UNIT-1
Basic Properties of Nucleus

Structure of the Unit

1.0 Objectives

In this unit ,we shall describe the certain basic properties of nucleus such as size, mass, angular momentum, magnetic moment ,electric quadrupole moment etc. and try to understand them by means of elementary theories.

1.1 Introduction

Main properties of atoms, molecules, solids and liquids can be explained on the basis of behavior of the electrons, nevertheless, role of the nucleus is important in nature. Applications of nuclear physics have had enormous effects on mankind. The most spectacular application of nuclear physics is nuclear energy .The energy characteristic of atoms is of the order of eV whereas of nucleus is of the order of MeV . In this unit we introduce some of its most basic properties. In the last we shall describe the semiempirical mass formula by employing liquid drop model.

1.2 Nuclear Radius and Nuclear Density

The size of nucleus was first investigated in the α particle scattering experiments of Rutherford. In this experiment, the distance of closest approach provides the information about the nuclear radius of the order of 10^{-14}m.

The most accurate results involve scattering of high energy relativistic electrons (of about 200 MeV kinetic energy) from thin target of the material under study. The electrons having such high energies have wavelengths comparable with the radius of nucleus. As nuclear forces do not act on an electron, so we have advantage with electrons that their electromagnetic interaction with the nucleus (nuclear charge) is well known. Thus electron scattering tells us the distribution of charge. If highly energetic neutrons are used as the scattering particles, then neutron scattering tells us the distribution of nuclear mass because neutron interacts only through the nuclear forces. If we assume a nucleus is an approximately spherically symmetric, we may express its size in terms of its radius R. Nuclear radius is measured in femtometer.

$$1 \text{ femtometer} = 1 \text{ Fermi} = 1 \text{ fm} = 10^{-15} m$$

The experimental results indicate that the radius R varies approximately as the cube root of the mass number and this relationship is usually expressed as

$$\boxed{R = R_0 A^{1/3}} \qquad (1)$$

where A is the mass number and R_0 is an empirical coefficient and its approximate value is

$$R_0 \approx 1.2 \times 10^{-15} m$$

Actual value of R_0 depends on the technique that used for determination of nuclear radius.

Nuclear Volume $V = \frac{4}{3}\pi R^3$ .From eq.(1) we have

$$V = \frac{4}{3}\pi R_0^3 A \qquad (2)$$

i.e. *volume of a nucleus is proportional to the number of nucleons.*

As the masses of a proton and a neutron are approximately equal, say m_p , then mass of nucleus *m* may be written as

$$m = m_p A \qquad (3)$$

Nuclear mass density $\rho_m = \frac{m}{V} = \frac{m_p}{\frac{4}{3}\pi R_0^3}$

which is independent of mass number A i.e. the mass density is approximately same for all nuclei.

We have m_p=1.67 × 10^{-27}kg and $R_0 \approx 1.2\text{x}10^{-15}$ m

Therefore $\rho_m \approx \frac{1.67\times10^{-27}}{\frac{4}{3}\pi\left(1.2\times10^{-15}\right)^3} = 2.3\times10^{17}\frac{kg}{m^3}$

i.e. ***nuclear mass density is of the order of*** $10^{17}\frac{\text{kg}}{\text{m}^3}$ **.** Thus we find that density of a nucleus has the extremely high value, neutron stars have densities of this magnitude.

Number of nucleons per unit volume = $\frac{\text{Mass Density}}{\text{Mass of a nucleus}}$

$$\cong \frac{2.3\times10^{17}}{1.6\times10^{-27}} \cong \boldsymbol{10^{44}\ \textbf{nucleons/m}^3}$$

Experimental observations for all nuclei are reasonably well approximated by following nuclear charge distribution (nuclear charge density):

$$\boxed{\rho(r) = \frac{\rho_0}{1+\exp\left[\frac{(r-R)}{t}\right]}} \qquad (4)$$

Above empirical equation represents *Fermi two parameter model,* where ρ_0 is the nucleon charge density near the centre of the nucleus and *r* is radial distance.

At distance r=R, from eq.(4) we have

$$\rho(r) = \frac{\rho_0}{1+1} = \frac{\rho_0}{2}$$

i.e. R is the radius at which the density has fallen to half its central value. Term t is nuclear surface thickness parameter. *The distance over which nuclear charge density* $\rho(r)$ *falls from* $0.9\,\rho_0$ *to* $0.1\,\rho_0$ *is 4.4 t.*

We can prove this by using eq.(4)

$$0.9\rho_0 = \frac{\rho_0}{1+\exp\left[\frac{r_1 - R}{t}\right]} \quad \Rightarrow \frac{r_1 - R}{t} = -ln9 \tag{5}$$

and

$$0.1\rho_0 = \frac{\rho_0}{1+\exp\left[\frac{r_2 - R}{t}\right]} \quad \Rightarrow \frac{r_2 - R}{t} = \ell n 9 \tag{6}$$

From eq.(5) & (6)

$$r_2 - r_1 = (2\,ln9)t \approx 4.4t$$

A plot of eq.(4) is shown below

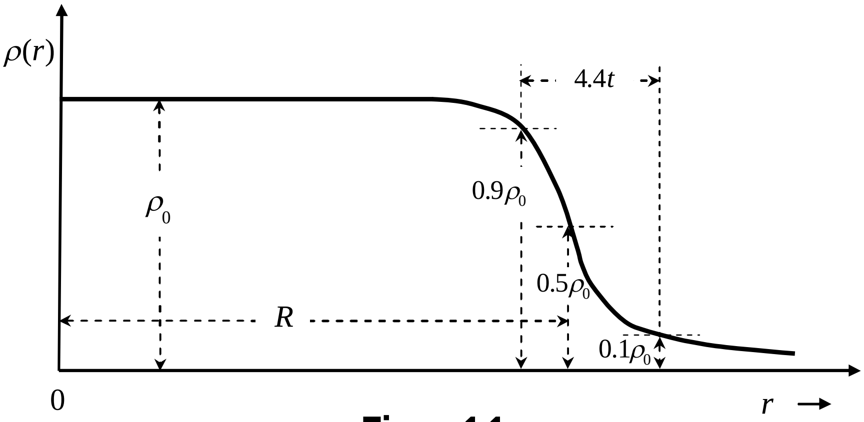


Figure 1.1

The charge densities of nucleons in $_{27}$Co and $_{83}$Bi nuclei versus radial distance from centre is plotted in figure (1.2).

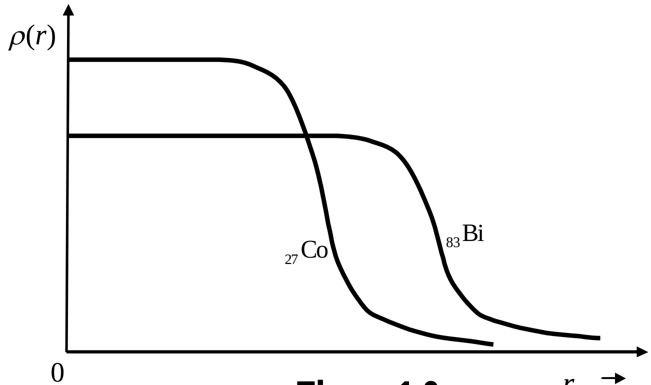


Figure 1.2

From the figure (1.2), it is evident that $\rho(0)$ (interior value of nuclear charge density) decreases slowly with increasing A (mass number).

The *charge density* $\rho(r)$ corresponds the density of the protons in the nucleus and $\rho_m(r)$ represents the density of all nucleons (matter) in the nucleus. Experimental results indicate that

$$\rho(r) \propto \frac{Z}{A}\rho_m(r)$$

Experimental observations show that $\rho_m(0)$ (interior value of nuclear mass density) is approximately the same for all nuclei.

1.3 Nuclear Spin (Total Angular Momentum)

Angular momentum of a nucleon can be described as:

(i) Spin Angular Momentum

Each nucleon (proton or neutron) has spin angular momentum

$$\boxed{|\vec{s}| = \sqrt{s(s+1)}\ \hbar = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\ \hbar = \frac{\sqrt{3}}{2}\hbar}$$

where *s = 1/2 spin angular momentum quantum number.*

Proton and neutron are fermions each with spin quantum number *s* =1/2 .

(ii) Orbital Angular Momentum

The magnitude of orbital angular momentum can be expressed as

$$\boxed{|\vec{\ell}| = \sqrt{\ell(\ell+1)}\,\hbar}$$

where ***l***= orbital quantum number.

(iii) Total Angular Momentum

The magnitude of the total angular momentum of the nucleon is

$$\boxed{\vec{J} = \sqrt{j(j+1)}\,\hbar}$$

The net angular momentum of the nucleus is the resultant of all the spin angular momenta and orbital angular momenta of the its constituent nucleons.

The magnitude of the nuclear angular momentum due to all nucleons is

$$\left|\vec{I}\right| = \sqrt{I(I+1)}\ \hbar$$

where I is called ***total angular momentum quantum number or nuclear spin*** which may be an integer or a half integer.

Greatest possible component of the total angular momentum along any direction is

$$I_Z = m_I \hbar$$

$m_I = -I, -I+1, \ldots\ldots\ldots, I-1, I$

where m_I = magnetic total angular momentum quantum number.

The word spin usually refers to the resultant angular momentum of a nucleus in nuclear physics, whereas, in atomic physics the word spin refers to the intrinsic spin angular momentum.

It is found that nuclei with even Z and even N have the total angular momentum zero, because pairs of protons are formed in such a way that their angular momenta cancel and similarly pairs of neutrons are formed in such a way that their angular momenta cancel.

The total angular momentum quantum number I is integral for nuclei with even mass number A and half integral for nuclei with odd mass number A.

Following conclusion about total angular momentum of a nucleus can be made

Mass Number A	***Proton Number Z***	***Neutron Number N***	***Nuclear spin I***
Even	***Even***	***Even***	***0***
	Odd	***Odd***	***1,2,3,....***
Odd	***Even***	***Odd***	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$
	Odd	***Even***	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

Shell model has been developed to find the angular momentum of a nucleus. ***Shell model energy diagram is given as:***

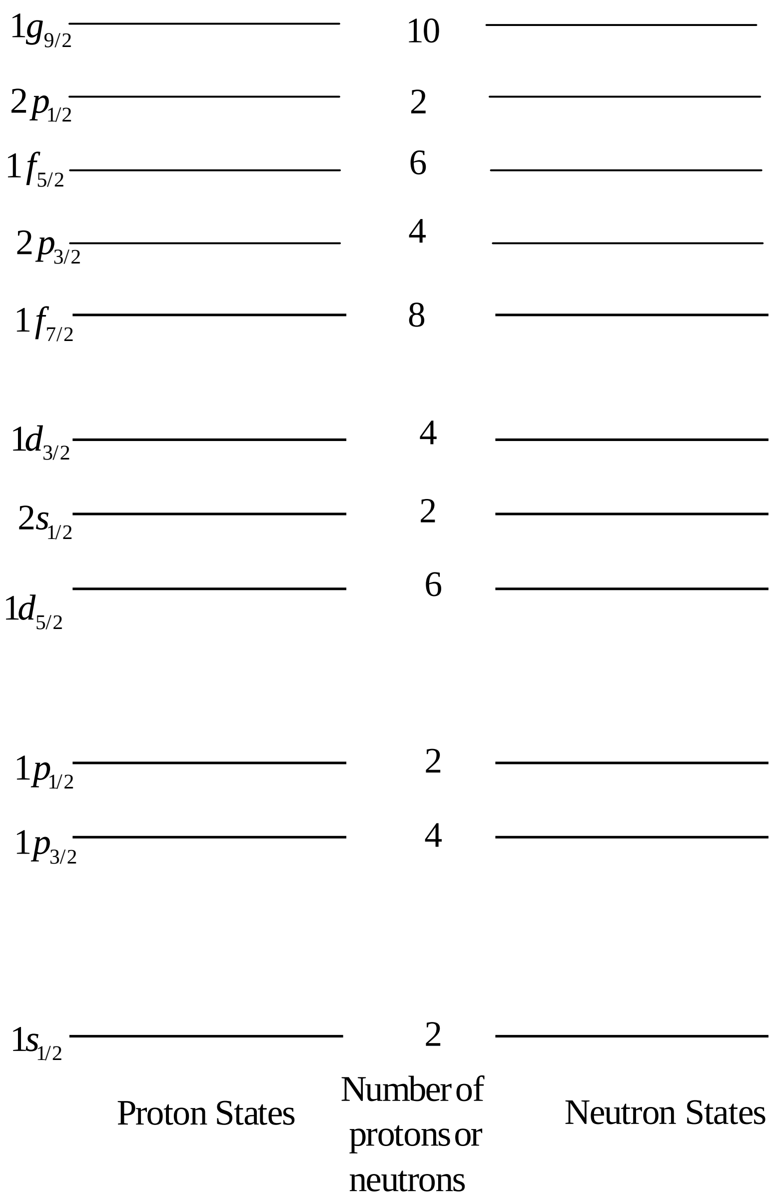


Figure 1.3

Proton and neutron states are filled separately. ***The filled shells have a total angular momentum I equal to zero.*** Angular momentum of nucleus is determined by the quantum state of single unpaired proton or neutron in the Shell theory. For example, we consider a $^{17}_{8}O$ nucleus which has 8 protons and 9 neutrons.

Quantum state (see figure 1.4) of the last single unpaired neutron is $1d_{5/2}$. Hence angular momentum of the nucleus is I=5/2.

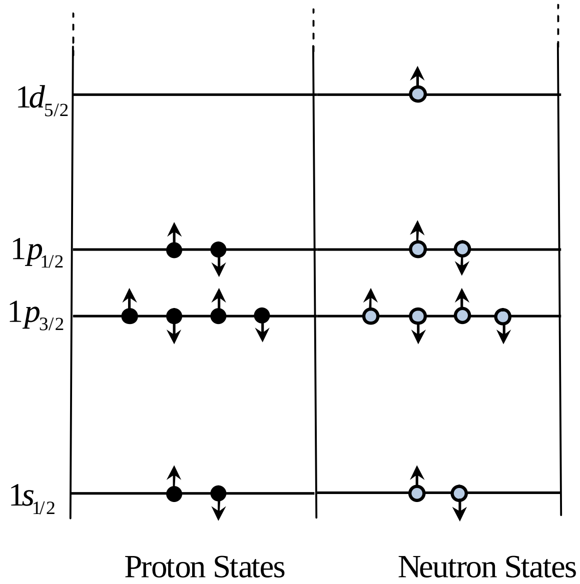


Figure 1.4 : *Quantum states of* ${}^{17}_{8}O$ *nucleus in shell model*

1.4 Parity

The parity of a wavefunction ψ is related to the symmetry properties of the wavefunction ψ.

If $|\psi(\vec{r})|^2 = |\psi(-\vec{r})|^2$

$\psi(\vec{r}) = \pm\psi(-\vec{r})$

If the spatial part of the wavefunction of a nucleus is unchanged when the space co-ordinates (x,y,z) are substituted by (–x, –y, –z)

i.e. ψ (–x, –y, –z) = +ψ (x,y,z) (7)

i.e. wavefunction is invariant under reflection (*function is symmetric as regards spatial inversion)* ,then system is said to have even parity.

If the spatial part of the wavefunction of a nucleus changes sign when the space co-ordinates (x,y,z) are substituted by (–x, –y, –z) i.e.

ψ (–x, –y, –z) = –ψ (x,y,z) (8)

,then system is said to have odd parity i.e. *function is antisymmetric as regards spatial inversion.*

The equations (7) & (8) may be combined in the form

ψ (–x, –y, –z) = Pψ (x,y,z)

$$\psi(-\vec{r}) = P\psi(\vec{r}) \qquad \text{where } P = \pm 1$$

P= +1 corresponds to even parity (positive parity)

P= –1 corresponds to odd parity (negative parity)

For Parity operator $\hat{P}$

$$\hat{P}\psi(\vec{r},t) \equiv P\psi(-\vec{r},t) \qquad \textit{\textbf{with eigenvalue P = ± 1}}$$

Parity is associated with quantum number ±1 and it is also denoted by symbol π.

In spherical polar coordinates (r,θ,ϕ,) a reflection about the origin is equivalent to the following transformation

$$\boxed{\begin{aligned} & r \to r \\ & \theta \to \pi - \theta \\ & \phi \to \phi + \pi \end{aligned}}$$

To a reasonably well approximation wavefunction ψ of a nucleus is the product of a function depending on space coordinates and a function depending on the spin orientation. It has been found that ***intrinsic parity of proton as well as of neutron is even i.e.*** $\boxed{P_{\substack{Intrinsic \\ Nucleon}} = +1}$

It is found *that* ***parity of a nucleus in a given state is related to orbital quantum number l in the following manner***

$$\boxed{P = (-1)^l}$$

The orbitals s,p,d,f,... correspond to l= 0,1,2,3,… respectively.

Parity is even for even l and parity is odd for odd l.

If $\vec{r}_1, \vec{r}_2, ...\vec{r}_A$ are coordinates of nucleons in the nucleus and $\psi_N(\vec{r}_1, \vec{r}_2, ...\vec{r}_A)$ represents the nuclear wavefunction in a state of definite parity, then

$$\psi_N(\vec{r}_1, \vec{r}_2, ...\vec{r}_A) = \pm\psi_N(-\vec{r}_1, -\vec{r}_2, ... -\vec{r}_A)$$

To a good approximation, the wavefunction ψ of the nucleus is the product of the wavefunctions of its constituents particles. If the nuclear particles have angular momentum quantum numbers l_1, l_2, ...respectively, then parity of the nucleus is the product over all nucleons is given by

$$P = P_1\, P_2\, P_3 .... = \prod_i P_{in}(i) P_l(i)$$

$$= \prod_i P_l(i) \qquad \{\because P_{\substack{\text{intrinsic}\\ \text{nucleon}}} = 1 \; for\; nucleon\}$$

$$= (-1)^{\ell_1}(-1)^{\ell_2}.......... = (-1)^{\ell_1+\ell_2+....}$$

$$\boxed{P = (-1)^{\Sigma \ell_i}}$$

If $\sum l_i =$ even then P=+1 and if $\sum l_i =$ odd then P= –1

The total angular momentum is generally called the nuclear spin and it is represented by I, but it is different from the spin angular momentum.

The parity of a nucleus is usually represented by a superscript + or – on the total angular momentum (spin) of the nucleus.

$$\boxed{I^P \equiv (\text{spin})^{\text{parity}}}$$

Spin-parity state of a nucleus is completely determined by a single unpaired proton or neutron.

For even Z - even N nuclei :

$$I^P = 0^+ \qquad \textit{(ground state)}$$

Inner shells are completely filled. Protons and neutrons in an even N-even Z nucleus tend to pair off separately.

For even Z-odd N nuclei or even N-odd Z nuclei:

Total angular momentum and parity are determined by the unpaired nucleon .

$$I = \ell \pm \frac{1}{2}, \qquad P=(-1)^l \qquad \text{(ground state)}$$

where ***l*** represents the orbital angular momentum quantum number of the unpaired nucleon.

For odd Z-odd N nuclei *:*

Parity $P = (-1)^{\ell_n + \ell_p}$

Parity is important quantity in physics. ***Parity is conserved in strong and electromagnetic interactions but parity is not conserved in weak interactions.***

1.5 Illustrative Examples

Example 1 What is the parity of the following quantum state

$$\psi = B\, r\, e^{\frac{-r}{a_0}} \sin\theta \; e^{-i\phi}$$

Sol. $\psi(-\vec{r}) = Bre^{-\frac{r}{a_0}} \sin(\pi-\theta)e^{-i(\pi+\phi)}$

$= Bre^{-\frac{r}{a_0}} \sin\theta\, e^{-i\phi}\, e^{-i\pi}$

$= Bre^{-\frac{r}{a_0}} \sin\theta e^{-i\phi}(-1)$

$= (-1)\psi(\vec{r})$

Hence parity P= −1

Example 2 Find the angular momentum and parity of the nucleus ^{41}Ca .

Sol. Quantum states of $^{41}_{20}Ca$ nucleus in shell theory are shown in figure given below

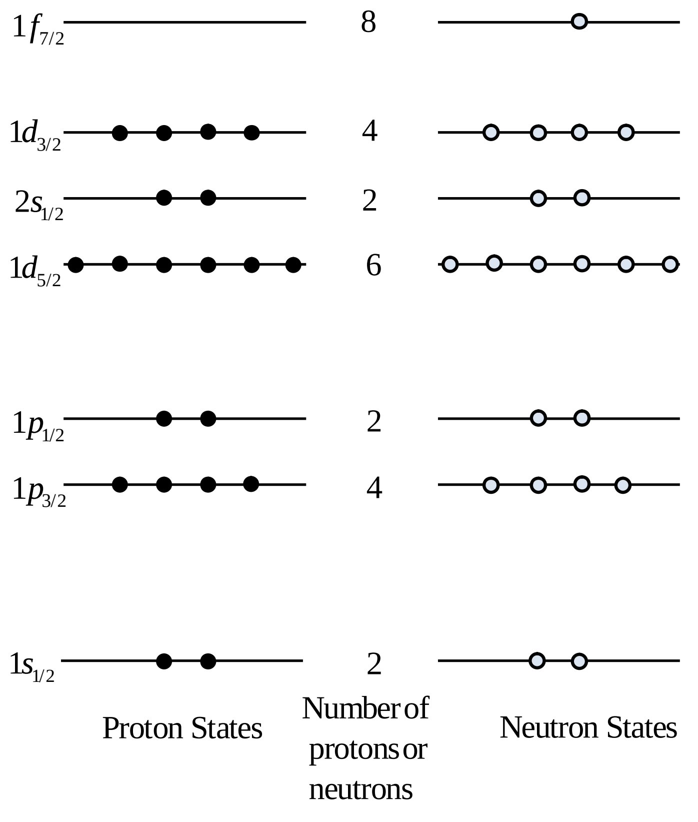


Figure 1.5

Nucleus $^{41}_{20}Ca$ has 20 protons and 21 neutrons. 20 protons and 20 neutrons form closed shells whereas 21st neutron goes to quantum state $1f_{7/2}$. The spin parity of $^{41}_{20}Ca$ is determined by the unpaired neutron in the state $1f_{7/2}$. For this state

$I = 7/2$ and $l=3$, Thus parity P= $(-1)^3 = -1$ and $I^P = \frac{7^-}{2}$

1.6 Self Learning Exercise-I

Q.1 What is the nature (shape) of the graph of $ln\left(\frac{R}{R_0}\right)$ versus $ln A$?

Q.2 What are the eigen values of parity operator ?

Q.3 Find the electric potential energy due to electric repulsion between two nuclei of $^{27}_{13}Al$ when they touch each other at the surface. (Assume that $R_0=1.1\times10^{-15}$m)

Q.4 Find the parity of $^{18}_{9}F$ nucleus.

1.7 Magnetic Moment

The spacing in hyperfine structure indicates that the magnitude of nuclear moments are of the order of $\frac{e\hbar}{2m_p}$ where m_p is the mass of the proton. The magnetic moment of a nucleus is expressed in terms of the ***nuclear magneton μ_N***

$$\boxed{\mu_N = \frac{e\hbar}{2m_p} = 5.05\times10^{-27}\,\frac{J}{T} = 3.15\times10^{-8}\,\frac{eV}{T}}$$

We know that ***Bohr Magneton*** $\boxed{\mu_B = \frac{e\hbar}{2m_e}}$

Thus $= \frac{\mu_B}{\mu_N} \approx 1836$

Spin Magnetic Moment:

A free proton has spin magnetic moment component in any direction (say z direction) is given by

$$\boxed{\left(\mu_{sp}\right)_z = 2.793\ \mu_N}$$

*The **spin magnetic moment of the proton is parallel to its spin angular momentum**.*

The spin magnetic moment component of a neutron in any direction (say z direction) is given by

$$\boxed{\left(\mu_{sn}\right)_z = -1.913\ \mu_N}$$

It means that ***spin magnetic moment of the neutron is opposite to its spin angular momentum.***

In order to understand the magnetic moments of a proton and a neutron (neutral particle), internal structures of them are considered.

We can express the spin magnetic moment for proton and neutron as

$$\boxed{\vec{\mu}_s = g_s\left(\frac{e}{2m_p}\right)\vec{s}}$$

and $\boxed{\mu_{sz} = g_s \mu_N m_s}$

where ***magnetic spin quantum number m_s= ±1/2***

g_s = nuclear g factor

For proton g_{sp}=+5.5855 $\because (\mu_{sp})_z = +2.793\mu_N$

For neutron g_{sn}=−3.826 $\because (\mu_{sn})_z = -1.913\mu_N$

Orbital Magnetic Moment:

There may be orbital angular momentum due to motion of the nucleons within the nucleus. The component of the orbital magnetic moment of a proton along the z axis (arbitrary direction) is

$$\boxed{M_{Lz} = \frac{e}{2m_p}L_z = \frac{e\hbar}{2m_p}m_\ell = \mu_N m_\ell}$$

m_l = magnetic orbital quantum number

Neutron does not have the orbital magnetic moment because it has no charge.

For proton g_{lp} =1

For Neutron g_{ln}=0

Resultant Magnetic Moment:

To a good approximation, resultant magnetic moment of a nucleus is directly proportional to the nucleus spin I and we can write

$\mu_{nucleus}=\mu_N g\, I$

Here *g* is the characteristic of each nucleus.

Nucleus with zero nuclear spin (total angular momentum) has no magnetic moment. Thus even N - even Z nuclei have no magnetic moment. Paired nucleons do not contribute to the magnetic moment.

Magnetic moments of electrons and nucleus interact and this interaction splits the atomic levels which gives rise to the ***hyperfine structure*** of the lines of the atomic spectra.

It is found that many nuclei are in the shape of an ellipsoid instead of sphere. ***Deviation of charge distribution of nucleus from a spherical shape is a measure of nuclear electric quadrupole moment***.

Quadrupole moment Q is defined as

$$\boxed{Q = \int \left(3z^2 - r^2\right) \rho \, dV}$$

where is ρ the nuclear charge density, dV = volume element

S.I. unit of Q is C-m²

Sometimes Q is also defined as

$$\boxed{Q = \frac{1}{e}\int (3z^2 - r^2)\, \rho \, dV}$$

where e=1.6x10^{-19} C and *then unit of Q will be* ***barn*** where $1 Barn = 10^{-28} m^2$

If the nucleus has spherically symmetric charge distribution, then it has no electric quadrupole moment or higher electric moments.

The charge distribution will be stretched in the z direction (prolate shape) if quadrupole moment is positive. If quadrupole moment is negative, then charge distribution will be in oblate shape.

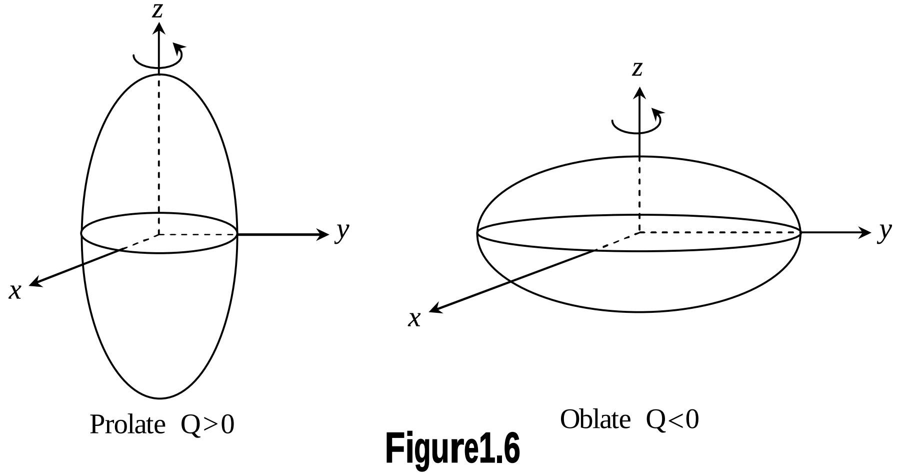


Figure1.6

It is observed that nuclei of both magic N and Z have zero quadrupole moments and hence are spherical.

1.8 Binding Energy

Nucleus is assumed to be composed of neutrons and protons. When neutrons and protons combine to form a nucleus, there is a loss in mass. So binding energy of the nucleus is the energy equivalent of the missing mass of the nucleus. If Δm be the missing mass of the nucleus, then binding energy E_b may be expressed as

$$E_b = \Delta m c^2 \quad \text{where } c = 3\times 10^8\, m/s$$

When the nucleons which are initially far away from each other are brought closer to form the nucleus , the amount of energy released is called the binding energy of the nucleus.

Alternatively ,we can say that the amount of energy required to separate the constituent nucleons to large distances is called the binding energy of the nucleus. The term missing mass Δm is known as ***mass defect***. The greater value of the binding energy of nucleus means that the more energy is needed to break the nucleus into its constituent particles. Thus binding energy is related to stability of the nucleus. Stable nuclei have positive value of the binding energy. Nuclear mass is found to be always less than the sum of the masses of constituent nucleons. The principle of equivalence of mass and energy confirms the idea of mass defect.

The binding energy of a nucleus of rest mass ${}^{A}_{Z}m$ composed of nucleons of rest masses m_i is written as

$$E_b = \left(\sum_i m_i - {}^{A}_{Z}m\right)c^2$$

If mass number of nucleus is A and there are Z protons and (A−Z) neutrons , then binding energy is stated as

$$\boxed{E_b = \left[Zm_p + (A-Z)m_n - {}^{A}_{Z}m\right]c^2 \qquad (in\, Joule)}$$

Here m_p and m_n are the rest masses of the proton and neutron respectively. In above expression masses are taken in kg.

$$\boxed{E_b = \left[Zm_p + (A-Z)m_n - {}^{A}_{Z}m\right]931.49\, MeV} \qquad (9)$$

Here all masses are taken in ***unified atomic mass unit u***.

$$\boxed{1u = 931.49\frac{MeV}{c^2}}$$

$$1u=\frac{\text{rest mass of one neutral }{}^{12}_{6}\text{C atom}}{12}\equiv\frac{1.99265\times10^{-26}\,Kg}{12}$$

$$\boxed{1u\equiv1.66054\times10^{-27}\,Kg}$$

Atomic mass unit (symbol : a.m.u.) was based on oxygen and it was replaced by unified atomic mass unit (symbol: u) in 1961 to take standard same form in physics and chemistry. Note that 1 a.m.u. can also be taken as $1amu\equiv931.49\frac{MeV}{c^2}$

Nuclear binding energy is of the order of MeV whereas binding energy of electrons in atom is of the order of eV. Hence binding energy of electrons in atom is negligible in comparison with nuclear binding energy. So without appreciable error , binding energy of the nucleus may be approximated as

$$\boxed{E_b=\left[ZM_H+(A-Z)m_n-{}^{A}_{Z}M_{atom}\right]c^2} \tag{10}$$

where M_H is the rest mass of the hydrogen atom.

In addition to masses of protons , the term ZM_H includes the masses of *Z* electrons. Similarly the term ${}^{A}_{Z}M_{atom}$ also contains the contribution of masses of Z electrons. Hence ,in the above expression of the binding energy E_b contributions of masses of electrons cancel out.

Packing Fraction:

It is defined as

Packing Fraction $f=\frac{M-A}{A}$,where *M* is the atomic mass of the neutral atom.

Above expression may be written as $M=A(1+f)$

Packing fraction f is a function of mass number A .

Unified Atomic Mass Unit is defined for carbon as $M\left({}^{12}_{6}C\right)=12.0000000\ u$

Hence by definition, ***packing fraction is zero for*** ${}^{12}_{6}C$.

Variation of Binding Energy per Nucleon with Mass Number:

Average binding energy per nucleon is more useful parameter for measurement of stability of a nucleus. It is defined as

Average binding energy per nucleon $\overline{E}_b=\frac{\text{Total binding energy of the nucleus}}{\text{Total number of nucleons in the nucleus}}=\frac{E_b}{A}$

For example, let's consider nucleus ${}^{4}_{2}He$ which has binding energy $28.3\,MeV$,then

$$\bar{E}_b = \frac{E_b}{A} = \frac{28.3}{4} \cong 7.07\frac{MeV}{Nucleon}$$

The binding energy per nucleon as a function of mass number A is plotted in figure(1.7).

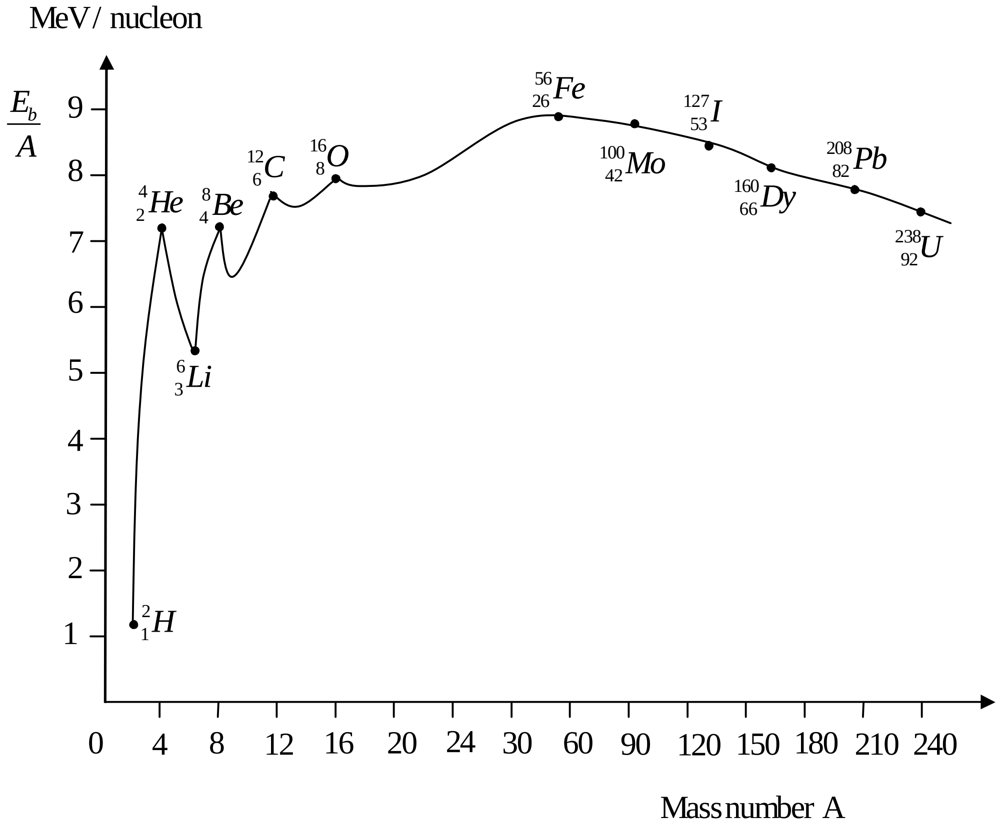


Figure 1.7

The binding energy per nucleon versus mass number characteristic curve has following main features:

(i) Binding energy per nucleon is lower for both light nuclei (A≲30) and heavy nuclei (A≳170). On the average, nuclei of intermediate masses (A≃50-80) are the most stable.

(ii) The binding energy per nucleon is fairly constant for the nuclei of middle mass numbers (about 30 < A < 170). In this region $\bar{E}_b$ has value about $8\,MeV$.

With further increase in the mass number A , the binding energy per nucleon decreases slowly to about $7.6\,MeV$ for A≃240. This happens due to long range repulsive Coulombic force between the protons in the nucleus.

(iii) The peak at A=4 for nucleus ${}_{2}^{4}He$ indicates the unusual high stability of the nucleus (alpha particle) ${}_{2}^{4}He$ which is made of two protons and two neutrons. Similarly there is a also rapid rise in the value of $\bar{E}_b$ for light nuclei with maxima for the even Z-even N nuclei such as ${}_{6}^{12}C$, ${}_{8}^{16}O$ .At these nuclei $\bar{E}_b$ is remarkably greater than those of their adjacent neighbours.

(iv) ***The curve has its maximum of*** $8.8 MeV$ ***when the mass number is 56 that is an iron isotope*** ${}_{26}^{56}Fe$ ***which is the most stable nucleus.***

(v) If a heavy nucleus of very high mass number is split into two medium mass fragments, this process is known as fission. In the fission process, energy is liberated because medium mass product nuclei have higher binding energy per nucleon compared to original heavy nucleus.

For example ${}_{92}^{238}U$ (for which $\bar{E}_b$ is about $7.6 \frac{MeV}{Nucleon}$) splits into two fragments of equal masses say mass number of 119. Approximate value of $\bar{E}_b$ is $8.5 \frac{MeV}{Nucleon}$ for nuclei having A=119. So gain in binding energy per nucleon is $8.5 - 7.6 = 0.9 \frac{MeV}{Nucleon}$ .Hence energy released in the process is about $238 \times 0.9 \simeq 210 MeV$

(vi) In nuclear fusion , two or more nuclei of very small mass number A combine to form a medium nucleus of higher mass number A and energy is released in this process because product nucleus has higher average binding energy per nucleon.

1.9 Semi Empirical Mass Formula

Scientists developed nuclear liquid drop model to give physical insight into nuclear properties .In this model nucleus is assumed like a liquid drop in which nucleons are closely packed. For expressing the atomic mass ,in 1935 ,***Van- Weizsacker developed a formula which is known as semi empirical mass formula*** in which certain properties of classical liquid drop is used.

From eq.(10) binding energy of the nucleus is given by

$$E_b = \left[ZM_H + (A-Z)m_n - {}_{Z}^{A}M_{atom} \right] c^2$$

$$ {}_Z^A M_{atom} = \left[ZM_H + (A-Z)m_n - \frac{E_b}{c^2} \right] \tag{11} $$

where ${}_Z^A M_{atom}$ is the mass of the neutral atom .

Now we discuss the various terms that contribute in the binding energy

(a) Volume Energy E_V

This term is based on ***saturation property of nuclear forces***. Nuclear forces among nucleons are very strong and have ***very short range about 3fm***. We can visualize each nucleon as a sphere and these are assumed to be closely packed in which each nucleon touches the 12 neighbouring nucleons. It can be assumed that interaction between any two nearest neighbouring nucleons ,results in certain interaction energy. Total interaction energy of such type depends on number of adjacent pairs of nucleons, i.e. depends on the mass number (total number of nucleons in the nucleus). Since volume of the nucleus is directly proportional to A ,so this type of interaction energy is related to volume of the nucleus. Attractive nuclear forces results in negative interaction energy but binding energy is taken as positive. Hence binding energy corresponding to this interaction can be approximated as

Volume Binding Energy $E_v = a_v A$

where a_v is positive constant.

(b) Surface Energy E_S

Nucleons on the surface have fewer neighbours and they are not completely surrounded .The nucleon on the surface feels attractive forces only from one side whereas the nucleon in the interior feels attractive forces from all sides. In the volume energy term ,it was assumed that each nucleon interacts with other nucleons equally from all sides, so a term that is proportional to the surface area of nucleus must be subtracted to reduce the binding energy. This negative correction constitutes the surface energy term E_S which represents the loss of binding energy.

$$ E_S = -\alpha R^2 $$

$$ \Rightarrow E_S = -a_S A^{2/3} \qquad \because R = R_0 A^{1/3} $$

Since lighter nuclei have greater fraction (ratio of number of nucleons on the surface to those in the interior volume), so surface energy term is the most significant for lighter nuclei.

(c) Coulomb Energy

Coulombic repulsion force between protons is long range force. The Coulomb potential energy (of Z protons packed together in spherical symmetric manner) is proportional to number of proton pairs $\frac{Z(Z-1)}{2}$ and is inversely proportional to nuclear radius.

The contribution to the binding energy is expressed as

$$E_C \propto \frac{Z(Z-1)}{R}$$

$$\Rightarrow E_c = -a_c \frac{Z(Z-1)}{A^{1/3}}$$

The Coulombic repulsive energy term lowers the binding energy and increases the mass , hence it opposes nuclear stability .For heavier nuclei $Z \gg 1$,hence E_C can be approximated as

$$E_C \cong -a_C \frac{Z^2}{A^{1/3}}$$

(d) Asymmetry Energy

The asymmetry energy E_a arises due to unequal number of neutrons and protons in the nucleus. To get the best agreement with predicted binding energy ,it can be written as

$$E_a = -a_a \frac{(N-Z)^2}{A} \qquad \text{Here neutron excess} \equiv (N-Z)$$

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

The contribution of the asymmetry energy to the binding energy is negative because it decreases the binding energy of the nucleus .This correction term cannot be understood with simple liquid drop model ,it is a purely quantum mechanical effect which is related with nuclear energy levels. To be in the stable state ,nucleus should occupy the lowest energy state. The asymmetry energy E_a is zero for Z=N that results in greater stability of the nucleus.

(e) Pairing Energy

The nuclei having even numbers of both protons and neutrons are strongly favoured and most stable in nature whereas nuclei having odd numbers of both protons and neutrons are the least stable. Hence this pairing effect (spin consideration) is taken in the pairing energy which can be expressed empirically as

$$E_p = (\pm, 0)\frac{a_p}{A^{3/4}}$$

The pairing energy is positive for even- even nuclei and zero for odd-even nuclei or even-odd nuclei and negative for odd-odd nuclei i.e.

$$E_p = \frac{a_p}{A^{3/4}} \qquad \text{for even Z and even N}$$

$$E_p = 0 \qquad \text{for even Z and odd N}$$

$$\text{or odd Z and even N}$$

$$E_p = -\frac{a_p}{A^{3/4}} \qquad \text{for odd Z and odd N}$$

Here a_p is assumed an approximately constant coefficient.

The total binding energy of a nucleus of atomic number Z and mass number A is written as

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

Semiempirical Binding Energy Formula

$$\boxed{E_b = a_v A - a_s A^{2/3} - a_c \frac{Z(Z-1)}{A^{1/3}} - a_a \frac{(A-2Z)^2}{A}(\pm, 0)\frac{a_p}{A^{3/4}}} \qquad (12)$$

From eq.(11) Atomic mass ${}_Z^AM_{atom} = \left[ZM_H + (A-Z)m_n - \frac{E_b}{c^2}\right]$

Semiempirical mass formula

$${}_Z^AM_{atom} = \left[ZM_H + (A-Z)m_n - \frac{1}{c^2}\left\{a_v A - a_s A^{2/3} - a_c \frac{Z(Z-1)}{A^{1/3}} - a_a \frac{(A-2Z)^2}{A}(\pm, 0)\frac{a_p}{A^{3/4}}\right\}\right] \qquad (13)$$

A set of constants a_v, a_s, a_c, a_a and a_p have been determined as

$$a_v = 14.1\ MeV$$

$$a_s = 13.0\ MeV$$

$$a_c = 0.595\ MeV$$

$$a_a = 19.0\ MeV$$

$$a_p = 33.5\ MeV$$

Other sets of constants have also been developed by empirically fitting the observed mass.

Eq.(13) is known as the semiempirical mass formula because the constants a_v, a_s, a_c, a_a and a_p are determined empirically by fitting observed atomic masses. The semiempirical mass formula predicts the binding energies which are remarkably close to the observed values except those of very small A. The discrepancies between predicted mass values and observed mass values are the least.

1.10 Illustrative Examples

Example 3 Calculate the atomic mass of ${}^{9}_{4}Be$ .The binding energy of the nuclide ${}^{9}_{4}Be$ is $58.11628\,MeV$

Given that atomic mass $M\left({}^{1}_{1}H\right)=1.00782\ u$,

Mass of neutron $m_n=1.00866\ u$ and $1\,u \equiv 931.5\dfrac{MeV}{c^2}$

Sol. $E_b=\left[\left\{4M\left({}^{1}_{1}H\right)+5m_n\right\}-M\left({}^{9}_{4}Be\right)\right]c^2$

$$\Rightarrow M\left({}^{9}_{4}Be\right)=\left[\left\{4M\left({}^{1}_{1}H\right)+5m_n\right\}-\frac{E_b}{c^2}\right]$$

$$=\left[\left\{4\times1.00782\ u+5\times1.00866\ u\right\}-\frac{58.11628\,MeV}{c^2}\right]$$

$$=\left[\left\{4\times1.00782\ u+5\times1.00866\ u\right\}-\frac{58.11628\,u}{931.5}\right]$$

$$=\left[\left\{4.03128\ u+5.04330\ u\right\}-0.06239u\right]$$

$$M\left({}^{9}_{4}Be\right)=9.01219u$$

Example 4 Calculate the binding energy of the last neutron in the nucleus ${}^{17}_{8}O$. Given that atomic masses

$M\left({}^{17}_{8}O\right)=16.99913\ u$, $M\left({}^{16}_{8}O\right)=15.99492\ u$, $M\left({}^{1}_{1}H\right)=1.00782\ u$

Mass of neutron $m_n=1.00866\ u$ and $1u \equiv 931.49\dfrac{MeV}{c^2}$

Sol. The binding energy of a nucleon is the energy required to remove that nucleon from the nucleus.

Binding energy of the last neutron

$$E_{bn}=\left[\left\{M\left({}^{16}_{8}O\right)+m_n\right\}-M\left({}^{17}_{8}O\right)\right]c^2$$

$$=\left[\left\{M\left({}^{16}_{8}O\right)+m_n\right\}-M\left({}^{17}_{8}O\right)\right]\frac{931.49MeV}{c^2}c^2$$

$$=\left[\left\{15.99492+1.00866\right\}-16.99913\right]931.49MeV$$

$$=\left[17.00358-16.99913\right]931.49MeV$$

$$=\left[0.00445\right]\times 931.49MeV$$

$$E_{bn}=4.15MeV$$

1.11 Self Learning Exercise-II

Q.1 What is the value of nuclear magneton ?

Q.2 Binding energy per nucleon is maximum for iron isotope ${}^{56}_{26}Fe$. Is this statement true?

Q.3 Calculate the binding energy of nucleus ${}^{238}_{92}U$ .Also find the binding energy per nucleon of the nucleus. Given that atomic masses

$M\left({}^{238}_{92}U\right)=238.05076u$, $M\left({}^{1}_{1}H\right)=1.00782\ u$

Mass of neutron $m_n=1.00866\ u$ and $1u\equiv 931.49\frac{MeV}{c^2}$

Q.4 Explain the pairing energy term in semiempirical mass formula.

1.12 Summary

- Nuclear radius $R=R_0A^{1/3}$
- *Nuclear mass density is of the order of* $10^{17}\ \frac{\text{kg}}{\text{m}^3}$.
- Greatest possible component of total angular momentum of a nucleus along any direction is $I_Z=m_I\hbar$

  $m_I=-I,-I+1,........,I-1,I$

  where m_I = magnetic total angular momentum quantum number.
- For Parity operator $\hat{P}$ we have $\hat{P}\psi(\vec{r},t)\equiv P\psi(-\vec{r},t)$ with *eigen value P = ± 1*

  It is found *that parity of nucleus in a given state is related to orbital quantum number l in the following manner* $P=(-1)^l$
- Quadrupole moment Q is defined as

$Q = \int \left(3z^2 - r^2\right) \rho \, dV$

where is ρ the nuclear charge density, dV = volume element, *S.I. unit of Q is C-m²*

Sometimes Q is also defined as $Q = \frac{1}{e} \int (3z^2 - r^2) \rho \, dV$

If the nucleus has spherically symmetric charge distribution, then it has no electric quadrupole moment or higher electric moments.

- Binding energy of the nucleus $E_b = \left[Zm_p + (A-Z)m_n - {}^{A}_{Z}m \right] 931.49 \, MeV$

  Here all masses are taken in *u* where $1u = 931.49 \frac{MeV}{c^2}$

  $$E_b = \left[ZM_H + (A-Z)m_n - {}^{A}_{Z}M_{atom} \right] c^2$$

  The curve plotted binding energy per nucleon versus mass number has its maximum of $8.8 MeV$ when the mass number is 56 that is an iron isotope ${}^{56}_{26}Fe$ which is the most stable nucleus.

- Semiempirical binding energy formula

  $$E_b = a_v A - a_s A^{2/3} - a_c \frac{Z(Z-1)}{A^{1/3}} - a_a \frac{(A-2Z)^2}{A} (\pm, 0) \frac{a_p}{A^{3/4}}$$

1.13 Glossary

Nucleon : protons and neutrons

Even -even nuclei: nuclei having even Z and even N

Parity: The parity of a wave function ψ is related to the symmetry properties of the wavefunction ψ. Parity operator $\hat{P}$ we have $\hat{P}\psi(\vec{r},t) \equiv P\psi(-\vec{r},t)$ with *eigen value P = ± 1*

1.14 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: Straight line $ln\left(\frac{R}{R_0}\right) = \frac{1}{3} ln A$ with slope $\frac{1}{3}$.

Ans.2: ± 1

Ans.3: Nuclear radius $R = R_0 A^{1/3} = 1.1 \times 10^{-15} (27)^{1/3}$

$= 3.3 \times 10^{-15}$m

Mutual electric potential energy $U = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{R}$

$$U = \frac{9x10^9(13x1.6x10^{-19})(13x1.6x10^{-19})}{3.3x10^{-15}}$$

$= 73.75 \times 10^6 \times 1.6 \times 10^{-19}$ Joule

$= 73.75$ MeV

Ans.4: According to shell model 9th proton and 9th neutron are unpaired and each lies in the respective states $^1d_{5/2}$

Hence $l_n=2$ and $l_p=2$

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

Answers to Self Learning Exercise-II

Ans.1: $\mu_N = \frac{e\hbar}{2m_p} = 5.05 \times 10^{-27}\frac{J}{T} = 3.15 \times 10^{-8}\frac{eV}{T}$

Ans.2: True

Ans.3: Binding energy

$$E_b = \left[ZM_H + (A-Z)m_n - {}^A_Z M_{atom}\right]c^2$$

$$E_b = \left[\left\{92M\left({}^1_1H\right) + 146m_n\right\} - M\left({}^{238}_{92}U\right)\right]c^2$$

$$= \left[\left\{92 \times 1.00782u + 146 \times 1.00866u\right\} - 238.05076u\right]c^2$$

$$= [1.93304]uc^2$$

$$= [1.93304] \times 931.49\,MeV$$

$$= 1800.61\,MeV$$

Binding energy per nucleon $\frac{E_b}{A} = \frac{1800.61}{238}\frac{MeV}{Nucleon} = 7.57\ \frac{MeV}{Nucleon}$

1.15 Exercise

Q.1 What is the value of the electric quadrupole moment of nucleus which has spherically symmetric charge distribution ?

Q.2 What is the order of nuclear mass density ?

Q.3 Magnetic moments of electrons and nucleus interact and this interaction splits the atomic levels which gives rise to the…………….(fine/hyperfine) structure of the lines of the atomic spectra.

Q.4 What is the value of 1 Barn ?

Q.5 Define mass defect and packing fraction.

Q.6 Explain the asymmetry energy term in semiempirical mass formula.

Q.7 Compare the nuclear density of ${}_1^1H$ with its atomic density (Assume the atomic radius is equal to the first Bohr orbit).

Q.8 Write the main features of curve of binding energy per nucleon versus mass number.

Q.9 Find the spin-parity of the following nuclei

(i) ${}_{19}^{39}K$ (ii) ${}_{8}^{17}O$ (iii) ${}_{7}^{15}N$

Q.10 Describe the semiempirical mass formula for the nucleus.

1.16 Answers to Exercise

Ans.1: Zero.

Ans.2: Nuclear mass density is of the order of $10^{17}\frac{kg}{m^3}$.

Ans.3: hyperfine structure

Ans.4: $1 Barn = 10^{-28} m^2$

Ans.7: Over 10^{14} times

Ans.9: (i)

	$1s_{1/2}$	$1p_{3/2}$	$1p_{1/2}$	$1d_{5/2}$	$2s_{1/2}$	$1d_{3/2}$
Protons	2	4	2	6	2	3=2+1
Neutrons	2	4	2	6	2	4

Quantum state $1d_{3/2}$ i.e. $3/2^+$

(ii) Quantum state $1d_{5/2}$ i.e. $5/2^+$

(iii) Quantum State $1p_{1/2}$ i.e. $1/2^-$

References and Suggested Readings

1. Herald A. Enge, Introduction to Nuclear Physics (1966), Addison Wesley Publishing Company.
2. Bernard L. Cohen, Concepts of Nuclear Physics (2002), Tata McGraw-Hill.
3. Irving Kaplan, Nuclear Physics (Second Edition 2002), Narosa Publishing House.
4. R.R. Roy & B.P. Nigam, Nuclear Physics (2000), New Age International (P) Ltd.
5. Kenneth S. Krane, Introductory Nuclear Physics (2008), Wiley India Pvt. Ltd.
6. Robert Eisberg & Robert Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles (2006) ,John Wiley & Sons (Asia) Pte. Ltd.
7. Arthur Beiser, Shobhit Mahajan & S.Rai Choudhury, Concepts of Modern Physics (Seventh Edition 2015), McGraw-Hill.
8. D.C.Tayal, Nuclear Physics (Fourth Edition 2001), Himalaya Publishing House.
9. Robert D. Evans, The Atomic Nucleus (1955), McGraw-Hill Book Company ,Inc.
10. J.B. Rajam ,Atomic Physics (Seventh Edition 2002), S. Chand & Company Ltd.
11. Young & Freedman, University Physics, (Eleventh Edition 2004), Pearson Education, Inc.
12. David Halliday, Robert Resnick & Kenneth S. Krane, Physics Volume -II (Fifth Edition 2004) ,John Wiley & Sons (Asia) Pte. Ltd.
13. Marcelo Alonso & Edward J. Finn, Physics (1999), Addition Wesley Longman , Inc.

UNIT-2
Two Nucleon System and Forces

Structure of the Unit

2.0 Objectives

After interacting with the material presented here students will be able to understand

- general nature of nuclear force
- properties of nuclear force and
- the general form of nuclear potential.

2.1 Introduction

At the beginning of the twentieth century, the science of physics knew about three basic forces: gravitational, electric, and magnetic. All forces, whether they were "action at a distance" or field forces, could be always interpreted as one these three forces and it was believed that all other forces like elastic forces, collision forces, etc could be understood in terms of these three forces.

By the end of first quarter of the twentieth century a fourth force was found. With electrostatic, magnetic, and gravitational forces, measurement could be made in the laboratory or on a macroscopic scale and the laws governing these forces were established. But entirely new methods were required to study the nuclear binding forces; by the 1960's the form of the laws governing these forces had not been established on a firm basis.

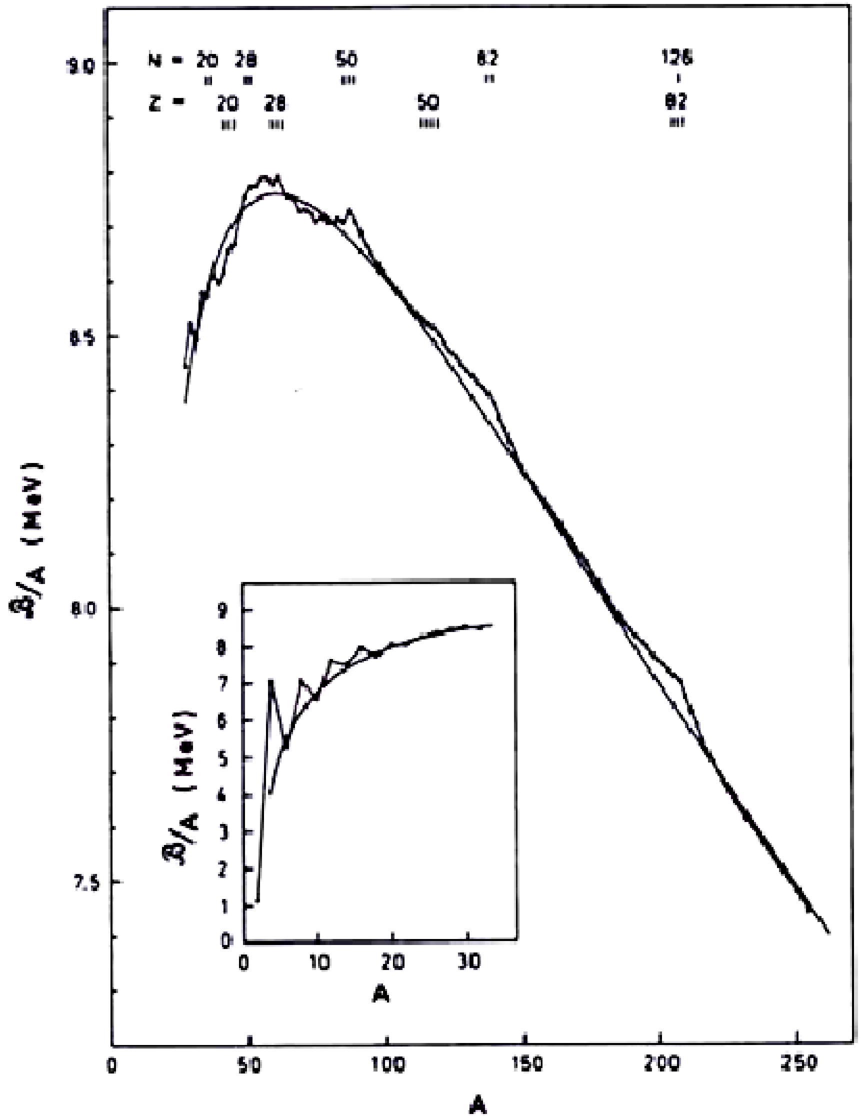
2.2 General Nature of the Force between Nucleons

We can enumerate the following properties of nuclear force on the basis of various observations and empirical facts:

1. **Nuclear force is always attractive** between two neutrons, or two protons or neutron and proton. Existence of neutrons and protons in a bound state is itself an evidence of this.
2. **Nuclear force is short ranged.** If it were not so, all the nucleons in different nuclei will coalesce into one big nucleus and everything will probably turn into a huge nucleus like a super-neutron star, and there will be no more a variety of elements in nature.
3. **Nuclear force is very strong**. This is evident from the large binding energy of nuclei (about 8 MeV per nucleon). The average binding energy of electrons in atoms is in the range of eV to keV only.
4. **Nuclear force saturates.** This is actually an outcome of the short range nature of the nuclear force. Each nucleon in a nucleus interacts with its neighbors only. As a result the binding energy per nucleon rises rapidly for light mass nuclei and quickly saturates

Figure shows the measurements of the energy needed to strip out a nucleon from a nucleus as a function of the number of nucleons in the nucleus, i.e. the binding energy per nucleon, rises rapidly up to A~10-20 and then levels off at approximately 7.5 MeV/nucleon.

If we assume that a nucleon interacts with all the other nucleons in the nucleus then there should be A(A-1)/2 pairs of nuclei. Since the binding energy increases with the number of interactions BE ~ A(A-1)/2. Then BE/A would be linear, which it is but only roughly up to around A~10.



The binding energy curve suggests that nucleons only interact with their nearest neighbours. The range of the force must be less than the size of a mass-10 nucleus, which is around 1.2x101/3= 2.6 fm. This property is described as saturation of the nuclear force.

5. **Nuclear force is charge symmetric.** It is same for a p-p and an n-n pair (ignoring the Coulomb repulsion between p-p). As an example consider the following evidence for charge symmetry.

^3H	^3He
Z=1, N=2	Z=2, N=1
2 p-n pairs and 1 n-n pair	2 p-n pair and 1 p-p pair
BE=8.48MeV	BE=7.71MeV

The difference in the BE between the two is 0.77 MeV. $^3_2He1$ assuming to be a uniformly charged sphere of radius 2.24 Fermi, the difference is almost entirely accounted for by Coulomb energy implying that p-p and n-n interaction is same.

6. **Nuclear force is charge independent.** The force is same for n-p as it is for n-n and p-p pairs provided the n-p pair is in the same isospin state (T=1). A p-p and an n-n pair can occupy isospin T=1 state only. If the n-p pair also occupies T=1 state then the force is the same.

One cannot say from mirror nuclei anything about n-n and p-p forces compared to n-p forces. But if we gradually change the individual nucleon types, one by one, into the other we generate a series of nuclei with the same mass, but a range different numbers of protons and neutrons. To make a fair comparison for the strong interactions, we can again correct for the Coulomb effects and the difference in the proton and neutron masses.

For example, the 0+ ground states of 30_{Si} and 30_S, and an excited 0^+ state in 30P are at a very similar mass-energy. The 2^+ states of 30_{Si} and 30_S also have an *isobaric analogue* in 30P, as do other levels. Transition probabilities and reaction rates based on strong interactions involving these states also show similarities.

Consider the changes in going from 30_{Si} and 30_P. A neutron turns into a proton. We already know that the n-n and p-p forces are similar. So the experimental similarity of the 30Si level scheme with a subset of states in the 30P level scheme must imply that the n-p force must also be of similar strength. *Nuclear forces display charge independence.*

7. **Nuclear force is spin dependent.** As an example, deuteron in its ground state (and the only bound state) exists only in spin triplet state. The spin singlet state is unbound. This property will be further discussed in chapter 3.

8. **Nuclear force has a tensor nature.** The arrangement of nucleon spins in a nucleus – whether two nucleons are placed side by side or, one on top of the other although total spin is 1 in both the cases - makes a difference in their binding howsoever small.

The tensor dependence is generally expressed by the term,

$$S_{12} = \frac{1}{r^2}[3(\vec{\sigma}_1.\vec{r})(\vec{\sigma}_2.\vec{r}) - (\vec{\sigma}_1.\vec{\sigma}_2)r^2]$$

If σ_1 and σ_2 are parallel to r and if the two are perpendicular to r, the value of (σ_1. σ_2) is different in the two cases even for the same value of the total spin i.e. σ. The magnetic moment of deuteron cannot be explained without the tensor nature of nuclear force.

9. **Nuclear force also has velocity dependence** or, a dependence on the spin-orbit term. It is given be a term like

$$V_{12} = \frac{1}{2}\vec{L}(\vec{\sigma}_1 + \vec{\sigma}_2)V_{LS}(r)$$

It is attractive when L and S (=1/2(σ_1+σ_2)) are parallel and repulsive when they are anti-parallel.

10. **Nuclear force has an exchange character.** This is a purely quantum feature and may be understood by knowing the way nuclear force is mediated. Two nucleons, when interacting with each other, can exchange their spin, isospin, or a combination of both. These are represented by Bartlett (B), Heisenberg (H), and Majorana (M) terms which contribute to the force according to the signs given below:

	Even *l*, +ve parity		Odd *l*, -ve parity	
	s=1	s=0	s=1	s=0
W	+1	+1	+1	+1

B	+1	-1	+1	-1
M	+1	+1	-1	-1
H	+1	-1	-1	+1

The sign depends on the nature of state (the l-value, s-value and the parity). W represents the Wigner term which is no exchange at all. Bartlett force leads to spin exchange, Majorana force to isospin exchange and Heisenberg force to a combination of spin and isospin.

2.3 Self Learning Exercise-I

Q.1 Explain the evidence for attractive nature of nuclear forces.

Q.2 Draw binding energy per nucleon graph.

Q.3 Write down the term which represent the tensor dependence of nuclear force.

Q.4 Define the exchange character of nuclear force.

Q.5 Write down the properties of nuclear forces.

2.4 General Form of Two Nucleon Interaction

The interaction of two nucleons at low energy can be described by a potential of the form

$$V(r) = V_{cent}(r) + V_{SS}(r) s_1.s_2 + V_T(r)[3(s_1.r)(s_2.r)/r^2 - s_1 s_2]$$
$$+ \mathrm{V}_{\mathrm{LS}}(r)(s_1 + s_2).L + V_{LS}(r)(s_1.L)(s_2.L) + V_{PS}(r)(s_1.p)(s_2.p)$$

Where

r denotes the relative distance of the nucleons with spins s_1 and s_2,

p is the relative momentum and

L is the total orbital angular momentum.

The potential neglects the inner structure of the nucleons and is therefore valid only for bound states and for low-energy NN scattering, from which its form can be derived. Interpretation of the different terms:

1. Central potential.
2. Central spin-spin interaction.
3. Tensor (non-central) potential. It has the same spin dependence as the magnetic interaction of two magnetic moments. This term is the only one which may lead to a mixing of different orbital angular momentum in the physical state.
4. LS coupling, similar to atomic physics, but caused by the strong force.
5. and 6 terms respect basic symmetries but may often be neglected due their quadratic dependence on p.

To describe nuclei, additional many-body forces have to be taken into account, leading to a still higher level of sophistication.

2.5 Properties of Nuclear Force

In this section we summarize the main features of the inter nucleon force.

Interaction between nucleons consists to lowest order of an attractive central potential

In most of nuclear calculation we use a square-well form of potential, which simplifies the calculations and reproduces the observed data fairly well. Other more realistic forms could just as well have been chosen but the essential conclusions would not change (in fact, the effective rang approximation is virtually independent of the shape assumed for the potential). *The* common characteristic of these potentials is that they depend only on the inter nucleon distance *r.* We therefore represent this central term as $V_c(r)$. The experimental program to study $V_C(r)$ would be to measure the energy dependence of nucleon-nucleon parameters such as scattering phase shifts, and then to try to choose the form for $V_C(r)$ that best reproduces those parameters.

The Nucleon - Nucleon interaction is strongly spin dependent

This observation follows from the failure to observe a singlet bound state of the deuteron .and also from the measured differences between the singlet and triplet cross sections (discussed in Chapter 3). What is the form of an additional term that must be added to the potential to account for this effect? Obviously the term must depend on the spins of the two nucleons, s_1 and s_2 but not all possible combinations of s_1 and s_2 are permitted. The nuclear force must satisfy certain symmetries, which restrict the possible forms that the potential could have. Examples of these symmetries are *parity (r ~ -r*) and *time reversal (t ~ - t).* Experiments indicate that, to a high degree of precision (one part in 10^7 for parity and one part in 10^3 for time reversal), the inter nucleon potential is invariant with respect to these operations. Under the parity operator, which involves spatial reflection, angular momentum vectors are unchanged. This statement may seem somewhat surprising, because upon inverting a coordinate system we would naturally expect all vectors defined in that coordinate system to invert. However, angular momentum is not a true or polar vector; it is a pseudo or axial vector that does not invert when *r ~ - r.* This follows directly from the definition *r* X *p* or can be inferred from a diagram of a spinning object. Under the time-reversal operation, all motions (including linear and angular momentum) are reversed. Thus terms such as s_1 or s_2 or a linear combination $As_1 + Bs_2$ in the potential would violate time-reversal invariance and cannot be part of the nuclear potential; terms such as s_1^2 , s_2^2 or $s_1.s_2$ are invariant with respect to time reversal and are therefore allowed. (All of these terms are also invariant with respect to parity.) The simplest term involving both nucleon spins is $s_1.s_2$. Let's consider the value of $s_1.s_2$ for singlet and triplet states. To do this we evaluate the total spin $S = s_1 + s_2$

$$S^2 = S.S = (s_1 + s_2).(s_1 + s_2)$$
$$= s_1^2 + s_2^2 + 2s_1.s_2$$

Thus

$$s_1.s_2 = \frac{1}{2}(S^2 - s_1^2 - s_2^2)$$

To evaluate this expression, we must remember that in quantum mechanics all squared angular momenta evaluate as

$$s^2 = \hbar^2 s(s+1)$$

$$\langle s_1.s_2 \rangle = \frac{1}{2}[S(S+1) - s_1(s_1+1) - s_2(s_2+1)]\hbar^2$$

With nucleon spins s_1 and s_2 of 1/2, the value of $s_1.s_2$ is, for triplet (S = 1) states:

$$\langle s_1.s_2 \rangle = \frac{1}{2}[1(1+1) - \frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1)]\hbar^2 = \frac{\hbar^2}{4}$$

and for singlet (S = 0) states:

$$\langle s_1.s_2 \rangle = \frac{1}{2}[0(0+1) - \frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1)]\hbar^2 = -\frac{3\hbar^2}{4}$$

Thus a spin-dependent expression of the form $s_1.s_2 V_s(r)$ can be included in the potential and will have the effect of giving different calculated cross sections for singlet and triplet states. The magnitude of V_s can be adjusted to give the correct differences between the singlet and triplet cross sections and the radial dependence can be adjusted to give the proper dependence on energy.

We could also write the potential including V_c and V_s as

$$V(r) = -\left(\frac{s_1.s_2}{\hbar^2} - \frac{1}{4}\right)V_1(r) + \left(\frac{s_1.s_2}{\hbar^2} + \frac{3}{4}\right)V_3(r)$$

where $V_1(r)$ and $V_3(r)$ are potentials that separately give the proper singlet and triplet behaviors.

The inter Nucleon potential includes a noncentral term, known as a tensor potential

Evidence for the tensor force comes primarily from the observed quadrupole moment of the ground state of the deuteron (Chapter 3). An s-state (l = 0) wave function is spherically symmetric; the electric quadrupole moment vanishes. Wave functions with mixed l states must result from noncentral potentials. This tensor force must be of the form *V(r),* instead of *V(r).* For a single nucleon, the choice of a certain direction in space is obviously arbitrary; nucleons do not distinguish north from south or east from west. The only reference direction for a nucleon is its spin, and thus only terms of the form *s* • *r* or *s* X *r,* which relate *r* to the direction of *s,* can contribute. To satisfy the requirements of parity invariance, there must be an even number of factors of *r,* and so for two nucleons the potential must depend on terms such as $(s_1 \bullet r)(s_2 \bullet r)$ or $(s_1 \times r) \bullet (s_2 \times r)$. Using vector identities we can show that the second form can be written in terms of the first and the additional term $s_1 \bullet s_2$, which we already included in *V(r).* Thus without loss of generality we can choose the tensor contribution to the inter nucleon potential to be of the form $V_T(r)s_{12}$, where $V_T(r)$ gives the force the proper radial dependence and magnitude, and

$$S_{12} = 3(s_1.r)(s_2.r)/r^2 - s_1.s_2$$

which gives the force its proper tensor character and also averages to zero over all angles.

The Nucleon - Nucleon force is charge symmetric

This means that the proton-proton interaction is identical to the neutron-neutron interaction, after we correct for the Coulomb force in the proton-proton system. Here "charge" refers to the character of the nucleon (proton or neutron) and not to electric charge. Evidence in support of this assertion comes from the equality of the pp and nn scattering lengths and effective ranges. Of course, the pp parameters must first be corrected for the Coulomb interaction. When this is done, the resulting singlet pp parameters are

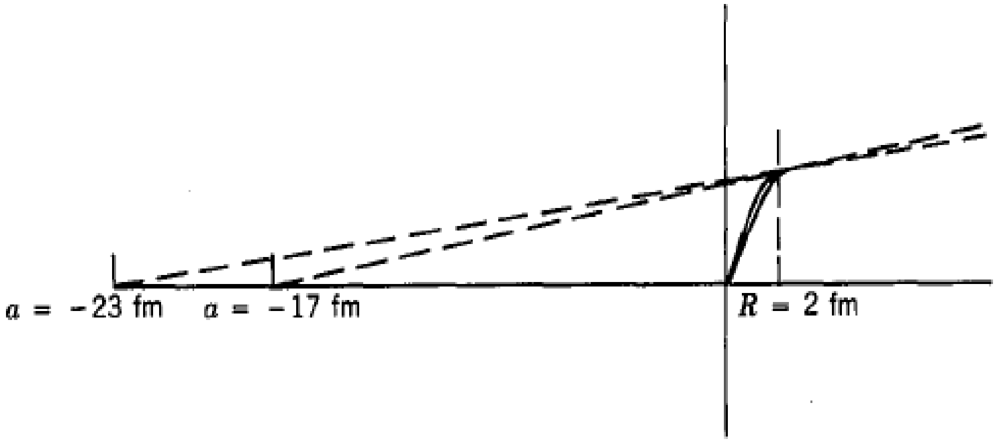
$$a = -17.1 \pm 0.2 \text{ fm}$$

$$r_0 = 2.84 \pm 0.03 \text{ fm}$$

These are in very good agreement with the measured nn parameters ($a = -16.6 \pm 0.5$ fm, $r_0 = 2.66 \pm 0.15$ fm), which strongly supports the notion of charge symmetry.

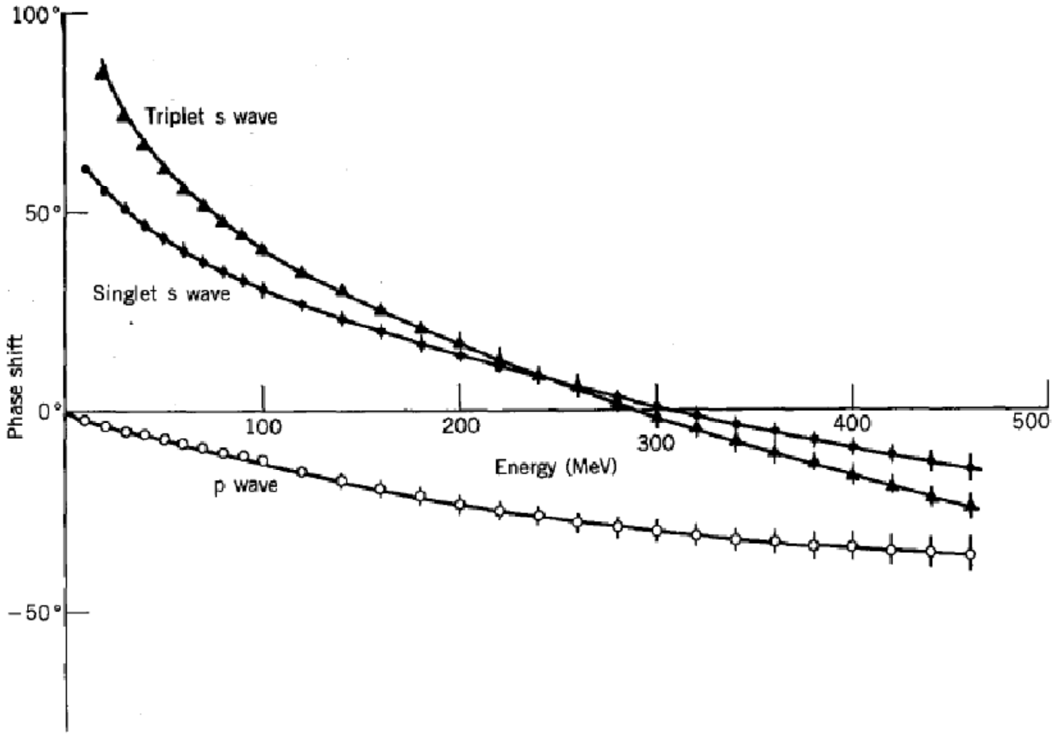
The Nucleon - Nucleon Force Is Nearly Charge Independent

This means that (in analogous spin states) the three *nuclear* forces nn, pp, *and* pn are identical, again correcting for the p'p Coulomb force. Charge independence is thus a stronger requirement than charge symmetry. Here the evidence is not so conclusive; in fact, the singlet np scattering length (- 23.7 fm) seems to differ substantially from the pp and nn scattering lengths (-17 fm).



However, we see from figure that large negative scattering lengths are extraordinarily sensitive to the nuclear wave function near $r = R$, and a very small change in ψ; can give a large change in the scattering length. Thus the large difference between the scattering lengths may correspond to a very small difference (of order 1 %) between the potentials, which is easily explained by the exchange force model.

The Nucleon - Nucleon interaction becomes repulsive at short distances



This conclusion follows from qualitative considerations of the nuclear density: as add more nucleons the nucleus grows in such a way that its central density remains roughly constant, and thus something is keeping the nucleons from crowding too closely together. More quantitatively, we can study nucleon-nucleon scattering at higher energies. Figure shows the deduced singlet s-wave phase shifts for nucleon-nucleon scattering up to 500 MeV. (At these energies, phase shifts from higher partial waves, p and d for example, also contribute to the cross sections. The s-wave phase shifts can be easily extracted from the differential scattering measurements of $d\sigma/d\Omega$ vs *(θ* because they do not depend on θ.*)* At about 300 MeV, the s-wave phase shift becomes *negative,* corresponding to a change from an attractive to a repulsive force. To account for the repulsive core, we must modify the potentials we use in our calculations. For example, again choosing a square-well form to simplify the calculation, we might try

$$
\begin{aligned}
V(r) &= +\infty && r < R_{core} \\
&= -V_0(R) && R_{core} \le r \le R \\
&= 0 && r > R
\end{aligned}
$$

and we can adjust *R core* until we get satisfactory agreement with the observed s-wave phase shifts. The value $R_{core} \cong 0.5$ fm gives agreement with the observed phase shifts.

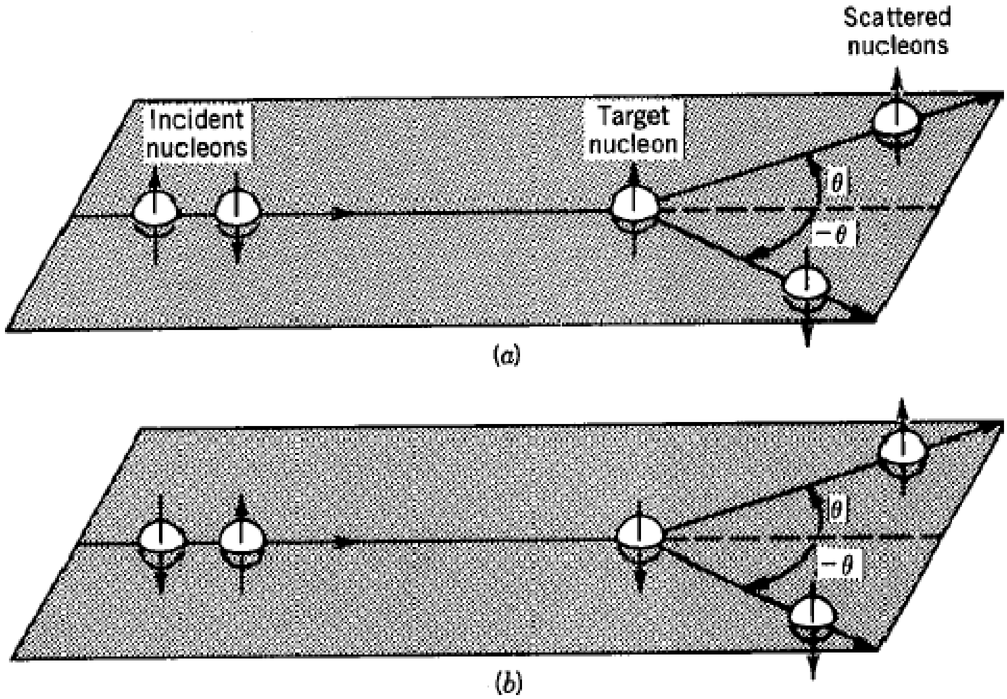
The Nucleon - Nucleon interaction may also depend on the relative velocity or momentum of the nucleons

Forces depending on velocity or momentum cannot be represented by a scalar potential, but we can include these forces in a reasonable manner by introducing terms linear in *p,* quadratic in *p,* and so on, with each term including a characteristic *V(r).* Under the parity operation, $p \to -p$, and also under time reversal $p \to -p$. Thus any term simply linear in *p* is unacceptable because it violates both parity and time-reversal invariance. Terms of the form *r.p* or *r* X *p* are invariant with respect to parity, but still violate time reversal. A possible structure for this term that is first order in *p* and invariant with respect to both parity and time reversal is $V(r)(r \times p) \cdot S$, where $S = s_1 + s_2$ is the total spin of the two nucleons. The relative angular momentum of the nucleons is $l = r \times p$, and therefore this term, known as the *spin-orbit term* in analogy with atomic physics, is written $V_{so}(r) l.S$. Although higher-order terms may be present, this is the only first-order term in *p* that satisfies the symmetries of both parity and time reversal.

The experimental evidence in support of the spin-orbit interaction comes from the observation that scattered nucleons can have their spins aligned, or *polarized,* in certain directions. The polarization of the nucleons in a beam (or in a target) is defined as

$$P = \frac{N(\uparrow) - N(\downarrow)}{N(\uparrow) + N(\downarrow)}$$

where $N(\uparrow)$ and $N(\downarrow)$ refer to the number of nucleons with their spins pointed up and down, respectively. Values of P range from + 1, for a 100% spin-up polarized beam, to -1, for a 100% spin-down polarized beam. An unpolarized beam, with $P = 0$, has equal numbers of nucleons with spins pointing up and down.



Consider the scattering experiment shown in figure, in which an unpolarized beam (shown as a mixture of spin-up and spin-down nucleons) is incident on a spin-up target nucleon. Let's suppose the nucleon-nucleon interaction causes the incident spin-up nucleons to be scattered to the left at angle θ and the incident spin-down nucleons to be scattered to the right at angle $-\theta$. Part *b* of the figure shows the *same experiment* viewed from below or else rotated 180° about the direction of the incident beam. We can also interpret figure *b* as the scattering of an unpolarized beam from a spin-down target nucleon, and once again the spin-up incident nucleons scatter to the left and the spin-down nucleons scatter to the right. The results would be the same, even in an unpolarized target, which would contain a mixture of spin-up and spin-down nucleons: when an unpolarized beam is scattered from an unpolarized target, the spin-up scattered nucleons appear preferentially at θ and the spin-down scattered nucleons at $-\theta$.

Although this situation may appear superficially to violate reflection symmetry (parity), you can convince yourself that this is not so by sketching the experiment and its mirror image. Parity is conserved if at angle θ we observe a net polarization *P,* while at angle $-\theta$ we observe a net polarization of -P.

Now let's see how the spin-orbit interaction can give rise to this type of scattering with polarization.

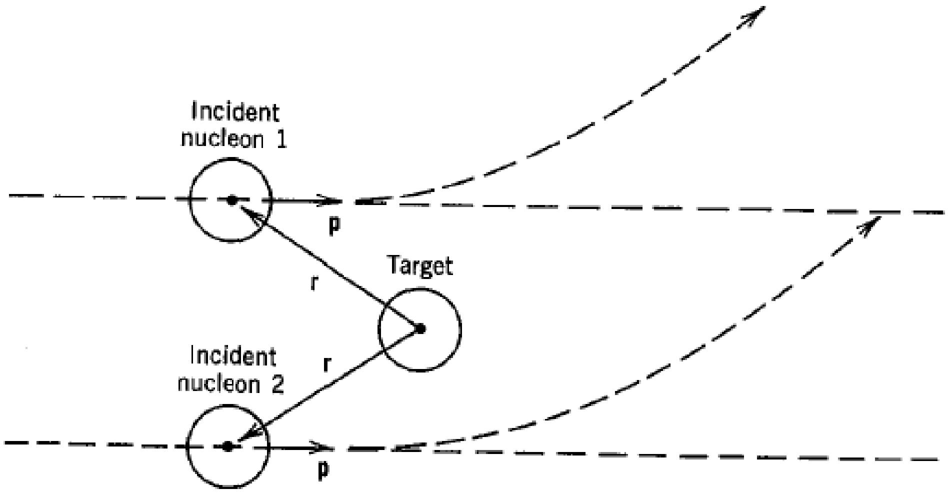


Figure shows two nucleons with spin up incident on a spin up target, so that S = 1. (Scattering that includes .only s waves must be spherically symmetric, and therefore there can be no polarizations. The p-wave *(t*= 1) scattering of identical nucleons has an anti symmetric spatial wave function and therefore a symmetric spin wave function.) Let's assume that $V_{so}(r)$ is negative. For incident nucleon 1, l= *r* X *p* is down, and therefore l· S is negative because l and S point in opposite directions. The combination $V_{so}(r)l\cdot$ S is positive and so there is a repulsive force between the target and incident nucleon 1, which is pushed to the left. For nucleon 2, *l* points up, l· S is positive, and the interaction is attractive; incident nucleon 2 is pulled toward the target and also appears on the left side. Spin-up incident nucleons are therefore preferentially scattered to the left and (by a similar argument) spin-down nucleons to the right. Thus the spin-orbit force can produce polarized scattered beams when unpolarized particles are incident on a target.

At low energy, where s-wave scattering dominates, we expect no polarization. As the incident energy increases, the contribution of p-wave scattering increases and there should be a corresponding increase in the polarization. The general topic of polarization in nuclear reactions is far more complicated than we have indicated in this brief discussion.

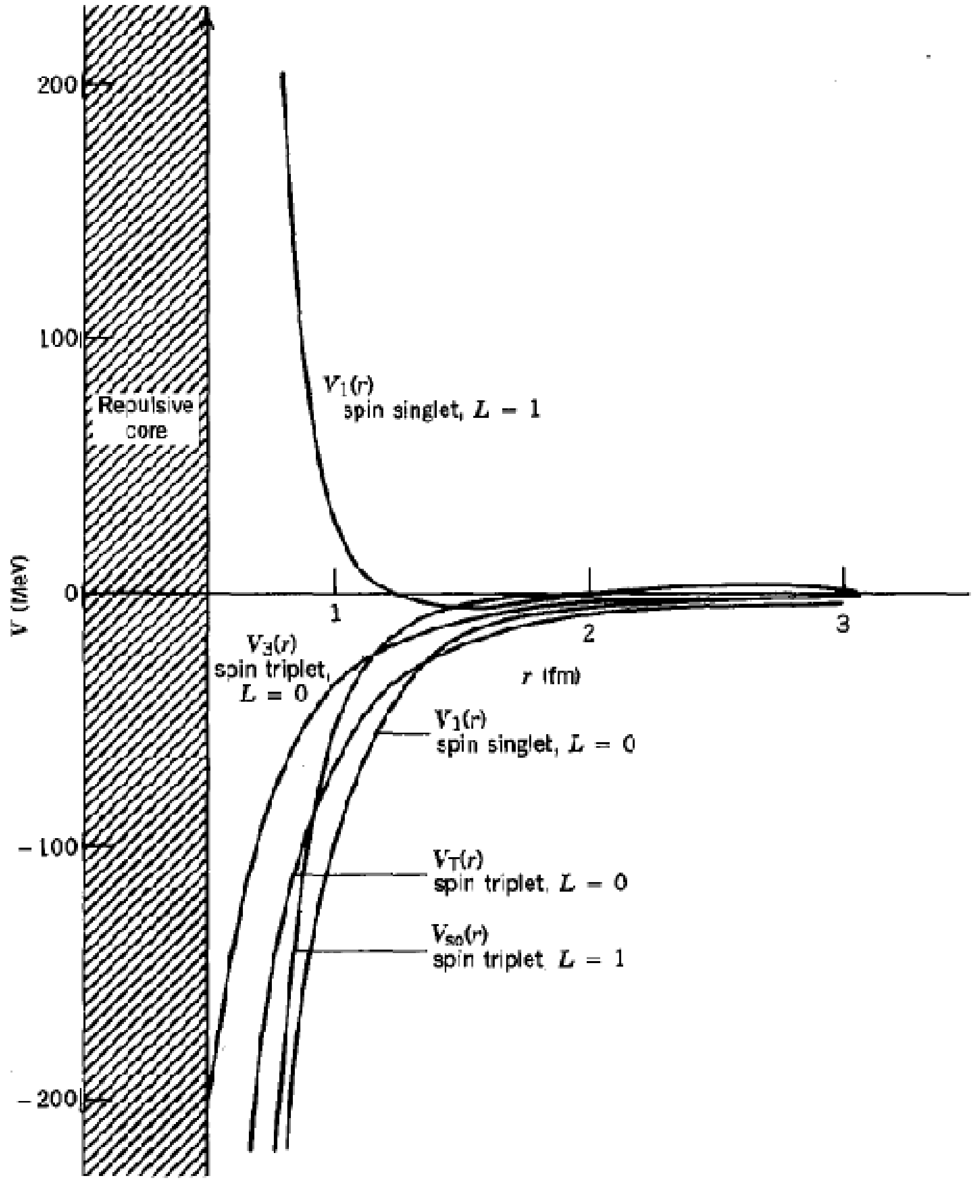


Figure shows some representative nucleon-nucleon potentials.

2.6 Self Learning Exercise-II

Q.1 What is polarization?

Q.2 Write down the evidence for the tensor force.

Q.3 Explain that the Nucleon - Nucleon interaction is strongly spin dependent.

Q.4 Write down and explain the general form of two nucleon interaction

2.7 Summary

In this chapter we have discussed general nature of nuclear force. We have also discussed various properties of nuclear forces with their evidences. This chapter also gave a brief idea of the general form of two nucleon interaction which includes central, noncentral and velocity dependent potentials terms.

2.8 Glossary

Spin: Spin is a characteristic property of elementary particles

Isospin: Particles appear to arrange themselves in sets of particles of different electric charge, but nearly the same mass. They are individually labeled with a quantum number of -1, 0, 1, or other multiples of these. Hadrons have Isospin. Leptons have a similar arrangement and are labeled with "weak isospin" according to their roles in the Standard Model. This is not the same as generic "isospin."

Nuclear force: The force that holds the nucleus together. Originally thought to be the exchange of pions, as suggested by Yukawa. Pions are now known to not be elementary themselves, but quarks which are held together by gluons.

Nucleon: The generic name for neutrons and protons, reflecting the fact that their Strong Interactions are identical.

Quantum Number: Quantum mechanics is full of integers which describe certain quantum states. In atoms, these quantum numbers come from the solutions to the Schroedinger equation, in which the principle quantum number, n, is identical to the original idea of Bohr's that electron orbits are fixed in radius and energy. There are quantum numbers for angular momentum, spin, and other characteristics. Transitions among states follow "selection rules" that relate the before and after values of the quantum numbers of the atomic states. In elementary particle physics Quantum Numbers appear to be inherent to particular particles and are "additive" meaning that in many cases they are conserved…that the sum before an interaction or decay must equal the same ones after the interaction or decay. This is especially true in the Strong Interactions, but also in the Weak Interactions. Examples of inherent quantum numbers are: Baryon Number, Lepton Number, Electric Charge, Isospin, and Strangeness.

Polarization: The polarization of a wave is the direction in which it is oscillating. The simplest type of polarization is linear, transverse polarization. Linear means that the wave oscillation is confined along a single axis, and transverse means that the wave is oscillating in a direction perpendicular to its direction of travel. Laser light is most commonly a wave with linear, transverse polarization. If the laser beam travels along the x-axis, its electric field will oscillate either in the y-direction or in the z-direction. Gravitational waves also have transverse polarization, but have a more complicated oscillation pattern than laser light.

2.9 Answers to Self Learning Exercise

Answers to Self Learning Exercise-I

Ans.1: Existence of neutrons and protons in a bound state is the evidence for attractive nature of nuclear forces.

Ans.2: See Section 2.2

Ans.3: $S_{12} = \frac{1}{r^2}[3(\vec{\sigma}_1.\vec{r})(\vec{\sigma}_2.\vec{r}) - (\vec{\sigma}_1.\vec{\sigma}_2)r^2]$

Ans.4: See Section 2.2

Ans.5: See Section 2.2

Answers to Self Learning Exercise-II

Ans.1: See Glossary

Ans.2: The evidence for the tensor force comes primarily from the observed quadrupole moment of the ground state of the deuteron

Ans.3: Section 2.5

Ans.4: Section 2.4

2.10 Exercise

Q.1 Justify the existence of tensor forces in the nucleus.

Q.2 What are the properties of nuclear forces?

Q.3 Write a short note on

a. Spin dependence of nuclear force

b. Charge symmetry of nuclear force

c. Charge independence of nuclear force

d. Saturation property of nuclear force

References and Suggested Readings

1. Theoretical Nuclear Physics by J.M. Bhatt and V.E. Weisskipf.
2. Nuclear Physics by B.K. Agarwal 1989.
3. Nuclear Physics by R.R. Roy and B.P. Nigam, 1979.
4. Concept of Nuclear Physics by B.L. Cohen, 1988.
5. Nuclear Physics by I. Kaplan, 1963.
6. Nuclear Physics by D. C Tayal.
7. Introductory Nuclear Physics by Kenneth S. Krane.

UNIT-3
The Deuteron

Structure of the Unit

3.0 Objectives

The main aim of this chapter is to study the Basic properties of deuteron viz, its binding energy, its size, spin, magnetic and quadrupole moments etc. After going through this chapter you should be able to:

- Understand the various properties of deuteron.
- Analyze the existence of ground and excited states of deuteron.

3.1 Introduction

In the previous chapter we have discussed various properties of nuclear force and potential. The actual properties of the nuclear potential are quite complicated. We can find out about the potential in two main ways. One is scattering of nucleons of each other or from nuclei. The other is to study any stable states that might result from this interaction. There are of course 3 possibilities: pn, pp, nn. It turns out that only one of these forms a stable nucleus. We will discuss why, and what this means. In this instance we will study the nucleus ^{2}H, the deuteron, which is the nucleus formed when a proton and neutron combine. It is the simplest nucleus and in a sense is the nuclear equivalent of the H atom in atomic studies. Unfortunately, unlike the H atom, it does not have any excited states, so there is no information available from its spectroscopy. None the less the fact that it is bound at all reveals a lot about the nuclear force. (of course if it were not bound, we wouldn't be here to study nuclear physics, since this nucleus is the basis for fusion to all the heavier nuclei in the universe)

Some Facts about the deuteron

1. A deuteron (^{2}H nucleus) consists of a neutron and a proton.
2. It is the simplest bound state of nucleons and therefore gives us an ideal system for studying the nucleon-nucleon interaction.
3. An interesting feature of the deuteron is that it does not have excited states because it is a weakly bound system
4. In analogy with the ground state of the hydrogen atom, it is reasonable to assume that the ground state of the deuteron also has zero orbital angular momentum **L = 0**
5. However the total angular momentum is measured to be **J = 1** (one unit of $h/2\pi$) thus it follows that the proton and neutron spins are parallel

   $\mathbf{s_n + s_p = 1/2 + 1/2 = 1}$
6. The implication is that two nucleons are not bound together if their spins are anti-parallel, and this explains why there are no proton-proton or neutron-neutron bound states.
7. The parallel spin state is forbidden by the Pauli exclusion principle in the case of identical particles
8. The nuclear force is thus seen to be spin dependent.

3.2 Analysis of the Ground State ($3S^1$) of Deuteron using a Square Well Potential

The deuteron is the simplest system of bound nucleons. Its ground state is the only known bound state of two nucleons:

— There are no bound states between two protons, respectively, two neutrons.

— Excited states of the deuteron are unbound.

Hence, the single bound state of nucleons offer us only very restricted possibilities to study NN interactions. Nonetheless, the ground state properties of the deuteron already tell us some important features of the binding force.

Properties of the deuteron:

Mass: 1.876 139 MeV, determined by mass spectroscopy using penning trap techniques

Binding energy: 2.225 MeV (i.e. $\sim$ 1.1 MeV per nucleon), determined from measurement of the gamma energy in radiative capture, n (p, γ) d. Compared to typical binding energies per nucleon of heavier nuclei ($\sim$ 8 MeV), the deuteron is a weakly bound nuclear system. The binding is so weak that there are no excited bound states.

Spin: J = 1, deduced from observed number of hyperfine components.

Magnetic moment: $\mu_d = 0.857\ 393\ \mu_N$, measured via nuclear magnetic resonance. The value is close to the sum of the magnetic moments of the free proton and the free neutron,

$$\mu_p + \mu_n = 2.792\ \mu_N - 1.913\ \mu_N = 0.879\ \mu_N$$

This implies that the deuteron is essentially a state, where the two spins 1/2 of the nucleons are parallel and add to J = 1 (remember the opposite signs of the proton and neutron magnetic moments). This corresponds to an S state (no orbital angular momentum).

Electric quadrupole moment: $Q_d = 2.86 \times 10^{-27}\ \text{cm}^2$, deduced from the magnetic field dependence of hyperfine lines of deuterium. The reason for the deuteron being not spherically symmetric is a non-central part in the NN force, the so-called tensor force. It admixes a state with orbital angular momentum to the ground state, meaning that the deuteron is not a pure S state. Since the strong force conserves parity (remember that the orbital angular momentum of a state influences its parity by a factor $(-1)^l$), the admixture must be a state with l = 2 (i.e. a D state), in order to have the same quantum numbers J^P .

— The sizes of both the magnetic moment and the quadrupole moment can be derived from a wavefunction

$$|\Psi_d\rangle = 0.98\,|^3S_1\rangle + 0.20\,|^3D_1\rangle$$

where the deuteron is found with 4 % probability in the state $^3D_1$.

To simplify the analysis of the deuteron, we assume that the nucleon-nucleon potential is *a three-dimensional square well*, as shown in the figure:

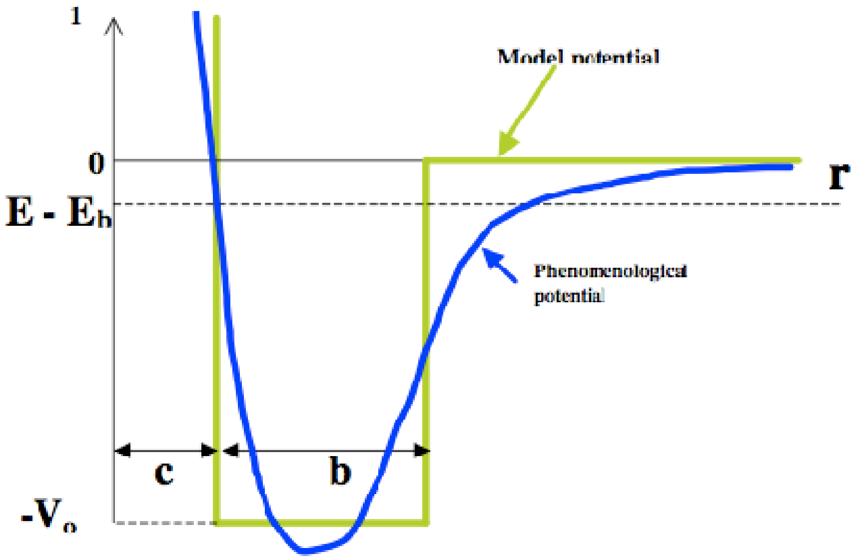


Figure1

$$V(r) = -V_0 \quad \text{for r < R}$$
$$V(r) = 0 \quad \text{for r > R}$$

In figure 2 ,here r represents the separation between the proton and the neutron, so R is in effect a measure of the diameter of the deuteron.

The dynamical behavior of a nucleon must be described by the Schrödinger's equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + V(r)\Psi(r) = E\Psi(\vec{r})$$

where m is the nucleon mass.

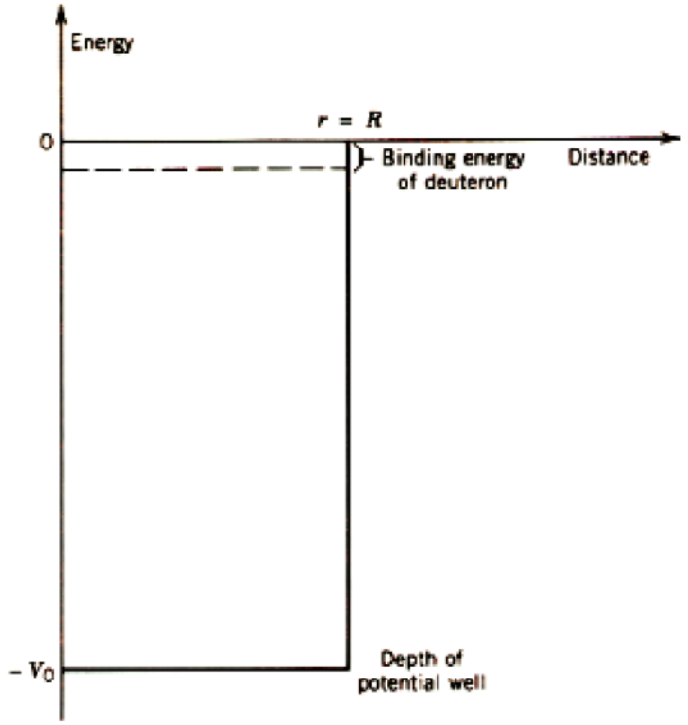


Figure 2

If the potential is not orientationally dependent, a central potential, then the wave function solution can be separated into radial and angular parts:

$$\Psi(r) = R(r)Y_{l\,m}(\theta,\phi)$$

Substitute *R*(*r*) = *u*(*r*)/*r* in to the Schrödinger's equation the function *u*(*r*) satisfies the following equation;

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left\{V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right\}u(r) = Eu(r)$$

The solution *u*(*r*) is labeled by two quantum numbers *n* and *l* so that:

$$u(r) \rightarrow u_{nl}(r)$$

The full solution Ψ(***r***) then can be written as

$$\Psi(\vec{r}) = \psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

with

$$R_{nl}(r) = \frac{u_{nl}(r)}{r}$$

Where

n: the principal quantum number which determines
the energy of an eigenstate.

l: the orbital angular momentum quantum number.

m: the magnetic quantum number, $-l \leqq m \leqq l$.

The angular part of the solution $Y_{lm}(\theta,\phi)$ is called the “spherical harmonic” of order l, m and satisfies the following equations:

$$\hat{L}^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm}(\theta,\phi)$$

and $$\hat{L}_Z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi)$$

where $$\hat{L}^2 \equiv -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right]$$

and $$\hat{L}_Z \equiv -i\hbar\frac{\partial}{\partial\phi}$$

For the case of a three dimensional square well potential with zero angular momentum (l = 0), which we use as the model potential for studying the ground state of the deuteron, the Schrödinger’s equation can be simplified into:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} - V_0 u(r) = Eu(r) \quad \text{for r<R}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} = Eu(r) \qquad \text{for r>R}$$

I. When *r* < *R*

The Schrödinger’s equation is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} - V_0 u(r) = Eu(r)$$

This equation can be rearranged into:

$$\frac{d^2u}{dr^2} + k_1^2 u(r) = 0$$

With $$k_1 \equiv \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$

and the solution is

$$u(r) = A\sin k_1 r + B\cos k_1 r$$

To keep the wave function finite for $r \to 0$

$$\lim_{r\to 0}\psi(r) = \lim_{r\to 0}\frac{u(r)}{r} = 0$$

The coefficient B must be set to zero. Therefore the acceptable solution of physical meaning is

$$u(r) = A\sin k_1 r$$

II. When *r* > *R*

The Schrödinger's equation is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} = Eu(r)$$

the solution is

$$u(r) = Ce^{-k_2 r} + De^{+k_2 r}$$

with $\quad k_2 = \sqrt{\frac{-2mE}{\hbar^2}}$

To keep the wave function finite for $r \to \infty$

$$\lim_{r\to\infty} u(r) = 0$$

The coefficient D must be set to zero. Therefore the acceptable solution of physical meaning is

$$u(r) = Ce^{-k_2 r}$$

Applying the continuity conditions on $u(r)$ and du/dr at $r = R$, we obtain

$$k_1 \cot k_1 R = -k_2$$

This transcendental equation gives a relationship between V_0 and R.

From electron scattering experiments, the *rms* charge radius of the deuteron is known to be about 2.0 fm. Taking R = 2.0 fm we may solve from above equation the value of the potential depth V_0. The result is V_0 = 36 MeV. From the observed binding energy, the size of the deuteron can be defined by $\frac{1}{k_2} = 4.3\,fm$, which is about twice that of the range of the potential. This explains the fact that the deuteron is a loosely bound state. (Its binding energy is 1.113 MeV per nucleon compared with the average value of over 8 MeV per nucleon in nuclei.)

Since $V_0 >> E$

$$\cot k_1 R = -k_2 / k_1 \cong -\sqrt{E / V_0}$$

Hence $\cot k_1 R \cong 0$

$$k_1 R \cong \frac{\pi}{2}, \frac{3\pi}{2}, \ldots$$

or $V_0 R^2 \cong \frac{\hbar^2 \pi^2}{4M}, \frac{\hbar^2 9\pi^2}{4M}, \ldots$

u(r) cannot have a node inside the well, for this would indicate that u(r) and hence wave function, is not the lowest (ground) energy level (Contradiction of our hypothesis)

Hence only the first term retained, and

$$V_0 R^2 \cong \frac{\hbar^2 \pi^2}{4M}$$

This relationship is known as **Range depth relationship**. The ground state wave function together with the range and depth of the potential and the ground state binding energy of the deuteron are shown in figure.

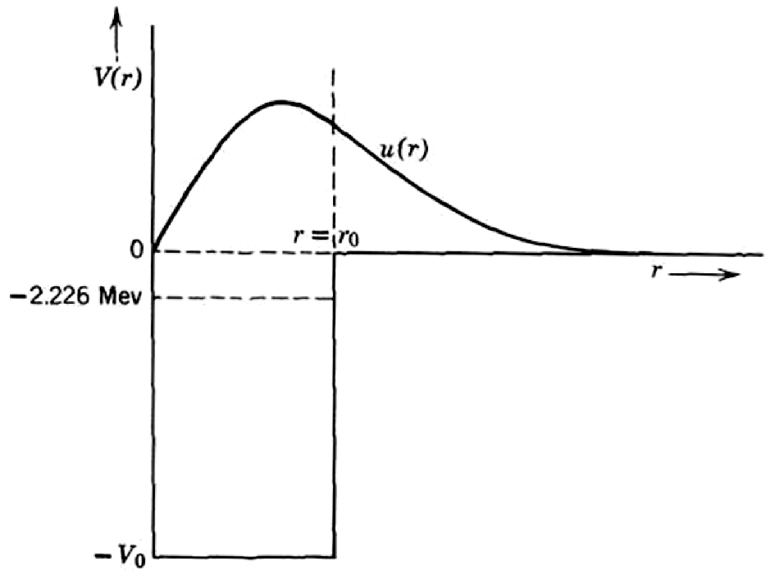


Figure 3

3.3 Self Learning Exercise-I

Q.1 State clearly the definition of nuclear quadrupole moment.

Q.2 Draw three-dimensional square well nucleon-nucleon potential.

Q.3 Write down the basic properties of deuteron.

Q.4 Derive the range depth relationship of the Deuteron.

3.4 Excited States of Deuteron

Extending the calculations of the bound state to cases where the orbital angular quantum number ***l*** is greater than zero leads to a result that deuteron cannot exist in these states. For the extreme case, binding energy E_B~0, k_1R is still only slightly greater than $\pi/2$, since the binding energy E_B of the ground state has already been found negligible compared to the potential well depth V_0. For the first excited state k_1R would have to be greater than $3\pi/2$, since the wave function *u(r)* would have to have a radial node inside the well. But from equation: k_1R must certainly be less than π for all positive values of binding energy.

We shell here prove that for ($l\neq0$) no bound state exists. It shall be assumed that the potential is central and of square well type. The differential equation to be used in this case ($l\neq0$), is which through the substitution $u(r) = r\psi(r)$ takes the form

$$\frac{d^2u(r)}{dr^2}+\frac{M}{h^2}\left[E-V(r)-\frac{l(l+1)h^2}{Mr^2}\right]u(r)=0.$$

With r > ***R***

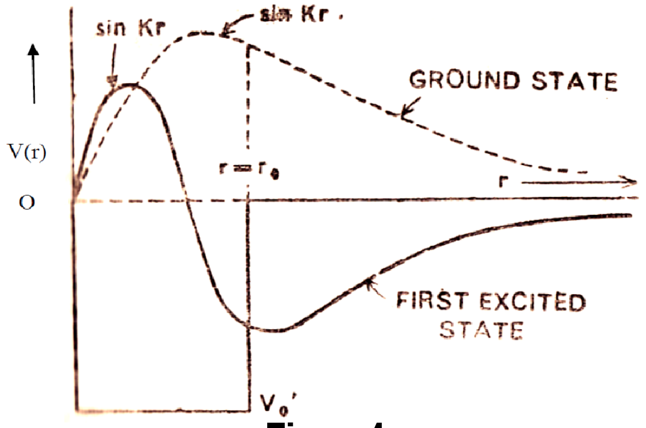


Figure 4

On comparing these equations, we find that it is equivalent to an S-wave radial equation with potential

$$V_{eff}(r) = V(r) + \frac{l(l+1)h^2}{Mr^2}$$

The second term on R.H.S. is called the centrifugal potential as its space derivative gives the classical centrifugal force. This potential is repulsive, there forces '*l*' increases, the binding energy of the lowest bound state decreases.

Returning back to equation and setting *l=1*, the next acceptable value of *l* after 0, we then get,

$$\frac{d^2u(r)}{dr^2} + \frac{M}{h^2}\left[\frac{2h^2}{Mr^2}\right]u(r) = 0.$$

Now $E = -E_B'$ the binding energy of deuteron in the *p* state *(l=1)* and using a square well potential $V = V_0'$ for r < R, for the *p*- state, equation may be written as

for r < ***R***
$$\frac{d^2u(r)}{dr^2} + \frac{M}{h^2}\left[V_0' - E_B' - \frac{2h^2}{Mr^2}\right]u(r) = 0$$

and for r > ***R***
$$\frac{d^2u(r)}{dr^2} + \frac{M}{h^2}\left[E_B + \frac{2h^2}{Mr^2}\right]u(r) = 0$$

Now letting

$$k_1' = \sqrt{\left[\frac{M}{h^2}(V_0' - E_B')\right]}$$

and
$$k_2' = \sqrt{\left(\frac{ME'_B}{h^2}\right)}.$$

The above equation may be written as

$$\frac{d^2u(r)}{dr^2} + \left[k_1'^2 - \frac{2}{r^3}\right]u(r) = 0$$

For r < ***R***

and
$$\frac{d^2u(r)}{dr^2} - \left[k_2'^2 - \frac{2}{r^3}\right]u(r) = 0$$

for r > ***R***

The least well depth, just repaired to produce this bound state, is the one for which the binding energy *E_B'* is just equal to zero, *i.e.,* when $k_2'=0$ and

$$k_1'=\sqrt{\left(MV_0'/h^2\right)}=k_0$$ (say).

If we put $k_0R=x$, the wave equation reduces to

$$\frac{d^2u(r)}{dx^2}+u(r)-\frac{2u(r)}{x^2}=0$$

for $x<k_0R$

and $$\frac{d^2u(r)}{dx^2}-\frac{2u(r)}{x^2}=0$$

for $x>k_0R$

The solution of equation with the correct boundary condition becomes

for $x>k_0R,\qquad u(r)=A_2x^{-1}$

To solve equation, we make the substitution $v=xu(r)$, so that

$$\frac{dv}{dx}=x\frac{du(r)}{dx}+u$$

and $$\frac{d^2v}{dx^2}=x\frac{d^2u(r)}{dx^2}+2\frac{du(r)}{dx}$$

and it can then be re-written as follows

for $x<k_0R.\qquad \dfrac{d^2v}{dx^3}-\dfrac{2}{x}\dfrac{dv}{dx}+v=0$

Differentiating this equation with respect to x, we get

for $x>k_0R\qquad \dfrac{d^3v}{dx^3}-\dfrac{2}{x}\dfrac{d^2v}{dx^2}+\dfrac{2}{x^2}\dfrac{dv}{dx}+\dfrac{dv}{dx}=0$

Dividing this equation by x throughout , we get

for $x<k_0R\qquad \dfrac{1}{x}\dfrac{d^3v}{dx^3}-\dfrac{2}{x^2}\dfrac{d^2v}{dx^2}+\dfrac{2}{x^3}\dfrac{dv}{dx}+\dfrac{1}{x}\dfrac{dv}{dx}=0$

Now since

$$\frac{d^2}{dx^2}\left(\frac{1}{x}\frac{dv}{dx}\right)=\frac{1}{x}\frac{d^3v}{dx^3}-\frac{2}{x^2}\frac{d^2v}{dx^2}+\frac{2}{x^3}\frac{dv}{dx'}$$

then the equation may be re-written as

for $x < k_0 R$ $$\frac{d^2}{dx^2}\left(\frac{1}{x}\frac{dv}{dx}\right)+\frac{1}{x}\frac{dv}{dx}=0$$

Now since $u(r)=vx^{-1}$, must vanish for x = 0, the solution of above equation is found to be

for $x < k_0R$. $$\frac{1}{x}\frac{dv}{dx}=A_1\sin x$$

Integrating it, we get

for $x < k_0R$, $$v = xu(r) = A_1(\sin x - x\cos x)$$

To satisfy continuity condition at the boundary ($r=R$ *or* $x=k_0R$), these solutions yields,

at $x = k_0R$ $$\frac{d}{dx}(\sin x - x\cos x) = 0$$

or $x \sin x = 0$ at $x = R$

or $k_0R \sin k_0R = 0$ at $x = k_0R$

The smallest positive root of this equation is $k_0R = \pi$. Hence a bound state of the deuteron for $l \neq 0$ can exist only if $k_0R < \pi$ and this contradicts the previous statement that $k_0R \simeq \pi$. Therefore we conclude that no bound states exist for deuteron when $l \neq 0$, *i.e.,* deuteron does not possess any excited state.

3.5 Deuteron Structure

The deuteron is the only bound state of 2 nucleons, with isospin T = 0, spin-parity = 1+, and binding energy E_B=2.225 MeV. For two spin half nucleons, only total spins S = 0, 1 are allowed. Then the orbital angular momentum is restricted to $J - 1 < l < J + 1$, i.e., l = 0, 1 or 2. Since the parity is $\Pi = (-)^l = +$, only $l = 0$ and $l = 2$ are allowed; this also implies that we have S = 1.

If the hamiltonian is

$$H = -\frac{\hbar^2}{M}\frac{1}{r}\frac{d^2}{dr^2} + \frac{\hbar^2}{M}\frac{L^2}{r^2} + V_C(r) + V_T(r)S_{12}$$

using the following relation,

$$S_{12}Y_{001} = \sqrt{8}Y_{211}$$
$$S_{12}Y_{211} = \sqrt{8}Y_{011} - 2Y_{211}$$
$$L^2Y_{011} = 0$$
$$L^2Y_{211} = 6Y_{211}$$

we find the radial equations

$$\left[\frac{\hbar^2}{M}\frac{d^2}{dr^2} + E - V_c\right]u_s = \sqrt{8}V_T u_D$$

$$\left[\frac{\hbar^2}{M}\left(\frac{d^2}{dr^2} - \frac{6}{r^2}\right) + E + 2V_T - V_c\right]u_D = \sqrt{8}V_T u_s$$

These equations can be solved numerically.

Other important information on the structure of the deuteron comes from the values of the magnetic moment μ and quadrupole moment Q:

$$\mu = 0.8574\ \mu_N$$
$$Q = 0.2857\ \text{e}-\text{fm}^2$$

Since Q≠0, the deuteron cannot be pure $l = 0$. But generally $l = 0$ is energetically favored for a central potential. Therefore, we write the deuteron wave function as a linear combination of S and D- waves

$$\psi = a\psi_{3S_1} + b\psi_{3D_1}$$
$$= [aR_0Y_{011} + bR_2Y_{211}]\psi^T_{00}$$

where a and b are constants with $\sqrt{a^2+b^2}=1$. R_0 and R_2 are the radial wave functions, the isospin wave function is written as

$$\psi^T{}_{00} = \frac{1}{\sqrt{2}}[\chi_p(1)\chi_n(2) - \chi_n(1)\chi_p(2)]$$

3.6 Magnetic Moment

We first consider the implications of the magnetic moment. The magnetic moment operator is

$$\mu = \mu_N \sum_i (g_s s_{zi} + g_l l_{zi})$$

where $g_s = 4.7\tau_i + 0.88$, where the first term is isovector, and the second term is isoscalar. $g_l = (\tau_i + 1)/2$. Since the deuteron is an iso-scalar particle, let us consider only the iso-scalar magnetic moment. Then, the above equation becomes,

$$\mu = \mu_N \sum_i (0.88 s_{zi} + 0.5 l_{zi})$$

Note that since T = 0 only the isoscalar magnetic moment operator contributes to μ:

$$\mu = \mu_N \sum_{i=1}^{2} (0.88 \langle S_{zi} \rangle_{M=1} + 0.5 \langle L_{zi} \rangle_{M=1})$$

$$= \mu_N [0.88 \langle S_z \rangle + 0.5 \langle L_z \rangle]$$

$$= \mu_N [0.88 \langle S_z \rangle + 0.5 M]$$

$$= \mu_N [0.88 \langle S_z \rangle + 0.5]$$

where we have used the fact that the sum of the two orbital angular momenta can be decomposed into the sum of the center-of-mass angular momentum and relative angular momentum. The center-of-mass angular momentum gives no contribution.

Let us now calculate the matrix element of S_z

$$\langle Y`_{011} | S_z | Y`_{011} \rangle = 1$$

$$\langle Y`_{211} | S_z | Y`_{011} \rangle = 1$$

$$\langle Y`_{211} | S_z | Y`_{211} \rangle = \sum_{M_s} | \langle 2(1 - M_s) 1 M_s | 11 \rangle |^2 = -\frac{1}{2}$$

Thus, for pure ***l*** = 0 or ***l*** = 2 states we would have the values $\mu = 0.88\mu_N$, $0.31\mu_N$. More generally we obtain the relation

$$\mu = [a^2 (0.88) + b^2 (0.31)] \mu_N = (0.88 - 0.57 b^2) \mu_N$$

Therefore, the experimental value $\mu_D = 0.857\mu_N$ implies that $b^2 = 0.04$. However, in more sophisticated treatments one finds that it is quantitatively important to explicitly include the effects of meson exchanges on the magnetic moment.

3.7 Quadrupole Moment

Now we consider the quadrupole moment of the deuteron. Using the definition of

$$Q = e\sqrt{\frac{16\pi}{5}} \int \psi^*_{J=M=1} \left[\sum_{i=1}^{2} \frac{\tau_{3i} + 1}{2} r_i^2 Y_{20} \right] \psi_{J=M=1} d^3 r$$

$$= e\sqrt{\frac{16\pi}{5}} \int \psi^*_{J=M=1} \left[\frac{r_i^2}{4} Y_{20} \right] \psi_{J=M=1} d^3 r$$

Here we have used the fact that for each nucleon the distance from the center of mass is only half the distance between them, r_i= r/2. Now using the expressions for the wave function introduced above

$$Q = e\sqrt{\frac{16\pi}{5}}\left\{\begin{array}{l} |a^2|\int\left[\frac{r^2}{4}R_0^2 r^2 dr\right]\int Y_{00}^* Y_{20} Y_{00}\, d\Omega + 2\,\mathrm{Re}(ab^*)\int\left[\frac{r^2}{4}R_0 R_2 r^2 dr\right] \\ \quad \times\sum_M \langle S=1, M_s=1 \| S=1, M_s = 1-M\rangle \int Y_{00}^* Y_{20} Y_{2M}\, d\Omega \times \langle 1(1-M)2M \| 11\rangle \\ \quad +|b^2|\int\left[\frac{r^2}{4}R_2^2 r^2 dr\right]\sum_M \langle 1(1-M)2M \| 11\rangle \int Y_{2M}^* Y_{20} Y_{2M}\, d\Omega \end{array}\right\}$$

After evaluating the angular integrals and putting in the CG coefficients, one finds

$$Q = e\sqrt{\frac{16\pi}{5}}\left\{\frac{\sqrt{2}}{10}\mathrm{Re(ab^*)}\int\left[r^4 R_0 R_2 dr\right] - \frac{|b^2|}{20}\int\left[r^4 R_2{}^2 dr\right]\right\}$$

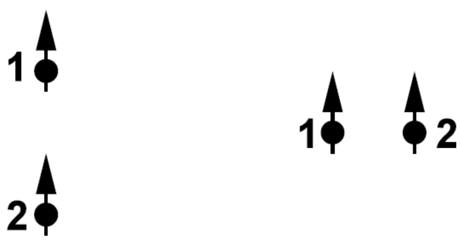
To proceed further we need to evaluate the radial integrals, so we would need to solve the radial Schrodinger equation and obtain the radial wave functions. Clearly, for a given potential model this is (in principle) possible. For our purposes, we will use our knowledge that b = 0.2 ≪ 1 from the magnetic moment analysis and keep only the first term. This will give us an approximate expression that we can set equal to the experimental value Q_{exp} = 0.286 e fm^2 to obtain the result

$$Q \cong e\frac{0.2\sqrt{2}}{10}\int r^4 R_0 R_2 dr = 0.286 efm^2$$

Solving for the unknown radial integral yields

$$\int r^4 R_0 R_2 dr \cong 10.1\, fm^2$$

for the radial integral. This value seems quite reasonable given that the mean squared charge radius of the deuteron is 4.0 fm^2.



To elucidate the effect of the tensor (non central) force on the structure of the deuteron let's consider the quadrupole moment, for which we need to use the M =

1 state. The dominant S-D interference term in the quadrupole moment has $M_S = 1$. So the spins of both the two nucleons are predominantly aligned parallel to z. Let's simply take $\sigma_1 = \sigma_2 = +z$, and then $\sigma_1 \cdot \sigma_2 = +1$. Then we need to consider the relative orientation of r, and we will focus (see Fig. on two extreme cases: (a) r||z and (b) r $\perp$ z).

In case

(a) $\sigma_1 \cdot r = \sigma_2 \cdot r = 1$, so we have $S_{12} = +2$ for this geometrical arrangement. This is a prolate configuration so we expect Q > 0 for case (a).

(b) In case (b) we have $\sigma_1 \cdot r = \sigma_2 \cdot r = 0$ so $S_{12} = -1$ and the oblate shape relative to the z axis would imply Q < 0.

Since experimentally Q > 0, case (a) must be energetically favored which corresponds to $V_T(r)<0$. This then gives an attractive force when the configuration is such that $S_{12} > 0$ (case (a)) and a repulsive force when $S_{12} < 0$ (case (b)).

Given $V_C(r)$ and $V_T(r)$, this is an eigenvalue problem for k^2 with a free parameter to be determined: the ratio b/a. It was shown by Rarita and Schwinger that large class of potentials can solve these equations with the constraints E_B = 2.225 MeV and Q = 0.286e-fm^2.

3.8 Self Learning Exercise-II

Q.1 Define magnetic moment.

Q.2 Explain that "no bound states exist for deuteron".

Q.3 Calculate the magnetic and Quadrupole moment of Deuteron.

3.9 Answer to Self Learning Exercise

Answer to Self Learning Exercise-I

Ans.1: See Glossary

Answer to Self Learning Exercise-II

Ans.2: See Glossary

3.10 Exercise

Q.1 Solve the Schrodinger equation for the deuteron in a S-state under the assumption of square well potential.

Q.2 Show that deuteron has the D-state admixture

3.11 Summary

After going through this chapter, you would be able to achieve the aforesaid objectives. Now we recall what we have discussed so far.

