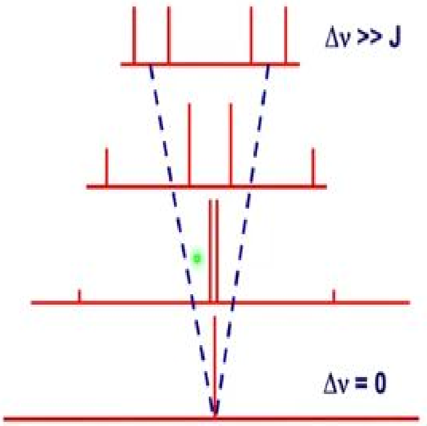
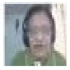
One and Two Dimensional NMR Spectroscopy for Chemists
Prof. N. Suryaprakash
NMR Research Centre
Indian Institute of Science, Bangalore

Lecture - 31
Eigen values of A2 and AMX spin systems

Welcome back, in last one or two classes, we have been discussing about the nomenclature of the coupled spin systems. How to identify them using Pople nomenclature; and in the last class particularly, we took example of two coupled spin system. For example a weakly couple two-spin system which are identified as A and X. I clearly mentioned to you in such a coupled spin system, A will give two lines of equal intensity, X will give two lines of equal intensity.

(Refer Slide Time: 00:58)





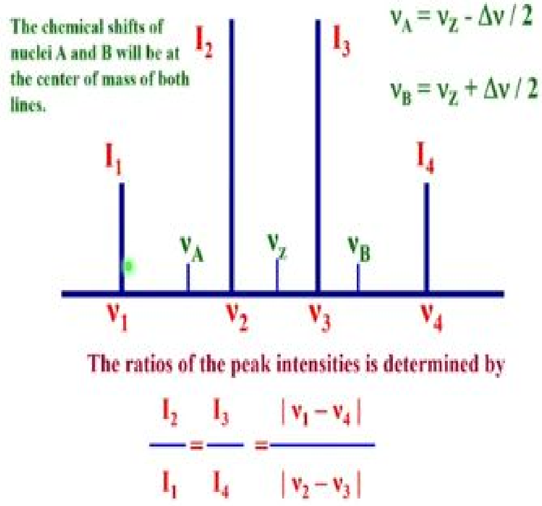
So finally you can get the chemical shift from the center of those doublets, also the doublet separations, if you measure, you will be getting J coupling. And we extended this logic, when the chemically separation become much smaller compared to J coupling, we got a AB pattern. I showed you how the AB pattern was there; wherein two central lines were of equal intensity which were much intense peaks compared to two lines of outer transitions which were of very weak intensity.

And I also mentioned to you the separation of the two outer lines, any two outer lines you take, on either side; right side or left side, it gives J coupling. And if you want to get the chemical shifts of this, especially strongly coupled which is identified as AB spins system, I told you it is not possible to get the individual chemical shifts. In strongly coupled spins, we can only get the difference in the chemical shifts.

So how do you get the chemical shift difference in AB spectrum? I showed you, you have to take the difference of the frequency between the first line and the last line of the four transitions. First and fourth transitions of the four transitions difference you take. Similarly take the difference of the second and third; multiply these two factors; take this square root of that. That will give you chemical shift difference between two coupled spins, in strongly coupled AB.

I also told you how to calculate the intensity ratio. You have to take I2 by I1, it is nothing but the the ratio of outer transitions to that of the inner transitions which we worked out.

(Refer Slide Time: 02:49)



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

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

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

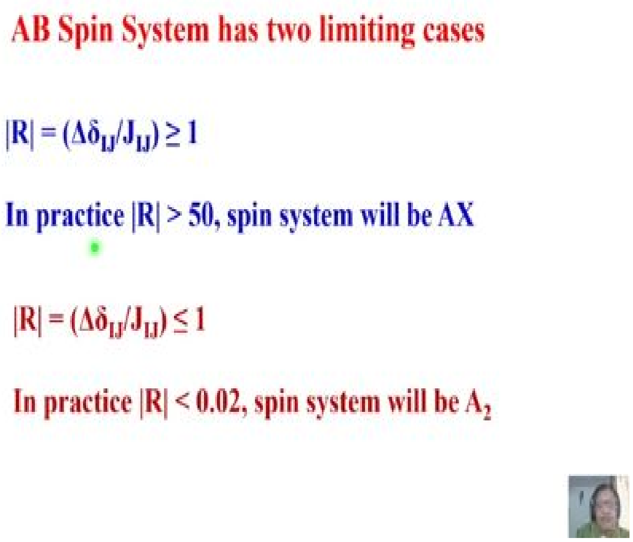
The ratios of the peak intensities is determined by

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

I showed you clearly what happened? For example we saw a situation like this; I2 by I1, this is ratio of inner line to the outer line, if you consider, this is the frequency separation between two outer lines divided by frequency separation between two inner lines. This also I told you, as you keep on increasing this, this separation becomes smaller and smaller, and the central peaks becomes larger and larger in intensities, as I told you.

For example take I said, if you take this to be very large value v1- v4; and this because very, very small, then the intensity ratio is very large; that is internal peaks; these two peaks have more intensity than outer lines.

(Refer Slide Time: 03:38)



AB Spin System has two limiting cases

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

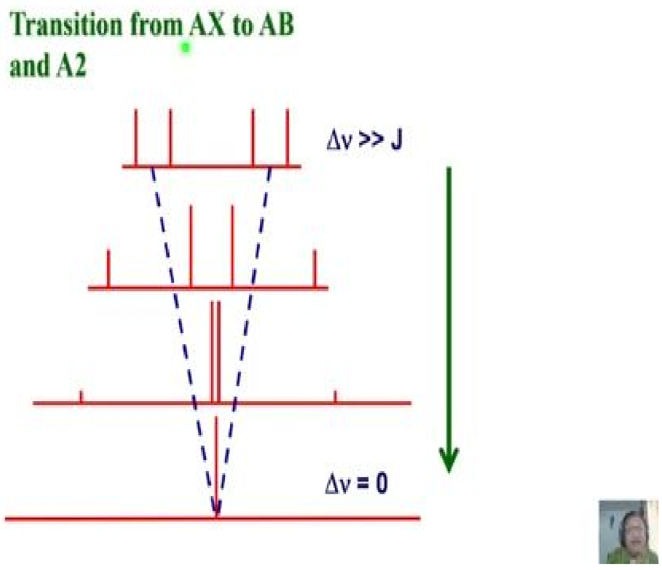
In practice $|R| > 50$, spin system will be AX

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

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

That is all we explained; I also told you root of this, and I also I told about the limiting case when the chemical shift become small, AX will become AB. AB will become A2. When the chemical shifts overlaps, it will become a A2 spin system and the coupling is not reflecting spectrum.

(Refer Slide Time: 03:55)



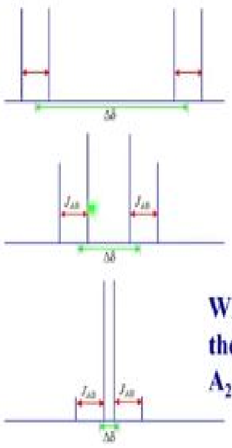
Transition from AX to AB and A2

Now how we see the transition from AX to AB? This is a very simple example, I am showing you; this is a perfect AX system. You can see both the lines are of equal intensity. Now what I am going to do is the chemical shift separation in this case is sufficiently larger than J coupling, what we will do is; we will try to make it more strongly coupled. How do we do? You keep on reducing the chemical shift separation between these two.

This you know, how to calculate the AB, so when you keep reducing the chemical shift separation; you see what is happening. The central peak starts increasing in intensity; this keeps coming down. Slowly keep on varying, there is a smooth transition; keeps on going smoothly internal lines always keep increasing in the intensity; outer lines start moving far apart. At the same time intensity of the outer lines starts decreasing. And you will come to a situation when the chemical shift difference between two coupled spins is exactly 0, there is no difference at all. They are equivalent spins and the overlap of the chemical shifts, and the J coupling is not reflected in the spectrum then you get a single transition. So you can see the transition from AX to AB and to A2.

