

# NMR SPECTROSCOPY

SEM-4, CC-8  
PART-5, PPT-17

## Contents (Part-5)

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Dr. Kalyan Kumar Mandal  
Associate Professor  
St. Paul's C. M. College  
Kolkata

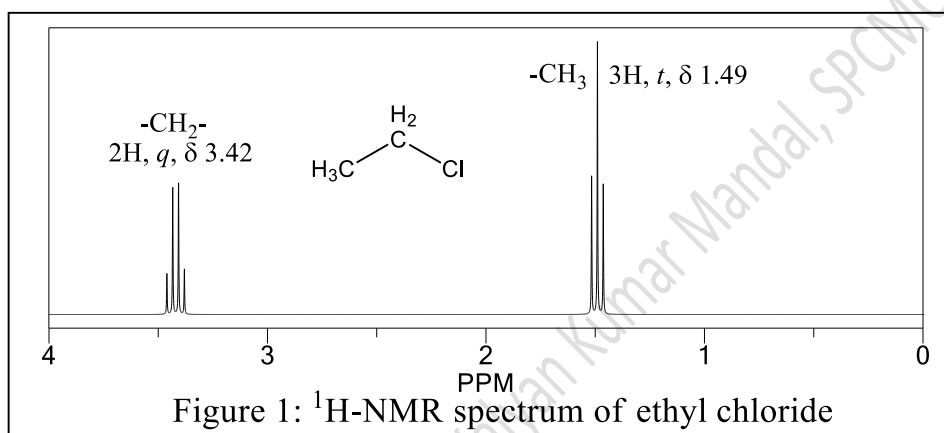
Lecture material prepared by Dr. Kalyan Kumar Mandal, SPCMC, Kolkata

## Nuclear Magnet Resonance (NMR) Spectroscopy (PART-5, PPT-17)

### Spin-Spin Coupling

Chemical shift of protons gives an idea about the nature of the protons in the molecule. The number of proton/s giving the signal can be obtained from the intensity of the signal which are obtained by an integration curve. Some of the signals appear as a singlet, doublet, triplet, quarter, and multiplet. The multiplicities of the signals provide information about the environment of the neighbouring proton/s.

Following things are obtained in the  $^1\text{H}$ -NMR spectrum of a compound, for instance  $\text{CH}_3\text{CH}_2\text{Cl}$  (Figure 1). As expected,  $\text{CH}_3$ , and  $\text{CH}_2$  protons appeared at different positions in the spectrum as they are nonequivalent, and have different chemical shifts.



These signals, however, do not necessarily occur as single peaks (singlets). Ethyl chloride (Figure 1) affords a triplet for the methyl protons, and a quartet for the methylene protons in the integrated intensity ratio of 3:2, respectively. The intensity of the components of the triplet is in the ratio of 1:2:1, and that of the quartet is in the ratio of 1:3:3:1.

The splitting of the signals does not affect the overall integrated intensities of the multiplets which still correspond to the number of underlying protons. The spacings of the components of the methyl triplet are equal, and are also equal to the spacings of the components of the methylene quartet. In ethyl chloride, methyl protons ( $\text{CH}_3$ ) have two neighbouring equivalent protons ( $\text{CH}_2$ ), and it is observed that it appears as a three-line signal (a *triplet*). Again, methylene protons ( $\text{CH}_2$ ) has threeneighbouring equivalent protons ( $\text{CH}_3$ ), and the signal is split into four lines (a *quartet*).

### Multiplicity of a Signal

Therefore, the number of lines (multiplicity) observed in the NMR signal for a group of protons is, therefore, not related to the number of protons in that group; the multiplicity of lines is related to the number of protons in neighbouring groups.

**(n + 1) rule:** The simple rule to find the multiplicity of a signal from a group of protons is the number of the neighbouring (n) equally coupled protons plus 1 (one).

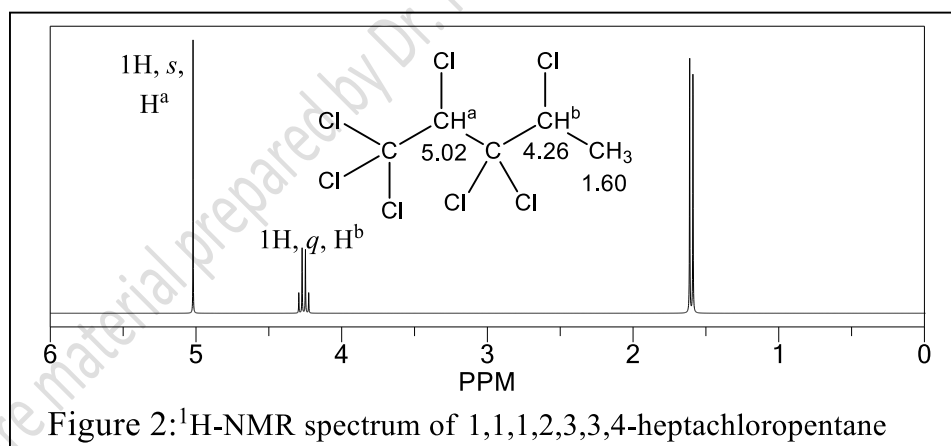
As a generalization, it can be said that if a proton (or protons) is coupled with  $n$  other *equivalent* protons, then it will give rise to  $(n + 1)$  peaks. Thus in an ethyl group, the methylene protons are coupled to three adjacent equivalent protons, and hence their resonance is split into  $(3 + 1) = 4$  lines. The methyl protons are coupled to the two equivalent methylene protons, and their resonance is, therefore, split into  $(2 + 1) = 3$  lines.

