with increase value of Δv due to which it is difficult to detectt he over tone band beyond the third. Overtone bands are sufficiently weak in intensity but even then they can be studied experimentaly due to their appearence in shorter wave lengths region.

Vibration bands are almost invariably observe in absorption. The equation (16.10) would also represents the frequency for absorption fundamental and overtone bands with the difference that now transition will occur from $v = 0,$ to $v = 1$, $v = 0$ to $v = 2$, $v = 0$ to $v = 3$ i.e. they are reversed. The three absorption transitions are shown in Fig. 16.4. At room temperature nearly all the molecules in a particular sample have only the zero point vibrational energy and exist in $v = 0$ state. The absorption of radiation must therefore result in transition starting from $v = 0$.

Force Constant for HCl : To a good approximation three spectral lines lie very close to ω_e, $2\omega_e$ and $3\omega_e$. The spectrum of HCl shows a very intense absorption at $2886\,\text{cm}^{-1}$ (hence the fundamental band ω_e) a weaker one at $5668\,\text{cm}^{-1}$ (first overtone band 2 ω_e) and a very weak one

$8347\,\mathrm{cm}^{-1}$ (second over tone band $3\omega_e$). If we wish to fnd the equlibrium frequency of the molecule from these data, we must solve any two of the following equations.

$$\omega_e(1-2x) = 2886$$

$$2\omega_e(1-3x) = 5668$$

$$3\omega_e(1-3x) = 8347$$

we find $\omega_e = 2989\,\mathrm{cm}^{-1}, x = 0.0174$. Thus we see that unlike ideal harmonic oscillator for real anharmonic molecules the observed fundamental absorption frequency may differ considerably from the equilibrium frequency. For infinitesimal displacement (small amplitude) force constant can be determined by

$$K = 4\pi^2\ m'\ C^2\ \omega_e{}^2$$

For HCl molecule : $m' = 1.63\times10^{-24}\,\mathrm{gm},\ w_e = 2989\,\mathrm{cm}^{-1}$ so that

$$K = 4\times(3.14)^2\times(1.63)\times10^{-24}\times\left(3\times10^{10}\right)^2\times(2989)^2$$

$$= 5.1574\times10^5 \text{ dynes / cm}$$

For harmonic oscillator with $\omega = 2886\,\mathrm{cm}^{-1}$ for HCl molecule we get force constant equal to 4.8×10^5 dynes / cm. Which is smaller than for an harmonic oscillator calculated using $\omega_e = 2989\,\mathrm{cm}^{-1}$ instead of ω.

Some molecular data for diatomic molecules determined by infra-red spectroscopy are being recorded in the table.

Example : A problem : The fundamental band for CO is centered at 2143.3 cm^{-1} and first over tone at $2459.7\,\mathrm{cm}^{-1}$. Calculate ω_e and $\omega_e x$.

Solution : We know that frequencies of fundamental and first overtone bands are given by

$$v_1 = (1-2xe)\,\omega_e$$

$$v_2 = (1-3xe)\,2\omega_e$$

Dividing $\frac{v_1}{v_2} = \frac{1-2x}{(1-3x)2}$ or $2v_1 - 6x\,v_1 = v_2 - 2x\,v$

i.e. $x(2v_2 - 6v_1) = v_1 - 2v_1$

$$x = \left(\frac{v_2 - 2v_1}{2v_2 - 6v_1}\right) = \left[\frac{4259.7 - 4286.6}{8519.4 - 12859.8}\right]$$

$$x = \frac{26.9}{4340.4} = 0.006$$

Also $2v_1 - v_2 = 2\omega_e x$

$$\omega_e x = \frac{2v_1 - v_2}{2} = \frac{4.286 - 4259.7}{2}$$

$$\omega_e x = \frac{26.9}{2} = 13.45\,\text{cm}^{-1}$$

Table 16.1

Some molecular data for diatomic moles determined by Infrared spectroscopy

Molecule	Vibration (cm^{-1})	Anharmonity constant x_e	Force constant dynes / cm	Inter nuclear Distance r_{eq} ($\overset{0}{A}$)
HF	4138.5	0.2018	9.66×10^5	0.927
HCl	2390.6	0.0174	5.16×10^5	1.274
HBr	2649.7	0.0171	4.12×10^5	1.414
HI	2309.5	0.0172	3.14×10^5	1.609
CO	2169.7	0.0061	19.00×10^5	1.103

16.3 Molecule as a Vibrating Rotator :

Fine Structure of Infra-red Bands : Ignoring Interaction of Vibrational and Rotational energies :

Hitherto we have considered rotation and vibration quite separately. Observed fine structure of the rotation bands gives ample evidence that a simultaneous rotation and vibration do occur.

A: Diatomic molecule as rigid rotator and harmonic oscillator : The near infra-red spectra of molecules consist of bands (not lines) each band being composed of close lines arranged in a particular manner. This observed fine structure suggests that in a vibrational transition the molecule also changes its rotational energy state, that is it must be treated as a vibrating rotator. As a first approximation, we consider that a diatomic molecule can execute rotation and vibrations quite independently i.e. there i s no interaction between rotational and vibrational energies. We can then take the combined rotational vibrational energy to be simply the sum of the separate energies i.e.

$$E_{total} = E_{rot} + E_{vib} \text{ ergs} \quad \text{--------------} \ (16.11)$$

If we first assume that diatomic molecule to be having as a linear harmonic oscillator and a rigid rotator the combined energy will be

$$E_{vr} = G(v) + F(J) = \left(v + \frac{1}{2}\right) hc\omega + \frac{h^2}{8\pi^2 I} J(J+1)$$

Suppose a simultaneous transition from the vibrational and v' to the level v'' and from the rotational level J' to the level J'' occurs. Then change in energy on using the above equation

$$E'_{vr} - E''_{vr} = (v' - v'')\, hc\omega + \frac{h^2}{8\pi^2 I}\left\{J'(J'+1) - J''(J''+1)\right\}$$

and the corresponding frequency of radiation arising due to this transition will be

$$\upsilon = \frac{Evr' - Evr''}{hc} = (v' - v'')\omega + B\left\{J'(J'+1) - J''(J''+1)\right\} \quad \text{--------} \ (16.12)$$

where $B = \dfrac{h}{8\pi^2 Ic} = \dfrac{h}{8\pi^2 m' r^2 c}$

B. Diatomic molecule as a non-rigid rotator and anharmonic oscillator : If we consider the diatomic molecule as the non-rigid rotator and anharmonic oscillator then the combined energy will be

$$E_{rv} = G(v) + F(J)$$

$$E_{rv} = hc\left[BJ(J+1) - DJ^2(J+1)^2 + H + J^3(J+1)^3 + \cdots\cdots\cdots\right]$$

$$\left(v+\frac{1}{2}\right)\omega_e - x\left(v+\frac{1}{2}\right)^2\omega_e + \cdots\cdots$$

Initially we ignore the small centrifugal distortion constant D, H etc. therefore

$$E_{rv} = hc\left[BJ(J+1) + \left(v+\frac{1}{2}\right)\omega_e - x\left(v+\frac{1}{2}\right)^2\omega_e\right] \quad \text{----------} \ (16.13)$$

By neglecting D, we are again treating here the molecule as rigid yet vibrating. We have mentioned earlier that B is about 10 cm^{-1} or less while D is only some 0.01% of B. Since a good infrared spectrometer has a resolving power of about 0.5 cm^{-1} it is obvious that D is negligible to a very high degree of accuracy.

It may be shown that the selection rules for the combined vibrational and rotational motion are the same as those for rotation and vibration separately. Therefore

$\Delta v = \pm 1, \pm 2$ etc.,

$\Delta J = \pm 1$

Relevent energy levels and transitions are shown in fig. 16.5, denoting rotational quantum numbers in $v=0$ state as J'' and $v=1$ state as J' (single prime is used for upper state and double for lower state).

An analytical expression for the spectrum can be obtained by applying the above selection rules to the energy levels. Considering only $v=0$ to $v=1$ transition, we have ingeneral the frequency of the transition as

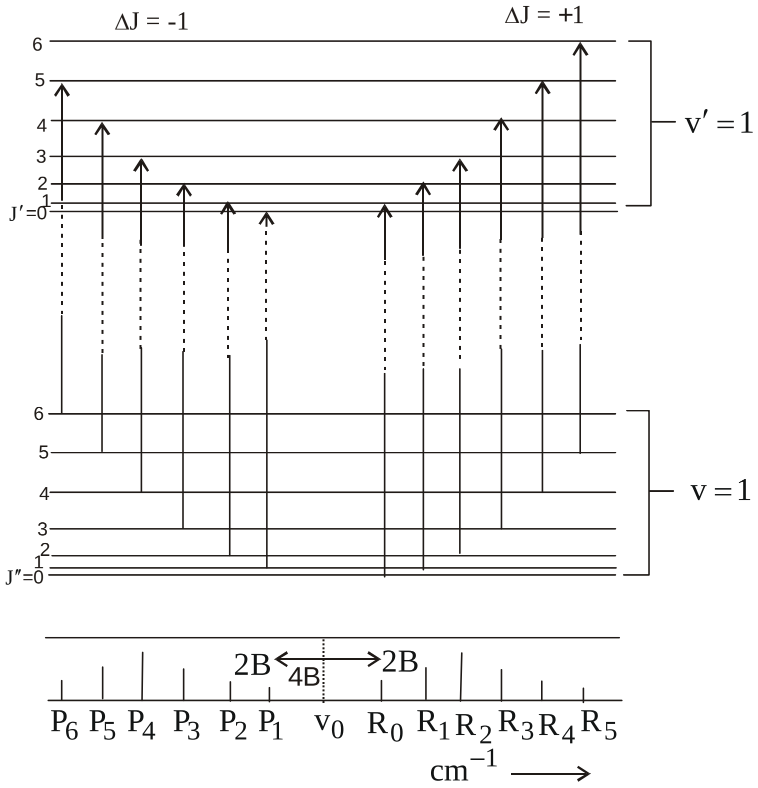


Fig. 16.5 : Some transitions between the rotational - vibrational energy levels of a diatomic molecule together with the spectrum arising from then (absorption spectra). Note that lines in P and R branches are shown equidistant.

$$\upsilon = \frac{E'_{r,\,v=1} - E''_{r,\,v=0}}{hc}$$

$$= BJ'(J'+1) + \frac{3}{2}\omega_e - \frac{9}{4}x\omega_e - \left\{BJ''(J''+1) + \frac{1}{2}\omega_e - x\omega_e\right\}$$

$$= \upsilon_0 + B(J'-J'')(J'+J''+1)\,cm^{-1} \text{ -------------- (16.14)}$$

Where $\omega_e(1-2x)$ we have written υ_0. It is the wave number of the pure vibrational transition (for which $J' = J'' = 0$) which is not allowed (as $\Delta J \neq 0$) and corresponds to the missing line in the band. υ_0 is knownl as the wave number of the 'band origin'.

Because we have taken rotation to be independent of vibrational changes B will remain same is the upper and lower vibrational states. Now we can have

R branch $\Delta J = +1$, i.e. $J' = J'' + 1$ or $J' - J'' = +1$. Hence

$$\upsilon(R) = \upsilon_0 + 2B(J''+1)\,cm^{-1},\ J''=0,1,2,.......$$ --------- (16.15)

P branch : $\Delta J = -1$ i.e. $J'' = J'+1$ or $J' - J'' = -1$. Hence

$$\upsilon_P = \upsilon_0 - 2B(J'+1)\,cm^{-1},\ J'=0,1,2,....$$

$$\upsilon(P) = \upsilon_0 - 2BJ'',\ \ J'' = 1,2,3,$$ ----------- (16.16)

Discussion : Equation (16.15) and (16.16) can be combine in the form

$$\upsilon = \upsilon_0 + 2Bm\ cm^{-1}$$ ------------- (16.17)

where $m = \pm 1,\ \pm 2,\ \pm 3$ etc.......

(i) m cannot be zero since this implies J' or J'' to be -1. The frequency υ_0 is usually called band origin. Equation (16.17) represents the combined vibration rotation spectrum. Such a spectrum will thus consist of equally spaced lines with a spacing $2B$ one each side of the band origin υ_0 but since $m \neq 0$ the line at υ_0 it will not appear (absense of Q branch).

(ii) **P branch :** Equation (16.17) gives a series of lines with a constant frequency separation $2B\,cm^{-1}$ lying on the lower frequency (longer wave length) side of the centre of the band (of frequency υ_0) when m has negative values. These lines constitute the fine structure of what is known as the P branch of the vibration rotation band. The frequencies of this branch are given by equation (16.16).

(iii) **R branch :** For positive values of m, similar series of lines with a constant frequency separation of $2B\,cm^{-1}$ appears on the higher frequency (shorter wave length) side of the centre of the band. This serives is termed as R branch of vibration rotation band. The frequencies of this branch are given by (16.15).

We note that value of m in equation (16.17) cannot be zero so that the line of frequencies corresponding to the centre of the band should be absent. Thus lines arising form

ΔJ	-2	-1	0	1	+2	
are called	O	P	Q	R	S	branches

The theoritical predictions are in agreement with the experimental. In fig. 16.6, the relation vibration bands of hydrogen chloride (HCl) are shown. It is found to consist of a number of lines with an approximate constant frequency of separation $2B\,cm^{-1}$. As expected there is a gap at the of the band and threrefore spacing between the lines immediately on each side of the centre is thus $4B\,cm^{-1}$.

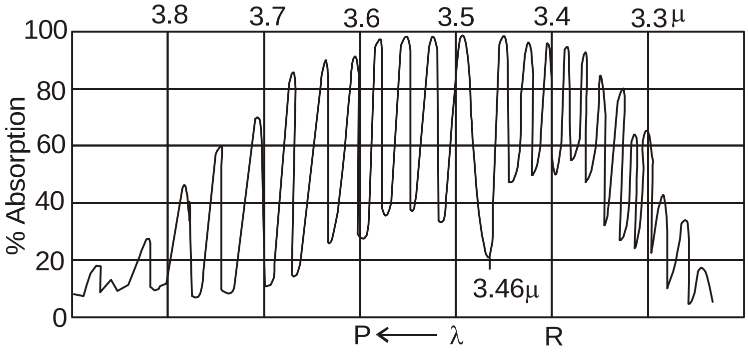


Fig. 16.6 Principle absorption band of HCl in the near infrared

16.4 Summary

(1) Vibrating diatomic molecule also contains rotational lines to start with vibrating diatomic molecule is approximated to a linear harmonic oscillator energy level, frequency of this trnansition is evaluated.

(2) Homo nuclear diatomic molecules such as H_2, N_2, O_2 do not posess dipole moment and hence do not exhibit vibrational spectra. Vibrational spectra is known only in absorption.

(3) Transition rule and selection rules for vibrating diatomic molecule is $\Delta v = \pm 1$ and $v_\upsilon = \omega$.