- We have learnt the basic properties of deutron, its charge (+e), mass (~2.014 amu), its radius (2.1 fermi), its binding energy (=2.225$\pm$.003 Mev), Spin and statistics (Bose-Einstein) and the electric quadrupole moment Q_d =0.00282 barn.
- The study of deuteron problem, although hopelessly limited in as much as deutron possesses only the ground state and no-excited states exist for the bound neutron-proton system, gives invaluable clues about the nature of the nuclear force.
- We learnt that neutron and proton can form stable combination (deuteron) only in the triplet state means when the n & p spins are parallel. The singlet state, i.e. a state of antiparallel n-p spins being unbound.
- The existence of non-zero magnetic moment and electric quadrupole moment for deutron suggests that at least a part of the neutron proton force acting in deutron is non-central.

3.12 Glossary

Barn: A unit of cross-section, a barn is equal to 10^{-28} m^2.

Cross-section: a measure of the likelihood of a given process occurring at an accelerator. The idea is that two objects with a larger cross-sectional area are more likely to hit one another. So, larger cross-sections mean that a process is more likely to occur. Cross-sections are measured in barns, 10^{-28} m^2. A barn is an extremely large cross-section in particle physics. Many interesting cross-sections are measured in pb (picobarns), which are equal to 10^{-12} barns.

The magnetic moment: (or magnetic dipole moment) of an object is a measure of the object's tendency to align with a magnetic field. It is a vector quantity, with the positive direction defined by the way the object responds to a magnetic field: The object will tend to align itself so that its magnetic moment vector is parallel to the magnetic field lines. There are two sources for a magnetic moment: the motion of electric charge and spin angular momentum. For example, a loop of wire with a current running through it will have a magnetic moment proportional to the current and area of the loop, pointing in the direction of your right thumb if your fingers are curling in the direction of the current. Alternatively, an electron, which is a spin-1/2 fermion, has an intrinsic magnetic moment proportional to its spin.

Quadrupole Moment: the quantity that characterizes the deviation from spherical symmetry of the electrical charge distribution in an atomic nucleus. It has the dimension of area and is usually expressed in sq cm. For spherical symmetry the nuclear quadrupole moment $Q = 0$. If a nucleus is extended along the axis of symmetry, then Q is a positive quantity, but if the nucleus is flattened along the axis, it is negative. The value of the nuclear quadrupole moment varies over a wide range.

References and Suggested Readings

1. "The Two Nucleon Problem" by M. Sugrwara and Hulthen.
2. "Nuclear Two Body Problems and Elements of Nuclear Forces" Experimental Nuclear Physics by N. F. Ramsey.
3. Lectures on Nuclear Theory by Landau, Plenum.
4. Elementary Nuclear Theory, 2nd ed. by Bethe and Morrison.
5. The Atomic Nucleus by R D. Evans.
6. Atomic and Nuclear Physics by Brijlal and Subhraininyan.
7. Nuclear Physics by D. C Tayal.
8. Nuclear Physics by Irving Kaplan

UNIT-4
Nucleon-Nucleon Scattering and Potentials: Part-I

Structure of the Unit

4.0 Objectives

After interacting with the material presented here students will be able to

- Learn n-p scattering at low energies with specific square well potential.
- Comparatively study the results of low energy n-p scattering.
- Know the spin dependence and scattering length.

4.1 Introduction

Having ascertained that nuclei are quantum mechanical systems composed of nucleons, it is quite plausible to study the nuclear forces under the simplest possible conditions. The simplest case in which the nuclear force is effective is when:

1. When the two nucleons are bound together.The three possible bound states of a two nucleon system, di-neutron (*nn)*, di-proton (*pp)* and deuteron (*np*), nature has provided us with only the deuteron and the other two are unstable.
2. When the two nucleons are in free state and one is made to impinge on the other, i.e. The scattering processes.

   In practice, it is not possible to make a neutron target and therefore scattering experiments are limited only to neutron proton (*np*) scattering and proton-proton (*pp*) scattering.

The first case we discussed in previous chapter and second case we will discuss in our upcoming two chapters. In this chapter we will focus only on np scattering.

The first question arises in our mind is that, What is Scattering? The answer is, when an intense and collimated beam of nucleons is born barded on target nuclei the interactions between incident nucleus and target nuclei takes place. As a result we may observe the following two possibilities:

1. The interaction does not change the incident particles, *i.e.,* incoming and outgoing particles are the same. The change is in the path of incoming nucleons, *i.e.,* they are deviated from their original path. This process is known as scattering, In scattering processes the outgoing particles may have same energy as that of incident particles or may have the changed energy value. The former is known as elastic scattering and latter is known as inelastic scattering.
2. The second possibility is that the outgoing particles are different from the incident particles. Then the interaction process is known as nuclear reaction. In nuclear reaction we have two alternatives:

   It should be remembered that any of the above alternative may occur, either alone or with other competing processes.

Among the nucleon-nucleon scattering, neutron proton (*n-p)* scattering is the simplest one, because here the complications due to coulomb forces are not present. The neutron neutron (*n-n*) scattering is not practically possible because of the non availability of neutron target (because neutron decays into proton in a few minutes). However, their are evidences to support if *n-n* forces are similar to *p-p* forces, a bound state for two neutrons cannot exist.

4.2 Neutron-Proton Scattering at Low Energy assuming Central Potential with Square Well Shape

In np scattering neutron proton system is analyzed in the state of positive energy, *i.e.,* in a situation when they are free. In the experiment, a beam of neutrons from an accelerator is allowed to impinge on a target containing many essentially free protons. The simplest substance is hydrogen gas but in some cases other substances like thin nylon sheet and paraffin are used. Hence, it is natural to think that in target protons are not free but are bound in molecules. The molecular binding energy is so small about 1*eV*, therefore, for the impinging neutrons of energy greater than 1*eV*, protons are treated as free. The presence of electrons also do not affect the process because they are too light to cause any appreciable trouble to incoming neutrons. When neutrons impinge on protons, some of them are captured to form deuteron and balance of energy is radiated in the form of γ rays; but the great majority of neutrons undergo elastic scattering. In the process, the interaction between two nucleons is of such an order that the neutrons changed their velocities in magnitude as well as in direction.

Neutron – Proton Scattering at Low Energies

In the low energy range most of the measurements of scattering cross section are due to Melkonian and Rainwater et.al. A beryllium target bombarded at by deuterons accelerated in a cyclotron, provided the neutron beam which was shot at a target containing free protons.

Results from figure 1 show that the scattering cross section depends very much on the energy of the incident neutrons. At low energies below 10 Mev, the scattering is essentially due to neutrons having zero angular momentum (***l***=0) and hence in the centre of mass system, the angular distribution of scattered neutrons is isotropic. In order to avoid complications due to Coulomb forces we shall consider the scattering of neutrons by free protons viz. those not bound to molecules. However in practice the protons are of course bound to molecules but the molecular binding energy is only about 0.1 ev. Therefore if the incident neutrons have an energy greater than about 1ev. The protons can be regarded as free.

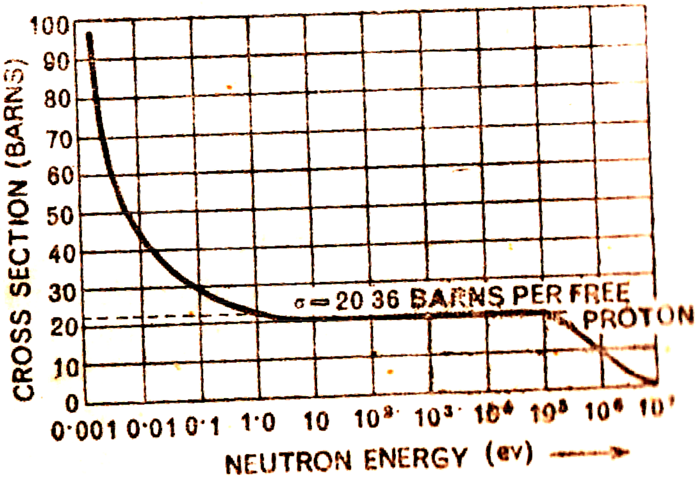


Figure 1: np scattering cross section

In describing elastic scattering events like the scattering of neutrons by free protons it is more convenient to use the center of mass system. The quantum mechanical problem describing the interaction between two particles, in the center of mass system, is equivalent to the problem of interaction between a reduced mass such as the system. Although while wording out the following theory we shall think in terms of a neutron being scattered by a proton but it applies equally well to spin less, reduced mass particle which is being scattered by a fixed force center.

Let us suppose that the neutron and the proton interact via a spherically symmetric force field whose potential function is *V* (r), where *r* is the distance between the particles.

The Schrodinger equation for a central potential *V* (r) in the center of mass system, for the *n-p* system is

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

Where *M* is the reduce mass of the *n-p* system.

To analyze the scattering event, we have to solve this equation under proper boundary conditions. In the immediate vicinity of the scattering center, the action will be violent and its description is difficult. At a considerable distance from the scattering center where the experimentalist lies in wait for the scattered particles, things will however be simpler. For scattering the boundary condition is that at large distances from the scattering center the wave should be made up of two parts:

1. an incident plane wave that describes the unscattered particles and superimposed upon it,
2. an outgoing scattered spherical wave which emanates from the scattering center. To solve in asymptotic form,

$$\psi = \psi_{inc} + \psi_{sc}$$

The wave function that describes an incident plane wave (a beam of particles) moving in the positive z-direction is

$$\psi_{inc} = e^{ikz} = e^{ikz}\cos\theta,$$

Where $k = \sqrt{\left(\frac{ME}{h^2}\right)}$

which is a solution of the wave equation with V(r) set equation zero,

$$\left[\nabla^2 + \frac{ME}{h^2}\right]\psi_{inc} = 0,$$

Setting V(r) equal to zero in this manner actually amounts to switching off the scattering potential and there by eliminate scattering so that the total wave function becomes identical with the incident wave function. The wave function represents one particle per unit volume since the square of the wave function is equal to unity. Having known the form of the incident wave function, the next problem is to devise a suitable form for the scattered wave function. This obviously is

$$\psi_{sc} = f(\theta)\frac{e^{ikr}}{r},$$

For large r $f(\theta)$ in this expression indicate amplitude of the scattered wave in the direction θ. This wave function is a necessary consequence of the assumption that the scatterer simply scatters the particles and does not absorb them at all.

The probability density and hence the number of scattered particles per unit volume shall be proportional to $|\psi_{sc}|^2$. If scattering is considered to be isotropic, the density (number per unit volume) of scattered particles through a large spherical shell of radius r is inversely proportional to r^2 since the volume of the spherical shell, being given by $4\pi r^2$ *dr*, is proportional to r^2 and density therefore is proportional to $1/r^2$ which is also proportional to $|\psi_{sc}|^2$. Hence $1/r^2$ dependence of ψ_{sc}.

Therefore the wave function, in a form we are actually interested *viz*. asymptotic, may be written as. $\psi = \psi_{inc} + \psi_{sc} = e^{ikz} + f(\theta)\dfrac{e^{ikr}}{r}.$

Now, in Fourier analysis we often expand as arbitrary function into a sense of harmonic functions of various frequencies. So we expand the incident plane wave function e^{ikz} in terms of Legendre Polynomials $P_l(\cos\theta)$ and write.

$$\psi_{inc} = e^{ikrcos\theta} = \sum_{l=0}^{\infty} B_l(r)P_l(\cos\theta)$$

where ***l*** is an integer representing the various partial waves. This particular way of writing the wave function is termed as the partial wave expansion.

The radial functions $B_1(r)$ in this equation are given by

$$B_l(r) = i^l(2l+1)\,j_l(kr),$$

Where *$J_l(kr)$* is the Spherical Bassel function which is related to the ordinary Bessel function through the formula

$$j_l(kr) = \left(\frac{\pi}{2kr}\right)^{1/2} J_{l+1/2}(kr)$$

and can be represented as $j_l(kr) = (-kr)^l\left[\dfrac{1}{kr}\dfrac{d}{d(kr)}\right]^l\left(\dfrac{\sin kr}{kr}\right)$

Whence asymptotically

$$j_l(kr)_{r\to\infty}\frac{\sin\left(kr-\frac{l\pi}{2}\right)}{kr}$$

Asymptotically, $B_l(r)$ from is given by

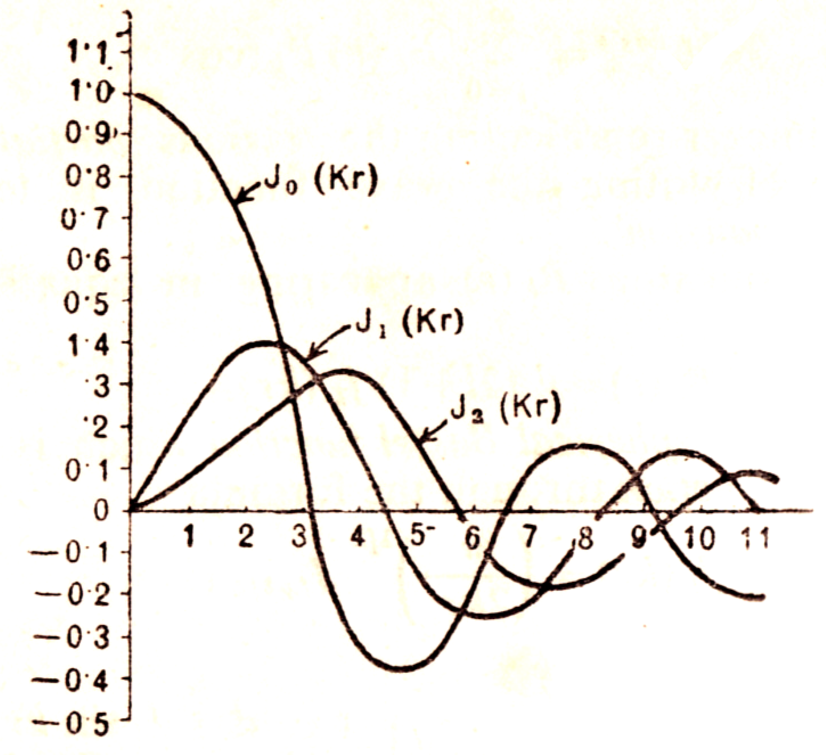
$$B_l(r)_{r\to\infty} \to i^l(2l+1)\frac{\sin\left(kr-\frac{l\pi}{2}\right)}{kr}$$

$$\cong \frac{1}{2ikr} i^{l}(2l+1).\left[e^{i(kr-l\pi/2)-e^{-i(kr-l\pi/2)}}\right]$$

The Spherical Bessel function $J_l(kr)$ for various values of *l* are given below

$$j_2(kr)=\left[\frac{3}{(kr)^3}-\frac{1}{kr}\right]\sin(kr)-\frac{3\cos(kr)}{(kr)^2}.$$

These functions are plotted in the Fig.



Similarly $f(\Theta)$ may also be expanded in terms of the Legendre Polynomials as follows

$$f(\theta)=\frac{i}{2k}\sum_{l=o}^{\infty} f_1(2l+1)P_1(\cos\theta).$$

Substituting from equation in equation we obtain

$$\psi=\psi_{inc}+\psi_{sc}\approx\sum_{l=0}^{\infty}\left[i^{l}(2l+1)\,j_l(kr)+f_l\frac{e^{ikr}}{r}\right]P_1(\cos\theta).$$

Since each term in the equation with a specific value of the orbital angular momentum quantum number l, represents a solution of the wave equation in spherical polar co-ordinates for constant potential energy. Therefore the expansion classifies the particles in the beam according to their angular momenta which is of great practical importance since at lower energies below 10 Mev, most of the scattering is due to *l=0* particles, *i.e.* the number of partial waves is severely limited in this case and it suffices to study the scattering only for *l*=0, *i.e.* S-wave.

For *l*=0

$$B_0(r) = \frac{\sin(kr)}{kr} \approx 1 - \frac{(kr)^2}{6} + ...$$

and for *l*=1

$$B_1(r) = 3i\left[\frac{\sin(kr)}{kr} - \frac{\cos(kr)}{kr}\right]$$

$$\cong 3i\left[\frac{kr}{3} - \frac{(kr)^3}{30} + ...\right].$$

$$\therefore \left|\frac{B_1\ (r)}{B_0\ (r)}\right| \cong (kr)^2.$$

We have found out the ratio of the square, since the probability density is determined by $B_l^2(r)$. To have an idea of the magnitude of this ratio, let us consider a neutron of energy 1 Mev in the L-system, it will be 0.5 Mev in the *C-M* system. Neutron momentum then is

$$p = (2ME)^{\frac{1}{2}} = \left[\frac{2\times1.67\times10^{-24}\times1.6\times10^{-6}}{2}\right]$$

$$= 1.63\times10^{-15}\, gm.cm./\sec.$$

and its wave number $k = \frac{p}{h} = \frac{1.63\times10^{-15}}{1.0545\times10^{-27}} = 1.55\times10^{12}\, cm.^{-1}$

If we assume the nuclear forces to have a range *r* = 2 Fermi, then

$$\left|\frac{B_1(r)}{B_0(r)}\right|^2 \cong (kr)^2 = \left(1.55\times10^{12}\times2\times10^{-13}\right) = \left(0.31\right)^2 = 0.0961,$$

i.e. at an energy of 1 Mev only about 9% of the scattering is due to neutrons with *l*=1. Similar calculation for a neutron of energy 10 Mev raises this percentage to about 49%. Therefore in the energy range below 10 Mev. S-wave scattering (*l*=0) is predominant.

4.3 Results of Low Energy n-p Scattering

The theory for the scattering cross-section developed in the previous section is in fact a theory for the phase shift δ_l which in turn depends up on the assumptions regarding the nature of the scattering potential *V(r)*. We now proceed to carry out the calculations for the same rectangular potential well as was assumed in sections for the deuteron ground state.

The radial Schrodinger equation for *l*=0, *viz*. equation inside and outside the nuclear square potential well may be written as

$$\frac{d^2u(r)}{dr^2}+\frac{M}{h^2}(E+V_0)u(r) \qquad \text{for } r < r_0,$$

$$\frac{d^2u(r)}{dr^2}+\frac{M}{h^2}Eu(r)=0 \qquad \text{for } r > r_0,$$

Since in the present case of *n-p* scattering, the negative binding energy is replaced by a small positive energy E which is much smaller than the well-depth V_0. These equation may be written as

$$\frac{d^2u_i}{dr^2}+K^2u_i=0 \qquad \text{for } r < r_0,$$

$$\frac{d^2u_0}{dr^2}+k^2u_0=0 \qquad \text{for } r > r_0,$$

Where u_i is the wave function inside the well and u_0 that outside the well and

$$K^2=\frac{M(E+V_{0)}}{h},k^2=\frac{ME}{h^2}.$$

Equation has the solution $u_i = A\sin Kr$

And equation has the solution $u_0 = C\sin kr + D\cos kr,$

Which may be written as $u_0 = B\sin(kr+\delta_0).$

In order to understand the significance of the phase shift δ_0, the Schrodinger equation would be equation *V*(r) set equal to zero, the solution of which would have to be of the form

$$u(r) = \sin kr.$$

Since it must vanish at *r*= *o*. The solution which holds good only outside the well.

Thus δ_0 is the phase shift at large distances introduced by switching on the scattering potential.

We now require that the solution and join smoothly at $r = r_0$ *i.e.* the logarithmic derivative must be continuous at $r=r_0$ *viz,*

$$\frac{1}{u_i}\frac{du_i}{dr}\bigg|_{r=r_0} = \frac{1}{u_0}\frac{du_0}{dr}\bigg|_{r=r_0}$$

This condition, with the aid of equation gives

$$K\cot Kro = k\cot(kr_0 + \delta_0)$$

This result may be compared with the continuity condition equation for the ground state of the deuteron *viz.*

$$\frac{\sqrt{\{M(V_0 - E_B)\}}}{h}\cot\left(\left[\frac{\sqrt{\{M(V_0 - E_B)\}}}{h}\right]r_0\right) = -\gamma$$

where $\gamma = \sqrt{\frac{ME_B}{\hbar^2}}$

To simplify the matching condition in case of *n-p* scattering, we assume that inside the well, the scattering wave function is not much different from the deuteron wave function. This appears quite reasonable since the two situations differ only in that the total energy *E* in this case although small, is positive whereas the deuteron binding energy E_B is small, but negative. We therefore assume that the logarithmic derivative $K\cot Kr_0$ of the inside wave function for scattering could be approximated by the value of the logarithmic derivative of the ground state wave function of deuteron *viz.* γ . Hence from

$$k\cot\left(kr_0 + \delta_0\right) = -\gamma$$

At this point we introduce another approximation that r_0 is very small (possibly zero) compared to $k = \sqrt{(MF/h)}$ so that kr_0 may be neglected in the above equation and then

$$k\cot\delta_0 = -\gamma \text{ or } \cot\delta_0 = -\gamma/k$$

Now the total scattering cross-section for l=0 from equation is given by

$$\sigma_{sc,0} = \frac{4\pi}{k^2}\sin^2\delta_0 = \frac{4\pi}{k^2}\cdot\frac{1}{(1+\cot^2\delta_0)} = \frac{4\pi}{k^2}\cdot\frac{1}{(1+\gamma^2/k^2)}$$

$$= \frac{4\pi}{k^2+\gamma^2} = \frac{4\pi h^2}{M(E+E_B)}.$$

where we have substituted the values of k^2 and γ^2 from equations and respectively.

4.4 Self Learning Exercise-I

Q.1 What is Scattering?

Q.2 Draw a neutron proton scattering cross section graph.

Q.3 Write down the Schrodinger equation, for the *n-p* system, for a central potential *V* (r) in the center of mass system.

Q.4 Discuss in detail the results of low energy np scattering.

4.5 Spin Dependence and Scattering Length

Spin dependence:

E. P. Wigner suggested that the inter-nucleon forces are spin-dependent. Since neutron and proton are $\frac{1}{2}$ spin particles, therefore in *n-p* scattering the neutron and proton spins may either be parallel or anti parallel. In deuteron the bound state of the *n-p* system, whose binding energy $E_{B,}$ the neutron and proton spins are parallel and therefore this equation possibly holds good for parallel spin case.

The state of parallel spins, is a triple state and has a statistical weight 3 corresponding to the three allowed orientations of the angular momentum vector under an external magnetic field. The state of anti parallel spins is a singlet state on account of the non orientability of a vector of zero length and has a statistical weight.

In a scattering experiment in general neutron and proton spins are randomly oriented and so are the spins of neutrons in the incident beam and therefore singlet and triplet state of the *n-p* system will occur in proportion to the statistical weight factors for these states which are $\frac{1}{2}$ and $\frac{3}{4}$ respectively. The total scattering cross-section therefore shall be made up of two parts, $\delta_{t,0}$- the cross-section for scattering in the triplet state and $\delta_{s,0}$ the scattering cross-section in the singlet state, as follows

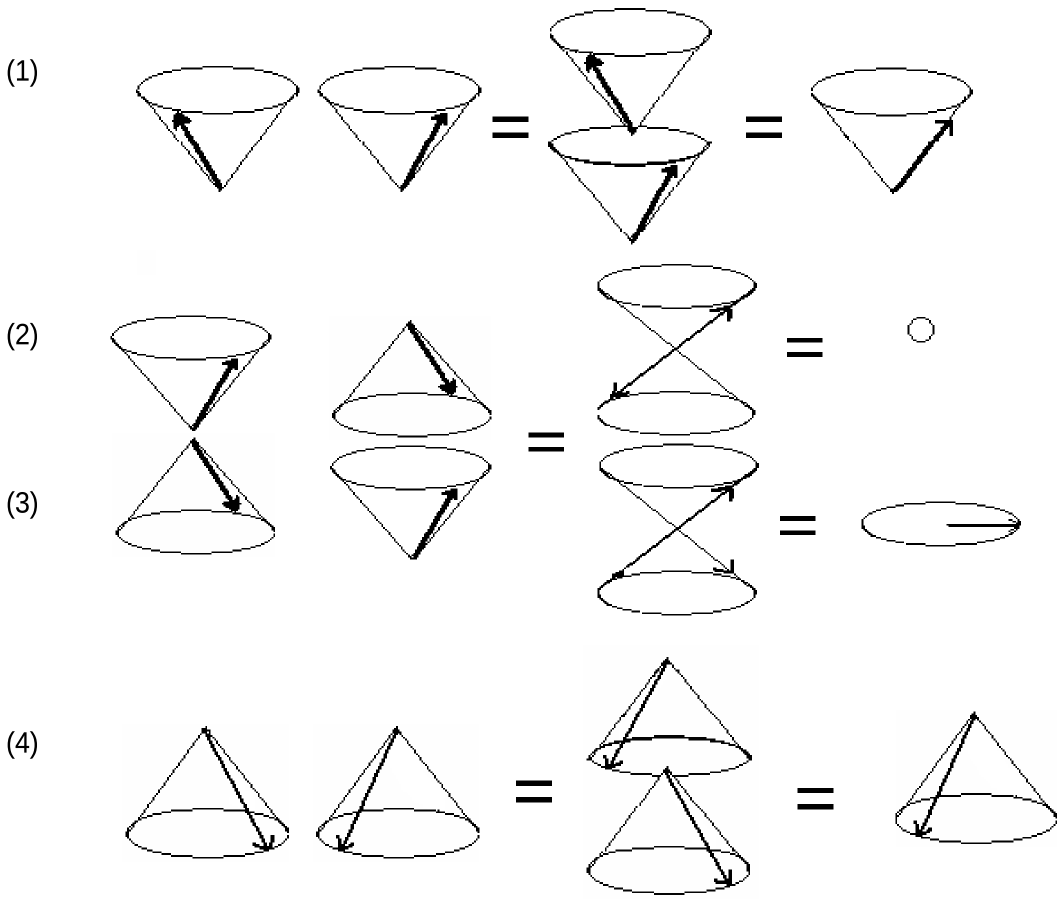
$$\sigma_0 = \frac{3}{4}\sigma_{t,0} + \frac{1}{4}\sigma_{s,0}$$

We therefore take σ_t= 4.6 b and using the measured value of σ = 20.4 b for the low-energy cross section, we deduce

$$\sigma_s = 67.8 \text{ b}$$

This calculation indicates that there is an enormous difference between the cross sections in the singlet and triplet states that is, the nuclear force must be spin dependent.

From a naïve point of view, in a random distribution of spins as in *n-p* scattering, the two spins are as often parallel as antiparallel giving equal statistical weights to the two states. However quantum mechanically, the spin direction cannot be defined as uniquely as a vector in space and hence the statement ‘spin pointing up’ simply tells that the spin vector points somewhere along a cone around the vertical direction. The following figure depicts schematically the four equally likely situations for the relative spins of the two particles.



Figures (1) and (4) correspond to a total spin unity corresponding to the magnetic quantum number values +1 and -1 respectively. In cases (2) and (3) the z-components add up to zero but since the spins are not aligned along the z-direction, they may add up to zero as in case (2) resulting in a singlet state or may add up to a total spin perpendicular to the z-axis as in case (3) giving rise to a triplet state.

Scattering Length:

Fermi and Marshall introduced a very useful concept the 'scattering length *a*' for the discussion of nuclear scattering at very low incident neutron energy.

$[i.e.E \rightarrow 0$ and hence $k = \sqrt{\left\{\left(\frac{ME}{h^2}\right)\right\}} \rightarrow 0$

which is defined as follows:

$$a = \underset{k\rightarrow 0}{Lim}\left(-\frac{\sin\delta_0}{k}\right);$$

With this definition, equation giving the total scattering cross section form S-wave (l=0) may be written for very low incident neutron energy as

$$\underset{k\rightarrow 0}{Lim}(\sigma_{sc}) = \underset{k\rightarrow 0}{Lim}\left(\frac{4\pi\sin^2\delta_0}{k^2}\right) = 4\pi a^2$$

Equation then indicates that 'a' has the geometrical significance of being the radius of a hard sphere surrounding the scattering center from which neutrons are scattered and so has the dimensions of length, hence the name scattering length.

Now it is to be noted from equation that as $k \rightarrow 0$ (*i.e.,*) as the energy *E* of the incident neutron approaches 0, δ must approach either 0 or π otherwise the cross-section at zero neutron energy would become infinite which is physically absurd. Therefore at very low incident neutron energies ($E \rightarrow 0$), equation reduces to

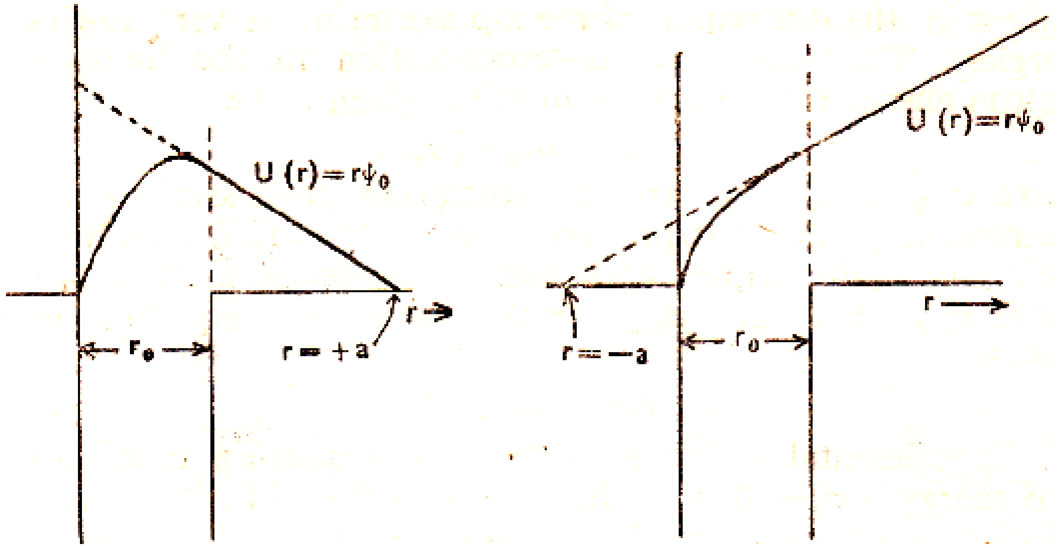
$$a = -\frac{\delta_0}{k}$$

Then at very low incident neutron energies, the wave function outside the range of nuclear force as expressed by equation may be written as

$$\underset{k\rightarrow 0}{Lim}u\ (r) = \underset{k\rightarrow 0}{Lim}(r\psi_0) = \underset{k\rightarrow 0}{Lim}\left[e^{i\delta_0}\frac{\sin(kr+\delta_0}{k}\right]$$

The equation then gives a simple graphical interpretation of the scattering length. This equation represents a straight line for U(r) and the scattering length 'a' is the intercept on the *r*-axis. This is indicated in Figure.

Having defined the scattering length by means of equations an inquisitive reader may ask quite naturally what is the significance of positive or negative scattering length ? or what is the significance of attaching a positive or a negative sign with at the scattering length? It tells us whether the system has a bound or an unbound state.



From figure it is clear that positive scattering length indicates a bound state and negative scattering length indicates a virtual or unbound state. Since the deuteron wave unction, *i.e.*, the wave function for the bound state of *n-p* system, must curve towards the *r*-axis in order to match the exponentially decaying solution (c.f. equation *i.e.* $r > r_0$ will give rise to a positive intercept on the *r*-axis indicating thereby a positive scattering length. For unbound state the wave function has to match with an increasing solution outside the range r_0 and then extrapolation of U(r) shall produce a negative intercept on the *r*-axis implying thereby a negative scattering length.

4.6 Coherent Scattering of Neutrons by Protons in Ortho and Para Hydrogen Molecules

We can verify our conclusions about the singlet and triplet cross sections in a variety of ways. One method is to scatter very low energy neutrons from hydrogen *molecules.* Molecular hydrogen has two forms, known as orthohydrogen and parahydrogen. In orthohydrogen the two proton spins are parallel, while in parahydrogen they are antiparallel. The difference between the neutron scattering cross sections of ortho- and parahydrogen is evidence of the spin-dependent part of the nucleon-nucleon force. Our discussion of the cross section for neutron-proton scattenng is inadequate for analysis of scattering of neutrons from H2 molecules. Very low energy neutrons *(E* < 0.01 eV) have a de Broglie wavelength larger than 0.05 nm, thus greater than the separation of the two protons in H2. The uncertainty principle requires that the size of the wave packet that describes a particle be no smaller than its de Broglie wavelength. Thus the wave packet of the incident neutron overlaps simultaneously with both protons in H2, even though the range of the nuclear force of the individual neutron-proton interactions remains of the order of 1 fm. The scattered neutron waves $\psi 1$ and $\psi 2$ from the two protons will therefore combine *coherently;* that is, they will interfere, and the cross section depends on $|\psi 1 + \psi 2|^2$, not $|\psi 1|^2 + |\psi 2|^2$. We cannot therefore simply add the cross sections from the two individual scatterings. (At higher energy, where the de Broglie wavelength would be small compared with the separation of the protons, the scattered waves would not interfere and we could indeed add the cross sections directly. The reason for choosing to work at very low energy is partly to observe the interference effect and partly to prevent the neutron from transferring enough energy to the H_2 molecule to start it rotating, which would complicate the analysis. The minimum rotational energy is about 0.015 eV, and so neutrons with energies in the range of 0.01 eV do not excite rotational states of the molecule.)

4.7 Conclusions of these Analysis regarding Scattering Lengths

To analyze the interference effect in problems of this sort, we introduce the *scattering length a,* defined such that the low-energy cross section is equal to $4\pi a^2$

$$\lim_{k\to 0}\sigma = 4\pi a^2$$

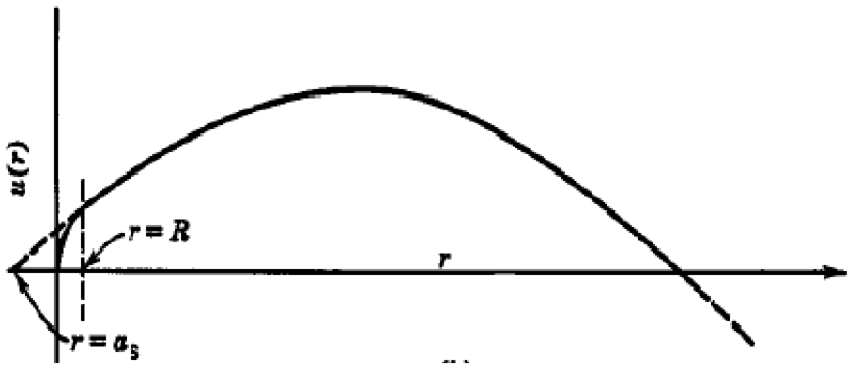
$$a = \pm\lim_{k\to 0}\frac{\sin\delta_0}{k}$$

The choice of sign is arbitrary, but it is conventional to choose the minus sign.

Even though the scattering length has the dimension of length, It is a parameter that represents the strength of the scattering, *not* its range. To see this, we note from above equation that δ_0 must approach 0 at low energy in order that *a* remain finite. The scattered wave function can be written for small δ_0 as

$$\psi_{\text{scattered}} \approx A\frac{\delta_0}{k}\frac{e^{ikr}}{r} = -Aa\frac{e^{ikr}}{r}$$

Thus *a* gives in effect the amplitude of the scattered wave.



The sign of the scattering length also carries physical information. Figure shows representations of the triplet and singlet scattered wave functions *u(r).* The triplet wave function for $r < R$ looks just like the bound state wave function for the deuteron: *u(r)* "turns over" for r < *R* to form the bound state. The value of a_t is therefore positive. Because there is no singlet bound state, *u(r)* does not turn over for $r < R$, so It reaches the boundary at $r = R$ with positive slope When we make the smooth connection at $r = R$ to the wave function beyond the potential and extrapolate to *u(r)* = 0, we find that *as,* the singlet scattering length, is negative.

Our estimate σ_t = 4.6 b from the properties of the deuteron leads to a_t = + 6.1m, and the estimate of σ_s = 67.8b needed to reproduce the observed total cross section gives a_s = -23.2 fm.

The theory of neutron scattering from ortho and parahydrogen gives

$$\sigma_{para} = 5.7(3a_t + a_s)^2$$

$$\sigma_{ortho} = \sigma_{para} + 12.9(a_t - a_s)^2$$

where the numerical coefficients depend on the speed of the incident neutron.

The measured cross sections corrected for absorption, for neutrons of this speed are σ_{para} = 3.2 ± 0.2 b and σ_{ortho} = 108 ±1 b. If the nuclear force were independent of spin, we would have $\sigma_t = \sigma_s$ and thus $a_t = a_s$; thus σ_{para} and σ_{ortho} would be the same. The great difference between the measured values shows that $a_t \neq a_s$, and it also suggests that a_t and a_s must have different signs, so that $-3a_t = a_s$ in order to make σ_{para} small. Solving equations for a_s and a_t gives

a_s = -23.55 ± 0.12 fm

a_t = +5.35 ± 0.06 fm

consistent with the values deduced previously from σ_t and σ_s. There are several other experiments that are sensitive to the singlet and triplet scattering lengths; these include neutron diffraction by crystals that contain hydrogen (such as hydrides) as well as the total reflection of neutron beams at small angles from hydrogen-rich materials (such as hydrocarbons). These techniques give results in good agreement with the above values for a_s and a_t".

The theory we have outlined is valid only for l = 0 scattering of low-energy incident particles. The *l* = 0 restriction required particles of incident energies below 20 MeV, while our other low energy approximations required eV or keV energies. As we increase the energy of the incident particle, we will violate σ long before we reach energies of 20 MeV. We therefore still have *l*= 0 scattering, but at these energies (of order 1 MeV) equations $\psi_{\text{scattered}} \approx A\frac{\delta_0}{k}\frac{e^{ikr}}{r} = -Aa\frac{e^{ikr}}{r}$ *are* not valid. This case is generally treated in the effective range approximation, in which we take

$$k \cot \delta_0 = 1/a + 1/2\, r_0 k^2 + \ldots$$

and where terms in higher powers of *k* are neglected. The quantity *a* is the zero-energy scattering length we already defined (and, in fact, this reduces to $a = \pm\lim_{k\to 0}\frac{\sin\delta_0}{k}$ in the *k* ~ 0 limit), and the quantity r_0 is a new parameter, the *effective range.* One of the advantages of this representation is that *a* and r_0 characterize the nuclear potential independent of its shape; that is; we could repeat all of the calculations done in this section with a potential other than the square well, and we would deduce identical values of *a* and r_0 from analyzing the experimental cross sections. Of course there is an accompanying disadvantage in that we can learn little about the shape of the nuclear potential from an analysis in which calculations with different potentials give identical results!

Like the scattering lengths, the effective range is different for singlet and triplet states. From a variety of scattering experiments we can deduce the best set of l= 0 parameters for the neutron-proton interaction:

a_s = -23.715 ± 0.015 fm

r_{0s} = 2.73 ± 0.03 fm

a_t = 5.423 ± 0.005 fm

r_{0t} = 1.748 ± 0.006 fm

As a final comment regarding the singlet and triplet neutron-proton interactions, we can try to estimate the energy of the singlet n-p state relative to the bound triplet state a_t - 2.22 MeV. Using Equations we would deduce that the energy of the singlet state is about + 77 keV. Thus the singlet state is only slightly unbound.

4.8 Self Learning Exercise II

Q.1 Which state is known as triplet state.

Q.2 Define scattering length and its physical significance.

Q.3 Explain that the nuclear force must be spin dependent.

Q.4 Discuss Coherent scattering of neutrons by protons in ortho and Para hydrogen molecules.

4.9 Summary

In this chapter we have discussed n-p scattering at low energies with square well potential. We also discussed that the nuclear forces are spin dependent i.e., nuclear forces not only depend upon the separation distance but also upon the spin orientations of two nucleons. They are independent of the shape of nuclear potential.

4.10 Glossary

Angular Momentum : A measure of the momentum of a body in rotational motion about its centre of mass. Technically, the angular momentum of a body is equal to the mass of the body multiplied by the cross product of the position vector of the particle with its velocity vector. The angular momentum of a system is the sum of the angular momenta of its constituent particles, and this total is conserved unless acted on by an outside force.

Neutron : One of the two main building blocks (along with the proton) of the nucleus at the centre of an atom. Neutrons have essentially the same mass as a proton (very slightly larger) but no electric charge, and are made up of one "up" quark and two "down"quarks. The number of neutrons in an atom determines theisotope of an element. Outside of a nucleus, they are unstable and disintegrate within about ten minutes.

Nucleus: The tight cluster of nucleons (positively-charged protons and zero-charged neutrons, or just a singleproton in the case of hydrogen) at the centre of an atom, containing more than 99.9% of the atom'smass. The nucleus of a typical atom is about 100,000 smaller than the total size of the atom(depending on the individual atom).

Proton : One of the two main building blocks (along with the neutron) of the nucleus at the centre of an atom. Protons carry a positive electrical charge, equal and opposite to that of electrons, and are made up of two "up" quarks and one "down" quark. The number of protons in an atom's nucleus determines its atomic number and thus which chemical element it represents.

Spin: Spin is a characteristic property of elementary particles

4.11 Answers to Self Learning Exercise

Answers to Self Learning Exercise-I

Ans.1: When an intense and collimated beam of nucleons is born barded on target nuclei the interactions between incident nucleus and target nuclei takes place. The interaction does not change the incident particles, *i.e.,* incoming and outgoing particles are the same. The change is in the path of incoming nucleons, *i.e.,* they are deviated from their original path. This process is known as scattering

Ans.2: section 4.2

Ans.3: $\left[\nabla^2 + \frac{M}{h^2}\{E - V(r)\}\right]\psi = 0$

Answers to Self Learning Exercise-II

Ans.1: The state of parallel spins is called triplet state.

Ans.2: 'a' has the geometrical significance of being the radius of a hard sphere surrounding the scattering center from which neutrons are scattered and so has the dimensions of length, hence the name scattering length.

$$a = \lim_{k\to 0}\left(-\frac{\sin\delta_0}{k}\right);$$

Ans.3: $\sigma_0 = \frac{3}{4}\sigma_{t,0} + \frac{1}{4}\sigma_{s,0}$

where σ_t= 4.6 b and σ = 20.4 b (for the low-energy cross section), we deduce σ_s = 67.8 b

This calculation indicates that there is an enormous difference between the cross sections in the singlet and triplet states that is, the nuclear force must be spin dependent.

4.12 Exercise

Q.1 Write short note on scattering length.

Q.2 Discuss Neutron-proton scattering at low energy.

References and Suggested Readings

1. Elementary Nuclear Theory by Bethe and Morrison.
2. The Atomic Nucleus by R D. Evans.
3. Atomic and Nuclear Physics by Brijlal and Subhraininyan.
4. Nuclear Physics by D. C Tayal.
5. Nuclear Physics by Irving Kaplan.
6. Introductory Nuclear Physics by Kenneth S. Krane

UNIT-5
Nucleon-Nucleon Scattering and Potentials : Part-II

Structure of the Unit

5.0 Objectives

After interacting with the material presented here students will be able to understand

- Hamada- Johnston hard core potential
- Reid hard core and soft core potentials and
- One boson Exchange Potentials

5.1 Introduction

The interaction between two nucleons is basic for all of Nuclear Physics. The traditional goal of Nuclear Physics is to understand properties of atomic nuclei in terms of the "bare" interaction between pairs of nucleons. With starting of Quantum Chromo Dynamics (QCD), it became clear that the NN interaction is not fundamental. Nevertheless, even today, in any approach towards a nuclear structure problem, one assumes the nucleons to be elementary particles. The failure or success of this approach may then teach us something about the relevance of sub nuclear degrees of freedom. A large number of physicists, all over the world, have investigated the NN interaction for the past 70 years. This interaction is the empirically best known piece of strong interactions; in fact, for no other sample of strong force a comparable amount of experimental data has been accumulated. The oldest attempt to explain the nature of the nuclear force is due to Yukawa. According to this theory massive bosons (mesons), mediate the interaction between two nucleons. Although, in the light of QCD, meson theory is not perceived as fundamental anymore, the meson exchange concept continues to represent the best working model for a quantitative Nucleon-Nucleon potential. Most basic questions were settled in the 1960's and 70's such that in recent years we could concentrate on the subtleties of this peculiar force.

5.2 Boson Exchange Potentials

The potential acting between a pair of particles due to the exchange of a meson has a range of the order of the meson Compton wavelength that is inversely proportional to the meson mass. Since the π meson is the lightest boson that can be exchanged between a pair of nucleons, the OPEP determines the long-range part (beyond the pion Compton wavelength) of the two-nucleon potential. If one wants information on the two-nucleon potential at intermediate- and short-ranges, one is then faced with the computation of the potential arising from the exchange of the heavier bosons and two, three,… pions. Since this computation is comparatively more difficult, thus at the potentials constructed based on symmetries (e.g., Breit and coworkers potential), it is determined phenomenologically; while at the meson theory of the two-nucleon potential, these exchanges are considered explicitly. It is understood that multi-meson systems most often have strongly correlated resonance states behaving as a single boson. It is therefore speculated that some of these multi-meson resonances, when exchanged between two nucleons may dominate the intermediate- and short-range behavior of the two-nucleon potential. The potential computed in this way is called the one-boson-exchange potential (OBEP). Besides the exchange of one π meson, also other exchanges have been explicitly considered in the OBEP. A main difference amongst workers on the meson theoretic two-nucleon potential lies in their manner of treatment of the two-pion system. An approach in which the effect of the two-pion system is parameterized through one or two isoscalar (T=0), scalar (J=0) mesons is one such treatment. In another development of the theory, the effect of the S-state of the two-pion system is parameterized through the scattering length and effective range. In yet another attempt the effect of two-pion continuum is considered in more detail and the resultant potential taken into account explicitly. Various authors also differ in the details of their method of computing the potential. Broadly speaking, conventional field-theoretical techniques and the dispersion theoretic method are the two principal methods of solving the problem that we do not express these methods in details here. Therefore, in other words, the boson exchange potentials are based on effective field theory and are expanded to nucleon-nucleon, pion-nucleon, and pion-pion interactions. These models do not any reference to QCD, but the baryon and meson fields have been considered as the asymptotic states that absorb all effects from quark-gluon dynamics. The discovery of the spin-one or vector mesons ρ and ω with the masses around 770-780 MeV was provided a progress and led to the expansion of the OBE potentials. In these models, the unrelated single exchange contributions of the pseudoscalar mesons π (138) , η (549) and the vector mesons ρ (769), ω(783) as well as the scalar meson δ (983) have been considered and iterated into the scattering equation. In addition, the two-pion exchange associated with the fictional scalar sigma meson with the masses around 400-800 MeV was demonstrated. The core region was finally parameterized by the phenomenological form factors related to the meson-nucleon vertices. Finally, those form factors formed the substructure of QCD. Such OBE potentials provided the first quantitative approximation of data. Many models of these potentials exist that each have owns definite and separable features. It is now known that these are the standard NN potentials, of course. A few examples are

Nijmegen, Paris, and Bonn potentials. Broadly speaking, in this quark-antiquark pair (=meson) exchange model, we have the following features:

a. It is similar to quark exchange (just reverse direction of one quark).
b. It gives a very good description of many aspects of NN potential.
c. It is preferred because meson states are color-neutral and have relatively low mass (larger range).
d. It studies OPEP and generalizes to other mesons- so far only model that gives perfect agreement with data, especially for long-range part.

5.3 Basic Potentials

The range of the nucleon-nucleon interaction is divided to the three parts: the short-range ($r \leq 1$ fm), the intermediate-range (1 fm$\leq r \leq 2$ fm), and the long range ($r \geq 2$ fm). For the long-range part, one-pion exchange (OPE) has usually been considered. The short-range part has often been discussed phenomenologically; in some models, form factors are introduced to regularize the potential at the origin whereas in other models a hard core is used. The first logical approach to describe the intermediate-range region was to include the two-pion exchange (TPE) contributions. However, these TPE models, did not give a satisfactory description of the NN scattering data, mainly due to a lack of a sufficient spin-orbit force. Gammel, Christian, and Thaler hinted the necessity of a spin-orbit force, when they tried to fit all of the data available at that time with a phenomenological velocity dependent (local) potential as:

$$V = V_C(r) + V_T(r)\, S_{12}$$

for each of four spin and isospin combinations and they failed. In 1975, the simultaneous construction of the purely phenomenological potentials by Gammel-Thaler and the semi-phenomenological Singell-Marshak potential, where both models introduced phenomenological spin-orbit potentials, began. The Gammel-Thaler model gave a good fit to scattering data up to 310 MeV. The Singell-Marshak model, consisting of the TPE Gartenhaus potential together with a phenomenological spin-orbit force, was successful up to 150 MeV. Okubo-Marshak showed that the most general two nucleon potential, considering symmetry conditions, is as follows:

$$V(r,\sigma_1,\sigma_2,\tau_1,\tau_2) = V_0(r) + V_\sigma(r)(\sigma_1.\sigma_2) + V_\tau(r)(\tau_1.\tau_2) + V_{\sigma\tau}(r)(\sigma_1.\sigma_2)(\tau_1.\tau_2)$$
$$+V_{LS}(r)(\tau_1.\tau_2) + V_{LS\tau}(r)(L.S)(\tau_1.\tau_2)$$
$$+V_T(r)S_{12} + V_{T\tau}(r)S_{12}(\tau_1.\tau_2)$$
$$+V_Q(r)Q_{12} + V_{Q\tau}(r)Q_{12}(\tau_1.\tau_2)$$
$$+V_{pp}(\sigma_1.p)(\sigma_2.p) + V_{pp\tau}(r)(\sigma_1.p)(\sigma_2.p)(\tau_1.\tau_2)$$

where L, S, and Q_{12} are spin-orbit and quadratic spin-orbit- operators, respectively.

$$Q_{12} = \frac{1}{2}\{(\sigma_1.l)(\sigma_2.l) + (\sigma_2.l)(\sigma_1.l)\}$$

Twelve terms are given by twelve radial functions $V_0(r)$, ... We can obtain the V(r)'s from our knowledge from the basic nature of the nuclear force such as the meson exchange and or from the semi-empirical procedure by fitting some assumed forms of the radial dependence to experimental data. When our understanding of QCD is fully developed in the future, it will be possible to determine these functions from first principles. The first four terms are the central force terms and in this case, L and S are the good quantum numbers. In the presence of the other terms, two-nucleon system is invariant only in the combined space of L and S labeled by J;

$$V_{ls}(r) = V_{LS}(r)L.S + V_{LS\tau}(L.S)(\tau_1.\tau_2)$$

The reason for these two terms comes from the possibility that the radial dependence of the isospin-dependent and of the isospin-independent parts may be different from each other, for example as the result of different mesons being exchanged. The six and the seven terms are the tensor force. The ninth and the tenth quadratic spin-orbit terms enter only when there is momentum dependence in the potential. The last two terms are often dropped since for elastic scattering, they can be expressed as a linear combination of other terms. Their contributions therefore cannot be determined using elastic scattering, for which most of our information on NN interaction is derived. Then, soon after, better potential forms were constructed. Some examples are Hamada-Johnston, Yale, and the various hard- and soft-core models constructed by Reid. Before going into the treatment of other potentials, it is useful to mention that most of the experimental elastic phase shifts are extracted from the pp and np differential cross sections. In these models, the data are fitted up to the energy range 0-350 MeV, because, as already mentioned, in higher energies (with the threshold 270 MeV) the pion production and other relativistic effects become important and the Schrödinger two-nucleon equation is therefore no longer sufficient.

Hamada-Johnston and Yale group potentials reproduce all the two-body scattering data (including the polarization parameters) as a function of energy over the energy range of several hundred MeV. The Yale potential was especially designed to reproduce the phase shifts in various two-nucleon states as smooth functions of energy. As a first step, the phase parameters (phase shifts, and the mixing parameter in the case of coupled states) were determined as a function of energy by direct fit to all the scattering and polarization data. The setting up of the potential with its parameters adjusted to reproduce the phase parameters may be regarded as the second step in this type of work. The first step, namely the determination of the phase parameters as a function of energy has been practiced very efficiently by several groups of workers including the Yale, Livermore, and other- teams. The actual procedure, now almost standardized, entails expressing the scattering amplitude as the sum over partial waves up to a certain maximum orbital angular momentum $l_{\max}$ (the usual value chosen for $l_{\max}$ is more or less 5). The contribution of all higher partial waves is then taken to be represented by the one-pion exchange contribution (OPEC) to the scattering amplitude. The Yale group took the OPEP as a given component of the potential and then determined the rest of the potential by fitting the energy-dependence phase parameters up to l_{max}.

5.4 Hamada-Johnston Potential

The Hamada-Johnston (HJ) potential is a leading phenomenological NN (pp+np here) energy-independent potential. It described well the scattering data below 350 MeV and deuteron properties as well as the effective-range parameters. The general form of HJ potential reads

$$V = V_c(r) + V_t(r)S_{12} + V_{ls}(r)L.S + V_{ll}L_{12},$$

where

$$S_{12} = 3(\sigma_1.r)(\sigma_2.r) - (\sigma_1.\sigma_2),$$
$$L_{12} = (\delta_{lj} + \sigma_1.\sigma_2)L^2 - (L.S)^2$$

and

$$V_c(r) = 0.08(\frac{1}{3}m_{pi})(\tau_1.\tau_2)(\sigma_1.\sigma_2)Y(x)[1 + a_c Y(x) + b_c Y^2(x)]$$

$$V_t(r) = 0.08(\frac{1}{3}m_{pi})(\tau_1.\tau_2)Z(x)[1 + a_t Y(x) + b_t Y^2(x)]$$

$$V_{ls}(r) = m_{pi} G_{ls} Y^2(x)[1 + b_{ls} Y(x)]$$

$$V_{ll}(r) = m_{pi} G_{ll} x^{-2} Z(x)[1 + a_{ll} Y(x) + b_{ll} Y^2(x)]$$

in which m_{pi}, x and M are the pion mass (139.4 MeV), the inter nucleon distance measured in the units of the pion Compton's wavelength (r_0 = 1.415 fm), and the nucleon mass (taken to be 6.73µ), respectively. Note that

$$x = \mu r,\ \mu = m_{pi}c/h = r^{-1}_0$$

$$Y(x) = \frac{e^{-x}}{x}, Z(x) = \left(1 + \frac{3}{x} + \frac{3}{x^2}\right)Y(x)$$

We should note that the quadratic spin-orbit potential was mainly introduced to describe np data satisfactorily.

For the r large enough, $V_c(r)$ and $V_t(r)$ reduce to the well-known OPEP with the pseudo vector coupling constant of 0.08.

The coefficients a_c, b_c, a_t and b_t represent the potential diversion from OPEP at small r's.

- G_{ls} is the strength of the short ranged spin orbit potential $V_{ls}(r)$ and is depended on the parity of state.
- G_{ll}, as the strength of $V_{ll}(r)$, originated from special evaluations, is determined phenomenologically.

All the coefficients are determined from the detailed fit to scattering data.

The hard cores are considered for all states with their radius at x_c = 0.343. The HJ potential, as originally proposed, included a strong long-range quadratic spin-orbit potential in triplet even states, and also a strong short-range spin-orbit potential in triplet (*l* = j)-odd states, where it is known that the latter does not exist. So, the potential for triplet-odd states was modified as follows: It was defined to be -0.26744 m_{pi} around $x_c < x \leq 0.487$ and by above standard relations for $x > 0.487$. The values of the binding energy, electric quadratic moment, effective-range, D-state probability and the asymptotic D-wave to S-wave ratio of deuteron were determined by the potential to be 2.226 MeV, 0.285 fm^2, 1.77 fm, 6.97 % and $A_D/A_S = 0.02656$, respectively.

An improvement of HJ potential was made in (we call it Massachusetts-group potential) to replace mainly the HJ hard cores (for $x \leq x_c$) by finite square-well cores. Outside the square-well radius (for $x > x_c$), the potential is the same as HJ except for a few changes in parameters such as considering the pion mass differences, and that the a_c values of the singlet even and triplet-odd states as well as the triplet-odd b_c are changed slightly. The pion mass splitting leads to charge-independent breaking (CIB) while CS is still preserved. Now, m_{pi} is replaced by the effective pion mass and $x_c = 0.4852$, which in turn implies the larger coreradius of 0.7 fm. Describing NN scattering data and deuteron properties with the potential were good. Indeed, the main aim to form the latter potential was to show that the hard cores were not necessary since all data could be described by the finite soft-core potentials.

5.5 Yale-Group Potential

The Yale-group potential is a pp+np phenomenological potential similar to HJ potential that is fitted to its time phase parameters as well. There, an one pion exchange potential (OPEP) is included directly and the quadratic spin-orbit potential is considered in a somewhat different form than that of HJ. The whole NN potential reads

$$V = V^{(2)}{}_{OPEP} + V_c(r) + V_t(r)S_{12} + V_{ls}(r)L.S + V_{ql}[Q_{12} - (L.S)^2],$$
$$[Q_{12} - (L.S)^2] = (L.S)^2 + L.S - L^2$$

where

$$V^{(2)}{}_{OPEP}(r) = \left(\frac{g^2_{pi}}{12}\right) m_{pi} c^2 \left(\frac{m_{pi}}{M}\right)^2 (\tau_1.\tau_2)[(\sigma_1.\sigma_2) + S_{12}[1 + \frac{3}{x} + \frac{3}{x^2}]\frac{e^{-x}}{x}$$

This OPEP is used for the distances larger than nearly 3fm, with the same parameter definitions as in HJ potential. For the coupling constant, $g^2_{pi}/14 = 0.94$ is used in singlet-even states and 1 elsewhere. For singlet-even and triplet-odd states, the neutral-pion mass ($m_{pi} = m_{\pi 0}$) is used while for singlet-odd and triplet-even states, a mean of the charged- and neutral-pion masses [$m_{pi} = (m_{\pi 0} + 2m_{\pi\pm})/3$] is used. The hard-core radius is considered at $x_c = 0.35$, and except in the OPEP part, all the radial functions V_c, V_t, V_{ls} and V_{ql} are taken as

$$V = \sum_{n=1}^{7} a_n \frac{e^{-2x}}{x^n}$$

The potential's parameters are determined by fitting to data for various states and involved potentials. It is also notable that HJ and Yale potentials are OPEP for L > 5, and that the Yale potential sets $V_{ls} = 0$ for J> 2.

5.6 Reid68 and Reid-Day Potentials

Reid68 Potential

Among the failures of HJ and Yale hard-core potentials were that they could not reproduce reasonable results when applying to many-body calculations. It appeared that the **Reid soft-core potentials** were better.

The Reid potentials are static and local phenomenological potentials similar to those of HJ and Yale. Reid determined the potential for each two-nucleon state independent of the other states. So, one may suppose that this approach is problematic in that, with many two-nucleon states each with its own potential, fitting the experimental data could be probably meaningless. But, because the highest energy in the analyses was about 350 MeV, just the two-nucleon states with $J \leq 2$, which are more important in nuclear calculations, were considered in practice.

Reid used only a central potential in the singlet and uncoupled triplet-states while, for the coupled triplet-states, he used

$$V = V_c(r) + V_t(r)S_{12} + V_{ls}(r)L.S$$

which has the central, tensor and usual spin-orbit components. For the LR part, he used the OPEP of as a tail attached to the potential, with $g^2_{pi} = 14$, $m_{pi} = 138.13$ MeV, M = 938.903 MeV and $\mu = 0.7\text{fm}^{-1}$. On the other hand, to remove the x^{-2} and x^{-3} behaviors at small distances, an short range [SR] potential was subtracted from the tensor part of the potential. For the medium range [MR's], the potentials were expressed as the sums of the Yukawa's functions of e^{-nx}/x, where n was an integer. The SR repulsions were also some combinations of the severe hard-core and the

Yukawa soft-core potentials–It is mentionable that the criterion for a potential to be soft-core is that the wave functions do not vanish in nonzero radiuses. For the hard-core radius, when needed, the radiuses of $x_c \leq 0.1$ could be used there. One should, of course, note that because of fitting the potentials to the energies often below 350 MeV, finding a unique formalism for the SR part was almost difficult. Finally, it is notable that the Reid potentials did not describe well some of the scattering data and deuteron properties at that time. It was also hinted the need for velocity-dependence and non locality in NN potentials, imposed by experimental data.

Reid-Day Potential

The Reid68 soft-core potentials up to the higher partial waves to solve three-body equation in nuclear matter calculations. In fact, he used three two-nucleon potentials in calculations. The first one (called V_2) was just the central part of the Reid68 potential in $3S_1 - 3D_1$ channel for all states. The second one (called V_6(Reid)) had four forms for the four (S,T) states. Indeed, in the latter case, for all S = 0 states, just two central $V_c(r)$ potentials (Reid68 $1S_0$ and $1P_1$ for T = 1 and T = 0 respectively) were used; meanwhile for all S = 1 states, just two central $V_c(r)$ and two tensor $V_t(r)$ potentials (Reid68 $3P_2 - 3F_2$ and $3S_1 - 3D_1$ for T = 1 and T = 0 respectively) were used. The third one (called Full-Reid potential that we call Reid-Day potential) used the original Reid68 potentials for all J $\leq$ 2 states; meanwhile for the states with J $\geq$ 3, he set up the potentials based on the Reid68 ones almost roughly. Clearly, for the states up to J = 5, the potential structures were similar to the original Reid68 ones. For example, in the coupled sate of $3D_3 - 3G_3$, he used

$$V_c(r) = -10.463Y(x) - 103.4Y^2(x) - 419.6Y^4(x) + 9924.3Y^6(x)$$

$$V_t(r) = -10.463\left[Z(x) - \left(\frac{12}{x} + \frac{3}{x^2}Y^4(x)\right)\right] + 351.77Y^4(x) - 1673.5Y^6(x)$$

$$V_{ls}(r) = 650Y^4(x) - 5506Y^6(x)$$

where x = 0.7r, and r is the inter nucleon distance measured in fm as usual. For all other not clearly mentioned states, he used the V_6(Reid) potentials. Therefore, that new expansion was not based on any fundamental underlying argument on NN interaction, and was just to sake of applying the wanted potentials in some nuclear calculations.

5.7 Self Learning Exercise -I

Q.1 What is the extra term which included in Yale potential over HJ potential

Q.2 What is the physical significance of Compton wavelength?

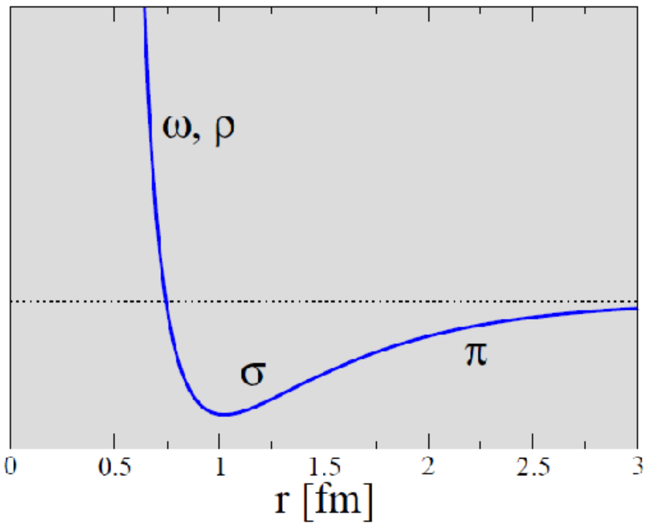
Q.3 Write down the different range of nucleon-nucleon interaction.

Q.4 Write down the expression for HJ potential.

Q.5 What is the failure of HJ and Yale potential.

5.8 One Boson Exchange Potential

The nucleon-nucleon (NN) interaction has a complex structure as schematically depicted in figure.



The central part of the nucleon-nucleon potential consists of a short range repulsive part, an intermediate range attractive and a long range part. In modern relativistic potentials based on field theory this interaction is described by the exchange of various mesons which act as exchange bosons. The most important are the non-strange mesons π, ρ, ω and σ. The total NN-interaction is given by the superposition of the contributions from the various mesons. These contributions are characterized by the coupling strength g_i, the meson mass m_i and the character of the meson which determines the Lorentz structure of the meson nucleon vertex Γ_i (scalar, vector, . . .).

Coupling strength: g_i with sign attractive +

repulsive –

Meson mass: m_i determines the range

Meson-nucleon vertex: Γ_i determines the Lorentz structure

First of all we give a short overview of the different mesons and the corresponding coupling properties:

- π-meson: m_π = 138 MeV, spin S=0, isospin I=1

  pseudoscalar coupling where the tensor force is the most important part, long range interaction

  $$L_{\pi NN} = \frac{f}{m_\pi}\overline{\psi}(x)i\gamma_5\vec{\tau}\psi(x)\overline{u}(x)$$

- σ-meson: $m_\sigma \approx$ 550MeV , S=0, I=0

  scalar coupling, attractive, intermediate range interaction

  $$L_{\sigma NN} = g_\sigma \overline{\psi}\psi(x)\phi(x)$$

- ω-meson: m_ω = 783 MeV, S=1, I=0

  vector coupling, repulsive, short range interaction

  $$L_{\omega NN} = -g_\omega \overline{\psi}\gamma_\mu \psi(x)\omega^\mu(x)$$

- ρ-meson: m_ρ = 770 MeV, S=1, I=1

  vector and tensor coupling, short range interaction

  $$L_{\rho NN} = -g_\rho \overline{\psi}(x)\gamma_\mu \vec{\tau}\psi(x)\rho^\mu(x) + \frac{g_\rho{}^T}{2M}\overline{\psi}(x)\sigma_{\mu\nu}\vec{\tau}\psi(x)\partial^\nu \rho^\mu(x)$$

Mesons with isospin I = 1 are isovector particles and couple to the isospin of the nucleon, i.e. they distinguish between protons and neutrons, mesons I = 0 are isoscalar and do not distinguish. The ρ-meson has a vector coupling and a tensor coupling. The pion nucleon coupling strength f is determined by some fundamental QCD relations (Effective chiral QCD Lagrangian). For all other mesons the coupling strengths g_i are fixed from empirical nucleon-nucleon scattering data.

Modern Boson-Exchange potentials describe NN-scattering data with high precision. Such potentials were developed in the mid eighties. Typical examples are the so-called Bonn and Nijmegen potentials developed by the Bonn-Julich and the Nijmegen (Netherlands) research groups. In addition to the mesons discussed above such potentials contain in addition an isoscalar pseudoscalar meson, the so-called η -meson, and an isovector scalar meson, the so-called δ-meson. Thus they are based on a complete set of non-strange mesons (mesons which have no strange quark content) with masses below 1 GeV. The model parameters, i.e. the meson-nucleon coupling strengths (and additional parameters for form factors) are fitted to NN-scattering data (about 3000 data points for proton-proton and proton-neutron scattering).

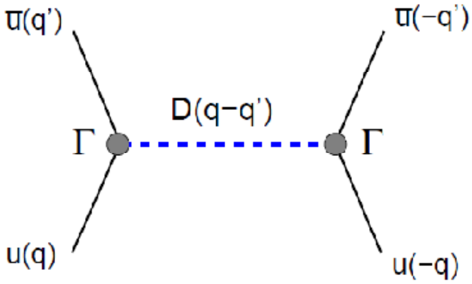


Figure 2: Schematic representation of the one-boson exchange diagram.

Spin-structure of one-boson-exchange potentials

An expansion in 1/M to leading order yields the non-relativistic form of the scalar and vector potentials.

1. Scalar potential, generated by the σ-meson

$$V_s(r) = -\frac{g_s^2}{4\pi}\frac{e^{-m_s r}}{r} + \frac{g_s^2}{4\pi}\frac{1}{2M^2 r^2}\frac{d}{dr}\left(\frac{e^{-m_s r}}{r}\right)L.S$$

   where S = 1/2 ($\sigma_1 + \sigma_2$) is the total spin and L the total angular momentum of the two-nucleon system.

2. Vector potential, represented by ω- and ρ-mesons

$$V_V(r) = -\frac{g_V^2}{4\pi}\frac{e^{-m_V r}}{r} + \frac{g_v^2}{4\pi}\left(3+4\frac{g_T}{g_v}\right)\frac{1}{2M^2 r^2}\frac{d}{dr}\left(3+4\frac{g_T}{g_v}\right)L.S$$

$$+\frac{g_v^2}{4\pi}\left(1+\frac{g_T}{g_v}\right)^2\frac{m_V^2}{4\pi}(\sigma_1\times\nabla)(\sigma_2\times\nabla)\frac{e^{-m_V r}}{r}$$

Momentum space representation of the OBE potentials

We want now first to evaluate the Feynman-diagram which corresponds to a one-meson exchange. For the moment we disregard the isospin. In the two-nucleon center-of-mass system the incoming nucleons have momenta ±q, the outgoing nucleons have momenta ±q ′. The nucleons are on-shell and therefore we have

$$E = \sqrt{M^2 + q^2}$$
$$E' = \sqrt{M^2 + q'^2}$$

Since we consider only elastic scattering, energy-momentum conservation implies

$$|q'| = |q|$$
$$E = E'$$

Applying the Feynman rules for evaluating the meson exchange potential $V_\alpha(q,q')$ where the index α stands for the various types of possible mesons exchanged

$\alpha = \pi, \sigma, \rho, \cdots$, one finds

$$V_\alpha = g_1 u_1(q')\Gamma_1 u_1(q) D_\alpha(q-q') g_2 u_2(q')\Gamma_2 u_2(q)$$

D_α represents the meson propagator. The meson propagator is different for (pseudo)-scalar and vector particles and reads

$$D_\alpha = \frac{P_\alpha}{(q-q')^2 - m_\alpha^2}$$

where P_α depends on the type of interchanged meson:

$$P_\alpha = \begin{cases} 1 & \text{(pseudo) scalar meson: } \sigma, \pi \\ -g^{\mu\nu} & \text{vector meson: } \omega, \rho \end{cases}$$

The $\Gamma_{1,2}$ matrices are the so-called vertex-functions or meson-nucleon couplings which are given by

Particle :	σ– meson	Pion	ω – meson
Γ :	1	γ_5	γ^μ .

We now give a basic example to illustrate our findings. Consider the case that a scalar meson (σ) is exchanged. This is the simplest example, but the other amplitudes can be evaluated in an analogous way. We discuss elastic, i.e. on-shell scattering with

$$E = E'.$$

In this case V_σ becomes

$$V_\sigma(q) = g_\sigma^2 \frac{u_1(q')u_1(q)u_2(-q')u_2(-q)}{-(q'-q)^2 - m_\sigma^2}$$

To compute V_σ, we use

$$\begin{aligned} u_1(q')u_1(q) &= u_1^\dagger(q')\gamma^0 u_1(q) \\ &= \sqrt{\frac{(E'+M)(E+M)}{4EE'}}\left(1, \frac{-\sigma.q'}{E'+M}\right)\begin{pmatrix} 1 \\ \frac{-\sigma.q'}{E'+M} \end{pmatrix} \\ &= \frac{E+M}{2E}\left(1 - \frac{q'.q + i\sigma_1.(q'\times q)}{(E+M)^2}\right) \end{aligned}$$

and we insert following relation

$$(\sigma.a)(\sigma\cdot b) = a\cdot b + i\,\sigma\cdot(a\times b)\,.$$

Now we introduce the momentum transfer

$$k \equiv q' - q$$

and the center-of-mass momentum

$$P = 1/2(q + q')$$

The vector product reads in terms of c.m. momentum and momentum transfer

$$n = q \times q' \equiv P \times k\,.$$

Furthermore, in the nonrelativistic limit with $E \cong M$, one obtains

$$E = \sqrt{M^2 + q^2} = M\left(1 + \frac{q^2}{2M^2} + \ldots\right)$$

The total matrix element for the scalar σ exchange contains two vertices of type $\bar{u}u$ and the meson propagator. The latter is taken in its static form $(-1)/(k^2 + m^2)$. Altogether, this yields in the non-relativistic limit, the scalar potential of form

$$V_\sigma(k) = -\frac{g_\sigma^2}{k^2+m_\sigma^2}\left[1+\frac{\frac{1}{2}(\sigma_1+\sigma_2)(-i)k\times P}{2M^2}\right]$$

We recognize an attractive Yukawa potential and the spin-orbit potential which is the second term in brackets. It corresponds to O_4 of the complete operator expansion given below.

The complete OBE potentials as e.g. the Bonn potentials can be reduced to a nonrelativistic representation by expanding the full field-theoretical OBE Feynman amplitudes into a set of spin and isospin operators

$$V = \sum_i [V_i + V'_i \, \tau_1.\tau_2]O_i$$

The operators O_i obtained in this low energy expansion, assuming identical particle scattering and charge independence, are defined as

$$O_1 = 1$$
$$O_2 = \sigma_1.\sigma_2$$
$$O_3 = (\sigma_1.k)(\sigma_2.k)$$
$$O_4 = \frac{i}{2}(\sigma_1+\sigma_2).n$$
$$O_5 = (\sigma_1.n)(\sigma_2.n)$$

Where

$k = q' - q$,

$n = q \times q' \equiv P \times k$

and $P = 1/2\,(q + q')$ is the average momentum.

The potential forms V_i are then functions of k, P, n and the energy. In order to perform a non-relativistic reduction, usually the energy E is expanded in k^2 and P^2

$$E(q) = (k^2/4 + P^2 + M^2)^{1/2} \simeq M + k^2/8M + P^2/2M$$

and terms to leading order in k^2/M^2 and P^2/M^2 are taken into account. The meson propagators $D_\alpha(k^2)$ are approximated by their static form $(-1)/(k^2+m^2)$.

$$O_1 = 1$$
$$O_2 = \sigma_1.\sigma_2$$
$$O_3 = S_{12} = 3(\sigma_1.r)(\sigma_2.r) - \sigma_1.\sigma_2$$
$$O_4 = L.S$$
$$O_5 = Q_{12} = \frac{1}{2}[(\sigma_1.L)(\sigma_2.L) + (\sigma_2.L)(\sigma_1.L)]$$

These operators are the well known central, spin-spin, tensor, spin-orbit and quadratic spin-orbit operators, respectively. The total angular momentum is denoted by L = r × P and the total spin S = 1/ 2 (σ_1 +σ_2).

5.9 Self Learning Exercise-II

Q.1 Draw the schematic diagram of nucleon-nucleon (NN) interaction.

Q.2 Give a short overview of different mesons and corresponding coupling properties.

Q.3 Explain the momentum space representation of the OBE potential.

5.10 Summary

In this chapter we discussed various types of nuclear potentials. This chapter started with the introduction of nuclear potentials and followed by HJ, Reid and OBEP.

5.11 Glossary

Nuclear force: The force that holds the nucleus together. Originally thought to be the exchange of pions, as suggested by Yukawa. Pions are now known to not be elementary themselves, but quarks which are held together by gluons.

Boson: A particle having spin that is an integer multiple of $\hbar$.

Meson: A particle (such as the pion) made of quark-antiquark pairs.

Interaction : Influence of a physical body on another body or the coupling between a field and its source. Interactions can be of the most diverse types, e.g. gravitational interaction, electromagnetic interaction, weak interaction, strong interaction.

5.12 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: OPEP

Ans.2: Compton wavelength is kind of the quantum mechanical cutoff - the length scale below which quantum mechanics can not be simply ignored in favor of classical approximations.

Ans.3: Range of the nucleon-nucleon interaction is divided to the three parts: the short-range ($r \leq 1fm$), the intermediate-range ($1fm \leq r \leq 2fm$), and the long range ($r \geq 2fm$).

Ans.4: Section 5.4

Ans.5: Failure of HJ and Yale hard-core potentials were that they could not reproduce reasonable results when applying to many-body calculations.

Answers to Self Learning Exercise-II

Ans.1,2,3: See Section 5.7

5.13 Exercise

Q.1 Write down the expression for OPEP.

Q.2 Write a short note on

- OBEP
- Hamada-Johnston Potential
- Reid potential

References and Suggested Readings

1. Advances in Nuclear Physics By Michel Baranger, Erich Vogt, 2012
2. Concepts of Nuclear Physics By Bernard Leonard Cohen, 1971.
3. The Nucleon-nucleon Interaction and the Nuclear Many-body Problem by Gerald E. Brown and T.T.S. Kuo 2010

UNIT-6
Interaction of Radiation and Charged Particle with Matter

Structure of the Unit

6.0 Objectives

From this chapter student should develop their understanding of the various ways photons, charged particles and neutrons can interact with matter and the concepts, such as mass attenuation coefficient, stopping power and range, that have been invented in order to aid that understanding. These ideas are the basis for the later study of the effects of x rays, gamma radiation and other ionizing radiations on living things.

6.1 Introduction

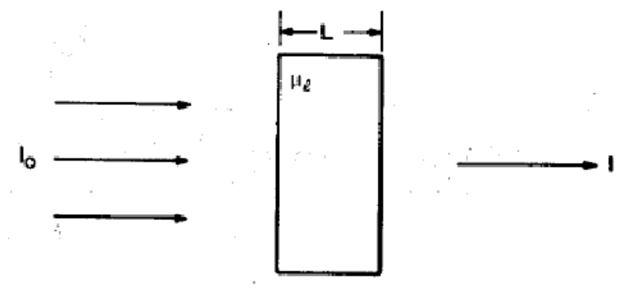
Gamma-rays, x-rays, neutrons, and neutrinos all have no net charge - they are electro-statically neutral. In order to detect them they must interact with matter and produce an energetic charged particle. In the case of gamma and x-rays, a photo-electron is produced. In the case of neutrons, a proton is given kinetic energy in a billiard ball like collision.

Knowledge of gamma-ray interactions is important to the Non Destructive Assayist(NDA) in order to understand gamma-ray detection and attenuation. A gamma ray must interact with a detector in order to be “seen.” Although the major isotopes of uranium and plutonium emit gamma rays at fixed energies and rates, the gamma-ray intensity measured outside a sample is always attenuated because of gamma-ray interactions with the sample. This attenuation must be carefully considered when using gamma-ray NDA instruments. This chapter discusses the exponential attenuation of gamma rays in bulk materials and describes the major gamma-ray interactions, gamma-ray shielding, filtering, and collimation. The treatment given here is necessarily brief.

6.2 Law of Absorption and Attenuation Coefficient

Gamma rays were first identified in 1900 by Becquerel and Villard as a component of the radiation from uranium and radium that had much higher penetrability than alpha and beta particles. In 1909, Soddy and Russell found that gamma-ray attenuation followed an exponential law and that the ratio of the attenuation coefficient to the density of the attenuating material was nearly constant for all materials

Law of Gamma-Ray Attenuation



$$I = I_0 e^{-\mu_\ell L}$$

Figure1

Figure1 illustrates a simple attenuation experiment. When gamma radiation of intensity I_0 is incident on an absorber of thickness L, the emerging intensity (I) transmitted by the absorber is given by the exponential expression

$$I = I_0 e^{-\mu_l L}$$

where μ_l is the attenuation coefficient (expressed in cm^{-1}). The ratio I/I_0 is called the gamma-ray transmission.

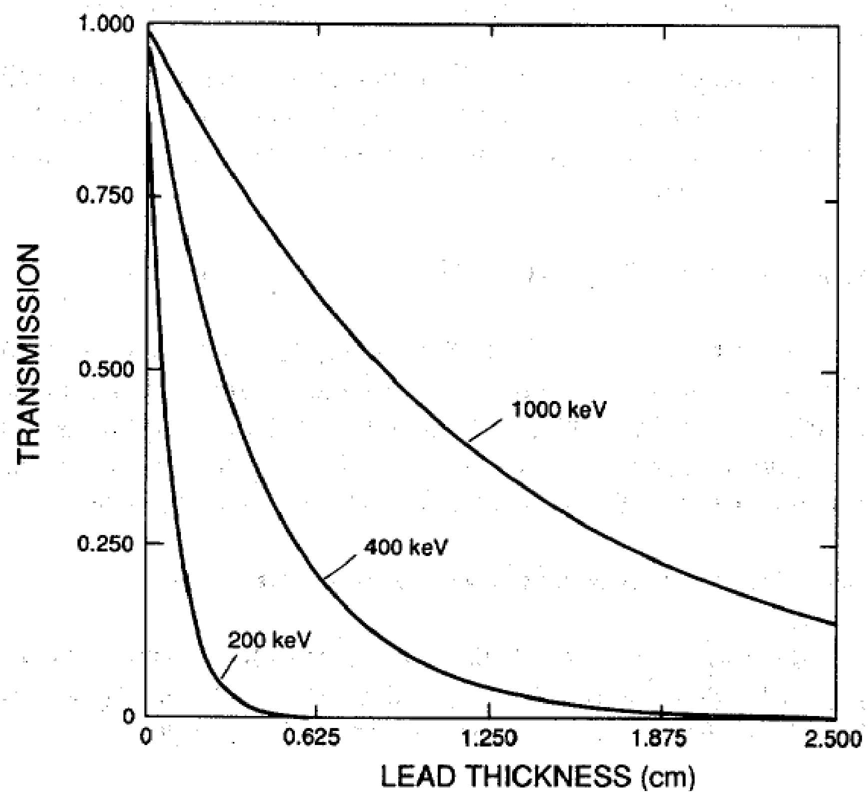


Figure 2

Figure illustrates exponential attenuation for three different gamma-ray energies and shows that the transmission increases with increasing gamma-ray energy and decreases with increasing absorber thickness. Measurements with different sources and absorbers show that the attenuation coefficient μ_l depends on the gamma-ray energy and the atomic number (Z) and density (ρ) of the absorber. The reciprocal of the attenuation coefficient $1/\mu_l$ has units of length and is often called the mean free path. The mean free path is the average distance a gamma ray travels in the absorber before interacting; it is also the absorber thickness that produces a transmission of l/e, or 0.37.

Mass Attenuation Coefficient

The linear attenuation coefficient is the simplest absorption coefficient to measure experimentally, but it is not usually tabulated because of its dependence on the density of the absorbing material. For example, at a given energy, the linear attenuation coefficients of water, ice, and steam are all different, even though the same material is involved.

Gamma rays interact primarily with atomic electrons; therefore, the attenuation coefficient must be proportional to the electron density P, which is proportional to the bulk density of the absorbing material. However, for a given material the ratio of the electron density to the bulk density is a constant, Z/A, independent of bulk density. The ratio Z/A is nearly constant for all except the heaviest elements and hydrogen.

$$P = Z \rho / A$$

where

P = electron density

Z = atomic number

ρ = mass density

A = atomic mass.

The ratio of the linear attenuation coefficient to the density (μ_l/ρ) is called the mass attenuation coefficient μ and has the dimensions of area per unit mass (cm^2/gm). The units of this coefficient hint that one may think of it as the effective cross-sectional area of electrons per unit mass of absorber. The mass attenuation coefficient can be written in terms of a reaction cross section, $\sigma(cm^2)$:

$$\mu = \frac{N_0 \sigma}{A}$$

where N_0 is Avagadro's number (6.02×10^{23}) and A is the atomic weight of the absorber. The cross section is the probability of a gamma ray interacting with a single atom. The mass attenuation coefficient, can be rewritten as

$$I = I_0 e^{-\mu\rho L} = I_0 e^{-\mu x}$$

$$x = \rho L$$

where $x \equiv mass\,thickness\left(\frac{cm^2}{gm}\right)$

6.3 Interaction Processes

The gamma rays interact with detectors and absorbers by three major processes: photoelectric absorption, Compton scattering, and pair production and fall in the range 10 to 2000 keV and. In the photoelectric absorption process, the gamma ray loses all of its energy in one interaction. The probability for this process depends very strongly on gamma-ray energy E_γ and atomic number Z. In Compton scattering, the gamma ray loses only part of its energy in one interaction. The probability for this process is weakly dependent on E and Z. The gamma ray can lose all of its energy in one pair-production interaction. However, this process is relatively unimportant for fissile material assay since it has a threshold above 1 MeV.

Photoelectric Absorption

A gamma ray may interact with a bound atomic, electron in such a way that it loses all of its energy and ceases to exist as a gamma ray (Figure3).

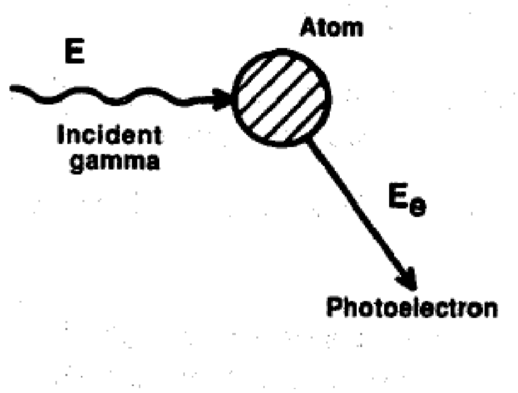


Figure 3

Some of the gamma-ray energy is used to overcome the electron binding energy, and most of the remainder is transferred to the free electron as kinetic energy. A very small amount of recoil energy remains with the atom to conserve momentum. This is called photoelectric absorption because it is the gamma-ray analog of the process discovered by Hertz in 1887 whereby photons of visible light liberate electrons from a metal surface. Photoelectric absorption is important for gamma-ray detection because the gamma ray gives up all its energy, and the resulting pulse falls in the full-energy peak.

The probability of photoelectric absorption depends on the gamma-ray energy, the electron binding energy, and the atomic number of the atom. The probability is greater the more tightly bound the electron; therefore, K electrons are most affected (over

80% of the interactions involve K electrons), provided the gamma-ray energy exceeds the K-electron binding energy. The probability is given approximately by Equation,

$$\tau \propto Z^4 / E^3$$

which shows that the interaction is more important for heavy atoms like lead and uranium and low-energy gamma rays:

where τ = photoelectric, mass attenuation coefficient.

This proportionality is only approximate because the exponent of Z varies in the range 4.0 to 4.8. As the gamma-ray energy decreases, the probability of photoelectric absorption increases rapidly. Photoelectric absorption is the predominant interaction for low-energy gamma rays, x rays, and bremsstrahlung.

The energy of the photoelectron E_e released by the interaction is the difference between the gamma-ray energy E_γ and the electron binding energy E_b:

$$E_e = E_\gamma - E_b$$

In most detectors, the photoelectron is stopped quickly in the active volume of the detector, which emits a small output pulse whose amplitude is proportional to the energy deposited by the photoelectron. The electron binding energy is not lost but appears as characteristic x rays emitted in coincidence with the photoelectron. In most cases, these x rays are absorbed in the detector in coincidence with the photoelectron and the resulting output pulse is proportional to the total energy of the incident gamma ray. For low-energy gamma rays in very small detectors, a sufficient number of K x rays can escape from the detector to cause escape peaks in the observed spectrum; the peaks appear below the full-energy peak by an amount equal to the energy of the x ray.

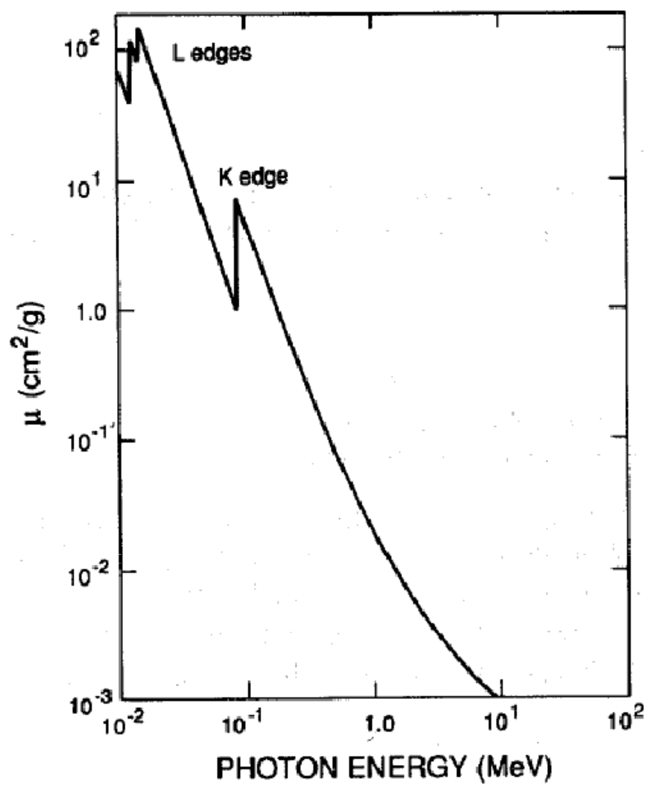


Figure 4

Figure shows the photoelectric mass attenuation coefficient of lead. The interaction probability increases rapidly as energy decreases, but then becomes much smaller at a gamma ray energy just below the binding energy of the K electron. This discontinuity is called the K edge below this energy the gamma ray does not have sufficient energy to dislodge a K electron. Below the K edge the interaction probability increases again until the energy drops below the binding energies of the L electron; these discontinuities are called the L_I, L_{II}, and L_{III} edges. The presence of these absorption edges is important for densitometry and x-ray fluorescence measurements.

Compton Scattering

Compton scattering is the process whereby a gamma ray interacts with a free or weakly bound electron ($E_\gamma >> E_b$) and transfers part of its energy to the electron (Figure5).

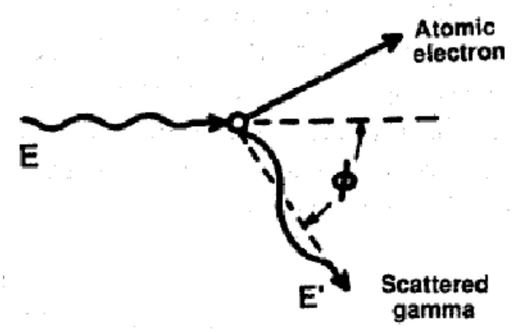


Figure 5

Conservation of energy and momentum allows only a partial energy transfer when the electron is not bound tightly enough for the atom to absorb recoil energy. This interaction involves the outer, least tightly bound electrons in the scattering atom. The electron becomes a free electron with kinetic energy equal to the difference of the energy lost by the gamma ray and the electron binding energy. Because the electron binding energy is very small compared to the gamma-ray energy, the kinetic energy of the electron is very nearly equal to the energy lost by the gamma ray:

$$E_e = E_\gamma - E'$$

where E_e = energy of scattered electron

E_γ = energy of incident gamma ray

E' = energy of scattered gamma ray.

Two particles leave the interaction site: the free electron and the scattered gamma ray. The directions of the electron and the scattered gamma ray depend on the amount of energy transferred to the electron during the interaction.

$$E' = m_0c^2 / (1 - \cos\phi + m_0c^2 / E)$$

Equation gives the energy of the scattered gamma ray.

Where m_0c^2 = rest energy of electron = 511 keV

ϕ = angle between incident and scattered gamma rays.

This energy is minimum for a head-on collision where the gamma ray is scattered 180°and the electron moves forward in the direction of the incident gamma ray. For this case the energy of the scattered gamma ray is given by

$$E'(\min) = m_0c^2 / (2 + m_0c^2 / E) \cong m_0c^2 / 2 = 256keV;$$
$$E >> m_0c^2 / 2$$

and the energy of the scattered electron is given by

$$E_e(\max) = E / (1 + m_0c^2 / 2E) \cong E - m_0c^2 / 2 = E - 256keV;$$
$$E >> m_0c^2 / 2$$

For very small angle scatterings ($\phi \cong 0$), the energy of the, scattered gamma ray is only slightly less than the energy of the incident gamma ray and the scattered electron takes very little energy away from the interaction. The energy given to the scattered electron ranges from near zero to the maximum given by above equation.

Pair Production

A gamma ray with an energy of at least 1.022 MeV can create an electron-positron pair when it is under the influence of the strong electromagnetic field in the vicinity of a nucleus (Figure).

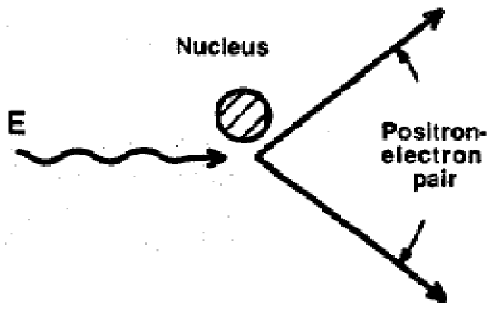


Figure 6

In this interaction the nucleus receives a very small amount of recoil energy to conserve momentum, but the nucleus is otherwise unchanged and the gamma ray disappears. This interaction has a threshold of 1.022 MeV because that is the minimum energy required to create the electron and positron. If the gamma ray energy exceeds 1.022 MeV, the excess energy is shared between the electron and positron as kinetic energy. This interaction process is relatively unimportant for nuclear material assay because most important gamma-ray signatures are below 1.022 MeV.

The electron and positron from pair production are rapidly slowed down in the absorber. After losing its kinetic energy, the positron combines with an electron in an annihilation process; which releases two gamma rays with energies of 0.511 MeV. These lower energy gamma rays may interact further with the absorbing material or may escape. In a gamma-ray detector, this interaction often gives three peaks for a high-energy gamma ray. The kinetic energy of the electron and positron is absorbed in the detector. One or both of the annihilation gamma rays may escape from the detector or they may both be absorbed. If both annihilation gamma rays are absorbed in the detector, the interaction contributes to the full-energy peak in the measured spectrum; if one of the annihilation gamma rays escapes from the detector, the interaction contributes to the single-escape peak located 0.511 MeV below the full-energy peak; if both gamma rays escape, the interaction contributes to the double-escape peak located 1.022 MeV below the full-energy peak. The relative heights of the three peaks, depend on the energy of the incident gamma ray and the size of the detector. ‘These escape peaks may arise when samples of irradiated fuel, thorium, and 232Uare measured because these materials have important gamma rays above the pair-production threshold.

6.4 Target and Projectile Dependence of all three Processes

The relative importance of the three main interaction mechanisms depends on the energy of the incident photon and the nature of the absorbing material. In general terms the photoelectric effect is most important at low energies. At higher energies Compton scattering becomes the main energy loss mechanism. At still higher photon energies Compton scattering is less effective. Above 1.1 MeV pair production becomes possible and is the dominant effect for energies greater than a few MeV. We can specify the energies at which relative importance of the effects changes by defining the energy at which they have the same value of the mass attenuation coefficient, μ_m.

Let E(pe,C) be the energy at which an incident photon loses energy at the same rate by both the photoelectric (pe) and Compton (C) effects. Its value is given by the point at which the photoelectric and Compton curves cross on the graph of attenuation coefficient and energy (Figure7).

Similarly E(C,pp) is the energy at which an incident photon loses energy at the same rate by both Compton scattering and by pair production (pp). The values of these changeover energies depend on the nature of the material; both E(pe,C) and

E(C,pp) vary with the atomic number, Z, of the absorbing material, as shown in figure.8

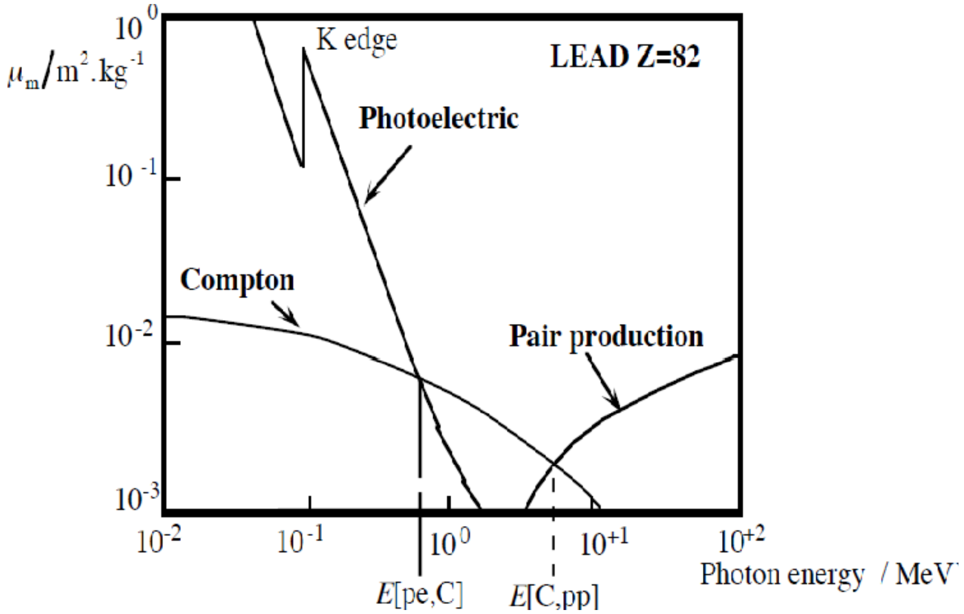


Figure:7

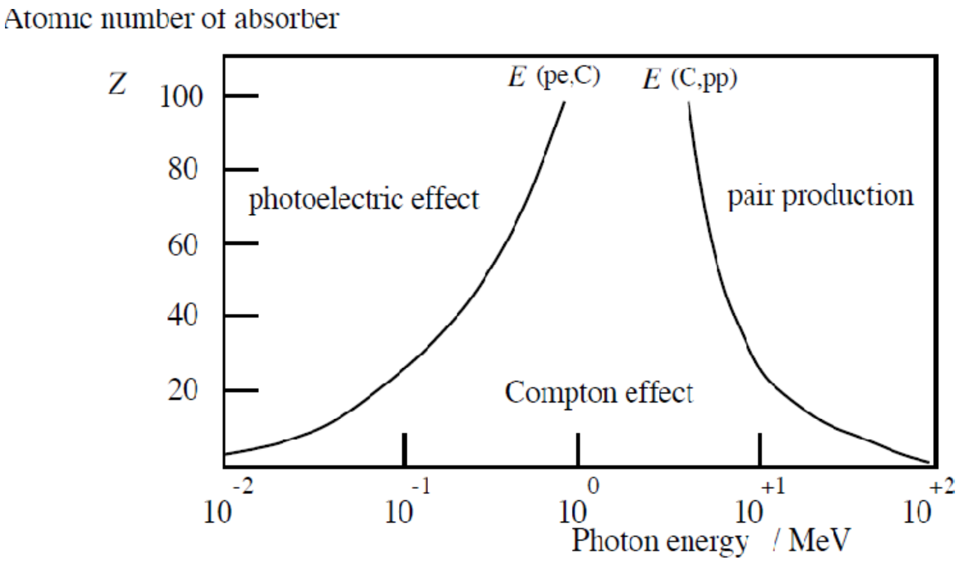


Figure:8

The total mass attenuation coefficient is just the sum of all the contributions from the different processes

$$\mu_m[tot] = \mu_m[pe] + \mu_m[C] + \mu_m[pp]$$

This total mass attenuation coefficient describes the decrease of the original incident radiation. The total linear attenuation coefficient is given by

$\mu_l\,[tot] = \mu_m[tot]\rho$.

Compton scattering produces a photon of reduced energy which nevertheless may interact again. Similarly the electrons and positrons produced in pair production may have large energies which they carry with them deeper into the material. Hence the exponential decrease law using the mass attenuation coefficient underestimates the total amount of radiation energy penetrating materials.

6.5 Self Learning Exercise-I

Q.1 Which process of attenuation is dominant for 10 MeV photons?

Q.2 Write down the law of absorption.

Q.3 The mass attenuation coefficients for photons in lead are shown in the accompanying diagram. Label the curves according to the process they represent.

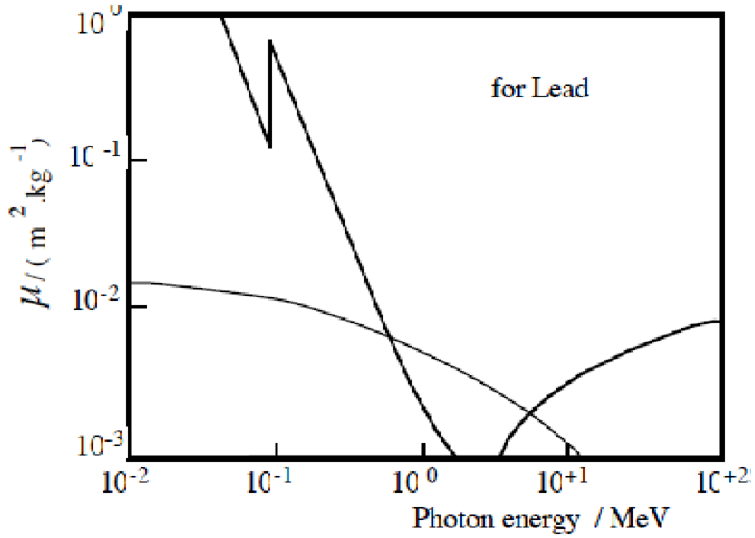


Figure:9

Q.4 Pair production by photons has two restrictions. The first is that the energy of the photons must be greater than 1.02 MeV and the second is that pair production can occur only near a heavy charged particle. Explain the reasons behind these restrictions.

6.6 Interactions of Charged Particles with Matter

Charged particles, such as electrons, protons and alpha particles, interact with matter electromagnetically or through one of the two kinds of nuclear interactions, the weak interaction or the strong interaction. The electromagnetic interaction involving collisions with electrons in the absorbing material is by far the most common. Neutral particles such as the neutron can interact only through the nuclear interactions. Thus charged particles can be detected directly by their electromagnetic interactions whereas neutral particles have to suffer nuclear interactions which produce charged particles before their presence can be detected.

Electromagnetic interactions:

The electromagnetic interaction consists mainly of two mechanisms: (a) excitation and ionization of atoms, and (b) bremsstrahlung, the emission of electromagnetic radiation (photons) when a charged particle is severely accelerated, usually by interaction with a nucleus. A third kind of interaction, producing Cherenkov radiation, while playing an important role in the detection of very high energy charged particles, absorbs only a small amount of energy. The contribution of each mechanism depends on the charge, mass and speed of the incident particle as well as the atomic numbers of the elements which make up the absorbing material.

Individual interactions – scattering:

Unlike photons, each charged particle suffers many interactions along its path before it finally comes to rest, but only a small fraction of its energy is lost at each interaction. For example, a typical alpha particle might make fifty thousand collisions before it stops. Hence the energy loss can usually be considered as a continuous process. Charged particles are deflected or scattered at each interaction. Although the amount of scattering at each collision may be small, the cumulative effect may be quite a large change in the direction of travel. Occasionally an incident particle will pass very near a nucleus and then there will be a single large deflection. This nuclear scattering effect is most pronounced for light incident particles interacting with heavy target nuclei.

Stopping power:

There are several ways of describing the net effects of charged-particle interactions, the rate of energy loss along the particle's path, $-dE/dx$, being most important. Here E is the particle's energy and x is the distance travelled. This rate of energy loss with distance travelled depends on the material and is called the **linear stopping power**, S_l, of the material:

$$S_l = -\frac{dE}{dx}$$

A common unit for linear stopping power is MeV.m^{-1}. In general the stopping power will vary as the particle loses energy so it depends on the charged particle's energy. The linear stopping power of a material also depends on the density of electrons within the material (and hence on the atomic numbers of the atoms) as well as the energy of the particle. So a more fundamental way of describing the rate of energy loss is to specify the rate in terms of the density thickness, rather than the geometrical length of the path. So energy loss rates are often given as the quantity called the **mass stopping power**:

$$S_l = -\frac{dE}{d(\rho x)} = -\frac{1}{\rho}\frac{dE}{dx}$$

where ρ is the density of the material and ρx is the density-thickness.

6.7 Energy Loss of Charged Particles due to Ionization

The dominant mechanism of energy loss at lower (non-relativistic) energies is the electromagnetic interaction between the moving charged particle and atoms within the absorbing material. Since the electromagnetic interaction extends over some distance, it is not necessary for the charged particle to make a direct collision with an atom; it can transfer energy simply by passing close by. However, since the internal energy of an atom is quantized, only certain restricted values of energy can be transferred. The incident particle can transfer energy to the atom, raising it to a higher energy level (excitation) or it may transfer enough energy to remove an electron from the atom altogether (ionisation). Although this fundamental mechanism operates for all kinds of charged particles, there are considerable differences in the overall patterns of energy loss and scattering between the passage of light particles (electrons and positrons), heavy particles (muons, protons, alpha particles and light nuclei), and heavy ions (partially or fully ionised atoms of high Z elements). Most of these differences arise from the dynamics of the collision process. In general, when a massive particle collides with a much lighter particle, the laws of energy and momentum conservation predict that only a small fraction of the massive particle's energy can be transferred to the less massive particle. The actual amount of energy transferred will depend on how closely the particles approach and restrictions imposed by quantization of energy levels. The largest energy transfers occur in head-on collisions.

In non-relativistic newtonian dynamics, when an object A (mass *M*) hits a stationary object B (mass *m*) head-on the laws of dynamics predict that the energy lost by the incident particle is

$$K_{\mathrm{B}} = 4K_{\mathrm{A}} \frac{mM}{(M+m)^2}$$

where K_A is the kinetic energy of the incident particle. For the case $M >> m$ this becomes

$$K_{\mathrm{B}} = 4K_{\mathrm{A}} \frac{m}{M}$$

The energy transferred is a very small fraction of the incident particle's energy. However when $M = m$ then all the kinetic energy is transferred to the target ($K_B = K_A$) and the projectile stops. This result is strictly true only for particles travelling with speeds much less than that of light (non-relativistic speeds) but similar results are obtained also for relativistic particle speeds. When the collision is not head-on the energy transfer to the target is less and of course the energy loss of the incident particle is correspondingly less as well.

Energy loss by heavy particles:

When a massive particle collides with an electron the energy lost at each collision is relatively small. For example, a slow alpha particle hitting an electron transfers a maximum of only 0.05% of its energy to the electron. Since head-on collisions are rare, usually the energy loss is much lower. Many collisions are needed to significantly reduce the incident particle's energy. Therefore we can consider the energy loss as a continuous process. Although the energy given to an electron may be a small fraction of the incident energy, it may be sufficient to ionize the atom and for the ejected electron to travel some distance away from the interaction point, leaving a trail of excited and ionized atoms of its own. These 'knock-on' electrons can leave tracks called delta rays. Mostly, however, the knock-on electrons will lose their energy within a very short distance of the interaction point.

The energy dependence of the rate of energy loss (stopping power) by excitation and ionization of heavy particles for some typical materials is shown in figure.

This graph is a plot of the energy-loss rate as a function of the kinetic energy of the incident particle.

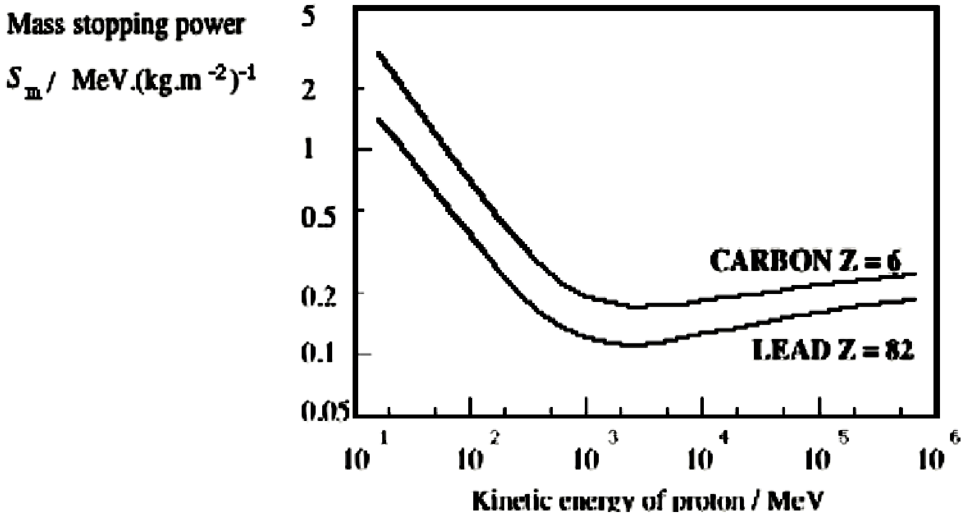


Figure:10

Note that the stopping power is expressed using density-thickness units. To obtain the energy loss per path length you would need to multiply the energy loss per density-thickness (shown on the graph) by the density of the material. As for photon

interaction, it is found that when expressed as loss rate per density-thickness, the graph is nearly the same for most materials. There is, however, a small systematic variation; the energy loss is slightly lower in materials with larger atomic numbers. The diagram shows the rate of energy loss for the extreme cases of carbon ($Z = 6$) and lead ($Z = 82$). At high incident energies there is also some variation with density of the same material because a higher density of atomic electrons protects the more distant electrons from interactions with the incident particle. This results in lower energy loss rates for higher densities.

For low energies the stopping power varies approximately as the reciprocal of the particle's kinetic energy. The rate of energy loss reaches a minimum, the minimum ionization point, and then starts to increase slowly with further increases in kinetic energy. Minimum ionization occurs when the particle's kinetic energy is about 2.5 times its rest energy, and its speed is about 96% of the speed of light in vacuum. Although the energy loss rate depends only on the charge and speed of the incident particle but not on its mass it is convenient to use kinetic energy and mass rather than the speed. At minimum ionization the energy loss is about 0.2 MeV.(kg.m^{-2})$^{-1}$ (= 3 × 10^{-12} J.m^2.kg^{-1} in SI units), decreasing slightly with increasing atomic number of the absorbing material. The distance that a particle penetrates a material before it loses all its kinetic energy is called the range of that particle. Energy loss along the path is shown in figure11.

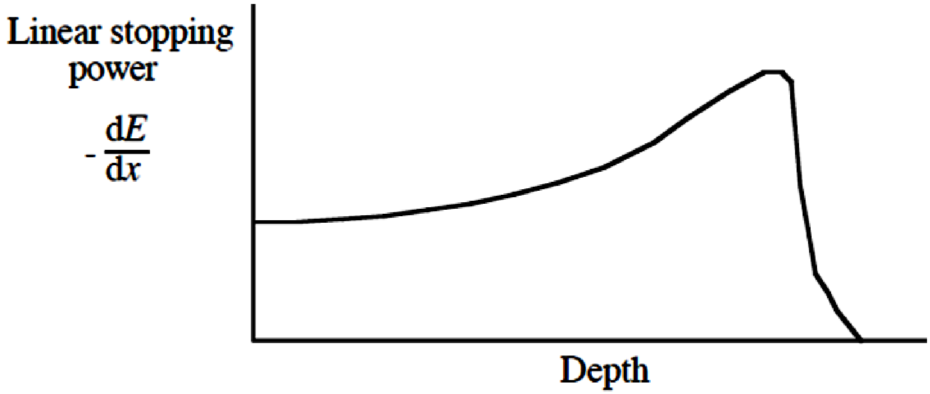


Figure:11

The rise near the end of the path is due to the increased energy loss rate at low incident energies. At very low speeds the incident particle picks up charge from the material, becomes neutral and is absorbed by the material.

For a given material the range will be the nearly the same for all particles of the same kind with the same initial energy. The number of particles as a function of distance along the path is shown in figure12.

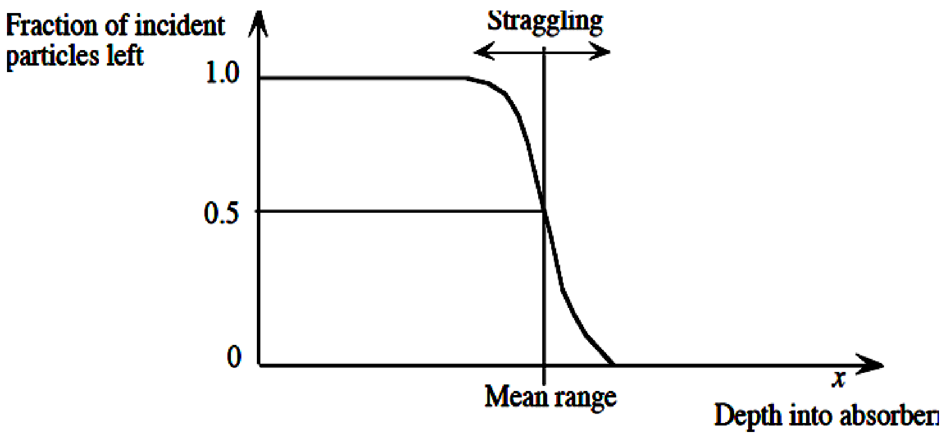


Figure 33: Range and straggling

A small variation in the range, called straggling, is due to the statistical nature of the energy loss process which consists of a large number of individual collisions.

The actual number of collisions is always subject to some fluctuation. In spite of that, the average range can be used to determine the average energy of the incident particles.

Energy loss by electrons and positrons:

Electrons and positrons also lose energy by ionization but there are several differences. There is a slight difference between the interactions of positrons and electrons, resulting in a slightly higher energy loss for the positrons. Both, however, have lower loss rates at high energies than heavier particles travelling at the same speed. Because of its light mass an electron is easily scattered in collisions with other electrons. The resulting erratic path will be longer than the linear penetration (range) into the material and there will be greater straggling.

6.8 Bremsstrahlung

The name bremsstrahlung comes from the German; the literal translation is 'braking radiation'. It occurs when a charged particle is accelerated - that is whenever its speed or direction of motion changes. The effect is most noticeable when the incident particle is accelerated strongly by the electric field of a nucleus in the absorbing material. An accelerated charged particle radiates electromagnetic energy (photons). Since the effect is much stronger for lighter particles, it is much more important for beta particles (electrons and positrons) than for protons, alpha particles, and heavier nuclei. At particle energies below about 1 MeV the energy loss due to radiation is very small and can be neglected. Radiation loss starts to become important only at particle energies well above the minimum ionization energy. At relativistic energies the ratio of loss rate by radiation to loss rate by ionization is approximately proportional to the product of the particle's kinetic energy and the atomic number of the absorber. So the ratio of stopping powers is

$$\frac{S_l[rad]}{S_m[coll]} = \frac{1}{E'} ZE$$

where *E* is the particle's kinetic energy, *Z* is the mean atomic number of the absorber and *E′* is a proportionality constant; $E' \approx 800$ MeV.

The kinetic energy at which energy loss by radiation equals the energy loss by collisions is called the **critical energy**, E_c. Approximately

$$E_c \approx \frac{E'}{Z} \approx \frac{800MeV}{Z}$$

Another quantity of interest is the **radiation length**, defined as the distance over which the incident particle's energy is reduced by a factor e^{-1}(0.37) due to radiation losses alone. Some typical values are given in table.

Material	**Critical energy E_c / MeV**	**Radiation length L / m**	**Density× radiation length ρL / kg.m-2**
Air	**102**	**200**	**362**
Water	**92**	**0.36**	**361**
Aluminium	**51**	**0.089**	**240**
Iron	**27**	**0.018**	**140**
Lead	**9.5**	**0.0056**	**64**

Bremsstrahlung by a high energy electron results in a high energy photon as well as a high energy electron. Pair production by high energy photons results in a high energy electron and a high energy positron. In both cases two high energy particles are produced from a single incident particle. Furthermore the products of one of these processes can be the incident particles for the other. The result can be a cascade of particles which increases in number, while decreasing in energy per particle, until the average kinetic energy of the electrons falls below the critical energy. The cascade is then absorbed by ionization losses. Such cascades, or showers, can penetrate large depths of material.

6.9 Self Learning Exercise-II

Q.1 Define linear stopping power.

Q.2 Draw a 'Range and straggling curve'.

Q.3 Explain the phenomena behind the energy loss of charged particles due to ionization.

Q.4 Explain why "bremsstrahlung" is a more important energy loss mechanism for electrons than for protons travelling through matter.

6.10 Summary

In this chapter we discussed various interaction phenomena of radiation and charged particle with matter. This chapter started with the introduction of law of absorption and attenuation coefficient followed by photon interaction with matter via Photoelectric effect, Compton scattering and pair production. After that we also discussed the interaction of charged particles with matter. At last we also discussed the Bremstrahlung energy which is nothing but the 'braking radiation'.

6.11 Glossary

Electromagnetic radiation: Radiation consisting of electric and magnetic waves that travel at the speed of light. Examples: light, radio waves, gamma rays, x-rays.

Gamma ray : A highly penetrating type of nuclear radiation, similar to x-radiation, except that it comes from within the nucleus of an atom, and, in general, has a shorter wavelength.

Ionizing radiation: Radiation that is capable of producing ions either directly or indirectly.

Scattering:A process that changes a particle's trajectory. Scattering is caused by particle collisions with atoms, nuclei and other particles or by interactions with electric or magnetic fields. If there is no change in the total kinetic energy of the system, the process is called elastic scattering. If the total kinetic energy changes due to a change in internal energy, the process is called inelastic scattering.

6.12 Answers to Self Learning Exercises

Answers to Self Learning Exercise- I

Ans.1: Pair production

Ans.2: See Section 6.2

Ans.3,4: See Section 6.3

Answers to Self Learning Exercise- II

Ans.1: The rate of energy loss with distance travelled depends on the material and is called the linear stopping power, S_l, of the material

$$S_l = -\frac{dE}{dx}$$

A common unit for linear stopping power is $MeV.m^{-1}$.

Ans.2,3: See Section 6.7

Ans.4: See Section 6.8

6.13 Exercise

Q.1 Define straggling.

Q.2 Explain why energy loss rate by "Bremsstrahlung" is greater for electrons travelling through lead than for electrons travelling through water.

Q.3 Write a short note on

1. Photoelectric effect
2. Pair production
3. Compton effect

References and Suggested Readings

1. The Atomic Nucleus by R. D. Evans, 1955.
2. Radiation Detection and Measurement by G. F. Knoll, 1979.
3. Elementary Nuclear Theory by Bethe and Morrison.
4. Nuclear Physics by D. C Tayal.
5. Nuclear Physics by Irving Kaplan.
6. Introductory Nuclear Physics by Kenneth S. Krane
7. R.R. Roy and B.P. Nigam: Nuclear Physics, 1979.

UNIT-7
Detectors-I

Structure of the Unit

7.0 Objectives

After going through this lesson, you would be able to understand

1. some of the most useful procedures for the detection and measurement of radiations like Alpha & Beta particles.
2. the way in which the measurements of radiations are carried out.

7.1 Introduction

Experiments in Nuclear and Particle Physics depend upon the detection of primary radiation/particle and that of the product particles if any. The detection is made possible by the interaction of nuclear radiation with atomic electrons directly or indirectly.

The same detector may be used to study different types of radiation according to different phenomena. Thus, G.M. counters register all sorts of charged particles through ionization effects. Scintillation counters detect gamma rays by photoelectric effect, Compton scattering or pair production depending on gamma ray energy.

The detection efficiency of an instrument is of great consideration in an investigation. The detection efficiency which is the probability of detection when the particle crosses it, varies widely. In most of the direct ionizing radiation, it is nearly 1. After an event is detected, most of the instruments lose their sensitivity for certain time called “Dead time”. In order that the counter efficiency be high, it is important that the dead time be smaller than the mean time interval between successive events. If r is the counting rate and t_d is the dead time then for high efficiency, the condition $rt_d \ll 1$, must be satisfied.

A perfect detector might have the following characteristics

i. 100 percent detection efficiency
ii. high-speed counting and timing ability
iii. good energy resolution
iv. linearity of response
v. application to virtually to all types of particles and radiations
vi. large dynamic range
vii. virtually no limit to the highest energy detectable
viii. reasonably large solid angles of acceptance
ix. discrimination between types of particles
x. directional information
xi. low background, and
xii. picturization of the event.

7.2 Ionization Methods for Measurement of Radiation

Different types of detectors can be characterized by the nature of the interaction of radiation with matter. Gas filled detectors operate by utilizing the ionization produced by radiation as it passes through a gas. Such a counter consists of two electrodes to which a certain electrical potential is applied. The space between the electrodes is filled with a gas. Ionizing radiation, passing through the space between the electrodes dissipates part or all of its energy by generating electron-ion pairs. They are charge carriers that move under the influence of the electric field. This induces a current on the electrodes, which may be measured or through appropriate electronics, the charge produced by the radiation may be transformed into a pulse, in which case particles are counted individually. A nucleonic pulse originates as transient voltage change across the output end of a radiation detector, as a result of charge deposited in the detector by the passage of ionizing radiation.

Radiation detector generating a charge pulse can be represented by a circuit diagram shown in the Fig.

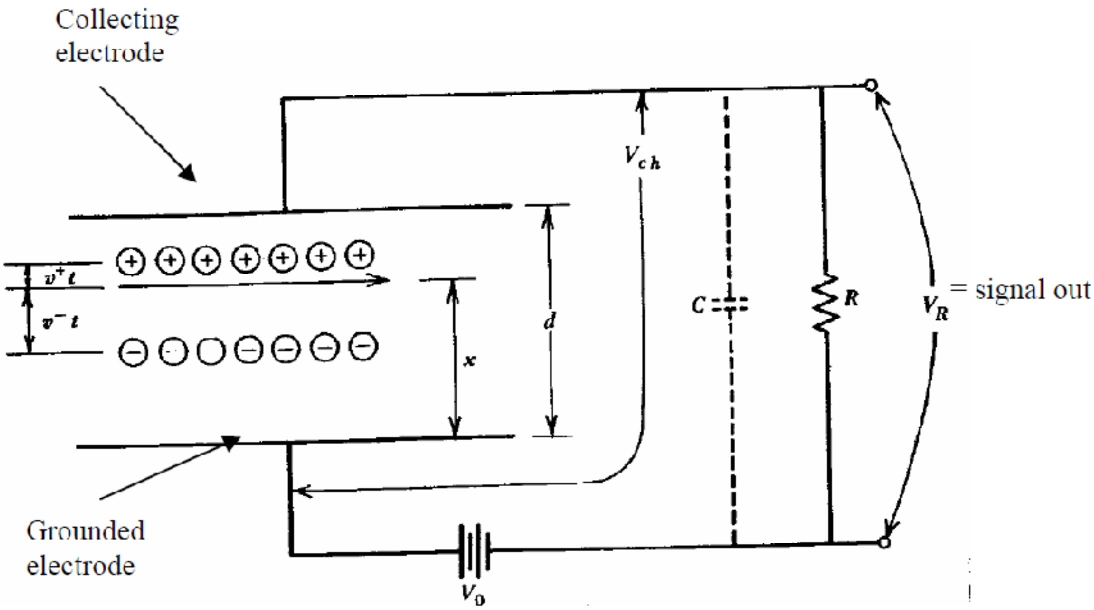


Figure 4: *The electronic circuit of ionization chamber*

Relationship between High Voltage and charge collected:

A radioactive source of constant intensity is placed at a fixed distance from a gas counter. The high voltage (HV) applied to the counter may be varied with the help of a potentiometer. An appropriate meter measures the charge collected per unit time. If the HV applied to the counter is steadily increased, the charge collected per unit time changes as shown in Fig.

