Magnetic Resonance Spectroscopy - Theory
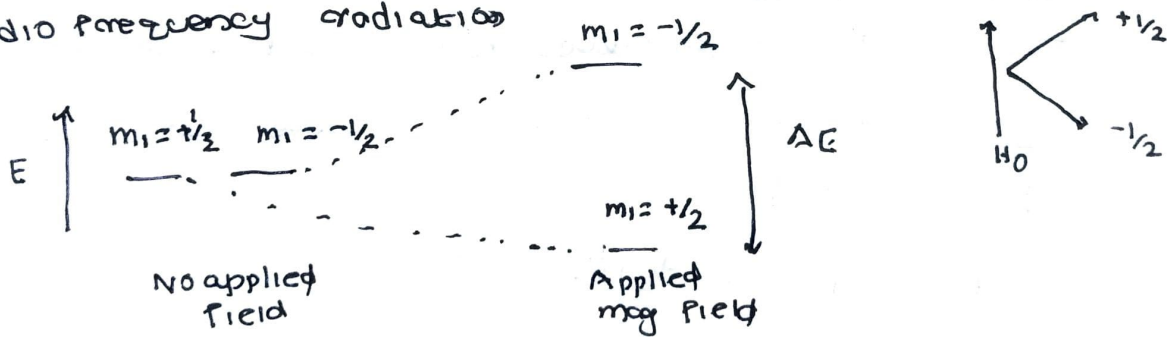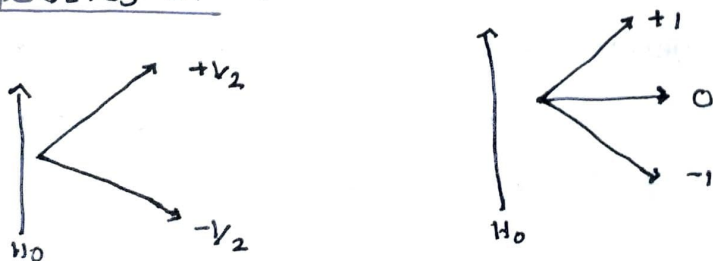
Protons and neutrons both have a spin quantum no of ½, and when the spins of all these particles are paired there will be no net spin and the nuclear spin quantum no I will be zero. when $I = ½$ there is one net unpaired spin and this unpaired spin imparts a nuclear magnetic moment, μ to the nucleus. The distribution of +ve charge in a nucleus of this type is spherical. ($eQ = 0$). NMR spectroscopy is often concerned with nuclei of spin $I = ½$ and also can result from nuclei for which $I \geq 1$, but not obtained for $I = 0$.

Unpaired nuclear spin leads to a nuclear magnetic moment and the allowed orientations of the nuclear magnetic moment vector in a magnetic field are indicated by the nuclear spin angular momentum quantum number, m_I. This quantum number takes on values $I, I-1 \cdots (-I+1), -I$. when $I = ½$ $m_I = ±½$ ($+½$ - alignment with applied field, $-½$ - oppose to the field when $I = 1$ $m_I = 1, 0, -1$ (op with, Perpendicular, opposed to the field). In the absence of external mag field all orientations of the nuclear magnetic moment are degenerate, however in the presence of ext. mag field this degeneracy will be removed and transition occur b/w these states by absorbing radio frequency radiation

The Quantum Mechanical Description of the NMR experiment

Properties of $\vec{I}$

Quantized orientation of m_I for $I = ½$ and $I = 1$

Quantum mechanics shows that for $I = \frac{1}{2}$ there are two allowed orientations of the spin angular momentum vector in a magnetic field and indicates that there is necessary requirement to induce transition b/ween these 2 states by the application of an oscillating magnetic field with energies corresponding to r.f. radiation. The necessary direction for this field can be determined from a consideration of the spin angular momentum operators. The $\hat{I}^2$ operator has eigenvalues $I(I+1)$ (as in atoms where the orbital angular momentum operator $L^2 \psi = I(I+1) h^2 \psi$). Any one of the components of $\hat{I}$ (eg: $\hat{I}_z$) commutes with $\hat{I}^2$, so we can specify eigenvalues of both $\hat{I}^2$ and $\hat{I}_z$. The eigenvalues of $\hat{I}_z$ are given by $I, (I-1), \cdots -I$. In general, if two operators commute, then there exist simultaneous eigenfunctions of both operators for which eigenvalues can be specified.