(Refer Slide Time: 05:17)

Transformation of AX to AB spin System



When Δν/J = 0, then it will be an A_2 spin system

This is a clear example how AX will become AB; but nevertheless separation between the outer lines; any two outer lines you take, this or this,it6 always gives the J coupling, irrespective of the strength of couplings; I told you. Even though it is strongly coupled, to whatever the extent of strong coupling, does not matter but outer two lines, if you take these two lines or these two lines this separation always gives JAB or you can take this, which gives you J coupling. J coupling is easy to extract, only this chemical shift you cannot get individually you get only difference.

(Refer Slide Time: 05:49)

A_2 Spin Systems

Now you go to another spin system. This is a another possibility for two couple spin system, it is called A2, what is A2?

(Refer Slide Time: 06:04)

A_2 (Two Spins are Very Strongly Coupled)

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

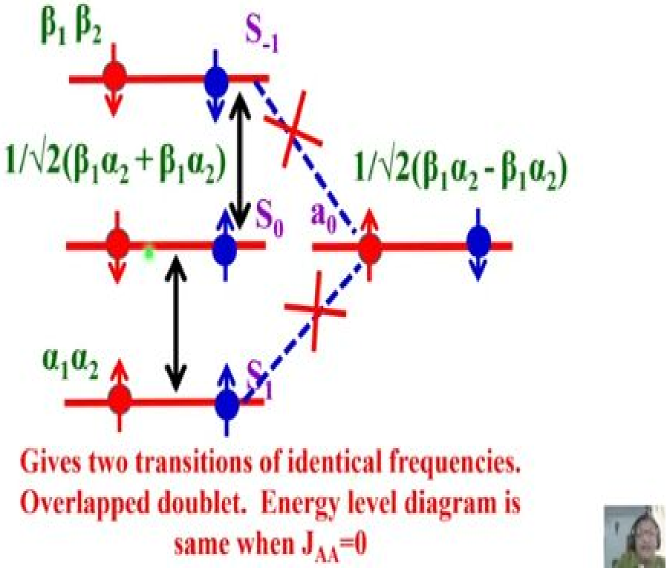
Only Homonuclear A_2

Heteronuclear A_2 spin system is impossible

The coupling between A and A is 0, the coupling is now reflected at all. I just now for the sake of understanding I have written here A and look at this thing, JAA or I can call it A1 and A2 does not matter. JAA of 2 protons coupling is 0 or not reflected in the spectrum; and the chemical shifts are exactly equal, again the equivalent spins for delta deeta is 0. Delta delta is 0 and coupling is also 0 or non-zero; this is called A2 spin system very strongly coupled spin system.

Remember AB strongly coupled spin system. Between AB and A2, A2 is most strongly coupled system and this is possible only in the homonuclear case. Heteronuclear A2 is impossible, because they are different chemicals shifts, the resonating frequencies are different, proton comes at 500 megahertz, fluorine comes at 470 megahertz. If you take such heteronuclear spins how can we think of AB or A2, it is impossible. So A2 spin system in heteronuclear is impossible; it has to be always homonuclear.

(Refer Slide Time: 07:16)



Gives two transitions of identical frequencies. Overlapped doublet. Energy level diagram is same when J_{AA}=0

This is the thing, now let us try to see how many transitions we get in A2. Remember you worked out the energy level diagram for AX. I did not write for AB; of course, we can also work it out, I leave it to your judgement to think what to do and you will work out the energy level diagram. But one thing you have to bear in mind; there is a mixed states in the AB, it is not pure states.

For example, alpha alpha, alpha beta, beta, beta alpha and beta beta are the product functions which are nothing but the wave functions for the weakly coupled system. But it is not the same for strongly coupled spins, there is a mixed state, in which case you have to take into account instead of pure states, especially alpha beta and beta alpha will turn out to be different like this, you have to take that into account. So you go ahead and practice it there is unlimited amount of information available NMR, you can keep discussing many things. I did not work out.

But A2 I will give, which is a special case. In the case of A2, again when you have two spins this one possibility both spins are down, beta beta state. One another possibility both are up; alpha alpha state. Again, it is strongly coupled, there is a mixture of states here, you see the wave functions are not just the product functions, you see this energy state should be written as 1 over 2 times square root of (beta1 alpha2 + alpha1 beta2) of course, it should be alpha 1 beta2, I think there is mistake I have made.

So similarly this will become negative. This is positive, this is negative. So in which case these two energy states, they are; alpha1 beta2 + beta1 alpha2; that it should be alpha1beta 2 + beta1 alpha 2. Similarly alpha1 beta2 - beta1 alpha2, so please read this correctly, this is not beta1 alpha2, it is is alpha1 beta2. Same here, it is alpha1 beta2. This is a while preparing the slide I have made a mistake, I am sorry about it, I apologise for that.

Please read it carefully, do not go by what is written here. Listen to what I am telling; this is alpha1 beta2 this is alpha1 beta2. So these three states are called symmetric states, these are triplet states; we call it symmetric state. Whereas this state is anti-symmetric state. What is symmetric state and what is anti symmetric state? Of course I do not want to go to details, you read yourself a little bit of quantum mechanics fundamentals, you will understand.

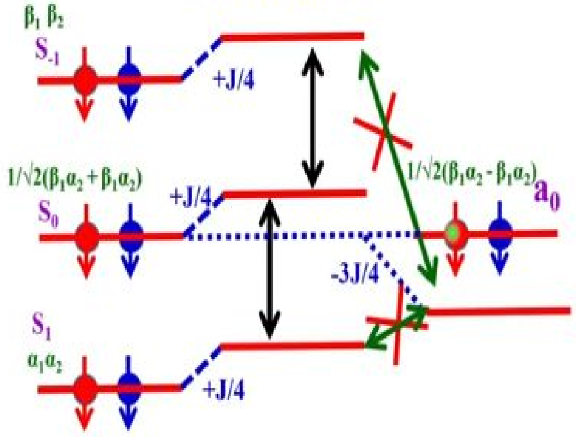
Now what are the allowed transitions here? I will tell you. This transition is allowed. Whereas symmetric to anti-symmetric transitions are not allowed. This is a case in A2; A2 has one anti symmetric transition, which I have written as is a0. There are three symmetric transitions S-1, S0 and S1, S1 corresponds to spin state where total magnetic quantum number for the state is 1. For this state the total magnetic quantum number is 0. For this state the total magnetic quantum number is -1. In this case also total magnetic quantum number for this state is 0. since the anti symmetric state; I wrote it as a0. It is a symmetric state; S0, S-1 and S1. Now the allowed transitions are only these 2, and this is not allowed. And what is the frequency separation of these two? Exactly same, you can find out the frequency separation in this case, it is exactly same.

It is a classic example of a situation; JAA=0. In A2 spin system there can be coupling, remember there can be coupling still did not get reflected in the spectrum. I gave you example of hydrogen molecule HH coupling is 276 hertz, it is present. But you do not see it in the spectrum. That is one case. But it can still be equivalent system like A2; but the coupling can still be 0 and this is a case where coupling is 0.

Now we are getting two transitions which perfectly overlap, exactly overlap and you are going to get only one peak; and that is what happens.

(Refer Slide Time: 11:42)

When $J_{AA} > 0$



Gives two transitions of identical frequencies.
Overlapped doublet.

Now, I consider a situation where the coupling is present. This is also possible, like hydrogen molecule. Now they are chemically equivalent plus coupling is also present, again write down for energy states; three symmetric and one anti-symmetric. Again here again I made a mistake it is alpha1 and beta2, this is beta1 alpha2.

