Advanced NMR Techniques in Solution and Solid State

Prof. N. Suryaprakash
Professor and Chairman (Retd)
NMR Research Centre
Indian Institute of Science – Bengaluru

Module-18
Quantum Mechanical Analysis of Coupled Spin Systems
Lecture – 18

Welcome back, in the last class we discussed about the strongly coupled spin system, we worked out quantum mechanically what are the energy levels and the frequency of transitions. And of course before that, we also worked out what are the energy of transitions and quantum mechanically, Eigen values and transition frequencies were worked out for weakly coupled 2 spins, which was AX and then extended to AB.

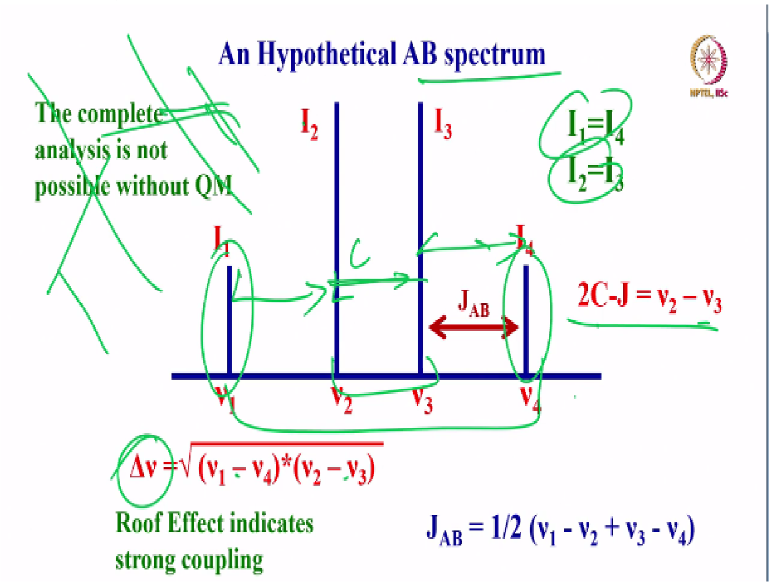
One important thing I also said in the AX case, we consider the situation J = 0; and considered the situation J not equal to 0, when J is not equal to zero, we have off-diagonal elements coming into the picture, which is equal to JAX, we saw that half JAX term was there. And then we also saw that JAX that when we calculated Eigen values and the transitions, we saw when chemical shift separations called quite large, that JAX can be ignored.

So, we got all the 4 energies of the four energy states and then got the frequency of the transitions and found out from the centre of the chemical shift of each of these coupled spins. Let us say A and X, let us say I consider A there will be 2 transitions which are separated by half JAX one to the right and one to the left; same in the case of AB, but intensities are same Whereas, in the case of the AB, it is not like that, because we have to consider JAB term also in the energy levels E2 and E3.

Because chemical shift shift separation is comparable to JAB in this case, and we showed that outer 2 transitions of the 4 lines give rise to J coupling irrespective of the strength of the coupling and centre to transitions you take the frequency separation, take the frequency separation the outer 2 transitions, multiply these 2; and take the square root of that what you are going to get is a chemical shift difference between A and B.

So, in the strongly coupled case, spectra are not spectra amenable to first order analysis and you get only chemical shift difference. That is what I said four intensities here are not exactly equal, unlike the intensities in AX case. Here you are going to get different spectrum that is what we are going to see today.

(Refer Slide Time: 02:39)



An Hypothetical AB spectrum

The complete analysis is not possible without QM

$I_1=I_4$

$I_2=I_3$

$2C\text{-}J = \nu_2 - \nu_3$

$\Delta\nu = \sqrt{(\nu_1 - \nu_4)*(\nu_2 - \nu_3)}$

Roof Effect indicates strong coupling

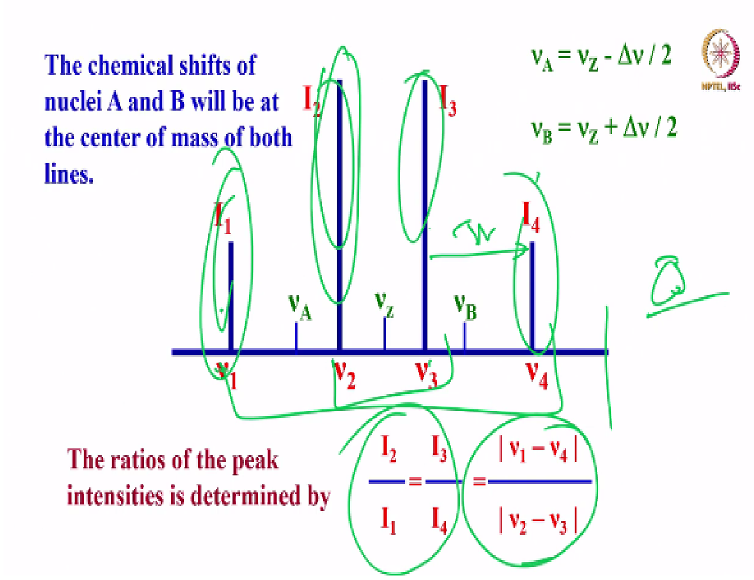
$J_{AB} = 1/2\,(\nu_1 - \nu_2 + \nu_3 - \nu_4)$

Look at this one. Today, what we are seeing the intensity of the AB spectrum and I have written a stick plot of this hypothetical AB spectrum, it is the stick plot. Now we see 2 transitions I1 and I4 they are of equal intensity. And there are 2 transitions at the centre these 2 are of equal intensity. Unlike the AX case all 4 are not of equal intensity. And we worked out also I1 = I4, I2 = I3 and we found out this chemical shift separation is given by 2C – J. And we found out frequency separation delta AB is nothing but frequency separation between this and this and this and this multiply these 2 and take a square root of that. And JAB is always the frequency separation of the outer two transitions. This is a typical AB spectrum; remember outer lines have always weaker intensity compared to central transitions. Of course in the realistic case, what happens is these 2 lines will not be exactly equal.

They will be like this, some may be slightly tending towards this; that shows it is called a roof effect which tells you the direction in which these 2 spins are coupled. Anyway, this is not important, which we discuss in the first course; the elementary course. So, in this case of course, complete analysis is not possible without quantum mechanics, of course in the AB cases somehow we can get the information, except individual chemical shifts.

But if you go to higher spins more than 2, eg. 3 spins coupled, 4 spins coupled it is impossible to get without getting into quantum mechanics and also even simulation. This quantum mechanical analysis here by this way is not the pretty simple, beyond 3 interacting spins it is going to be very tough; you have to resort to numerical analysis using computers.

(Refer Slide Time: 04:25)



The chemical shifts of nuclei A and B will be at the center of mass of both lines.

$\nu_A = \nu_Z - \Delta\nu / 2$

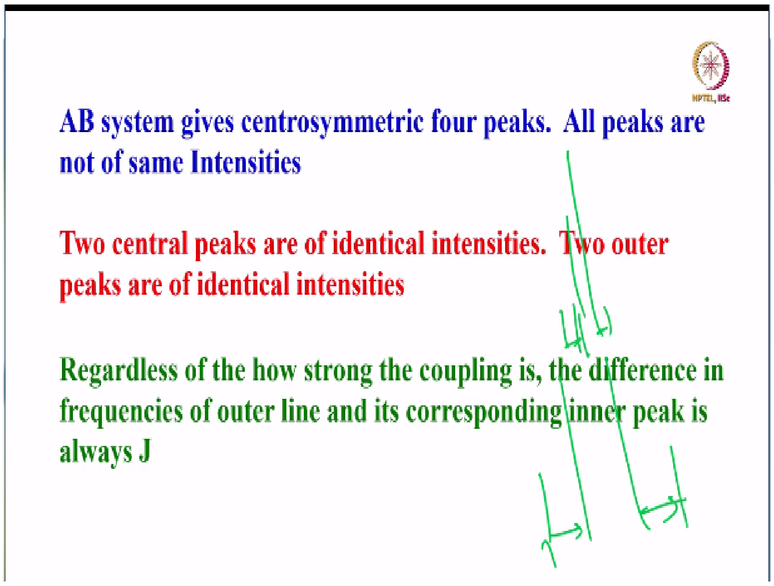
$\nu_B = \nu_Z + \Delta\nu / 2$

The ratios of the peak intensities is determined by

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

So, now the ratio of peak intensities also we can consider that it can be easily obtained by taking into account the frequency separation. nu 1 – nu 4 you take the ratio of the frequency of placement 1 and 4 and 2 and 3 these correspond to intensities ratio, I 2 / I 1 or equal to I 3 / I 4. So, if I want to take this intensity of this peak intensity ratio of one of the central lines with that of the outermost lines, next to each other. That is the adjacent lines of central and outer most lines, you consider, that is nothing but this frequency separation divided by this frequency separation. That gives you a ratio the intensity of the peak. See please remember this is J and I have to get this one, nu 2 – nu 3, you have to consider separation of 1 and 4 and 2 and 3, if you take the ratio you will get ratio between this and this or this and this.

