One and Two Dimensional NMR Spectroscopy for Chemists

Prof. N. Suryaprakash
NMR Research centre
Indian Institute of Science - Bengaluru

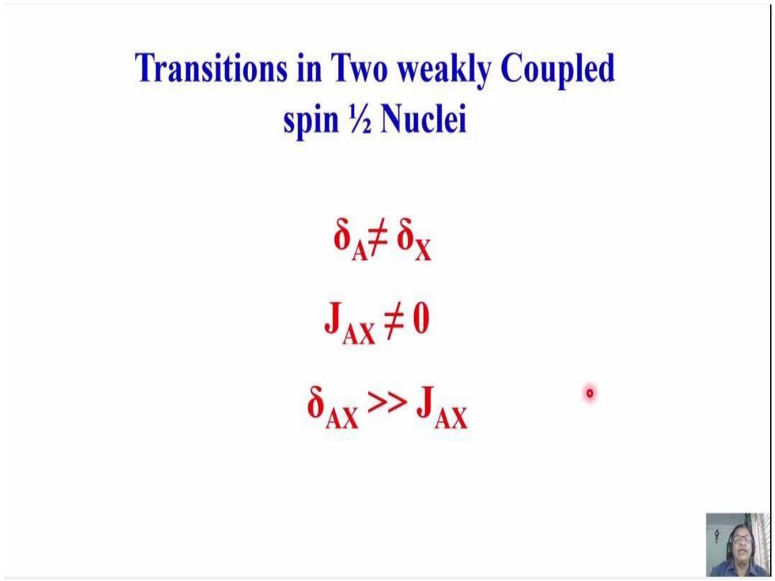
Lecture - 20
Energy level of coupled spins

Welcome back. So, we have been discussing scalar couplings since last 2 classes. I hope that you are all with me. You may please recollect, what did we discuss in the last class. In the last class I discussed about the interaction between 2 nuclear spins. The mechanism of J coupling what happens, how the energy levels will be there when 2 spins are coupled or with the coupling constant 0, or coupling constant nonzero and we worked out the energy level diagram for homonuclear spins and also heteronuclear spins, for two coupled spin system.

And we also found out what are the possible transitions for 2 coupled spins. Just by looking at the energy level diagram, we found out what is the total magnetic quantum number for each energy state, and applied the selection rules, we could find out which transition, I would say, belong to which spin. So in a 2 coupled spin system, I would say with coupling constant zero or 2 non interacting spins, we observed there are 4 possible transitions, 2 for A and 2 for X.

Since the frequency being same in both the spins, 2 transitions of A overlapped and also 2 transitions of X overlapped. As a consequence, what happened? we got only 2 peaks for 2 spins which are non-interacting. Today let us continue further and see what happens if you bring in the coupling between these two spins.

(Refer Slide Time: 02:24)

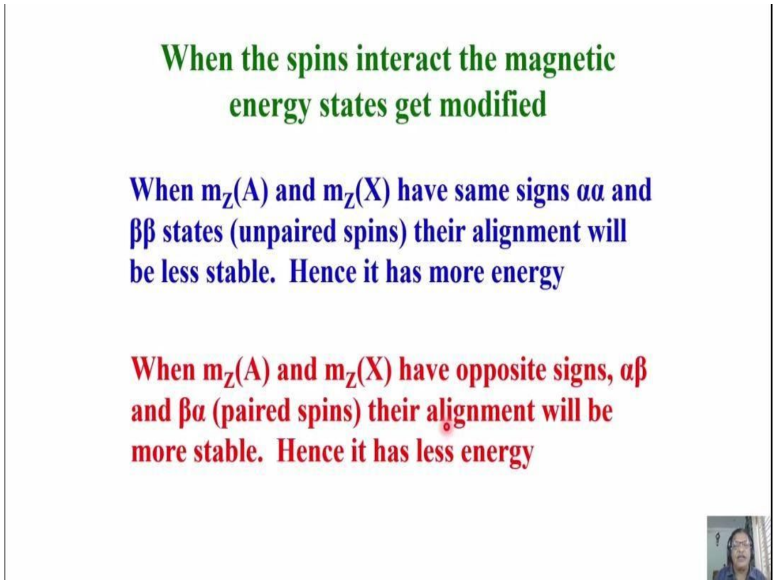


This is the case of a 2 spin half nuclei, where chemical shifts are not same, that means they are not equivalent spins. They are not equivalent nuclei. Like another condition I have put JAX is not equal to 0, there exists a substantial amount of interaction between these 2 spins. The interaction strength is how much, that will decide later, but one conditions JAX is nonzero. And I have also put a condition the chemical shift separation between these 2 nuclei is very much larger than the coupling constant.

