One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture - 21
Spin System Classification and Multiplicity

Welcome back. In the last class, we discussed about scalar interaction and worked out the energy level diagram for 2 coupled spin system, weakly coupled spin system A and X. We identified the 4 energies and total magnetic quantum number of each energy state and found out the allowed transitions. For each of these spins, we found out the 2 transitions for the A and 2 transitions for X. Of course from the energy level diagram I explained to you alpha alpha and beta beta are unpaired states, and they get destabilized and have a higher energy and moves up by J / 4. Whereas, alpha beta and beta alpha are paired states, they are stabilized. So, they have low energy and push us down by the same amount, by J / 4. So, when we worked out we found out for 2 coupled spin system, we get 4 peaks 2 for A, and 2 for X. From the center of the chemical sheet A, there are 2 peaks, which are; one peak to the right by J / 2, and one peak to the left by J / 2. It is the same for X.

Then we further we went to 3 spin system, and I showed 8 possible energy states. I worked out what is the magnetic quantum number of each energy state and I explained to you that there are 12 possible transitions here, 4 for A, 4 for M and 4 for X.

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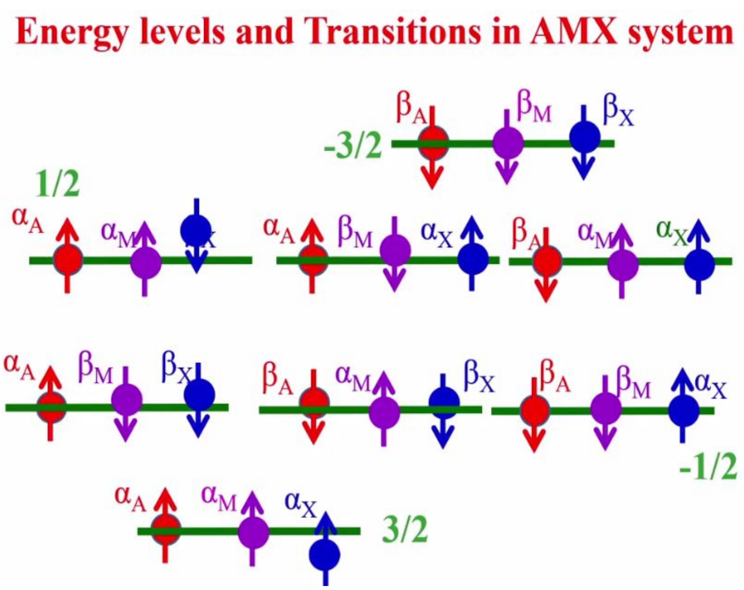

I explained to you in this diagram, I showed you, this is the energy state with a total magnetic quantum number for this -3 / 2. And each of these energy state has total magnetic quantum number of half, and this one has magnetic quantum number of each energy state as minus half, and for this it is 3 / 2. Pertaining to the orientation of different spins, different magnetic moments, whether it is up or down, we can work out all the energy states, what are possible energy states; and we found out also what are the allowed transitions for are all the 3 spins; A, M and X. I do not want to go into the details, because we discussed this last in the class.

Just to see only A transitions, or we will see the X transitions. In this case, beta of X is changing to alpha of X with the change in the magnetic quantum number between these 2 energies states is 1; from 3 / 2 to minus half is 1, half to - 3 / 2 is -1, it is allowed transition. But when you see here when this spin is undergoing transition, or spin flip; we call flipping of the state from alpha to beta, beta to alpha, these 2 spins have the same state. They will not get disturbed, see, this alpha A, remains alpha A, alpha M remains alpha M. So, only this transition is for X because that is changing the state. Remember for the transition the spins has to undergo transition from alpha to beta or beta to alpha state. Otherwise, the transition cannot be seen, you understand this one. So, now, let us see few things. Next transition; again X; alpha X to beta X, it is a plus half to minus half transition; plus half to minus half, that is allowed, because it turns out to be one. Another one, this is also allowed. This is also X transition and this is also X transition. So, like that I showed 4 transitions will be there 4 for A, 4 for M, and 4 for X.

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Wave functions and Energy states for AMX Spin System

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

$$Fz = \sum_I m_i (i)$$

So, without going into the details further we will go further; we can see what are the possible functions and energy states. We found out what are the wave functions, or in simple terms, the energy states correspond to alpha alpha alpha with the spin the magnetic quantum number of total is 3 / 2 half half half, all those things. Now, you can find out the transitions. What are the transitions allowed here. The first state here correspond to sum of all the 3 chemical shifts A and M and X, half of that then you will take the sum of (JAM, JAX and JMX) / 4.

Now, you can find out which are the transitions that are allowed. If I take, for example, this to this difference, this will cancel out, this will cancel out, only new ν_X will be retained and then this will cancel, when I take the difference this will cancel out, and this and this will be retained. So, you can find out all the possible transition frequencies and you can work out how many transition frequencies are there; and with respect to the center of the chemical shift of them, how the peaks have moved. How much they have moved, so, you can find out.

