

# NMR Spectroscopy

Lecturer: Komalharini Tiwari  
(M.Sc. Bioinformatics, PG Dipl. Data Science)

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# Outline:

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1. Introduction of NMR
2. Mechanism of Resonance
3. Shielding and De-shielding
4. Principles of NMR Spectroscopy
5. Spin Quantum Number
6. Instrumentation and Working
7. Solvents used in NMR Spectroscopy
8. Chemical Shift (Theory, Factors affecting and Numerical Problems)
9. Number of Signals in NMR & Types of Couplings
10.  $^{13}\text{C}$ -NMR Spectroscopy
11. Fourier Transform NMR
12. Numericals

# Introduction:

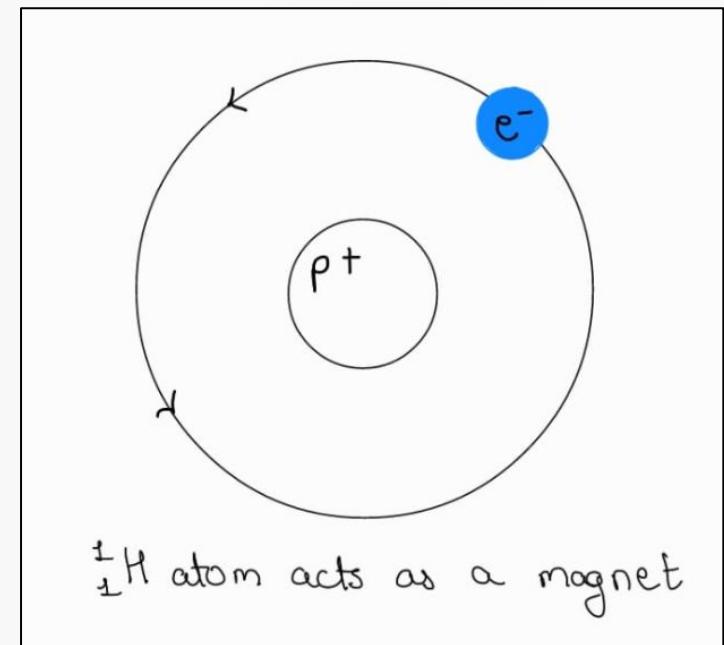
- NMR is the most powerful tool available for organic structure determination. EMR used: Radio waves
- Proton is present in the nuclei, which shows the spin moment. Due to this spin, the proton acts as a small magnet. Due to EMR, the resonance will take place in this small magnet.
- Criteria:
  - Spin quantum number  $> 0$ ; then NMR active
  - Spin quantum number  $= 0$ ; then NMR inactive (when the atomic number and atomic mass number are 0)

NMR Inactive atoms

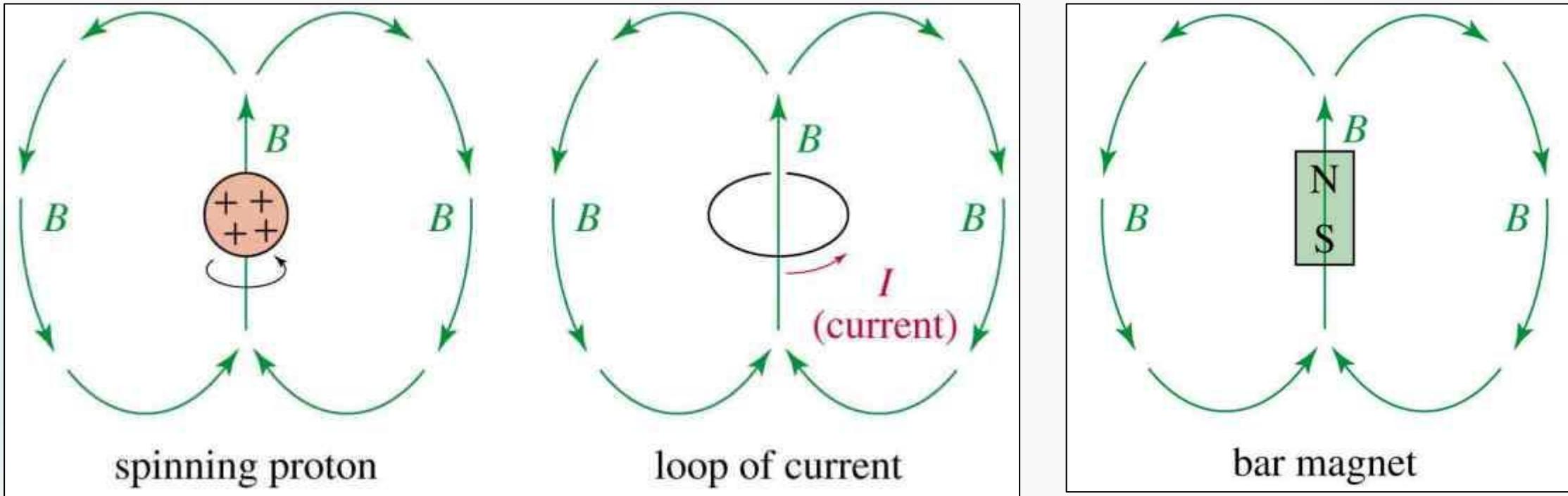
$^{12}_{6}\text{C}$ ,  $^{16}_{8}\text{O}$

NMR Active atoms

$^{1}H$ ,  $^{13}_{6}\text{C}$ ,  $^{14}_{7}\text{N}$ ,  
 $^{17}_{8}\text{O}$ ,  $^{19}_{9}\text{F}$ ,  $^{31}_{15}\text{P}$ ,  
 $^{35}_{17}\text{Cl}$



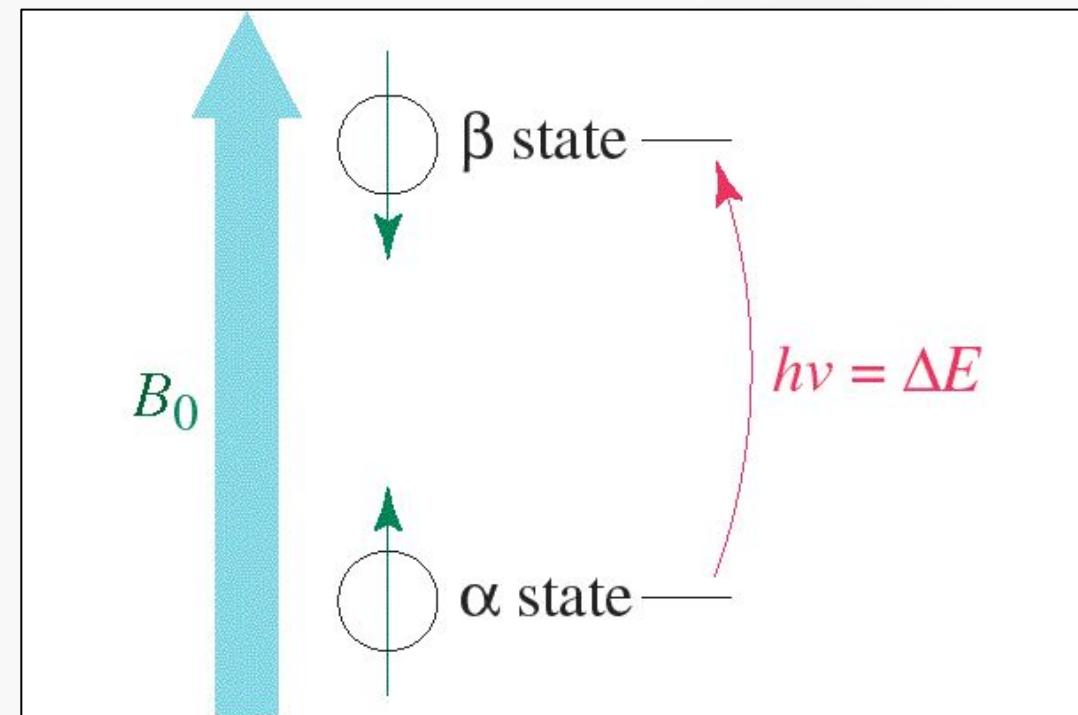
# Nuclear Spin



- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.
- When placed in an external field, spinning protons act like bar magnets.