(4) Because expermintal evidence vibrational spectra is different from what has been said above and there by vibrating diatomic molecule has been considered as anharmonic oscillator, energy level have been given. The transition and selection rules not dictate.

$\Delta v = \pm 1, \pm 2, \pm 3$ etc.,

The energy spectram and frequency of vibration has been shown. As an example HCl molecule is taken and force constant has been calculated. Co molecule is also taken as an example.

(5) Vibrating rotator has been taken and the fine structure of infra-red bands have been evaluated. Even here the interaction between vibrational and rotational energies has been ignored. Diatomic molecule has been treated as rigid rotator and harmonic oscillator and later as diatomic molecule has been treated as non-rigid rotater and anharmonic oscillator.

(6) P branch lines and R branch lines are distinguished Q branch lines are absent which are identified at the centre of the band origin.

16.5 Key Words

Vibrating diatomic mole, Harmonic oscillator, Vibrational quantum number, zero-point energy term value, homo nuclear and hetero nuclear molecules, dipole moment, Hermite polynomial, force constant, Anharmonic oscillator, Morse Curve, Parabolic, Fundamental band, First over tone (Second harmonic) Fine structural of infrared bands.

16.6 Review Questions

(1) Treating the diatomic molecule as vibrating as a harmonic oscillator, obtain the energy levels, frequency (wave number) expressing, Sketch the potential energy diagram, explain the inference to be drawn from the curve.

(2) Treating the diatomic molecule as vibrating anharmonic oscillator, obtain the energy levels frequency (wave number expression, obtain the energy diagram, Illustrate the important features of the energy diagram. Distinguish between harmonic oscillator and anharmonic oscillator.

(3) Treating the diatomic molecule as a vibrating rotator and as like a rigid rotator anharmonic oscillator draw the transitions between different energy levels. Explain P, Q, R branch of lines. Illustrate with an example.

16.7 Text and Reference Books

(1) Elements of spectroscopy by Gupta Kumar Sharma, Pragathi Publication.
(2) Molecular Structure and Spectroscopy by G. Aruldhas (PHI)
(3) Fundamentals of Molecular Spectroscopy by C N Banwell, Tata McGraw Hill

Unit - IV

Lesson - 17

VIBRATING ROTATOR -

INTERACTION OF VIBRATIONAL AND ROTATIONAL ENERGIES

Aim : To know and study the molecule as a vibrating rotator with interaction between vibrational and rotational energy levels. To determine the change in the spectra due to isotopic effect. To highlight the applications of vibration spectroscopy.

To know about IR spectrometer and to understand about vibrational spectroscopy of poly atomic molecule and finally to tell about essential features of vibrational spectroscopy.

Objectives of the lesson :

1. The molecule as a vibrating rotator and having significant interaction between vibrational and rotational energies, to draw energy levels, frequency of separation, transition level through diagram.
2. To look into the effect of Isotopic substitution of vibrational energy levels.
3. To highlight the essential features of vibrational spectroscopy along with important applications of vibrational spectroscopy
4. Through a sketch diagram (Block diagram) to know about IR spectrometer and different parts.
5. To understand vibrational rotational spectroscopy of polyatomic molecules.

Structure of the lesson :

17.1 Introduction of Vibrating Rotator

If we do not take interaction of vibrational and rotational energies into consideration R branch lines and P branch lines are equidistant. That is these lines form two branches of equidistant lines. But in practice it is not observed like this. In fact the separation between the lines of one branch slowly decreases (R branch) and of other branch slowly increases (P branch) as we move towards higher and higher lines of the branch. This is attributed to vibration - rotation interaction.

Though it is assumed that vibration and rotation can proceed quite independently of each other but it is not so. As a molecule vibrates some 10^3 times during the course of a single motion the bond length also changes continually during the motion. A change in bond length will also change the moment of inertia and constant $B \left[\text{since } I = m'r^2 \text{ and } B = \frac{h}{8\pi^2 Ic}\right]$. Thus ineraction betweent he two energies occurs. An increase in vibration energy is accompanied by an increase in the vibrational amplitude. Since, B the rotational constant depends on $\left[\frac{1}{r^2}\right]$ (r represent internuclear distance or bond length) it will depend upon the vibrational quantum number v. An increase in vibration energy will lead to an increase in the average band length r_{av}, rotational constant B is smaller in the upper vibrational state than in the lower. An equation of the form

$$B_v^* = B_e^\dagger - \alpha\left(v + \frac{1}{2}\right) + \cdots\cdots \text{ --------- } (17.1)$$

gives the value of B_v, the rotational constant in vibrational level v, interms of the equilibrium value B_e and α, a small positive constant for each molecule. (i.e. corresponding to the equlibrium state of the molecule) of the order of 0.02 B_e to 0.05 B_e.

[$^*B_v$ can be defined in the usual manner by $B_v = \frac{h}{8\pi^2 I_v c}$, where I_v is the moment of Inertia of the molecule with vth vibrational level given by $I_0 = m'r_v{}^2$, $r_v{}^2$ is the means square of the internuclear distance in that level. When amplitude of vibration is small, we define the quantity B_e as, $B_e = \frac{h}{8\pi^2 I_e c}$, with $I_e = m' r_e^{\,2}$ where $r_e^{\,2}$ refers to the internuclear distance in the equilibrium state of the molecule].

In the same way the constant D_v, which allows for the nonrigidity of the molecule is related to the equailibrium value D_e by

$$D_v = D_e + B_e\left(v+\frac{1}{2}\right) \quad \text{------------ (17.2)}$$

Where B_e is small compared to D_e which itself is small. Taking above points into consideration, the rotational energy of a diatomic molecule can be modified to take the form

$$E_r = B_v\, J(J+1)hc - D_v J^2 (J+1)^2 hc \quad \text{-------- (17.3)}$$

where B_v and D_v bear the same significance as explained in equations (1) and (2) and refer to the particular vibrational level indicated by quantum number v.

In the lowest state $(v=0)$ these become B_0 and D_0 quite identical with the quantities B and D respectively. Further since in equation (17.2) B_e is small compared to D_e, we write D_e instead of D_v. This equation (17.3) take the form

$$E_r = B_v J(J+1)hc - D_v J^2 (J+1)^2 hc + \cdots\cdots \quad \text{---------- (17.4)}$$

where D_e is regarded as constant for all vibrational levels. The total vibrational and rotational energy allowing for interaction in terms

$$\boxed{\begin{aligned} &E_{vr} = \left(v+\frac{1}{2}\right)hc\,\omega_e - \left(v+\frac{1}{2}\right)^2 hc\,x\,\omega_e + \cdots\cdots \\ &B_v\, J(J+1)hc\; - D_e J^2 (J+1)^2 hc + \cdots\cdots \end{aligned}} \quad \text{--------- (17.5)}$$

The expression gives the frequencies of the lines constituting P and R branches of vibrational band i.e.

$$J-1 \text{ to } J\,;\; \upsilon(P) = \upsilon_0 - (B_{v'} + B_{v''})J + (B_{v'} - B_{v''})J^2 + 4D_e J^3 + \cdots\cdots \quad \text{----- (17.6)}$$

J to $\mathrm{J}-1;\ \upsilon(\mathrm{R}) = \upsilon_0 + (\mathrm{B}_{\mathrm{v}'} + \mathrm{B}_{\mathrm{v}''})\mathrm{J} + (\mathrm{B}_{\mathrm{v}'} - \mathrm{B}_{\mathrm{v}''})\mathrm{J}^2 - 4\mathrm{D}_e\mathrm{J}^3 \cdots\cdots$ -------- (17.7)

where $\mathrm{J} = 1,\ 2, 3, \cdots\cdots$

The constants $\mathrm{B}_{\mathrm{v}'}$ and $\mathrm{B}_{\mathrm{v}''}$ are the values of $\mathrm{B_V}$ in the initial (upper) and final (lower) states involved in the vibrational transition. v_0 is the frequency of the centre of the band

If we ignore, D_e, then equation (17.6) and (17.7) can be written as

$$\upsilon_{\mathrm{P,R}} = \upsilon_0 + (\mathrm{B}_{\mathrm{v}'} + \mathrm{B}_{\mathrm{v}''})\mathrm{m} + (\mathrm{B}_{\mathrm{v}'} - \mathrm{B}_{\mathrm{v}''})\mathrm{m}^2\ \mathrm{cm}^{-1}$$

where $\mathrm{m} = +1,\ +2, +3$ for R branches

and $\mathrm{m} = -1,\ -2,\ -3$ for P branches

Discussion :

(i) As we know that the average inter nuclear distance (r_e) increases with vibraitonal energy, the vibrational constant $\mathrm{B_v}\left(= \dfrac{\mathrm{h}}{8\pi^2\ \mathrm{Ic}} = \dfrac{\mathrm{h}}{8\pi^2\ \mathrm{m}'\ \mathrm{r}_e{}^2\ \mathrm{c}}\right)$ is small in the upper vibrational state than in the lower. Since $\mathrm{B}''_{\mathrm{v}}$ denotes lower state we have always $\mathrm{B}_{\mathrm{v}'} < \mathrm{B}_{\mathrm{v}''}$. It means band head appears in R branch on the high wave number side of the origin. Such a band is said to be degrade towards the red. Thus in vibration - rotation spectra bands are degraded to read only.

But later in electronic spectra we shall observe that since $\mathrm{B}_{\mathrm{v}'} - \mathrm{B}_{\mathrm{v}''}$ would belong to different electronic staates, $(\mathrm{B}_{\mathrm{v}'} - \mathrm{B}_{\mathrm{v}''})$ may be negative or positive, that is $\mathrm{B}_{\mathrm{v}'} > \mathrm{B}_{\mathrm{v}''}$ or $\mathrm{B}_{\mathrm{v}'} < \mathrm{B}_{\mathrm{v}''}$ both are possible. Therefore in electronic band system both red and violet degraded bands have been observed.

(ii) If molecule possesses a resultant angular momentum, so that there is a probability of the transition for which $\Delta\mathrm{J}$ is zero, then the expression for the frequency Q branch is $(\mathrm{J}\ \text{to}\ \mathrm{J})$

$\upsilon(\mathrm{Q}) = \upsilon_0 + (\mathrm{B}_{\mathrm{v}'} - \mathrm{B}_{\mathrm{v}''})\mathrm{J} + (\mathrm{B}_{\mathrm{v}'} - \mathrm{B}_{\mathrm{v}''})\mathrm{J}^2$ ------------ (17.8)

Where $\mathrm{J} = 0, 1, 2, 3, \cdots\cdots\cdots\cdots$

which accounts for the fact that Q branch is observed to have a number of very closely spaced lines. When vibrational quantum numbers v' and v'' differ by 3 or 4 at most the difference $\left(B_{v'} - B_{v''}\right)$ must be small and hence the lines be closely spaced.

(iii) From equation (17.6) and (17.7) we find that the frequency separation $\Delta\upsilon$ of successive lines in the P and R branches as respectively, given by

$$\left.\begin{aligned}\Delta\upsilon(P) &= 2B_{v'} - \left(B_{v'} - B_{v''}\right) 2J + \cdots\cdots\cdots \\ \Delta\upsilon(R) &= 2B_{v'} - \left(B_{v'} - B_{v''}\right) 2J + \cdots\cdots\cdots\end{aligned}\right\} \text{-------- (17.9)}$$

which shows that the frequency separation of successive lines in the vibration band will not be constant in either branch.

As for both P or R branches we have $B_{v'} < B_{v''}$ the separation between lines of R branch will decrease with increasing J values where as separation between lines of P branch will increase with increasing J values.

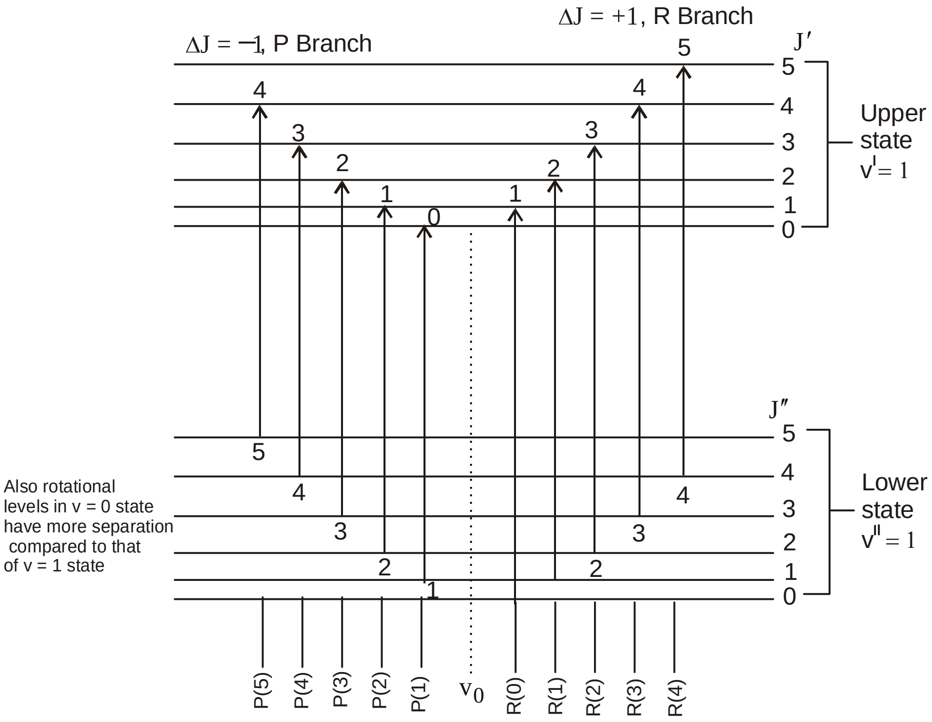


Fig. 17.1 P & R branches of rotation - vibration spectra, Note that lines in R branch & also in P branch are not equidistant

$B_{v'}$ refers to the upper and $B_{v''}$ to the lower state. Further $B_{v'} < B_{v''}$, factor B_v decreases slightly with increasing v, the spacings between the rotational levels associated with vibrational state $v=1$ are slightly smaller than those between the rotational levels associated with vibrational state $v = 0$.

Applications : We can evaluate witht he help of rotation vibration spectra, the equilibrium moments of inertia I_e and the corresponding nuclear separations r_e. For this B_v values for two or theree vibrational levels are determined from the analysis of the frequencies of the lines in P and R branches of the various vibration - rotation bands of a given diatomic molecule. From these the value of rotational constant B_e is calculated on using the equation (17.1). B_e then provides the value of I_e since $B_e = \frac{h}{8\pi^2 I_e c}$. Further $I_e = m' r_e^2$ and r_e, the inter nuclear distance in the equilibrium state of the molecule can be determined. The data for most abundant isotopic form of each of the hydrogen halides are given in the table below.