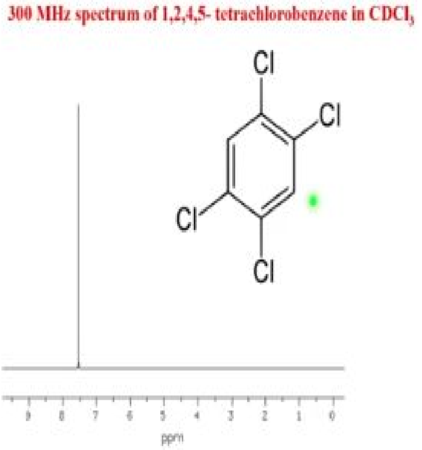
Now when the coupling is there, a very interesting thing happen? All these energy levels are shifted up by J /4. This is for all th ethree symmetric states; An A2 spin system the energy level move by J / 4. They get destabilized to an extent of J /4, all of them. What happens to anti-symmetric state? This gets this stabilized by a factor of -3J / 4 or you may ask me a question how did I arrive at this number and everything; extensive calculations can be done and it can be shown.

But please believe my words this is what happens. Now all the three symmetric states get destabilized and more by J /4 and the anti-symmetric state gets stabilized and comes down energy by -3J / 4; all these will go up + J by 4. Now find out the transitions here. Again, this is a transition, these two are allowed transitions; this transitions and this transition. Identical frequencies; again because energy separation has not changed, where all of them are moved up by the same amount compared to previous example. You remember the previous example, here they have the same energy separation, same frequency you are going to get. So it will overlap here also. But same because all the three energy states have destabilized by same amount, moved by only J / 4, all of them equally. For frequency, there is no difference in the frequency; again both the transitions are having identical frequencies and they overlap.

Yet again symmetric to antisymmetric transitions are not allowed, in this case also so. What does it mean? Here also you are going to get only single peak; okay, which are overlapped. The two peaks are there, which are overlapped and you get a single peak. So what is the conclusion? In A2 spin system, whether you have a J coupling or there is no J coupling, does not matter; you always get a single peak. Though there are two frequencies, they overlap and you give rise to single frequency.

You see the difference, if you should go to AX spin system. I got 4 lines, it is by general equation; number of transitions allowed we be ${}^{2N}C_{N-1}$. When two spins are coupled we should get 4 peaks we got 4 for AX, 4 for AB, But in the A2, remember that 2 spin are coupled. I am showing only two transitions. What happened to the remaining two? This is a special case, that is why I show you; in this case there is a anti-symmetric state and symmetric to anti symmetric state transitions are not allowed. As a consequence A2 spin system always gives two peaks of identical frequency, they overlap and the resulting spectrum will be a single frequency, single peak. This is important thing.

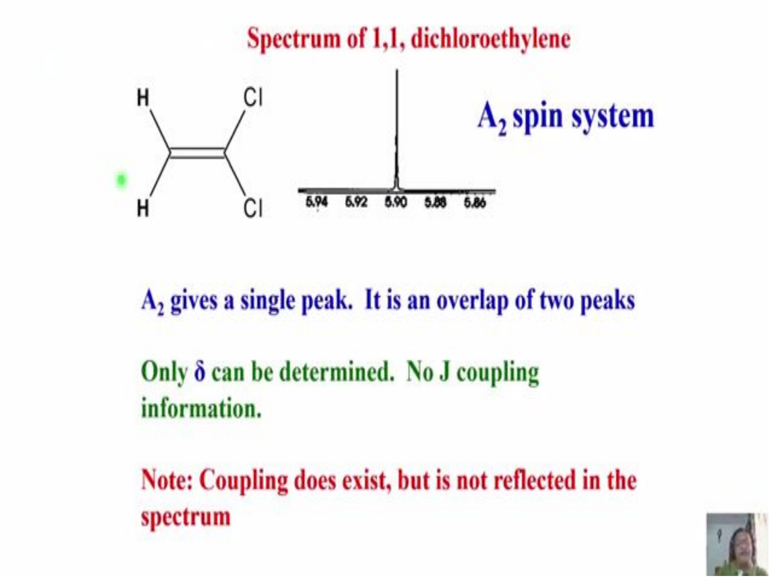
(Refer Slide Time: 15:24)


300 MHz spectrum of 1,2,4,5- tetrachlorobenzene in $CDCl_3$

And this is a classic example of A2 spin system, look at this. Here, 1, 2, 4, 5 tetra substituted benzene. This is tetra 1, 2, 4, 5 tetrachlorobenzene. Now this proton and this proton are chemically equivalent, and you will not see J coupling at all. It is perfect example of an A2 spin system. If this spectrum is taken in any spectrometer, for that matter, it will remain A2 only.

It will not become AB or AX in any spectrometer, it always remains A2 because there are only two protons, in this case both are chemically equivalent and gives rise to a single peak. Now the question comes what happened to the coupling? is there a J coupling? Of course there is a J coupling here. Meta coupling is of the order of 0.5 Hz to one Hz. It is there it is a classic example I showed you for A2 spin system. All the three in symmetric states are destabilized moves up by J by 4, anti-symmetric state gets stabilized comes down by -3J by 4. There is a decrease in the energy for this by -3J / 4. That is the situation here, there is a coupling nevertheless all the allowed transitions between symmetric states will overlap, and will give a single peak.

(Refer Slide Time: 16:47)


Spectrum of 1,1, dichloroethylene

A_2 spin system

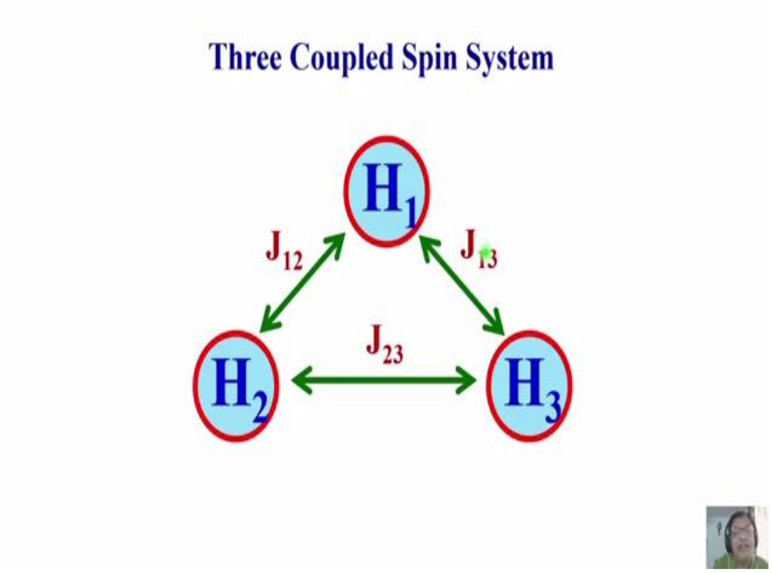
A_2 gives a single peak. It is an overlap of two peaks

Only δ can be determined. No J coupling information.

Note: Coupling does exist, but is not reflected in the spectrum

Another example, a classic example for this. This also is a case where A2 with a J coupling present. So what is the information you get, no J coupling information only chemical shift in A2 spin system. Measure the frequency position of this, you will say what is the chemical shift. No other information you can derive in this case, okay?

(Refer Slide Time: 17:12)

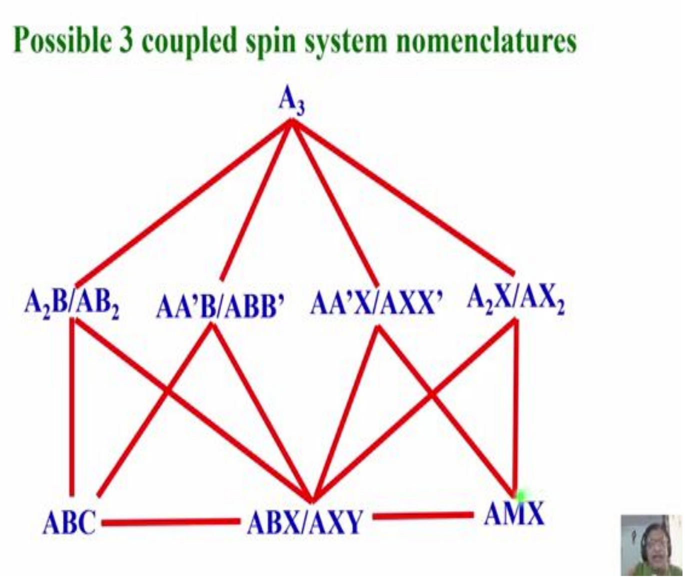

Three Coupled Spin System

Now I will go to another example of 3 coupled spin system. One or two simple examples I will show you, so that we can quickly wind up this topic; otherwise we can go on and on and on and on, talk about this coupled spin system; 3, 4 spins. With three spins, there are n number of possibilities, each of them can be analyzed, worked out and see this type of spectrum we get.

