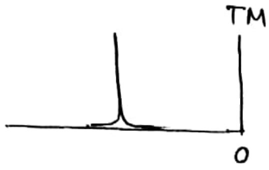
Spin - Spin Coupling — Spin - Spin Splitting.

i) The splitting of NMR signals in proton NMR spectra

CH_3COCH_3 :

Fig 1:



CH_3CHO :

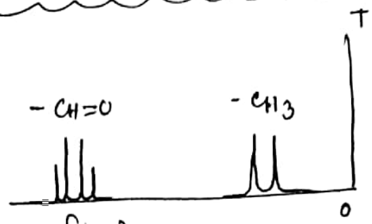


Fig 2

$ClCH_2CHO$:

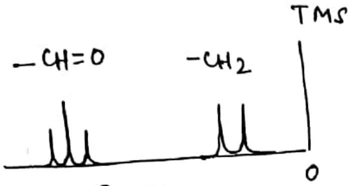


Fig 3

Cl_2CHCHO :

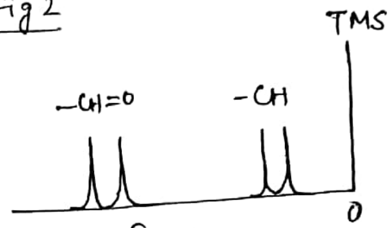


Fig 4

Cl_3CCHO

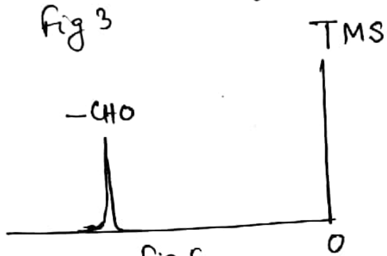


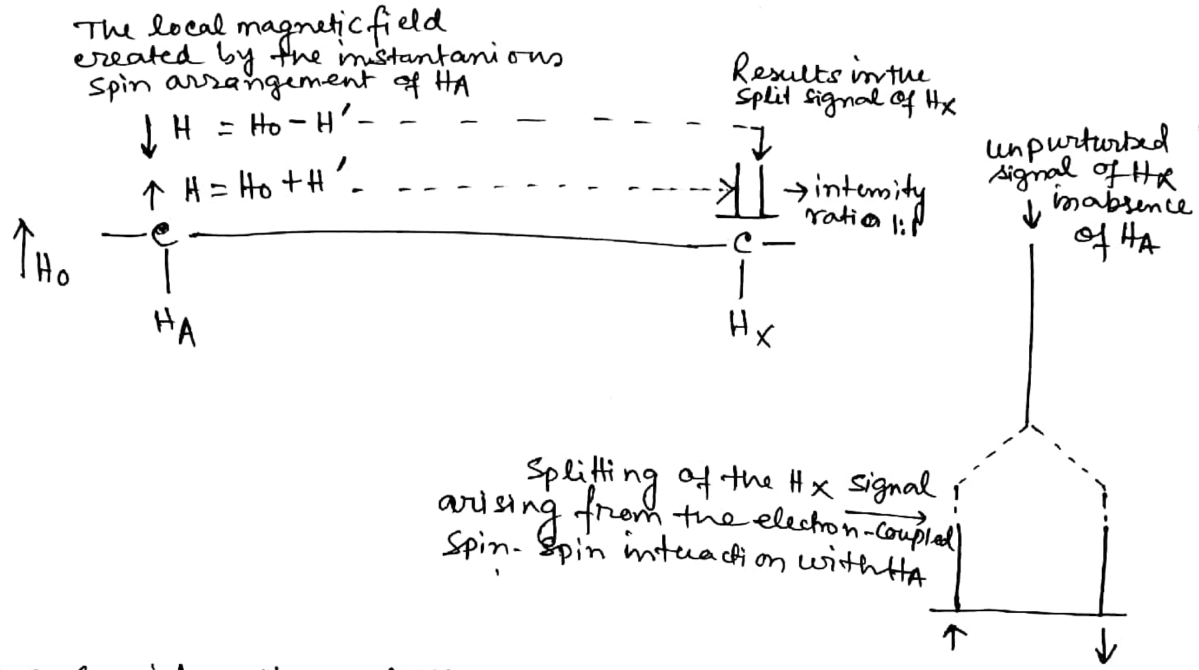
Fig 5

[The number of lines (multiplicity) observed in the NMR signal for a group of protons is not related to the number of protons in that group; the multiplicity of lines is related to the number of protons in neighbouring group.]