Table 17.1 : Inter-nuclear distance from vibrational - rotation spectrum

Substance	$B_e\ cm^{-1}$	$I_e\left(gm-cm^2 \times 10^{-40}\right)$	$r_e\,(cm) \times 10^{-8}$
HF	20.967	1.335	0.9266
HCl	10.591	2.644	1.747
HBr	8.471	3.304	1.414
HI	65.51	4.272	1.604

17.2 Isotopic Effect in Vibrational Bands

The two isotopic forms of the same molecule have different reduced masses but force constants would remain the same. From the expression $K = 4\pi^2 \omega_e^2 m^1 c^2$, for force constant, it is evident that equilibrium vibration frequencies of the two forms will differ. Let ω_1 and ω_2 be the values of ω_e for the two isotopic forms and m_1' and m_2' be their respective reduced masses, then form the rotatioon force constant $K = 4\pi^2 \omega_e^2 m' c^2$, it follows that

$$\frac{\omega_2}{\omega_1} = \left[\frac{m_1'}{m_2'}\right]^{1/2} = \rho \text{ ------------- } (17.10)$$

or $\omega_2 = \rho\,\omega_1$.

Anharmonity constant x from theoretical considerations is proportional to the equilibrium frequency so that we can write

$$x_2 = \rho\, x_1 \text{ ----------- } (17.11)$$

Now we know that

$v_{\upsilon\to 0}\, v\,\omega_e - \{1-(v+1)x\}\, v\,\omega_e$ gives the general expression for the frequency of the centre of any band involving lower vibrational level of $v=0$. Writing that equation

$$v_{\upsilon\to 0} = v\,\omega_e - \{v(v+1)\}\, x\,\omega_e$$

which with the aid of equations (17.1) and (17.2) gives

$${}_1\upsilon_{v\to 0} = v\,\omega_1 - \{v(v+1)\}\, x_1\, \omega_1$$

and $${}_2\upsilon_{v\to 0} = v\,\rho\omega_1 - \{v(v+1)\}\,\rho^2\, x_1\,\omega_1$$

The subscripts 1 and 2 refer to the isotopic forms of the same molecule. The frequency difference of the centres of the two isotopic bands called isotopic shift, $\Delta\upsilon_i$ is the

$$\Delta\upsilon_i = (1-\rho)\{1-(v+1)(1+\rho)\,x_1\}\, v\,\omega_1 \text{ -------- } (17.12)$$

The relation gives the isotopic shift for

(i) Fundamental band $(v=1 \text{ to } v=0)$

$$\Delta\upsilon_i(1) = (1-\rho)\{1-2(1+\rho)\,x_i\}\ \omega_1$$

(ii) First over tone band $(v=2 \text{ to } v=0)$

$$\Delta\upsilon_i(2) = (1-\rho)\{1-3(1+\rho)\,x_1\}\, 2\omega_1 \qquad (17.13)$$

(iii) Second overtone band $(v=3 \text{ to } v=0)$

$$\Delta\upsilon_i(3) = (1-\rho)\{1-4(1+\rho)\,x_1\}\, 3\omega_1$$

Thus we find that if x_1 and ω_1 are known for one isotopic form of the molecule, it is possible to calculate the frequency shift corresponding to another isotopic form of the same diatomic molecule. The isotopic shift depends upon the factor $(1-\rho)$ and since $\rho=\left[\frac{m_1'}{m_2'}\right]^{1/2}$ the former also depends upon the ratio of the reduced masses. Isotopic shift increases with the increase in $(1-\rho)$. Isotopic exchange as we have seen, changes the frequency of the centre (origin) of the band. Further from the equation (17.6) and (17.7) we note that rotational lines in the band involve the frequency of the origin (υ_0) as the constant term and thus a shift in the frequency of the origin will result in the shifting of all the lines by the same amount as a whole. If $\rho>1$ the isotopic shift $\Delta\upsilon_i$ is in the direction of lower frequency whereas if $\rho<1$ the shift in the opposite direction. The vibrational isotopic shift expected according to the theory was first noticed by Loomis and independenly by Kratzer in the rotation vibration spectrum of HCl. Since Cl has two isotopes Cl^{35} and Cl^{37} two bands should appear in the spectrum of HCl are corresponding to HCl^{35} and another to HCl^{37}. The band belong to HCl^{37} should be shifted by a small amount towards longer wave length with respect to the band belonging to HCl^{35}. Experimental investigation of the rotation - vibration bands of HCl actually showed doubling of all lines. Every line has a companion of weaker intensity to the wave length side with a constant frequency separation of $\Delta\upsilon_i$ to a first approximation Fig. 17.2.

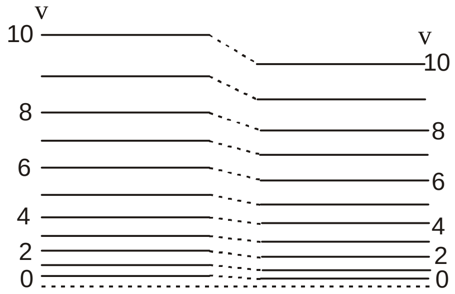


Fig. 17.2 Vibrational level of two isotopic molecules

Table 17.2

Observed and calculated vibrational isotopic displacement for the Infra red HCl bands

Band	$\Delta\upsilon$ obs	$\Delta\upsilon$ Calculated
1 - 0	2.01	2.105
2 - 0	4.00	4.053
3 - 0	5.834	5.845

Problem : If fundamental band of HCl^{35} lies at 3.46 μ. Calculate the corresponding band of HCl^{37}

$$m_1' = \frac{35}{36}\,\frac{1}{N_0}, \quad m_2' = \frac{37}{38}\cdot\frac{1}{N_0}$$

such that $\left(\frac{m_1'}{m_2'}\right)^{1/2} = \rho = 0.998$

Isotopic shift of the fundamental band is given by

$$\Delta\upsilon = (1-\rho)\{1-(v+1)\,(1+\rho)x\}\,v\,\omega_e$$

If anharmonicity constant is taken to be zero, that

$$\Delta\upsilon = (1-\rho)\,\omega_e = 0.002\ \omega_e$$

$$\Delta\upsilon = 5.78\,cm^{-1}$$

$$\upsilon = 2890.1 + 5.78 = 2895.88\,cm^{-1}$$

$$\lambda = 3.45\,\mu$$

17.3 Applictions of Vibrational Spectroscopy

(i) **Determination of force constant :** The force constant which is a measure of stiffness of the band of a molecule can be evaluated.

(ii) **Determination of moments of inertia :** The moment of inertia can be deduced from the rotational structure of the vibration band.

(iii) **Determination of molecular shape :** The molecular shape (whether linear or bent) can be deduced from the number of absorption bands observed in the vibrational of the molecule.

(iv) **Indication of the presence of certain groups in the molecule :** Bands or groups within a large molecule sometimes vibrate with a frequency that is little affected by the rest of the molecule. Therefore those groups will show absorption at their characteristic frequencies or conversely, absorption at a frequency that is characteristic of a particular group can be taken as an indication of the presence of that group in the compound under study. For example all compounds with single Carbon-hydrogen bonds show a bond near 3.5μ due to $C-H$ stretching mode and all compounds containing a Carbonyl group have a bond due to a $C=O$ streaching mode near 6μ. The study of the infrared absorption spectrum of a large molecule gives the indication of a particular group being present.

(v) **Identification of unknown compounds by matching :** The vibrational spectra are used in verifying the identity of a compound by matching its infrared spectrum to that a known sample. If the infrared spectrum of two substances are identical, the compounds are also identical. The complex spectra (above 7μ called finger print region) due to large molecules are used in such attempts of matching.

17.4 General Experimental Arrangement

Infrared spectra that are of chief practical significance lie in the range of 2.5μ to 25μ. For spectroscopic study of the spectra, the basic requirements are a source, a disprersion element and a detector. The choice depends upon the wave length region under consideration. The block diagram of the arrangement used to observe the absorption spectra is shown in Fig. 17.3.

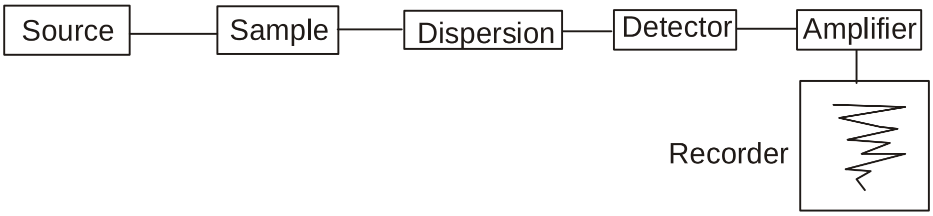


Fig. 17.3 Arrangement for the Observation of Absorption spectra - single beam

For absorption spectra a source that emits all wave lengths over a useful interval of wave lengths is used and radiation is focussed on to the entrance slit of monochromator. The term monochromater applies to those instruments in which a second slit is placed in the focal plane. This slit isolates a particular narrow band of wavelength of radiation which is refocused on to a detector whose output is a measure the energy at the chosen wavelength band.

The recorder then shows the graph that predicts the energy reaching the detector at each wave length. To determine absorption wave length interval is covered again without absorbing sample. Soure and detectors should remain stable for the period of two scans. (with and withoug sample)

We take up the parts of arrangement for infrared region

(i) **Radiation Source :** A hot strip of material emitting all frequencies in accordance with black body radiation law is preferred as an infrared source. The emission maximum lies in the near infrared. The energy at each frequency increases with source temperature.

There are two common sources

(a) **Nearest Filament (Glower) :** It is maximum of Zirconium and Yttrium oxides which is formed into a small hollow rods about 2 mm in diameter and 80 mm in length. The filament is heated to a surface temperatures 1500^0C and 2000^0C. It furnishes maximum radiation at about 1.4μ.

(b) **Glober Source :** It is a rod sintered silicon carbide about 50 mm in length and 4 mm in dia meter. It is self-starting and is heated to 1300^0C to 1700^0C. The maximum radiation occurs about 1.9μ. This is more satisfactory for work at wavelengths longer there 15μ because its radiant energy output decreases less rapidly compared to Nearest source.

(ii) **Sample :** Gas samples are studied in glass cells that are about 10 cm in length closed at their ends with rock salt windows. The cell is evacuated and the sample is filled through a stop cock or needle valve. The window material which is transponent over infrared region to all the radiation to enter the sample should be inert. Sodium chloride is transponent at wave lengths as long as 16μ. Potassium Chloride can be used up to 2μ and Cesium Chloride to 40μ.

Samples that are liquid at room temperature are usually scanned in their pure form. The sample thickness should be chosen so that the transmittance lies between 15 and 70 percent. For most liquids this will represent a very thin layer of the order of 0.01 - 0.05 mm.

Solid samples as such cannot be used because the particles would reflect and scatter incident radiation resulting in low transmittance. The solid samples whenever possible are dissolved and examined as dilute solutions. However not all substances can be dissolved in reasonable concentration in a solvent which is non absorbing in the region of interest. For the range $2.5-15.4\mu$ a mixture of Carbon tetrachloride and Carbon disulphide is satisfactory. There is also KBr pellet technique and Potassium bromide and pressing the mixture into a transponent disc in an evacuable dye under high pressure.

Some window materials are listed in table

(iii) **Mirrors :** Mirrors are used for collimating and focusing of radiations in infrared region. The advantages of mirrors over lenses in this region is that

(a) They do not require focussing. If the minor is focussed for sodium D lines, the spectrum will be infocus to the farthest infrared.

(b) They can be used upto farthest infrared where even fluorite and rock salt absorb the radiations.

(iv) **The dispersing media :** Media used for dispersion are prisms of suitable material, gratings or their combination. The choice of prism material depends upon the region of spectrum under investigation. Some prism and window materials for infrared region are tabulated below.

Table 17.3

Prism and Window Materials for the Infrared

Material	Suitable range for window	Optimum range as prisms
Glass	$3000\,m\mu$ to $2.6\,\mu$	$3000\,m\mu$ to $2.0\,\mu$
Fused Silica	$185\,m\mu$ to $4.0\,\mu$	$185\,m\mu$ to $3.5\,\mu$
Lithium Fluoride	$115\,m\mu$ to $7.0\,\mu$	$600\,m\mu$ to $6.0\,\mu$
Calcium Fluride	$125\,m\mu$ to $10.0\,\mu$	$200\,m\mu$ to $9.0\,\mu$
Barium Fluoride	$200\,m\mu$ to $13.5\,\mu$	$300\,m\mu$ to $13.0\,\mu$
Zinc Sulphide	$150\,m\mu$ to $13.0\,\mu$	----
Sodium Chloride	$200\,m\mu$ to $17.0\,\mu$	$200\,m\mu$ to $15.0\,\mu$
Silver Chloride	$10\,m\mu$ to $25.0\,\mu$	-----
Potassium Bromide	$200\,m\mu$ to $26.0\,\mu$	10 to $25\,\mu$
Cesium Iodide	1 to $40\,\mu$	10 to $38\,\mu$

Higher dispersions can be obtained from a reflection grating substituted in place of the prism in the Liltrow mount. Granting are unstable only over a short spectral range.

(v) Detectors : Thermopiles, Bolometers and Golay cells are used as detectors. They measure the radiant energy by virtue of its heating effect.

Thermopile is a series of thermo couples linked together and thus acts on the principle of thermo couple i.e. an emf is generated when one of the two metal junction is heated by radiant energy, emf developed is proportional to the radiant energy falling on hot junction.

Bolometers give an electrical signal as a result of the change in resistance of a metallic conductor with temperature.

Golay cell consists of a small metal cylinder closed by a blackened metal plate at one end by a flexible metallised diaphragm at the other. This cylinder is filled with Xenon and sealed. Where the radiation fall on blackened plate gas expands and deforms the metallised diaphram. Light from a lamp inside the detector housing can be focussed upon the diaphragm which reflects the light on to photocell.

The motion of diaphragm moves the light beam across the photocell surface and changes the photo cell output.

A double beam arrangement : In double beam arrangement two equivalent beams are taken from the source. One beam passes through the sample while the other beam called as refence beam passes through a variable and calibrated attenuator.

Then both beams are presented to monochromator detector system on alternate half cycles by means of a rotating mirror. As the monochromator scans the wave length range, the detector and amplifier system notes and discriminates between two signals. Any difference between then as will occur because of the aborption by the sample is used by the servo amplifier to actuate a motar drive the attennator into the reference beam. This results in the reduction of comparison beam such that there in no difference between the two beams. Servo amplifier acts in a direction as to connect for any difference between the two beams and thus maintains balance. The absorption by the sample is given by the position of the attenuator at each wave length. An electrical or mechanical connection between attenuater and recorder enable a curve to be drawn on a paper moving forward as the wave length changes. Fig. 17.4 shows the arrangement.