Take for example, this peak, take the difference between 1 and 2. If I take 1 - 2, this will get cancelled, this will get cancelled, you will get; $\nu_{X/2}$ plus $\nu_{X/2}$. How much? See do not get confused here. Look at this one. When I am going to see this one, take the difference, this term gets cancelled out, this term get cancelled out, and we will get $\nu_{X/2}$ plus $\nu_{X/2}$; it is ν_X. And then when I take the difference, this will cancel out, this will cancel out; and this will add up and this will add up.

What does it mean? At the center of the chemical shift position of $\nu_{X.,}$ From that position, actually one peak. If you take the difference, it is JAX / 4 and -JAX / 4, it will become J AX / 2. From the position of chemical shift of X, 1 peak is there which is moved by J / 2 of AX coupling. There is another peak which moves to the right by J / 2 of MX coupling, you can simply find out other one also like this.

You can see one more where the couplings (peaks) will be moving to the left. What is that, you can find out, which is which. So, again another transition you can similarly find out, there will be 2 transitions moving to the left of X. Remember in the AX spin system, we have 1 transitions each from the center chemical shift. But in this case, from the center of the chemical shift of this for each proton, there will be 2 transition to the right and 2 transition to the left depending upon the couplings; from the center, for example for the X transition here, you are going to have 2 peaks 1 separated by J / 2 half of JAX, other by half of JMX. Other one you can find out. Let me see which is that one. To retain νX, you take this one, take this one now, what happens νX will be retained and similarly, these 2 couplings will be retained and this gets cancelled out. It means you get 2 peaks from the centre of the chemical shift position of νX, here 2 peaks will come to the right. So, you get for each spin at the respective chemical shift position, the 2 peaks on the right, 2 on the left, separated by, each of them, JAX and JMX. Understand. From the center of the chemical shift position half JAX to the right and half MX peak to the right. From the chemical shift position νX; half JMX to the left, half JMX to the left. So, similarly you can work out for M and workout for A, all the chemical shift positions has 4, 4 peaks from the center.

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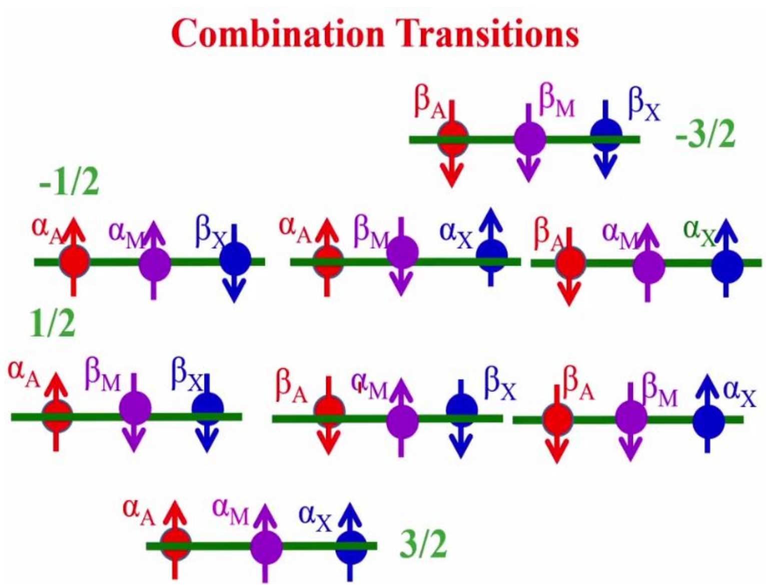

In addition to that, are there any additional transition possible here? If you carefully see, look at this one, plus half to minus half , it is 1, all the 3 spins are changing positions here. Look at it, alpha X is going to beta X here, Alpha M is going to beta M, beta A is going to alpha A. All the 3 spins are changing states from alpha to beta, it is allowed. See any one spin can change the state of alpha to beta or beta to alpha, that is fine. But all the 3 can change, no problem, but only thing is the selection rules should be obeyed.

So, this total difference in the magnetic quantum number between these 2 energy states, either +1 or -1, that is obeyed. This is called combination transition. Please remember, when 1 spin was changing, the particular 1 spin was flipping from alpha to beta or beta to alpha like this, this was called single transition, single quantum transition particular to 1 spin, 1 transition. But here all the three are getting changed, this is called combination transition. Is there any other combination transition, you can think of? What about this? This of course, we did, what about this? here also alpha A is changing to beta A, beta M is changing to alpha M, alpha X is changing to beta X, that is also allowed. This is another combination transition, these 3 completely changing, it is also allowed. What about this one? again allowed; alpha A will change to beta A, beta M to alpha M, alpha X to beta X. This also allowed, and the transition you can see it is between plus half and minus half, you understand about this thing. So, now, these are all allowed transitions. In this case, not 1 spin, all the 3 spins are changing the state from alpha to beta and beta to alpha, vice versa. These are combination transitions; 3 combination transitions are also there.