A wider generalization would be  $S = 2nI + 1$  where  $S$  is the number of lines formed by coupling, i.e., multiplicity,  $n$  is the number of equivalent neighbouring nuclei which are causing the coupling, and  $I$  is the spin quantum number of the nuclei causing the coupling. This generalization is correct only when the coupled nuclei have a spin of  $1/2$ .

Thus in considering the multiplicity of the  $\text{CH}_2$  protons in the  $-\text{CH}_2-\text{CH}_3$  group,  $n$  will refer to the number of protons with which the  $\text{CH}_2$  protons are coupled, which in this case is three, whereas  $I$  will refer to the spin quantum number of the nuclei with which the  $\text{CH}_2$  protons are coupled, which in this case is  $1/2$ .

### Spin-Spin Coupling

It is to be noted that area under a one-proton signal is always the same whether it is a singlet, doublet, triplet, quartet or a multiplet. This statement is true in all cases with any fixed number of proton/s forming the signal. The spectrum in Figure 2 shows two one-proton signals, more downfield proton appears as a *singlet*, but the other as a *quartet*, though the area/integration under each signal is the same.



### Spin-Spin Coupling/Spin-Spin Splitting

The following questions need to be considered to understand the spin-spin coupling phenomenon between the protons.

- Why does the multiplicity arise?
- Why the spacings between the lines in a multiplet are equal?
- What is the implication of the spacing?

Splitting of the spectral lines arises because of a *coupling* interaction between the neighbouring protons attached to the same carbon or to adjacent carbon atoms, and is

related to the number of possible spin orientations that these neighbours can adopt. The phenomenon is called either *spin-spin splitting* or *spin-spin coupling*.