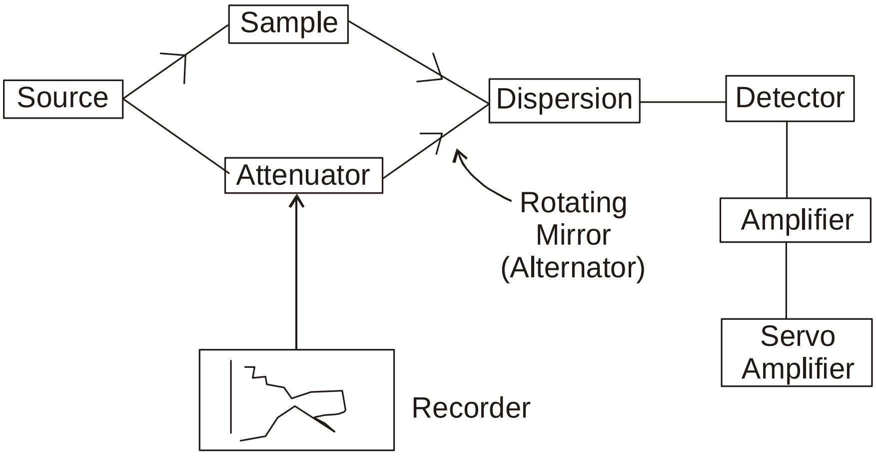


Fig. 17.4 Double beam spectrometer arrangement

17.5 Vibration of Polyatomic molecules

A molecule of n atoms has 3n degrees of freedom. The translational movement uses 3 rotation uses 3 of 3n degrees. Hence a non linear atom has $(3n-6)$ degrees of freedom. If the molecule is linear there is n_0 rotation about the bond axis and it will have $(3n-5)$ degrees of freedom. The $(3n-6)/(3n-5)$ vibrations are called the internal vibrations or normal vibrations or fundamental vibrations of the molecule. A normal vibration is defined as a molecular motion in which all the atoms move in phase and with the same frequency. During a normal vibration the centre of gravity of the molecule remains unchanged. Since a molecule having n atoms has $(n-1)$ bands. Out of the $3n-6/3n-5$ vibrations $(n-1)$ would be bond stretching $(2n-5)/(2n-4)$ would be deformation vibrations. In large molecules the nature of normal vibrations along with the symbols used for classification is discussed below in some molecules.

17.5.1 Normal vibrations of CO_2 and H_2O molecules : The CO_2 molecule is linear and will have 4 normal vibrations. They are depicted in fig. 17.5.

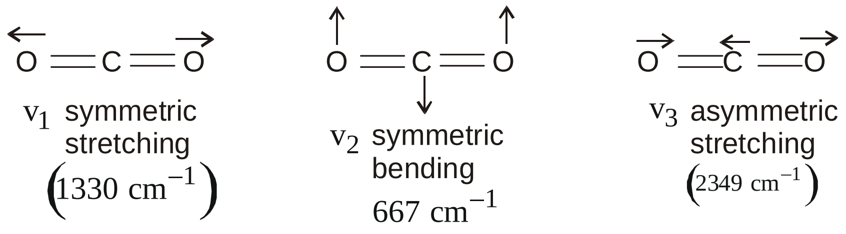


Fig. 17.5 The normal vibrations of CO_2 molecule. The solid arrows indicate the direction of motion of atoms in a particular instant

The first and second vibrations are completely symmetric. Hence they are labelled as symmetric stretching and symmetric bending modes respectively. There is an alternative way of looking at the system. These two vibrations are unchanged in character, when the molecule is rotated by 180^0 about an axis perpendicular to the bond axis and passing through the Carbon atoms.

The vibrations are labelled as υ_1, υ_2 and υ_3 (Fig. 17.5). By convention it is the practice to label vibrations in decreasing frequency with in their symmetry type. Thus the symmetric vibrations one labelled υ_1 (highest frequency) and υ_2 (next highest) and the asymmetric one as υ_3. The υ_2 vibration actually consists of 2 vibrations - one in the plane of the paper and the other in a plane perpendicular to it. Hence it is doubly degenerate. The observed vibrational frequencies are given in brackets.

The three normal modes of the non-linear triatomic water molecule one as shown in Fig. 17.6

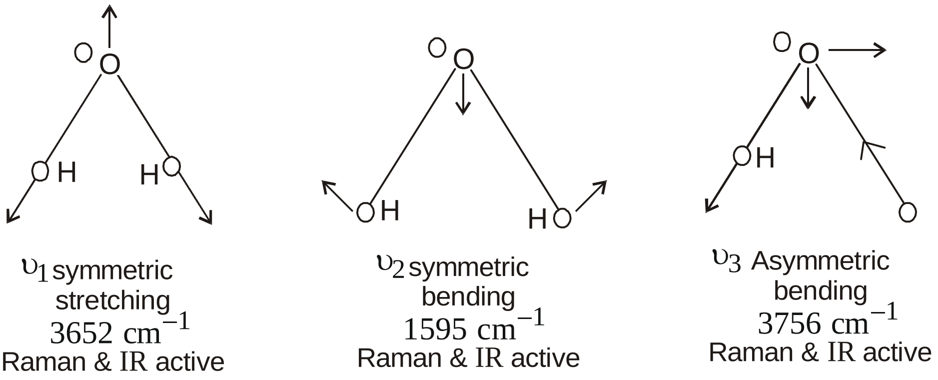
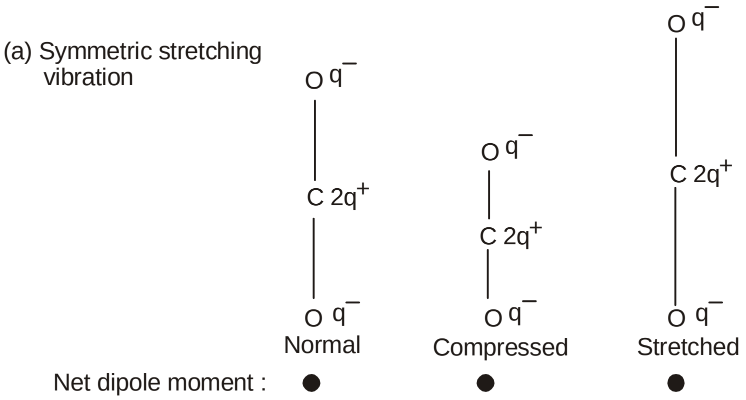


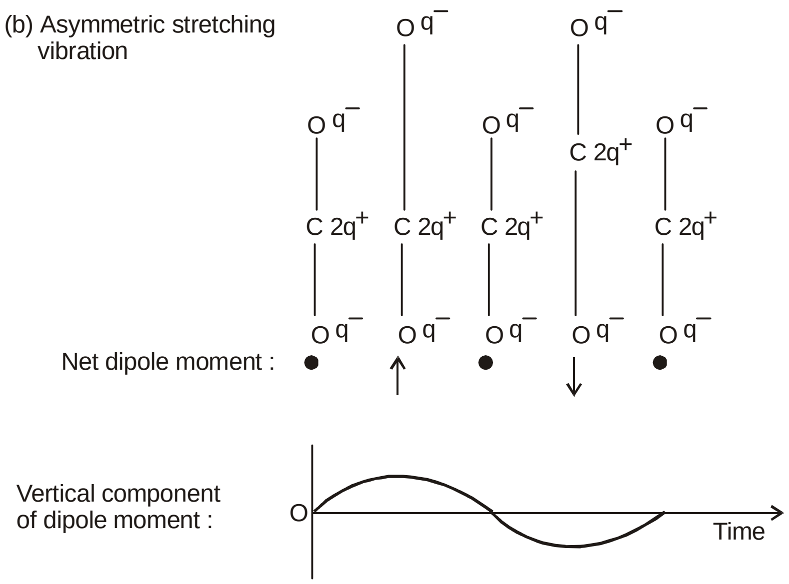
Fig. 17.6 The normal modes of water molecule

17.5.2 : Dipole moment Change in CO_2 molecule : The CO_2 moleule, though electrically neutral has a small positive change $2q^+$ one on the Carbon atom and a small negative change q^- on each of the oxygen atom.

The system then constitutes two oppositely oriented dipoles. In the equilibrium position, its dipole moment is zero since the moments of the two dipoles are equal and oppositely oriented. During symmetric stretching vibration there is no net change in the dipolemoment. Hence it is IR inactive. The υ_2 and υ_3 vibrations produce a change in dipole moment during vibration. Hence they are IR active.



Vertical component of dipole moment : No change during vibration



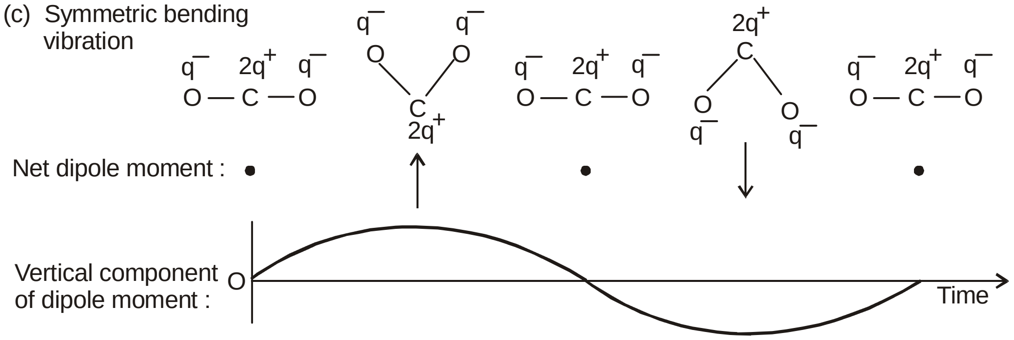


Figure 17.7 illustrates how vertical component of the dipole moment of CO_2 changes during its normal vibrations.

17.5.3 Hydrogen Bonding : Formation of the hydrogen bond (H bond) also affects the vibrational frequencies of solids considerably. The H - bond is defined as a bond between an atom B and the hydrogen atom of a covalent bond $A-H$ forming the group $A-H\ldots\ldots B$. Atoms A and B have electro negativities greater than H. Generally it can be considered as a proton shared by two lone pair electrons. It is an important form of molecular association and can be of both inter, and intramolecular type. Different types of studies are needed to understand the strength of H-bond.

A large number of studies of H bonded systems show the following affects with the formation of a H-bond.

(i) Shifting of a υ_{A-H} stretching vibration to lower frequencies with broadening and increase in intensity as the strength of the H-bond becomes stronger. Typical line widths of υ_{A-H} for weak, medium, and strong H - bonded systems are of the order of $10, 10^2$ and $10^3\,\text{cm}^{-1}$ respectively.

(ii) Shifting of δ_{A-H} deformation band to higher frequencies without appreciable changes in line width and intensity.

(iii) Appearance of new bands corresponding to $H\ldots\ldots B$ stretching and deformation at low frequencies.

(iv) Shifting of the vibrational modes involving the hydrogen band acceptor atom B. This shift is generally much smaller than those found for doner A - H vibrations.

17.5.4 Rotation Vibration Spectra of Polyatomic molecules : The rotation - vibration spectra of diatomic molecules give rise to equally spaced lines for P and R branches in the first approximation for the vibrations to be IR active, there must be a change of dipole moment during the vibration. For complex molecules vibrations can be divided into two categories vibrations causing a dipole change (i), parallel to the major axis of rotational symmetry and (ii) perpendicular to the major axis of rotational symmetry. These are called parallel and perpendicular vibrations respectively. Often the selction rules are different for parallel and perpendicular vibrations. The selection rules also depend on the shape of the molecules.

17.5.5 Linear molecules : The selection rules for the parallel vibration $\Delta\upsilon=\pm1$ and $\Delta J=\pm1$ are identical with those for diatomic molecules. The spectra will have the P and R branches with almost equally spaced lines. The spacing between lines is likely to be less as the moment of inetia is expected to be large. When the moment of inertia is extremely large the individual lines of the branches coalesce resulting in two lines.

For perpendicular vibrations the spectrum will have P, Q, R branches. If the B values of upper and lower vibrational states are equal all $\Delta J=0$ transitions give line at the bond centre resulting in an intense Q branch line. This line is likely to be broadened a little as the B values of the involved states are to likely to differ slightly. The rotational energy levels and the transitions are carried out in the usual manner. Poly atomic molecules not having a permanent dipole moment do not show pure rotational spectrum. However such molecules show vibrational spectrum in the IR region and some times with the rotational fine structure. In such cases one can estimate the rotational constant B which gives the bond length value. We see the influence of nuclear spin on the spectra of linear molecules possessing a centre of symmetry (eg : $CO_2,\ H-C\equiv C-H\cdots\cdots\cdots$) In CO_2 every alternate rotational level is completely unoccupied since the spin of the nucleus is zero and so the alternate various the P and R branches have zero intensity. This leads to a line spacing of 4B instead of the usual 2B. This effect of nuclear spin will not be there in the absense of centre of symmetry.

In the case $H-C\equiv C-H$, the nuclear spin H is not zero and the alternate lines have an intensity ratio ${(I+1)}/{I}$ where I is the spin of the hydrogen nucleus. This intensity change is in addition to the relative intensity factor due to Boltzmann distribution and degeneracy.

17.6 Salient features of Vibrational Rotational Spectra

(i) When there are transitions between vibrational states of the same electronic state of the molecule, we get vibrational rotational molecular spectra.

Such a spectra is observed in the near infrared region $(1\mu-100\mu)$ of electro magnetic spectrum.

(ii) Vibrational rotational spectra like pure rotational spectrum are observed only for molecules that have permanent dipole moment such as HCl, HCN, HF, the hetero nuclear diatomic molecules.

(iii) The inter nuclear distance changes when the nuclei of these molecules vibrate relative to each other. Thus these molecules possess an oscillating dipole moment. Which according to classical electrodynamics exists radiation of frequency that fall in the near infrared region. Conversely if an electro magnetic radiation falls on such a molecule than oscillating dipole interacts with the incident radiation and can absorb radiation of frequency of near infrared region.

(iv) In practice, vibrational rotational spectra are observed in absorption.

For HCl Molecule :

(a) Spectrum for a molecule has intense band (called fundamental band) Fig. (17.8)

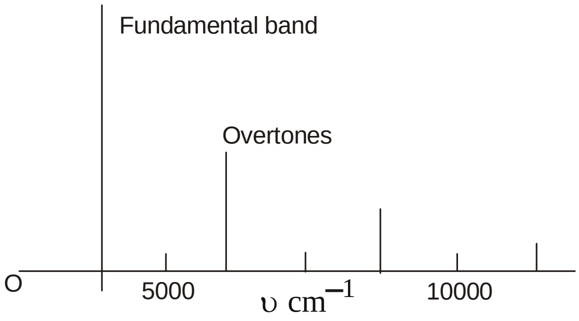


Fig. 17.8 : Spectrum of HCl molecule

(b) Spectrum consists of weak bands (over tones) that appear at wave numbers approximately double, triple,... of the fundamental band.

