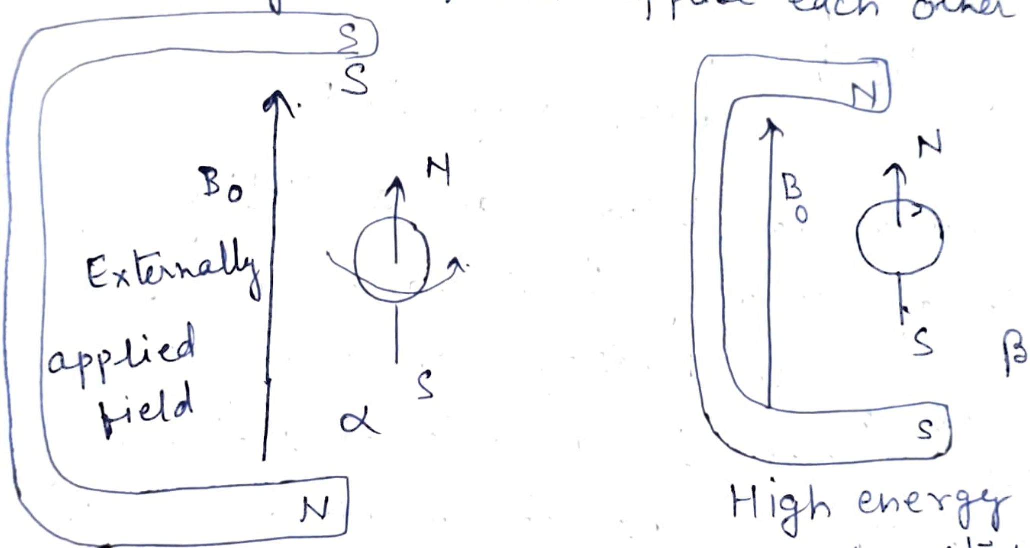
Nuclear Magnetic Resonance Spectroscopy

Introduction: The nucleus of a Hydrogen atom behaves as a spinning bar magnet as it Possesses both electric and magnetic ~~field~~ spin. Like any other spinning charged body, the nucleus of Hydrogen atom also generates a magnetic field.

• Nuclear magnetic Resonance involves the interaction between an oscillating magnetic field of electromagnetic radiation and the magnetic energy of the Hydrogen or some other nuclei when these are placed in an external static magnetic field. The sample absorbs electromagnetic radiations in radiowave region at different frequencies since the absorption depends upon the type of protons or certain nuclei contained in the sample.

Any nucleus consisting of either an odd number of Protons or an odd number of neutrons or both has the property of nuclear spin. Ex ^{1}H ^{13}C ^{19}F nuclei possess spin but ^{12}C, ^{16}O do not.

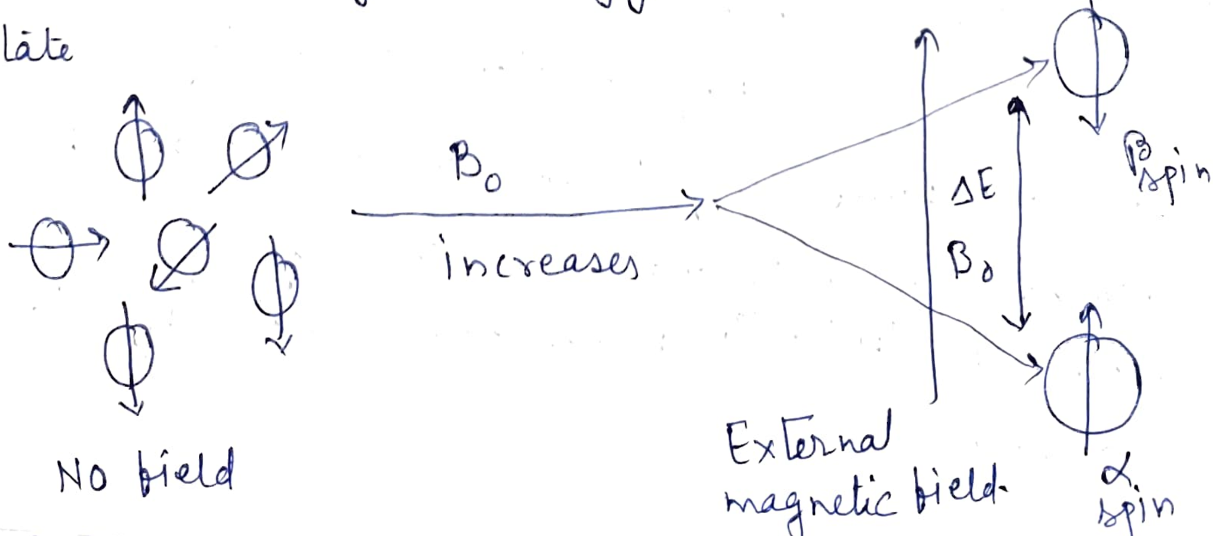
Now when a spinning proton (small bar magnet) is placed in an external magnetic field, it can align itself in one of the two possible orientations with respect to the applied field (i) low energy alignment of the nucleus in which the magnetic field of the nucleus is in the same direction as the applied magnetic field and (ii) High energy orientation in which the two magnetic fields oppose each other