(Refer Slide Time: 05:29)



AB system gives centrosymmetric four peaks. All peaks are not of same Intensities

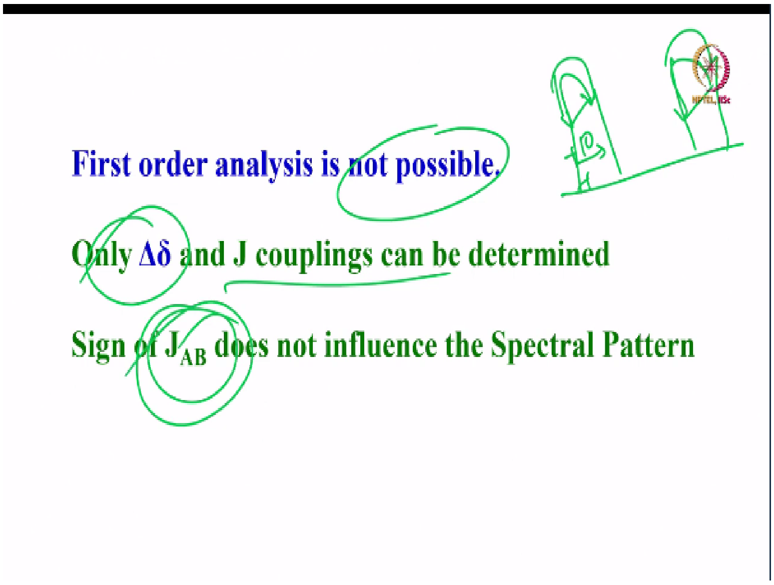
Two central peaks are of identical intensities. Two outer peaks are of identical intensities

Regardless of the how strong the coupling is, the difference in frequencies of outer line and its corresponding inner peak is always J

AB system gives centrosymmetric 4 lines. They are symmetric with respect to the center, all peaks are not of same intensity. You understand that 2 central peaks are identical intensity, 2 outer peaks are of identical intensity, that is what we observed in the hypothetical stick plot and regardless of the strength of the coupling, the outer 2 lines always gives corresponding J coupling. For example I consider the case like this, this give this J; the coupling may become small, let us say does not matter.

Nevertheless, I have to take the outer lines separation; consecutives outer lines, 2 outer lines to get the J coupling. Whatever may be the strength of the coupling? You get separation with the 2 consecutive outer lines.

(Refer Slide Time: 06:16)



First order analysis is not possible.

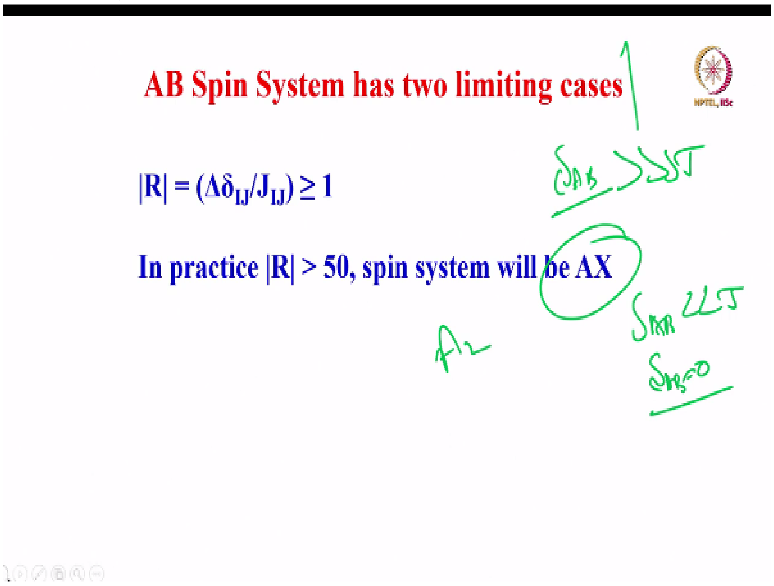
Only Δδ and J couplings can be determined

Sign of J_{AB} does not influence the Spectral Pattern

And as I told you first order analysis is not possible; in strongly coupled cases. you can get the only difference of the chemical shifts, and J coupling of course, we can obtain. And sign of the couplings will not affect the spectrum. This I have been telling you. Even in the first class, also even in the previous course, even in this course, earlier with our 2 classes, I told you in the one dimensional NMR spectrum. The sign of the coupling do not influence the spectral pattern

Does not matter you take a large chemical shift separation or let us say we have AX spin system with a coupling constant of 10 Hz, which is positive, you make it 10 Hz negative. This line will become here, this line will come here. Similarly, this will come here, this will come here; pattern remain same, you will not find the difference at all. So, that is why I said one dimensional NMR spectrum will not give you the information about the sign of the coupling. Here also as I said; again I am repeating the sign of JAB does not influence the spectral pattern.

(Refer Slide Time: 07:16)



AB Spin System has two limiting cases

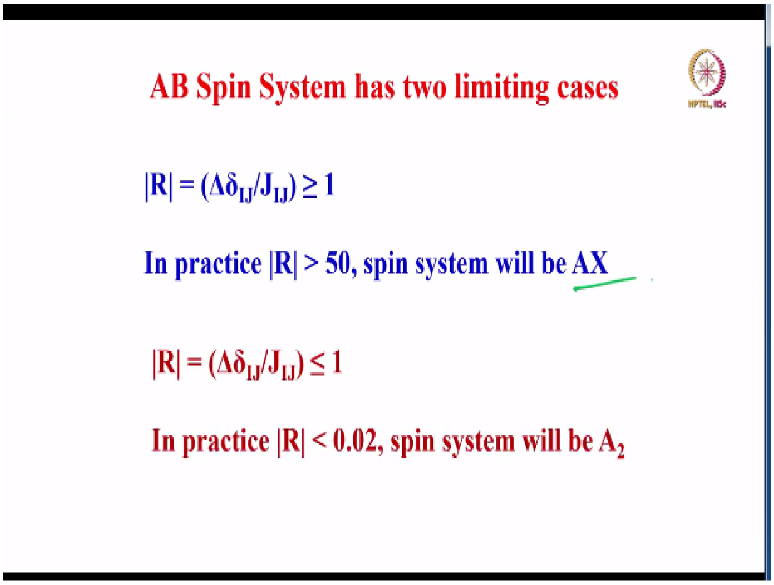
$|R| = (\Delta\delta_{IJ}/J_{IJ}) \geq 1$

In practice $|R| > 50$, spin system will be AX

So, AB has now 2 limiting cases; one, what happens is the chemical shift separation becomes very, very large. It is very simple. We already discussed delta AB chemical shift separation between these 2 become very, very large than J, it is AX case; it will become AX. Now go to a situation delta AB becomes very, very small compared to J or almost delta AB will become equal to 0. I say there is no chemical shift difference at all, then what will happen? It is called A2 spin system.

So, this important thing you should remember, when the chemical separation in the limiting example of this case, when J coupling is 0, you are going to get AB as A2. So, this is the limiting example of AB. In one case it can become AX in other cases it can become A2. This is A2. So, depending upon strength of the coupling and the chemical shifts.

(Refer Slide Time: 08:13)



AB Spin System has two limiting cases

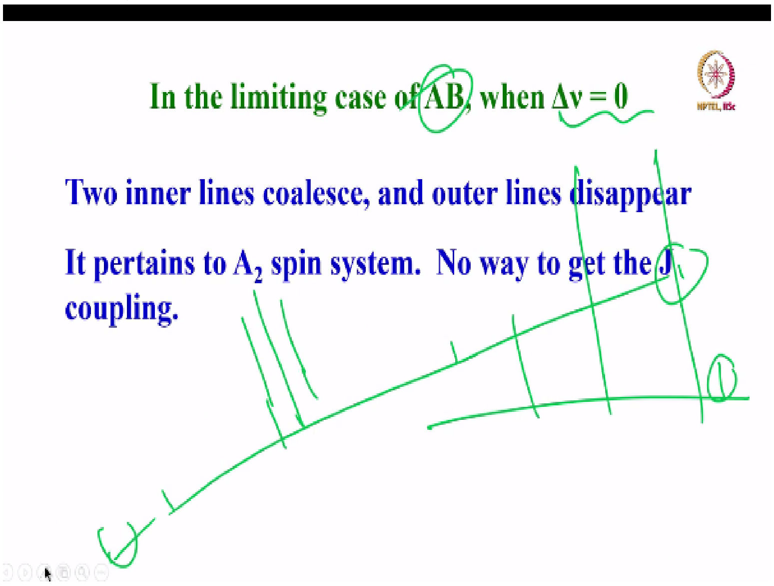
$|R| = (\Delta\delta_{IJ}/J_{IJ}) \geq 1$

In practice $|R| > 50$, spin system will be AX

$|R| = (\Delta\delta_{IJ}/J_{IJ}) \leq 1$

In practice $|R| < 0.02$, spin system will be A_2

(Refer Slide Time: 08:18)



In the limiting case of AB, when $\Delta\nu = 0$

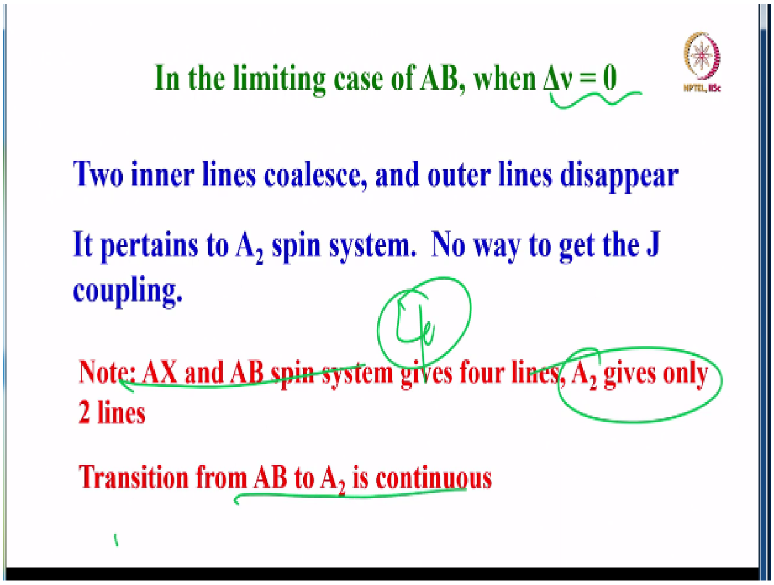
Two inner lines coalesce, and outer lines disappear

It pertains to A_2 spin system. No way to get the J coupling.