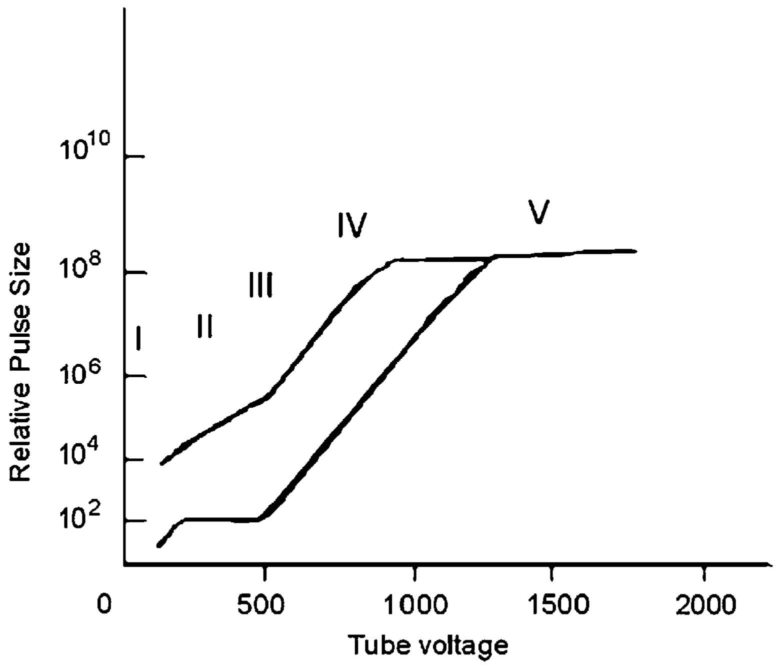


Figure 2: *Characteristics of a gas filled detector*

Region I : When the voltage is very low, the electric field in the counter is not strong, electrons and ions move with relatively slow speeds, and their recombination rate is considerable. As V increases, the field becomes stronger, the carriers move faster, and their recombination rate decreases up to the point where it becomes zero. Then the entire charge created by the ionizing radiation is being collected. That gives the saturation current known as Ionization region current.

Region II : The recombination rate is zero and no new charge is produced. This is indicated as Ion saturation in Fig2.

Region III : The electric field is so strong, in a certain fraction of the counter volume, that the electrons from the primary ionization acquire enough energy between collisions to produce additional ionizations. The gas multiplication factor: Ks i.e., the ratio of the total ionization produced divided by the primary ionization is, for a given voltage, is independent of the primary ionization. The output of the counter is proportional to the primary ionization. The pulse height of the output is proportional to the energy dissipated inside the counter. Therefore, particle identification and energy measurement are possible.

Region IV : Beyond the proportional region, the electric field inside the counter is so strong that a single electron-ion pair generated in the chamber is enough to initiate an avalanche of electron-ion pairs. This avalanche will produce a strong signal with shape and height independent of the primary ionization and the type of particle, a signal that depends only on the electronics of the counter. This region is called the Geiger-Muller region.

Different types of gas filled counters take their name from the voltage region in which they operate-

Region	Name of the counter
I	Ionization chamber
III	Proportional counter
IV	GM counter

7.3 Ionization Chamber

Operate in the ionization region. No charge multiplication takes place. Output signal is proportional to the particle energy dissipated in the detector. Since the signal is not large, only strongly ionizing particles such as alpha, protons, fission fragments and other heavy ions are detected.

7.4 Proportional Counters

Operate in region III. Charge multiplication takes place. Output signal is still proportional to the energy deposited in the counters. Measurement of particle energy is possible. Identification of the type of particle is possible.

7.5 Geiger-Muller Counter (GM Counter)

Operate in region IV. It can be used for any kind of radiation. The signal is independent of the particle energy and its type. It provide information only about the number of particles. It has relatively long dead time (200 to 300 μs).

General Principles: A widely used radiation detector is a Geiger Muller detector tube. Cross sectional view of a typical GM tube is shown in Fig.3. A GM tube consists of a very fine central anode and a shell, which serves as the cathode. The region surrounding the anode is filled with a gas, usually argon or neon, specially selected for the ease with which it can be ionized. A high electrical field is maintained between the electrodes.

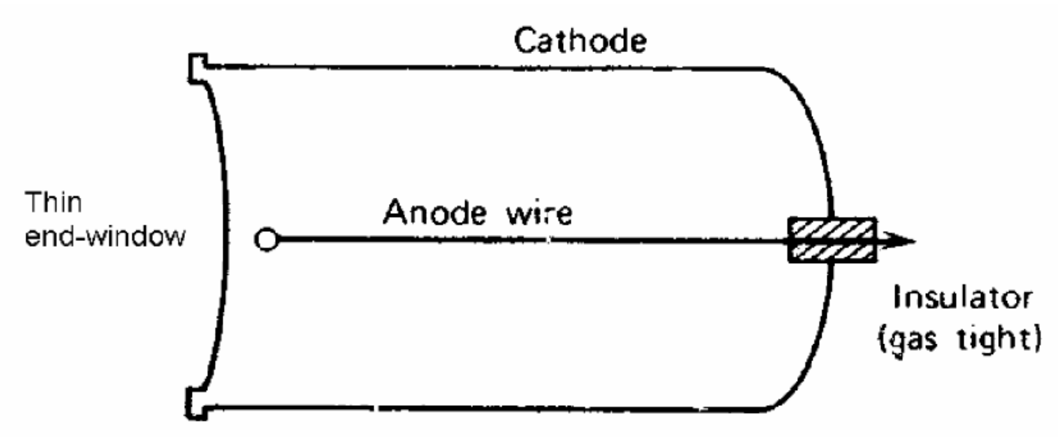


Figure:3

The sensitive volume is the portion surrounding the anode responding to the specific radiation. An energetic charged particle traversing through the sensitive volume will have high probability of producing one or more ion pairs (electron and positive ion). The electron is accelerated towards the anode and in a short distance, gains sufficient kinetic energy to produce a second ion pair in a chance encounter with a gas atom. These two electrons will now produce additional ion pairs and thus an avalanche is developed in which an enormous number of electrons of the order of 10^{10} are eventually collected by the anode. This charge which will be collected in about 0.25μs, appears across the capacitance of the tube plus the associated circuitry to produce a voltage pulse of amplitude ranging from 0.25 to 10 volts with a duration of about 100μs. These values depend upon the design of the tube, its operating voltage and the characteristics of the external circuit. When the voltage across the tube is such that it is operating in the GM region, all pulses are of equal size irrespective of the number of ion pairs formed in the initial ionizing event.

Operating Characteristic of a GM Tube :

When the tube is exposed to a constant radiation intensity and the voltage applied on the tube is slowly increased, a voltage will be reached at which GM tube begins to produce pulses as indicated by the recorder. This is the starting potential. As the voltage is increased, very rapid increase in counting rate is observed. This voltage is known as the threshold. Beyond the threshold further increase in the voltage over certain range will produce little effect on the counting rate. This region is known as the plateau. It should have a slope of less than 10% per 100 volts for good tubes. Within the plateau region, the proper operating voltage is selected. The operating voltage should be selected relatively close to the threshold voltage (within the lower 25% of the plateau) to preserve the life of the tube. Also the operating voltage should be selected at a point where the plateau shows minimum slope. If the voltage is increased beyond the plateau region, the counting rate begins to increase rapidly and the region of continuous discharge is reached. The shape of the high voltage (HV) plateau is as shown in the Fig. and explained as follows.

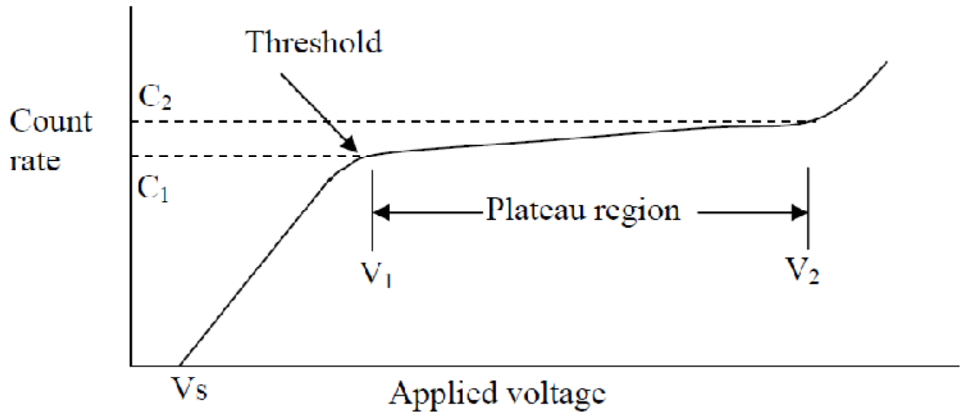


Figure 4

For very low voltage ($V < V_s$) the counting rate is zero. The scaler does not receive any signal because all the pulses are below the discriminator level. The counting rate keeps increasing with high voltage (HV), since more and more pulses are produced with a height above the discriminator level. This continues up to the point when $V = V_1$. For $V > V_1$, all the pulses are now above the discriminator level. Since all the pulses are counted, each pulse being recorded as one regardless of its height, the counting rate does not change. This continues up to $V = V_2$. Beyond that point, the counting rate will start increasing again because the HV is so high that spurious & double pulses may be generated. Counter should not be operated beyond $V = V_2$

Quenching of the discharge:

When the electrons are accelerated in the strong field surrounding the wire they produce, in addition to a new avalanche of electrons, considerable excitation of the atoms and molecules of the gas. These excited atoms and molecules produce photons when they de-excite. The photons in turns, produce photoelectrons in other parts of the counter. Thus the avalanche, which was originally located close to the wire, spreads quickly in most of the counter volume. During all this time, the electrons are continuously collected by the anode wire, while the much slower moving positive ions are still in the counter and form a positive sheath around the anode. When the electrons have been collected, this positive sheath, acting as an electrostatic screen, reduces the field to such an extent that the discharge should stop. However, this is not the case because the positive ions eject electrons when they finally strike the cathode, and since by that time the field has been restored to its original value, a new avalanche starts and the process just described is repeated. Clearly some means are needed by which the discharges is permanently stopped or quenched. Without quenching, a GM tube would undergo repetitive discharging. There are two general methods of quenching the discharge.

External Quenching : In external quenching, the operating voltage of the counter is decreased, after the start of the discharge until the ions reach the cathode, to a value for which the gas multiplication factor is negligible. The decrease is achieved by a properly chosen RC circuit. The resistance R (10 ohms or more) is so high that the voltage drop across it due to the current generated by the discharge (i_d) reduces the voltage of the counter below the threshold needed for the discharge to start ($V_o - i_d R$). The time constant RC is much longer than the time needed for the collection of the ions. As a result the counter is inoperative for an unacceptably long period of time. In other words, its dead time is too long.

Internal quenching : The internal quenching method is accompanied by adding to the main gas of the counter a small amount of a polyatomic organic gas or a halogen gas. These have relatively large molecules, which tend to absorb the fluorescent emissions of the noble-gas atoms. They also have smaller excitation potentials than the latter, so their de- excitation photons have insufficient energy to ionize the gas and propagate the discharge further. For satisfactory photon quenching, the absorption spectrum of the quenching agent should match the emission spectrum of the noble gas. Methane and ethanol both satisfy these requirements.

GM counters using an organic gas as quenching agent have a finite lifetime because of the dissociation of the organic molecules. Usually the GM counters last for 10^8 to 10^9 counts. The lifetime of a GM detector increases considerably if a halogen gas is used as the quenching agent. The halogen molecules also dissociate during the quenching process but there is a certain degree of degeneration of the molecules which greatly extends the useful lifetime of the counter.

Sensitivity of a GM tube :

GM tubes are not equally sensitive to α, β and γ radiations. Once the radiation reaches the sensitive volume of the counter, the efficiency of detection is 100% for α, nearly 100% for β and only 1 or 2% for γ radiation.

Dead Time and Recovery Time of GM Tubes :

It is found on close observation of oscilloscope that a small vertical pulse can sometimes be seen closely following one of the normal height for a particular applied voltage. These pulses occur when one ionizing event follows another at an interval too short for the counter to have completely recovered, a situation due to the fact that the positive ion sheath has not reached the cathode when the second ionizing event occurs. The longer the interval between the ionizing events the larger the second pulse will be, until it reaches its maximum. The time interval between the first full pulse and the detectability of another full pulse depends on the characteristics of the counter tube and is known as resolving time. This time interval is made up of two parts. The first part is the dead time and is the time after a count during which no pulse can be registered at all, even if an ionizing event occurs, because the electric field has collapsed and has not yet been re-established. The second part is the recovery time, a time of increasing sensitivity, during which an ionizing event will give a pulse of amplitude less than that which is characteristic of the particular tube at the applied voltage. During this time the electric field is growing to its maximum value. At the end of the recovery time a full pulse is recorded. This is illustrated in given Fig5 below.

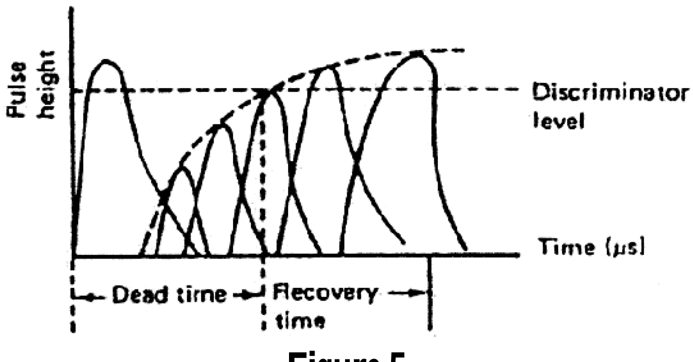


Figure 5

Consider two radioactive sources of strength S_1 and S_2. Let n_1, n_2 be the respective count rates recorded and n_{12} be the count rate recorded when sources are taken together. Let τ be the resolving time. Let N_1, N_2 and N_{12} be the corrected count rates respectively. Then we have

$$N_1 = \frac{n_1}{1-n_1\tau};\ N_2 = \frac{n_2}{1-n_2\tau};\ N_{12} = \frac{n_{12}}{1-n_{12}\tau}$$

we have

$$N_1 + N_2 = N_{12}$$

substituting value of N_1, N_2 and N_{12} in above equation.

$$\frac{n_1}{1-n_1\tau} + \frac{n_2}{1-n_2\tau} = \frac{n_{12}}{1-n_{12}\tau}$$

solving the above equation and neglecting the higher powers of τ we get

$$\tau = \frac{n_1 + n_2 - n_{12}}{2n_1 n_2}$$

7.6 Self Learning Exercise-I

Q.1 Which type of particles towards GM counter is most sensitive?

Q.2 What is Giger region .

Q.3 What is dead time?

Q.4 Write down the principle of GM counter.

7.7 Scintillation Counter

Construction: Scintillation counter consists of a photomultiplier tube to which is fixed a scintillator. A high voltage (~kV) is applied between the photo-cathode and the anode. The dynodes incorporated in the tube produce electron multiplication and by the use of a voltage divider provide progressively larger voltage between cathode and anode. Scintillators exist in several forms, crystals (organic or inorganic), liquids, plastic solids and gases. The scintillation phenomenon depends on the fact that suitable “flours” give off pulses of light when traversed by a charged particle.

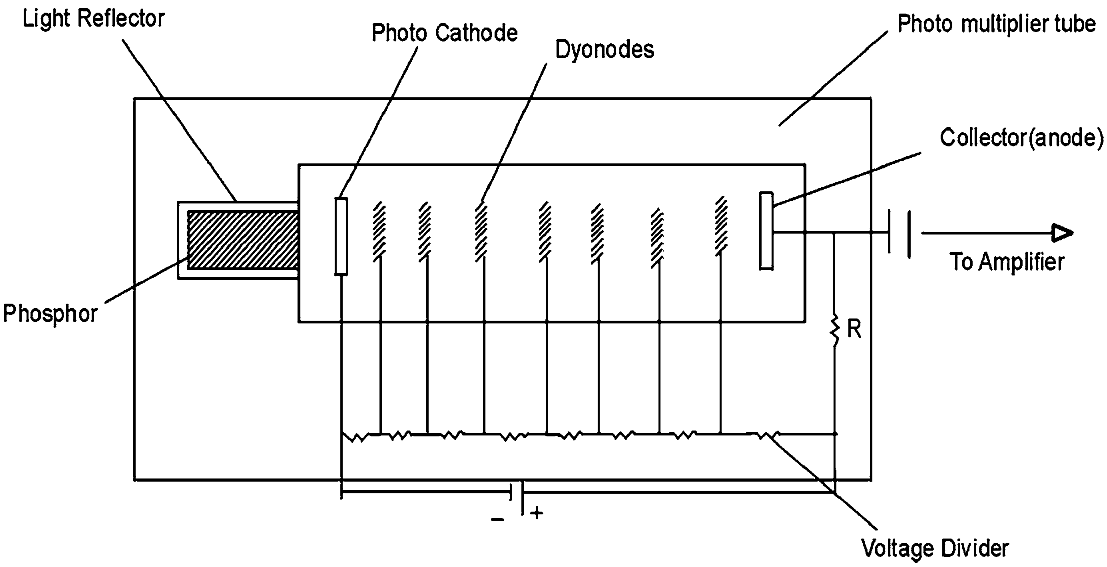


Figure 6: *Block diagram of a scintillation counter.*

This light is directed on to a photomultiplier cathode where it ejects electrons by photo-electric effect. These electrons are multiplied in the dynode structure of the tube. In each stage the number of secondary electrons is multiplied which are finally collected at the anode and recorded as a pulse by suitable circuits. The phosphor is in optical contact with the tube and is protected from external light. A reflector surrounding the phosphor enhances light falling on the photo-cathode for higher efficiency.

Mechanism: A charged particle passing through the phosphor loses energy by ionization, excitation and dissociation of molecules close to its path, ultimately light is emitted. The solid phosphor scan be basically divided into

i. organic

ii. inorganic crystals.

There are several important differences between the characteristics of organic and inorganic scintillators, in regard to lifetimes, linearity of energy response, temperature effects, fluorescence and conversion efficiency and v_{max} at which maximum number of photons are emitted. The basic difference in the mechanism for the light production is that light emitted by an inorganic crystal is primarily due to the crystal structure, where as organic substances exhibit luminescence by virtue of molecular properties.

Desirable Characteristics of Luminescent Materials:

i. The phosphor must have high efficiency for conversion of incident energy of radiation or particles into that of the emitted luminescence. In the case of inorganic phosphor material a small percentage impurity is essential while for organic phosphors, material must be pure.

ii. The spectrum of the emitted light must closely match the spectral response of the cathode of the photomultiplier used.

iii. The luminescent material must be transparent to their own luminescence radiation.

iv. The material used must be a large optically homogeneous mass, either as a single crystal without defects or in solution, solid or liquid, moulded or machined to any convenient shape.

v. The phosphor must have a high stopping power for the radiation to be detected.

vi. The rise and decay of luminescence during and after excitation should occur in a short time.

vii. The phosphor must be stable against vacuum conditions and under prolonged irradiation.

viii. The refractive index μ of the crystal should not be too high, otherwise light will not be able to come out easily due to internal reflections.

Organic Scintillators:

- **Main mechanism** is believed to be that of collisions which are responsible for the energy transfer from the molecules, either by excitation transfer or by a dipole resonance interaction.
- The energy response, is not quite linear.
- Light output is very much dependent upon the nature of the particle.
- Lifetime is of the order of 10^{-9} to 10^{-8} sec.
- The phenomenon of phosphorescence is absent.
- The fluorescent conversion efficiency is generally smaller than the inorganic phosphors, conversion efficiency.

Examples: anthracene, (λ_{max} = 4400 A), diphenylacetyline, terphenyl naphthalene and stilbene.

Organic phosphors are extensively used for fast neutron detection. The interactions of fast neutrons with hydrogen produce fast recoil protons which can be detected with high efficiency in large crystals.

Inorganic Scintillators:

- In inorganic crystals, for example alkali halides notably NaI with thallium impurity, charged particles may raise electrons into the conduction bands or into excitation levels. The electron and the hole left move rapidly throughout the crystal as an exciton until captured by the imperfection, giving up the energy in the form of vibrational transfer or until captured by an impurity. The impurity gets excited and acts as a scintillator. In the case of halides, thallium is added as an impurity to the extent of 0.1 to 0.2 percent. These crystals are highly transparent to their own radiation.
- The light output from inorganic crystals like NaI is very nearly proportional to energy loss down to about 1 MeV for protons and about 15 MeV for α's.
- The life time is of the order of 10^{-6} sec.
- The phenomenon of phosphorescence which is delayed emission of photons can in certain cases cause generation of secondary pulses which are indistinguishable from the primary pulses. As sodium iodide is deliquescent, it must be protected from moisture; nevertheless it is the most widely used inorganic phosphor. Large size crystals up to several inches in diameter and length are available. It has a high density and contains high Z atoms of Iodine and is an efficient detector for gamma rays as the absorption cross section for the three important processes, photoelectric, Compton and pair-production vary as $Z^{4.5}$, Z and Z^2 respectively. Of the other inorganic phosphors, zinc sulphide is useful for alpha-particle detection and lithium iodide for neutron detection, the relevant nuclear reaction being

  $$6Li + n \rightarrow 3H + 4He + 4.8 \text{ MeV}$$

- **Examples**: NaI (thallium activated, λ_{max} 4100 A), cesium iodide (cooled to 77 K), zinc sulphide (copper activated) and lithium iodide (europium activated).

- Some of the inorganic phosphors have a high value of the refractive index ($\sim$2). Difficulty is experienced in getting light out of them.

Photo-Multiplier (PM) Characteristics:

The desired characteristics of Photo-multiplier (PM) are:

1. PM must have a photo cathode of large cathode area with an end-window.
2. PM must be of a high efficiency for converting photons into photo-electrons.
3. PM must provide a high gain.
4. It must provide a good signal-to-noise ratio. In the absence of light the output from a photomultiplier consists of numerous pulses (noise) of various sizes, principally due to thermal emission of electrons from the photo-cathode. This constitutes the so-called dark current which depends on the photo-cathode material. It can be reduced by cooling the cathode.
5. **Examples:** 56 AVP (Philips), 6810 A, 7264 (RCA), 6292 Du Mont. The number of dyonodes varies from 10 to 15.

Light Collection:

A crystal scintillation counter is normally placed in a metal container. When hygroscopic alkali halides are used, they are protected against moisture by sealing the container. Good optical contact is made between the surface of phosphor and the end face of PM with a layer of clear vacuum grease and by placing a good reflector in optical contact with other crystal surfaces so that light which would otherwise escape will be returned to the photomultiplier with improved efficiency. A highly polished foil or a diffuse reflector such as magnesium oxide is used as a specular reflector. When the arrangement is such that the PM can not be in direct contact with the scintillator, lucite pipes can be used.

Electronic Equipment:

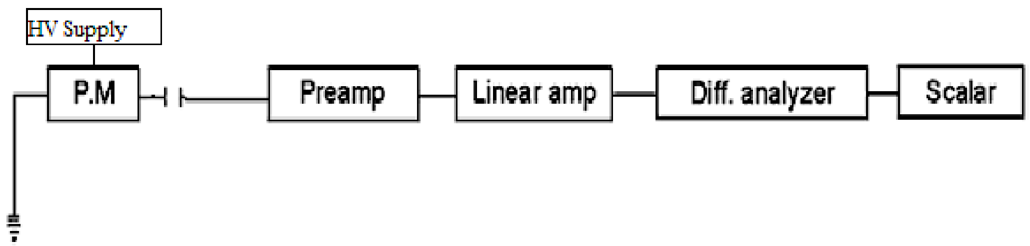


Figure:7

Figure7 is a block diagram of the electronic equipment attached to the PM. Pulses from the anode of the PM which are small are passed through a pre-amplifier and then to a linear amplifier and through a "window" of the differential analyzer, and finally counted by the scalar. The high voltage can be varied to suite the given PM. The gain of linear amplifier can be varied so that the input fed to the differential analyzer is within the range of operation. The differential analyzer accepts pulses of height between V and $V+\Delta V$, where ΔV is the width of the window. The pulse height is proportional to E_γ.

Gamma Ray Spectroscopy with NaI (TL) Scintillator:

At low γ ray energy (< 100 keV) photoelectric absorption is the dominating process. As $\sigma_{ph} \propto Z^{4.5}$, most of the absorptions occur in Iodine, with the K-shell electron (ionization energy E_k = 29 keV). The vacancy caused by the ejection of electron is filled in by radiative transitions (mainly X-rays) from electrons belonging to upper levels. If the resulting X-rays get absorbed then full energy (E_γ) is available and this corresponds to photo peak in the pulse height distribution. However, in few events the X-rays escape. Hence energy equal to ($E_\gamma - E_k$) is available. This results in the "Iodine escape peak". The ratio of photons under escape peak to those under photo-peak depends on E_γ crystal size and experimental geometry.

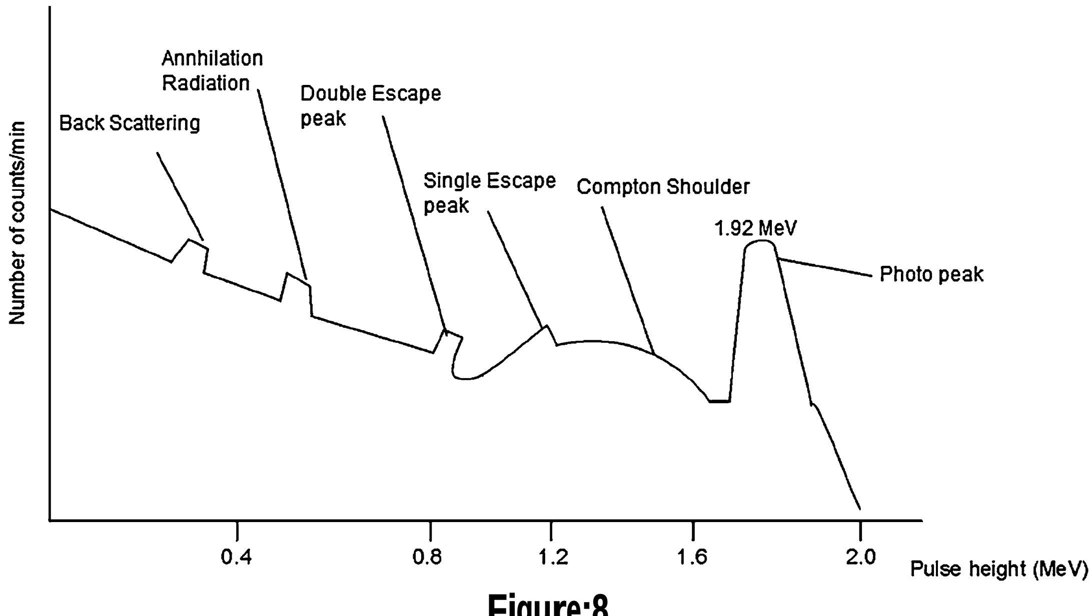


Figure:8

For E_γ > 100 keV, Compton scattering also becomes significant. The "escape peak" is not significant when the mean absorption length of the incident γ –rays becomes greater than that of iodine X-rays. In the case of single Compton scattering, the energy of escape radiation extends from $E`$ to $E\gamma$, where $E` = E_\gamma /(1 + 2\alpha)$ with $\alpha = E_\gamma/mc^2$ corresponds to the energy of the scattered photon at 180◦ (back scattering). The corresponding energy deposited ranges from (E_γ –$E`$) to 0. There will be a broad Compton distribution with the Compton edge occurring at energy ($E_\gamma – E`$). There can also be external Compton scattering from material outside such as the PM shielding. This gives rise to the "back scattering peak".

In the case of multiple Compton scattering the energy of escaping radiation extends from 0 to E_γ and the corresponding energy deposited is E_γ to 0. For $E_\gamma > 2mc^2$ (threshold for pair production) two other peaks are observed, a single escape peak at ($E_\gamma - mc^2$) and a double escape peak at ($E_\gamma - 2mc^2$).

Below figures (9,10) show typical spectra obtained from γ rays incident on NaI crystal from Cs-137 (661 keV) and Co-60 (1.17 MeV and 1.33 MeV), respectively. The 661 keV photo peak, Compton shoulder, back scattering from material of the phosphor and noise are indicated. The decay scheme is also shown.

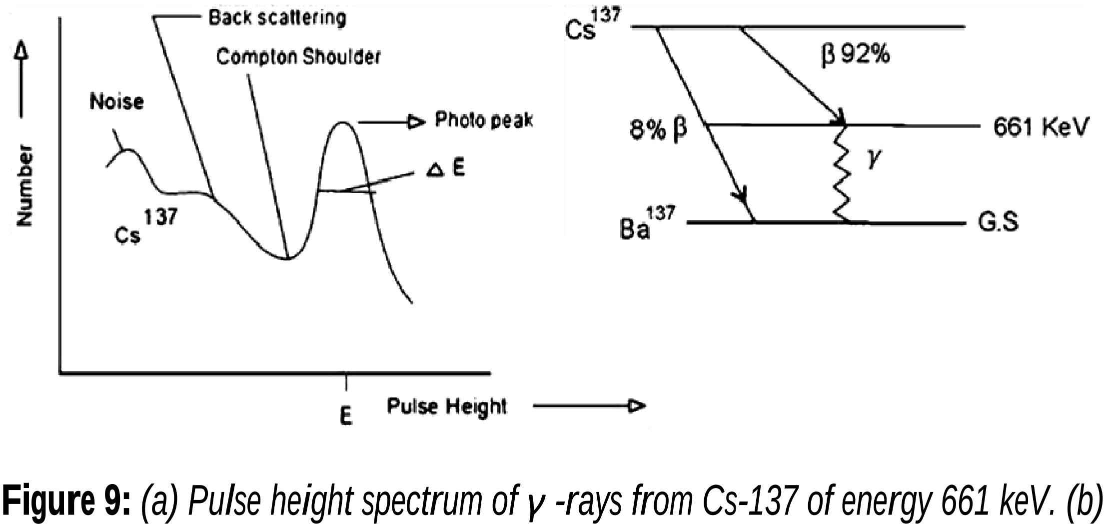


Figure 9: *(a) Pulse height spectrum of γ -rays from Cs-137 of energy 661 keV. (b) Decay scheme for Cs^{137}*

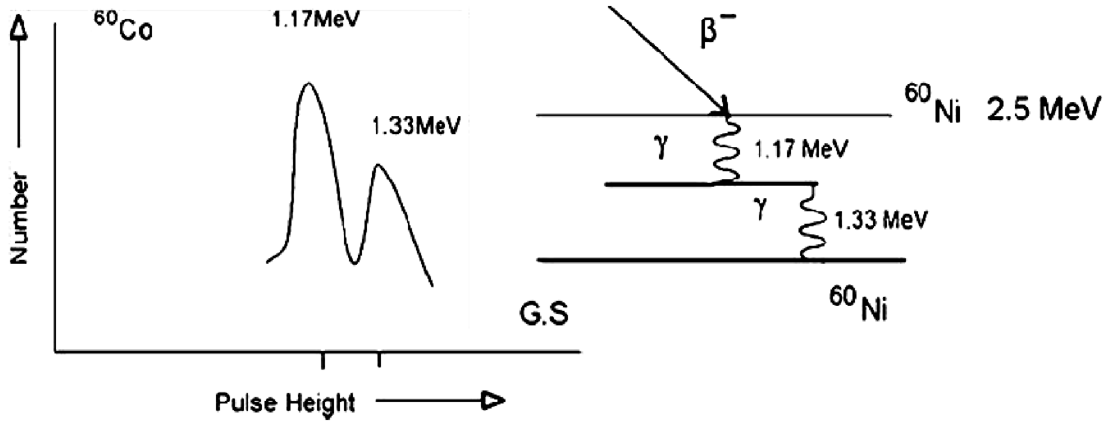


Figure 10: *(a) Pulse height spectrum of γ -rays of energy 1.17 MeV and 1.33 MeV. The origin of γ -rays is shown in the decay scheme. (b) Decay scheme for ^{60}Co*

Energy Resolution:

The photo peaks shown in above Figs, are not sharp. It is important that the spread in photo peaks be as small as possible, otherwise γ-rays of neighboring energies cannot be resolved. Many factors contribute to the energy resolution of a scintillation counter. These factors are:

i. Fluorescent radiation conversion efficiency (*f*)
ii. Efficiency for the collection of light by the cathode (*b*)
iii. Efficiency for the conversion of photo-electrons (*c*)
iv. Efficiency for collection of electrons which are accelerated to the first dynode (*p*)
v. Total multiplication from all the dynodes (*M*)

If *E* is the particle energy and ε the average energy of the photons generated in the crystal, then the number of photons emitted is Ef/ε. It follows that the number of electrons finally collected at the output of the PM tube is equal to $(Ef/\varepsilon)bcpM$. For various reasons there will be variation in the factors *f, b, c,p* and*M*. Of various factors, however, the variation in *c* which arises due to the statistical fluctuations in the number of photo-electrons released from the photo cathode is decisive for the pulse height and is therefore the ultimate factor which limits the resolution. The best resolution that is achieved is 6 % for 661 keV γ-rays from Cs-137 using NaI phosphor and a 6292 Du Mont P.M. Note that $\Delta E \propto \sqrt{E\gamma}$, so that the energy resolution, $\Delta E/E \propto 1/\sqrt{E\gamma}$.

Applications and Advantages

1 Fast Timing-

For investigations which involve fast timing, the scintillation counters have a decisive advantage over visual detectors. This aspect has been exploited in the lifetime measurements of $\pi+$, $K+$, capture times of $\mu-$ and in the discovery of $p-$ by time of flight method. In conjunction with Cerenkov counter or other scintillation counters, it can be used as a "telescope" in coincidence or anti-coincidence to avoid unwanted particles or events.

2 Scintillation Spectroscopy

Spectrometry of heavy charged particles by scintillation technique is usually done with the use of inorganic crystals. However, a number of organic compounds are also found useful. Organic scintillators like anthracene have a linear response for electrons, but for heavier particles the pulse-height energy relationship exhibit nonlinearity. For this reason, organic scintillators are preferred to inorganic crystals for electron spectroscopy as their effective low atomic number causes substantial improvement for backscattering compared with inorganic crystals, except for very low energy electrons.

3 Gas Scintillation Counters

Gas scintillation counters have the merit of short decay times ($\sim 10^{-9}$ s), large light output per MeV independent of ionization density, and their availability in a wide range of Z and density. Fission fragments in the presence of heavy background of α's can be discriminated. Also, because of low stopping power and small pulse height for γ-rays of nuclear origin, relativistic charged particles can be separated from an intense γ radiation background

7.8 Self Learning Exercise-II

Q.1 Differentiate between the characteristics of organic and inorganic scintillators.

Q.2 What are the desirable Characteristics of Luminescent Materials.

Q.3 Write down the characteristics of Photo-Multiplier (PM).

7.9 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: Charge particles

Ans.2: Beyond the proportional region, the electric field inside the counter is so strong that a single electron-ion pair generated in the chamber is enough to initiate an avalanche of electron-ion pairs.

Ans.3: After an event is detected, most of the instruments lose their sensitivity for certain time called "Dead time".

Ans.4: See Section 7.5

Answers to Self Learning Exercise-II

Ans.1: organic and inorganic scintillators are different not only in regard to lifetimes, linearity of energy response, temperature effects, fluorescence and conversion efficiency and v_{max} at which maximum number of photons are emitted but also in the mechanism for the light production. light emitted by an inorganic crystal is primarily due to the crystal structure, where as organic substances exhibit luminescence by virtue of molecular properties.

Ans.2: See Section 7.7

Ans.3: See Section 7.7

7.10 Exercise

Q.1 Compare and contrast ionization chambers, proportional counters, and Geiger-Muller tubes.

Q.2 Describe the construction and explain the operation of a photomultiplier tube.

7.11 Summary

In this chapter we discuss various types of detectors. Firstly we introduce Ionization chamber followed by Proportional counter, Geiger-Muller counter and Scintillation counter.

7.12 Glossary

Background radiation : The radiation of man's natural environment originating primarily from the naturally radioactive elements of the earth and from the cosmic rays. The term may also mean radiation extraneous to an experiment.

Geiger counter : A Geiger-Müller detector and measuring instrument. It contains a gas-filled tube which discharges electrically when ionizing radiation passes through it and a device that records the events.

Ionizing radiation : Radiation that is capable of producing ions either directly or indirectly.

Scaler : An electronic instrument for counting radiation induced pulses from radiation detectors such as a Geiger-Muller tube.

Scintillation counter : An instrument that detects and measures gamma radiation by counting the light flashes (scintillations) induced by the radiation.

References and Suggested Readings

1. Particle Physics by A. Kamal 2014.
2. Engineering Physics, by Raghuvanshi, G. S. Raghuvanshi.
3. Nuclear and particle physics by B. R. Martin 2006.
4. Nuclear Energy by Raymond L. Murray, 2000.
5. R.R. Roy and B.P. Nigam: Nuclear Physics (Willey -Easter, 1979).

UNIT-8
Detectors-II

Structure of the Unit

8.0 Objectives

After interacting with the material presented here students will be able to understand the working of

- Diffused junction detector
- Surface barrier detectors and
- Nuclear detectors
- Multiwire proportion chambers

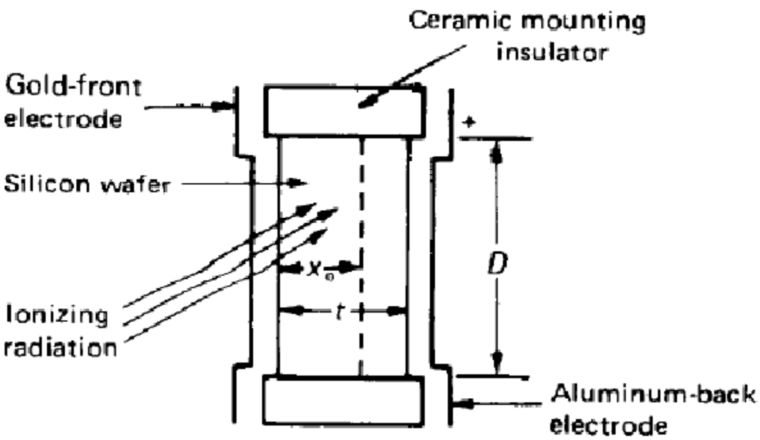
In this chapter we will also discuss nuclear emulsion and the techniques and analysis of tracks.

8.1 Solid State Detectors (Diffused Junction Detector, Surface Barrier Detectors)

The several types of semiconductor detectors that exist today differ from one another because of the material used for their construction or the method by which that material is treated. The rest of this section describes briefly the method of construction and the characteristics of the most successful detectors -made of silicon or germanium-and two promising ones made of CdTe and HgI_2.

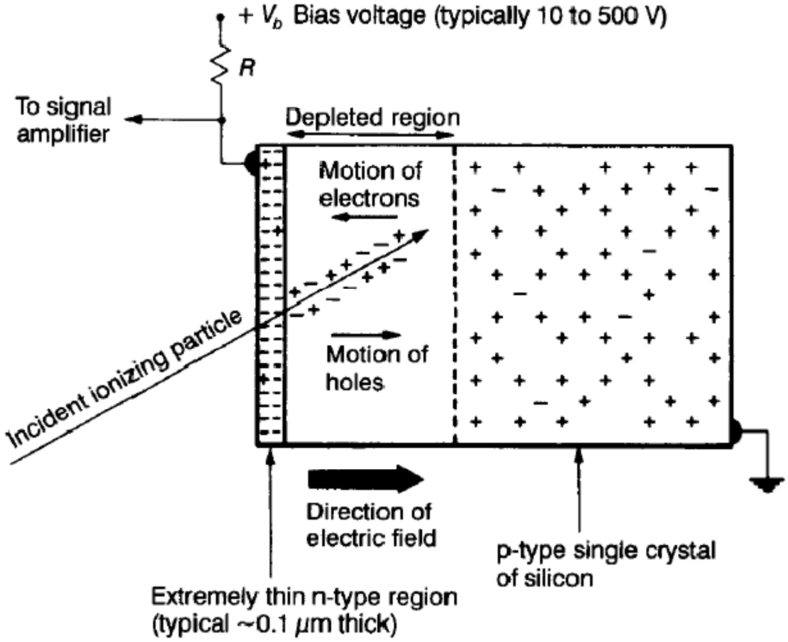
1. Surface Barrier Detectors:

Silicon of high purity, usually n-type, is cut, ground, polished, and etched until a thin wafer with a high-grade surface is obtained. The silicon is then left exposed to air or to another oxidizing agent for several days. As a result of surface oxidization, surface energy states are produced that induces a high density of holes and form, essentially, a p-type layer on the surface (Figure). **A** very thin layer of gold evaporated on the surface serves as the electrical contact that will lead the signal to the preamplifier. In Fig., *X,,* is the depth of the sensitive region, *t* is the total silicon thickness, and D is the diameter of the detector. The size of the detector is the length (or depth) *Xo.*



2. Diffused-Junction Detectors:

Silicon of high purity, normally p-type, is the basic material for this detector type. As with surface-barrier detectors, the silicon piece has the shape of a thin wafer. **A** thin layer of n-type silicon is formed on the front face of the wafer by applying a phosphorus compound to the surface and then heating the assembly to temperatures as high as 800-1000" C for less than an hour. The phosphorus diffuses into the silicon and "dopes" it with donors (Figure). The n-type silicon in front and the p-type behind it form the p-n junction.



Both surface-barrier and diffused-junction detectors are used for the detection of charged particles. To be able to measure the energy of the incident radiation, the size *Xo* of the detector should be at least equal to the range of the incident particle in silicon. The value of X_0, depends on the resistivity of the material (which in turn, depends on impurity concentration) and on the applied voltage.

8.2 Nuclear Track Detectors

The passage of highly ionizing radiation through an insulating solid leaves a wake of destruction in the material. In covalently bonded materials, the chemical structure of the material along the track can be significantly and permanently changed by the passage of a single energetic ion. Certain polymeric (plastic) materials and the mineral mica (a form of silicon dioxide) are particularly sensitive to such radiation damage. The original radiation damage remains localized on the molecular scale but is not visible without enhancement. However, the track can be expanded by chemical etching from the molecular scale (nanometers) up to the microscopic scale (μm).

Advantages: Nuclear track detectors are very simple and very efficient detectors of rare events that produce highly ionizing radiation. Carefully prepared and scanned track detectors have been used to identify individual rare decays. The detectors are integrating in that the damage caused by a track is not spontaneously repaired.

Drawback: The drawback to track detectors is that the tracks are small and can only be observed with a microscope. In the past, scanning by eye was extremely labor intensive and prone to error. Modern computer---controlled scanning has improved the speed and reliability of the analysis.

Plastic track detectors that are sensitive to alpha particles are used extensively in commercial radon detectors. Chemical etching of the material takes place on all surfaces that are exposed to the etching solution. The exposed surfaces of the material are eroded along with the material along the track. Therefore, the rate of etching has to be carefully controlled to get the maximum amount of information from the track.

Notice that etching of a uniform track will generally form a circular cone because the material will be more easily removed from the surface than from deep along the track. Mica tracks are diamond-shaped due to the lattice structure as opposed to being circular.

Nuclear emulsions are closely related "track detectors" that trace their origins to the original discovery of radiation by Becquerel. Nuclear emulsions are very fine-grained photographic film. The film is "exposed" by the passage of radiation through it and the grains of AgC1 are activated by the ionization. The film is developed and with careful handling and microscopic observation, the track or path of individual particles can be traced. Occasionally, a particle interacts with a nucleus in the emulsion, creating many fragments or particles, and the tracks of the reaction products can be traced. The emulsion is also sensitive to the rate of ionization and the nature of the particle in each track can often be determined. On the other hand, most people are familiar with the shadow images of skeletal features taken with x-rays. The x-rays are absorbed and scattered more efficiently by the heavy elements in bones (essentially calcium) than by the light elements in soft tissue (carbon, oxygen, hydrogen) and create a shadow. The grains in the emulsion are then exposed by the transmitted x-rays and are developed to form the negative image.

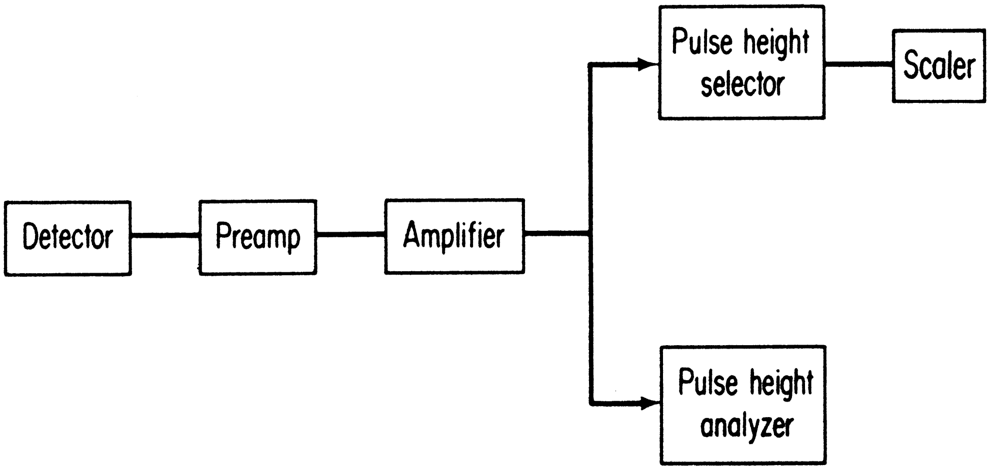
8.3 Nuclear Electronics and Data Collection

All of the nuclear radiation detectors produce electronic pulses in response to the interaction of some ionizing radiation. These signals are processed by standardized nuclear instrumentation modules (NIM) electronics to count the number of pulses or to more fully analyze the size or even the shape of the signal. In addition, computer-based electronics in the CAMAC (Computer Automated Measurement and Control) system are used to measure the time relationships of pulses, the pulse heights, and the signal shapes. The signals are recorded and stored by computers for later analysis. An important feature of scientific studies with radio activities and with nuclear beams is that the data must be collected as rapidly as possible usually during a very limited time. A radioactive source will decay away after being produced and cannot be "stopped" because the scientist is not ready to use it. Similarly, the nuclear reactions induced by particle beams take place in a very short time and must be recorded when they occur. Then after a set of events has been collected “on-line,” the data are analyzed “off-line.”

We will give a very brief overview of the kinds of modules used. CAMAC and NIM electronics fall into three broad categories,

- linear electronics that maintain a linear relationship to the size of the initial signal,
- logic circuits that provide only a standard (or single sized) pulse indicating that a given logical condition was met, and
- data-acquisition modules to measure the signals and record the data.

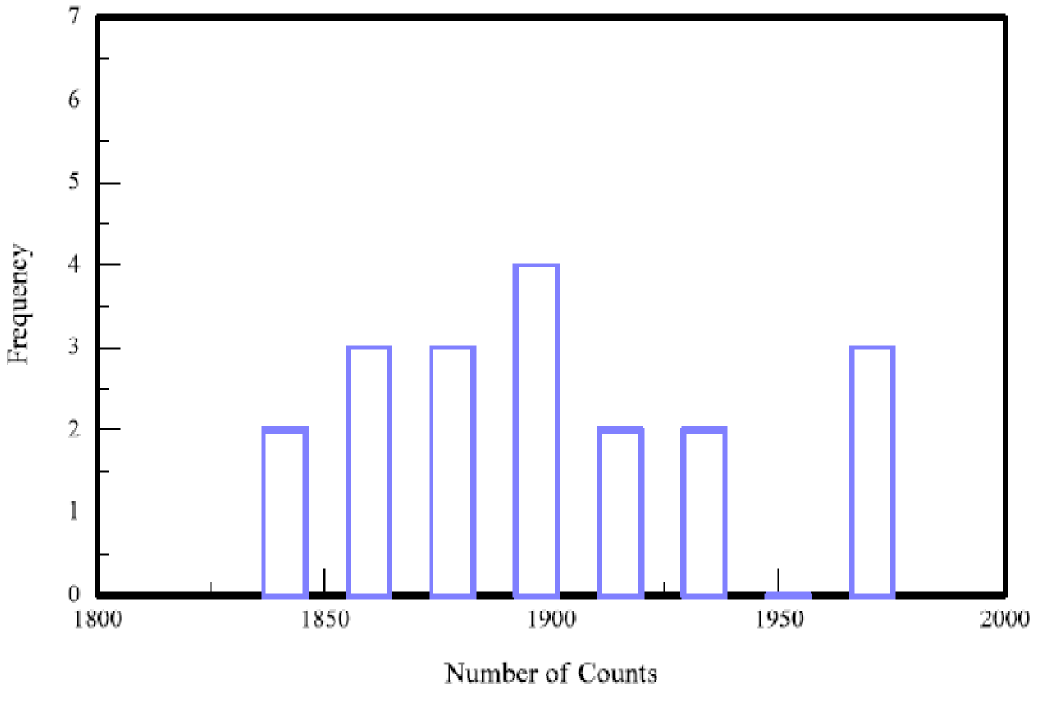
One should realize that with modern high density electronics the functions that we will describe can correspond to a single electronic module or may be condensed into a single integrated circuit. Therefore, we will only describe the functions performed by the electronic modules and not specific equipment. The output of most detectors is an electrical pulse that carries information about the energy deposited in the detector, the time of the interaction, etc. Linear electronics are described as modules that preserve and extract information about the energy deposit in the detector from the detector signal.



A typical pulse-height analysis system is shown in figure. The signal from the detector is given a preliminary amplification and shaping by a preamp before being sent through a coaxial cable to a linear amplifier. This is done to prevent noise in the cable from destroying the tiny detector signal. In the amplifier the signal is further amplified and shaped before analysis. The height of the pulse is related to the energy deposited in the detector. The analog-to-digital converter (ADC) converts the signal from the amplifier into digital data (a number of standard pulses) thus measuring its size. The ADC could be contained on a plug-in card in a personal computer (used to measure the distribution of pulses from a single detector monitoring a radioactive source) or it might be one of many identical ADC units in a CAMAC module (used to record the signals from many detectors monitoring nuclear collisions simultaneously) .Logic modules are used to monitor the counting rate of single detectors and the relative times at which radiation is detected. A fast signal derived from the detector itself, the preamplifier, or from a timing-filter amplifier is sent to a discriminator. The discriminator produces an output pulse with a fixed shape (generally square) and size when the input signal crosses a reference. Discriminators usually have multiple identical output signals. The logic pulses can be sent to a scalar that simply counts the number of pulses, to a count rate meter to monitor radiation rates or doses, and to a time-to- amplitude converter (TAC) to measure the relative times of arrival of two or more logic signals.

8.4 Nuclear Statistics

Radioactive decay is a random process. The number of nuclei in a sample of radioactive material that decay in any time period is not a fixed number but will differ, usually, for various time periods. This point can be readily shown by making repeated measurements of the activity of a long-lived radionuclide, each for the same time duration. The results of such an experiment might be shown in as a distribution function, by "binning" the data (Figure: Typical Sequence of Counts of a long-Lived Sample (^{170}Tm)*).

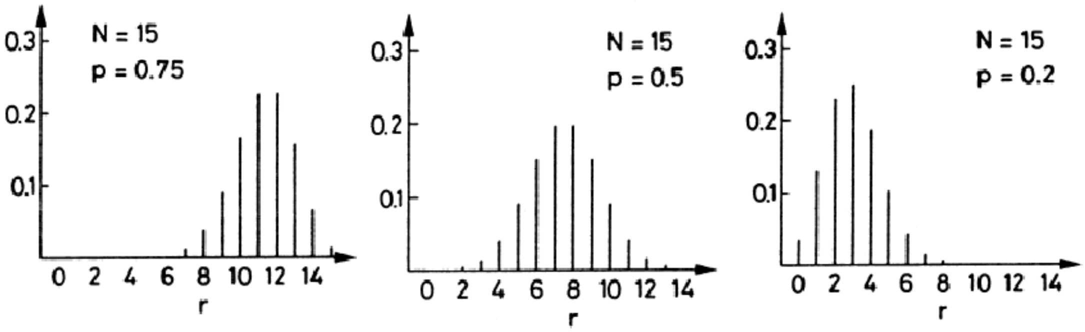


We can now ask ourselves if we can understand this distribution function. Statisticians have given us mathematical models that describe these and other similar distribution functions. As a background for our discussion of how to extract the maximum amount of information from these data, let us consider some of these models. The most general model to describe radioactive decay is the *binomial distribution.* For a process that has two outcomes (success or failure, decay or no decay), we can write for the distribution function P(x)

$$P(x) = \frac{n!}{(n-x)!x!} p^x (1-p)^{n-x}$$

where n is the number of trials where each trial has a probability of success p and

P(x) is the predicted probability of getting x successes. Applying this distribution to radioactivity, P(x) might be taken as the probability of getting x counts in a given time interval and p=λΔt where Δt is a time short compared with the measurement time and the half-life. Note that x and n are both integers. Typical binomial distribution functions are shown in Figure.



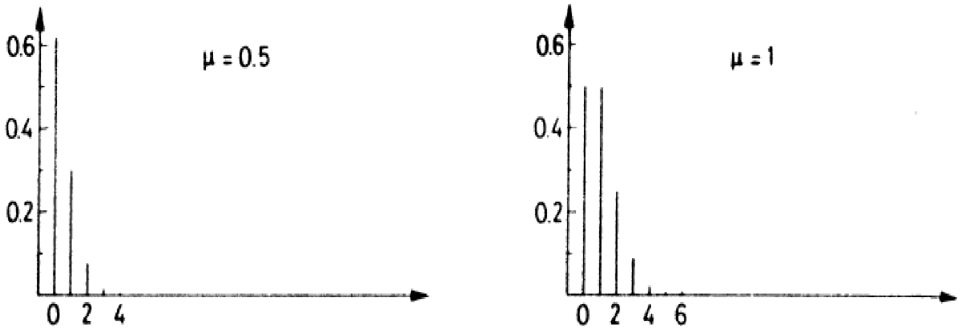
The binomial distribution function is cumbersome and a simplification can be made. If the probability of success p is small (p<<1) (the measurement time is very short compared with the half-life), we can approximate the binomial distribution by the Poisson distribution. The Poisson distribution is written as

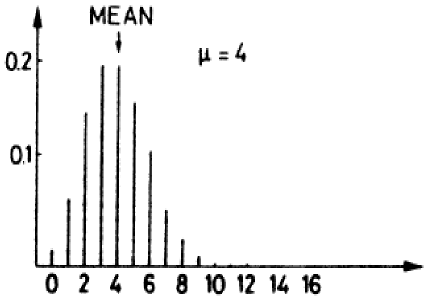
$$P(x) = \frac{{x_m}^x}{x!}\exp(-x_m)$$

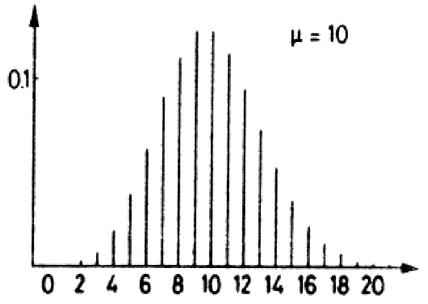
where x_m= pn

Thus we have a simplified distribution characterized by one parameter, x_m compared to two parameters in the binomial distribution. The Poisson distribution is an asymmetric distribution as shown in Figure.

Besides being a more tractable function to use, the Poisson distribution has certain important properties that we will use in analyzing radioactivity data.







Let us consider a parameter, the *variance*, σ_2, which expresses something about the width of the distribution of values about the mean, x_m.

For a set of N measurements, we can calculate

$$\sigma^2 = \frac{\sum_{i=1}^{N}(x_i - x_m)^2}{N-1}$$

For a binomial distribution

$$\sigma^2 = np(1-p)$$

Which is cumbersome to use but, for a Poisson distribution, we can show that

$$\sigma^2 = x_m$$

$$\sigma = (x_m)^{1/2}$$

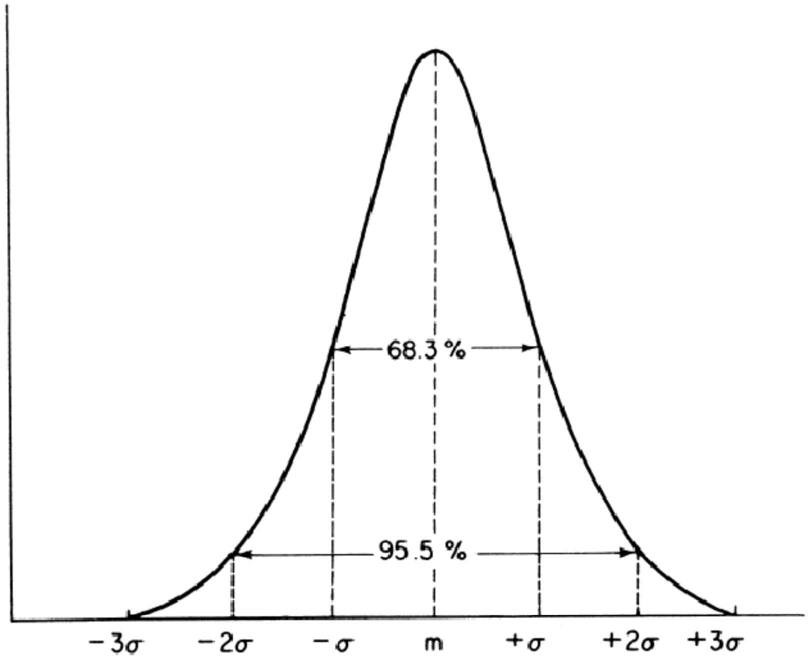
This illustrates the important point that these distribution functions are models, not physical laws, and when they are applied to finite data sets, their predictions may deviate from observation. The Poisson distribution can be applied also to describe the action of detectors. For example, suppose the interaction of a γ-ray photon with an inefficient scintillator produced, on average, 3.3 photoelectrons from the photocathode. The probability of producing no photoelectrons (not seeing the event) is given by the Poisson distribution as

P(0)= exp(-3.3) = 3.7%

Thus 3.7% of the events will be missed due to "statistical fluctuations". A further simplification of the parent binomial distribution occurs when the number of successes is relatively large, *i.e.*, we get more than about 30 counts in a measurement. Then the binomial distribution can be represented as a *normal* or *Gaussian distribution*. Here we write

$$P(x) = \frac{1}{\sqrt{2\pi x_m}} \exp\left(-\frac{(x - x_m)^2}{2x_m}\right)$$

This analytical approximation is symmetric. As shown in Figure, 68.3% of the measured values lie within $\pm 1\sigma$ of the mean, x_m.



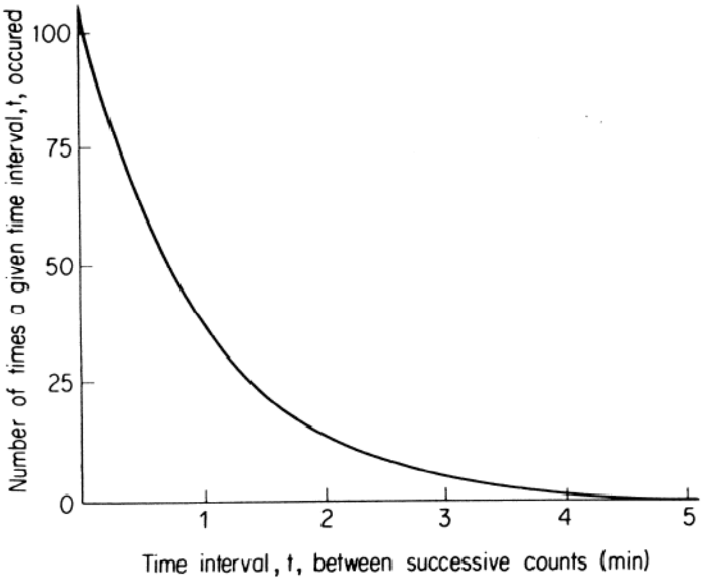
Furthermore 95.5% of all measurements lie within $\pm 2\sigma$ of the mean and 99.7% lie within $\pm 3\sigma$ of the mean. The full width at half maximum (FWHM) is 2.35σ .

Thus for a single measurement of a count rate of 100, we would estimate that σ = 10. We could say, with a 68.3% chance of being correct that the true rate was between 100-10=90 and 100+10=110. With 95.5% certainty, we could say the true rate lies between 80 and 120. Generalizing, we can quote the results of a measurement as x'+ $n\sigma$ where n is related to the probability that an infinite number of measurements would give a value within the quoted range. For n = 0.6745,1,1.6449,1.96,2,2.5758,3, the "confidence limits" are 50%, 68.3%, 90%,95%,95.5%, 99%, and 99.7%, respectively. Commonly people will quote the results of a measurement as $x \pm \sigma$. One should remember that doing so means one will be wrong 31.7% of the time, *i.e.*, the mean count rate will be outside $x \pm \sigma$. If this risk is not acceptable, one should pick a greater confidence level, *i.e.*, 2 σ, 3 σ, etc. Another distribution function of interest relates to the distribution of time intervals between successive counts. We know the average time between counts is (1/count rate). The distribution of time intervals is given by the *interval distribution*. This distribution (applicable to all random events) states that for a process with an average time between events tm, the probability of getting a time t between successive events is

$$I(t) = \frac{1}{t_m}\exp(-t/t_m)dt$$

For radioactive decay $t_m = 1/\lambda$

This distribution function is shown in Figure.



Note the most probable time between events is zero. Random events (counts, natural disasters, etc.) occur in "bunches." Let us summarize how we describe the statistical uncertainty in measurements of radioactivity. If we measure the activity of a sample (+background) as 64 counts in 1 minute, then we estimate

(S+B)=64cpm

with an uncertainty σ_{S+B}

σ_{S+B}= 8 cpm

What if a second measurement with no sample showed a background of 10 counts in 1 minute? We would then estimate

$B = 10$ cpm

$\sigma_B = (10)^{1/2} = 3.2$ cpm

If we consider two independently determined numbers and their uncertainties (standard deviations), $A \pm \sigma_a$, $B \pm \sigma_b$, we can write down, some rules for the uncertainty in the result of some common mathematical operations. We would calculate that for our sample and background counting case,

Net rate = (sample + background) - (background)

=64 -10= 54cpm

Uncertainty in net rate = $(8^2 + 3.2^2)^{1/2} = 8.6$ cpm

Up to now we have carefully restricted our discussion of nuclear statistics to cases where l-min counts were taken. If the number of counts recorded in 1 min was x, then the counting *rate* has been quoted as $x \pm (x)^{1/2}$ cpm. Suppose, however, that we recorded 160 counts in 5 min. What would be the standard deviation of the average counting rate (in cpm)? The best estimate of the mean number of counts in the 5-min period would by $160 \pm (160)^{1/2}$ that is, 160 ± 13 counts. The average rate would be 160/5 ± 13/5 = 32 ± 3 cpm. In general, therefore, the rate R is given as

R=(number of counts recorded)/(measurement time)=x/t

The standard deviation of the rate, σ_R, is

$$\sigma_R = (x)^{1/2}/t = (R*t)^{1/2}/t = (R/t)^{1/2}$$

Thus for the preceding example we could have calculated directly that

$$\sigma_R = (R/t)^{1/2} = (32/5)^{1/2} = 3$$

Often we wish to compute the average of two numbers, x_1, and x_2, both of which have an uncertainty denoted by their standard deviations σ_1 and σ_2, respectively. The best average of these two numbers is not the simple average but weighted average x_m, given by

$$x_m = \left(\frac{x_1}{\sigma_1^2} + \frac{x_2}{\sigma_2^2}\right) / \left(\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2}\right)$$

$$x_m = \frac{x_1 + w x_2}{1 + w}$$

where $w = \left(\frac{\sigma_1}{\sigma_2} \right)^2$

In short, each number is weighted by the inverse of its standard deviation squared. For the weighted average of N values, x_i, with standard deviation, σ_i, we have

$$x_m = \sum_{i=1}^{N} \left(\frac{x_i}{\sigma_i^{\,2}} \right) / \sum_{i=1}^{N} \left(\frac{1}{\sigma_i^{\,2}} \right)$$

The uncertainty or standard deviation of x is given by

$$\sigma_{x_m} = \left[1 / \sum_{i=1}^{N} \left(\frac{1}{\sigma_i^{\,2}} \right) \right]^{1/2}$$

For example, suppose that we make two independent measurements of an activity, obtaining results of 35 ± 10cpm and 46 ± 2cpm. The weighted average of the two measurements is

$w= (10/2)^2=25$

$x_m = (35+25.46)(1+25) \cong 46$ cpm

The standard deviation of the weighted average is

$\sigma_x= ((100+(25)^2(4))/(26^2))^{1/2}$

$$\sigma_x = \frac{1}{\left[\frac{1}{100} + \frac{1}{4} \right]^{1/2}} \simeq 2$$

Thus we would say that the average rate was 46 ± 2 cpm.

Rejection of Abnormal Data

In our discussions so far, we have only considered the uncertainty in the experimental data due to the randomness of radioactive decay. But there may also be systematic error that contributes to the overall uncertainty in the data. As a result, when we make repeated measurements of a sample activity under seemingly identical situations, we will find occasionally one measurement that differs from the others by a large amount. If included in the average, this abnormal observation may cause significant error. When are we justified in rejecting such data? One criterion for rejecting such data is to reject suspected values that deviate from the mean by more than 2σ or 3σ. The probabilities of ccurrence of such deviations are 4.5 and 0.27%, respectively. What about the question of whether a detector or counting system is working properly? For example, the data in do not exactly match a Poisson or normal distribution. Was the counting system malfunctioning? One parameter that we can calculate that will help us answer such questions is χ^2 (chi-squared). Formally

$$\chi^2 = \frac{\sum_{i=1}^{N}(x_i - x_m)^2}{x_m}$$

Setting Upper Limits When No Counts Are Observed

Suppose our experiment failed to detect a type of decay we were seeking: What can we say about its occurrence? The simplest answer is what is termed the *"one-event upper limit"*. We assume that you had detected one event, and calculate the resulting decay rate, cross section, etc., taking into account detection efficiencies, solid angles, etc. A more sophisticated answer can be obtained by using the properties of a Poisson distribution. The probability of observing n events if the mean value is μ is given as

$$\rho(n/\mu) = \frac{\mu^n}{n!} = e^{-\mu}$$

The probability of observing 0 events in a time period T for a process with mean rate λ is

$$\rho(0/\lambda t) = e^{-\lambda t}$$

It can be shown that the upper limit on the rate (when zero counts are observed), λ_0, is given by

$$\lambda_0 = -\frac{1}{T}\ln(1 - CL)$$

Where CL is the confidence limit you wish to attach to your upper limit. (If you want to quote an upper limit with 95% confidence, then CL = 0.95.)

8.5 Self Learning Exercise-I

Q.1 Write down the formula for binomial distribution.

Q.2 Write down the drawback of Nuclear Track Detectors.

Q.3 Sketch figure of Diffused junction detector.

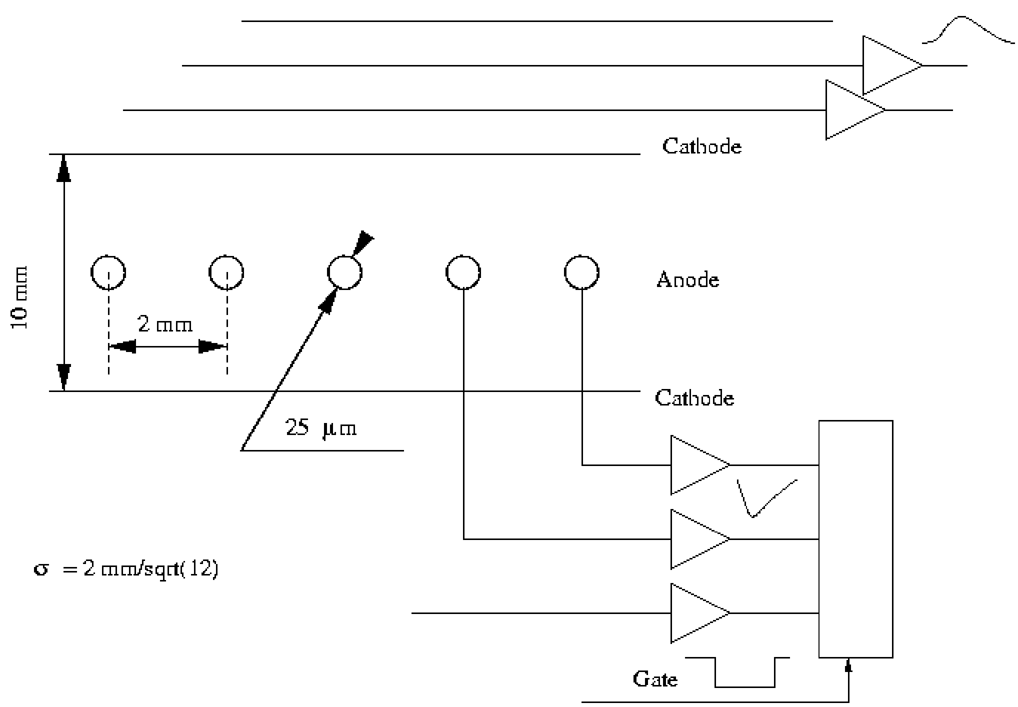
Q.4 Explain the nuclear detector electronics.

8.6 Multi-Wire Proportional and Drift Chambers

The proportional chamber advances by virtue of the fact the voltage pulse it measures is able to provide information on the particle's energy as well.

The multi-wire proportional chamber or MWPC advances this further - instead of having one anode wire surrounded by a cathode wall or plate, multiple 'sense wires' are equidistantly spaced symmetrically between two parallel plates. Wire spacings are typically a few millimetres. A nearly uniform electric-field develops between the cathode plates, distorted only near the sense wires. Each wire acts as a separate counter - when a charged particle passes through the chamber leaving a trail of electron-ion pairs, the electrons drift to the nearest wire and cause a voltage pulse. By placing another such configuration at 90^0 to the first, thus forming a grid, and marking off the wires that produce a pulse, the path of the charged particle is revealed.

Multiwire Proportional Chamber

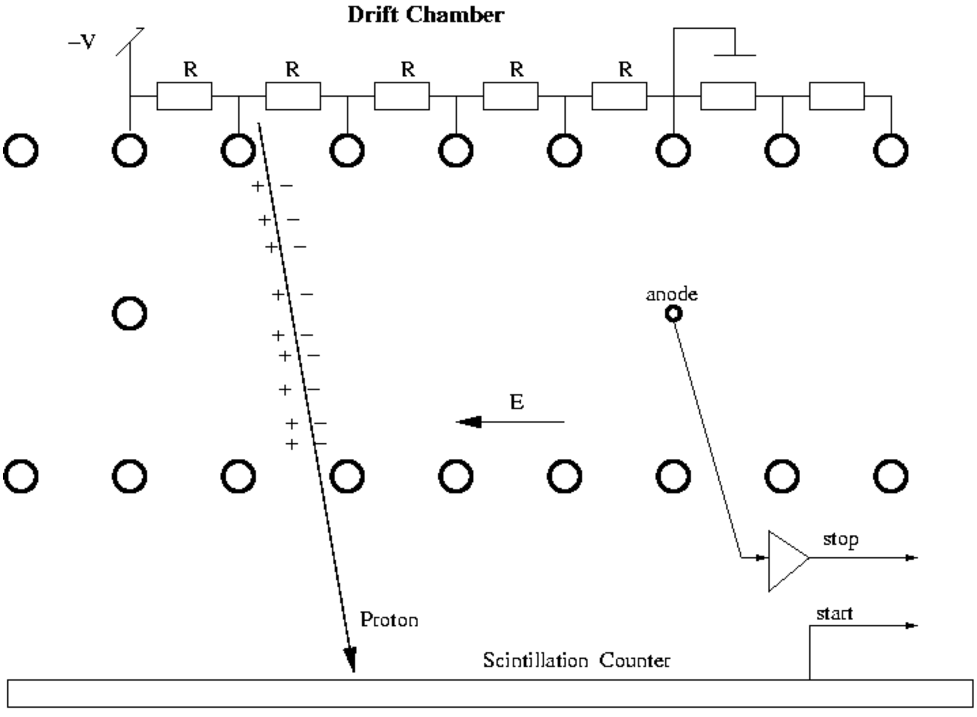


Applying a magnetic field perpendicular to the direction the particle is travelling in, will cause it to spiral due to the Lorentz force. This will reveal how the particle is charged and what its momentum is.

A typical gas composition for multi-wire proportional chambers is the ‘magic gas’ mixture comprising 75% argon + 24.5% isobutane + 0.5% freon.

Drift chambers:

The resolution of multi-wire proportional chambers can be dramatically enhanced by taking into consideration the time the electrons take to drift from the point where they were liberated to the sense wire, where they are detected. Thus one can infer the distance at which the charged particle passed the wire. This improves the spatial resolution and allows for wider wire spacing on the order of centimeters. Wider wire spacing distort the uniform field less, but increase the drift time, hence these ‘drift chambers’ are not ideal for use in colliders with high collision rates, or in triggers. In order to calculate the distance an electron has travelled it is necessary to understand its velocity in the electric-field. The uniformity of the field must be more carefully controlled than it is in a multiwire proportional chamber: to this end, the anode sense wires are alternated with cathode field wires that ‘correct’ the field distortion caused by the sense wires, restoring uniformity throughout the chamber. Drift velocities under electric-fields



Drift Distance = Drift Velocity * Time

8.7 Nuclear Emulsions

Composition:

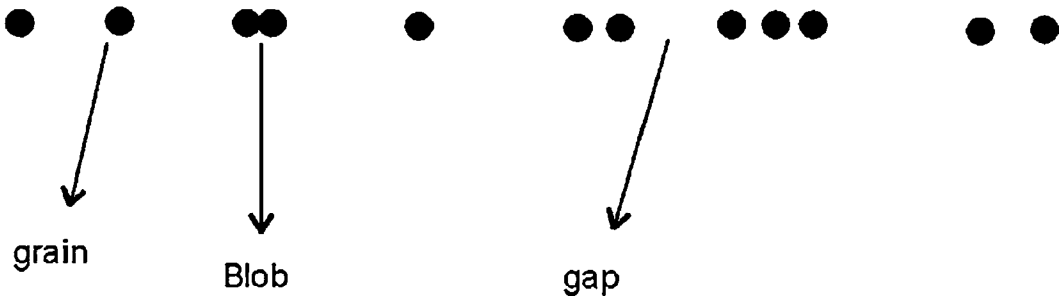
Photographic Emulsions or Nuclear Emulsions differ from ordinary optical emulsions by a higher silver-bromide content, smaller average crystal diameter and much greater thickness. The silver-halide (mainly silver bromide with 5 % silver-iodide) crystals are embedded in gelatin (HCNO). The gelatin is usually made from clippings of calf hide, ear and cheek or from pig skin and bone. The main function of gelatin is to keep the silver halide crystals well dispersed in the medium and to prevent clamping of the crystals. Atomwise, the AgBr group and HCNO groups compromise 25%and 75 % respectively. But the interactions with medium and high energy particles take place with a frequency of 70 % in AgBr, 20 % in CNO and 5 % in H. The emulsion sheets called pellicles of standard size 400μm or 600μm are stacked with one on the top of the other before the exposure in order to increase the volume. A variety of emulsions of different crystal sizes have been manufactured which differ in sensitivity. The type G_5, L_5 (Ilford), NTB (Kodak), ET-7A (Fuji) and Nikfi-R with crystal size in the range 0.2μm–0.28μm are highly sensitised and are capable of recording relativistic particles ($\beta \sim 1$). K_2 and L_2 are less sensitised and record protons up to β=0.4. K_1 is less sensitised and record less protons up to β=0.12. K_0 is least sensitised and is used mainly for fission studies.

Latent Image:

When a charged particle moves through emulsion energy is absorbed by the silver halide crystal, and under the action of reducing agent is converted into metallic silver. The physical condition which renders the crystal developable is called “latent image”. The latent image will fade if too much time elapses between irradiation and development, similar to ordinary photography.

Processing:

Stripped emulsions are first mounted on glass before processing. For uniform development, it is essential that the developer, for example amidol, permeates the thickness of emulsion. For this reason, the plates are bathed in the developer at low temperature (0–5°C) so that the developer is permitted to penetrate but the development will not ensue. Now, if the temperature is raised to say 23°C, the development ensues. This is called high temperature development. After the development stage, the plates are “fixed”, washed and dried in alcohol.



Techniques:

Events are analyzed with the aid of special type of microscopes with smooth movable stages and high power oil objectives and eyepieces with graticules capable of giving magnifications as high as 2700. After processing, normal emulsion shrinks by a factor of 2–2.5. The shrinkage factor is taken into account in the dip measurements of angles. For particles, which stop within the emulsion stack, Range-Energy Relation of the type (1-101) is used.

Ionization measurements are made either by counting grains or blobs for relativistic particles or by counting blobs and gaps of length > l, for non-relativistic particles, and determining the exponent g from the relation

$$H = Be^{-gl}$$

where H and B are gap and blob density, respectively. Blobs are unresolved grains and gap is the space separating two successive grains or blobs, as shown in Fig.

For energetic particles, the parameter $p\beta$ (momentum times velocity) can be found out from multiple scattering measurements by essentially measuring the y-coordinates of the track along the axis, at constant intervals called “cell’s”. The arithmetic average of second differences is given by,

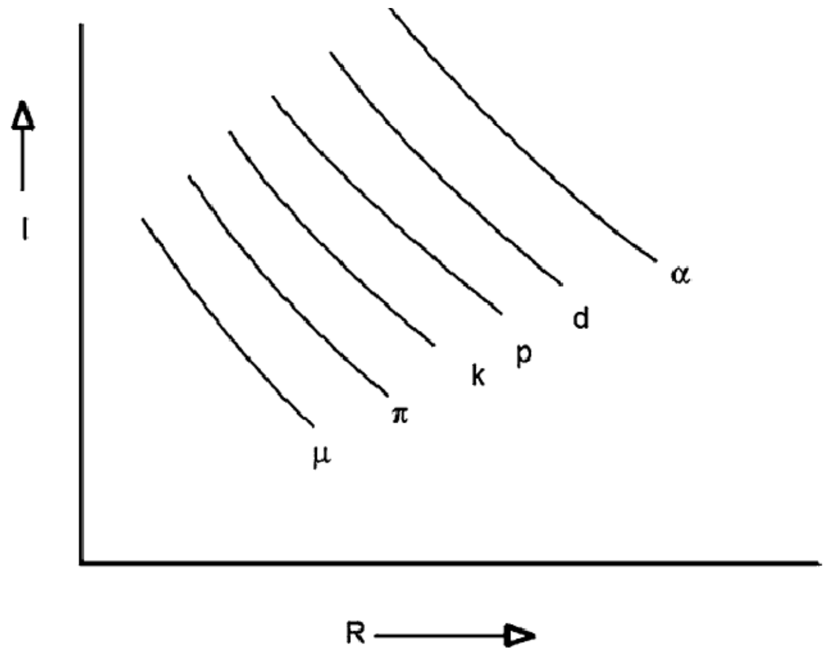
$$\langle | D_2 | \rangle = \langle | y_1 - 2y_{i+1} + y_{i+2} | \rangle$$

and $p\beta$ is given by the relation

$$p\beta = \frac{Kt^{\frac{3}{2}} \times 18.1}{|D_2|}$$

where K = 28 is the scattering constant, for β >1, D_2 is in μm, t = cell length in mm and p in GeV/c. The quantity $t^{3/2}$ arises due to the fact that the scattering angle $\theta = D/t$. The factor 18.1 arises due to conversion of degrees into radians. The choice of cell-length is such that the signal-to-noise ratio is greater than 2–3. Multiple scattering technique with constant cell method works provided the energy loss over the tracks is not significant. In order that the method be useful, it is important that the spurious scattering and distortion resulting from the processing of mulsions be small and that the stage noise, which arises due to the non-linear motion of the stage be negligible.

Charge of the particle can be determined from δ-ray counting *(*AAK*, 1, 1)* or from photometric measurements; for example, the fluxes of heavy primaries of Cosmic rays have been determined from emulsion exposures in balloons or rockets following this procedure.

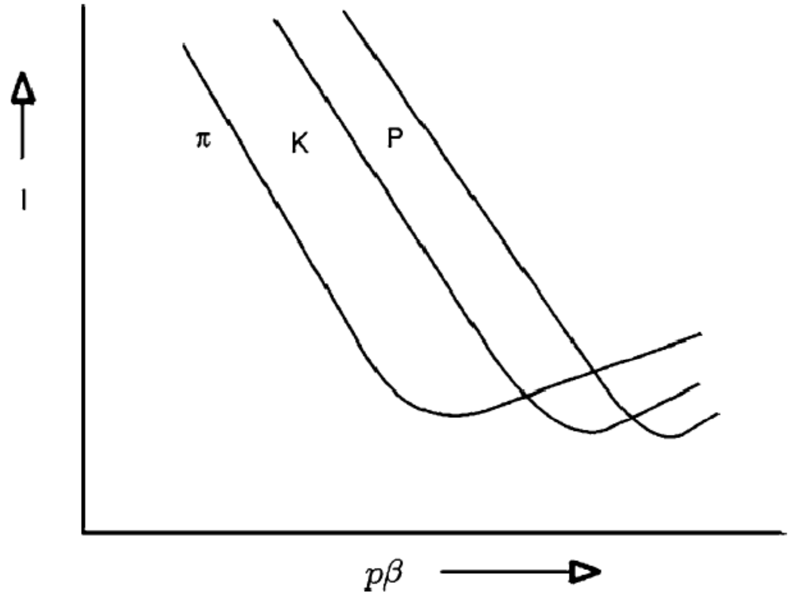


Particles are identified from their mass determinations. In this context we recall from *(*AAK*, 1, 1)*,

i. Range measurement gives energy of the particle
ii. Ionization measurement gives the velocity
iii. Multiple Scattering measurements give $p\beta$.
iv. δ-ray density measurement gives z of the particle.

For singly charged particles, combination of any two parameters arising in (i), (ii) and (iii) uniquely fixes the mass of the particle since velocity must be eliminated. Thus, the plot of ionization (*I*) versus residual range (*R*) gives a family of curves for particles of different mass, Fig. Notice that for the given *I*, the ranges are in the ratio of the masses. The method is very extensively used for particles which are brought to rest. Masses can be estimated with an accuracy of about 10% from a single measurement.

The method can be extended for identifying particles which are not arrested in the emulsion stack, if an appreciable change in ionization over a known distance is determined.



At higher energies, combination of (ii) and (iii) in favorable cases permits the identification of particles. (Fig) At still higher energies, the curves cross each other and the identification becomes difficult or even impossible. On the other hand, energy measurements can seldom be made from multiple scattering method with an accuracy better than 10–15 % due to the presence of spurious scattering. At energies greater than few GeV, the measurements are rendered meaningless if the noise due to spurious scattering competes with the Coulomb's signal. Sometimes in favorable cases it has been possible to extend the energy measurements up to 15–20 GeV in cosmic ray jets by making relative scattering measurements—a method in which multiple scattering measurements are made with reference to a neighboring track due to an ultra relativistic particle so that spurious scattering and stage noise which affect both the tracks similarly are eliminated.

Advantages:

1. **High Stopping Power and High Spatial Resolution**

2. **High Angular Resolution** The angular resolution is unsurpassed. This aspect has been exploited in the determination of the magnetic moment of Λ^0.

3. **Compactness** In situations where compactness of equipment is essential, emulsions can be conveniently used. For example, they can be sent in balloons or rockets to high altitudes and recovered conveniently after the required exposure. Further, they are economical.

4. **Radiation Length** Because of high stopping power and short radiation length huge electromagnetic cascades can be contained in a large stack and the complete development and final degradation can be studied in detail.

5. **Loading** It is possible to load emulsions with H_2O, D_2O, Li_2SO_4, $Th(NO_3)_4$, UO_2 etc. to study reactions with elements which are not contained in normal emulsions.

Limitations:

1. **Composition Invariability**

The composition of nuclear emulsions can not be changed arbitrarily so that interaction studies are limited only to those nuclei which are present in normal emulsions, although loaded emulsions in limited concentration have been used with some difficulty.

2. **Minuteness of Volume** Because of minuteness of volume of emulsion under study in the microscope it is exceedingly difficult to find correlated events even 1 cm or so apart.

3. **Continuous Sensitivity** Because of continuous sensitivity the background tracks are a source of nuisance. The best available emulsions from the stand point of sensitivity lack discrimination and all highly ionizing particle tracks are saturated.

4. **Distortion and Spurious Scattering**

Emulsion which has a gelatin base is subject to distortion in the processing regime. This can seriously affect the range and angle measurements. Spurious scattering can interfere with Coulomb's signal in multiple scattering measurements.

5. **Scanning** It usually takes several months involving a large group of Physicists

and scanners to scan and analyze events of statistical significance.

6. **The Study of Elementary Interactions**

Since only 5 % of the interactions take place with hydrogen and 95 % in complex nuclei of emulsion, the interactions in the latter are obscured by secondary effects. Although hydrogen density in emulsions is comparable with that in hydrogen bubble chamber, the latter is by far better suited in so far as the elementary interaction studies are concerned.

Discoveries Made with Photographic Emulsions

Major discoveries of fundamental importance included the particles π^+, π^-, π^0, K^+, K^- mesons, several decay modes of K^+ mesons (two-body and three-body decay modes), the hyperons, hyper fragment, double-hyper fragment, the composition of primary cosmic rays etc. Reliable mass measurements of various types of mesons and the Σ^+ and Λ^0 hyperons, and their mean life times were first carried out in emulsions.

8.8 Self Learning Exercise- II

Q.1 Define latent image?

Q.2 What is the gas composition used in multi-wire proportional chambers?

Q.3 Write down the advantage and limitation of nuclear emulsion.

Q.4 Discuss workings of Multi-Wire Proportional and Drift Chambers.

8.9 Summary

In this chapter we discussed various types of detector and nuclear detector techniques.

8.10 Glossary

Background radiation: The radiation of man's natural environment originating primarily from the naturally radioactive elements of the earth and from the cosmic rays. The term may also mean radiation extraneous to an experiment.

Ionizing Radiation : Radiation capable of producing ions or charged particles. Ionizing radiation includes alpha, beta, gamma, and X-rays.

Multiwire Proportional Counter : Particle detector using changes in the current in wires due to the passage of ionizing particles nearby.

8.11 Answer to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: $P(x) = \frac{n!}{(n-x)!x!} p^x (1-p)^{n-x}$

Ans.2: See section 8.2

Ans.3: See section 8.1

Ans.4: See section 8.3

Answers to Self Learning Exercise-II

Ans.1: The physical condition which renders the crystal developable is called "latent image".

Ans.2: Mixture comprising 75% argon + 24.5% isobutane + 0.5% freon.

Ans.3: Section 8.7

Ans.4: Section 8.6

8.12 Exercise

Q.1 Write a short note on

(i) Diffused junction detector, (ii)Surface barrier detectors

(iii) Multiwire proportional chamber (iv)Nuclear emulsions

Q.2 Explain Different type of distribution function use to analyze nuclear data.

References and Suggetsed Readings

1. Measurement and Detection of Radiation by Nicholas Tsoulfanidis, 2013.
2. Modern Nuclear Chemistry by Walter D. Loveland, David J. Morrissey, Glenn T. Seaborg, 2005.
3. Particle Physics by Anwar Kamal, 2014
4. Engineering Physics, by Raghuvanshi, G. S. Raghuvanshi.
5. Nuclear and particle physics by B. R. Martin 2006
6. Nuclear Energy by Raymond L. Murray, 2000.
7. R.R. Roy and B.P. Nigam: Nuclear Physics, 1979.

UNIT-9
Complex Nuclei : Shell Theory

Structure of the Unit

9.0 Objectives

After interacting with the material presented here students will be able to understand the nuclear shell structure. They can also be able to calculate parity, spin and magnetic moment of a given nucleus.

9.1 Introduction

There are two basic types of simple nuclear model-

1. Collective body with no individual particle states. An example is the Liquid Drop Model which is the basis of the semi-empirical mass formula.

2. Individual particle model with nucleons in discrete energy states for example the Fermi Gas Model or the Shell Model.

   In this chapter we will discuss details of nuclear shell model.

9.2 Magic Numbers

The binding energies predicted by the Liquid Drop Model underestimate the actual binding energies of "magic nuclei" for which either the number of neutrons $N = (A - Z)$ or the number of protons, Z is equal to one of the following "magic numbers" 2, 8, 20, 28, 50, 82, 126. This is particularly the case for "doubly magic" nuclei in which both the number of neutrons and the number of protons are equal to magic numbers.

For example for $^{56}Ni_{28}$ (nickel) the Liquid Drop Model predicts a binding energy of 477.7MeV, whereas the measured value is 484.0 MeV. Likewise for $^{132}Sn_{50}$ (tin) the Liquid Drop model predicts a binding energy of 1084 MeV, whereas the measured value is 1110 MeV. There are other special features of magic nuclei:

- The neutron (proton) separation energies (the energy required to remove the last neutron (proton)) peaks if N (Z) is equal to a magic number.
- There are more stable isotopes if Z is a magic number, and more stable isotones if N is a magic number.
- If N is magic number then the cross-section for neutron absorption is much lower than for other nuclides.
- The energies of the excited states are much higher than the ground state if either N or Z or both are magic numbers.
- Elements with Z equal to a magic number have a larger natural abundance than those of nearby elements.

9.3 The Shell Theory Potential

The first step will be to identify a suitable average potential for the nucleons. One obvious difference distinguishing nuclei from atoms is that the Coulomb potential is not going to hack it. In the electron structure of an atom the electrons repel each other, and the only reason the atom stays together is that there is a nucleus to attract the electrons. But inside a nucleus, the nucleons all attract each other and there is no additional attractive core. Indeed, a Coulomb potential like the one used for the electrons in atoms would get only the first magic number, 2, right, predicting 10, instead of 8, total particles for a filled second energy level.

A better potential is needed. Now in the center of a nucleus, the attractive forces come from all directions and the net force will be zero by symmetry. Away from the center, the net force will be directed inwards towards the center to keep the nucleons together inside the nucleus. The simplest potential that describes this is the harmonic oscillator one. For that potential, the inward force is simply proportional to the distance from the center. That makes the potential energy V proportional to the square distance from the center, as sketched in figure (a).

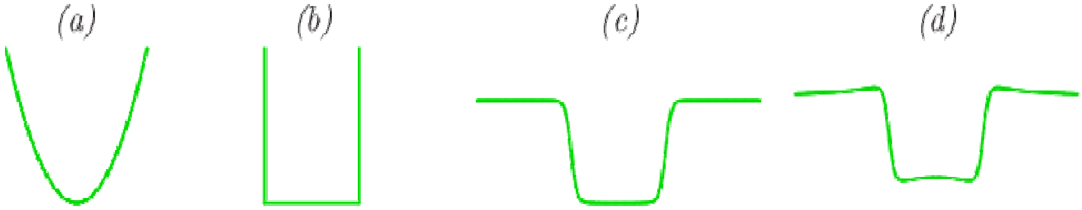


Figure 5 (a) harmonic oscillator, (b) impenetrable surface, (c) Woods-Saxon, (d) Woods-Saxon for protons.

The energy eigenvalues of the harmonic oscillator are

$$E_n = (n + 1/2)\hbar\omega, \qquad \text{n=1,2,3...}$$

Also, in spherical coordinates the energy eigenfunctions of the harmonic oscillator can be taken to be of the form,

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Here **l** is the azimuthal quantum number that gives the square orbital angular momentum of the state as $l(l+1)\hbar^2$; m is the magnetic quantum number that gives the orbital angular momentum in the direction of the arbitrarily chosen z-axis as mh, and m_s is the spin quantum number that gives the spin angular momentum of the nucleon in the z-direction as m_sh. The spin up state with m_s=1/2 is commonly indicated by a postfix $\uparrow$, and similarly the spin-down one m_s=1/2 by $\downarrow$.

Compared to the Coulomb potential of the hydrogen electron, the major difference is in the number of energy states at a given energy level n. While for the Coulomb potential the azimuthal quantum number ***l*** can have any value from 0 to n-1, for the harmonic oscillator l must be odd or even depending on whether n-1 is odd or even.

It does not make a difference for the lowest energy level n=1; in that case only l= 0 is allowed for either potential. And since the number of values of the magnetic quantum number m at a given value of l is 2l+1, there is only one possible value for m. That means that there are only two different energy states at the lowest energy level, corresponding to m_s=1/2 respectively -1/2. Those two states explain the first magic number, 2. Two nucleons of a given type can occupy the lowest energy level; any further ones of that type must go into a higher level.

In particular, helium-4 has the lowest energy level for protons completely filled with its two protons, and the lowest level for neutrons completely filled with its two neutrons. That makes helium-4 the first doubly-magic nucleus. It is just like the two electrons in the helium *atom* completely fill the lowest energy level for electrons, making helium the first noble gas.

At the second energy level n=2, where the Coulomb potential allows both l= 0 and l= 1, only l= 1 is allowed for the harmonic oscillator. So the number of states available at energy level n- 2 is less than that of the Coulomb potential. In particular, the azimuthal quantum number l= 1 allows 2l+1= 3 values of the magnetic quantum number m, times 2 values for the spin quantum number m_s. Therefore, l= 1 at n= 2 corresponds to 3 times 2, or 6 energy states. Combined with the two l= 0 states at energy level n=1, that gives a total of 8. The second magic number 8 has been explained! It requires 8 nucleons of a given type to fill the lowest two energy levels.

It makes oxygen-16 with 8 protons and 8 neutrons the second doubly-magic nucleus. Note that for the electrons in atoms, the second energy level would also include two l= 0 states. That is why the second noble gas is neon with 10 electrons, and not oxygen with 8.

Before checking the other magic numbers, first a problem with the above procedure of counting states must be addressed. It is too easy. Everybody can evaluate 2l+1 and multiply by 2 for the spin states! To make it more challenging, physicists adopt the so-called spectroscopic notation in which they do not tell you the value of l. Instead, they tell you a letter like maybe p, and you are then supposed to figure out yourself that l= 1. The scheme is:

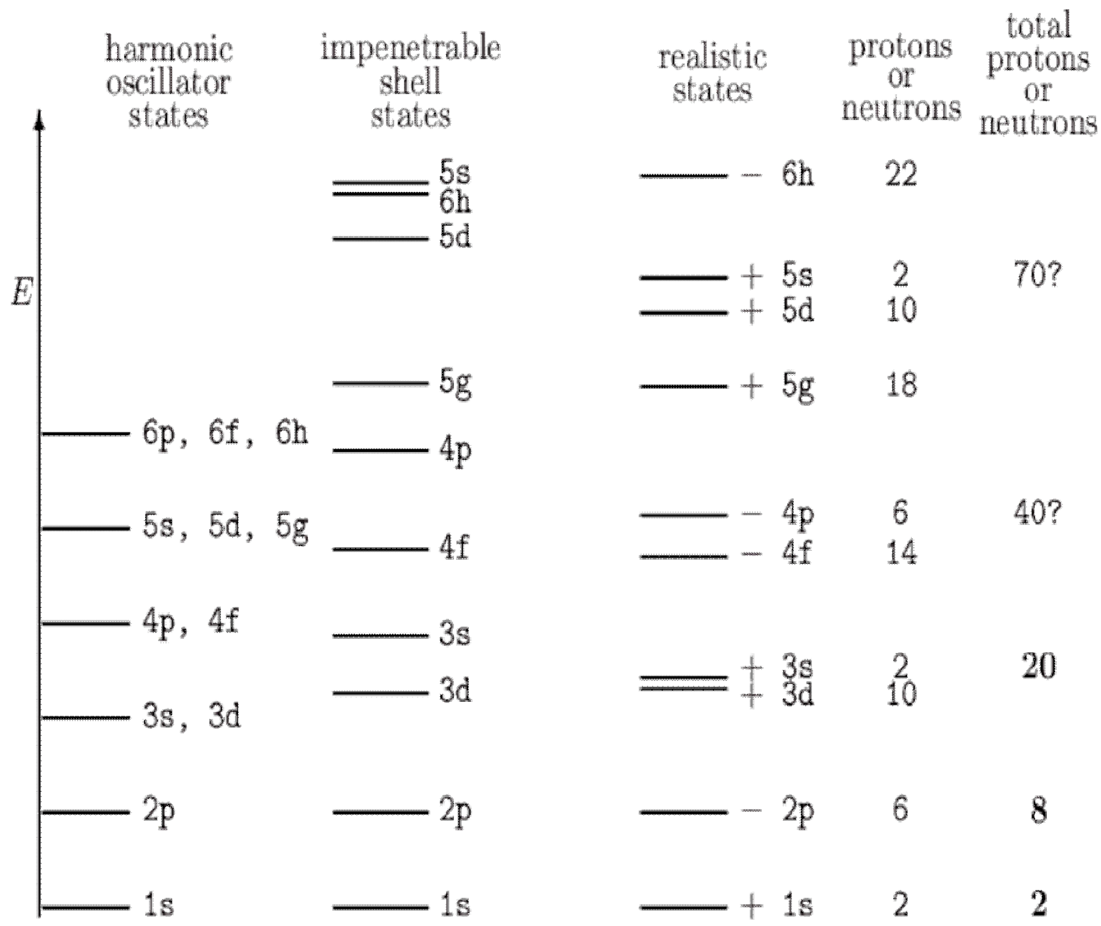
$$\text{s, p, d, f, g, h, i, [j], k, } \ldots \quad \Longrightarrow \quad l = 0, 1, 2, 3, 4, 5, 6, 7, 8, \ldots$$

The latter part is mostly alphabetic, but by convention j is not included. Using spectroscopic notations, the second energy level states are denotated as

$$\psi_{21mm_s} \quad \Longrightarrow \quad 2p$$

where the 2 indicates the value of n giving the energy level. The additional dependence on the magnetic quantum numbers m and m_s is kept hidden from the uninitiated.

In these terms, the energy levels and numbers of states for the harmonic oscillator potential are as shown in figure. The third energy level has 2 3s states and 10 3d states. Added to the 8 from the first two energy levels, that brings the total count to 20, the third magic number.



Unfortunately, this is where it stops. The fourth energy level should have only 8 states to reach the next magic number 28, but in reality the fourth harmonic oscillator level has 6 4p states and 14 4f ones. Still, getting 3 magic numbers right seems like a good start.

The logical next step is to try to improve upon the harmonic oscillator potential. In an average nucleus, it can be expected that the net force on a nucleon pretty much averages out to zero everywhere except in a very thin layer at the outer surface. The reason is that the nuclear forces are very short range; therefore the forces seem to come equally from all directions unless the nucleon is very close to the surface. Only right at the surface do the particles experience a net inward attraction because of the deficit of particles beyond the surface to provide the full compensating outward force. This suggests a picture in which the nucleons do not experience a net force within the confines of the nucleus. However, at the surface, the potential ramps up very steeply. As an idealization the potential beyond the surface can be taken infinite.

That reasoning results in the impenetrable-shell. It too is analytically solvable, The energy levels are shown in figure. Unfortunately, it does not help any explaining the fourth magic number 28.

It turns out that once again the Saxon-Woods model is a reasonable guess, i.e.

$$V(r) = -\frac{V_0}{1+\exp((r-R)/\delta)}$$

Unfortunately, the fourth magic number remains unexplained. In fact, any reasonable spherically symmetric spatial potential will not get the fourth magic number right.

9.4 Allowed Orbits in the Shell Theory Potential

Eventually, Mayer in the U.S., and independently Jensen and his co-workers in Germany, concluded that spin had to be involved in explaining the magic numbers above 20. To understand why, consider the six 4p and fourteen 4f energy states at the fourth energy level of the harmonic oscillator model. Clearly, the six 4p states cannot produce the eight states of the energy shell needed to explain the next magic number 28. And neither can the fourteen 4f states, unless for some reason they split into two different groups whose energy is no longer equal.

Why would they split? In nonquantum terms, all fourteen states have orbital and spin angular momentum vectors of exactly the same lengths. What is different between states is only the direction of these vectors. And the absolute directions cannot be relevant since the physics cannot depend on the orientation of the axis system in which it is viewed. What it can depend on is the relative alignment between the orbital and spin angular momentum vectors. This relative alignment is characterized by the dot product between the two vectors.

Therefore, the logical way to get an energy splitting between states with differently aligned orbital and spin angular momentum is to postulate an additional contribution to the Hamiltonian of the form

$$\Delta H \propto L.S$$

Here L is the orbital angular momentum vector and S the spin one. A contribution to the Hamiltonian of this type is called an spin-orbit interaction, because it couples spin with orbital angular momentum. Spin-orbit interaction was already known from improved descriptions of the energy levels of the hydrogen atom. However, that electromagnetic effect is far too small to explain the observed spin-orbit interaction in nuclei. Also, it would get the sign of the correction wrong for neutrons.

While nuclear forces remain incompletely understood, there is no doubt that it is these much stronger forces, and not electromagnetic ones, that provide the mechanism. Still, in analogy to the electronic case, the constant of proportionality is usually taken to include the net force on the nucleon and an additional factor 1/r to turn orbital momentum into velocity. None of that makes a difference for the harmonic oscillator potential, for which the net effect is still just a constant. Either way, next the strength of the resulting interaction is adjusted to match the experimental energy levels.

However, consider the *net* angular momentum operator

J=L+S

If you expand its square magnitude

$$J^2 = (L+S).(L+S) = L^2 + 2L.S + S^2$$

you see that the spin-orbit term can be written in terms of the square magnitudes of orbital, spin, and net angular momentum operators:

$$-L.S = -\frac{1}{2}[J^2 - L^2 - S^2]$$

Therefore combination states that have definite square net angular momentum J^2 remain good energy eigenfunctions even in the presence of spin-orbit interaction.

Now a quick review is needed of the weird way in which angular momenta combine into net angular momentum in quantum mechanics. In quantum mechanics, the length of the final vector must be quantized as $\sqrt{j(j+1)}\hbar$ where the quantum number j must satisfy $|l-s| \leq j \leq |l+s|$ and must change in integer amounts. In particular, since the spin is given as s=1/2, the net angular momentum quantum number j can either be l-1/2 or l+1/2. (If l is zero, the first possibility is also ruled out, since square angular momentum cannot be negative.)

For the 4f energy level l= 3, so the square net angular momentum quantum number j can only be 5/2 or 7/2. And for a given value of j, there are 2j+1, values for the quantum number m_j giving the net angular momentum in the chosen z-direction. That means that there are six states with j=5/2 and eight states with j=7/2. The total is fourteen, still the same number of independent states at the 4f level. In fact, the fourteen states of definite net angular momentum j can be written as linear combinations of the fourteen states. Pictorially,

$$7\ 4\mathrm{f}\uparrow \text{ and } 7\ 4\mathrm{f}\downarrow \text{ states} \quad \Longrightarrow \quad 6\ 4\mathrm{f}_{5/2} \text{ and } 8\ 4\mathrm{f}_{7/2} \text{ states}$$

where the spectroscopic convention is to show the net angular momentum j as a subscript for states in which its value is unambiguous. The spin-orbit interaction raises the energy of the six 4f5/2 states, but lowers it for the eight 4f7/2 states. In fact, from above, for any state of definite square orbital and square net angular momentum,

$$-L.S = -\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$$

$$= \begin{cases} \frac{1}{2}l(l+1)\hbar^2 & \text{for } j = l\text{-}\frac{1}{2} \\ -\frac{1}{2}l\hbar^2 & \text{for } j = l\text{-}\frac{1}{2} \end{cases}$$

The eight 4f7/2 states of lowered energy form the shell that is filled at the fourth magic number 28.

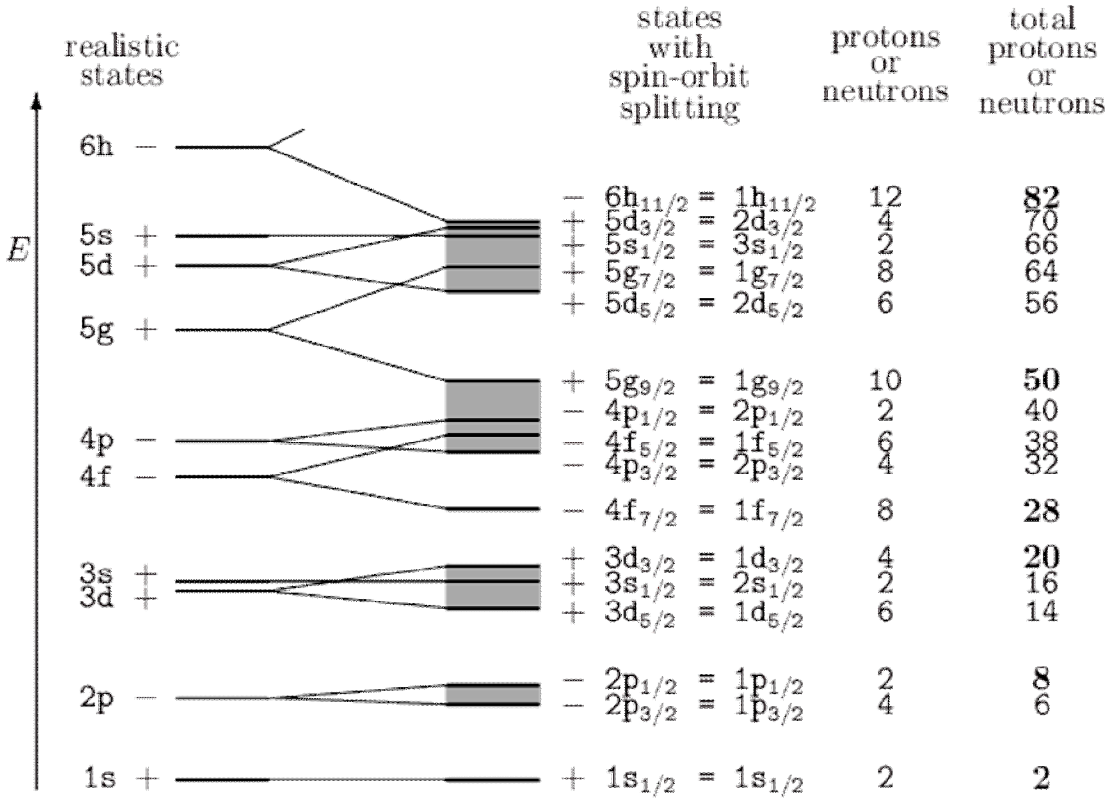


Figure 6 Schematic effect of spin-orbit interaction on the energy levels. The ordering within bands is realistic for neutrons. The designation behind the equals sign is the official one.

Figure shows how the spin-orbit splitting of the energy levels gives rise to the remaining magic numbers. In the figure, the coefficient of the spin orbit term was simply taken to vary linearly with the energy level n. The details depend on whether it is neutrons or protons, and may vary from nucleus to nucleus. Especially for the higher energy bands the Coulomb repulsion has an increasingly large effect on the energies of protons.

The major shells, terminated by magic numbers, are shown as grey bands. In the numbering system followed here, a subshell with a different number as the others in the same major shell comes from a different harmonic oscillator energy level.

9.5 Self Learning Exercise-I

Q.1 Write down top five magic numbers

Q.2 Draw Woods Saxon potential for protons.

Q.3 What is spin orbit coupling?

Q.4 Write down draw backs of Liquid drop model.

9.6 Filling of the Orbits in the Shell theory Potential

Nuclear states have an intrinsic spin and a well defined parity, p=±1, defined by the behaviour of the wavefunction for all the nucleons under reversal of their coordinates with the centre of the nucleus at the origin.

$$\psi(-r_1,-r_2,...-r_A) = p\psi(r_1,r_2,...r_A)$$

The spin and parity of nuclear ground states can usually be determined from the shell model. Protons and neutrons tend to pair up so that the spin of each pair is zero and each pair has even parity (p = 1). Thus we have

- Even-even nuclides (both Z and A even) have zero intrinsic spin and even parity.
- Odd A nuclei have one unpaired nucleon. The spin of the nucleus is equal to the j value of that unpaired nucleon and the parity is $(-1)^l$, where l is the orbital angular momentum of the unpaired nucleon.

Example $^{47}Ti_{22}$ (titanium) has an even number of protons and 25 neutrons. 20 of the neutrons fill the shells up to magic number 20 and there are 5 in the 1f7/2 state (l = 3, j = 7/2) Four of these form pairs and the remaining one leads to a nuclear spin of 7/2 and parity $(-1)^3 = -1$.

- Odd-odd nuclei. In this case there is an unpaired proton whose total angular momentum is j_1 and an unpaired neutron whose total angular momentum is j_2. The total spin of the nucleus is the (vector) sum of these angular momenta and can take values between $|j_1 - j_2|$ and $|j_1 + j_2|$ (in unit steps). The parity is given by $(-1)^{(l1+l2)}$, where l_1 and l_2 are the orbital angular momenta of the unpaired proton and neutron respectively.

Example $^{6}Li_{3}$ (lithium) has 3 neutrons and 3 protons. The first two of each fill the 1s level and the third is in the 1p3/2 level. The orbital angular momentum of each is l = 1 so the parity is (−1)×(−1) = +1 (even), but the spin can be anywhere between 0 and 3.

9.7 Magnetic Dipole Moments

Since nuclei with an odd number of protons and/or neutrons have intrinsic spin they also in general possess a magnetic dipole moment.

The unit of magnetic dipole moment for a nucleus is the "nuclear magneton" defined as

$$\mu_N = \frac{e\hbar}{2m_P}$$

which is analogous to the Bohr magneton but with the electron mass replaced by the proton mass. It is defined such that the magnetic moment due to a proton with orbital angular momentum l is μ l.

Experimentally it is found that the magnetic moment of the proton (due to its spin) is

$$\mu_p = 2.79\mu_N = 5.58\mu_N s, \quad (s = 1/2)$$

and that of the neutron is

$$\mu_n = -1.91\mu_N = -3.82\mu_N s, \quad (s = 1/2)$$

If we apply a magnetic field in the z-direction to a nucleus then the unpaired proton with orbital angular momentum l, spin s and total angular momentum j will give a contribution to the z− component of the magnetic moment

$$\mu^z = (5.58 s^z + l^z)\,\mu_N.$$

As in the case of the Zeeman effect, the vector model may be used to express this as

$$\mu^z = \frac{(5.58\langle s.j\rangle + \langle l.j\rangle)}{\langle j^2\rangle} j^z \mu_N$$

Using $\langle j^2\rangle = j(j+1)\hbar^2$

$$\langle s.j\rangle = \frac{1}{2}(\langle j^2\rangle + \langle s^2\rangle - \langle l^2\rangle)$$

$$=\frac{\hbar^2}{2}[j(j+1)+s(s+1)-l(l+1)]$$

$$\langle l.j\rangle=\frac{1}{2}(\langle j^2\rangle+\langle l^2\rangle-\langle s^2\rangle)$$

$$=\frac{\hbar^2}{2}[j(j+1)+l(l+1)-s(s+1)]$$

We end up with expression for the contribution to the magnetic moment

$$\mu^z=\frac{(5.58[j(j+1)+s(s+1)-l(l+1)]+[j(j+1)+l(l+1)-s(s+1)])}{2j(j+1)}j\mu_N$$

and for a neutron with orbital angular momentum **l′** and total angular momentum **j′** we get (not contribution from the orbital angular momentum because the neutron is uncharged)

$$\mu^z=\frac{(5.58[j`(j`+1)+s`(s`+1)-l`(l`+1)]}{2j`(j`+1)}j`\mu_N$$

Thus, for example if we consider the nuclide ^{7}**Li**3 for which there is an unpaired proton in the 2p3/2 state (**l** = 1, **j** = 3/2 then the estimate of the magnetic moment is

μ =3.79μN

The measured value is 3.26μN so the estimate is not too good. For heavier nuclei the estimate from the shell model gets much worse.

The precise origin of the magnetic dipole moment is not understood, but in general they cannot be predicted from the shell model. For example for the nuclide $^{17}F_9$ (fluorine), the measured value of the magnetic moment is 4.72μN whereas the value predicted form the above model is −0.26μN. There are contributions to the magnetic moments from the nuclear potential that is not well-understood.

9.8 Shell Model Failures

1. Excited States:

As in the case of Atomic Physics, nuclei can be in excited states, which decay via the emission of a photon (gamma ray) back to their ground state (either directly or indirectly). Some of these excited states are states in which one of the neutrons or protons in the outer shell is promoted to a higher energy level.

However, unlike Atomic Physics, it is also possible that sometimes it is energetically cheaper to promote a nucleon from an inner closed shell, rather than a nucleon form an outer shell into a high energy state. Moreover, excited states in which more than one nucleon is promoted above its ground state is much more common in Nuclear Physics than in Atomic Physics.

Thus the nuclear spectrum of states is very rich indeed, but very complicated and cannot be easily understood in terms of the shell model. Most of the excited states decay so rapidly that their lifetimes cannot be measured. There are some excited states, however, which are metastable because they cannot decay without violating the selection rules. These excited states are known as “isomers”, and their lifetimes can be measured.

2. Imperfect Pairing:

In case of titanium-47, the shell model predicts that there will be five neutrons in an unfilled 4f7/2 subshell. It is believed that this is indeed correct. The unperturbed shell model makes no predictions about the nuclear spin. However, the odd-particle shell model says that in the ground state the nuclear spin should be that of the odd neutron, 7/2. But it is not, the spin is 5/2. The pairing of the even number of neutrons in the 4f7/2 shell is not complete. While unfortunate, this is really not that surprising. The perturbation Hamiltonian used to derive the prediction of nucleon pairing is a very crude one. It is quite common to see subshells with at least three particles and three holes (three places for additional particles) end up with a unit less spin than the odd-particle model predicts. It almost happened for oxygen-19.

3. Wrong Shell:

Fluorine-19 shows a more fundamental failure of the shell model. The shell model would predict that the odd proton is in the 3d5/2 state, giving the nucleus spin 5/2 and even parity. In fact, it should be just like fluorine-17. For the unperturbed shell model, the additional two neutrons should not make a significant difference. But the nuclear spin is1/2, and that means that the odd proton must be in the 3s1/2 state. Which show that the unperturbed shell model cannot qualitatively explain this swapping of the two states.

It is the theoretician’s loss, but the experimentalist’s gain. The fact that fluorine has spin one-half makes it a popular target for nuclear magnetic resonance studies.

Spin one-half nuclei are easy to analyze and they do not have nontrivial electric fields that mess up the nice sharp signals in nuclei with larger spin.

And maybe the theoretician can take some comfort in the fact that this complete failure is rare among the light nuclei. In fact, the main other example is fluorine-19's mirror twin neon-19. Also, there is an excited state with the correct spin and parity just above the ground state. But no funny business here; if you are going to call fluorine-19 almost right, you have to call fluorine-17 almost wrong.

Note also how low the ½- excited state has become. Maybe this can be somewhat understood from the fact that the kicked-up 2p1/2 proton is now in a similar spatial orbit with three other nucleons, rather than just one like in the case of fluorine-17. In any case, it would surely require a rather sophisticated perturbed shell model to describe it, one that includes nucleons of both type in the perturbation.

And note that formulating a perturbed shell model from physical principles is not easy anyway, because the basic shell model already includes the interactions between nucleons in an average sense. The perturbations must not just identify the interactions, but more importantly, what part of these interactions is still missing from the unperturbed shell model.

4. Promotion:

Selenium-77 illustrates a more fundamental reason why the odd particle may end up in the wrong state. The final odd neutron would normally be the third one in the 5g9/2 state. That would give the nucleus a net spin of 9/2 and positive parity. There is indeed a low-lying excited state like that. (It is just above a 7/2 one that might be an effect of incomplete pairing.) However, the nucleus finds that if it promotes a neutron from the 4p1/2 shell to the 5g9/2 one just above, that neutron can pair up at higher angular momentum, lowering the overall nuclear energy. That leaves the odd neutron in the 4p1/2 state, giving the nucleus a net spin of 1/2 and negative parity. Promotion happens quite often if there are more than 32 nucleons of a given type and there is a state of lower spin immediately below the one being filled.

5. Non spherical nucleus:

Tantalum-181 is an example nucleus that is not spherical. For it, the shell model simply does not apply as derived here. So there is no need to worry about it. Which is a good thing, because it does not seem easy to justify a 7/2+ ground state based on the shell model. Nonspherical nuclei appear near the stable line for mass numbers of about 150 to 190 and above 220. There are also a few with mass numbers between 20 and 30.

Preston & Bhaduri give an extensive table of nucleons with odd mass number, listing shell occupation numbers and spin. Notable is iron-57, believed to have three neutrons in the 4p3/2 shell as the shell model says, but with a net nuclear spin of ½-. Since the three neutrons cannot produce that spin, in a shell model explanation the 6 protons in the 4f7/2 shell will need to contribute. In general the table shows that the ground state spin values of spherical nuclei with odd mass numbers are almost all correctly predicted if you know the correct occupation numbers of the shells. However, predicting those numbers for heavy nuclei is often nontrivial.

9.9 Self Learning Exercise-II

Q.1 Calculate magnetic moment of ^{7}Li3

Q.2 What is a "halo nucleus,"

Q.3 Give the spin and parity, as expected from the shell model, of the ground states of ^{173}Yb.

Q.4 Write a short note on "Failures of nuclear shell model"

9.10 Summary

The unit starts with the introduction of Nuclear models followed by a detailed discussion of nuclear shell model.

9.11 Glossary

Angular Momentum : A measure of the momentum of a body in rotational motion about its centre of mass. Technically, the angular momentum of a body is equal to the mass of the body multiplied by the cross product of the position vector of the particle with its velocity vector. The angular momentum of a system is the sum of the angular momenta of its constituent particles, and this total is conserved unless acted on by an outside force.

Neutron : One of the two main building blocks (along with the proton) of the nucleus at the centre of an atom. Neutrons have essentially the same mass as a proton (very slightly larger) but no electric charge, and are made up of one "up" quark and two “down” quarks. The number of neutrons in an atom determines the isotope of an element. Outside of a nucleus, they are unstable and disintegrate within about ten minutes.

Nucleus : The tight cluster of nucleons (positively-charged protons and zero-charged neutrons, or just a single proton in the case of hydrogen) at the centre of an atom, containing more than 99.9% of the atom’s mass. The nucleus of a typical atom is about 100,000 smaller than the total size of the atom(depending on the individual atom).

Proton : One of the two main building blocks (along with the neutron) of the nucleus at the centre of an atom. Protons carry a positive electrical charge, equal and opposite to that of electrons, and are made up of two “up” quarks and one “down” quark. The number of protons in an atom’s nucleus determines its atomic number and thus which chemical element it represents.

Spin : Spin is a characteristic property of elementary particles

9.12 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: 2, 8, 20, 28, 50

Ans.3: $\Delta H \propto L.S$

Here L is the orbital angular momentum vector and S the spin one. A contribution to the Hamiltonian of this type is called an spin-orbit interaction, because it couples spin with orbital angular momentum.

Ans.4: See Section 9.2

Answers to Self Learning Exercise-II

Ans.1: $\mu = 3.79\mu N$

Ans.2: A nucleus whose radius is noticeably larger than that predicted by the liquid drop formula.

Ans.3: 5/2-

9.13 Exercise

Q.1 Give the spin and parity, as expected from the shell model, of the ground states of

7Li, 5N, 29Si, 43Ca, 87Ru, 133Cs.

Q.2 Write down a short note on nuclear shell model.

References and Suggested Readings

1. Concepts of Nuclear Physics by Bernard L. Cohen, 1971
2. Introductory Nuclear Physics, by K.S. Krane, 1988.
3. Structure of the Nucleus by M.A. Preston and R.K. Bhaduri,1975.
4. Theory of Nucleus. By A. Sitenko and V. Tartakovskii,1997.
5. The shell model Nobel Lecture by Maria Goeppert Mayer,1963.

UNIT-10
Beta Decay

Structure of the unit

10.0 Objectives

The nucleus decays through various forms of β decay : β^+, β^- and electron capture. The reader learn about allowed and forbidden beta transitions and $f\,t$ –values. Fermi and Gamow Teller transitions are explained so that the student can differentiate between two types of transitions .V−A theory of beta decay is introduced so that the reader learns the concept of parity violation in the context of beta decay process.

10.1 Introduction

The decay processes falling under beta decay category are described with proper theoretical models using concepts and tools of quantum mechanics and quantum field theory. The Fermi Kurie plot and parity non conservation are deduced from the theoretical (phenomenological) models. The concept of *f t* values and Fermi and Gamow –Teller transitions are introduced to understand the experimental observations .The better comprehension of beta decay processes comes from recognition of the role of weak interaction in the phenomena.

10.2 General Characteristics of Weak Interaction

Nuclear beta decay is only one class of phenomena out of many other classes of phenomena occurring due to weak interaction .The weak interaction not only produces transitions between nuclear states but a wide categories of phenomena involving leptons, mesons, hadrons etc. The weak processes cannot be observed because these are slower by several orders of magnitude compared with competing electromagnetic and strong processes. The studies of weak processes can be made in the areas where faster electromagnetic and strong processes are forbidden and suppressed by selection rules.

Let us consider the basic weak reactions in nuclei which produce nuclear transitions .

The decay of a free neutron and a bound proton are

$$n \rightarrow p + e^- + \bar{\nu}_e \tag{10.1}$$

and
$$p_{bound} \rightarrow n + e^+ + \nu_e \tag{10.2}$$

The decay of hadrons ,for example

$$\begin{aligned} \pi^+ &\rightarrow \mu^+ + \nu_\mu \\ &\rightarrow e^+ + \nu_e \end{aligned} \tag{10.3}$$

$$\begin{aligned} \pi^- &\rightarrow \mu^- + \bar{\nu}_\mu \\ &\rightarrow e^- + \bar{\nu}_e \end{aligned} \tag{10.4}$$

$$\Sigma^- \rightarrow n + \pi^- \tag{10.5}$$

$$\begin{aligned}\kappa^+ &\to \pi^+ + \pi^o \\ &\to \pi^+ + \pi^- + \pi^+\end{aligned} \tag{10.6}$$

The decay of nucleons [given by eq.(10.1) and (10.2)] and decay of hadrons [given by eq.(10.3) and (10.4)] are called semi- leptonic processes as these processes involve leptons also.