$$\hat{I}^2 \hat{I}_z - \hat{I}_z \hat{I}^2 = 0 \quad \text{ie} \quad [\hat{I}^2, \hat{I}_z] = 0$$

Similar equations can be written for $\hat{I}_x$ and $\hat{I}_y$ ie

$$[\hat{I}^2, \hat{I}_x] = [\hat{I}^2, \hat{I}_y] = 0$$

However $\hat{I}_z$ does not commute with $\hat{I}_x$ or $\hat{I}_y$, eg:

$$\hat{I}_z \hat{I}_y - \hat{I}_y \hat{I}_z \neq 0$$

Eigenvalues for $\hat{I}^2$ exist and if we decide to specify eigenvalues for $\hat{I}_z$, then eigenvalues for $\hat{I}_x$ and $\hat{I}_y$ do not exist.

$$\hat{I}_z \alpha = (+\tfrac{1}{2}) \alpha \qquad \alpha, \beta - \text{Spin wave functions}$$

$$\hat{I}_z \beta = (-\tfrac{1}{2}) \beta$$

$$\hat{I}_x \alpha = (\tfrac{1}{2}) \beta \qquad \hat{I}_x \beta = (-\tfrac{1}{2}) \alpha$$

$$\hat{I}_y \alpha = (\tfrac{1}{2}) i\beta \qquad \hat{I}_y \beta = (-\tfrac{1}{2}) i\alpha$$

Thus $\hat{I}_z$ operator yields eigenvalues. Since operation on α gives back α and operation on β - gives β, but the $\hat{I}_x$ and $\hat{I}_y$ operators do not yield eigenvalues since operation on α produces β and operation on β yields α. The average value for the property of $\hat{I}_x$ or $\hat{I}_y$ is given by an equation

$$\frac{\int \psi^* \, op \, \psi \, d\tau}{\int \psi^2 \, d\tau}$$

Transition probabilities

If the alternating field applied is written in terms of amplitude H_x^0, we get a perturbing term in the Hamiltonian of the form of eq^n

$$\hat{H}_{pert} = -\gamma h \, H_x^0 \, \hat{I}_x \cos \omega t$$

The eq^n describing the probability of a transition in the nmr is given by

$$P = 8\pi \gamma_N^2 H_1^2 \, |\langle \psi^{ex} | \hat{I}_x | \psi \rangle|^2 \, g(\omega)$$

where $g(\omega)$ = General line shape function, which is an empirical function that describes how the absorption varies near resonance. In brief, simply placing a sample in a magnetic field, H_0 removes the degeneracy of the m_i states. Now a radio frequency source is needed to provide $h\nu$ to induce the transition. Absorption of energy occurs provided that the magnetic vector of the oscillating electromagnetic field, H_1 has a component perpendicular to the steady field H_0 of the magnet. Otherwise if H_1 is parallel to H_0, the oscillating field simply modulates the applied field, slightly changing the energy levels of the spin system, but no energy absorption occurs.

Chemical Shift — The shift of the resonance line of a given compd from that of standard reference sample is called chemical shift (δ) of the molecule. -In a typical NMR-spectrum, the magnetic field is plotted versus absorption. TMS which is unreactive and its resonance region which does not overlap the other resonances resonances of the molecules are typically used as reference compound, (usually in non aqueous solvents). In water due to its limited solubility, Salt of the anion $(CH_3)_3 Si \, CD_2 CD_2 COO^-$ are commonly used as reference material. Chemical shift δ is defined as

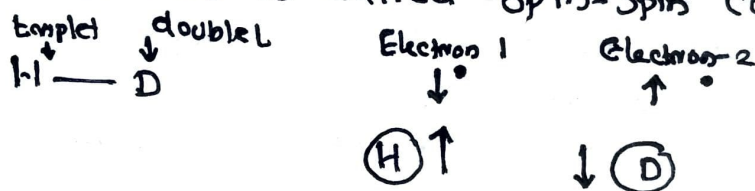$$\delta = \frac{\Delta \times 10^6 \, (Hz)}{\text{fixed frequency of the probe}, \nu_0 \, (MHz)} \quad ppm$$

The chemical shift of a solute molecule in a solvent will be influenced not only by shielding of electrons but also by the

Volume diamagnetic susceptibility of the solvent (diff diamagnetic susceptibility of molecules in different solvents). when the measurement are made by external standard method. So in this case the chemical shift value will be concentration dependent. However the contribution to the measured δ from the volume diamagnetic susceptibility of the solvent can be more easily minimized by using an internal standard. Under these conditions the standard is subjected to the same volume susceptibility as is the solute and the effects will tend to cancel when the difference Δ is calculated.