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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

But, generally the combination transitions, if you calculate, if you work out the frequency like this, the transition frequencies of combination transitions arise always at the sum and difference of the values of the chemical shift. It comes at the sum and difference of the chemical shift positions, look at this; and it contains no J information at all. It does not contain J information. You see here, it is coming only at sum and difference of the chemical shift positions. You understand? This is the situation here. And these are generally very weak intensities, and generally not seen. Seen only the stronger coupled spins, especially the weak coupling systems, the A, M and X these transitions are not allowed, or not seen. They are allowed, but not seen. Whereas, in the strongly coupled spin system, which I am going to explain to you later, these 3 transitions are allowed, are seen; but not in AMX system, remember this point.

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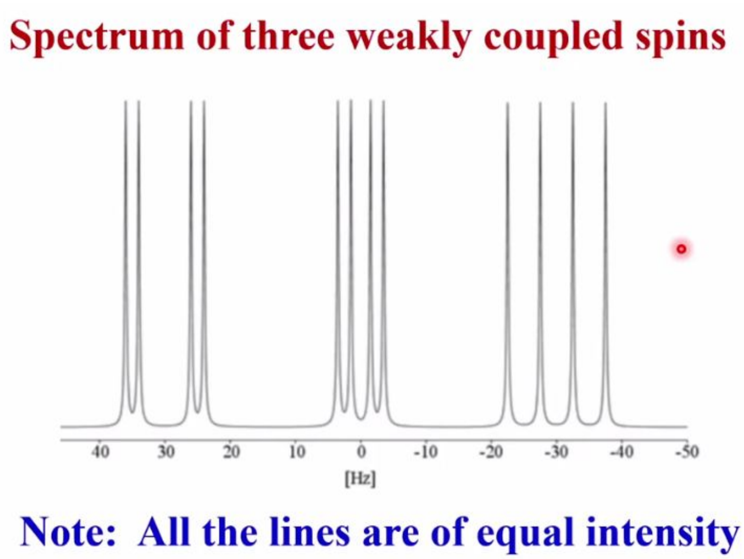

And this is a typical example of a spectrum, AMX spectrum. Typical example of AMX spectrum, where 4 transitions are there for A, 4 for M and 4 for X. see 4 for A, 4 for M, and 4 for X. Which is a A, which is M is my convention, the way. I can call this as A, I can call this as M, I can call this as X; or whatever the way I want, that is the way I define, labeling is my choice. So, now if we look at it, each spin, very interesting thing is, you are seeing for each of them 4 peaks. 4 for this, 4 for this, and 4 for A. From the center of these you have 2 peaks on either side.

It could be JAX, JMX or whatever it is. So, each of these peaks at the chemical shift position, each of the 4 peaks, if you finalize, you get 2, 2 coupling information, understand. And the interesting thing is, all are equal intensity, similar to a AX spin system, where 2 spins coupled, we understood and there is a JAX, 2 coupled system we got 4 peaks, all are equal intensity. Here also all the peaks are of equal intensity. This is purely perfect AMX weakly coupled spin system.

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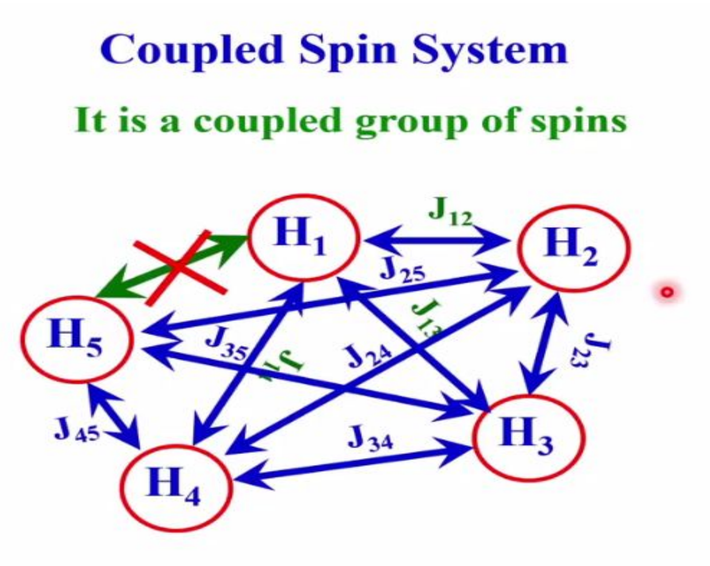

Now, I will give you some additional information, which you must know. Please understand, carefully listen to me. These are all information, which you require very often. If you want to understand NMR in depth, these are subtle information, but you need to know these things. I am now going to introduce what is called coupled spin system.

What do you mean by a couple spin system? We have A, M and X. All the 3, we understood this is coupled spin system. In the previous example of 3 spins you know, I took this, I called it A, M and X. A is coupled to M is also coupled to X, M is couple to A, M is coupled to X, X is coupled to M, X is also couple to A. So, these are all coupled spin system, it is a group of spin system, coupling can be there among all of them. Let us say, I consider five different types of protons are there in a molecule, 5 chemically inequivalent protons, all are different.

Let me concentrate on proton 1. It can have a coupling with this proton 2, it is possible. That is called J12 coupling. This can have a coupling with this one, that is J13, we can also have a coupling with this one, it is J14 and it can also have a coupling between 2 and 5 and not one, 2 can have coupling with 5, 5 can have coupling with 3, 2 can have coupling with 3, 3 can have coupling with 4, 4 can have coupling with 5, what about 1 and 5, this is also allowed, this is another coupling here.