So, in the limiting case of AB, when delta nu = 0; what is going to happen? Very interesting case; when chemicals shift different becomes 0. Two inner lines will collapse, 2 outer lines will disappear, very interesting. Now you have 4 lines here, these lines, these lines as you keep on making it stronger and stronger, that is keeping J coupling constant, the chemical shift difference become smaller and smaller, then what will happen? You will see these outer lines keeps going away far away from this, and the with the reduced intensity.

And when it becomes very, very strongly coupled outer lines almost become negligible and disappears. When it becomes exactly A2 this will disappear and these 2 lines overlapped, these 2 peaks overlapped. So, in A2 case it is a special example of AB where you do not get 4 peaks, you get only 2 peaks very interesting. How it happens I am going to explain to you now, we will see.

(Refer Slide Time: 09:18)



In the limiting case of AB, when $\Delta\nu = 0$

Two inner lines coalesce, and outer lines disappear

It pertains to A_2 spin system. No way to get the J coupling.

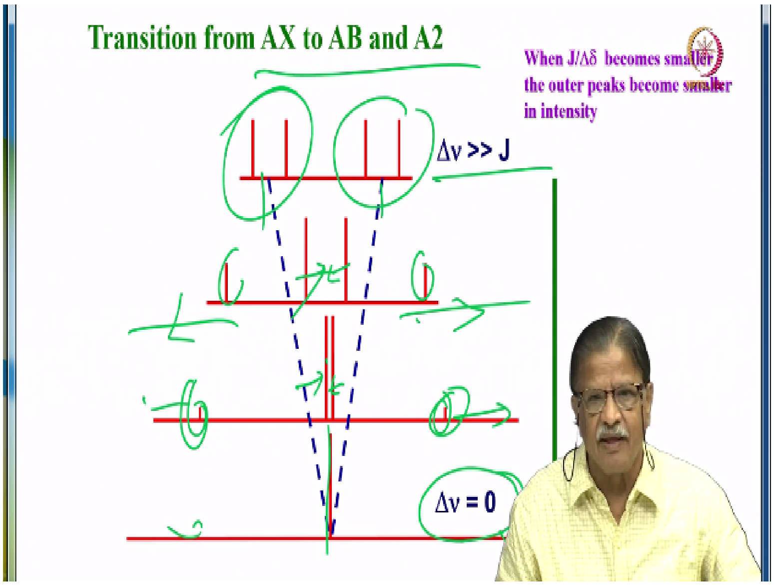
Note: AX and AB spin system gives four lines, A_2 gives only 2 lines

Transition from AB to A_2 is continuous

AX and AB spin system gives 4 lines whereas A2 is going to gives you 2 lines; AB and AX will give you 4 lines. We saw that we worked out the Eigen values and the energy of the transitions everything; but A2 gives only 2 lines. What does it mean? Why it happens? We will see again; we can work out quantum mechanically because then we can work out the n number of spin system; I wanted to give you an idea how to quantum mechanically workout for the coupled spin system.

We are taking 2 examples AX and AB that is enough; No need to go further for 3 spin 4 spin or strongly coupled or weakly coupled etcetera. But simply remember A2 gives 2 peaks and transition from AB to A2 is going to be continuous; and it is like this.

(Refer Slide Time: 10:05)



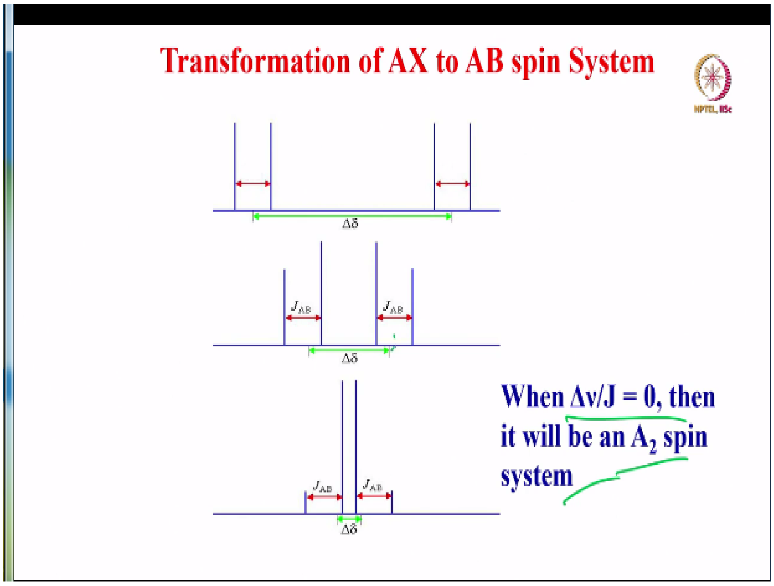
Transition from AX to AB and A2

When J/Δδ becomes smaller the outer peaks become smaller in intensity

I have AX spin system as you know well separated 2 lines for A, and 2 lines for X well separated to doublets. Now chemical shift separation is quite larger here; make a situation chemical shift become smaller and smaller; then outer lines keeps moving away. So, inner lines, inner peaks start moving inside, only outer peaks go out. Again it goes further out and this becomes further in; inner peaks keeps coming closer and closer, outer peaks keeps going far away from each other.

And then the intensity of this keeps on reducing, and the intensity of these peaks keep on increasing and come to a situation delta nu = 0, this will disappear; there are no outer peaks here. Only these 2 will overlap and gives rise a single peak. This is a transition which goes from AX to AB; it is always smooth keeps going like this.

(Refer Slide Time: 11:02)

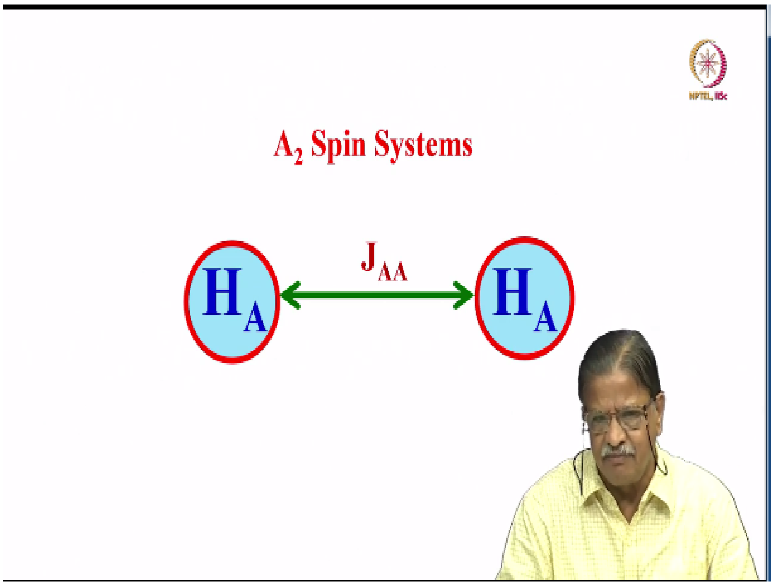


Transformation of AX to AB spin System

When $\Delta\nu/J = 0$, then it will be an A_2 spin system

Of course AX to AB also we can think of like this, I mean a different case delta nu / J = 0. Then it will be an A2 spin system. We went from AB to A2. Now we can go to AX to AB. And further, when they become strongly coupled, you can see that the outer peak become very, very small in intensity.