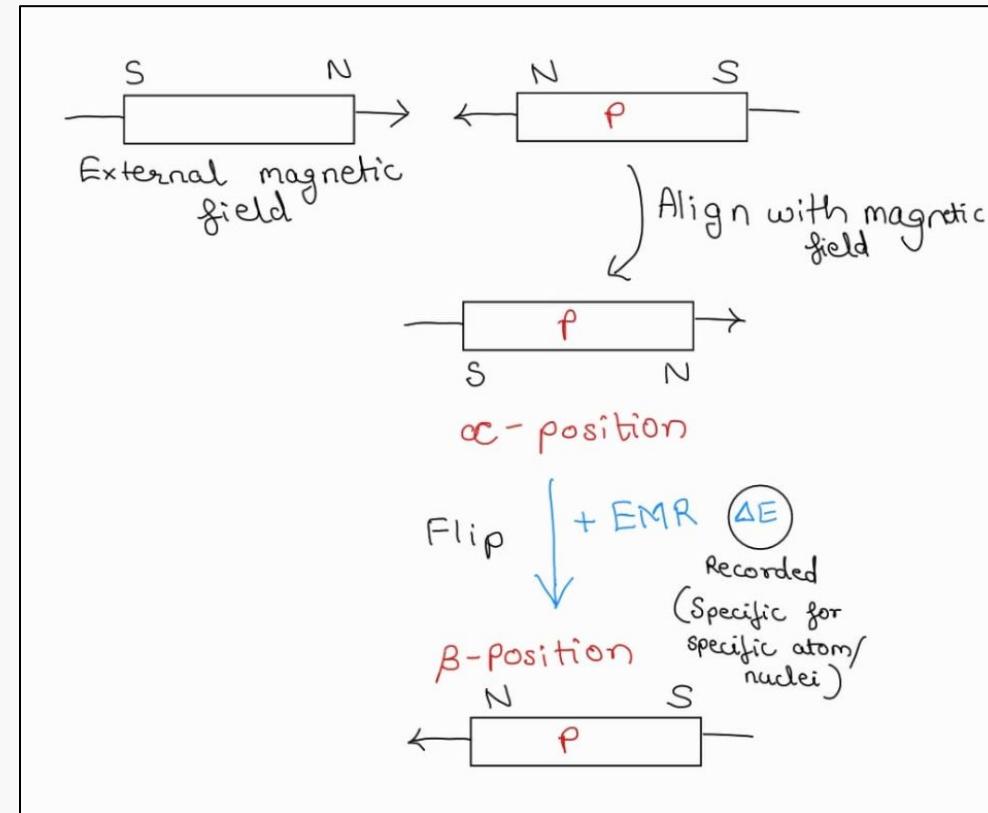
# Two Energy States:

- The magnetic fields of the spinning nuclei will align either with the external field or against the field.
- A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.

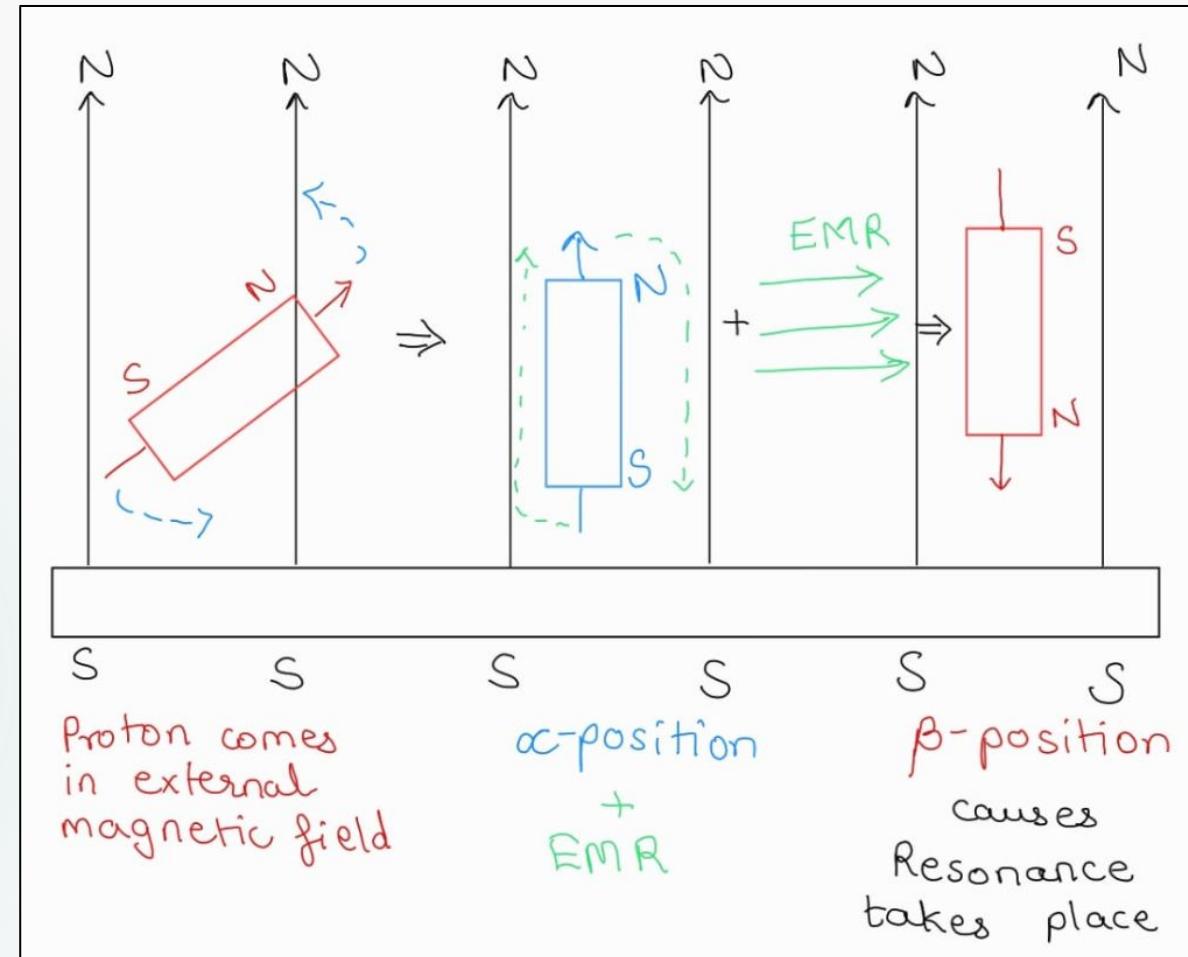


# Mechanism of NMR Spectroscopy:

- Resonance takes place when two magnets come in contact and repulsion causes the proton magnet to flip.
- After absorption of Energy from EMR, the magnet flips back to the beta position.
- The energy ( $\Delta E$ ) is recorded and is used to characterize the atom/nuclei in NMR.
- Energy difference is proportional to the magnetic field strength.

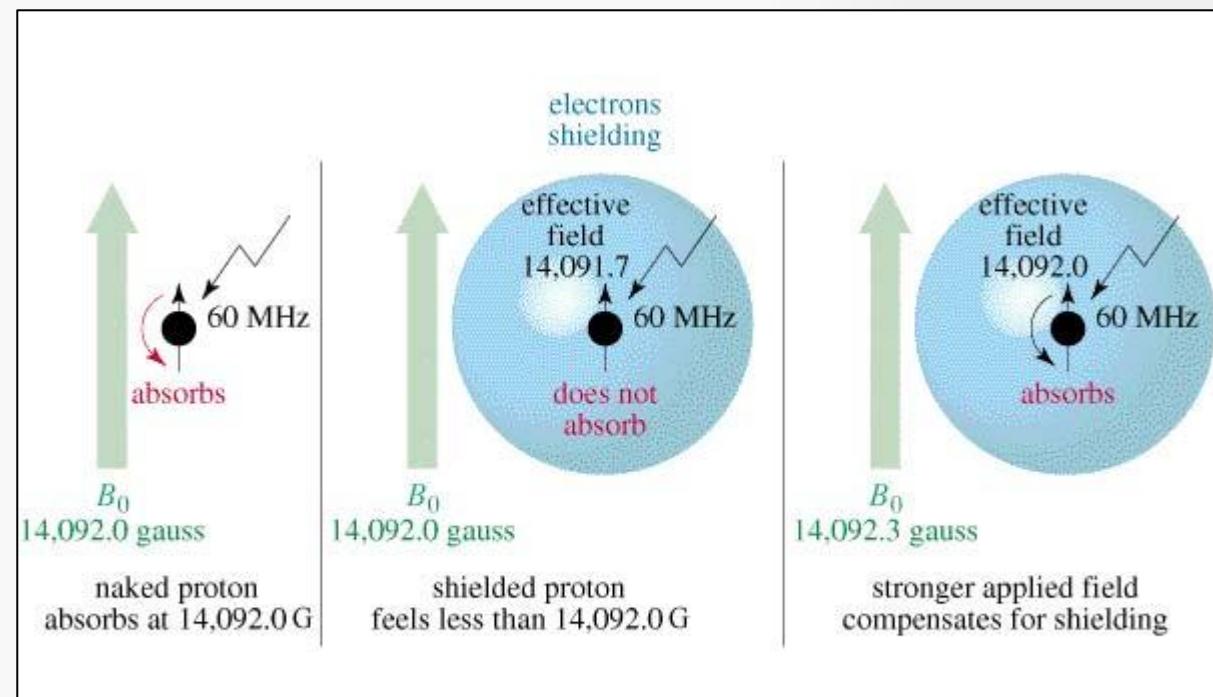
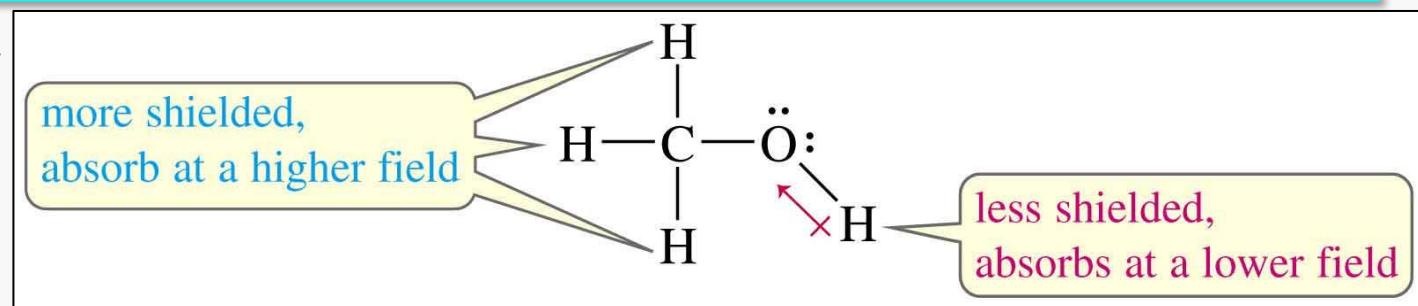


