

Lecture 24 Title : Nuclear magnetic resonance spectroscopy (N.M.R)

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In this lecture we will describe the static magnetic field interaction with the nuclear spin.

The spectroscopy developed on this concept is known as Nuclear magnetic resonance spectroscopy (N.M.R).

We will go through the theory of this interaction, its consequence and the applications.

The fine structure seen in high resolution spectrum is very useful to determine the structure of molecule.

This spectroscopy has wide application in various fields of science.

In 1944, Rabi (Columbia) won the Nobel prize "for his resonance method for recording the magnetic properties of atomic nuclei".



Nuclear magnetic resonance spectroscopy: It is commonly referred to as NMR, and is a technique which exploits the magnetic properties of certain nuclei to study physical, chemical, and biological properties of matter. The most interesting isotope ^{12}C has nuclear spin 0 and does NOT exhibit magnetic resonance. The same goes for ^{16}O and ^{32}S (the naturally occurring isotopes). Fortunately, the most abundant isotope ^1H has $I = \frac{1}{2}$ and so it does exhibit magnetic resonance. And also ^{13}C , ^{19}F , ^{31}P and ^{15}N exhibit nuclear magnetic resonance. Thus the wide applications of N.M.R. are based on ^1H and ^{13}C .

When hydrogen (^1H) or a proton having $I = \frac{1}{2}$ is introduced into a magnetic field, the energy level splits into two corresponding to the two projections of its spin $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$. This way the degeneracy of m_I is removed due to the magnetic field.

As described in previous lecture, the interaction energy of proton with the magnetic field is described as

$$\begin{aligned} E_{mag} &= -\langle I m_I | g_I \mu_B \vec{I} \cdot \vec{B}_0 | I m_I \rangle \\ &= -g_I \mu_B B_0 \langle I m_I | \vec{I}_z | I m_I \rangle \dots\dots\dots(24.1) \\ &= -g_I \mu_B B_0 m_I = -g_N \mu_B^N B_0 m_I \end{aligned}$$

Where g_N is the nuclear Lande g-factor, μ_B^N is the nuclear Bohr magneton and B_0 is the applied magnetic field in the Z-direction of the laboratory frame.

It is clear from equation-24.1 that the energy difference corresponding to $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$ depends on the magnetic field strength. Referring to the following figure-24.1, it is seen that when an electromagnetic field is incident, the magnetic dipole transition takes place between $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$.

$$g_N = 5.5857$$

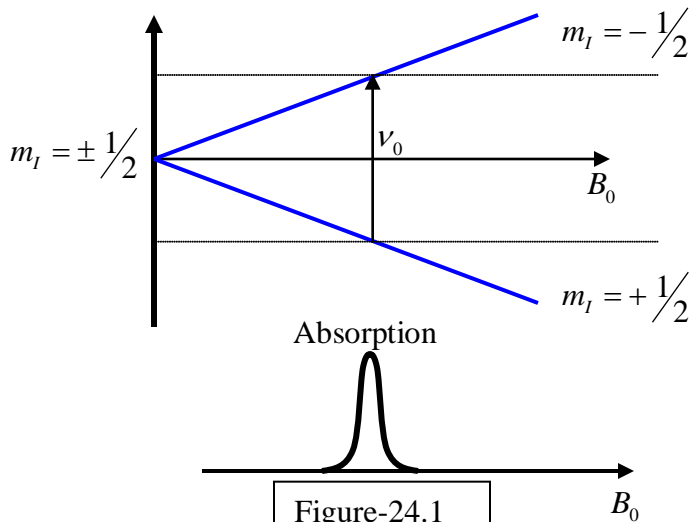
And

$$\mu_B^N = 5.05 \times 10^{-27} \text{ joule / Tesla}$$

$$\begin{aligned} \frac{\nu_0}{B_0} &= \frac{g_N \mu_B^N}{h} = \frac{5.585 \times 5.05 \times 10^{-27}}{6.626 \times 10^{-34}} \\ &= 4.257 \times 10^7 \\ &= 42.57 \text{ MHz / Tesla} \end{aligned}$$