In 3 spin we have 10 possible spin systems, if I go to 4 spin. I will give one example, 33 possible combinations I can think of, and for each of them we may have to find out the energy states frequencies and transitions. This is not going to be one hour or one day it is going to be a one semester course, but we will not go into more details. I will give you one weakly coupled spin system, another simple example of 3 coupled spins.

This is just you always come across in your day-to-day analysis of this spectrum. That is why, I will give simple example. Three coupled spin system are like this, proton1, proton 2 and proton 3 there is a coupling between these two 1, 2, 1, 3 and 2, 3. So as I said if there is n coupled spin system, we have n chemical shifts. n (n -1) /2; that is 3 (3 – 1) / 2; there are only 3 couplings. And $^{2N}C_{N-1}$ transitions will be possible. Maximum 15 transitions, from which you can get 3 chemical shifts, and 3 coupling constants, that is all you will get from that. But the spectrum pattern varies depending upon the spin system, depending upon the chemical shift equivalence, and couplings are present or not. We will take simple example like this

(Refer Slide Time: 18:53)



Possible 3 coupled spin system nomenclatures

A_3

A_2B/AB_2

AA'B/ABB'

AA'X/AXX'

A_2X/AX_2

ABC

ABX/AXY

AMX

See these are the possible combinations you can think of, all can be chemically equivalent, you know, like A2 spin system, we discussed earlier. All of them can have same chemical shifts and the coupling constants can be 0. Or maybe there, or may not be there. Or I would not say 0, it may be 0 or non 0, but it is not reflected the spectrum. It is a classic example of A3, you can have A2B or AB2, AA'B, ABB prime, AA prime, AMX or AXX prime.

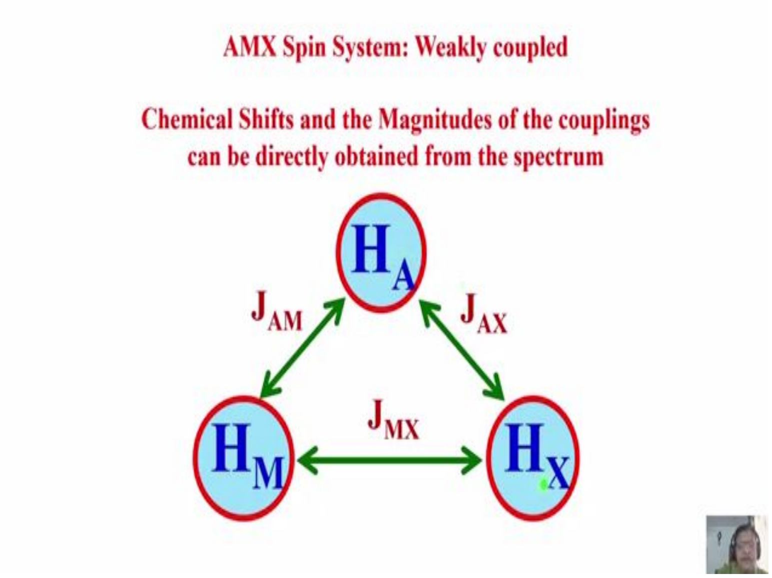
In this case A2B two are chemically equivalent like A2 strongly coupled and these two together have the same chemical shift and strongly coupled can have a coupling with another proton again, it can be a strong coupling. You understand two spins like similar A2 what we observed this can together coupled to another proton with a strong coupling effect it can have a strong coupling.

Here you consider the situation AA' B, AA' means that chemically equivalent but the coupling is visible in this spectrum. Here coupling is invisible in the spectrum. Here the coupling is seen in this spectrum, and these two individually can have coupling, with a strong coupling, this can interact with this, can interact with this, and their chemical shift separation is much much smaller compared to J coupling. As a consequence, this is a very strongly coupled spin system. You understand that.

Similarly, on the other end these two can be chemically equivalent with the J coupling observed in this spectrum, but these individually can have a weak coupling with another. It is called AA'X, or these two can be chemically equivalent like A2, coupling is invisible in the spectrum but together it can have a coupling, weak coupling with another proton it is A2X.

Similarly all the 3 can be strongly coupled, all the 3 couplings can be visible in the spectrum in which case it is ABC, or ABX. AMX is a weakly coupled spin system. So, varieties of combinations here, just for 3 spins; see how many types and each of them we can start discussing, the individual type of spectrum.

(Refer Slide Time: 21:04)

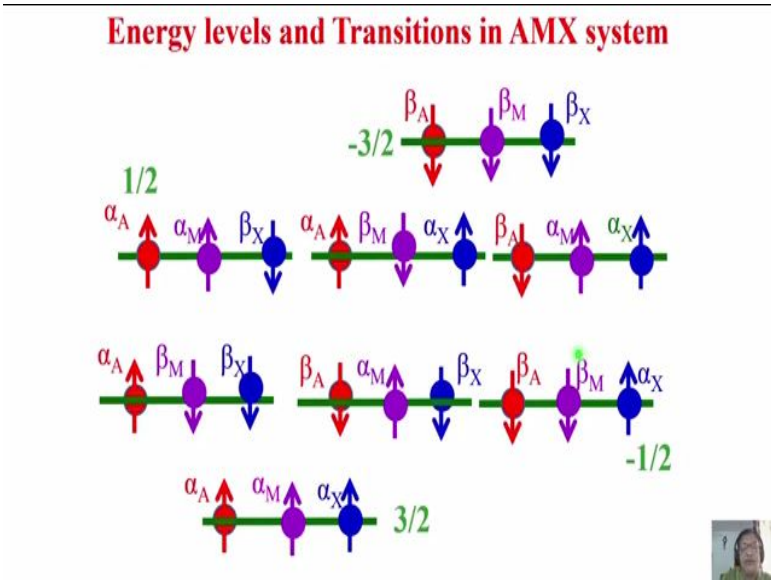


AMX Spin System: Weakly coupled

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

Well start with AMX why I took AMX very simple example. Because these are weakly coupled spin system. I told you look at the letters I have written A to M far away letters M to X far away. The letters I have written; AMX clearly tells me this is a weakly coupled spin system. So this coupling between A and M is JAM; this is JAX this is JMX. So 3 couplings and 3 chemicals shifts are there.