You understand what I mean? In the previous example, we saw 2 peaks for non-interacting spins chemical shift of X, chemical shift of A, remember, one was here and one was here. And this separation we can measure; this is δ_{AX}, the difference between the chemicals shift of A and X. Let us say this is about 20 ppm, 20 ppm in 500 megahertz if you take, it is 1000 hertz, whereas coupling constant JAX is normally of the order of 15 or 20 hertz or less than that.

This is the condition I am assuming. I am assuming the chemical shift separation between the 2 spins is sufficiently large, very much larger than the coupling constant. Why I am going to do that, when you go further after few classes, you will understand what is strong coupling, what is weak coupling and how to get the transitions in a strongly coupled spin system, weakly coupled spin system, all those things we will discuss. OK. At that time I will tell you all the details, but at the moment simply understand, this is by assumption.

(Refer Slide Time: 04:27)



Now, when these 2 spins interact the magnetic energy gets modified. Earlier, they were not interacting, in the previous example, we had 4 energy levels, beta beta, alpha, beta, beta alpha, alpha alpha. So, there were the energy levels for total magnetic quantum number of the energy states, - 1, 0, 0 and 1. It what easy to understand. Now when the spins interact some interesting thing do happen, please understand.

Now, let us say a magnetic quantum number of spins A and spin X, have same signs, means, take alpha alpha both have same signs, plus half, plus half, what is the another energy state where the spins have the same sign, it is beta beta. So, when the magnetic quantum number of A and magnetic quantum of number X have same signs; that is alpha alpha and beta beta states are unpaired spins. You understand, they are unpaired. Only when they are different spin orientations, alpha and beta; they are paired.

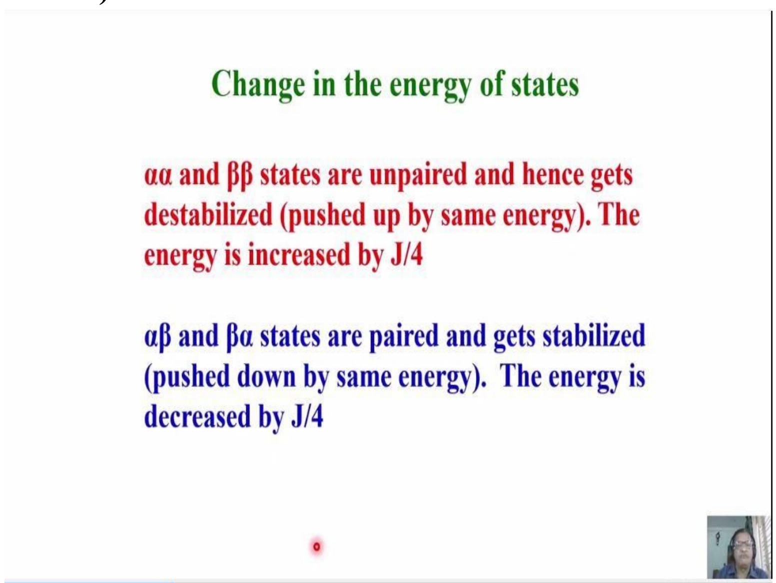
When they are unpaired spins, what happens? The energy levels are less stable. The alignment is less stable because we know that it is unpaired; you have studied in chemistry like Pauli's principle, everything you know, it is now not paired. It is unpaired, as a consequence, to get themselves paired it has more energy. If they are unpaired, it has less energy. When they are unpaired, that is, alpha alpha and beta beta states will have more energy.

Similarly what happens to opposite signs, for example alpha beta and beta alpha, OK; alpha, beta and beta alpha, are paired spins. When the spins are paired, the alignment is more stable.

Remember, alpha alpha and beta beta? They were unpaired. They were less stable, but the alpha beta and beta alpha are more stable states; so that means it has less energy. Do you understood the point, always do not get confused, what happens when the interaction is there, when there is non interaction.

For non interacting spins there was no change energy levels, beta beta was here, alpha alpha was here and alpha beta, beta alpha was here, it is very clear, but when the spins start interacting for energy levels something is going to happen, it would not remain same. What happens alpha alpha and beta beta have more energy, whereas beta alpha and alpha beta states have less energy.