(c) On close examination the fundamental band is found to consist of two close maxima (Fig. 17.9) which is isotopic effect.

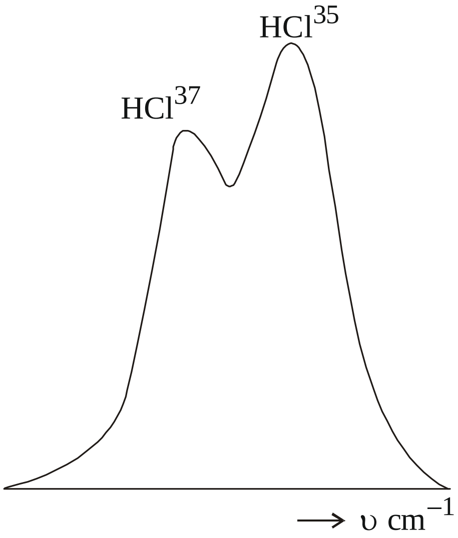


Fig. 17.9 : Spectrum of HCl molecule

(d) (i) Under high resolution it is found that each band consists of a series of lines that are not equidistant.

(ii) A line is found missing in the centre of the band and is called null line or zero gap.

(iii) Lines seen to converge towards high wave number side and the band is said to be degraded towards the low wave number side i.e. towards the red.

17.7 Summary

(1) Whether is no interaction between vibrational and rotational energies, the lines of P and R are equidistant.

(2) Because there interaction between vibration and rotation, the separation of line in R branch slowely decreases and that of P branch slowly increases as we move higher and higher linear of branch.

(3) B_e and D_e are defined, B_e is small compared D_e which it self is small.

(4) By means of rotation vibration spectra the equilibrium moment of inertia and the corresponding inter nuclear distance r_e can be evaluated precisely.

(5) The isotopic effect in vibrational bands course a shift given by $(1-\rho)$ and ρ is given by $\left[\frac{m_1'}{m_2'}\right]^{1/2}$.

(6) Further vibrational spectroscopy is helpful in calculating force constant K and also to determine the molecular shape whether linear or bent.

(7) Two types of schematic representation of IR spectrometers have been presented.

(8) Vibrations of poly atomic molecules, the degrees of freedom, number of independent vibrations have been presented. Further the examples of CO_2 and H_2O also presented.

(9) Certain other important information like dipole moment change, Hydrogen bonding, vibrational rotational spectra of polyatomic molecules have been discussed briefly.

(10) Lastly the salient features of vibrational rotational spectra is also added.

17.8 Key Words

Vibrating rotator, Isotopic effect, Diatomic molecule, Polyatomic molecule, P branch, R branch of lines Q branch line, force constant moment of inertia, internuclear distance, Normal vibrations, hydrogen bonding, linear molecule dipole moment.

17.9 Review Questions

(1) By considering the molecule as vibrating rotator and considering the interaction between vibration and rotational energy levels; obtain the energy levels and frequency of separation and draw three transitions and highlight essential features.

(2) What do you infer by isotopic effect and illustrate through a diagram and taking HCl as an example.

(3) Sketch the block diagram of IR spectrometer explain the different parts of the instrument. Write down the applications of vibrational spectroscopy and also list out salient features of vibrational spectroscopy.

(4) Write down about vibrational spectroscopy of poly atomic molecules. Discuss about the features of different molecular studies of polyatomic molecules.

17.10 Text and Reference Books

(1) Elements of Spectroscopy by Gupta, Kumar Sharma (Pragati Prakashan)

(2) Fundamentals of Molecular Spectroscopy by CN Banwell (Tata Mcgraw Hill)

(3) Molecular Structure and Spectroscopy by G. Aruldhas

Unit - IV

Lesson - 18

PROBLEMS IN MOLECULAR SPECTROSCOPY

Aim : To work out the different problems of molecular spectroscopy.

1. Diatomic molecule as a rigid rotator and also as a nonrigid rotator.
2. Diatomic molecule as a vibrating rotator with no interaction in between vibrational and rotational energies.
3. Diatomic molecule as a vibrating rotator with considerable interaction in between vibrational and rotatinal energies.
4. Diatomic molecule as a vibrating rotator, rotating as a non rigid rotator and vibratig unlike as a harmonic oscillator but as anharmonic oscilator with interaction of vibrational and rotational energies.

Objective of the lesson :

To carry out different type of problems by looking the 4 points cited in the aim of the lesson.

Structure of the lesson :

18.1 Problems in rotational spectroscopy

1. What is the change in the rotational constant B when hydrogen is replaced by deuterium in the hydrogen molecule ?

Denoting the isotopically substituted hydrogen by primes

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu},\ \mu = \frac{m_H}{2},\ \mu' = \frac{m_D}{2} = m_H$$

$$\frac{B}{B'} = \frac{m_H}{\frac{m_H}{2}} = 2,\ B' = \frac{B}{2}$$

Change in rotational constant $B - B' = B - \frac{B}{2} = \frac{B}{2}$

2 The first line in the rotation spectrum of Carbon monoxide has a frequency of $3.8424\,\text{cm}^{-1}$. Calculate the rotational constant and the $C-O$ band length in Carbon monoxide. Avagadro number is 6.022×10^{23}, given $2B = 3.8424\,\text{cm}^{-1}$, $B = 1.9212\,\text{cm}^{-1}$.

$$I = \mu r^2 = \frac{h}{8\pi^2 Bc},\ r^2 = \frac{h}{8\pi^2 \mu Bc}$$

$$\mu = \frac{12\times15.9949}{27.9949\times6.022\times10^{23}} = 1.1385\times10^{-23}\,\text{gm}$$

$$r^2 = \frac{h}{8\pi^2 \mu BC} = \frac{6.625\times10^{-27}}{8\pi^2\times1.1385\times10^{-23}\times1.9212\times3\times10^{10}}$$

$$r = 1.131\times10^{-8}\,\text{cm} = 1.131\,\overset{0}{A}$$

3 What is the average period of rotation of HCl molecule if it is in the $J=1$ state. The inter nuclear distance of HCl is 0.1274 nm. Given the mass of hydrogen and Chlorine atoms as $1.673\times10^{-27}\,\text{Kg}$ and $58.06\times10^{-27}\,\text{Kg}$ respectively.

Rotational energy of classical rotator = $\frac{1}{2}I\omega^2$

Rotational energy of quantum rotator = $\frac{h^2}{8\pi^2 I}J(J+1)$

Equating the two $\omega^2 = \frac{h^2 J(J+1)}{4\pi^2 I^2}$

$$I=\mu r^2=\frac{1.673\times10^{-27}\times58.06\times10^{-27}}{59.733\times10^{-27}}\left(0.1274\times10^{-9}\right)^2$$

$$=0.0264\times10^{-45}\,\mathrm{Kg\,m^2}$$

$$\omega=\frac{h\sqrt{J(J+1)}}{2\pi I}=\frac{6.625\times10^{-34}\times\sqrt{2}}{2\pi\times0.0264\times10^{-45}}=56.4829\times10^{11}$$

Period of rotation $T=\frac{2\pi}{\omega}=\frac{2\pi}{56.4829\times10^{11}}=1.112\times10^{-12}\,\mathrm{sec}$

4 The first rotational line $^{12}C\ ^{16}O$ is observed at $3.84235\ \mathrm{cm}^{-1}$ and that of $^{13}C\ ^{16}O$ at $3.67337\ \mathrm{cm}^{-1}$. Calculate the atomic weight of ^{13}C assuming the mass of ^{16}O to be 15.9949.

Writing B for the rotational constant of $^{12}C\,^{16}O$ and B' for that of $^{13}C\,^{16}O$, we have

$\frac{B}{B'}=\frac{I'}{I}=\frac{\mu'}{\mu}$. Let the atomic weight of ^{13}C be m.

$$\therefore\ \frac{\mu'}{\mu}=\frac{27.9949}{12\times15.9949}\times\frac{m\times15.9949}{m+15.9949}$$

$$\frac{B}{B'}=\frac{3.84235}{3.67337}=1.046$$

Equating the two and simplifying $m=13.001$

Atomic weight of ^{13}C is 13.001.

5. Rotational and distortion constants of HCl molecule are $10.593\,\mathrm{cm}^{-1}$ and $5.3\times10^{-4}\,\mathrm{cm}^{-1}$ respectively. Estimate the vibrational frequency and force constant of the molecule.

Centrefugal distortion constant $D=\frac{4B^3}{\bar{\upsilon}^2}$

$$\bar{\upsilon}=\left[\frac{4\times(10.593)^3}{5.3\times10^{-4}}\right]^{1/2}=2995.2\,\mathrm{cm}^{-1}$$

Force constant $K = 4\pi^2 C^2 \mu \bar{\upsilon}^2$. Therefore

$$\mu = \frac{1.673\times10^{-27}\times58.06\times10^{-27}}{59.733\times10^{-27}} = 1.6261\times10^{-27}\ \mathrm{Kg}$$

$$K = 4\pi^2\left(3\times10^8\right)^2\times1.6261\times10^{-27}\times\left(2995.2\times10^2\right)^2$$

$$=(577.17)\times10^{16}\times10^{-27}\times10^4\times\ 8.971223\times10^6$$

Force constant $K = 517.8\ \mathrm{N\,m^{-1}}$

6. Three consequitive lines in the rotational spectrum of diatomic molecule are observed at 84.544, 101.355 and 118.112 $\mathrm{cm^{-1}}$. Assign these lines to their appropriate $J'' \to J'$ transitions and deduce values of B and D. Hence evaluate the approximate vibrational frequency of the molecule.

Frequency $J \to J+1$ transition,

$$\bar{\upsilon}_I = 2B(J+1) - 4D(J+1)^3$$

$$84.544 = 2B(J+1) - 4D(J+1)^3$$

$$101.355 = 2B(J+2) - 4D(J+2)^3$$

$$118.112 = 2B(J+3) - 4D(J+3)^3$$

From the first two equations

$$16.811 = 2B - 4D(J+2)^3 - (J+1)^3$$

Since $D \ll B$ approximate value of B can be obtained by neglecting the term in D, with

$2B \simeq 16.811$, again neglecting the term in D

$84.544 = 16.811(J+1)$

$J = 4.03 \simeq 4$ connected to the integer.

Therefore the line 84.544 $\mathrm{cm^{-1}}$. Correspond to $J=4 \to J=5$, transition, the one at 101.355

is due to $J \rightarrow 5$ to $J \rightarrow 6$ and the one at 118.112 cm^{-1} is due to $J=6 \rightarrow J=7$ with these values

$$84.544 = 2B \times 5 - 4D \times 125$$

$$101.355 = 2B \times 6 - 4D \times 216$$

Solving $B=8.473\,cm^{-1},\ D=3.7\times10^{-4}\,cm^{-1}$

$$D=\frac{4B^3}{\bar{\upsilon}^2}$$

$$\bar{\upsilon}^2 = \frac{4\times(8.473)^3}{3.7\times10^{-4}},\ \bar{\upsilon} = 2564.4\,cm^{-1}$$

7. The observed rotational spectrum of HF shows the $J=0 \rightarrow J=1$, absorption at $41.11\,cm^{-1}$, the spacing between adjacent absorptions is $40.08\,cm^{-1}$ around $J=5 \rightarrow J=6$ transitions and only $37.81\,cm^{-1}$ around $J=10 \rightarrow J=11$ transition. Calculate B values and I values from these three given data what explanation can you give for this

Around $J=0$ to $J=1$, $2B=41.11\,cm^{-1}$ $B=20.56\,cm^{-1}$

Around $J=5$ to $J=6$, $2B=40.08\,cm^{-1}$ $B=20.04\,cm^{-1}$

Around $J=10$ to $J=11$ $2B=37.81\,cm^{-1}$, $B=18.91\,cm^{-1}$

$$B=\frac{h}{8\pi^2 Ic}$$

$B=20.56\,cm^{-1}$ gives $I=\dfrac{6.625\times10^{-34}}{8\pi^2(20.56)\,3\times10^{8}} = 1.362\times10^{-47}\,Kg.\,m^2$

$B=20.04\,cm^{-1}$ gives $I=1.3971\times10^{-47}\,Kg.\,m^2$

$B=18.91\,cm^{-1}$ gives $I=1.4841\times10^{-47}\,Kg.m^2$

Including centrifugal distortion the expression for the frequency of a transition is

$$\bar{\upsilon} = 2B(J+1) - 4D(J+1)^3$$

As the term $4B(J+1)^3$ is always positive, the separation between energy levels decreases as J increases. In otherwords in the excited states the amplitude of vibration of the atoms are expected to be larger which increases the moment of inertia $I=\mu r^2$.

8. The rotational constant for $H^{12}C\ ^{14}N$ and $D^{12}\,C\ ^{14}N$ are 1.4782 and $1.2077\,cm^{-1}$ respectively. Calculate moment of inertia of these molecules and inter nuclear distances of $C-H$ and $C\equiv N$ bonds.

Moment of Inertia of HCN, $I=\dfrac{6.625\times10^{-34}}{8\pi^2\times147.82\times3\times10^8}$

$$= 1.894\times10^{-46}\ Kg\,m^2$$

Moment of Inertia of DCN, $I=\dfrac{6.625\times10^{-34}}{8\pi^2\times120.77\times3\times10^8} = 2.3182\times10^{-46}\ Kg\,m^2$

From previous equations

$$I=\frac{m_H\,m_C\,r_{CH}^2+m_C\,m_N\,r_{CN}^2+m_H\,m_N\,(r_{CH}+r_{CN})^2}{m_H+m_C+m_N}$$

$$I'=\frac{m_D\,m_C\,r_{CH}^2+m_C\,m_N\,r_{CN}^2+m_D\,m_N\,(r_{CH}+r_{CN})^2}{m_D+m_C+m_N}$$

where

$m_H = 1.008, \quad m_D = 2.014$

$m_C = 12.00, \quad m_N = 14.003$

These atomic weights have to be divided by the Avagadro number 6.022×10^{23}, to get the mass in gram, substituting values of the masses

$$11.406\times10^{-20} = 0.4478\,r_{CH}^2 + 6.2210\,r_{CN}^2 + 0.5226(r_{CH}+r_{CN})^2$$

$$13.960\times10^{-20} = 0.8862\,r_{CH}^2 + 5.9976\,r_{CN}^2 + 1.0066(r_{CH}+r_{CN})$$

on simplification $r_{CH} = 1.06\,A^0,\ r_{CN} = 1.157$

9 In the rotational transition for $J = 0$ to $J=1$, the absorption lines occur at $1.153\times10^{11}\text{Hz}$ in $C^{12}\,O^{16}$ and $1.102\times10^{11}\,\text{Hz}$ in $C^n\,O^{16}$. Find the mass number of $C^n\,O^{16}$

Mass of $C^{12} = 12\,M_H$

Mass of $O^{16} = 16\,M_H$

Since force constant of the bond involved in CO molecule will not be affected by Isotopic substitution. We can write

$$K = 4\pi^2\,\upsilon_1^2\,m_1' = 4\pi^2\,\upsilon_2^2\,m_2' \quad \text{-------------- (1)}$$

where $\upsilon_1 =$ frequency of the absorption in case of $C^{12}\,O^{16}$.