(Refer Slide Time: 21:34)



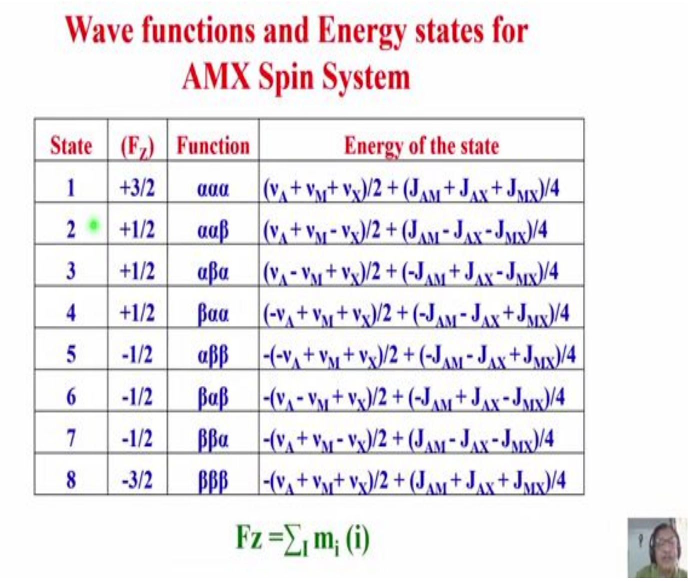
Energy levels and Transitions in AMX system

Let us see what we are going to see. This I already explained to you, when I explained the number of allowed transitions in a three spin case, in a weakly coupled case. We know what is the total magnetic moment of this energy state, and these energy states and these three and this,

This is - 3 /2 because all these spins are oriented anti parallel to magnetic field. Here all the magnetic moments are in the directions 3 / 2. Here 2 up 1 down same energy for all the three states. Here 2 down and 1 up same energy for all the 3 energy states. – 3/2; - 1/ 2, Now allowed transitions are between to these 2. This to this, this to this and this to, all are allowed. Now based on this we have worked out and last time we saw how many transitions are possible; 4 for X, for M and 4 for A, all those things we observed.

I do not want to go to the details clearly, now I have been showing you these are allowed transitions, because change the magnitude quantum number between two energy states is only one. So this is why we got 12 transitions.

(Refer Slide Time: 22:44)



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	$-(v_A + v_M + v_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4$

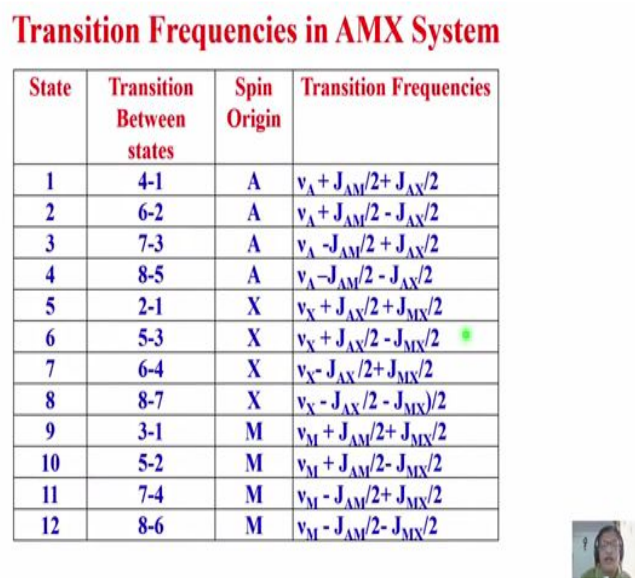
$Fz = \sum_I m_i (i)$

These are the 12 transitions which can be worked out. This is the wave function, it is nothing but a product function. Always in the weakly coupled spin system, wave function is just a product functions; jalpha alpha alpha you have to take. But in the strongly coupled case, you know in the case of AB and A2, I did not write the product function. In A2 I wrote it is alpha beta + beta alpha by root 2 alpha beta - beta alpha by root 2.

So we have 2 different mixes states. They are there getting mixed up, the wave functions are mixed there, but here it is a pure function. The wave functions functions are nothing but the wave functions. Again go to the quantum mechanical analysis, get the frequencies of each of the transitions or Eigen values first, and then differences of the Eigen values you find out, and you get the frequencies of the transitions.

And all I told you is like we saw in the diagram which corresponds to νx, which corresponds to νM and which correspond to νA.   You can identify 12 possible transitions, for example 3 / 2 to 1/ 2; this is allowed transition; 1 to 2; if you look at what is 1 to 2 allowed, it is the x transition and when I take the difference. νA, νM gets canceled out, it is the X transitions; like that you can identify what are the X transitions, M transitions and A transitions. You will definitely get 12 peaks here. So I have not worked out, but you please remember this very important, do not forget this.

(Refer Slide Time: 24:06)



Transition Frequencies in AMX System

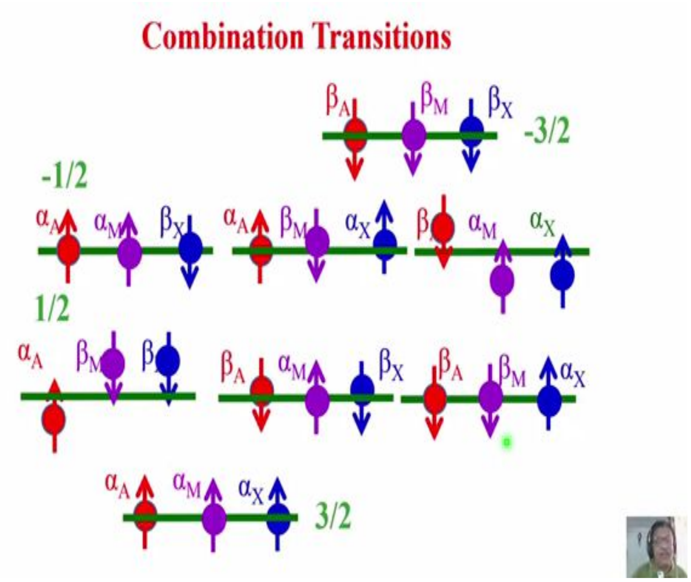
State	Transition Between states	Spin Origin	Transition Frequencies
1	4-1	A	$\nu_A + J_{AM}/2 + J_{AX}/2$
2	6-2	A	$\nu_A + J_{AM}/2 - J_{AX}/2$
3	7-3	A	$\nu_A - J_{AM}/2 + J_{AX}/2$
4	8-5	A	$\nu_A - J_{AM}/2 - J_{AX}/2$
5	2-1	X	$\nu_X + J_{AX}/2 + J_{MX}/2$
6	5-3	X	$\nu_X + J_{AX}/2 - J_{MX}/2$
7	6-4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

Now it is already done here; state one, 4 to 1 is transition, A; 2 to 1, you go back to that table find out this, depending upon which are the energy states to consider for transitions. It is going from letter 3 to 1. Take an example here, 3 to 1 is, If you take the difference this gets cancelled out this gets cancelled out, It is M transition, true, what is 3 to 1, M transition, you see. And then you can also get from this.

From this what is written in this bracket, you can find out what are the contributions of J, in this case when you are observing M you get AM and MX coupling. True, it has to be right? when A is active spin, you always get the coupling between active and passive spins, that is what I said, so when you are observing M you get AM and MX couplin. And there are 4 peaks; 2 peaks will move to the left from the center of this. Or from the chemical shift position of M, which is J / 2 of AM and J /2 of MX.

As a consequence, you can find out from the center, which is half of JM, and which is half of JMX. But then totally you will get 4 peaks. If you can measure the separations of that you can find out JAM and JMX very easyly. Like 4 transitions will give you 2 couplings.

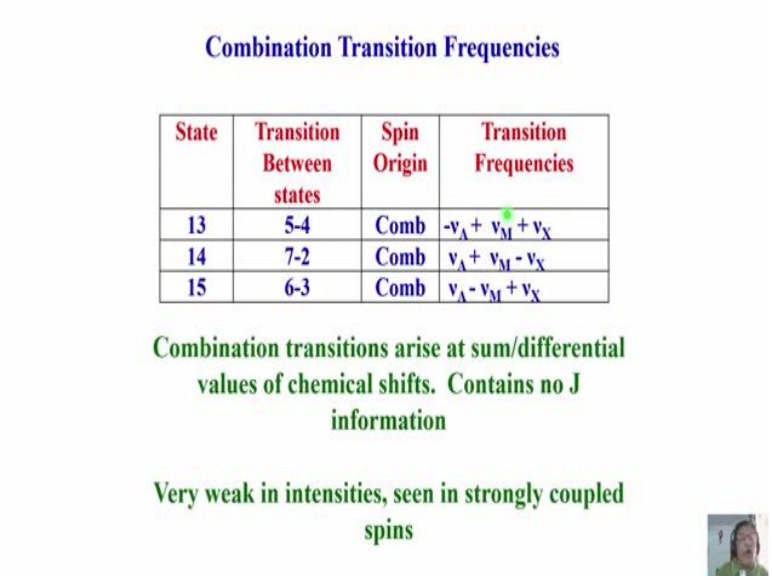
(Refer Slide Time: 25:41)



Combination Transitions

So that is okay, and also there are combination transitions, I said. All the three spins can go simultaneously from plus half to minus half. This is changing the magnetic quantum number of these two energy states by plus one or minus one; but all these 3 spins are undergoing transitions, the combination transition 1, this is 2, 3 all the 3 are allowed.