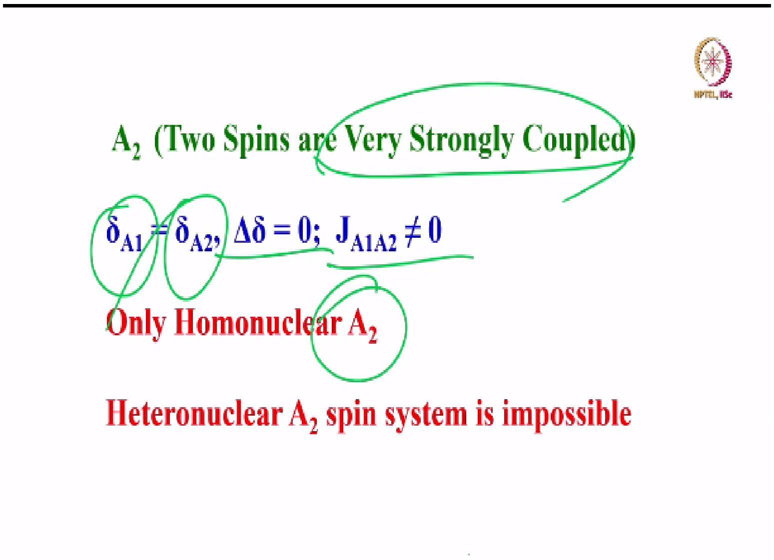
(Refer Slide Time: 11:28)



A_2 Spin Systems

So, this is the way we can understand AX and AB spin systems. Now we will go the A2 spin system without going into the rigorous mathematics. I will show you this is a situation we have coupling between these 2; AA it is present, you may not see that.

(Refer Slide Time: 11:45)



A_2 (Two Spins are Very Strongly Coupled)

$\delta_{A1} = \delta_{A2}$, $\Delta\delta = 0$; $J_{A1A2} \neq 0$

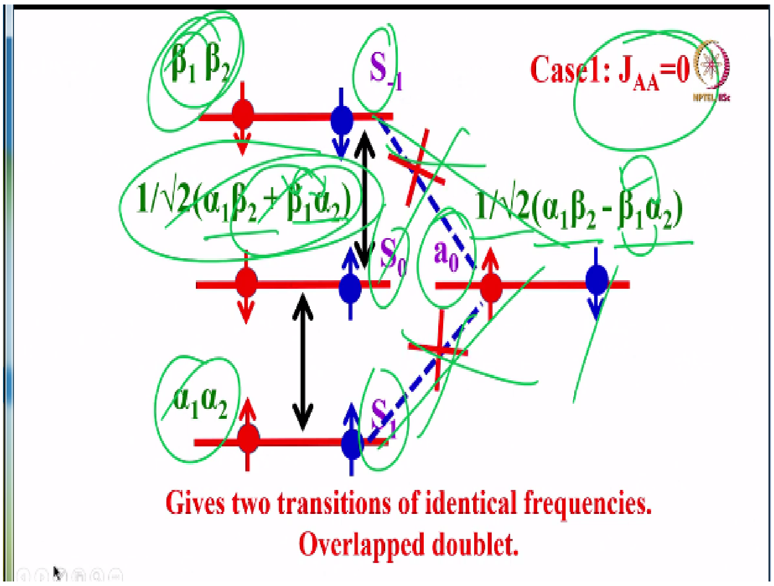
Only Homonuclear A_2

Heteronuclear A_2 spin system is impossible

A2 is a situation where 2 spins are very, very strongly coupled, because there is no chemical shift difference at all; both are identical; and delta A1 = delta A2; both chemical shift are same. So, delta delta is 0, and J A1A2 is not zero. See in the magnetically equivalent spins case, I told you there exist J coupling, remember there exists J coupling, but you do not see in the spectrum, they are not reflected in the spectrum.

Similarly, in the case of homonuclear A2 there exists J coupling between the 2 A spins, but you may not be able to see that. Heteronuclear is not possible because the chemical shift difference is quite large. So, homonuclear A2 is present.

(Refer Slide Time: 12:33)



Case1: $J_{AA}=0$

Gives two transitions of identical frequencies.
Overlapped doublet.

And this is what happens; without going into the rigorous mathematics. I will show you in the A2 case, we 4 energy levels beta beta and alpha alpha for 2 spins 1 and 2. There are 2 other transitions remember in earlier case weakly coupled to alpha beta and beta alpha. And I told you in the AB case, we can also write like this cos of alpha beta plus sin of beta alpha; in other cases it was negative I wrote but anyway, I did not work out everything, but this is what it turns out to be.

So, in this case these 2 energy states can be written as; 1 divided by square root of 2 into alpha 1 beta 2 + beta 1 alpha 2; and the other 1 over square root of 2 into alpha 1 beta 2 - beta 1 alpha 2. These are the 2 energy states. Now, one interesting thing you should observe; this is a symmetric state; symmetric state means if you interchange this one alpha beta to beta alpha, the sign will not change; whereas, this anti symmetric state if you interchange this alpha beta make it beta alpha the sign will change. It is not anti symmetric state, these are all called symmetric states.

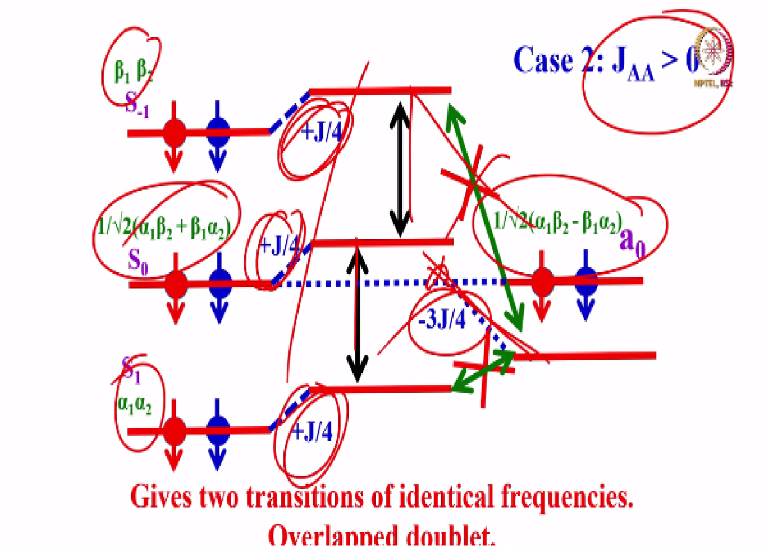
There are 3 symmetric states and one anti symmetric state in A2 coupled spin system. One important rule you should understand. Transition between symmetric to anti symmetric are forbidden, it is not allowed. Only transition between symmetric states are allowed or only between anti symmetric states are allowed. No transition between symmetric to anti symmetric states are allowed. That is one of the rule you should remember that; as a consequence, only these transitions are allowed.

Now, I am considering a situation JAA = 0; when J AA = 0, very interesting thing is going to happen. Please remember when JAA = 0. So, J AA when it is equal to 0 what is going to happen is, we are considering only situation, these 2 energy transitions are allowed, whereas, transition between this to this are not allowed. And these transition frequencies are same, this transition frequency and this transition frequency are same; identical. And this is not allowed. So, in the A2 spin system you can consider a situation; again coupling can be 0.

These are magnetically equivalent; does not mean coupling is zero or coupling need not be present, coupling can be present coupling cannot be present also, it could be 0 or nonzero. Now, I consider situations JAA = 0, then what I am going to see I am telling you this is not allowed. Only 2 transitions are allowed between three symmetric states; between this to this is allowed and this to this allowed; the identical frequencies. As a consequence what will happen it will overlap.

That is why in the A2 spin system we are going to get only single frequency, single peak with 2 frequencies identical and overlapped. Unlike AX and AB which gives 4 transitions when 2 spins are coupled, in the A2 case, you get only single transition which is nothing but 2 frequencies which are overlapped; you do not get 4 peaks in A2 case.

(Refer Slide Time: 16:03)



Gives two transitions of identical frequencies. Overlapped doublet.

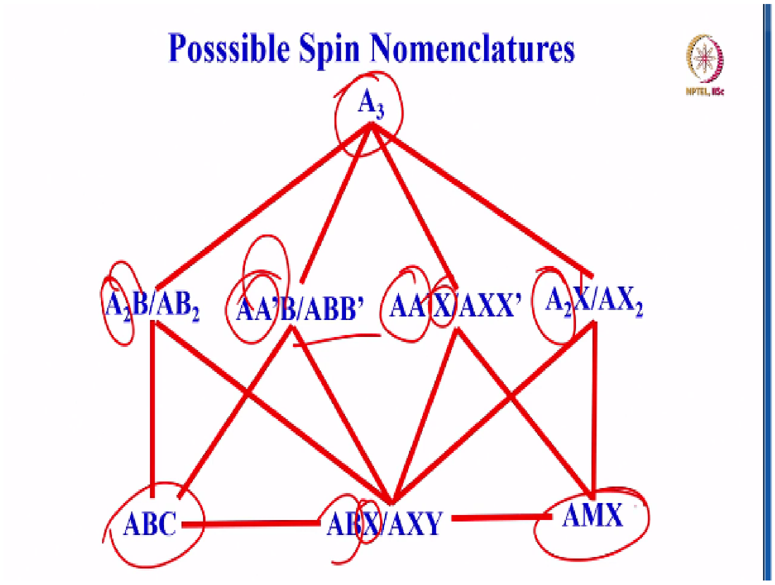
Now, what happens in a situation JAA is not zero, it could be positive or negative; does not matter, I consider situation JAA non zero; greater than 0. Now, what will happen is all the 3 symmetric states are lifted up by J/4. I did not work on rigorously with mathematics; from what I showed you simply you know the wave functions you know the energy Eigen state beta beta is there and this is alpha beta + beta alpha by root 2.