$m_1' =$ reduced mass of $C^{12}\,O^{16} = \dfrac{12\times16}{12+16} = \dfrac{192}{28}\text{amu}$

$\upsilon_2 =$ Frequency of absorption live in case of $C^n\,O^{16}$.

$m_2' =$ reduced mass of C^nO^{16}

$$= \frac{16\,n}{16+n}\text{amu}$$

Therefore from (1)

$$m_2' = \left[\frac{\upsilon_1}{\upsilon_2}\right]^2 m_1' \quad \text{or}$$

$$\frac{16\,n}{n+16} = \left[\frac{1.153\times10^{11}}{1.102\times10^{11}}\right]\times\frac{192}{28}$$

Further on simplification $n = 14$ amu

10 The moment of inertia of the CO molecule is $1.46\times10^{-46}\,\text{Kg}\,\text{m}^2$. Calculate the energy in eV and the angular velocity in the lowest rotational energy of the CO molecule.

$$E_r = \frac{h^2}{8\pi^2 I}$$

For the lowest energy level $J=0$, so that

$$E_r = \frac{h^2}{8\pi^2 I}$$

Putting $I = 1.46\times10^{-46}\ \text{Kg.m}^2$

$$h = 6.62\times10^{-34}\ \text{Joule sec}\cdot$$

We have $E_r = \dfrac{\left[(6.62)10^{-34}\right]^2}{8\cdot(3.14)^2\times\left(1.46\times10^{-46}\right)}\text{Joule}$

$$= \frac{\left[6.62\times10^{-34}\right]^2}{8\times(3.14)^2\times\left[1.46\times10^{-46}\right]\times(1.6)\times10^{-19}}\text{ev}$$

$$= 2.37\times10^{-4}\ \text{eV}$$

Angular velocity will be given by

$$E_r = \frac{1}{2}I\omega^2 \text{ or } \omega = \sqrt{\frac{2E_r}{I}}$$

$$\omega = \left[\frac{2\times2.37\times10^{-4}\times1.6\times10^{-19}}{1.46\times10^{-46}}\right]^{1/2} = 7.21\,\text{rad/sec}$$

11. The OH radical has a moment of Inertia of $1.48\times10^{-40}\ \text{gm. cm}^2$. Calculate its inter nuclear distance. Also calculate for J = 5 its angular momentum and angular velocity. Determine the energy absorbed in the J = 6 to J = 5 transition in cm^{-1} and erg/molecule.

Solution : The reduced mass of OH radical is given by

$$m'OH = \frac{M_O m_H}{M_O + m_H} = \frac{\left(\frac{16}{N_O}\right)\left(\frac{1}{N_O}\right)}{\left(\frac{16+1}{N_O}\right)} = \frac{16}{17}\left(\frac{1}{N_O}\right) \text{gm}$$

where $N_O = 6.023 \times 10^{23}$ Avagadro's number.

$$m'_{OH} = \frac{16}{17} \times \frac{1}{6.023 \times 10^{23}} = 1.56 \times 10^{-24} \text{ gm.}$$

Inter nuclear distance is given by

$$r^2_{OH} = \frac{I_{OH}}{m'_{OH}} = \frac{1.48 \times 10^{-40} \text{ gm cm}^2}{1.56 \times 10^{-24} \text{ gm}}$$

or $r_{OH} = 0.95 \times 10^{-8} \text{ cm} = 0.95 \overset{0}{A}$

Angular momentum is given by

$$L = I\omega = \sqrt{J(J+1)} \frac{h}{2\pi}$$

For $J = 5$, $L = I\omega = \sqrt{(5)(5+1)} \cdot \frac{6.62 \times 10^{-27} \text{ erg sec}}{(2 \times 3.14)}$

$$= 5.77 \times 10^{-27} \text{ erg. sec}$$

and the corresponding angular velocity is

$$\omega = \frac{L}{I} = \frac{5.77 \times 10^{-27} \text{ erg sec}}{1.48 \times 10^{-40} \text{ gm cm}^2} = 3.90 \times 10^{13} \text{ rad/sec}$$

Further we have $\upsilon_r = B\left[J'(J'+1) - J''(J''+1)\right]$

For the problem $J' = 6,\ J'' = 5$, so that

$$\upsilon_r = B\left[6(6+1) - 5(5+1)\right] = 12B$$

$$= 12 \times \frac{h}{8\pi^2 \, Ic} = \frac{12 \times 6.62 \times 10^{-27} \, \text{erg sec}}{8(3.14)^2 \left(1.48 \times 10^{-40} \, \text{gm cm}^2\right) \times 3 \times 10^{10} \, \text{m/sec}}$$

$$\upsilon_r = 227 \, \text{cm}^{-1}$$

The corresponding energy in erg / molecule is given by

$$E_r' - E_r'' = hc\upsilon = (6.62)10^{-27} \, \text{erg sec}\left(3 \times 10^{10} \, \text{cm/sec}\right) 227\text{cm}^{-1}$$

$$= 4.50 \times 10^{-14} \text{ erg / molecule}$$

12 The number of lines in band are given by $\upsilon_r = 1000(2n-1)\text{cm}^{-1}$ and $\upsilon_r = -1000(2n+1)\text{cm}^{-1}$ for n positive and n negative respectively. Calculate the moment of inertia of spectrum emitting system.

Solution : Given

$$\upsilon_r = 1000(2n-1) = 1000, \ 3000, \ 5000 \text{ for } n \text{ positive}$$

and $\upsilon_r = -1000(2n+1) = -1000, \ -3000, \ -5000$ for n negative

The separation between adjacent lines as given by both the cases is

$$2B = 2000 \text{ cm}^{-1}$$

$$B = 1000 \text{ cm}^{-1}$$

But $I = \dfrac{h}{8\pi^2 Bc} = \dfrac{6.63 \times 10^{-27}}{8(3.14)^2 \times 1000 \times 3 \times 10^{10}}$

$$= 2.8 \times 10^{-42} \, \text{gm} - \text{cm}^2$$

13 The spacing of a series of lines in the microwave spectrum of $A\ell H$ is constant at 12.604 cm^{-1}. Calculate the moment of Inertia and the internuclear distance of the $A\ell H$ molecule what are the energy of rotation and the rate of rotation when $J = 15$.

Given $h = 6.62 \times 10^{-27}$ erg sec, $c = 3.0 \times 10^{10}$ cm / sec

$m' \, AlH = 0.9718 \, au \qquad N_O = 6.023 \times 10^{23}$

Solution : Given that $2B = 12.604 \, cm^{-1}$

or $B = 6.302 \, cm^{-1}$

The moment of inertia of the rotating molecules is the

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.62 \times 10^{-27} \, erg \, sec}{8(3.14)^2 (6.302) 3 \times 10^{10} \, cm / sec}$$

$$= 4.44 \times 10^{-40} \; gm - cm^2$$

The reduced mass of AlH molecule is

$$m'_{AlH} = 0.9718 \text{ au} = \frac{0.9718}{6.023 \times 10^{-23}} gm$$

$$\boxed{= 1.613 \times 10^{-24} \, gm} \qquad \left[1au = \frac{1}{N_O} gm \right]$$

Inter nuclear distance is given by :

$$r^2_{AlH} = \frac{I_{Al-H}}{m' \, AlH} = \frac{4.44 \times 10^{-40} \, gm - cm^2}{1.613 \times 10^{-24} \, gm}$$

or $r_{AlH} = 1.66 \times 10^{-8} \, au = 1.66 \, \overset{0}{A}$

Rotational energy of the molecule is given by

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) = B \, hc(J)(J+1)$$

For $J = 15$, we have

$$E_r = \left(6.302 \, cm^{-1}\right) \times \left(6.62 \times 10^{-27} \, erg \, sec\right) \left(3 \times 10^{10} \, cm / sec\right) \times 15(15+1)$$

$$=3.0\times10^{-13}\ \text{Erg / molecule.}$$

As $E_r = \frac{1}{2}I\omega^2$

$$\omega = \sqrt{\left(\frac{E_r}{I}\right)} = \left[\frac{2\times3.0\times10^{-13}}{4.44\times10^{-40}}\right]^{1/2} = 3.68\times10^{13}\ \text{rad / sec}$$

14 The $J=1\leftarrow0$ transition in HCl occurs at $20.68\,\text{cm}^{-1}$. Regarding the molecule to be a rigid rotator, calculate the wave length of the transition $J=15\leftarrow14$.

$$\upsilon_{r\ 1\leftarrow0} = 2B(J+1) \qquad \text{(for } J\ 1\leftarrow0\text{)}$$

$$= 2B(0+1) = 2B$$

$$2B = 20.68\,\text{cm}^{-1}$$

For $(\upsilon_r)\ 15\leftarrow14 = 2B(J+1) = 2B(14+1)$

$$= 20.68\times15 = 310.2\ \text{cm}^{-1}$$

Corresponding wave length $\lambda = \frac{1}{\upsilon_r} = \frac{1}{310.2}$

$$32.23\times10^{-4}\,\text{cm} = 32\,\mu\cdot$$

15. The infrared spectrum of $H^1\,Br^{79}$ consists of a series of lines spaced 17cm^{-1} apart. Find the internuclear distance of $H^1\,Br^{79}$.

Given $h=6.62\times10^{-27}\,\text{erg.sec., } c=3\times10^{10}\ \text{cm / sec}\cdot$

$N_O = 6.023\times10^{23}$.

Here separation between 2 successive lines is $2B$, so that

$$2B=17\,\text{cm}^{-1}$$

$$B = 8.5\,\text{cm}^{-1}$$

The moment of the inertia of the molecule is

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.62\times10^{-27}\ \text{erg sec}}{8(3.14)^2(8.5)\text{cm}^{-1}\times3\times10^{10}\ \text{cm/sec}}$$

$$= 3.29\times10^{-40}\ \text{gm}-\text{cm}^2$$

and reduced mass is $m' = \frac{m_H + m_{Br}}{m_H + m_{Br}}\cdot\frac{1}{N} = \frac{1\times79}{1+79} = \frac{1}{6.023\times10^{23}}$

$$= 1.64\times10^{-24}\ \text{gm}$$

Inter nuclear distance $r^2 = \frac{I}{m'} = \frac{3.29\times10^{-40}}{1.64\times10^{-24}} =$

or $r = 1.42\,\overset{0}{A}$

16. In the infrared spectrum of HCl molecule the first line falls at $20.8\,\text{cm}^{-1}$. Calculate the moment of inertia, reduced mass and bond length of the molecule.

Solution : given that

$$2\frac{h}{8\pi^2 Ic} = 20.8\,\text{cm}^{-1},\ 2B = 20.8\,\text{cm}^{-1}$$

$$B = 10.4\,\text{cm}^{-1}$$

The moment of inertia is

$$I_{HCl} = \frac{h}{8\pi^2 Bc} = \frac{6.62\times10^{-27}\ \text{erg sec}}{8(3.14)^2(10.4)\ 3\times10^{10}\ \text{cm/sec}}$$

$$= 2.716\times10^{-40}\ \text{gm}-\text{cm}^2$$

Reduced mass of HCl is

$$m' = \frac{m_1\ m_2}{\left(m_1 + m\right)} \cdot \frac{1}{N_O} = \left[\frac{1.008 \times 35.46}{1.008 + 35.46}\right] \cdot \frac{1}{6.024 \times 10^{23}}$$

$$= \frac{35.74368}{36.468} \cdot \frac{1}{6.024 \times 10^{23}}$$

$$m' = 1.627 \times 10^{-24}\ \text{gm}$$

Bond length of HCl molecule

$$r^2{}_{H-Cl} = \frac{I_{HCl}}{m'} = \frac{2.716 \times 10^{-40}}{1.627 \times 10^{-24}} = 1.66933 \times 10^{-10}$$

$$= 1.29 \times 10^{-8}\ \text{cm} = 1.29\ \overset{0}{A}$$

17. The bond length of HF molecule is 0.0927 nm. Calculate the moment of inertia, rotational constant in Joules and cm^{-1},

Solution : Given $r_{H-F} = 0.0927\,nm = 9.27 \times 10^{-11}\,m$

Therefore $r_{HF}^2 = 85.9329 \times 10^{-22}\ m^2$

We have

$$r_{HF}^2 = \frac{I_{HF}}{m'\,HF}$$

$$\therefore I_{HF} = \left(r_{HF}^2\right) m'_{HF}$$

$$m'_{HF} = \frac{m_H\ m_F}{m_H + m_F} \cdot \frac{1}{N_O} = \frac{1.008 \times 19}{1 + 19} = \frac{19}{20} \times \frac{1}{6.023 \times 10^{23}}$$

$$1.577 \times 10^{-24}\ \text{gm} = 1.577 \times 10^{-27}\ \text{Kg}$$

$$I_{HF} = \left(85.9329\right) 10^{-22}\ m^2 \left(1.577\right) 10^{-27}\ \text{Kg}$$

$$I_{HF} = 135.516 \times 10^{-49}\ \text{Kg} - m^2$$

or $1.35\times10^{-47}\ \mathrm{Kg-m^2}$

$1.35\times10^{-43}\ \mathrm{Kg-cm^2} = 1.35\times10^{-40}\ \mathrm{gm-cm^2}$

Rotational constant $B = \frac{h}{8\pi^2\, Ic}\ \mathrm{cm^{-1}}$

$$B = \frac{6.62\times10^{-27}\ \mathrm{erg\,sec}}{8(3.14)^2\, 1.35\times10^{-40}\times3\times10^{10}} = \frac{6.62}{315.45}\times10^{3}\ \mathrm{cm^{-1}}$$

$$= 0.0209\times10^{3}\ \mathrm{cm^{-1}}$$

Rotational constant $B = 20.9\,\mathrm{cm^{-1}}$

Energy $= hC\bar{\upsilon} = 6.62\times10^{-27}\times3\times10^{10}\times20.9\,\mathrm{cm^{-1}}$

$$415.074\,\mathrm{erg}\ \ 10^{-17}\ \mathrm{ergs}$$

$$= 4.15\times10^{-22}\ \mathrm{Joules/molecules}\quad 4.15\times10^{-15}\ \mathrm{ergs\ /\ molecules}$$

18. How many revolutions pur second does a CO molecule make when $J=3$, The CO bond length is 0.1131 nm.

The angular momentum is given by

$$L = I\omega = \sqrt{J(J+1)}\ \frac{h}{2\pi},\ \text{for } J=3,$$

$$L = I\omega = \sqrt{3(3+1)}\cdot\frac{6.62\times10^{-27}\ \mathrm{erg\,sec}}{2\times(3.14)}$$

$$L = I\,\omega\cdot = 3.65\times10^{-27}\ \mathrm{erg\,sec}.$$

Bond length $r_{CO} = 0.1131\times10^{-9}\ \mathrm{m}$.