For

$$B_0 = 1.141 \text{ T}, \quad \nu_0 = 60 \text{ MHz}$$

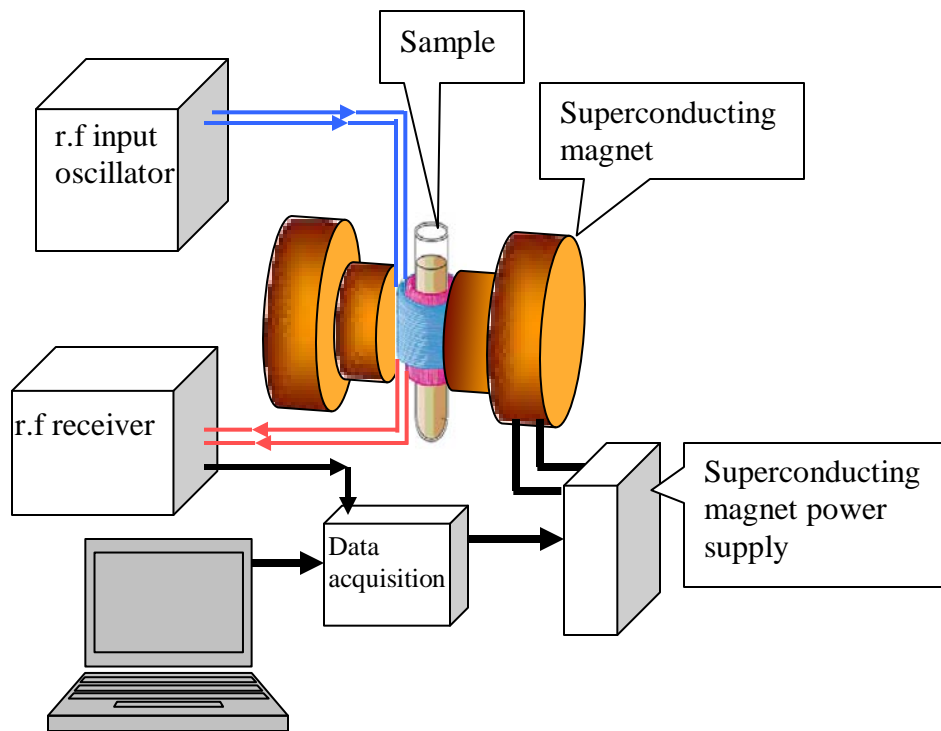


And for $B_0 = 7.04 \text{ T}$, $\nu_0 = 300 \text{ MHz}$, so for the transition the radio frequency (r.f) is needed.

The block diagram of the experiment setup is shown in figure-24.2

It consist of

1. A source of radio frequency radiation.
2. A receiver coil.
3. A d.c magnetic field.
4. A sweep generator for varying the magnetic field.
5. A data acquisition system.



For experiment,

- Sample is placed between the poles of a powerful magnet, made of superconductor.
- The radio frequency (r.f) field is generated in the coil connected to the r.f oscillator.
- The detector coil is placed at right angles to both the direction of the magnetic field and the transmitter coil.
- The magnet is provided with the sweep coils which are used to vary the magnetic field.

In general, the r.f. frequency is kept fixed. The magnetic field is varied until the resonance condition is reached. The nuclear magnetic moment transition induces an emf in the detector coil, which is amplified and then recorded as resonance absorption.

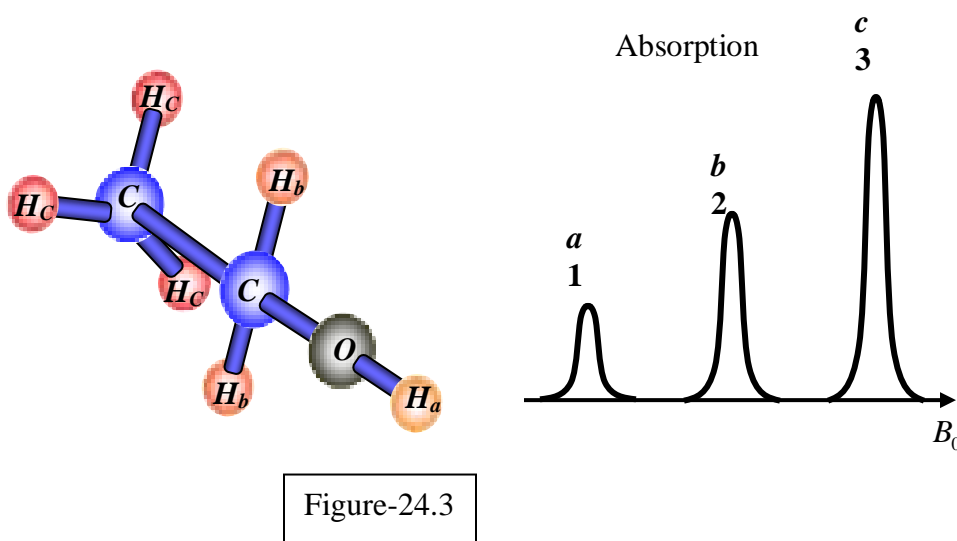
- Homogeneity of the magnetic field is achieved by spinning the sample tube with an appropriate frequency. In this way, all the nuclei experience an average magnetic field.
- The sensitivity is achieved by cooling the sample because,

$$\frac{n_{-1/2}}{n_{+1/2}} = e^{-g_N \mu_B^N B / kT}$$

Where the electron population in the $m_l = +1/2$ state $n_{+1/2}$ and that in $m_l = -1/2$ state $n_{-1/2}$

- According to the theory, we should expect that all protons in ^1H have the resonance the same magnetic field.
- However, in actual case, this is not observed.