And this is alpha beta - beta alpha by root 2 and you know the Hamiltonian for H0 and H1; you can write down and work it out very easily; simple arithmetic. So, I did not work out but already I showed you for 2 cases, but remember in this case what will happen is all the 3 symmetric states are lifted up by J/4 and on the other hand the anti symmetric state is lifted down, I mean down by minus 3J/4. These 3 will go up; this will come down, the anti symmetric state, this is what is going to happen.

So, but still, what is happening? this transition is not allowed. So, as a consequence what is going to happen? again you are going to get these transition frequencies which are identical, because all the 3 energy states are shifted up by same amount of J/4. So, the difference remains same as a consequence whether the J coupling is 0 or nonzero in A2 coupled spin system, you always get 2 transitions of identical frequencies and in both the cases the transitions from symmetric to anti symmetries are forbidden, not allowed; as a consequence in the A2 case.

You always get single frequency which is nothing but 2 peaks overlapped. Now, what happens if I take the example of a 3 coupled spin system? what do we get out of it? should we analysis this? remember, it is going to be very very terrible job for you.

(Refer Slide Time: 17:55)



Posssible Spin Nomenclatures

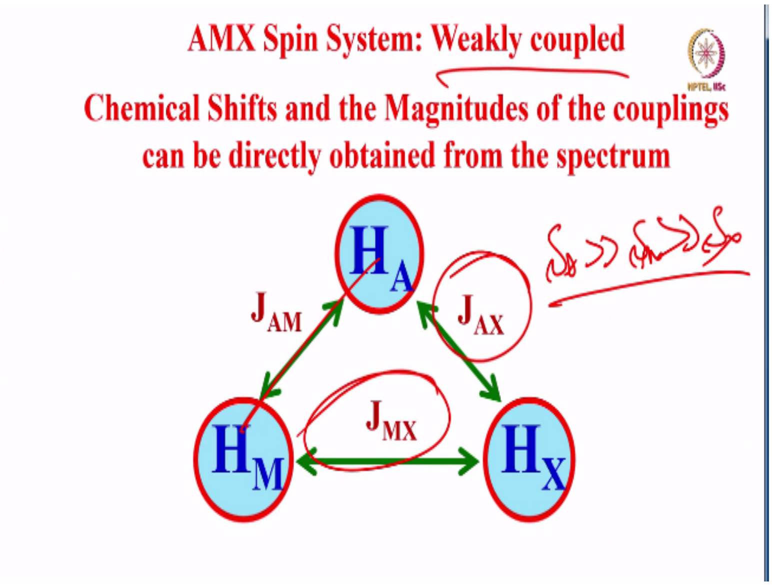
A_3

A_2B/AB_2 $AA'B/ABB'$ $AA'X/AXX'$ A_2X/AX_2

ABC ABX/AXY AMX

There are various possible combinations you can think of in 3 spin case. For example, all the 3 spins can be magnetically equivalent, A3, 2 can be strongly coupled and magnetically equivalent A2 and these 2 together with the third spin can be strongly coupled, but they are not equivalent. Similarly 2 can be chemically equivalent and both are strongly coupled to third spin. This is possible and 2 are strongly coupled and both of them are weakly coupled to the third one. Two are magnetically equivalent very strongly coupled A2 and both are weakly coupled to third one. And all the 3 are weakly coupled non-equivalent; both are strongly coupled and weakly coupled to the third one; and all the three can be weakly coupled varieties of possible combinations you can think in spin Nomenclature. We are still remaining in 3 spins case. Imagine you go to 4 spins 5 spins umpteen number of possibilities you can think. For each of them if you want to work out quantum mechanically It is going to take you all your lifetime, no it is not easy. It will take enormous amount of time. It is not difficult, you can work it out where you are working out pages and pages and pages of calculations to get the Eigen values and Eigen functions. So, it is not worthwhile doing that. But anyway in the olden days people have already worked out some of the cases it is available in the books. But we have shown for 2 spins, AX, AB and A2. Now we will see the simple case AMX without going through rigorous mathematics

(Refer Slide Time: 19:28)



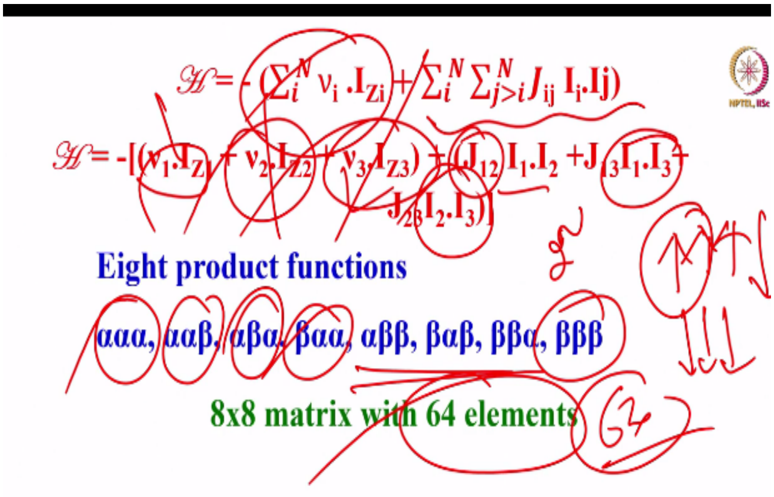
AMX Spin System: Weakly coupled

Chemical Shifts and the Magnitudes of the couplings can be directly obtained from the spectrum

How the AMX works, AMX 3 weakly coupled chemical shifts are far away separated; delta A is very much greater than delta M; which is very much greater than delta X. This is a condition and there exists a coupling between A and M. There exists a coupling between A and X. There exists a coupling between M and X. There are 3 couplings and 3 different chemical shifts.

And all are weakly coupled because we are representing by 3 different alphabets in the roman alphabets, which are far away separated. So, it is a 3 weakly coupled AMX spin system; pretty easy to analysis. That is why I took it, if you go back to ABC, here, it is much difficult. So, that is why I took the simplest one to show you in the three spins case.

(Refer Slide Time: 20:12)



$$\mathcal{H} = -(\textstyle\sum_i^N \nu_i . I_{Zi}) + \sum_i^N \sum_{j>i}^N J_{ij}\, I_i . I_j)$$

$$\mathcal{H} = -[(\nu_1 . I_{Z1} + \nu_2 . I_{Z2} + \nu_3 . I_{Z3}) + (J_{12} I_1 . I_2 + J_{13} I_1 . I_3 + J_{23} I_2 . I_3)]$$

Eight product functions

ααα, ααβ, αβα, βαα, αββ, βαβ, ββα, βββ

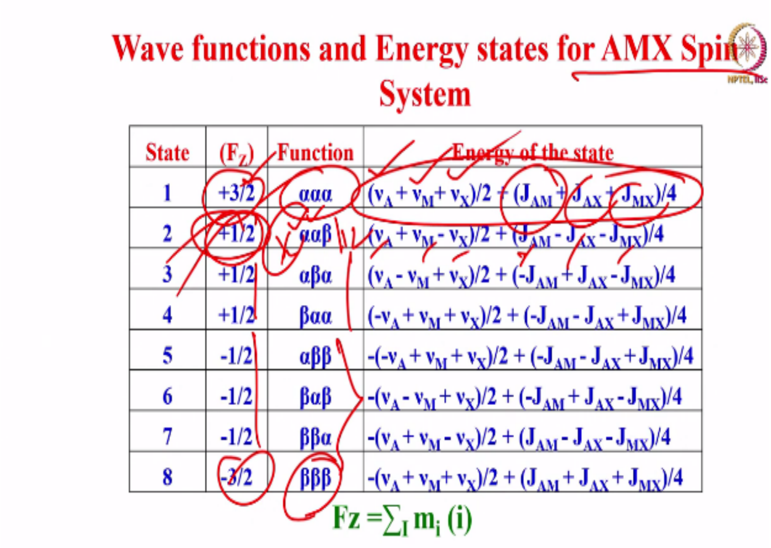
8x8 matrix with 64 elements

Write down the Hamiltonian again. Now, this H0 one Zeeman term is coming taking into account and now this is the J coupling term, take the J coupling term, same, what we wrote a general term. Previous case we detect 2 spins, now we have to detect 3 spins, how do we detect 3 spins? Now chemical shift of one, its Zeeman interaction with external magnetic field, chemical shift 2 and its Zeeman interaction, Zeeman interaction of spin 3. Zeeman interaction of spin 1, Zeeman interaction of spin 2, Zeeman interaction of spin 3. Then J12 I1.I2; J13 I1.I3, J23 I2.I3. Remember each of these term you have to expand in terms of Ix, Iy and Iz and then construct the Hamiltonian and there are 8 product functions; remember, alpha alpha alpha, alpha alpha beta, alpha beta alpha, beta alpha alpha and these 3 and finally beta beta beta.