(Refer Slide Time: 07:32)

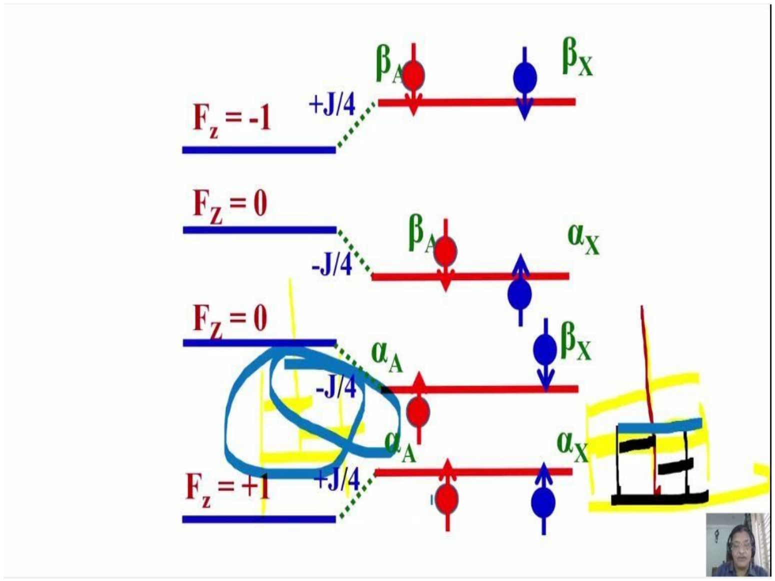


Now, because of this, there is a change in the energy of the states, OK. When they are interacting there is a change in the energy of the states. What is the change in the energy of the states? Alpha alpha and beta beta are unpaired hence gets destabilized, when they get destabilized they are pushed up by some energy. Alpha alpha and beta beta, when they are pushed up, destabilized and they go up. How much it goes up, it goes up by a factor of J / 4 where J is the interaction strength, or coupling constant between the A and X.

So, by 1/ 4th of the coupling, they are pushed up, alpha alpha will go up, beta beta also will go up. They are destabilized states. What about alpha beta and beta alpha, they are paired. When they get stabilized, they do not get pushed up, they are push down by the same energy. Understand a point now. Instead of going up these 2 states come down by the same amount of energy. So, alpha alpha and beta beta goes up, increases in the energy by J / 4.

Alpha beta and beta alpha states because they are paired, they get stabilized and there is decrease in energy by J / 4. But the quantum of change of energy pushing up, pushing down is the same. Both are J / 4, in one case it pushes up and in other case it pushes down. Please remember this point.

(Refer Slide Time: 09:09)



Now, how it works. So let us see, these are the 4 states. so see earlier I wrote 4 energy states like this alpha alpha, beta, beta, alpha beta and beta alpha, like these 4 different states. Instead of that I am now writing them vertically, because I wanted to show you how to transition. It is only a different way I am writing, that is all, but everything is same. Do not get confused. I am trying in a different style. To explain it better. That is all. Now what are these 4 energy states? This is total magnetic quantum number of this state, which is - 1.

This is 0. This is 0 and This is + 1. It corresponds to beta beta, beta alpha, alpha, beta and alpha alpha states. What did I say? These 2 states beta beta and alpha alpha, they get destabilized. So, pushes up by J / 4 both his energy level went up, look at it, it was here, they have moved up by J / 4. So, now, they have a different energy levels instead of here, they are more here, both of them. Now, what did I say for alpha beta and beta alpha states they get stabilized, and move down by the same amount.

This goes up + J / 4 comes down by - J / 4, by the same amount, they get stabilized by this energy. Now, what is happening, the energy levels you see, now, they are not identical to what would have happened without interaction. Because of the interaction, now energy levels and the separations are different. It is not same? So, what to do? Now, let us see what is going to happen for these 2. Now, same transitions,

What are the transitions? Now, you know, this is beta beta, beta alpha, alpha beta, alpha alpha,. Now I am writing like this; what is going to happen, apply the same selection rule. What are the allowed transitions here? The number of allowed transitions do not change, it remains same 4 transitions are there. Identify which are the 4 transitions. This is – 1, and - 1 to 0 this transition is allowed, which is the transition? beta X is getting changed to alpha X. See the difference? Beta X is getting changed to alpha X.