Spin-Spin Splitting

The coupling interaction between two or more protons/nuclei, most often through the bonds, results in splitting of the spectral lines. This is called Spin-Spin coupling.

triplet   doublet   Electron 1   Electron 2
H-l —— D

(H)↑   ↓(D)

Consider the simple HD molecule. Since the magnetic moment of proton and duetron are different, they show resonances at different magnetic fields. The spin of proton is $\frac{1}{2}$ and that of deuteron is one. The system has two electrons. The proton spin interacts with the spin of electron 1 and as a consequence, their spins will be antiparallel. This electron in turn interacts with electron 2, forcing its spin to be antiparallel with its spin. Electron 2 in turn interacts with the deuteron nucleus and as a consequence, their spins will be antiparallel. In other words, as a result of the interaction, via the electron cloud, if the spin of proton is 'up' the spin of the deuteron would be 'down'. This indirect interaction b/wn two nuclei via the electron cloud is termed as the 'indirect spin-spin interaction' or electron coupled spin-spin interaction. when

the proton spin interacts with the deuteron spin it 'sees' the three different orientations of the deuteron spin $(I=1, 2I+1=3)$. Hence the spectrum of proton splits into three components of equal intensity. In the same way, the deuteron spin 'sees' the two orientations of the proton spin via the electron cloud in the molecule Splitting deuteron spectrum in to 2 components. Similar effects are observed for other molecules also, and which is the basis of splitting of signals

① Quantum Mechanical Description of Coupling

AX System

Any molecule possessing two hydrogen atoms that are widely different chemical shifts and that couple together to give rise to a pair of doublets with all the four lines of equal intensity. Such a system is called an AX system. eg: $Cl_2C\text{—}CHO$. Here the system involves two protons at widely different. chemical shift (widely seperated letters of the alphabet). By convention the proton absorbing at a lower field is given the earlier letter of the alphabet.

AB System

An AB System consists of two mutually coupled nuclei A and B which are not coupled to any other protons and have the chemical shift difference $(\delta_A - \delta_B)$ comparable in magnitude to the coupling constant J_{AB}. As the chemical shift difference between interacting nuclei (Δv) approaches in magnitude to the value of the coupling constant blwn them, the simple splitting rules already considered is no longer apply. The pattern of splitting in the multiplet becomes distorted, extra lines appear in the spectrum and the bands are no longer symmetrical. Thus it is not possible to deduce chemical shift and coupling constant values by inspection. They can be obtained using the following prescriptions.

(1) Numbering the bands serially from 1 to 4, in order of increasing shielding, the coupling constant is given by
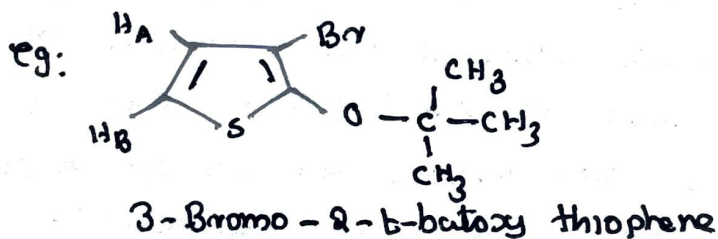
$$J_{AB} = \nu_1 - \nu_2 = \nu_3 - \nu_4$$