For example, when experiment is done with ethanol ($\text{CH}_3\text{-CH}_2\text{-OH}$), three peaks were observed with relative intensity 1:2:3 corresponding to one, two and three protons as shown in figure-24.3.



This implies that the actual magnetic fields seen by the protons are different from the applied magnetic field B_0 .

So, if we write the effective field

$$B = B_0(1 - \sigma)$$

Where σ = Screening constant ($\approx 10^{-5}$ for protons)

The value of σ depends on the chemical environment around the nucleus.

Let us consider, two types of environment of the nucleus and because of that two resonance lines for nucleus of type A and type B. So,

$$\begin{aligned} B_B - B_A &= B_o(1 - \sigma_B) - B_o(1 - \sigma_A) \\ &= B_o(\sigma_A - \sigma_B) \\ &= B_o \delta_{AB} \end{aligned}$$

In terms of resonant frequency

$$\begin{aligned} \nu_B - \nu_A &= \nu_o(1 - \sigma_B) - \nu_o(1 - \sigma_A) \\ &= \nu_o(\sigma_A - \sigma_B) \\ &= \nu_o \delta_{AB} \end{aligned}$$

This $\delta_{AB} = \sigma_A - \sigma_B$ is known as chemical shift. It is expressed as

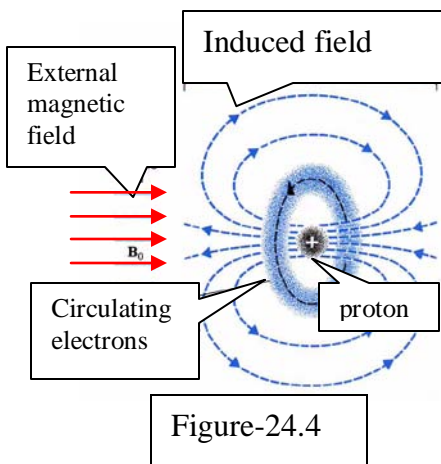
$$\delta_{AB} = \frac{\nu_B - \nu_A}{\nu_o} \times 10^6 \text{ ppm} \dots\dots\dots(24.2)$$

What influences the chemical shift?

(a) Shielding effects:

When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied magnetic field as shown in figure 24.4.

This ultimately decreases the effective magnetic field felt by the proton, shifting the signal to the higher magnetic field. This is called local diamagnetic shielding.



(b) De-shielding effect:

- (a) When H atom is bonded with an electronegative atom, this electronegative atom attracts the electron towards it. Thus the density of the electron cloud decreases and as a result de-shields the nucleus. In this cause the resonance occur at a lower magnetic field. The magnitude of the de-shielding rapidly decreases as the distance between the proton and electronegative atom increases.
- (b) In a paramagnetic substance the electron distribution is anisotropic about the atom. In this case, the electron circulation about the nucleus generates a magnetic field. This result in de-shielding the nucleus.
- (c) In aromatic protons, such as in benzene molecule, the circulating current due to the delocalized π electrons produces a magnetic dipole. The induced field at the proton is parallel to the applied field and the result is therefore de-shielding.

The following figure explains the resonance condition for shielding and de-shielding condition.