The decay of hadrons without any lepton are called non leptonic processes [given by eq.(10.5) and (10.6)].

The decay of leptons are ,for example ,

$$\mu^+ \to e^+ + \nu_e + \overline{\nu}_\mu \tag{10.7}$$

This is pure leptonic process.

Now it is clear that weak processes are of three types: pure leptonic ,semi leptonic and non leptonic and non leptonic .Beta decay is basically semi leptonic nucleon decays causing nuclear transitions and an integral part of weak processes.

We will now consider the general characteristics of weak interaction processes.

(i) Universal Strength:

The weak interaction exhibits the same interaction strength in all types of the processes like pure leptonic , semi leptonic and non leptonic processes. This universal weak coupling constant , designated by Fermi coupling constants, has the same value.

$$\begin{aligned}G_F &= 1.43584 \pm 0.00003 \times 10^{-62}\ J - m^3 \\ &= 1.166637 \pm 0.00002 \times 10^{-11} (\hbar c)^3 (MeV)^{-2}\end{aligned} \tag{10.8}$$

whether it is measured through super allowed β -decay in nuclei or from muon decay or from other weak processes.

(ii) W^+, W^- and Z^o Vector Bosons are Weak Interaction Carriers:

The vector Bosons carry the weak interaction as photons carry electromagnetic interaction. The masses of the vector bosons are

$$\left.\begin{aligned}M_{W^\pm} c^2 &= 80.9 \pm 1.4 GeV \\ M_{Z^o} c^2 &= 91.9 \pm 1.8 GeV\end{aligned}\right\} \tag{10.9}$$

(iii) Range of weak interaction is very short ($\simeq 10^{-3}\, fm$):

The characteristic range of the weak interaction can be calculated using Heisenberg's uncertainty relation

$$\Delta r\left(\Delta pc\right) \geq \frac{\hbar c}{2} \tag{10.10}$$

and taking $Mc^2 \approx 100\, GeV$ as typical mass of weak vector boson ,we get

$$\Delta r \simeq \frac{\hbar c}{2Mc^2} \simeq \frac{200 MeV\ fm}{2\times 100 GeV} \approx 10^{-3}\, fm \tag{10.11}$$

We see that range of the weak interaction is approximately three orders of magnitude smaller than long range of the nuclear force (10^{-3} times smaller).

(iv) SU_3 Flavour Symmetry Mixing:

Fundamentally , beta decay may be viewed as one type of quark transformed into another through exchange of charged vector boson. In general one type of particle (quark or lepton) changes into another particle through exchange of $W^{\pm}\ and\ Z^{o}$ in the weak interaction processes .When a quark decays into another quark, it does not necessarily have a definite flavour i.e. it may result in Flavour Mixing.

The customary Transformation for weak decay among four quarks u,d,c and s can be expressed in terms of the Cabbibo angle , θ_c

$$j^{+}_{weak} = \left(\bar{u}\ \bar{c}\right)\begin{bmatrix} cos\,\theta_c & sin\,\theta_c \\ -sin\,\theta_c & cos\,\theta_c \end{bmatrix}\begin{pmatrix} d \\ s \end{pmatrix} \tag{10.12}$$

The more general case of the transformation for weak decay among all six quarks u,d,c,s,t and b can be expressed using the 3×3 Kobayashi –Maskawa matrix:

$$j^{+}_{weak} = \left(\bar{u}\ \ \bar{c}\ \ \bar{t}\right)\begin{bmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{bmatrix}\begin{pmatrix} d \\ s \\ b \end{pmatrix} \tag{10.13}$$

The nine matrix elements are functions of three mixing angles and a phase factor. In the nuclear beta decay ,we are concerned with transformation between *u* and *d* quarks. Let us view (10.1) and (10.2) decays in terms of quark weak transformations:

$$n \to p + e^- + \bar{\nu}_e$$

$$\Rightarrow (u\,d\,d) \to (u\,u\,d) + W^-$$
$$\qquad\qquad\qquad\qquad\qquad \hookrightarrow e^- + \bar{\nu}_e$$

$$\Rightarrow d \to u + W^- \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(10.14)}$$
$$\qquad\qquad \hookrightarrow e^- + \bar{\nu}_e$$

$$p \to n + e^+ + \nu_e$$

$$\Rightarrow (u\,u\,d) \to (u\,d\,d) + W^+$$
$$\qquad\qquad\qquad\qquad\qquad \hookrightarrow e^+ + \nu_e$$

$$\Rightarrow u \to d + W^+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(10.15)}$$
$$\qquad\qquad \hookrightarrow e^+ + \nu_e$$

The Feynman diagrams for β^- *and* β^+ decays are shown in figure (10.1) and figure (10.2).

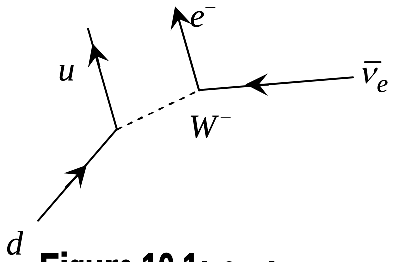


Figure 10.1: β^- *decay*

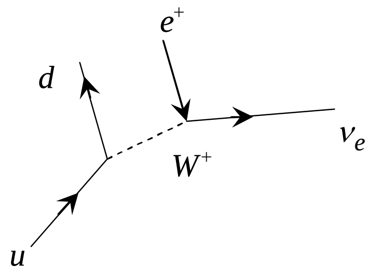


Figure 10.2: β^+ *decay*

(v) Parity Nonconservation:

The parity transformation is the operation which inverts the spatial coordinates and physically described as taking mirror image of the coordinate system. The parity of a particle (Fermion) and its antiparticle (Fermion) are opposite to each other .The parity of π is taken as negative. The formal definition of parity operator P is given as

$$P\,\psi(\vec{r}) = \psi(-\vec{r}) = \pm\psi(\vec{r}) \qquad \text{(10.16)}$$

Here + sign corresponds to positive parity (even) while – sign refers to negative parity (odd) of the function $\psi(\vec{r})$ .If a function does not fall into any of these two categories is said to have nondefinite parity .It is helpful to consider the parity of following type of nature of operators/functions:

S.No.	Type of operator / Function	Symbol	Parity
1.	Usual vector/Polar vector (example: $\vec{r}, \vec{p}$)	V	Odd
2.	Axial Vector Example: $\vec{L}, \vec{S}, \vec{r} \times \vec{p}$	A	Even
3.	Scalar Example: density ,numerical constants like e,1,π; dot product of two axial vectors or of two polar vectors	S	Even
4.	Pseudo Scalar Examples: Scalar product of an axial and a polar vector	P	Odd

Now let us consider the angular distribution of electrons emitted in β^- decay with given momentum $\vec{p}$; energy E and spin $\vec{\sigma}$, denoted by $W(\theta)$.The expression for $W(\theta)$ is given by

$$W(\theta) = 1 + a\frac{\vec{\sigma}.\vec{p}}{E}$$

$$W(\theta) = 1 + a\frac{v}{c}cos\theta \tag{10.17}$$

where θ: angle of electron emission between momentum $\vec{p}$ and its angular momentum $\vec{J}$.

The first term is a scalar while the second is a pseudo scalar in eq.(10.17) and if $a \neq 0$,then these two terms will behave differently under parity operation. It will lead to different angular distribution under spatial coordinate inversion and parity violation of $W(\theta)$.The experimental measurement of $W(\theta)$ in the $^{60}_{27}Co$ nucleus β^- decay experiment carried out by Wu and others confirmed this strange conclusion .The existence of two decay modes of K^+ in nature (10.6) (final states having two and three pions) also confirmed parity nonconservation in weak interactions. Hence parity non conservation is a basic characteristic of weak processes.

10.3 Nuclear Beta Decay and Lepton Capture

The nuclei ,which lie above the stability region ,emit electrons ,antineutrinos and daughter nuclei with same mass number A remain as residual nuclei, but atomic number increased by unity. In β^- decay ,a neutron is replaced by/transformed into a proton ,and parent and daughter nuclei are isobars consequently.

The process can be expressed as :

$$ {}_{Z}^{A}X \rightarrow {}_{Z+1}^{A}Y + e^- + \bar{\nu}_e \tag{10.18}$$

The more precise expression can be written as

$$ {}_{0}^{1}n \rightarrow {}_{1}^{1}p^+ + {}_{-1}^{0}e^- + {}_{0}^{0}\bar{\nu}_e \tag{10.18a}$$

The following observations can be expressed explicitly

(i) X and Y are isobars. Nucleons are conserved ;A=A.

(ii) Electric charge is conserved ; $0 = +1e - 1e \Rightarrow 0 = 0$

(iii) Intrinsic spin is conserved

(iv) Leptons are conserved.

For Example

$$ {}_{6}^{14}C \rightarrow {}_{7}^{14}N + e^- + \bar{\nu}_e \tag{10.18 b}$$

${}_{6}^{14}C$ is a β^- emitter.

Similarly ,for β^+ decay ,the process can be expressed as

$$ {}_{Z}^{A}X \rightarrow {}_{Z-1}^{A}Y + e^+ + \nu_e \tag{10.19}$$

The more precise expression can be written as

$$ p^+ \rightarrow n + e^+ + \nu_e \tag{10.19a}$$

The following observations can be made explicitly

(i) X and Y are isobars.Nucleons are conserved ; A=A

(ii) Leptons are conserved; $0 = -1 + 1$

(iii) Electric charge is conserved; $+1e = +1e$

(iv) Intrinsic spin is conserved.

We can take following Example

$$ {}^{11}_{6}C \to {}^{11}_{5}B + e^{+} + \nu_e \tag{10.19b}$$

${}^{11}_{6}C$ is a β^{+} emitter.

Similarly ,for electron capture (E C),the process can be expressed as

$$ {}^{A}_{Z}X + e^{-} \to {}^{A}_{Z-1}Y + \nu_e \tag{10.20}$$

The more precise expression can be written as

$$ p^{+} + e^{-} \to n + \nu_e \tag{10.20a}$$

Again , following observations can be made explicitly

(i) X and Y are isobars.Nucleons are conserved; A=A

(ii) Electric charge is conserved; $+1e - 1e = 0 + 0 = 0$

(iii) Leptons are conserved.

(iv) Intrinsic spin is conserved.

We take another example as

$$ {}^{7}_{4}Be + e^{-} \to {}^{7}_{3}Li + \nu_e \tag{10.20b}$$

$$\left[T_{1/2} = 53.4d \quad ,Q = 0.86MeV\right]$$

*Special Note :*Positron $\left(e^{+}\right)$ was theoretically predicted by Dirac (1927) and experimentally verified by Anderson (1932).

10.4 Energy Consideration in β^{-},β^{+} and Electron Capture Reactions

Let us consider the relation between the atomic mass and the nuclear mass.

$$ M(Z,A) = N(Z,A) + Zm_e - B_Z \tag{10.21}$$

$$ M^{*}(Z,A) = N(Z,A) + Zm_e - B_Z^{*}(K \to P,...) \tag{10.21a}$$

where

$M(Z,A) \cong$ mass of the atom (Z,A) in ground state

$m_e \cong$ mass of the free electron

$N(Z,A) \cong$ mass of the nucleus (Z,A) in ground state

B_Z : Binding energy of all orbiting electrons of atom $M(Z,A)$ in ground state.

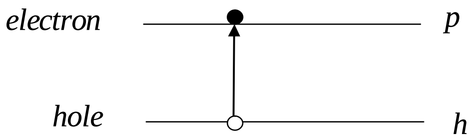
$$= \sum_{i=1}^{Z} b_i$$

$M^*(Z,A)$:mass of the atom (Z,A) in excited state {hole- particle pair $(h\text{-}p\ pair)$}

$B_Z^*(K \to P)$: Binding energy of all orbiting electrons of atom in $M^*(Z,A)$ in excited state $(h\text{-}p\ pair)$

$$= \sum_{i=1}^{Z} b_i + (b_P - b_K)$$

$$= B_Z - \varepsilon_{ph} \tag{10.22}$$



The difference in binding energy B_Z of Z orbiting electrons of the atom $M(Z,A)$ and the binding energy $B_{Z\pm1}$ of $Z \pm 1$ electrons of the atom $M(Z \pm 1, A)$ is very small. The difference is $\Delta B \simeq 10\text{-}50\ keV$ typically.

The masses $M(Z,A)$, $N(Z,A)$ and m_e are the order of MeV. The ratio $\frac{\Delta B}{\Delta M}$ in β processes is of the order of 0.1% or less.

The Q value for β^- decay:

$${}_Z^AX \to {}_{Z+1}^{A}Y + e^- + \bar{\nu}_e$$

$(n \to p^+ + e^- + \bar{\nu}_e)$ is given as

$$Q_{\beta^-} = N_Z - N_{Z+1} - m_e \tag{10.23}$$

If we change nuclear masses into atomic masses then

$$Q_{\beta^-} = \left[\left(M_Z + B_Z - Zm_e\right) - \left\{M_{Z+1} + B_{Z+1} - (Z+1)m_e\right\}\right] - m_e$$

$$Q_{\beta^-} = \left[\left(M_Z + B_Z\right) - \left\{M_{Z+1} + B_{Z+1}\right\}\right] \tag{10.24}$$

The Q value for β^+ decay:

$$ {}_{Z}^{A}X \rightarrow {}_{Z-1}^{A}Y + e^+ + \nu_e $$

$\left(p \rightarrow n + e^+ + \nu_e\right)$ is given as:

$$ Q_{\beta^+} = N_Z - N_{Z-1} - m_e \tag{10.25} $$

Changing nuclear masses into atomic masses ,we can rewrite above relation as

$$ Q_{\beta^+} = \left[\left(M_Z + B_Z - Zm_e\right) - \left\{M_{Z-1} + B_{Z-1} - (Z-1)m_e\right\}\right] - m_e $$

$$ Q_{\beta^+} = \left[\left(M_Z + B_Z\right) - \left(M_{Z-1} + B_{Z-1}\right)\right] - 2m_e \tag{10.26} $$

The Q value for EC

$$ {}_{Z}^{A}X + e^- \rightarrow {}_{Z-1}^{A}Y + \nu_e $$

$\left(p^+ + e^- \rightarrow n + \nu_e\right)$ is given as

$$ Q_{EC} = N_Z + m_{e^-} - N_{Z-1} - b_Z^e(K) \tag{10.27} $$

where $b_Z^e(K)$: binding energy of K electron. Changing nuclear masses into atomic masses ,we can rewrite above relation

$$ Q_{EC} = M_Z - M_{Z-1}^* \tag{10.28} $$

$$ Q_{EC} = \left(M_Z + B_Z\right) - \left(M_{Z-1} + B_{Z-1}\right) - b_Z^e(K) $$

Hence we notice that EC (electron capture) decay demands that mass difference of parent- daughter must be at least greater than or equal to binding energy of K or L or any other shell. The Q value in this case is sum of kinetic energy of daughter nucleus and neutrino.

10.5 Fermi Theory of Beta Decay

In the beta decay a nucleon changes into another type of nucleon and electron (positron) and antineutrino (neutrino) are created. Fermi assumed parity conservation but his calculations involved only scalar quantities .The results of his theory still stand in large measure, inspite of the fundamental changes produced by the parity violation.

The theory explained:

(1) Form of beta spectra : Number of electrons in beta process/energy interval $\frac{dN_e}{dE_e}$ versus energy of electron E_e .

(2) The relation between maximum energy of beta decay and mean life time.

(3) The classification of beta transitions and establishment of selection rules.

The transition probability for beta transition is given by Golden Rule of time dependent perturbation theory:

$$\omega = \frac{2\pi}{\hbar}\left|H_{if}\right|^2 g\left(E_f\right) \tag{10.29}$$

where

$H_{if} \equiv$ Matrix element of beta interaction

$g\left(E_f\right) \equiv$ Density of final energy states of final products of beta process

$\omega \equiv$ Probability of transition

The relation is applicable because universal Fermi coupling constant G_F and universal vector coupling constant $G_{V\beta}$ are very small.

Let us consider the transition

$$^A_Z X \rightarrow {}^A_{Z+1}Y + e^{-1} + \bar{\nu}_e$$

$$\left(n \rightarrow p^+ + e^- + \bar{\nu}_e\right)$$

Then $\psi_f \equiv \psi_Y \psi_{e^-} \psi_{\bar{\nu}_e}$

$$\psi_i \equiv \psi_X \tag{10.30}$$

Now Fermi assumed the form of interaction

$$\hat{H} = G_{V\beta}\hat{M} \tag{10.31}$$

where $G_{V\beta} = \left(1.4029 \pm 0.0022\right) \times 10^{-62}\, Jm^3$

$$= \left(1.1396 \pm 0.0018\right) \times 10^{-11} \left(\hbar c\right)^3 \left(MeV\right)^{-2}$$

$$= \left(0.875 \pm 0.002\right) \times 10^{-4} MeV\left(fm\right)^3$$

We have discussed G_F earlier in equation (10.2).

The matrix element of beta process is

$$H_{if} = G_{V\beta} \int \psi_Y^* \psi_{e^-}^* \psi_{\bar{\nu}_e}^* M \psi_X \, d\tau \tag{10.32}$$

Taking $\psi_{\bar{\nu}_e}^* = \psi_{\nu_e}$

$$H_{if} = G_{V\beta} \int \psi_Y^* \psi_{e^-}^* \psi_{\nu_e} M \psi_X \, d\tau$$

Let us consider parent nucleus X at rest ,then momentum conservation yields

$$\vec{P}_R + \vec{P}_e + \vec{P}_{\bar{\nu}_e} = \vec{P}_X = 0 \tag{10.33}$$

The energy conservation leads to

$$E_o = E_R + E_e + E_{\bar{\nu}_e} \tag{10.34}$$

Let us take the case when electron and neutrino are considered as a pair and the nucleus and this pair share the momentum i.e.

$$\vec{P}_{R\,max} + \vec{p}_{e\bar{\nu}_e\,max} = 0 \tag{10.35}$$

Then $\quad E_o = E_{R\,max} + E_{e\bar{\nu}_e\,max} \qquad (10.36)$

Eq.(10.35) and eq.(10.36) imply

$$\vec{P}_{R\,max} = -\vec{p}_{e\bar{\nu}_e\,max}$$

$$\Rightarrow E_{R\,max} = \frac{P_{R\,max}^2}{2A.M.}$$

$$= \frac{p_{e\bar{\nu}_e\,max}^2}{2A.M.} = \frac{E_{e\,max}^2 - m_e^2 c^4}{2A.M.\, m_e c^2} m_e$$

$$\Rightarrow E_{R\,max} = \frac{m_e}{2A.M.} \frac{\left(E_{e\,max}^2 - m_e^2 c^4\right)}{m_e c^2} \tag{10.37}$$

where

$A =$ Mass number of daughter nucleus

$m_e \equiv$ mass of electron emitted in β decay

$M \equiv$ Mass of a nucleon

The ratio $\frac{E_{R\,max}}{E_{e\bar{\nu}_e\,max}}$ can be evaluated as

$$\frac{E_{R\,max}}{E_{e\,max}} = \left(\frac{m_e}{2AM}\right)\left[\frac{E_{e\,max}^2 - m_e^2 c^4}{E_{e\,max}\; m_e c^2}\right]$$

Take the typical values

$$m_e \simeq \frac{1}{2}MeV \;, M \simeq 1000 MeV \;,\; A \sim 10 \text{ ,then}$$

$$\frac{m_e}{2AM} \simeq 3\times 10^{-5} \;,\; m_e c^2 \sim \frac{1}{2}MeV \;, E_{e\,max} \simeq 10 MeV$$

$$\frac{E_{e\,max}^2 - m_e^2 c^4}{E_{e\,max}\; m_e c^2} \simeq 20$$

Hence $\frac{E_{R\,max}}{E_{e\,max}} \simeq 60\times 10^{-5} \approx 10^{-3}$ (10.38)

Hence we conclude that recoil energy can be neglected.

Now approximate energy momentum conservation relations can now be written

$$\vec{P}_R + \vec{p}_e + \vec{p}_{\nu_e} = 0$$

$$E_e + E_{\nu_e} = E_o \qquad (10.39)$$

The energy in β decay process is shared by electron and neutrino effectively.

10.6 Electron Energy Spectrum and Fermi Kurie Plot

Wavefunctions of anti neutrino and electron:

The neutrino interacts very weakly with nucleons and move with $v_\nu \cong c$. It is, therefore , reasonable to use plane wave free particle wavefunction

$$\psi_{\nu_e} = \frac{1}{\Omega^{1/2}} e^{-i\left(\vec{p}_\nu . \vec{r}\right)/\hbar} \qquad (10.40)$$

where $\Omega \equiv$ volume of the box enclosing the system.

The electron interacts with nucleons but its velocity is very high, so we can neglect the electromagnetic interaction. The electron wavefunction can also be taken as plane wave free particle wavefunction:

$$\psi_e^* = \frac{1}{\Omega^{1/2}}\, e^{-i\left(\vec{p}_e.\vec{r}\right)/\hbar} \tag{10.41}$$

Further

$$\psi_e^*\psi_{\nu_e} = \frac{1}{\Omega}\, e^{-i\left(\vec{p}_e+\vec{p}_{\nu_e}\right).\vec{r}/\hbar}$$

$$= \frac{1}{\Omega}\left[1 - \frac{-i\left(\vec{p}_e+\vec{p}_{\nu_e}\right).\vec{r}}{\hbar} - \frac{\left\{\left(\vec{p}_e+\vec{p}_{\nu_e}\right).\vec{r}\right\}^2}{2\hbar^2} + \frac{i\left\{\left(\vec{p}_e+\vec{p}_{\nu_e}\right).\vec{r}\right\}^3}{6\hbar^3} + \ldots.\right]$$

Taking $p_e \simeq p_{\nu_e} \simeq m_e c$, $2m_e c^2 \simeq 1MeV$,$R = 10\,fm$

and $\frac{2m_e c^2}{\hbar c}R \simeq \frac{10MeV\ \ fm}{200MeV\ \ fm} \simeq \frac{1}{20}$,we get

$$\psi_e^*\psi_{\nu_e} = \frac{1}{\Omega}\left[1 - i\frac{1}{20} - \frac{1}{2}\left(\frac{1}{20}\right)^2 + \frac{i}{6}\left(\frac{1}{20}\right)^3 + \ldots\right]$$

$$= \frac{1}{\Omega}\left[1 - \frac{1}{8}.10^{-2} - i\left(\frac{1}{2}.10^{-1} - \frac{1}{48}.10^{-3}\right) + \ldots.\right]$$

$$\psi_e^*\psi_{\nu_e} \approx \frac{1}{\Omega} \tag{10.42}$$

We see that electron -neutrino field is weak in comparison to short range strong interaction among nucleons. The β decay process is analogous to emission of electromagnetic radiation with electron -neutrino field in place of photon .This makes the matrix element

$$H_{if} = \frac{G_{V\beta}}{\Omega}\int \psi_Y^* M \psi_X\, d\tau$$

$$= \frac{G_{V\beta}}{\Omega}\left|M_{if}\right| \qquad (10.43)$$

We assume that all partitions of energy $E_0 = E_e + E_{\nu_e}$ are equally probable. This means that the transition probability of beta decay is proportional to the volume of accessible phase space in that transition.

The number of states dN_e corresponding to appearance in volume Ω of electron with momentum in p_e and $p_e + dp_e$ range is :

$$dN_e = \frac{4\pi\Omega}{h^3} p_e^2 dp_e \qquad (10.44)$$

Similarly number of states dN_{ν_e} corresponding to appearance in volume Ω of neutrino with momentum in p_{ν_e} and $p_{\nu_e} + dp_{\nu_e}$ range is

$$dN_{\nu_e} = \frac{4\pi\Omega}{h^3} p_{\nu_e}^2 dp_{\nu_e} \qquad (10.45)$$

Hence the number of states for electron -neutrino pair is given by

$$d^2N = \left(\frac{4\pi\Omega}{h^3}\right)^2 p_e^2 p_{\nu_e}^2 dp_e dp_{\nu_e} \qquad (10.46)$$

For a fixed electron energy E_e , the relation

$$E_0 = E_e + E_{\nu_e} \qquad \Rightarrow dE_0 = dE_{\nu_e}$$

For neutrino $\Rightarrow \frac{E_{\nu_e}^2}{c^2} = \frac{\left(E_0 - E_e\right)^2}{c^2} = p_{\nu_e}^2$

$$E_{\nu_e} = p_{\nu_e} c$$

$$\Rightarrow \frac{dE_{\nu_e}}{c} = dp_{\nu_e} \qquad (10.47)$$

For electron

$$E_e^2 = p_e^2 c^2 + m_e^2 c^4$$

$$\frac{dE_e}{c} = dp_e \tag{10.48}$$

Using eq. (10.47) and (10.48), we get dN as

$$d^2N = \left(\frac{4\pi\Omega}{h^3}\right)^2 p_e^2 p_{\nu_e}^2 dp_e dp_{\nu_e}$$

$$d^2N = \left(\frac{4\pi\Omega}{h^3}\right)^2 p_e^2 \left(\frac{E_0 - E_e}{c}\right)^2 dp_e \frac{dE_0}{c} \tag{10.49}$$

The density of states $\rho\left(E_0\right)$ can be written as

$$\frac{d^2N}{dE_0} = \frac{1}{c^3}\left(\frac{4\pi\Omega}{h^3}\right)^2 p_e^2 \left(E_0 - E_e\right)^2 dp_e$$

$$\rho\left(E_0\right) dp_e = \frac{1}{c^3}\left(\frac{4\pi\Omega}{h^3}\right)^2 p_e^2 \left(E_0 - E_e\right)^2 dp_e \tag{10.50}$$

The probability of transition using eq.(10.29) employing Fermi Golden rule

$$\omega\left(p_e\right) dp_e = \frac{2\pi}{\hbar}\left|H_{if}\right|^2 \rho\left(E_0\right) dp_e$$

$$= \frac{2\pi}{\hbar}\frac{G_{V\beta}^2}{\Omega^2}\left|M_{if}\right|^2 \frac{1}{c^3}\left(\frac{4\pi\Omega}{h^3}\right)^2 p_e^2 \left(E_0 - E_e\right)^2 dp_e$$

$$\omega\left(p_e\right) dp_e = \frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{\left|M_{if}\right|^2}{\hbar^7 c^3} p_e^2 \left(E_0 - E_e\right)^2 dp_e \tag{10.51}$$

$$\omega\left(E_e\right) dE_e = \frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{\left|M_{if}\right|^2}{\hbar^7 c^3}\left(E_0 - E_e\right)^2 p_e E_e dE_e \tag{10.52}$$

The $\left|M_{if}\right|$ is independent of p_e and dp_{ν_e} for allowed transitions. This fact produces beta decay spectrum.

The plot between $\omega\left(p_e\right)$ versus E_e is shown in figure.

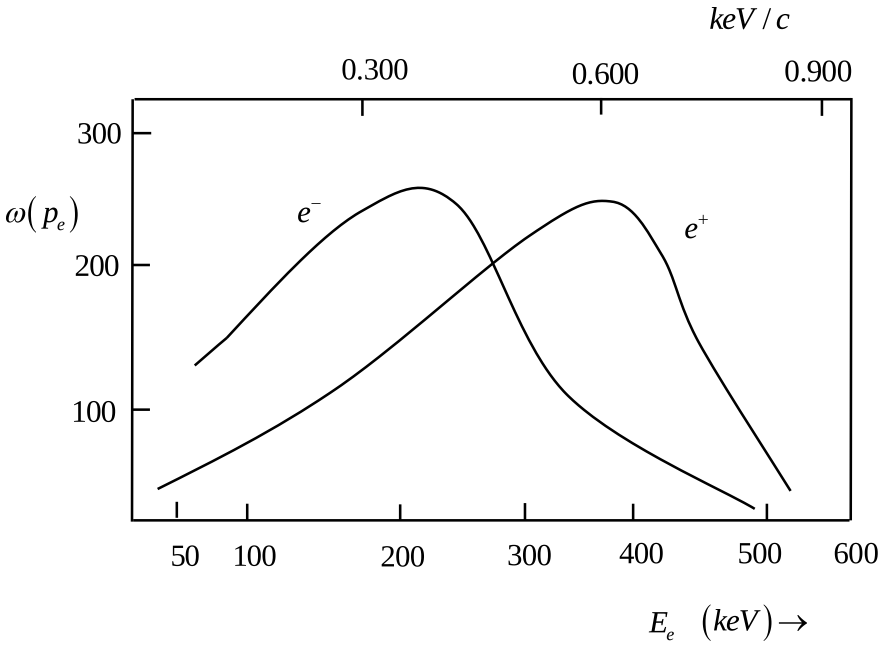


Fig10.3 : *Momentum spectra for* ^{64}Cu ***electrons and positrons [Wu & Albert (1949)]***

Generally $\left[\dfrac{\omega(p_e)}{p_e^2 F(Z,E_e)}\right]^{1/2}$ versus (E_e) is plotted .It is straight line and called Fermi Kurie plot.

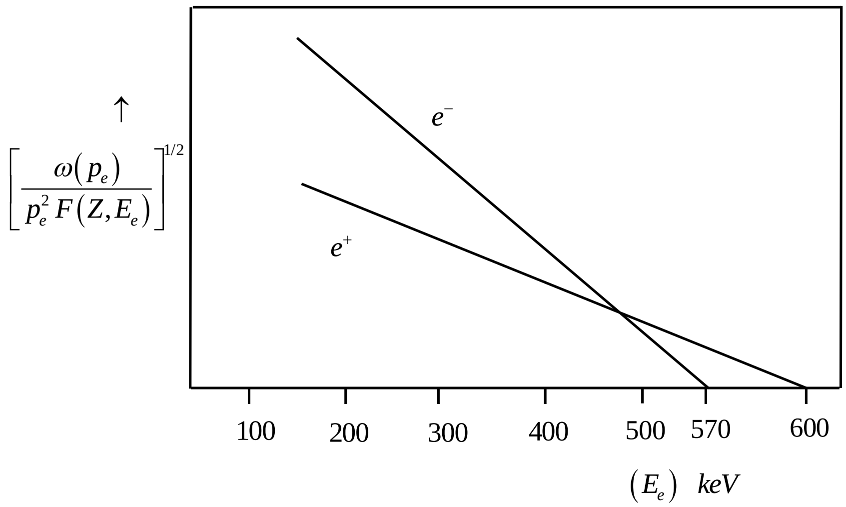


Figure 10.4 : *The Fermi Kurie plot of* ^{64}Cu ***beta spectra .End points are*** $571keV(e^-)$ ***and*** $657\,keV(e^+)$ ***[Owen &Cook (1949)]***

The departure from the straight line are attributed to a dependence of M_{if} on p_e such as occurs in forbidden transitions according to eq.(10.41) and (10.42).

Coulomb Factor $F\left(Z,E_e\right)$ is defined as

$$F\left(Z,E_e\right)=\frac{\left|\psi_e(0)\right|^2_{Coulomb}}{\left|\psi_e(0)\right|^2_{free}} \tag{10.53}$$

Coulomb factor takes care of the fact that electrons are not really free but interacting with nucleons (Coulomb interaction).

The corrected expression for (10.52) is

$$\omega\left(p_e\right)dp_e=\frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{\left|M_{if}\right|^2}{\hbar^7c^3}F\left(Z,E_e\right)p_e^2\left(E_0-E_e\right)^2 dp_e$$

$$\omega\left(E_e\right)dE_e=\frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{\left|M_{if}\right|^2}{\hbar^7c^5}F\left(Z,E_e\right)\left(E_0-E_e\right)^2 p_eE_edE_e \tag{10.54}$$

All momenta are expressed in terms of $p_e=\eta m_ec$ and all energies in terms of

$E_e=\varepsilon_e m_e c^2$, $E_0=\varepsilon_0 m_e c^2$

We get above equations in unitless variables.

$$\omega(\eta)d\eta=\frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{m_e^5c^4}{\hbar^7}\left|M_{if}\right|^2F\left(Z,\varepsilon_e\right)\left(\varepsilon_0-\varepsilon_e\right)^2\eta^2d\eta$$

$$\omega\left(\varepsilon_e\right)d\varepsilon_e=\frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{m_e^5c^4}{\hbar^7}\left|M_{if}\right|^2F\left(Z,\varepsilon_e\right)\left(\varepsilon_0-\varepsilon_e\right)^2\eta\varepsilon_ed\varepsilon_e \tag{10.55}$$

The decay constant λ can be expressed as

$$\lambda_\beta=\int_0^{\eta_0}\omega(\eta)d\eta=\frac{\left|M_{if}\right|^2}{\tau_0}\int_0^{\eta_0}F\left(Z,\varepsilon_e\right)\left(\varepsilon_0-\varepsilon_e\right)^2\eta^2d\eta \tag{10.56}$$

where $\frac{1}{\tau_0}=\frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{m_e^5c^4}{\hbar^7}$ (10.57)

$\tau_0=$ Universal Time constant for beta process.

The estimate for τ_0 is

$$\tau_0 \cong \frac{1}{1.03\times 10^{-4}} s \simeq 9.709\times 10^3 s \simeq 2.7 hrs \tag{10.58}$$

Taking $$f\left(\eta_0\right) = \int_0^{\eta_0} F\left(Z,\varepsilon_e\right)\left(\varepsilon_0 - \varepsilon_e\right)^2 \eta^2 d\eta \tag{10.59}$$

λ_β can be expressed as

$$\lambda_\beta = \frac{\left|M_{if}\right|^2}{\tau_0} f\left(\eta_0\right) \tag{10.60}$$

Here we have defined

$f\left(\eta_0\right) \equiv$ Coulomb Fermi Factor

From the decay law

$$N = N_0 e^{-\lambda_\beta t} \tag{10.61}$$

We get half life as

$$\lambda_\beta = \frac{ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} = \frac{\left|M_{if}\right|^2}{\tau_0} f\left(\eta_0\right) \tag{10.62}$$

We can write $\left(h\text{-}p\ pair\right)$

$$6728 s \simeq 1.9 hrs$$

The product of Coulomb Fermi Factor and half life of nucleus for beta decay is called comparative half life $f\,t_{1/2}$ or usually written as *ft.*

10.7 Parity Conserved Selection Rules for Fermi and Gamow Teller Transitions

Selection Rules

Angular momentum conservation dictates

$\vec{I}_f = \vec{I}_i + \vec{L}_\beta$ (Fermi Type)

$\vec{I}_f = \vec{I}_i + \vec{L}_\beta + \hat{\mathbb{1}}$ (Gamow Teller Type)

In the Fermi Type transitions emitted light particles have their spins antiparallel.

Singlet state $e\uparrow \quad \bar{\nu}_e\downarrow \quad \Rightarrow S_{eZ} = -S_{\nu Z}$

But in the Gamow Teller type transitions emitted light particles have their spins parallel.

Triplet state $e\uparrow \quad \bar{\nu}_e\downarrow \quad \Rightarrow S_{eZ} = +S_{\nu Z}$

Parity changes are determined by

$$\pi_f = \pi_i(-1)^{L_\beta}$$

The total orbital angular momenta carried by $(e,\bar{\nu}_e)$ light particles is denoted by $\vec{L}_\beta$.

We assume that $(e,\bar{\nu}_e)$ are emitted by the point nucleus.

$$\frac{R}{\lambda_{e\ or\ \bar{\nu}_e}} << 1 \text{ hence } \vec{k}.\vec{r} = 0$$

But if we consider

$$\frac{R}{\lambda_{e\ or\ \bar{\nu}_e}} < 1 \text{ then}$$

$$\psi_e(0) \neq 1 \quad \text{but} \quad \simeq 1 + i\vec{k}_e.\vec{r} + ...$$

$$\psi^*_{\bar{\nu}_e}(0) \neq 1 \quad \text{but} \quad \simeq 1 + i\vec{k}_{\bar{\nu}_e}.\vec{r} + ...$$

The inclusion of $\vec{k}.\vec{r} \quad \rightarrow L_\beta = 1$

$$\left(\frac{\vec{k}.\vec{r}}{2}\right)^2 \quad \rightarrow L_\beta = 2$$

The wavefunctions should be considered in the volume Ω rather than at the centre.

Relativistic consideration is required .

These modifications produce nonlinearity in Kurie plots and higher order transitions occur for $L_\beta \geq 0$.

So we classify the transitions as

If $\quad L_\beta = 0 \quad$ allowed

$L_\beta = 1$ Forbidden Ist Order

$L_\beta = 2$ Forbidden 2nd Order

Transition	L_β	ΔI (Fermi)	$\Delta\pi$ (Fermi)	ΔI (G.T.)	$\Delta\pi$ (G.T.)
Allowed	0	0	No	(0),1	No
First Forbidden	1	(0),1	Yes	0,1,2	Yes
Second Forbidden	2	(1),2	No	2,3	No
Third Forbidden	3	(2),3	Yes	3,4	Yes
Fourth Forbidden	4	(3),4	No	4,5	No

Those not possible ,if either I_i or I_f is zero, are in parenthesis.

The Gamow Teller transitions for which $\Delta I = L + 1$ only then these transitions are called unique transitions or pure transitions.

The mixing of Fermi and Gamow Teller transitions changes the shape of Curie plots.

General Selection rules

Fermi $\Delta I = \pm n, \pm(n-1)$

$$\pi_f = \pi_i(-1)^n$$

Gamow Teller $\Delta I = \pm n, \pm(n+1)$

$$\pi_f = \pi_i(-1)^n$$

10.8 *f t* Values and Forbidden Beta Transitions

The allowed or forbidden nature of transitions is often determined from the measurement of $ft\tfrac{1}{2}$ values.

$ft\tfrac{1}{2}$ value depends upon

- Z
- End point energy ε_0
- Half life $t_{1/2}$

$ft\frac{1}{2}$ has large variations so $log_{10}\ ft\frac{1}{2}$ is considered

$log_{10}\ ft\frac{1}{2}$ value	Type of transition
2.7-3.7	Super allowed
4-5.8	allowed
6-10	First forbidden
10-14	Second Forbidden
14-17	Third Forbidden
17-24	Fourth Forbidden

We can take following examples:

Fermi type:

$L_\beta = 0 \qquad {}^{14}_{8}O \rightarrow {}^{14}_{7}N^* + e^+ + \nu_e$

$\left[0^+ \rightarrow 0^+\right]$

$L_\beta = 1 \qquad {}^{87}Kr \rightarrow {}^{87}Rb + e^- + \bar{\nu}_e$

$\left[\frac{5}{2} \rightarrow \frac{3}{2}\right]$

${}^{111}Ag \rightarrow {}^{111}Cd + e^- + \bar{\nu}_e$

$\left[\frac{1}{2} \rightarrow \frac{1}{2}\right]$

$L_\beta = 2 \qquad {}^{135}Cs \rightarrow {}^{135}Bi + e^- + \bar{\nu}_e$

$\left[\frac{7}{2} \rightarrow \frac{3}{2}\right]$

$L_\beta = 3 \qquad {}^{87}Rb \rightarrow {}^{87}Sr + e^- + \bar{\nu}_e$

$\left[\frac{3}{2} \rightarrow \frac{9}{2}\right]$

$L_\beta = 4 \qquad {}^{115}In \rightarrow {}^{115}Sn + e^- + \bar{\nu}_e$

$\left[\frac{9}{2} \rightarrow \frac{1}{2}\right]$

Gamow Teller type:

$L_\beta = 0$ $\quad {}^{6}_{2}He \rightarrow {}^{6}_{3}Li + e^- + \bar{\nu}_e$

$\left[0^+ \rightarrow 1^+\right]$

$L_\beta = 1$ $\quad {}^{37}S \rightarrow {}^{37}Cl + e^- + \bar{\nu}_e$

$\left[\frac{7}{2} \rightarrow \frac{3}{2}\right]$

$L_\beta = 1$ $\quad {}^{85}Kr \rightarrow {}^{85}Rb + e^- + \bar{\nu}_e$

$\left[\frac{9}{2} \rightarrow \frac{5}{2}\right]$

$L_\beta = 2$ $\quad {}^{10}Be \rightarrow {}^{10}B + e^- + \bar{\nu}_e$

$\left[0 \rightarrow 3\right]$

$L_\beta = 2$ $\quad {}^{22}Na \rightarrow {}^{22}Ne + e^- + \bar{\nu}_e$

$\left[3 \rightarrow 0\right]$

10.9 Experimental Verification of Parity Violation

If the process and its parity reversed process both occur in nature with the same probability ,then the process is said to be parity invariant.

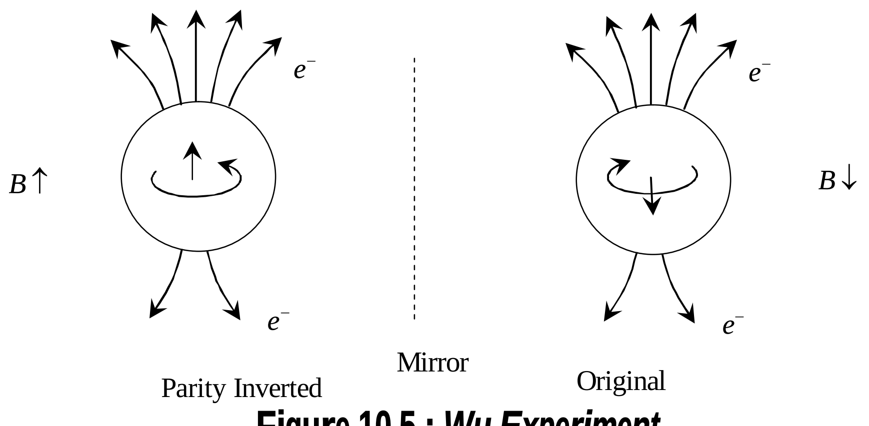


Figure 10.5 : *Wu Experiment*

The counts observed in original set up in the direction of opposite to the field are 40% higher than that in the direction of field but this observation is not maintained in parity inverted set up.

Electrons were emitted preferentially in the opposite direction of the nuclear spin.

$$^{60}Co \to {}^{60}Ni^* + e^- + \bar{\nu}_e$$

Backward emission is 40% higher .[Wu and coworkers]

Hence in weak interaction neutrinos and electrons are left handed. Yang and Lee suggested that in beta decay and in general in weak processes, parity is violated so Lagrangian density and matrix element both must have even and odd couplings.

Parity Violation τ - θ Puzzle :

	P	$Mode$
$K^+ \to \pi^0\pi^+$	$(-1)^2 = 1$	τ
$K^+ \to \pi^+\pi^-\pi^+$	$(-1)^3 = -1$	θ
$K^+ \to \pi^+\pi^0\pi^0$	$(-1)^3 = -1$	θ

K^+ decay forced to argue that Parity invariance fails in weak processes [Yang &Lee]

10.10 V−A Theory of Fermi Beta Decay with Parity Conserving and Nonconserving Terms

Now we shall discuss the arguments to establish the V−A form of weak interaction.

Let us write the most general matrix element for the beta decay of neutron.

$$n \to p + e^- + \bar{\nu}_e$$

That is consistent with Lorentz invariance and Lepton –Baryon conservation.

$$M = g \sum_{nucleons} \sum_j \int d\Omega \left[\bar{\Psi}_p \hat{O}_j \Psi_n \right] \left[\bar{\Psi}_e \hat{O}_j \left(C_j - C'_j \gamma_5 \right) \Psi_{\nu_e} \right]$$

$\sum_{nucleons}$ it is summed over all nucleons inside the nucleus.

$\sum_j$	j	$\hat{O}_j$	Symbol	Meaning
	$j=1$	1	S	Scalar
	$j=2$	γ^μ	V	Vector
	$j=3$	$\sigma^{\mu\nu}$	T	Tensor

	$j=4$	$\gamma^{\mu}\gamma_5$	A	Axial Vector
	$j=5$	γ_5	P	Pseudo scalar

$\sum_j$: It is summed over all type couplings SVTAP and each has left and right handed terms.

$$\left(C_j - C'_j\gamma_5\right) = \left(C_j - C'_j\right)\left(\frac{1+\gamma_5}{2}\right) + \left(C_j + C'_j\right)\left(\frac{1-\gamma_5}{2}\right)$$

$\left(\frac{1+\gamma_5}{2}\right)$: Right handed term (10.63)

$\left(\frac{1-\gamma_5}{2}\right)$: Left handed term (10.64)

We use the definitions of γ matrices

We obtain

$$\hat{O}_j\left(1\pm\gamma_5\right) = \left(1\pm\gamma_5\right)\hat{O}_j \quad \text{for } j = \underset{S}{1}\ ,\ \underset{T}{3}\ ,\ \underset{P}{5} \tag{10.65}$$

$$\hat{O}_j\left(1\pm\gamma_5\right) = \left(1\mp\gamma_5\right)\hat{O}_j \quad \text{for } j = \underset{V}{2}\ ,\ \underset{A}{4} \tag{10.66}$$

Now we use the experimental fact that all electrons and neutrinos are left handed so $\hat{O}_j\left(\frac{1+\gamma_5}{2}\right)$ terms will vanish.

Hence $C_j = C'_j$ (Wu-Experiment)

Now $\hat{O}_j\left(1-\gamma_5\right) = \left(1-\gamma_5\right)\hat{O}_j$ for $j = \underset{S}{1}\ ,\ \underset{T}{3}\ ,\ \underset{P}{5}$

$\hat{O}_j\left(1-\gamma_5\right) = \left(1+\gamma_5\right)\hat{O}_j$ for $j = \underset{V}{2}\ ,\ \underset{A}{4}$ (Wu-Experiment)

Therefore

$$\hat{O}_j\left(C_j - C'_j\gamma_5\right) = \sum_{j=1,3,5} C_j\left(1-\gamma_5\right)\hat{O}_j + \sum_{j=2,4} C_j\left(1+\gamma_5\right)\hat{O}_j$$

We now apply the result of ^{152}Eu Goldhaber experiment which measures circular polarization of γ photons. It results in the assignment of helicity of neutrinos.

$$h\left(\overline{\nu}_e\right) = -1 = \frac{\vec{\sigma}.\vec{P}}{|\sigma||P|} \cong \frac{v}{c} \qquad \left(m_{\nu_e} = 0\right) \quad \text{(Experiment-Goldhaber)}$$

$$\frac{C_S}{C_V} = -0.001 \pm 0.006$$

$$\frac{C_T}{C_A} = -0.004 \pm 0.001 \qquad (10.67)$$

Next we consider that neutrons in β^- decay are not relativistic and transfer of momentum of the order of $q \simeq 1MeV$

This introduces $\frac{v^2}{c^2} \simeq 10^{-6}$ factor in $|M|^2$ calculation.

It shows that C_P is negligible [Exp-$\frac{v^2}{c^2}$]

Hence C_S, C_T, C_P all are negligible .

Christensen et.al. (1969) measured decay rates of $0^+ \to 0^+$ transitions in

$$^{10}C \to {}^{10}B$$
$$^{14}O \to {}^{14}N$$

and concluded that $C_V = 1$ [Experiment –Christensen]

Krohn et.al (1975) measured neutron's mean life time which yielded

$$\lambda = \frac{C_A}{C_V} = 1.258 \pm 0.015 \qquad \text{[Experiment-Krohn]}$$

Now $\sum_{V,A} \overline{\Psi}_e C_j \left(1+\gamma_5\right) \hat{O}_j \psi_{\nu_e} = \overline{\Psi}_e C_V \left(1+\gamma_5\right)\gamma^\mu \psi_{\nu_e} + \overline{\Psi}_e C_V \lambda \left(1+\gamma_5\right)\gamma^\mu \psi_{\nu_e}$

$$= \overline{\Psi}_e C_V \left(1+\gamma_5+\lambda+\lambda\gamma_5\right)\gamma^\mu \psi_{\nu_e} \qquad \left(\because \gamma_5^2 = 1\right)$$

$$= \overline{\Psi}_e C_V \left(1+\lambda\gamma_5\right)\left(1+\gamma_5\right)\gamma^\mu \psi_{\nu_e}$$

$$= \left(1-\lambda\gamma_5\right)\overline{\Psi}_e C_V \left(1+\gamma_5\right)\gamma^\mu \psi_{\nu_e}$$

$$= \left(1-\lambda\gamma_5\right)\overline{\Psi}_e C_V \gamma^\mu \left(1-\gamma_5\right)\psi_{\nu_e}$$

$$= \left(1-\lambda\gamma_5\right)\overline{\Psi}_e C_V \gamma^\mu \left(1-\gamma_5\right)\psi_{\nu_e}$$

Hence We justify (V−A) law for beta decay and weak processes in general using the empirical fact of parity violation.

10.11 Self Learning Exercise

Q.1 Describe Fermi theory of β decay and derive transition probability for β decay.

Q.2 Describe τ-θ puzzle and Wu experiment of parity violation in β decay of ^{60}Co.

Q.3 Discuss energetics of β^- decay , β^+ decay and EC processes.

10.12 Summary

- β^- decay : ${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + e^- + \bar{\nu}_e$; $Q_{\beta^-} = \left[\left(M_Z + B_Z\right) - \left\{M_{Z+1} + B_{Z+1}\right\}\right]$

  β^+ decay : ${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + e^+ + \nu_e$; $Q_{\beta^+} = \left[\left(M_Z + B_Z\right) - \left(M_{Z-1} + B_{Z-1}\right)\right] - 2m_e$

  Electron capture(EC) : ${}^{A}_{Z}X + e^- \rightarrow {}^{A}_{Z-1}Y + \nu_e$; $Q_{EC} = \left(M_Z + B_Z\right) - \left(M_{Z-1} + B_{Z-1}\right) - b^e_Z(K)$

- general characteristics of weak interaction processes.
  - (i) universal weak coupling constant
  - (ii) W^+, W^- and Z^o Vector Bosons are Weak Interaction Carriers:
  - (iii) Range of weak interaction is very short ($\simeq 10^{-3}\ fm$):
  - (iv) SU_3 Flavour Symmetry Mixing:
  - (v) Parity Nonconservation

- The probability of transition by Fermi Golden rule

$$\omega\left(E_e\right)dE_e = \frac{1}{2}\frac{G_{V\beta}^2}{\pi^3}\frac{\left|M_{if}\right|^2}{\hbar^7 c^5}F\left(Z,E_e\right)\left(E_0 - E_e\right)^2 p_e E_e dE_e$$

- General Selection rules for beta decay

  Fermi $\Delta I = \pm n, \pm(n-1)$; $\pi_f = \pi_i(-1)^n$

  Gamow Teller $\Delta I = \pm n, \pm(n+1)$; $\pi_f = \pi_i(-1)^n$

- The allowed or forbidden nature of transitions is often determined from the measurement of $ft_{1/2}$ values.

- Yang and Lee suggested that in beta decay and in general in weak processes, parity is violated.

10.13 Glossary

β **decay :** β^{+}, β^{-} and electron capture

GT Transitions : Gamow Teller Transitions

10.14 Exercise

Q.1 Describe Fermi theory of β decay and obtain the expression for partial decay λ_{β} for for β channel.

Q.2 Distinguish between Fermi and Gamow Teller transitions by giving one example for each case.

Q.3 Give salient points of hypothesis of Fermi theory of β decay and derive expression for $f\,t_{1/2}$ value (comparative half life).

Q.4 Derive transition probability for β decay using Fermi theory. Discuss Fermi Kurie plots.

Q.5 Write short notes on

(i) Basic characteristics of weak interaction (ii) Cabbio angle

(iii) Kobayashi Maskawa Matrix (iv)Vector Bosons W^{+}, W^{-} and Z^{0}

Q.6 Write basic steps of $V-A$ Fermi theory explaining the meaning of S, V, A, T, P terms.

References and Suggested Readings

1. Nuclei and Particles by Emilio Segre
2. Nuclear Physics by R.R. Roy and B.P. Nigam
3. Introductory Nuclear Physics by Samuel S.M. Wong
4. Elements of Nuclear Physics by W.E. Burcham
5. Theoretical Nuclear Physics by John M. Blatt &Victor F. Weisskopf.
6. Nuclear Physics by S.N. Ghosal
7. Nuclear Models by Walter Greiner & Joachein A. Mahrun
8. Introductory Nuclear Physics by Kenneth S. Krane

UNIT-11
Gamma Ray Emission

Structure of the unit

11.0 Objectives

The reader learns about electromagnetic transition probabilities and selection rules for multipoles.

11.1 Introduction

Gamma ray is an electromagnetic wave. Gamma decays have theoretical and practical importance in nuclear physics as gamma rays are source of information about nuclear energy levels. The concept of quantized electromagnetic field is introduced. Weisskopf single particle estimates for transition probabilities are discussed. In this unit we also study internal conversion and nuclear isomerism. We have used CGS units in this unit.

11.2 The Quantized Electromagnetic Field

The vector electromagnetic potential $\vec{A}(\vec{r},t)$ is taken as the principal dynamic field which is constrained by Coulomb Gauge (Transverse Gauge). The vector field fulfils the gauge condition

$$\vec{\nabla}.\vec{A}=0 \tag{11.1}$$

and in the absence of charges or currents, the wave equation

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-\nabla^2\right)\vec{A}=0 \tag{11.2}$$

The electromagnetic fields are given in terms of $\vec{A}(\vec{r},t)$ by

$$\vec{E}=-\frac{1}{c}\frac{\partial\vec{A}}{\partial t},$$

$$\vec{H}=\vec{\nabla}\times\vec{A} \tag{11.3}$$

The energy density of the field is

$$E_{em}=\frac{1}{8\pi}\left(\left|\vec{E}\right|^2+\left|\vec{H}\right|^2\right) \tag{11.4}$$

With a plane waveform for vector electromagnetic potential

$$\vec{A}_k(\vec{r},t)=\vec{A}_0\,cos\left(\vec{k}.\vec{r}-\omega t\right) \tag{11.5}$$

The above equations (11.3) & (11.4) become

$$\vec{E}_k=-k\vec{A}_0\,sin\left(\vec{k}.\vec{r}-\omega t\right) \quad ,$$

$$\vec{H}_k=-\vec{k}\times\vec{A}_0\,sin\left(\vec{k}.\vec{r}-\omega t\right) \tag{11.6}$$

and the energy density of the field will take the form

$$E_{em}=\frac{1}{8\pi}k^2\left|\vec{A}_0\right|^2 \tag{11.7}$$

For a vector field corresponding to one photon of energy $\hbar\omega$ in the system volume V , the amplitude of the electromagnetic vector potential becomes

$$\left|\vec{A}_0\right|=\sqrt{\frac{8\pi\hbar\omega}{k^2V}}=\sqrt{\frac{8\pi\hbar c^2}{\omega V}} \tag{11.8}$$

Taking $\omega=ck$,the corresponding complex expression of the dynamic vector potential which yields the same average energy density is

$$\vec{A}(\vec{r},t)=\varepsilon\sqrt{\frac{2\pi\hbar c^2}{\omega V}}\left[a_0e^{i\left(\vec{k}.\vec{r}-\omega t\right)}+a_0^*e^{-i\left(\vec{k}.\vec{r}-\omega t\right)}\right] \tag{11.9}$$

where a_0 is a complex number with $|a_0| = 1$ which determines the phase of the wave and ε is the unit vector indicating the polarization .We know that electromagnetic waves are transverse in nature and there are two independent polarization directions $\varepsilon_l \;, l = 1,2$ both fulfilling $\vec{\varepsilon}_l . \vec{k} = 0$

The classical interaction Hamiltonian density is

$$H = -\frac{1}{c} \; \vec{j}\,(\vec{r}).\vec{A}(\vec{r}) \tag{11.10}$$

With $\vec{j}\,(\vec{r})$ the current density .The transition matrix element between ψ_i and ψ_f nuclear states which describes emission of a photon is

$$\int d^3\vec{r} \left\langle \psi_f, \gamma \right| -\frac{1}{c} \; \hat{j}\,(\vec{r}).\vec{A}(\vec{r}) \left| \psi_i, no\ \gamma \right\rangle \tag{11.11}$$

and for absorption of a photon

$$\int d^3\vec{r} \left\langle \psi_f, no\ \gamma \right| -\frac{1}{c} \; \hat{j}\,(\vec{r}).\vec{A}(\vec{r}) \left| \psi_i, \gamma \right\rangle \tag{11.12}$$

The electromagnetic vector potential operator should thus contains two Hermitian conjugate parts involving creation and annihilation operators for photon. Hence a_0 and a_0^* amplitudes in equation (11.9) must be replaced by $\beta^\dagger$ and β, the creation and annihilation operators for photons.

The matrix element for emission of a photon of energy $\hbar\omega$,the total time dependent phase is

$$\frac{i}{\hbar}\left(E_f - E_i\right)t + i\phi = \frac{i}{\hbar}\left(E_f - E_i\right)t + i\omega t \tag{11.13}$$

with ϕ the unknown phase for creation of a photon in the radiation field .The conservation of energy implies $E_f = E_i - \hbar\omega$ and consequently we have $\phi = \omega t$.

The annihilation operator and creation operator are associated with outgoing plane waves ($\vec{k}$) and incoming plane waves $\left(-\vec{k}\right)$ respectively. The mode of the field is thus specified by wavevector $\vec{k}$ and polarization index μ. The electromagnetic vector potential operator will thus be specified by indices defining mode. The energy of electromagnetic field is given correctly by number of photons if normalization factor $\sqrt{\dfrac{2\pi\hbar c^2}{\omega V}}$ is ensured . The electromagnetic vector potential operator summed over all modes $\left(\vec{k},\mu\right)$ is

$$\hat{A}(\vec{r},t)=\sum_{\mu}\sqrt{\frac{2\pi\hbar c^2}{\omega V}}\left[\hat{\beta}_{k\mu}\varepsilon_{\mu}^{*}e^{i\left(\vec{k}.\vec{r}-\omega t\right)}+\beta_{k\mu}^{\dagger}\varepsilon_{\mu}e^{-i\left(\vec{k}.\vec{r}-\omega t\right)}\right] \tag{11.14}$$

The choice of ε_{μ} and angular momentum projection μ should go with creation operator $\beta_{k\mu}^{\dagger}$.

The total energy of this field integrated over the volume V is given by

$$\hat{H}=\sum_{k,\mu}\hbar\omega_k\left(\beta_{k\mu}^{\dagger}\hat{\beta}_{k\mu}+\frac{1}{2}\right) \tag{11.15}$$

and the total momentum is

$$\hat{p}=\sum_{k,\mu}\hbar\vec{k}\beta_{k\mu}^{\dagger}\hat{\beta}_{k\mu} \tag{11.16}$$

The photon states are treated as eigen states of the momentum operator $\hat{p}$. The interaction with nuclei is best understood if we use angular momentum eigen states.

Note on ε_{μ}:

The photon of energy $\hbar\omega$ has an intrinsic angular momentum of $1\hbar$ with basis vectors ε_{μ} given by spherical unit vectors e_{μ} $,\mu=-1,0,1.$

The normalized vectors are

$$e_{+1}=-\frac{1}{\sqrt{2}}\left(\hat{e}_x+i\hat{e}_y\right)$$

$$e_0=\hat{e}_z$$

$$e_{-1}=\frac{1}{\sqrt{2}}\left(\hat{e}_x-i\hat{e}_y\right) \tag{11.17}$$

Spherical basis vectors are complex vectors and orthogonal

$$e_{\mu}^{*}e_{\mu'}=\delta_{\mu\mu'} \tag{11.18}$$

The Condon-Shortley choice of phases yields the property

$$e_{\mu}^{*}=(-1)^{\mu}e_{-\mu} \tag{11.18a}$$

The careful reader will notice that this is analogous to spherical harmonics.

Any vector $\vec{a}$ can be decomposed in spherical basis in the following manner

$$\sum_{\mu=-1}^{1} a_{\mu}^{*} e_{\mu} = a \tag{11.19}$$

a_1: describes a vector with positive angular momentum of unit 1 about z axis.

The Hamiltonian for the charged particle is written as

$$H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 \tag{11.20}$$

which is sum of free particle Hamiltonian H_0 and the coupling with the external electromagnetic field giving perturbing Hamiltonian H'

$$H = H_0 + H' \tag{11.21}$$

Comparing (11.20) and (11.21) ,we get

$$H' = -\frac{q}{2mc}\left(\vec{p}.\vec{A} + \vec{A}.\vec{p}\right) + \frac{q^2}{2mc^2}\left(\vec{A}.\vec{A}\right)$$

$$\Rightarrow H' = -\frac{q}{mc}\vec{A}.\vec{p} + \frac{q^2}{2mc^2}\left(\vec{A}.\vec{A}\right) \tag{11.22}$$

Using $\vec{p} = -i\hbar\vec{\nabla}$ and $\vec{\nabla}.\vec{A} = 0$

($\vec{\nabla}.\vec{A}$ is known as transversality condition)

$\vec{A}.\vec{p} = \vec{p}.\vec{A}$ was obtained and used .The quadric term $\vec{A}.\vec{A}$ involves two photons at same time and therefore will be ignored because our interest is in lower order phenomena. H' may be written in terms of a current density $\hat{j}$

$$\hat{j} = q\vec{v} = \frac{q}{m}\hat{p} \tag{11.23}$$

The perturbing Hamiltonian H' (neglecting quadratic term) is

$$H' = -\frac{1}{c}\vec{A}.\ \vec{j} \tag{11.24}$$

$$= -\frac{1}{c}\sum_{\mu=1}^{4} A_{\mu}\ j_{\mu} \tag{11.25}$$

where $A_{\mu} = \left(\vec{A}, iV\right)$ and $j_{\mu} = \left(\vec{j}\,, i\rho c\right)$.

In the region , outside any sources, the electromagnetic vector potential is the solution of the partial differential equation

$$\left(\nabla^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)A_\mu(\vec{r},t)=0 \qquad (11.26)$$

The 3 vector potential $\vec{A}(\vec{r},t)$ can be expanded in terms of components characterized by definite wavenumber $\vec{k}$ as

$$\vec{A}(\vec{r},t)=\sum_k \vec{A}_k(\vec{r})e^{-i\omega t} \qquad (11.27)$$

where $\omega=ck$. In this relation ,time dependence is separated.

The spatial dependence of $\vec{A}(\vec{r},t)$ is given and constrained by

$$\left(\nabla^2+k^2\right)\vec{A}_k(\vec{r})=0 \qquad (11.28)$$

The solution of this equation can be written as

$$\hat{A}(\vec{r},t)=\frac{1}{N}\sum_{k,\mu}\left[\hat{\beta}_{k\mu}\varepsilon^*_\mu e^{i\left(\vec{k}.\vec{r}-\omega t\right)}+\beta^\dagger_{k\mu}\varepsilon_\mu e^{-i\left(\vec{k}.\vec{r}-\omega t\right)}\right] \qquad (11.29)$$

$\varepsilon^*_\mu e^{i\left(\vec{k}.\vec{r}-\omega t\right)}$ and $\varepsilon_\mu e^{-i\left(\vec{k}.\vec{r}-\omega t\right)}$ can be expanded in terms of eigen functions of angular momentum operators,

$$\hat{A}(\vec{r},t)=\sum_{\lambda,\mu}\vec{A}_{\lambda\mu}(\vec{r},t) \qquad (11.30)$$

$\vec{A}_{\lambda\mu}(\vec{r},t)$ are vector functions of spherical tensor of ranks (λ,μ) which satisfy the relations

$$\vec{J}^2\vec{A}_{\lambda\mu}(\vec{r},t)=\lambda(\lambda+1)\vec{A}_{\lambda\mu}(\vec{r},t)\ ,$$

and $$J_z\vec{A}_{\lambda\mu}(\vec{r},t)=\mu\vec{A}_{\lambda\mu}(\vec{r},t) \qquad (11.31)$$

$\vec{A}_{\lambda\mu}(\vec{r},t)$ can be expressed in terms of vector spherical harmonics defined by

$$\vec{X}_{\lambda\mu}=\frac{\vec{l}}{\sqrt{\lambda(\lambda+1)}}Y_{\lambda\mu}(\theta,\phi) \qquad (11.32)$$

$\vec{A}_{\lambda\mu}(\vec{r},t)$ appearing in (11.30) and (11.31) can be expanded in terms of electric and magnetic 2^λ poles spatially.

$$\vec{A}_{\lambda\mu}(\vec{r})=C^E_{\lambda\mu}\vec{A}_{\lambda\mu}(E\text{-}\lambda,\vec{r})+D^M_{\lambda\mu}\vec{A}_{\lambda\mu}(M\text{-}\lambda,\vec{r}) \qquad (10.33)$$

Symbols mean as

$\vec{A}_{\lambda\mu}(E\text{-}\lambda,\vec{r}) \equiv$ Electric multipole 2^{λ} pole type vector potential

$\vec{A}_{\lambda\mu}(M\text{-}\lambda,\vec{r}) \equiv$ Magnetic multipole 2^{λ} pole type vector potential

$\vec{A}_{\lambda\mu}(E\text{-}\lambda,\vec{r})$ and $\vec{A}_{\lambda\mu}(M\text{-}\lambda,\vec{r})$ are solutions of Helmholtz equation

$$\left(\nabla^2 + k^2\right)\vec{A}_{\lambda\mu}(G\text{-}\lambda,\vec{r}) = 0 \tag{10.34}$$

where $G = E, M$

The relations between fields and vector potential near the source are given by

$$\vec{E}(E\text{-}\lambda,\vec{r}) = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A}(E\text{-}\lambda,\vec{r}) = ik\vec{A}(E\text{-}\lambda,\vec{r})$$

$$\vec{H}(E\text{-}\lambda,\vec{r}) = \vec{\nabla}\times\vec{A}(E\text{-}\lambda,\vec{r}) = -ik\vec{A}(E\text{-}\lambda,\vec{r})$$

$$\vec{E}(M\text{-}\lambda,\vec{r}) = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A}(M\text{-}\lambda,\vec{r}) = ik\vec{A}(M\text{-}\lambda,\vec{r})$$

$$\vec{H}(M\text{-}\lambda,\vec{r}) = \vec{\nabla}\times\vec{A}(M\text{-}\lambda,\vec{r}) = -ik\vec{A}(M\text{-}\lambda,\vec{r}) \tag{11.35}$$

The magnetic 2^{λ} pole radiations obey equations

$$\left(\nabla^2 + k^2\right)\vec{E}(M\text{-}\lambda,\vec{r}) = 0,$$

$$\vec{\nabla}.\vec{E}(M\text{-}\lambda,\vec{r}) = 0$$

$$\vec{H}(E\text{-}\lambda,\vec{r}) = -\frac{i}{k}\sqrt{\frac{\varepsilon}{\mu}}\;\vec{\nabla}\times\vec{E}(M\text{-}\lambda,\vec{r})$$

$$\vec{r}.\vec{E} = 0 \tag{11.36}$$

Similarly ,the electric 2^{λ} pole radiations obey equations

$$\left(\nabla^2 + k^2\right)\vec{H}(M\text{-}\lambda,\vec{r}) = 0$$

$$\vec{\nabla}.\vec{H}(E\text{-}\lambda,\vec{r}) = 0$$

$$\vec{E}(M\text{-}\lambda,\vec{r}) = \frac{i}{k}\sqrt{\frac{\mu}{\varepsilon}}\;\vec{\nabla}\times\vec{H}(E\text{-}\lambda,\vec{r})$$

and $\vec{r}.\vec{H} = 0$ (11.37)

In terms of spherical harmonics ,the electric and magnetic multipole radiations or transitions can be expressed in the following forms

$$\vec{A}_{\lambda\mu}(E\text{-}\lambda,\vec{r}) = -\frac{i}{k}\vec{\nabla}\times\left(\vec{r}\times\vec{\nabla}\right)\left[j_\lambda(kr)Y_{\lambda\mu}(\theta,\phi)\right]$$

and $$\vec{A}_{\lambda\mu}(M\text{-}\lambda,\vec{r}) = \left(\vec{r}\times\vec{\nabla}\right)\left[j_\lambda(kr)Y_{\lambda\mu}(\theta,\phi)\right] \qquad (11.38)$$

where $j_\lambda(kr)$ is spherical Bessel function of order λ and $Y_{\lambda\mu}(\theta,\phi)$ is spherical harmonics of ranks (λ,μ).

We can now express the multipole (λ,μ) part of the perturbing Hamiltonian H' [refer to eq.(11.24)] in the form:

$$\hat{O}_{\lambda\mu}(E\text{-}\lambda) = -\frac{i}{ck^{\lambda+1}}\frac{(2\lambda+1)!!}{(\lambda+1)}\;\hat{j}\;(\vec{r}).\vec{\nabla}\times\left(\vec{r}\times\vec{\nabla}\right)\left[j_\lambda(kr)Y_{\lambda\mu}(\theta,\phi)\right]$$

and $$\hat{O}_{\lambda\mu}(M\text{-}\lambda) = -\frac{1}{ck^{\lambda}}\frac{(2\lambda+1)!!}{(\lambda+1)}\;\hat{j}\;(\vec{r}).\left(\vec{r}\times\vec{\nabla}\right)\left[j_\lambda(kr)Y_{\lambda\mu}(\theta,\phi)\right] \qquad (11.39)$$

where $(2\lambda+1)!! = 1\cdot3\cdot5\cdots(2\lambda+1)$

The $\hat{O}_{\lambda\mu}(E\text{-}\lambda)$ and $\hat{O}_{\lambda\mu}(M\text{-}\lambda)$ are scalar operators in the nuclear and electromagnetic fields. So multipole part of current density $\hat{j}\;(\vec{r})$ can make a nonvanishing contribution in the transition for $(\lambda,-\mu)$ multipole only. The spherical Bessel function may be expanded in power series as

$$j_\lambda(kr) \simeq \frac{(kr)^\lambda}{(2\lambda+1)!!}\left[1-\frac{1}{2}\frac{(kr)^2}{(2\lambda+3)}+...\right] \qquad (11.40)$$

The γ ray involved in nuclear transitions here energies $E_\gamma < 10MeV$ typically. The corresponding wavenumbers of order

$$k \simeq \frac{E_\gamma}{\hbar c} \simeq \frac{10\,MeV}{200\,MeV.fm} \simeq \frac{1}{20}\,fm^{-1}\ or\ less.$$

The multipole operators cannot have contributions from the regions outside the nucleus because they act on nuclear wavefunctions. This leads us to the $r \simeq R$ (nuclear radius) ,but the highest value of $R\left({}^{208}Pb\right) \simeq 7\,fm.$ As a result , $kr \simeq \frac{1}{20}\,fm^{-1}.7\,fm \simeq \frac{1}{3} < 1.$ The spherical Bessel function (refer to equation 11.40) thus converges very fast and we may approximate it by just retaining the first term alone. This yields

$$j_\lambda(kr) \simeq \frac{(kr)^\lambda}{(2\lambda+1)!!}$$

which means $j_\lambda(kr) \propto (kr)^\lambda$. Physically , the observation that wavelength λ of γ energies $E_\gamma \lesssim 10MeV$ is $\frac{2\pi\hbar c}{E_\gamma} \gtrsim \frac{2\pi \times 200MeV\ fm}{10MeV} \gtrsim 120\ fm$. This is very large in comparison to nuclear dimension /radius. This is the reason of calling it long wavelength limit of radiation.

Applying the Fermi Golden Rule to calculate the transition probability for multipole 2^λ radiation from initial nuclear state $\left|J_i M_i \zeta\right\rangle$ to final nuclear state $\left|J_f M_f \xi\right\rangle$.

$$\begin{aligned} W\ \left(\lambda; J_i\zeta \to J_f\xi\right) &= \frac{2\pi}{\hbar}\left|\left\langle J_i, \zeta\right| H' \left| J_f, \xi\right\rangle\right|^2 \rho\left(E_f\right) \\ &= \frac{8\pi(\lambda+1)}{\lambda\left[(2\lambda+1)!!\right]^2} \cdot \frac{k^{2\lambda+1}}{\hbar} B\left(\lambda\ ; J_i\zeta \to J_f\xi\right) \end{aligned} \tag{11.41}$$

where $B\left(\lambda\ ; J_i\zeta \to J_f\xi\right)$ is the reduced transition probability .The reader should note that the reduced transition probabilities are dimensional physical quantities. For electric 2^λ pole transitions, $B(E\text{-}\lambda)$ are measured in $e^2 fm^{2\lambda}$ units and for magnetic 2^λ pole transitions, $B(M\text{-}\lambda)$ are measured in $\mu_N^2 fm^{(2\lambda-2)}$ units. The transition probability W is the number of decays per unit time. The expressions for transition probabilities are

$$W\ (E\text{-}\lambda) = \alpha\hbar c \frac{8\pi(\lambda+1)}{\lambda\left[(2\lambda+1)!!\right]^2} \frac{1}{\hbar}\left(\frac{1}{\hbar c}\right)^{2\lambda+1} E_\gamma^{2\lambda+1}[MeV]\, B(E\text{-}\lambda)\left[e^2 fm^{2\lambda}\right] \tag{11.42}$$

$$W\ (M\text{-}\lambda) = \alpha\hbar c\left(\frac{\hbar}{2M_p c}\right)^2 \frac{8\pi(\lambda+1)}{\lambda\left[(2\lambda+1)!!\right]^2} \frac{1}{\hbar}\left(\frac{1}{\hbar c}\right)^{2\lambda+1} E_\gamma^{2\lambda+1}[MeV]\, B(M\text{-}\lambda)\left[\mu_N^2 fm^{(2\lambda-2)}\right] \tag{11.43}$$

Table 11.1

Electromagnetic transition probabilities for the lowest four multipoles.

$W\ (E1) = 1.59\times10^{15}\, E_\gamma^3 B(E1)$	$W\ (M1) = 1.76\times10^{13}\, E_\gamma^3 B(M1)$
$W\ (E2) = 1.23\times10^{9}\, E_\gamma^5 B(E2)$	$W\ (M2) = 1.35\times10^{7}\, E_\gamma^5 B(M2)$
$W\ (E3) = 5.71\times10^{2}\, E_\gamma^7 B(E3)$	$W\ (M3) = 6.31\times10^{0}\, E_\gamma^7 B(M3)$
$W\ (E4) = 1.70\times10^{-4}\, E_\gamma^9 B(E4)$	$W\ (M4) = 1.88\times10^{-6}\, E_\gamma^9 B(M4)$

$E_\gamma\,[MeV]\,, B(E\text{-}\lambda)$ in $\left[e^2\, fm^{2\lambda}\right]$ and $B(M\text{-}\lambda)$ in $\left[\mu_N^2\, fm^{(2\lambda-2)}\right]$

11.3 Weisskopf Single Particle Estimates for Transition-Probabilities

We can enumerate the motivation for having reasonable estimates for transition probabilities between initial and final nuclear states:

1. We can simplify the tedious and lengthy calculations by making a few reasonable assumptions and approximations.
2. We can make an estimate of sizes of $B(E\text{-}\lambda)$ and $B(M\text{-}\lambda)$ that are expected on the average. $W\ (E\text{-}\lambda)$ and $W\ (M\text{-}\lambda)$ are dominated by energy dependent factor $k^{2\lambda+1}$ but $B(E\text{-}\lambda)$ and $B(M\text{-}\lambda)$ are intimately linked with transition matrix element.
3. These estimates provide the basis with which observed transition rates can be compared with theoretical estimates.

$E\text{-}\lambda$ Transitions:

The average of r^λ is

$$\left\langle r^\lambda \right\rangle = \frac{3}{\lambda+3} r^\lambda\, A^{\left(\frac{\lambda}{3}\right)} \tag{11.44}$$

where $r_0 = 1.2\, fm$.

The estimate for reduced transition probabilities $B(E\text{-}\lambda)$ is taken as

$$B_{est}\left(E\text{-}\lambda\right)=\frac{1}{4\pi}e^{2}\left\langle r^{\lambda}\right\rangle^{2} \tag{11.45}$$

Using eq.(11.44) and (11.45) we obtain Weisskopf Single Particle estimate for electric 2^{λ} pole transition probability is expressed as

$$B_{W}\left(E\text{-}\lambda\right)=\frac{1}{4\pi}\left(\frac{3}{\lambda+3}\right)^{2}(1.2)^{2\lambda}A^{2\lambda/3}\left[e^{2}\,fm^{2\lambda}\right] \tag{11.46}$$

M–λ Transitions:

The average of $r^{(\lambda-1)}$ may be taken to be

$$\left\langle r^{(\lambda-1)}\right\rangle=\frac{3}{\lambda+3}r_{0}^{\lambda-1}A^{\left(\frac{\lambda-1}{3}\right)} \tag{11.47}$$

The factors related to gyromagnetic ratios can be reasonably averaged to

$$\lambda\left(2\lambda+1\right)\left(g_{s}-\frac{2g_{l}}{\lambda+1}\right)^{2}\simeq 10 \tag{11.48}$$

The Weisskopf Single Particle estimate for magnetic 2^{λ} pole transition probability is expressed as

$$B_{W}\left(M\text{-}\lambda\right)=\frac{10}{\pi}\left(\frac{3}{\lambda+3}\right)^{2}(1.2)^{(2\lambda-2)}A^{(2\lambda-2)/3}\left[\mu_{N}^{2}\,fm^{(2\lambda-2)}\right] \tag{11.49}$$

The results of (11.46) and (11.49) may be substituted into (11.41),(11.42),(11.43) to produce the Weisskopf units for transition probability

$$W_{W}\left(E\text{-}\lambda\right)=\alpha\hbar c\frac{8\pi\left(\lambda+1\right)}{\lambda\left[(2\lambda+1)!!\right]^{2}}\frac{1}{\hbar}\left(\frac{1}{\hbar c}\right)^{2\lambda+1}\frac{1}{4\pi}\left(\frac{3}{\lambda+3}\right)^{2}E_{\gamma}^{2\lambda+1}\left[MeV\right]$$
$$\cdot(1.2)^{2\lambda}A^{2\lambda/3}\left[e^{2}\,fm^{2\lambda}\right] \tag{11.50}$$

$$W_{W}\left(M\text{-}\lambda\right)=\alpha\hbar c\left(\frac{\hbar}{2M_{p}c}\right)^{2}\frac{8\pi\left(\lambda+1\right)}{\lambda\left[(2\lambda+1)!!\right]^{2}}\frac{1}{\hbar}\left(\frac{1}{\hbar c}\right)^{2\lambda+1}E_{\gamma}^{2\lambda+1}\left[MeV\right]\frac{10}{\pi}\left(\frac{3}{\lambda+3}\right)^{2}$$
$$\cdot(1.2)^{(2\lambda-2)}A^{(2\lambda-2)/3}\left[\mu_{N}^{2}\,fm^{(2\lambda-2)}\right] \tag{11.51}$$

The explicit values in terms of nucleon number /mass number A and transition energy $E_{\gamma}(MeV)$ are listed in table 11.2.

Table11.2

Weisskopf Single Particle Estimates for $(E\text{-}\lambda)$ and $(M\text{-}\lambda)$ transition probabilities and widths.

Multipole λ	$(E\text{-}\lambda)$	$(M\text{-}\lambda)$
1	$W\ (s^{-1}) = 1.02\times10^{14}\ A^{2/3}E_\gamma^3$ $\Gamma(MeV) = 6.75\times10^{-8}\ A^{2/3}E_\gamma^3$	$W\ (s^{-1}) = 3.15\times10^{13}\ E_\gamma^3$ $\Gamma(MeV) = 2.07\times10^{-8}\ E_\gamma^3$
2	$W\ (s^{-1}) = 7.28\times10^{7}\ A^{4/3}E_\gamma^5$ $\Gamma(MeV) = 4.79\times10^{-14}\ A^{4/3}E_\gamma^5$	$W\ (s^{-1}) = 2.24\times10^{7}\ A^{2/3}E_\gamma^5$ $\Gamma(MeV) = 1.47\times10^{-14}\ A^{2/3}E_\gamma^5$
3	$W\ (s^{-1}) = 3.39\times10\ A^{2}E_\gamma^7$ $\Gamma(MeV) = 2.23\times10^{-20}\ A^{2}E_\gamma^7$	$W\ (s^{-1}) = 1.04\times10\ \ A^{4/3}E_\gamma^7$ $\Gamma(MeV) = 6.85\times10^{-21}\ A^{4/3}E_\gamma^7$
4	$W\ (s^{-1}) = 1.07\times10^{-5}\ A^{8/3}E_\gamma^9$ $\Gamma(MeV) = 7.02\times10^{-27}\ A^{8/3}E_\gamma^9$	$W\ (s^{-1}) = 3.27\times10^{-6}\ A^{2}E_\gamma^9$ $\Gamma(MeV) = 2.16\times10^{-27}\ A^{2}E_\gamma^9$
5	$W\ (s^{-1}) = 2.40\times10^{-12}\ A^{10/3}E_\gamma^{11}$ $\Gamma(MeV) = 1.58\times10^{-33}\ A^{10/3}E_\gamma^{11}$	$W\ (s^{-1}) = 7.36\times10^{-13}\ A^{8/3}E_\gamma^{11}$ $\Gamma(MeV) = 4.84\times10^{-34}\ A^{8/3}E_\gamma^{11}$

In terms of Weisskopf units, the measured reduced rates have been observed to vary several orders of magnitude in different nuclei and sometimes even for the transitions within the same nucleus. This enhancement of a transition with respect to the single particle Weisskopf estimates indicates the collective motion of a several nucleons in a coherent manner .This will produce nuclear vibrations and rotations.

11.4 Selection Rules and Parity

If for a transition of certain multipolarity λ, the transition element vanishes then the transition is called “forbidden”. If , on the otherhand ,for a transition of certain multipolarity λ, the transition element does not vanish ,then the transition is called “allowed” .This criterion yields *selection rules*.

Let us consider the transitions of multipolarities λ and $\lambda' = \lambda + 1$ of E and M types .The ratios

$$R(E\text{-}\lambda) = \frac{W_W(E\text{-}\lambda+1)}{W_W(E\text{-}\lambda)}$$

and $$R(M\text{-}\lambda) = \frac{W_W(M\text{-}\lambda+1)}{W_W(M\text{-}\lambda)}$$

can be estimated approximately using (11.50) and (11.51). The ratios $\tilde{R}(M\text{-}\lambda, E\text{-}\lambda)$ also.

We obtain *k* for $1MeV\ \gamma$ ray to be $\frac{1}{200}\,fm^{-1}$ and taking *r* to measure up to 1fm .

We get $R(E\text{-}\lambda) \approx (kr)^2 \simeq \left(\frac{1}{200}\right)^2 \simeq 3\times10^{-5}$

and $R(M\text{-}\lambda) \simeq 3\times10^{-5}$ (11.52)

The factor $\left(\frac{\hbar}{2M_Pc}\right)^2$ is approximated to be (taking $\hbar c \simeq 200MeV\ fm$ and $M_pc^2 \simeq 940MeV$)

$$\left(\frac{\hbar}{2M_Pc}\right)^2 = \left(\frac{200}{2\times940}\right)^2 \simeq \left(\frac{1}{10}\right)^2 \simeq 10^{-2}$$

This leads to

$$\tilde{R}(M\text{-}\lambda, E\text{-}\lambda) \simeq \left(\frac{\hbar}{2M_pc}\right)^2 \simeq 10^{-2} \qquad (11.53)$$

Transition between initial $\left(J_i^{\pi_i}\right)$ and final nuclear state $\left(J_f^{\pi_f}\right)$ is usually dominated by the lowest order process allowed by angular momentum and parity selection rules because of the large reduction in probability with increasing multipolarity order λ. The angular momentum carried by γ photon is $\lambda\hbar$ for transition of λ order.

The law of conservation of total angular momentum gives an additional vectorial relation between $\vec{J}_i, \vec{J}_f$ and $\vec{\lambda}$. Here $\vec{\lambda}$ is the angular momentum carried by the 2^λ -pole radiation ,and a relation between their z components m_i, m_f and μ.

The transition amplitude vanishes unless

$$\vec{J}_i = \vec{J}_f + \vec{\lambda} \text{ and } m_i = m_f + \mu \tag{11.54}$$

The equation further signifies

$$\left|J_i - J_f\right| \le \lambda \le J_i + J_f \tag{11.55}$$

If $J_i = 0, J_f = 0$ then $0 \to 0$ transition is absolutely forbidden.

The parity of multipole radiation is specified by the parity of the magnetic field $\vec{H}_{\lambda\mu}(E\text{-}\lambda)$ and $\vec{H}_{\lambda\mu}(M\text{-}\lambda)$ which are $(-1)^\lambda$ and $-(-1)^\lambda$. We have chosen this because the parity of the perturbing Hamiltonian H' (refer to eq.11.24) has the parity of the $\vec{H}$ field. The parity of current density $\vec{j}$ is negative and the parity of $\vec{A}$ is opposite to that of $\vec{H}$.

Now consider a nuclear transition from initial state $|i\rangle$ to final state $|f\rangle$ with π_i and π_f parities. The conservation of parities demand the relation between initial and final states parities as following

$$\pi_i = \pi_f (-1)^\lambda \quad \text{for } (E\text{-}\lambda) \text{ radiation}$$

and $$\pi_i = \pi_f (-1)^{\lambda+1} \quad \text{for} (M\text{-}\lambda) \text{ radiation} \tag{11.56}$$

11.5 Internal Conversion and Pair Production

When an excited nucleus makes a transition from one level to another by emission of γ photon (electromagnetic radiation) when it is isolated and deprived of all its atomic electrons. The presence of orbital electrons makes possible a different process:

The excited nucleus loses excitation and transfers it to one of the electron of K or L or M shell. This process is called conversion electrons.

The another competing process of emission of γ radiation can be compared for a given transition from an excited state.

The ratio of average number of conversion electrons and average number of γ photons is called conversion coefficient .

$$\alpha = \frac{N_e}{N_\gamma} \tag{11.57}$$

The partial conversion coefficient α_K , α_L ,...are ratios for K,L,.. electrons ejection respectively.

$$\alpha = \alpha_K + \alpha_L + \alpha_M + ...$$

The energy of conversion of electron from K shell is given as

$$E_K^{CE} = E_i - E_f - b_Z^h(K) \tag{11.58}$$

The conversion electron spectrum is discrete and not continuous such as in β^- decay where it is continuous and broad peaked.

If energy of nuclear excitation is greater than $2m_ec^2$, then pair production may occur .

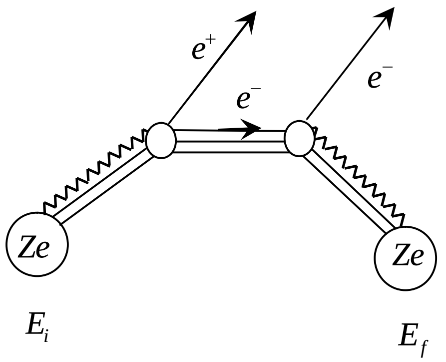


Figure11.1: *Pair production in the presence of a heavy nucleus Ze*

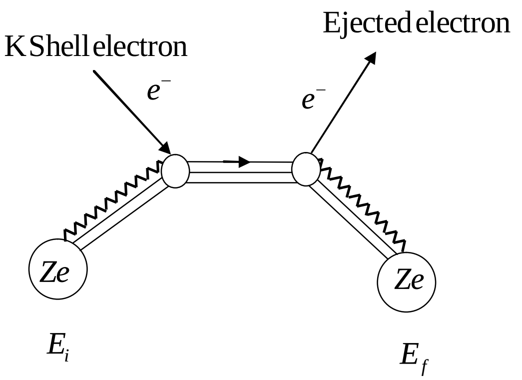


Figure 11.2 : *Internal conversion of an orbital electron due to electromagnetic interaction with a nucleus.*

Nuclear Isomerism

Some time a nucleus releases energy decaying into lower state with a life time of the order of 100ms to several years. The nucleus may then β decays into a new nucleus . These states of longer lifetime are called isomer states. This phenomenon is called nuclear isomerism .The isomer levels are shown in figure 11.3.

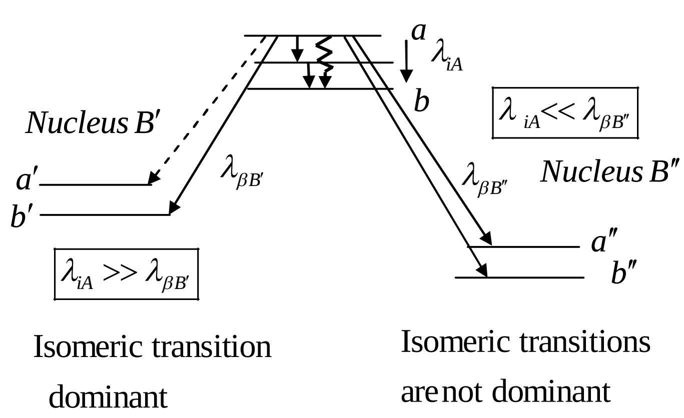


Figure :11.3

The schematic diagram explaining two types of nuclear isomers through β decay into daughter nuclei B' and B'' of a parent nucleus A.

11.6 Self Learning Exercise

Q.1 Write multipole expansion of electromagnetic field in presence of the sources of radiation.

Q.2 Write the expression for the Weisskopf single particle estimates of the transition probability for the multipole radiation of order λ. Discuss the result.

11.7 Summary

- For a vector field corresponding to one photon of energy $\hbar\omega$ in the system volume V ,the amplitude of the electromagnetic vector potential is

$$\left|\vec{A}_0\right| = \sqrt{\frac{8\pi\hbar\omega}{k^2 V}} = \sqrt{\frac{8\pi\hbar c^2}{\omega V}}$$

- The total energy of this field integrated over the volume V is given by

$$\hat{H} = \sum_{k,\mu} \hbar\omega_k \left(\beta^{\dagger}_{k\mu}\hat{\beta}_{k\mu} + \frac{1}{2}\right)$$ and the total momentum is $$\hat{p} = \sum_{k,\mu} \hbar\vec{k}\beta^{\dagger}_{k\mu}\hat{\beta}_{k\mu}$$

- $\vec{A}_{\lambda\mu}(E\text{-}\lambda,\vec{r})$ and $\vec{A}_{\lambda\mu}(M\text{-}\lambda,\vec{r})$ are solutions of Helmholtz equation

$$\left(\nabla^2 + k^2\right)\vec{A}_{\lambda\mu}(G\text{-}\lambda,\vec{r}) = 0$$ where $G = E, M$

Magnetic 2^{λ} pole radiations	Electric 2^{λ} pole radiations
$\left(\nabla^2+k^2\right)\vec{E}(M\text{-}\lambda,\vec{r})=0$, $\vec{\nabla}.\vec{E}(M\text{-}\lambda,\vec{r})=0$ $\vec{H}(E\text{-}\lambda,\vec{r})=-\frac{i}{k}\sqrt{\frac{\varepsilon}{\mu}}\ \vec{\nabla}\times\vec{E}(M\text{-}\lambda,\vec{r})$ $\vec{r}.\vec{E}=0$	$\left(\nabla^2+k^2\right)\vec{H}(M\text{-}\lambda,\vec{r})=0$ $\vec{\nabla}.\vec{H}(E\text{-}\lambda,\vec{r})=0$ $\vec{E}(M\text{-}\lambda,\vec{r})=\frac{i}{k}\sqrt{\frac{\mu}{\varepsilon}}\ \vec{\nabla}\times\vec{H}(E\text{-}\lambda,\vec{r})$ $\vec{r}.\vec{H}=0$

- The expressions for transition probabilities are

$$W\ (E\text{-}\lambda)=\alpha\hbar c\frac{8\pi(\lambda+1)}{\lambda\left[(2\lambda+1)!!\right]^2}\frac{1}{\hbar}\left(\frac{1}{\hbar c}\right)^{2\lambda+1}E_{\gamma}^{2\lambda+1}[MeV]\,B(E\text{-}\lambda)\left[e^2\,fm^{2\lambda}\right]$$

$$W\ (M\text{-}\lambda)=\alpha\hbar c\left(\frac{\hbar}{2M_p c}\right)^2\frac{8\pi(\lambda+1)}{\lambda\left[(2\lambda+1)!!\right]^2}\frac{1}{\hbar}\left(\frac{1}{\hbar c}\right)^{2\lambda+1}E_{\gamma}^{2\lambda+1}[MeV]B(M\text{-}\lambda)\left[\mu_N^2\,fm^{(2\lambda-2)}\right]$$

- The transition amplitude vanishes unless

  $\vec{J}_i=\vec{J}_f+\vec{\lambda}$ and $m_i=m_f+\mu$

  If $J_i=0, J_f=0$ then $0\to 0$ transition is absolutely forbidden.

  The relation between initial and final states parities as following

  $\pi_i=\pi_f(-1)^{\lambda}$ for $(E\text{-}\lambda)$ radiation and

  $\pi_i=\pi_f(-1)^{\lambda+1}$ for $(M\text{-}\lambda)$ radiation

- The excited nucleus loses excitation and transfers it to one of the electron of K or L or M shell. This process is called conversion electrons.

11.8 Glossary

Coulomb Gauge : The vector field fulfils the gauge condition $\vec{\nabla}.\vec{A}=0$

$\boldsymbol{j_{\lambda}(kr)}$**:** spherical Bessel function of order λ

$\boldsymbol{Y_{\lambda\mu}(\theta,\phi)}$ **:** spherical harmonics of ranks (λ,μ)

11.9 Exercise

Q.1 Define transition probability for emission of a multipole radiation of order

(λ,μ) by a nucleus .Discuss briefly spin and parity selection rules for these transitions .

Q.2 For transitions between low lying states of nuclei (using long wavelength approximation) show that $\left(\frac{\hbar}{M_p cR}\right) \approx \frac{v}{c}$

Q.3 Write short note on

(i) Internal conversion of electrons

(ii) Parity and selection rules for emission of multipole radiations in nuclei.

(iii) $0 \rightarrow 0$ Transitions in nuclei.

Q.4 When the transition probability is larger than the Weisskopf estimates of the single particle transition probability for multipole radiation of order λ,for a nucleus what are the possible reasons ?

Q.5 What are the conventional units of reduced transition probabilities $B\left(E-\lambda\,;\,J_i\zeta \rightarrow J_f\xi\right)$ and $B\left(M-\lambda\,;\,J_i\zeta \rightarrow J_f\xi\right)$? Show that the difference of dimensions between these units by analyzing the units dimensionally .

Q.6 Calculate ratios

$$R_E = \frac{W_W\left(E-\lambda+1\right)}{W_W\left(E-\lambda\right)}, \quad R_M = \frac{W_W\left(M-\lambda+1\right)}{W_W\left(M-\lambda\right)} \quad \text{and} \quad \tilde{R}_{ME} = \frac{W_W\left(M-\lambda\right)}{W_W\left(E-\lambda\right)}$$

by making approximations .The symbols have their usual meaning.

References and Suggested Readings

1. Nuclei and Particles by Emilio Segre
2. Nuclear Physics by R.R. Roy and B.P. Nigam
3. Introductory Nuclear Physics by Samuel S.M. Wong
4. Elements of Nuclear Physics by W.E. Burcham
5. Theoretical Nuclear Physics by John M. Blatt &Victor F. Weisskopf.
6. Nuclear Physics by S.N. Ghosal
7. Nuclear Models by Walter Greiner & Joachein A. Mahrun
8. Introductory Nuclear Physics by Kenneth S. Krane

UNIT-12
Sommerfeld Theory of Hydrogen Atom

Structure of the Unit

12.0 Objectives

Bohr was able to calculate the radii as well energies of the stationary orbit around the nucleus in an atom and those calculated values were found to be in a good agreement with the experimental values. He also gave the Hydrogen ion spectrum. For these reasons, his theory was widely accepted throughout the world. But a few years later, the use of high resolving power spectrometer revealed fine structure of the hydrogen spectral lines which couldn't explained by Bohr's model .To explain hydrogen fine structure ,Sommerfeld extended Bohr Theory .In this chapter we will study about Bohr- Sommerfeld theory.

12.1 Introduction

In 1916,Sommerfeld, in an attempt to explain the fine structure of hydrogen atom, extended Bohr's model by considering that the electron could revolve in elliptic orbits also, apart from Bohr's circular orbits. He estimated the size and shape of the possible elliptic orbit and the total energy of an electron revolving in such orbit. According to Sommerfeld, the stationary orbits in which electrons are revolving around the nucleus in the atom are not circular but elliptical in shape. It is due to the influence of the centrally located nucleus. The electron revolves in elliptical path with nucleus at one of its foci. So there will be a major and a minor axis of the path. He said that with the broadening of the orbit, the lengths of the two axes approach to equal value and ultimately become equal i.e. the path become circular. So we can say that the circular path is just one special case elliptical path.

12.2 Sommerfeld's Elliptic Orbits

Let us consider an electron mass (m), and charge (-e) is revolving around nucleus (charge +Ze) in an elliptic orbit(Fig.1), where a and b are the semi-major and semi-minor axes of ellipse respectively.

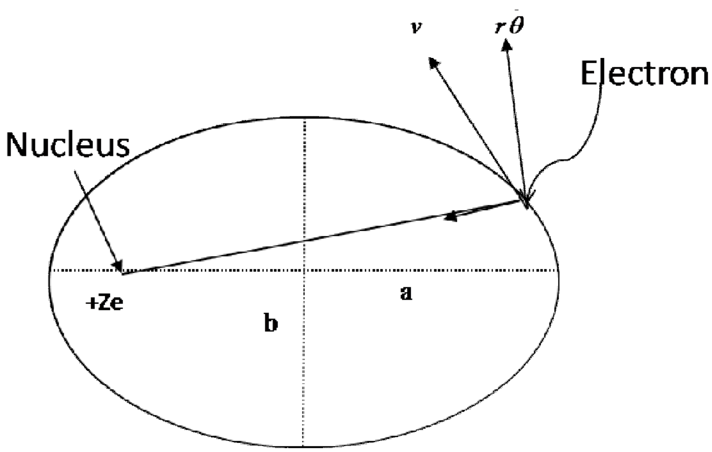


Figure 1. A*n electron of mass (m), and charge (-e) is revolving around nucleus (charge +Ze) in an elliptic orbit.*

The r and θ are the polar coordinates of electron at instantaneous position. It should be periodic functions of time, must be quantized separately,where the p and j are the radial and angular momentum of the electron respectively.

Then according to Wilson –Sommerfeld quantization rules, we know

$$\oint p dr = n_r h \tag{1}$$

and $\int_0^{2\pi} j\, d\theta = lh$ (2)

where n_r and l are integers, known as radial and azimuthal quantum numbers respectively.

In second integral, according to classical mechanics, the angular momentum **j** of any isolated system is constant. Thus,

$$j \int_0^{2\pi} d\theta = lh$$

or $$j = \frac{lh}{2\pi} \tag{3}$$

This condition of the orbital angular momentum is similar to Bohr model.

To solve the first integral,

$$p = m\dot{r} \tag{4}$$

and $$j = mr^2\dot{\theta}, \tag{5}$$

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

The polar equation of the ellipse

$$\frac{1}{r} = \frac{1}{a}\frac{1-\varepsilon\cos\theta}{1-\varepsilon^2} \tag{6}$$

where $\sqrt{1-\varepsilon^2} = \frac{b}{a}$

Taking differentiation of r with respect to θ, we get

$$-\frac{1}{r^2}\frac{dr}{d\theta} = \frac{1}{a}\frac{\varepsilon\sin\theta}{1-\varepsilon^2} \tag{6.a}$$

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

Using equation (6)

$$\frac{1}{r}\frac{dr}{d\theta} = -\frac{\varepsilon\sin\theta}{1-\varepsilon\cos\theta}$$

By squaring the both sides of above equation, we get

$$\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 = \frac{\varepsilon^2\sin^2\theta}{(1-\varepsilon\cos\theta)^2} \tag{7}$$

Now, $p = m\dot{r} = m\frac{dr}{dt} = m\frac{dr}{d\theta}\frac{d\theta}{dt} = m\frac{dr}{d\theta}\dot{\theta}$

Using equation (5),we have $p = \frac{j}{r^2}\frac{dr}{d\theta}$ (8)

We can write $dr = \frac{dr}{d\theta}d\theta$

$$\therefore \; pdr = j\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 d\theta$$

Using equation (7), we get

$$pdr = j\frac{\varepsilon^2 \sin^2\theta\, d\theta}{(1-\varepsilon\cos\theta)^2}$$

Hence the integral in equation (1) becomes

$$j\int_0^{2\pi}\frac{\varepsilon^2\sin^2\theta\, d\theta}{(1-\varepsilon\cos\theta)^2} = n_r h \tag{9}$$

Solution of this integration is

$$\int_0^{2\pi}\frac{\varepsilon^2\sin^2\theta\, d\theta}{(1-\varepsilon\cos\theta)^2} = 2\pi\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right) \tag{10}$$

Using eq.(10) in eq.(9),we get

$$2\pi j\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right) = n_r h$$

From eq.(3) put value of j

$$lh\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right) = n_r h$$

or $\frac{1}{\sqrt{1-\varepsilon^2}} - 1 = \frac{h}{l}$

or $\sqrt{1-\varepsilon^2} = \frac{l}{n_r+l}$

But we know from property of ellipse

$$\sqrt{1-\varepsilon^2} = \frac{b}{a} \therefore \frac{b}{a} = \frac{l}{n_r+l} \tag{11}$$

where n_r and l are integers,

$$n_r + l = n,$$

We can write

$$\sqrt{1-\varepsilon^2} = \frac{l}{n} \tag{11.a}$$

So $\frac{b}{a} = \frac{l}{n}$ (12)

This is quantum condition for elliptic orbits.

Here n is principal or total quantum number. When *n* = *l*, *b* = *a* and ε = 0, the orbit becomes circular. *l* cannot be zero, since the ellipse would then degenerate into a straight line passing through the nucleus. Also *l* cannot be greater than *n*, since *b* is always less than *a*. Hence for a given value of *n*, quantum number *l* can take only *n* different values, which means that there can be only *n* elliptical orbits of different eccentricities.

Total energy of an electron in an elliptical orbit

Let us now calculate total energy of an electron in elliptic orbit. It will be sum of the kinetic energy K and the potential energy U. Then total energy of an electron will be

$$E = K + U \tag{13}$$

The kinetic energy of an electron $K = m\left(\dot{r}^2 + r^2\dot{\theta}^2\right)$

using eq.(4) and (5),we get

$$K = \frac{1}{2m}\left(p^2 + \frac{j^2}{r^2}\right)$$

The potential energy of an electron $U = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$

Putting the values of K and U in equ.(13), we have

$$E = \frac{1}{2m}\left(p^2 + \frac{j^2}{r^2}\right) - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \tag{14}$$

Using eq.(8)

$$E = \frac{j^2}{2mr^2}\left[\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 + 1\right] - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

or $$\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 = \frac{2mEr^2}{j^2} + \frac{mZe^2r}{2\pi\varepsilon_0 j^2} - 1 \tag{15}$$

From eq.(6.a)

$$\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2 = \frac{1}{a^2}\frac{r^2\varepsilon^2\sin^2\theta}{(1-\varepsilon^2)^2} = \frac{\varepsilon^2 r^2\,(1-\cos^2\theta)}{[a(1-\varepsilon^2)]^2}$$

$$\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2 = \frac{r^2\,(\varepsilon^2 - \varepsilon^2\cos^2\theta)}{[a(1-\varepsilon^2)]^2} \tag{16}$$

Using eq.(6)

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

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

Squaring both sides of equation, we get

$$(\varepsilon\cos\theta)^2 = \left(1-\frac{a}{r}(1-\varepsilon^2)\right)^2 \tag{17}$$

Putting the value of eq.(17) in eq.(16)

$$\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2 = \left[\frac{r}{a(1-\varepsilon^2)^2}\right]^2 \left[\varepsilon^2 - \left\{1-\frac{a}{r}(1-\varepsilon^2)\right\}^2\right]$$

$$= \frac{r^2}{a^2(1-\varepsilon^2)^2}\left[\varepsilon^2 - \left\{1+\frac{a^2}{r^2}(1-\varepsilon^2)^2 - \frac{2a(1-\varepsilon^2)}{r}\right\}\right]$$

$$= \left[\frac{r^2\varepsilon^2}{a^2(1-\varepsilon^2)^2} - \frac{r^2}{r^2(1-\varepsilon^2)^2} + \frac{2r}{a(1-\varepsilon^2)} - 1\right]$$

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

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

$$= -\frac{r^2}{a^2(1-\varepsilon^2)} + \frac{2r}{a(1-\varepsilon^2)} - 1 \tag{18}$$

Comparing the coefficient of r^2 and r from equations (15) and (18), we get

$$\frac{2mE}{j^2} = -\frac{1}{a^2(1-\varepsilon^2)} \tag{19}$$

and
$$\frac{mZe^2}{2\pi\varepsilon_0 j^2} = \frac{2}{a(1-\varepsilon^2)} \tag{20}$$

From equation (19)

$$E = -\frac{j^2}{2ma^2(1-\varepsilon^2)} \tag{21}$$

Putting the value of $(1-\varepsilon^2)$ into equation (21) from equation (20),we get

$$E = -\frac{j^2}{2ma^2}\left[\frac{amZe^2}{4\pi\varepsilon_0 j^2}\right]$$

$$E = -\frac{Ze^2}{8\pi a\varepsilon_0} \tag{22}$$

Again substituting for a from equation (20),we get

$$E = -\left(\frac{Ze^2}{8\pi\varepsilon_0}\right)\left(\frac{mZe^2}{2\pi\varepsilon_0 j^2}\right)\left(\frac{1-\varepsilon^2}{2}\right)$$

$$E = -\left[\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2}\right]\frac{(1-\varepsilon^2)}{j^2}$$

Putting the value of $(1-\varepsilon^2)$ and j from eq.(3) and (11.a) respectively, we get

$$E = -\left[\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2}\right]\left[\frac{l^2}{n^2}\right]\left[\frac{4\pi^2}{l^2h^2}\right]$$

$$E = -\frac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2} \tag{23}$$

This equation shows the energy of an electron in elliptical orbit which is exactly the same as for the Bohr's circular orbit. The energy of electron still independent on the azimuthal quantum number l. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition. Hence Sommerfeld's attempt to explain the fine structure of spectral lines failed.

Size and Shape of Sommerfeld's Orbits:

From equation (22),we have

$$a = -\frac{Ze^2}{8\pi E\varepsilon_0}$$

From equation (23) substituting the value of E, we get

$$a = \frac{n^2h^2\varepsilon_0}{\pi mZe^2} \tag{24}$$

$$a = \frac{n^2 r_b}{Z} \tag{25}$$

where $r_b = \frac{h^2\varepsilon_0}{\pi me^2} = 0.0529\ nm$ (Bohr radius)

Again using equation (12)

$$b = \frac{al}{n}$$

Substituting value of a from equation (25), we get

$$b = \frac{nl}{z} r_b \tag{26}$$

We can determine the size and shape of Sommerfeld's elliptic orbits from equation (25) and (26).The length of semi-major axis is determined by the principal quantum number n, while the length of the semi-minor axis depends upon the azimuthal quantum number l as well as on n .

For a given value of n, the possible values of l are 0,1,2,3..... n, when we consider $l = 0$,the ellipse reduces to a straight line and the electron then passes through the nucleus traversing the orbit. This leads to the collapse of the atom. Therefore the value of $l = 0$ is forbidden. Thus for given value n, quantum number l can take n different possible values 1,2,3....... n. This means for a given n, there are n orbits of different eccentricities which will be occupied by the electron. Let us consider hydrogen atom (Z=1).

For first orbit $n = 1$, Since $n_r + l = 1$;

$$l \neq 0 \Longrightarrow l = 1$$

Thus with $n = l$ and $n_r = 0$, a=r_b and b=r_b

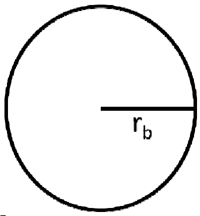


Figure 2 : n=1, *l*=1

This shows circular orbit of radius r_b(Fig.2) which is exactly same as the Bohr's consideration. For $n = 2$, Possible values of l are 1and 2. we get

(1) $l = 2$, then $a = 4r_b$, $b = 4r_b$

(2) $l = 1$, then $a = 4r_b$, $b = 2r_b$

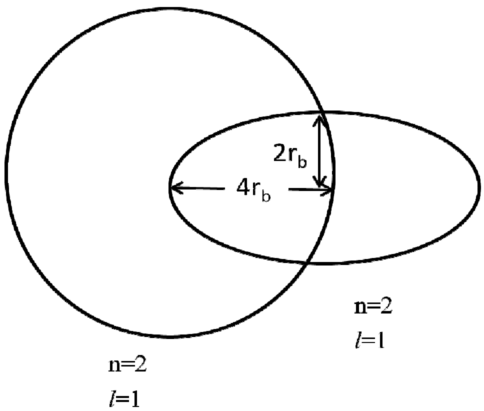


Figure 3.n=1, n=2 orbits.

From above given combination for $n = 2$,we have a Bohr's circular orbit of radius $4r_b$ and an elliptic orbit with semi-major axis $4r_b$ and semi-minor axis $2r_b$(Fig.03). But all these orbits have same energy E given by equation (23).

For $n = 3$,Possible values of l are 1,2 and 3. we get

(1) $l = 3$, then $a = 9r_b$, $b = 9r_b$

(2) $l = 2$, then $a = 9r_b$, $b = 6r_b$

(3) $l = 1$, then $a = 9r_b$, $b = 3r_b$

Thus we find one Bohr's circular orbit of radius $9r_b$, remaining two are elliptic orbits with same semi-major axis $9r_b$ and different semi-minor axes $6r_b$ and $3r_b$ which is shown in below figure(04).These all three orbits have same energy.

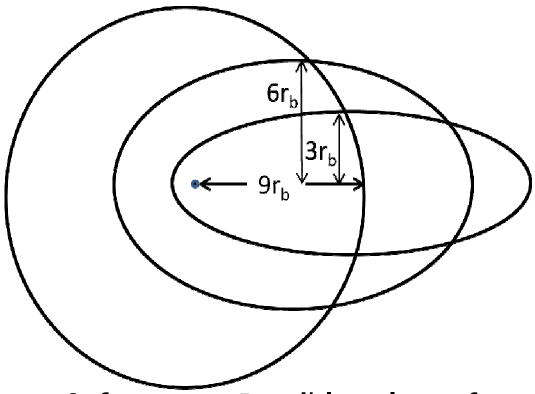


Figure 4: for $n = 3$, Possible values of l are 1,2 and 3.

We can see that for each value of the principal quantum number n, there will be n different allowed orbits. One of these will be circular, which is explained by the original Bohr theory. Other will be elliptic, all having the same semi-major axis, but different semi-minor axes.

The electron is moving in different possible orbits for a given n, but the energy of electron remains same in all orbits associated to n. Thus we conclude that Sommerfeld's introduction of elliptic orbits do not include new energy levels, hence it cannot explain the fine structure. The orbits associated to same energy known as degenerate. To represent the different orbits in another notation corresponding to azimuthal quantum number $l = 1,2,3,4$,etc.. It is described by the letters s,p,d,f etc. respectively. In this notation, the orbit determined by $n = 3$ and $l = 1$ is represented by 3s. Similarly 4f will represent the orbit $n = 4$ and $l = 4$.

12.3 Sommerfeld's Relativistic Correction

An electron has the ratio $v/c \cong 10^{-2}$ or less in innermost orbit of hydrogen atom. Due to this, relativistic correction will arise. In elliptic orbit, the velocity of an electron varies point to point in orbit. It is a maximum at nearest the nucleus and a minimum farther away from the nucleus. According to the theory of relativity, we know that the variation of velocity means variation of mass of the electron.

Taking this effect into account, Sommerfeld calculated the total energy of an electron in an orbit which is characterized by the quantum numbers *n* and ***l*** *as*

$$E = -\frac{m_0 Z^2 e^4}{8\,\varepsilon_0^2 n^2 h^2}\left[1 + \frac{Z^2 \propto^2}{n}\left(\frac{1}{l} - \frac{3}{4n}\right)\right]$$

where $\propto = \frac{e^2}{8\varepsilon_0\, hc} = \frac{1}{137}$ is "fine -structure constant". It is dimensionless quantity and equal to the ratio of the velocity of electron in the first Bohr orbit of hydrogen to the velocity of light c in vacuum.

The above expression may also be written as

$$E = -\frac{R_\infty Z^2 hc}{n^2}\left[1 + \frac{Z^2 \propto^2}{n}\left(\frac{1}{l} - \frac{3}{4n}\right)\right]$$

where $R_\infty = \frac{m_0 e^4}{\varepsilon_0^2 h^3 c} = 1.097 \times 10^7 m^{-1}$ is Rydberg constant for an infinitely heavy nucleus.

The term values of the hydrogen –like atom are

$$T = -\frac{E}{hc} = \frac{R_\infty Z^2}{n^2}\left[1 + \frac{Z^2 \propto^2}{n}\left(\frac{1}{l} - \frac{3}{4n}\right)\right]$$

or $$T = \frac{R_\infty Z^2}{n^2} + \frac{R_\infty Z^4 \propto^2}{n^3}\left(\frac{1}{l} - \frac{3}{4n}\right)$$

The first term is similar to Bohr derivation for circular orbits. The second term is the relativisitic correction ΔT, so we can write

$$\Delta T = \frac{R_\infty Z^4 \propto^2}{n^3}\left(\frac{1}{l} - \frac{3}{4n}\right)$$

Because $R_\infty \propto^2 = 5.84\ cm^{-1}$

So $$\Delta T = \frac{5.84\, Z^4}{n^3}\left(\frac{1}{l} - \frac{3}{4n}\right) cm^{-1} \qquad (27)$$

Finally we can calculate the relativistic shift in the energy levels of various ***l*** values for each Bohr energy level *n* with the help of the last expression.

12.4 Shortcomings of Bohr- Sommerfeld Theory

There are given some shortcomings of Bohr-Sommerfeld theory as following-

(1) Bohr's theory able to calculate the energies of the allowed states of an atom and the frequency of radiation emitted or absorbed in transitions between allowed states. But it is unable to calculate the rate at which such transitions take place and intensity of the spectral lines.

(2) The theory fails for atoms which have more than one electron ,for example neutral helium atom which has only two electrons. It is applicable only to one-electron atoms like hydrogen, hydrogen isotopes, singly-ionized helium etc.

(3) Even it was unable to explain the fine structure of spectral lines in the simplest hydrogen atom.

(4) There were not given proper reason for the introduction of quantum numbers. The quantum numbers were introduced by Bohr as a postulate.

(5) Both the theories could not explain the distribution and arrangement of electrons in atoms.

(6) Both the theories could not explain anomalous Zeeman effect and Stark effect.

12.5 Illustrative Examples

Example1: Calculate the energy shift from Bohr level of an electron in hydrogen atom in state of n=1 quantum number using Sommerfeld's relativistic correction.

Sol. Given principal quantum number n=1, and for hydrogen atom Z=1

Azimuthal quantum number for *n*=1 will be ***l***=1

Energy shift from Bohr level

$$\Delta T = \frac{R_\infty Z^4 \propto^2}{n^3}\left(\frac{1}{l} - \frac{3}{4n}\right),$$

$$\therefore R_\infty \propto^2 = 5.84\ cm^{-1}$$

Then, putting the given values, we get

or $$\Delta T = \frac{5.84\ cm^{-1}}{1}\left(\frac{1}{1} - \frac{3}{4}\right)$$

or $$\Delta T = \frac{5.84\ cm^{-1}}{4}$$

Shift from Bohr level

$$\Delta T = 1.46\ cm^{-1}$$

Example 2: Calculate the ionization energy of hydrogen atom.(h=6.63 x 10^{-34} J.s, e = 1.6 x 10^{-19} C, m = 9.1 x 10^{-31} kg , and ε_0 = 8.85 x 10^{-12} $C^2/N\text{-}m^2$)

Sol. In case of hydrogen atom (Z=1) ionization energy means binding energy the electron to the nucleus, which is equal to the energy of the lowest state corresponding to n=1.

$$E = -\frac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2}$$

Using above equation for ionization potential (n=1,Z=1)

$$E = -\frac{me^4}{8\varepsilon_0^2 h^2}$$

$$= -\frac{(9.11\ X\ 10^{-31}\ kg)(1.60\ X\ 10^{-19}\ C)^4}{8(8.85\ X\ 10^{-12}\frac{C^2}{N-m^2})^2(6.63\ X\ 10^{-34} J\ S)^2}$$

$$= -2.17\ X\ 10^{-18}\ J = -13.6\ eV \qquad \therefore 1\ eV = 1.60\ X\ 10^{-19} J$$

12.6 Self Learning Exercise -I

Q.1 What will be shape of orbit corresponding to principal quantum number n=2 ?

Q.2 Why did Sommerfeld introduce relativistic correction?

12.7 Interpretation of Quantum Numbers for Hydrogen Atoms

We consider a simplest bound system, one-electron atom like hydrogen atom that occurs in nature. It have a positively charged nucleus and negatively charged electron(-e), moving under their coulomb attraction and bound together by the attraction. The state of the electron around the nucleus in terms of its location relative to the nucleus and the energy associated with it is described by a set of quantum numbers. Each electron is characterized by four quantum numbers called the principal (total) quantum number, the azimuthal (orbital) quantum number, the magnetic orbital quantum number and the magnetic spin quantum numbers. Now we want to describe in term of size, shape, orientation of the orbit in space and spin around the nucleus.

(1) The total and principal quantum number(*n*)

This is identical with the one used in Bohr-Sommerfeld's theory. It can take values 1, 2, 3, 4, ..., ∞. This denotes the major axis of the ellipse with which the energy of the electron is associated and hence pertains to the main energy level or shell. These energy levels having values of *n* = 1, 2, 3, 4, etc. These values represented by symbols of shells K, L, M, N, etc.

The energy (E) of different levels is inversely proportional to n^2. That is

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

(2)The orbital quantum number (*l*) –

This quantum number is an integer and for a given value of n, it can take any of the values 0, 1, 2, 3,4, ..., (n – 1). It divides the main shell into n slightly different energy levels of sub shells so that the number of sub shells in main shell is represented by its principal quantum numbers. It means the shell with principal quantum number n=1 or K-shell has only one sub shell represented as s-sub shell (*l*=0).

This quantum number is called the angular momentum quantum number,which represents mechanical angular momentum of the electron. The orbital angular momentum L is written as

$$L = l\frac{h}{2\pi}$$, where *l*=0, 1, 2, 3.....etc.

According to quantum mechanics, the value of orbital angular momentum L is not equal to $l\frac{h}{2\pi}$ but given by

$$L = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$$

The L-shell will have two sub-shells having values *l*=0 and *l*=1. They are represented as *s* and *p* sub-shells. Thus we can find different sub-shells associated to different shells.

(3)Magnetic orbital quantum number (m_l)-

An electron revolves around the nucleus possesses angular momentum interacts with an external magnetic field B. The magnetic quantum number m_l represents the direction of L by determining the component of L in the field direction. This is known as space quantization.

$$L_z = m_l\frac{h}{2\pi}$$

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

The possible values of m_l for given value of l ranges from $+l$ to $-l$. The number of possible orientations of the angular momentum vector L in magnetic field will be $2l + 1$.

For $l = 0$, $L_z = 0$ (only single value)

$$l = 1, \quad L_z = \frac{h}{2\pi}, 0, -\frac{h}{2\pi}$$

Similarly we can find out different $L_z$values associated to different l.

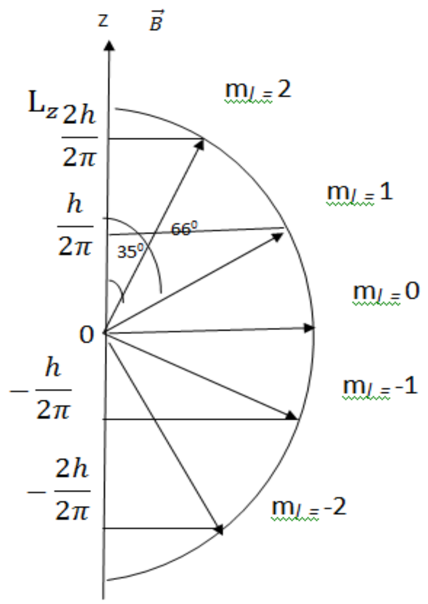


Figure 5:-*Space quantization of orbital angular momentum.*

The magnetic spin quantum number(m_s):-

In 1925 ,two Dutch graduate students, Samuel Goudsmit and George Uhlenbeck, proposed that every electron have an intrinsic angular momentum called spin, whose magnitude is half (1/2).It is same for all electrons and associated with this angular momentum is magnetic moment.

The quantum number *s* describes the spin angular momentum of the electron. It follows both Dirac's theory and from spectral data. The angular momentum S due to electron spin is given in terms of the spin quantum number *s* by

$$\vec{S} = \sqrt{s(s+1)}\frac{h}{2\pi} = \frac{\sqrt{3}}{2}\frac{h}{2\pi}$$

The space quantization of electron spin is described by the spin magnetic quantum number m_s. The spin angular momentum vector can have the 2*s*+1=2 orientations specified by m_s= +1/2 (spin up) and m_s= -1/2 (spin down).

Z-component of spin angular momentum

$$S_z = m_s\frac{h}{2\pi} = \pm\frac{1}{2}\frac{h}{2\pi}$$

12.8 Electron Probability Density

The electron in a hydrogen atom is described by the Schrodinger equation. The time independent Schrödinger equation in spherical polar coordinates (r,θ,Φ) can be solved by separation of variable in the form

$$\Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\,\Phi(\varphi)$$

Quantum mechanically, we cannot consider an electron as moving around the nucleus in definite orbits. It is probabilistic phenomena. In three dimensions, probability density $\Psi^2(r,\theta,\varphi)$ gives the probability per unit volume for the electron to be found in a small volume element at the coordinate (r,θ,Φ).

$$\Psi^2(r,\theta,\varphi) = |R|^2|\Theta|^2|\Phi|^2$$

where $|\Psi|^2 = \Psi\Psi^*$, etc.