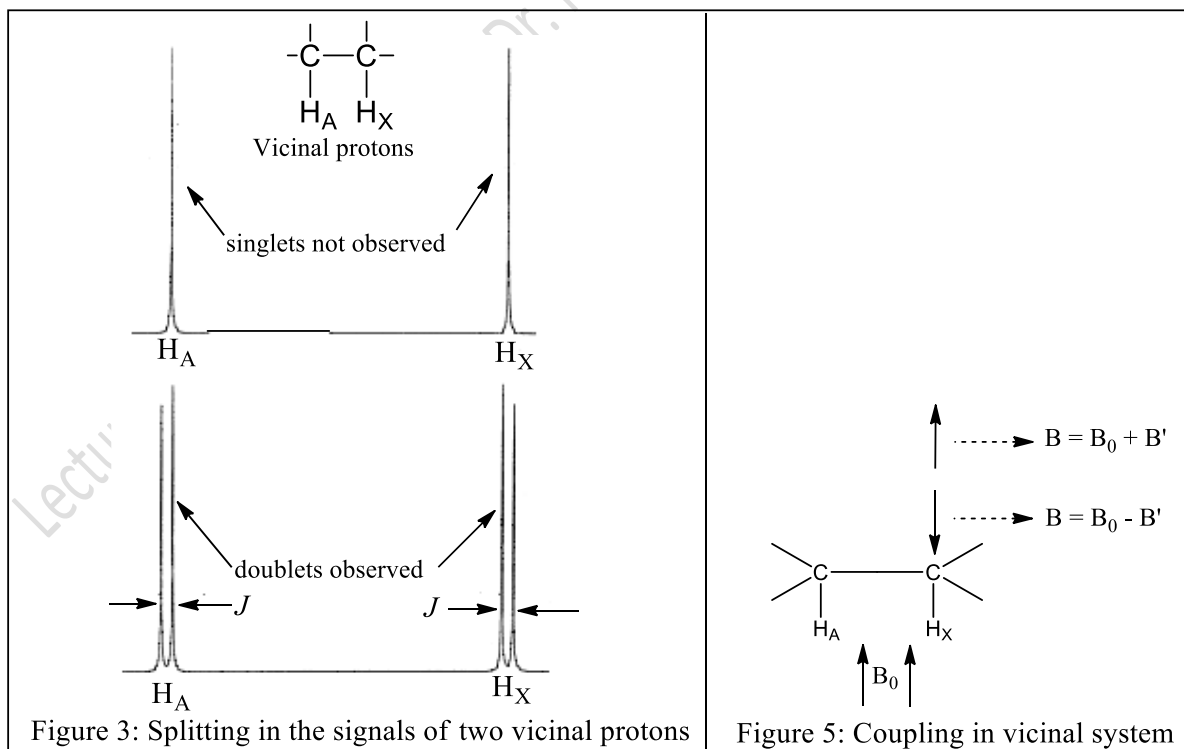
### Theory of Spin-Spin Splitting

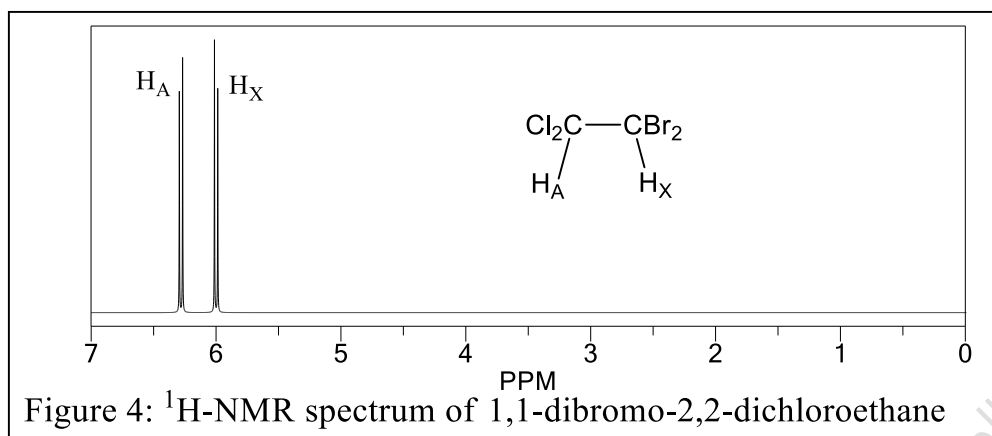
The multiplicity of the signal arises due to the actual magnetic field of a proton is modified by the instantaneous spin arrangement, either parallel or antiparallel, of the neighbouring proton and their attainment magnetic fields which are transmitted through the bonded electrons.

The diagram in Figure 3 represents a molecule containing two vicinal nonequivalent protons ( $H_A$  and  $H_X$ ) similar to the protons in 1,1-dibromo-2,2-dichloroethane. These protons with different magnetic environments come to resonance at different positions in its  $^1\text{H-NMR}$  spectrum (Figure 4). They do not give rise to single peaks (singlets) but doublets. The separation between the lines of each doublet is equal; this spacing is called the *coupling constant*,  $J$ .

### Why does the signal for proton A split into a doublet?

$H_X$  can exist in two possible spin orientations, one having spin parallel and another antiparallel to the external magnetic field as shown in Figure 5. There will be the generation of two local magnetic fields due to these two possible spin orientations.





A simplistic explanation is that the resonance position for proton A depends on its total magnetic environment; part of its magnetic environment is the nearby proton X, which is itself magnetic, and proton X can have its nuclear magnet either aligned with proton A or opposed to proton A. Thus, proton X can either increase the net magnetic field experienced by proton A (X aligned) or decrease it (X opposed); in fact, it does both. The two spin orientations of proton X create two different magnetic fields around proton A; in roughly half of the molecules the spin orientation of proton X creates a shielding field around proton A, and in the other half a deshielding field. Therefore, proton A comes to resonance, not once, but twice, and proton A gives rise to a doublet.

Similarly, proton A is a magnet having two spin orientations with respect to proton X, and therefore, proton A creates two magnetic fields around proton X. Consequently, Proton X comes to resonance twice in the NMR spectrum. This mutual magnetic influence between protons A and X is not transmitted through space, but via the bonded electrons in the intervening bonds.

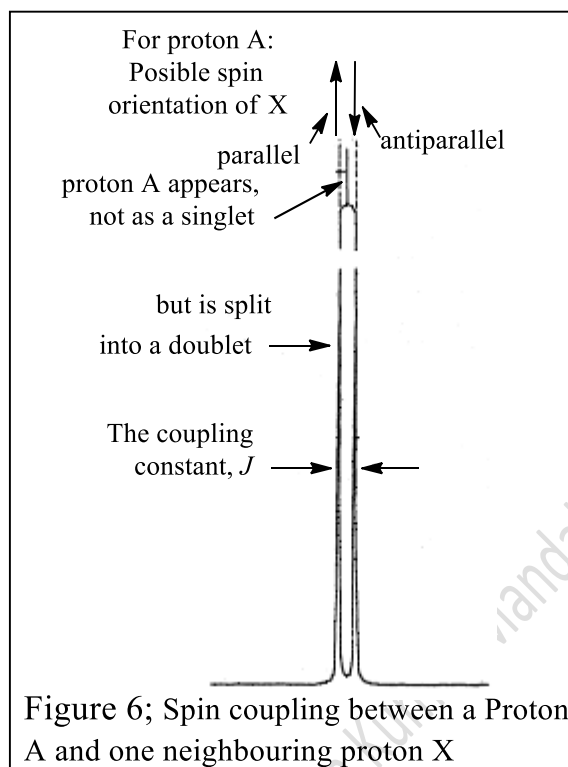
The nuclear spin of proton A couples with the electron spin of the  $\text{C-H}_A$  bonding electrons; these, in turn, couple with the  $\text{C-C}$  bonding electrons and then with the  $\text{C-H}_X$  bonding electrons. The coupling is eventually transmitted to the spin of the  $\text{H}_X$  nucleus. This *electron-coupled spin-spin* interaction operates strongly through one bond or two bonds, and weakly through three or more bonds.

The possible spin orientations of coupling protons can be represented as in Figure 6. Proton A can 'see' proton X as aligned (parallel  $\uparrow$ ) or opposed (antiparallel  $\downarrow$ ). These two spin orientations correspond effectively to two different magnetic fields. Therefore, proton A comes to resonance twice.