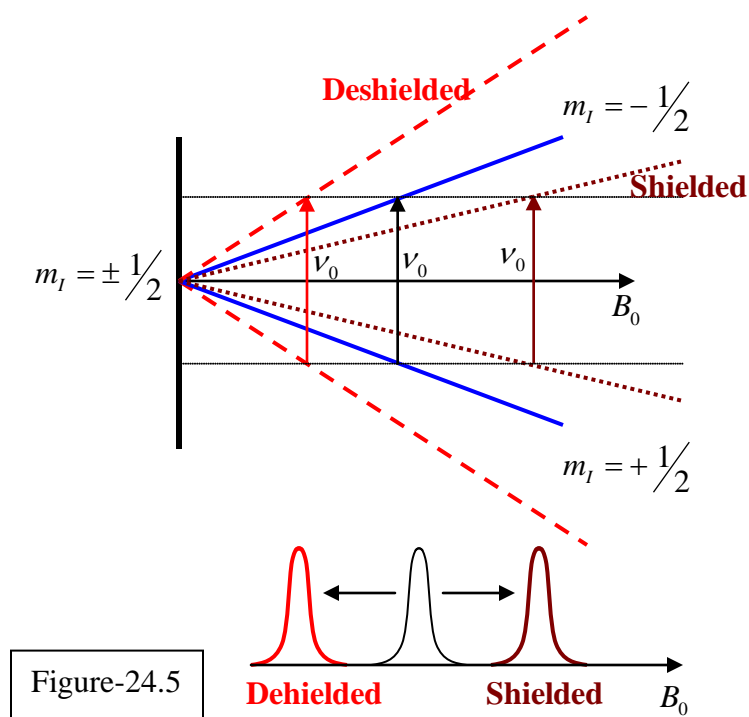


Figure-24.5

From the above de-shielding effect discussion we note that, in NMR spectrum

- (1) Number of peaks = no. of H environments
- (2) Position of the peak depends on the chemical environment.

Area under the peak = relative number of H in the chemical environment

Referring to figure 24.3 for the case of ethanol,

Since, $H_a \rightarrow$ close to oxygen atom \rightarrow more de-shielding \rightarrow resonance at lowest magnetic field. Also only one H contribution to the intensity

$H_b \rightarrow$ Two bonds away \rightarrow middle peak, two H atoms contribution to the intensity, and

$H_c \rightarrow$ Far away \rightarrow less de-shielding \rightarrow highest magnetic field, three H in the methyl group, thus intensity is thrice that of intensity of H_a .

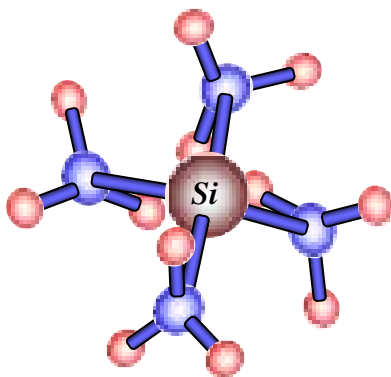
In practice, chemical shift is measured with reference to tetramethylsilane. It is chemically inert so,

$$\delta_{sample,TMS} = \frac{\nu_{sample} - \nu_{TMS}}{\nu_o} \times 10^6 \text{ ppm} \dots\dots\dots(24.3)$$

This will come as '-ve number, so, τ scale is introduced,

$$\tau = 10.00 + \delta_{sample,TMS}$$

Tetramethyl silane (TMS) $[\text{Si}(\text{CH}_3)_4]$ is used as reference because it is soluble in most organic solvents, is inert, volatile, and has 12 equivalent ^1H and 4 equivalent ^{13}C . TMS signal is set to 0.



Spin-Spin Coupling :

When N.M.R spectrum is recorded under high resolution, it is observed that ;

- 1) The peak corresponding to H_b splits into four peaks with intensity pattern 1:3:3:1
- 2) The peak corresponding to H_c splits into three peaks with intensity pattern 1:2:1

The splitting of the lines arises as a result of the nuclear spin-spin interaction with the neighboring protons. Such coupling between pairs of nuclear spins is an important feature of nuclear magnetic resonance (NMR) spectroscopy as it can provide detailed information about the structure and conformation of molecules.

In the following we will discuss the theory of this spin-spin coupling.

For a proton $m_I = \pm \frac{1}{2}$. Let us denote $m_I = +\frac{1}{2}$ as α and $m_I = -\frac{1}{2}$ as β , then possible combinations for the CH_2 group and CH_3 group are given in table-24.1 and table-24.2 respectively.

Table-24.1

| $-CH_2$ group | $\sum m_I$ | degeneracy |
|----------------------------|------------|------------|
| $\alpha\alpha$ | +1 | 1 |
| $\alpha\beta, \beta\alpha$ | 0 | 2 |
| $\beta\beta$ | -1 | 1 |

Table-24.2

| $-CH_3$ group | $\sum m_I$ | degeneracy |
|---|------------|------------|
| $\alpha\alpha\alpha$ | +3/2 | 1 |
| $\alpha\alpha\beta, \alpha\beta\alpha, \beta\alpha\alpha$ | +1/2 | 3 |
| $\beta\beta\alpha, \beta\alpha\beta, \alpha\beta\beta$ | -1/2 | 3 |
| $\beta\beta\beta$ | -3/2 | 1 |

The interaction of the two types of nuclei A and B with the applied magnetic field is given by

$$H_{Zeeman} = -g_N \mu_B^N I_z^A B_0 (1 - \sigma_A) - g_N \mu_B^N I_z^B B_0 (1 - \sigma_B) \dots\dots\dots(24.4)$$

Now we will introduce the spin-spin interaction term in the Hamiltonian

$$H_{sc} = J \mathbf{I}^A \cdot \mathbf{I}^B$$

Where J is the spin-spin coupling constant.