We will start with this one; alpha A is getting changed to beta A; this allowed transition because this also 0 to – 1 and - 1 to 0 is also allowed. Here beta beta is not changing, but alpha A and beta A is changing, so X transition is not affected. So, this only A transition; X spin is not affected here. Now, what about the other one, this is also alpha A going to beta A; and beta A is coming to alpha A, this is also allowed transition; from 0 to + 1. The difference is 1. 1 to 0 is again allowed. So, - 1 and + 1 is the change in the magnetic quantum number between 2 different energy states, it is + 1 or - 1 allowed. So what are these transitions; 2 A transitions? But what is the change you are observing? The same thing we observed for uncoupled spins. Now, what is the difference here? Look at it, this is moved by J / 4, this is a moved down by J / 4. The separation is now, difference if you take, it is J / 2; positive J / 2? do you understand it is J / 2 what about this difference? this is also J / 2.

Now, what is happening is, one of the peaks is moving by J / 2 other is moving down by another J / 2? See, now, if this is the chemical shift, let us say, of A transitions, A spin. Now, when it splits into 2 because of this energy level, one transition as higher frequency by J / 2 other has lower frequency by J / 2; higher frequency moves from the chemical shift by J / 2 other has lower frequency by J / 2; because this energy separation is smaller, less frequency.

So if this is the chemical shift of mine, what is less frequency, less frequency is to the right, so this peak comes to the right, what about this peak? this is higher frequency, move to the left. So, in the center, the peak which was there, split into 2, and 1 peak move to the right side, 1 peak move to the left side by the same amount. This moved to the left by J / 2. This move to the right by J / 2 and what is the difference between these 2 peaks now, you understand? Now what I am going to explain to you is this.

Now, there was a peak here. This peak is moved by here and this peak move here. This is moved by J / 2. And this is also moved by J / 2; what is the difference between these and these J. This is J coupling between A and X. You understand the logic now, this peak central peak split into 2 of equal intensity; this moves to the right, the one which moves to the right is lower frequency; this peak moves to the left is at higher frequency which is this peak. So we have 2 peaks.

Now because of different frequencies; unlike in the previous example, there is no overlap, there are 2 distinct peaks at different frequencies. You understand this point now.

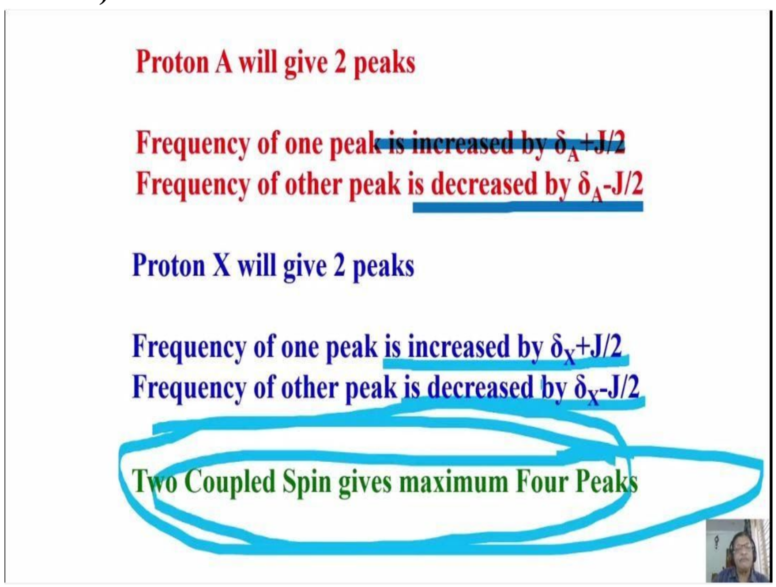
What about this one? Now we will go to X transition. Now, what are the allowed transitions of X? You see this one. This is allowed, because this energy state magnetic quantum number 0, the magnetic quantum number - 1 is allowed , the difference is 1, but here A is not changing, only X is changing.

So, A spin is still, in both these cases, remaining the beta state. Whereas the X spin is changing its state from alpha to beta and beta to alpha. And remember, this energy separation is a higher frequency because larger energy spread now. What about this one? another 1, that is also allowed now, this has come down by J / 4, this has gone up by J / 4. Now the difference is same, but now it is a lower frequency. Again now what I am going to do is, take this example for X.

X was like this earlier. now, because of this 1 peak, which is lower energy, or lower frequency comes here, higher energy or higher frequency comes here. So, these are the doublets now, and what is this separation? This is J / 2 and this is J / 2. What is this separation? It is J. Exactly like this, you get the same doublet, this is J and this is also J, and the centre of this is what? chemical shift of X, and the centre of this is what? chemicals shift of A, and this separation is J, this separation is also J between A and X.