Low energy
more stable

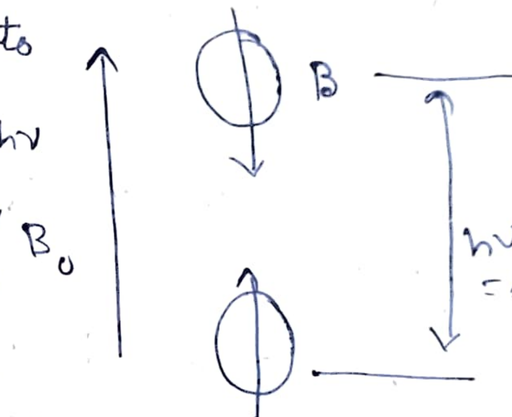
High energy
less stable

The lower energy state is called α spin state and higher energy state is called β spin state



A transition from the low energy state of a nucleus to the high energy state (blip) can be obtained by providing an energy equal to the difference in energy between the two states ΔE. This energy can be supplied by electromagnetic radiation.

The energy required to bring about the transition $\Delta E = h\nu$ or to flip the proton depends upon the strength of External magnetic field. Stronger the field, greater will be the tendency of the nuclear magnet to remain lined up with it and higher will be the frequency of the radiation needed to flip the proton to higher energy state.



$$\Delta E = h\nu = \frac{\gamma \cdot h \cdot B_0}{2\pi}$$

γ is gyrometric ratio & its value for each nucleus is $26753\ s^{-1}\ gauss^{-1}$. In a 14092 gauss field, a 60 MHz frequency photon is required to flip a Proton. which is much lower and absorption is from Radio wave region.

The precessing proton will absorb energy from the radio frequency source only if the precessing frequency is the same as the frequency of the radio frequency beam. when this occurs, the nucleus and radio frequency beam are said to be in resonance. Hence the term Nuclear magnetic resonance.

[Precessing frequency may be defined as the no. of revolutions per second made by the magnetic moment vector of the nucleus around the external field]

<u>NMR</u> <u>spectrum</u>: The technique consists of exposing the protons in an organic molecule to a powerful magnetic field. The Protons will precess at diffrent frequencies. Now we irradiate these precessing Protons with steadily changing frequencies and observe the frequency at which absorptions occur.

It is generally more convenient to keep the radio frequency constant and the strength of the magnetic field is constantly varied. At some Value of the field strength, the energy required to flip the proton matches the energy of the radiation. Absorption occurs and a signal is observed. Such a spectrum is called NMR spectrum.