The wave function $\Psi(r,\theta,\varphi)$ is symmetrical about the z-axis. So $|\Psi|^2$ depends only $|R|^2$ and $|\Theta|^2$. Firstly we will discuss the dependence of $|\Psi|^2$ on $|R|^2$. For this we define the radial probability density $P(r)$, this is defined so that $P(r)dr$ gives the probability that regardless the direction, electron will be found to the lie between two spheres whose radii are r and $r + dr$, the volume dV between these spheres is $4\pi r^2 dr$. So we can write

$$P(r)dr = \Psi^2(r)dV = \Psi^2(r)4\pi r^2 dr \tag{28}$$

The graph of $P(r)$ against r/r_b, where r_b is Bohr radius ,is given below for values of n and l (state 1s, 2s and 3s for the hydrogen atom (z=1) are shown in Fig.6.

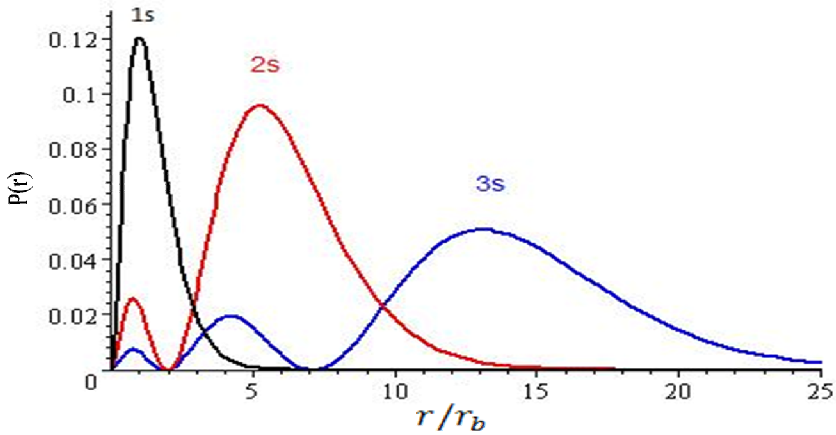


Figure: 6 Graph between P(r)and r/r_b

We can see from fig.6 the electron is most likely to be found at the locations of Bohr orbits. Now we will consider the dependence of $|\Psi|^2$ on $|\Theta|^2$ (directional) which is shown Fig.7 and Fig.8. The form of $|\Theta|^2$ in terms of polar diagram in which the origin is at r = o and the z- axis is taken along the direction from which the angle θ is measured.

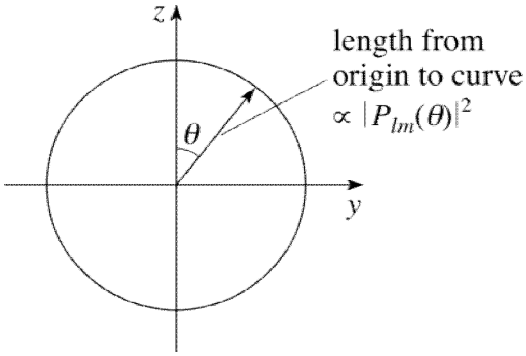


Fig.7 Polar diagram for s-state ***l*** = 0, m_l = 0

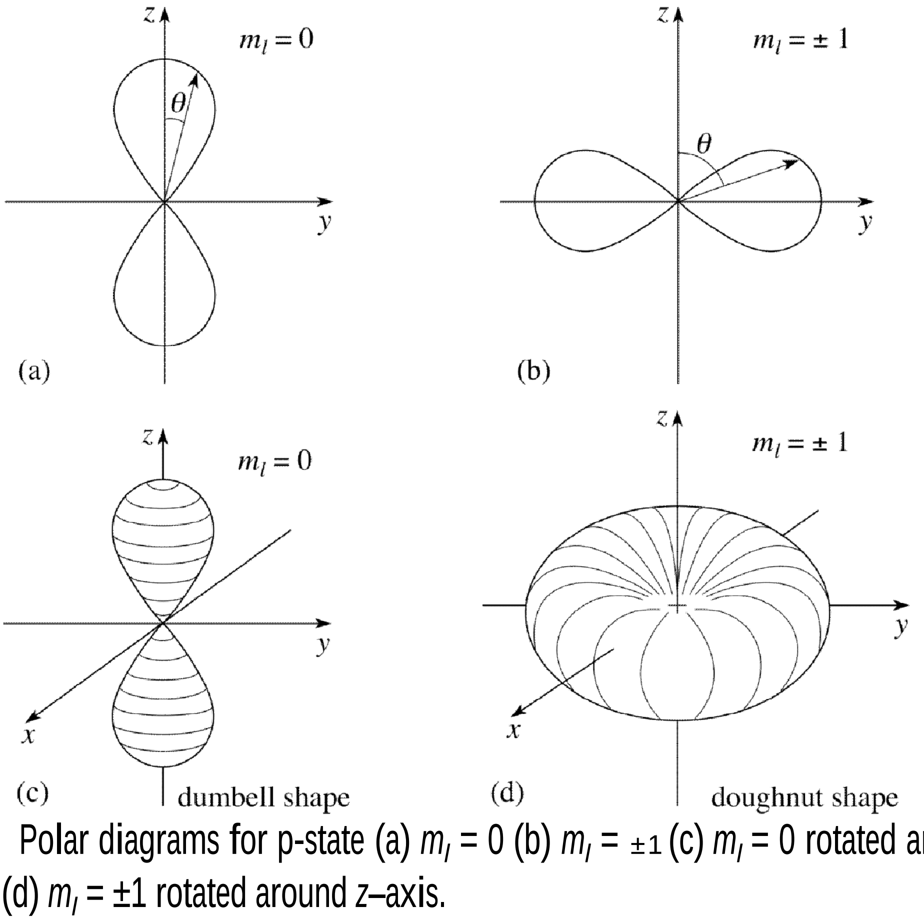


Fig. 8. Polar diagrams for p-state (a) m_l = 0 (b) m_l = ±1 (c) m_l = 0 rotated around *z*–axis, (d) m_l = ±1 rotated around *z*–axis.

From above figures we can say $|\Theta|^2$ is constant for an s-state (l=0) and for other states it varies with θ and takes largest value in definite direction.

12.9 Orbital Angular Momentum

An electron revolves around nucleus in atom which has an orbital angular momentum $\vec{L}$ which have direction along the orbital axis. The angular momentum $\vec{L}$ of a particle bound to and moving around a coordinate origin is defined by the equation

$$\vec{L}=\vec{r}\times\vec{p},$$

where $\vec{r}$ and $\vec{p}$ are a position vector with respect to origin and linear momentum vector respectively. The rectangular components of $\vec{L}$ are

Using cross product,

$$L_x = yp_z - zp_y$$
$$L_y = zp_x - xp_z$$
$$L_z = xp_y - yp_x$$

where x,y,z are the components of $\vec{r}$, and p_x,p_y,p_z are the components of $\vec{p}$.

Using equivalent differential operator for momentum components

$$p_x = -\frac{i}{2}\frac{h}{\pi}\frac{\partial}{\partial x}, p_y = -\frac{i}{2}\frac{h}{\pi}\frac{\partial}{\partial y}, p_z = -\frac{i}{2}\frac{h}{\pi}\frac{\partial}{\partial z}$$

Now we get rectangular component of angular momentum in quantum mechanical operators, which are

$$\hat{L}_x = -\frac{i}{2}\frac{h}{\pi}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = -\frac{i}{2}\frac{h}{\pi}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

and

$$\hat{L}_z = -\frac{i}{2}\frac{h}{\pi}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

In spherical polar coordinates these operators become

$$\hat{L}_x = \frac{i}{2}\frac{h}{\pi}\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \quad (29)$$

$$\hat{L}_y = \frac{i}{2}\frac{h}{\pi}\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \quad (30)$$

and $\hat{L}_z = -\frac{i}{2}\frac{h}{\pi}\frac{\partial}{\partial\varphi}$ (31)

The square of the magnitude of the angular momentum vector $\vec{L}$ is

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

The corresponding operator is

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Put the squares of $\hat{L}_x$,$\hat{L}_y$,$\hat{L}_z$ from equation (29),(30),(31) we get

$$\hat{L}^2 = -\frac{h^2}{4\pi^2}\left[\left\{\sin^2\varphi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\cos^2\varphi\ \frac{\partial^2}{\partial\varphi^2} + \sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\varphi}\right)\right\}\right.$$
$$+\left\{\cos^2\varphi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\sin^2\varphi\frac{\partial^2}{\partial\varphi^2}\right.$$
$$\left.\left.-\cos\varphi\frac{\partial}{\partial\theta}\left(\cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\left(-\cos\varphi\frac{\partial}{\partial\theta}\right)\right\} + \left\{\frac{\partial^2}{\partial\varphi^2}\right\}\right]$$

By more solving, we get final solution

$$\hat{L}^2 = -\frac{h^2}{4\pi^2}\left[\frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \cot\theta\frac{\partial}{\partial\theta}\right]$$

$$= -\frac{h^2}{4\pi^2}\left[\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

or $\hat{L}^2 = -\frac{h^2}{4\pi^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$ (32)

It is operator of the square of the angular momentum.

By applying the operator $\hat{L}_z$ to the one –electron atom wave function

$$\Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\,\Phi(\varphi)$$

This gives $\hat{L}_z\Psi = -\frac{i}{2}\frac{h}{\pi}\frac{\partial\Psi}{\partial\varphi}$

or $\hat{L}_z\Psi = -\frac{i}{2}\frac{h}{\pi}\ R\,\Theta\frac{\partial\Phi}{\partial\varphi}$ (33)

The function $\Phi(\varphi)$ for the atom is given by

$$\Phi = A\,e^{im_l\varphi}$$

By differentiating w.r.t φ, we get

$$\frac{\partial\Phi}{\partial\varphi} = A\,im_l e^{im_l\varphi} = im_l\,\Phi$$

Put this value in equation v, we get

$$\hat{L}_z\Psi = -\frac{i}{2}\frac{h}{\pi} im_l \, R\,\Theta\Phi$$

$$\hat{L}_z\Psi = m_l \frac{h}{2\pi}\Psi$$

Given above equation shows the wave functions Ψ of the one-electron atom are the eigenfunction of $\hat{L}_z$ having eigenvalues given by

$$L_z = m_l \frac{h}{2\pi} \tag{34}$$

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

12.10 Illustrative Examples

Example 3: Calculate the two possible orientations of spin vector S with respect to a magnetic field.

Sol. The magnitude of spin angular momentum S,

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

and z-component

$$S_Z = m_S\frac{h}{2\pi}, \qquad m_S = \pm 1/2$$

The angle between S and the z- axis is determined by the quantum numbers m_S and S,

$$\cos\theta = \frac{s_z}{s} = \frac{m_s}{\sqrt{s(s+1)}} = \frac{2}{\sqrt{3}} m_s, \qquad (\because s=1/2)$$

For m_S=+1/2,we get

$$\cos\theta = +\frac{1}{\sqrt{3}} = 0.577 \quad \therefore \theta = \cos^{-1}(0.577) = 54.7^0$$

For m_S = - 1/2,we get

$$\cos\theta = -\frac{1}{\sqrt{3}} = -0.577 \quad \therefore \theta = \cos^{-1}(-0.577) = 125.3^0$$

Example 4: Find the possible values of the components of angular momentum along a specified direction for an electron orbit with quantum number ***l***=1.

Sol. For the given electron ***l***=1 (p-electron) and s = 1/2

The two possible values of ***j*** are

$$j = l \pm s = 1 \pm 1/2 = 3/2 \text{ and } ½$$

For ***j***=*3/2,* the possible values m_j are

$$m_j = \frac{3}{2}, \frac{1}{2}, -\frac{3}{2}, -\frac{1}{2}$$

For ***j**=1/2*, the possible values m_j are

$$m_j = \frac{1}{2} \;, -\frac{1}{2}$$

Z – Component of total angular momentum will be

$$j_z = m_j \frac{h}{2\pi} \;,$$

So the possible values for z-component of total angular momentum

$$\pm \frac{3}{2}\left(\frac{h}{2\pi}\right), \pm \frac{1}{2}\left(\frac{h}{2\pi}\right)$$

Example 5: How many revolutions does an electron in n=3 state of a hydrogen atom make before dropping to the n=1 state? The average life time of an excited state is 10^{-8} second. (R_∞ =1.097 × $10^7 m^{-1}$)

Sol. For hydrogen atom Z=1

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

$$f = v/2\pi r$$

For finding the value of v from Bohr postulates for condition of mechanical stability of electron is

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

and quantum condition is

$$mvr = \frac{nh}{2\pi} \qquad (n=1,2,3.......)$$

We find from above equations

$$v = \frac{e^2}{2nh\varepsilon_0} \text{ and } r = \frac{n^2h^2\varepsilon_0}{\pi me^2}$$

Thus $$f = \frac{me^4}{4{\varepsilon_0}^2n^3h^3} = \frac{me^4}{4{\varepsilon_0}^2h^3c}\left(\frac{2c}{n^3}\right) = R_\infty\left(\frac{2c}{n^3}\right)$$

For the n = 3 state, the frequency of revolution is

$$f = R_\infty\left(\frac{2c}{n^3}\right)$$

$$f = \frac{(1.097 \times 10^7 m^{-1})(3.0 \times 10^8\, ms^{-1}}{9} = 3.66 \times 10^{14} s^{-1}$$

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

$$=(3.66 \times 10^{14} s^{-1}) \times 10^{-8}\, s = 3.66 \times 10^6$$

12.11 Self Learning Exercise- II

Q.1 What is the meaning of degeneracy of the elliptic orbits in Sommerfeld's theory of elliptic orbits?

Q.2 Calculate the possible orientations of the total orbital angular momentum vector $\vec{L}$ corresponding to $l = 1$ with respect to a magnetic field along the z-axis.

Q.3 Show that the ionization potential of Li^{++} is nine times the value for hydrogen atom.

12.12 Summary

The unit starts with Sommerfeld's elliptic orbit. Find the derivation for energy, shape and size for different elliptical orbits. Sommerfeld's model can't explain fine structure of spectral lines. We introduce relativistic correction for single electron atoms.

Further, quantum numbers and electron probability density are introduced for hydrogen atom .We try to draw polar diagrams for different energy states. In last, we defined orbital angular momentum. There involved many solved and unsolved problems time to time after derivation.

12.13 Glossary

Degenerate–Two or more quantum states that share or relate the same quantum numbers.

Stationary -Remaining in the same condition or state

12.14 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: There will be to two possible orbits

(i) Circular (with radius $2r_b$)

(ii) Elliptical (with semi-major axis $a = 4r_b$ and semi-minor axis $b = 2r_b$)

Ans.2: To explain fine structure of hydrogen spectral lines.

Answers to Self Learning Exercise-II

Ans.1: Orbits have common value of energy known as degenerate orbit and such property of orbits known as degeneracy.

Ans.2: $\cos\theta = 0.7071, 0, -0.7071, \theta = 45^0, 90^0, 135^0$

Ans.3: Using $E_1 = -R_\infty Z^2 hc$

12.15 Exercise

Q.1 Describe Bohr's atom model. Assuming that the nucleus is infinitely heavy and the electron has mass *m* and charge *e*, find out the energy of the electrons moving in the *n*th orbit. Calculate the ionization potential of hydrogen atom.

Q.2 Calculate the time taken by the electron to traverse the first Bohr's orbit in hydrogen spectrum.

Q.3 What are the salient features of Bohr-Sommerfeld atom model ?

Q.4 How many revolutions does an electron in the $n = 2$ state of a hydrogen atom make before dropping to the $n = 1$ state? (The average life time of an excited state is about 10^{-8} s).

Q.5 Calculate the possible orientations of the total angular momentum vector $\vec{J}$ corresponding to j=5/2 with respect to a magnetic field along the z-axis.

12.16 Answers to Exercise

Ans.1: See in section 12.2

Ans.2: 15.26 $\times 10^{-5}$ sec.

Ans.3: See in section 12.3 & 12.4

Ans.4: 8.2 $\times 10^{6}$

Ans.5: $32.22^0, 59.53^0, 80.27^0, 99.72^0, 120.46^0, 147.77^0$

References and Suggested Readings

1. Raj Kumar, Atomic and Molecular Spectra: LASER, Fifth edition (2008), Kedar Nath Ram Nath.
2. Arthur Beiser, Concept of Modern Physics, Sixth edition (2006), Tata McGraw-Hill .
3. R. Resnick, D. Halliday, K. S Krane,Physics (Volume - I) 5th Edition (English) Wiley India Pvt. Ltd. 2002.

UNIT-13
Vector Atom Model

Structure of the Unit

13.0 Objectives

This chapter is focused on the development of Vector Atom model, which was conceptualized with two features, namely, the quantization of space (orientations of orbits) and electron spin. The idea of quantization of orientations was introduced by the concept of projection of each quantized orbit on the field direction. This laid down the introduction of additional quantum numbers, namely magnetic orbital (m_l) and spin quantum number (m_S). With complete nomenclature of quantum numbers of single electron system, say Hydrogen atom, this model neatly explains the periodic table as well as describe the magnetic properties of electron (atom) and the total angular momentum results from L-S coupling. Stern – Gerlach experiment provides the direct experimental evidences for the existence of spin of electron and discrete orientations of orbits, when an atom is placed in a strong non – uniform magnetic field.

13.1 Introduction : Vector Atom Model

The vector-atom model is an extension of Rutherford-Bohr-Sommerfeld atom model. Rutherford-Bohr-Sommerfeld atom model successfully explains single valence atom, *i.e.* Hydrogen atom but incapable of resolving the spectroscopic issues of atoms contains more valence electrons. Thus, to overcome the limitation of Bohr-Sommerfeld model as well as to explain new experimental phenomena, like anomalous Zeeman's effect, Paschen's–Back effect, Stark effect. Further, the theory proposed by Bohr and Sommerfeld are two dimensional while an atom is a three dimensional entity. Therefore, to incorporate the three-dimensional concept and to explain the complexity of the spectral distributions, extension of Bohr-Sommerfeld model was given by Uhlenbeck and Goudsmit, known as Vector-Atom model. The vector atom model basically deals with the total angular momentum of an atom which is results of the combination of orbital and spin angular momenta. The main two features of vector atom models are, namely, spinning electrons and space Quantization of electron orbits.

13.2 Spinning of Electrons

Since the Bohr-Sommerfeld model couldn't explain completely the spectral behavior of Hydrogen atom and thus it became necessary to address some other properties of moving electron. To describe the multiple character of spectral lines, i.e. multiplets (for example double of sodium, triplet of magnesium and mercury) and also to account the behavior of spectral lines under the effect of magnetic field, Uhlenbeck and Goudsmit proposed the hypothesis of spinning electrons in order to explain some of spectral phenomena such as Zeeman effect, fine structure etc. According to its, electron revolves about its own axis while revolving in its orbit around the nucleus. Thus moving electron has two kinds of motion, orbital motion and spin motion.

As we know that circular motion of a mechanical body leads to mechanical angular momentum, similarly a charge body, i.e. electron produces a circular current which also rotates with body. This circular current then gives rise to a magnetic moment. Therefore, concept of electron spin introduces two angular momentum and two magnetic moments: one from is due to orbital motion while other is due to spin motion. The total angular momentum of the electron is the sum of orbital and spin angular momentum. Similarly, the total magnetic moment is the sum of orbital and spins magnetic moment.

The spinning motion of electron is quantized in both magnitude and direction. The intrinsic spin angular momentum is given by

$$\vec{p}_s = \vec{s}\hbar \tag{1}$$

The intrinsic spin angular momentum is as shown in Fig. (13.1) spin angular momentum can take only two orientations in the presence of magnetic field.

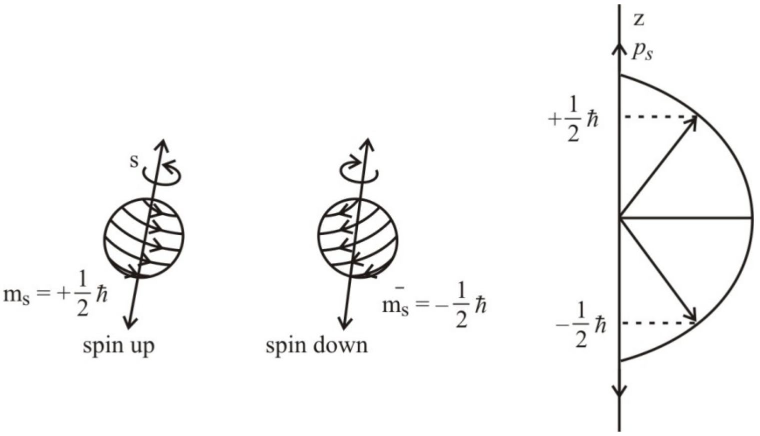


Fig.: 13.1

The projection of $\vec{p}_s$ is given by

$$p_{s_z} = m_s\hbar \tag{2}$$

with analogy, the orbital angular momentum vector and spin angular momentum vector can have two values (2*s*+1). For example, if $s = \frac{1}{2}$, m_s can have only two values, namely $+\frac{1}{2}$, or $-\frac{1}{2}$, *i.e.* spin-up (parallel) and spin-down (anti parallel) directions correspondingly and thus p_s can take only two orientations.

13.2.1 Intrinsic Magnetic Momentum

Due to the spinning of electron, a circular current is produced which generates a magnetic field. This field is the same as the produced by a bar magnet and characterized by magnetic moment μ_s is given by

$$\vec{\mu}_s = 2\frac{e}{2m}.\vec{p}_s \tag{3}$$

13.3 Space Quantization

In Bohr's model, electron has only one quantum number, namely, principal quantum number *n* to describe the motion of electron motion. Thus electron has only one degree of freedom in Bohr's model. Later on, according to Sommerfeld, electron revolves in elliptical orbits which are two dimensional and hence electron has two degree of freedom. Therefore, two quantum numbers namely, principal quantum number *n* and the azimuthal quantum number *k*. But in general, an atom is a three-dimensional body and therefore, possesses three degree of freedom. Since, classically, electron orbit may orient in all possible directions in space, *i.e.* may take different orientations in the atom, as shown in Fig. (13.2).

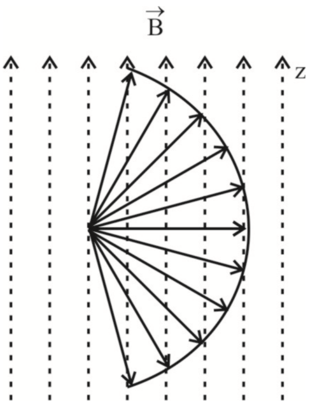


Fig.: 13.2

Thus, third quantum number quantizes the orientation of elliptical orbit in three-dimensional space does not change original Sommerfeld orbits, but according to rule of space quantization, out of infinite possible orientations only certain discrete orientations are allowed. Therefore, the orientation of an orbit is needed to fixed up.

13.3.1 Orientations of the Orbit

The preferred direction or orientation of an orbit can be find out with the help of orbital angular momentum vector p_l which is directed along the axis of rotation of electron and perpendicular to the plane of orbit (Fig. 13.3).

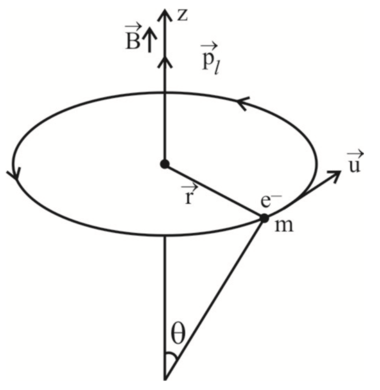


Fig. :13.3

The rotating electron about the nucleus forms a current loop has magnetic moment $\mu = IA$, where I is the current in loop and A is the area vector. The energy of charged loop is given by $\mu B\cos\theta$. Since an orbiting electron possesses angular momentum (p_l) which interacts with external magnetic field. Therefore according to quantum theory vector p_l can have certain discrete directions relative to external magnetic field direction, known as space quantization. The space quantization of an orbit is specified by projection of its orbital angular momentum onto direction of external magnetic field (along z-direction).

The orbital angular momentum is given by

$$\vec{p}_l = \frac{lh}{2\pi} = \vec{l}\hbar \qquad (4)$$

According to space quantization, p_l can have only those orientation for which its component in the field direction $\vec{B}$ will take integral values of $\hbar$. From Fig. (13.4), $p_l \cos\theta$ is given by

$$p_{l_z} = p_l \cos\theta = m_l\hbar \qquad (5)$$

where m_l is known as orbital magnetic quantum number and θ is the angle between p_l and field direction since m_l has to be an integer and $\cos\theta$ cannot exceed unity, thus the permitted values of m_l are from $+l$ to $-l$, *i.e.* take following values:

$$l,(l-2),(l-2)......,1,\,0,-1,-2,......(l-2),-l$$

This implies that for each value of l, there will be $(2l+1)$ values that m_l can have and p_l can have $(2l+1)$ possible directions.

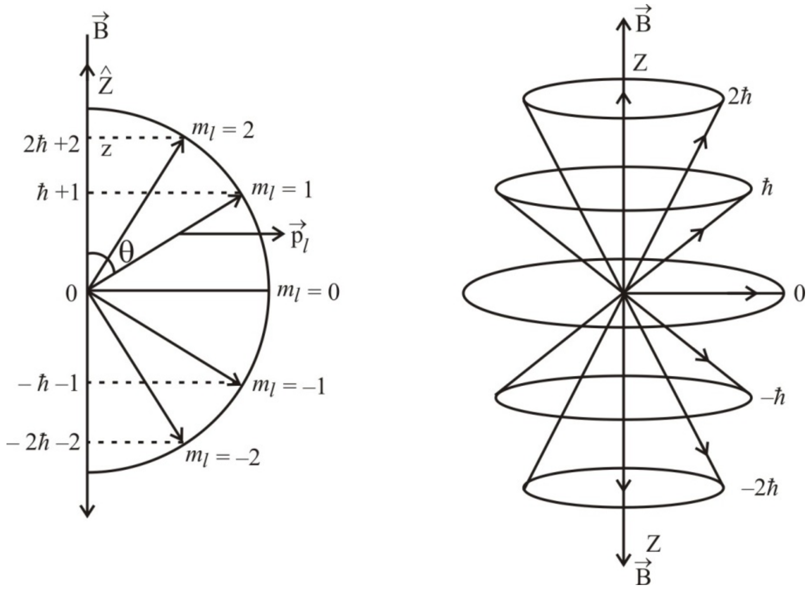


Fig.: 13.4: Space quantization of p_l for $l = 2$)

When an atom is subjected to magnetic field, the energy of the electron in its orbit varies for all relative orientation of p_l with respect to field direction.

Now the electron is visualized as three dimensional motion quantized by three quantum number n, l and m_l.

As both the orbital angular momentum p_l and intrinsic spin angular momentum p_s that determine the state by quantized vectors and added up as per the rules of vectors, the atom model is known as Vector Atom model.

Thus, the introduction of quantization of space and quantization of spin of electron further lead to same new quantum number which we will discuss in next.

13.4 Quantum Number's and Their Physical Interpretation

In Bohr's Sommerfeld model, two quantum numbers, namely, principal and azimuthal quantum numbers are defined, which are not enough to describe the motion of an electron in its orbit. But in vector atom model, each component is assigned as quantum number whose numerical value may be thought of as the length of vector and therefore following quantum numbers are used to describe the motion of an electron completely.

(i) **Principal Quantum Number (*n*):–** Classically, the principal quantum number '*n*' represents ordinal number of particular orbit occupied by electron are defined as K, L, M, N orbit for n = 1, 2, 3, 4 respectively. But in quantum mechanics, no definiteness is allowed.

The quantum number '*n*' can take on the integral values 1, 2, 3, 4 …. ∞ and governs the total energy $\left(E_n \propto \frac{1}{n^2}\right)$ and major axis of elliptical orbit, even it gives the large mean distance of the electron from the nucleus. Thus, the K, L, M, N …. not only represents the mean distance but also a group of electrons at the means distance from the orbit.

(ii) **An Orbital Quantum Number (*l*):–** The orbital quantum number *l* can take on values 0, 1, 2, 3, ……. (n – 1) for each n and governs the orbital angular momentum (p_l). It is to be noted that *l* can have value zero but it is not allowed for *k* (azimulthal quantum number), because of the relation $l = k - 1$.

Angular momentum according to wave mechanics is given by

$$p_l = \sqrt{l(l+1)}\,\hbar \tag{6}$$

Orbital have the same value of l defines the natural series 0, 1, 2, 3, ….. are labeled as (*s*) sharp, (*p*) principal, (*d*) diffuse, (*f*) fundamental …… given to the lines in the hydrogen spectra.

(iii) **Spin Quantum Number (*s*):–** As we have discussed that the quantization of spin of electron was needed to explain fine structure of spectral line spin of electron can take ½ only and relates to the intrinsic, property known as spin angular momentum as

$$p_s = \sqrt{s(s+1)}\,\hbar \tag{7}$$

For single electron system $p_s = 0.866\hbar$

(iv) **Total Angular Momentum Quantum Number (*j*):–** It is also known as inner quantum number. This denotes the total angular momentum of the electron which arises due to orbital motion and spinning of electron.

For a single electron system, vector $\vec{l}$, i.e. p_l and s , *i.e.* $\vec{p}_s$ couple vectorially in a weak field to given vector $\vec{j}$, *i.e.* $\vec{j} = \vec{l} \pm \vec{s}$ and the total angular momentum of the electron is p_j *i.e.* $\vec{p}_j = \vec{p}_l \pm \vec{p}_s$. The quantized total angular momentum is given by

$$p_j = \sqrt{j(j+1)}\hbar \tag{8}$$

where j is positive and always ½ integral for a single electron. Each l level degenerates into two j levels, namely $l+\frac{1}{2}$ and $l-\frac{1}{2}$.

When an atom is subjected to a magnetic field, three more quantum numbers are associated with electron due to space quantization.

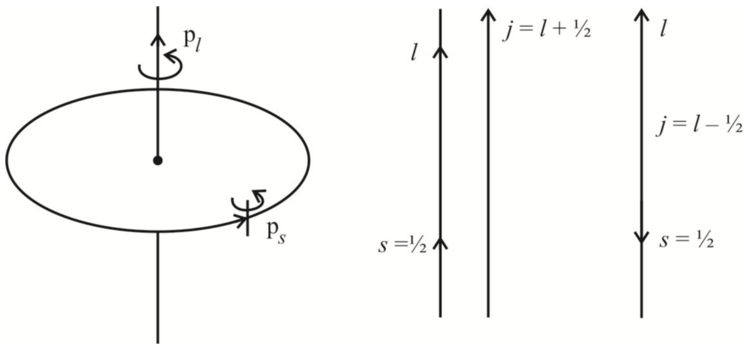
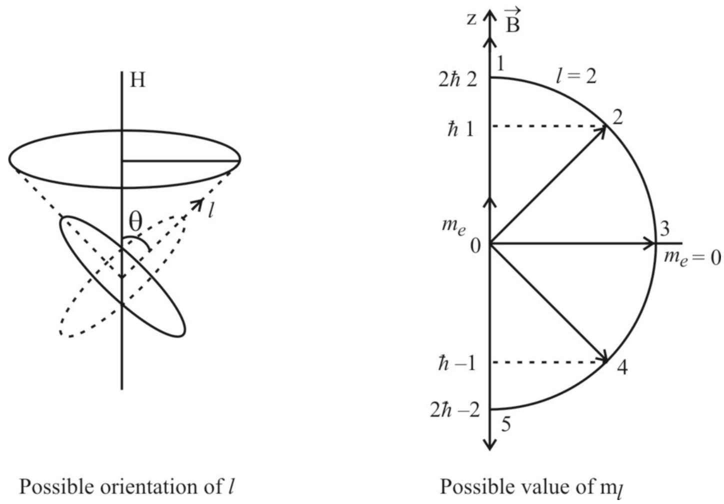


Fig. 13.5

(v) Magnetic Orbital Quantum Number (m_l):– m_l is the numerical value of the projection of orbital quantum no. (vector l) in the magnetic field direction, ***i.e.*** l precesses about the magnetic field direction and forms a cone about axis. Due to the rule of space quantization, projection of l must be quantized in the field direction then l can have orientation in certain directions and m_l may also be an integer, is given by

$$m_l = l\cos\theta \quad (9)$$

Possible values of m_l are $m_l = l, (l-1), (l-2)........0,......\ -1,......-2....(l-1).......-l$ ***i.e.*** $(2l+1)$ possible orientations of l.



Possible orientation of l

Possible value of m_l

Fig. 13.6

The negative values of m_l represent that component of angular momentum is oriented opposite to the direction of magnetic field. Fig. (13.6) shows the orientations of l and possible values of m_l for $l=2$.

(vi) Magnetic Spin Quantum Number (*m_s*):– Similar the orbital angular momentum, m_s is the numerical value of the projection of the spin vector '*s*' on the field direction and spin vectors can have only (2*l* +1) values from –*s* to +*s* at unit interval.

(vii) Total Magnetic Quantum Number (*m_j*):– It is the numerical value of the projection of total angular momentum in the field direction. Since, j can have only ½ integral values m_j also assumes half integral values. The permitted orientation of j are $(2j+1)$ and hence possible values of m_j are $-j,(-j+1)$ …….. $(j-1)$, i.e., $(2j+1)$ excluding zero.

13.5 Magnetic Moment of an Electron in an Atom and Lande's g- Factor

Electron magnetic moment, *i.e.*, electron magnetic dipole moment is the magnetic moment of an electron produced by intrinsic properties of spin and electric charge.

In an atom, it is known that an electron revolves around the nucleus with certain angular velocity ω in a orbit of radius *r.* This revolution of electron produces the angular momentum about the centre of the path, is given by

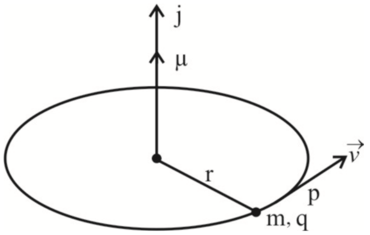


Fig.: 13.7

$$p_l = m\omega r^2 \qquad (\because v = r\omega) \qquad (10)$$

which is quantized along the perpendicular direction to the plane of orbit.

From, classical electrodynamics, we know that when a charged body rotates, it produces magnetic field due to current. This creates magnetic dipoles of equal magnitude but opposite polarity, which gives rise to the orbital magnetic moment.

Thus, an electron would gives rise to a current in a complete revolution of time period T is

$$i = \frac{Q}{T} = -\frac{e}{T} \tag{11}$$

As we also know that the field due orbital circuital current does not depend upon the shape *x* and having orbital magnetic moment

$$\mu_l = iA \tag{12}$$

where $A = \pi r^2$ (Area of orbit)

$$\Rightarrow \qquad \mu_l = -\frac{e}{T}\pi r^2 = -\frac{e\omega}{2\pi}\pi r^2 \qquad (\because T = 2\pi / \omega)$$

$$= -\frac{e}{2m} m\omega r^2$$

$$\mu_l = -\frac{e}{2m} p_l \tag{13}$$

–ve sign indicates that μ_e and p_l are oppositely oriented. The numerical value of the ratio of μ_e and p_e, *i.e.* $\frac{|\mu_l|}{|p_l|} = \frac{e}{2m} = g_l$ is known as gyromagnetic ratio.

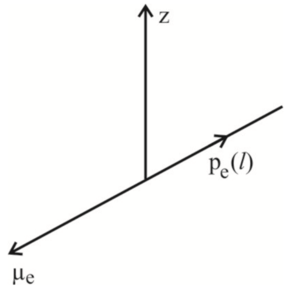


Fig. 13.8

From the quantization of angular momentum $(\vec{p}_l = \vec{l}\hbar)$, the orbital magnetic moment $\vec{\mu}_l = -\frac{\vec{l}e\hbar}{2m}$ Joule/Tesla (14)

For the case of ground state of hydrogen atom (*n* =1), this orbital magnetic moment is called Bohr-Magneton, given by

$$\mu_B = \frac{e\hbar}{2m} = \frac{1.6\times10^{-19}\times1.05\times10^{-34}}{2\times9.1\times10^{-31}} \text{ J/T}$$

$$= 9.27\times10^{-24} \text{ J/T} \tag{15}$$

Thus, equation (14) is written more correctly as

$$\vec{\mu}_l = -g_l \mu_B \vec{l} \tag{16}$$

Similarly, further, electron possesses an intrinsic spin angular momentum, hence, it will also have a spin magnetic moment, following the equation (16), spin magnetic moment can be written as

$$\vec{\mu}_s = -g_s \mu_B \vec{s} \tag{17}$$

Since spin of electron also leads to a mechanical momentum $(\vec{p}_s)$, thus the ratio of spin magnetic moment to spin mechanical momentum is

$$\frac{|\vec{\mu}_s|}{|\vec{p}_s|} = \frac{-e}{m} \tag{18}$$

Since the spin frequency is twice as large as orbital frequency, thus we may write

$$g_s = 2$$

here g_s is called "spin-g factor", which gives the numerical measure of magnetic moment in units of Bohr magneton.

Quantum mechanically, we have

$$\vec{\mu}_l = -g_l \frac{e}{2m} \vec{l} \tag{19}$$

$$\vec{\mu}_s = -g_s \frac{e}{2m} \vec{s} \tag{20}$$

The total magnetic moment of the atom is the vector sum of orbital and spin magnetic moment

$$\vec{\mu}_j = -g \frac{e}{2m} \vec{j} \tag{21}$$

This g is called Lande's g- factor.

The potential energy of atomic magnet associated with orbital magnetic moment is given by

$$V_m = -\vec{\mu}_B . \vec{B} = -\mu . B \cos\theta \tag{22}$$

where θ is the angle that the angular momentum makes with the field direction, is given by (according to the rule of space quantization).

$$l \cos\theta = m_l \tag{23}$$

and also from equation (14) $\mu = -\frac{el\hbar}{2m}$

then $V_m = \frac{e\hbar}{2m} B m_l$ (24)

13.6 Larmor Precession (Larmor's Theorem)

In physics, Larmor precession is the precession of the magnetic moment of any object with magnetic moment in an external magnetic field. The concept of precession is illustrated below for the earth well as for a spinning top. On both cases the external force is just gravity.

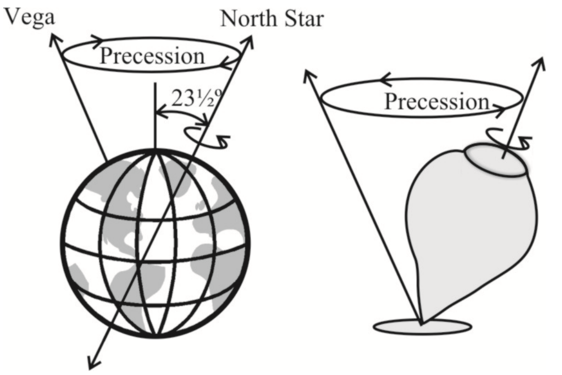


Fig. 13.09

When a magnetic moment is placed in a magnetic field, it is aligned with the field. Classically, a magnetic moment can be realized as a current in a loop and the influence for being aligned by the external magnetic field can be treated as torque. When a magnetic moment directed at some finite angle with respect to magnetic field direction, the field will exert torque ($\vec{\tau} = \vec{\mu} \times \vec{B}$) on the magnetic moment, which causes the precession about the magnetic field. Since the magnetic moment is associated with angular momentum $\vec{J}$ precesses about an axis parallel to the magnetic field.

The phenomena of precession can be described in term of (a) angle between symmetry axis and angular momentum vector, denoted by θ, and (b) angular velocity $\omega_p = \frac{d\phi}{dt}$, where the angular displacement $\Delta\phi$ in the time internal Δt is $\Delta\phi\Delta t$ obviously.

From the Fig. (13.10), it can be easily written that

$$\Delta j \approx J \sin\theta (\omega_p \Delta t) \tag{25}$$

For an infinitesimally small $\Delta\phi$ and ΔJ, we may write

$$\frac{dJ}{dt} = \omega_p J \sin\theta \tag{26}$$

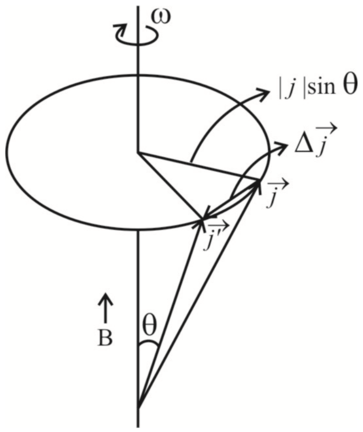


Fig. 13.10

But the angular momentum cannot change if there is no torque, infact, rate of change of angular momentum is equal to torque, given by

$$\vec{\tau} = \vec{\mu} \times \vec{B} = \mu B \sin\theta \tag{27}$$

Thus, one may have

$$\mu B \sin\theta = \omega_p J \sin\theta$$

$$\omega_p = \frac{\mu B}{J}$$

where $\frac{\mu}{J} = \frac{e}{2m} g$

$$\therefore \qquad \omega_p = g \frac{e}{2m} B \tag{28}$$

which states that angular velocity of the precession is proportional to the magnitude of the external field and the proportionality constant $\left(\frac{ge}{2m}\right)$. Thus the frequency of the precession i.e. is given by

$$f_p = \frac{\omega_p}{2\pi} = g \frac{eB}{4\pi m} \tag{29}$$

Since according to the classical theory, in an atom, the electron orbit and spin should precess in a magnetic field which holds good in quantum mechanical treatment also but the meaning of precession in quantum mechanics is usually referred as Larmor' precession and frequencies above are often defined as Larmor' frequencies, where the constant $\left(\frac{ge}{2m}\right)$ is usually written as γ, known as gyromagnetic (magnetogyric) ratio. Thus,

$$\omega_p = \gamma B \tag{30}$$

For a single electron system it is quite simple to understand the behavior of system. But it becomes more complicated when many electrons are involved, which further become more complicated when external magnetic field is introduced. To resolve the issue, Larmor has proved a theorem that basically state that "*motion of the system is the same as it would be in the absence of the field except that a uniform rotation around the axis of magnetic field.*"

More specifically, the added rotation will have an angular frequency in an external magnetic field, equal to

$$\omega_L = \frac{e}{2m}.B \tag{31}$$

which is the same formula, as we have observed for angular velocity of the precession when $g = 1$.

So, when an atom is placed in an external field $\vec{B}$, the electron orbit precesses about the field direction as axis. The electron orbital angular momentum $\vec{L}$ traces a cone around the $\vec{B}$ such that the angle between $\vec{L}$ & $\vec{B}$ remains constant

i.e. $\quad \vec{B} = B\hat{z}$

and $\quad L_Z = |\vec{L}|\cos\theta$

But quantum mechanically, $|\vec{L}| = \sqrt{l(l+1)}\hbar \;\Rightarrow\; L_Z = m_l\hbar$

$$\Rightarrow \qquad \cos\theta = \frac{L_Z}{|\vec{L}|} = \frac{ml}{\sqrt{l(l+1)}} \tag{32}$$

Thus, angle θ can have discrete values as m_l has $(2l+1)$ possible orientations with respect to magnetic field. This is known as space quantization

13.7 Spin-Orbit Coupling : Vector Atom Model

The total angular momentum of an atom results from the combination of the orbital and spin angular momenta of its electrons. The total angular momentum of one electron atom is given by the vector sum of $\vec{l}$ and $\vec{s}$, *i.e.* $\vec{j} = \vec{l} + \vec{s}$.

This leads to the vector model of atom. Since the magnitude of the angular momentum $\vec{l}$ of an atomic electron is given by

$$|\vec{l}| = \sqrt{l(l+1)}\hbar \tag{33}$$

and its z-component $l_z = m_l \hbar$

Similarly the magnitude of spin angular momentum $\vec{s}$ is given by

$$|\vec{s}| = \sqrt{s(s+1)}\,\hbar \tag{34}$$

and its –component $s_z = m_s \hbar$

Total angular momentum $\vec{j} = \vec{l} + \vec{s}$. Then, the magnitude and z-component of $\vec{j}$ are given by according to usual quantization condition

$$|\vec{j}| = \sqrt{j(j+1)}\,\hbar \tag{35}$$

and $\quad j_z = m_j \hbar$

The possible values of m_j ranges from $-j$ to $+j$ in integral steps. We may write

$$j_z = l_z \pm s_z \tag{36}$$

and $\quad m_j = m_l \pm m_s \qquad (37)$

In case of one electron system, there are only two relative orientations possible, corresponding to

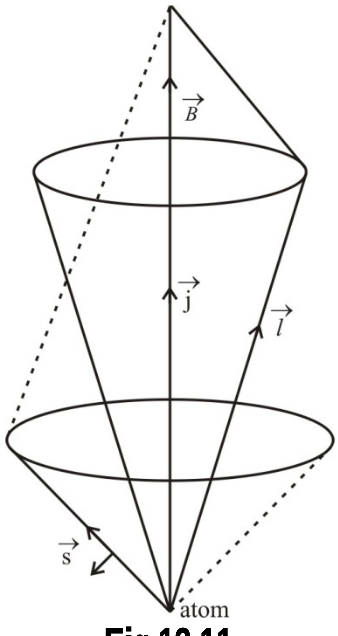


Fig.13.11

$j = l + s$ so that $j > l$

$j = l - s$ so that $j < l$

The angular momenta of an atomic electron interacts magnetically, thus known as spin-orbit interaction. The torque due to $\vec{l}$ and $\vec{s}$ exert on each other which cause then to precess uniformly about their resultant $\vec{j}$. If no external torque acts on it, then total angular momentum $\vec{j}$ is conserved. Thus the angle between $\vec{l}$ and $\vec{s}$ would remain conserved.

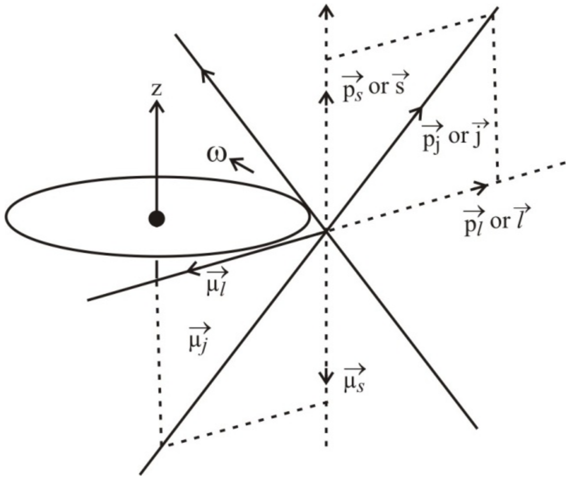


Fig. 13.12

$$|\vec{j}|^2 = |\vec{l}|^2 + |\vec{s}|^2 + 2|\vec{l}||\vec{s}|\cos(\vec{l},\vec{s}) \tag{38}$$

$$\Rightarrow \quad \cos(\vec{l},\vec{s}) = \frac{|\vec{j}|^2 - |\vec{l}|^2 - |\vec{s}|^2}{2|\vec{l}||\vec{s}|}$$

$$= \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}} \tag{39}$$

From the fig. 13.12, it is noted that $\vec{l}$ and $\vec{s}$ cannot be parallel or antiparallel to each other. For a weak external field $\vec{B}$, the vector precesses around $\vec{B}$ and spatially quantized. However, as $\vec{B}$ increase, the $\vec{l}$ and $\vec{s}$ are uncoupled and precesses independently around $\vec{B}$ and spatially quantized independently.

13.8 Quantum Numbers for Multielectron Atom

For a single electron (single valence) atom, letters are used to describe the different quantum numbers were all small and so was the letters *s*, *p*, *d*, *f*….. whereas, for a complete atom, *i.e.* multielectron system, capital letters are used for various quantum numbers.

(i) $\vec{L}$ **:–** As we have now understood that for a single valence electron system (Hydrogen atom and alkali metals), the total angular orbital momentum for the atom is the same as for a single electron. Thus, the value of L is the same as *l* value, when there is more than one electron in an atom then discrete values of ***l*** is assigned each electron must be added up vectorially to obtain resultant orbital angular momentum of the atom.

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + ... = \sum_i \vec{l}_i \qquad (40)$$

If all $l_i's$ are in same direction, $\vec{L}$ becomes maximum equal to $\sum_i \vec{l}_i$. The minimum possible value for L could be zero ,but if one of the $l_i's$ is larger than the sum of all others, minimum value is not zero.

For two electron atom, value of $\vec{L}$ for the atom is written as

$$L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2) ....(l_1 - l_2) \qquad (41)$$

For example, say $l_1 = 2$ & $l_2 = 1$, than L can have only one of the value 3, 2 or 1. (see Fig.13.12).

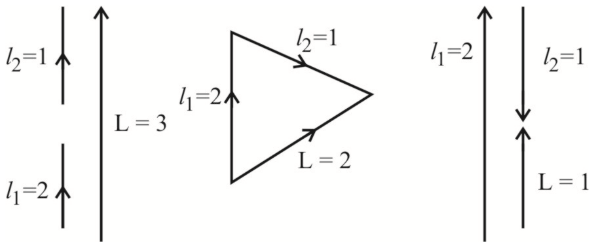


Fig. 13.12

(ii) $\vec{S}$ **:–** As we know already that value of spin for each and every electron is ½ which could be either parallel or antiparallel to the preferred direction. Unlike the case of $\vec{L}$, each electron is assigned with a discrete and definite value of spin $\vec{s}_i$ and all $\vec{s}_i$ combine to form a resultant $\vec{S}$ for the atom. For *N* electrons, possible values for *S* can be written as

$$\frac{N}{2}, \left(\frac{N}{2} - 1\right), \left(\frac{N}{2} - 2\right), ... \frac{1}{2} \text{ or } 0 \qquad (42)$$

The minimum possible value is either ½ if *N* is odd or zero if *N* is even.

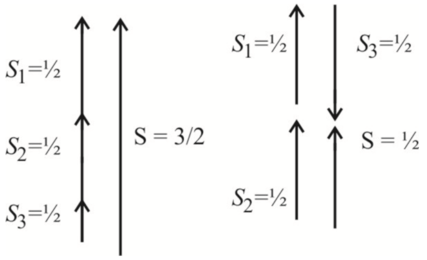


Fig. 13.13

Since $\vec{L}$ & $\vec{S}$ are associated with their corresponding magnetic moment and thus interaction between $\vec{L}$ and $\vec{S}$ yields total angular momentum $\vec{J}$. The possible descrete value of $\vec{J}$ depends upon the possible allowed orientation of $\vec{L}$ and $\vec{S}$.

(iii) $\vec{J}$ **:–** In quantum mechanics, total angular momentum of the atom is essentially the function of $\vec{J}$ and it is written as $\sqrt{J(J+1)}\hbar$ and have certain discrete values in between

$$|\vec{L}+\vec{S}|,|\vec{L}+\vec{S}-1|.........|\vec{L}-\vec{S}| \tag{43}$$

The minimum and maximum values of $\vec{J}$ are obtained by subtracting and adding values of $\vec{L}$ and $\vec{S}$.

If L>S, then $\vec{J}$ can have $(2\vec{S}+1)$ possible values for a given L and if L< S than $\vec{J}$ will have $(2L+1)$.

13.9 Spectral Terms and Their Notations

The spectral behavior of an element is characterized by the outermost electrons which are not interlocked in closed shells. To describe the state of electron, small letters (*l,s,j*) are used while the capital letters *L*, *S*, and *J* describe the state of complete atom as whole.

For the case of single electrons system, the value of *L*, *S* and *J* are the same as that of *l*, *s*, and *j* because inner most electrons do not contribute to the total angular momentum. The multiplicity of a state is decided by $(2S+1)$. Thus, for single electron system $\left(S=+\frac{1}{2}\right)$. The multiplicity of state is two ,corresponding to the values $\left(L+\frac{1}{2}\right)$ and $\left(L-\frac{1}{2}\right)$ for *J* in addition to the ground state. But for multielectron system S can have any value not precise to $\frac{1}{2}$. For example, three electron system $S=\frac{1}{2}$ or $\frac{1}{3}$, thus multiplicity of the state is either double or quarter except the ground state.

Therefore to describe the state of an atom, it is defined as

$$nL_j^{2S+1}$$

For example, the state having j and $J=\frac{3}{2}$ then state is defined as $2P_{3/2}$ which clearly illustrates that the value of *L* is given by the capital letter. Here the values of *n* (principal quantum number) is 2. Further, state of the system may also be defined as

$$nl^{x}\,{}^{2S+1}L_{J}$$

Where ***l*** is the orbital quantum number of electron, ***i.e.***, *s*, *p*, *d*, …….. and *x* is the number of electrons in that orbital (x is 1 or 2 for s orbital, 1 to 6 for *p* orbital). Actually nl^{x} is the configuration of the outermost electrons.

13.10 Description of Ground State

For one electron system, $S=\pm\frac{1}{2}$ with respect to L. Thus, $J=L+\frac{1}{2}$ and $L-\frac{1}{2}$ ***i.e.*** double. But for the ground state $L=0$ and then $J=+\frac{1}{2}$ or $-\frac{1}{2}$. We know the value of *J* is given by $(L+S)$ or $(L-S)$ and must be positive, thus the possibility of $-\frac{1}{2}$ is not allowed. Hence, for a single electron system, ground state is always singlet. Whereas, for mutli-electron system, $J=S$ as $L=0$ for ground state, thus J can have any value as S can, ***i.e.*** $0,\frac{1}{2},\frac{3}{2}$...... .If $L<S$, multiplicity of the state is given by $(2L+1)$ yield to the possible values of J as one (*L*= 0) and thus state is singlet.

13.11 Stern-Gerlach Experiment and Electron Spin

In 1922, this experiment was performed by O. Stern and Gerlach, which directly manifest the main features of vector atom model. This experiment demonstrates that an atom in a magnetic field can take only certain discrete orientations and also exhibits the existence of electron spin and provides experimental verification of vector atom model. Since, the atom is considered as a small magnet, where the magnetism arises due to spin (spin angular momentum) and orbital (orbital angular momentum) motions of the electrons. When this atomic magnet is placed in a homogeneous (uniform) magnetic field, i.e. having equal and opposite magnetic strength, it gets aligned in the direction of magnetic field and does not experience any translatory motion, i.e. the magnet moves in a straight path without any deviation. But when this atomic magnet is placed in non-uniform magnetic field ,then the magnet not only align along the direction of magnetic field but also have translatory motion, *i.e.* the projector is a curved path due to displacement.

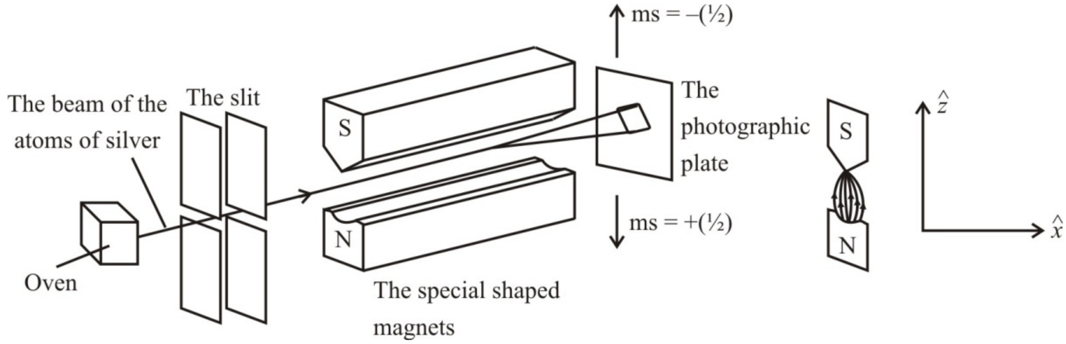


Fig. 13.14: The Stern-Gerlach experiment.

The plan of experimental arrangement is shown in Fig. 13.14. The substance of neutral silver atoms is heated up in an electrical oven. On heating, substance emits a beam of neutral atoms in all direction and collimated by few slits and then passes through a non-homogeneous magnetic field. The nonuniform magnetic field is produced by specially designed pole-pieces, whose cross sectional view is shown separately. The atomic beam is then made to strike on a photographic plate. The magnetic field is made more intense and more non-uniform as much as possible. On developing the photographic plate, none trace of direct beam is observed rather two traces are obtained which are symmetric with respect to the direct beam. This implies that the beam is splitted in two discrete directions, one is in +z direction and other in –z direction. The same has been observed for different atoms.

Interpretation of results:– In the case of silver, a straight line is obtained without field and double trace with some irregularities is obtained in the presence of field. The irregularities in double trace occur due to irregularities of magnetic field near the knife-edge of the poles of magnets.

Some important features of vector atom model can be explained easily.

(a) Spin of the electron:– It was ascertained by using beam of Hydrogen atoms. The atom consists of single electron in ground state (s-state; ***l*** = 0). If there were no spin then j would also be zero $(j = l + s)$, so that $m_j = (2j+1) = 1$ implies that splitting of line will not take place and thus $\mu = m_j g = 0$. But it has been found the beam to be splitted in two symmetrically deflected components giving rise to two traces. This occur when the existence of electron spin is admitted and a value ½ is assigned to spin quantum number. Thus, $j=l\pm\frac{1}{2}s=0\pm\frac{1}{2}=\pm\frac{1}{2}$ so that $2j+1=2$, then naturally μ will have two values +1 and –1. Hence, two traces obtained are in complete agreement with theory.

(b) Quantization of Space: Classically, atomic magnets can orient-themselves in any direction should give diffused path instead of two distinctly visible traces. But due to quantization of spin, only certain discrete orientations are permissible. If we consider silver atom belonging to one electron in its ground state then $l=0$ and $j=s$, and the possible orientation will be $(2j+1)=2$, i.e. we must get double trace which shows that the atoms passing through the field become oriented in space in discrete directions. Therefore H, Na, K, Cu, Ag belong to one electron system showing the value $s=\frac{1}{2}, l=0$, for ground state. Then $2j+1=2$, traces are possible. Further $\mu=m_j g$ have +1 and –1, two discrete possible orientations. But in case of many electron system, number of traces depends upon the value of s. Zn, Cd, and Hg have 2 s-electrons in their outermost orbit and their normal state is defined by ${}^1s_0$ which mean $j=0$. Thus $\mu=0$, which means that application of field brings no effect. In the case of Ni, Co, Fe the effect observed clearly due to large value of electron spin.

Therefore, Stern-Gerlach experiment not only verifies the main features of vector atom model but also establishes the fact that diamagnetic substances do not have resultant magnetic moment while paramagnetic substances do have, which agree with experimental data.

13.12 Illustrative Examples

Example 13.1: An electron is in $2p$ state of Hydrogen atom. Find the magnitude of orbital angular momentum and z-component of $\vec{l}$.

Sol: $\because$ The orbital angular momentum is given by

$$|\vec{l}|=\sqrt{l(l+1)}\,\hbar$$

and for *p*-state, $l=1$ $\Rightarrow$ $|\vec{l}|=\sqrt{2}\hbar$

Also z-component of l is defined as

$$l_z=m_l\hbar$$

where $m_l = -1, 0, +1$ for $l = 1$ (p state), hence $l_z = \hbar, 0, -\hbar$

Example 13.2 What are the possible orientation of $\vec{j}$ for the $j = 3/2$ and $j = \frac{1}{2}$ states which correspond to $l = 1$.

Sol: For any value of total orbital angular momentum I, the possible orientations aregiven by

m_j as $-j$ to $+j$.

i.e., for $j = 3/2$ state, $m_j = -3/2, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

and for $j = \frac{1}{2}$ state $m_j = -\frac{1}{2}, \frac{1}{2}$.

Example 13.3: For one electron atom, calculate $|\vec{l}|, |\vec{s}|, |\vec{j}|$ for a p-electron.

Sol: For electron in p-state $l = 1, s = \frac{1}{2}$.

Thus j will have two values:

(i) $\vec{j} = \vec{l} + \vec{s} = 1 + \frac{1}{2} = \frac{3}{2}$

(ii) $\vec{j} = \vec{l} - \vec{s} = 1 - \frac{1}{2} = \frac{1}{2}$

Therefore $|\vec{l}| = \sqrt{l(l+1)}\,\hbar = \sqrt{2}\hbar$

and $|\vec{s}| = \sqrt{s(s+1)}\,\hbar = \sqrt{\frac{3}{2}}\hbar$

$$|\vec{j}| = \sqrt{j(j+1)}\hbar = \sqrt{\tfrac{3}{2}(3/2+1)}\,\hbar = \sqrt{\frac{15}{2}}\,\hbar \text{ for } j = \tfrac{3}{2}$$

$$= \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1)}\hbar = \frac{\sqrt{3}}{2}\hbar \text{ for } j = \tfrac{1}{2}$$

Example 13.4: Determine the orbital state for $n = 3, s = \frac{1}{2}$

Sol: For $n = 3$ the corresponding value of l are 0, 1, 2.

(i) $l = 0,\ s = \dfrac{1}{2}$ ($l = 0$ state)

$\Rightarrow j = l + s = \dfrac{1}{2}$ then corresponding state is $3s_{\frac{1}{2}}$

(ii) $l = 1, s = \frac{1}{2}$ (($l = 1$ p state)

$\Rightarrow j = l \pm s = \frac{3}{2}, \frac{1}{2}$ then corresponding states are $3p_{3/2}, 3p_{1/2}$

(iii) $l = 2,\ s = \frac{1}{2}$ (($l = 2$; d state)

$\Rightarrow j = l \pm s = \frac{5}{2}, \frac{3}{2}$ then corresponding states are $3d_{5/2}, 3d_{3/2}$

$\because$ Orbital states are defined by nl_j^{2s+1}, where $(2s+1)$ is known as spin multiplicity.

Example 13.5: What would be the total quantum number $\vec{j}$ for two electrons with same $l = 1$ and $s = \frac{1}{2}$.

Sol: $l_1 = l_2 = 1$ for both electrons,

then $|L| = |(l_1 + l_2)|, |(l_1 + l_2 - 1)| \ldots\ldots |(l_1 - l_2)| = 2, 1, 0$

Similarly, $s_1 = s_2 = \frac{1}{2}$ for both electrons

$$|s| = |s_1 + s_2| + |s_1 + s_2 - 1| \ldots\ldots |s_1 - s_2|$$

Then, the allowed values for J are as follows:

(i) $L = 2,\ s = 1;\ J = L + S, \ldots to \ldots\ldots L - S = 3, 2, 1$

(ii) $L = 2,\ S = 0;\ J = 2$

(iii) $L = 1,\ S = 1 \Rightarrow J = 2, 1, 0$

(iv) $L = 0,\ S = 1 \Rightarrow J = 1$

(v) $L = 1,\ S = 0 \Rightarrow J = 1$

(vi) $L = 0,\ S = 0 \Rightarrow J = 0$

Example 13.6: State ${}^2s_{3/2}$ is possible or not?

Sol: For s-state $l = 0$ as $s = \frac{1}{2}$ given $j = l + s = \frac{1}{2}$ there ${}^2s_{3/2}$ cannot exist, but ${}^2s_{1/2}$ can exist.

Example 13.7: Calculate the possible two orientations of spin vector $\vec{s}$ with respect to a magnetic field direction.

Sol: $\because s = \sqrt{s(s+1)}\hbar$ where $s = \frac{1}{2}$ and $z-$component of spin angular momentum $s_z = m_s\hbar$, where $m_s = \pm\frac{1}{2}$.

Therefore $\cos\theta = \frac{s_z}{3} = \frac{m_s\hbar}{\sqrt{s(s+1)}\hbar} = \frac{m_s}{\sqrt{s(s+1)}}$

for $m_s = \pm\frac{1}{2}$,

$$\cos\theta_1 = \frac{1}{\sqrt{3}} = 0.577 \Rightarrow \theta_1 \cong 54^0 55'$$

and $\cos\theta_2 = -\frac{1}{\sqrt{3}} = -0.577 \Rightarrow \theta_2 \cong 125^\circ 14'$

Hence, two possible orientations are 54º55' & 125º14'.

Example 13.8 For the electron is $2D_{5/2}$ state, calculate (i) possible values of m_j and J_z, (ii) possible orientations of $\vec{J}$ in vector space.

Sol: For $2D_{5/2}$ state, $l=2, s=\frac{1}{2}$ and $j=\frac{5}{2}$

(i) The possible of $m_j=+\frac{5}{2},+\frac{3}{2}+\frac{1}{2},-\frac{1}{2},-\frac{3}{2},-\frac{5}{2}$ and z-component of total orbital angular momentum

$$J_z=m_j\hbar=\frac{5}{2}\hbar,\frac{3}{2}\hbar,\frac{1}{2}\hbar,-\frac{1}{2}\hbar,-\frac{3}{2}\hbar,-\frac{5}{2}\hbar$$

(ii) Possible orientation of $\vec{j}$ in space are given by

$$\cos\theta=\frac{m_j}{\sqrt{j(j+1)}}=\frac{2m_j}{\sqrt{35}}$$

$\cos\theta=\pm.35,\pm.51,\pm.17$ respectively for $\pm\frac{5}{2},\pm\frac{3}{2},\pm\frac{1}{2}$

13.13 Self Learning Exercise

Q.1 What is the total angular momentum of an atom?

Q.2 What is Bohr magneton ?

Q.3 For an electron in $p_{3/2}$ state, find the values of m_j and j_z.

Q.4 What would be the total quantum number $\vec{j}$ for electron with $l_1=1$ and $l_2=2$.

Q.5 How the different atomic energy levels in atom are designated ?

13.14 Summary

So far, this unit initializes with the description of Vector Atom model, where the atom is treated three dimensional entity rather a two dimensional system. Giving the understanding of the quantization of space and spin, magnetic momenta of the atom have been described. The behavior of atom in the presence of magnetic field has been understood with the concept of precession as Larmor's precession (frequency). Coupling of spin and angular momentum have been understood in the Vector Atom model. Extending the idea of coupling for many electrons system has been summarized. Finally, experimental verification of features of the Vector Atom model has been studied by Stern – Gerlach experiment.

13.15 Glossary

Quantization : It is the process of converting a continuous range of values into a finite range of discreet values.

Orientation : Position or alignment relative to points of the compass or other specific directions

Moment : It is a combination of a physical quantity and a distance. The moment of a force is a measure of its tendency to cause a body to rotate about a specific point or axis.

Precession : It is a change in the orientation of the rotational axis of a rotating body *or* the slow movement of the axis of a spinning body around another axis due to a torque (such as gravitational influence) acting to change the direction of the first axis.

13.16 Answers to Self Learning Exercise

Ans.3: $m_j = +\frac{3}{2}\ to\ -\frac{3}{2}$; $j_z = +\frac{3}{2}\hbar\ to\ -\frac{3}{2}\hbar$

Ans.4: L = 4, 3, 2; S = 1, 0.

13.17 Exercise

Section A : Very Short Answer Type Questions

Q.1 Why the concept of electron spin was introduced ?

Q.2 Comment on angular momentum conservation.

Q.3 What do you understand by Larmor' precession and Larmor's frequency ?

Q.4 What is dipole moment ?

Section B: Short Answer Type Questions

Q.5 For a d-electron, find the value of $\vec{s}, \vec{l}$ and $\vec{j}$.

Q.6 If an electron is in 4d level of hydrogen atom, calculate the magnitude and orbital angular momentum along with its possible z-components.

Q.7 Obtain the orbital states (term values) for electron with $l_1 = 1$ and $l_2 = 2$.

Q.8 Calculate the possible orientations of the total angular momentum vector $\vec{j}$ corresponding to $j = 3/2$ with respect to magnetic field.

Q.9 A beam of electrons enter a uniform magnetic field of flux density 1.2 Tesla. Find the energy difference between the electrons whose spin are parallel and antiparallel to the field.

Q.10 What do you mean by space quantization ? Explain by drawing a suitable diagram.

Q.11 Discuss the origin of vector atom model.

Q.12 What are quantum numbers ? Explain the significance of each in the theory of atom.

Section C: Long Answer Type Questions

Q.13 Derive an expression for total magnetic moment of an atomic electron.

Q.14 What do you mean by spinning of an electron ? How the spin electron coupled with orbital motion of electron ?

Q.15 What are quantum numbers ? Explain the significance of each in the theory of atom.

Q.16 Obtain an expression for Larmor frequency. Calculate it is the case of electron when a magnetic field of 10^4 Weber/m^2 is applied to it.

Q.17 Describe Stern-Gerlach experiment neatly. How it verifies the features of vector atom model ?

Q.18 In Stern-Gerlach experiment, what happens if ions are used instead of atomic beam is non-homogenous magnetic field ?

13.18 Answers to Exercise

Ans.5: For d-electron $l = \sqrt{6}\hbar$; $s = \sqrt{\frac{3}{2}}\hbar$; $j = \sqrt{\frac{35}{2}}\hbar$

Ans.6: $L = \sqrt{6}\hbar$; $L_z = +2\hbar$ to $-2\hbar$

Ans.8: $\theta \cong 392^\circ, 75^\circ, 105^\circ, 140.8^\circ$

Ans.9: $\because V_m = \pm \frac{e\hbar}{2m}\vec{B}$

Energy difference $\Delta V_m = \frac{2e\hbar}{2m}\vec{B} = 1.39 \times 10^{-4}$ eV.

Ans.17: $\because$ Larmor frequency $f = \frac{e}{4\pi m}B$

$e = 1.6 \times 10^{-19}$ C, $m = 9.1 \times 10^{-31}$ kg, $B = 10^4$ Weber/m^2

$f = 1.4 \times 110^{14}$ per second.

Ans.18: In Stern-Gerlach experiment, a beam of neutral atom **–s** is passed in a non homogeneous magnetic field and each atom experiences a transverse force depending upon the orientation of applied field. If ions were used, they would experience Lorentz force instead of transverse force and their deflection would no longer be transverse and hence no traces would be obtained.

References and Suggested Readings

1. Bransden and Joachain, Physics of Atoms and Molecules, (2009), Benjamin Cummings.
2. Raj Kumar, Atomic and Molecular Spectra: Laser , Kedarnath Ram Nath Pub.
3. S.L. Gupta, V. Kumar, R.C. Sharma, Elements of Spectroscopy, Pragati Prakashan.
4. Rajam J B, Atomic Physics (2007), S. Chand & Co., New Delhi.
5. S.N. Thakur and D.K. Rai, Atom, Laser and Spectroscopy, PHI Learning Pvt. Ltd.
6. Fewkes J.H. and Yarwood J. Atomic Physics Vol II (1991) Oxford University Press.
7. Rita Kakkar, Atomic and molecular spectroscopy, Cambridge University Press (2015).
8. http://users.aber.ac.uk/ruw/teach/327/lsjj.php
9. http://www.chem.uwimona.edu.jm/courses/RScoupling.html
10. http://physics.nist.gov/Pubs/AtSpec/
11. http://nptel.ac.in/courses/

UNIT-14
Spin Orbit Interaction and Identical Particles

Structure of the Unit

14.0 Objectives

The fine structure observed in hydrogen spectral lines were first explained by Sommerfeld. He used the relativistic variation of mass of the electron moving into elliptic orbits. A more perfect picture of fine structure was given by Quantum mechanics using spin-orbit coupling and taking into account the relativistic corrections. The current unit describes in detail the spin-orbit interaction and fine structure of hydrogen spectral lines. The chapter also explains the structure of multi electron systems.

14.1 Spin-Orbit Interaction

The spin-orbit interaction, which is the interaction between electron's spin angular momentum ***S*** and its orbital angular momentum ***L*** is responsible for the fine structure of the excited states of one electron systems.

If the electron is moving in an electric filed ***E***, the field can be expressed in terms of a scalar potential *V(r)* as,

$$\boldsymbol{E} = gradV(r)$$

Where, r is the distance between the electron and the nucleus.

The orbital motion of the electron with velocity ***v*** in the electric field ***E*** produces a magnetic field ***B***, which is given by,

$$\boldsymbol{B} = \frac{1}{c^2}\boldsymbol{E} \times \boldsymbol{v} \quad = \frac{1}{c^2 r}\frac{dV(r)}{dr}(\boldsymbol{r} \times \boldsymbol{v})$$

The orbital angular momentum of the electron ***L*** is given by m $\boldsymbol{r} \times \boldsymbol{v}$, so the above expression can be written as

$$\boldsymbol{B} = \frac{1}{mc^2 r}\frac{dV(r)}{dr}\boldsymbol{L}$$

In terms of electron's spin angular momentum ***S***, the magnetic potential energy can be written as

$$\Delta E_{l,s} = -\boldsymbol{\mu_s}.\boldsymbol{B}$$

$\boldsymbol{\mu_s}$ is given by,

$$\boldsymbol{\mu_s} = -g_s(\frac{e}{2m})\boldsymbol{S}$$

where g_s=2. Thus the magnetic potential energy in terms of electron's spin angular momentum can be written as,

$$\Delta E_{l,s} = \frac{e}{m}\boldsymbol{S}.\boldsymbol{B}$$

Substituting for **B,** we get

$$\Delta E_{l,s} = \frac{e}{m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\boldsymbol{S}.\boldsymbol{L}$$

This is the expression for magnetic potential energy in a frame where the electron is at rest. In a frame where, the nucleus is at rest, the energy get reduced by a factor two. The origin of this factor in the spin orbit Hamiltonian on relativistic transformation is known as "Thomas precession". Including the correction factor, the spin-orbit interaction energy can be written as

$$\Delta E_{l,s} = \frac{e}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\boldsymbol{S}.\boldsymbol{L}$$

The above expression can also be expressed in terms of quantum numbers ***l**, s,*and ***j***

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

$$\boldsymbol{J}.\boldsymbol{J} = (\boldsymbol{L} + \boldsymbol{S}).(\boldsymbol{L} + \boldsymbol{S})$$

$$\boldsymbol{J}.\boldsymbol{J} = \boldsymbol{L}.\boldsymbol{L} + \boldsymbol{S}.\boldsymbol{S} + 2\boldsymbol{S}.\boldsymbol{L}$$

Since $\boldsymbol{S}.\boldsymbol{L} = \boldsymbol{L}.\boldsymbol{S},$

$$\boldsymbol{S}.\boldsymbol{L} = \frac{\mathbf{1}}{\mathbf{2}}(\boldsymbol{J}.\boldsymbol{J} - \boldsymbol{L}.\boldsymbol{L} - \boldsymbol{S}.\boldsymbol{S})$$

$$= \frac{\mathbf{1}}{\mathbf{2}}(J^2 - L^2 - S^2)$$

$$= \frac{\mathbf{1}}{\mathbf{2}}[j(j+1) - l(l+1) - s(s+1)]\left(\frac{h}{2\pi}\right)^2$$

Substituting the expression for ***S.L***, the expression for spin-orbit interaction energy can be written as

$$\Delta E_{l,s} = \frac{eh^2}{16\pi m^2c^2}[j(j+1) - l(l+1) - s(s+1)]\overline{\frac{1}{r}\frac{dV(r)}{dr}}$$

This is the general expression for spin-orbit interaction energy of an atom. In the above expression, the average value of $\frac{1}{r}\frac{dV(r)}{dr}$ has been taken over the unperturbed motion since it is not constant during the electron motion.

For a given atom, the average value of $\frac{1}{r}\frac{dV(r)}{dr}$ can be calculated using the potential function ***V(r)***, and the radial probability density.

Spin-Orbit Interaction Energy for Hydrogen like Atom

In case of hydrogen atom, the electron moves in a Coulombian field. The potential energy is given by,

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze}{r}$$

Using this expression for potential in the expression for spin-orbit interaction energy can be written as

$$\Delta E_{l,s} = \frac{Ze^2h^2}{4\pi\varepsilon_0\,(16\pi m^2c^2)}[j(j+1) - l(l+1) - s(s+1)]\overline{\frac{1}{r^3}}$$

where the average value of $\frac{1}{r^3}$ is given as,

$$\overline{\frac{1}{r^3}} = \frac{Z^3}{a_0^3n^3l^3\left(l+\frac{1}{2}\right)(l+1)}$$

$a_0 = 4\pi\varepsilon_0\,\frac{h^2}{4\pi^2me^2}$ is the radius of the smallest Bohr orbit of the Hydrogen atom. Using these, the final expression for the energy reduces to

$$\Delta E_{l,s} = \frac{R_\infty\,\alpha^2Z^4hc}{2n^3l\left(l+\frac{1}{2}\right)(l+1)}[j(j+1) - l(l+1) - s(s+1)]$$

where, $R_\infty = \frac{me^4}{8\varepsilon_0^2h^3c}$ is known as Rydberg constant, and $\alpha = \frac{e^2}{2\varepsilon_0hc} = \frac{1}{137}$ is known as fine structure constant and is dimensionless.

Now, for a single electron system, $S = \frac{1}{2}$

$$j = l \pm \frac{1}{2}$$

Substituting these values of j in the expression for energy, the energy shift corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ can be given as,

$$\Delta E = \frac{R_\infty\,\alpha^2Z^4hc}{2n^3l\left(l+\frac{1}{2}\right)(l+1)}[2l+1]$$

$$\Delta E = \frac{R_\infty \alpha^2 Z^4 hc}{n^3 l(l+1)}$$

This expression shows that,

Heavier atoms $\Longrightarrow$ larger spin-orbit coupling

Larger n $\Longrightarrow$ smaller spin-orbit coupling

14.2 Quantum Mechanical Relativistic Correction

In order to calculate the energy shift, which is due to the relativistic effects, the relativistic Hamiltonian of the electron with rest mass m_0 , can be written as

$$H = K + V$$

where $K = (p^2c^2 + m_0^2c^4)^{\frac{1}{2}} - m_0c^2$ is the relativistic kinetic energy, and *V* is the potential energy.

Substituting for *K*, in the expression for *H* and after simplification, the expression for relativistic Hamiltonian can be written as,

$$H = (p^2c^2 + m_0^2c^4)^{\frac{1}{2}} - m_0c^2 + V$$

$$= \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3c^2} + \cdots \dots \dots \dots . +V$$

The first term is the standard non-relativistic expression for kinetic energy. The second term is the lowest-order relativistic correction to this energy. There the correction to Hamiltonian is,

$$\Delta H_{rel} = -\frac{1}{8m_0^3c^2}p^4$$

This can be considered as a perturbation term, which using equivalent differential operator for *p*, can be written as

$$= -\frac{1}{8m_0^3c^2}\left(-\frac{ih}{2\pi}\frac{\partial}{\partial q}\right)^4$$

$$= -\frac{1}{8m_0^3c^2}\frac{h^4}{16\pi^4}\nabla^4$$

If ψ_0 is the unperturbed wavefunction of the hydrogen atom, the first-order energy shift due to the relativistic correction is given by,

$$\Delta E_{rel} = -\int \psi_0^* \left(\frac{h^4/16\pi^4}{8m_0^3c^2} \right) \nabla^4 \psi_0 d\tau$$

Upon evaluating the integral , the correction in the energy is given as

$$\Delta E_{rel} = -\frac{2R_\infty \alpha^2 Z^4 hc}{n^3}\left(\frac{1}{2l+1} - \frac{3}{8n}\right)$$

where R_∞ is the Rydberg constant, and α is fine structure constant.

14.3 Hydrogen Fine Structure

The term shift due to spin-orbit interaction is given by,

$$\Delta T_{l,s} = -\frac{\Delta E_{l,s}}{hc}$$

Thus the net term-shift due to spin-orbit interaction and relativistic effects, which combine in a liner manner is given by,

$$\Delta \boldsymbol{T} = \Delta T_{l,s} + \Delta T_{rel} = \frac{\Delta E_{l,s}}{hc} + \frac{\Delta E_{rel}}{hc}$$

where the expressions for $\Delta E_{l,s}$ and ΔE_{rel} has been derived in the previous sections.

For a single electron system, $S = \frac{1}{2}$, hence for $j = l + s = l + \frac{1}{2}$ and $j = l - s = l - \frac{1}{2}$, the net term shift is given as

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3}\left(\frac{1}{l+1} - \frac{3}{4n}\right)$$

and

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3}\left(\frac{1}{l} - \frac{3}{4n}\right)$$

In terms of ***j***, the two equations can be combined to a single equation:

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3}\left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right)$$

This equation was also obtained by Dirac using quantum mechanical treatment of hydrogen like atom and hence this equation is also known as Dirac equation.

Sommerfeld's formula: Sommerfeld also derived a relativistic equation for energy levels of hydrogen-like atoms.

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

In his equation $j + \frac{1}{2}$ is replaced by k.

Comparison of energy levels of hydrogen atom

$$R_\infty = 1.097 \times 10^7 m^{-1}, \alpha = \frac{1}{137}, Z = 1\ (For\ hydrogen)$$

Let us consider Bohr levels corresponding to n=1, 2, 3

Bohr level	Sommerfeld levels		Dirac levels		
n	k	ΔT (cm^{-1})	l	$j = l \pm \frac{1}{2}$	ΔT (cm^{-1})
1	1	1.46	0	$\frac{1}{2}$	1.46
2	2	0.091	1	$\frac{3}{2}, \frac{1}{2}$	0.091, 0.456
	1	0.456	0	$\frac{1}{2}$	0.456
3	3	0.018	2	$\frac{5}{2}, \frac{3}{2}$	0.018, 0.054
	2	0.054	1	$\frac{3}{2}, \frac{1}{2}$	0.054, 0.162
	1	0.162	0	$\frac{1}{2}$	0.162

Fig. 1(a), (b),and (c) shows the energy level for hydrogen atom as predicted by Sommerfeld and Dirac for levels n=1, 2, and 3. Both the predictions are similar in case of hydrogen atom.

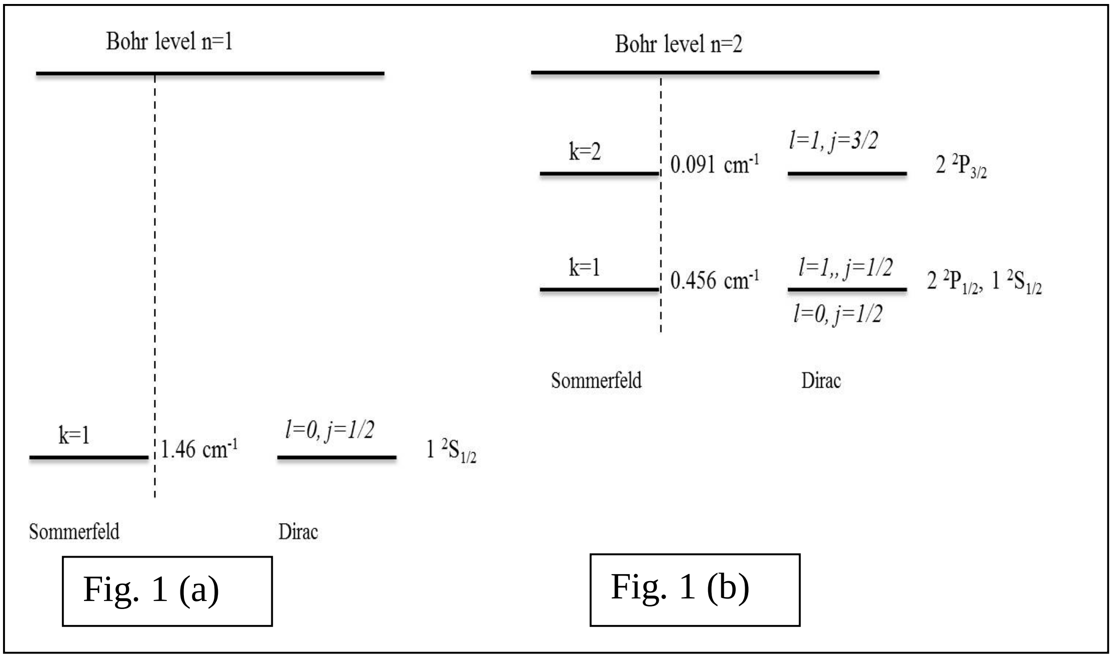


Fig. 1 (a) Fig. 1 (b)

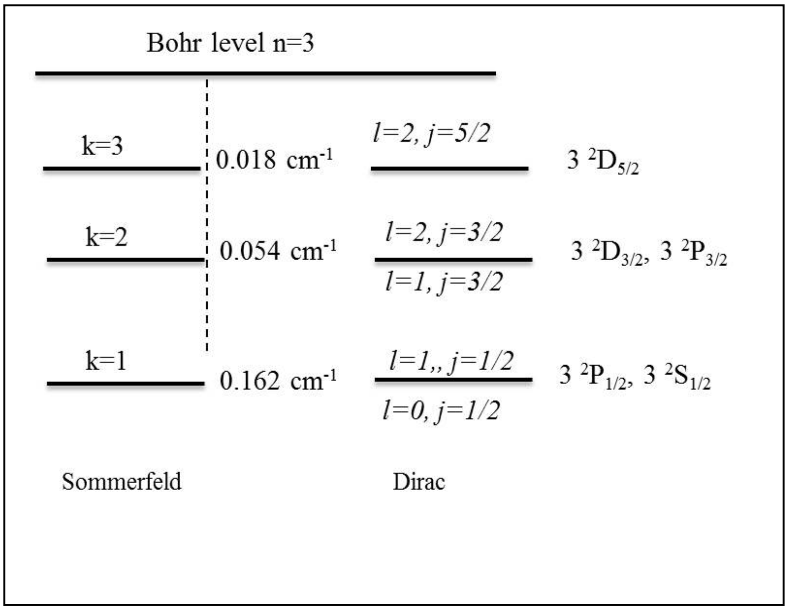
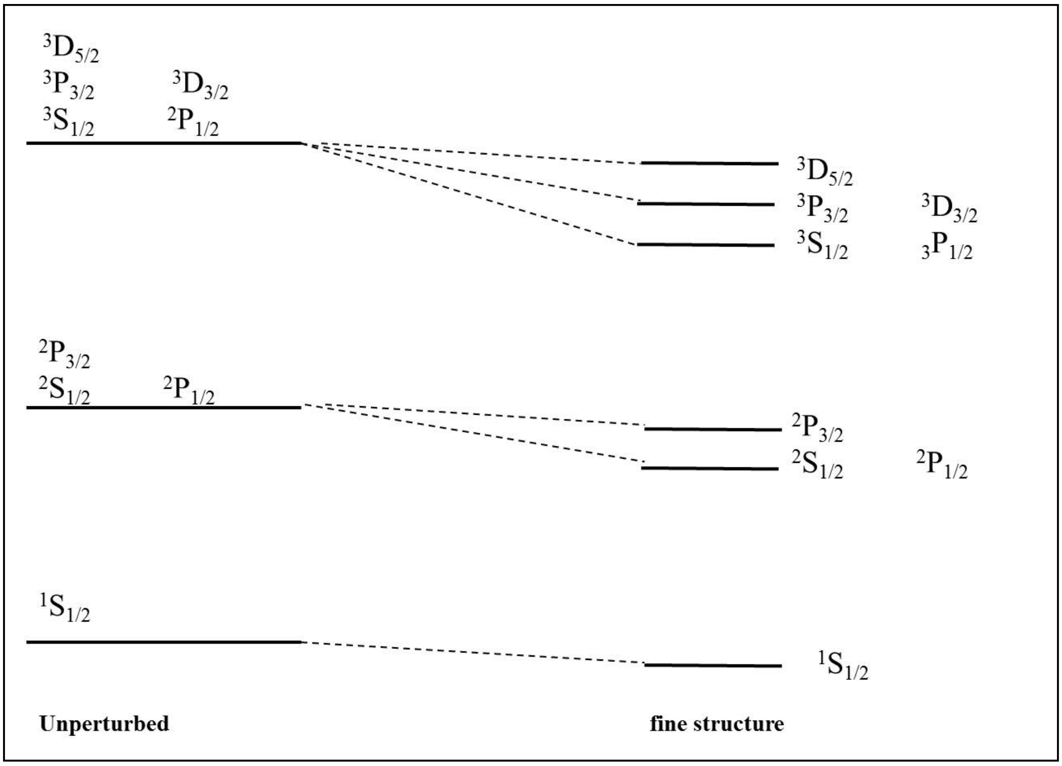


Fig. 1 (c)

Fine Structure of Hydrogen



Effect of the fine structure energy-shift on then=1,2 and 3 states of hydrogen atom.

For n=1, in the absence of fine structure, there are two $^1S_{1/2}$ states. The fine structure induced energy shift is same for both the states. Hence fine structure doesn't break the degeneracy of this state of hydrogen atom.

For n= 2, there are two $^2S_{1/2}$, two $^2P_{1/2}$, and four $^2P_{3/2}$ states. All these states are degenerate. Fine structure breaks the degeneracy of the states relative to $^2P_{3/2.}$

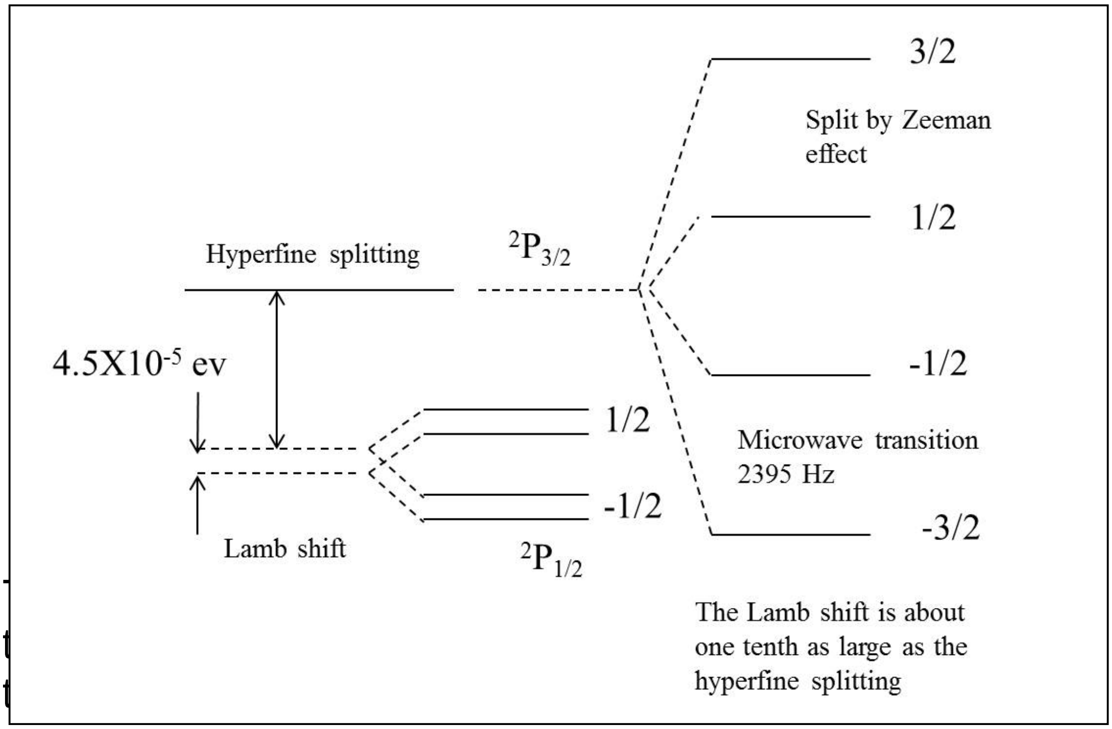
For n=3, there are two $^3S_{1/2}$, two $^3P_{1/2}$, four $^3P_{3/2}$, four $^3D_{3/2}$, and six $^3D_{5/2}$. All of these states are degenerate. Fine structure breaks these states into three groups: $^3S_{1/2}$, and $^3P_{1/2}$, $^3P_{3/2}$, $^3D_{3/2}$, and $^3D_{5/2}$ states.

14.4 Lamb Shift

The Dirac theory applied to hydrogen-like atoms predicts that the energy levels of the hydrogen electron should depend only on the principal quantum number ***n.*** Hence the states with same ***n ,*** and the same total angular momentum quantum number ***j*** are degenerate. Thus, according to Dirac theory, the $2^2P_{1/2}$ and $2^2S_{1/2}$ states of hydrogen are degenerate. However it was found that $2^2P_{1/2}$ was lower than $2\,^2S_{1/2}$. This effect was first measured by Lamb and Rutherford in 1947 in the experiment on the hydrogen microwave spectrum. They showed that for hydrogen-like atoms states of particular n, having same j but different ***l*** values are not degenerate but separated. The shift of the $2^2S_{1/2}$ level above the $2^2P_{1/2}$ level is called *Lamb shift.*

Measurements of Lamb shift:

The Lamb shift is extremely small and is difficult to measure as a splitting in the optical or uv spectral lines. However it is possible to make use of transitions directly between the sublevels by going to other regions of the electromagnetic spectrum. Willis Lamb made his measurements of the shift in the microwave region. He formed a beam of hydrogen atoms in the $2s_{(1/2)}$ state. These atoms could not directly take the transition to the $1s_{(1/2)}$ state because of the selection rule which requires the orbital angular momentum to change by 1 unit in a transition. Putting the atoms in a magnetic field to split the levels by the Zeeman effect, he exposed the atoms to microwave radiation at 2395 MHz (not too far from the ordinary microwave oven frequency of 2560 MHz).



magnetic field splitting of these levels correspond to 1057 MHz. By the Planck relationship, this energy separation was about 4.372×10^{-6} eV.

Significance of the Lamb Shift

When the Lamb shift was experimentally determined, it provided a high precision verification of theoretical calculations made with the quantum theory of electrodynamics. These calculations predicted that electrons continually exchanged photons, this being the mechanism by which the electromagnetic force acted. The effect of the continuous emission and absorption of photons on the electron g-factor could be calculated with great precision.

The tiny Lamb shift, measured with great precision, agreed to many decimal places with the calculated result from quantum electrodynamics. The measured precision gives us the electron spin g-factor as

g=2.002319304386

14.5 Illustrative Examples

Example 1: If the doublet splitting of the first excited state $2^2P_{3/2}$-$2^2P_{1/2}$ of **He⁺** is 5.84 cm^{-1}. Calculate the corresponding separation for **H**.

Sol: The doublet splitting of a one-electron atomic state arising due to spin-orbit interaction is given by

$$\Delta T = \frac{\Delta E}{hc} = \frac{R_\infty \alpha^2 Z^4}{n^3 l(l+1)}$$

where R_∞ is Rydberg constant, α is fine structure constant, and Z is atomic number.

For a given state (n, *l* constant), $\Delta T \propto Z$

For **He^+,** Z=2 and for **H**, Z=1. Hence,

$$\frac{\Delta T_{He^+}}{\Delta T_H} = \frac{(2)^4}{(1)^4} = 16$$

$$\Delta T_H = \frac{1}{16} \Delta T_{He^+}$$

$$\Delta T_H = \frac{1}{16} \times 0.584\ cm^{-1}$$

$$\Delta T_H = 0.365\ cm^{-1}$$

14.6 Self Learning Exercise-I

Q.1 What is the significance of quantum number J ?

Q.2 What J is equal to ?

Q.3 What is Rydberg constant ?

Q.4 What is the value of fine structure constant ?

Q.5 The doublet splitting of the first excited state $^2P_{3/2}$- $^2P_{1/2}$ of H atom is 0.365 cm^{-1}. Calculate the corresponding separation for Li^{++}.

14.7 Identical Particle exchange Symmetry of Wavefunctions

Identical particles: A system is said to be consist of identical particles if on interchanging the position and co-ordinates of any two particles there is no way to know that a change has been made in the system.

In classical description of system containing identical particles, a label can be assigned to identical particles. For e.g., in a box containing electrons, the electrons can be labeled as *a* and *b*. While the electrons travel in their well-defined trajectories, at any given instance it can be told that which electron is *a* and which electron is *b*. However, in a quantum mechanical description it will not be possible as the uncertainty principle doesn't allow us to observe the motion of the electron without disturbing the system. Though it can be stated that at a given point of time an electron was located but not which electron it was. In other words, due to the overlapping of the wavefunctions of the two electrons, it is impossible to say which wavefunction was associated with which particle. Therefore, the indistinguishability of identical particles must be taken into account in the quantum mechanical description of identical particles.

Consider a system of two electrons. The Hamiltonian for the system can be written as $H = H_a + H_b$ where H_a , and H_b are the hamiltonians for the individual electrons.

The wavefunction for the system can be written as the product of the individual wavefunctions.

$$\psi(a,b) = \psi(a)\psi(b)$$

If the electron *a* is in state 1, and electron b in state 2, then the total wavefunction can be written as

$$\psi(a,b) = \psi_1(a)\psi_2(b)$$

$$\psi_{12} = \psi_1(a)\psi_2(b)$$

The probability density function for this system will be

$$\psi_{12}^*\psi_{12} = \psi_1^*(a)\psi_2^*(b)\psi_1(a)\psi_2(b)$$

On interchanging the states i.e. electron *a* is in state 2, and electron b in state 1, the total wavefunction will be,

$$\psi_{21} = \psi_2(a)\psi_1(b)$$

The probability distribution function for this new arrangement would be

$$\psi_{21}^*\psi_{21} = \psi_2^*(a)\psi_1^*(b)\psi_2(a)\psi_1(b)$$

Since the electrons are indistinguishable, changing the labels should not change any of the physically measurable quantity. If we change the labels in $\psi_{12}^*\psi_{12}$, then

$$\psi_1^*(a)\psi_2^*(b)\psi_1(a)\psi_2(b) \rightarrow \psi_1^*(b)\psi_2^*(a)\psi_1(b)\psi_2(a)$$

This interchange leads to the distribution function $\psi_{21}^*\psi_{21}$ which is different than $\psi_{12}^*\psi_{12}$. Thus merely changing the labels of the electrons resulted into the change of the probability density. Hence for a two electron system, the wavefunctions described above doesn't properly represent the system.

Consider a system of ***N*** particles. Let us say that the total wavefunction of the system is ψ(a,b,…..N). As we know that the Hamiltonian of a system is invariant with respect to the position and spin of the particles, let us consider an operator $\boldsymbol{C_{ab}}$, whose action is to interchange the coordinates of any two particles. i.e.

$$\boldsymbol{C_{ab}}\psi(a,b,\ldots..N) = \psi(b,a\ldots..N)$$

$\boldsymbol{C_{ab}}$ is also linear like parity operator.

$$\boldsymbol{C_{ab}}\,\psi = \alpha\psi$$

where α is the eigenvalue. Operating once more,

$$\boldsymbol{C_{ab}^2}\,\psi = \alpha^2\psi$$

By definition, the operator after two operations brings back the system into the original state. Hence

$$\boldsymbol{C_{ab}^2}\,\psi = \psi$$

So that $\alpha^2 = 1$

Or, $\alpha = \pm 1$

Thus, $\boldsymbol{C_{ab}}\psi(a,b,\ldots..N) = \pm\,\psi(a,b\ldots..N)$

On comparison we get,

ψ(b,a,………..N)=± ψ(a,b,………..N)

Thus if the two particles of the system are changed, the wavefunction either remain unchanged or changes its sign. Thus with respect to the exchange of the particles, the wavefunctions are either symmetric or antisymmetric.

The particles, which can be described by symmetric wavefunction are known as bosons . Thus for a boson,

ψ(a,b,………..N)=+ ψ(b,a,………..N)

All particles having integer spins are bosons.

The particles which can be described using antisymmetric wavefunction are known as fermions. Thus for a fermion

ψ(a,b,………..N)=- ψ(b,a,………..N)

Particles having half-integral spin are known as fermions. Electrons are fermions.

14.8 Formulation of Pauli's Principle

Wolfgang Pauli, in 1925, gave his exclusion principle to explain the arrangement of electrons in an atom according to which, "no two electrons in an atom can have identical quantum numbers". This is an example of a general principle which applies all the particles having half-integer spin (fermions). It does not apply to particles of integer spin (bosons).

Consider a system of two identical and non-interacting particles *a*, and *b*. The total Hamiltonian of the system can be written as,

$$\boldsymbol{H} = \boldsymbol{H_a} + \boldsymbol{H_b}$$

Where $\boldsymbol{H_a}$, and $\boldsymbol{H_b}$ are Hamiltonians for separate particles. The wavefunction for the two electron system would be

$$\psi(a,b) = \psi(a)\psi(b)$$

If the particle a is in quantum state 1,and particle b is in quantum state 2, then the combined wavefunction of the system is

$$\psi_{12}(a,b) = \psi_1(a)\psi_2(b)$$

If the particles exchange their respective states, the new wavefunction would be

$$\psi_{21}(a,b) = \psi_2(a)\psi_1(b)$$

Since the particles are identical and indistinguishable, both ψ_{12} and ψ_{21} will equally describe the system. Hence a linear combination of these two will be more appropriate to describe the system. Thus

$$\psi(a,b) = \frac{1}{\sqrt{2}}[\psi_1(a)\psi_2(b) \pm \psi_2(a)\psi_1(b)]$$

where, $\frac{1}{\sqrt{2}}$ is the normalization factor. With the exchange of co-ordinates, this wavefunction is either symmetric (+ sign) or ant symmetric (-sign).

Symmetric $\psi_{Bosons}(a,b) = \frac{1}{\sqrt{2}}[\psi_1(a)\psi_2(b) + \psi_2(a)\psi_1(b)]$

Antisymmetric $\psi_{Fermions}(a,b) = \frac{1}{\sqrt{2}}[\psi_1(a)\psi_2(b) - \psi_2(a)\psi_1(b)]$

Thus, if both the particles are in same state,

$$\psi_{Bosons}(a,b) \neq 0$$
$$\psi_{Fermions}(a,b) = 0$$

Thus, no two fermions can occupy the same quantum states. It can be stated as, in a multi-electron system, it is impossible for two electrons to have the same values of all the quantum numbers. Another statement is that, with respect to the exchange of the particles, the total wavefunction for two identical fermions is antisymmetric. This means that the wavefunction changes its sign if the space *and* spin co-ordinates of any two particles are interchanged. In other words, it can also be stated as if two particles are described by antisymmetric wavefunction, they cannot occupy the same quantum state. Thus a multielectron system must be described by an antisymmetric wavefunction.

14.9 Atomic Orbits and the Hund's Rule

Filling of subshells having more than one orbital are done according to the ***Hund's rule.*** In 1927 Hund formulated two empirical rules.

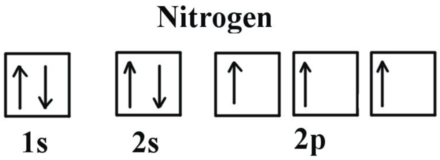
Hund's rule -I: Of the states arising from a given electron configuration, the lowest in energy is the one having highest multiplicity. In other words, electron pairing will not take place in orbitals of same energy (same sub-shell) until each orbital is first singly filled with parallel spin. This is known as Hund's rule of maximum multiplicity.

Hund's rule -II: For a given multiplicity, the lower in energy is the one with higher L value.

In the process of assigning the electrons to an orbital, the electron first fill all the orbitals having same energy before it pairs with another electron in a half-filled orbital. The atoms in their ground states tend to have as many unpaired electrons as possible.

For *Example : Nitrogen Atoms*

Consider the correct electron configuration of the nitrogen (Z = 7) atom: $1s^2\ 2s^2\ 2p^3$



The p orbitals are half-filled; there are three p orbitals and three electrons. This is because the three electrons in the 2p subshell will fill all the empty orbitals first before pairing with electrons in them.

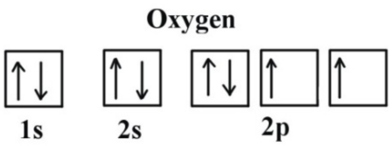
Hund's Rule Explained

According to the first rule, an electron first fills an empty orbital before it decides to pair up. Negatively charged electrons repel each other. Hence to minimize the repulsion, electrons tend to occupy their own orbitals rather than sharing an orbital with another electron. Furthermore, the calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

For the second rule, unpaired electrons in singly occupied orbitals have the same spins. Once the spin of the first electron in a sublevel is chosen, however, the spins of all of the other electrons in that sublevel depend on that first spin.

Example: Carbon and Oxygen

Consider the electron configuration for carbon atoms: $1s^2 2s^2 2p^2$: The two 2s electrons will occupy the same orbital, whereas the two 2p electrons will be in different orbital (and aligned the same direction) in accordance with Hund's rule.



Consider also the electron configuration of oxygen. Oxygen has 8 electrons. The electron configuration can be written as $1s^2 2s^2 2p^4$. To draw the orbital diagram, begin with the following observations: the first two electrons will pair up in the 1s orbital; the next two electrons will pair up in the 2s orbital. That leaves 4 electrons, which must be placed in the 2p orbitals. According to Hund's rule, all orbitals will be singly occupied before any is doubly occupied. Therefore, two p orbital get one electron and one will have two electrons. Hund's rule also stipulates that all of the unpaired electrons must have the same spin. In keeping with convention, the unpaired electrons are drawn as "spin-up"..

14.10 Illustrative Examples

Example 1: Show that the total number of electrons in a shell is $2n^2$, where n is the principle quantum number of the shell.

Sol: To define the state of an electron, we need a set of four quantum numbers:

n, l, m_l, and m_s.

For a given n, the azimuthal quantum number l, can take values

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

For each l, m_l can take values:

$m_l = -l, \ldots 0, \ldots\ldots +l$

that is a total of $(2l+1)$ values. For each of these values, the magnetic spin quantum number m_s, can be either +1/2 or -1/2. Thus for a given l, there are $2(2l+1)$ sets of quantum numbers. Summing over all the possible values of l, for a given n, the number of the possible sets of quantum numbers l, m_l, m_s,

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

$$=2[1+3+5+7+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2(n-1)+1]$$

$$=2[1+3+5+7+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2n-1]$$

$$=2 \times \frac{n}{2}[1+2n-1] = 2n^2$$

14.11 Self Learning Exercise-II

Q.1 Calculate the energy of transition involving $n_1=6$ to $n_2=3$ in a hydrogen atom.

Q.2 What are the ground state configuration of

(a) Ar (b) K (c) Cl

Q.3 State Hund's rule.

Q.4 Calculate the wavelength of first line in Lyman series of hydrogen spectrum.

Q.5 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n= 2 of He^+ spectrum ?

14.12 Summary

The current unit summarizes the observed fine structure in hydrogen spectral lines. The quantum mechanical description of spin-orbit interaction has been discussed in detail. The model by Sommerfeld uses classical mechanics to evaluate the energy shift while the theory by Dirac has used quantum mechanical description. The theory by Dirac predicted a double-degeneracy of most levels. The fine structure of H_α lines has also been discussed. A quantum mechanical description of multi-electron systems and Pauli's exclusion principle has also been discussed in detail.

14.13 Glossary

Shell : Orbitals with same value of the principal quantum number *n* comprise a shell.

Energy level : In an atom a location or orbital above the ground state in which an electron is found when it gains a specific amount of energy.

Energy-level diagram : A diagram showing the arrangement of an atom's energy levels.

Excited state : A state of an atom ion or molecule with a higher energy than the ground state.

Balmer line : An emission or absorption line in the spectrum of hydrogen caused by an electron transition between the second and higher energy levels.

14.14 Answers to Self Learning Exercises

Answers to Self Learning Exercise – I

Ans.1: In lighter elements, spin-orbit coupling is small, while in heavier elements it is large. Hence the new quantum number j becomes important. This quantum number gives the total angular momentum.

Ans.2: $j=l+s$

Ans.3: See section 14.1.

Ans.4: Fine structure constant α=1/137

Ans.5: 29.6 cm^{-1}

Answers to Self Learning Exercise – II

Ans.1: -1.819×10^{-19} J

Ans.2: (a)$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(b)The abbreviated electron configuration for potassium is: K [Ar] $4s^1$

(c)The configuration for chlorine is: Cl $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$.

Ans.3: See section 14.9

Ans.4: 1215 A^0.

Ans.5: The transition n_2=2 to n_1=1 (Lyman series) in hydrogen atom has the same wavelength as the Balmer series transition n_2=4 to n_1=2 of of He^+ spectrum

14.15 Exercise

Q.1 Calculate the spin-orbit interaction splitting of a level corresponding to n=2 and ***l***=1 of hydrogen atom.

Q.2 Show that f orbital can accommodate 14 electrons ?

Q.3 A state is denoted as $^4D_{5/2}$. What are its values of ***l**,s,**j***.

Q.4 The numerical value of the first orbit of hydrogen is ?

Q.5 What is the value of Rydberg constant for hydrogen ?

14.16 Answers to Exercise

Ans.1: 0.365 cm^{-1}

Ans.2: See section 14.10 Example 1.

Ans.3: *s=3/2, **l**=2, **j**=5/2*

Ans.5: See section 14.1.

References and Suggested Readings

1. C. N. Banwell and E. M. McCash, Fundamentals of Molecular Spectroscopy, 4thEd., Tata-McGraw-Hill, 1994.
2. G. Aruldhas, Molecular Structure and Spectroscopy ,PHI Learning Pvt. Ltd., 01-Feb-2004
3. H. S. Randhawa, Modern Molecular Spectroscopy, McMillan India Ltd., 2003

UNIT-15
LS & jj Couplings

Structure of the Unit

15.0 Objectives

In the following discussion, we will study the characteristics, namely, the spectra of elements, that have two or more than two electrons in their valence shell, for which one has to follow the various coupling schemes, as these facilitate the understandings of possible transitions occur in between the filled/half filled shells. Thus, the possibilities and effects of *LS*- and ***jj***- couplings will be of our main discussion as these have direct consequences in the atomic spectra. New Terms (states) arise after the various interactions, are of great importance, have been explained. Further, some restrictions, namely, selection rules, Hund's rules, and Lande's interval rules are important to study the exact behavior of atomic transitions and thus experimental spectra, thus have been paid attention.

15.1 Introduction

The spectra of elements (Be, Mg, Ca, Zn, Sr, Ba, Cd and Hg) resemble with the spectrum of He in same way. During the excitation of atoms, the excitations of either single electron or both electrons are possible resulting into the spectra. Due to two valence electrons, the choice for the transition increases and therefore, we obtain a large number of spectra lines of these alkaline-earth elements. The series, like principal, sharp, diffuse and fundamental are observed, where one corresponds to singlet and other belongs to triplet. It has been found that energy levels are also influenced when a single electron transition takes place between these, which is not the same as in the case of alkali elements. To understand the spectra of alkaline earths, it was proposed that, (i) all s vectors ,all ***l*** vectors are strongly coupled individually with little effect of s vector on ***l*** vector individually, and (ii) the s vector of single electron combined with ***l*** vector of same electron to give ***j*** with negligible influence on other electrons and thus, finally we get single resultant *J*. The wide spectrum containing number of lines is obtained when suitable *selection principle* is applied to the quantum number *J*. Therefore, we get the resultant vectors *S*, *L* and *J* which are governed by the selection principles.

15.2 Coupling Schemes

The atoms may have two or more electrons with different orbital and spin momenta, therefore there are many ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together and varied. The interactions that can occur are of three types. (*note: A brief about the coupling has been discussed in the section 13.7 & 13.8*)

(a) *Orbit-Orbit (l-l) coupling* :

For any electron in the atom, potential energy of repulsion is similar in magnitude to that due to the attraction by the nuclear charge. Under the assumption, each electron is described with orbital quantum number l_i that can have certain discrete values. Resultant angular momentum of an atom, which in turn will also have discrete values, is obtained by vector addition of the individual l_i yielding its value that depends on the number, the magnitude & direction of each of the electron's angular momentum.

For two valence electrons atom, resultant angular momentum is given by $L = \sum l_i$ (termed as ***ll***- or orbit-orbit coupling) with maximum value when all the moments are in the same direction, i.e. $L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2)..........., |l_1 - l_2|$. Further, the electrons do influence one another's motion and thus this interaction has the effect that l's are no longer constant in time; rather possesses precessional motion about the resultant analogous to the precession of ***l*** and s about their resultant ***j***. Stronger the interaction, greater will be the precessional velocity of the electrons which is reflected in the separations of different values of *L* (Terms of an atom). The Terms having $L = 0,1,2,3,4......$ are designated as S, P D, F…. respectively. In general, the term values for various configurations of two electron system are given below:

l_1	l_2	Electrons	L	Term Symbols
0	0	s, s	0	S
0	1	s, p	1	P
0	2	s, d	2	D
1	1	p, p	2, 1, 0	D, P, S

1	2	p, d	3, 2, 1	F, D, P
2	2	d, d	4, 3, 2, 1, 0	G, F, D, P, S

For three electrons system, vector addition of each of L (derived taking two electrons) is taken with ***l*** of third electron to obtain the final states/ Terms.

(b) *Spin-Spin (s-s) coupling* :

Electrostatic forces, apart from the orbital motion, also affect the spin motion of electrons. As in the case of orbital angular momentum, one can obtain the resultant spin of the atom by taking that spins of the individual electrons in an atom, are either parallel or antiparallel to one another. The resultant spin motion of a system of several electrons is derived exactly the same way as for the orbital angular momentum; that is by taking vector addition of individual spin angular momentum, $S = \sum s_i$ (termed as ss- or spin-spin coupling). Since spin angular momentum of individual electron can be $\pm\frac{1}{2}\hbar$, their resultant, *S* will also have only discrete values with maximum when all the spins are in the same direction and minimum of 0 or 1/2, respectively depending upon whether the number of electrons is even or odd.

The electron spins in helium can be either $\uparrow\downarrow$ (anti-parallel) or $\uparrow\uparrow$ (parallel) giving *S* = 0 or 1, respectively. So is the case with all two valence electrons systems. Obviously, there will be two different Term series, one with *S* = 0 and second having *S* = 1. In three electrons system, spin directions can be $\uparrow\downarrow\downarrow$ or $\uparrow\uparrow\downarrow$ and $\uparrow\downarrow\uparrow$ or $\uparrow\uparrow\uparrow$. As the electrons are indistinguishable, first three combinations yield *S* = 1/2 and the fourth gives *S* = 3/2. The magnitude of the resultant spin is given by $S = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2)............, |s_1 - s_2|$

(c) *Spin-Orbit (s-l) coupling*: This occurs between the resultant spin and orbital momenta of an electron which gives rise to *J*, the total angular momentum quantum number.

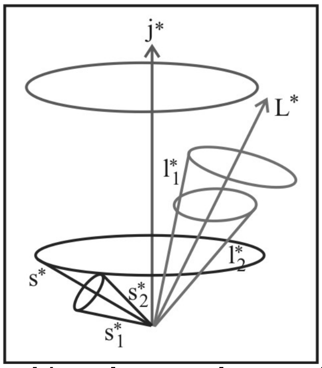
Mainly, there are two principal coupling schemes used:

(i) Russell-Saunders or LS- coupling

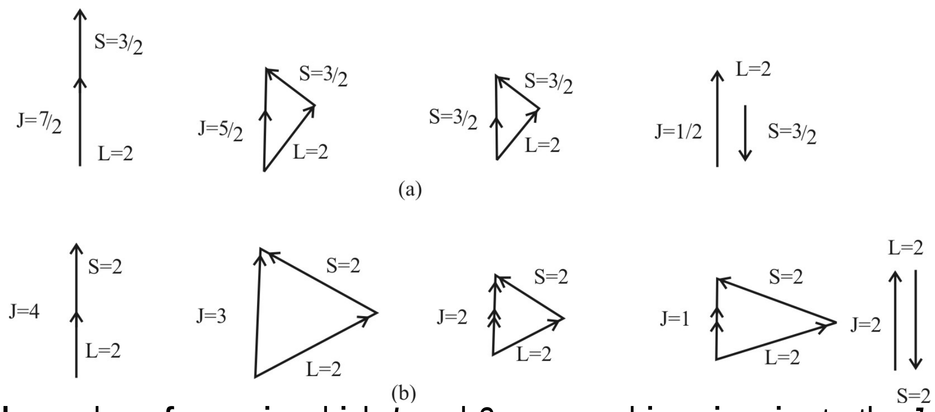
(ii) jj- coupling

15.2.1 Russell-Saunders (LS) Coupling:

The orbital angular momenta of the electrons are coupled to give a total orbital angular momentum $L = \sum l_i$ and (ii) The spins of the electrons are coupled to give a total spin $S=\sum s_i$. Strong coupling of ***l***'s and *s*'s is electrostatic in nature. In addition to these electrostatic forces, there are magnetic forces, one due to orbital motion of the electrons and another caused by their spin motions. These motions about their respective resultants provide the magnetic moments (μ_L because of orbital and μ_S due to spin motions). These two interact weakly. One may visualize as if a small magnet of magnetic moment μ_S is subjected to an internal magnetic field of magnetic moment μ_L . This weak interaction will make *L* and *S* to precess around their resultant, *J*. Therefore, like that of the precession of ***l*** and *s* about their resultant ***j***, the relative motion of *L* and *S* is governed by their resultant which remains not only fixed in space but also constant in time. That is, *L* and *S* perform precessional motion together as a rigid body about their resultant J. The combination of a particular *S* value with a particular *L* value comprises a spectroscopic *term*, the notation for which is ^{2s+1}L . The quantum number 2*S* + 1 is the *multiplicity* of the term. The ***S*** and ***L*** vectors are coupled to obtain the total angular momentum, ***J = S + L***, for a level of the term; the level is denoted as $^{2s+1}L_j$. *J* will be an integer (0,1,2,3…) when *S* is an integer for even number of electrons and J will be an half integer (1/2, 3/2, 5/2, …..) when *S* is a half integer for odd number of electrons. Coupling of l 's to *L* and *s*'s to *S* and finally the coupling of *L* and *S* to yield the resultant angular momentum *J* is termed as LS- coupling or Russell- Saunders coupling, shown below.



For example, an atom with only one electron in ground state (***l*** = 0), *L* will have only one value 0, since the value of *S* is ½ and thus *J* = +1/2. While for an atom having two electrons such that one with ***l*** = 0 and other in excited state with ***l*** = 1, then $L=l_1+l_2$ an $S=s_1+s_2$ gives: *L* = 1 and *S* = 1 (if electron spins are parallel) or *L* = 1 and *S* = 0 (if electron spins are anti-parallel).Therefore, *J* = 0, 1, 2 are designated by $^3P_0$, $^3P_1$, $^3P_2$, i.e. P state is splitting into triplet.

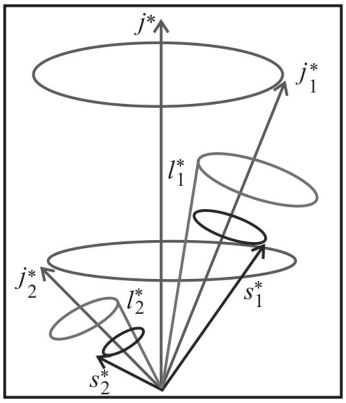


Possible number of ways in which L and S may combine give rise to the J values (non negative) are $(2S+1)$ if L>S and $(2L+1)$ if L<S. This type of coupling is commonly used in explaining the spectra of second group.

In this coupling scheme, it is assumed that: spin-spin coupling > orbit-orbit coupling > spin-orbit coupling. It is a good approximation for lighter atoms (say up to atomic number 30 or so); for higher atomic number spin-orbit coupling is more prominent leading to ***jj***- coupling scheme

15.2.2 jj- Coupling:

Consider a two valence electrons atom, one with quantum numbers l_1 and s_1 and the second with l_2 and s_2. Different types of interactions among the four quantum numbers are possible. First, l_1 interacts strongly with l_2 yielding L and s_1 with s_2 leading to S; finally L couples weakly with S to form LS-coupling. Second possibility, though rare one, is l_1 may interact with spin s_2 of the other electron and l_2 with spin s_1 of the first. Such inter electrons interactions are very weak to observe; therefore will not be considered. Third possibility is predominant & frequent in heavy atoms (large volume) where the electrons are situated at larger distances and the electrostatic interaction among them diminishes in comparison with the interaction of individual electron's orbital motion with its own spin motion. Thus, l_1 interacts strongly with its own spin $s_1(j = l + s)$ leading to resultant angular momentum j_1 of one electron and l_2 with its own s_2 to yield j_2 for the second electron; finally j_1 couples weakly with j_2 to form ***jj***-coupling. The total angular momentum of the atom is given by $J = \sum j_i$. Therefore, for two valence electrons atom $J = (j_1 + j_2), (j_1 + j_2 - 1), (j_1 + j_2 - 2)............, |j_1 - j_2|$. The coupling scheme is shown in the next figure , where *LS*- coupling, i.e. orbital and spin angular moments are combined horizontally, then vertically ***jj***- coupling, i.e. orbital and spin angular moments are combined vertically, then horizontally.



15.3 Selection Rules for Two Valence Electrons

If two electrons contribute in producing the spectra then only those transitions are allowed in which two electrons jump with the emission of radiations of single frequency. On the other hand if only one electron transits ,then value of ***l*** changes by unity and of other does not change and if both electrons transit such that ***l*** values change by unity and the other does not change or change by two. In these two types of coupling due to other terms, additional conditions are also required-

(i) In L-S coupling: $\Delta L = 0, \pm 1$; $\Delta S = 0$; $\Delta J = 0, \pm 1$ ($0 \to 0$ not allowed).

(ii) In j-j coupling: $\Delta j_1 = 0$; $\Delta j_2 = 0$ or ± 1; and $\Delta J = 0, \pm 1$ ($0 \to 0$ not allowed).

Quantum mechanically, even terms combine with odd terms and odd terms combine with even terms. The even terms are those for which $l_1 + l_2$ = even and others are odd.

It has been observed that presence of extra electrons other than valence electrons, the spectra become complicated (e.g. spectra of Hg is more complicated than of He). As the number of more than two electrons increases, the complexity increases because of number of terms arises due to various combinations of spin and orbital vectors. In complex spectra, in addition to ordinary series of singlet, doublet and triplet, there exists a multiple level of series like four, five, six, seven or eight with equal spaced. Experimentally, it has been found that these levels are either all or all odd in the spectrum.

Following table lists resultant spin quantum number and the possible multiplicities for various numbers of electrons.