Various possible combination you can think of; the orientations of all the 3 can be alpha, all the 3 can be beta, these 2 can be alpha and this can be beta like that all the combinations you can think of, there are 8 possible product functions. That is why I said for N interacting spins there are 2 to the power of N product functions. So, in the 2 spins we have 4, 3 spin we have 8; go to 4 spins you have 16 product functions. Imagine 16 into 16 that is the big matrix your to analysed.

Here already 8 into 8, 64 by 64 matrix, 8 into 8 64 64 elements will be there, 8 by 8 matrix you have to analysis like 4 by 4, 16 by 16 is another big matrix for 4 spins. So, we have to analysis this 8 by 8 matrix, it is very difficult, all 64 elements if you want to work out; it to runs into tons and tons of pages for calculations. So, we will not worry about it. We will see what are the Eigen values and the transition frequencies in the simplest possible way.

(Refer Slide Time: 22:25)



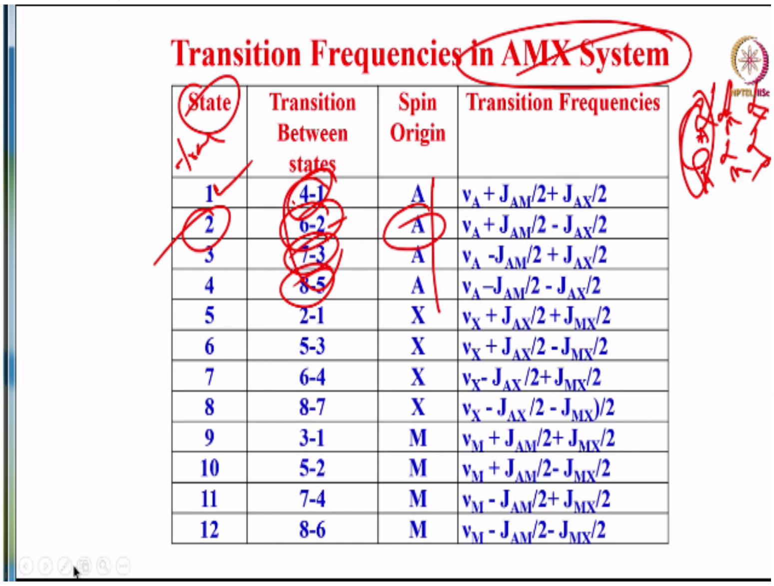
Wave functions and Energy states for AMX Spin System

State	(F_Z)	Function	Energy of the state
1	+3/2	ααα	$(v_A + v_M + v_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4$
2	+1/2	ααβ	$(v_A + v_M - v_X)/2 + (J_{AM} - J_{AX} - J_{MX})/4$
3	+1/2	αβα	$(v_A - v_M + v_X)/2 + (-J_{AM} + J_{AX} - J_{MX})/4$
4	+1/2	βαα	$(-v_A + v_M + v_X)/2 + (-J_{AM} - J_{AX} + J_{MX})/4$
5	-1/2	αββ	$-(-v_A + v_M + v_X)/2 + (-J_{AM} - J_{AX} + J_{MX})/4$
6	-1/2	βαβ	$-(v_A - v_M + v_X)/2 + (-J_{AM} + J_{AX} - J_{MX})/4$
7	-1/2	ββα	$-(v_A + v_M - v_X)/2 + (J_{AM} - J_{AX} - J_{MX})/4$
8	-3/2	βββ	$-(v_A + v_M + v_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4$

$Fz = \sum_I m_i (i)$

The wave functions are, as I told you, the product functions especially in the weakly coupled case, you do not have to worry about alpha beta + beta alpha by root 2, alpha beta - beta alpha by root 2 which I said in the earlier case; same here instead of AMX if you make A3 you get symmetric, anti symmetric states everything. Since I am considering AMX, a weakly coupled, simply I wrote product functions and the FZ; the total spin magnetic quantum number for this energy state is 3/2, because we have all the 3 spins up; alpha alpha alpha; half half half will become 3/2 and energy state 2 plus half; 2 up and 1 down; the sum turns out to be plus half, similarly here, these 2 are situation sum terms have to be half, here these 3, 2 down 1 up, the sum turns out to be minus half. And all the 3 are down sum is – 3 / 2 and very very easily energy states have been worked out, very simple for us. Imagine it is not simple, if I have to work out. Again I try to write down, then calculate each elements of the matrix find out which are 0 which are nonzero and then you have to construct the energy states like this. So, simplify the one, the first energy state is simple nu A nu M nu X is then all the 3 chemicals shift divided by 2 and JAM; JAX and JMX divided by four. The second energy state nu A + nu M -nu X are divided by 2, and J AM – J AX - J MX / 4. Like this very easily all the 8 energy states are worked out. Now for all the 8 energy states, how many transitions you can obtain? Very simple.

(Refer Slide Time: 24:15)



Transition Frequencies in AMX System

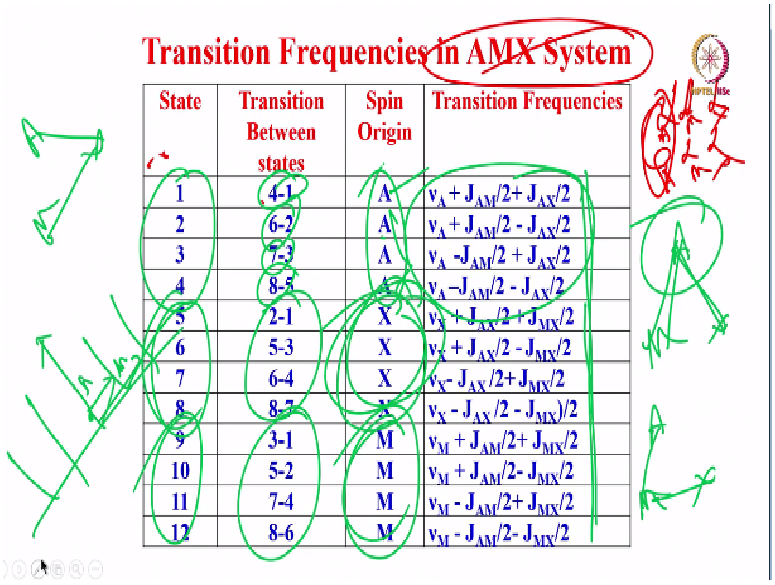
State	Transition Between states	Spin Origin	Transition Frequencies
1	4-1	A	$\nu_A + J_{AM}/2 + J_{AX}/2$
2	6-2	A	$\nu_A + J_{AM}/2 - J_{AX}/2$
3	7-3	A	$\nu_A - J_{AM}/2 + J_{AX}/2$
4	8-5	A	$\nu_A - J_{AM}/2 - J_{AX}/2$
5	2-1	X	$\nu_X + J_{AX}/2 + J_{MX}/2$
6	5-3	X	$\nu_X + J_{AX}/2 - J_{MX}/2$
7	6-4	X	$\nu_X - J_{AX}/2 + J_{MX}/2$
8	8-7	X	$\nu_X - J_{AX}/2 - J_{MX})/2$
9	3-1	M	$\nu_M + J_{AM}/2 + J_{MX}/2$
10	5-2	M	$\nu_M + J_{AM}/2 - J_{MX}/2$
11	7-4	M	$\nu_M - J_{AM}/2 + J_{MX}/2$
12	8-6	M	$\nu_M - J_{AM}/2 - J_{MX}/2$

You find out what are the transitions which are allowed according to our selection rule. For the transitions frequency if you go for the AMX system, the transition between 4 and 1 is allowed; 6 to 2 is allowed; 7 to 3 and 8 to 5 allowed. I mean instead of state 1 I would say transition; that is easy to instead of statements you may get confused with the energy state.

So, I will consider there are transitions, transition 1, is between the transitions states 4 and 1 which correspond to transition A spin; understand.

Now I consider transition 2, the transition 2 is between 6 and 2; it again correspond to A spin because the one of the spin which is undergoing transition is for A spin; for example alpha alpha alpha, beta alpha alpha if right, if the transition undergoes between alpha to beta, these correspond A spin, I wrote it right, I can write it AM and X. So, here A spin is undergoing transition from alpha to beta or beta to alpha. So, this is called A transition. So, like that, if you can work out from the energy states, you can see transition from 4 to 1, and work out all these things.