Substituting $g_N \mu_B^N B_0 = \nu_0$, we get

$$H = -\nu_0 (1 - \sigma_A) I_z^A - \nu_0 (1 - \sigma_B) I_z^B + J \mathbf{I}^A \cdot \mathbf{I}^B \dots\dots\dots(24.5)$$

Now,

$$\mathbf{I}^A \cdot \mathbf{I}^B = I_x^A I_x^B + I_y^A I_y^B + I_z^A I_z^B$$

The energies can be obtained by solving the Schrodinger equation

$$H\psi = E\psi$$

$$\text{Where, } \psi = \sum_i c_i \phi_i$$

The possible combinations are,

$$\phi_1 = \alpha(A) \alpha(B) \quad \phi_2 = \alpha(A) \beta(B)$$

$$\phi_3 = \beta(A) \alpha(B) \quad \phi_4 = \beta(A) \beta(B)$$

Let us take that the ψ is normalized, then

$$E = \langle \psi' | H | \psi \rangle$$

We construct the determinant to solve E

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - E \end{vmatrix} = 0 \dots\dots\dots(24.6)$$

Now $I^+ = I_x + i I_y$

$$I^- = I_x - i I_y$$

We know that,

$$\begin{aligned} I^+ |\alpha\rangle &= 0 & I^+ |\beta\rangle &= \alpha \\ I^- |\alpha\rangle &= \beta & I^- |\beta\rangle &= 0 \end{aligned}$$

And,

$$I^{A+} I^{B-} = (I_x^A I_x^B + I_y^A I_y^B) + i(I_y^A I_x^B - I_x^A I_y^B)$$

$$I^{A-} I^{B+} = (I_x^A I_x^B + I_y^A I_y^B) - i(I_y^A I_x^B - I_x^A I_y^B)$$

$$I_x^A I_x^B + I_y^A I_y^B = \frac{1}{2}(I^{A+} I^{B-} + I^{A-} I^{B+})$$

Substituting in equation-24.5

$$H = -\nu_0(1-\sigma_A)I_z^A - \nu_0(1-\sigma_B)I_z^B + J \left[I_z^A I_z^B + \frac{1}{2}(I^{A+} I^{B-} + I^{A-} I^{B+}) \right]$$

The various terms can easily be deduced as

$$H_{11} = -\frac{\nu_0}{2}(1-\sigma_A) - \frac{\nu_0}{2}(1-\sigma_B) + \frac{J}{4}$$

$$H_{22} = \frac{\nu_0}{2}(1-\sigma_A) - \frac{\nu_0}{2}(1-\sigma_B) - \frac{J}{4}$$

$$H_{33} = -\frac{\nu_0}{2}(1-\sigma_A) + \frac{\nu_0}{2}(1-\sigma_B) - \frac{J}{4}$$

$$H_{44} = \frac{\nu_0}{2}(1-\sigma_A) + \frac{\nu_0}{2}(1-\sigma_B) + \frac{J}{4}$$

$$H_{23} = H_{32} = \frac{J}{2}$$

All other terms will be zero. So the determinant in equation-24.6 will be

$$\begin{vmatrix} -\frac{\nu_0}{2}(1-\sigma_A) - \frac{\nu_0}{2}(1-\sigma_B) + \frac{J}{4} - E & 0 & 0 & 0 \\ 0 & \frac{\nu_0}{2}(1-\sigma_A) - \frac{\nu_0}{2}(1-\sigma_B) - \frac{J}{4} - E & \frac{J}{2} & 0 \\ 0 & \frac{J}{2} & -\frac{\nu_0}{2}(1-\sigma_A) + \frac{\nu_0}{2}(1-\sigma_B) - \frac{J}{4} - E & 0 \\ 0 & 0 & 0 & \frac{\nu_0}{2}(1-\sigma_A) + \frac{\nu_0}{2}(1-\sigma_B) + \frac{J}{4} - E \end{vmatrix} = 0$$