### Theory of Spin-Spin Splitting (AX spectrum)

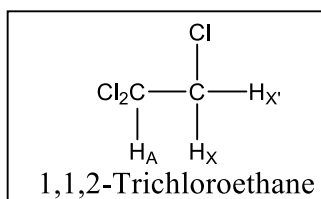
The same argument explains why proton X appears as a doublet. The proton A and proton X of 1,1-dibromo-2,2-dichloroethane give rise to this characteristic pair of doublets, caused by two protons undergoing spin coupling; such a spectrum is called an AX spectrum. Since the

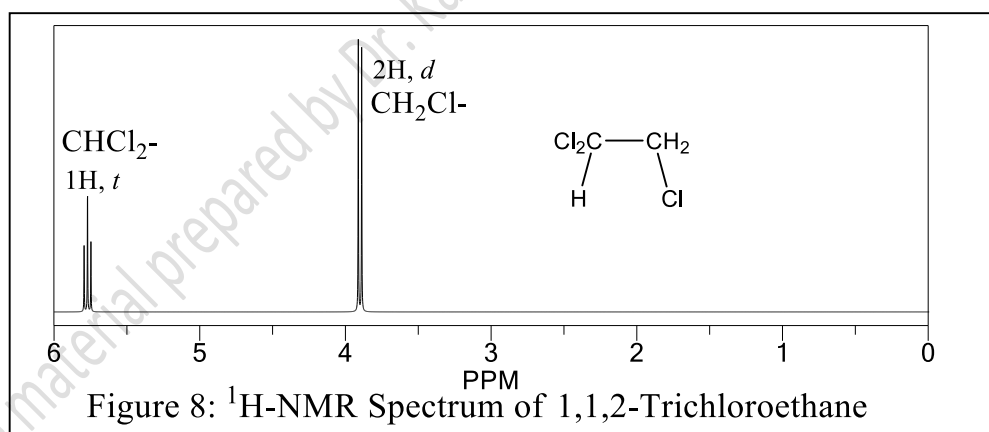
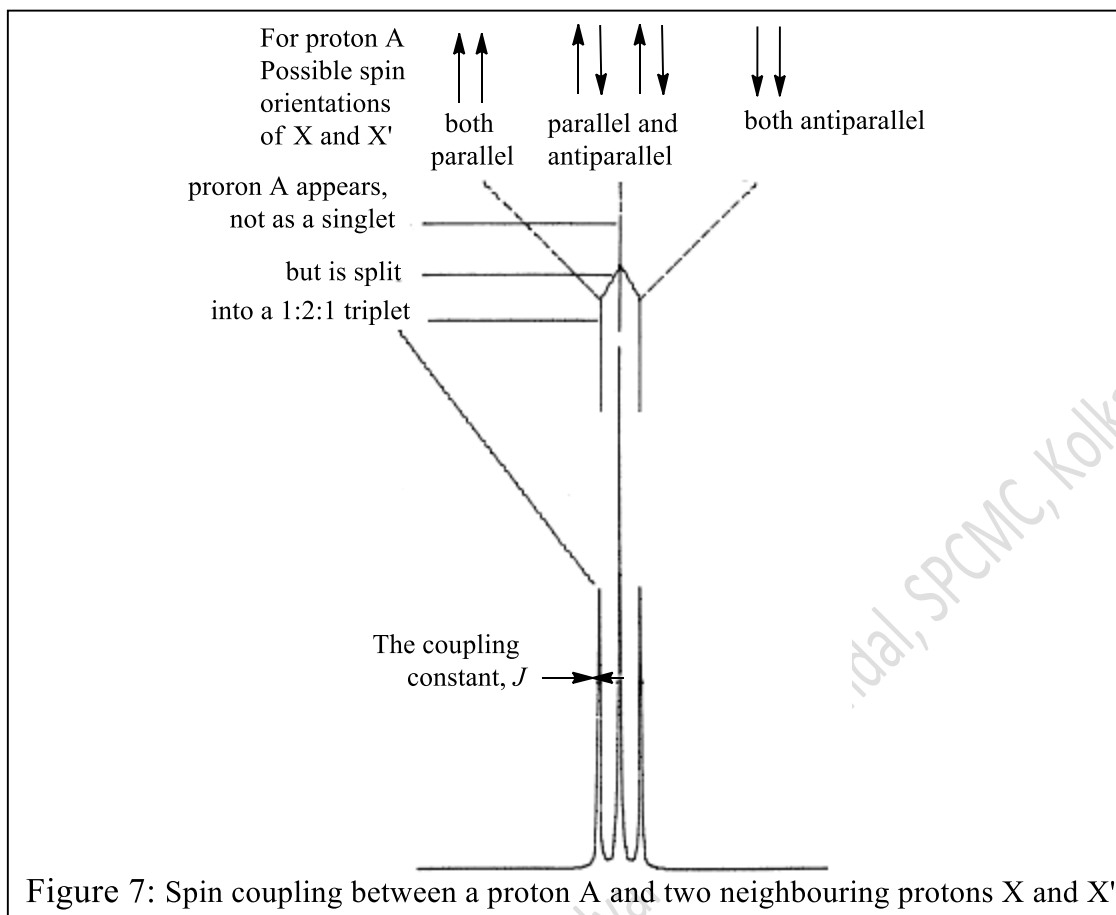
probability of the two spin orientations of protons A and X arising is equal in molecules throughout the sample, the two lines in each doublet are of equal intensity.