(Refer Slide Time: 26:04)



Combination Transition Frequencies

State	Transition Between states	Spin Origin	Transition Frequencies
13	5-4	Comb	$-\nu_A + \nu_M + \nu_X$
14	7-2	Comb	$\nu_A + \nu_M - \nu_X$
15	6-3	Comb	$\nu_A - \nu_M + \nu_X$

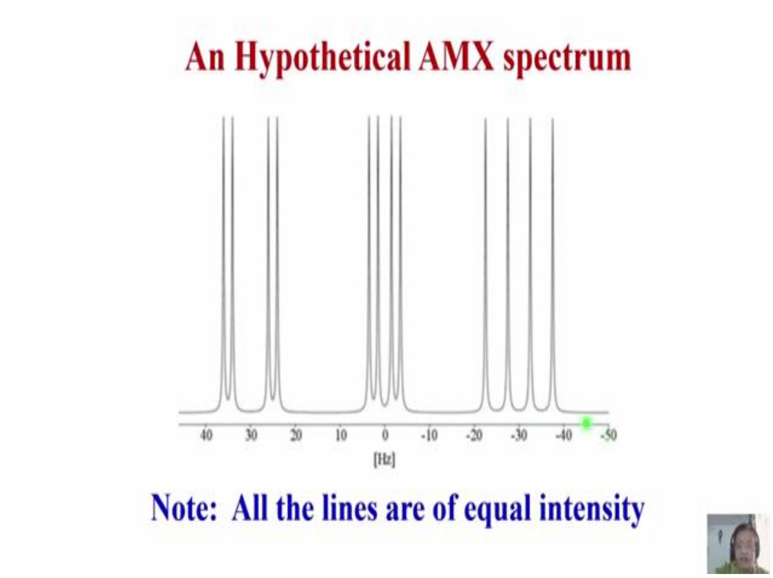
Combination transitions arise at sum/differential values of chemical shifts. Contains no J information

Very weak in intensities, seen in strongly coupled spins

So essentially you get 3 combinations transitions. What are you going to get here? Look at this parameter; in the previous case, there were JAM, JMX, half of that, all those things were there, here nothing. So the combination transitions will not give you coupling information. It only gives you chemical shifts, actually. It only arises at sum or difference of chemical shifts, if you find out 5 to 4 combination transition it comes at sum of νM or νX and from that νA chemical shift has to be subtracted.

In fact if you know these three combination transitions, and you have three equation and three unknowns, you can solve it and get the chemical shifts of all the three easily, you can find out it exactly matches with what you can get from the 12 peaks. So this also possible. So combination transitions give you only chemical shift information. And they are very weak in intensity. Normally in weakly coupled you dont see. Very rarely it is seen. But in strongly coupled especially, ABC all 15 peaks are seen, including 3 combination transitions. All 15 will be seen. So strongly coupled case this combination transitions becomes more intense.

(Refer Slide Time: 27:17)



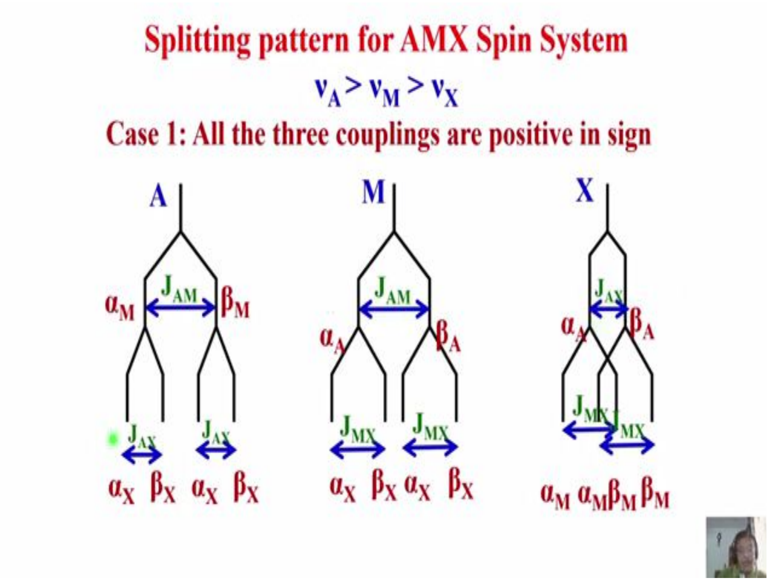
An Hypothetical AMX spectrum

Note: All the lines are of equal intensity

These are the points. And this is a hypothetical AMX spin system. What did I say when I took the example of AX, always in weakly coupled spin system intensities are very well defined. There is no intensity anomaly at all. All peaks are of equal intensity 1 : 1:1 :1 ratio. This correspond to one spin. It could be A, this is M, this is X; all are of equal intensity. This separation is larger, maybe one coupling is larger and other is smaller.

This has two couplings. If it is A you have JAX and JAM, if this is M you have JAM and JMX, if this is X you have JAX and JMX completely. Very easily you can get, I can analyze this spectrum and get coupling information and the center of this multiplet gives you chemical shift, the center of this gives you chemical shift. This gives you chemical shift. So AMX chemical shift are known, very easy analysis.

(Refer Slide Time: 28:19)



Splitting pattern for AMX Spin System

$\nu_A > \nu_M > \nu_X$

Case 1: All the three couplings are positive in sign

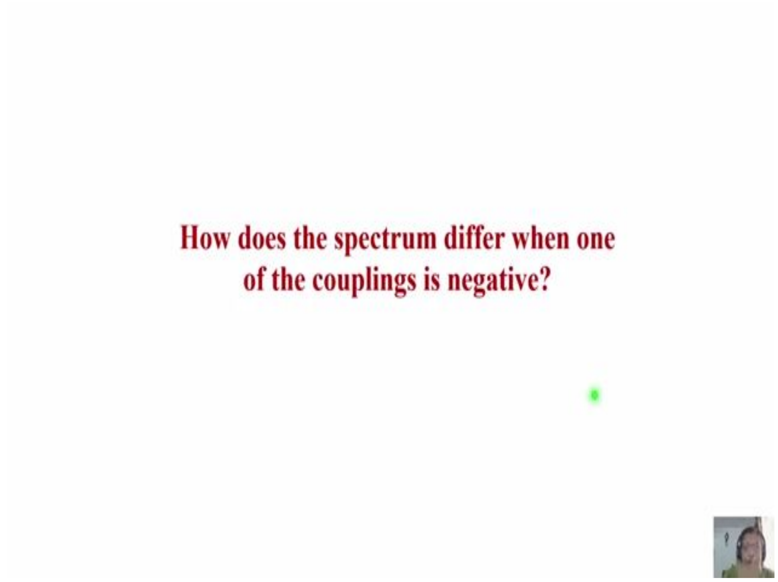
Now, let us see this splitting pattern for AMX, and we will try to analyze in a simple way. I consider situation νA is greater than νM greater than νX. All the three couplings are positive in sign. I know chemical shifts like this. I have considered A, M and X. A is here. M is here and X is here.

You know, this is a splitting pattern I get. Why νA splits into doublet because of M because of alpha and beta states of M. Okay? I did not write but this is a JAM, coupling.