So, one of them is enough to get the decoupling but both doublet are require you get the chemical shift. Are you all with me? I hope you will be able to follow what I am trying to say, I am now trying to tell you about what is the type of doublet you got. This is the 1 peak. Now after splitting it, splitting pattern is, let us say, this is J / 2, this is J / 2 and this is the line, and this is J / 2 and this is J / 2. Now, this separation, I will use a different color, this separation correspond to J, exactly what you see for this peak. Please remember, what you are seeing here is exactly same. Are you understanding? this is what it is.

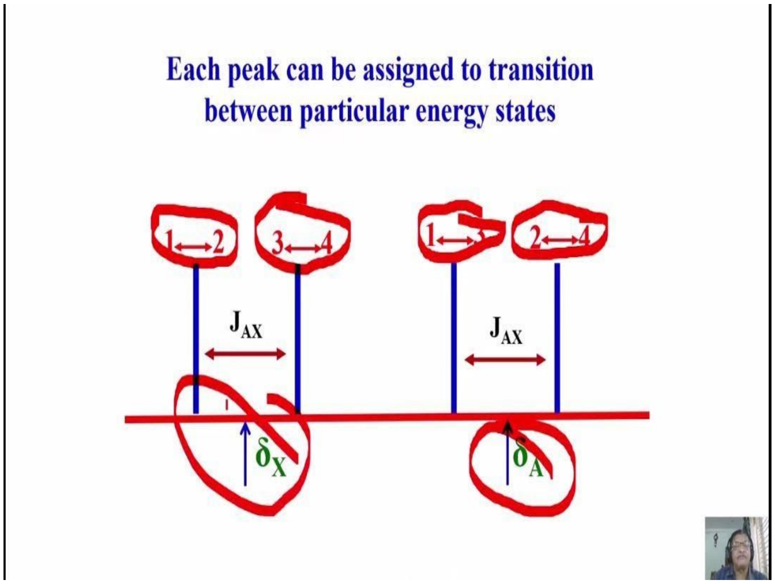
(Refer Slide Time: 18:58)



So, now 1, 2, 3 and 4, 4 transitions are observed. What did you understand? proton A, will give 2 peaks frequency of one of them is increased by J / 2 and frequency of other is decreased by J / 2. Now go to the next one, proton X also gives 2 peaks. In this case what is happening is frequency of one of them is increased by J / 2 other is decreased by J / 2. Please do not get confused. Now, in this coupled case also 4 transitions are there.

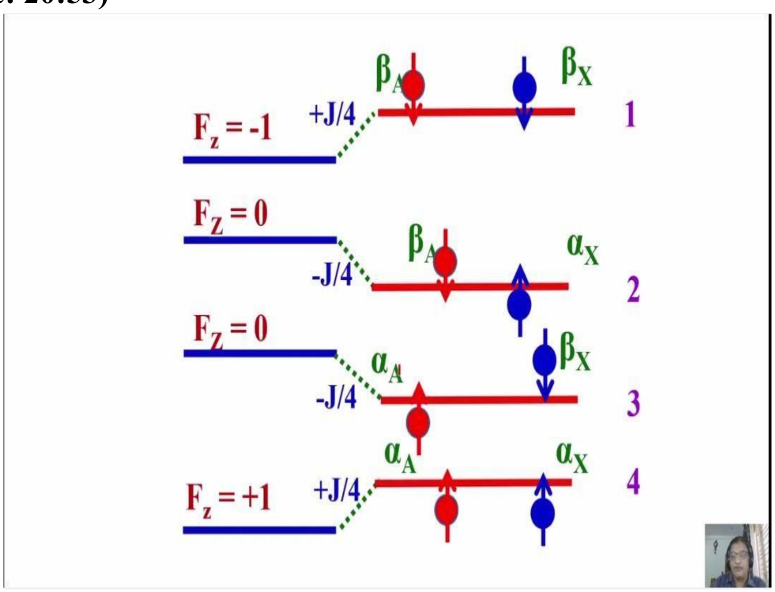
So, there are 4 distinct transitions, it can give you the coupling information unlike in the previous example. So, the two couple systems can now give maximum of 4 peaks, that is what we understood. In the previous case also, whether it is coupled or non-coupled, JAX is 0 will give 4 peaks, but we detect only 2, because 2 overlap. Here you get all the 4 peaks. This is what the example that we took for 2 coupled spin system.