# Mechanism of NMR Spectroscopy

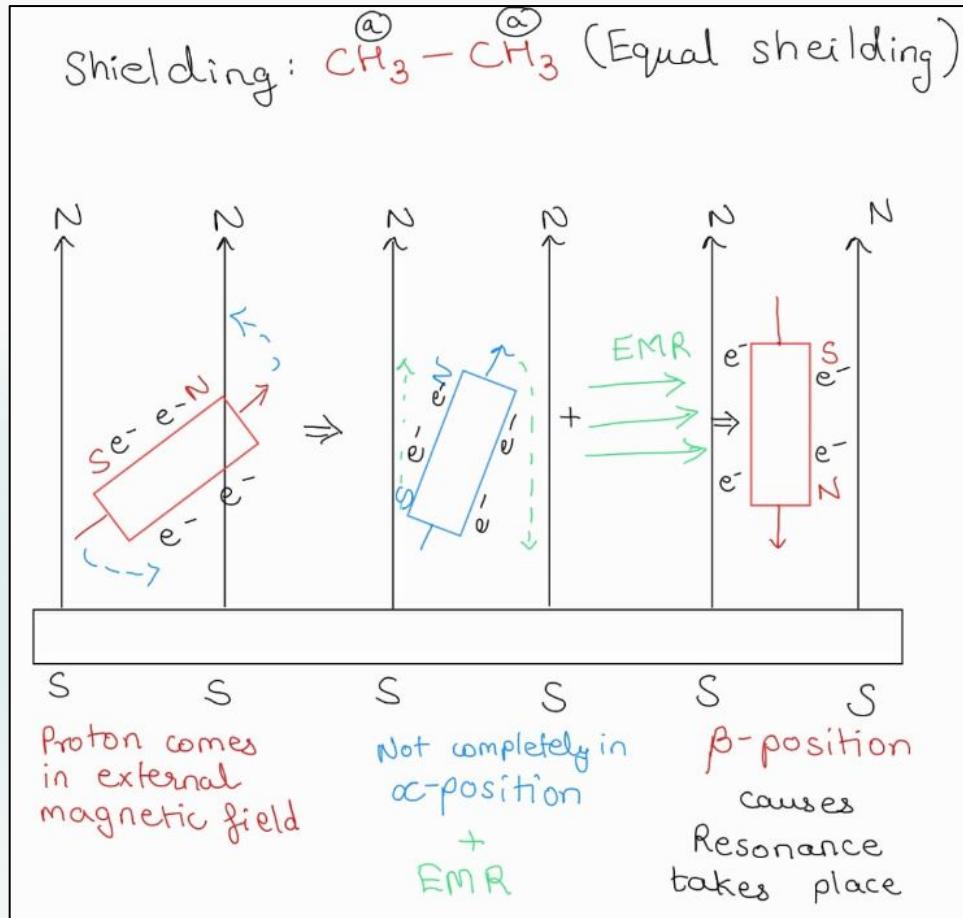


# Shielding & De-shielding:

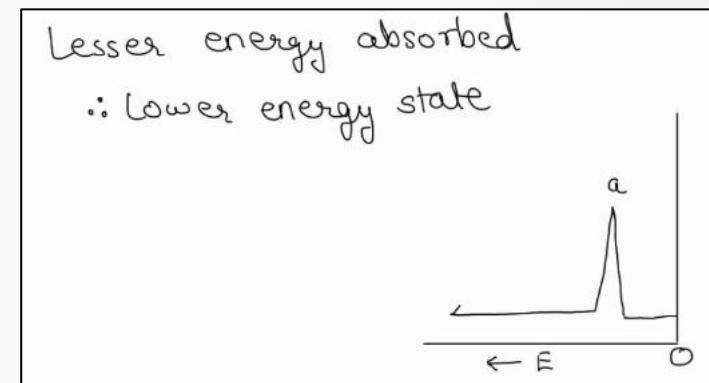
- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.
- Shielded protons: Magnetic field strength must be increased for a shielded proton to flip at the same frequency.
- Depending on their chemical environment, protons in a molecule are shielded by different amounts.



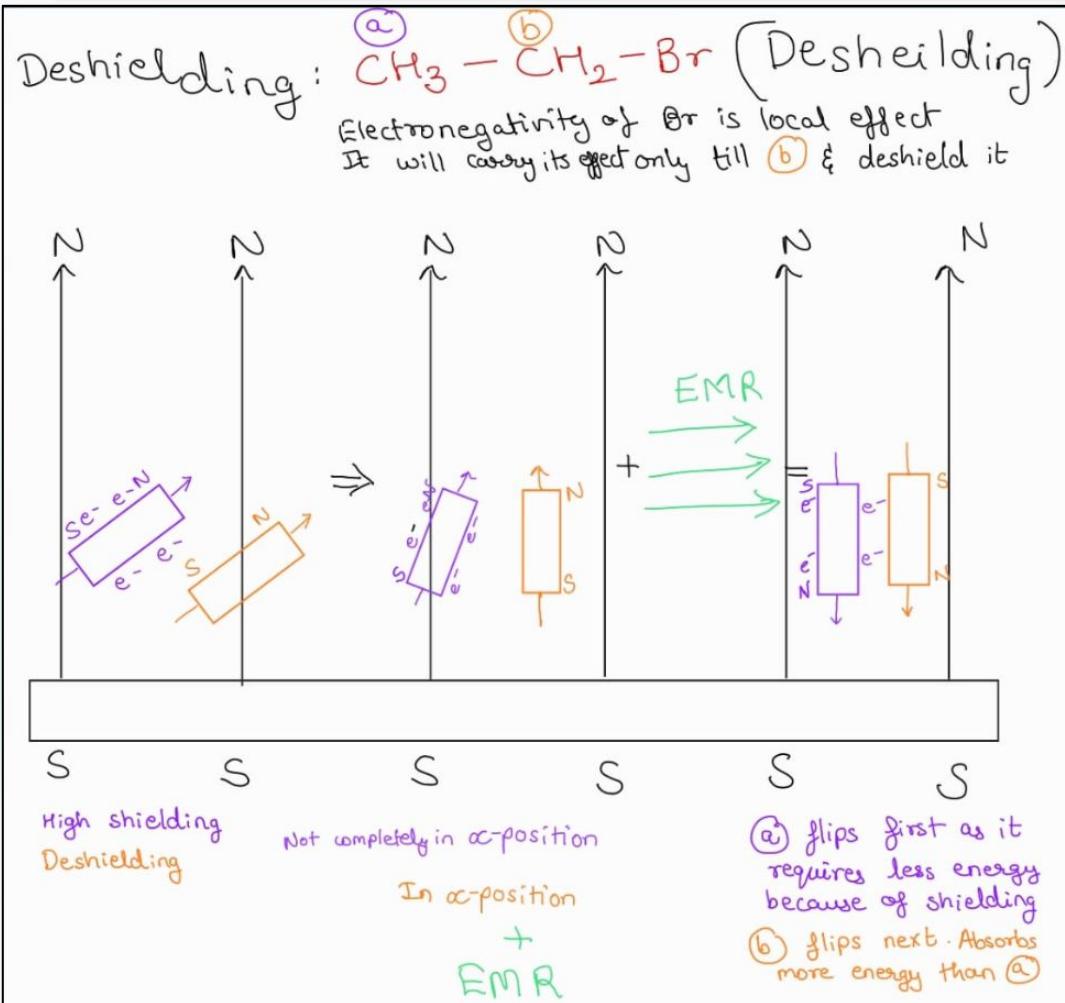
# Shielding Effect



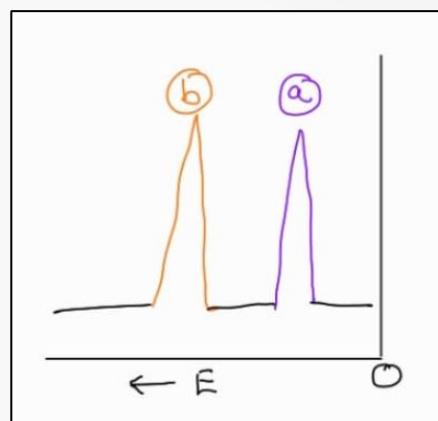
- Equal shielding around all protons.
- Because of shielding, the proton magnet does not align completely with the external magnetic field.
- Hence, less energy is required for it to convert into beta position.