From the determinant we get,

$$E_1 = \nu_0 \left(-1 + \frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right) + \frac{J}{4}$$

$$E_4 = \nu_0 \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right) + \frac{J}{4}$$

$$E_1 = -M + \frac{J}{4}$$

$$E_4 = M + \frac{J}{4} \quad \text{where} \quad M = \nu_0 \left(1 - \frac{\sigma_A}{2} - \frac{\sigma_B}{2} \right)$$

To get the other two roots we have to solve the following determinant

$$\begin{vmatrix} \frac{\nu_0}{2}(1-\sigma_A) & \frac{J}{2} \\ -\frac{\nu_0}{2}(1-\sigma_B) - \frac{J}{4} - E & \frac{J}{2} \\ \frac{J}{2} & -\frac{\nu_0}{2}(1-\sigma_A) \\ & +\frac{\nu_0}{2}(1-\sigma_B) - \frac{J}{4} - E \end{vmatrix} = 0$$

We obtain,

$$E = -\frac{J}{4} \pm \sqrt{\frac{\nu_0^2 \delta^2}{4} + \frac{J^2}{4}}$$

Where, $\delta = \sigma_A - \sigma_B$.

So we have now,

$$\begin{aligned} E_2 &= -\frac{J}{4} - \frac{1}{2} \sqrt{\nu_0^2 \delta^2 + J^2} \\ &= -\frac{J}{4} - \frac{1}{2} \nu_0 \delta \left(1 + \frac{J^2}{2\nu_0^2 \delta^2} + \dots \right) \end{aligned}$$

$$\begin{aligned} E_3 &= -\frac{J}{4} + \frac{1}{2} \sqrt{\nu_0^2 \delta^2 + J^2} \\ &= -\frac{J}{4} + \frac{1}{2} \nu_0 \delta \left(1 + \frac{J^2}{2\nu_0^2 \delta^2} + \dots \right) \end{aligned}$$

The energy level diagram is shown in figure-24.6

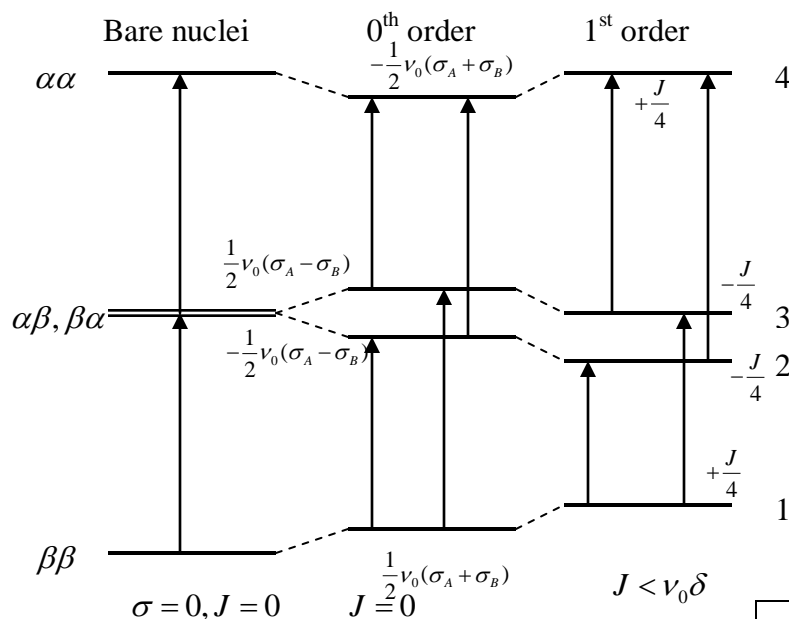


Figure-24.6

The transitions are

$$E_2 - E_1 = -\frac{J}{2} + M - \frac{1}{2}v_0\delta\left(1 + \frac{J^2}{2v_0^2\delta^2} + \dots\right)$$

$$E_3 - E_1 = -\frac{J}{2} + M + \frac{1}{2}v_0\delta\left(1 + \frac{J^2}{2v_0^2\delta^2} + \dots\right)$$

$$E_4 - E_2 = \frac{J}{2} + M + \frac{1}{2}v_0\delta\left(1 + \frac{J^2}{2v_0^2\delta^2} + \dots\right)$$

$$E_4 - E_3 = \frac{J}{2} + M - \frac{1}{2}v_0\delta\left(1 + \frac{J^2}{2v_0^2\delta^2} + \dots\right)$$

Figure -24.7 shows the splitting of the transitions when $J \neq 0$. It should be noted that the interaction between the two nonequivalent protons (having different chemical shift) gives rise to the splitting of the transitions. The separation between these transitions depends on the interaction term J .