What about 1 and 5, 1 and 5 there is no coupling, J coupling is 0, but this is a part of the coupled spin system. Remember, there is coupling of 5 to many other protons and coupling is also there with 4 to other protons. So it is a part of a coupled spin system. Whenever there is a group of spins which are coupled among themselves, we call it a spin system, a coupled spin system. There may be several couplings present. No problems. One of them can be 0 also. So for example, this coupling is 0, J 15, does not matter, but all 5 protons form a system. It is a coupled spin system, you understand what a coupled spin system? It is a coupled group of protons where each of them coupled among themselves, there may or may not exist coupling of 1 or 2, does not matter, but they all form a system where one is coupled to other, they are coupled among themselves. And some of the couplings can be 0, but spin must be a part of the system. It is a part of the coupled spin system you see, for all these things. It may not be coupled to this, but this is coupled to other spins, because others are coupled to this. It is spin system.

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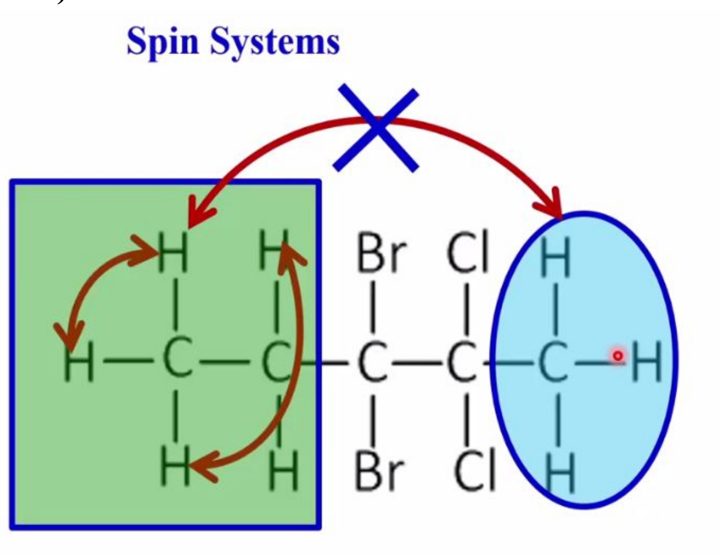

Now, simple example of a spin system is like this. In this example, you take there are 3 protons here, CH3 and a CH2. Just an example I am giving, This CH3 can couple to CH2, it is allowed, because there is no problem, the 3 bond coupling is possible. This can couple to this and this can couple to this. No problem. But if you see 1, 2, 3, 4 bonds away 1, 2, 3, 4, 5 bond away. So this CH cannot couple to CH3, CH2, and this CH3 coupling is 0, there is a break in the system now, break in the coupling. So, that means what happens is, this coupling exists, this coupling exists and this coupling do not exist. This is one coupled spin system. And it is another coupled spin system. Understand, here, none of these protons are coupled to any of them. So it does not form a part of the coupled spin system. For the part of the coupled spin system, all the coupling may not be there, at least some of them should be there. If all couplings are 0, that means it is not in the coupled spin system.

In this example of the molecule, there are 2 spin systems. This one form one coupled spin system. This forms another couple spin system. I hope you are all able to understand. I hope you are all with me. If, let us say, there was 1 proton here, and this coupling was there, and it was there, this coupling may be 0, but still it would have been a part of the entire group, and would have been part of coupled spin system. But because there is a breakage in the chain here, and none of these protons are coupled with this, they are all different spin systems. They do not form one spin system together.

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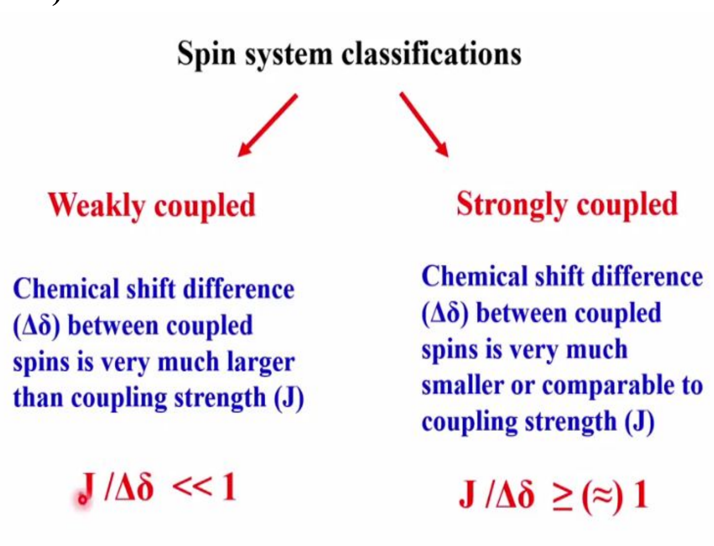

Now, the spin system, we can classify, very easy. There is a rule for it, we can classify. What do you mean by classifying a spin system? I can classify them as weakly coupled and strongly coupled. Remember, when I was analyzing the 2 spin system AX, I said, they weakly coupled, what did I say, because the chemical shift separation of these 2 should be larger, sufficiently larger, than coupling between them.