(2) The chemical shift is obtained as

$$\delta_A - \delta_B \;(\delta_{AB}) = \sqrt{(\nu_1 - \nu_4)(\nu_2 - \nu_3)}$$

(3) If I_x = intensity of line x then, the intensities are in the ratio

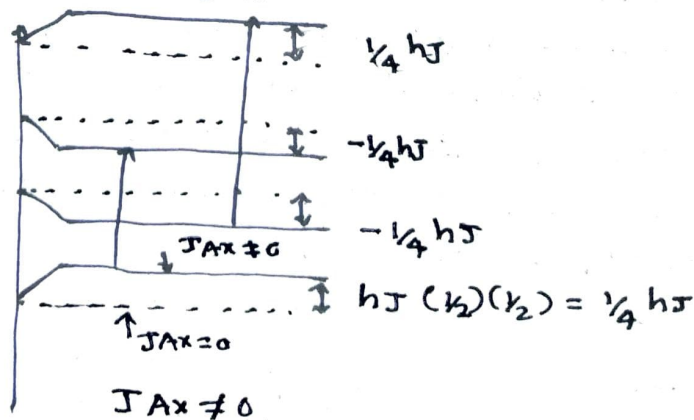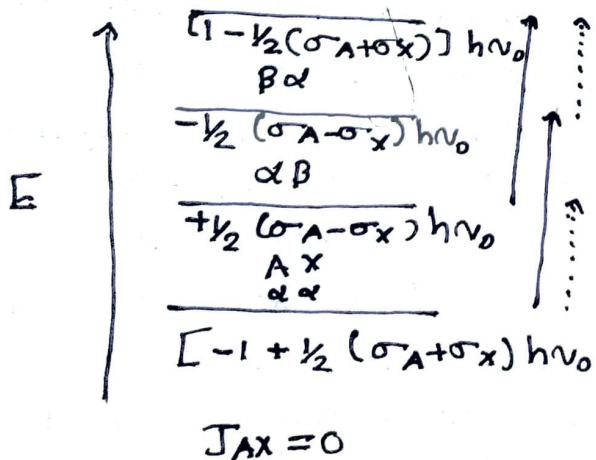$$\frac{I_3}{I_4} = \frac{I_2}{I_1} = \frac{(\nu_1 - \nu_4)}{(\nu_2 - \nu_3)}$$

Nuclei exhibiting these characteristics are said to be strongly coupled and are designated by adjacent letters in the alphabet. Two such nuclei constitute an AB system.

eg:

3-Bromo-2-t-butoxy thiophene

AX System

The energy of a System X_j (AX system) of X_j protons whose shift differences are larger than J is given by equation

$$E = -h \sum_j \nu_0 (1 - \sigma_j) m_j + h \sum_{j<k} J_{jk}\, m_j m_k \quad —①$$

Energies for the AX system in a magnetic field $[1(A) = \frac{1}{2}$, $1(x) = \frac{1}{2}]$.

When $J_{AX} = 0$, the energy levels for the $\overset{+\frac{1}{2}+\frac{1}{2}}{\alpha \alpha}$, $\overset{+\frac{1}{2}-\frac{1}{2}}{\alpha \beta}$, $\overset{-\frac{1}{2}+\frac{1}{2}}{\beta \alpha}$, $\overset{-\frac{1}{2}-\frac{1}{2}}{\beta \beta}$ nuclear spin configurations are given above. The A nuclear spin state is listed first and that of X nucleus listed as second

for eg: α, α $(A = +\frac{1}{2}$ $X = +\frac{1}{2})$

$$-h\left[(\nu_0 (1-\sigma_A)(\frac{1}{2}) + \nu_0 (1-\sigma_x) \frac{1}{2}\right] = \left[-1 + \frac{1}{2}(\sigma_A + \sigma_x)\right] h\nu_0 \text{①}.$$

The solid arrows indicate the transition for the A type nucleus and the dashed arrow for X nucleus. The selection rule is $\Delta m_1 = 1$. The two transitions of nucleus A are degenerate. So without any coupling single peak would be observed for A. Similarly a single peak is obtained for X.

When $J_{AX} \neq 0$, the the $J_{JK} \, m_j \, m_K$ term modify the energies, ie $\alpha\alpha$ energy is raised by $(\frac{1}{4})Jh$ and $\beta\alpha$ is lowered by $(\frac{1}{4})Jh$. Thus $\alpha\alpha \rightarrow \beta\alpha$ transition occurs at a frequency $J/2$ lower than the corresponding transition in the $J_{AX} = 0$, and $\alpha\beta \rightarrow \beta\beta$ transition is at a frequency $J/2$ higher than that of the $J_{AX} = 0$ transition. Thus the frequency separation b/wn the two peaks is equal to J in the $J_{AX} \neq 0$.

Eqn ① is first order solution of the chemical shift coupling constant problem. It applies only when the chemical shift difference Δ of the nuclei is large compared to their coupling constant J (usually $\Delta \sim 5J$)

AB System

Considered AB system for which $1(A) = \frac{1}{2}$ $1(B) = \frac{1}{2}$. We can solve the energies using equation

$$\int \psi^* \hat{H} \psi \, d\tau = \frac{E}{h} \int \psi^* \psi \, d\tau$$

$$\hat{H} = -\nu_0 (1-\sigma_A) \hat{I}_{ZA} - \nu_0 (1-\sigma_B) \hat{I}_{ZB} + J_{AB} \hat{I}_A \cdot \hat{I}_B$$

The so nuclear spin functions are $\phi_1 = |\alpha\alpha\rangle$, $\phi_2 = |\alpha\beta\rangle$
$\phi_3 = |\beta\alpha\rangle$ $\phi_4 = |\beta\beta\rangle$

The solution will give four energies in terms of frequencies.