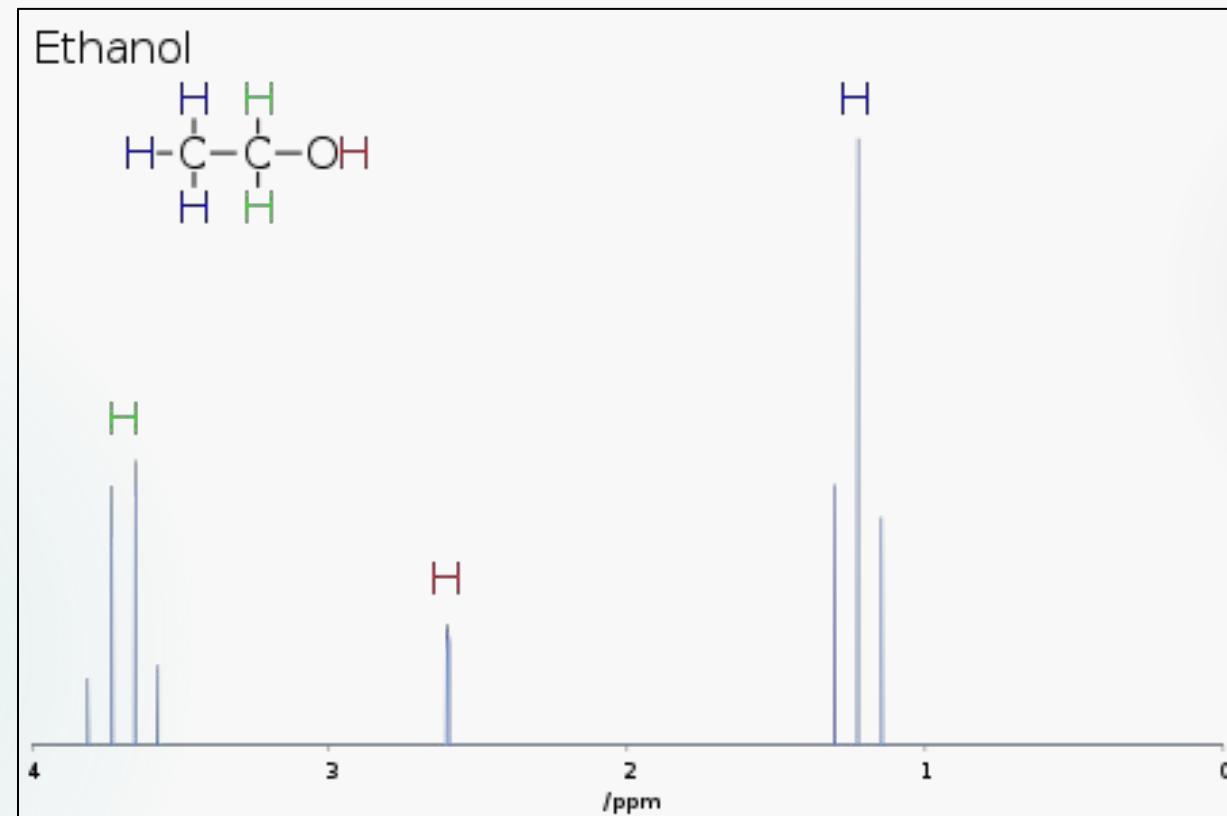
# De-shielding Effect



- For the protons in  $-\text{CH}_3$  atom, shielding is seen.
- Because of the electronegative  $-\text{Br}$  atom, there is de-shielding from the  $-\text{CH}_2$  atom.
- For  $-\text{CH}_3$  protons, lower energy is required to convert into beta-position. However, higher energy is required for the nuclei in alpha-position to convert to beta-position.
- Using the extra energy remaining after the conversion of the shielded proton, the de-shielded proton will also flip to beta-position.



# Example:



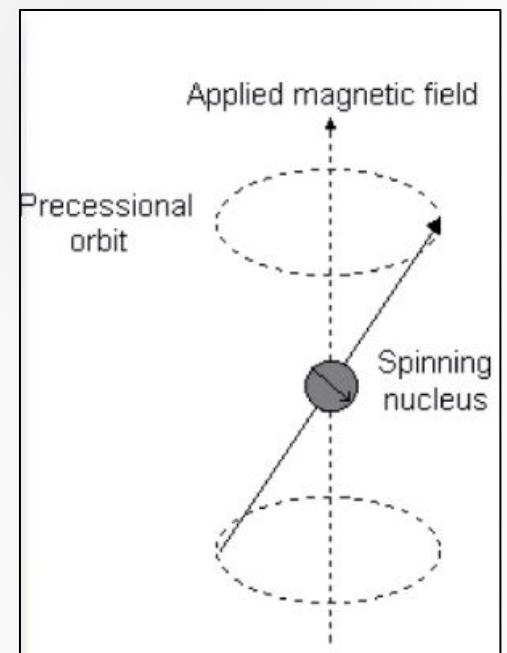
# Resonant Frequency:

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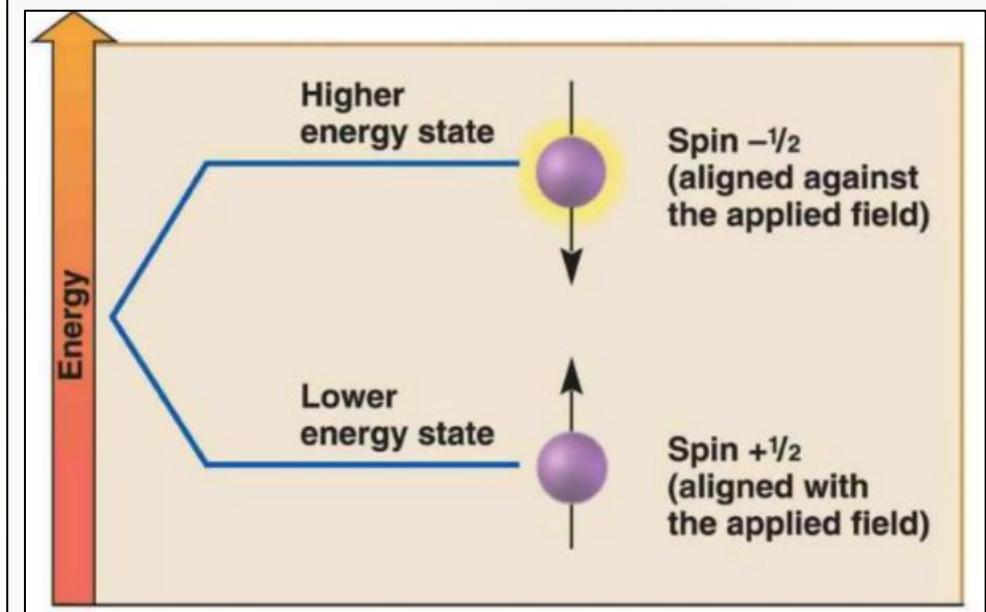
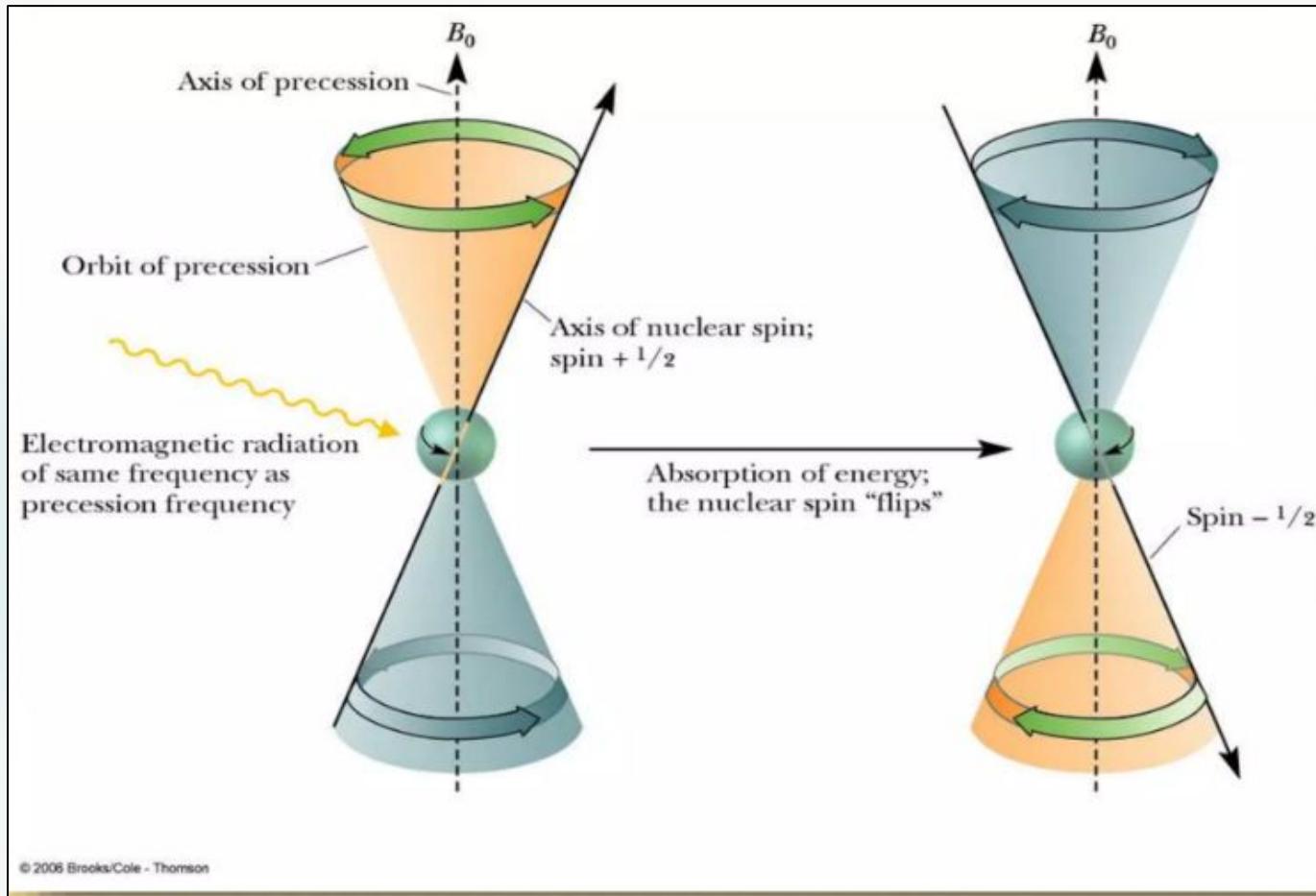
- Resonant frequency: Frequency required to convert in beta-position.
- In other words, when placed in a magnetic field, NMR active nuclei (such as  $^1\text{H}$  or  $^{13}\text{C}$ ) absorb electromagnetic radiation at a frequency characteristic of the isotope.
- The resonant frequency, the energy of the radiation absorbed, and the intensity of the signal are proportional to the strength of the magnetic field.
- 2 types of Operations of NMR:
  - Magnetic field will be constant and EMR will be changing.
  - Electromagnetic Radiation frequency will be constant and magnetic field will be changing (More commonly used).