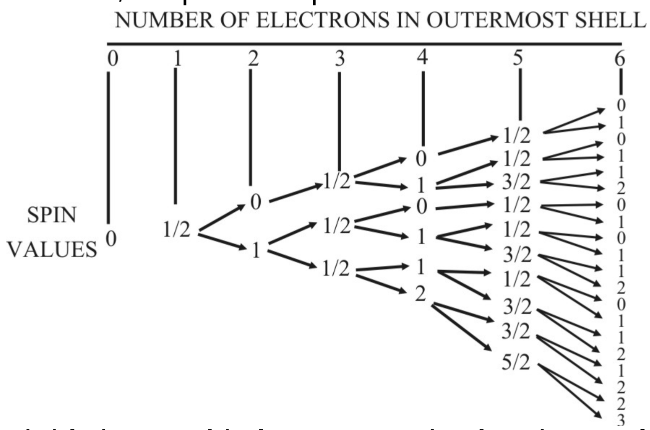
No. of Electrons	Spin Values	Possible Mulitplets (2S+1)
1	1/2	2 (Doublet)
2	0,1	1 (Singlets), 3 (Triplets)
3	½, 3/2	2(Doublets), 4 (Quartets)
4	0,1,2	1 (Singlets), 3 (Triplets), 5 (Quintets)
5	½, 3.2, 5/2	2 (Doublets), 4 (Quartets), 6 (Sextets)

15.4 Terms in Many Electron System

Due to the contribution of additional terms, the atoms have been classified broadly into two categories: the one, in which spin-spin correlation as deciding factors has LS- coupling, and the other class in which spin-orbit interaction predominates has j-j coupling.

15.4.1 Terms due to LS- coupling:

To find out the possible terms, Branching rule is used according to which if the atom is ionized completely, the electrons return to it one after the another to form a neutral atom. Thus, the possible spin combinations can be found out.



We can understand this by considering an atom having three valence electrons in following way:

(i) Consider an atom having three valence electrons like *2s 3p 4d*.

(ii) To find the possible values of S, spin of two electrons are combined first and the third electron is allowed to combine with each of them. From the above branching scheme, two sets of doublet ($S = 1/2$) states and one set of quartet ($S = 3/2$) are observed.

(iii) For the L values, first combining the orbital motions of first two electrons and then combined the third one with each of them. Combination of first two p states results (l + 1) to (l - 1) values, i.e. 2, 1, 0, known as terms S, P, D.

(iv) Now, third d electron is added to these three terms as

$$S + d \rightarrow 0 + 2 = 2 \qquad\qquad \rightarrow D$$

$$P + d \rightarrow (2+1)\,to\,(2-1) \rightarrow 3, 2, 1 \qquad \rightarrow F, D, P$$

$$D + d \rightarrow (2+2)\,to\,(2-2) \rightarrow 4, 3, 2, 1, 0 \rightarrow G, F, D, P, S$$

(v) Finally, introducing LS- coupling gives rise to J states, i.e. $J = L \pm S$.

The two sets of doublet will have the following states-

$^2D_{3/2,5/2}$

$^2F_{5/2,7/2}$, $^2D_{3/2,5/2}$, $^2P_{1/2,3/2}$,

$^2G_{7/2,9/2}$, $^2F_{5/2,7/2}$, $^2D_{3/2,5/2}$, $^2P_{1/2,3/2}$, $^2S_{1/2}$,

i.e. total 34 terms. In quartet set, the following we have

$^4D_{1/2,\,3/2,\,5/2,7/2}$,

$^4P_{1/2,\,3/2,\,5/2}$ $^4D_{1/2,\,3/2,\,5/2,7/2}$ $^4F_{3/2,\,5/2,\,7/2,9/2}$,

$^4S_{3/2}$ $^4P_{1/2,\,3/2,\,5/2}$ $^4D_{1/2,\,3/2,\,5/2,7/2}$ $^4F_{3/2,\,5/2,\,7/2,9/2}$ $^4G_{5/2,\,7/2,\,9/2,11/2}$,

i.e. in all 31 terms. Thus, total 65 distinct levels.

15.4.2 Terms due to jj- coupling:

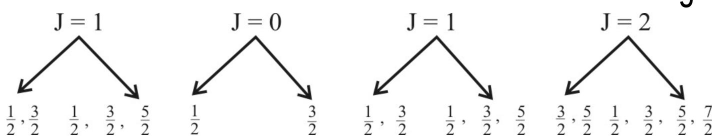
Here we consider only the addition of one electron to parent system, generated with one or more valence electrons. Meaning of parent system is, the energy level of an ionized atom to which we add another electron via. jj- coupling to form new energy level for neutral atom.

Let us understand this with a simple example. Consider a parent system having sp configuration and we are going to add p electron to this system. Possible terms of parent system are as follows:

$$l_1 \pm s_1 = j_1 = 1/2$$

$$l_2 \pm s_2 = j_2 = 1/2,\ 3/2$$

Thus, $J = j_1 \pm j_2 = 1, 0, 1, 2$. Now, then adding up the p electron has j values ½ or 3/2 to these and thus the final total 18 terms will have the following J values.



15.5 Terms in Equivalent Electron System

15.5.1 LS- Coupling:

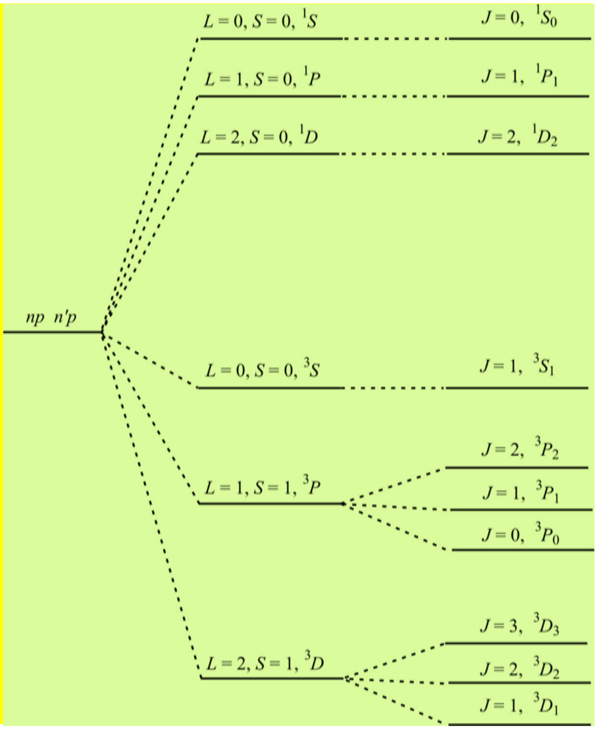
We understand this by the following cases-

(i) ***Two s- electrons (Unexcited He atom)***: Here we have $l_1 = 0$, $l_2 = 0$ and $s_1 = 1/2$, $s_2 = 1/2$. To know the possible terms, following the same procedure as outlined in section 15.5.1, the spin combination results to S = 0 and 1, for which there is only one possible L value, i.e. $L = 0$. Thus the terms are $^3S_1$ and $^1S_0$. Let as assume that if the electrons have principal quantum number $n = 1$ and $n = 2$, i.e. one electron is in excited state then the lowest existing state will be $^3S_1$. But for the unexcited state, two electrons will be completely in same structure and thus become indistinguishable, the ground state of helium atom is $^1S_0$.

(ii) ***Two p- electrons (Unexcited carbon atom)***: Very first, let us consider the case of *two non-equivalent pp- electrons*, i.e. say np and np'. The following calculation give rise to the possible terms-

$$l_1 = 1, l_2 = 1 \Rightarrow L = 2,1,0 \text{ and } s_1 = s_2 = 1/2 \Rightarrow S = 1,0$$

Therefore, the Terms are: ^3D, ^3P, ^3S (triplets) and ^1D, ^1P, ^1S (singlets); six in all. J values for each of the triplet and singlet states are:



For $^3D, J = 3,2,1$; Terms are $^3D_3, {}^3D_2, {}^3D_1$ $({}^3D_{3,2,1})$. Each will have slightly different energy. For $^3P, J = 2,1,0$; Terms are $^3P_2, {}^3P_1, {}^3P_0$ $({}^3P_{2,1,0})$. Each will have slightly different energy. For $^3S, J = 1$; Term is $^3S_1$. It may be written as ^3S since J is equal to S. For $^1D, J = 2$, Term is $^1D_2$; For $^1P, J = 1$, Term is $^1P_1$; For $^1S, J = 0$, Term is $^1S_0$. Like in triplets case, *J* value of the singlet *S* is not usually written.

Now we switch over to the case of the *equivalent pp- electrons*, then the Pauli's principal restricts the combination which have the same set of quantum numbers. Whereas, for non-equivalent electrons, values of *n* & or *l* are different implying that Pauli's principle is satisfied. However, when *n* and *l* are same then m_l and or m_s must have different values to meet the requirements of Pauli's Exclusion principle. By doing so, some of the states which are possible for the non-equivalent electrons may not exist for the equivalent electrons. Thus, in our case, each of the two p electrons has $m_l = 1, 0, -1$ and can have $m_s =$ either +1/2 or -1/2. Therefore, each of the m_l values can have m_s either +1/2 or -1/2. Values are tabulate below labeling with *a, b, c, d, e, f*.

m_l	1	0	-1	1	0	-1
m_s	½	½	½	-½	- ½	- ½
	a	*b*	*c*	*d*	*e*	*f*

If two p equivalent electrons exist, the number of possible combinations out of the six different columns taking two at time is $^6C_2 = \frac{6!}{\{(6-2)! \times 2!\}} = 15$, which are

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

This means that out of 36 magnetic field levels only 15 strong field levels exist when the electrons are two p electrons. Further, we have to calculate the values of M_L, M_S, and M_J for which the energy levels are excluded according to Pauli's principal. Thus, these possible combinations provide the following values of M_L, M_S, and M_J.

M_L	1	0	2	1	0	-1	1	0	-1	0	-1	-2	1	0	1
M_S	1	1	0	0	0	1	0	0	0	0	0	0	-1	-1	-1
M_J	2	1	2	1	0	0	1	0	-1	0	-1	-2	0	-1	-2
Group	=	=	$\vert$	$\vert$	$\vert$	=	=	__	$\vert$	=	=	$\vert$	=	=	=

Starting with the highest value of M_L and according to quantization rule, it should be equal to the highest value of *L*. Maximum value of M_L is 2 with M_S. Since M_L being space quantized value of *L*, value of *L* must therefore be 2, representing possibly ${}^1D_2$ term. If this is so, there must be combinations $M_L = 1, 0, -1, -2$ each having M_S = 0. All these are shown in dark boxes (indicated by | in the last row). Then there are three groups of $M_L = 1, 0, -1$; where the largest value of M_L is +1 and largest value of M_S is +1 ,then they must belong to ${}^3P$ state and for the value of M_L is 0 and -1 ,the M_S has +1, 0 and -1 which correspond to ${}^3P$ state (indicated by = in the last row). Further, the remaining term has M_L = 0 and M_S = 0 belongs to ${}^1S_0$ state (indicated by – in last row). The number of states is reduced to three ${}^1D_2, {}^3P, {}^1S_0$ as against the six for the two non-equivalent p electrons.

Terms of equivalent electrons can easily be calculated using *Breit's method* as explained below: For pp electronic configuration, $m_l = 1, 0, -1$ for each of the two electrons & m_s is either +1/2 or -1/2. Writing m_{l1} and m_{l2} in a horizontal row and column (written in bold). Similarly, writing the values of m_{s1} and m_{s2} as shown in following tables. Fill the body of the tables with $\sum m_l = M_L$ and $\sum m_s = M_S$.

Table 1

$m_{l1}\rightarrow$		**1**	**0**	**-1**
$m_{l2}\downarrow$	**1**	2	1	0
	0	1	0	1
	-1	0	-1	-2
		L = 0	L = 1	L = 2

$m_{s1} \rightarrow$		**+ ½**	**- ½**
$m_{s2} \downarrow$	**+ ½**	1	0
	- ½	0	-1
		S = 0	S = 1

Table 2

Equivalent electrons for a given values of *n* and ***l***, can have either same m_s or same values of m_l. If m_s values are same then some combinations of m_l will not be allowed and vice versa.

If m_s ***are same***: M_L values on the diagonal of the table 1 have same m_l and therefore, not allowed. Likewise, M_L values above the diagonal are mirror image of the values below the diagonal; hence forbidden. What is left are $M_L = 1, 0, -1$ which are the magnetic quantum numbers corresponding to *L* = 1. The combinations of M_L and M_S which are left and allowed by the Pauli's exclusion principle are

$$\sum m_s = M_S = 1 \text{ or } -1 \quad (1)$$

$$\sum m_l = M_L = 1, 0\ -1 \quad (2)$$

Each of the M_L value combines with each of the M_S value yielding $M_L = 1, 0, -1$ for each of the M_S values, that is 1 and -1 all alone has no meaning unless there is another combination with M_S = 0 and $M_L = 1, 0, -1$. This deficiency may be fixed up from the following considerations when same m_l is considered.

If m_l ***values are same***: Electrons can't have same values of m_s (that is allowed value of M_S is 0 only) but, on the other hand, each of the electrons is free to have any of the value of m_l. Pauli's principle, therefore allows the following combinations.

$$M_L = 2, 1, 0, -1, -2 \text{ with } M_S = 0 \quad (3)$$

$$M_L = 1, 0, -1 \text{ with } M_S = 0 \quad (4)$$

$$M_L = 0 \text{ with } M_S = 0 \quad (5)$$

Relations (1), (2) and (4) lead to *L* = 1 and *S* =1 giving the Term ^3P; (3) and (5) yield the Terms ^1D and ^1S respectively. Thus two equivalent p electrons yield Terms (states) ^1S, ^3P, and ^1D.

Similar mechanism can be followed for calculating the Terms (states) for other different number of equivalent p– electron systems.

(iii) Three equivalent p- electrons (Unexcited Nitrogen atom): Possible number of combinations is 20. The values of M_L and M_S can be grouped as

$$\left.\begin{array}{l} M_L \\ M_S \end{array}\right\} \begin{array}{c|c|c} 1,\ 0,\ -1 & 2, 1, 0, -1, -2 & 0 \\ \frac{1}{2}, \quad -\frac{1}{2} & \frac{1}{2}, \quad -\frac{1}{2} & \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \end{array}$$

The spectral Terms for normal nitrogen atom are

$$L = 1, S = \tfrac{1}{2} \qquad {}^2P_{3/2,\,1/2}$$

$$L = 2, S = \tfrac{1}{2} \qquad {}^2D_{5/2,\,3/2}$$

$$L = 0, S = \tfrac{3}{2} \qquad {}^2S_{3/2}$$

Spectral Terms for excited nitrogen atom are

$$\left.\begin{array}{r} {}^1S \\ +\,{}^2P \end{array}\right\} \left.\begin{array}{l} L = 0,\ S = 0 \\ L = 1,\ S = \frac{1}{2} \end{array}\right\} \left.\begin{array}{l} L = 1 \\ S = \frac{1}{2} \end{array}\right\} \qquad {}^2P$$

$$\left.\begin{array}{r} {}^1D \\ +\,{}^2P \end{array}\right\} \left.\begin{array}{l} L = 2,\ S = 0 \\ L = 1,\ S = \frac{1}{2} \end{array}\right\} \left.\begin{array}{c} L = 3, 2, 1 \\ S = \frac{1}{2} \end{array}\right\} \qquad {}^2F, {}^2D, {}^2P$$

$$\left.\begin{array}{r} {}^3P \\ +\,{}^2P \end{array}\right\} \left.\begin{array}{l} L = 2,\ S = 1 \\ L = 1,\ S = \frac{1}{2} \end{array}\right\} \left.\begin{array}{c} L = 2, 1, 0 \\ S = \frac{3}{2}, \frac{1}{2} \end{array}\right\} {}^4D, {}^4P, {}^4S, {}^2D, {}^2P, {}^2S$$

(iv) *Four equivalent p electrons*: In all possible combination is ${}^6C_4 = 15$. With the same reasons, the final spectral Terms are ${}^1S_0$, ${}^3P_{0,1,2}$ and ${}^1D_2$, which is the same as due to two p – electrons.

(v) *Two equivalent d- electrons*: The possible values of m_l and m_s for one d-electron are

m_s	½	½	½	½	½	-½	-½	-½	-½	-½
m_l	2	1	0	-1	-2	2	1	0	-1	-2
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*

Totally, in all there are 10 states and the possible combinations are ${}^{10}C_2 = 45$.

Adding the values of m_l and m_s to these combinations, we get ${}^1S$, ${}^3P$, ${}^1D$, ${}^3F$ and ${}^1G$

15.5.2 jj- Coupling:

Consider the case of three equivalent p- electrons in ***jj***- coupling. The possible values of quantum number m_j are listed below:

j	3/2	3/2	3/2	3/2	½	-½
m_j	3/2	½	-½	-3/2	½	-½
	a	*b*	*c*	*d*	*e*	*f*

Out of these six states, we can take three at a time with no two of same kind. The same combinations are obtained as in the case of LS- coupling.

$$j_1 = 3/2, j_2 = 3/2,\ j_3 = 3/2 \quad \Rightarrow m_j = 3/2, 1/2, -1/2, -3/2$$

$$j_1 = 3/2, j_2 = 3/2,\ j_3 = 1/2 \quad \Rightarrow m_j = 1/2, -1/2$$

$$5/2, 3/2, 1/2, -1/2, -3/2, -5/2$$

$$3/2, 1/2, -1/2, -3/2$$

$$j_1 = 3/2, j_2 = 1/2,\ j_3 = 1/2 \quad \Rightarrow m_j = 3/2, 1/2, -1/2, -3/2$$

These 20 terms correspond to five Terms: $(3/2, 3/2, 3/2)_{3/2}$, $(3/2, 1/2, 1/2)_{1/2}$, $(3/2, 3/2, 1/2)_{5/2}$, $(3/2, 3/2, 1/2)_{3/2}$ and $(3/2, 1/2, 1/2)_{1/2}$.

15.6 Hund's Rule

This rule is applicable only to LS coupling. In LS coupling, the effect of spin-spin interaction is usually larger compared to the electrostatic repulsion. It is found that largest S has lowest energy because the repulsion is taken inversely proportional to the distance between them. Further the electrostatic energy will be minimum, if the valence electrons are very far from each other. Therefore, the electrons of the lowest energy level's will be then arranged symmetrically around the nucleus. This symmetric configuration rotates like a rigid body, making thereby individual electrons to rotate in same direction which finally makes maximum possible value of *L*. Thus, the largest *L* value lies in the lowest energy level. These results are known as Hund's rules.

In multi-electron atoms, the energy states with maximum total spin are more bound as evident by their energy. It is because, no spatial orbital m_l of a given sub shell (***l*** value) will have two electrons unless all others have one electron each. For example, a p^4 sub shell has occupancy of its electrons as $(\uparrow\downarrow)(\uparrow)(\uparrow)$

rather than $(\uparrow\downarrow)(\uparrow)(\downarrow)$ or $(\uparrow\downarrow)(\uparrow\downarrow)(\;)$. It has been shown, that with symmetric spin eigen function, the electrons are far apart resulting in less screening of the nuclear charge by the inner electrons. This result in more binding and therefore, lowering of the states of large more total spin.

Hund's rules may be restated as follows:

(i) For a given electron configuration, the Term with maximum multiplicity (2S+1) are lowest.

(ii) Among the Terms with same multiplicity, Terms having largest orbital angular momentum *L* lie lowest on energy scale.

The rule holds good for the case of electron configuration involving normal state (example- nitrogen, carbon, scandium etc.).

15.7 Lande's Interval Rule

The rule determines the separation of fine structure line in LS- coupling. LS-coupling has the characteristics that the separation between the triplets and the singlets is large compared to the separation between the multiplet fine structure which, in turn, follows Lande' interval rule. These characteristics help recognize the coupling.

As, it is known that fine structure of a level for a given value of L and S is due to spin-orbit interaction and thus the change in the energy is calculated with the help of perturbation theory. The change in the energy value is given by

$$\Delta E = \tfrac{A}{2}[J(J+1) - L(L+1) - S(S+1)], \qquad (6)$$

where A is constant.

Thus, the energy values corresponding to the fixed *L* and *S* values are given by

$$\begin{aligned} E_J &= E_0 + \Delta E \\ &= E_0 + \tfrac{A}{2}[J(J+1) - L(L+1) - S(S+1)] \end{aligned} \qquad (7)$$

$$E_{J+1} = \tfrac{A}{2}[(J+1)(J+2) - L(L+1) - S(S+1)] \qquad (8)$$

Thus, the separation between two consecutive levels of fine structure levels is $E_{J+1} \rightarrow E_J = \Delta E_{(J+1)-J} = A(J+1)$, i.e. proportional to (*J+1*). In other words, separation is proportional to the larger *J* value. Consequently, for a triplet, one may writes

$$\Delta E_{(J+2)-(J+1)} \propto (J+2)$$

$$\Delta E_{(J+1)-J} \propto (J+1)$$

$$\left[\Delta E_{(J+2)-(J+1)}\right] \Big/ \left[\Delta E_{(J+1)-J}\right] = (J+2)/(J+1)$$

That is ratio of the two consecutive separations is equal to the ratio of the larger J values. This is known as Lande' interval rule. Therefore, for $^3P_{0,1,2}$; $^3D_{1,2,3}$ and $^3F_{2,3,4}$ are in the ratio of 1:2 ; 2:3 and 3:4 respectively.

15.8 Normal and Inverted Terms

When fine structure levels are arranged in upward direction in the increasing order of *J* value such that the level with smallest *J* values lie lowest, knows as normal Terms whereas, the inverted Terms is defined for those when the energy levels of fine structure are arranged in upward direction with the decreasing order of *J* value such that level with largest *J* value lies lowest. From experimental evidences, it has also been noticed that normal Terms appear when the electronic configuration of the concerned element has less than half filled subshell of electrons, while if the subshell are more than half filled, then inverted Terms appear.

For example, the ground ^3P term of carbon, formed from two equivalent p electrons, forms a normal multiplet and the ground state $^3P_0$. On the other hand, the ground ^3P term of oxygen, formed from four equivalent p electrons, forms an inverted multiplet and the ground state is $^3P_2$. For atoms having a ground configuration with an exactly half filled orbital, the ground term is always an *S* term, for which the only one state (ground state) arise. For example, the ground state of chromium is ^7S ,because the quantum numbers ***l*** = 0 and *S* = 3, and *J* can take only value 3, and the ground state is $^7S_3$.

Further, the fine structure of spectrum of an element also generated due to the interaction, namely, spin –orbit interaction. Thus, it is possible that order of energy levels may also governed by spin-orbit interaction energy. Now when the interaction energy results negative, the Terms are inverted and for positive energy it turns to the normal Terms.

15.9 Order of Fine Structure Multiplets

15.9.1 LS Coupling:

The effects of various terms, like interaction energy due to spin-orbit, spin-spin, orbit –orbit as well as due to electron spin - nuclear spin and nuclear spin – orbital motion and also electrostatic energy of electrons in attraction and repulsion, splits up the unperturbed energy levels into many levels and the resultant of those, of course, lie in a order obeying the Pauli's principle, Hund's rule and Lande's interval rule.

a. In LS coupling, spin-spin correlation is most dominating factor and because of it unperturbed energy levels split up into a large number of well spaced levels. The number is equal to the possible values of *S*. While calculating the possible *S* values, in accordance with the Pauli's principle, the split levels lie in an order of decreasing *S* such that the level with the largest value of *S*, lies lowest.

b. The second dominating factor is electrostatic effect, which further influences and splits up each of the above levels. The number of levels is equal to the possible values of *L*, which can be formed from the individual angular momenta of a given number of valence electrons following the Pauli's principle. These levels lie in order of decreasing *L* for a given value of S such that the level with largest *L* value lies lowest.

c. The next effective term is spin-orbit interaction. This interaction splits the level into (2S+1) or (2L+1) levels, whichever is smaller. Here the level with lowest value of J lies lowest and others in increasing order of *J* value.

15.9.2 jj- Coupling:

a. In this coupling, spin-orbit interaction is the most dominating factor and it splits up the unperturbed level into a number of well separated levels. The level with smaller *j* value will lie deepest as it has lowest energy.

b. Next effective factors are electrostatic energy and spin-spin interaction, which contribute in splitting up each of the above levels into a large number of levels characterized by different values of *J*. The level with lowest value of *J* lies lowest, again in accordance with the Pauli's principle.

15.10 Selection Rules

In order to have complete understanding about the exact nature of the transitions, it is required to know the rules, namely, Selection Rules which govern the allowed changes in various quantum numbers when an atom jumps from one state to other. The selection rules for complicated atom are almost same as for the two electron system. Other selection rules can also be obtained using the symmetry properties of the states and of the interaction dipole. A detailed analysis leads to the following selection rules.

15.10.1 Selection Rules for LS- Coupling

The selection rules, when LS coupling is pertinent are similar to those for one-electron systems. Although, the selection rules for one electron atoms are based on mathematics of dipole moment, the selection rules for many electrons are based on both mathematics and experimental proof. In LS coupling ,the main quantum numbers are *L*, *S*, M_L an M_S. Since the spin does not exist in perturbing Hamiltonian so one have the selection rule $\Delta S = 0$. As for the case of Hydrogen atom, the parity must change. The parity is given by the value of *l* (odd or even) of jumping electron must change by unity, i.e. $\Delta(\sum l_i) = \pm 1$, where $\Delta(\sum l_i)$ is the change in the sum of individual angular momentum quantum numbers for the electrons. For total orbital angular momentum, in addition to the selection rule $\Delta L = \pm 1$. As a whole, for an atom the selection rules for other quantum numbers are: $\Delta L = 0, \pm 1$; $\Delta J = 0, \pm 1$ but transitions $j = 0 \rightarrow 0$ is not allowed. $\Delta M_j = 0, \pm 1$ but $M_j = 0 \rightarrow 0$ is not allowed when $\Delta J = 0$.

15.10.2 Selection Rules for jj- Coupling

The selection rules when ***jj***- coupling pertains may be deduced from general angular momentum. Although *L* and *S* are no longer treated as good quantum number but *J*, M_j and individual ***j*** are good. In most common type of spectra, transitions between the levels take place only when one electron makes the jump at a time. The orbital quantum number of jumping electron must change by unity, i.e. $\Delta L = \pm 1$. Thus, the inner quantum number of jumping electron must change by unity or by 0, i.e. $\Delta \boldsymbol{j} = 0, \pm 1$, but for all other electrons must not change, i.e. $\Delta \boldsymbol{j} = 0$. As a whole, the other quantum numbers changes as: $\Delta J = 0, +1$; $j = 0 \rightarrow 0$ is not allowed. $\Delta M_j = 0, \pm 1$ but $M_j = 0 \rightarrow 0$ is not allowed when $\Delta J = 0$.

15.11 Illustrative Examples

Example 1: Find the values of *s*, *L* and *J* for the representation of electron states: ${}^1S_0$, ${}^3P_2$, ${}^2D_{3/2}$ and ${}^5F_5$.

Sol. (i) ${}^1S_0$: 2s+1=1$\Rightarrow$s=0; S$\Rightarrow$L=0; $\Rightarrow$J = 0.

(ii) $^3P_2$: 2s+1=3$\Rightarrow$s=1; P$\Rightarrow$L=1; $\Rightarrow$J = 2

(iii) $^2D_{3/2}$: 2s+1=2$\Rightarrow$s=1/2; D$\Rightarrow$L=2; 3/2 $\Rightarrow$J = 3/2

(iv) $^5F_5$: 2s+1=5$\Rightarrow$s=2; F$\Rightarrow$L=3; 5$\Rightarrow$J = 5

Example 2: Find Term values (states) for the electronic configuration *pd* of an atom under LS- and jj- coupling schemes.

Sol. Given that $l_1 = 1, l_2 = 2$ an $s_1 = s_2 = 1/2$.

(i) Under LS- coupling scheme

$L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2) .... |l_1 - l_2| = 3, 2, 1$, which is F, D, and P states.

$S = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2) .... |s_1 - s_2| = 1, 0$, i.e. (2S+1) = 3, 1.

Thus corresponding Terms are: $^3F, ^3D, ^3P$ (triplets) and $^1F, ^1D, ^1P$ (singlets). Therefore, the *J* values for each of the triplet and singlet states as given by $J = (L + s), (L + S - 1), ... |L - S|$

For ^3F and $J = 4, 3, 2$; Terms are $^3F_{4,3,2}$;

For ^3D and $J = 3, 2, 1$; Terms are $^3D_{3,2,1}$.

For ^3P and $J = 2, 1, 0$; Terms are $^3P_{2,1,0}$;

For ^1F and *J* = 3, Term is $^1F_3$;

For ^1D and *J* = 2, Term is $^1D_2$;

For ^1P and *J* = 1, Term is $^1P_1$.

(ii) Under jj- coupling scheme

$j_1 = (l_1 + s_1), (l_1 - s_1 - 1), ... |l_1 - s_1| = 3/2, 1/2$

$j_2 = (l_2 + s_2), (l_2 - s_2 - 1), ... |l_2 - s_2| = 5/2, 3/2$

Each of j_1 value combines with each of the j_2 value give four Terms, represented by $(3/2, 5/2), (3/2, 3/2), (1/2, 5/2)$, and $(1/2, 3/2)$. *J* values for each of the combinations is given by

$J = (j_1 + j_2), (j_1 + j_2 - 1), (j_1 + j_2 - 2) .... |j_1 - j_2|$.

For $(3/2, 5/2)$; J = 4, 3, 2, 1; Terms are $(3/2, 5/2)_{4,3,2,1}$.

For $(3/2, 3/2)$; J = 3, 2, 1, 0; Terms are $(3/2, 3/2)_{3,2,1,0}$.

For $(1/2, 5/2)$; J = 3, 2; Terms are $(1/2, 5/2)_{3,2}$.

For $(1/2, 3/2)$; J = 2, 1; Terms are $(1/2, 3/2)_{2,1}$.

Example 3: A two electron atom in an excited state has one electron in d- state and one in f- state, coupled according to *LS* scheme. Show that there are 20 possible Terms (states), which are either singlet or triplets. Write them.

Sol. Given $l_1 = 2$, $l_2 = 3$ and $s_1 = s_2 = 1/2$.

From these, we have *L* = 5, 4, 3, 2, 1 corresponding to *H, G, F, D* and *P* states and *S* = 1, 0. Under *LS*- coupling scheme, we get following J values

L	***S***	***J***	**States**	***J=L***	***S***	**States**
5	1	6, 5, 4	$^3H_{6,5,4}$	5	0	$^1H_5$
4	1	5, 4, 3	$^3G_{5,4,3}$	4	0	$^1G_4$
3	1	4, 3, 2	$^3F_{4,3,2}$	3	0	$^1F_3$
2	1	3, 2, 1	$^3D_{3,2,1}$	2	0	$^1D_2$
1	1	2, 1, 0	$^3P_{2,1,0}$	1	0	$^1P_1$

Example 4: Write the complete ground state term in *LS* notation, i.e. $^{2s+1}L_J$, for the elements in the first row of the periodic table, i.e. Li through Ne.

Sol.

Li: $1s^2 2s$; $L = 0; S = 1/2; J = 1/2 \ \therefore \ ^2S_{1/2}$

Be: $1s^2 2s^2$; $L = 0; S = 0; J = 0 \ \therefore \ ^1S_0$

B: $1s^2 2s^2 2p$; $L = 1; S = 1/2; J = 3/2, 1/2 \ \therefore \ ^2P_{1/2}$

C: $1s^2 2s^2 2p^2$; the possible terms are ^3P, ^1D, ^1S and by Hund's rule, the lowest-lying must be the triplet, since the p- shell is less than half full, i.e. $^3P_0$.

N: $1s^2 2s^2 2p^3$; the possible terms are ^4S, ^2D, ^2P. The quartet will lie lowest. Since $L = 0$, because *l* = 0 and thus there is only one value of *J* for this state, i.e. $^4S_{3/2}$.

O: $1s^2 2s^2 2p^4$; the possible terms are ${}^3P$, ${}^1D$, ${}^1S$ (same as carbon), so by Hund's rule, Since the *p*-shell is more than half full and the highest *J* lies lowest, i.e. ${}^3P_2$

F: $1s^2 2s^2 2p^5$; Possible states are the same as boron, except the highest *J* will lie lowest, i.e. ${}^2P_{3/2}$

Ne: $1s^2 2s^2 2p^6$; Closed shell configuration so the ground state is the same as helium, ${}^1S_0$.

Example 5: (a) Write all terms for the electron configuration $npn'p$ in both the *LS*- and ***jj***-coupling notation.

(b) Make a diagram similar to Figure 3 for the ***jj***-coupling states showing the effects of spin-orbit interaction and exchange and electrostatic repulsion. Put all terms in proper order.

Sol.(a) *LS*- coupling: Given $S = 0,1; L = 0,1,2$

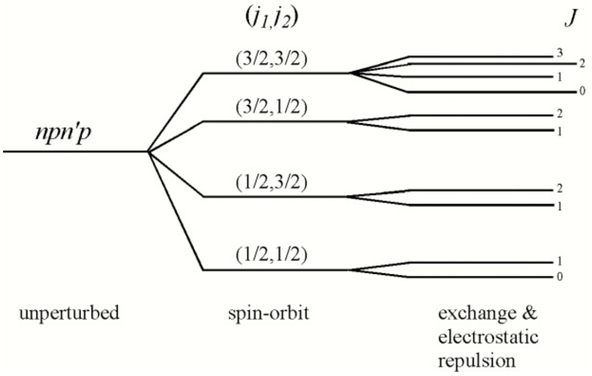
Possible states: ${}^3D_{3,2,1}; {}^3P_{2,1,0}; {}^3S_1; {}^1D_2; {}^1P_1; {}^1S_0$

jj- coupling: $j_1 = \frac{3}{2}, \frac{1}{2}; j_2 = \frac{3}{2}, \frac{1}{2}; J = 3,2,1,0$

Possible states:

$$\left(\frac{1}{2}\frac{1}{2}\right)_0; \left(\frac{1}{2}\frac{1}{2}\right)_1; \left(\frac{1}{2}\frac{3}{2}\right)_2; \left(\frac{1}{2}\frac{3}{2}\right)_1; \left(\frac{3}{2}\frac{1}{2}\right)_2; \left(\frac{3}{2}\frac{1}{2}\right)_1; \left(\frac{3}{2}\frac{3}{2}\right)_3; \left(\frac{3}{2}\frac{3}{2}\right)_2; \left(\frac{3}{2}\frac{3}{2}\right)_1; \left(\frac{3}{2}\frac{3}{2}\right)_0$$

(b)



15.12 Self Learning Exercise

Q.1 What states arise from the terms (a) ${}^3S$, (b) ${}^4P$, (c) ${}^5D$ and (d) ${}^2F$?

Q.2 What terms arise from the excited configurations (a) $1s^2 2s^2 2p^1 4f^1$, and (b) $1s^2 2s^2 3d^1 4f^2$ of carbon atom?

Q.3 Compare the terms arise from two non-equivalent p electrons with those that arise from two equivalent p electrons.

15.13 Summary

Starting with the spectra of two valence electrons as case study and extended the idea for many electron systems for understanding the complicated (complex) spectra. Proceeding in sequence, we have studied well the Russell-Saunder's (*LS*) and ***jj***- coupling and derived the spectral terms, namely, S, P, D, F…. for the new energy levels generated after the splitting of original levels, which occur after the various types of possible interactions. Effects of LS and jj- coupling have been studied for equivalent and non-equivalent electrons system. Further, the Selection rules have been followed for possible interactions and thus spectral terms. A brief about the rules, namely, Hund's rule, Lande's Interval rule have been outlined for complete explanation of experimental multiplets of fine structure. Substantive examples have also been worked out for better understanding.

15.14 Glossary

Multiplet: (i) A spectral line having more than one component, representing slight variations in the energy states characteristic of an atom. (ii) Any group of subatomic particles that are similar in most properties, but have different electric charges, such as the nucleons, which form a doublet, or the pions, which form a triplet.

Spectral Term: It is an abbreviated description of the angular momentum quantum numbers in multi electron system.

Fine Structure: The presence of groups of closely spaced lines in spectra corresponding to slightly different energy levels

Hyperfine Structure: It is the different effects leading to small shifts and splitting in the energy levels of atoms, molecules and ions.

Coupling: It is an indirect interaction between two nuclear spins which arises from hyperfine interactions between the nuclei and local electrons

Precession: A change in the orientation of the rotational axis of a rotating body or the slow movement of the axis of a spinning body around another axis due to a torque acting to change the direction of the first axis.

15.15 Exercise

Q.1 Find the *LS* terms that arise from the following configurations:

(a) *nsnp* (b) *npnd* (c) $(np)^2 ns$

Q.2 Write all terms for the electron configuration np^2 in both *LS*- and ***jj***-coupling notation. (b) Make a diagram showing the transition from *LS*- to ***jj***-coupling. Put all terms in proper order.

Q.3 Deduce the spectral Terms arising from the configuration 3pnd in the case of jj- coupling. Which of the terms is likely to be the lowest in energy?

Q.4 Calculate all spectral terms for three equivalent p- electrons in unexcited nitrogen atom.

References and Suggested Readings

12. Bransden and Joachain, Physics of Atoms and Molecules, (2009), Benjamin Cummings.
13. Raj Kumar, Atomic and Molecular Spectra: Laser , Kedarnath Ram Nath Pub.
14. SL Gupta, V Kumar, RC Sharma, Elements of Spectroscopy, Pragati Prakashan.
15. Rajam J. B., Atomic Physics (2007), S Chand & Co, New Delhi.
16. S.N. Thakur and D.K. Rai, Atom, Laser and Spectroscopy, PHI Learning Pvt. Ltd.
17. Fewkes J.H. and Yarwood J. Atomic Physics Vol II (1991) ,Oxford University Press.
18. Rita Kakkar, Atomic and molecular spectroscopy, Cambridge University Press (2015).
19. http://users.aber.ac.uk/ruw/teach/327/lsjj.php
20. http://www.chem.uwimona.edu.jm/courses/RScoupling.html
21. http://physics.nist.gov/Pubs/AtSpec/
22. http://nptel.ac.in/courses/

UNIT-16
Spectra of Alkali and Alkaline Earth Elements

Structure of the Unit

16.0 Objectives

In this chapter, we will concentrate on the fine structure of the one electron atoms. The cause of this fine structure is the interaction between the orbital angular momentum and the spin angular momentum. The chapter will also review the origin for this interaction and the effect of the coupling between orbital and spin on the spectral lines.

16.1 The Spinning Electron

In spectroscopy, Fine structure is the splitting of the main spectral lines of an atom into two or more components. Each component represents a slightly different wavelength. In alkali metals such as sodium and potassium, there are two components of fine structure, which are called doublets. For e.g. the yellow D-line of Sodium consists two close lines, the wavelengths of which are 5890 and 5896 A^o.

In the spectral lines of different series, the nature of fine structure is different. Experimental findings reveal that emission spectra of the alkali atoms can be analyzed into so called four chief series with the peculiarities as given below.

1. All the lines of sharp series consist of doublets; separation between the doublet components remain constant as far as the series extends.
2. Similarly, each line of the principal series is also a doublets, however the separation between the doublet components decreases rapidly as the series extends to higher members.
3. Third series initially consists of triplets (three components) followed by apparent doublets; separation between the outer components remain constant as far as the series extends. Series is termed as diffuse series.
4. Fourth series, termed as Fundamental series, lies in far infra-red region and consists of very close lying doublets.

In general, for lighter atoms the fine structure splitting of spectra lines is small which increases with the increase in the atomic number.

Explanation of fine structure:

Fine structure is produced when an atom emits light in making the transition from one energy state to another. The split lines, which are called the fine structure of the main lines, arise from the interaction of the orbital motion of an electron with the quantum mechanical "spin" of that electron. An electron can be thought of as an electrically charged spinning top, and hence it behaves as a tiny bar magnet. The spinning electron interacts with the magnetic field produced by the electron's rotation about the atomic nucleus to generate the fine structure. Due to the spin-orbit interaction, the orbital angular momentum ***l*** is coupled to the spin angular momentum **s**. The quantum number ***j***, which is also known as 'inner quantum number' can take values between ***l+s*** to ***l-s***. As *s* can take only ½ value, each energy level gets split into two, one corresponding to ***j=l+1/2*** and another ***j=l-1/2***. The complete notation of the levels will be as given below:

Level	*l*	*s*	*Multiplicity (2s+1)*	*j(=l±s)*	*Full notation*
S	*0*	*1/2*	*2*	*1/2*	$^2S_{1/2}$
P	*1*	*1/2*	*2*	*3/2, 1/2*	$^2P_{3/2}$, $^2P_{1/2}$
D	*2*	*1/2*	*2*	*5/2, 3/2*	$^2D_{5/2}$, $^2D_{3/2}$
F	*3*	*1/2*	*2*	*7/2, 5/2*	$^2F_{7/2}$, $^2F_{5/2}$

The component corresponding to smaller **j** value is stable and hence lies deeper in the doublet. This is due to the fact that, in the stable state, the spin magnetic moment $\boldsymbol{\mu}_s$ of the electron has the same direction of the magnetic field **B**, which is produced by the orbiting electrons. This is also the same direction as that of the orbital angular momentum ***l.*** Since μ_s and spin angular momentum s has opposite direction, ***l*** is also opposite to **s**. Hence in the more stable state, ***j*** takes the value ***l-s***.

Calculation of Level splitting due to Spin-Orbit interaction:

The expression for spin-orbit interaction energy can be written as [Ref: Unit 14]

$$\Delta E_{l,s} = \frac{eh^2}{16\pi^2 m^2 c^2}[j(j+1) - l(l+1) - s(s+1)]\overline{\frac{1}{r}\frac{dV(r)}{dr}} \qquad \textbf{(1)}$$

For ***l=0***, the spin-orbit interaction energy $\Delta E_{l,s} = 0$. For other values of *l*, $\Delta E_{l,s}$ assumes two values: one positive and another negative.

According to Hartree theory, in an alkali atom, the optical electron in a shell n is considered to be moving in a potential field

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Z_n e}{r}$$

where Z_n is a constant and equals to $Z(r)$. $Z(r)$is given by

$$Z(r) \rightarrow Z \; as \; r \rightarrow 0$$
$$Z(r) \rightarrow 1 \; as \; r \rightarrow \infty$$

$Z_n e$ is the effective nuclear charge for shell n.

Substituting the expression for the potential in the expression of spin-orbit interaction energy and after solving, eq. (i) can be written as:

$$\Delta E_{l,s} = \frac{Ze^2h^2}{4\pi\varepsilon_0\,(16\pi^2m^2c^2)}[j(j+1) - l(l+1) - s(s+1)]\overline{\frac{1}{r^3}}$$

where the average value of $\frac{\mathbf{1}}{\boldsymbol{r^3}}$ is given as,

$$\overline{\frac{1}{r^3}} = \frac{Z^3}{a_0^3 n^3 l^3 \left(l + \frac{1}{2}\right)(l+1)}$$

$a_0 = 4\pi\varepsilon_0 \frac{h^2}{4\pi^2 me^2}$ is the radius of the smallest Bohr orbit of the Hydrogen atom. Using these, the final expression for the energy reduces to

$$\Delta E_{l,s} = \frac{R_\infty \alpha^2 Z_n^4 hc}{2n^3 l \left(l + \frac{1}{2}\right)(l+1)}[j(j+1) - l(l+1) - s(s+1)]$$

where, $R_\infty = \frac{me^4}{8\varepsilon_0^2 h^3 c}$ is known as Rydberg constant, and $\alpha = \frac{e^2}{2\varepsilon_0 hc} = \frac{1}{137}$ is known as fine structure constant and is dimensionless.

The term shift due to spin-orbit interaction is

$$\Delta T_{l,s} = -\frac{\Delta E_{l,s}}{hc}$$
$$= \frac{R_\infty \alpha^2 Z_n^4}{2n^3 l \left(l + \frac{1}{2}\right)(l+1)}[j(j+1) - l(l+1) - s(s+1)]$$

Now, for a single electron system, $S = \frac{1}{2}$

$$j = l \pm \frac{1}{2}$$

Substituting these values of j in the expression for energy, the term shift corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ can be given as,

$$\Delta T'_{l,s} = \frac{R_\infty \alpha^2 Z_n^4}{2n^3 l\left(l + \frac{1}{2}\right)(l + 1)} l$$

$$\Delta T''_{l,s} = \frac{R_\infty \alpha^2 Z_n^4}{2n^3 l\left(l + \frac{1}{2}\right)(l + 1)} (l + 1)$$

Thus due to the spin-orbit interaction, each level gets split into two levels corresponding to two values of ***j***. The separation between these two levels is

$$\Delta T = \Delta T''_{l,s} - \Delta T'_{l,s}$$

Substituting the values of R_∞ and $\alpha = \frac{1}{137}$ we get,

$$\Delta T = 5.84 \frac{(Z - \sigma)^4}{n^3 l(l + 1)} \ cm^{-1}$$

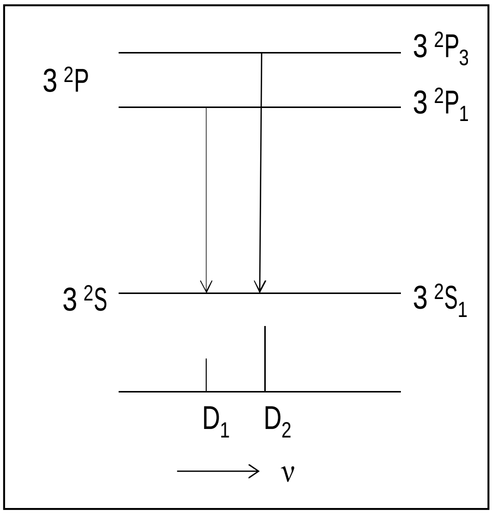
This formula gives the doublet separation, which is remarkably good in agreement with experimental variation. This shows that (i) The level splitting for an alkali atom increases with the increase in atomic number (ii) For the same ***l***, the level spitting decreases with increasing n and (iii) For the same n, it decreases with increasing n.

16.2 Intensity Ratio for Doublets

The line intensities in doublet spectra show that:

(1) The strongest line in any doublet arises from transition in which j and ***l*** change in one way.
(2) When there is more than one such line, the line involving the larger j value is strongest.

For eg. in the principle series doublet shown above, the line arising from the transition $^2P_{3/2}$-$^2S_{1/2}$ is stronger than $^2P_{1/2}$-$^2S_{1/2}$. The reason is that in the first transition, j changes by 1 and ***l*** changes by -1 while in the second transition j changes by 0 and ***l*** changes by -1.

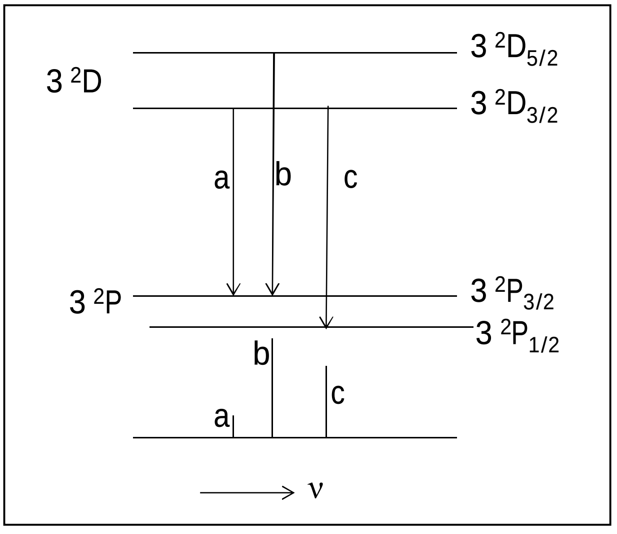


The intensity ratio is then defined as,

$$\frac{I_b}{I_a} = \frac{2\left(\frac{3}{2}\right)+1}{2\left(\frac{1}{2}\right)+1} = \frac{4}{2} = 2:1$$

The same holds for the members of principal series.

Let us consider another example. The diffuse series compound doublet:



The lines ***a*** and ***c*** start from $^2D_{3/2}$ while the line b starts from $^2D_{5/2}$. Therefore,

$$\frac{I_b}{I_a+I_c} = \frac{2\left(\frac{5}{2}\right)+1}{2\left(\frac{3}{2}\right)+1} = \frac{6}{4} = \frac{3}{2} \qquad \text{(i)}$$

Line ***c*** ends on $^2P_{1/2}$ while lines ***a*** and ***b*** end on $^2P_{3/2}$. Thus

$$\frac{I_c}{I_a+I_b} = \frac{2\left(\frac{1}{2}\right)+1}{2\left(\frac{3}{2}\right)+1} = \frac{2}{4} = \frac{1}{2} \qquad \text{(ii)}$$

Solving (i) and (ii) we get,

$$a : b : c = \frac{1}{9} : 1 : \frac{5}{9}$$

$$a : b : c = 1 : 9 : 5$$

If the line ***a*** is not resolved from line ***b*** **,**then we shall see two lines having intensity ratio

$$(1 + 9) : 5 = 2 : 1$$

16.3 Illustrative Examples

Example 1: The first member of the principle series of sodium has a wavelength of 5893 A^0. First excited *s* state of sodium lies 3.18 eV above the ground state. Find the length of the first member of the sharp series. Given $e=1.60\times10^{-19}$C, $c=3\times10^8\ ms^{-1}$

Sol. The first member of the principal series corresponds to the transition 3p-3s. The energy corresponding to this transition (wavelength =5893 A^0) is

$$E_1(3p\text{-}3s)=hc/\lambda$$

$$= 3.375 \times 10^{-19} J$$

$$= 2.11\ eV$$

The energy corresponding to the first excited state 4s of Sodium relative to the ground state 3s is:

$$E_2(4s\text{-}3s)=3.18\ eV$$

The first member of sharp series corresponds to the transition from 4s-3p. The energy corresponding to this transition is:

$$E(4s\text{-}3p)= E_2(4s\text{-}3s)- E_1(3p\text{-}3s)$$

$$=3.18\ eV-2.11\ eV$$

$$=1.07\ eV$$

Corresponding wavelength is

$$\lambda = hc/E = 11618\ A^0$$

16.4 Self Learning Exercise-I

Q.1 Write down the normal electronic configuration of Helium and lithium atoms. Determine the states to which these configurations give rise.

Q.2 Calculate the wavelength of the line corresponding to 2p-2s transition in Lithium. The 2p level lies 1.85 eV higher than the 2s level.

Q.3 Define intensity ratio of doublets.

16.5 Vector Model for Two-Valence Electron Atom

Alkaline Earth atoms like Beryllium, Magnesium, Zinc, Cadmium, Mercury, Calcium and others in group IIA and IIB of the periodic table contain two valence electrons and give rise to series of singlet and triplet spectral lines. The analysis of these spectra by Russell and Saunders in 1925 was an important development in the theoretical understanding of atomic spectroscopy. The current topic deals with the observed spectral features and finally the vector model description of the atom that emerged out of these studies.

In the vector atom mode, the orbital angular momentum of each electron is represented by $\boldsymbol{l}$, and the spin angular momentum by $\boldsymbol{s}$. Under varying circumstances, the vector $\boldsymbol{l}$ and $\boldsymbol{s}$, combine to form resultant vectors in terms of which the observed properties can be explained.

In alkaline earth metals, the vector atom model consists of vectors $\boldsymbol{l_1}, \boldsymbol{l_2}, \boldsymbol{s_1}, \boldsymbol{s_2}$ and their resultant $\boldsymbol{J}$. The formation of $\boldsymbol{J}$ can be understood in terms of L-S and j-j coupling.

L-S Coupling:

This coupling occurs in the lighter atoms. In the vector model of L-S coupling, the angular momentum vector of individual electrons $\boldsymbol{l_1}$, $\boldsymbol{l_2}$ precess rapidly. The corresponding quantum number **L** can then take the values from $|\boldsymbol{l_1} - \boldsymbol{l_2}|$ to $|\boldsymbol{l_1} + \boldsymbol{l_2}|$. The various terms according the values of L=0,1,2… are termed as *S,P,D*,…

Similarly the spin angular momentums $\boldsymbol{s_1}, \boldsymbol{s_2}$ combines to form a resultant angular momentum **S**. It can take values between $|\boldsymbol{s_1} - \boldsymbol{s_2}|$ to $|\boldsymbol{s_1} + \boldsymbol{s_2}|$. Since $\boldsymbol{s_1}, \boldsymbol{s_2}$ can have values ½, S=0, 1. The multiplicity 2S+1 has values 1 and 3. Thus the two valence electron system leads to singlet and triplet states.

As a result of spin-orbit interaction, **L** and **S** couples with each other to form the total angular momentum vector **J**. The value of J is given by, **J=L+S.** The quantum number **J** thus takes values from |L-S | to |L+S |.

This shows that the spin orbit interaction breaks each level which is characterized by an L value in a number of fine structure characterized by a J-value. The collection of fine-structure levels is known as a 'multiplet'.

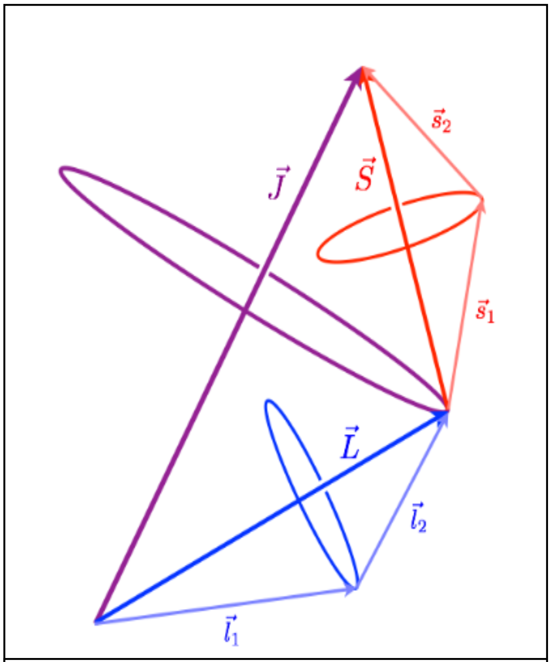


Fig: L-S coupling

Eg. Calcium atom (Ca)

The ground state configuration of Ca is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

For the two optically active electrons we have, ***l_1=0, l_2=0*** and ***s_1=1/2, s_2=1/2***

Thus, L=0 (S-term)

S=0, 1

J=0, 1

The terms are $^1S_0$ and $^3S_1$. Since the two valence electrons in $4s^2$ are equivalent, the term $^3S_1$ is excluded by Pauli's principle. Hence the normal atom gives rise to a singlet-S terms i.e. $^1S_0$ only.

j-j Coupling:

In light atoms, the interactions between the orbital angular momenta of individual electrons is stronger than the spin-orbit coupling between the spin and orbital angular momenta. These cases are described by "L-S coupling". However, for heavier elements with larger nuclear charge, the spin-orbit interactions become as strong as the interactions between individual spins or orbital angular momenta. In those cases the spin and orbital angular momenta of individual electrons tend to couple to form individual electron angular momenta.

In j-j coupling, the orbital angular momentum ***l***, and spin ***s***, of each electron are first coupled to form a total angular momentum ***j***, for that electron. These single-electron total angular momenta are then combined into a total angular momentum **J**, for the group of electrons. This is in contrast to LS coupling, where the total orbital angular momentum L and total spin S, of the system are calculated first and then combined to the total angular momentum J, of the whole system.

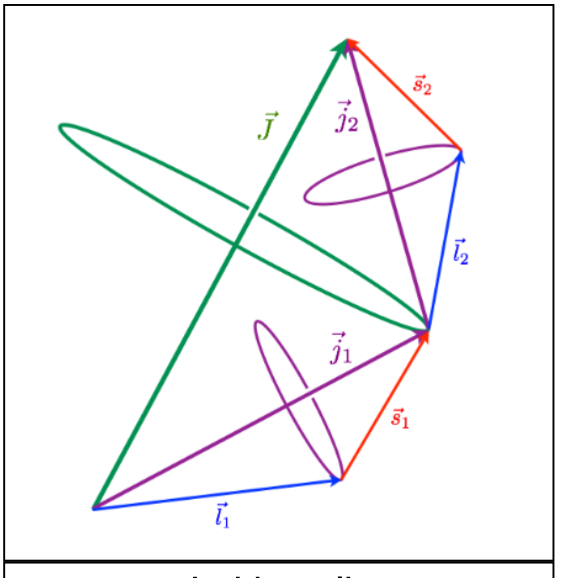


Fig: j-j coupling

16.6 Interaction Energy in LS and JJ Coupling

Due to the spin orbit interaction, the atomic term consists of different energies.

Each of them is slightly different and corresponds to different J values. Thus the multiplet splitting increases rapidly with increase in atomic number Z.

As we already know, the interaction energy for a single electron atom is given by,

$$-\Delta T_{l,s} = \frac{R_\infty \alpha^2 Z^4}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$$= a\frac{j^{*2} - l^{*2} - s^{*2}}{2}$$

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

$$s^{*2} = s(s+1)$$

In case of two optical electrons, there are four angular momentum, i.e. l_1^*, l_2^*, s_1^*, s_2^*. The possible interactions are,

(1) l_1^* with l_2^*

(2) s_1^* with s_2^*

(3) l_1^* with s_1^*

(4) l_2^* with s_2^*

(5) l_1^* with s_2^*

(6) l_2^* with s_1^*

The interactions (1) and (2) dominate over (3) and (4). Interactions (5) and (6) are negligible.

Using equation (1), the energies corresponding to interactions (1), (2), (3), and (4) can be written as,

$$\Delta T_1 = a_1 l_1^* l_2^* \cos\left(l_1^*, l_2^*\right)$$

$$\Delta T_2 = a_2 s_1^* s_2^* \cos\left(s_1^*, s_2^*\right)$$

$$\Delta T_3 = a_3 l_1^* s_1^* \cos\left(l_1^*, s_1^*\right)$$

$$\Delta T_4 = a_4 l_2^* s_2^* \cos\left(l_2^*, s_2^*\right)$$

In LS coupling, l_1^* and l_2^* precess rapidly around their resultant L^*. Using Cosine law, we can write:

$$L_*^2 = l_1^{*2} + l_2^{*2} + 2l_1^* l_2^* \cos(l_1^*, l_2^*)$$

$$\Delta T_1 = \frac{1}{2} a_1 (L_*^2 - l_1^{*2} - l_2^{*2})$$

Similarly $\boldsymbol{s_1^*}$ and $\boldsymbol{s_2^*}$ precess rapidly around their resultant S^*.

$$S_*^2 = s_1^{*2} + s_2^{*2} + 2s_1^* s_2^* \cos(s_1^*, s_2^*)$$

This gives,

$$\Delta T_2 = \frac{1}{2} a_1 (S_*^2 - s_1^{*2} - s_2^{*2})$$

To calculate the interaction energy between $\boldsymbol{l_1^*}$ and $\boldsymbol{s_1^*}$ and between $\boldsymbol{l_2^*}$ and $\boldsymbol{s_2^*}$ the average values of cosine must be calculated. The average values are given by,

$$\overline{\cos(l_1^*, s_1^*)} = \cos(l_1^*, L^*) \cos(L^*, S^*) \cos(S^*, s_1^*)$$

$$\overline{\cos(l_2^*, s_2^*)} = \cos(l_2^*, L^*) \cos(L^*, S^*) \cos(S^*, s_2^*)$$

Substituting the average values of the cosines in equation (ii), we get

$$\Delta T_3 + \Delta T_4 = [a_3 l_1^* s_1^* \cos(l_1^*, L^*) \cos(S^*, s_1^*) + a_4 l_2^* s_2^* \cos(l_2^*, L^*) \cos(S^*, s_2^*)] \cos(L^*, S^*)$$

Using cosine law and after simplification, we get

$$= \left[a_3 \frac{l_1^{*2} + L^{*2} - l_2^{*2}}{2L^{*2}} \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2S^{*2}} + a_4 \frac{l_2^{*2} + L^{*2} - l_1^{*2}}{2L^{*2}} \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2S^{*2}}\right] \frac{J^{*2} - L^{*2} - S^{*2}}{2}$$

This after further simplification can be written as,

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} A (J^{*2} - L^{*2} - S^{*2})$$

where $A = a_3 \alpha_3 + a_4 \alpha_4$

and, $\alpha_3 = \frac{l_1^{*2} + L^{*2} - l_2^{*2}}{2L^{*2}} \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2S^{*2}}$

$$\alpha_4 = \frac{l_2^{*2} + L^{*2} - l_1^{*2}}{2L^{*2}} \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2S^{*2}}$$

We can now write any fine-structure term by the formula,

$$T = T_0 - \Delta T_1 - \Delta T_2 - \Delta T_3 - \Delta T_4$$

where, T_0 is a hypothetical term which accounts for the center of gravity of entire electron configuration.

16.7 Illustrative Examples

Example 2. Consider a carbon atom whose electrons are in the configuration $(1s)^2 (2s)^2$ 2p 3p. List all expected terms on the basis of the *LS* (Russell-Sanders) coupling scheme.

Sol. $(1s)^2$ couples to L=0, S=0. (Pauli Exclusion Principle)

$(2s)^2$ couples to L=0, S=0. (Pauli Exclusion Principle)

The 2p and 3p electrons both have l=1, s=1/2. This can lead to L=2,1,0, S=0,1.

We therefore can form the following terms: $^1D_2$, $^3D_{123}$, $^1P_1$, $^3P_{012}$, $^1S_0$, $^3S_1$

Example 3 Scandium has a ground state configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ 3d. Consider a transition from the ground state $4s^2$ 3d to the excited state 3d 4s 4p.

Assuming *LS* coupling find L, S, and J values for the terms derived from the $4s^2$ 3d and 3d 4s 4p configurations.

Write down each term in standard notation.

Sol. *LS* coupling: L=2; S=1/2

Possible terms: $^2D_{5/2}$, $^2D_{3/2}$

16.8 Self Learning Exercise-II

Q.1 The atomic number of Carbon is 6.

(i) State its electronic configuration.

(ii) Calculate the spectroscopic terms for this configuration.

(iii) If one of the 2p electrons gets excited to the M-shell, what other spectroscopic terms will be possible?

Q.2 Write down the electronic configuration of N^+ and deduce the spectral terms.

Q.3 Obtain the terms for the ground state of neutral oxygen atom.

16.9 Summary

The closely spaced groups of lines observed in the spectra of the lightest elements, notably hydrogen and helium. The components of any one such group are characterized by identical values of the principal quantum number n, but different values of the azimuthal quantum number ***l*** and the angular momentum quantum number **j**.

In atoms having several electrons, this fine structure becomes the multiplet structure resulting from spin-orbit coupling. This gives splitting of the terms and the spectral lines that are "fine'' for the lightest elements but that are very large, of the order of an electronvolt, for the heavy elements.

Careful examination of the spectra of alkali metals show that each member of some of the series is closed doublets. For example, sodium yellow line, corresponding to 3p-3s transition, is a close doublet with separation of $6A^0$while potassium (K) has a doublet separation of $34A^0$ and so on. Further investigations show that only the S-terms are singlet, while all the other terms P, D, F etc. are doublets. Such doublet structure in energy is observed for all the atoms possessing a single valence electron i.e., in the outer most shell. Usually the doublet spacing is small compared to the term difference (for Na the main D line is centered at $5893A^0$; D_2= 5890 A^0 and D_1 = $5896A^0$) and hence it is called fine structure.

16.10 Glossary

Ground state: The state of lowest intramolecular energy.

Line width: The width of a spectral line.

Quantum Number : According to quantum mechanics, the distribution of electrons labels the state of the electron and specifies the value of a property in an atom.

n- Principal Quantum Number (shell number): The average distance of the electron from the nucleus in a particular orbital; can have integral values of 1, 2, 3, and so forth.

l*- Angular Momentum Quantum Number: (subshell of one shell):** Its value reflects the orbital shape; it correlates with n; (l***=n-1); which reveals 0 for the s, 1 for p, 2 for d, 3 for f.

16.11 Answers to Self Learning Exercises

Answers to Self Learning Exercise-I

Ans.1: $^{2}He: 1s^{2}, {}^{1}S_{0}$

$^{3}Li: 1s^{2}, 2s, {}^{2}S_{1/2}$

Ans.2: 6719 A^{0}

Ans.3: See section 16.2

Answers to Self Learning Exercise-II

Ans.1: (i) $1s^{2}\ 2s^{2}\ 2p^{2}$ (ii) $^{1}S, {}^{1}D, {}^{3}P$ (iii) 2p 3s: $^{1}P\ {}^{3}P$

2p 3p: $^{1}S\ {}^{1}P\ {}^{1}D; {}^{3}S\ {}^{3}P\ {}^{3}D$

2p 3d: $^{1}P\ {}^{1}D\ {}^{1}F; {}^{3}P\ {}^{3}D\ {}^{3}F$

Ans.2: $1s^{2}\ 2s^{2}\ 2p^{2}; {}^{1}S_{0}{}^{1}D_{2}{}^{3}P_{0,1,2}$

Ans.3: $^{1}S_{0}{}^{1}D_{2}{}^{3}P_{0}{}^{3}P_{1}{}^{3}P_{2}$

16.12 Exercise

Q.1 What is the significance of quantum number J ?

Q.2 What J is equal to ?

Q.3 What are the possible values of J ?

Q.4 Distinguish between LS (RS) and jj coupling.

16.13 Answers to Exercise

Ans.1: In lighter elements spin-orbit coupling is small, while in heavier elements, it is large or appreciable. Hence, the new quantum number J becomes important. This quantum number gives the total angular momentum.

Ans.2: $j = l + s$

Ans.3: J = L+S, L+S-1,......, L-S

Ans.4: Russell – Saunders is known as RS coupling. According to this scheme, electronic repulsions are stronger than spin -orbit coupling. In lighter elements, spin -orbit coupling is small and hence RS coupling is valid.

Specifically, it is valid for first transition series (3d elements). But in the case of heavier elements, spin- orbit coupling is more powerful than electron repulsions. Hence, jj coupling is more important than RS coupling. In RS coupling, configuration is split into terms by electron repulsion and these are further split into states by spin -orbit coupling. But jj coupling is exactly the reverse of RS coupling. Thus, in jj coupling, configuration is split into levels by spin -orbit coupling and not terms. These levels are split further by electron repulsions.

References and Suggested Readings

1. A. Beiser, Concept of Modern Physics (1987), McGraw Hill Co. Ltd, New Delhi
2. J. B. Rajam, Atomic Physics (2007), S Chand & Co, New Delhi
3. J.H. Fewkes and J. Yarwood Atomic Physics Vol II (1991) Oxford University Press
4. B.H. Bransden and C.J. Joachain, Physics of Atoms and Molecules 2nd Ed. (2009), Pearson Education, New Delhi.
5. *C.N. Banwell*, and E. Mccash, *Fundamentals of Molecular&Spectroscopy*. McGraw-Hill Education (India) Pvt Limited, 1994
6. Atom, Laser And Spectroscopy By S. N. Thakur, D. K. Rai

UNIT-17
Zeeman Effect and Paschen -Back Effect

Structure of the Unit

17.0 Objectives

To describe an atom we have to give a unique set of discrete energy states. When that atom gets excited through heating or some other way, the atom makes transitions between these quantized energy states. When atom (electron) comes back to ground state it emits a photon (light). If we record the emitted photon on a screen, we get a spectrum which shows the quantized nature of energy levels.

When we apply magnetic field to it, these energy levels can shift from original state. This effect is known as Zeeman Effect.

Dutch physicist Pieter Zeeman studied this effect for splitting of spectral lines into several components in the presence of a static magnetic field. In 1896, Zeeman observed that when a sodium source was placed in an external magnetic field, the yellow D lines were split into several components. Faraday had performed the same experiment some thirty years earlier, but had failed to observe an effect because of low resolution of his spectrograph. Splitting of spectral lines was predicted by Faraday on the basis of classical theory by Lorentz and first observed by Zeeman. This effect is named after Pieter Zeeman as Zeeman Effect and he shared 1902 Nobel Prize in Physics with Hendrik Lorentz.

17.1 Introduction

When we look at a light source with line spectrum, which is placed in an external magnetic field, the spectral lines emitted by the atoms of the source will split into a number of polarized components. If we put the magnetic field than the splitting will be proportional to the strength of applied magnetic field. Due to Zeeman Effect some degenerate energy levels will split into several non-degenerate energy levels with different energies and due to this effect we get few new transitions which can be seen as new spectral lines in the atomic spectrum.

We look at the *singlet* spectral line right angles to the magnetic field direction than it will split into three plane-polarized components: un-shifted central line in which electric vector is vibrating parallel to the magnetic field (called π component) and two other lines equally displaced on both sides with electric vector vibrating perpendicular to the magnetic field (called σ components). This effect in known as 'normal' Zeeman Effect and it is called a 'normal triplet'.

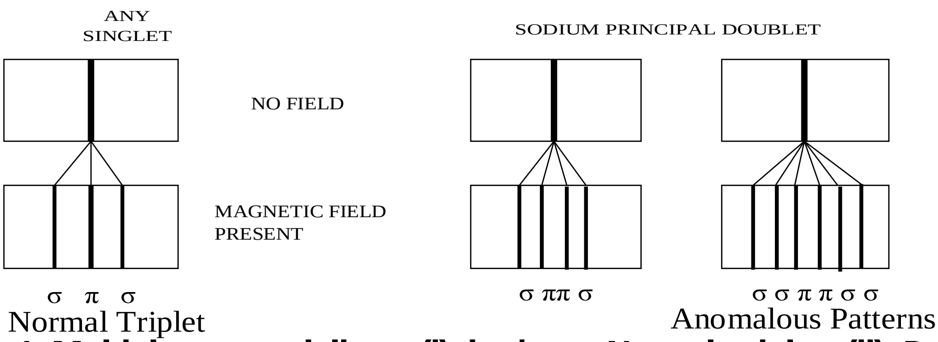


Fig 1 Multiplet spectral lines, (i) it shows Normal triplet, (ii) D_1 and D_2 component of sodium line.

If we measure the fine-structure components of a multiplet spectral line, we get complex Zeeman pattern. For example, due to Zeeman effect D_1 and D_2 components of sodium yellow doublet split in four and six lines respectively. This effect is known as 'anomalous' Zeeman effect. Zeeman splitting is smaller in comparison to fine-structure splitting.

17.2 Experimental Set-up for studying Zeeman Effect

To make experimental setup for studying Zeeman Effect, we need high resolving power and large light-gathering power. Schematic diagram of constant-deviation prism spectrometer arrangement is given in figure 2.

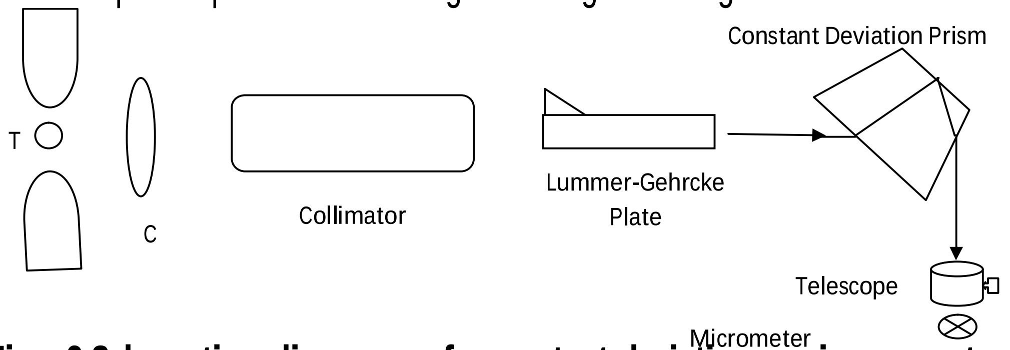


Fig 2.Schematic diagram of constant-deviation prism spectrometer arrangement.

Here (in figure 2), T is a neon discharge tube (line source) placed between the poles of an electromagnet. (If we want to look at another spectrum like cadmium lamp, sodium etc., then we have to use corresponding lamp)C is positive lens which is also known as condenser lens. Lens should be adjusted in the position that the light coming from the capillary part of the tube can be focused on the slit of the collimator of the spectrometer. A high resolving optical device should be kept between the collimator and constant deviation prism. In above setup, we kept a Lummer-Gehreke plate (L-G plate)as a high resolving optical device. A telescope is fitted with a micrometer eyepiece to measure the light emerging from the prism. It emerges at the right angles to its initial direction.

For the above setup, we have to follow these steps:

(i) In first step, we keep the electromagnet off. Remove the focusing (condenser) lens C, L-G plate and micrometer eyepiece. In this state collimator slit will be fairly wide opened. In telescope, we can see images of pole-pieces and the neon tube. The pole-piece and the neon tube are so adjusted that the image of the pole-piece appears central in the field of view, and the neon tube is symmetrical between the pole-pieces.

(ii) Put the focusing lens C in between the electromagnet and slit of the collimator, such that it's aperture is fully illuminated. The image of the aperture should fill the field of view. The micrometer eyepiece should be kept in position and focused on the crosswire. Now, on looking through it, a bright spectrum of neon light is seen.

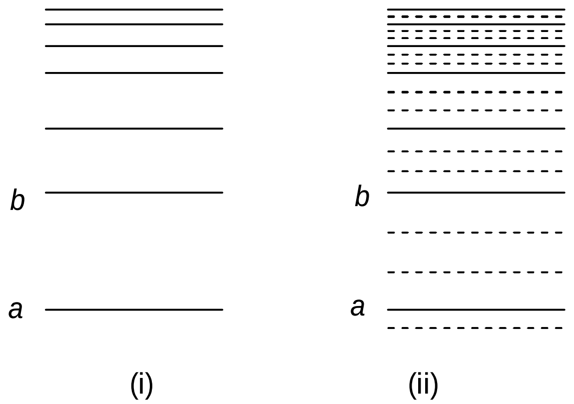


Fig 3. View at eyepiece.(i)Before switching on electromagnet.(ii) After switiching on electromagnet.

(iii) Mount the L-G plate on its stand which is kept in position on the spectrograph. Look through the eyepiece, each spectral line shows a few orders. We can adjust the plate in various directions using screws. To get bright and sharp fringe-system, we have to fairly rotate the screws.

(iv) Recognize the *singlet* yellow line (λ = 5852 Å) of the spectrum and set the cross-wire on a few successive orders (fringes). We have to take micrometer reading.

(v) Now, switch on the electromagnet and adjust the current on the scale where we can get the magnetic field about 4000 Gauss. Each order will split into three components: one, which is not displaced from the original line and other two will be symmetrically displaced. By putting the crosswire on each (displaced and not displaced line) we can take these reading through micrometer.

(vi) Change the value of current to get the spectrum on another magnetic field and repeat the process. For example magnetic field is 7000 Gauss and 10k Gauss. Now, we have to perform the same process for *singlet* red line (λ = 6266 Å) of the neon spectrum.

17.3 Explanation of Normal Zeeman Effect

All lines due to transition between the singlet (S = 0) states of an atom or the normal Zeeman Effect can be explained from the classical electron theory. It can be also explained from the quantum theory with the ignorance of electron spin.

In quantum theory, an atom with electrons more than one possesses an orbital angular momentum $\vec{L}$ with an orbital magnetic moment $\vec{\mu_L}$. A ratio known as gyromagnetic ratio (or sometimes magnetogyric ratio; ratio of magnetic moment to angular momentum of a particle) can be given by

$$\left|\frac{\vec{\mu_L}}{\vec{L}}\right| = \frac{e}{2m}$$

Here e is the charge of an electron ($1.6 \times 10^{-19}\ C$) and m is the mass of elctron. Magnetic moment and angular momentum of an electron have opposite in direction because the elctron is a *negatively* charged particle.

When we put an atom in an external magnetic field $\vec{B}$ (say along Z-axis), then the angular momentum of vector $\vec{L}$ will precess around the field direction with quantized components. These components can be given by

$$L_z = \frac{h}{2\pi} = \hbar$$

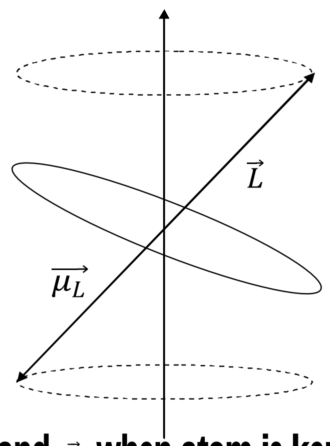


Fig 4. Directions of $\vec{\mu_L}$ and $\vec{L}$, when atom is kept in magnetic field $\vec{B}$.

where the M_L is magnetic orbital quantum number which can have values:

$M_L = L, L-1, \ldots, -L,$

So, total number of values of M_L is $(2L + 1)$. This precession is known as 'Larmor precession', this implies that in a magnetic field, each L-level will split in $(2L + 1)$ levels and each characterized by a M_L value.

According to Larmor's theorem, the angular velocity of precession is given by

$$\omega = \left|\frac{\overrightarrow{\mu_L}}{\vec{L}}\right| B = \frac{e}{2m} B.$$

Interaction energy of such precession can be calculated by multiplying the angular velocity and the projection of angular momentum $\vec{L}$ along magnetic field. In this case it is z-component of $\vec{L}$ because magnetic field is along z-axis. So, interaction energy is: $\Delta E = \omega L_z = \frac{e}{2m} B M_L \frac{h}{2\pi}$

$$\Rightarrow \Delta E = \frac{eh}{4\pi m} B M_L$$

Interaction energy as a function of wave number is

$$-\Delta T = \frac{\Delta E}{hc} = \frac{eB}{4\pi mc} M_L$$

Since, magnetic field B is uniform or same for all levels for a given atom, so, we can write

$$-\Delta T = \frac{\Delta E}{hc} = \frac{eB}{4\pi mc} M_L$$

Where L' is called 'Lorentz unit'. So, for each level M_L, change in energy from its original level is ΔT and it is proportional to the magnetic field B. Here L' is the wave-number separation between any two consecutive Zeeman levels for any value of L.

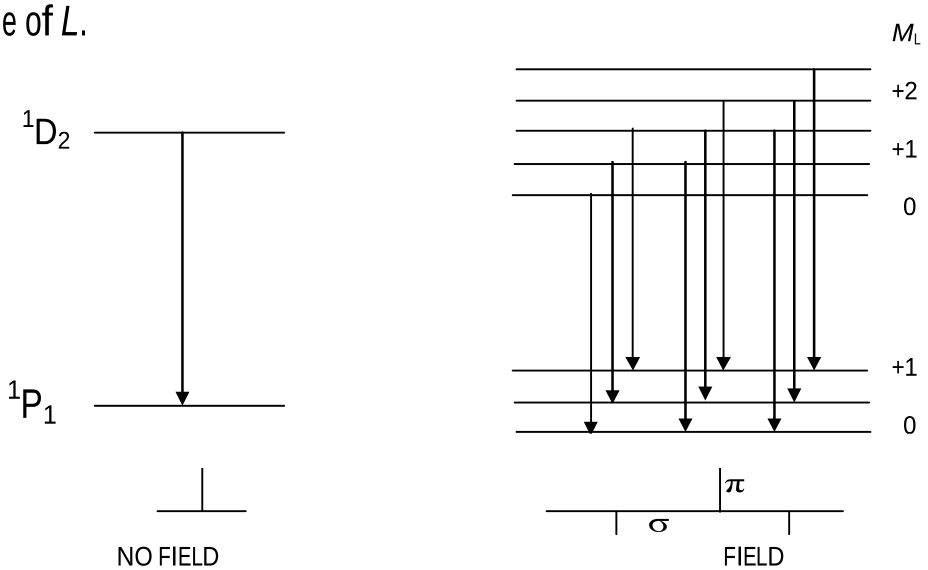


Fig 5. Transition $^1D_2 - {}^1P_1$ (L = 2 to L =1 transition)

Now, consider transition $^1D_2 - {}^1P_1$. $^1D_2$ corresponds L = 2 and S = 0, $^1P_1$ correspond to L = 1 and S = 0 states. So, in simple words we can say transition from L = 2 to L = 1 transitions. In presence of weak magnetic field these will split into (2 L + 1) levels. So, respectively it will split into 5 and 3 equidistant energy levels. Corresponding M_L values are 2, 1, 0, -1, -2; for L = 2 and 1, 0, -1 for L = 1.

There are only few optical transitions are possible. These transition rules are known as selection rules. These rules for magnetic quantum number (M_L) can be derived by quantum mechanics. For this process selection rules are:

$$\Delta M_L = \begin{cases} \pm 1, & for\ \sigma - component \\ 0, & for\ \pi - component \end{cases}$$

From this rule, we get nine-transitions but Zeeman splitting is same for transitions corresponding to ΔM_L correspond in wave number. So, in this case we get only three component line which is a normal *triplet* pattern. From selection rules, we get one component in the position of the field line, known as π-component and two symmetrically displaced σ-components. Separation between consecutive Zeeman levels is equal to the wave-number separation between consecutive components. Wave-number separation is given by

$$\Delta \upsilon = L' = \frac{eB}{4\pi mc}$$

Putting $e = 1.6 \times 10^{-19}$ C, $m = 9.1 \times 10^{-31}$ kg and $c = 3\times10^{8}$ m/s,

we get $\Delta\upsilon$ = 46.7 B /m

where B is in Tesla (N/A-m).

Other than selection rules, quantum mechanics give us the information of polarization rules also. Transition $\Delta M_L = 0$ results in spectral line polarized with the electric vector parallel to magnetic field (π-component). While transition $\Delta M_L = \pm 1$ gives lines polarized with electric vector perpendicular to magnetic field (σ-component).

Both σ-components together have the same intensity as the π-component has. This intensity ratio of the components can be derived from the correspondence principle. Thus, the normal Zeeman Effect is fully explained.

17.4 Zeeman Effect in Hydrogen

When an external magnetic field is applied, sharp spectral lines like the n=3⟶ 2 transition of hydrogen split into multiple closely spaced lines. This splitting comes from the interaction between the magnetic field and orbital angular momentum associated with magnetic dipole moment. In absence of the magnetic field, energy levels in hydrogen atom depend only upon principle quantum number *n*. So, emitted light will be with same wavelength.

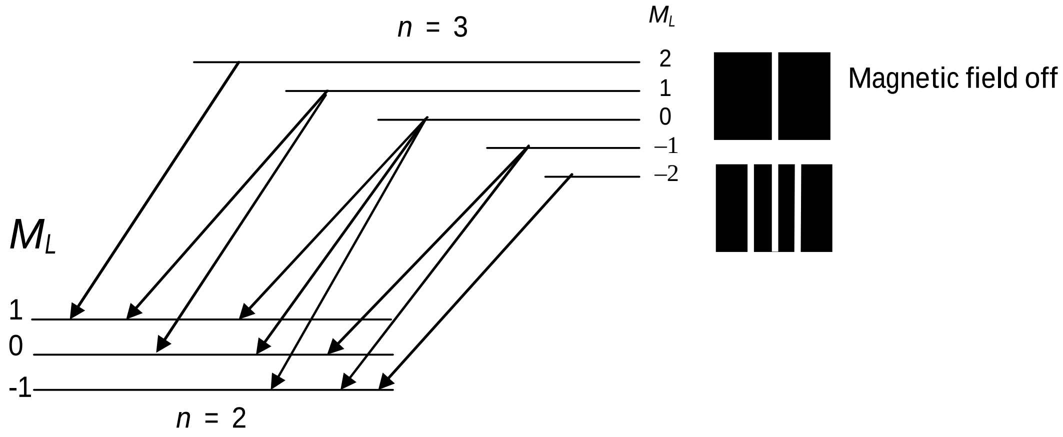


Fig 6. Zeeman splitting in Hydrogen

Here selection rules are same as in previous section. Allowed values of change in magnetic quantum numbers ΔM_L are ±1 and 0.

17.5 Illustrative Examples

Example 1: Calculate the number of energy levels corresponding to energy level *n* = 3 or $E_3 = -E_0/9$.

Sol. For hydrogen atom, energy eigenvelues depend only on principle quantum number *n*. For any value of principle quantum number there are *l* number of orbital angular momentum (*L* = 0, 1, 2, …*n* – 1). For every value of *L*, there are 2*L* + 1 different magnetic quantum states. So:

For *n* = 3: There are 3 values of *L* = 0, 1 , 2 and there corresponding magnetic quantum numbers are {0},{ –1, 0, +1}, {–2, –1, 0, 1, 2} respectively.

So, there are 1 + 3 + 5 = 9 degenerate states. In absence of external magnetic field, all states are same energy but different quantum numbers.

Example 2: Calculate the value of the Bohr magneton for energy difference between m_l = 0 and +1 components of 2P state of atomic Hydrogen placed in 2T magnetic field.

Sol. Bohr magneton is $\mu_B = \frac{e\hbar}{2m}$

$$= \frac{(1.6 \times 10^{-19} C)(1.05 \times 10^{-34}\ J - s)}{2(9.11 \times 10^{-31} Kg)} = 9.27 \times 10^{-24} J/T$$

So the splitting energy $\Delta E = \mu_B B \Delta M_L = 1.16 \times 10^{-0.4} eV$

17.6 Self-Learning Exercise-I

Q.1 Give electronic structure of neon. (Use standard notations).

Q.2 A hydrogen atom is placed in a 2T magnetic field. Considering normal Zeeman Effect for splitting of n = 2 and n = 3 levels.

(a)What is the separation in energy between adjacent M_L levels for the same L?

(b)How many different wavelengths will be there for 3D to 2P transitions, if allowed values of change in M_L are only 0, ±1 ?

Q.3 An atom emits a photon with wavelength 600 nm with transition from L = 1 state to L = 0 state. Determine the shifts in the enrgy levels and in the wavelength resulting from the interaction of the magnetic field 2T and the atom's orbital magnetic moment.

17.7 Explanation of Anomalous Zeeman Effect

When we look at the spectral lines, from the transition between components of multiplet levels (closely spaced spectral lines), we get complex Zeeman pattern. The explanation of this anomalous Zeeman Effect can be done considering electron “spin”.

Anomalous Zeeman Effect was discovered by Thomas Preston in Dublin in 1897. It can be observed in atoms with non-zero spin or atoms with odd number of electrons.

It is happening because of *L*-*S* coupling which is also known as spin-orbit interaction. Coupling of spin and angular momentum gives us total angular momentum. According to vector model of atom, orbital angular momentum vector and spin angular momentum precesses more rapidly about total angular momentum $\vec{J}$. If we apply magnetic field *B* then $\vec{J}$ precesses about magnetic field vector at the Larmor frequency.

When an atom is placed in a weak magnetic field, which does not decouple $\vec{L}$ and $\vec{S}$, along the Z-axis, the magnetic moment of the atom associated with the total angular momentum causes the vector $\vec{J}$ to precess slowly around the magnetic field. The motion is quantized such that the projection of $\vec{J}$ along the field direction, J_z takes discrete values given by M_J(h/2π), where

$$M_J = J, J\text{-}1, J\text{-}2, \ldots, -J.$$

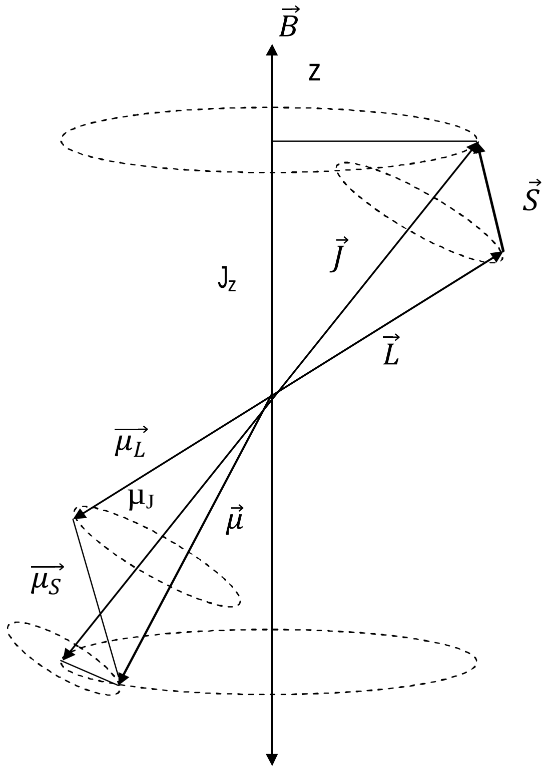


Fig 7. Anomalous Zeeman Effect: total magnetic moment $\vec{\mu}$ (=$\overrightarrow{\mu_L} + \overrightarrow{\mu_S}$) is not exactly antiparallel to $\vec{J}$

Total values of M_J will be 2 J + 1. Due to precession of $\vec{J}$ around $\vec{B}$ we get a small change in energy of atom and its discrete orientations break each (fine-structure) J-level into (2 J + 1) Zeeman levels. The separation between the Zeeman levels depends on the strength of the magnetic field and the total magnetic moment of the atom.

To calculate the separations between Zeeman levels, let us consider the simplest case of a single valence-electron atom. Since atom has single valence-electron, so that valence electron is alone responsible for the angular momentum and the magnetic moment of the atom. Classically the gyromagnetic ratio is $\frac{e}{2m}$. Since this is the ratio of orbital magnetic moment $|\overrightarrow{\mu_L}|$ and angular momentum $\vec{L}$.

Similarly, for studying anomalous Zeeman effect, we require ratio of spin magnetic moment $|\vec{\mu_S}|$ and spin angular momentum $|\vec{S}|$. This ratio is confirmed with quantum mechanics as twice of that of $\vec{L}$. Because of this inequality of these ratios, total magnetic moment $\vec{\mu}$ ($=\vec{\mu_L} + \vec{\mu_S}$) will not exactly antiparallel to $\vec{J}$.

Since total angular momentum is invariant, $\vec{L}$, $\vec{S}$, $\vec{\mu_L}$, $\vec{\mu_S}$ and $\vec{\mu}$ precess around $\vec{J}$. In this precession, component of magnetic moment vector perpendicular total angular momentum will have continual change in direction which gives average to zero. Only parallel component remains a constant of magnitude μ_J. Magnetic moment of atom is also due to parallel component. Thus

$$\mu_J = \text{component of } \vec{\mu_L} \text{ along } \vec{J} + \text{component of } \vec{\mu_S} \text{ along } \vec{J}$$

$$= |\vec{\mu_L}| \cos(\vec{L},\vec{J}) + |\vec{\mu_S}| \cos(\vec{S},\vec{J})$$

$$= \frac{e}{2m}|\vec{L}|\cos(\vec{L},\vec{J}) + \frac{2e}{2m}|\vec{S}|\cos(\vec{S},\vec{J})$$

But $|\vec{L}| = \sqrt{L(L+1)}\,\frac{h}{2\pi}$

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

So,

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

Vectors $\vec{L}$, $\vec{S}$ and $\vec{J}$ make an obtuse-angled triangle, so using triangle property, we have by cosine law

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

and

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

So,

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

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

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

The quantity inside the brackets was first described by Alfred Lande in 1921. It is named after him and known as 'Lande g-factor', that is

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

Relative separation of Zeeman levels for different terms can be directly explained with g-factor. The expression for g-factor for a multi-electron atom under *L*-*S* coupling is same as explained in previous sections.

The expression for the total magnetic moment of the atom now becomes

$$\mu_J = g\frac{e}{2m}\sqrt{J(J+1)}\frac{h}{2\pi} = g\frac{e}{2m}|\vec{J}|.$$

Let us now calculate the magnetic interaction energy. From the previous expression, we get

$$\frac{\mu_J}{|\vec{J}|} = g\frac{e}{2m}.$$

So, ratio of total magnetic moment to the total angular momentum in states can be determined by g ,where the angular momentum is partly orbital and partly spins. (for S = 0 and so J= L, g = 1; for L = 0 and so J = S, g =2).

From Larmor's theorem, angular velocity (or angular frequency) of precession of $\vec{J}$ around the magnetic field $\vec{B}$ is

$$\omega = \frac{\mu_J}{\vec{J}}B = g\frac{e}{2m}B.$$

The energy of precession is equal to product of the projection of $\vec{J}$ along $\vec{B}$ and the angular velocity. In our case magnetic field is along Z-axis, so projection of total angular momentum along magnetic field is the z-component of total angular momentum. That is :

$$J_z = M_J\frac{h}{2\pi}.$$

Thus $\Delta E = \omega J_Z = g\frac{e}{2m}BM_J\frac{h}{2\pi}$

$$\Rightarrow \Delta E = gM_J\frac{eh}{2\pi m}B.$$

Interaction energy, in terms of wave-number is

$$-\Delta T = \frac{\Delta E}{hc} = gM_J \frac{eB}{4\pi mc}.$$

Here $\frac{\mathrm{eB}}{4\pi\mathrm{mc}}$ is the Lorentz unit L'. Thus

$$-\Delta T = gM_J L'.$$

This is the expression the Zeeman shift of a single valance electron system. This is also for the weak-field magnetic interaction energy. The expression for the atoms having two or more valence electrons under L–S coupling is same as one-electron system. For one-electron system, we can see that each J-level splits into (2 J + 1) equal energy spaced Zeeman levels corresponding to the possible values of M_J. The Zeeman splitting depends on the value of g for different levels or we can say it is different for different J-levels. This means that the relative separations of the Zeeman levels of one term and those of another can be determined by the g-factor alone.

Let us consider the Zeeman splitting of sodium of the resonance lines D_1 and D_2. These lines arise from the transitions

$$2P_{\frac{1}{2}} \rightarrow 2S_{\frac{1}{2}} \text{ and } 2P_{\frac{3}{2}} \rightarrow 2S_{\frac{1}{2}}$$

We know that

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

So, the Zeeman levels, g-factors and the Zeeman shifts for the involving terms in these transitions are as follows:

Terms	No. of Zeeman levels (2J+1)	g	M_J (+J, …. J)	Shift in Lorentz unit gM_J
$2S_{\frac{1}{2}}$ $\left(L = 0, S = \frac{1}{2}, J = \frac{1}{2}\right)$	2	2	$\frac{4}{3}$	± 1
$2P_{\frac{1}{2}}$ $\left(L = 1, S = \frac{1}{2}, J = \frac{1}{2}\right)$	2	$\frac{2}{3}$	$\frac{4}{3}$	$\pm\frac{1}{3}$

$2P_{\frac{3}{2}}$ $\left(L = 1, S = \frac{1}{2}, J = \frac{3}{2}\right)$	4	$\frac{4}{3}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	$\pm 2, \pm\frac{2}{3}$

The splitting of these terms has been displayed in figure bellow:

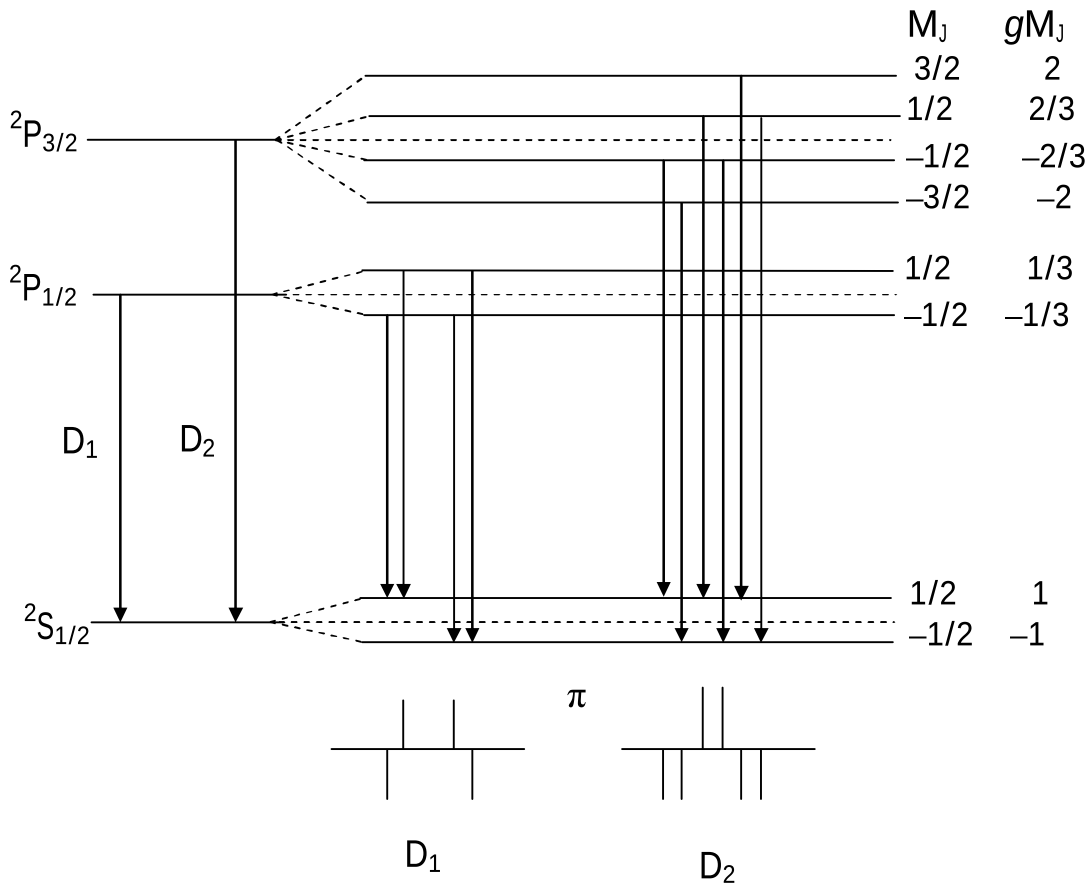


Fig 8. $Transitions\ from\ 2P_{\frac{1}{2}} \rightarrow\ 2S_{\frac{1}{2}}\ \ and\ \ 2P_{\frac{3}{2}}\ \rightarrow\ 2S_{\frac{1}{2}}$.

Applying the selection rules

$$\Delta M_J = 0, \pm 1 \text{ (but } M_J = 0 \nleftrightarrow M_J = 0 \text{ if } \Delta J = 0)$$

We obtain that the D_1 line will split in four Zeeman components and the D_2 line splits in six components. The components corresponding to $\Delta M_J = 0$ will polarize with electric vector perpendicular to the field (σ-components).

The intensities of the Zeeman components given by following rules:

(i) The sum of all the transitions starting from any initial Zeeman level is equal to the sum of all transitions starting from any other level having the same principle quantum number *n* and azimuthal quantum number ***l*** values.

(ii) The sum of all transitions arriving at any Zeeman level is equal to the sum of all transitions arriving at any other level having the same principle and azimuthal values.

17.8 Zeeman Effect in Sodium

Sodium light consists bright doublet which is responsible for the bright yellow light. This can be used to demonstrate several influences. From this we can study splitting of the emission lines of atomic spectra. We get doublet from the transition from 3P to 3S levels. These are same as in hydrogen atom. Since principal quantum number is same and only there is a change in orbital quantum number. 3S (orbital quantum number is 0) is lower than the 3P (L = 1). So, it is also a good example of the dependence of atomic energy levels on angular momentum. The 3S electron is effectively less shielded than the 3P electron, so the 3S level is more tightly bound. Here doublet shows the smaller dependence of the atomic energy levels on the total angular momentum. Because of magnetic energy of the electron spin, in the presence of the internal magnetic field caused by orbital motion, the 3P level splits into two states with total angular momentum J = 3/2 and J = ½. This effect is known as spin-orbit effect. If we apply additional external magnetic field, these levels will split further by the magnetic interaction. It depends on the energies on the z-component of the total angular momentum. This splitting gives the Zeeman effect for sodium.

17.9 Paschen-Back Effect

Paschen-Back Effect is the splitting of atomic energy levels in the presence of strong magnetic field. To observe this effect magnetic field should be sufficiently large to disrupt the coupling of orbital angular momentum and spin angular momentum.

External magnetic field in the Zeeman Effect is weak in comparison to the internal fields due to spin angular momentum and orbital motion of valence electrons of atom. However the strength of external magnetic field is not sufficient to disrupt spin-orbit coupling. If we increase the strength of external magnetic field, separations between multiplet fine structure components increase. For more magnetic field it will increase more and up to the separation become greater than fine-structure components. The anomalous Zeeman pattern then changes again like a normal Zeeman pattern. This is the condition when spin-orbit coupling is disrupted by external magnetic field. This process can be explained in the following way:

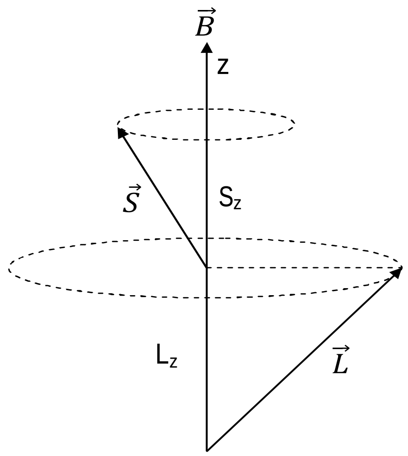


Fig 9. Cartoon diagram for showing respective direction of $\vec{L}$ and $\vec{S}$ and their components.

When we apply external magnetic field stronger than the internal fields, the magnetic coupling between total angular momentum and external magnetic field exceeds the coupling of spin-orbit. The precession of $\vec{J}$ about $\vec{B}$ become faster then $\vec{L}$ and $\vec{S}$ precession about $\vec{J}$. When we apply these conditions than $\vec{L}-\vec{S}$ coupling will partially break down which implies that $\vec{J}$ is not fixed in magnitude any more. If we increase magnetic field $\vec{B}$ more than $\vec{L}$ and $\vec{S}$ start precessing independently about $\vec{B}$. In this state their quantized components along field direction (here we took it in Z-axis) will be L_z and S_z. Magnitudes of these components will be $M_L\hbar$ and $M_S\hbar$ respectively and magnetic quantum numbers M_L and M_S will have discrete values as follows:

$$M_L = L, L-1, L-2, \ldots, -L$$

and $$M_S = S, S-1, S-2, \ldots, -S$$

By Larmor's theorem, the angular velocities of any precession are given by the product of magnetic field and corresponding ratio of magnetic moments with the angular momenta. So for $\vec{L}$ and $\vec{S}$

$$\omega_L = \frac{e}{2m}B \quad \text{and} \quad \omega_S = 2\frac{e}{2m}B$$

Since the energy of any precession is equal to the product of the projection of the corresponding angular momentum vector along the magnetic field direction and angular velocity. That is

$$\Delta E_L = \omega_L L_Z = \frac{e}{2m} B M_L \frac{h}{2\pi}$$

and $$\Delta E_S = \omega_S S_Z = 2\frac{e}{2m} B M_S \frac{h}{2\pi}$$

Main energy shift ΔE from unperturbed energy level is the sum of these two interaction energies. So,

$$\Delta E = \Delta E_L + \Delta E_S$$

$$= (M_L + 2M_S)\frac{eB}{4\pi mc},$$

Or in Lorentz unit of $\frac{eB}{4mc}$,

$$-\Delta T = (M_L + 2M_S)L'$$

This expression is for strong magnetic field interaction energy, where we ignore spin-orbit interaction at all. It shows that each free level will shift into $(2L + 1)(2S + 1)$ magnetic levels. Because $(2L + 1)$ values comes from M_L and $(2S + 1)$ from M_S.

As a specific example, in strong magnetic field, let us consider the transitions

$$2P \rightarrow 2S$$

This transition is responsible for the D_1 and D_2 lines of sodium $2P_{\frac{1}{2}} \rightarrow 2S_{\frac{1}{2}}$. In presence of strong magnetic field, these levels and magnetic shifts for multiplet terms are given in following table:

Term	No. of strong-field levels $(2L+1)(2S+1)$	M_L	M_S	Shift in Lorentz unit $(M_L + 2M_S)$
$^2P\left(L = 1, S = \frac{1}{2}\right)$	6	1, 0 -1	½, - ½ ½, - ½ ½, - ½	2, 0 1, –1 0, –2
$^2S\left(L = 0, S = \frac{1}{2}\right)$	2	0	½, - ½	1, –1

The strong-field splitting of the terms and have been shown in figure bellow:

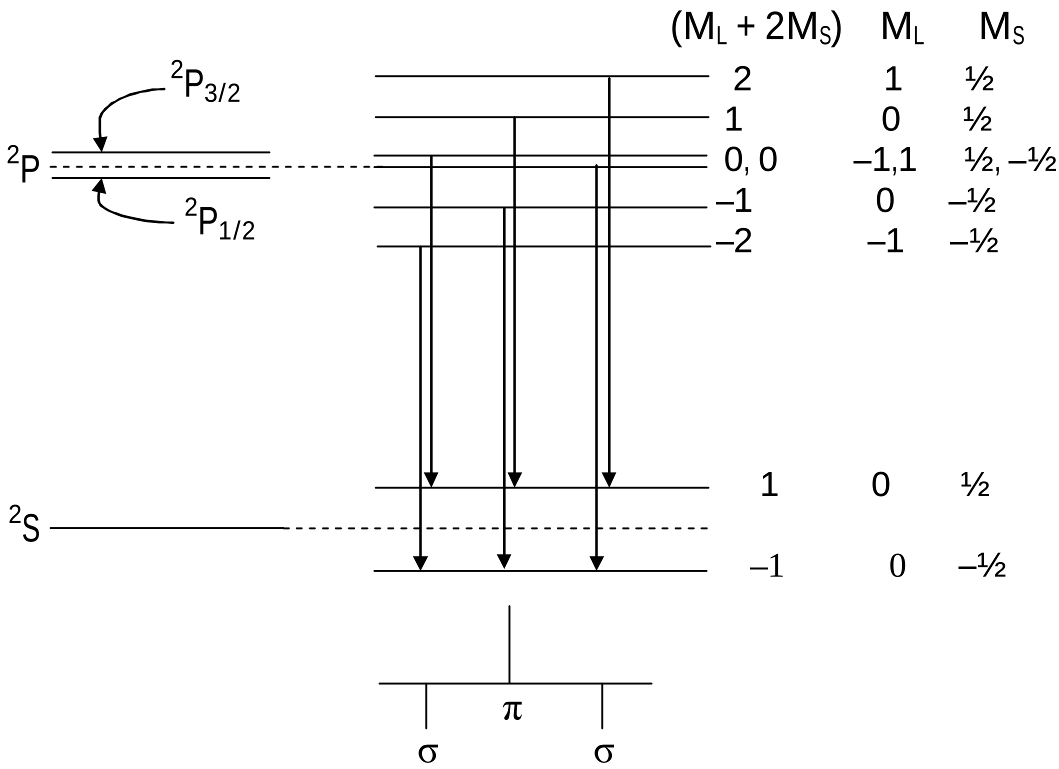


Fig 10.Strong field splitting of the terms ^2P and ^2S

Selection rules in presence of a strong field for above transitions are:

$\Delta M_L = 0$ (Components polarized parallel to the field)

$\Delta M_L = \pm 1$ (Components polarized perpendicular to the field)

$\Delta M_S = 0.$

When these selection rules are applied we get a pattern same as a normal Zeeman triplet.

Spit-Orbit Correction: In practice, the residual spin-orbit coupling changes the relative energies of the components of different terms. Due to this we can add a small term aM_LM_s in the expression for the magnetic interaction energy. Now interaction energy in Lorentz term will become

$$-\Delta T = (M_L + 2M_S)L' + aM_LM_S.$$

This implies that each of two σ-components of normal Zeeman triplet will split in narrow doublet, triplet and so on. In this $2P \rightarrow 2S$ transition, each σ-component will split into a doublet with a separation just two-thirds that of the field-free double.

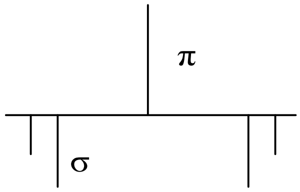


Fig 11. Strong-Field Pattern with Spin-Orbit Coupling

Experimentally, the Paschen-Back effect has been observed for very narrow multiplets only. For example Li doublet having a field-free separation of $0.34cm^{-1}$.Since ordinarily available magnetic field, for example 4.3Tesla magnetic field can produce a magnetic splitting of about 2 cm^{-1} and Paschen-Back Effect occurs when the magnetic splitting exceeds the fine-structure (field-free) splitting. So, for Li doublet it is larger than the fine-structure splitting. Because of this Paschen-Back effect can easily be observed. For sodium resonance doublet ($17cm^{-1}$) fine-structure splitting is much higher. So, to observe this effect in sodium, we need an abnormally large field.

Here we have already considered the cases when the external field is either very weak (Zeeman effect) or very strong (Paschen-Back effect) as compared to the internal field in the atom. For intermediate fields (comparable with internal field) complicated patterns are obtained.

17.10 Transitions from Weak to Strong Field

The number of magnetic levels into which a given state is split doesn't depend on the magnetic field strength. This number is called the 'quantum weight'.

In a weak field, a level with a given inner quantum number J will split into $(2J+1)$levels where orientations of J in external magnetic field is $(2J+1)$. In case of an atom with one valance electron, J can have only two values $L+\frac{1}{2}$ and $L-\frac{1}{2}$, so that level will split into

$$\left\{2\left(L+\frac{1}{2}\right)+1\right\}+\left\{2\left(L-\frac{1}{2}\right)+1\right\}=4L+2$$

levels. In a strong field, L alone has $(2L+1)$orientations and for each of these, S has $(2S+1)$, giving altogether

$$(2L+1)(2S+1)=4L+2 \qquad \text{[Since S = ½]}$$

levels, same as in a weak field.

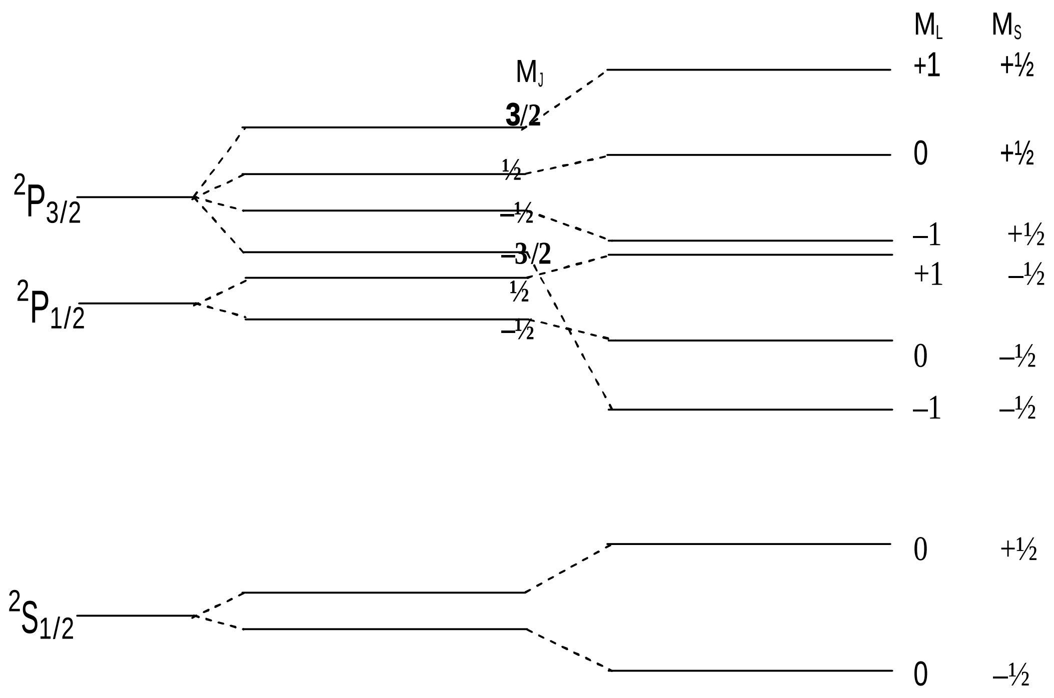


Fig12.*Transition of the magnetic levels corresponding to the states $^2S_{½}$,$^2P_{½}$ and $^2P_{3/2}$.*

In a weak field, we characterize each of the magnetic levels by the quantum numbers J and M_J while in a strong field M_L and M_S are the characteristic quantum numbers. Now, we have to look at the levels J and M_J , which reread a particular level with M_L and M_S when the field is increased. Here, things to be noted that the sum of the projections of the angular momentum vectors on magnetic field does not change. In presence of weak field this projection is M_J and in presence of a strong magnetic field it is M_L+ M_S. Hence the first rule of transition is

$$M_J = M_L + M_S$$

This is insufficient to correlate all weak and strong field levels. Since there are cases when there are more than one level with the same value of M_J. Hence next restriction is that there will not be any two levels with the same M_J cross each other.

17.11 Zeeman Effect in Some Transitions (examples)

(i) $1F_3$ — $1D_2$: It is a singlet-singlet transition. It will give a normal Zeeman triplet.

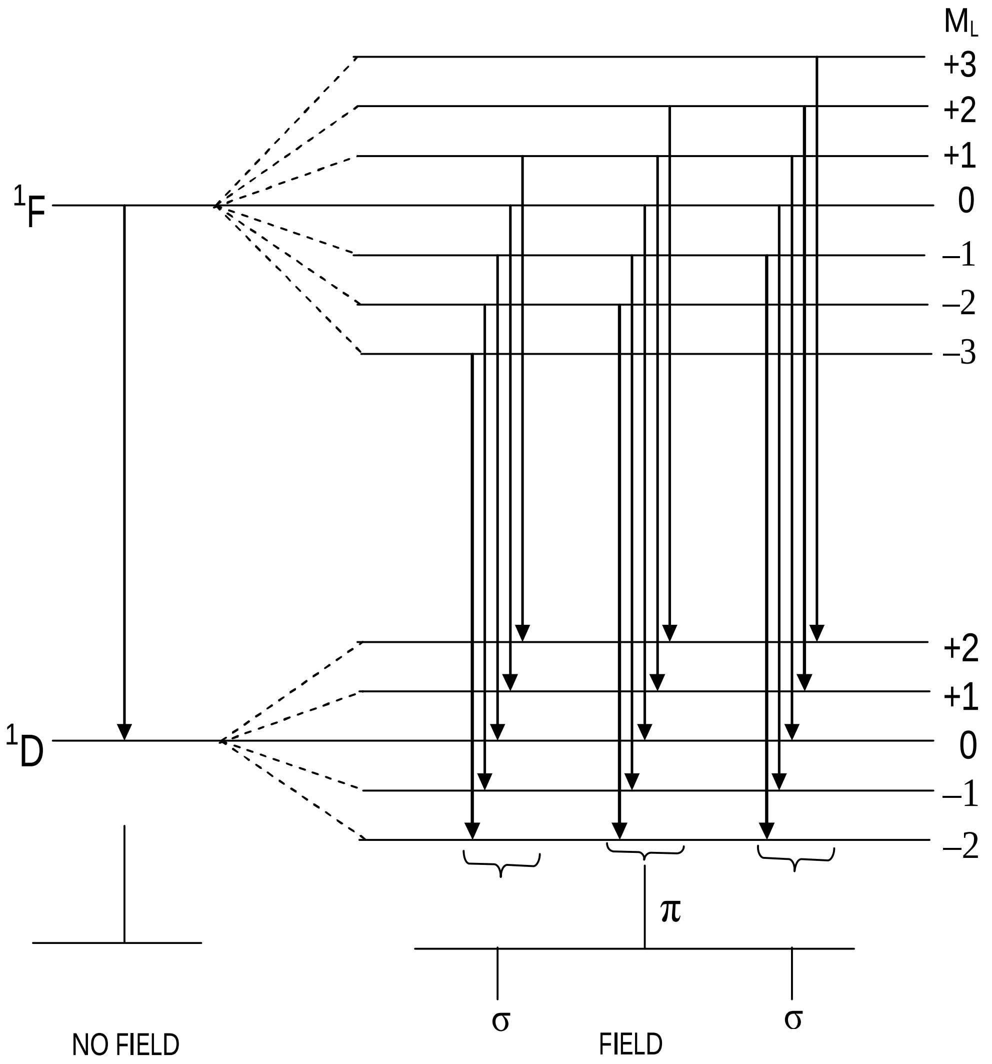


Fig 13.Splitting of $^1F_3$ – $^1D_2$, single-singlet transition.

The terms ^{1}F and ^{1}D correspond to L = 3 and L = 2 respectively. In presence of a weak magnetic field it will break into (2L + 1) = 7 and 5 Zeeman components respectively. The M_L values characterizing the Zeeman levels are 3, 2, 1, 0, -1, -2, -3 and 2, 1, 0, -1, -2 respectively.

Since for singlet terms (S = 0, J = L) the Lande g-factor is 1. The separation between consecutive Zeeman levels is the same for both terms equal to one Lorentz unit. The splitting of the terms is shown in figure .

The selection rules $\Delta M_L = 0, \pm 1$. From these rules we get 15 transitions. Since the Zeeman splitting is same for both terms so, all transitions corresponding to same

ΔM_L coincide in wave number. Hence we obtain only three Zeeman component lines; the π-component corresponding to $\Delta M_L = 0$ and two π-components corresponding to $\Delta M_L = \pm 1$. This is normal Zeeman triplet.

(ii) $\boldsymbol{2D_{\frac{3}{2}} - 2P_{\frac{1}{2}}}$: It is a doublet-doublet transition. So, the Zeeman pattern would be anomalous. The weak-field interaction energy of a one-electron atom is given by

$$\Delta T = gM_J L',$$

where L' is the Lorentz unit. The Lande g-factor is

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

The Zeeman levels, g-factors and the Zeeman shifts for the given terms $2P_{\frac{1}{2}}$ and $2D_{\frac{3}{2}}$ are as follows:

Term	No. of Zeeman levels (2J +1)	*g*	M_J (+J, …. –J)	Shift in L' unit g M_J
$2P_{\frac{1}{2}}$ $\left(L = 1, S = \frac{1}{2}, J = \frac{1}{2}\right)$	2	$\frac{2}{3}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{3}, -\frac{1}{3}$
$2D_{\frac{3}{2}}$ $\left(L = 2, S = \frac{1}{2}, J = \frac{3}{2}\right)$	4	$\frac{4}{5}$	$\frac{2}{3}$	$\frac{6}{5}, \frac{2}{5}, -\frac{2}{5}, -\frac{6}{5}$

The splitting of these terms has been displayed in figure14:

The selection rule is $\Delta M_J = 0, \pm 1$.

There are in all six allowed transitions ,hence six Zeeman components. Transitions corresponding to $\Delta M_J = 0$ give π-components polarized parallel to the magnetic field and transitions corresponding to $\Delta M_J = \pm 1$ give σ-components polarized perpendicular to the field as shown in the energy level diagram.

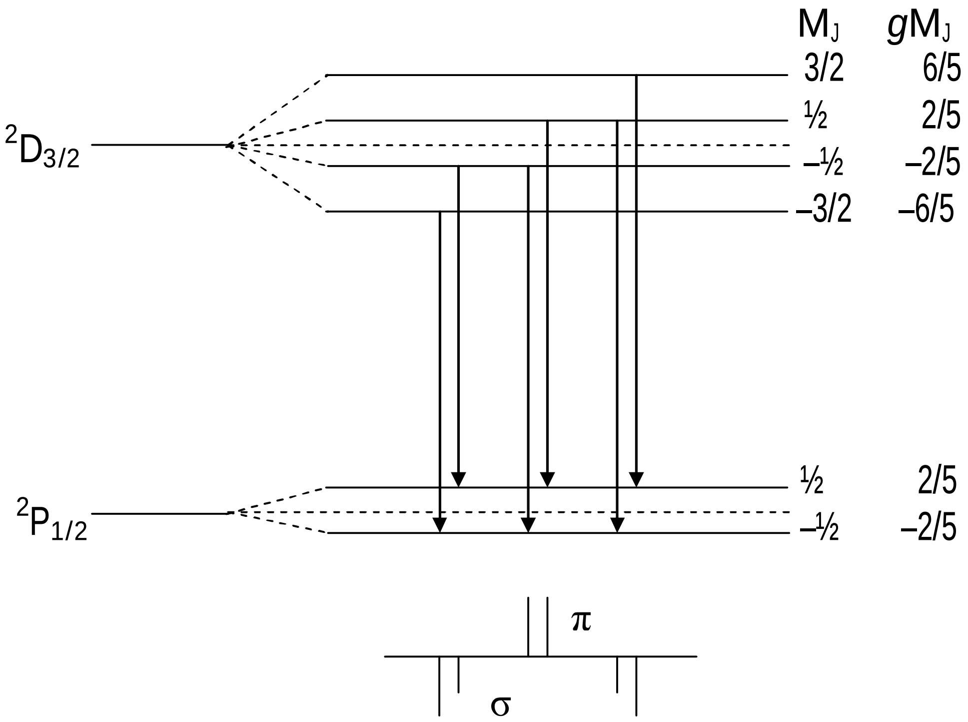


Fig 14. *Zeeman shifts for the given terms* $2P_{\frac{1}{2}}$ *and* $2D_{\frac{3}{2}}$, *doublet-doublet transition*

(iii) $\boldsymbol{2D_{\frac{5}{2}} - 2P_{\frac{3}{2}}}$**:** It is again a doublet-doublet transition so that the Zeeman pattern would be anomalous.