(Refer Slide Time: 25:44)



Transition Frequencies in AMX System

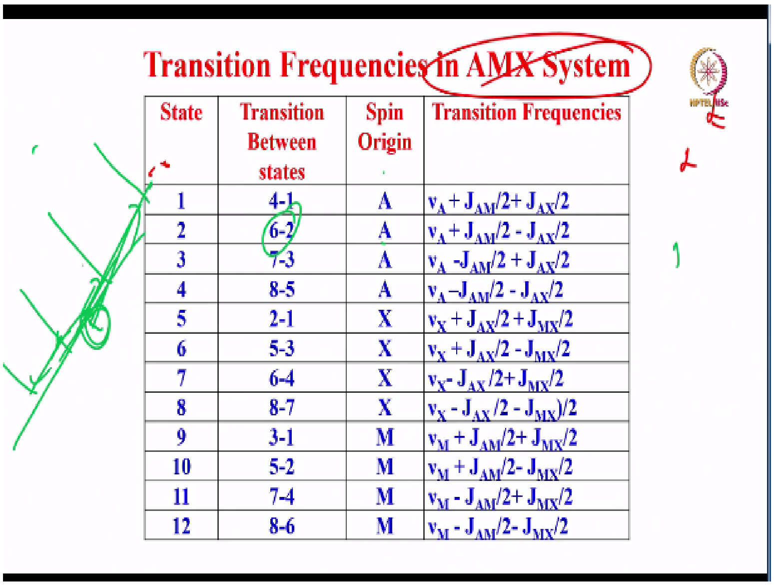
State	Transition Between states	Spin Origin	Transition Frequencies
1	4-1	A	$\nu_A + J_{AM}/2 + J_{AX}/2$
2	6-2	A	$\nu_A + J_{AM}/2 - J_{AX}/2$
3	7-3	A	$\nu_A - J_{AM}/2 + J_{AX}/2$
4	8-5	A	$\nu_A - J_{AM}/2 - J_{AX}/2$
5	2-1	X	$\nu_X + J_{AX}/2 + J_{MX}/2$
6	5-3	X	$\nu_X + J_{AX}/2 - J_{MX}/2$
7	6-4	X	$\nu_X - J_{AX}/2 + J_{MX}/2$
8	8-7	X	$\nu_X - J_{AX}/2 - J_{MX})/2$
9	3-1	M	$\nu_M + J_{AM}/2 + J_{MX}/2$
10	5-2	M	$\nu_M + J_{AM}/2 - J_{MX}/2$
11	7-4	M	$\nu_M - J_{AM}/2 + J_{MX}/2$
12	8-6	M	$\nu_M - J_{AM}/2 - J_{MX}/2$

See for example, 4 to 1 is A transition 6 2, 7 3, 8 5 you can calculate yourself, you will find out the difference between the transitions. The origin of the spin for all of them, the transition which is undergoing is A spin. A spin is the one which is undergoing flipping, they are called A transitions. If you consider the energies other transitions 5 6 7 and 8 which is between 2 and 1, 5 3, 6 4 they all pertain to X transitions, where the X spin is undergoing flipping from alpha to beta or beta to alpha. Again these are the energy states, these are the difference of the Eigen values.

Now, go to a situation of remaining 4 transitions, they are all from 3 1, 5 2, 7 4, 8 6 states and they all pertain to M transitions, where M spin is undergoing flipping from alpha to beta, beta to alpha. So, there are 3 product functions. Among the 3, any one of the spin can undergo flipping from alpha to beta, beta to alpha. If A spin is flipping from alpha to beta or beta to alpha that corresponds to A transition. If M is flipping from alpha to beta or beta to alpha that is M transition. Similarly, if X is flipping from alpha to beta or beta to alpha that is X transition.

So, in AMX spins case, you have got 12 transitions 4 transitions correspond to A, 4 correspond to M and 4 correspond to X. And you can find out all the frequencies here. Very interesting thing, you have to see here, each spin is coupled to other spins. You consider AM and X. A is coupled to M, A is also coupled to X. Now, I consider AM and X, M is coupled to A, M is also coupled to X, I consider AM and X, A is coupled to X and M is also coupled to X. So, each spin is coupled to the remaining 2 spins. What is the type of spectrum you are going to get? 4 peaks you have got for each of them. But remember the JAX case I told you from the chemical shift at the centre of A there are 2 peaks which are separated by half of J AX one towards the plus JAX, others towards the minus JAX; the separation gives JAX in the AX case. But in the AMX case you are getting 4 peaks, where easily extend the logic. For example, if I consider A, A is coupled to M and A is coupled to X. So, at the chemical shift of A I get from that centre 2 peaks on either side; one correspond to JAX, other correspond to JAM very easy. Exactly the same logic I hope it is very clear for you to understand if not I hope if it is not clear for you, I will tell you very simply; take one example and explain to you. I consider let us say chemical shift of A; this A spin.

(Refer Slide Time: 28:55)

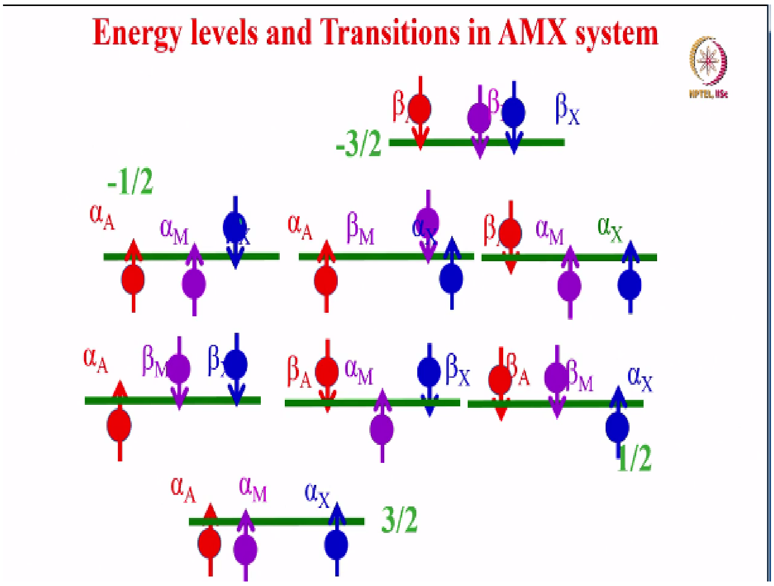


Transition Frequencies in AMX System

State	Transition Between states	Spin Origin	Transition Frequencies
1	4-1	A	$v_A + J_{AM}/2 + J_{AX}/2$
2	6-2	A	$v_A + J_{AM}/2 - J_{AX}/2$
3	7-3	A	$v_A - J_{AM}/2 + J_{AX}/2$
4	8-5	A	$v_A - J_{AM}/2 - J_{AX}/2$
5	2-1	X	$v_X + J_{AX}/2 + J_{MX}/2$
6	5-3	X	$v_X + J_{AX}/2 - J_{MX}/2$
7	6-4	X	$v_X - J_{AX}/2 + J_{MX}/2$
8	8-7	X	$v_X - J_{AX}/2 - J_{MX})/2$
9	3-1	M	$v_M + J_{AM}/2 + J_{MX}/2$
10	5-2	M	$v_M + J_{AM}/2 - J_{MX}/2$
11	7-4	M	$v_M - J_{AM}/2 + J_{MX}/2$
12	8-6	M	$v_M - J_{AM}/2 - J_{MX}/2$

A spin is here. Now I get 2 peaks here and 2 peaks here; you can see here; from A chemical shift plus A, there are 2 peaks, JAM/2 and JAX/2 on either side; +JAM /2 and the +JAX /2 on one side. Similarly, minus AM/2 minus AX/2 on other side. There are 2 peaks on either side of each chemical shift which is nothing but half the chemical J coupling of remaining 2 spins. So, now this is the active spin I am seeing, it is giving rise to coupling with the passive spins; each is going to be 2 lines on either side. One Separation gives you one of the passive coupling, other separation gives you other passive coupling; not complete J coupling, but half of the value. And if you take the separation for corresponding peaks from the other side, you are going to get both the couplings.

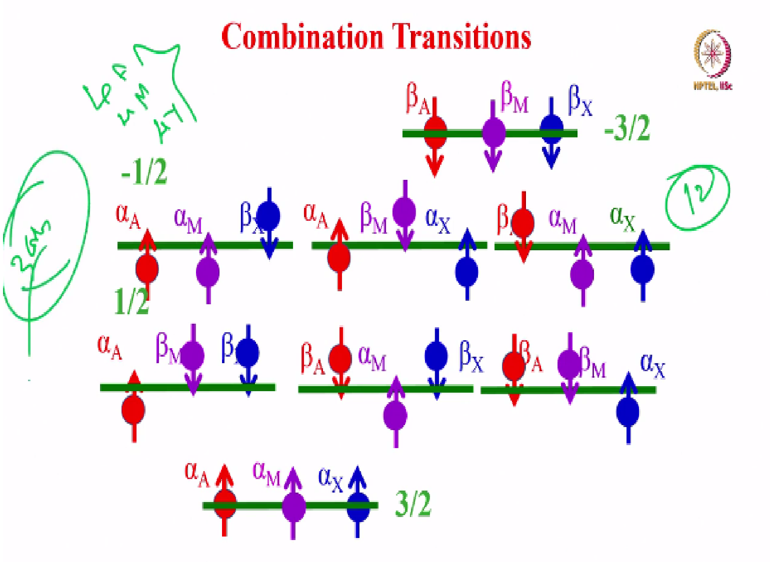
(Refer Slide Time: 29:43)



Energy levels and Transitions in AMX system

So, energy level transitions very easily you can understand. This correspond X transition from plus 3/2 to minus ½, here X is undergoing transition. Similarly, X is undergoing here; X is undergoing transition. So, there are 4 X transitions. Now, this is A transition, this is A transition, this is A transition; there are 4 A transitions. Now, next is M transition this is M, this is M, this is M and last is M. There are 4 M transitions, 4A transitions and 4X transitions.