# Principle of NMR:

- Proton spins around its own axis and generates a magnetic field. It then aligns with the external magnetic field. EMR is absorbed and it goes to a higher energy level and opposes the external magnetic field.
  - When the proton goes from a low energy level to a higher energy level because of absorption of EMR, resonance takes place.
1. Spinning nucleus
  2. Effect of external magnetic field
    - ▶ Proton is aligned (low energy and parallel)
    - ▶ Proton opposes (high energy and antiparallel)
  3. Precessional motion:
    - ▶ When exposed to an external magnetic field, protons precess.
    - ▶ The movement of precession can be likened to the wobbling motion seen when a spinning top is spun.
    - ▶ The handle of the spinning top follows a circular path.
  4. Precessional frequency
  5. Energy Transition



# NMR Flipping Phenomenon:



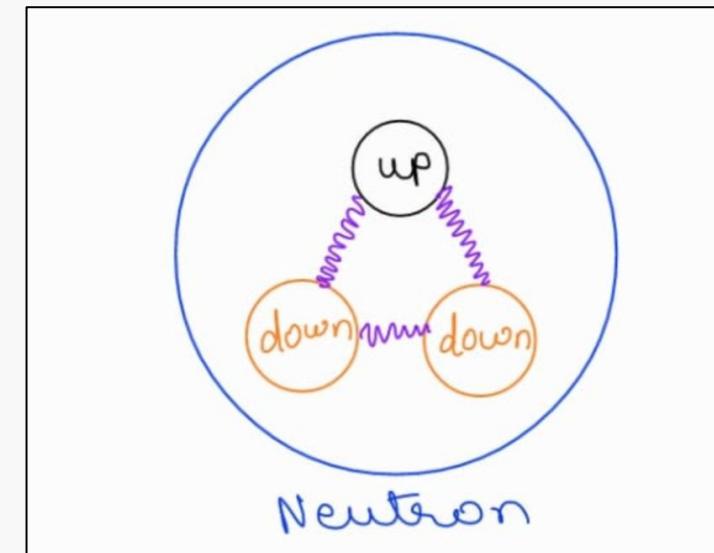
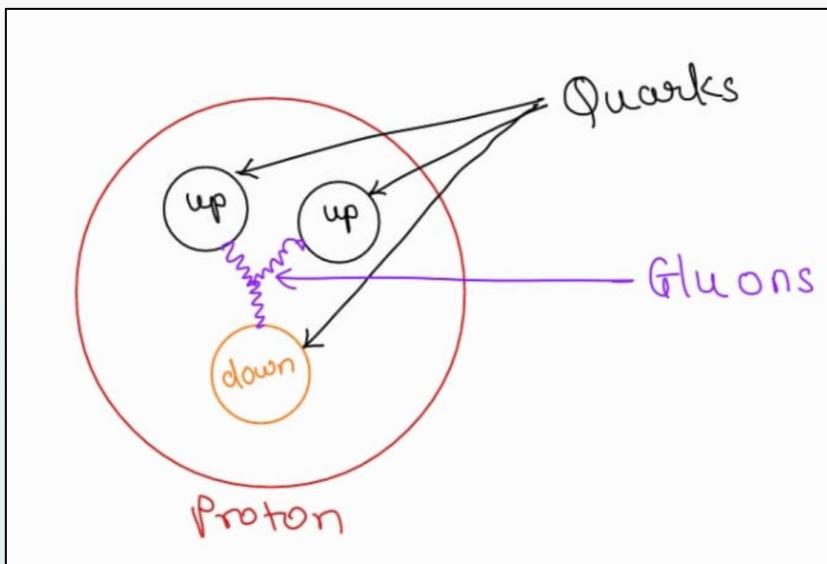
# Spin Quantum number:

- $I = 0$ ; NMR inactive
- $I > 0$ ; NMR active
- Atomic no. = # of Protons present in nuclei of atom
- Atomic mass no. = # of protons + # of neutrons present in nuclei of atom
- Composition of nuclear matter:
  - Quarks: Elementary particle  
Fundamental constituent of matter
  - Gluons are essential for attaching the quarks.
- Refer notes

Atomic mass	Proton	Neutron	Spin Quantum number	Examples
Even	Even	Even	0	$^{12}\text{C}_6$ $^{16}\text{O}_8$ $^{32}\text{S}_{16}$
Odd	Odd	Even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$	$^{11}\text{B}_5$ $^{19}\text{F}_9$
Odd	Even	Odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$	$^{13}\text{C}_6$
Even	Odd	Odd	1	$^2\text{H}_2$ $^{14}\text{N}_7$

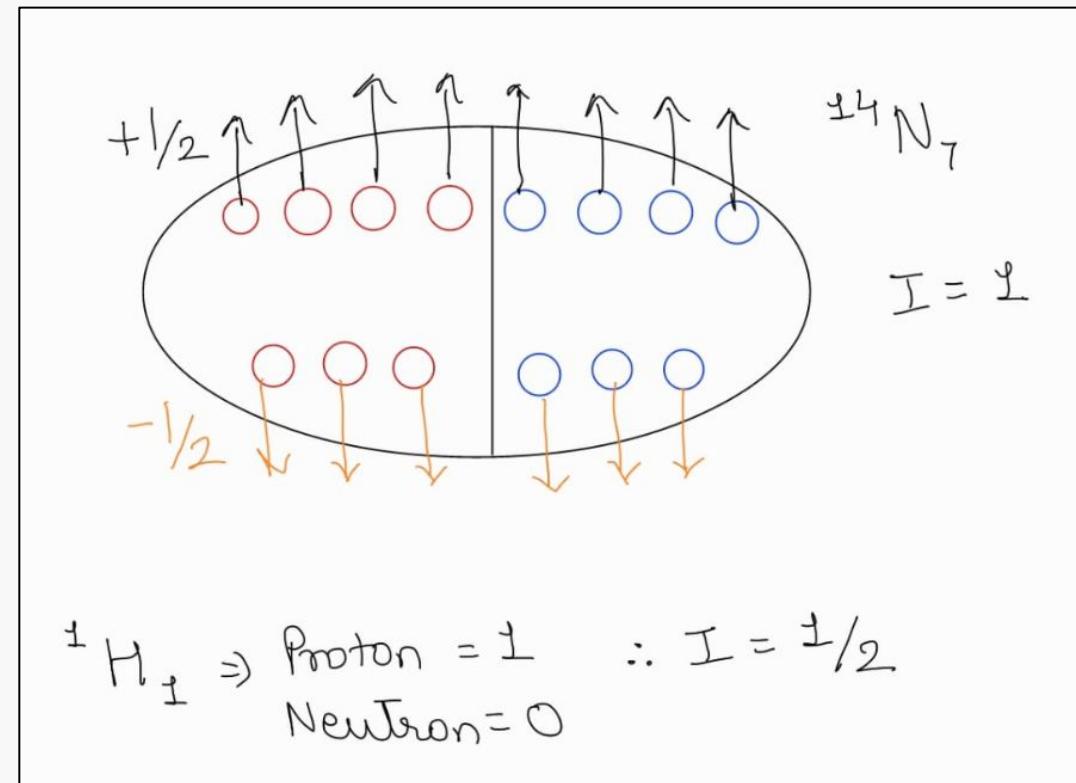
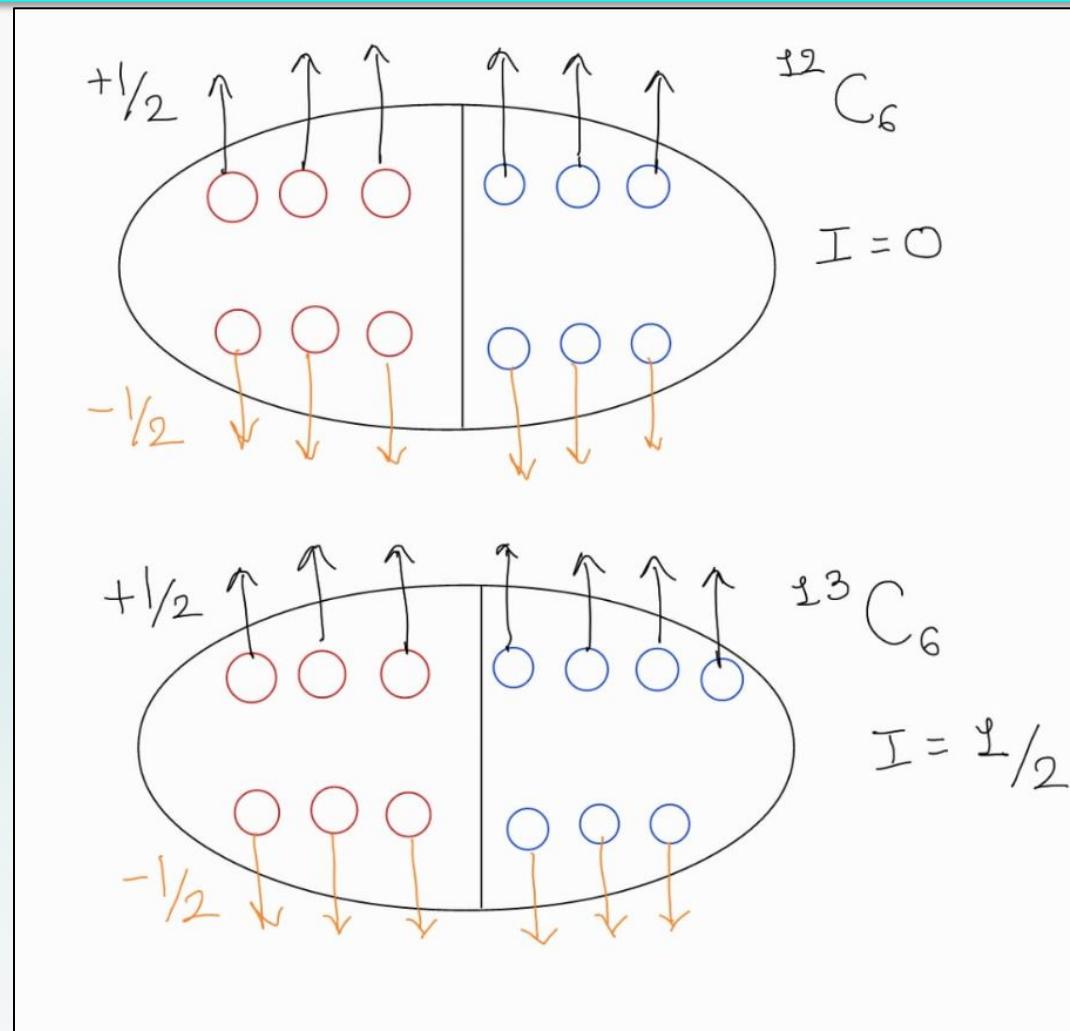
or