The Zeeman levels, g-factors and the Zeeman shift for the given terms $2P_{\frac{3}{2}}$ and $2D_{\frac{5}{2}}$ are as follows:

Term	No. of Zeeman levels (2J +1)	*g*	M_J (+J, …. –J)	Shift in L' unit g M_J
$2P_{\frac{3}{2}}$ $\left(L = 1, S = \frac{1}{2}, J = \frac{3}{2}\right)$	4	$\frac{4}{3}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$\frac{6}{3}, \frac{2}{3}, -\frac{2}{3}, -\frac{6}{3}$
$2D_{\frac{5}{2}}$ $\left(L = 2, S = \frac{1}{2}, J = \frac{5}{2}\right)$	6	$\frac{6}{5}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	$\frac{15}{5}, \frac{9}{5}, \frac{3}{5}, -\frac{9}{5}, -\frac{15}{5}$

The splitting of these terms has been displayed in figure given bellow:

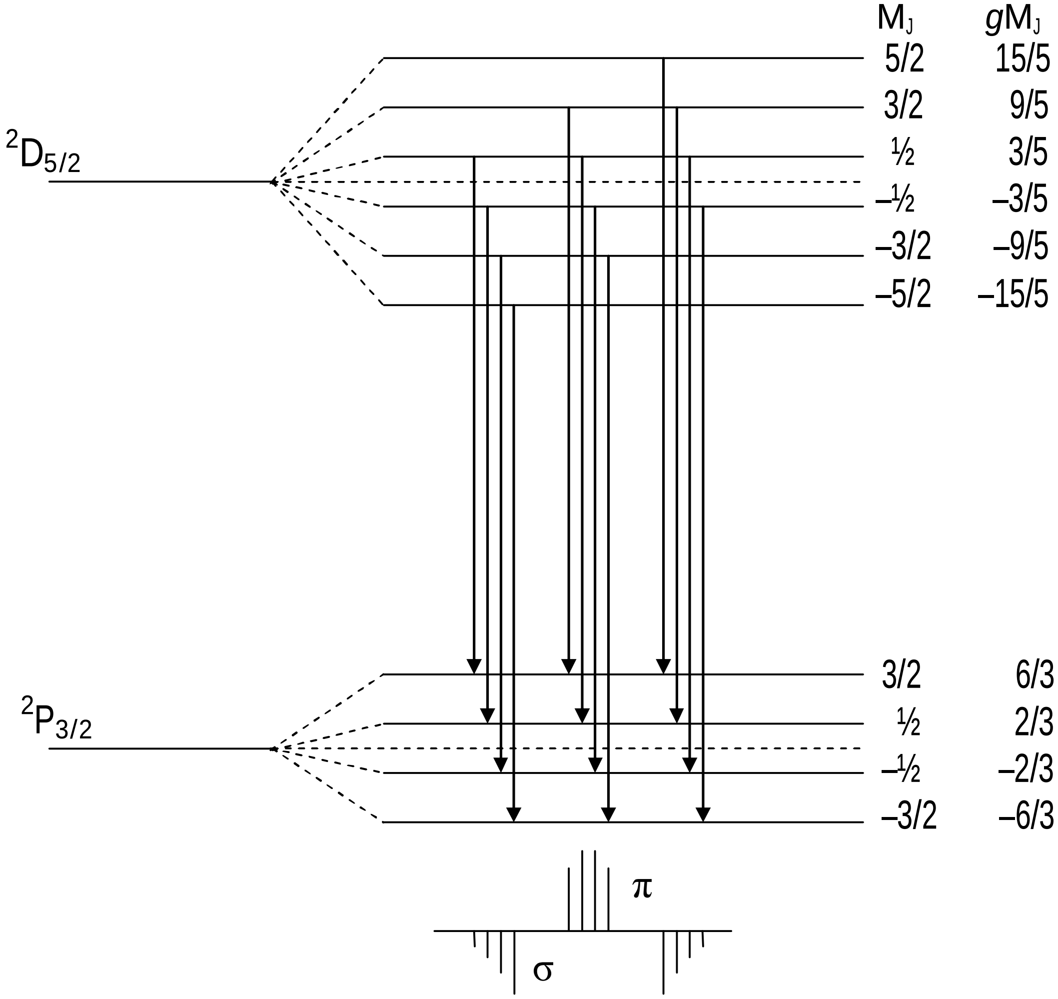


Fig 15*.Double-doublet transition $^2D_{5/2}$ – $^2P_{3/2}$. The complete Zeeman pattern of 12 components*

The selection rule in operation is $\Delta M_J = 0, \pm 1$.

There are four allowed transitions corresponding to $\Delta M_J = 0$ which give π-components while the all four transitions each corresponding to $\Delta M_J = \pm 1$ give σ-components.

(iv) Principal Series Triplet ^{3}P – ^{2}S or $3P_{0,1,2} - 3S_1$: The fine-structure transitions are:

$$3P_0 - 3S_1;\ 3P_1 - 3S_1;\ 3P_2 - 3S_1$$

The *g*-factor and Zeeman shifts for the unperturbed levels $3P_0$, $3P_1$, $3P_2$ and $3S_1$ are as follows:

Unperturbed level	No. of Zeeman levels (2J+1)		M_J (+J, … -J)	Shift in Lorentz unit gM_J
$3P_0$ (L = 1, S = 1, J = 0)	1	$\frac{0}{0}$	0	0
$3P_1$ (L = 1, S = 1, J = 1)	3	$\frac{3}{2}$	1, 0, – 1	$\frac{3}{2}, 0, -\frac{3}{2}$
$3P_2$ (L = 1, S = 1, J = 2)	5	$\frac{3}{2}$	2, 1, 0, – 1, – 2	$\frac{6}{2}, \frac{3}{2}, 0, -\frac{3}{2}, -\frac{6}{2}$
$3S_1$ (L = 0, S = 1, J = 1)	3	2	1, 0, – 1	2, 0, -2

The magnetic splitting of levels is shown in figure bellow:

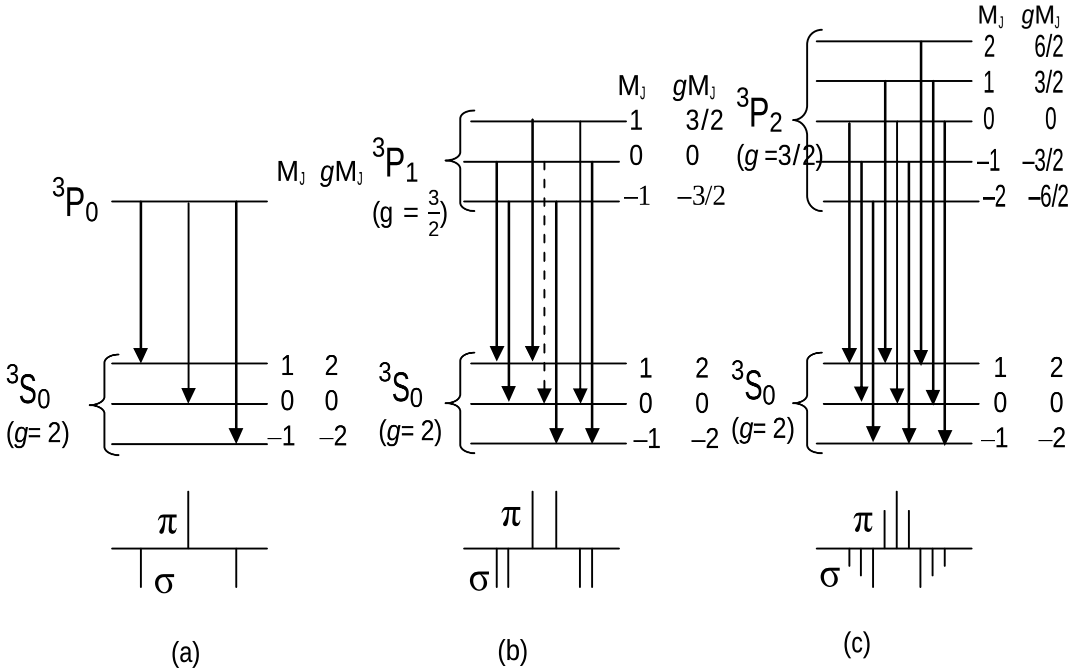


Fig 16. Splitting of $^3P_{0,1,2}$ and $^3S_1$ level in magnetic field.

From selection rules $\Delta M_J = 0, \pm 1$ (but $\Delta M_J = 0 \nleftrightarrow M_J = 0$ if $\Delta J = 0$) we get, three Zeeman components in the transition $3P_0 - 3S_1$; six in $3P_1 - 3S_1$ and nine in $^3P_2$ – $^3S_1$. The Zeeman transition $M_J = 0 \to M_J = 0$ in $3P_1 - 3S_1$ is forbidden. Since, at the same time $\Delta J = 0$. This transition is indicated by a dotted line in figure.)

Energy-level diagram for the Zeeman patterns are shown in figure. While the qualitative structure of each pattern depends only on two unperturbed levels for the values of *J*. The energy separations depend on *g* and hence on other properties like coupling conditions and on other quantum numbers.

All the three patterns in this transition are symmetrical with regard to wave number, intensity and polarization of the components. The π-components form a central group and polarized with electric vector parallel to magnetic field. The σ-components form two symmetrically displaced groups and the components are equidistant in each and electric vector perpendicular to the field. The sum of the intensities of the π-components are equal to that of the σ-components.

(v) $\boldsymbol{3P_1 - 3D_2}$: It is a triplet-triplet transition. It would give an anomalous Zeeman pattern in a 'weak' external magnetic field. The Zeeman shifts of the various forms an unperturbed level are given by

$$-\Delta T = gM_J L',$$

where L' is the Lorentz unit and g is given by

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

The Zeeman levels, g-factors and the shifts from the given unperturbed levels $3D_2$ and $3P_1$ are given in following table:

Unperturbed level	No. of Zeeman levels (2J + 1)	G	$M_J(+J, \ldots, -J)$	Shift in Lorentz unit gM_J
$3D_1$ (L = 2, S = 1, J = 2)	5	$\frac{7}{6}$	2, 1, 0, -1, -2	$\frac{14}{6}, \frac{7}{6}, 0, -\frac{7}{6}, -\frac{14}{6}$
$3P_2$ (L = 1, S = 1, J = 1)	3	$\frac{3}{2}$	1, 0, -1	$\frac{3}{2}, 0, -\frac{3}{2}$

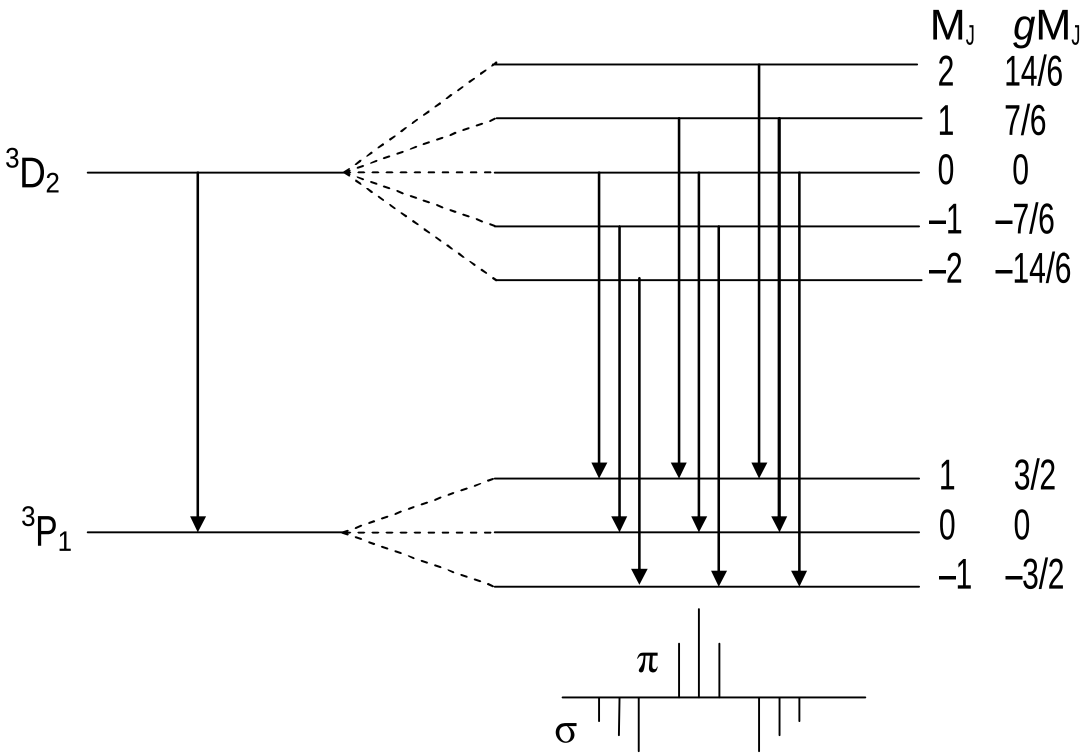


Fig 17.Triplet-triplet transition $^3P_1$ - $^3D_2$

From selection rules $\Delta M_J = 0, \pm 1$ ($M_J = 0 \nleftrightarrow M_J = 0$ if $\Delta J = 0$) we get 9 allowed transitions. $\Delta M_J = \pm 1$ each give three σ components. The complete pattern with Zeeman splitting of the levels $^3D_2$ and $^3P_1$ isfigure.

(vi) $\boldsymbol{3D_3 - 3P_2}$**:** This is also a triplet-triplet transition. This would give an anomalous Zeeman pattern in a 'weak' external magnetic field.

Zeeman levels, *g* factors and the shifts from the unperturbed levels $3D_2$ and $3P_2$ are given in following table:

Unperturbed level	No. of Zeeman levels (2J + 1)	g	M_J $(+J, \dots, -J)$	Zeeman Shift in Lorentz Unit gM_J
$3D_3$ $\left(L = 2, S = 1, J = 3\right)$	7	$\frac{4}{3}$	3, 2, 1, 0, -1, -2, -3	$\frac{12}{3}, \frac{8}{3}, \frac{4}{3}, 0, -\frac{4}{3}, -\frac{8}{3}, -\frac{12}{4}$

$3P_2$ $\begin{pmatrix} L = 1, S = 1, \\ J = 2 \end{pmatrix}$	5	$\frac{3}{2}$	2, 1, 0, -1, -2	$\frac{6}{2}, \frac{3}{2}, 0, -\frac{3}{2}, -\frac{6}{2}$

The splitting of these levels are shown in figure bellow:

From selection rules $\Delta M_J = 0, \pm 1$ ($M_J = 0 \nleftrightarrow M_J = 0$ if $\Delta J = 0$) we get, 15 allowed transitions. From the rule $\Delta M_J = \pm 1$ we get, five σ-components. The complete pattern is shown in the energy-level diagram.

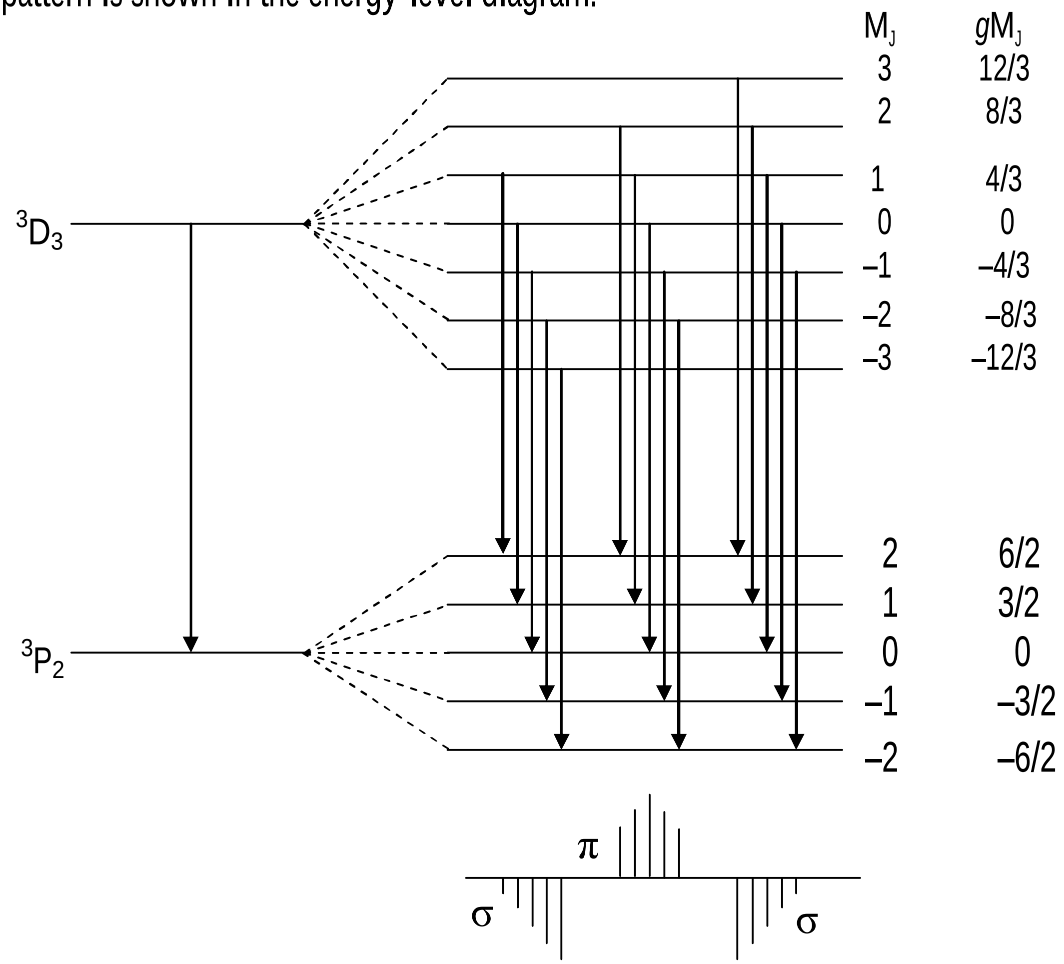


Fig 18.Splitting of $^3D_3$ – $^3P_2$ levels.

7.12 Illustrative Examples

Example-3: Calculate the distance between Zeeman components of a spectral line of wavelength 4500 Å. If a sample of a certain element is kept in a magnetic field. Given Flux density 0.3 Tesla, $e/m = 1.76 \times 10^{11}$ C/kg, $c = 3 \times 10^8$ m/s.

Sol. The wave-number separation between the components of a normal Zeeman triplet is given by

$$\Delta\nu = \frac{eB}{4\pi mc} = \left(\frac{e}{m}\right)\frac{B}{4\pi c}$$

Putting the given values, we get

$$\Delta\nu = \frac{(1.76 \times 10^{11}\, C/kg)0.3\, N/A - m}{4 \times 3.14 \times (3.0 \times 10^{8}\, m/s)}$$
$$= 14.0\, m^{-1}$$

Now, $\nu\lambda = 1$

or $\nu\Delta\lambda + \lambda\Delta\nu = 0$

or $|\Delta\lambda| = \frac{\lambda\Delta\nu}{\nu} = \lambda^2\Delta\nu$

$$= (4500 \times 10^{-10} m)^2 (14.0\, m^{-1})$$
$$= 283.5 \times 10^{-14} m$$
$$= 0.02835\, \text{Å}$$

Example-4: Evaluate the Lande *g*-factor in the 2p3s configuration for the $3P_1$ of the atom and use the result to predict the splitting of the level. Atom is in an external magnetic field of 0.1 Tesla.

Sol. For the $3P_1$ level, we have

$$L = 1, S = 1, J = 1,$$

So
$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$
$$= 1 + \frac{1(1+1) - 1(1+1) + 1(1+1)}{2 \times 1(1+1)}$$
$$= 1 + \frac{1}{2} = \frac{3}{2}$$

For J = 1, the possible values of M_J are 1, 0, -1 and so the level is split into three components. The wave-number shift of the components is given by

$$\Delta T = gM_J \frac{eB}{4\pi mc}$$

The Zeeman level corresponding to $M_J = 0$ remains unshifted while those corresponding to $M_J = \pm 1$ are shifted by

$$\Delta T = \pm g \frac{eB}{4\pi mc}$$

$$= \pm \frac{3}{2} \frac{(1.6 \times 10^{-19})(0.1\, N/A - m)}{4 \times 3.14 \times (9.1 \times 10^{-31} kg)(3 \times 10^8\, m/s)}$$

$$= \pm 7.0 m^{-1}$$

$$= \pm 0.07 cm^{-1}$$

17.13 Self-Learning Exercise-II

Q.1 Calculate the effective magnetic field experienced by the electron in the 3P levels of sodium atom.

Q.2 Suppose the sodium D_1 line emitted in a magnetic field is observed to be split into 4-components. What is the magnetic field B ? (Given values are: Wavelength difference = 0.022 nm, D_1 line is at 589.5 nm)

Q.3 Calculate the number of energy levels corresponding to energy level n = 2 or $E_3 = -E_0/4$.

Q.4 Calculate the number of transitions between $1D_2$ and $1P_1$ states due to normal Zeeman Effect.

17.14 Summary

American solar astronomer George Ellery Hale observed Zeeman Effect in the solar spectra in 1908. This sprctra indicate the existence of strong magnetic fields in sunspots. Such fields can be of the order of 0.1 Tesla or higher. Zeeman Effect is utilized in many laser cooling applications such as a magneto-optical trap and the Zeeman slower. Zeeman Effect is also useful to measure magnetic field strength and orientations in Tokamak plasma. It can also measure temperature from Zeeman components.

17.15 Glossary

Multiplet : A group of spectral lines.

LS coupling : Coupling of angular momentum and spin angular momentum of an electron.

Bohr magneton : A physical constant (it can be different for spin and angular).

Selection rules : Constrains of the possible transitions of from one quantum state to another.

Zeeman energy : Potential energy of magnetized particles in external magnetic field.

g factor : Dimensionless quantity for magnetic moment and gyromagnetic ratio.

17.16 Answers to Self-Learning Exercises

Answers to Self-Learning Exercise- I

Ans.1: $1S^2\ 2S^2\ 2P^6$

Ans.2: (a) 1 and 9.274×10^{-24} J/T (b) 9

Ans.3: Wavelength shift = 0.034 nm

Answers to Self-Learning Exercise- II

Ans.1: 18 T

Ans.2: 0.51 T = 5100 Gauss

Ans.3: 6

Ans.4: 9 (will give only 3 spectral lines.)

17.17 Exercise

Q.1 Describe an experimental set-up to study Zeeman Effect.

Q.2 What do you understand by anomalous Zeeman Effect ? Discuss the Zeeman pattern of the resonance (D_1 , D_2) lines for sodium.

Q.3 Distinguish between normal Zeeman, anomalous Zeeman and Paschen-Back effects. Determine the Lande g-values for the various levels of multiplets.

Q.4 Calculate splitting of term $4D_{½}$ in arbitrary magnetic field.

Q.5 In one electron atom, determine Zeeman transition line for $2D_{3/2} – 2P_{3/2}$.

Q.6 In one electron atom, determine Zeeman transition line in $2D_{5/2} – 2P_{3/2}$.

Q.7 Calculate g-factor for 3P term.

Q.8 Write down the number of Zeeman levels (2J + 1) for $2P_{3/2}$ term.

Q.9 Write down the values of L, S and J for $2D_{5/2}$ term.

Q.10 What are the possible values of M_J for $2P_{3/2}$.

17.18 Answers to Exercise

Ans.1: See section 17.2.

Ans.2: See section 17.7 and 17.8

Ans.3: See section 17.9

Ans.4: 0

Ans.5: 10

Ans.6: 12

Ans.7: $3P_{0,1,2}$: g = 0/0. 3/2, 3/2

Ans.8: 4

Ans.9: L = 2, S = ½, J = 5/2.

Ans.10: ±3/2, ±1/2.

References and Suggested Readings

1. Nobel Lectures: Physics, Vol. 1, Elsevier, Amsterdam, 1967.
2. R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles. 2nd ed., Wiley, New York, 1985.
3. W. A. Hilton, Am. J. Phys. 30, 724 (1962).
4. Feynman, Richard P., Leighton, Robert B., Sands, Matthew (1965). The Feynman Lectures on Physics 3. Addison-Wesley. ISBN 0201021153

UNIT-18
The Stark Effect and Hyperfine Structure of Spectral Lines

Structure of the Unit

18.0 Objectives

In 1913, German physicist Johannes Stark studied Hydrogen atom emission in electric field of a condenser. In presence of external electric field (of the order of 10^5 V/cm), he observed the shifting and a splitting of the spectral lines of the Balmer series of hydrogen (emission spectra). Observable amount of splitting or shifting is known as Stark shift. It is also known as Stark splitting. In previous chapter, we have already studied Zeeman Effect where a spectral line split into several components due to external magnetic field; similarly Stark effect is electric analogue of Zeeman Effect.

18.1 Introduction

The Strak Effect is a result of interaction of external electric field with electric moment of the atom. Interaction energy can be defined as $W = -\vec{p}.\vec{E}$

where $\vec{p}$ is the electric dipole momentof electron in atom. Electric dipole moment comes in picture because of charge distribution and it can be calculated with the charge distribution. Here we will study two aspects of the Stark Effect: the linear effect and the quadratic effect. Here we will see that the linear effect is due to a dipole moment which is induced by the external electric field. For simplicity fine and hyperfine structure effect will be neglected. We can explain and study the molecule formation from atoms, broadening of spectral lines and dielectric constants with the study of Stark Effect.

18.2 Stark Effect of Hydrogen Atom

In Stark Effect, if we take observations from different positions, then we get some different results. In particular and for simplicity we look at perpendicular and parallel to the applied electric field. When we look at perpendicular to electric field then we get two plane-polarized lines or components. One component is parallel to electric field vector, called π – component and another is perpendicular to electric field vector, called σ – component. If we observe parallel to electric field then we get only one unpolarized component, known as σ– component. Few initial observations of Stark Effect are as:

(i) In general, all hydrogen lines are in symmetrical patterns but the pattern mainly depends on the principal quantum number *n*. Number of Stark lines and width of pattern increases with *n*.

(ii) Wavenumber shifts are same for all hydrogen lines. It is integral multiples of a unit which is proportional to the strength of the electric field.

(iii) Polarization properties of Stark lines are same as Zeeman lines. Only, the $\pi-$ component shows more shift than the $\sigma-$ component.

(iv) Ordering of Stark components is in the increasing order of principal quantum number n as H_α, H_β, H_γ.

(v) For lower energy states symmetrical splitting is proportional to the field intensity and for higher states Stark components show unidirectional displacements proportional to the square of the field strength. This is called second-order Stark Effect.

18.3 Weak-field Stark Effect in Hydrogen

Since, orbital angular momentum $\vec{l}$ and spin angular momentum $\vec{s}$ of the electron of a hydrogen atom have magnetic interaction. When we apply an external electric field $\vec{F}$,then it will interact with total angular momentum$\vec{j}$. If field interaction energy with electron's total angular momentum is less than the magnetic interaction energy between orbital momentum and spin momentum then the Stark splitting will be much smaller compared with the fine-structure splitting. Such a field is known as weak-field.

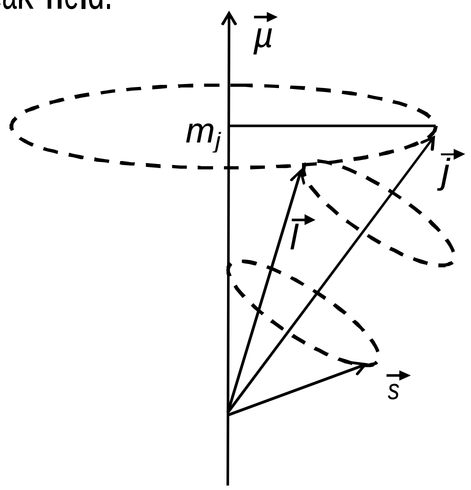


Fig 19.*Schematic diagram of l-s coupling*

We get $\vec{j}$ by the coupling of $\vec{l}$ and $\vec{s}$. Therefore $\vec{j}$ precesses around $\vec{F}$ with projection $m_j\, h/2\pi$,

$$m_j = +j,\ \ j-1,\ \ j-2, \ldots, -j.$$

So, unlike the Zeeman levels, the Stark levels $+m_j$ and $-m_j$ arise from a given unperturbed level which have same energy.

Selection rules for weak-field Stark effect are the same as those for the Zeeman effect, that is

$\Delta m_j = 0$ gives π components

$\Delta m_j = \pm 1$ gives σ components

Following these selection rules, each of the fine-structure components I, II, III, IV, V in H_α should show a symmetrical Stark pattern. The weak-field Stark pattern has never been observed.

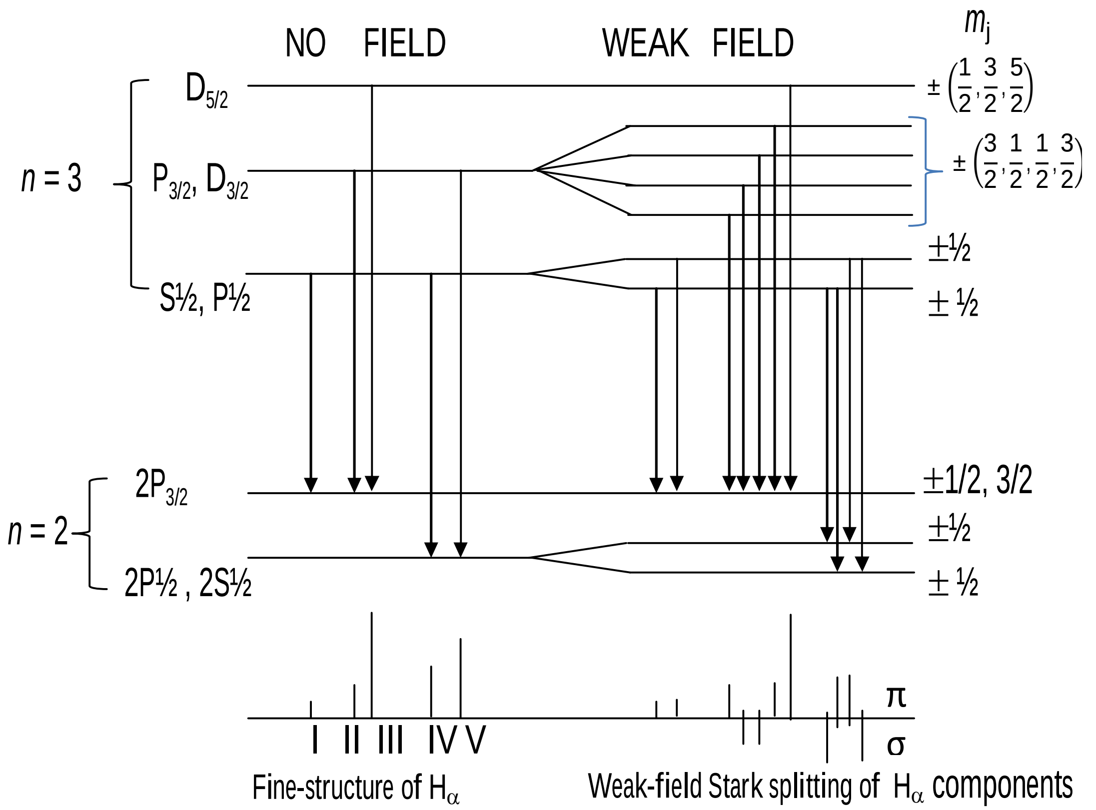


Fig 20. *Energy levels of H-atom for the transitions n = 3 and n = 2.*

18.4 Strong-Field Stark Effect in Hydrogen

When we apply an electric field $\vec{F}$ on hydrogen which has the interaction energy with electron's angular moment $\vec{j}$, such that it is greater than the magnetic interaction energy between electron's orbital momentum $\vec{l}$ and spin momentum $\vec{s}$. Therefore, the Stark splitting of the energy levels due to the electric field will be larger than the fine-structure splitting. This is known as the 'strong' field for which first-order Stark effect in hydrogen has actually been observed. In such strong field, magnetic coupling between $\vec{l}$ and $\vec{s}$ is breakdown and $\vec{l}$ get quantized. It precesses independently around the applied electric field $\vec{F}$. The spin is however not acted on by $\vec{F}$.

In 1916, German physicists Karl Schwarzchild and Russian-American physicists Paul Sophus Epstein independently explained the observation of first-order Stark Effect in hydrogen and they explained the same for ionized helium by quantizing a hydrogen-like atom in an electric field. At that time electron spin was not discovered. For this explanation, they used Bohr-Sommerfeld quantum theory, which is known as old quantum theory. This was taken an outstanding triumph for the old quantum theory because the results given by this theory were very little altered by quantum mechanical treatment.

Let an electron is moving in a Kepler ellipse. If we will apply homogeneous electric field $\vec{F}$ along *z*-axis than it will behave differ than magnetic field. If we average the center of gravity of the electron for the Kepler motion then it will not coincide with the nucleus which forms an electric dipole. Electric field applies a torque on the orbital dipole which causes a precession of the orbital about the *z*-axis. However, in presence of magnetic field the orbital angular momentum $\vec{l}$ is not a constant and the orbital quantum number l is no longer a "good" quantum number. The projection of $\vec{l}$ along electric field (*z*-axis) is l_z, given by $m_l\, h/2\pi$, where m_l is the electric quantum number. l_z is still a constant of motion and m_l retains its strict meaning. Energy value in parabolic coordinates depends on field-free energy of atom E_0, Bohr radius a_0, principle quantum number n and two new parabolic quantum numbers n_1 and n_2. These parabolic quantum numbers are defined as:

$$m_l = n - n_2 - n_1 - 1$$

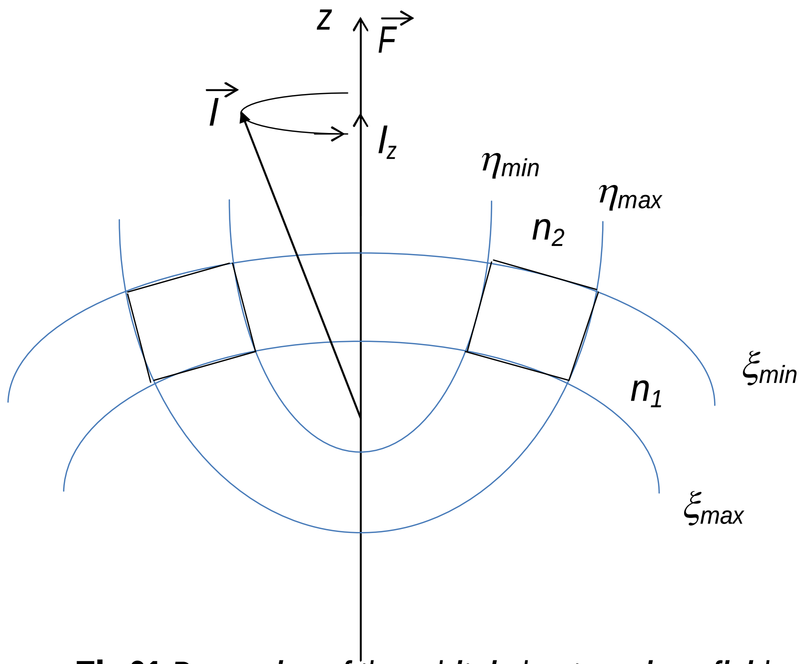


Fig 21.*Precession of the orbital about z-axis or field axis.*

Since, allowed values are

$$n = 1, 2, 3, \ldots . \infty$$
$$m_l = 0, \pm 1, \pm 2, \ldots . , \pm(n-1)$$
$$n_1 = 0, 1, 2, 3, \ldots . , n-1$$
$$n_2 = 0, 1, 2, 3, \ldots . , n-1$$

n_1 limits the electron's motion to the region between the two paraboloids of revolution ξ and ξ_{max}; while n_2 limits it to the region intersected by the two pairs of paraboloids, the electron has three periodic motions, one around the field $\vec{F}$ given by m_l and one each along the ξ and η coordinates given by n_1 and n_2. Since the last two periods are not necessarily the same, the orbit is not closed and the electron in time covers every point in the intersected region.

18.5 Illustrative Examples

Example1. Prove that the Stark-shift for the ground state (n = 1) of hydrogen is zero.

Sol. Shift is given by the

$$-\Delta T = \frac{\Delta E}{hc} = \frac{3a_0 e}{2Zhc} Fn(n_2 - n_1)$$

Putting the values of a_0, e, h, c and Z (=1 for H-atom)we get

$$-\Delta T = \frac{3 \times 0.53 \times 10^{-10} m \times 1.6 \times 10^{-19}}{2 \times 6.63 \times 10^{-34} J\ s \times 3 \times 10^{8} ms^{-1}} F\ n(n_2 - n_1)$$

$$= 6.4 \times 10^{-5}\ Fn(n_2 - n_1) cm^{-1}.$$

(Here field F is expressed in Volt/cm.)

Allowed values of n , n_2 and n_1 can be get from $m = n - n_2 - n_1 - 1$. Here $m = 0$, $n = 1$. So, $n_2 - n_1 = 0$. This implies that the Stark-shift for ground state of hydrogen is zero.

Example 2. Excluding nuclear spin, write down the configuration of $n = 2$ in hydrogen atom.

Sol. For a given ***j*** there are 2***j*** + 1 degenerate sublevels can be written:

$2S_{1/2} \Rightarrow |2S_{1/2}, +1/2\rangle, |2S_{1/2}, -1/2\rangle$

$2P_{1/2} \Rightarrow |2P_{1/2}, +1/2\rangle, |2P_{1/2}, -1/2\rangle$

$2P_{3/2} \Rightarrow |2P_{3/2}, +3/2\rangle, |2P_{3/2}, +1/2\rangle, |2P_{3/2}, -1/2\rangle, |2P3/2, -3/2\rangle$

When angular momentum and spin will not couple (strong field) then these levels will split as given bellow:

$|2S1/2, \pm 1/2\rangle = |2S, 0\rangle \otimes |\pm 1/2\rangle$

$|2P1/2, \pm 1/2\rangle = (1/\sqrt{3})|2P, 0\rangle \otimes |\pm 1/2\rangle - \sqrt{(2/3)}\, |2P, \pm 1\rangle \otimes |\mp 1/2\rangle$

$|2P3/2, \pm 1/2\rangle = \sqrt{(2/3)}\, |2P, 0\rangle \otimes |\pm 1/2\rangle + (1/\sqrt{3})|2P, \pm 1\rangle \otimes |\mp 1/2\rangle$

$|2P3/2, \pm 3/2\rangle = |2P, \pm 1\rangle \otimes |\pm 1/2\rangle$

18.6 Hyperfine Structure of Spectral Lines

When we increase the resolution of instruments by taking high resolution instruments to observe the Stark Effect, we get further splitting into more components. Order of this splitting is very much smaller than ordinary splitting multiplet. This further splitting is known as 'hyperfine structure' and it is caused by properties of the atomic *nucleus*.

To study hyperfine structure experimentally, we need a light source which gives extremely sharp lines. In hyperfine structure, there are two types of nuclear effects. First is the presence of isotopic species in the given sample or study element. Isotope produces spectral lines at slightly different wavenumbers relative to each other. Second type of effect comes from charged nucleus possesses as spin angular momentum and the associated magnetic dipole moment. Hyperfine splitting of the spectral terms comes from the interaction between internal magnetic field (produced by orbital motion of electron) of atom and spin magnetic dipole moment of the nucleus.

18.7 Isotope Effects

Many elements have different contents of isotopic atoms. Since, different isotopes of an element have same number and same arrangement of extra-nuclear electrons. But isotopes have different masses from each other. Since Rydberg constant for an atom depends on the nuclear mass, through the reduced mass of the atom. Different isotopes have slightly different values of Rydberg constant. Correspondingly, the same transitions in different isotopes give rise to slightly different wavenumbers.

In hydrogen atom variation in Rydberg constant can be observed easily. First four members of Balmer series, H_α , H_β , H_γ and H_δ (each) has a very weak companion on the short-wavelength side at distances of 1.79, 1.33, 1.19 and 1.12 Å respectively. These shifts agree with the theoretical values if the companions are attributed as due to presence of an isotope of mass 2 (deuterium) and it was in this way that the existence of heavy hydrogen was first established.

Hydrogen isotope shift is the simplest case. Many cases of isotope-shift are not as simple. In many earths and heavier atoms, isotope shift comes due to their different radii with masses, not due to their masses only. These calculations can be understood purely with Columbian interaction.

18.8 Self-Learning Exercise- I

Q.1 Write down the degenerate states in $n = 3$ subspace.

Q.2 Write down the first order stark splitting of the level $n = 3$ for hydrogen.

Q.3 A particle of charge q and mass m, which is moving in a one-dimensional harmonic potential of frequency ω, is subjected to a weak electric field E in z-direction.

a. Find expression for energy.
b. Calculate the energy to first nonzero correction and compare it with above result.

18.9 Illustrative Examples

Example 1 Calculate the shift for H_β line (4861.33 Å).

Sol. For this transition, we have from Balmer's formula

$$\frac{1}{\lambda_H} = R_H\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\frac{1}{\lambda_D} = R_D\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

So,

$$\frac{\lambda_D}{\lambda_H} = \frac{R_H}{R_D}$$

$$\frac{\lambda_D - \lambda_H}{\lambda_H} = \frac{R_H - R_D}{R_D}$$

$$\Delta\lambda = \lambda_D - \lambda_H = -\lambda_H\left(\frac{R_D - R_H}{R_D}\right)$$

$$= -4861.33\ \text{Å}\left(\frac{109707.4\ \text{cm}^{-1} - 109677.6\ cm^{-1}}{109707.4\ cm^{-1}}\right)$$

$$= -1.32\ \text{Å}$$

Example 2: An atom with nuclear spin is ***I*** = 3, have 2 levels which are designations $2D_{3/2}$ and $2P_{1/2}$. Find the expected number of components in the hyperfine structure of the corresponding spectral line.

Sol. For the state $2D_{3/2}$, we have

$$J = 3/2,\ I = 3$$

The allowed values of the *hyperfine structure* quantum number F are

$$F = J+I,\ J+1-1,\ \ldots,\ |J-I|$$

$$= 9/2,\ 7/2,\ 5/2,\ 3/2.$$

Thus, for this state there are four *hyperfine structure* levels.

For the state $2P_{1/2}$, we have

$J = ½ , I = 3$

So, $F = 7/2 , 5/2.$

This state has only 2 *hyperfine structure* levels.

$\Delta E = 0 , \pm 1.$

Hence allowed transitions from the levels of one state to those of the other are:

$9/2 \rightarrow 7/2$, $7/2 \rightarrow 7/2$, $7/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$, $5/2 \rightarrow 5/2$ and $3/2 \rightarrow 5/2$

(all are from $2D_{3/2} \rightarrow 2P_{1/2}$)

So, total transitions are 6.

18.10 Nuclear Spin and Hyperfine Splitting

Isotope effect has its limitations. In many cases, this fails to explain the hyperfine structure. Hyperfine components are often greater than the number of isotopes. Similarly, some elements show hyperfine structure, even those are only isotope in that element. For example bismuth exists as a single isotope, but shows six hyperfine components in its line wavelength 4722 Å. Similarly, the number of components of different lines is frequently quite different for one and the same element.

In 1924, Pauli gave an explanation about hyperfine structure. According to him when it assumed that the atomic nucleus possesses an intrinsic spin angular momentum $\vec{I}$ and which is associated a magnetic dipole moment $\vec{\mu_I}$. Same as in the case of spinning electron, the magnitude of the nuclear angular momentum is

$$|\vec{I}| = \sqrt{I(I+1)}\frac{h}{2\pi}$$

Where ***I*** is nuclear spin quantum number. It has different for different masses number nuclei. It is also different for different isotopes of same element.

Since $\vec{L}$, $\vec{S}$ and $\vec{J}$ have quantized components along an axis in space. So the component of $\vec{I}$ along the *z*-axis is

$$I_z = M_I \frac{h}{2\pi}$$

where $M_I = I, I-1, I-2, \dots, -I$

Nuclear proton produces a magnetic moment $\vec{\mu_l}$ when it is in motion. This is proportional to the angular momentum and which we can be written as

$$\vec{\mu_l} = g_l \left(\frac{e}{2m_p}\right) \vec{I}$$

Here *e* and m_p are respectively the charge and mass of proton. The quantity g_l is called the 'nuclear g factor'. The magnitude of the nuclear magnetic moment is

$$\mu_l = g_l \left(\frac{e}{2m_p}\right) \sqrt{I(I+1)} \frac{h}{2\pi}$$

$$= g_l \sqrt{I(I+1)} \frac{eh}{4\pi m_p}$$

Here $\frac{eh}{2\pi m_p}$ forms a natural unit for the measurement of nuclear magnetic moment and is called the 'nuclear magneton'μ_N. It is 1/1836 times the Bohr magneton (because mass of proton is 1836 times the mass of electron). Thus,

$$\mu_l = g_l \sqrt{I(I+1)}\, \mu_N$$

The component of μ_l along z-axis is

$$\mu_{lz} = g_l M_l \mu_N$$

where $M_l = I, I-1, I-2, \ldots, -I$.

Since the maximum value of M_l is I, the maximum observable component of μ_l is $g_l I \mu_N$, and is commonly called the 'nuclear magnetic moment'. It is roughly 1000 times smaller than electron magnetic moment.

Atomic Vector Model: Let us now construct the vector model with nuclear spin taken into account. The total angular momentum of the whole atom is the sum of three angular momenta: the electron orbital angular momentum $\vec{L}$, the electron spin angular momentum $\vec{S}$ and the nuclear spin angular momentum $\vec{I}$. That is, the total angular momentum is

$$\vec{F} = \vec{L} + \vec{S} + \vec{I} = \vec{J} + \vec{I}$$

As a result of interaction between electron orbit and spin, $\vec{L}$ and $\vec{S}$ precess rapidly around their resultant $\vec{J}$. Further, the interaction between the nuclear magnetic moment and the magnetic field produced by the orbital and spin motions of the atomic electrons couples $\vec{I}$ with $\vec{J}$ and causes these vectors to precess around their resultant $\vec{F}$. This precession is however, about 1000 times slower than that of $\vec{L}$ and $\vec{s}$ about $\vec{J}$ because nuclear magnetic moment is so much smaller than electron magnetic moment. Correspondingly the energy differences are very much smaller.

The *hyperfine structure* quantum number *F* can take the values:

$$F = J+I,\ J+I-1,\ J+I-2,\ \dots,\ |J-I|$$

having $2J + 1$ values if $I \geq J$ or $2I+1$ values if $I \leq J$. This means that as a result of $I - J$ interaction, each fine structure *J*-level splits into $2J+1$ (if $I \geq J$) or $2I+1$ (if $I \leq J$) *hyperfine structure* levels, each characterized by an *F* value.

Interaction Energy: The $\vec{I} - \vec{J}$ interaction energy can be shown to be given by

$$E_{I,J'} = \frac{1}{2}A'[F(F+1) - I(I+1) - J(J+1)],$$

where A' is a constant. The various *hyperfine structure* levels of a given term of a given atom have the same *I* and same *J*, but differ in *F*. Hence the separation between two *hyperfine structure* levels can be obtained by substituting first *F*+1, then *F*, in the above equation and taking the differences. This gives

$$\Delta E' = \frac{1}{2}A'[(F+1)(F+2) - F(F+1)]$$

$$\Delta E' = A'(F+1)$$

Thus, the energy interval between consecutive *hyperfine structure* levels *F* and *F*+1 is proportional to the larger of the *F* values (Lande's interval rule). The order of *hyperfine structure* levels in some of the multiplets is normal (smallest *F* level deepest) while in others it is inverted (largest level deepest).

The selection rule for F for electric dipole transitions is similar to that for J:

$$\Delta F = 0, \pm 1 \text{ but } F = 0 \not\longleftrightarrow F = 0$$

18.11 Intensity Ratio and Determination of Nuclear Spin

When the *hyperfine structure* components are observed due to the splitting of only one of the terms, a measurement of the intensity ratio of the observed components leads to the determination of nuclear spin. This is based on the 'sum rule', according to which the sum of the intensities of the all the transitions starting from or ending on the same level is proportional to the statistical weight 2*F*+1 of that level. This situation arises in the *hyperfine structure* of the resonance lines of sodium. In this case the ratio of the intensities of the two observed *hyperfine structure* components is equal to the ratio of the weights (2*F*+1) of the hyperfine structure levels of the term $2S_{½}$,where *I* is unknown. The *F* values of the two *hyperfine structure* levels of the term $2S_{½}$ (*J* = ½) would be *I* + ½ and *I* – ½ . Hence

$$\text{Intensity ratio} = \frac{2\left(I+\frac{1}{2}\right)+1}{2\left(I-\frac{1}{2}\right)+1} = \frac{I+1}{I}$$

Thus, if intensity ratio is known, we can calculate nuclear spin I.

When *I* has been obtained, the *g*-factor and the magnetic moment of the nucleus can be solved from the magnitude of the *hyperfine structure* splitting by using the theoretical formulae.

When the *hyperfine structure* components are observed due to the splitting of both the terms as in Bi line 4722 Å, then also an analysis of the hyperfine structure can also lead to the determination of nuclear spin.

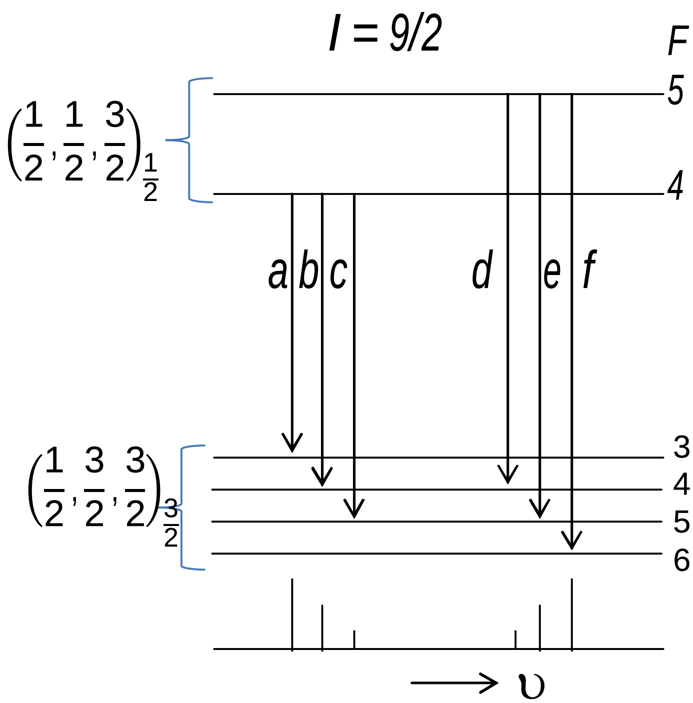


Fig 22. *Hyperfine structure for Bi*

When all the hyperfine components are fully resolved (like Bi) then constant wavenumber differences occur between pairs of components.

$$c - b = e - d$$

and $$d - b = e - c.$$

These differences correspond to level differences in the lower and the upper state respectively, We arrange the wavenumbers of the hyperfine component in a square array such that along each row and along each column they increase (or decrease) regularly and the differences between them in two successive rows and successive columns is constant. Then, all the components in any row correspond to the same upper *hyperfine structure* level, while all those in any column correspond to the same lower *hyperfine structure* level. This will enable us to construct *hyperfine structure* energy for the upper and the lower states.

18.12 Back Goudsmit Effect in Hyperfine Structure

When we apply strong magnetic field $\vec{B}$ so the velocity of precession of $\vec{F}$ about the field direction becomes greater than that of $\vec{J}$ and $\vec{I}$ about $\vec{F}$, an effect like Pascen-Back effect will occurs in the *hyperfine structure* pattern. This effect is called 'Back-Goudsmit effect'. Since, weak coupling of $\vec{J}$ and $\vec{I}$, the Back-Goudsmit effect occurs at fields much lower than those at which Paschen-Back effect sets in fine-structure.

More precisely, magnetic field which is weak for fine structure is a strong field for hyperfine structure. In this type of field the coupling between $\vec{J}$ and $\vec{I}$ breaks down and each precesses independently around $\vec{B}$ with quantized components along the field direction. These components take values $\vec{J}$ and $M_I \frac{h}{2\pi}$ respectively.

where

$$M_J = J, J - 1, J - 2, \ldots, -J$$

and $$M_I = I, I-1, I-2, \ldots, -I$$

The total interaction energy of the atom consists of

(i) the energy of interaction between $\vec{J}$ and $\vec{B}$

(ii) the energy of interaction between $\vec{I}$ and $\vec{B}$.

By Larmor's theorem, the angular velocities of precession of $\vec{J}$ and $\vec{I}$ are given by B times the corresponding ratios between the magnetic moment and angular momentum. That is,

$$\omega_J = Bg_J \frac{e}{2m}$$

and

$$\omega_l = Bg_l \frac{e}{2m_p} = Bg_l \frac{e}{2m}\frac{m}{m_p}$$

18.13 Self-Learning Exercise- II

Q.1 Find the expected number of components in the hyperfine structure of the spectral line correspond to nuclear spin I = 3 and designations $2D_{3/2}$ and $2P_{1/2}$.

Q.2 What is the degeneracy of the fine-structure components of $3D_3$.

18.14 Summary

Effect of magnetic effect on atomic structure can be measured with Zeeman Effect. Similarly, Stark effect gives understanding of electric effect for same. It explains the behavior of molecules due to presence of an external electric field. It is also an application of quantum mechanical approaches. Even it can be observed in semi-classical ground. Hyperfine splitting is very much useful in astrophysics, nuclear technology and quantum computing.

18.15 Glossary

Multiplet : A group of spectral lines.

Dipole moment : Mathematical product of the separation of the ends of a dipole and the magnitude of the charges (in simplest case).

Balmer series : Spectral emission lines of the hydrogen atom.

Electric field : A vector field that associates to each point in space the Coulomb force.

Nuclear magneton : Magnetic dipole moments of heavy particles such as nucleons and atomic nuclei.

18.16 Answers to Self-Learning Exercises

Answers to Self-Learning Exercise- I

Ans.1: The n = 3 level consists 9 states:

$|3, 0, 0\rangle$, $|3, 1, -1\rangle$, $|3, 1, 0\rangle$,

$|3, 1, 1\rangle$, $|3, 2, -2\rangle$, $|3, 2, -1\rangle$,

$|3, 2, 0\rangle$, $|3, 2, 1\rangle$ and $|3, 2, 2\rangle$

Here every state represents $|n, l, m\rangle$, n is principle quantum number, l is azimuthal quantum number and m is magnetic quantum number after splitting.

Ans.2: First order Stark Effect splits the n = 3 into 5 sublevels with different degeneracy:

Degeneracy	States
1	$|3, 0, 2\rangle$
2	$|3, -1, 2\rangle$, $|3, 1, 2\rangle$
3	$|3, -2, 1\rangle$, $|3, 0, 2\rangle$, $|3, 2, 2\rangle$
2	$|3, -1, 1\rangle$, $|3, 1, 1\rangle$
1	$|3, 0, 1\rangle$

Ans.3: The interaction between the oscillating charge and the external electric field gives rise to a term H_P= qEX,

$$H = H_0 + H_P = -\frac{h}{4m\pi}\frac{d^2}{dX^2} + \frac{1}{2}m\omega^2X^2 + qEX$$

(a) Let us take a variable change y = X + qE/mω^2

$$H = \frac{h^2}{8m\pi^2}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2y^2 - \frac{q^2E^2}{2m\omega^2}$$

This is Hamiltonian of a harmonic oscillator from which a constant, $q^2E^2\omega^2/2m$ is subtracted. So, exact energy eigenvalue is:

$$E_n = \left(n + \frac{1}{2}\right)\frac{h\omega}{2\pi} - \frac{q^2E^2}{2m\omega^2}$$

(b) Since, if we apply weak electric field, we can calculate terms corresponding to H_P as perturbation

First order correction is zero and second order correction is

$$E_n^{(2)} = -\frac{q^2E^2}{2m\omega^2}$$

Total energy = ground state energy + perturbed energy

$$E_n = \left(n + \frac{1}{2}\right)\frac{h\omega}{2\pi} - \frac{q^2E^2}{2m\omega^2}$$

This agrees with previous result.

Answers to Self-Learning Exercise- II

Ans.1: For the state $2D_{3/2}$, we have

$J = 3/2$, $I = 3$.

Allowed *hyperfine structure* quantum number F are:

$F = J + I, J + I - 1, \ldots, |J - I|$

For state $2P_{1/2}$, we get

$J = 1/2$, $I = 3$

So, $F = 7/2, 5/2$

Ans.2: $J = 3$, $I = 3/2$.

The allowed values of hyperfine structure quantum number F are

$F = J + I, J + I - 1, \ldots, |J - I|$

$$= \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}.$$

Thus there are 4 *hyperfine structure* components whose designations which are

$$^{3}_{\frac{9}{2}}D_3\ ,\ ^{3}_{\frac{7}{2}}D_3\ ,\ ^{3}_{\frac{5}{2}}D_3\ ,\ ^{3}_{\frac{3}{2}}D_3$$

18.17 Exercise

Q.1 What do you understand about nuclear spin and hyperfine splitting ?

Q.2 What is Stark Effect ?

Q.3 Discuss weak field Stark effect.

Q.4 Discuss strong field Stark Effect.

Q.5 Explain transitions of Stark effect components in hydrogen.

Q.6 Explain a simple way to determine nuclear spin.

Q.7 How can we measure the isotopes in an element ?

Q.8 What is Back Goudsmit effect ?

Q.9 What is the difference between Goudsmit effect and Paschan back effect ?

Q.10 Give some areas which has application for hyperfine structure.

18.18 Answers to Exercise

Ans.1: See section 18.10

Ans.2: See section 18.1

Ans.3: See section 18.2

Ans.4: See section 18.3

Ans.5: See section 18.3 and 18.4

Ans.6: See section 18.6

Ans.7: See section 18.7

Ans.8: See section 18.12

Ans.9: See section 18.12

Ans.10: See section 18.14

References and Suggested Readings

1. H.W. Kroto, Molecular Rotation Spectra, Dover, New York (published in 1992)
2. H. Friedrich, Theoretical Atomic Physics. Springer-Verlag, Berlin (published in 1990)
3. The Modern Theories (1800-1950). American Institute of Physics
4. Harald A. Enge, Introduction to Nuclear Physics. Addison Wesley (published in 1966)
5. Nouredine Zettili, Quantum Mechanics: Concepts and Applications

UNIT-19
Introduction to Molecular Spectra

Structure of the Unit

19.0 Objectives

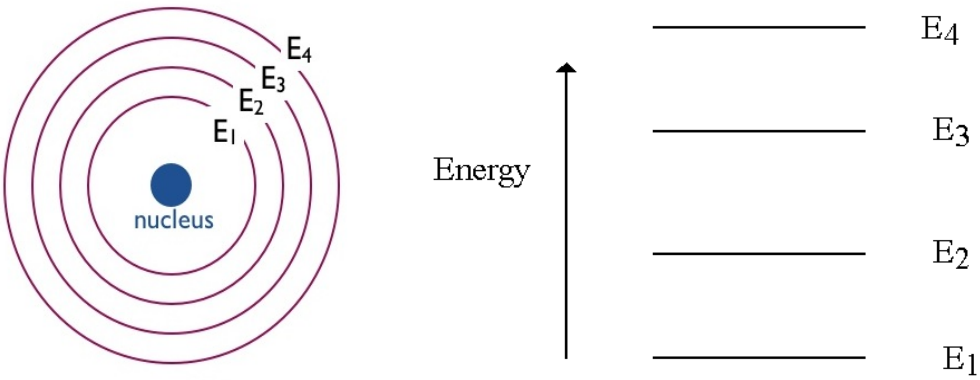
The objective of this chapter is to make familiar the readers with the basics of molecular spectroscopy i.e. interaction of radiation with the molecules of matter. The existence of various energy levels of molecules in the solids, the separation between these energy levels and the regions of existence of spectra in the electromagnetic spectrum will be presented. The basic idea regarding the features of molecular spectra related to instrumentation will also be presented.

19.1 Introduction

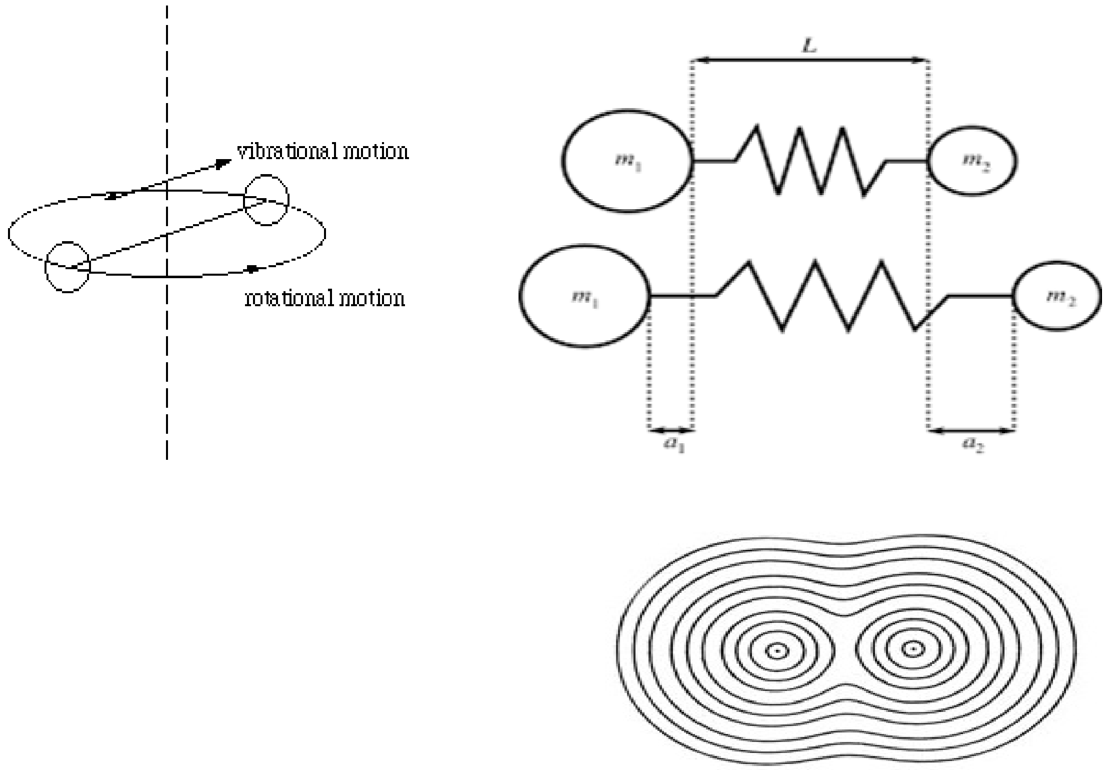
In this chapter the basic features of molecular spectroscopy and the energy levels of the molecules are explained. The origin of energy levels of the molecules in the crystals, the separation between various energy levels and the regions of the spectrum (Far IR, NIR and UV-Visible) accompanying the transition between these energy levels are discussed. Some features of molecular spectra in view of instrumentation like signal-to-noise ratio, width of spectral line, resolving power, etc. are explained.

19.2 Introduction to Molecular Spectroscopy

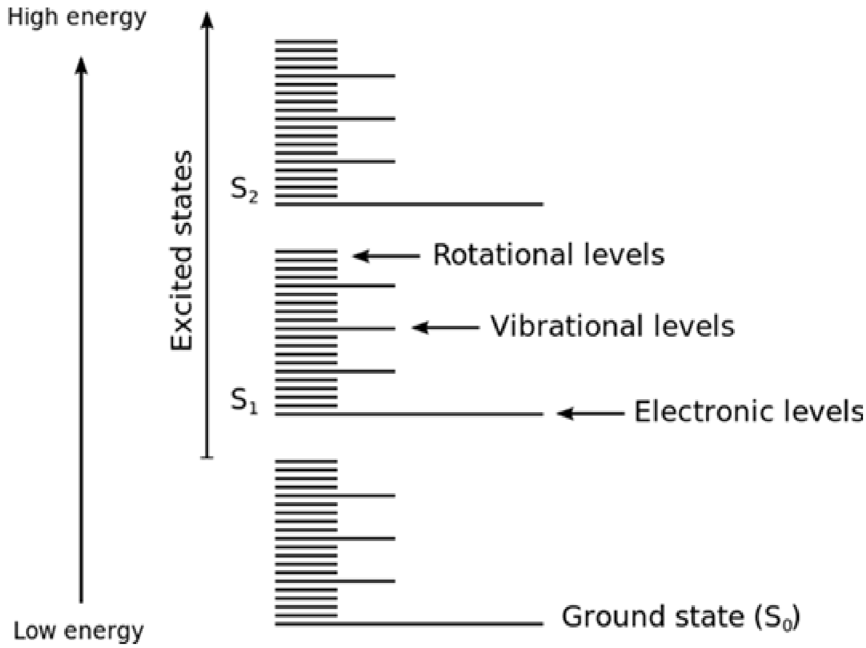
The interaction of Electromagnetic radiations with matter is called as spectroscopy. The electromagnetic radiations act as a probe to obtain the information about the atoms and molecules which are very small enough to see. The interaction of radiation with matter can influence the matter or/and radiations. This interaction of radiation with matter provides the information about the matter i.e. its constituents like atoms or molecules, binding between the atoms, structure and shape of the molecules etc. The molecular spectra are different to as that of atomic spectra. The atomic spectra contain discrete spectral lines and hence called as line spectra. The molecular spectra are complicated as compared to atomic spectra. These spectra contain a number of lines separated by small spacing forming a band. Due to this reason the molecular spectra are called as band spectra. The intensity of lines varies from one edge to another edge of a band.



Atomic Energy Levels



Diatomic Molecule



Molecular Energy Levels

19.3 Separation of Electronic and Nuclear Motion : The Born-Oppenheimer Approximation

The energy levels in molecules are different as compared to an atom. In molecules nuclear motion also contributes to energy levels (rotational and vibration levels). The allowed energy levels can be obtained by solving the Schrodinger equation as:

$$H\varphi = E\varphi$$

In the molecules ,the nuclei and electrons are interacting. The electrons are very light particles as compared to nuclei. Therefore the motion of electrons and nuclei are considered to be separated to good approximation. This separation of electronic and nuclear motions is called as Born-Oppenheimer approximation. So by using this approximation the Schrodinger Equation can be solved in two steps:

1. The wave equation is solved for electronic motion by considering nuclei are to fixed.
2. After this the wave equation is solved for the motion of nuclei and the eigen values of electronic wave equation are considered to be part of potential energy.

The Hamiltonian for a molecule consisting of ***j*** nuclei and ***i*** electrons is given by

$$H = -\sum_{j=1}^{m} \frac{h^2}{8\Pi^2 m_j} \nabla_j^2 + \sum_{i=1}^{n} \frac{h^2}{8\Pi^2 m} \nabla_i^2 + V_{ne} + V_{ee}$$

Where first term of L.H.S. is the operator for kinetic energy for nuclei, second term is the operator for kinetic energy operator for electrons, third term is potential energy function for nuclear-nuclear interactions, fourth term is the potential energy function for the nuclear-electron interaction and the last term is due to potential energy function for electron-electron interactions.

By considering the nuclei in a fixed position, the kinetic energy of nuclei is taken as zero and V_{nn} is treated as constant. So the Hamiltonian for the electron will be

$$H_e = -\sum_{i=1}^{n} \frac{h^2}{8\Pi^2 m} \nabla_i^2 + V_{ne} + V_{ee}$$

The Nuclear Hamiltonian is given by

$$H_n = -\sum_{j=1}^{m} \frac{h^2}{8\Pi^2 m_j} \nabla_j^2 + V_{nn}$$

So the total Hamiltonian is given by

$$H = H_n + H_e$$

Now according to Born-Oppenhiemer, the wave function of the molecule can be written as product of electronic and nuclear wave functions

Let φ is the wavefunction of the molecule and φ_e and φ_n are the wavefunctions of electrons and the nuclei so,

$$\varphi = \varphi_e \varphi_n$$

Let E is the total eigen value of the total eigen function then

$$H \varphi = E \varphi$$

$$H(\varphi_e \varphi_n) = E(\varphi_e \varphi_n)$$

$$[-\sum_j \frac{h^2}{8\Pi^2 M_j} \nabla_j^2 - \sum_i \frac{h^2}{8\Pi^2 m} \nabla_i^2] \Psi_e \Psi_n + (V_{nn} + V_{ne} + V_{ee}) \Psi_e \Psi_n = E \Psi_e \Psi_n$$

Using

$$\nabla_j^2 \Psi_e \Psi_n = \Psi_e \nabla_j^2 \Psi_n$$

$$\nabla_i^2 \Psi_e \Psi_n = \Psi_n \nabla_i^2 \Psi_e$$

$$[-\frac{h^2}{8\Pi^2 M_1} \nabla_1^2 - \frac{h^2}{8\Pi^2 M_2} \nabla_2^2 + V(r)] \Psi = E\Psi$$

$$(H_e + E_e) = -[\sum_j \frac{h^2}{8\Pi^2 M_j} \nabla_j^2 + E_e + V_{nn}]$$

$$-\Psi_e \sum_j \frac{h^2}{8\Pi^2 M_j} \nabla_j^2 \Psi_n - \Psi_n [\sum_i \frac{h^2}{8\Pi^2 m} \nabla_i^2 + V_{ne} + V_{ee}] \Psi_e + V_{nn} \Psi_e \Psi_n = E \Psi_e \Psi_n$$

In the above equation

$$H_e \Psi_e = [\sum_i \frac{h^2}{8\Pi^2 m} \nabla_i^2 + V_{ne} + V_{ee}] \Psi_e$$

If the eigen values of the electronic wavefunction is E_e then

$$H_e \Psi_e = E \Psi_e$$

So,

$$-\Psi_e \sum_j \frac{h^2}{8\Pi^2 M_j} \nabla_j^2 \Psi_n + E_e \Psi_n \Psi_e + V_{nn} \Psi_e \Psi_n = E \Psi_e \Psi_n$$

$$(H_n + E_e)\Psi_n = E\Psi_n$$

$$\Psi = \Psi_e \Psi_v \Psi_r \Psi_t$$

$$E = E_e + E_v + E_r + E_t$$

$$\frac{d^2 f}{dr^2} + \frac{8\Pi^2 \mu}{h^2}[E - V(r) - \frac{J(J+1)h^2}{8\Pi^2 \mu r^2}]\mathrm{f} = 0$$

$$V'(r) = V(r) + \frac{J(J+1)h^2}{8\Pi^2 \mu r^2}$$

$$R(r) = \frac{1}{r} f(r)$$

$$-[\sum_j \frac{h^2}{8\Pi^2 M_j} \nabla_j^2 + E_e + V_{nn}]\Psi_n = E\Psi_n$$

$$(H_n + E_e)\Psi_n = E\Psi_n$$

In the above equation E_e is the eigen value of the electronic wavefunction and act as part of potential energy for nuclear motion. So, the effective Hamiltonian for molecular wavefunction is

$$(H_e + E_e) = -[\sum_j \frac{h^2}{8\Pi^2 M_j} \nabla_j^2 + E_e + V_{nn}]$$

First the equation is solved for a given electronic state of the molecule for a range of values of inter-nuclear co-ordinates. It will give values of φ_e and E_e as a function of nuclear co-ordinates. After obtaining E_e, the above Schrodinger wave function φ_n and eigen value É are determined. Different sets of wavefunction φ_n and eigen value É are obtained for each electronic state of the molecule. Finally, the total wavefunction $\varphi=\varphi_n\varphi_e$ is determined.

19.4 Types of Molecular Energy states and associated Spectra

Born-Oppenheimer approximation stated that motions of the electrons in a molecule can be treated separately from those of nuclei and that the electronic motion can be solved by assuming the nuclei to be fixed. The electronic energy E_e and nuclear-nuclear interaction energy then act as an effective potential for the motion of the nuclei.

The nuclear motion in a molecule is further divided into vibration, rotation, and translational motions. In the approximation the electronic, vibration, rotation and translation motions are considered to be independent. The Hamiltonian of molecules is written as

$$H = H_e + H_v + H_r + H_t$$

where

$$H_e\Psi_e = E_e\Psi_e$$
$$H_v\Psi_v = E_v\Psi_v$$
$$H_r\Psi_r = E_r\Psi_r$$
$$H_t\Psi_t = E_t\Psi_t$$

The total wavefunction is written as

$$\Psi = \Psi_e\Psi_v\Psi_r\Psi_t$$

and the total energy is given by

$$E = E_e + E_v + E_r + E_t$$

For simplicity we here consider a diatomic molecule. The Schrodinger wave equation for nuclear motion of the diatomic molecule is as

$$[-\frac{h^2}{8\Pi^2 M_1}\nabla_1^2 - \frac{h^2}{8\Pi^2 M_2}\nabla_2^2 + V(r)]\Psi = E\Psi$$

where V(r) is the effective potential energy contributed from the nucleus-nucleus interaction and electronic energy state, Ψ is the eigen function and E is the eigen value. The above equation can be transformed into polar co-ordinates. The radial part of this equation is given by

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{8\Pi^2\mu}{h^2}[E - V(r) - \frac{J(J+1)h^2}{8\Pi^2\mu r^2}]R = 0$$

where J is the total angular momentum of the molecule and J=0, 1, 2, 3, 4......

Let us now consider

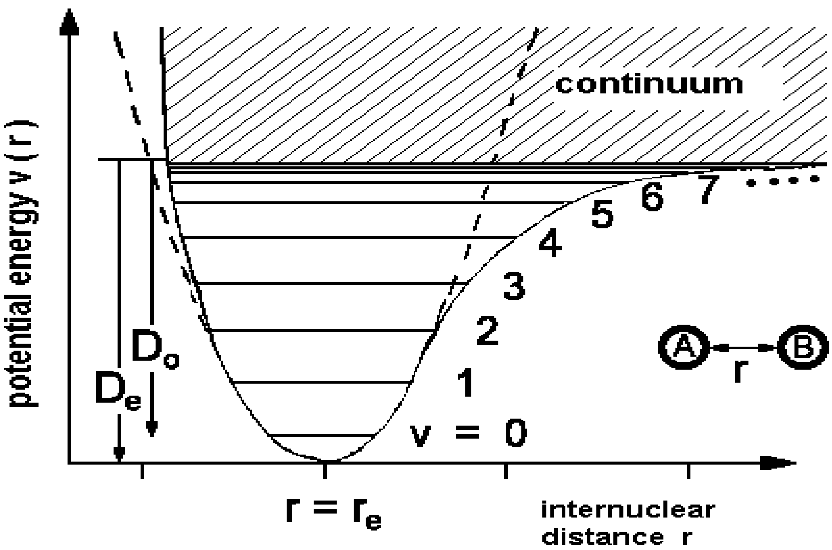
$$R(r) = \frac{1}{r}f(r)$$

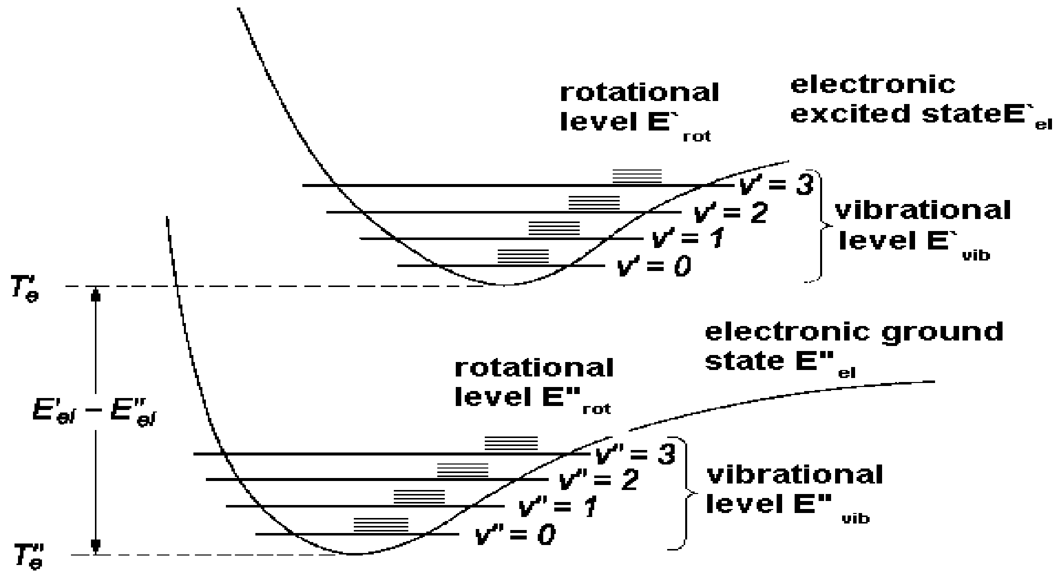
Then the above equation get converted into

$$\frac{d^2 f}{dr^2} + \frac{8\Pi^2\mu}{h^2}[E - V(r) - \frac{J(J+1)h^2}{8\Pi^2\mu r^2}]\mathrm{f} = 0$$

Let $$V'(r) = V(r) + \frac{J(J+1)h^2}{8\Pi^2 \mu r^2}$$

Here E_e is the eigen value of the electronic wavefunction, V_{nn} is the potential energy due to nucleus-nucleus interactions and the term $\frac{J(J+1)h^2}{8\Pi^2 \mu r^2}$ is due to centrifugal potential energy arising due to superposition of rotational motion on the vibrations of particles. The variation of potential V(r) is as shown below





If the nuclear vibrations are small oscillations so V(r) can be expanded by Taylor's series as

$$V(r) = V(r_e) + (\mathrm{r} - \mathrm{r}_e)[\frac{\delta V(r)}{\delta r}]_{r=r_e} + \frac{1}{2}(r - r_e)^2[\frac{\delta^2 V(r)}{\delta^2 r}]_{r=r_e} + ...$$

If $V(r_e)=0$ and at $r=r_e$, $\frac{\delta V(r)}{\delta r}=0$, so

$$V(r) = \frac{1}{2}(r - r_e)^2[\frac{\delta^2 V(r)}{\delta^2 r}]_{r=r_e}$$

The potential energy is a parabolic function near $r=r_e$ for small displacement. The molecule in this case can be treated as harmonic oscillation. Here $r=r_e$ is the equilibrium inter-nuclear separation and at this the potential energy is minimum.

If nuclear-nuclear interaction is ignored then $V(r)_{min}=E_e$. When two atoms are brought nearer to form a stable molecule, the electronic energy decreases rapidly while the energy of repulsion increases. For certain inter-nuclear separation the total potential energy is minimum i.e. for $r-r_e$, V(r)=Min. It is called as equilibrium inter-nuclear position. The two nuclei vibrate about their equilibrium position along the inter-nuclear axis and it also rotates about the centre of mass. So, we can conclude now the following from the potential energy V(r):

1. The energy at minimum of V(r) is called as electronic energy E_e if the nuclei are fixed.
2. The energy of nuclear vibrations about the nuclear position r_e under the potential function V(r) is called as vibration energy E_v and is given by quantum number *v*.
3. The energy of rotation of the molecule E_r is given by quantum number J.

   So the total energy of the molecule is given by

$$\mathrm{E} = \mathrm{E}_e + E_v + E_r$$

In terms of wavenumber

$$\frac{E}{hc} = \frac{E_e}{hc} + \frac{E_v}{hc} + \frac{E_r}{hc}$$

or

$$\overline{v} = \overline{v}_e + \overline{G}(v) + \overline{\mathrm{F}}(v, \mathrm{J})$$

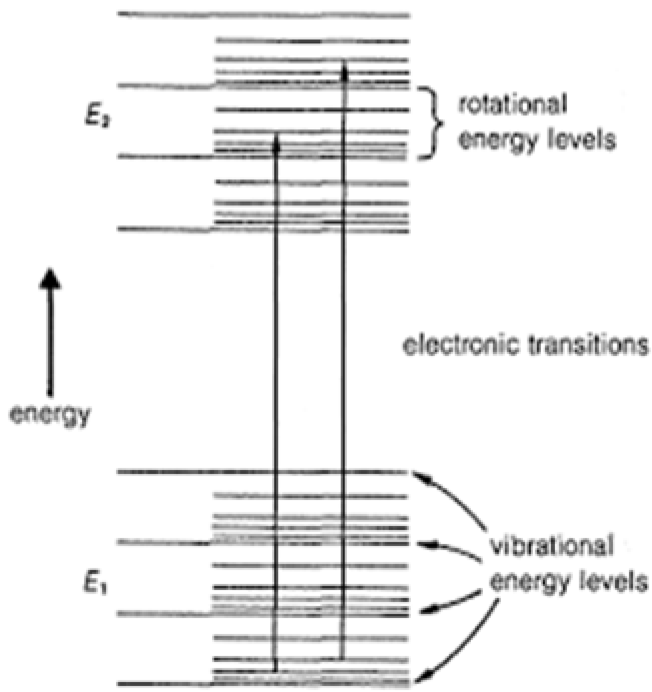
where

$\bar{v}_e$ = Electronic term

$\bar{G}(v)$ = Vibration term

$\bar{F}(v, J)$ = Rotation term

As a result a molecule has number of quantized electronic levels. The transition between two electronic levels results in a radiations that fall in the UV-Visible region. Within each electronic level a number of vibration energy levels exist. The spacing between these levels decreases with increasing vibration quantum number (v). A transition between vibration levels results in the emission of radiations that fall in the near Infra-red region. Also each vibration level is associated with a number of rotational levels. The spacing between these levels increases with increase in rotational quantum number. A transition between two rotational levels gives rise to emission of radiations that fall in the far Infra-red region.



Transitions In Molecular Energy Levels

A spectral line in each band arises due to change in the energies E_e, E_v and E_r

$$\bar{v} = \frac{E' - E''}{hc}$$

$$\bar{v} = \frac{E'_e - E''_e}{hc} + \frac{E'_v - E''_v}{hc} + \frac{E'_r - E''_r}{hc}$$

$$\bar{v} = \bar{v}_e + \bar{v}_v + \bar{v}_r$$

Here $\bar{v}_e > \bar{v}_v > \bar{v}_r$.

So now summarize the following:

1. For a given band $\bar{v}_e$ and $\bar{v}_v$ are constant while $\bar{v}_r$ changes from line to line. The position in the band $\bar{v}_v$ =0 is called as origin of band.
2. For a system of bands $\bar{v}_e$ is constant while $\bar{v}_v$ changes from band to band. The position in the system $\bar{v}_v$ =0 and $\bar{v}_v$ =0 is called system origin.
3. The electronic band system lies in UV-Visible region.
4. The vibration-rotation band arises due to transition between two vibrational levels of the same electronic state. The lines of the band result from the transition between rotational levels of one vibrational level to the rotational levels of other vibrational levels. Such band lies in near Infra-red region.
5. For a given electronic and vibrational level as same, the transition between two rotational levels give rise to pure rotational bands. These lines fall in Far Infra-red region.

19.5 Types of Molecular Spectra (Characteristics of Band Spectra)

The molecular spectra under low dispersion appear as continuous bands. The intensities of a band decrease from one edge to other. With an instrument having high resolving power band spectra are found to have internal structure as:

- Each band is composed of large number of lines having very small separations. There is a strong overlapping of the lines in higher wavelength region i.e. near band head.
- There exist a group of bands in a definite sequence.
- The bands are very close to each other so forming a band system.

19.6 Regions of Molecular Spectrum

The molecules have electronic, vibrational and rotational levels. All these levels are quantized. The transition between these energy levels due to absorption or emission of energy will result in number of spectral lines in the spectrum of the molecule. The interactions of molecules with electromagnetic radiations mainly fall in following regions:

If the energy of the excited state is E' and the ground state is E'' then the frequency of the spectral line is as

$$\nu = \frac{E' - E''}{h} \quad \text{Hz.}$$

$$\bar{\nu} = \frac{E' - E''}{hc} \ \text{cm}^{-1}$$

1. UV-Visible or Electronic Spectra: The electronic transitions in a molecule require energy of the order of 5-10 eV. The wavenumber and wavelength corresponding to 5 eV is

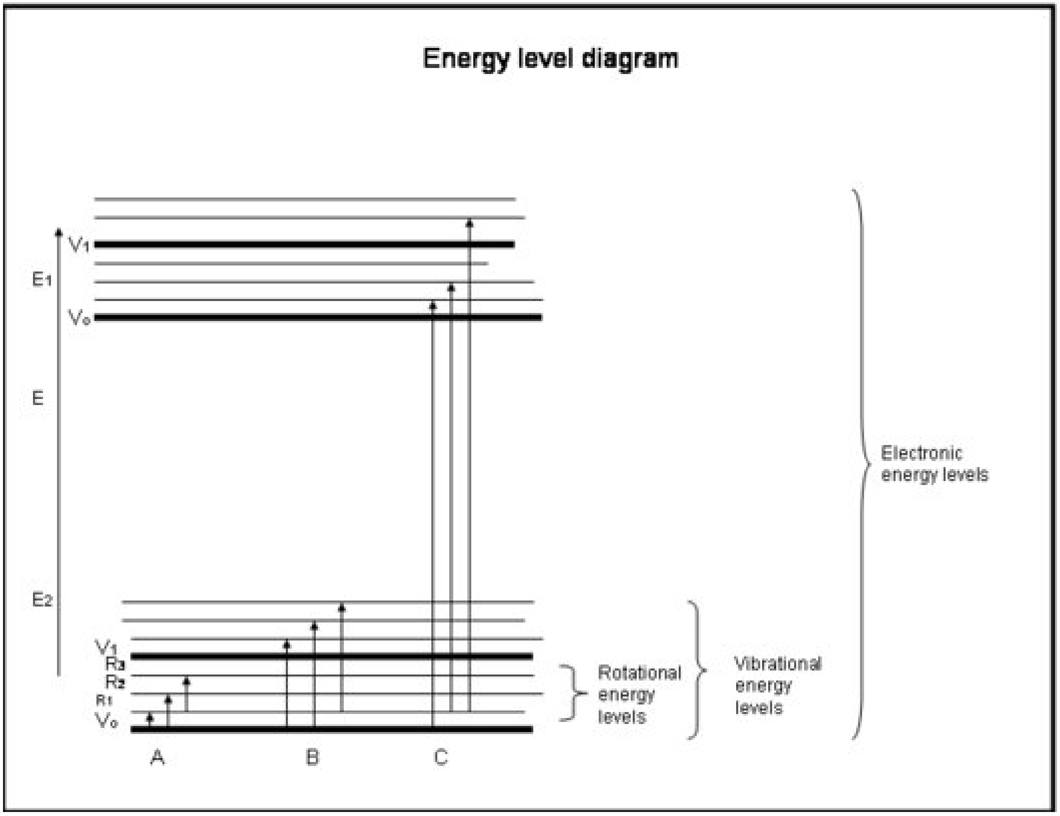
$$\bar{\nu} = \frac{5 \times 1.6 \times 10^{-19}}{6.6 \times 10^{-34} \times 3 \times 10^{8}}$$
$$\approx 4.04 \times 10^{6} m^{-1}$$
$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{4.04 \times 10^{6}}$$
$$\approx 25 \times 10^{-6} cm \approx 2500 A^{o}$$

This lies in the UV or short wavelength visible region. In each electronic state there are a number of possible vibrational states. Also in a vibrational state there is a set of rotational states.

2. Near Infra-red Spectra or Vibrational-rotational spectra: The vibrational levels are separated from each other by an energy gap of order 0.1 eV. The wavenumber and wavelength corresponding to 0.1 eV is

$$\bar{\nu} = \frac{0.1 \times 1.6 \times 10^{-19}}{6.6 \times 10^{-34} \times 3 \times 10^{8}}$$
$$\approx 8 \times 10^{4} m^{-1}$$
$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{8 \times 10^{4}}$$
$$\approx 12.5 \times 10^{-6} \mu m \approx 125000 A^{o}$$

These transitions fall in the near Infra-red region. The vibrational transitions are always accompanied by change in rotational levels. So such spectra are called as vibrational-rotational spectra.



3. Far Infra-red Spectra or Pure rotational Spectra: The vibrational levels are separated from each other by an energy gap of order 0.005 eV. The wavenumber and wavelength corresponding to 0.005 eV is

$$\bar{v} = \frac{0.005 \times 1.6 \times 10^{-19}}{6.6 \times 10^{-34} \times 3 \times 10^{8}} \approx 4040 m^{-1}$$

$$\lambda = \frac{1}{\bar{v}} = \frac{1}{4040} \approx 2.47 \times 10^{-4} m \approx 2470000 A^{o}$$

19.7 Signal-to-Noise Ratio and Resolving Power

1. Signal-to-Noise Ratio: In spectrometers some electronics amplification devices are used to magnify the signal produced by the detector, the recorded spectrum has a background of random fluctuations caused by spurious electronic signals produced by the source or detector or may be generated by amplifying device. These fluctuations are called as “noise”. In order that a spectral line should appear as such and can easily be distinguished from noise the intensity of spectral line should be at least three or four times that of noise

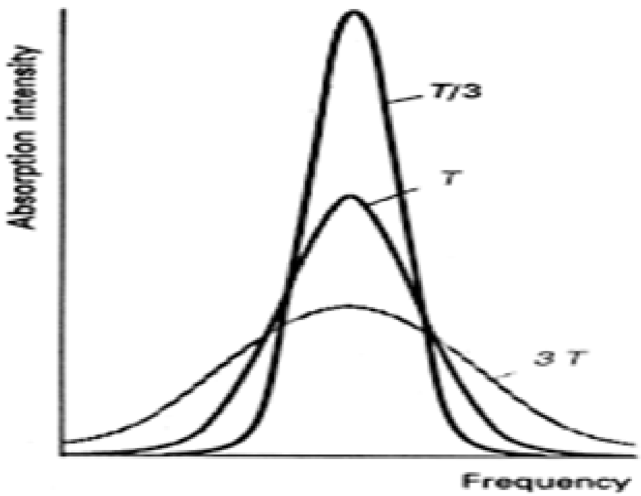
signal. By using computer averaging technique the signal-to-noise ratio can be improved.

2. Resolving Power: The resolving power is related to ability of the spectrometer to distinguish between different spectral lines situated close to each other. By decreasing the slit width of the spectrometer the resolving power can be improved. The sensitive detector can also enhance the resolving power.

19.8 Width of Spectral Line

When we record the absorption or emission spectrum then we find broader spectral lines instead of sharp lines. The design of the spectrometer can improve the resolving power but the width of the spectral line of any atomic or molecular spectrum cannot be reduced below an inherent width of that line. This width arises due to non-sharp single energy levels of the atoms or molecules. There is a width of energy of the state involves in the transition. The following factors contribute to the width of a spectral line:

1. **Collision Broadening**: In the liquid and gases phases the atoms and molecules are in continuous motion and they collide with each other. Due to these collisions a change in the electronic, vibrational and rotational levels take place causing the broadening of the spectral lines. In case of solids the spectra are sharper as compared to liquid or gases phases.
2. **Doppler Broadening**: Due to motion of molecules in liquid and gases phases there is a Doppler shift in the spectral line. Due to this shift the lines get broader.



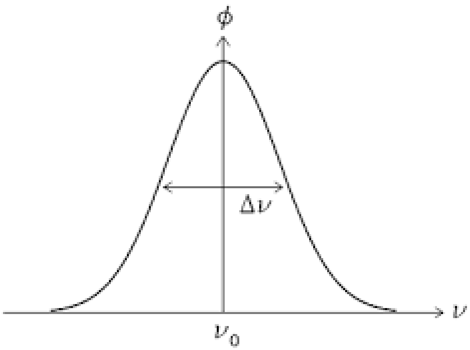
3. **Natural Broadening**: In the atoms or molecules which are at rest the energy levels are not sharp as stated by Heisenberg uncertainty principle. According to this principle if the system exists in an energy state for a time Δt seconds then the energy of that state will be uncertain by an amount ΔE.

$$\Delta E.\Delta t \approx \frac{h}{2\Pi} \approx 10^{-34}\, Js$$

Here h is the Planck's constant. The lower energy state is sharp while upper state is not sharp. So the spectral line has finite width as

$$\Delta E = \frac{h}{2\Pi.\Delta t}$$

$$\Delta \nu = \frac{1}{2\Pi.\Delta t}$$



19.9 Intensity of Spectral Line

The intensity of a spectral line depend the following factors:

1. **Transition Probability**: The transition probability is related to fact that the transition between two states is allowed or forbidden i.e. the transition probability is non-zero or zero. The probability of transition is related to derivation of selection rules for the transition between two levels.
2. **Population of two states**: The intensity of a spectral line depends upon the population of that state from which the transition takes place.

   Suppose there are N molecules distributed over two states of energies as E_1 and E_2 such that $E_2 > E_1$, then from statistical mechanics

$$N_1 = Ne^{\frac{-E_1}{kT}}$$

$$N_2 = Ne^{\frac{-E_2}{kT}}$$

$$\frac{N_2}{N_1} = e^{\frac{-(E_2-E_1)}{kT}} = e^{\frac{-\Delta E}{kT}}$$

3. **Path Length of Sample**: The sample absorbs the radiations which are incident on it. If the path of the sample is increased then more and more radiation will be absorbed. The absorbance of a sample is given by

$$A = \log(\frac{I_0}{I}) = \varepsilon cl$$

c = Concentration

ε = Molecular absorption coefficient.

l = Path length

9.10 Self Learning Exercise

Q.1 Why molecular spectra are called as band spectra.

Q.2 Write the total wavefunction for a molecule and explain it.

Q.3 Write the order of wavelength of each region of molecular spectra.

Q.4 Explain Signal-to-Noise ratio.

Q.5 Explain the intensity of a spectral line. On which factors the intensity of the line depends?

19.11 Summary

The unit has introduced the concepts of molecular energy levels. How these energy levels arise due to mutual interaction between the atoms of the molecule. The total potential energy function of the molecule is calculated and then the Schrodinger wave equation is solved by using Born- Oppenheimer approximation. The molecule has three types of energy levels i.e. electronic, vibrational and rotational energy levels. The transitions between these levels give rise to molecular spectra i.e. band spectra. In the later section of unit order of energies involving the transitions between these levels and the corresponding regions of their fall are discussed. Finally there is a discussion on the width of spectral line and their origin as well how the spectrometer will be able to record the spectral line precisely.

19.12 Glossary

Band : Group of energy levels separated by small energy gap

Spectra : Plural of spectrum

Spectrometer : Instrument to record the spectrum.

Hamiltonian : Total energy operator in quantum mechanics.

Eigen value : Value of a physical quantity in quantum mechanics

Centrifugal : Towards the centre

Interaction: Influencing by a force

Width : Interval

Noise : Unwanted signal

Resolve : Keep separation

Spurious: Duplicate

19.13 Exercise

Q.1 What is the difference between atomic and molecular spectrum.

Q.2 What is origin of band spectra of molecules ?

Q.3 Explain the Born-Oppenheimer approximation.

Q.4 Write the total Hamiltonian for a Molecule.

Q.5 Write the effective potential energy function for a molecule and explain it.

Q.6 Write the various regions of molecular spectra.

Q.7 What is the order of energy of quanta of various regions of molecular spectrum.

Q.8 Write the order of frequencies of different region of molecular spectra.

Q.9 Draw the energy level diagram of molecular levels.

Q.10 Write the characteristics of molecular spectra.

Q.11 How the Signal-to-Noise can be improved ?

Q.12 What is the resolving power of spectrometer ? How the resolving power can be improved ?

Q.13 Explain the width of a spectral line. Explain the various factors on which the width of line depends upon ?

References and Suggested Readings

1. Colin N. Banwell and Elaine M. McCash*: Molecular Spectroscopy*, Tata Mcgraw-Hill Education Private Limited, New Delhi, 1994.
2. J. M. Holias*: Modern Spectroscopy* , John Wiley & Sons, England, 1987.
3. S.L. Gupta, V. Kumar and R.C. Sharma: *Elements of Spectroscopy,* Pragati Prakashan, Meerut, 1990.
4. Raj Kumar: *Atomic & Molecular Spectra: LASER*, Kedar Nath Ram Nath, Meerut, 2007.

UNIT-20
Microwave Spectroscopy

Structure of the Unit

20.0 Objectives

This unit is designed to let readers with the knowledge of pure rotational spectra of molecules. The basic features of the molecular spectra, energy of rotational levels of a diatomic molecule as rigid and non-rigid rotator and the transition between these energy states will be explained. The various types of polyatomic molecules and the rotational spectra of some simple polyatomic molecule will also be discussed.

20.1 Introduction

The pure rotational spectra are shown by those molecules which have permanent electric dipole moment. The salient features of the pure rotational spectra, rotational spectra of a rigid and non-rigid diatomic molecule, intensity of spectral lines and selection rules for transition between rotational levels are discussed. The various types of polyatomic molecules and the spectra of symmetric top molecule are explained.

20.2 Salient Features of Rotational Spectra

1. The spectral lines which are observed in far Infra-red region in the wavelength range greater than 200μm are due to transitions between rotational energy levels of the molecule.
2. The change in these transitions is of the order of 0.0005 eV.
3. Only those molecules which have permanent electric dipole moment can give rise to rotational spectra. It is the basic requirement to show rotational spectra by the molecules.
4. The homo-nuclear molecules like H_2 , O_2 , N_2 , etc. do not show rotational spectra.
5. Only the hetero-nuclear molecules like HF, HCl, HBr, etc. show the rotational spectra.
6. The rotational spectra are observed in absorption mode.
7. From the spectral lines of rotational spectra the moment of inertia of the molecule and inter-nuclear distance can be calculated.
8. The polar molecules interact with electric field of Infra-red radiations to absorb energy and will show absorption spectra.
9. The rotational spectral lines are observed at equidistance on wavenumber scale.

20.3 Molecular Requirement for Rotational Spectra

The basic requirement for the emission or absorption of radiations by transitions between rotational energy states is that the molecule must have a permanent electric dipole moment. This can be explained on the basis of theory of classical electrodynamics. According to this theory a rotating molecule can lead to emission of radiations if the dipole moment of hetero-nuclear molecule changes. All hetero-nuclear molecules have a permanent electric dipole moment. During the rotation of the molecule this dipole moment changes periodically in a particular direction with frequency of rotation $\upsilon_{rot.}$ of the molecule, so as per classical theory of electrodynamics it will emit the radiation of frequency $\upsilon_{rot.}$. The homo-nuclear molecules have no electric dipole moment and hence there is no emission of radiations.

Similar to emission the Infra-red radiations can be absorbed by rotating molecules if they have permanent electric dipole moment is present. The molecules interact with oscillating electric field of the incident radiation to absorb rotation energy and produce absorption lines.

Suppose the electric field of the electromagnetic wave at any instant of time pushes the positive ions in the upward direction and negative ions in the downward direction. As a result the molecule will rotate faster. If frequency of radiations coincides with that of molecular rotation ,then in the next half cycle, the molecule will rotate faster as compared to previous half cycle. As a result the molecule will be excited to higher rotational state. So the absorption spectrum is only observed when the molecule has electric dipole moment.

20.4 The Molecule as Rigid Rotator : Explanation of Rotational Spectra

Let us consider a hetero-nuclear diatomic molecule having masses of two atoms as m_1 and m_2. The bond between two atoms is rigid i.e. not flexible. Let r be distance between two atoms which remain constant. Let r_1 and r_2 be the distance atoms m_1 and m_2 from the centre of mass C of the molecule. The molecule is rotating about an axis passing through the centre of mass and perpendicular to inter-nuclear axis. From the property of centre of mass as

$$m_1 r_1 = m_2 r_2$$

$$r = r_1 + r_2$$

$$r_1 = r - r_2$$

$$m_1 (r - r_2) = m_2 r_2$$

$$m_1 r = (m_1 + m_2) r_2$$

$$r_2 = \frac{m_1 r}{(m_1 + m_2)}$$

Similarly $$r_1 = \frac{m_2 r}{(m_1 + m_2)}$$

The moment of inertia of the molecule about the axis of rotation is given by

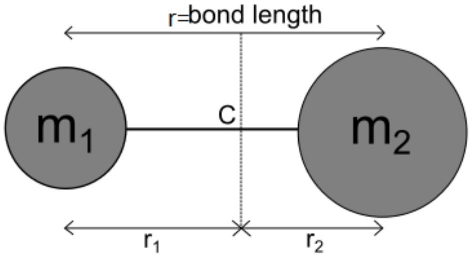
$$I = m_1 r_1^2 + m_2 r_2^2$$

$$I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2}{(m_1 + m_2)^2}[m_2 + m_1] r^2 = \frac{m_1 m_2}{(m_1 + m_2)} r^2 = \mu r^2$$

where $$\mu = \frac{m_1 m_2}{(m_1 + m_2)}$$

μ is called as reduced mass of the molecule.



In order to find the energy of rotation of molecule we have to solve the Schrodinger's wave equation as

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

In terms of spherical polar co-ordinates the Schrodinger wave equation is

$$\frac{1}{r^2}\frac{\delta}{\delta r}(r^2 \frac{\delta \psi}{\delta r}) + \frac{1}{r^2 Sin\theta}\frac{\delta}{\delta \theta}(Sin\theta \frac{\delta \psi}{\delta \theta}) + \frac{1}{r^2 Sin^2\theta}\frac{\delta^2 \psi}{\delta \phi^2} + \frac{8\pi^2 \mu}{h^2} E\psi = 0$$

Since r is fixed so the differentiation with respect to r are taken as zero

$$\frac{1}{Sin\theta}\frac{\delta}{\delta \theta}(Sin\theta \frac{\delta \psi}{\delta \theta}) + \frac{1}{Sin^2\theta}\frac{\delta^2 \psi}{\delta \phi^2} + \frac{8\pi^2 I}{h^2} E\psi = 0,$$

where $I = \mu r^2$,I is the moment of inertia of the molecule.

Let us now separate the variables θ and ϕ as

Let $\psi(\theta,\phi) = \Theta(\theta).\Phi(\phi)$

$$\frac{1}{Sin\theta}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})\Phi(\phi)+\frac{1}{Sin^2\theta}\frac{\delta^2\Phi(\phi)}{\delta\phi^2}\Theta(\theta)+\frac{8\pi^2 I}{h^2}E\Theta(\theta).\Phi(\phi)=0$$

Dividing by $\Theta(\theta).\Phi(\phi)$

$$\frac{1}{Sin\theta}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})\frac{1}{\Theta(\theta)}+\frac{1}{Sin^2\theta}\frac{\delta^2\Phi(\phi)}{\delta\phi^2}\frac{1}{\Phi(\phi)}+\frac{8\pi^2 I}{h^2}E=0$$

Multiplying the equation by $Sin^2\theta$

$$\frac{Sin\theta}{\Theta(\theta)}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})+\frac{1}{\Phi(\phi)}\frac{\delta^2\Phi(\phi)}{\delta\phi^2}+\frac{8\pi^2 I}{h^2}E.Sin^2\theta=0$$

$$\frac{Sin\theta}{\Theta(\theta)}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})+\frac{8\pi^2 I}{h^2}E.Sin^2\theta=-\frac{1}{\Phi(\phi)}\frac{\delta^2\Phi(\phi)}{\delta\phi^2}$$

Let us consider $-\frac{1}{\Phi(\phi)}\frac{\delta^2\Phi(\phi)}{\delta\phi^2}=M^2$

$$\frac{\delta^2\Phi(\phi)}{\delta\phi^2}=-M^2\Phi(\phi)$$

$$\frac{\delta^2\Phi(\phi)}{\delta\phi^2}+M^2\Phi(\phi)=0 \qquad \text{(A)}$$

and

$$\frac{Sin\theta}{\Theta(\theta)}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})+\frac{8\pi^2 I}{h^2}E.Sin^2\theta=M^2$$

On multiplying by $\frac{\Theta(\theta)}{Sin^2\theta}$ to above equation

$$\frac{1}{Sin\theta}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})+\frac{8\pi^2 I}{h^2}E.\Theta(\theta)=M^2\frac{\Theta(\theta)}{Sin^2\theta}$$

$$\frac{1}{Sin\theta}\frac{\delta}{\delta\theta}(Sin\theta\frac{\delta\Theta(\theta)}{\delta\theta})+[\frac{8\pi^2 I}{h^2}E-\frac{M^2}{Sin^2\theta}]\Theta(\theta)=0 \qquad \text{(B)}$$

The solution of the equation (A) is

$$\Phi_M(\phi)=Ae^{iM\phi}$$

where, $M = 0,\pm1,\pm2,\pm3.......etc.$

In order to solve equation (B), we consider the following

Let $\mathrm{x} = \mathrm{Cos}\,\theta$ and $P(x) = \Theta(\theta)$

Then $\mathrm{Sin}^2\theta = 1 - x^2$ and $\frac{\delta\Theta(\theta)}{\delta\theta} = \frac{\delta P}{\delta x}\frac{\delta x}{\delta\theta} = -\frac{\delta P}{\delta x} Sin\theta$

Let us treat $\frac{d}{d\theta}(....) = -Sin\theta \frac{d}{d\theta}(....)$ as an operator, so the equation (B) become

$$\frac{1}{Sin\theta}[-Sin\theta \frac{d}{dx}\{-Sin\theta \frac{dP(x)}{dx} Sin(\theta)\}] + [\frac{8\pi^2 IE}{h^2} - \frac{M^2}{Sin^2\theta}]P(x) = 0$$

$$[\frac{d}{dx}(1-x^2)\frac{dP(x)}{dx}] + [\frac{8\pi^2 IE}{h^2} - \frac{M^2}{(1-x^2)}]P(x) = 0$$

$$(1-x^2)\frac{d^2P(x)}{dx^2} - 2\,\mathrm{x}\frac{dP(x)}{dx} + [\frac{8\pi^2 IE}{h^2} - \frac{M^2}{(1-x^2)}]P(x) = 0 \qquad \text{(C)}$$

This equation is identical to associated Legendre's differential equation if we replace $\frac{8\pi^2 IE}{h^2}$ by J(J+1) or $E = \frac{h^2 J(J+1)}{8\pi^2 I}$, here J is a positive integer. So the solution of the above (C) equation will be

$$\Theta_{I,M}(\theta) = N.\mathrm{P}_J^{|M|}(x) = N.\mathrm{P}_J^{|M|}(\mathrm{Cos}\,\theta)$$

M has values as, M=J, J-1, J-2, J-3, ---------, -J+1, -J.

So, the complete wave function is given

$$\psi(\theta,\phi) = N.\mathrm{P}_J^{|M|}(\mathrm{Cos}\,\theta)A.e^{iM\phi}$$

The rotational energy states are given by

$$E_J = \frac{h^2 J(J+1)}{8\pi^2 I}$$

where $\frac{h^2 J(J+1)}{4\pi^2}$ is the eigen value of the square of the angular momentum as

$$\hat{L}^2\psi = \frac{h^2 J(J+1)}{4\pi^2}\psi \text{ , J=0, 1, 2, 3, 4, ..., etc.}$$

and $\frac{Mh}{2\pi}$ are the eigen values of Z-components of the angular momentum as

$$\hat{L}_Z\psi = \frac{Mh}{2\pi}\psi \text{ , } M = 0, \pm 1, \pm 2, \pm 3, ..., etc.$$

The angular frequency of rotation is given by

$$\omega_{rot} = \frac{L}{I} = \frac{h}{2\pi I}\sqrt{J(J+1)}$$

and the frequency of rotation is given by

$$\upsilon_{rot} = \frac{\omega}{2\pi} = \frac{h}{4\pi^2 I}\sqrt{J(J+1)}$$

Rotational Spectrum: The energy of a rigid rotator is given by

$$E_J = \frac{J(J+1)h^2}{8\pi^2 I}$$, where J=0, 1, 2, 3, 4, ..., etc.

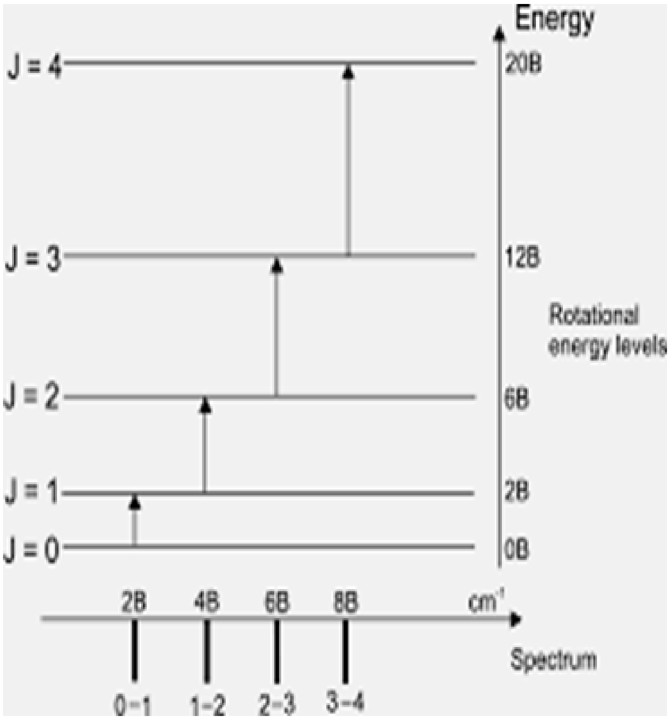
Corresponding to different values of J ,there will be different energy states of rotations of a diatomic molecule. In term of wavenumber

$$F(J) = \frac{E}{hc} = \frac{h}{8\pi^2 Ic}J(J+1)$$

$$F(J) = BJ(J+1)$$

where $\mathrm{B} = \frac{h}{8\pi^2 Ic}$, B is called as rotational constant.

If J=0, 1, 2, 3, 4, 5, ..., etc., then, F(J)=0, 2B, 6B, 12B, 20B, ..., etc.



When the transitions take place between an upper level and lower level of rotational levels, then the wave number of absorbed radiation will be

$$\bar{\nu} = F(J') - F(J'')$$

$$\bar{\nu} = BJ'(J'+1) - BJ''(J''+1) \qquad \text{(D)}$$

The selection rule for the transitions to take place is

$$\Delta J = \pm 1$$

If $J' = J'' + 1$, then from equation (D) we have

$$\bar{\nu} = B(J''+1)(J''+2) - BJ''(J''+1), \quad \bar{\nu} = 2B(J''+1)$$

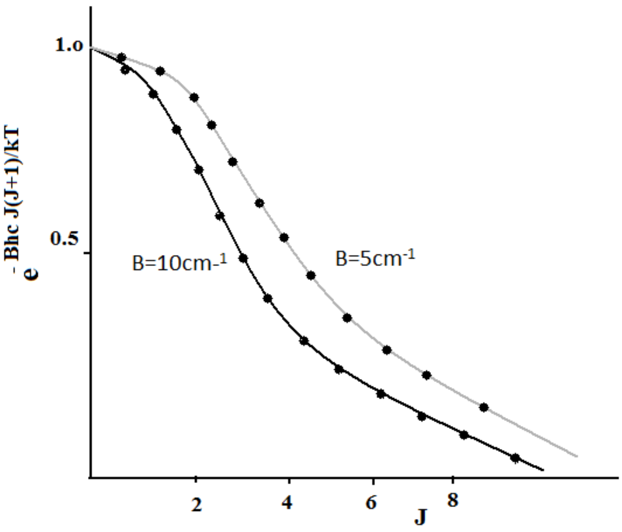
From the above we see that the absorption spectrum of a rigid rotator contains a series of equidistant lines having separation 2B.

20.5 The Intensities of Spectral Lines

The spectral lines are observed in the rotational spectra of molecule for $\Delta J = \pm 1$. The probability of these transitions is same irrespective of levels involved in the transitions. But the intensity of the spectral lines emerging due to transitions between pair levels having different values of J is not same. This is related to the different number of molecules in a state ,therefore the number of molecules undergoing transitions from different levels will be different. The intensity of spectral line is proportional to number of molecule in the initial state. The number of molecules in a state is given by

$$N_J = N_0 e^{\frac{-E_J}{kT}} = N_0 e^{\frac{-BhcJ(J+1)}{kT}},$$

Here T is the temperature and K is the Boltzmann constant.



As the value of J and B increases N_J decreases. The population of the level is proportional to degeneracy of a rotational level i.e. for a given value of J there will be (2J+1) sublevels of same energy. So the population of a level is given by

$$N_J = (2J+1)N_0 e^{\frac{-E_J}{kT}} = (2J+1)N_0 e^{\frac{-BhcJ(J+1)}{kT}}$$

20.6 Diatomic Molecule as a Non-Rigid Rotator

From the experimental investigation of the spectral lines of rotational spectra it is found that the spectral lines are equally spaced but the separation between lines decreases on wavenumber scale as the value of rotational quantum number J increases. From the calculation of rotational constant it is found that the bond length increases with increase in J , so the rigidity of the rotator is under question. We may here conclude that with increase in J value the increase in bond length is due to elastic nature of the bond up to some extent. The centrifugal force tends to increase the bond length at higher value of J. As a result of change in bond length due to stretching or compressing the molecule periodically, it is assumed the molecules may have vibrational energy. If the motion is simple harmonic the force constant is given by

$$k = 4\pi^2 \bar{v}^2 c^2 \mu \qquad \text{or} \qquad \bar{v}^2 = \frac{k}{4\pi^2 c^2 \mu}$$

By considering the effect of non-rigidity of the bond the rotational energy levels are as

$$E = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2 (J+1)^2$$

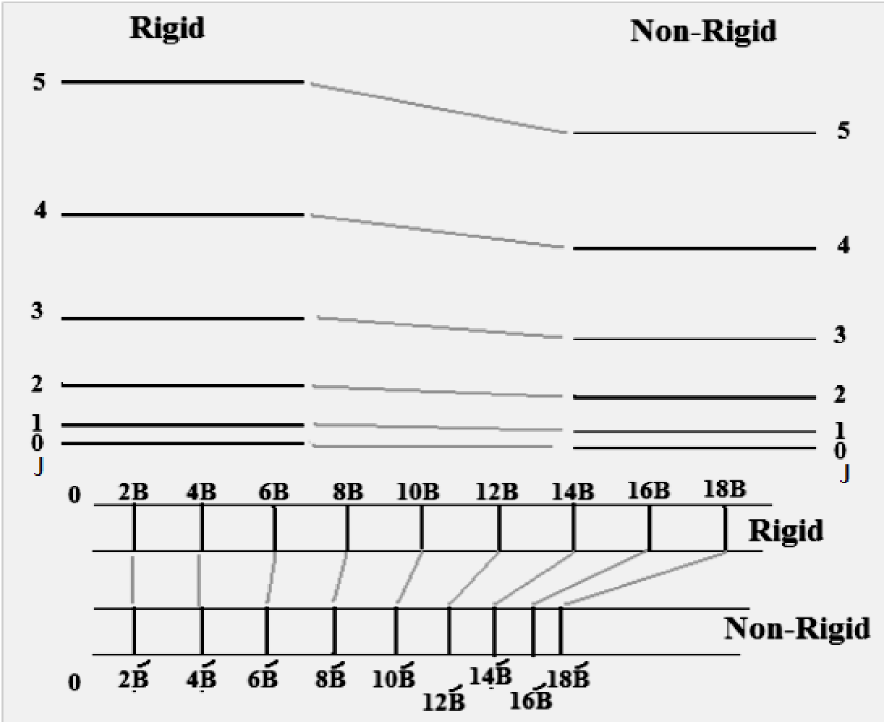
$$F(J) = \frac{E}{hc} = BJ(J+1) - DJ^2(J+1)^2$$

where $B = \frac{h^2}{8\pi^2 Ic}$ and $D = \frac{h^3}{32\pi^4 I^2 r^2 kc}$ and $D = \frac{4B^3}{\bar{v}^2}$

Here D is called as centrifugal distortion constant. So the energy of rotational energy level of high J values is lowered as shown above. The wavenumber of the transition between two levels

$$\bar{v} = F(\mathrm{J+1}) - \mathrm{F(J)} = \mathrm{B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2} - J^2(J+1)^2]$$

$$\bar{v} = F(\mathrm{J+1}) - \mathrm{F(J)} = 2\,\mathrm{B(J+1)} - 4\,\mathrm{D(J+1)^2}$$



Rotational Energy Levels of Rigid and Non-Rigid Rotator

The selection rule for transition is $\Delta J = \pm 1$. Due to centrifugal distortions the spectral lines are not equally spaced particularly at higher value of J.

20.7 Isotopic Effect

If any atom in the molecule is replaced by its isotope then the reduced mass of the molecule μ changes. Due to this change the moment of inertia changes but the inter-nuclear distance remains the same.

Before the isotopic exchange in the molecule

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}, \text{ and } I = \mu r^2$$

If m_1 is exchanged by its isotopic mass m' then

$$\mu' = \frac{m_1' m_2}{(m_1' + m_2)}, \text{ and } I' = \mu' r^2$$

Due to isotopic exchange the rotational energy values and the frequency separation of successive lines in the rotational spectrum changes. If m' >m_1 then μ' >μ and I' >I. So rotational constant B changes as

As, $B = \frac{h^2}{8\pi^2 Ic}$, so due to isotopic exchange it become $B' = \frac{h^2}{8\pi^2 I'c}$, so B´<B, and $F'(J) = B'J(J+1)$, F´(J)<F(J). So the wave number after the isotopic exchange is given by

$$\bar{v}' = 2B'(J+1), \text{ so } \bar{v}' < \bar{v}$$

So the separation of levels for heavier isotopes will be smaller as compared to original mass. If $m_1' < m_1$, then $\bar{v}' > \bar{v}$ i.e. for lighter isotopic exchange, the separation between levels is higher as compared to original mass.

So we conclude that the spectral lines will be closer on isotopic substitution if $m_1' > m_1$ and wider if $m_1' < m_1$ as compared to m_1. The isotopic effect increases with increase in value of J.

20.8 Rotational Spectra of Polyatomic Molecule

In order to understand the spectra of polyatomic molecule ,we must be aware of the principal moment of inertia, angular momentum and kinetic energy of the polyatomic molecule.

1. Principal Moment of Inertia : Suppose there are N atoms in a polyatomic molecule. Then there will be 3N degrees of freedom, out of these three belong to rotation of whole molecule about three mutually perpendicular axes. The moment of inertia of N atoms about any axis of rotation is written as

$$I = m_1 r_1^2 + m_2 r_2^2 + m_3 r_3^2 + m_4 r_4^2 + \ldots\ldots + m_N r_N^2$$

Now there exists one direction of three mutually perpendicular axis for which corresponding moment of inertia are maximum or minimum. The axis along these directions pass through centre of mass. The maximum and minimum values are called as principal moment of inertia. They are I_a, I_b and I_c with $I_a \le I_b \le I_c$.

2. Angular Momentum: The angular momentum is given by

$$\vec{L} = I\vec{\omega}$$

In terms of inertial tensor

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

In terms of principal moment of inertia the above can be written as

$$\begin{pmatrix} L_a \\ L_b \\ L_c \end{pmatrix} = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix} \begin{pmatrix} \omega_a \\ \omega_b \\ \omega_c \end{pmatrix}$$

3. Kinetic Energy in terms of Principal Moment of Inertia: The kinetic energy of the molecule in terms of principal moment of inertia is given by

$$K = \frac{1}{2}[I_a\omega_a^2 + I_b\omega_b^2 + I_c\omega_c^2]$$

$$K = [\frac{L_a^2}{2I_a} + \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c}]$$

4. Types of Molecules on the basis of Principal Moment of inertia: On the basis of principal moment of inertia of the molecule the molecules are classified as

(a) Asymmetric Tops: Three moment of inertia are different i.e.

$$I_a \neq I_b \neq I_c$$

(b) Symmetric Tops: Two moments of inertia are equal i.e.

$I_a = I_b < I_c$, for oblate symmetric top

$I_a < I_b = I_c$, for prolate symmetric top

(c) Spherical Tops: Three moments of inertia are equal i.e.

$$I_a = I_b = I_c = I$$

(d) Linear or Diatomic Molecule: Two moment of inertia are equal and one is zero i.e.

$$I_a = 0, I_b = I_c$$

20.9 Rotational spectra of Symmetric Top Molecules

In the symmetric molecule two moments of inertia are equal and one is different. The examples of such molecules are CH_3Cl and NH_3. The rotational energy of the molecule is given by

$$E_r = \frac{L_a^2}{2I_a} + \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c}$$

For a linear molecule it is assumed that the total angular momentum is quantized as

$L = \sqrt{J(J+1)}\frac{h}{2\pi}$, where J = 0, 1, 2, 3, 4, ..., etc.

The rotational energy of such molecules depend upon two quantum numbers J and K because J may not be directed perpendicular to top axis (I_a axis or unique principal axis). K is the component of vector J along top axis and K is also quantized.

$$L_a = \frac{Kh}{2\pi}, K = 0, \pm1, \pm2, \pm3, ..., etc.$$

$$L^2 = L_a^2 + L_b^2 + L_c^2$$

$$L^2 - L_a^2 = L_b^2 + L_c^2 = J(J+1)\frac{h^2}{4\pi^2} - K^2\frac{h^2}{4\pi^2}$$

So the rotational energy is given by

For Prolate type Molecule

$$E_r = \frac{K^2h^2}{8\pi^2 I_a} + \frac{J(J+1)h^2}{8\pi^2 I_b} - \frac{K^2h^2}{8\pi^2 I_b}$$, as $I_b = I_c$

$$E_r = \frac{J(J+1)h^2}{8\pi^2 I_b} + (\frac{h^2}{8\pi^2 I_a} - \frac{h^2}{8\pi^2 I_b})K^2$$

The term value is given by

$$F(J,K) = \frac{E_r}{hc} = \frac{J(J+1)h}{8\pi^2 I_b c} - (\frac{h}{8\pi^2 I_a c} - \frac{h}{8\pi^2 I_b c})K^2$$

$$F(J,K) = BJ(J+1) + (A-B)K^2$$

Where $$B = \frac{h}{8\pi^2 I_b c}, A = \frac{h}{8\pi^2 I_a c}$$

The quantum numbers J and K can take the values as

J = 0, 1, 2, 3, 4, ..., etc.

K = 0, ±1, ±2, ±3, ±4, ...etc.

So all values having K>0 are double degenerate.