Here is the A spin, and here is X spin, the chemical shift separation maybe 500 hertz, coupling is about 10 hertz. Where is 10 hertz? and where is 500 hertz chemical shift separation. It is quite large right? the chemical shift separation. That is why we call such system, the chemical shift separation is sufficiently large, several orders of magnitude larger than the coupling, we call them as weakly coupled spin system. On the other hand, is a chemical shift separation is comparable or equal to J coupling they are strongly coupled.

I give an example here; look at this one, if I take the J over delta delta, what is J? J is actually if you see that, J will be about 10 hertz, and take as 10 hertz. And divide by the chemical shift separation. Let us say, 500. What is the difference now, it is we much, much smaller than 1. If you look at it much much smaller. Now come here, in this case J and delta are comparable, J is 10 hertz and delta delta separation is also, let us say, 15 hertz, what it this? this is of the order of 1, here is much, much smaller

Here,10 / 500 or 10 by, let us say, 1000 I will take for easy to compare. Then it is 0.001, which is much smaller than 1, and this is a weakly coupled spin system, whereas this one is strongly coupled spin system. Do you understand this one? please do not get confused. In this example, what I am trying to say, In this case, J / delta is much, much smaller, delta delta chemical shift separation much, much smaller. That means, this has to be very large value, and a weakly coupling spin system, if they are comparable or of the order of 1, then it is a strongly couple spin system.

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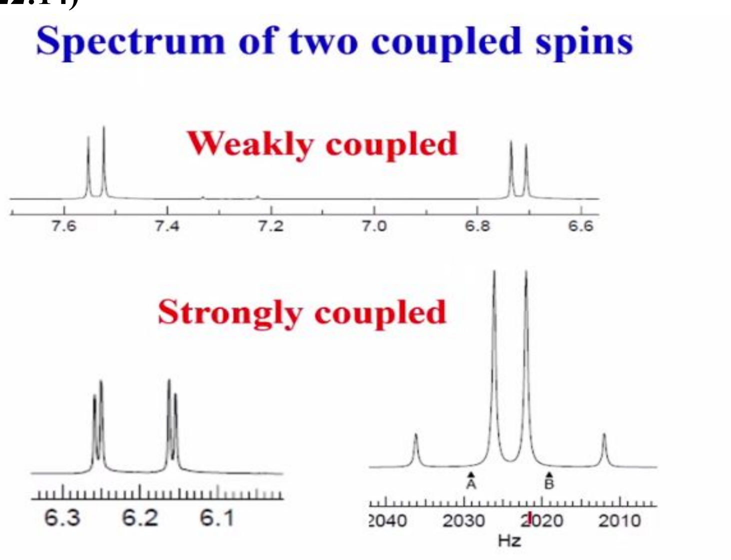

It is a very important point, you should remember. And this spectrum is entirely different, if it is strongly coupled and if it is weakly coupled. And especially when they are very, very strongly coupled, the spectrum will appear entirely different. Remember that point, look at the example of this spectrum of 2 coupled spins. We took the example of 2 coupled spins system, AX spin system right? we got 4 transitions, we calculated by looking at the transitions; 2 for A and 2 for X. That is what we observed. Here these are 2 for A and 2 for X.

This is a weakly couple spin system, look at the chemicals shift separation, about almost 7.52 and 6.72, about 1 ppm. In 500 megahertz, 1 ppm 500 hertz, what is this separation? it is only about 10 hertz. That is weakly coupled and they must be of equal intensity. See in principle all these 4 lines should be of equal intensity. Look at this one all this four peaks should be equal, but, do you see this, No, not of equal intensity, it means, it is still not 100% weakly coupled, there is some sort of a strong coupling character put in this system. There is some sort of a strong coupling character present in this. So, this is a weakly coupled, more or less you assume that equal intensity and weakly coupled.

What is a strongly coupled? strongly coupled looks like this. Look at this one. This spectrum is a 2 spin coupled, this is also 2 spin coupled. But this is 4 lines of equal intensity, well separated, whereas in this case look at it, it looks like 2 very strong peaks at the center, 2 very weak peaks outside. This is the pattern of a 2 coupled spin system, especially when they are strongly coupled. I am going to discuss more about strong and weak coupling, and try to analyze this theoretically, by using Pople nomenclature. How we can analyze the spectrum I will come to that later, we will use the Pople notation, when I say AX, AB, AMX, I use the term AX and AMX when do you want to use it? We will discuss all those things later.

So now with this idea, I hope you got some idea about the multiplicity, strong coupling weak coupling, spin system and also I explained to you what are the transitions for 3 spin system, like A, M and X weakly coupled, 4 A transitions we have got for A, 4 for M 4 for X, and we also saw in such system there are 3 combination transitions, where all the 3 spins can simultaneously change states from alpha to beta, and vice versa.