(Refer Slide Time: 20:12)



Now each peak can be assigned to transitions. Remember, each peak can be assigned to the transition. Look at this one we observe 1 to 2 transitions in the energy level, go back here, what is the energy level transition from 1 to 2. These correspond to alpha X is changing to beta X. So, it is a X transition, and X transition is what, this energy is larger and the frequency is larger. So, that means, it comes at higher frequency, this is X transition.

(Refer Slide Time: 20:53)



What about 3 to 4 transition, go back, 3 to 4 again alpha X is changing into beta X but state of A is not getting changed, both the spins, in this case, A is in alpha state. So, this is X transition, but it a lower frequency, so, lower energy separation means lower frequency. So, this corresponds to the transitions 3 to 4. So, the center of this was the chemical shift of X, now because of splitting, this move to the right by J / 2 this move to the left by J / 2. Let us look at A, exactly what happened at the X, happens to A spin also.

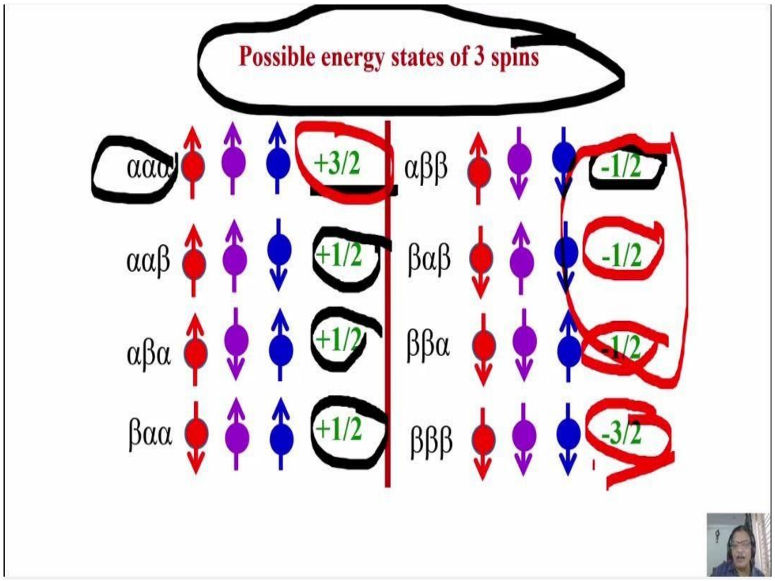
Now, go back. Here what is the transition between 1 and 3? it is A. Similarly, 2 and 4 is A. So, now look at this 1 to 3 is one transition for A, and other is other transition for A. But always remember, the center of this doublet give you chemical shift of A here and chemical shift of X here. Do not forget this. you understand, how we got the doublets in 2 coupled spin system, for each peak.

Now let us go further we will try to understand something more, very interesting thing we can do. We will go to the energy states for 3 coupled spin system, very complex. If you have not understood how we get 4 peaks in 2 peak system, it is even more difficult. Why? the possible energy states are much more here. How much was the energy states in the previous case, there were 4. There were 2 protons coupled remember, it is goes by the power, 2^2. So you got 4 energy states.

Now for 3 couple spin system, 2 cube. How much is 2 cube? It is 8, so there will be 8 energy states for this 3 coupled spin system. Let us again assume 3 spins, which are A, M and X, you understand. Three spins A, M and X, I use the same latter, do not take ABC that is not allowed. Why? you will understand when you go ahead later, it takes another 1 or 2 classes for you to come to that point, at least 2, 3 classes, you will not come to it till then. Afterwards. I will explain

You have to use only AM and X, because that is called weakly coupled. The chemical shift separation between them is larger than the coupling. So that is why I took A, M and X spin system. Three I labeled as A, M and X.

(Refer Slide Time: 24:05)



Now, what are the possible energy states for these three, you must understand what is the possible energy state for these 3 spins. In one case c all the 3 spins A M and X are in alpha alpha alpha. Now, what is the total magnetic quantum number of this energy state, alpha is half half half, simply add up all these three you get 3 / 2. Now, you can come to a situation, I am now considering 2 alpha 1 beta, can also consider 2 beta and 1 alpha that is another thing, that is how with 2 cube you have 8 energy states.