$$= 1.131\times10^{-10}\ \mathrm{m}$$

$$= 1.131\times10^{-8}\ \mathrm{cm}$$

$$r_{CO}^2 = 1.279 \times 10^{-16}\ cm^2$$

$$r_{CO}^2 = \frac{I_{CO}}{m'_{CO}} \quad \text{or} \quad I_{CO} = \left(r_{CO}^2\right)\left(m'_{CO}\right)$$

$$m'_{CO} = \frac{12\times16}{12+16}\cdot\frac{1}{N_O} = \frac{192}{28}\cdot\frac{1}{6.023\times10^{23}}$$

$$= 1.138\times10^{-23}\,gm$$

$$\therefore I_{CO} = \left(r_{CO}\right)\left(m'_{CO}\right) = \left(1.279\times10^{-16}\right)\left(1.138\right)\times10^{-23}$$

$$= 1.455\times10^{-39}\,gm - cm$$

$$L = I\omega = 3.65\times10^{-27}\,erg\ sec$$

$$\omega = \frac{L}{I} = \frac{3.65\times10^{-27}}{I} = \frac{3.65\times10^{-25}}{1.455\times10^{-39}}$$

$$\omega = 2.508\times10^{14}\ rad/sec$$

19. The microwave spectrum of CN radical shows a series of lines spaced by a nearly constant amount 3.798 cm^{-1} what is the bond length of CN.

given that $2B = 3.798\,cm^{-1}$ or $B = 1.899\,cm^{-1}$

Moment of inertia is calculated from

$$I_{CN} = \frac{h}{8\pi^2 Bc} = \frac{6.62\times10^{-27}}{8\left(3.14\right)^2\left(1.899\right)3\times10^{10}}$$

$$= 0.00147\times10^{-37}$$

$$I_{CN} = 1.47\times10^{-39}\,gm - cm^2$$

m' reduced mass $= \dfrac{12\times14}{12+14}\cdot\dfrac{1}{N_O} = \dfrac{168}{26} = \dfrac{1}{6.023\times10^{23}}$

$$=1.0728\times10^{-23}\,\text{gm}\,\cdot$$

Bond length r_{CN} is given through

$$r^2{}_{CN} = \frac{I_{CN}}{m'_{CN}} = \frac{1.47\times10^{-39}\,\text{gm cm}^2}{1.0728\times10^{-23}}$$

$$= 1.37\times10^{-16}$$

$$r_{CN} = 1.17\times10^{-8}\,\text{cm} = 1.17\,\overset{0}{A}$$

20. The spectrum between lines in the rotational spectrum of HCl molecule was found to be 20.92 cm^{-1}. Calculate the bond length

given that $2\dfrac{h}{8\pi^2 Ic} = 20.92\,\text{cm}^{-1}$

$$2B=20.92\,\text{cm}^{-1} \text{ or } B=10.46\,\text{cm}^{-1}$$

So the moment of inertia is

$$I_{HCl} = \frac{h}{8\pi^2 Bc} = \frac{6.62\times10^{-27}}{8(3.14)^2\,(10.46)3\times10^{10}}$$

$$2.674\times10^{-40}\,\text{gm}-\text{cm}^2$$

Reduced mass of the HCl is

$$m' = \frac{m_1\,m_2}{m_1+m_2}\cdot\frac{1}{N_O} = \frac{(1.008)\,(35.46)}{(1.008)+(3.546)}\cdot\frac{1}{6.024\times10^{23}}$$

$$= 1.627\times10^{-24}\,\text{gm}$$

Bond length of HCl is given by

$$r^2{}_{HCl} = \frac{I_{HCl}}{m'} = \frac{2.674\times10^{-40}\,gm-cm^2}{1.627\times10^{-24}\,gm}$$

$$r^2{}_{HCl} = 1.6435\times10^{-16}\,cm^2$$

$$r_{HCl} = 1.2819\times10^{-8}\,cm = 1.28\,A^0$$

18.2 Problems in Vibrational Spectroscopy

1. The frequency of OH stretching vibration in CH_3OH is $3300\,cm^{-1}$. Estimate the frequency of OD stretching vibration in CH_3OD.

We have $\frac{\upsilon_{OH}}{\upsilon_{OD}} = \sqrt{\frac{\mu_{OD}}{\mu_{OH}}} = \sqrt{\frac{16\times2}{18}\times\frac{17}{16\times1}} = 1.3744$

$$\upsilon_{OD} = \frac{\upsilon_{OH}}{1.3744} = \frac{3300}{1.3744} = 2401\,cm^{-1}$$

2. The normal mode of vibration of CO_2 molecule are $\upsilon_1 = 1330\,cm^{-1}$, $\upsilon_2 = 667\,cm^{-1}$, $\upsilon_3 = 2349\,cm^{-1}$. Evaluate zero point energy of CO_2 molecule.

The CO_2 molecule has 4 normal modes of vibration. The symmetric bending mode υ_2 is double degenerate

The zero point energy E_0 of CO_2 is $\frac{1}{2}hC\sum_{i=1}^{4}\bar{\upsilon}_i$

$$\sum_{i=1}^{4}\bar{\upsilon}_i = (1330+667+667+2349)\,cm^{-1} = 5013\times100\ m^{-1}$$

$$E_0 = \frac{1}{2}\times6.625\times10^{-34}\times3\times10^{10}\times5013\times100\,J$$

$$= 4.98\times10^{-20}\,J = 0.311\,eV$$

3. The equilibrium vibration frequency of the iodine molecule is $215\,\text{cm}^{-1}$ and the anharmonicity constant $x_e = 0.003$ what is the intensity of the hot band $\upsilon = 1 \rightarrow \upsilon = 2$ relative to that of the fundamental $\upsilon = 0 \rightarrow \upsilon = 1$. If the temperature is 300K.

The frequency of the fundamental $= \bar{\upsilon}_e\left(1 - 2x_e\right)$

$$= 215(1 - 2 \times 0.003)$$

$$= 213.11\ \text{cm}^{-1} = 213.11 \times 10^2\ \text{m}^{-1}$$

Let $N_0, N_1, N_2, \cdots\cdots\cdots\cdots$ be the population in $\upsilon = 0, 1, 2, \cdots\cdots\cdots\cdots$ states. The intensity of the fundamental I_0 is proportional to N_0 and that of the hot band I_1 is proportional to N_1. Hence $\frac{I_0}{I_1} = \frac{N_0}{N_1} = e^{\Delta E/kT}$.

Where ΔE is the energy separation between $\upsilon = 0$ and $\upsilon = 1$, states then

$$\frac{\Delta E}{kT} = \frac{213.11 \times 10^2 \times 6.625 \times 10^{-34} \times 3 \times 10^8}{1.381 \times 10^{-23} \times 300} = 1.02234$$

$$\frac{I_0}{I_1} = e^{1.02234} = 2.779$$

$$I_1 = \frac{I_0}{2.779} = 0.36\,I_0$$

4. The frequencies of vibration of the molecule in their $\upsilon = 0$ states are $\text{HCl}: 2885\,\text{cm}^{-1}$, $D_2: 2990\,\text{cm}^{-1}$, $\text{DCl}: 1990\,\text{cm}^{-1}$ and $\text{HD}: 3627\,\text{cm}^{-1}$. Calculate the energy charge of the reaction $\text{HCl} + D_2 \rightarrow \text{DCl} + \text{HD}$.

Solution : As the molecules are in the $\upsilon = 0$ state, it is sufficient that one calculates the zero point energies of the reactants and products for determining the energy change.

Sum of the zero point energies of HCl and D_2 given by

$$= \frac{1}{2}\left(2885 + 2990\right) \times 100 \times 6.625 \times 10^{-34} \times 3 \times 10^8\ \text{J}$$

$$= 58.382\times10^{-21}\,\mathrm{J}$$

Sum of the zero point energies of DCl and HD

$$= \frac{1}{2}\left(1990+3627\right)\times 100\times 6.625\times 10^{-34}\times 3\times 10^{8}\,\mathrm{J}$$

$$= 55.819\times 10^{-21}\,\mathrm{J}$$

Energy liberated or change in energy $= \left(58.382 - 55.819\right)\times 10^{-21}$

$$= 2.563\times 10^{-21}\,\mathrm{J}$$

Energy liberated per mole = $2.563\times10^{-21}\times6.02\times10^{23}\,\mathrm{J}$

Energy liberated $= 1.54\times 10^{3}\ \mathrm{J\,/\,mole}$

5. The fundamental and first overtone transition of $^{14}\mathrm{N}\,^{16}\mathrm{O}$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Evaluate the equlibrium vibration frequency, the anharmonicity constant zero point energy and the force constant of the molecule.

Solution :

Frequency of the Fundamental : $\bar{\upsilon}_e\left(1-2x_e\right) = 1876.06\,\mathrm{cm}^{-1}$

Frequency of the first overtone $=2\bar{\upsilon}_e\left(1-3x_e\right) = 3724\,\mathrm{cm}^{-1}$

From these two equations

$$\bar{\upsilon}_e = 1903.98\,\mathrm{cm}^{-1} \text{ and } x_e = 7.332\times10^{-3}$$

zero point energy $\varepsilon_0 = \frac{1}{2}\bar{\upsilon}_e\left(1-\frac{1}{2}x_e\right)$

$$= \frac{1}{2}\times1903.98\left(1-0.003666\right) = 94.85$$

Mass of $^{14}\mathrm{N} = 23.25\times 10^{-27}\,\mathrm{Kg}$

Mass of $^{16}\mathrm{N} = 26.56 \times 10^{-27}\,\mathrm{Kg}$

$$\mu = \frac{23.25 \times 25.56}{23.25 + 26.50} \times 10^{-27}\,\mathrm{Kg} = 12.3975 \times 10^{-27}\,\mathrm{Kg}$$

$$K = 4\pi^2 \mu c^2\, \bar{\upsilon}_e{}^2 = 4\pi^2 \times 12.3975 \times 10^{-27} \times 9 \times 10^{16} \times (1904 \times 100)^2$$

$$= 1.595 \times 10^{14} \times 10^{-27} \times 10^{16}$$

$$K = 1595\ \mathrm{N\ m^{-1}}$$

6. Estimate the position of the band centre and B value of the HCl molecule from the few lines of the P and R branches listed below.

Line	$\bar{\upsilon}\left(\mathrm{cm^{-1}}\right)$	Line	$\bar{\upsilon}\left(\mathrm{cm^{-1}}\right)$
P_1	2865.1	R_0	2906.24
P_2	2843.62	R_1	2925.90
P_3	2821.56	R_2	2944.90
P_4	2798.94	R_3	2963.29

$$\bar{\upsilon}_{P \cdot R} = \bar{\upsilon}_0 + 2B_m \qquad m = \pm 1, \pm 2, \pm 3, \cdots\cdots\cdots$$

$\bar{\upsilon}_0 =$ sum of the 8 readings divided by 8.

$$= \frac{23069.55}{8} = 2883.69\,\mathrm{cm^{-1}}$$

$$\bar{\upsilon}_{R_0} - \bar{\upsilon}_{P_1} = 4B = 41.14\,\mathrm{cm^{-1}}$$

$$\bar{\upsilon}_{R_1} - \bar{\upsilon}_{P_2} = 8B = 82.28\,\mathrm{cm^{-1}}$$

$$\bar{\upsilon}_{R_2} - \bar{\upsilon}_{P_1} = 12B = 123.34\,\mathrm{cm^{-1}}$$

$$\bar{\upsilon}_{R_3} - \bar{\upsilon}_{P_2} = 16B = 164.35\,\mathrm{cm^{-1}}$$

$$B = 10.28\,\text{cm}^{-1}$$

7. The fundamental band for HCl is centered at 2886 cm^{-1}. Assume that the inter nuclear distance is $1.276\,\text{A}^0$. Calculate the wave number of the first two lines of each of the P and R branches of HCl.

The reduced mass of HCl $= \dfrac{(1.008)\ 35.45}{(36.46)\,6.022\times10^{23}} = 1.6275\times10^{-24}\,\text{gm}$

Rotational Constant $B = \dfrac{h}{8\pi^2\,\mu r^2 c}$

$$= \frac{6.625\times10^{-27}}{8(3.14)^2\ 1.6275\times10^{-24}\ \left(1.276\times10^{-8}\right)^2\ 3\times10^{10}}$$

$$= 0.005655\times10^{-27+24+16-10}$$

$$B = 0.0105655\times10^3 = 10.5655\,\text{cm}^{-1}$$

$$\bar{\upsilon}_{PR} = \bar{\upsilon}_0 + 2B_m,\ m = \pm1,\ \pm2,\ \pm3,\cdots\cdots$$

$$\bar{\upsilon}_{P_1} = 2886 - 2\times10.5655 = 2864.869\,\text{cm}^{-1}$$

$$\bar{\upsilon}_{P_2} = 2886 - 4\times10.5655 = 2843.739\,\text{cm}^{-1}$$

$$\bar{\upsilon}_{R_0} = 2886 + 2\times10.5655 = 2907.131\,\text{cm}^{-1}$$

$$\bar{\upsilon}_{R_1} = 2886 + 4\times10.5655 = 2928.262\,\text{cm}^{-1}$$

8. The force constant of the bond in CO molecule is $187\,\text{N/m}$ and its reduced mass is $1.14\times10^{-26}\,\text{Kg}$. Compute the frequency of vibration of the CO molecule and the spacing between its vibration energy levels.

$$\omega = \frac{1}{2\pi}\sqrt{\frac{K}{m'}}$$

In this problem, $\upsilon = \frac{1}{2\pi}\sqrt{\frac{187\,\text{N/m}}{1.14 \times 10^{-26}\,\text{Kg}}} = 2.04 \times 10^{13}\,\text{sec}^{-1}$

The separation ΔE between the vibrational energy levels is

$$\Delta E = E_{\upsilon+1} - E_{\upsilon} = h\upsilon$$

$$6.63\times10^{-34}\,\text{Joule sec} \times 2.04\times10^{13}\,\text{sec}^{-1}$$

$$= 8.44\times10^{-2}\,\text{eV}$$

9. The molecules of HCl show a strong absorption line of wave length 3.456 micron. Assuming origin of line due to vibration. Calculate the force constant for HCl bond

Solution : Frequency of vibration is

$\upsilon = \frac{1}{2\pi}\sqrt{\frac{K}{m'}}$ or force constant is

$K = 4\pi^2 \upsilon^2 m'$ If $m_H = 1.0087$

$m_{Cl} = 35.453$

There $m' = \frac{m_H\ m_{Cl}}{m_H + m_{Cl}} = 0.98\,\text{amu}$

$$= 0.98 \times 1.67\times10^{-27}\,\text{Kg}$$

$$= 1.63 \times 10^{-27}\,\text{Kg}$$

Also, frequency of vibration

$$\upsilon = \frac{c}{\lambda} = \frac{3\times10^{8}\,\text{m/sec}}{3.465\times10^{-6}\,\text{m}}$$

The force constant is given by

$$K = 4\pi^2 \left[\frac{3\times10^{8}}{3.465\times10^{-6}}\right]^2 (1.63) \times 10^{-27} = 480\,\text{N/m}$$

10. Given that the spacing between the vibrational levels of a CO molecule is $8.45 \times 10^{-2}\,\text{eV}$. Calculate the value of the force constant K of the bond in CO molecule.