Normally, only once we will change from alpha to beta or beta to alpha, others will remain same, their state will not change. But in some examples, all can change, but still maintaining the selection rule. They are called combination transitions. All those things we understood, some information, about scalar coupling and everything. Now, most important part, we will understand how this scalar coupling influences the spectrum. So far, we took the example of 2 spins, and 3 spins, you got 4 peaks, you got 12 peaks in AMX, it is very easy. I can show you how we analyze later, we can easily get the chemical shifts and couplings.

What happens when the more protons are coupled? Will you get only 4 peaks of equal intensity will you get only 12 peaks of equal intensity? do not know? again depends upon the spin system, depends upon how strongly they are coupled, how weakly they are coupled, how the multiplicity will be there? whether it is 4 peaks, 10 peaks, 12 peaks, what is the pattern, we do not know. We have to understand that. As a consequence, I introduce to you, something about what is called multiplicity of this spin system, please remember, I am going to introduce to you about multiplicity of the spin system here.

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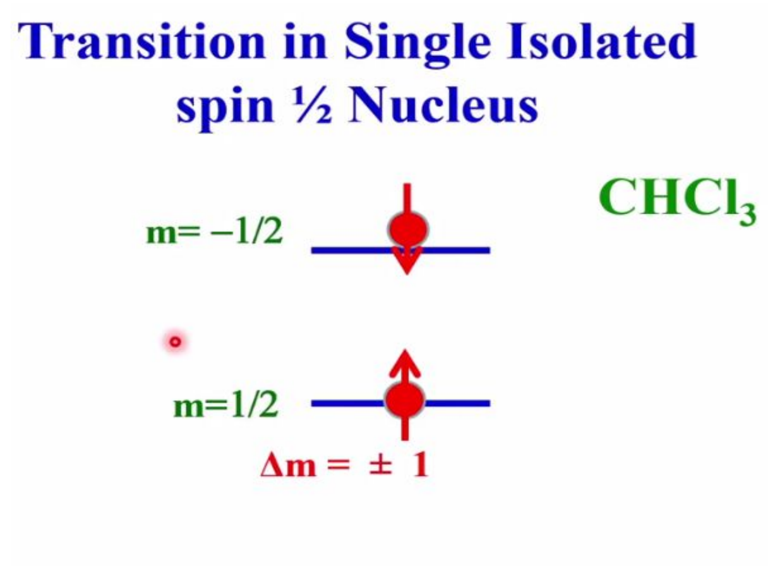

What is the multiplicity of the spin system? First, start with an isolated proton, isolated spin, or any molecule containing only 1 proton. Consider an example of CHCl3, I am looking at proton spectrum.

What are the other spins which can interact here? What are the other NMR active spins? carbon 13, chlorine 35 and it is a quadrupolar spin, we will ignore it. Assume that it does not couple. Carbon 13 is there, that can couple to this. But carbon 13 is a very low natural abundance, only 1%. This is what, remember. As a consequence, temporarily for the time being we will assume carbon 13 coupling to proton is not there. Even if it is there, we do not worry, ver small intensity peaks will be there, we will not bother about that coupling. We will assume that molecule has 99% carbon 12 attached to CHCl3. carbon 12 with CHCl3. We will consider 99% molecule, 1% will not worry. Then, if that is the case, it is like telling it is an isolated single spin system, because it does not couple to this, this does not couple to this. And we say it is carbon 12 isotopomer. What are the possible energy states for this, there are 2 orientations of the magnetic moments, plus half and minus half. The allowed transition, we have been discussing, the selection rule also we discussed. So, this spin can go from alpha to beta and beta to alpha, this transition is allowed, because minus half to plus half plus half to minus half is always plus or minus 1. So, this is analogous to a single spin, uncoupled spin system. In this case we get only a single transition. An isolated spin ½ always gives a single peak.

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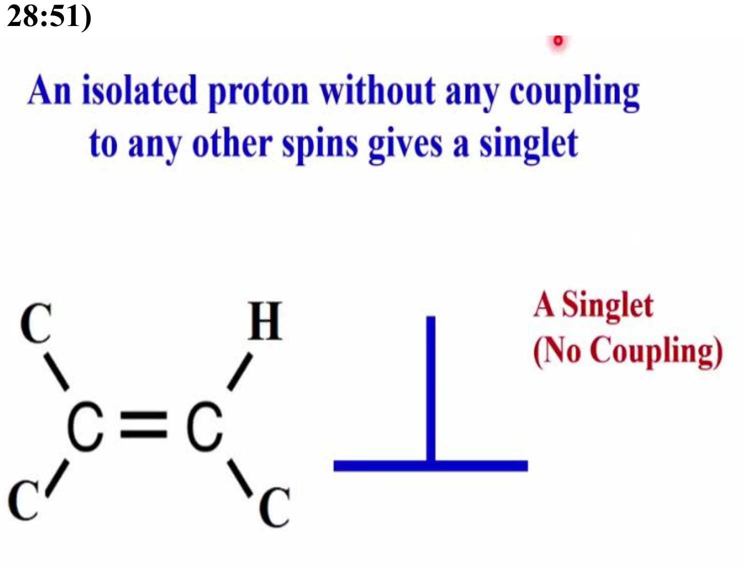

This is a classical example I will give you. Take an isolated proton without any coupling to any other spins. Take a molecule like this. An hypothetical molecule I have generated. I have put proton here, carbon with X, Y and Z. They are attached here and none of them coupled to this, then how many peaks you get? only 1 peak, it is a singlet, that is an example.