Further each line is split into a doublet because of coupling to X. So, this is JAX splitting. This is JAM. This is AX. Similarly M, M can split into a doublet because of alpha and beta of A and each line of doublet is further split into doublet because of alpha and beta states of X. So this gives you AM coupling this gives you MX coupling. Similarly, this gives you X, X will be split into doublet because of A, this gives you JAX coupling. And further split by M due to alpha and beta spin states of M, it gives you JMX. Okay. Very easily. I have written here. JAM, JAX, JAM. So what is that your observing here? In each of these things the same information can be obtained twice. That is what I was telling you, the single quantum transitions of spectrum has large number of frequency transitions, large number of transitions, they contain redundant information.

I do not need all the frequencies to analyze and get this particular information. Look at this one. I get JAM here. JAM here also. I get JAX here. I get JAX here also. I get JAM here. I get JAM here also. So you can get this parameter twice, two times you can get it. Okay, the spectrum is easily analyzable. In fact you do not need to analyze everything. if analyze this you get two couplings, if you analyze this you get other unknown third coupling also. So only for chemical shift you have to use these, otherwise from these two you can get all the three couplings.

(Refer Slide Time: 30:55)

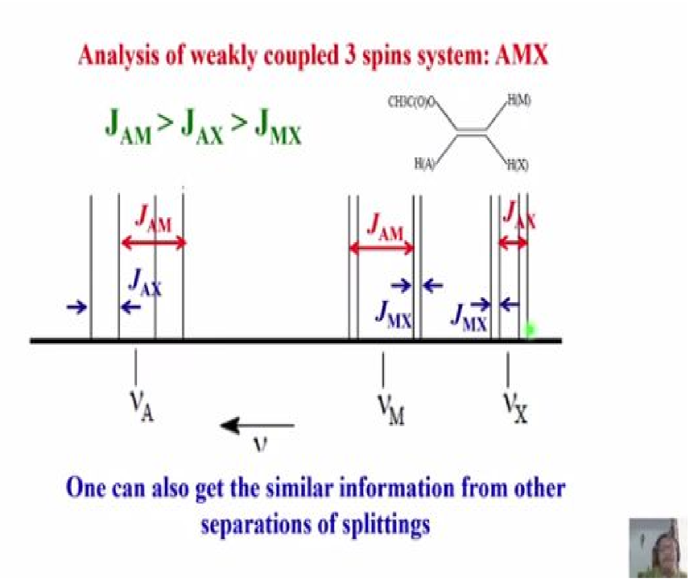


How does the spectrum differ when one of the couplings is negative?

Now I ask the question I was telling you one thing the spectrum is invariant within sign of the coupling. Let us say one of the couplings, there are three couplings, you know, AM, AX and MX. let us say one them is negative; actually change the sign, let us see what happens. This what you know, just now you worked out. Now I am going to make AM positive AX positive, only MX is negative.

Here is the X where here MX coupling is there here MX coupling is there. When I interchange change sign what happens, earlier I wrote this is alpha and beta state now it will become, this will become beta state this will become alpha state, what does it mean? The order of the transitions gets reversed, that is all. Nothing else, no difference you will see.

(Refer Slide Time: 31:48)



Analysis of weakly coupled 3 spins system: AMX

$J_{AM} > J_{AX} > J_{MX}$

One can also get the similar information from other separations of splittings

And this is a classic example of analysis of AMX spin exponent system, which is taken from the literature. Look at this is A spin, M spin and X spin very. Clearly written here A, M and X. Chemicals shifts, you do not have to worry, you directly get from the center of the multiplet. Also look at the condition here JAM is larger than JAX is larger than JMX. Why did I write like that? Look at the molecule, I have been telling you the trans coupling is larger than cis, and both of them are larger than germinal coupling.

This is precisely what we are seeing here. So, at the chemical shift of A, A can undergo coupling with them, trans coupling, the large coupling; may be this peak to this peak you may see one coupling or center of this doublet to center this doublet also we can measure, no problem. Initially it will be like this, the doublet. Each line of this doublet is further split because of coupling of A with X also. It is a vicinal coupling; and that is also quite large.

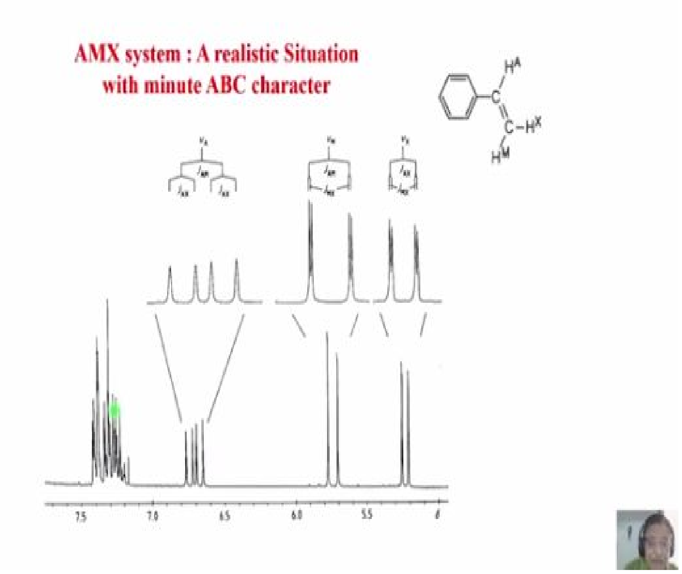
That is why this large coupling is trans, and this coupling is quite large also but less than trans it is a cis coupling or the vicinal coupling. Come to M now. At the M only one large trans coupling and small geminal coupling is there. So. the largest separation between this transition to this or theis to this from from central this doublet to centre this doublet, if you measure, that pertains trans coupling.

So what about this one, this correspond to geminal coupling this must be smaller. So while measuring the frequency J coupling, remember you can measure from this peak to this peak, this to this are same; or from center of this doublet to center of this doublet is same. Always this gives you trans coupling and each line of this doublet further split due to geminal coupling into two lines; because of this. That is why you get small doublets you measure this, you get geminal coupling.

This is what it is. Now, what about the X? X can have one vicinal coupling. This is of this order. And then in addition to that it has a geminal coupling. That is why from this to this, if you measure that is a general coupling. Or this to this, from the center of this doublet to centre of this doublet you measure it is a vicinal coupling, and each line of the doublet is split into doublet because of geminal coupling with the M and this is what the JMX.

So one can also get the similar information from other separations of splitting like this. Here I took this separation and I took this as the JAX. Similarly, you can look at this one, you can go back, and now use the other one this one I can use this one like this. So you can get this similar information from other separations of splittings. That is why I said it has redundant information.

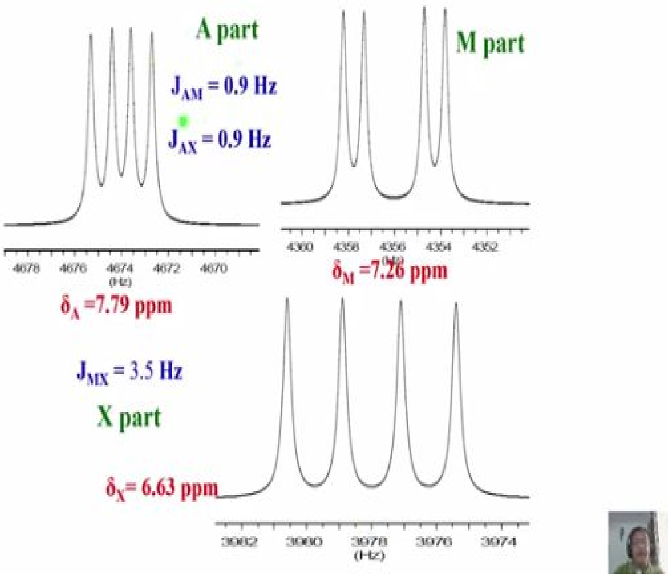
(Refer Slide Time: 35:04)



AMX system : A realistic Situation
with minute ABC character

Now AMX in a realistic situation like this, you see. This is one part A, M and X. This is AMX spin system, look at it. But do you call it a really AMX? No, look at the intensity, not exactly equal. They should be equal intensity 1 : 1 : 1 :1 ratio. They are not. So, I would say, it is close to AMX there is your minute ABC character present here. It is not a perfect weakly coupled spin system.