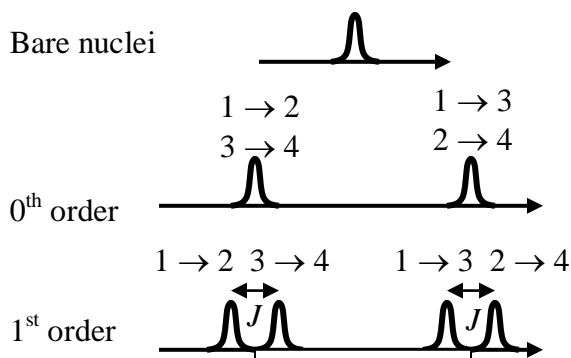


Figure-24.7

The splitting structure follows the Pascal's triangle discussed in the previous lecture. In figure 24.8 describes this method.

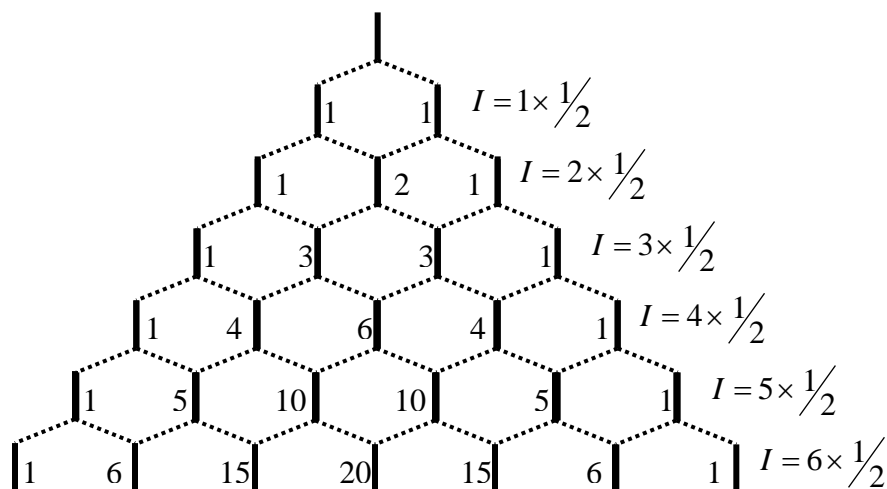


Figure-24.8

So if we again look at the fine structure of the ethanol given in figure-24.9, the line marked as b splits into four having intensity ratio 1:3:3:1 because of the $-CH_3$ group and the line marked as c splits into three with intensity 1:2:1 due to the $-CH_2$ group.

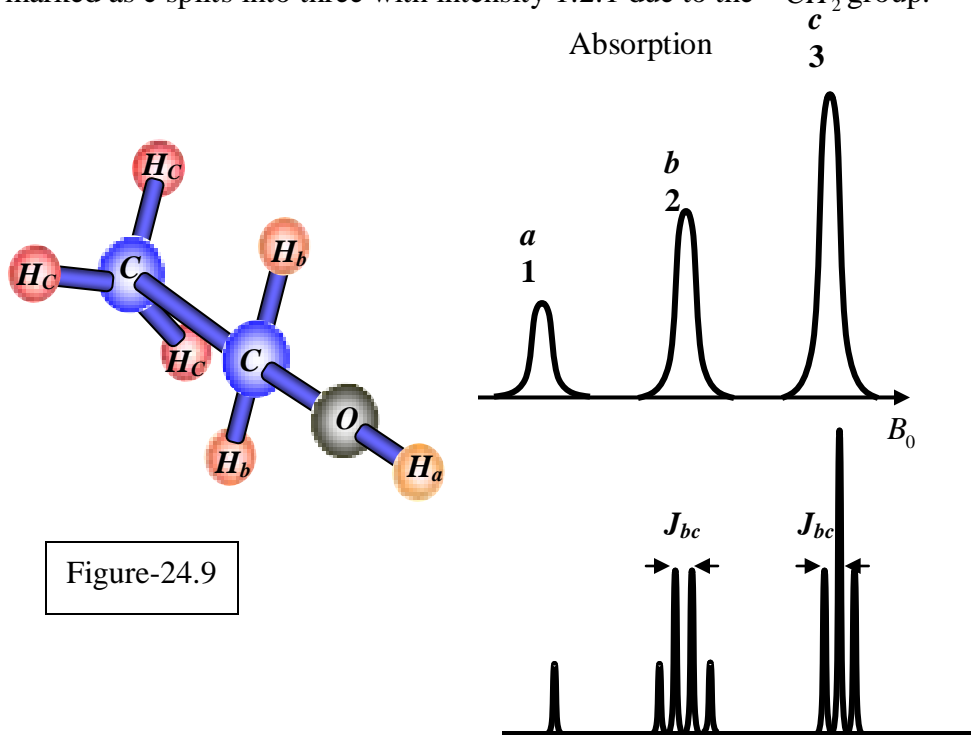


Figure-24.9

Let us take another example.