Solution : Given $\Delta E = 8.45 \times 10^{-2}\,\text{eV}$

Therefore $h\upsilon = \Delta E = 8.45 \times 10^{-2}\,\text{eV}$

$$= 8.45 \times 10^{-2} \times 1.602 \times 10^{-19}\,\text{J}$$

so that $\upsilon = \dfrac{8.45\times10^{-2} \times 1.602\times10^{-19}\,\text{J}}{6.63\times 10^{-13}\,\text{Joules / sec}}$

$$= 2.04 \times 10^{13}\,\text{sec}^{-1}$$

Reduced mass of CO $m' = 1.14 \times 10^{-26}\,\text{Kg}$

Force constant is

$$K = 4\pi^2\,\upsilon^2\,m' = 4\pi^2\left(2.04\times10^{13}\right)^2\left(1.14\times10^{-26}\right)$$

$$= 187\ \text{N / m}$$

11. Assume that force constant of H_2 molecule is same as that of D_2. The H_2 molecule shows an absorption line at $2.3\times10^{-6}\,\text{m}$. What will be the vibrational frequency observed from D_2.

Solution : Given that

$$K = 4\pi\,\upsilon_H^2\,m'_H = 4\pi^2\,\upsilon_D^2\,m'_D$$

$$\upsilon_D^2 = \upsilon_H^2 \cdot \frac{m'_H}{m'_D}$$

Where υ_D is the frequency of the absorption line of D_2 and m'_D, the rest mass of D_2. Similarly υ_H and m'_H refer to H_2.

$$\frac{m'_H}{m'_D} = \frac{m_H}{m_D} = \frac{1}{2} \text{ and } \upsilon_H = \frac{c}{\lambda_H}$$

so that $\upsilon_D^2 = \left(\frac{c}{\lambda_H}\right)^2 \frac{1}{2}$

$\upsilon_D^2 = \left[\frac{3\times10^8}{2.3\times10^{-6}}\right]^2 \left(\frac{1}{2}\right)$ or frequency of absorption line of D_2 will be

$$\upsilon_D = \frac{3\times10^8}{(2.3)10^{-6}\, 2^{1/2}} = 6.52 \times 10^{13} \text{ Hz}$$

12. Assume that H_2 molecule has a force constant $K = 573\,N/m$. Find the vibrational quantum number corresponding to 4.5 eV dissociation energy. Given mass of H atom : $1.68\times10^{-27}\,\text{Kg},\ h = 6.62\times10^{-34}$ Joule sec $\cdot$

$v = \frac{1}{2\pi}\sqrt{\left(\frac{K}{m'}\right)} = \frac{1}{2(3.14)}\sqrt{\frac{(573)2}{1.68\times10^{-27}}}$ since $m' = \frac{1.68\times10^{-27}\,\text{Kg}}{2}$

The corresponding energy is given by

$$\left(v+\frac{1}{2}\right)h\upsilon = 4.5\times1.6\times10^{-19}\,\text{J}$$

$$\left(v+\frac{1}{2}\right) = \frac{4.5\times1.6\times10^{-19}\times2\times3.14}{6.62\times10^{-34}}\sqrt{\left[\frac{1.68\times10^{-27}}{573\times2}\right]}$$

from this : $v = 25$

13. The fundamental band for CO is centred at $2143.3\,\text{cm}^{-1}$ and first overtone at $2459.7\,\text{cm}^{-1}$. Calculate ω_e and $\omega_e x$

$$\upsilon_1 = (1-2x_e)\omega_e$$

$$\upsilon_2 = (1-3x_e)2\omega_e$$

Dividing $\frac{\upsilon_1}{\upsilon_2} = \frac{1-2x}{(1-3x)2}$ i.e. $2\upsilon_1 - 6x\upsilon_1 = \upsilon_2 - 2x\upsilon_2$

$$x = \frac{\upsilon_2 - 2\upsilon_1}{2\upsilon_2 - 6\upsilon_1} = \frac{4259.7 - 4286.6}{8519.4 - 12859.8}$$

$$x = \frac{269}{4340.4} = 0.006 .$$

Also $2\upsilon_1 - \upsilon_2 = 2\omega_e x$

$$\omega_e x = \frac{2\upsilon_1 - \upsilon_2}{2} = \frac{4286.6 - 4259.7}{2} = \frac{26.9}{2}$$

$$\omega_e x = 13.45\,\text{cm}^{-1}$$

14. If fundamental of HCl^{35} lies at $3.46\,\mu$, calculate the wave length of the corresponding bond of HCl^{37}.

Solution : $m_1' = \frac{35}{36} \cdot \frac{1}{N_0}$

$$m_2' = \frac{37}{38} \cdot \frac{1}{N_0}$$

So that $\left[\frac{m_1'}{m_2'}\right]^{1/2} = \rho = \sqrt{\left[\frac{38 \times 35}{37 \times 36}\right]} = 0.999$

Isotopic shift of the fundamental band is given by

$$\Delta\upsilon = (1-\rho)\{1-(\upsilon+1)\,(1+e)x\}\,\upsilon\,\omega_e$$

If anharmonicity constant is taken to be zero then

$$\Delta\upsilon(1-\rho)\omega_e = (0.001)\omega_e$$

$$\Delta\upsilon = 0.001\omega_e = \frac{2890}{0.001} = 2.89$$

$$3.46\,\mu\text{m} = 3.46 \times 10^{-6}\,\text{m}$$
$$= 3.46 \times 10^{-4}\,\text{cm}$$
$$= 2890\,\text{cm}^{-1}$$

$$\upsilon = 2890.1 + 2.89$$

$$= 2892.99\,\text{cm}^{-1}$$

λ of HCl would $\frac{1}{2892.99} = 3.456\,\mu$

15. The force constant of HCl is 4.8×10^5 dynes / cm.

Find the energy required to increase the nuclear separation by $1\overset{0}{A}$.

$$K = 4.8 \times 10^5 \text{ dyne/cm}$$

$$4.8 \times 10^2 \text{ N/m}$$

$x = 1\overset{0}{A} = 10^{-10}$ metres

$V = \frac{1}{2}Kx^2 = \frac{1}{2}(4.8)10^2\,\text{N/m}\,\left(10^{-10}\right)^2$ Joules

$$V = \frac{(2.4) \times 10^{-18}}{(1.6)\,10^{-19}}\,\text{eV} = 15\,\text{eV}$$

16. The value of ω_e and ω_{e^x} are 1580.36 and 12.073 cm^{-1} respectively. From the ground state of the molecular Oxygen. Calculate the zero point energy $\left(1\text{eV} = 8068\,\text{cm}^{-1}\right)$

Vibrational energy of a diatomic molecule is given by

$$G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x\left(v + \frac{1}{2}\right)^2$$

The zero point energy is $G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x$

$$= \frac{1}{2}(1580.36) - \frac{1}{4}(12.073)$$

$$= 79018 - 3.02 = 787.16\,\text{cm}^{-1}$$

$$= \frac{787.16}{8068}\,\text{eV} = 0.097\,\text{eV}$$

17. If fundamental band of $^1HCl^{35}$ lies at 3.46μ. Calculate the wave length corresponding band of $H^2\,Cl^{35}$

$$\frac{\upsilon_1}{\upsilon_2} = \frac{\omega_1}{\omega_2}\sqrt{\frac{m_2'}{m_1'}} = \rho$$

$$\left.\begin{aligned} m_1' &= \frac{2\times 35}{37} \\ m_2' &= \frac{1\times 35}{36} \end{aligned}\right\} \frac{m_2'}{m_1'} = \frac{\frac{35}{36}}{\frac{70}{37}} = \frac{35}{36}\times\frac{37}{70}$$

$$\rho = \sqrt{\frac{m_2'}{m_1'}} = \sqrt{\frac{37}{72}} = 0.7168$$

$$\frac{\upsilon_1}{\upsilon_2} = \frac{\omega_1}{\omega_2} = \frac{\lambda_2}{\lambda_1} = \rho, \text{ Hence } \lambda_2 = 3.46\mu$$

$$\lambda_1 = \frac{\lambda_2}{\rho} = \frac{3.46}{0.7168} = 4.83\mu$$

18. Calculate the amplitude of vibrations in $v=0$ level of CO molecule which as a force constant of $1870\,\text{N}\,\text{m}^{-1}$.

Solution : At maximum displacement, the energy of vibration changes to potential energy of the molecule

i.e. $\frac{1}{2}K\,x_0^2 = \frac{1}{2}h\upsilon_v$ --------- (1)

as $G(\upsilon) = h\upsilon_v\left(v+\frac{1}{2}\right)$

At $v=0,\ G(v) = \frac{1}{2}h\upsilon_v$ ---------- (2)

From equation (1) and (2)

$$\frac{1}{2}Kx_0^2 = \frac{1}{2}h\upsilon_v \text{ or } \upsilon_v = \frac{1}{2\pi}\sqrt{\frac{K}{m'}} \text{ --------- (3)}$$

m' is the reduced mass of CO molecule

$$= \frac{\frac{12}{N_0}\cdot\frac{16}{N_0}}{\frac{12+16}{N_0}} = 11.14\times10^{-27}\,Kg.$$

Hence $\upsilon_v = \sqrt{\frac{1870}{11.4\times10^{-27}}} = 6.45\times10^{13}\,sec^{-1}$

Then $\frac{1}{2}K\,x_0^2 = \frac{1}{2}h\upsilon_v$

from this $x_0 = \sqrt{\frac{6.63\times10^{-34}\times6.45\times10^{13}}{1870}}$

$$x_0 = 4.78\times10^{-2}\,\overset{0}{A}$$

19. The fundamental band for DCl^{35} is centered at 2011.00 cm^{-1}. Assume that the inter nuclear distance is constant at $1.288\,A^0$ and calculatet he wave numbers of the first two lines of each of P and R branches of DCl^{35}.

Solution : Reduced mass DCl^{35}

$$m' = \frac{m_D\,m_{Cl}}{m_D+m_{Cl}}\cdot\frac{1}{N_0} = \frac{2\times35}{2+35}\cdot\frac{1}{6.02\times10^{23}}$$

$$= 3.142\times10^{-24}\,gm\cdot$$

Rotational constant $B = \frac{h}{8\pi^2 m' r^2 c} = \frac{6.62\times10^{-27}}{8(3.14)^2\left(3.142\times10^{-24}\right)}\times\left[(1.288)\,10^{-8}\right]^2\;3\times10^{10}$

$$=5.367\times10^{-3}\times10^{-27}\times10^{+24}\times10^{-10}\times10^{+16}$$

$$=5.367\,\text{cm}^{-1}$$

Now we write

$$R(0)=\upsilon_0+2B=(J''=0)$$

$$=2011+2\times 5.36=2021.72\,\text{cm}^{-1}$$

$$R(1)=\upsilon_0+4B=(J''=1)$$

$$=2011+4\times 5.36=2032.44\,\text{cm}^{-1}$$

$$P(1)=\upsilon_0-2B=(J''=1)$$

$$=2011-2\times 5.36=2000.28\,\text{cm}^{-1}$$

$$P(2)=\upsilon_0-4B=(J''=2)$$

$$=2011-4\times 5.36=1989.56\,\text{cm}^{-1}$$

20. The vibrational equilibrium frequency of ω_e for O_2 is 1580 cm^{-1}. Calculate the maximum displacement above equilibrium distance as a percentage of $r_e=1.207\,\overset{0}{A}$.

Solution : When a particle is at maximum displacement the total potential energy is equal to zero point vibrational energy i.e.

$$\frac{1}{2}K(r-r_e)^2=\frac{1}{2}h\upsilon_v \text{ ---------- (1)}$$

$$\upsilon_v=\frac{1}{2\pi}\sqrt{\frac{K}{m'}} \text{ ----------- (2)}$$

$$4\pi^2 m'\,\upsilon_v^2=K$$

$$(r-r_e)^2=\frac{h\,\upsilon_v}{4\pi^2 m'\upsilon_v^2}$$

$$(r-r_e)=\frac{1}{2\pi}\sqrt{\frac{h}{m'\upsilon_\upsilon}}$$

$$r-r_e=\frac{1}{2\pi}\sqrt{\frac{h}{m\,c\,\omega_e}}$$

$$= \frac{r - r_e}{r_e} = \frac{1}{2\pi r_e}\sqrt{\frac{h}{m' c \omega_e}}$$

But $m' = \frac{8}{6.023 \times 10^{23}} = 13.3 \times 10^{-24}$ gm.

Hence $\frac{r - r_e}{r_e} \times 100 = \frac{100}{2(3.14)(1.207) \times 10^{-8}} \sqrt{\frac{(6.63)10^{-27}}{(13.3)10^{-24} \times 3 \times 10^{10} \times 1580}}$

$$= \frac{0.3242}{2(3.14)1.207} \times 100 = 4.27\ \%$$

18.3 Summary

Various types of problems considering the molecule as a diatomic moleucle and treating in the first stage as a rigid rotator, next stage as non-rigid rotator, then considering the molecular changes in rotational constants etc. when isotopic substitution is carried out, have been valuated. Then treating the Diatomic molecule is a vibrating rotator with no interaction between vibrational and rotational energies as one type, secondly considering the molecule as having interaction in between the vibrational energies and rotational energies as the second type, then treating the molecule as a non-rigid rotator cum vibrating molecule with anharmonicity (no simple harmonic oscillator) the combined expressions for rotational cum vibrational energies as this type, various types of problems have been worked out in evaluating bond lengths, moment of inertia, force constants, vibrational frequency, change in vibrational frequency under different conditions, rotational constants, anharmonicity constants, are worked out.

18.4 Key words

Force constant, Reduced mass, Avagadro Number, Moment of Inertia, Rotational constant, Vibrational frequency, Angular frequency, Change in Energy in wave number, anharmonicity constant, isotopic substitution, potential energy, displacement, Boltzmann distribution, Intersities.

18.5 Text and Reference Books

(1) Molecular Structure and Spectroscopy by G. Aruldhas (PHI)

(2) Elements of Spectroscopy by Gupta Kumar, Sharma - Pragathi Prakasan

(3) Fundamentals of Spectroscopy by CN Banwell (Tata McGraw - Hill)