Position of signals

→ The number of signals in an nmr spectrum tells the no. of the sets of equivalent protons in a molecule

→ The position of the signals in the spectrum help us to know the nature of Protons ex: Aromatic, aliphatic acetylenic, vinylic, ~~etc~~. adjacent to some electron attracting or releasing groups. Each of these type of Protons will have a different electronic environment and thus they absorb at different applied field strength

When a molecule is placed in a magnetic field, its ~~so electro~~ spinning electrons produce induced magnetic field. This induced magnetic field can either oppose or reinforce the applied field at the proton. If the Induced field opposes the applied field, then the proton is said to be shielded. But if the induced field reinforces the applied field, the proton feels a higher field strength and thus such a proton is said to be deshielded.

Shielding shifts the absorption upfield and deshielding shifts the absorption downfield to get an effective field strength necessary for absorption.

<u>Chemical Shift (δ)</u>:- Such shifts (compared with a standard reference) in the positions of nmr absorption which arise due to the shielding or deshielding of protons by the elections are called chemical shifts(δ).

Tetramethyl silane is taken as reference for measuring chemical shift of various protons in a molecule. In tetramethyl silane the shielding of equivalent protons is greater than most of the organic compounds due to low EN of silicon. The nmr signal for a particular proton in a molecule will appear at different field strength compared to the signal for TMS.

<u>The difference in the absorption position of the proton with respect to TMS signal is called chemical shift.</u>

TMS is most convenient reference because of following characteristics:

(a) It is miscible with all organic solvents

(b) It is highly volatile and can be easily removed from system.

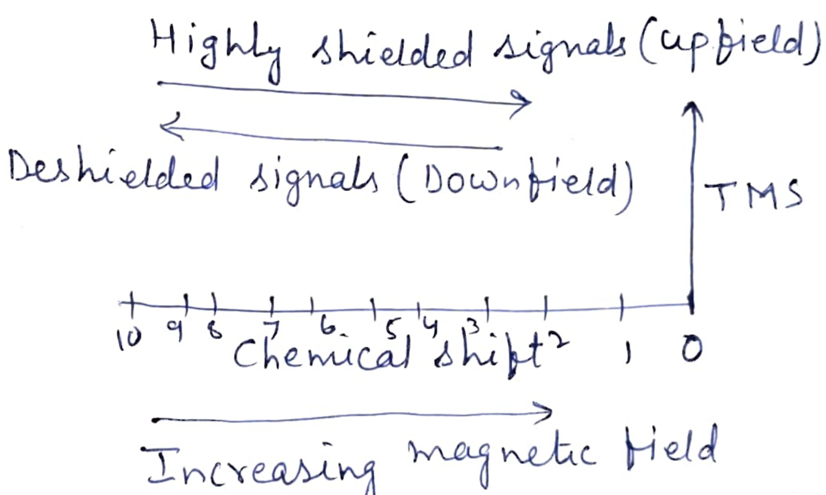
(c) It does not take part in intermolecular association with the sample.

$$\text{Chemical shift } \delta = \frac{\nu_{sample} - \nu_{ref}}{\text{operating frequency in megacycles/sec}}$$

$$\delta = \frac{\Delta \nu}{\text{operating frequency in megacycles (per sec)}}$$

$\Delta\nu$ is frequency shift. The value of δ is expressed in Parts per million. Most chemical shifts have values between 0 to 10. In the τ scale, signal for the standard reference, TMS is taken as 10 ppm. The two scales are related by the expression

$$\tau = 10 - \delta$$



NMR signal is plotted with magnetic field strength increasing to the Right. Thus, the signal for TMS (highly shielded) appears at the extreme right of spectrum with $\delta = 0$ ppm. Greater the deshielding of Protons, larger will be the value of δ. For most of the organic compounds, signals appear downfield to the left of TMS signal.

→ A compound shows a proton – NMR peak at 240 Hz down field from the TMS peak in a spectrometer operating at 60 MHz. What are the values of chemical shift δ.

$$\delta = \frac{\nu_{sample} - \nu_{ref}}{\nu_0}$$

$$\delta = \frac{240\ s^{-1}}{60 \times 10^6} \times 10^6\ ppm$$

$$\delta = 6\ ppm$$

$$\tau = 10 - 6\ ppm.$$