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

$$\frac{E_2}{h} = -(1/4) J - C \quad\quad\quad -③$$

$$C = \frac{1}{2} (J^2 + A^2)^{1/2}$$

$$\frac{E_3}{h} = -(1/4) J + C$$

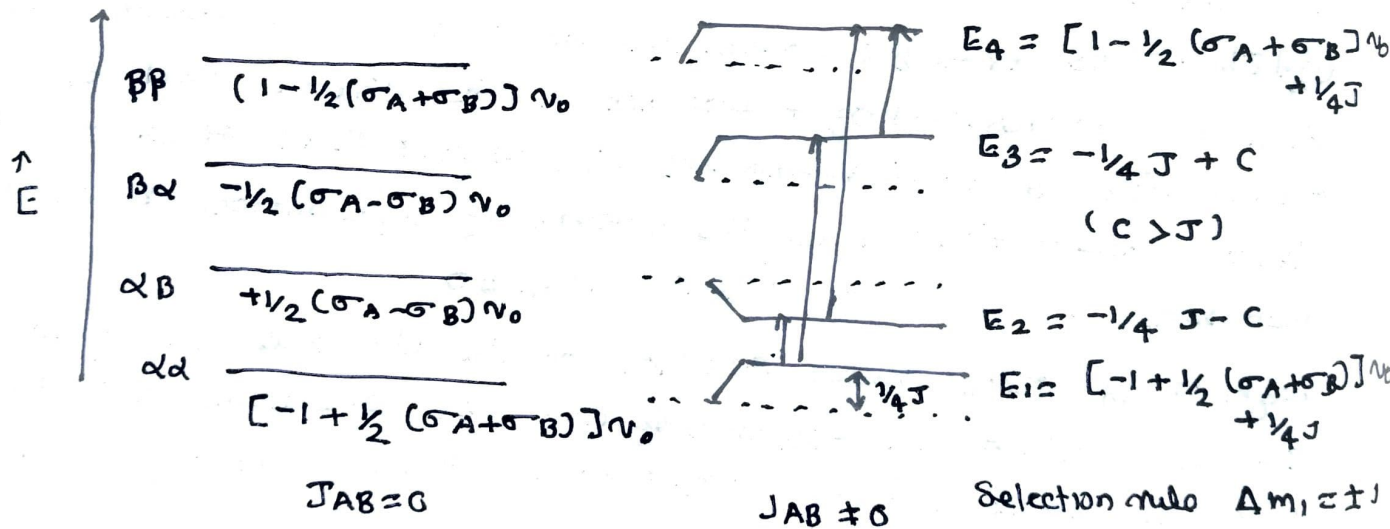$$\frac{E_4}{h} = \nu_0 \left[1 - (1/2) \sigma_A \right) - (1/2) \sigma_B \right] + J/4$$

The corresponding wave function are

$$\psi_1 = | \alpha\alpha \rangle$$
$$\psi_2 = \cos\omega | \alpha\beta \rangle - \sin\omega | \beta\alpha \rangle$$
$$\psi_3 = \sin\omega | \alpha\beta \rangle + \cos\omega | \beta\alpha \rangle$$
$$\psi_4 = | \beta\beta \rangle$$

$\beta\beta$	$[1 - 1/2 (\sigma_A + \sigma_B)] \nu_0$
$\beta\alpha$	$-1/2 (\sigma_A - \sigma_B) \nu_0$
$\alpha\beta$	$+1/2 (\sigma_A - \sigma_B) \nu_0$
$\alpha\alpha$	$[-1 + 1/2 (\sigma_A + \sigma_B)] \nu_0$

$J_{AB} = 0$

$$E_4 = [1 - 1/2 (\sigma_A + \sigma_B)] \nu_0 + 1/4 J$$

$$E_3 = -1/4 J + C \quad (C > J)$$

$$E_2 = -1/4 J - C$$

$$E_1 = [-1 + 1/2 (\sigma_A + \sigma_B)] \nu_0 + 1/4 J$$

$J_{AB} \neq 0$

Selection rule $\Delta m_i = \pm 1$

The second order energies (in frequency units) for an AB Spin System. (A) $J_{AB} = 0$ (B) $J_{AB} \neq 0$

When A and B have B have similar chemical shifts, all four transition will appear in a narrow region of the spectrum. The center of the spectrum is given by the average of the $E_1 \rightarrow E_2$ and $E_2 \rightarrow E_4$ transition energies or