Now, consider the situation, this is alpha, this is alpha this is beta, then what happens? Two 2 plus half and 1 minus half, you will get plus half. Consider this possibility alpha beta alpha that is plus half minus alpha plus half, again you have plus half. In this case beta alpha alpha that is minus half plus half plus half, that is again plus half. Now go to the other possible states now I am considering 2 betas, 1 alpha. So, this is 1 possible combination alpha beta beta. that is plus half minus half minus half. If you add up all the 3, you get minus half.

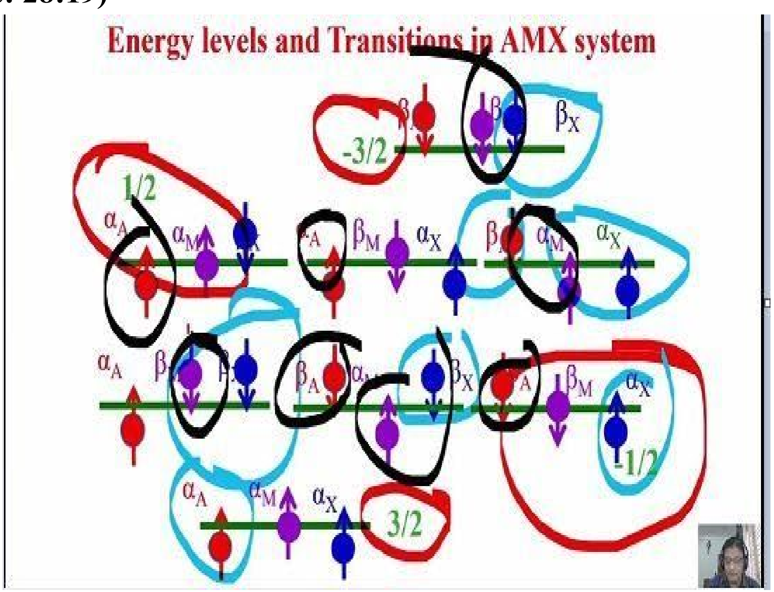
That is important point, you must remember. Now, next situation, beta alpha beta, this is beta, this is alpha, this is beta, what is the possibility now, what is the total number or magnetic quantum number of this energy state, minus half, plus half minus half, it is - 1 / 2. What about this one minus half, minus half, plus half; beta beta alpha, this is beta this is beta this is alpha, it turns out to be minus half. Now what about beta beta beta, all are 3 minus half minus half minus half; all are oriented with spin states down. Then possibility, add up everything, it is - 3 / 2.

These are the only possible energy states. You find out any other combination, it is not possible; you will not get it. So, when there are 3 spins coupled among themselves, the possible energy states are 2^3, there are 8 possibilities. Now, which are these states that have same energy; which are the states that have different energy? For example, this state this state and this state all are plus half, they have the same energy states. Remember, all are plus half plus half plus half, same energy state, this is 3 / 2, this is different energy state.

Similarly, this is minus half minus half minus half, all the 3 now have same energy, what about this is – 3/2. So, how many energy states we can think of, only 4 different energy states, out of each, one is 3 / 2 other is -3 / 2 the remaining 6 energy states out of these 3 are of equal energy and these 3 are of equal energy. So, there are 8 energy states out of which 2 are distinctly different like this, and these 2 are distinctly different in such a way, that these 3 have plus half energy and these 3 have minus half energy.

I am sure you are able to understand, I hope, do not get confused. I do not want to repeat, you understood now. This you can work out yourself, the possible permutation combinations you would have studied. So, if you work out that way and you will find out what the energy states here.

(Refer Slide Time: 28:19)