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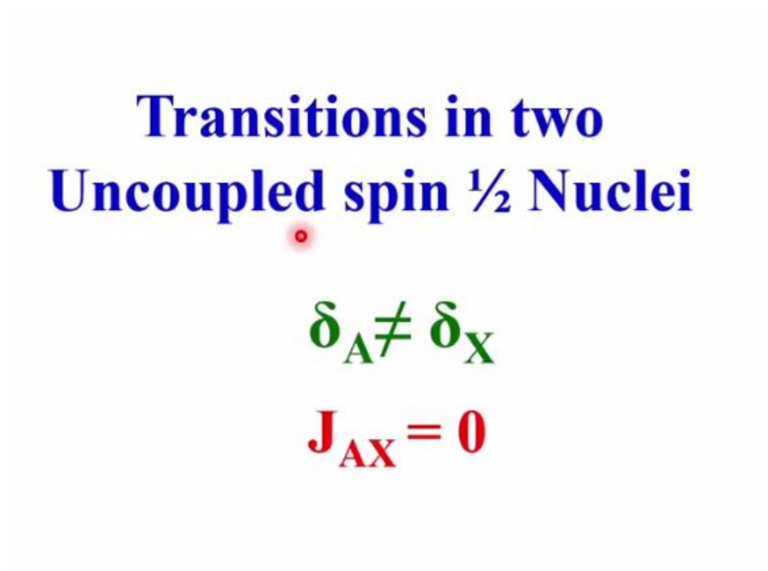

Now, we already discussed transition in two uncoupled spin system, J_{AX} is not equal to 0, we already discussed.

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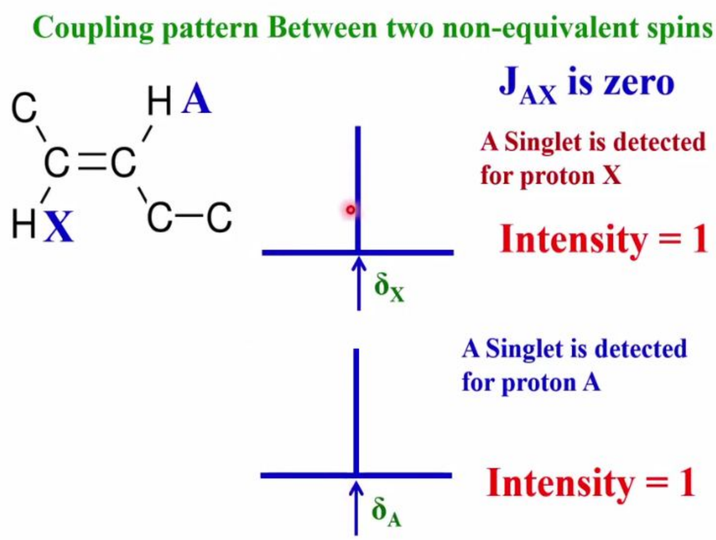

Now, take an example like this, proton A and X, assume this coupling is 0. When I make JAX as 0. What will happen? You will get 1 peak for X and 1 peak for A. Remember a singlet is detected for A, and a singlet is detected for X. This is what we observed. We have 2 spins, which were non-interacting, and we found from the energy level diagram, there are 4 transitions, 2 for A and 2 for X identical frequencies, they were overlapping. So, as a consequence we got 1 peak for A, 1 peak for X. please remember, we worked it out in one of the classes, may be 2 classes before, for 2 interacting spins we calculated, we found out the transitions. We got one transition each for A, 1 transition for X. In reality there are 2 peaks overlapped. Let us consider the intensity of this is one. They are all equal intensity, overlapped equal intensity will be there.

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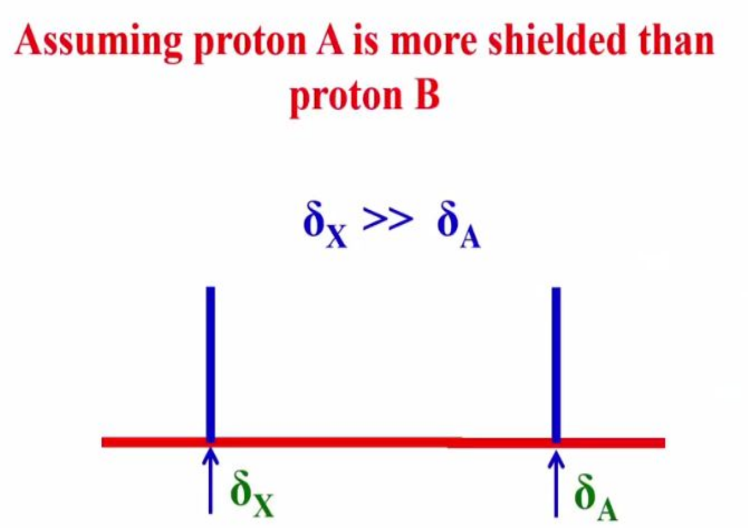

And if I assume similarly in the previous case, delta X is larger than delta A, I get only 2 peaks. This also we understood.