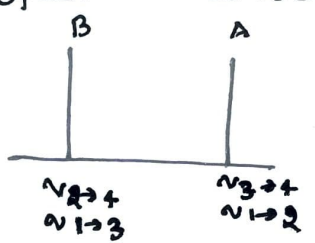$$(1/2) (E_2 - E_1 + E_4 - E_2) = \frac{E_4 - E_1}{2} = \nu_0 [1 - (1/2)\sigma_A - (1/2)\sigma_B]$$

AP

Effect of the relative magnitude of J and Δ on the Spectrum of an AB molecule

Transition	Separation from Center	Relative intensity
$1 \to 2$	$-(J/2)-c$	$1 - \sin 2\theta$
$1 \to 3$	$-(J/2)+c$	$1 + \sin 2\theta$
$2 \to 4$	$(J/2)+c$	$1 - \sin 2\theta$
$3 \to 4$	$(J/2)-c$	$1 + \sin 2\theta$

$$\sin 2\theta = J/2c \quad \text{and} \quad c = \tfrac{1}{2}(J^2 + \Delta^2)^{1/2}$$

AB Molecule

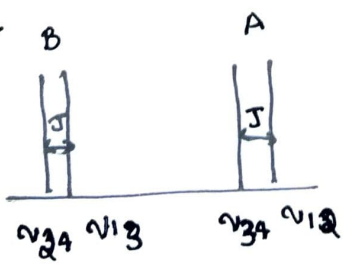**A.** $J=0$ and $\Delta \neq 0$

the $1 \to 2$ and $3 \to 4$ transitions are degenerate as are $1 \to 3$ and $2 \to 4$. The spectrum consist of two peaks one from A and one from B

$\nu_{2\to4}$
$\nu_{1\to3}$
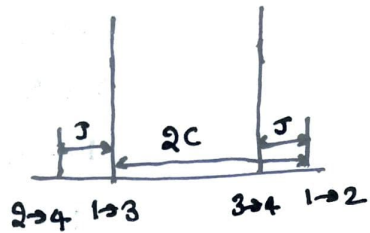
$\nu_{3\to4}$
$\nu_{1\to2}$

B. $J \neq 0$ $\Delta \neq 0$ but $J <<< \Delta$ - AX system

In this case $2\theta \to 0$ $(\tan 2\theta = J/\Delta)$, bec² Δ dominates c, then $\sin 2\theta = J/\Delta \approx 0$, then the intensities of all four transitions tend to become equal. The low field doublet is associated with nucleus B and the high field doublet with nucleus A. This is exactly what is predicted in the first order spectra and the doublet separation is simply J. In the real sense this corresponds to the AX case.
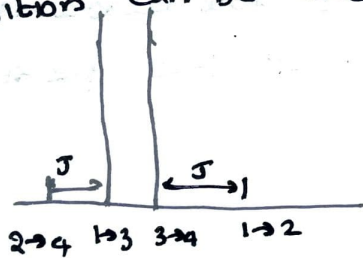

ν_{24} ν_{13}

ν_{34} ν_{12}

C. $\Delta \neq 0$, $J \neq 0$ but $J \approx \Delta$

when $J \approx A$ $\sin 2\theta$ is appreciable and positive. Therefore the $1 \to 3$ and $3 \to 4$ transitions will have equal intensities which are greater than those of $1 \to 2$ and $2 \to 4$. The separation b/w the outer pairs of lines is still equal to the coupling constants J and that b/w alternate line is $2C \cdot (A^2 + J^2)^{1/2}$

$2 \to 4$ $1 \to 3$ $3 \to 4$ $1 \to 2$

D. $J \neq 0$ A very small $(A < J)$

this is the case when σ_A and σ_B are almost equal, the value of $\sin 2\theta$ approaches unity and the $1 \to 2$ and $2 \to 4$ transition can be easily lost in base line noise

$2 \to 4$ $1 \to 3$ $3 \to 4$ $1 \to 2$

E. $J \neq 0$ but $\sigma_A = \sigma_B$ so $A = 0$

this is the case of equivalent protons. when $A = 0$ $\sin 2\theta$ equal unity and the $1 \to 2$ and $2 \to 4$ transitions have zero intensity. The $1 \to 3$ and $3 \to 4$ transition have intensity but they have same energy and occur at the centre of the spectrum. This gives the general rule that magnetically equivalent nuclei do not split each other.

$A = 0$