### Theory of Spin-Spin Splitting ( $AX_2$ spectrum)

Figure 7 represents the coupling that arises in the triplet signal in the  $^1\text{H-NMR}$  spectrum of 1,1,2-trichloroethane as shown in Figure 8.





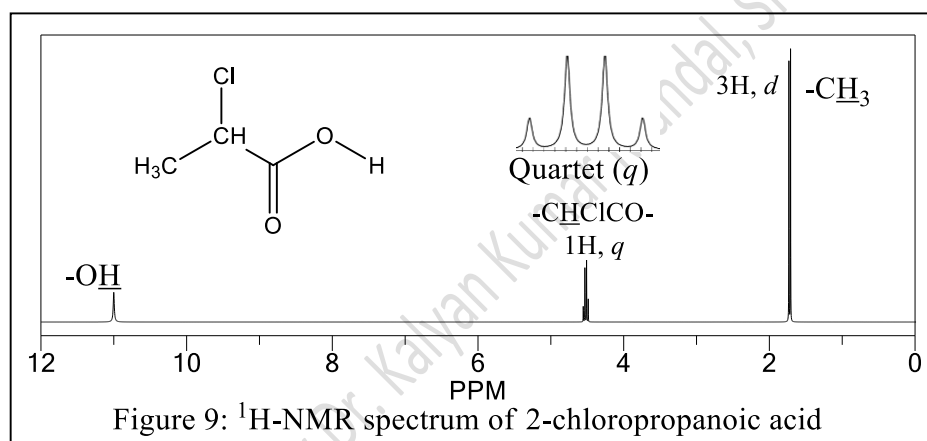
When proton A 'sees' the two neighbouring protons X and X', proton A can 'see' three different possible combinations of spin: (i) the nuclear spins of H<sub>X</sub> and H<sub>X'</sub> can both be parallel to H<sub>A</sub> (↑↑); (ii) both can be antiparallel to H<sub>A</sub> (↓↓); (iii) one can be parallel and the other antiparallel, and this can arise in two possible ways—H<sub>X</sub> parallel with H<sub>X'</sub> antiparallel (↑↓) or H<sub>X</sub> antiparallel with H<sub>X'</sub> parallel (↓↑).

Thus, three distinct energy situations, (i), (ii) and (iii), are created, and therefore, proton A gives rise to a triplet. The probability of the first two energy states arising is equal, but since the third state can arise in two different ways, it is twice as likely to arise; the intensity of the signal associated with this state is twice that of the lines associated with the first two states.

It can be seen in the spectrum of 1,1,2-trichloroethane that the relative line intensities in the triplet are 1:2:1. The spectrum of 1,1,2-trichloroethane, consisting of the characteristic doublet and triplet of two protons coupling with one proton, can be called an  $AX_2$  spectrum. The relative line intensities predicted by the above spin coupling mechanism are 1:1 in doublets and 1:2:1 in triplets.

### Theory of Spin-Spin Splitting ( $AX_3$ spectrum)

The spectrum of 2-chloropropanoic acid (Figure 9) contains a doublet and a quartet ( $J$ , 8 Hz), corresponding to the coupling of one proton with three neighbouring protons; this is an  $AX_3$  spectrum. The methyl protons have one neighbouring proton, and therefore, appear as a doublet. The methine proton has three neighbours, on the methyl group, and therefore  $(n + 1)$  is 4.



For this methine proton, the spin orientations of the methyl protons can be grouped together in various ways, and four arrangements are possible: (i) the methine proton can 'see' all three spins of the methyl protons parallel ( $\uparrow\uparrow\uparrow$ ); (ii) alternatively, two spins may be parallel with one antiparallel (and there are three ways in which this can arise-  $\uparrow\uparrow\downarrow$  or  $\uparrow\downarrow\uparrow$  or  $\downarrow\uparrow\uparrow$ ); (iii) then two spins can be antiparallel with one parallel (arising in three ways-  $\downarrow\downarrow\uparrow$  or  $\downarrow\uparrow\downarrow$  or  $\uparrow\downarrow\downarrow$ ); (iv) lastly, all three spins can be antiparallel ( $\downarrow\downarrow\downarrow$ ).

Four different energy combinations are produced; therefore, the methine proton comes to resonance four times, appearing as a *quartet*. The relative probabilities of these states arising are in the ratio 1:3:3:1 (a pattern of an expanded triplet is shown in Figure 9, and the line intensities in the quartet have the same ratio).