# Nuclear matter: Protons and Neutrons



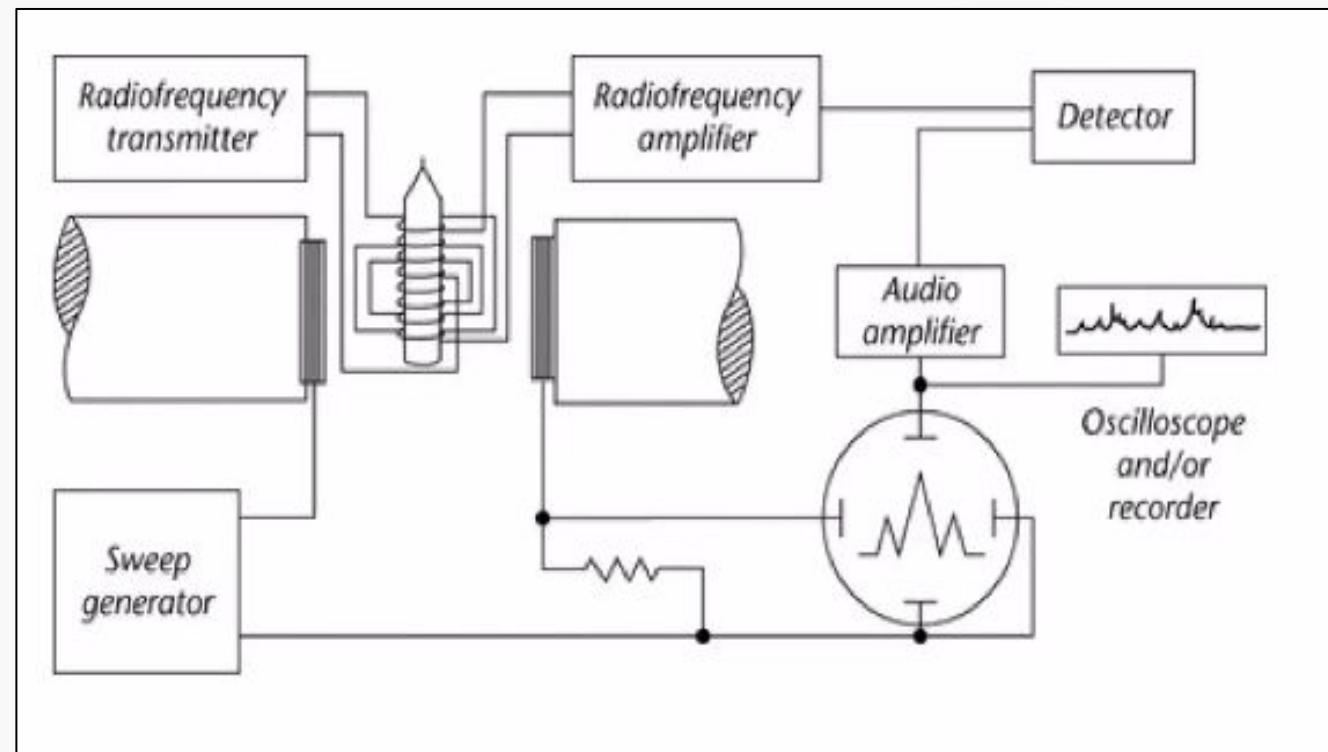
Electric charge in Quarks:  
Upward =  $\left(\frac{+2e}{3}\right)$   
Downward =  $\left(\frac{-e}{3}\right)$

# Spin Quantum number:



# Instrumentation:

1. Sample under investigation is taken in a glass tube
2. Radiofrequency source is made to fall on the sample by feeding energy into the coil wound around the sample holder
3. A signal is detected if nuclei in the sample resonate with the source
4. Energy is transferred via nuclei to the detector source
5. Output from the detector is fed to the recorder after amplification



# Instrumentation:

## 1. Sample Holder:

- A 5mm glass tube is used which can hold a 0.4 mL liquid sample.
- Microtubes are used for low volume.

## 2. Magnet:

- The accuracy and quality of NMR instrument are dependent on the strength of the magnet.
- Resolution of NMR peak will increase by increasing the strength of the magnetic field.
- 3 types:

1. Conventional ( used for 30-60 MHz frequency),
2. Permanent or Electromagnet (60, 90, 100 MHz)
3. Superconducting solenoids (470 MHz, high frequency)

## 3. Sweep Generator or magnet controller:

- A set of Helmholtz coils is located parallel to the magnet, which alters the strength of the magnetic field.

## 4. Rf Transmitter:

- Pair of coils mounted perpendicular to the path of field and receiver coil

## 5. Receiver coils & Amplifier:

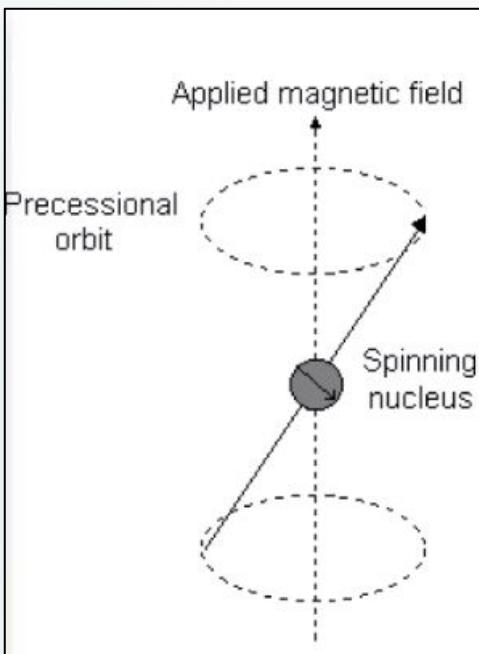
- Amplifies the received EMR by  $10^5$  times.

## 6. Detector:

- Detects signal produced by resonating nucleus.

# Larmour Equation:

- Gives the relationship between magnetic field and frequency.
- Slow precession in a small magnetic field
- Faster precession in larger magnetic field



Angular Precessional velocity

$$\omega = \gamma B_0 \quad \begin{matrix} \gamma \rightarrow \text{Gyromagnetic ratio} \\ \text{---(I)} \end{matrix}$$

$B_0 \rightarrow \text{External magnetic field}$

Larmour equation for NMR:

$$\nu = \frac{\gamma B_0}{2\pi} \quad \nu \rightarrow \text{Precessional frequency}$$

$$\gamma B_0 = 2\pi\nu \quad \begin{matrix} \text{---(II)} \end{matrix}$$

$$\omega = 2\pi\nu \quad \begin{matrix} \text{---(III)} \end{matrix}$$

$$\gamma = \frac{2\pi\mu}{hI} \quad \begin{matrix} \mu \rightarrow \text{Magnetic moment of} \\ \text{proton} \end{matrix}$$

$$h \rightarrow \text{Planck's constant}$$

$$I \rightarrow \text{Spin quantum no.}$$

# NMR Signals:

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- The **number** of signals shows how many different kinds of protons are present (in detail further).
- The **location** of the signals shows how shielded or de-shielded the proton is.
- The **intensity** of the signal shows the number of protons of that type.
- Signal **splitting** shows the number of protons on adjacent atoms.

