NMR Spectroscopy

Nuclear magnetic Resonance is a branch of spectroscopy in which radio frequency waves induce transition between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in a magnetic field.

Without the magnetic field the spin states of nuclei are degenerate i.e possess the same energy, and energy level transition is not possible. When a magnetic field is applied, the separate levels and radio frequency radiation can cause transitions between these energy levels.

(NMR spectroscopy is most often concerned with nuclei with $I = 1/2$) Examples of such nuclei are ^{1}H, ~~^{31}P~~ ^{31}P and ^{19}F. Spectra cannot be obtained from nuclei with $I = 0$. In special cases, spectra can be obtained from nuclei when $I \geq 1$

(Nuclear magnetic Resonance is a powerful tool for investigating nuclear structure.)

In nuclear magnetic resonance spectroscopy radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule

The magnetic energy levels are created by keeping the nuclei in a magnetic field.

Spin and an applied field

We have seen that all electrons have a spin of $\frac{1}{2}$ they have an angular momentum

of $\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\ \frac{h}{2\pi} = \frac{\sqrt{3}}{2}$

Many nuclei also posses spin
Let us consider the simplest nucleus
hydrogen atom which consist of only one proton
The proton has a spin of $\frac{1}{2}$

Thus if a particular nucleus is composed of 'P' protons and n neutrons its total mass is $P+n$
its total charge is P and the total spin will be a vector combination of $P+n$ spins each of magnitude $\frac{1}{2}$

Then the spin of hydrogen nucleus is (^{1}H) is $1/2$ since it contains one proton only, deuterium an isotope of hydrogen containing one proton and one neutrons (^{2}H) might have a spin of 1 or 0 depending on whether the proton and neutron spins are parallel or opposed.

1. Nuclei with both p and n even have zero spin (^{4}He, ^{12}C, ^{16}O etc)
2. Nuclei with both p and n odd (p+n = even) have integral spin (^{2}H, ^{14}N, ^{10}B)
3. Nuclei with odd mass have half-integral spin (^{1}H, ^{15}N)

The spin of a nucleus is usually given by the symbol I, called the spin no angular momentum of the nucleus

$$I = \sqrt{I(I+1)}\ h/2\pi = \sqrt{I(I+1)} \text{ units.}$$

The angular momentum vector cannot point in any arbitrary direction, but can point only along a particular reference direction so that the its components have half integral or integral value along that direction

$$I_z = I, I-1, \ldots 0, -1, -(I-1) - I \quad \left[\begin{array}{l}\text{for}\\ I \text{ integral}\end{array}\right]$$

or

$$I_z = I, I-1, \ldots \tfrac{1}{2}, -\tfrac{1}{2} \ldots, -I)$$

for (I half integral

Quantum Mechanical description of NMR

If a nucleus has spin, it behaves as a spinning finite spatial distribution of charge

One of the most important properties of a nucleus is its spin I or intrinsic spin angular momentum $I\hbar$. This gives rise to a magnetic moment μ to the nucleus.

The magnetic moment μ associated with the spin angular momentum is given by

$$\mu = \gamma I \hbar \quad \text{———} \quad 1$$

Here γ is a scalar called the gyromagnetic ratio and it may take +ve or −ve value.

An alternate expression for the magnetic moment is

$$\mu = g_N \cdot \mu_N I \quad \text{———} \quad (2)$$

where g_N - nuclear g factor. It is a dimensionless quantity

μ_N is the nuclear magneton

$$\mu_N = \frac{e\hbar}{2m_p} \quad \text{———} \quad (3)$$

Resonance condition:

When a nucleus of magnetic moment μ is placed in a magnetic field B_0, The interaction energy

$$E = -\mu \cdot B_0$$

$$= -\mu B_0 \cos\theta$$

Eqn $$E = \frac{-\mu B_0 m_I}{I} \quad \text{—— 4}$$

~~m_I – Projection of spin vector on magnetic field direction~~

~~m_I can have~~

m_I – Projection of spin vector I in any direction

m_I can have $(2I+1)$ values, so there are $2I+1$ equally spaced energy levels.

The energy separation between any two adjacent level is given by

$$|\Delta E| = \mu B_0 \frac{\Delta m_I}{I} = \frac{\mu B_0}{I}$$

$$= g_N \mu_N B_0$$

The basis of NMR experiment is to introduce a transition from a lower level to the next higher level. If ν is the frequency of the electromagnetic radiation that induces transitions between adjacent levels, Bohr's condition is then $h\nu = \frac{\mu B_0}{I} = g_N \mu_N B_0$

$$\nu = \frac{g_N \mu_N B_0}{h} \quad \text{—— (5)}$$

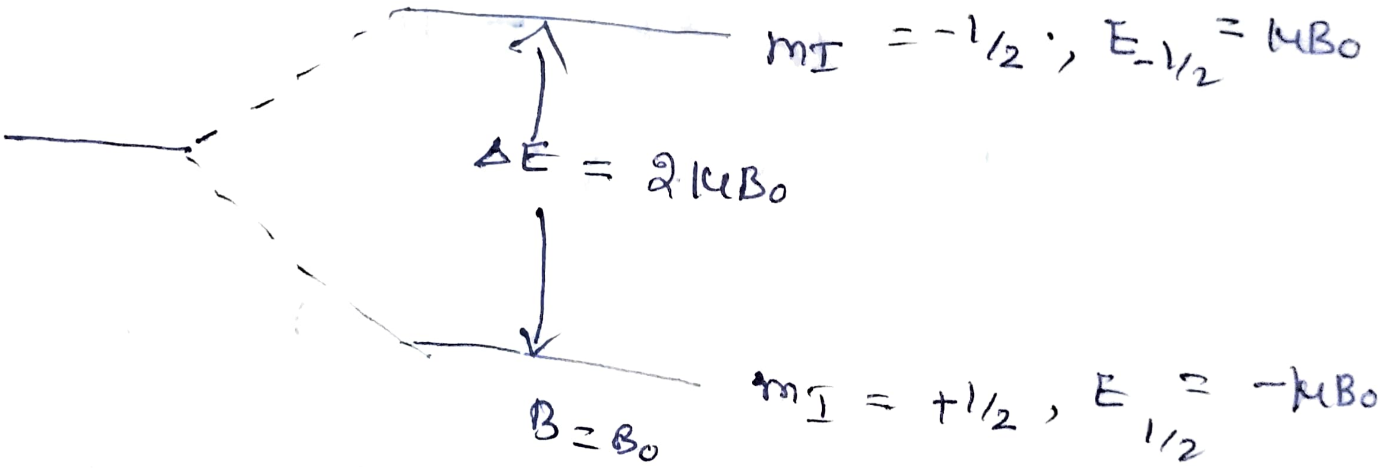
Eqn (5) is the resonance condition.

For a spin 1/2 system we will have 2 states, one corresponding to $m_I = 1/2$ and the other for $m_I = -1/2$

These energies are
$$\left.\begin{aligned} E_{1/2} &= -\mu B_0 \text{ and} \\ E_{-1/2} &= +\mu B_0 \end{aligned}\right\} \quad \text{— (6)}$$

The resonance condition reduces to

$$h\nu = 2\mu B_0$$



Coupling constants

The distance between the peaks in a given multiplet is a measure of the magnitude of splitting effect. It is refered to as coupling constant and is denoted by the symbol J. The numerical value of J is expressed in Hz or cps.

Unlike the chemical shifts, the values of J are independent of the applied field strength and depend only on the molecular structure.