### Multiplicity of a Signal: Line Intensities

A general prediction for the intensities of the multiplets can also be made. They are related to the coefficients of the binomial expansion  $(a + b)^n$  where  $n$  is related to the number of neighbouring proton, and is applicable to any value of  $n$ . When a proton or group of protons has one neighbouring proton, then  $n = 1$ , i.e.,  $(a + b)^1 = a + b = 1a + 1b$ , the ratio of the



coefficients is 1:1. When  $n = 2$ , i.e.,  $(a + b)^2 = a^2 + 2ab + b^2$ , the ratio of the coefficients is 1:2:1. When  $n = 3$ , i.e.,  $(a + b)^3 = a^3 + 3a^2b + 3ab^2 + b^3$ , the ratio of the coefficients is 1:3:3:1. These ratios, (1:1, 1:2:1, and 1:3:3:1 for  $n = 1, 2$ , and 3) are exactly the same with the ratio of the line intensities of a doublet, triplet, and a quartet, respectively.

### Line Intensities: Pascal's Triangle

The theoretical line intensity ratios of multiplets derived from the ' $n + 1$ ' Rule can be easily verified by following the entries in the mathematical mnemonic device called Pascal's triangle (Figure 10). Each entry in the triangle is the sum of the two entries above it and to its immediate left and right. The intensities of the outer peaks of a multiplet such as a *septet* are so small compared to the inner peaks that they are often obscured in the baseline of the spectrum.

1								Singlet						
	1	1						Doublet						
		1	2	1				Triplet						
			1	3	3	1		Quartet						
				1	4	6	4	1	Quintet					
					1	5	10	10	5	1	Sextet			
							1	6	15	20	15	6	1	Septet

Figure 10: Pascal's Triangle

### Coupling Constant, $J$

The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called coupling constant. This separation is a direct measure of the effectiveness of the electron coupled spin-spin interaction. The value of the coupling constant is independent of the strength of the applied magnetic field. It is measured in Hertz (Hz). It is denoted by the latter  $J$ .

The coupling constant,  $J$ , can have positive or negative values, but the sign of  $J$  cannot be directly extracted by observation. The number of bonds intervening between the coupling nuclei is important, since the coupling is transmitted via the electrons of these bonds.

It is a convenient notation to indicate this number as a superscript to the symbol for the coupling constant. Direct coupling as in the coupling of a proton with an attached carbon-13 nucleus, ( $^{13}\text{C}$ - $^1\text{H}$ ) is a one-bond coupling,  $^1J$ . The coupling between protons on a  $\text{CH}_2$  group is symbolized by  $^2J$ ; that between protons on adjacent carbons as  $^3J$ ; and so on.

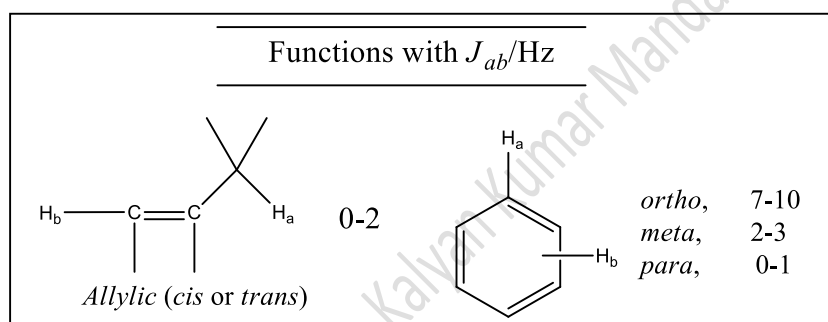
*Geminal coupling*, involving protons on  $-\text{CH}_2-$  groups, is strong,  $^2J$  being typically 12-18 Hz, but it will only be observed where the *geminal* protons have different chemical shift positions.

*Vicinal coupling* (three bonds separating the protons) varies from  $^3J = 0$  to  $^3J = 18$  Hz in rigid systems, but in freely rotating carbon chains (alkyl groups) it is usually around 8 Hz.

*Trans coupling* in alkenes ( $J$ , 13-18 Hz) is stronger than *cis* coupling ( $J$ , 10-12 Hz). Typical values, 16 Hz and 8 Hz, respectively.

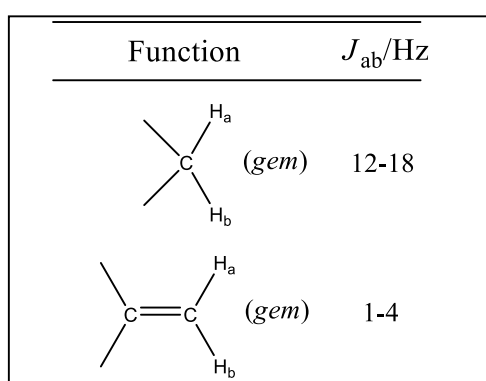
*Allylic coupling*, as in allyl chloride, is the four-bond coupling to be met in nonaromatic molecules and is very small ( $^4J$ , 0-2 Hz). The analogous coupling in aromatic systems (for example, between the methyl protons and the *ortho* protons in the ring) is also very small.

*Aromatic coupling* depends on whether the coupling protons are *ortho*, *meta* or *para* to each other, and in simple cases the coupling constant is definitive in deciding the orientation; thus,  $^3J_{ortho}$ , 7-10 Hz;  $^4J_{meta}$ , 2-3 Hz;  $^5J_{para}$ , 0-1 Hz.