- For example, in CH_3CHO, −CHO protons in Fig 1 have three neighbouring protons & the −CHO proton appears as four-line signal. Again −CH_3 protons of CH_3CHO have one neighbouring proton (the −CHO proton) and the signal is split into two line signal.
- Again in Cl−C(H)(H)−C(=O)−H, the −CHO proton in Fig 2 have two neighbouring H protons (−CH_2) & the −CHO proton appear as three line signal. Again −CH_2Cl protons of CH_2−CHO have one neighbouring proton (the −CHO proton) and the signal is split into two line signals.
- **(n+1) rule** : The simple rule is: to find the multiplicity of the signal from a group of protons, count the number of neighbours (n) and add 1.
- Splitting of the spectral lines arises because of coupling interaction between neighbouring protons, and is related to the number of possible spin orientations that these neighbors can adopt. The phenomenon is called spin-spin splitting or spin-spin coupling.

Explanation for the multiplicity of the signal of a proton or protons by an adjacent non-equivalent proton ~~or protons~~ or a group of protons.

(i) Multiplicity of the signal of proton(s) by one adjacent non-equivalent proton.



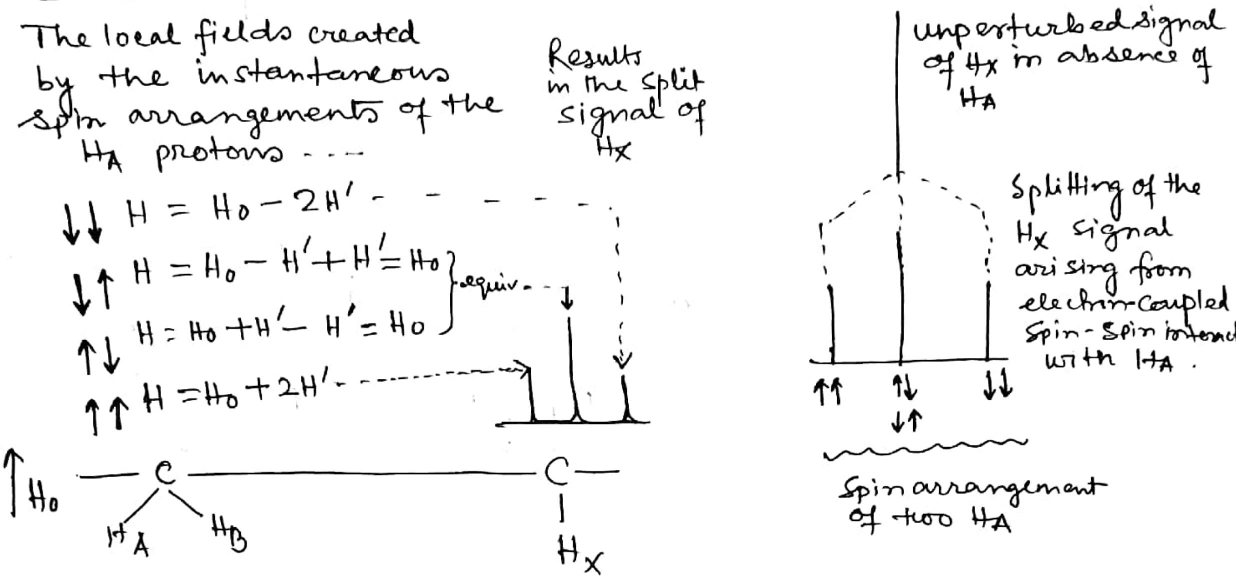
Let us consider the splitting of the H_X signal by H_A. The spin state of H_A may be either parallel (↑) or antiparallel (↓) with the external magnetic field. Accordingly, there will be two local fields $H = H_0 + H'$ and $H = H_0 - H'$. The magnetic effect of the two spin arrangements of H_A is transmitted through the bonded electrons to H_X. ~~when the~~ Thus proton H_A can either increase the net mag. field of H_X (when the spin of H_A is alligned) or decrease it (when the spin of H_A is opposed).

In fact it does both. Thus the two spin orientations of H_A create two different magnetic fields around H_X. Therefore H_X comes to resonance, not once, but twice, and so H_X gives rise to a doublet.

Since the probability of existence of each of the two spin arrangements of H_A is equal, it follows that the intensities of the two transitions will be in the ratio of 1:1 i.e the intensities of the component of doublet of H_X will be in the ratio of 1:1. The same explanation holds true for splitting of the H_A signal which also appears as a doublet in the ratio of 1:1.

The separation of the components of the doublet of H_X is same as that of the components of the doublet of H_A. This separation or spacing is called coupling constant or J.