(Refer Slide Time: 30:18)



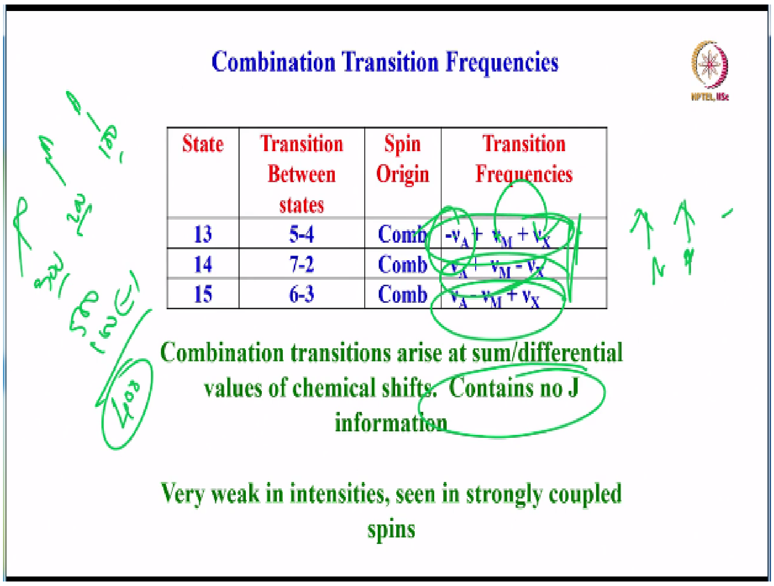
Combination Transitions

And here very interesting thing is going to happen. For example, there is a possibility these 3 can come to these 3; plus half to minus half is allowed, because they are change in the magnetic quantum number is plus 1 or minus 1; that is all the 3 spins are simultaneously changing, not one; In the previous example, in the previous slide, I showed you only A spin is changing or M is changing, X is changing; 4 such transitions for each we saw.

But in this case, for example, here, all the 3 are simultaneously undergoing change, that is why it is called a combination transition. And all the 3 spins flipped simultaneously from alpha to beta. And these are examples, where this transition is allowed, similarly this also allowed, all the 3 are changing; similarly this also followed. So, there are 3 combination transitions in thid 3 spin case in addition to 12 transitions; 4 for A, 4 for M and 4 for X. You are going to get 4 A, 4 M transitions, 4 X transitions, plus 3 combination transitions will be there.

So, there are 15 transitions for 3 coupled spin system. But interestingly, in the weakly coupled case all the 3 combination transitions are not usually seen, they are almost 0 intensity; you will not see.

(Refer Slide Time: 31:37)



Combination Transition Frequencies

State	Transition Between states	Spin Origin	Transition Frequencies
13	5-4	Comb	$-v_A + v_M + v_X$
14	7-2	Comb	$v_A + v_M - v_X$
15	6-3	Comb	$v_A - v_M + v_X$

Combination transitions arise at sum/differential values of chemical shifts. Contains no J information

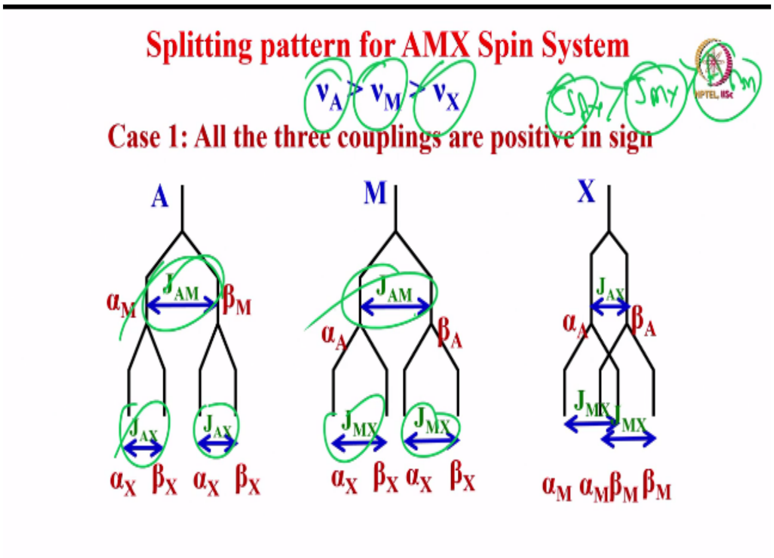
Very weak in intensities, seen in strongly coupled spins

But if you go to strongly coupled case you will see that. But where do these combination transitions will occur, they come only at the sum or difference of the chemical shifts. You can find out on this table, from this energy level diagram which are given. You go back here and you can find out transition which I showed you then you will find out the combination transition. The only thing is all of them will come at the sum or difference of the chemical shifts.

And because of that, combination transition contains no J information. See here, no J term coming, only – nu A + nu M + nu X; sum of 2 chemical shifts of nu M and X minus chemical shift of nu A. That is all you get from this combination transition. Another combination transition you get at the sum of chemical shift of A and M and minus of X.

For example, one chemical shift is coming at 100, other is 200, other is 300. Let us say this is A, this is M and this is X. Now combination transitions, that is a one of them will come with chemicals shifts M and X 200 + 300, ie. 500; minus nu A 100. So, at 400 you will see one combination transition, very weak intensities; peak that correspond to one of these combinations transition, there is no information you get out of it. So, very weak intensities you see them only in strongly coupled spin systems, not in this case.

(Refer Slide Time: 33:14)



Splitting pattern for AMX Spin System

$\nu_A > \nu_M > \nu_X$

Case 1: All the three couplings are positive in sign

So, splitting example of AMX I am going to give you like this a simple case, where all the 3 couplings are positive in sign like this. So, A can split with the M it gives doublet and they will further split with X gives a doublet of doublet. Similarly, M is coupled to A, gives doublet and coupled with the X gives doublet of doublet, X is coupled to A gives doublet, again coupled to M gives rise to doublet of doublet.

So, this gives to JAM, whereas this this separation gives you JAX. Similarly because M is coupled to A, this will give a JAM this will give you JMX, so like that all coupling information can be obtained. But of course, I did not want to show you here, there is an example what happens if the couplings; you see here I have taken the example; several conditions we can put, when nu A is greater than nu M greater than nu X, this is the pattern.

Now also I can think of what happens when JAX is greater than JMX is greater than JAM. What happenes is this is larger than this, larger than this, all combinations you could think of accordingly the pattern the spectrum changes. You can also think of what happens if one of the couplings is negative, other is positive, other 2 are positive, or 2 are negative one is positive, all the 3 are negative what will happen? Varieties of combinatioins you can think of; simply go back to the AMX case workout by yourself with a stick plot.

Consider a situation now JAX is greater than JMX. JAM have taken, make J AX very small compared to JMX or make one of the couplings 0. See how the pattern changes? In one case you will get only 2 lines instead of 4 lines. These are the things the splitting pattern; can be easily understood by quantum mechanical analysis. So, 3 spin case also it can be done, I did not explicitly do what I showed you the procedure to do that.

And AMX case I told you we get 4 for A, 4 for M and 4 for X transitions; 12 transitions plus 3 combination transition at sum and differences of the chemical shift of A, M and X, which are very weak intensities; they are not seen. Whereas, they are seen in the strongly coupled case. So, with this I am going to stop here before that I want to tell you; so far in the quantum mechanical analysis of the coupled spin system, we have discussed a lot, we started telling you how we can go ahead in making the analysis of the spectrum to get the chemical shift and coupling constants for all the coupled spins in system; what is this type of spectrum we get for weakly coupled, what is this type of spectrum we are going to get for strongly coupled spin system. We took the example of AX, we knew what are the wave functions, your wave functions are nothing but the product functions.

We constructed the Hamiltonian taking into account only the Zeeman interaction; considering J = 0, taking into account the J coupling present, which is nonzero then we constructed the Hamiltonian and then used this and we wanted to work out the Eigen values; for that we constructed a matrix; secular equation we got and then each and every element of the matrix were worked out.

And I showed you for 2 spin case there is 4 by 4 matrix; 16 elements and then out of which in the AX case, when J coupling is 0, we have only 4 diagonal elements and we get 2 transitions for each A and X which are overlapped when J= 0. When J is nonzero we said 4 peaks 2 for A and 2 for X well separated by JAX. And similarly for AB I said 4 peaks are there; outer peaks are of equal intensity, two central peaks are of equal intensity; outer peaks gives rise to J coupling, Central peak separation if you take multiply by outer peak separation and then take this square root of that, we are going to get the chemical shift difference. I told you in the strongly coupled case there is no way you can get the chemical shifts individually. You can get only the difference of chemical shifts. And I took the example of 3 spin weakly coupled and showed how the spectrum comes, how the combination transitions come and what are the possible spin states, what are the possible nomenclature in 3 coupled spins case.

And took the simplest stuff weakly coupled A, M and X and showed you how many peaks we get with a simple stick plot and also the transitions by taking into account different energy states, which already has been worked out. I did not explicitly worked out that, but took from the table and we worked out. So, with this I am going to stop. So, quantum mechanical analysis coupled spin system is complete. In the next class we will go to a different topic. Thank you.