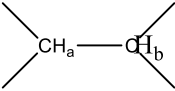
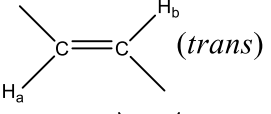
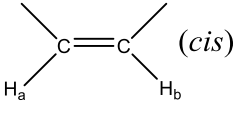
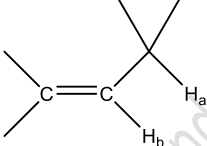
### Factors Influencing *Geminal* Coupling

The electronegativity of an attached substituent alters the values of *geminal* (*gem*) coupling. In groups such as  $-\text{CH}_2-\text{X}$  the *gem* coupling will range from 12 Hz to 9 Hz as the electronegativity of X is increased. These couplings can be measured only when the two *geminal* protons will have different  $\delta$  values, i.e., when they are diastereotopic. The magnitude of  $J_{gem}$  also varies with the C-C-C bond angle. *Geminal* coupling constant will have greatest magnitude (10-14 Hz) in the strain-free cyclohexanes and cyclopentanes. With increasing angular strain the value of  $J_{gem}$  drops.



## Factors Influencing Vicinal Coupling

The electronegativity of attached substituents alters the value of *vicinal* (*vic*) coupling, as it does that of *geminal* coupling. The more electronegative the substituent the smaller the value of  $J_{vic}$ , so that in unhindered alkanes the value is = 8 Hz, and in halogeno ethanes it is lowered to 6-7 Hz. The most important factor that influences  $J_{vic}$  is the dihedral angle,  $\phi$ , between the two vicinal C-H bonds. The dependence of  $J_{vic}$  with dihedral angle ( $\phi$ ) can be obtained qualitatively from Karplus equations:

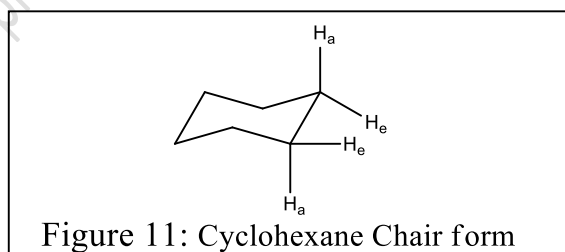
	Function	$J_{ab}/\text{Hz}$
	6-8	 13-18
	10-12	 4-10

$$\phi \text{ between } 0^\circ \text{ and } 90^\circ: J_{vic} = 8.5 \cos^2 \phi - 0.28$$

$$\phi \text{ between } 90^\circ \text{ and } 180^\circ: J_{vic} = 9.5 \cos^2 \phi - 0.28$$

To summarize the Karplus rules, the largest *vicinal* couplings arise with protons in the *trans* coplanar positions ( $\phi = 180^\circ$ ). *Vicinal* couplings for *cis* coplanar protons are almost as large ( $\phi = 0^\circ$ ). Very small couplings arise between protons at  $90^\circ$  to each other. Karplus equation can be applied successfully for the protons in chair cyclohexanes particularly in case of rigid systems as shown in Figure 11; *diaxial* protons have coupling constants around 8-13 Hz and this collates with their  $180^\circ$  orientation.

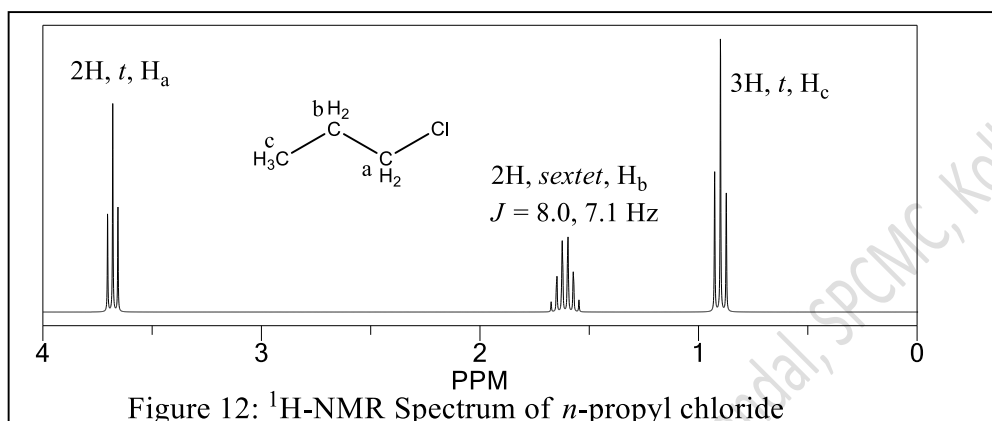
The *diequatorial* protons, or those with *axial/equatorial* relationship, have coupling constants around 2-5 Hz, corresponding to about  $60^\circ$  orientation.