(ii) Multiplicity of the signal of a proton or protons by two adjacent protons:



~~In the external magnetic field there can be eight possible instantaneous spin arrangements of the three H_A protons (i-viii)~~

The resonance position of H_X depends on its total magnetic environments part of which is due to the nearby H_A protons which are themselves magnetic. In the external magnetic fields there can be four possible instantaneous spin orientations of the two H_A protons w.r.t the external field: (i) both parallel (↑↑), (ii) one parallel and one antiparallel (↑↓) (iii) one antiparallel and one parallel (↓↑) & (iv) both antiparallel (↓↓). The spin arrangements (ii) and (iii) are equivalent and produces the same local mag. fields. Thus the two H_A protons would produce three different mag. fields, the effect of which are transmitted through the bonded electrons to H_X. Thus the spin orientations of two H_A protons would create three different magnetic fields around H_X. As a results H_X comes to resonance, not once, but thrice to give a triplet. Since the probability of the existence of each of the spin arrangement of H_A protons is equal and taking into account that (ii) and (iii) are equivalent, it follows that the intensities of the three transitions will be 1:2:1.

(iii) Multiplicity of the signals of a proton or a group of protons by three adjacent protons.

The local fields created by the instantaneous spin arrangement of the H_A protons

(viii) ↓↓↓ $H = H_0 - 3H'$

(vii) ↑↓↓ $H = H_0 + H' - 2H' = H_0 - H'$

(vi) ↓↑↓ $H = H_0 - H' + H' - H' = H_0 - H'$

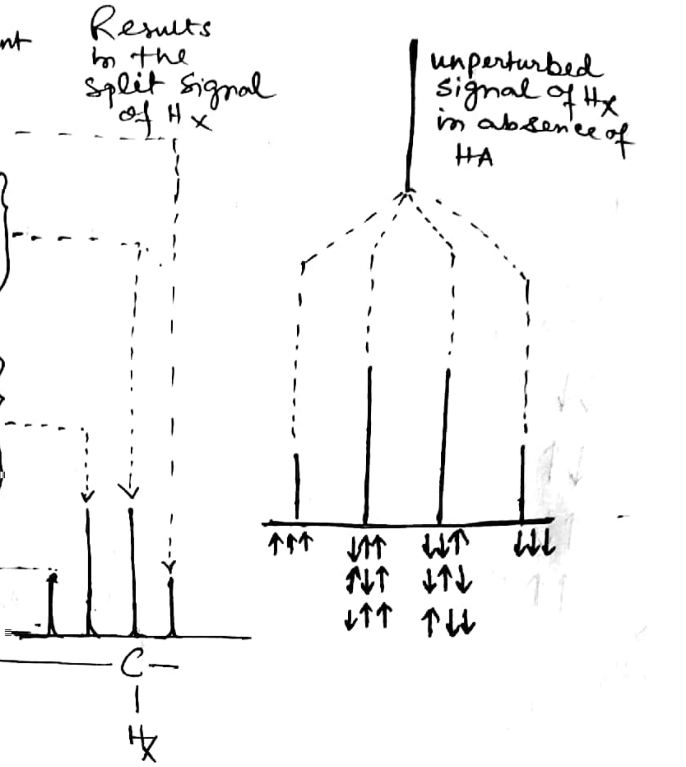
(v) ↓↓↑ $H = H_0 - 2H' + H' = H_0 - H'$

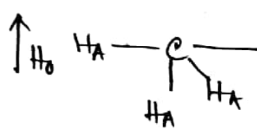
(iv) ↑↑↓ $H = H_0 + 2H' - H' = H_0 + H'$

(iii) ↑↓↑ $H = H_0 + H' - H' + H' = H_0 + H'$

(ii) ↓↑↑ $H = H_0 - H' + 2H' = H_0 + H'$

(i) ↑↑↑ $H = H_0 + 3H'$





In the external mag. field there can be eight possible instantaneous spin arrangements of the three H_A protons (i–viii) and the local mag. fields created these spin orientation are shown above. The spin arrangements (ii)–(iv) are equivalent and produce the same local mag. field. So also are the spin arrangement v–vii, each producing the same local magnetic fields. Thus there are four different local mag. fields created by the eight spin arrangements of the three H_A protons. These local mag. fields are transmitted through the bonded electrons to H_X, and produce four different magnetic fields around H_X.

As a result, H_X comes to resonance, not once, but four times to give a quartet, since the probability of the existence of each of the spin arrangement of H_A protons is equal and taking into consideration that (ii)—(iv) and (v)—(vii) are equivalent, it follows that the intensities of the four transitions will be 1:3:3:1.

General Rule for 1st order multiplicity.

If the chemical shift of the two interacting groups is large compared to the magnetude of splitting and if each nucleus in one group interacts with each and every nucleus in the 2nd group, the multiplet structure is governed by the following simple set of rules.

(i) Nuclei of equivalent group (eg CH_3-CH_3) do not interact with each other in such a way as to cause any observable multiplicity.