# Solvents used in proton-NMR:

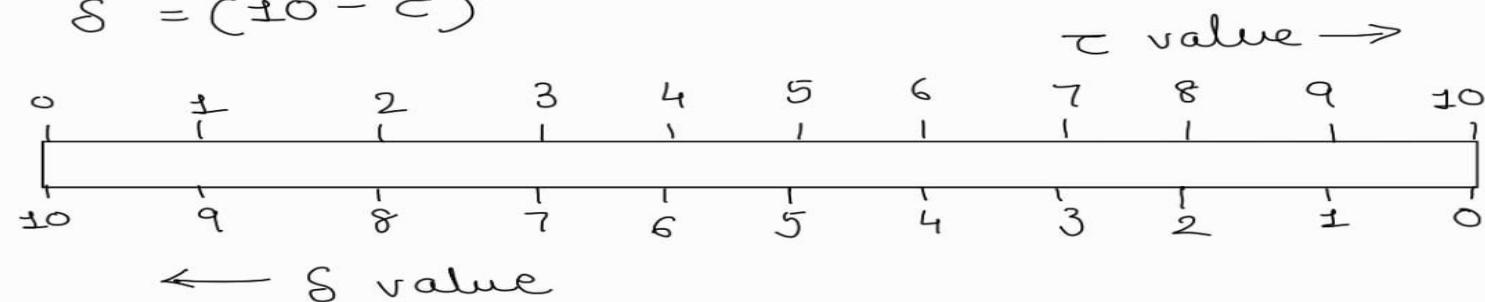
- Also known as  $^1\text{H}$  NMR
- Characteristics of solvents:
  - Chemically inert
  - Magnetically isotropic (gives the same reading from any direction in a magnetic field)
  - Free from any hydrogen ( $^1\text{H}$ ) atom (Otherwise, the solvent will give an NMR peak along with the sample) Deuterium can be used instead of hydrogen as solvent.
    - $^1\text{H}_1$  Hydrogen (Proton = 1, Neutron = 0, I =  $\frac{1}{2}$ )
    - $^2\text{H}_1$  Deuterium (Proton = 1, Neutron = 1, I = 1)
  - Should be able to dissolve the sample molecules in a reasonable quantity (approx. 10% or more).
- Polar solvents for polar compounds and non-polar for non-polar compounds.
- Commonly used solvents:
  - Carbon tetrachloride (CCl<sub>4</sub>)
  - Carbon disulphide (CS<sub>2</sub>)
  - Deuterochloroform (CDCl<sub>3</sub>)
  - Hexachloroacetone ((CCl<sub>3</sub>)<sub>2</sub>CO)
  - Deuterodimethyl Sulfoxide (Deuterium containing DMSO) ((CH<sub>3</sub>)<sub>2</sub>SO)
  - Deuterobenzene (C<sub>6</sub>D<sub>6</sub>)
- Hydrogen bonding:
  - It will increase  $\delta$  value and deshielding occurs
  - If electronegative groups are present in high concentrations, then electron cloud transfer takes place from hydrogen to the electronegative atom.
  - Ultimately H-bonding takes place and  $\delta$  value
  - Thus  $\delta$  value for the same substance will be different in different solvents.

# Chemical Shift Scale:

Chemical Shift value is denoted by  $\delta$  or  $\tau$

$$\tau = (10 - \delta) \quad \text{unit = ppm}$$

$$\delta = (10 - \tau)$$



← Deshielding

← Downfield

← High frequency

← High Chemical  
Shift value

Shielding →

Upfield →

Low frequency →

Low Chemical →  
Shift value

# Chemical Shift:

- Position of signal helps to understand the nature of the proton (aliphatic, aromatic, or aldehydic) in compounds.
- Different types of protons have different electronic environments; due to variations in an electronic environment, protons absorb at different strengths of the magnetic field.
- Electrons present outside the nucleus produce a secondary magnetic field which will either reinforce or oppose the primary (applied) magnetic field.
- Secondary magnetic field is opposed □ Shielding □ Upfield
- Secondary magnetic field is reinforced □ Deshielding □ Downfield
- Upfield/Downfield shifting is known as Chemical shift.

Type	$\delta$
Aliphatic alicyclic	0 to 2
$\alpha$ -substituted aliphatic	1 to 2
Alkyne	2 to 3
$\alpha$ -monosubstituted aliphatic	2 to 5
$\alpha$ -Desubstituted aliphatic	2.5 to 7.5
Alkene	4.5 to 7.5
Aromatic & Heteroaromatic	6 to 9
Aldehydic	9 to 10

# Note

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The unit in which a chemical shift is expressed is parts per million (ppm) of the total applied magnetic field. Since shielding and deshielding arise from induced secondary fields, the magnitude of the chemical shift is proportional to the strength of the applied field and consequently to the radiofrequency, the field must match. However, if it is expressed as a function of the applied field, that is, if the observed shift is divided by the particular radio frequency used, the chemical shift has a constant value that is independent of the radiofrequency and the magnetic field that the NMR spectrometer employs.

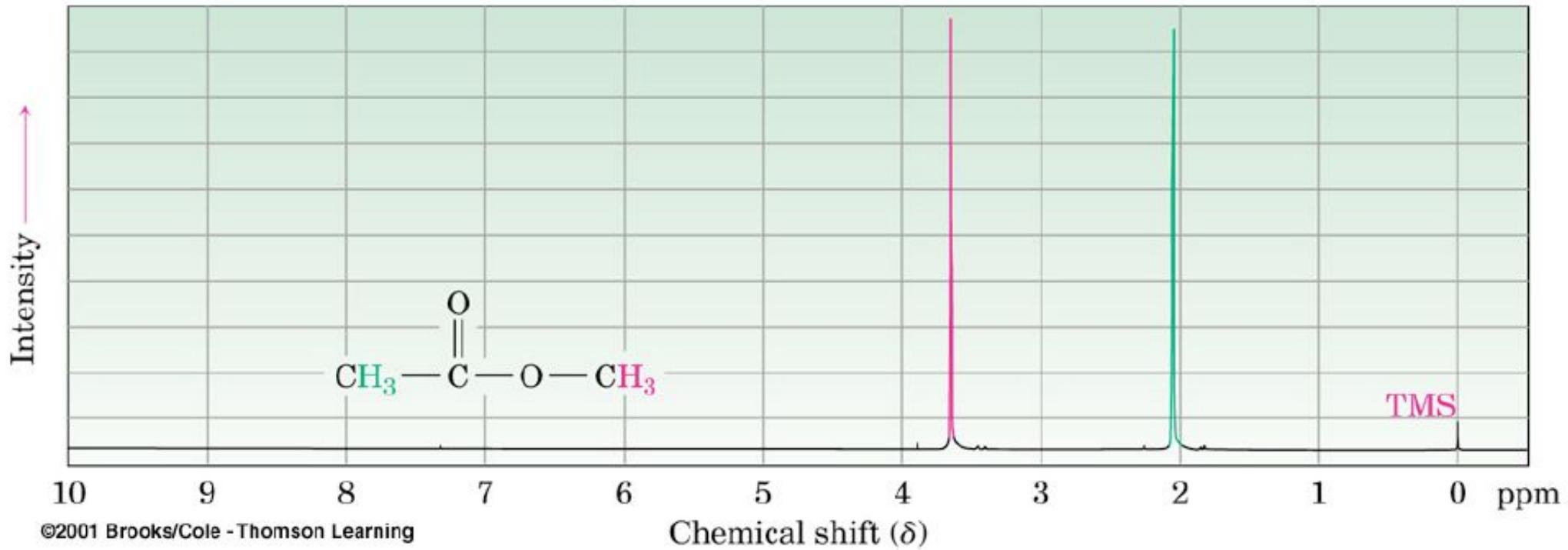
$\delta$  □ Chemical Shift value

If electronegative groups (such as -NH or -OH) are present in high concentrations, then electron cloud transfer takes place from hydrogen to the electronegative atom. Ultimately H-bonding takes place and  $\delta$  value will be increased and deshielding occurs in H-atoms. Thus  $\delta$  value for the same substance will be different in different solvents.

**Chemical shift:** the exact field strength (in ppm) of a nucleus comes into resonance relative to a reference standard (TMS)

Electron clouds “shield” nuclei from the external magnetic field causing them to absorb slightly higher energy

**Shielding:** influence of neighboring functional groups on the electronic structure around a nucleus and consequently the chemical shift of their resonance.