## Splitting of Multiplet Signals

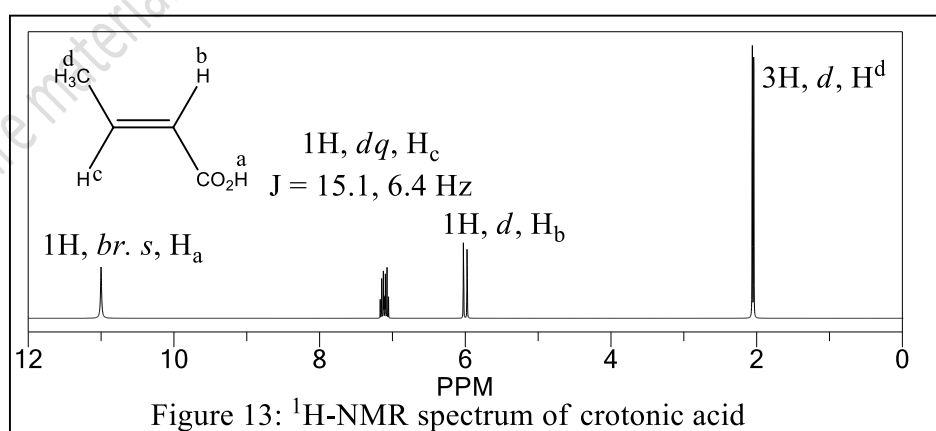
If the protons responsible for spin-spin coupling are not in exactly similar environment, the number of lines for a particular multiplet will be equal to  $(n_1 + 1)(n_2 + 1)(n_3 + 1) \dots$  where  $n_1$ ,  $n_2$ , and  $n_3$  are the number of protons in different environments. A few examples are listed below:

**Example-1:** In *n*-propyl chloride,  $\text{H}^{\text{c}}_3\text{C}-\text{CH}^{\text{b}}_2-\text{CH}^{\text{a}}_2-\text{Cl}$ ,  $\text{H}^{\text{a}}$  and  $\text{H}^{\text{c}}$  atoms are nonequivalent (with different chemical shifts) and thus, will influence the central methylene protons ( $\text{H}^{\text{b}}$ ) differently. Thus, the signal for central methylene protons ( $\text{H}^{\text{b}}$ ) is expected to be a multiplet consisting of 12 lines ( $n_1 + 1 = 2 + 1 = 3$ ;  $n_2 + 1 = 3 + 1 = 4$ ). But in actual practice, a multiplet consisting of 6 lines (*sextet*) is observed in the  $^1\text{H}$ -NMR spectrum (Figure 12) of *n*-propyl chloride.



This is because, though the protons  $\text{H}^{\text{a}}$  and  $\text{H}^{\text{c}}$  are nonequivalent, the coupling constant values,  $J_{\text{ab}}$  and  $J_{\text{bc}}$ , are close enough ( $J_{\text{ab}} = 7.1$  Hz and  $J_{\text{bc}} = 8.0$  Hz). Therefore, under the influence of five-adjacent protons, the  $\text{H}^{\text{b}}$  signal will be split into a *sextet* ( $n = 2 + 3 = 5$ ;  $n + 1 = 5 + 1 = 6$  lines) with intensity of the lines 1:5:10:10:5:1. Since,  $J_{\text{ab}}$  and  $J_{\text{bc}}$  are not exactly equal, the line intensities will be slightly asymmetrical than the predicted shape.

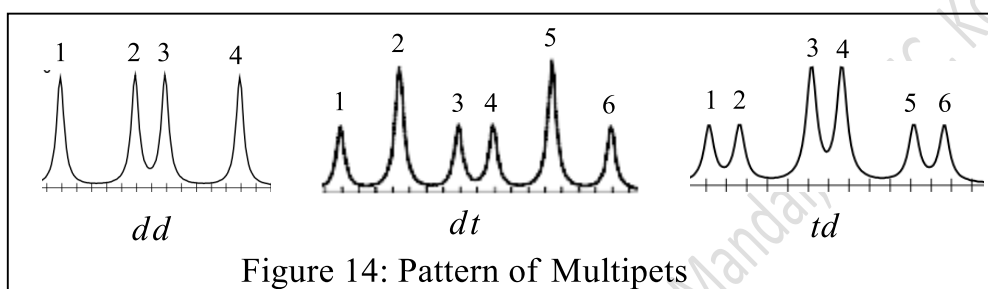
**Example-2:** The olefinic proton,  $\text{H}^{\text{c}}$  in crotonic acid (Figure 13) interacts with the other olefinic proton,  $\text{H}^{\text{b}}$  and also with the methyl protons ( $\text{H}^{\text{d}}$ ). These protons are nonequivalent, and also the two corresponding coupling constants are significantly different,  $J_{\text{bc}} = 15.1$  Hz and  $J_{\text{cd}} = 6.4$  Hz. Therefore, the signal for  $\text{H}^{\text{c}}$  will appear as a multiplet consisting of 8 lines ( $n_1 + 1 = 2$  and  $n_2 + 1 = 4$ ). This type of multiplet is classified as doublet of quartets (dq).



### Meaning of $dd$ , $dt$ , $td$ , $dq$ , $qd$

$dd$ : doublet of doublets       $dt$ : doublet of triplets  
 $td$ : triplet of doublets       $dq$ : doublet of quartets  
 $qd$ : quartet of doublets

$dd$  (4 lines),  $dt$  (6 lines),  $td$  (6 lines),  $dq$  (8 lines),  $qd$  (8 lines), etc., are the multiplets such that the biggest coupling constant determines the “first name” of the multiplet and the smallest coupling constant determine the “last name”. In this system of nomenclature, a doublet of triplets ( $dt$ ) is six-line pattern with one large coupling and two equal small couplings. Few patterns of multiplets are shown in Figure 14.



Lecture material prepared by Dr. Kalyan Kumar Mandal, Kolkata