(ii) The multiplicity of the band arising from a group of equivalent nuclei is determined by the neighboring group of equivalent nuclei. A neighbouring group of equivalent nuclei causes a multiplicity which is given by $(2nI+1)$, where n is the number of equivalent nuclei of spin number I. For hydrogen having I is $\frac{1}{2}$, this becomes $(n+1)$. If there are more than two interacting groups, the multiplicity of one (say A) is given by $(2n_B I_B+1)(2n_C I_C+1)\ldots\ldots$ for hydrogen this becomes $(n_B+1)(n_C+1)\ldots\ldots$

(iii) The intensities of a multiplet is symmetric about the midpoint of the band. The relative intensities of the components of doublet, triplet and quartet are given by the co-efficients of the terms in the expansion of $(x+1)^n$.

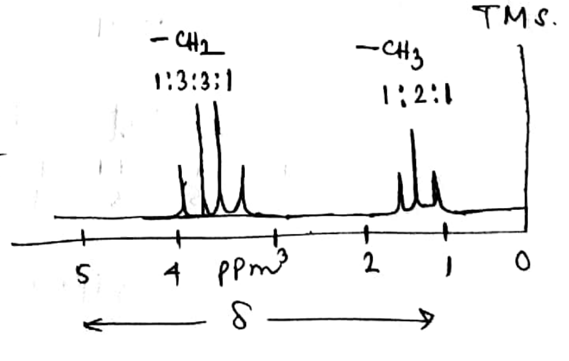
$$(x+1)^n = 1+nx+\frac{n(n-1)x^2}{2!}+\frac{n(n-1)(n-2)x^3}{3!}+\ldots\frac{n(n-1)(n-2)(n-r+1)x^r}{r!}$$

Thus, when $n=1$, the expression become $1+1.x$. The ratio of the coefficients, viz 1:1 gives the relative intensities of the components of a doublet.

① CH_3-CH_2-Cl

CH_3: δ 1.25; $(n+1)$, $n=2$ (2 neighbouring proton) $=(2+1)=3$ triplet

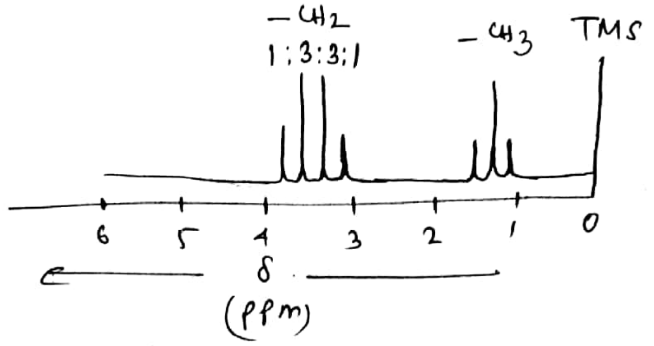
CH_2: δ 3.8-3.9; $(n+1)$ ($n=3$ as 3 neighbouring proton) $=(3+1)=4$ quartet



neighbouring proton = 3 ($-CH_3$)

$CH_3 - CH_2 - Br$

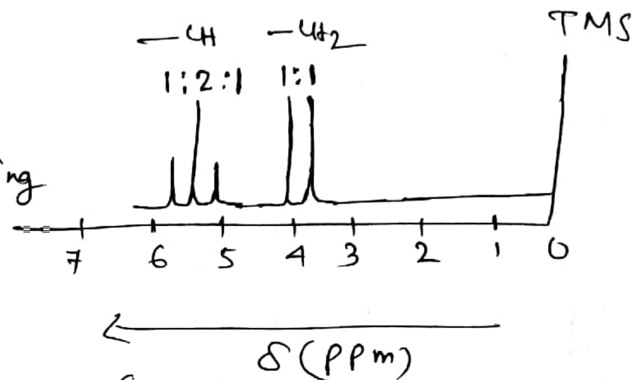
CH_3	CH_2
δ 1.2	δ 3.5
(t)	(q)
(n+1)	n+1
= 2+1	= 3+1
= 3	= 4



$Cl - CH_2 - CHCl_2$

δ 4 (d) as 1 neighbouring proton.

δ 5.8 (t) as 2 neighbouring proton ($-CH_2$)



Here two interacting group ($-CH_3$) & ($-OH$).

$CH_{3A} - CH_{2B} - OH_C$

CH_{3A}	CH_{2B}	OH_C
δ 1.07	δ 3.62	δ 5.28
(t)		(t)
(2+1) = 3		(2+1) = 3

CH_2: this protons are split into doublet of quartet.

$= (n_A+1)(n_C+1)$

$= (3+1)(1+1)$

$= 4 \times 2$

$= 8$

Therefore 8 lines are observed in its multiplet