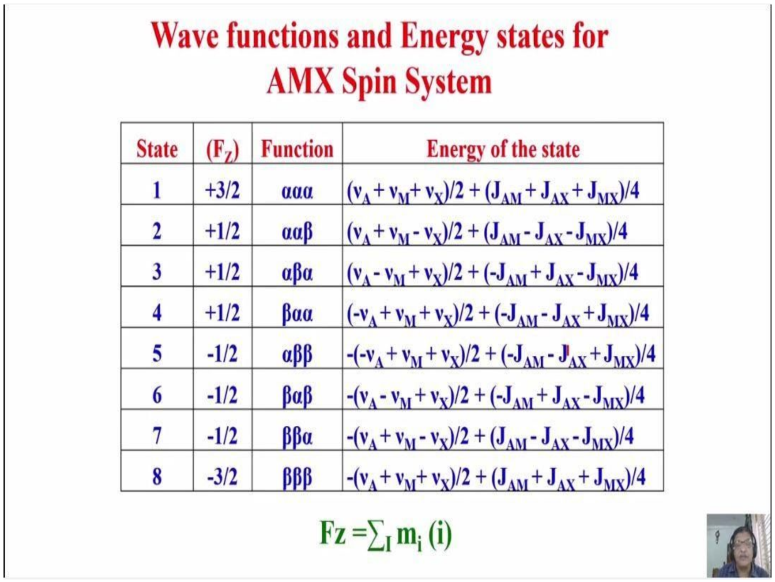
This is what it is. Now, I am going to write the energy levels and transitions in a AMX system in a very simple way. I said - 3 / 2 state here, which is minus half minus half minus half all 3 are down, this is plus half all are 2 up and down, all are 2 up and down you see, here 2 down 1 up so, this is a minus half energy, and what about this one? this is + 3 / 2, so now what we will do we will find out what are the allowed transitions.

Please remember what are allowed transitions? Change in the total magnetic quantum number between energy states must be either + 1 or – 1. Apply the selection rule - 3 / 2 to half, Is it allowed. Of course it is allowed, because if we take the difference, it is going to be 1 or this way is also allowed. Similarly, this to this is allowed, and 3 / 2 to 3 / 2 is not allowed. So, this to this allowed all these states, can have a transition from this, all these 3 states can have transitions from these, and all these 3 states can have transition from this.

Because plus half to minus half, minus half to plus half is 1, is allowed. So, there are various combinations of transitions which we can think of ,what are allowed and what not allowed. You understood what I am really trying to say. Let us take one example of 1 transition. What is this? alpha X is changing to beta X, allowed, because + 3 / 2 and half difference is 1, 3 / 2 minus half is 1. So, this is allowed. This transition corresponds to X. What about this 1, alpha X to beta X plus half to minus half, allowed, it is one transition. For this alpha of X is coming to beta of X, beta of X, is going to alpha X both are allowed. Now, go to the next 1, this 1, alpha of X coming to beta of X it is allowed. Go to the next 1. So, alpha of X again is going to beta of X and find out there are no other transitions correspond to X possible here. All others are for M and A and only X transitions are only these 4. No other transition is allowed for X, Look at it, all are A and M and only 4 possibilities like this. That means you got 4 transitions for X, understand what is the energy separation between them? you can work out, like the what we did for 2 spin system.

Now, let us see what is this? Here A is undergoing a transition from beta to alpha, alpha to beta, what about these 2? Remains same. they are not getting disturbed. What about this? That is allowed, beta A is coming to alpha A, is allowed. What about this? again what is happening there. Alpha A is changing to beta A. One more, this is also allowed, see alpha has in. See A has 4 transitions. Workout now, 4 for X, 4 for A, how many should be there for M? Exactly again 4. Look at this, alpha of M is changing into beta of M. What about here, alpha of M, is changing to beta of M. This one alpha of M changing into beta of M. So like this, we can work out ,beta of M changing to this.

(Refer Slide Time: 32:34)



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

$Fz = \sum_I m_i (i)$

So 4 transitions, and all these 4 transition we can work out. So what I am trying to say is, we can discuss about all the possible frequencies. And now we can calculate where do these peaks come? If I know the chemical shift of A, M and X, I can tell where the 4 peaks are coming, which are the couplings involved, like that. So, we will come to that. In the next class we will discuss these things.

But today what I wanted to tell you is, I want to tell you the allowed transitions in the couple 2 spin system, how we can get the transitions? What are the 4 transitions I explained to you, alpha alpha and beta beta states that unstable states, they push up in the energy by J / 4; beta alpha, and alpha beta, are stable states, they push down in energy by J / 4. As a consequence, if you look at the allowed transitions what you saw, 4 transitions, each 2 for A and 2 for X. From the center, the position of chemical shift, 1 peak go to the right by J / 2 and the other move to the left by J / 2. same thing for A, same thing for X. So, now, we extended the logic for AMX. We know there are 8 possible energy states, and we understood what are the transitions allowed? We found 4 transitions are there for A, 4 for M and 4 for X.

So how many lines we get? totally 12 lines. So AMX, 3 spin coupled, very weakly coupled, we have 12 lines.

So what are the 12 lines? we understand more when we come back tomorrow. Right now, this is the message, you please understand, go back and practice some of these things to understand. So we will discuss more about the energy states and frequencies everything tomorrow.