For a group given in figure-24.10,

Here, H_a , H_b and H_c are nonequivalent protons having different chemical shift. The low resolution spectrum is shown in this figure. J_{ab} is the coupling constant between H_a and H_b and J_{bc} is the coupling constant between H_b and H_c .

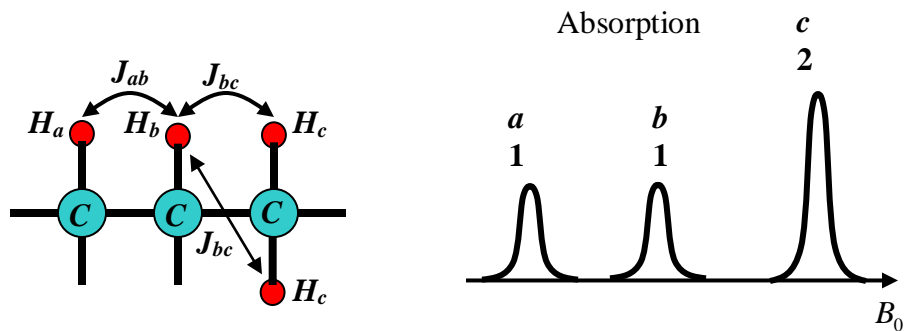


Figure-24.10

There are two situations

(a) $J_{ab} > J_{bc}$ or (b) $J_{ab} < J_{bc}$. The fine structure is shown in figure-24.11

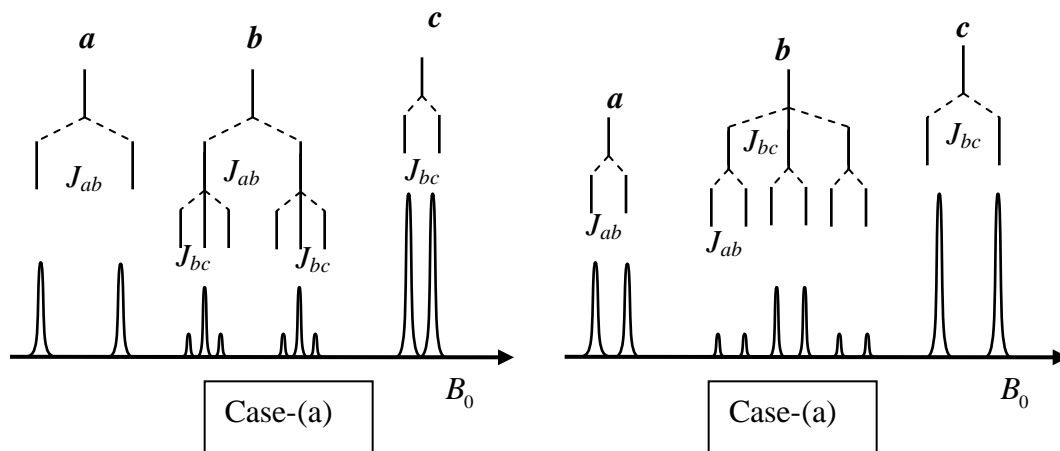


Figure-24.11

There are few points need to be remembered from the above discussions.

1. When two nuclei have the same chemical shift, only one line is observed even there is spin-spin interaction between them. This is why for the equivalent protons, no splitting is observed.
2. The major application of NMR spectroscopy is to determine the structure of the molecule. This requires the determination of the two quantities, chemical shift and the spin-spin coupling constant.
3. The chemical shift provides the information about the nature of the chemical group
4. The spin-spin coupling constant and the pattern help us to determine the arrangement of the atoms
5. The relative intensity of the peaks tells us about the ratio of the equivalent atoms in different chemical environment
6. There are more to learn about the complex structure and the kinetics and those are beyond the scope of this course.

Recap

In this lecture, we have learnt that due to the shielding and de-shielding of the protons, there is chemical shift.

This Chemical shift depends on :

- Electronegativity of nearby atoms
- Hybridization of adjacent atoms
- diamagnetic effects
- paramagnetic effects
- solvent effect

The fine structure of these transitions depends on the coupling of the intrinsic angular momentum of different protons.

Such coupling between pairs of nuclear spins is an important feature of nuclear magnetic resonance (NMR) spectroscopy as it can provide detailed information about the structure and conformation of molecules.