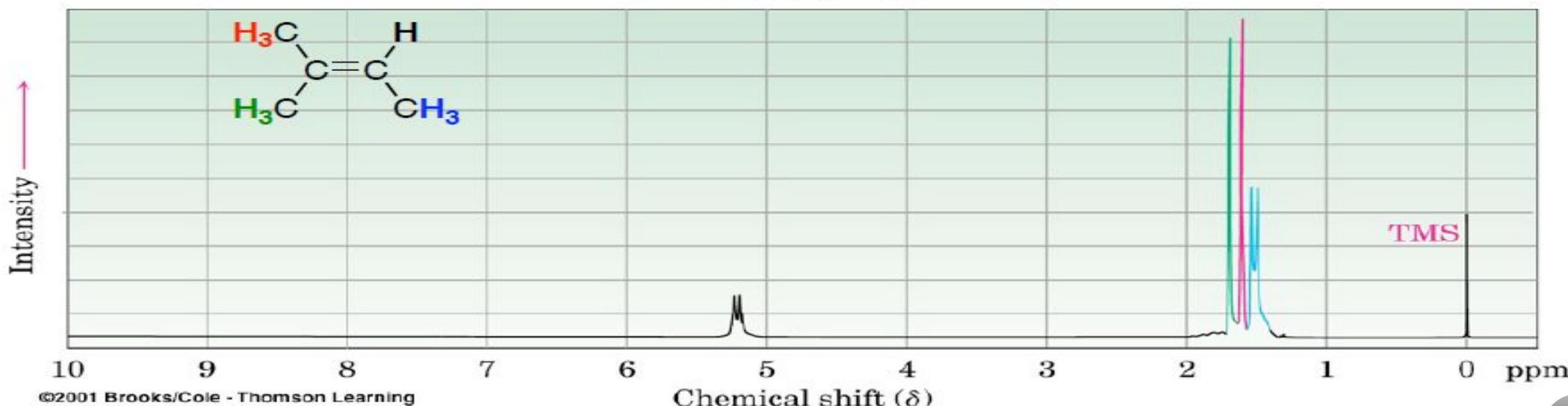
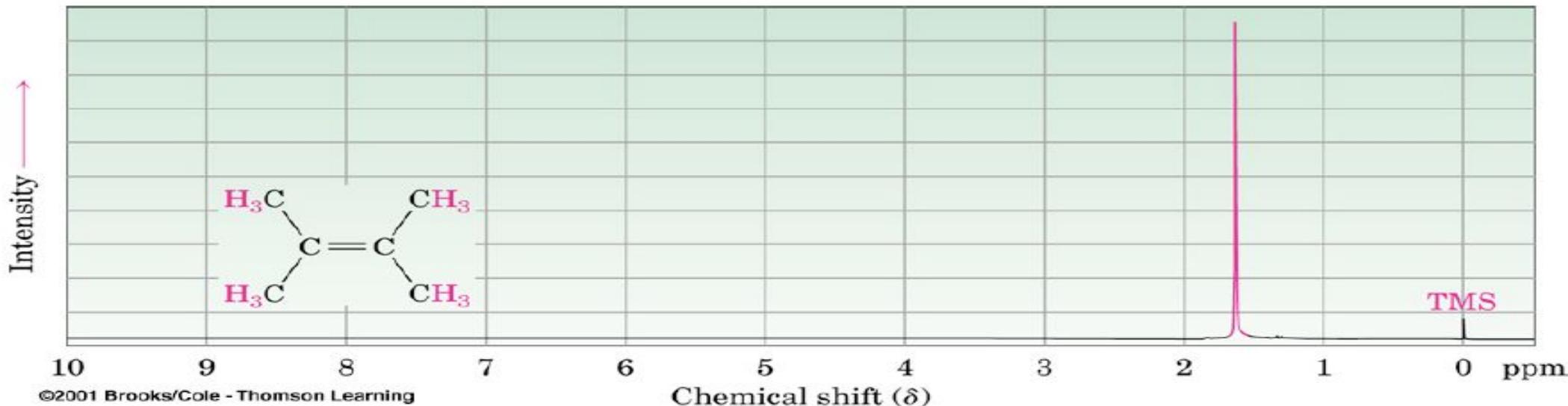


Vertical scale = intensity of the signal

Horizontal scale = chemical shift ( $\delta$ ), dependent upon the field strength of the external magnetic field; for  $^1\text{H}$ ,  $\delta$  is usually from 1-10 ppm

$$\delta = \frac{\nu - \nu_{\text{TMS}}}{\nu_0} = \frac{\text{chemical shift in Hz}}{\text{operating frequency in MHz}}$$

**Equivalence:** chemically and magnetically equivalent nuclei resonate at the same energy and give a single signal or pattern



# Location of Signals

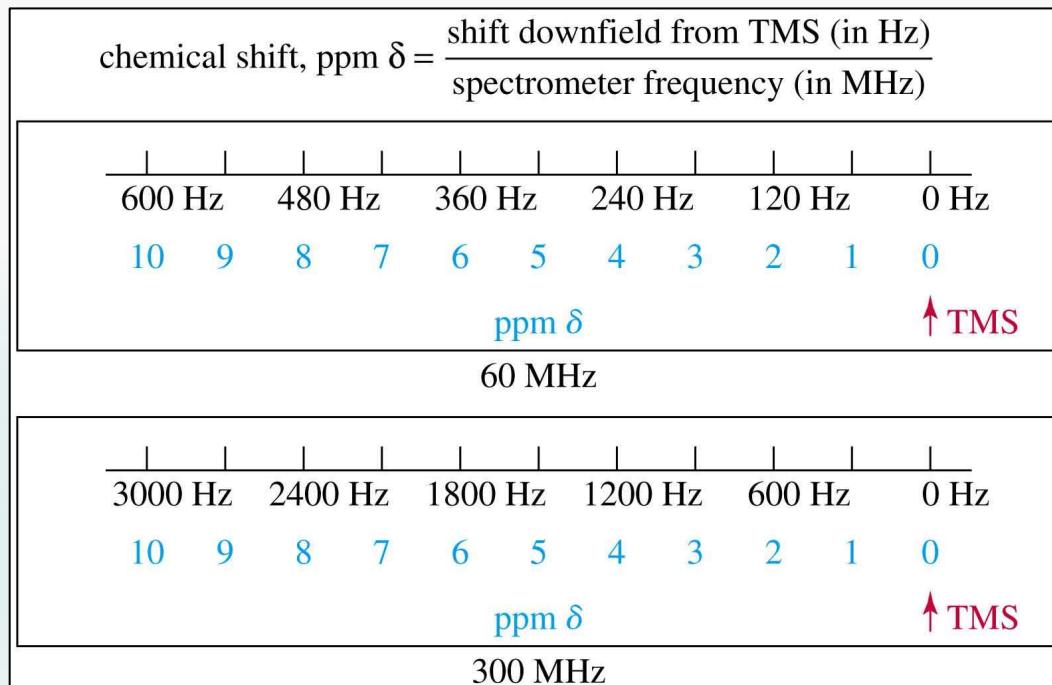
- More electronegative atoms de-shield more and give larger shift values.
- Effect decreases with distance.
- Additional electronegative atoms cause an increase in chemical shift.

**TABLE 13-2** Chemical Shifts of the Chloromethanes

Compound	Chemical Shift	Difference
$\text{H}-\text{C}-\text{H}$	$\delta 0.2$	
$\text{H}-\text{C}-\text{Cl}$	$\delta 3.0$	2.8 ppm
$\text{H}-\text{C}-\text{Cl}$	$\delta 5.3$	2.3 ppm
$\text{H}-\text{C}-\text{Cl}$	$\delta 7.2$	1.9 ppm

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

# Delta Scale & Typical Values:



**TABLE 13-3** Typical Values of Chemical Shifts

Type of Proton	Approximate $\delta$	Type of Proton	Approximate $\delta$
alkane ( $-\text{CH}_3$ )	0.9	$\begin{array}{c} >\text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{CH}_3 \end{array}$	1.7
alkane ( $-\text{CH}_2-$ )	1.3	$\text{Ph}-\text{H}$	7.2
alkane ( $-\text{CH}-$ )	1.4	$\text{Ph}-\text{CH}_3$	2.3
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{CH}_3 \end{array}$	2.1	$\text{R}-\text{CHO}$	9–10
$-\text{C}\equiv\text{C}-\text{H}$	2.5	$\text{R}-\text{COOH}$	10–12
$\text{R}-\text{CH}_2-\text{X}$ (X = halogen, O)	3–4	$\text{R}-\text{OH}$	variable, about 2–5
$\begin{array}{c} >\text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	5–6	$\text{Ar}-\text{OH}$	variable, about 4–7
		$\text{R}-\text{NH}_2$	variable, about 1.5–4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

# TMS

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## **Tetra methyl Silane (TMS)**

- TMS is used as a reference compound in NMR.
- $\delta$  value of TMS is considered to be 0 as it is highly shielded as compared to other organic compounds.
- Highly volatile so it can be removed easily
- Chemically stable so it will not take part in any chemical reaction.

(More information available in Reference materials.)

# Factors affecting Chemical Shift:

## 1. Inductive Effect:

- When a proton is attached to any electronegative group, then the proton will be deshielded and  $\delta$  value will increase.
- $\delta$  value increases with electronegativity as deshielding happens.
- $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_4$

## 2. Vander Waal's Deshielding (Steric effect)

## 3. Anisotropic effect

- Some sites (wrt bonds) are deshielded.

## 4. Hydrogen bonding

## 5. Hybridization of C-atom attached with H-atom(s)

- sp (1:1), sp<sup>2</sup> (1:2), sp<sup>3</sup> (1:3)
- Higher s character  $\rightarrow$  bonding electron is closer to C  $\rightarrow$  electrons are away from H-atom  $\rightarrow$  Deshielding

# Number of Signals in NMR:

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- The number of signals gives information about different sets of equivalent protons in a molecule.
- Each signal represents a set of equivalent protons.
- Magnetically equivalent protons are known as chemically equivalent and give a single signal in NMR.

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# Numerical problems

# References:

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- Principle and working of Nmr spectroscopy:  
<https://www.slideshare.net/ArpitSuralkar/principle-and-working-of-nmr-spectroscopy>
- NMR Instrumentation: <https://www.slideshare.net/AdityaSharma1550/nmr-instrumentation-241082791>
- Practice problems: <https://www.nmr.tips/indexe.html>

# Thank-You!