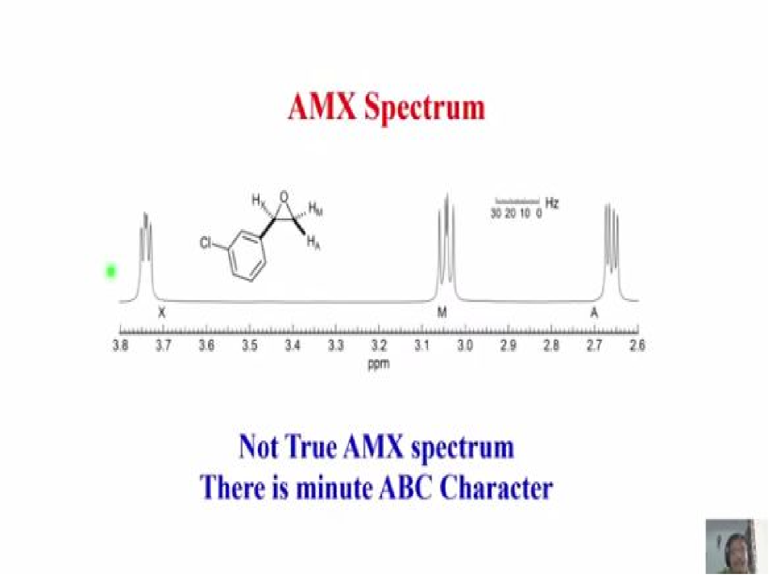
(Refer Slide Time: 35:39)



So you should understand. This is a classic example of AMX spin, it is the true 600 MHz spectrum of 2-furoic acid. Look at this one, A, M and X; all lines are equal intensity, very well separated. If you expand this you will get four lines, expand you will get 4 lines, this gives four lines. This centre gives you chemical shift of one A, this gives for M and this gives for X. If you analyze like I showed in the previous case, you get J couplings.

You see expansion here A part, M part and X part and the couplings have been measured very clearly. See the coupling is much, much smaller compared to chemical shift separation, here you see, it is quite larger here.

(Refer Slide Time: 36:20)

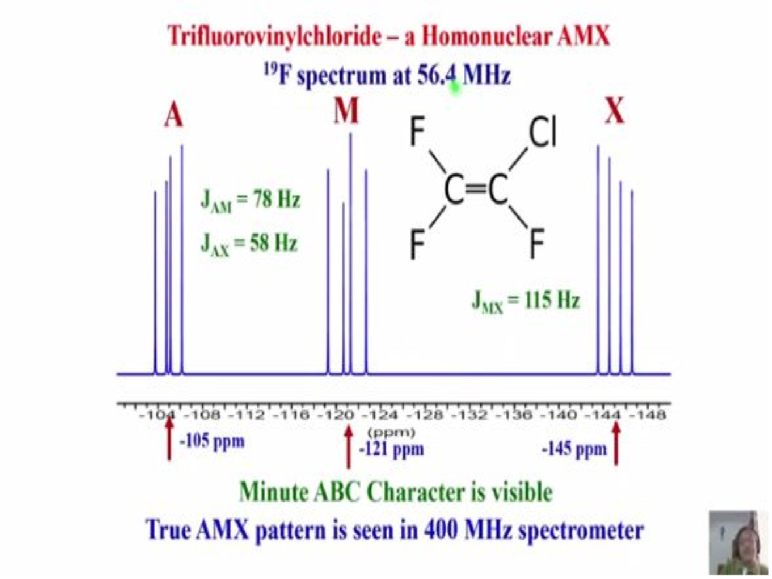


AMX Spectrum

Not True AMX spectrum
There is minute ABC Character

And this is an AMX spin system of this molecule,e three protons are present but you can see there is a minute ABC character also.

(Refer Slide Time: 36:30)



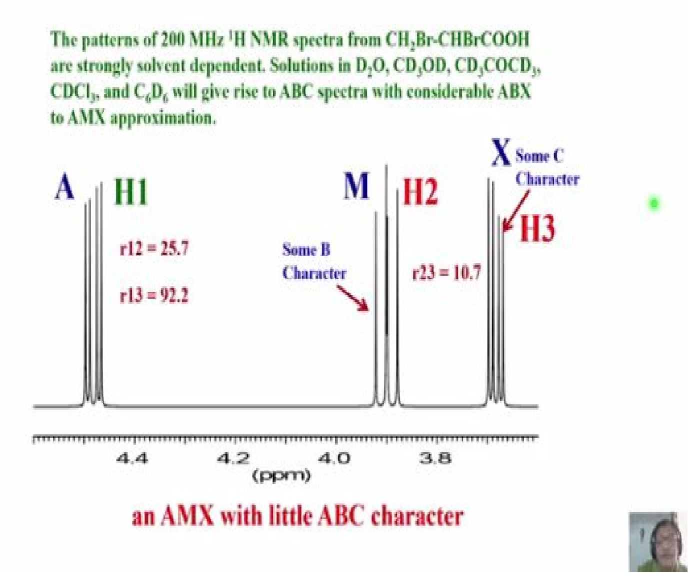
Trifluorovinylchloride – a Homonuclear AMX
^{19}F spectrum at 56.4 MHz

Minute ABC Character is visible
True AMX pattern is seen in 400 MHz spectrometer

Nevertheless, the analysis is possible, it is a true AMX spin system. this is also classic hetero nuclear. Not heteronuclear. This molecule has 3 fluorines, all the three fluorines are coupled again, vicinal, trans and geminal are different, as a consequence these three are well separated; well isolated chemical shifts are there, and they form AMX. Nevertheless there is a minute ABC character.

But you can go to very high field, this is almost at 100 megahertz or or 80 mega hertz I think. But if you go to 400 megahertz and take this spectrum, perfectly you will get all the lines of equal intensity.

(Refer Slide Time: 37:13)

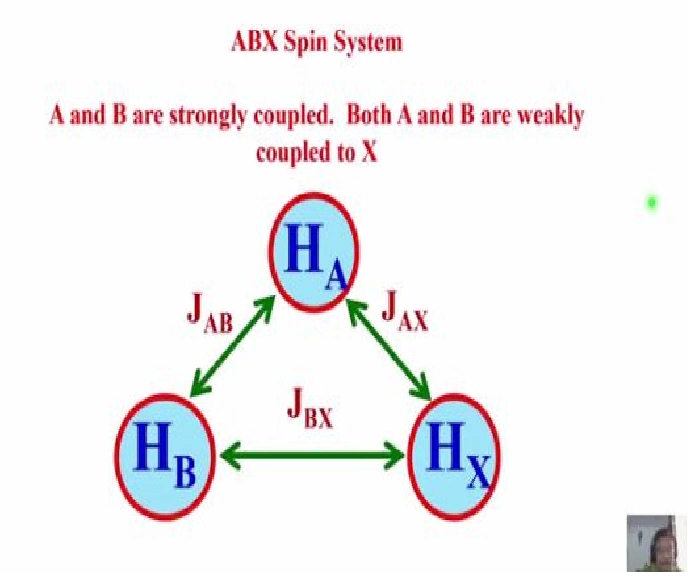


The patterns of 200 MHz ^{1}H NMR spectra from CH_2Br-$CHBrCOOH$ are strongly solvent dependent. Solutions in D_2O, CD_3OD, CD_3COCD_3, $CDCl_3$, and C_6D_6 will give rise to ABC spectra with considerable ABX to AMX approximation.

an AMX with little ABC character

So this what it is.

(Refer Slide Time: 37:22)



ABX Spin System

A and B are strongly coupled. Both A and B are weakly coupled to X

Now I will stop here, another two systems I will explain to you and then we will go to analyze the proton spectra later.