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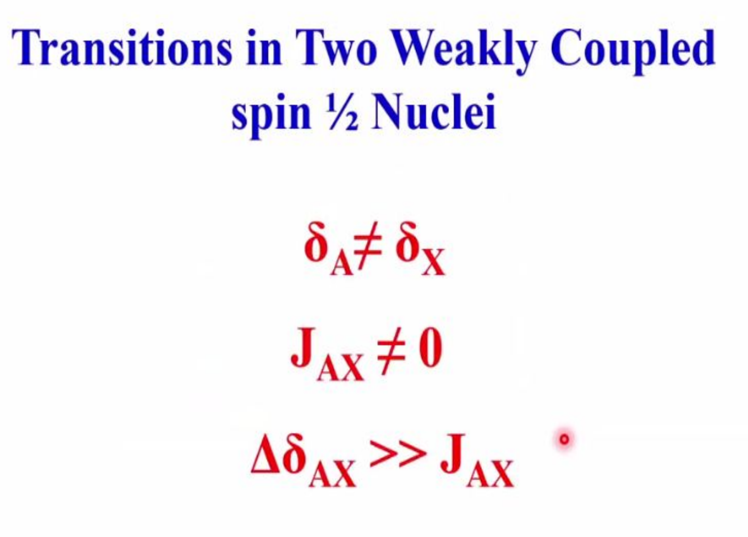

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Proton A will give 2 peaks

One peak is shifted by δ_A+J/2
Other is shifted by δ_A-J/2

Proton X will give 2 peaks

One peak is shifted by δ_X+J/2
Other is shifted by δ_X-J/2

Two Coupled Spin gives maximum Four Peaks

Of course, we understood this also, 2 weakly coupled spin system. Proton A gives 2 peaks, and proton X also gives 2 peaks. And we also got 4 peaks, this also we understood, because we discussed today.

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Interaction among spins in NMR are always mutual

If proton A is coupled to proton X

Proton X is also coupled to proton A

If peak of proton A is split into doublet because of its coupling with proton X

Doublet with Identical splitting is also seen for proton X

Now, one interesting important information I want to give you, please remember. The interactions among spins in NMR are always mutual. Remember, interactions among spins in NMR are always mutual. If proton A is coupled X, proton X is also coupled to A. Remember that. If proton A splits into doublet because of its coupling with X, similarly, doublet of identical splitting is also seen for X, because X is also coupled to A. It is one of the important points you remember, interaction among the spins in NMR is always mutual.

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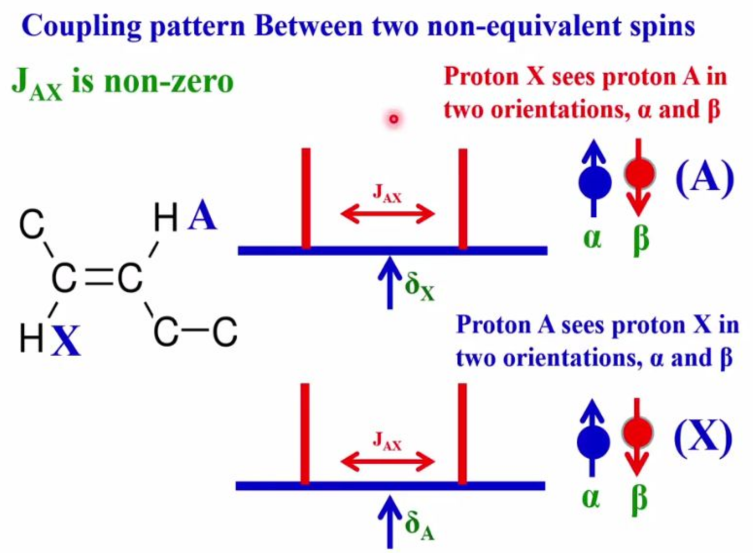

Now coupling between 2 nonequivalent spins, if I take, we already calculated from the energy level diagram which we have found out, it will give rise 2 peaks. Proton X sees A in 2 energy states, X will see A in 2 energy states. As a consequence, this will split into a doublet and this will also split into a doublet and this is JAX. This is equal to JAX, and the center gives chemical shift of X, and this gives you chemical shift of A.

So, what I will do is go about the multiplicity pattern for other spin systems. I am going to start later, from tomorrow. But today, I will stop at this place. We have understood quite a bit about scalar couplings today. Now we have come to the level of interpreting the multiplicity pattern. I just took the example of some hypothetical molecules, which you are told from the energy level diagram, and now I am telling you how does spectrum come. With this, we go further. One important point you must remember, what I said today. Interactions in NMR are always mutual. If A is coupled to X, X is also coupled to A. If X is split into doublet because of coupling with A, identically same doublet will be seen at A, because it is coupled to X. because of mutual interaction. So these are all important points, we use these quite a bit to analyze the spectrum. So, I stop here we will see tomorrow.