The selection rules for transitions are as

ΔJ = 0, ±1 and ΔK = 0

For absorption spectrum

ΔJ = +1 and ΔK = 0

For oblate type of the molecule

$I_a = I_b < I_c$, so

$$F(J,K) = BJ(J+1) - (B - C)K^2$$

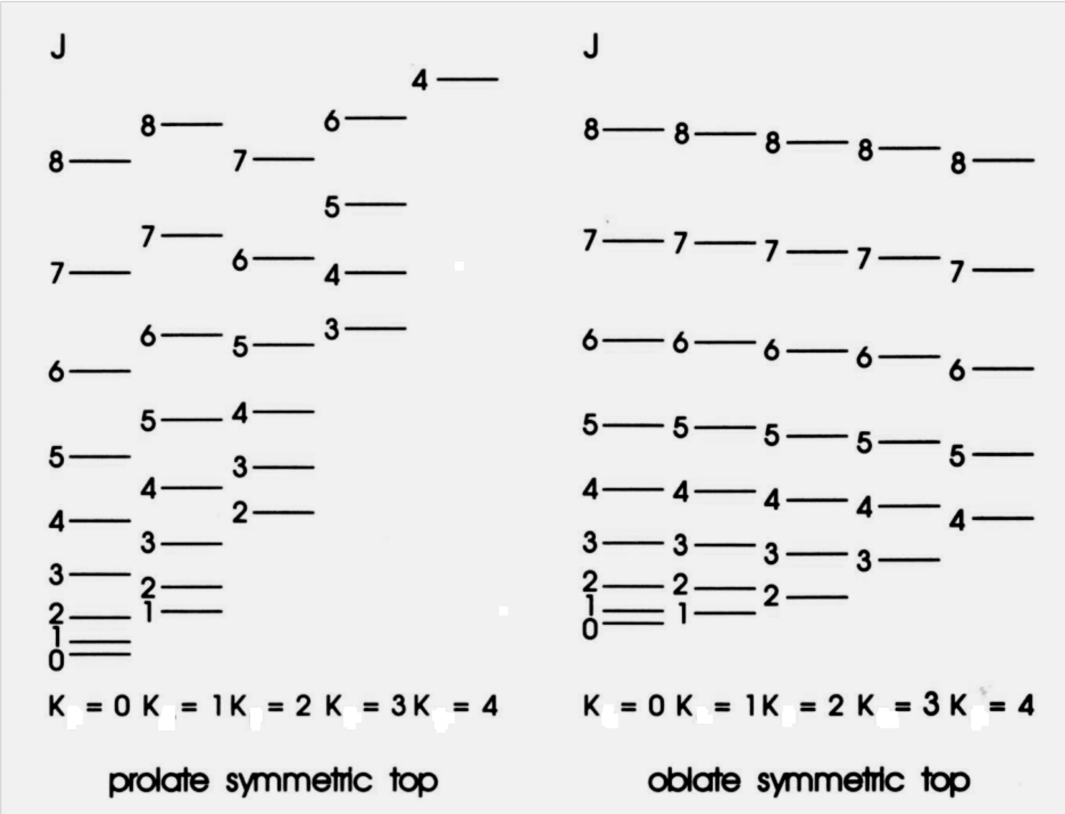
where $C = \dfrac{h}{8\pi^2 I_c c}$, and (B-C) is positive since $I_b < I_c$

The wave number of the pure rotational absorption spectral transition

$$\bar{v} = F(J+1, K) - F(J,K)$$

$$\bar{v} = [B(J+1)(J+2) + (A-B)K^2] - [BJ(J+1) + (A-B)K^2]$$

$$\bar{v} = 2B(J+1) \text{ cm}^{-1}$$



20.10 Illustrative Examples

Example1. The wavenumber of first line in the rotation spectrum of CO is 3.84235 cm^{-1}. Calculate the rotational constant, moment of inertia and bond length of the molecule. (Given mass of C=19.92168×10^{-27} kg and mass of O = 26.5636×10^{-27} kg)

Sol. Given that $\bar{v}_{0\to 1} = 3.84235 cm^{-1} = 2B$

So $\quad B = 1.92118\ cm^{-1}$

The moment of inertia of Co molecule is

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626\times10^{-34}}{8\times(3.14)^2\times3\times10^8\times1.92118\times10^2} = 1.457\times10^{-46}\,kgm^2$$

The reduced mass of the molecule is related to bond length as

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{19.92168\times10^{-27}\times26.56136\times10^{-27}}{(19.92168+26.56136)\times10^{-27}} = 11.38365\times10^{-27}\,kg$$

As $I = \mu r^2$, so $r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.45695\times10^{-46}}{11.38365\times10^{-27}}} = 1.131\times10^{-10}\,m$

Example 2 Wave number of J =0 to 1 transition in HCl molecule found at 20.68 cm^{-1}. Calculate the wavelength for the transition J = 14 to J = 15.

Sol. The wave number of the transition from J = J to J =J+1 is

$$\bar{\nu} = 2B(J+1)$$

For J = 0 to J = 1

$$\bar{\nu} = 2B$$

As $\quad \bar{\nu} = 20.68\ cm^{-1}$

So $\quad 2B = 20.68\ cm^{-1}$

$\quad B = 10.34\ cm^{-1}$

So the wavenumber for the transition J= 14 to J = 15 is

$\bar{\nu} = 2B(J+1)$, here J = 14

$$\bar{\nu} = 2B(14+1) = 2\times10.34\times15 = 310.2\,cm^{-1}$$

So the wavelength of the transition is

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{310.2} = 3.2\times10^{-3}\,cm = 32\,\mu m$$

Example 3 In the rotational spectra of $C^{12}O^{16}$ the first absorption line (J = 0 to J = 1) is observed at 1.153×10^{11} cycles/s and for $C^{n}O^{16}$ it is observed at 1.102×10^{11} cycles/s. Find the value of n for Carbon isotope. (Given that mass of C^{12} = 12 a.m.u. and mass of O^{16} = 16 a.m.u.).

Sol. Before isotopic exchange the rotational constant is

$$B = \frac{h^2}{8\pi^2 Ic}, \text{ and } \bar{\nu} = 2B(J+1)$$

After isotopic exchange the rotational constant is

$$B' = \frac{h^2}{8\pi^2 I'c}, \text{ and } \bar{\nu}' = 2B'(J+1)$$

$$\frac{\bar{\nu}}{\bar{\nu}'} = \frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu} = \frac{(12+16)}{12\times16} \times \frac{(n\times16)}{n+16}$$

$$\frac{1.153\times10^{11}}{1.102\times10^{11}} = \frac{28}{(12\times16)} \times \frac{(n\times16)}{(n+16)}$$

$$\frac{1.153}{1.102} = \frac{7}{3} \times \frac{n}{n+16}$$

$$\frac{3.459}{7.714} = \frac{n}{n+16}$$

$$(7.714 - 3.459)\times n = 3.459\times16$$

$$n = \frac{3.459\times16}{4.255} = \frac{55.344}{4.255} = 13.0068$$

So the isotope of Carbon is C^{13}.

20.11 Self Learning Exercise

Q.1 Why rotational is not observed for homo-nuclear molecules ?

Q.2 Give the examples of polar molecules.

Q.3 Discuss the pure rotational spectra of a rigid rotator. Show that the spectral lines are equally spaced on wavenumber scale.

Q.4 What is a symmetric molecule ? Explain oblate and prolate type of a symmetric molecule.

20.12 Summary

The aim of this unit is to study the pure rotational spectra of the diatomic and symmetric top molecules. The pure rotational spectra of the molecule lie in far Infra-red region of electromagnetic region. The pure rotational spectra are shown by hetero-nuclear molecules. These molecules have permanent electric dipole moment. The homo-nuclear molecules do not show the pure rotational spectra because they do not have permanent electric dipole moment. The mechanism of interaction of dipolar molecules with the electric field of electromagnetic field leading to change in the rotational state was discussed. The pure rotational spectrum of diatomic molecule have been discussed in detail. The energy levels and selection rules for transitions have been explained. The spectral lines are found to equally spaced on wave number scale. The effect of non-rigidity and isotopic exchange has been also discussed for a diatomic molecule. The shift in the spectral due to these effects has been presented. The introduction about the rotational spectra of polyatomic molecules has been also introduced and the rotational spectrum of symmetric top molecules has been discussed in detail. At last some problems related to the content of the units have been solved.

20.13 Glossary

Homo-nuclear : Same type of nucleus

Hetero-nuclear : Different type of nucleus

Polar : Having positive and negative charge

Oscillating : Periodically varying

Rigid : Hard to change

Flexible : Easy to change

Centrifugal : Away from centre

Distortion : Defects

Successive : Consecutives

Degenerate : Same energy

20.14 Exercise

Q.1 What is requirement for a molecule to show rotational spectrum ?

Q.2 How the polar molecules interact with electromagnetic radiations ?

Q.3 Write region of pure rotational spectrum and order of quanta of energy for transition between two levels.

Q.4 What is the order of wavelength of pure rotational spectra ?

Q.5 Write the Schrodinger's wave equation for a rigid rotator.

Q.6 Write the formula for population of a rotational level and its degeneracy.

Q.7 Discuss the dependence of intensity of spectral lines on the population of a rotational level.

Q.8 Write the formula for energy of rotation of a rigid rotator and the selection rules for transition between two levels.

Q.9 Discuss the effect of non-rigidity on the pure rotational spectra of a diatomic molecule.

Q.10 Discuss the effect of isotopic exchange on the pure rotational spectra of a diatomic molecule.

Q.11 Discuss the various types of polyatomic molecules on the basis of principal moment of inertia.

Q.12 Discuss the rotational spectrum of a symmetric top molecule.

References and Suggested Readings

1. Colin N. Banwell and Elaine M. McCash*: Molecular Spectroscopy*, Tata Mcgraw-Hill Education Private Limited, New Delhi, 1994.
2. J. M. Holias*: Modern Spectroscopy* , John Wiley & Sons, England, 1987.
3. S.L. Gupta, V. Kumar and R.C. Sharma: *Elements of Spectroscopy,* Pragati Prakashan, Meerut, 1990.
4. Raj Kumar: *Atomic & Molecular Spectra: LASER*, Kedar Nath Ram Nath, Meerut, 2007.

UNIT-21
Infrared Spectroscopy : Part-I

Structure of the Unit

21.0 Objectives

This chapter is aimed to provide knowledge to the readers about the population of vibrational energy levels of molecules. The different modes of vibrations of polyatomic molecules will be discussed. The instrumentation for recording the IR spectra of the molecules will be explained.

21.1 Introduction

The vibrational energy levels of the molecules are quantized. The population of these energy levels at any temperature will be discussed. The normal coordinates of vibrations and various modes of vibration of polyatomic molecules are explained with examples. The instrumentation required to record the IR spectra of the molecules is discussed i.e. FTIR spectrometer.

21.2 Salient features of Vibrational-Rotational Spectra

The salient features of vibrational-rotational spectra are as follows:

1. The vibrational-rotational spectra fall in the Near-Infra-Red (NIR) region of electromagnetic spectrum (1μm-100μm).
2. During the vibrational transitions between vibrational levels of molecule there is no change in the electronic state.
3. The vibrational transitions are always are accompanied by rotational transitions.
4. The vibrational-rotational spectra observed in absorption mode.
5. The vibrational-rotational spectra are observed for those molecules which have permanent electric dipole moments e.g. HCl, HBr, HI, HF, H_2O etc.
6. When the molecule vibrates, then the inter-nuclear distance changes. So, the dipole moment of the molecule also changes. The electric dipole moment of molecule oscillates and emits the radiation of frequency which lies in the Near-Infra-Red region.
7. The oscillating electric dipole moment also interacts with the incident radiations and absorbs the radiations of frequency of Near-Infra-Red region.
8. The vibrational-rotational spectra of diatomic molecules consist of an intense band called as fundamental band surrounded by weak bands called as overtones.

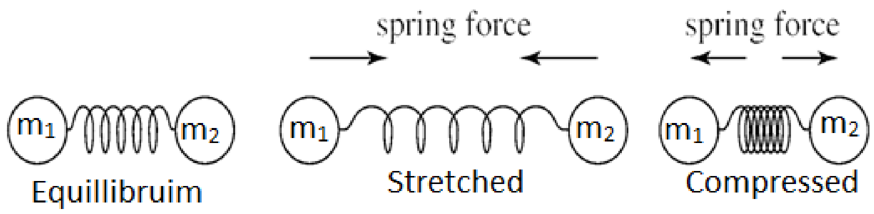
21.3 Vibrating Diatomic Molecule as Harmonic Oscillator

Let us consider a diatomic molecule which is vibrating and whose vibrations are treated as simple harmonic. Let r_e be the equilibrium length of the bond between two atoms of the molecule. At any instant of time during the vibration the bond length is r. The equation of motion the atoms in the molecules are as

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_e) \tag{A}$$

$$m_2 \frac{d^2 r_2}{dt^2} = -k(r - r_e) \qquad \text{(B)}$$

where m_1 and m_2 be masses of the two atoms, r_1 and r_2 be the position of two atoms from the centre of mass and k is the force constant.



From the properties of centre of mass we have

$$m_1 r_1 = m_2 r_2$$

$$r = r_1 + r_2$$

$$r_1 = r - r_2$$

$$m_1(r - r_2) = m_2 r_2$$

$$m_1 r = (m_1 + m_2) r_2$$

$$r_2 = \frac{m_1 r}{(m_1 + m_2)}$$

and

$$r_1 = \frac{m_2 r}{(m_1 + m_2)}$$

So by substituting the values of r_1 and r_2 in equation (A) and (B) we get the equation as

$$\left(\frac{m_1 \times m_2}{m_1 + m_2}\right) \frac{d^2 r}{dt^2} = -k(r - r_e) \qquad \text{(C)}$$

Since, r_e is constant so we can replace r by $(r - r_e)$ in equation (C)

$$\left(\frac{m_1 \times m_2}{m_1 + m_2}\right) \frac{d^2 (r - r_e)}{dt^2} = -k(r - r_e) \qquad \text{(D)}$$

Let $(r - r_e) = x$ and $\mu = \frac{m_1 \times m_2}{m_1 + m_2}$, so the equation (D) now become

$$\mu \frac{d^2 x}{dt^2} = -kx$$

$$\frac{d^2x}{dt^2}+\frac{k}{\mu}x=0$$

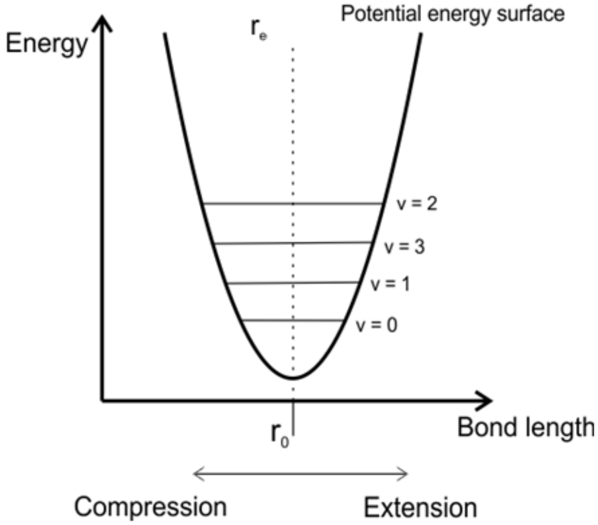
$$\frac{d^2x}{dt^2}+\omega^2x=0 \text{, where } \qquad \omega^2=\frac{k}{\mu}$$

The frequency of vibration is given by

$$\upsilon=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \text{ Hz.}$$

In terms of wave numbers

$$\bar{v}=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}=\frac{1}{\lambda}cm^{-1}$$



The energy of the vibrational energy levels is quantized. The allowed energies for the diatomic molecule can be determined by solving the Schrodinger's wave equation considering the potential to be harmonic as $V=\frac{1}{2}kx_0{}^2$. The energy of levels of diatomic molecule is given by the following equation

$$E_v=[v+\frac{1}{2}]h\upsilon=[v+\frac{1}{2}]hc\bar{v}$$

Here v is the vibrational quantum number which can take values as v = 0, 1, 2, 3, ..., etc.

In terms of term value the above equation is written as

$G(v)=[v+\frac{1}{2}]\overline{v}$, for v =0, 1, 2, 3, 4, ...etc the values of G(v) are as

$$G(v)=\frac{\overline{v}}{2},3\frac{\overline{v}}{2},5\frac{\overline{v}}{2},7\frac{\overline{v}}{2},.....etc.$$

So we observe a series of levels which are quantized and equispaced.

Suppose a transition takes place from higher vibrational energy state having quantum number v' to lower vibrational state having quantum number v'' ,then the frequency of radiation emitted given by

$$\upsilon=\frac{(E_{v'}-E_{v''})}{h}Hz$$

In term of wavelength

$$\overline{v}=\frac{(E_{v'}-E_{v''})}{hc}=G(v')-\mathrm{G(v'')}\,\mathrm{cm}^{-1}$$

The selection rule for transition is Δv = ±1.

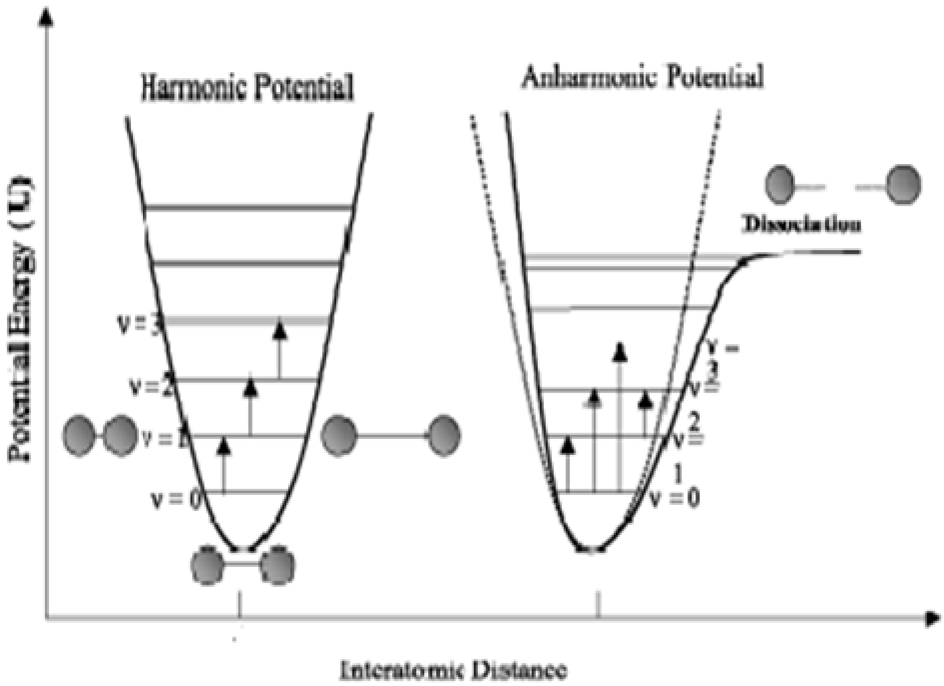
21.4 Vibrating Molecule as Anharmonic Oscillator

For a diatomic molecule as purely harmonic oscillator the change in vibrational quantum number is Δv = ±1 ,so there is one band for each mode of vibration. But experimentally there is strong band with one or two overtones or harmonics. The harmonics correspond to the frequencies that are resulted due to change in vibrational quantum number Δv = ±2, ±3,… etc. Thus the overtones correspond to transitions involving the change in vibrational quantum number Δv>1. Thus the dipole moment of the molecule is not linear with respect to inter-nuclear distance, implying the presence of anharmonicity in the molecular vibrations. The overtones are not observed exactly at $2\overline{v},3\overline{v}$,.. but at lower value side. It indicates that the vibrational energy levels are not equispaced but converges slowly as the vibrational quantum number increases. Due to presence of anharmonicity ,the potential energy curve is not strictly parabolic but its shape changes at higher values of quantum number v. The potential energy in this case is given by as

$$V(r)=(\frac{1}{2}\frac{\partial^2 V(r)}{\partial r^2})_{r=r_e}(r-r_e)^2+(\frac{1}{6}\frac{\partial^3 V(r)}{\partial r^3})_{r=r_e}(r-r_e)^3+....$$

$$V(r)=f(r-r_e)^2-g(r-r_e)^3$$

Where g<<f. So the real molecules do not obey Hook's law, there is anharmonicity present in their vibrations. The potential energy curve for such oscillators is as shown as below and by considering the above potential energy the Schrodinger equation is solved.



The allowed vibrational levels are given by following equation

$$E(v) = (v + \frac{1}{2})h\upsilon - (v + \frac{1}{2})^2 h\upsilon x + (v + \frac{1}{2})^3 h\upsilon y + ...$$

Here x and y are the anharmonicity constants.

In terms of term values the above equation is written as

$$G(v) = (v + \frac{1}{2})\overline{v} - (v + \frac{1}{2})^2 \overline{v}x + (v + \frac{1}{2})^3 \overline{v}y + ...$$

The quantity $\overline{v}$ is the line spacing of energy levels in terms of wavenumbers if the potential energy is purely parabolic, $\overline{v}x$ is the anharmonicity constant whose value is much smaller than $\overline{v}$ and is always positive. So the energy levels are not at equispaced as observed from above equation. As the value of vibrational quantum number v increases separations between levels decrease. The selection rules for transitions between vibrational levels after considering the anharmonicity are as

$\Delta v = \pm 1, \pm 2, \pm 3$, ..., etc.

These transitions are classified as fundamental band corresponding to transition v = 1 to v = 0 , first overtones or second harmonics for v = 2 to v = 0, and second overtone or third harmonics for v = 3 to v = 0, etc.

Suppose a transition takes place from an upper vibration state v' to lower state v'' then the frequency of radiation is given by

$$\upsilon_v = \frac{(E'_v - E''_v)}{h} \quad Hz$$

In terms of wave number

$$\bar{v}_v = \frac{(E'_v - E''_v)}{hc} = G(v') - G(v'')$$

$$\bar{v}_v = (v' - v'')\bar{v} - \{v'(v'+1) - v''(v''+1)\}x\bar{v}$$

Since vibrational quantum number is always is zero so v'' = 0 and v' = v, so the wavenumber of fundamental band overtones are

$\bar{v}_1 = (1-2x)\bar{v}$ Fundamental band.

$\bar{v}_2 = (1-3x)2\bar{v}$ First overtone.

$\bar{v}_3 = (1-4x)3\bar{v}$ Second overtone.

21.5 Vibrational Frequency and Force Constant for Anharmonic Oscillator

The vibrational frequency of harmonic oscillator is given by

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where k is force constant and μ is the reduced mass. The separation between the levels is constant and is equal to $\bar{v}$ in terms of wavenumber. In case of anharmonic oscillator the above formula holds for small amplitude of vibrations. The vibrational frequency of anharmonic oscillator in state v is given by

$$\upsilon = c\Delta G_v = c\frac{\Delta G_{v+\frac{1}{2}} + \Delta G_{v-\frac{1}{2}}}{2}$$

$$\upsilon = \frac{1}{2}c[\{G(v+1) - G(v)\} + \{G(v) - G(v-1)]$$

$$\upsilon = \frac{1}{2}c[G(v+1) - G(v-1)]$$

As we know that

$$G(v) = \overline{v}(v+\frac{1}{2}) - \overline{v}x(v+\frac{1}{2})^2$$

So,

$$\upsilon = \frac{1}{2}c[\{\overline{v}(v+\frac{3}{2}) - \overline{v}x(v+\frac{3}{2})^2\} - \{\overline{v}(v-\frac{1}{2}) - \overline{v}x(v-\frac{1}{2})^2\}]$$

$$\upsilon = \frac{1}{2}c[\{\overline{v}(v+\frac{3}{2} - v + \frac{1}{2}\} - \overline{v}x\{(v+\frac{3}{2})^2 - (v-\frac{1}{2})^2\}]$$

$$\upsilon = \frac{1}{2}c[2\overline{v} - \overline{v}x(4v+2)]$$

$$\upsilon = c[\overline{v} - \overline{v}x(2v+1)]$$

So as value of v increases ,the frequency of vibration decreases. From the vibrational frequency of small amplitude vibration ,we have

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = c\overline{v}$$

So the force constant is given by

$$k = 4\pi^2 \mu c^2 \overline{v}^2$$

21.6 Isotopic Effect in Vibrational Spectra

The isotopic forms of the molecule have different reduced masses ,but the force constant is same. From the value of force constant $k = 4\pi^2 \mu c^2 \overline{v}^2$, it is observed that the equilibrium vibrational wavenumber will be different for different isotopic form. Let $\overline{v}_1$ and $\overline{v}_2$ are the equilibrium wavenumbers for two isotopic forms having reduced masses μ_1' and μ_2'. The from the force constant we have

$$\frac{\overline{v}_2}{\overline{v}_1} = \rho = \sqrt{\frac{\mu_1'}{\mu_2'}}, \text{ or } \quad \overline{v}_2 = \rho \overline{v}_1 \qquad \text{(A)}$$

The anharmonicity constant is proportional to equilibrium constant so

$$x_2 = \rho x_1 \qquad \text{(B)}$$

So the wavenumber of the centre of any band involving lower vibrational level v = 0 is

$$\overline{v}_{v\to 0} = v[1-(v+1)x_1]\overline{v} \qquad (C)$$

So by using equations (A) and (B) in (C) we

$${}_1\overline{v}_{v\to 0} = v[1-(v+1)x_1]\overline{v}$$

$${}_2\overline{v}_{v\to 0} = v[\rho-(v+1)x_1\rho^2]\overline{v}$$

The above equations represent the wavenumbers of the isotopic forms of same molecule. The wavenumber difference of the centers of the two isotopic bands called as isotopic shifts, $\Delta\overline{v}_i$.

$$\Delta\overline{v}_i = (1-\rho)\{1-(v+1)(1+\rho)x_1\}\overline{v}_1$$

The isotopic shift for fundamental band, first overtone and second overtone are as

Fundamental Band v = 1 to v = 0

$$\Delta\overline{v}_i(1) = (1-\rho)\{1-2(1+\rho)x_1\}\overline{v}_1$$

First Overtone v = 2 to v = 0

$$\Delta\overline{v}_i(2) = (1-\rho)\{1-3(1+\rho)x_1\}2\overline{v}_1$$

Second Overtone v = 3 to v = 0

$$\Delta\overline{v}_i(3) = (1-\rho)\{1-4(1+\rho)x_1\}3\overline{v}_1$$

The isotopic shift depends upon the factor $(1-\rho)$. The shift increases with increase in $(1-\rho)$. If ρ>1, isotopic shift $\Delta\overline{v}$ is towards lower wavenumber and for ρ<1 the shift is towards higher wavenumber side.

21.7 Molecule as Vibrating Rotator

We have considered the vibrations and rotations of a diatomic molecule independently up to now. But a vibrating molecule is always associated with rotational motion so we have to consider the combined vibrational and rotational motion of the molecule. Let us discuss this combined motion under situations.

I. Molecule as Rigid Rotator and Harmonic Oscillator

The Near Infra-red spectra of the molecules consist of bands which composed of close lines arranged in a particular manner. This fine structure suggests that during the vibrational transition the rotational state of the molecule also changes. The molecule can be treated as vibrating rotator. Suppose the vibrations and rotations of molecules take place independently i.e. there is no interaction between two motions. The total energy of the molecule in this case can be written as

$$E_{vr} = E_{vib} + E_{rot}$$

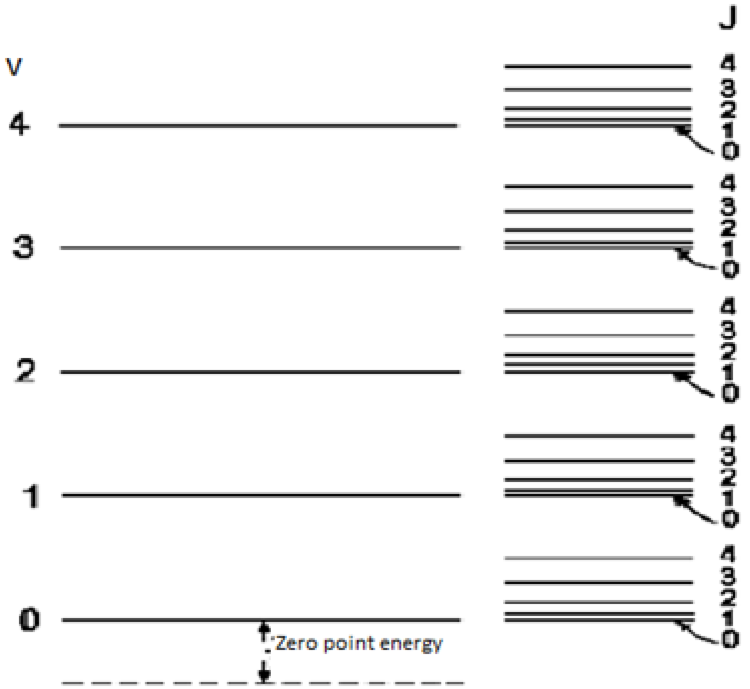
If the molecule is rigid rotator and harmonic oscillator ,then

$$E_{vr} = \{G(v) + F(J)\}ch$$

$$E_{vr} = (v + \frac{1}{2})hc\overline{v} + \frac{h^2}{8\pi^2 I} J(J+1)$$

Suppose a transition takes place from vibrational level v' to v'' level along with transition from rotational level J' to level J''. Then the change in energy accompanies the transitions is

$$\Delta E_{vr} = E'_{vr} - E''_{vr} = (v' - v'')hc\overline{v} + \frac{h^2}{8\pi^2 I}[J'(J'+1) - J''(J''+1)]$$



Vibrational -Rotational Levels of Diatomic Molecule

The wavenumber of radiation arising due to the transition is

$$\overline{v}_{vr} = \frac{E'_{vr} - E''_{vr}}{hc} = (v' - v'')\overline{v} + B[J'(J'+1) - J''(J''+1)] \text{ ,where } B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 \mu r^2 c}$$

II. Diatomic Molecule as Non-rigid and Anharmonic Oscillator

If the diatomic molecule is not rigid rotator and there is anharmonicity is present in the vibrations ,then the energy of the molecule is given by

$$E_{vr} = \{G(v) + F(J)\}ch$$

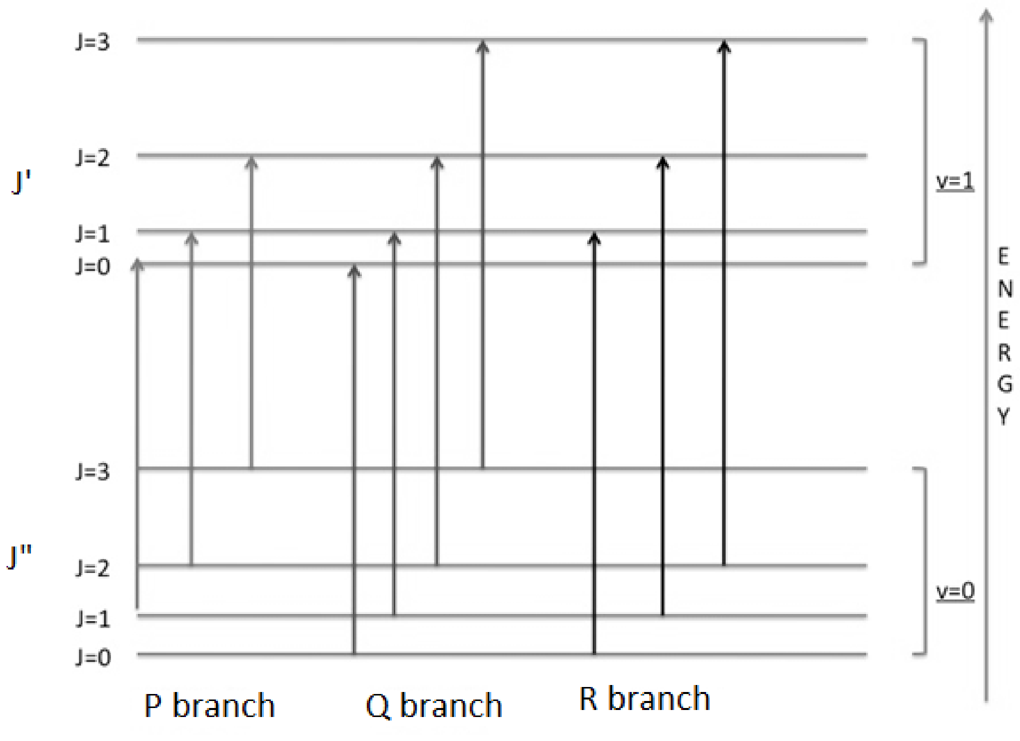
$$E_{vr} = ch[(v+\frac{1}{2})\overline{v} - x(v+\frac{1}{2})^2\overline{v}... + BJ(J+1) - DJ(J^2+1)^2 + ...]$$

If we neglect the small centrifugal distortions ,then we take D = 0 and others then the energy of the molecule in this case as

$$E_{vr} = ch[(v+\frac{1}{2})\overline{v} - x(v+\frac{1}{2})^2\overline{v} + BJ(J+1)]$$

The selection rules for combined vibrational and rotational transition are as

$$\Delta v = \pm 1, \pm 2, etc. \qquad \Delta J = \pm 1$$



Vibrational-Rotational Transitions

Let us consider two vibrational state designated by v = 0 and v = 1. The rotational states in v = 0 are denoted by J'' and in the state v = 1 are denoted by J'. For the transition from v = 0 to v = 1 the wave number of the radiation

$$\bar{v}_{vr} = \frac{E'_{r,v=0} - E''_{r,v=1}}{hc}$$

$$\bar{v}_{vr} = \{BJ'(J'+1) + \frac{3}{2}\bar{v} - \frac{9}{4}x\bar{v}\} - \{BJ''(J''+1) + \frac{3}{2}\bar{v} - \frac{1}{4}x\bar{v}\}$$

$$\bar{v}_{vr} = \bar{v}(1-2x) + B(J'-J'')(J'+J''+1) = \bar{v}_0 + B(J'-J'')(J'+J''+1)$$

where $\bar{v}_0 = \bar{v}(1-2x)$, it is the wave number of pure vibrational transitions ($J' = J'' = 0$).

$\bar{v}_0$ is called as wave number of the band origin.

Now let us consider

R Branch: $\Delta J = +1,\ i.e.\ (J'-J'') = +1 \qquad \bar{v}(R) = \bar{v}_0 + 2B(J''+1), J'' = 0,1,2,....$

P Branch $\Delta J = -1,\ i.e.\ (J'-J'') = -1 \qquad \bar{v}(P) = \bar{v}_0 - 2BJ'', J'' = 1,2,....$

In General $\bar{v}_{vr} = \bar{v}_0 + 2Bn$, where $n = \pm1, \pm2, \pm3....etc.$, $n \neq 0$

So the vibrational-rotational spectra of diatomic molecule consist of numbers of lines at a separation of 2B cm^{-1} around the centre of band.

21.8 Breakdown of Born-Oppenhemier Approximation: The Interaction of Rotations and Vibrations

If we do not consider the interaction between vibrational and rotational energies ,then the R and P branch lines are equidistant. But in actual practice the separation between the lines of one branch decreases (R branch) and of the other branch (P branch) increases. This is resulted due to interaction between vibrational and rotational motion of the molecule.

When a molecule vibrates ,then the bond length changes which cause the change in moment of inertia I and rotational constant B of the molecule. This is called as interaction between two motions. As the vibrational quantum number v increases ,the amplitude of vibrations increases ,hence the value of rotational constant decreases due to increase in average bond length. The dependence of rotational constant on vibrational quantum number can be expressed as

$$B_v = B_e - \alpha(v + \frac{1}{2}) + ...$$

where $\qquad B_v = \frac{h}{8\pi^2 I_v c}$ $\quad$ and $\quad$ $B_e = \frac{h}{8\pi^2 I_e c}$

Here I_v is the moment of inertia of molecule in v^{th} vibrational state, I_e is the moment of inertia in equilibrium state and α is a small positive integer of the order of $0.02B_e$ to $0.05B_e$. In the same way the non-rigidity constant of the molecule in the v^{th} state is given by

$$D_v = D_e + \beta(v + \frac{1}{2}) + ...$$

D_v is the no-rigidity constant in v^{th} state, D_e is non-rigidity constant in equilibrium constant and β is constant as compared to D_e. So the rotational energy is given by

$$E_r = B_v J(J+1)hc - D_v J^2 (J+1)^2 hc + ...$$

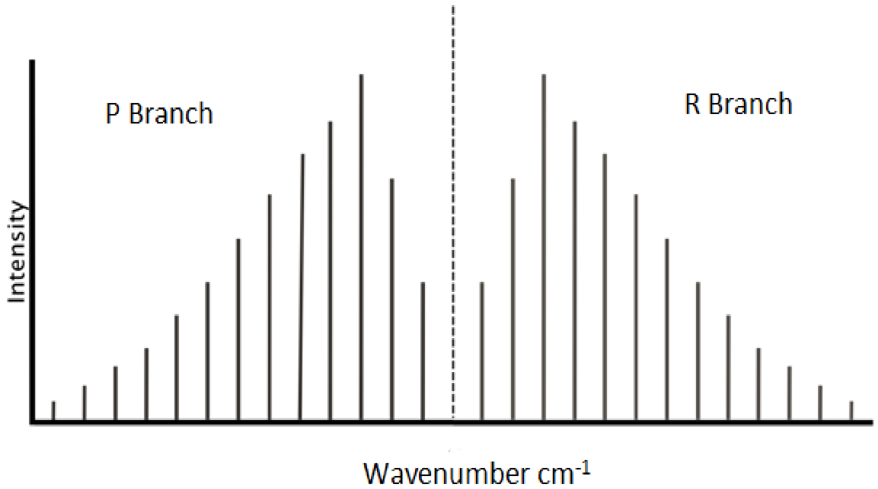


Figure : **Ideal Vibrational-Rotational Spectra**

The total energy of the molecule after considering the interaction between the vibrational and rotational motion is

$$E_{vr} = (v + \frac{1}{2})hc\overline{v} - (v + \frac{1}{2})^2 hcx\overline{v} + ... + B_v J(J+1)hc - D_v J^2 (J+1)^2 hc + ..$$

The wavenumber of the lines of P and R branches are

P Branch: $\quad \overline{v}(P) = \overline{v}_0 - (B'_v + B''_v)J + (B'_v - B''_v)J^2 + 4D_v J^3$

R Branch: $\quad \overline{v}(R) = \overline{v}_0 + (B'_v + B''_v)J + (B'_v - B''_v)J^2 - 4D_v J^3$

Here J = 0, 1, 2, 3, ...etc. and $\bar{v}_0$ is the wavenumber of the centre of band which is given as

$$\bar{v}_0 = (1-2x)\bar{v}, v = 1 \rightarrow v = 0$$

If we neglect the non-rigidity constant D_v ,then

P Branch: $\bar{v}(P) = \bar{v}_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$, m = -1, -2, -3, ...

R Branch: $\bar{v}(R) = \bar{v}_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$, m= +1, +2, +3, ...

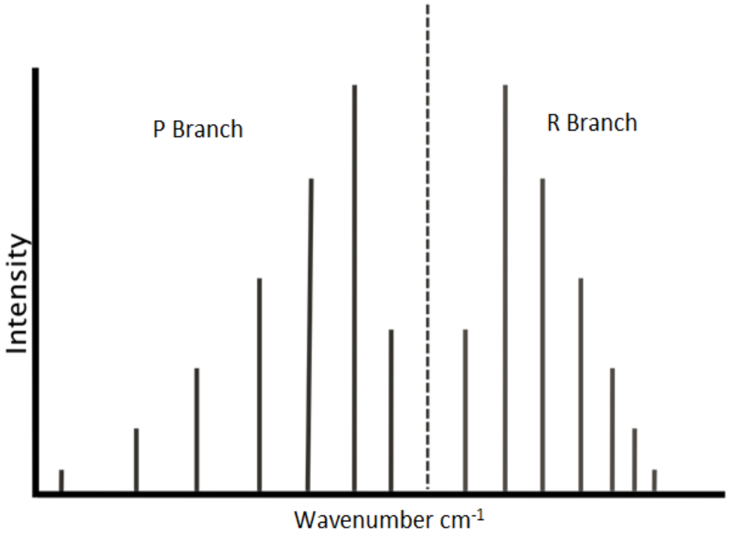


Figure: *Real Vibrational-Rotational Spectra (Fine Structure)*

So we Conclude the following from the above theory

1. As the vibrational energy increases ,the average inter-nuclear distance increases so the rotational constant B_v is smaller in the upper state than lower state. So $B_v' < B_v''$, means band head appears in R branch on high wavenumber side of the origin. Such a band is said to be degraded towards the red. So the vibrational-rotational spectra bands are degraded to red only.
2. The wavelength separation of successive lines in the P and Q branches are as

$$\Delta\bar{v}(P) = 2B'_v - (B'_v - B''_v)2J + ...$$

$$\Delta\bar{v}(R) = 2B'_v + (B'_v - B''_v)2J + ...$$

3. For both P and R branches $B_v' < B_v''$, so the separation between the lines of R branch decreases with increase in J values where as the separation between lines of P branch increases with increase in J.

21.9 Illustrative Examples

Example1 The value of $\overline{v}$ and $\overline{v}x$ are 1580.36 cm^{-1} and 12.073 cm^{-1} respectively for the ground state of molecular oxygen. Calculate the zero-point energy. (1eV = 8068 cm^{-1}).

Sol. The vibrational energy of the diatomic molecule is given by

$$G(v) = \overline{v}(v+\frac{1}{2}) - \overline{v}x(v+\frac{1}{2})^2$$

For zero point energy v = 0 so

$$G(0) = \overline{v}\frac{1}{2} - \overline{v}x\frac{1}{4}\ , \quad G(0) = 1580.36\times\frac{1}{2} - 12.073\times\frac{1}{4} = 790.18 - 3.02$$

$$G(0) = 787.16 \text{ cm}^{-1},\ G(0) = \frac{787.16}{8068} = 0.097eV$$

Example 2 The force constant of the bond in CO molecule is 190 N/m and its reduced mass is $1.15\times10^{-26}kg$. Calculate the frequency of vibration and spacing between the vibrational levels.

Sol. The frequency of vibration of the molecule is given by

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\times3.14}\sqrt{\frac{190}{1.15\times10^{-26}}}$$

$$\upsilon = 2.0467\times10^{13} \text{ Hz}$$

The separation between the two energy levels

$$\Delta E = E_{v+1} - E_v = h\upsilon$$

$$\Delta E = E_{v+1} - E_v = 6.63\times10^{-34}\times2.0467\times10^{13}$$

$$\Delta E = 6.63\times10^{-34}\times2.0467\times10^{13} = 13.5696\times10^{-21} \text{ J}$$

$$\Delta E = \frac{13.5696\times10^{-21}}{1.6\times10^{-19}}eV$$

$$\Delta E = 8.481\times10^{-2}eV$$

Example 3 HCl molecule absorbs wavelength 3.5 micrometer due to vibrational transitions. Find the force constant for HCl molecule.

Sol. The frequency of vibrations is given by

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2\upsilon^2\mu$$

Here $m_H = 1.0087$ a.m.u. and $m_{Cl} = 35.453$ a.m.u.

So the reduced mass of the molecule is given by

$$\mu = \frac{m_H m_{Cl}}{(m_H + m_{Cl})} = \frac{1.0087 \times 35.453}{(1.0087 + 35.453)} = 0.98 \text{ a.m.u.}$$

$$\mu = 0.98 \times 1.67 \times 10^{-27} \text{ kg.}$$

The frequency of vibration can also be written as

$$\upsilon = \frac{c}{\lambda} = \frac{3 \times 10^8}{3.5 \times 10^{-6}} = 8.571 \times 10^{13} \text{ Hz.}$$

So the force constant is now given by

$$k = 4 \times (3.14)^2 (8.571 \times 10^{13})^2 \times 1.63 \times 10^{-27}$$

$$k = 472.24 \text{ N/m}$$

Example 4 The fundamental band of a diatomic molecule is centered around 2145 cm^{-1} and first overtone at 4260 cm^{-1}. Find $\overline{v}$ and $\overline{v}x$.

Sol. The frequency of fundamental and first overtones are given by

$\overline{v}_1 = (1 - 2x)\overline{v}$ Fundamental band.

$\overline{v}_2 = (1 - 3x)2\overline{v}$ First overtone.

So, $\frac{\overline{v}_1}{\overline{v}_2} = \frac{(1 - 2x)}{(1 - 3x) \times 2}$

$$2\overline{v}_1 - 6\overline{v}_1 x = \overline{v}_2 - 2\overline{v}_2 x$$

$$(2\overline{v}_2 - 6\overline{v}_1)x = \overline{v}_2 - 2\overline{v}_1$$

$$x = \frac{(\overline{v}_2 - 2\overline{v}_1)}{(2\overline{v}_2 - 6\overline{v}_1)} = \frac{(4260 - 4290)}{(8520 - 12870)} = \frac{30}{4350}$$

$$x = 0.0069$$

As $2\overline{v}_1 - \overline{v}_2 = 2\overline{v}x$

$$\overline{v}x = \frac{(2\overline{v}_1 - \overline{v}_2)}{2} = \frac{4290 - 4260}{2} = 15 \text{ cm}^{-1}$$

$$\overline{v} = \frac{15}{x} = \frac{15}{0.0069} = 2174 \text{ cm}^{-1}$$

21.10 Self Learning Exercise

Q.1 What is the order of energy difference between vibrational levels of a molecule ?

Q.2 Discuss the anharmonicity present in molecular vibrations.

Q.3 Discuss the effect of isotopic exchange on the vibrational spectra of a diatomic molecule.

Q.4 Discuss the fine structure of the vibrational-rotational spectra.

21.11 Summary

The aim of this unit is to study the vibrational-rotational spectra of the diatomic molecules. First of all the pure vibrational motion of the molecule is considered and the energies levels are determined. After this effect of anharmonicity present in the molecule has been discussed. Due to anharmonic effect the presence of fundamental band, first overtones and second overtones were discussed. Effect of the isotopic exchange on the spectra has been also discussed. After considering the pure vibrational motion the rotational motion of the molecule is also considered. The two motions first treated as non-interacting and the total energy of the molecule has been calculated. The combined vibrational and rotational motion provides the presence different branches in the molecular spectra. Different cases were considered regarding the rigidity and non-rigidity of the bond as harmonic and anharmonic effect in the vibrations. At last the fine structure of the vibrational-rotational spectra have been discussed. The fine spectra are related to interaction of vibrational and rotational motion. The effect has been discussed in terms of separation between the lines of different branches.

21.12 Glossary

Homo-nuclear : Same type of nucleus

Hetero-nuclear : Different type of nucleus

Polar : Having +ive and –ive charge

Oscillating : Periodically varying

Rigid : Hard to change

Flexible : Easy to change

Distortion : Defects

Converge : Terminating

Degraded : Ending

21.13 Exercise

Q.1 Write the order of frequency and wavelength of NIR spectra.

Q.2 How the polar molecules interact with electromagnetic radiations ?

Q.3 Give the examples of polar molecules.

Q.4 Write the selection rules for transitions between the vibrational levels.

Q.5 Are the vibrations of a diatomic molecules are pure harmonic ?

Q.6 Discuss the effect of anharmonicity on the vibrational spectra.

Q.7 Discuss the fundamental band and various overtones in vibrational spectra.

Q.8 Discuss the effect of isotopic exchange on the fundamental and on the overtones of the vibrational spectra.

Q.9 Write the formula for calculation of force constant of bond in a diatomic molecule.

Q.10 Discuss the Vibrational-Rotational spectra of diatomic molecules. Discuss the various branches of the spectra.

Q.11 Write the selection rules for transitions in vibrational-rotational spectra.

Q.12 Discuss the effect of non-rigidity and anharmonicity on the NIR spectra.

References and Suggested Readings

1. Colin N. Banwell and Elaine M. McCash*: Molecular Spectroscopy*, Tata Mcgraw-Hill Education Private Limited, New Delhi, 1994.
2. J. M. Holias*: Modern Spectroscopy* , John Wiley & Sons, England, 1987.
3. S.L. Gupta, V. Kumar and R.C. Sharma: *Elements of Spectroscopy,* Pragati Prakashan, Meerut, 1990.
4. Raj Kumar: *Atomic & Molecular Spectra: LASER*, Kedar Nath Ram Nath, Meerut, 2007.
5. G.M. Barrow, Introduction to Molecular Spectroscopy, McGraw Hill, London, 1961.

UNIT-22
Infrared Spectroscopy : Part-II

Structure of the Unit

22.0 Objectives

This chapter is aimed to provide knowledge to the readers about the population of vibrational energy levels of molecules. The different modes of vibrations of polyatomic molecules will be discussed. The instrumentation for recording the IR spectra of the molecules will be explained.

22.1 Introduction

The vibrational energy levels of the molecules are quantized. The population of these energy levels at any temperature will be discussed. The normal coordinates of vibrations and various modes of vibration of polyatomic molecules are explained with examples. The instrumentation required to record the IR spectra of the molecules is discussed i.e. FTIR spectrometer.

22.2 Thermal Distribution of Vibrational and Rotational Levels

Vibrational Levels : According to Maxwell-Boltzmann distribution law the number of molecules in the v^{th} state, N_v, relative to lowest state, N_0, is given by

$N_v = N_0 e^{\frac{-G_0(v)hc}{kT}}$, k is the Boltzmann constant and T is the temperature. $G_0(v)$ is the energy term value of the transition from v^{th} state to zero state.

$$G_0(v) = G(v) - G(0)\,,\ G(v) = \bar{v}(v+\frac{1}{2}) - \bar{v}x(v+\frac{1}{2})^2$$

At room temperature the population of higher vibrational levels is very small as compared to lowest level v = 0. As the temperature increases the population of higher vibrational levels increases as shown in the graph 22.1.

Rotational Levels : The relative population of various rotational levels corresponding to a vibrational level is of different nature. A rotational state having rotational quantum number J is (2J+1) fold degenerate. The probability of a molecule to be in each degenerate state is equal. Let the molecules are in the lowest vibrational state v = 0, $N_{v=0}$, be the number of molecules in this state. These molecules are distributed in various rotational states. The number of molecules in a rotational state of a given vibrational state is as

$$N_J = \frac{N_{v=0}}{Z_r}(2J+1)e^{\frac{-F(J)hc}{kT}}$$

where Z_r is the rotational partition function which is given by

$$Z_r = \sum_{J=0}^{\infty}(2J+1)e^{\frac{-F(J)hc}{kT}}$$

$$Z_r = \sum_{J=0}^{\infty}(2J+1)e^{\frac{-BJ(J+1)hc}{kT}}$$

$$Z_r = \int_0^{\infty}(2J+1)e^{\frac{-BJ(J+1)hc}{kT}}dJ = \frac{kT}{hcB}$$

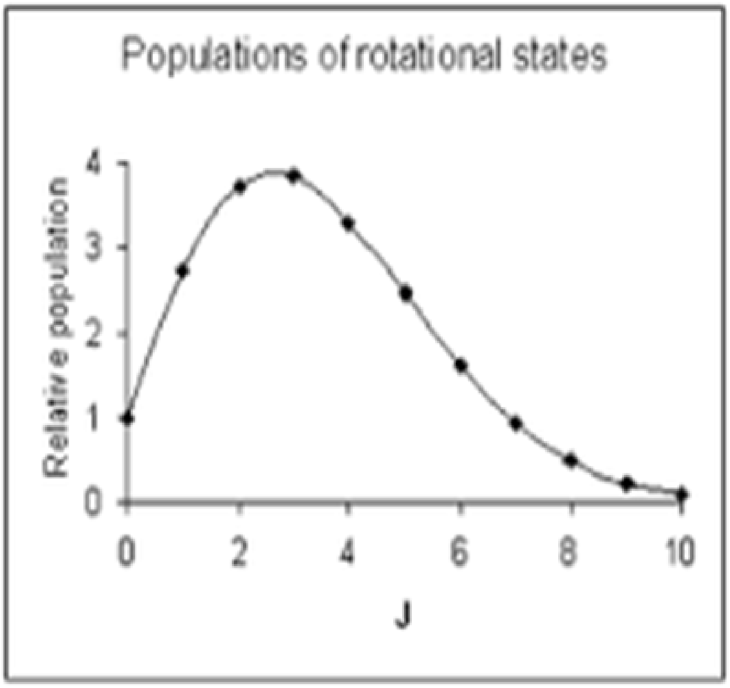


Figure:22.1 Population of Rotational levels

So $\frac{N_J}{N_{v=0}} = \frac{hcB}{kT}(2J+1)e^{\frac{-BJ(J+1)hc}{kT}}$

We see here that as the value of J increases, the value of $\frac{N_J}{N_{v=0}}$ first increases and then decreases. The value of J for which the population is maximum is calculated as $\frac{d}{dJ}(\frac{N_J}{N_{v=0}}) = \frac{d}{dJ}(\frac{hcB}{kT}(2J+1)e^{\frac{-BJ(J+1)hc}{kT}}) = 0$

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

Thus, the value of J at which the population is maximum, increases with decrease in B and increase in temperature. As the temperature of the molecular gas increases ,then the following effects are observed.

1. The extension of band takes place along both sides i.e. along P branch and R branch.
2. The intensity maxima in both branches moves farther from $\overline{v}_0$.
3. The intensity maximum is found for higher value of J.
4. The height of intensity maxima decreases.
5. The inequality between the intensity of two branches becomes less marked.

22.3 Vibrational Spectra of Polyatomic Molecules

A polyatomic molecule having N atoms have 3N degrees of freedom i.e. 3N co-ordinates are required to specify the positions of all nuclei. Out of these 3N degree of freedoms 3 are related to translational motion, 3(non linear molecule) or 2(linear molecule) are related to rotational motion and remaining 3N-6(non linear molecule) or 3N-5 (linear molecule) are related to vibrational motion. There will be 3N-6 or 3N-5 energy levels corresponding to these vibrations. So in the spectrum of the molecules having n atoms there will be 3N-6 (non linear molecule) or 3N-5(linear molecule) absorption bands.

Normal Co-ordinates and Normal Modes of Vibrations

For the analysis of spectra shown by polyatomic molecules ,the study of modes of vibrations is essential. Let us consider a linear diatomic molecule having 3N-6 degree of freedoms denoted by m and generalized coordinates q_1, q_2, q_3, ...q_m, representing the equilibrium state of each nucleus. The potential energy of can be expanded by Taylor's series in terms of these coordinates, i.e.

$$V = V_{eq} + \{\sum_i \frac{\partial V}{\partial q_i}\}_{eq} q_i + \{\frac{1}{2}\sum_{i,j} \frac{\partial^2 V}{\partial q_i \partial q_j}\}_{eq} q_i q_j + ...$$

If the equilibrium potential energy is taken as reference and chosen to be zero then

$V = \{\frac{1}{2}\sum_{i,j} \frac{\partial^2 V}{\partial q_i \partial q_j}\}_{eq} q_i q_j$, because $\{\frac{\partial V}{\partial q_i}\}_{eq} = 0$ in equilibrium position.

Let us consider that

$$b_{ij} = \{\frac{1}{2}\sum_{i,j}\frac{\partial^2 V}{\partial q_i \partial q_j}\}_{eq}\text{, then } V = \frac{1}{2}\sum_{i,j} b_{i,j} q_i q_j$$

The kinetic energy is given by

$$K = \frac{1}{2}\sum_{i,j} m_{i,j}\,\dot{q}_i\,\dot{q}_j\text{, where the coefficients are given by}$$

$$m_{i,j} = m_{j,i} = \sum_k m_k (\frac{\partial r_k}{\partial q_i})(\frac{\partial r_k}{\partial q_j}) = m_{i,j}(q_1, q_2, q_3, \ldots . q_m)$$

$$m_{i,j} = (m_{i,j})_{eq} + \sum_k (\frac{\partial m_{ij}}{\partial q_l}) q_l + \ldots\ldots$$

If we consider only the first term of the series ,then the kinetic energy is written as

$$K = \frac{1}{2}\sum_{i,j} a_{i,j}\,\dot{q}_i\,\dot{q}_j \text{ , where } a_{ij} = (m_{ij})_{eq}$$

The Lagrangian of the system is given by

$$L = K - V = \frac{1}{2}\sum_{i,j}(a_{ij}\,\dot{q}_i\,\dot{q}_j - b_{ij} q_i q_j)$$

The Lagrangian's equation of motion are

$$\sum_{i=1}^{m}[\frac{d}{dt}(\frac{\partial L}{\partial \dot{q}_i}) - \frac{\partial L}{\partial q_i}] = 0$$

$$\frac{d}{dt}[\frac{1}{2}\sum_j a_{ij}\,\dot{q}_j + \frac{1}{2}\sum_j b_{ij} q_j = 0$$

$$\sum_j a_{ij}\,\ddot{q}_j + \sum_j b_{ij} q_j = 0 \qquad \text{(A)}$$

It represents a set of m equations (i = 1, 2, 3, ..., m). The general solution of such equation is as

$$q_j = A_j Sin(\omega t + \alpha) \qquad \text{(B)}$$

where A_j is the amplitude and ω is the angular frequency which is given by

$$\omega = \sqrt{\lambda} = 2\pi\upsilon$$

By substituting from (B) in equation (A) we get

$$\sum_j (b_{ij} - a_{ij}\lambda)A_j = 0, i = 1,2,3...m$$

which gives a set of m simultaneous linear homogeneous equations in A's and if A's are not all to be zero then

$$\sum_j (b_{ij} - a_{ij}\lambda) = 0$$

or $$\begin{pmatrix} \\ b_{11} - a_{11}\lambda & .... & b_{1n} - a_{nn}\lambda \\ b_{21} - a_{21}\lambda & .... & b_{2n} - a_{nn}\lambda \\ .... & .... & .... \\ b_{n1} - a_{n1}\lambda & .... & b_{nn} - a_{nn}\lambda \end{pmatrix} = 0$$

This equation is an equation of m[th] degree giving m values of λ in terms of *a*'s and b's. These values of λ's or ω^2 are the normal frequency of vibrations of a polyatomic molecule.

We now consider the normal coordinates, such that each of them execute only one single frequency oscillations. Let us now transform the equations in q_i's to normal coordinates Q_j's as

$$q_i = \sum_{j=1}^{i} C_{ij}Q_j \quad \text{or} \qquad q = CQ$$

where (q) and (Q) are single column matrices. In order to write the equation of motion in terms of normal coordinates ,we have to find first the kinetic energy and potential energy and the Lagrangian in terms of Q's. The potential energy is given by

$V = \frac{1}{2}\sum_{i,j} b_{ij}q_iq_j$, which is a quadratic in q. Any quadratic expression is of the form can be written as

$$\alpha q_1^2 + \beta q_2^2 + 2\gamma q_1 q_2$$

which can be written as

$$(q_1, q_2)\begin{pmatrix} \alpha & \gamma \\ \gamma & \beta \end{pmatrix}\begin{pmatrix} q_1 \\ q_2 \end{pmatrix} = X^T UX$$

where $$X = \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}$$

$$U = \begin{pmatrix} \alpha & \gamma \\ \gamma & \beta \end{pmatrix}$$

$$X^T = (q_1, q_2)$$

Now we can write V as

$$V = \frac{1}{2} q^T b q$$

$$V = \frac{1}{2} C^T Q^T b C Q$$

$$V = \frac{1}{2} Q^T C^T b C Q$$

$$V = \frac{1}{2} Q^T \lambda Q$$

where $C^T b C = \lambda$

So the potential energy can be written as

$$V = \frac{1}{2} \sum_k \omega_k^2 Q_k^2$$

$$T = \frac{1}{2} \sum_{i,j} a_{ij} \dot{q}_i \dot{q}_j = \frac{1}{2} \dot{q}^T \alpha \dot{q}$$

$$T = \frac{1}{2} \dot{Q}^T C^T \alpha C \dot{Q} = \frac{1}{2} \dot{Q}^T \dot{Q} = \frac{1}{2} \sum \dot{Q}_k^2$$

where $C^T \alpha C = 1$

Therefore Lagrangian will be

$$V = \frac{1}{2} \sum_k \omega_k^2 Q_k^2$$

$$T = \frac{1}{2} \sum_{i,j} a_{ij} \dot{q}_i \dot{q}_j = \frac{1}{2} \dot{q}^T \alpha \dot{q}$$

$$T = \frac{1}{2} \dot{Q}^T C^T \alpha C \dot{Q} = \frac{1}{2} \dot{Q}^T \dot{Q} = \frac{1}{2} \sum_k \dot{Q}_k^2$$

$$C^T \alpha C = 1$$

$$L = T - V = \frac{1}{2} \sum_k \dot{Q}_k^2 - \frac{1}{2} \sum_k \omega_k^2 Q_k^2$$

$$\sum_{k=1}^{m} [\frac{d}{dt}(\frac{\delta L}{\delta \dot{Q}_k}) - (\frac{\delta L}{\delta Q_k})] = 0$$

$$\sum_{k=1}^{m}[\ddot{Q}_k + \omega_k^2 Q_k] = 0$$

$$\ddot{Q}_m + \omega_m^2 Q_m = 0$$

$$Q_m = A_m \cos\omega_m t + B_m \sin\omega_m t$$

which when used with

$$\sum_{k=1}^{m}[\frac{d}{dt}(\frac{\delta L}{\delta \dot{Q}_k}) - (\frac{\delta L}{\delta Q_k})] = 0$$

$$\sum_{k=1}^{m}[\ddot{Q}_k + \omega_k^2 Q_k] = 0$$

or $$\ddot{Q}_1 + \omega_1^2 Q_1 = 0$$

$$\ddot{Q}_2 + \omega_2^2 Q_2 = 0$$

$$\ddot{Q}_3 + \omega_3^2 Q_3 = 0$$

....

....

$$\ddot{Q}_m + \omega_m^2 Q_m = 0$$

Corresponding to Q_1 the frequency is ω_1 , for Q_2 it is ω_2 , and so on. The Q's are called as normal coordinates. The solutions to above equations are as

$$Q_1 = A_1 \cos\omega_1 t + B_1 \sin\omega_1 t$$

$$Q_2 = A_2 \cos\omega_2 t + B_2 \sin\omega_2 t$$

$$Q_3 = A_3 \cos\omega_3 t + B_3 \sin\omega_3 t$$

....

....

$$Q_m = A_m \cos\omega_m t + B_m \sin\omega_m t$$

Here ω_1, ω_2, ω_3, ...ω_m are called as normal frequencies.

22.4 Fundamental Vibrations and their Symmetry

Let us consider a molecule containing N atoms. The position of each atom can be specified by three coordinates i.e. x, y, and z coordinates. So there will be 3N coordinates i.e. molecule has 3N degree of freedom. Now the molecule is free to move in three dimensional space as a whole without change of shape. The translational motion uses three degree of freedom leaving 3N-3 as remaining. Also a non-linear molecule has three degree of freedom due to rotations . So the molecule is left with 3N-6 degree of freedom. The only other motion allowed to molecule is the internal vibrations, so a non-linear molecule will have 3N-6 degree of freedom due to internal vibrations. If the molecule is linear, then there will be 3N-5 degree of freedom due to internal vibrations. In both types of molecules there are N atoms, so there will be N-1 bonds (acyclic molecules) between the atoms. There will be N-1 vibrations are of bond stretching type motions and 2N-5 (non-linear) or 2N-4 (linear) are of bending type motions.

In case of diatomic molecule N=2 and 3N-5=1, so there is only one fundamental vibration. In case of tri-atomic non-linear molecule like H_2O, there are 3N-6=3 allowed vibrational modes called as normal modes. Theses modes of vibrations are shown as below.

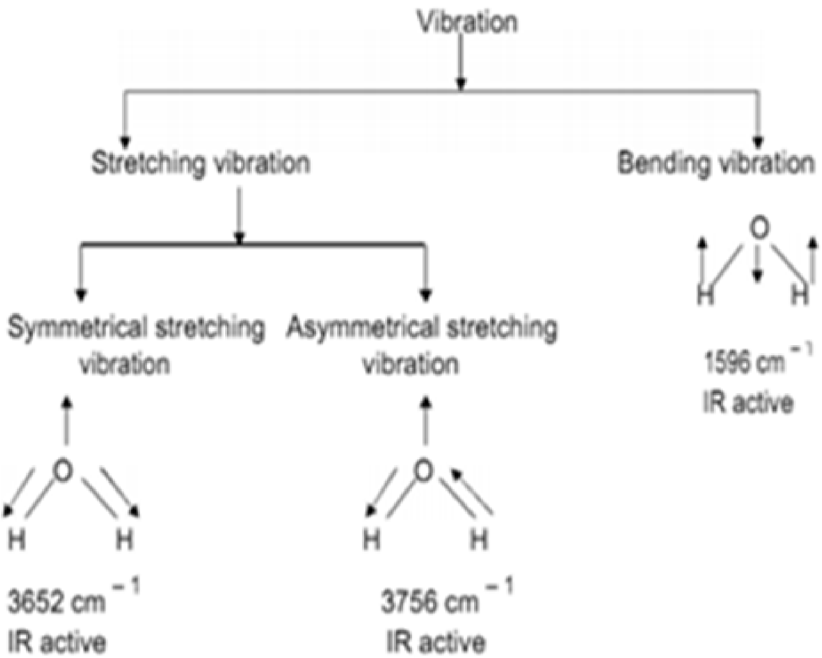


Figure 22.2 Vibrations of Water Molecule

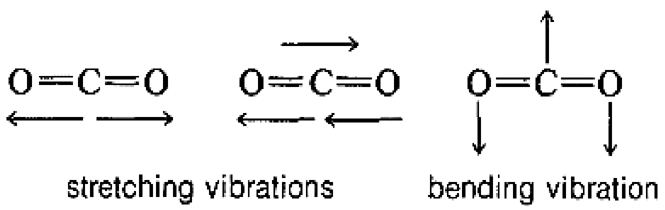


Figure 22.3 Vibrations of Carbon Dioxide Molecule

Each vibrational motion is labeled as symmetric or antisymmetric. If we rotate the vibrating molecule by 180^0 such that vibration is quite unchanged in character then it is called as symmetric vibrations. However if the rotation produces a vibration which is in antiphase with the original ,then such motion is called as antisymmetric stretching mode. The vibrations of water molecule and carbon dioxide molecule are shown in figure.

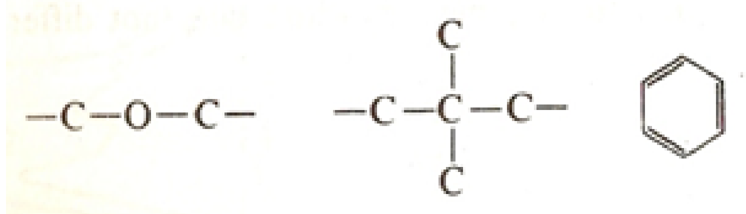
22.5 Analysis by Infrared Techniques

A complex molecule has 3N-6 or 3N-5 normal modes of vibrations. Each normal mode involves some displacement of all or nearly all the atoms in the molecule, but in some of the modes ,all atoms may undergo approximately the same displacement and in others the displacement of a small group of atoms may be much more vigorous than the remainder. Thus we may divide the normal modes into two groups as skeletal vibrations and characteristics group vibrations. The skeletal vibrations involve many of the atoms to same extent and the characteristic vibrations involve only a small portion of the molecule while others remain stationary.

22.5.1 Skeletal Vibrations

For organic molecules these fall in the range 1400-700 cm^{-1} and arise from linear or branched chain structure in the molecule. Thus each such group gives rise to several Skeletal modes of vibrations and hence several absorptions bands in the infra-red.

It is not possible to assign particular bands to specific vibrational mode, but the observed band is highly typical of a molecular structure under examination. Further a change in the chain or ring in the form of substitution results in a marked change in the pattern of absorption band. These bands are treated as fingerprint of a particular molecular structure.



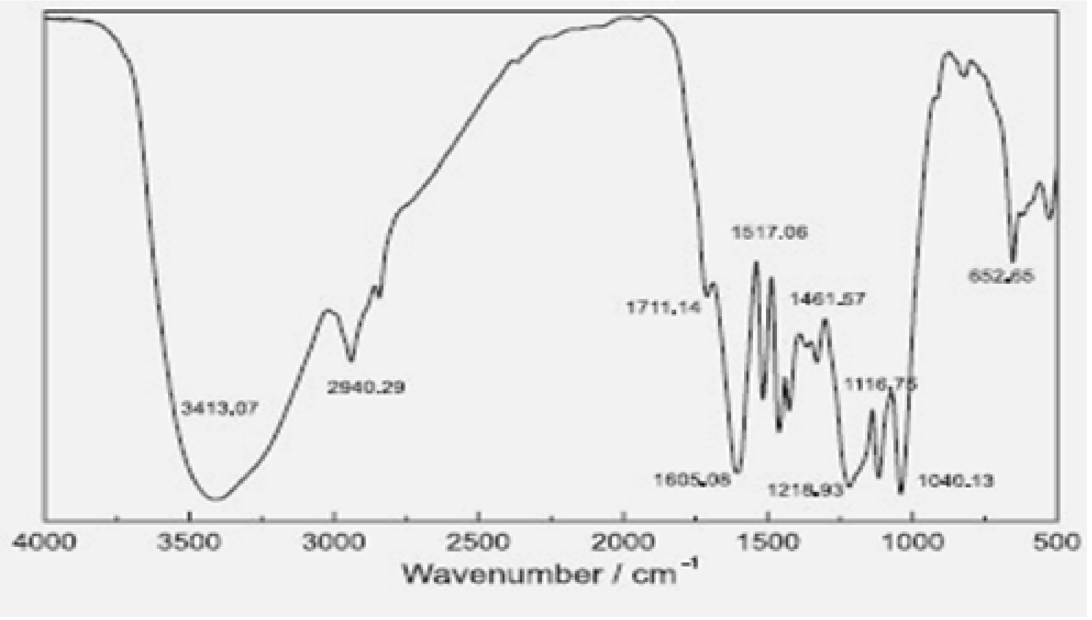


Figure:22.4 ***The adsorption bands at 1605 cm^{-1} and 1517 cm^{-1} were characteristic of phenyl ring skeletal vibrations of lignin macromolecules.***

22.5.2 Group Frequencies

The group frequencies are usually independent of the structure of the molecule as whole and fall in the regions well above and well below that of skeletal modes. The group frequencies of some functional groups are given in table below.

CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES

Bond	Compound type	Frequency range cm^{-1}
C—H	Alkanes	2850–2960 1350–1470
C—H	Alkenes	3020–3080 675–1000
C—H	Aromatic rings	3000–3100 675–870
C—H	Alkynes	3300
C=C	Alkenes	1640–1680
C≡C	Alkynes	2100–2260

Bond	Compound type	Frequency range cm^{-1}
C⋯C	Aromatic rings	1500, 1600
C—O	Alcohols, ethers, carboxylic acids, esters	1080–1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760
O—H	Monomeric alcohols, phenols	3610–3640
	Hydrogen-bonded alcohols, phenols	3200–3600
	Carboxylic acids	2500–3000
N—H	Amines	3300–3500
C—N	Amines	1180–1360
C≡N	Nitriles	2210–2260
—NO_2	Nitro compounds	1515–1560
		1345–1385

Table:22.1 ***Vibrational Frequencies of Functional Groups (cm^{-1})***

Shift in the characteristic frequencies occurs due to two major factors. Firstly the shift may arise due to interactions between the different molecules. Secondly, the shift in the frequencies is also due physical state of molecules. The more condensed phase gives lower frequencies particularly in case of polar molecules. In non polar molecules there is no shift in symmetric vibrations but a smaller shift in others.

22.6 Fourier-Transform Infrared Spectrometers

Fourier-transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an interferogram. The latter is a signal produced as a function of the change of path length between the two beams. The two domains of distance and frequency are inter-convertible by the mathematical method of Fourier-transformation. The basic components of an FTIR spectrometer are shown schematically in given Figure. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier-transformation. The major components of the spectrometer are discussed as

22.6.1 Michelson Interferometers

The most common interferometer used in FTIR spectrometry is a Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which can travel in a direction perpendicular to the plane ,a semi-reflecting film, the beam splitter, bisects the planes of these two mirrors. The beam splitter material has to be chosen according to the region to be examined. Materials such as germanium or iron oxide are coated onto an infrared-transparent substrate such as potassium bromide or caesium iodide to produce beam splitters for the mid- or near-infrared regions. Thin organic films, such as poly (ethylene terephthalate), are used in the far-infrared region. If a collimated beam of monochromatic radiation of wavelength λ (cm) is passed into an ideal beam splitter, 50% of the incident radiation will be reflected to one of the mirrors while 50% will be transmitted to the other mirror. The two beams are reflected from these mirrors, returning to the beam splitter where they recombine and interfere. The moving mirror produces an optical path difference between the two arms of the interferometer. For path differences of $(n + 1/2)\lambda$, the two beams interfere destructively in the case of the transmitted beam and constructively in the case of the reflected beam.

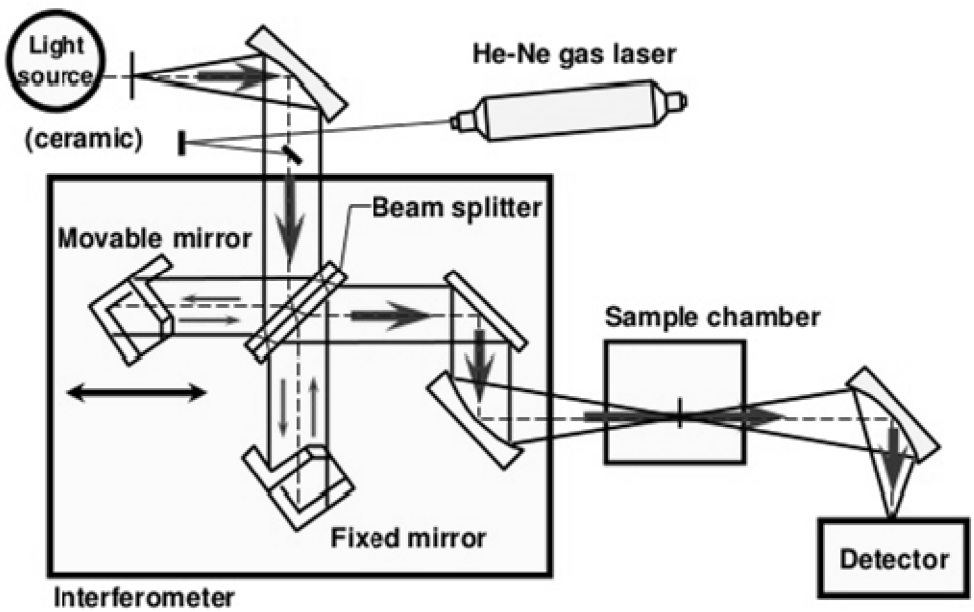


Figure 22.5 FTIR spectrometer

22.6.2 Sources and Detectors

FTIR spectrometers use a Globar or Nernst source for the mid-infrared region. If the far-infrared region is to be examined, then a high-pressure mercury lamp can be used. For the near-infrared, tungsten–halogen lamps are used as sources. There are two commonly used detectors employed for the mid-infrared region. The normal detector for routine use is a pyro-electric device incorporating deuterium tryglycine sulfate (DTGS) in a temperature-resistant alkali halide window. For more sensitive work, mercury cadmium telluride (MCT) can be used, but this has to be cooled to liquid nitrogen temperatures. In the far-infrared region, germanium or indium–antimony detectors are employed, operating at liquid helium temperatures. For the near-infrared region, the detectors used are generally lead sulfide photoconductors.

22.6.3 Fourier-Transformation

The essential equations for a Fourier-transformation relating the intensity falling on the detector *I(δ)* to the spectral power density at a particular wavenumber $\bar{v}$ is given by $B(\bar{v})$ as

$$I(\delta) = \int_{0}^{\infty} B(\bar{v}) \cos(2\pi \bar{v} \delta) d\bar{v}$$

where $$B(\bar{v}) = \int_{-\infty}^{\infty} I(\delta) \cos(2\pi \bar{v} \delta) d\delta$$

These two equations are inter-convertible and are known as a Fourier-transform pair. The first shows the variation in power density as a function of the difference in path length, which is an interference pattern. The second shows the variation in intensity as a function of wavenumber. Each can be converted into the other by the mathematical method of Fourier-transformation. The essential experiment to obtain an FTIR spectrum is to produce an interferogram with and without a sample in the beam and transforming the interferograms into spectra of (a) the source with sample absorptions and (b) the source without sample absorptions. The ratio of the former and the latter corresponds to a double-beam dispersive spectrum. The major advance toward routine use in the mid-infrared region came with a new mathematical method devised for fast Fourier-transformation (FFT). This was combined with advances in computers which enabled these calculations to be carried out rapidly.

22.6.4 Moving Mirrors

The moving mirror is a crucial component of the interferometer. It has to be accurately aligned and must be capable of scanning two distances so that the path difference corresponds to a known value. A number of factors associated with the moving mirror need to be considered when evaluating an infrared spectrum. The interferogram is an analogue signal at the detector that has to be digitized in order that the Fourier-transformation into a conventional spectrum can be carried out. There are two particular sources of error in transforming the digitized information on the interferogram into a spectrum. First, the transformation carried out in practice involves an integration stage over a finite displacement rather than over an infinite displacement. The mathematical process of Fourier transformation assumes infinite boundaries. The process of apodization is the removal of the side lobes (or pods) by multiplying the interferogram by a suitable function before the Fourier-transformation is carried out. A suitable function must cause the intensity of the interferogram to fall smoothly to zero at its ends. Most FTIR spectrometers offer a choice of apodization options and a good general purpose apodization function is the cosine function, as follows:

$$F(D) = [1 + \cos(\pi D)]/2$$

where D is the optical path difference. This cosine function provides a good compromise between reduction in oscillations and deterioration in spectral resolution. When accurate band shapes are required, more sophisticated mathematical functions may be needed. Another source of error arises if the sample intervals are not exactly the same on each side of the maxima corresponding to zero path differences. Phase correction is required and this correction procedure ensures that the sample intervals are the same on each side of the first interval and should correspond to a path difference of zero. The resolution for an FTIR instrument is limited by the maximum path difference between the two beams. The limiting resolution in wavenumbers (cm^{-1}) is the reciprocal of the path length difference (cm). For example, a path length difference of 10 cm is required to achieve a limiting resolution of 0.1 cm^{-1}. This simple calculation appears to show that it is easy to achieve high resolution. Unfortunately, this is not the case ,since the precision of the optics and mirror movement mechanism become more difficult to achieve at longer displacements of path lengths.

22.6.5 Signal-Averaging

The main advantage of rapid-scanning instruments is the ability to increase the signal-to-noise ratio (SNR) by signal-averaging, leading to an increase of signal-to-noise proportional to the square root of the time, as follows:

$$\text{SNR} \propto n^{1/2}$$

There are diminishing returns for signal-averaging in that it takes an increasingly longer time to achieve greater and greater improvement. The accumulation of a large number of repeat scans makes greater demands on the instrument if it is to exactly reproduce the conditions. It is normal to incorporate a laser monochromatic source in the beam of the continuous source. The laser beam produces standard fringes which can 'line-up' successive scans accurately and can determine and control the displacement of the moving mirror at all times.

22.6.6 Computers

The computer forms a crucial component of modern infrared instruments and performs a number of functions. The computer controls the instrument, for example, it sets scan speeds and scanning limits, and starts and stops scanning. It reads spectra into the computer memory from the instrument as the spectrum is scanned; this means that the spectrum is digitized. Spectra may be manipulated using the computer, for example, by adding and subtracting spectra or expanding areas of the spectrum of interest. The computer is also used to scan the spectra continuously and average or add the result in the computer memory. Complex analyses may be automatically carried out by following a set of pre-programmed commands. The computer is also used to plot the spectra.

22.6.7 Spectra

Early infrared instruments recorded percentage transmittance over a linear wavelength range. It is now unusual to use wavelength for routine samples and the wavenumber scale is commonly used. The output from the instrument is referred to as a spectrum. Most commercial instruments present a spectrum with the wavenumber decreasing from left to right. The infrared spectrum can be divided into three main regions: the far infrared (<400 cm^{-1}), the mid-infrared (4000–400 cm^{-1}) and the near-infrared (13000–4000 cm^{-1}).

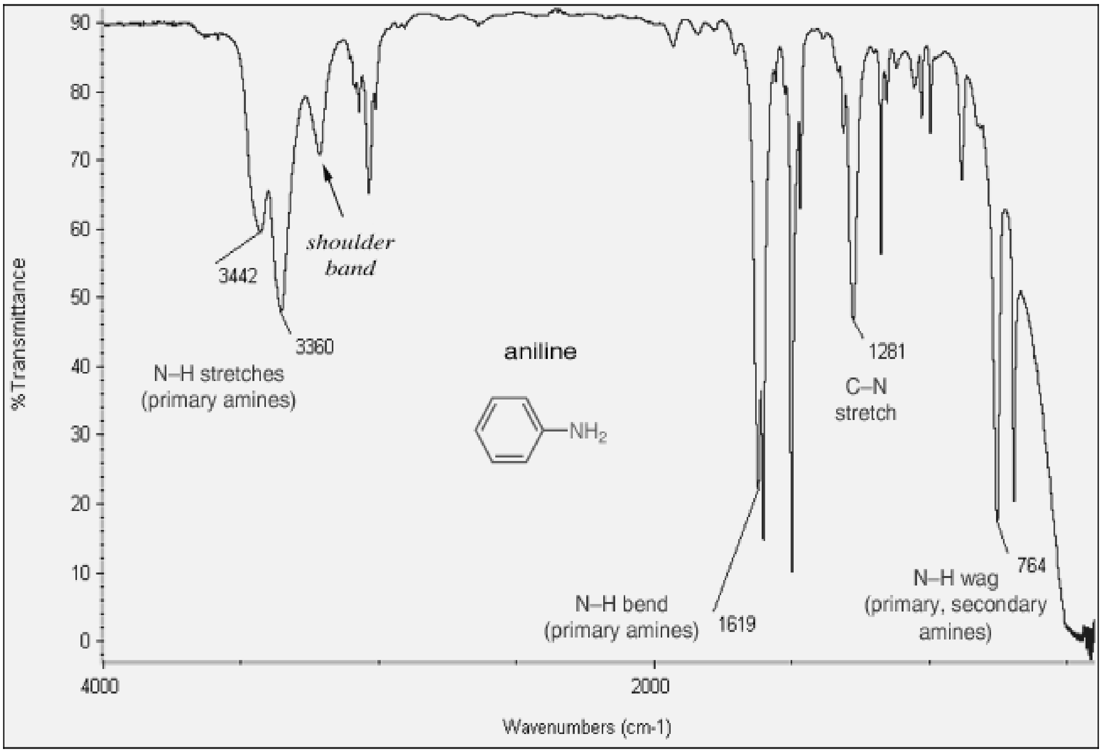


Figure 22.6. Typical FTIR spectra of Aniline

Many infrared applications employ the mid-infrared region, but the near- and far-infrared regions also provide important information about certain materials. Generally, there are less infrared bands in the 4000–1800 cm^{-1} region with many bands between 1800 and 400 cm^{-1}. Sometimes, the scale is changed so that the region between 4000 and 1800 cm^{-1} is contracted and the region between 1800 and 400 cm^{-1} is expanded to emphasize features of interest. The ordinate scale may be presented in % transmittance with 100% at the top of the spectrum. It is commonplace to have a choice of absorbance or transmittance as a measure of band intensity.

22.7 Self Learning Exercise

Q.1 Write the formula for population of a rotational level at any temperature.

Q.2 Write the Lagrangian of a system of a diatomic molecule.

Q.3 Write the Frequencies of vibration of C-H in alkenes, alkynes and aromatic ring.

Q.4 Write the use of moving mirror in FTIR spectrometer.

22.8 Summary

This unit deals with populations of vibrational and rotational levels at any temperature. The degeneracy of rotational level as well maximum population for a particular value of rotational quantum number has been discussed. The degree of freedoms of a molecules having N atoms as well vibrational degree of freedom have been discussed. The normal co-ordinates as well as normal mode of vibrations of a diatomic molecule have been explained. The skeletal vibrational frequency range and functional frequencies range is also discussed. Finally the instrumentation required to record the IR spectrum particularly FTIR has been discussed in detail. All the components of FTIR spectrophotometer have been discussed in detail.

22.9 Glossary

Degenerate : Number of states having same energy

Degree of freedom : Number of independent co-ordinates required to specify the state

Lagrangian : Total energy function mechanics

Linear : Along a line

Non-linear : Not along a line (bend)

Transparent : Able to pass

Splitter : Dividing into two or many

Interferometer : Instrument to record the interference

Interferogram : Interference pattern

22.10 Exercise

Q.1 Write the formula for population of a vibrational level at any temperature.

Q.2 Discuss the thermal distribution of vibrational and rotational levels.

Q.3 Write the various degree of freedom of a molecule having N atoms.

Q.4 Write the number of vibrational modes of a linear and non-linear molecule having N atoms.

Q.5 Write the Lagrangian equation of motion of a system of a diatomic molecule.

Q.6 Explain the normal modes and normal co-ordinates.

Q.7 Write the various modes of vibration of a linear and non-linear molecule with example.

Q.8 Write a short note on skeletal vibration.

Q.9 Write a short note on group frequencies.

Q.10 Write the general regions of skeletal and group frequencies.

Q.11 Write the Frequencies of vibration of C=C bond in alkenes, alkynes and aromatic ring.

Q.12 Write the basic components of FTIR spectrometer.

Q.13 Write the sources of IR and detectors of IR used in FTIR spectrometers.

Q.14 Discuss the construction and working of FTIR spectrometer.

References and Suggested Readings

1. Colin N. Banwell and Elaine M. McCash*: Molecular Spectroscopy*, Tata Mcgraw-Hill Education Private Limited, New Delhi, 1994.
2. J. M. Holias*: Modern Spectroscopy* , John Wiley & Sons, England, 1987.
3. S.L. Gupta, V. Kumar and R.C. Sharma: *Elements of Spectroscopy,* Pragati Prakashan, Meerut, 1990.
4. Raj Kumar: *Atomic & Molecular Spectra: LASER*, Kedar Nath Ram Nath, Meerut, 2007.
5. G.M. Barrow, *Introduction to Molecular Spectroscopy*, McGraw Hill, London, 1961.
6. B. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley & Sons, Ltd, 2004.

UNIT-23
Raman Spectra, Franck-Condon Principle

Structure of the Unit

23.0 Objectives

This unit is designed to provide basic knowledge about the one of most important phenomenon called as Raman Scattering or Raman Effect. The classical as well as quantum theories of Raman Effect will be discussed. It will be explained here that how the Raman scattering is related to vibration and rotational energy levels of the molecules and how it can provide the information about the molecular structure. The required instrumentation to observe Raman Scattering will also be discussed.

23.1 Introduction

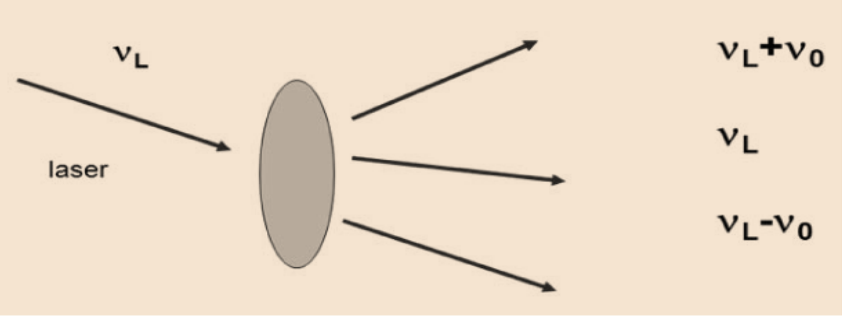
The scattering of electromagnetic radiation from the solid and there is a shift in frequency of electromagnetic radiation is called as Raman Effect. The scattering of these radiations by the solid is related to the vibrational and rotational energy levels of the molecules of the solids. Here the basic theories of Raman effect, origin of different spectral lines and various branches of these lines are explained. Finally the Raman Spectrometer is discussed in detail.

23.2 Raman Effect

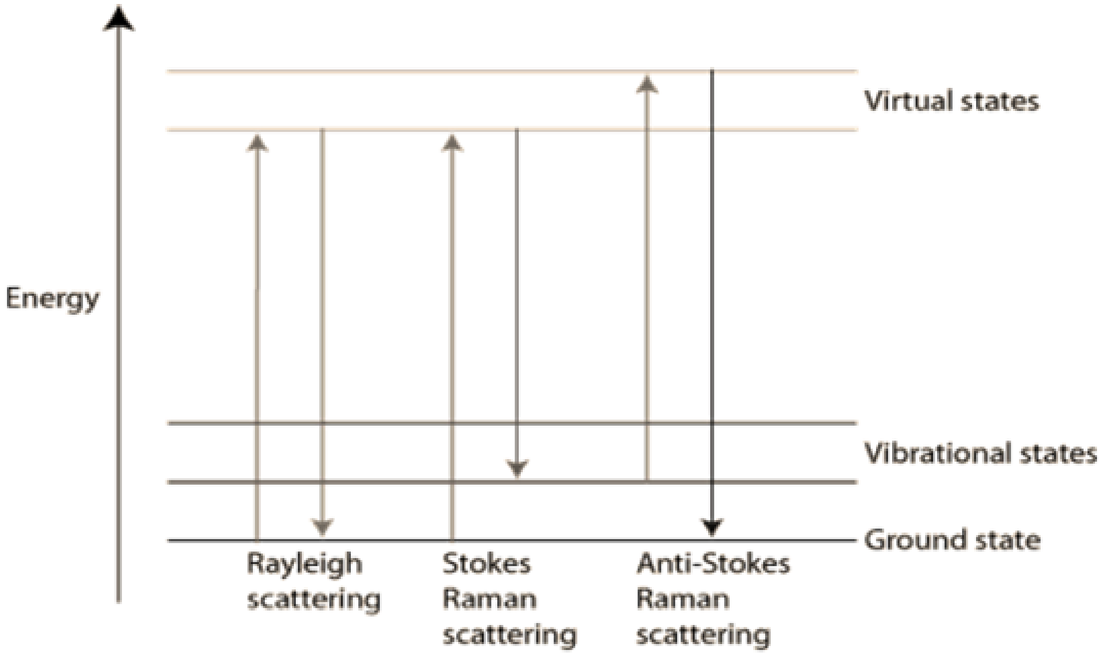
When a monochromatic radiations or radiations of very narrow frequency band are scattered by a solid then the scattered radiations not only consists of radiations of incident frequency but also radiations of frequencies above and below that of incident beam frequency. This type of scattering in which the frequency of incident beam undergoes a definite change was observed and was studied by Raman in 1928 and is called as Raman Effect. If $\bar{v}_i$ is the wavenumber of incident wave and $\bar{v}_s$ is the wavenumber of scattered wave then the Raman shift is given by

$$(\Delta\bar{v})_{rmn} = \bar{v}_i - \bar{v}_s$$

This difference is the characteristic of the material and it does not depend upon the wavenumber of the incident radiation. If $(\Delta\bar{v})_{rmn}$ is positive ,then Raman spectra is said to have Stokes lines and if $(\Delta\bar{v})_{rmn}$ is negative ,then the Raman spectra is said to have anti-Stokes lines.



The intensity of Stokes lines is higher as compared to anti-Stokes lines. The Raman shift $(\Delta\bar{v})_{rmn}$ lies within the range 100-3000 cm^{-1}, which fall in the far and near infra-red region of the spectrum. This shift suggests that the changes in the energy of scattered radiations in the Raman Effect correspond to the energy changes accompanying rotational and vibrational transitions in the molecules of the materials.



23.3 Classical Theory of Raman Effect

If an atom or a molecule is placed in an electric field ,then the electrons and the nuclei are displaced relative to each other i.e. an electric dipole moment is induced in the molecule due to this relative displacement of electrons and nuclei. It is also called as molecular polarization by the external electric field. Let E is the intensity of electric field and μ is the magnitude of induced dipole moment then

$$\mu = \alpha E$$

where α is the polarizability of the molecule. The intensity of the electric field of the electromagnetic wave of frequency υ can be expressed as

$$E = E_0 Sin(2\pi\upsilon t)$$

So the polarizability of the molecule is given by

$$\mu = \alpha E_0 Sin(2\pi\upsilon t)$$

So the interaction of radiation of frequency υ induces a dipole moment in the atom or molecule. This dipole moment oscillates with same frequency υ. So from the classical theory, this oscillating dipole will scatter or emit radiation of frequency υ i.e. frequency of incident radiations. It is called as Rayleigh scattering.

In the above discussion no internal motion i.e. rotation and vibration of the molecule is considered. Let us first consider the effect of vibrational motion of a diatomic molecule. When the two nuclei of the molecule vibrate along the line joining them then the polarizability of the molecule will change. The change in the polarizability α, with small displacement x from equilibrium position is given by

$$\alpha = \alpha_0 + \beta \frac{x}{A}$$

where α_0 is the equilibrium polarizability β is the rate of variation of polarizability with displacement and A is the vibrational amplitude. If the molecule executes the simple harmonic motion ,then the displacement from the mean position is given by

$$x = ASin(2\pi\upsilon_v t)$$

where υ_v is the frequency of vibration of the molecule. So the polarizability of the molecule is given by

$$\alpha = \alpha_0 + \beta Sin(2\pi\upsilon_v t)$$

So the induced dipole moment is given by

$$\mu = \alpha_0 E_0 Sin(2\pi\upsilon t) + \beta E_0 Sin(2\pi\upsilon t) Sin(2\pi\upsilon_v t)$$

$$\mu = \alpha_0 E_0 Sin(2\pi\upsilon t) + \frac{1}{2}\beta E_0 [Cos 2\pi(\upsilon - \upsilon_v)t - Cos 2\pi(\upsilon + \upsilon_v)t]$$

Thus the induced dipole moment oscillates with frequencies of radiations υ, $\upsilon + \upsilon_v$ and $\upsilon - \upsilon_v$. The first frequency is same as that of incident radiation i.e. Rayleigh scattering and last two frequencies are due to Raman scattering. The vibrational shift is equal to υ_v.

Now let us consider the effect of rotation of molecule on polarizability. During the rotation of the molecule the orientation of the molecule with respect to electric field of radiation changes, therefore the molecule is not isotropic, it shows different polarizability in different directions. The polarizability of the molecule varies with time. The variation of polarizability can be expressed as

$$\alpha = \alpha_0 + \beta' Sin 2\pi(2\upsilon_r)t$$

where υ_r is the frequency of rotation. The polarizability changes at a rate twice the frequency of rotation, therefore in place of υ_r we have written $2\upsilon_r$. The induced dipole moment is given by

$$\mu = \alpha_0 E_0 Sin(2\pi\upsilon t) + \beta' E_0 Sin(2\pi\upsilon t) Sin(4\pi\upsilon_r t)$$

$$\mu = \alpha_0 E_0 Sin(2\pi\upsilon t) + \frac{1}{2}\beta' E_0 [Cos 2\pi(\upsilon - 2\upsilon_r)t - Cos 2\pi(\upsilon + 2\upsilon_r)t]$$

The Raman lines will have frequencies υ, $\upsilon + 2\upsilon_r$ and $\upsilon - 2\upsilon_r$. The Raman shift will be $2\upsilon_r$ i.e. equal to twice the frequency of rotation.

So we conclude that in the scattered radiation, there will be vibrational lines at υ_v on either sides of Rayleigh line υ and also rotational Raman lines at $2\upsilon_r$ on either sides of υ. It is not necessary to have a permanent electric dipole moment to show Raman spectra. So the homo-nuclear molecules also show Raman spectra even though they are IR inactive.

23.3.1 Quantum Theory of Raman Effect

When electromagnetic waves are incident on the molecules of a substance then due to absorption of these radiations the molecules are raised to higher state. Now if the molecules return to their original state, then the frequency of radiation emitted is same as that of incident light, but if they return to a higher or lower state.

Let us consider a molecule in its initial state having energy E'' and it is exposed to incident radiations of wavenumber $\bar{v}_i$. Due to absorption of this radiation the molecule is raised to higher energy state having energy $E'' + hc\bar{v}_i$. Now suppose that the molecule returns to a level of energy level of energy E' lying above E'', by losing energy $hc\bar{v}_s$ and wavenumber of scattered radiations is $\bar{v}_s$.

$$E'' + hc\bar{v}_i - hc\bar{v}_s = E'$$

$$E' - E'' = hc(\bar{v}_i - \bar{v}_s) = hc(\Delta\bar{v})_{rmn} = \Delta E$$

The Raman shift is equal to the difference in energy of two levels represented by E' and E''. The sign of $(\Delta\bar{v})_{rmn}$ depends upon $(E' - E'')$, if $E' > E''$ then $(\Delta\bar{v})_{rmn}$ is positive and hence Raman Stokes lines are produced. If $E' < E''$ then $(\Delta\bar{v})_{rmn}$ is negative and hence Raman anti-Stokes lines are produced. Classically the intensity of Stokes and anti-Stokes lines should be same but experimentally it is found that the intensity of Stokes lines is higher as compared to anti-Stokes lines.

23.3.2 Probability of Transition in Raman Effect

When an atom or molecule is placed in electric field of intensity E the electrons and nuclei are displaced in such a manner so as to induce electric dipole moment μ given by

$$\mu = \alpha E$$

where α is the molecular polarizability. Now if the two nuclei vibrate along the line joining them ,then the polarizability will vary. For small displacement the variation in the polarizability is expressed as

$$\alpha = \alpha_0 + \beta \frac{x}{A},$$

where α_0 the equilibrium polarizability is β is the rate of variation of polarizability with displacement and A is amplitude of vibrations. Let us consider the x components of polarizability and determine the transition probability as

$$P_{mn}(x) = \int \psi_m^* (\alpha_{xx} E_x) \psi_n d\tau \qquad \text{(A)}$$

where α_{xx} is the polarizability in the x direction when the electric field E_x is acting in the same directions. The variation of polarizability α_{xx} during the oscillation of molecule is given by

$$\alpha_{xx} = \alpha_{xx}^0 + \beta_{xx} \frac{x}{A} \qquad \text{(B)}$$

Therefore from equation (A) and (B) we have

$$P_{mn}(x) = \alpha_{xx}^0 E_x \int \psi_m^* \psi_n d\tau + \frac{E_x}{A} \beta_{xx} \int \psi_m^* \psi_n d\tau \qquad \text{(C)}$$

So we conclude from equation (C) as

1. The first term of this equation is zero except m = n. This term gives rise to a transition which does not involve the vibrational or rotational transitions. This term gives the transition probability of Rayleigh scattering.
2. For Raman scattering m $\neq$ n, the first term is zero, while for non zero of second term β_{xx} must change during the vibrations.

3. For the molecule to be Raman active it is necessary that the molecular polarizability must change in any direction during the rotations of the molecule.

23.3.3 Vibrational Raman Spectra

The vibrational Raman spectrum arises due to transition of molecule from one vibrational level to other vibrational level of same electronic state. Quantum mechanically if β_{xx} is not zero, the molecule will show Raman scattering. From the study of matrix element $P_{mn}(x)$ of the polarizability, it is found that in case of harmonic oscillator the same selection rule holds for Raman scattering as in case of infra-red spectrum i.e.

$$\Delta v = \pm 1$$

The transition takes place only adjacent vibrational levels i.e. from one level to next upper level (Stokes lines) or to the next lower level (anti-Stokes lines). Thus in the Raman spectrum there will be one Stoke and one anti-Stoke line which are shifted by an amount $|\Delta\overline{v}|_{vib}$ to both sides of the original line.

$$|\Delta\overline{v}|_{vib} = G(v+1) - G(v) = \overline{v}$$

At ordinary temperature most of the molecules are in their lowest vibrational state i.e. v = 0, so majority of transitions will be of the type v = 0 to v = 1. A small number of molecules occupy the v = 1 level which may undergo the transitions as v = 1 to v =2 (Stokes line) or from v = 1 to v = 0 level (anti-Stokes line). The intensity of these will be weak because of small number of molecules in this state. Thus the intensity of the Stokes-Raman lines corresponding to transition v = 0 to v = 1 is much greater than that of anti-Stokes Raman lines corresponding to transition v = 1 to v = 0. At high temperature the number of molecules in higher vibrational levels increases so the intensities of anti-Stokes lines increases.

The vibrational energy of a diatomic molecule is given by

$$E_v = (v+\frac{1}{2})hc\overline{v} - (v+\frac{1}{2})^2 hcx\overline{v}$$

For transition v =0 to v = 1 giving very strong vibrational Raman line

$$E' - E'' = (1-2x)hc\overline{v}$$

The Raman shift is given by

$$(\Delta\overline{v})_{vib} = (1-2x)\overline{v} = \overline{v}_0$$

where $\overline{v}_0$ is equal to the frequency of the centre of the fundamental vibrational band in the infra-red spectrum of the molecule.

23.3.4 Rotational Raman Spectra

These spectra arise due to transition of the molecule from one rotational energy state to the other rotational state of the same vibrational state. These lines appear on both sides of Rayleigh line. The selection rule for rotational Raman transition is different from that of purely rotational transitions (for infra-red). For the Raman Effect the selection rules for transition between rotational levels are as

$$\Delta J = 0, \pm 2$$

The transition corresponding to $\Delta J = 0$ represents no change in the molecular energy i.e. there is same frequency of scattered Raman radiation (Rayleigh scattering). The transition corresponding to $\Delta J = +2$ gives Stokes lines while $\Delta J = -2$ gives the anti-Stokes lines.

The rotational energy levels of a linear molecule are represented by

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

For transition $\Delta J = +2$, the value of rotational shift of Stokes lines is given by

$$(\Delta\overline{v})_{rot} = \frac{h}{8\pi^2 cI}\{(J+2)(J+3) - J(J+1)\}$$

$$(\Delta\overline{v})_{rot} = 2B(2J+3), \text{ Where } B = \frac{h}{8\pi^2 cI}$$

For transition $\Delta J = -2$, the value of rotational shift of anti-Stokes lines is given by

$$(\Delta\overline{v})_{rot} = -2B(2J+3)$$

In more general for the Raman Shift due to rotational motion of the molecule is as

$$(\Delta\overline{v})_{rot} = \pm 2B(2J+3),$$

where J = 0, 1, 2, 3, ... etc.

The wavenumbers of the corresponding spectral lines are given by

$\overline{v} = \overline{v}_{exc} - (\Delta\overline{v})_{rot}$, where $\overline{v}_{exc}$ is the wavenumber of exciting radiations.

23.3.5 Vibrational-Rotational Raman Spectra

Theoretically it is possible for vibrational and rotational transitions to take place simultaneously in a Raman transition, the selection rule is as $\Delta v = \pm 1$ and $\Delta J = 0, \pm 2$.

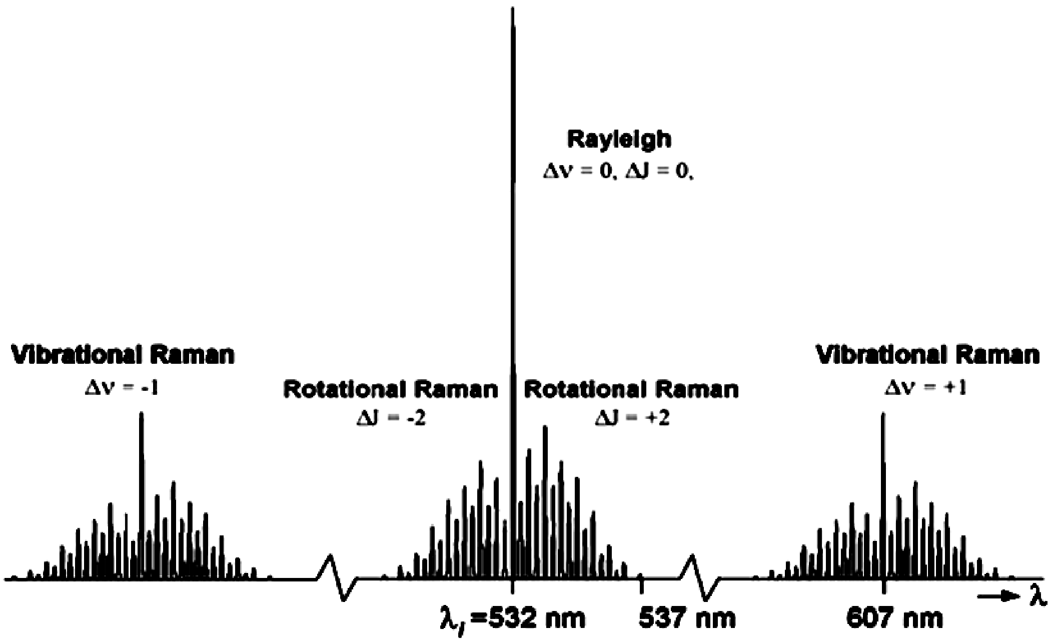
For a diatomic molecule vibrational-rotational energy levels are given by

$$E_{vr} = hc\{\bar{v}(v+\frac{1}{2}) - \bar{v}x(v+\frac{1}{2})^2\} + BhcJ(J+1)$$

where v = 0, 1, 2, 3 ...etc. and J = 0, 1, 2, 3..... , etc.

In terms of wavenumber

$$\bar{v}_{vr} = \bar{v}(v+\frac{1}{2}) - \bar{v}x(v+\frac{1}{2})^2 + BJ(J+1)$$



Applying selection rules

$\Delta J = 0$ $\quad\quad\Delta\bar{v}(Q) = \bar{v}_0$ cm^{-1}, For all J

$\Delta J = +2$ $\quad\quad\Delta\bar{v}(S) = \bar{v}_0 + B(4J+6)$ cm^{-1}, J = 0, 1, 2, 3, ...

$\Delta J = -2$ $\quad\quad\Delta\bar{v}(O) = \bar{v}_0 - B(4J+6)$ cm^{-1}, J = 2, 3,4, ...

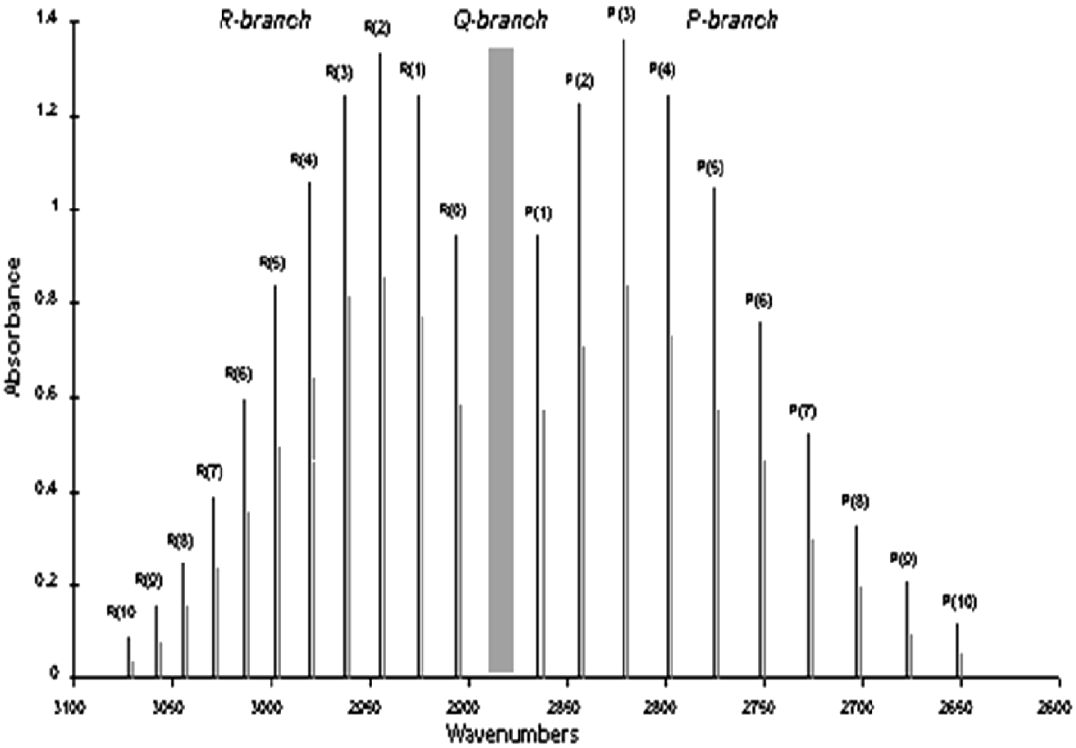
where $\bar{v}_0 = \bar{v}(1-2x)$, and O, Q, S refers to O branch, Q branch, R branch respectively.

The Stokes lines will occur at

$$\bar{v}(Q) = \bar{v}_{exc} - \Delta\bar{v}(Q) = \bar{v}_{exc} - \bar{v}_0 \text{ cm}^{-1}\text{, for all value of J}$$

$$\bar{v}(O) = \bar{v}_{exc} - \Delta\bar{v}(O) = \bar{v}_{exc} - \bar{v}_0 + B(4J + 6) \text{ cm}^{-1}\text{ , for J = 2,3,4, ..}$$

$$\bar{v}(S) = \bar{v}_{exc} - \Delta\bar{v}(S) = \bar{v}_{exc} - \bar{v}_0 - B(4J + 6) \text{ cm}^{-1}\text{, for J = 0, 1, 2, ...}$$



The anti-Stokes lines will occur at

$$\bar{v}(Q) = \bar{v}_{exc} + \Delta\bar{v}(Q) = \bar{v}_{exc} + \bar{v}_0 \text{ cm}^{-1}\text{, for all value of J}$$

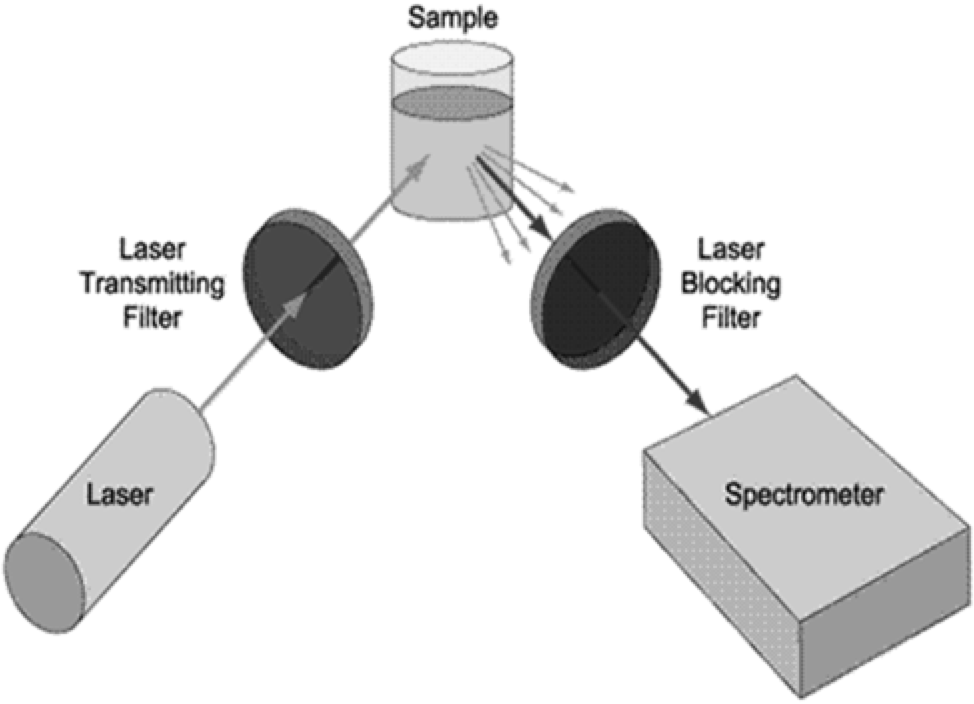
$$\bar{v}(O) = \bar{v}_{exc} + \Delta\bar{v}(O) = \bar{v}_{exc} + \bar{v}_0 - B(4J + 6) \text{ cm}^{-1}\text{ , for J = 2,3,4, ..}$$

$$\bar{v}(S) = \bar{v}_{exc} + \Delta\bar{v}(S) = \bar{v}_{exc} + \bar{v}_0 + B(4J + 6) \text{ cm}^{-1}\text{, for J = 0, 1, 2, ...}$$

23.4 Raman Spectrometer

The instrument required to record the Raman scattering is called as Raman Spectrometer. The recording of the Raman spectrum essentially requires illumination of sample with monochromatic radiations and detection of scattered radiations at right angle to incident radiations. The basic components of the Raman Spectrometer are as :

1. **Exciting source:** In the Raman spectrometer we need a monochromatic source of radiations. For this purpose one particular line of mercury arc spectrum is selected. The choice of the wavelength of this line depends upon the intensity of the line. Nowadays in Raman spectrometer a Helium-Neon laser beam is used.



2. **Sample Tube and Sample:** The material of the sample tube is either glass or quartz. The tube is shaped along with associated reflectors in a way so as to direct much of the incident light into the sample. The length of the tube is 20-30 cm and 12 cm in diameter. To avoid multiple reflections the back of the tube is horn-shaped and blackened. The other end of the tube is made optically flat so that scattered radiations do not suffer any distortion on their exit. The Raman tube is protected from heat generated by lamps by means of a glass jacket through which water circulates. The Raman spectrum can be recorded with solid, liquid and gas phase samples but the liquid sample is more preferred because it easy to handle it. The quantity of the liquid sample required is between 10-100 mL. Water is a good solvent because of its weak Raman spectrum.

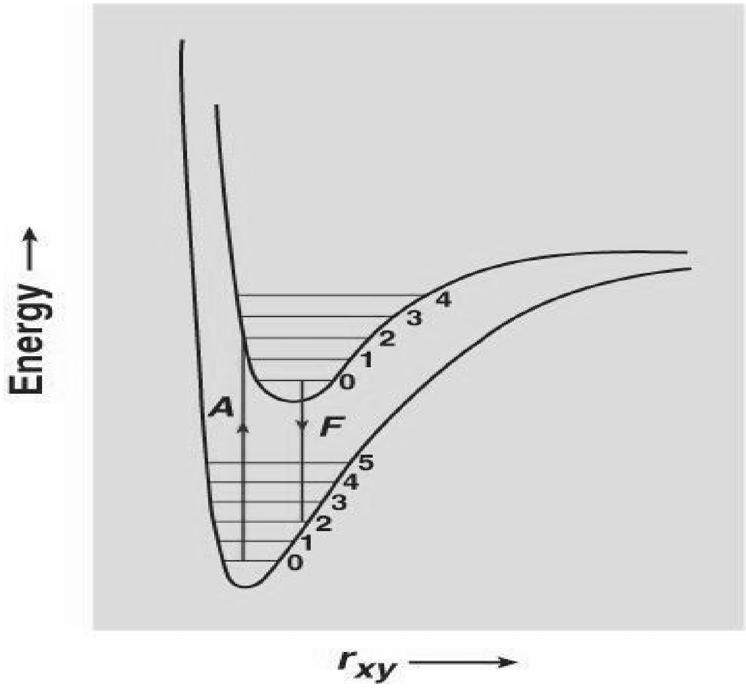
3. **Filters:** Liquid filters are placed between the source and the sample tube in order to remove high energy radiations that may cause photodecompositions, to

isolate single exciting line and to remove the continuous spectrum in the region occupied by the Raman line.

4. Optical system: The optical system is designed so that the maximum amount of scattered Raman radiation is accepted by the spectrometer. A suitable spectrograph, with prism or grating having wide aperture and medium dispersion is preferred.

23.5 Franck Condon Principle

The Franck Condon principle is related to electronic spectra of the molecules. The electronic spectra of the molecule arise when the electrons in the molecules are excited to higher energy state. The energy involved in this is large so the electronic spectra of the molecules fall in the visible and ultraviolet region of electromagnetic spectrum. The electronic spectra arise due to change in the arrangement of molecular electrons. A small change in electronic energy is accompanied by a large change in the vibrational energy of the molecule and a small change in vibrational energy is accompanied by a large change in rotational energy of the molecule. The vibrational energy changes cause the appearance of various bands and the rotational energy changes cause formation of various lines in each band.



The probability of transition between two given vibrational levels of two different electronic states is given by the Franck-Condon principle. According to this principle "The transition between two vibrational levels should start from extreme position of the levels and they are represented by vertical lines".

The rearrangement of the electrons in a molecule is 1000 times faster than the time period of vibrations of nuclei. During the electronic transition the inter-nuclear distance does not change appreciably so the transitions are represented by vertical lines. Further, the transitions are most probable when the nuclei in their mean positions. The nuclei spend maximum time in these states because of zero kinetic energy in these states. The square of the vibrational eigen function is maximum at extreme positions implying the probability of finding the nuclei is maximum there. However for lowest vibrational state v = 0, quantum mechanics predicts that the most probable position for nuclei is the equilibrium position r_e. Thus the most probable inter-nuclear distance for the vibrational levels other than v = 0, corresponds to extreme positions and mid-position for v =0. So, the transitions will start from extreme position for levels other than v = 0 and for v = 0 the transition will start from mid-point.

23.6 Illustrative Examples

Example 1 The wavelength of the exciting line in Raman scattering is 5460 A^0 and stokes line is observed at 5520 A^0. Find the wavelength of anti-Stokes line.

Sol. The Raman shift is given by

$$(\Delta\overline{v})_{rmn} = \overline{v}_i - \overline{v}_s$$

$$\overline{v}_i = \frac{1}{5460\times10^{-8}} = 18315 cm^{-1}$$

$$\overline{v}_s = \frac{1}{5520\times10^{-8}} = 18116 cm^{-1}$$

$$(\Delta\overline{v})_{rmn} = 18315 - 18116 = 199 cm^{-1}$$

The wavenumber of the anti-Stokes line is given by

$$(\overline{v}_s)_{anti-stokes} = \overline{v}_i + (\Delta\overline{v})_{rmn} = 18315 + 199 = 18514 cm^{-1}$$

The wavelength of anti-Stokes line is given by

$$\lambda = \frac{1}{18514} = 5401 A^\circ$$

Example 2 The exciting radiations has wavelength 4358 A° in Raman spectrum of a substance which show lines at $(\Delta\bar{v})_{rmn}$=608, 846, 995, 1599 and 3064 cm^{-1}. At what wavelength these lines will appear if the exciting source has wavelength 5461 cm^{-1}

Sol. The wavenumber of the exciting line

$$\bar{v}_i = \frac{1}{5461\times10^{-8}} = 18312cm^{-1}$$

Since the difference remains the same ,then the wavenumber of Raman lines are as

$$\bar{v}_s = \bar{v}_i - (\Delta\bar{v})_{rmn}$$

So the wavenumbers are as

$$\bar{v}_{s1} = 18312 - 608 = 17704cm^{-1}$$

$$\bar{v}_{s2} = 18312 - 846 = 17466cm^{-1}$$

$$\bar{v}_{s3} = 18312 - 995 = 17317cm^{-1}$$

$$\bar{v}_{s4} = 18312 - 1178 = 17134cm^{-1}$$

$$\bar{v}_{s5} = 18312 - 1599 = 16113cm^{-1}$$

$$\bar{v}_{s6} = 18312 - 3064 = 15248cm^{-1}$$

Example 3 A substance shows a Raman line at 4567 A^0 when exciting line 4358 A^0 was used. Find the positions of Stokes and anti-Stokes lines for the same substance when exciting line 4047 A^0 is used.

Sol. The Raman shift is given by

$$(\Delta\bar{v})_{rmn} = \bar{v}_i - \bar{v}_s$$

$$\bar{v}_i = \frac{1}{4358\times10^{-8}} = 22946cm^{-1}$$

$$\bar{v}_s = \frac{1}{4567\times10^{-8}} = 21896cm^{-1}$$

$$(\Delta\bar{v})_{rmn} = 22946 - 21896 = 1050cm^{-1}$$

The wavenumber of the other exciting line is

$$\bar{v}_i' = \frac{1}{4047\times10^{-8}} = 24710cm^{-1}$$

So the wavenumber of Stokes line is as

$$\bar{v}_{stoke} = 24710 - 1050 = 23660 cm^{-1}$$

and the wavenumber of anti-Stokes line is

$$\bar{v}_{anti-stoke} = 24710 + 1050 = 25760 cm^{-1}$$

The wavelengths of Stokes and anti-Stokes lines are

$$\lambda_{stoke} = \frac{1}{23660} = 4226.5 A^{\circ}$$

$$\lambda_{anti-stoke} = \frac{1}{25760} = 3882 A^{\circ}$$

Example 4 In the rotational Raman spectrum of a molecule the displacement from exciting line is represented by $(\Delta\bar{v})_{rot.} = \pm(62.4 + 41.6J)$ cm^{-1} . Calculate the moment of inertia of the molecule.

Sol. The rotational Raman shift is given by

$$(\Delta\bar{v})_{rot.} = 2B(2J+3)$$

$$(62.4 + 41.6J) = 2B(2J+3)$$

$$41.6(J + \frac{3}{2}) = 4B(J + \frac{3}{2})$$

$$B = \frac{41.6}{4} = 10.4 cm^{-1}$$

The rotational constant B is related to moment of inertia I as

$$B = \frac{h}{8\pi^2 Ic} \quad \text{so} \quad I = \frac{h}{8\pi^2 Bc}$$

$$I = \frac{6.62 \times 10^{-27}}{8 \times (3.14)^2 \times 10.4 \times 3 \times 10^{10}}$$

$$= 2.7 \times 10^{-40} gm.cm^2$$

23.7 Self Learning Exercise

Q.1 What is Raman Effect ?

Q.2 Explain the origin of Stokes and anti-Stokes lines.

Q.3 Discuss the quantum theory of Raman Effect.

Q.4 Write the selection rules for Raman vibrational-rotational transitions.

23.8 Summary

The aim of this unit is to study the spectroscopy technique known as Raman Effect. This technique can be used in place of IR spectroscopy technique but this technique is more versatile as compared to IR technique. The IR technique fails to provide information when the molecules are homo-nuclear in the materials. Since the principle of Raman Effect involves the polarization of molecules by the radiations ,so the information can also be obtained from this technique. Here first the definition of Raman Effect has been discussed and then its classical and quantum theories have been developed. The quantum theory is useful to provide the information about the intensity of Stokes and anti-Stokes lines. The selection rules for transitions among the various vibrational levels as well between rotational levels have been discussed. The basic components of Raman spectrometer have been discussed. Finally there is the discussion on the Franck-Condon principle which predicts the transition probability between two electronic states.

23.9 Glossary

Homo-nuclear : Same type of nucleus

Hetero-nuclear: Different type of nucleus

Polar : Having positive and negative charge

Oscillating : Periodically varying

Polarizability : measurement of tendency to be polarized

Band : Group of energy levels or spectral lines

Shift : Kind of displacement

Accompanying : Simultaneously

Photodecomposition : Dissociation by radiations

Scattering : Absorption and re-emission of radiations

Inter-nuclear : Between two nucleus.

23.10 Exercise

Q.1 What is Rayleigh line ?

Q.2 Explain Stokes and anti-Stokes lines ?

Q.3 Explain the variation of polarizability of molecule with the electric field of electromagnetic radiations.

Q.4 Explain why the intensity of Stokes and anti-stokes lines is not same?

Q.5 Write the basic components of Raman spectrometer.

Q.6 Explain the Franck-Condon principle.

Q.7 Discuss the classical theory of Raman Effect.

Q.8 Explain the fine structure of Raman spectral lines.

References and Suggested Readings

1. Colin N. Banwell and Elaine M. McCash*: Molecular Spectroscopy*, Tata McGraw-Hill Education Private Limited, New Delhi, 1994.
2. J. M. Holias*: Modern Spectroscopy* , John Wiley & Sons, England, 1987.
3. S.L. Gupta, V. Kumar and R.C. Sharma: *Elements of Spectroscopy,* Pragati Prakashan, Meerut, 1990.
4. Raj Kumar, *Atomic & Molecular Spectra: LASER*, Kedar Nath Ram Nath, Meerut, 2007.
5. G.M. Barrow, Introduction to Molecular Spectroscopy, McGraw Hill, London, 1961.