One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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Lecture 11: Scalar couplings

Welcome all of you. We started discussing another interesting interaction parameter which is called scalar coupling. I discussed a lot about scalar coupling and I did mention it is covalent bond mediated interaction. That means, one spin will give its polarization or magnetization to another spin for which it is interacting through what is called covalent bond. And there are several features I discussed about the scalar coupling such as, it is a scalar quantity, one spin can exhibit a homonuclear coupling, heteronuclear coupling, and one case spin can simultaneously experience several couplings of different interaction strengths; and then one spin when it interacts with another spin there is a multiplicity of the transition because of splitting of the energy levels. And as a consequence there will be complex multiplicity patterns. This multiplicity pattern depends upon the number of spin states available for the coupled spin. This is what I explained to you taking the example of two interacting spins A and X. When A is couplde with proton X then it will see X in two possible spin states alpha and beta. Similarly, X will see A in two possible spin states alpha and beta with different energies. As a consequence, I said we are going to get doublet for both of them. Like that we discussed a lot of things and introduced quite a bit about the scalar coupling. I took the example of only two protons and I said maximum of four transitions you can get for two coupled spins and then what happens if one proton is coupled to many other protons; or one proton coupled to several groups of protonswhat will happen? How the multiplicity comes all those things we have to discuss. It is this understanding of the multiplicity pattern is very important when we analyze the spectrum of proton or any other nuclei, where there is a complex multiplicity pattern. Unless you know the pattern what is the type of splitting pattern we get when one spin interacts with another spin or group of other spins, chemical equivalent or magnetically equivalent spins, how this splitting arises all those information is needed. We will try to understand this today by taking lot of examples.

Let me continue with this and I will start discussing about the multiplicity pattern of coupled spins. First thing of course, we discussed this at stretch also. If you consider an single isolated spin of nucleus, I took the example of CHCl3 where we have only single

proton. I am not worried about interaction with carbon 13 or chlorine. Then we have only two possible energy states m equal to minus half and m equal to plus half. And the transition between these two are allowed as per the selection rule, which I said change in the magnetic quantum number between any two states should be the either plus 1 or minus 1. And between these two states both the transitions between alpha to beta, and beta to alpha are allowed. So, as a consequence when this transition takes place we are going to get a single peak. This what we discussed earlier also, when we discussed some interaction parameters.

So, this is a simple logic an isolated proton without any coupling to any other spins always gives a singlet because there is no interaction at all, as in a simple example like CHCl3. or When I was explaining chemical shift, I said reference used is TMS. If it does not interact with any of your molecules all 12 protons of tetramethylsilane are magnetically equivalent. As a consequence it gives a single peak even though there are 12 protons like this. When there are single proton or groups of protons which are chemically or magnetically equivalent if they do not interact with any other spin you are going to get a singlet, it is a uncoupled spin.

Now, we will understand how do we get the transition when you have more number of spins. A simple example after single spin, it should be two coupled spins. We can take the example of transitions in two spins. These two spins could be interacting or non interacting. That means they can be coupled or uncoupled. If they are coupled that means there is a scalar coupling interaction between them. If there is no coupling the interaction J_{AX} is 0. However, there are two different spins, the chemical shifts are entirely different. Delta A and delta X are two different protons, with two different chemical shifts one for A and one for X. I have assumed a situation J_{AX} equal to 0. That means there is no coupling at all. An hypothetical molecule will consider; here proton A and proton X. And we assume there is no coupling between them. In such type of molecule there will be cis-trans coupling. But we will not worry about that. For this special case we assume there is no coupling and J_{AX} is 0. When I look at the spectrum of this for example X proton it gives raise to a single peak; a singlet is detected for X. What about A proton? A also gives raise to a singlet, because there is no interaction between A and X. I take this intensity as 1. There is no splitting. If 1 proton is there I told you the intensity corresponds to the proton count, Earlier I said when I was discussing chemical shifts so each of them is a single proton. A is single proton; X is single proton. We get only equal intensity peaks, one peak for each of them. If I assume the chemical shifts of X (delta X) is very much larger than A, that is the condition we have to consider for AX spin system, we will discuss later. I assume the condition chemical shift of X is more than that of A, that is, delta X is larger than delta A. Then I can simply say this is the spectrum we get for two uncoupled spins. One for X and one for A, two singlets of equal intensity.

Now what will happen; transition into weakly coupled spins, in which case chemical shifts are different, delta A and delta X like in the previous example they are different. But in this condition I am assuming J_{AX} is nonzero. That means there exists an interaction between A and X. Further I have assumed the condition the chemical shift difference between A and X spin; if A is here X is here; I can calculate what is the chemical shift of A and what is the chemical shift of X; and take the difference between these two. I call it as $\Delta\delta$, chemical shift difference between A and X spins; and I assume this to be very much larger than coupling constant. This is the assumption. Now let us see what happens to this type of interaction for two spins which are weakly coupled. But remember one thing, I want to tell you the interactions in NMR are always mutual. That means if A spin is interacting with the X spin in a molecule X is also interacting with A. The interactions are always mutual. If proton A is coupled to X; proton X is also coupled to A. If peak of proton A is split into a doublet because of X then obviously the peak of proton X is also split into a doublet because of A. The proton A will see X in two spin states. Similarly proton X will see A in two spin states; each of them will be a doublet. What is the type of coupling pattern we are going to see between two non-equivalent spins? They have to be non-equivalent as I said, if they are equivalent there won't be any coupling. When the chemical shifts are overlapping, exactly equal, of course there could be coupling. But we are assuming that they are non-equivalent. Now this is a hypothetical molecule again A and X; assuming there is no no other protons only two protons in this molecule. Consider proton A, it has two spin states alpha and beta. The proton X also has two spin states alpha and beta. Since J AX is non-zero there is an interaction between them. proton X sees proton A in these two orientations alpha and beta and then it splits into a doublet like this exactly from its center position of chemical shift. From the center two peaks move on either side. Fine that is a doublet. What happens to proton A? proton A now sees proton X again in two possible orientations, that is, alpha and beta. Exactly identical phenomenon. What will happen to X? two peaks it gives exactly from the center one peak moves at equidistance to the right, and the other peak moves at equidistance to the left. And if you measure this separation that is called J_{AX}; coupling constant between A and X spins.
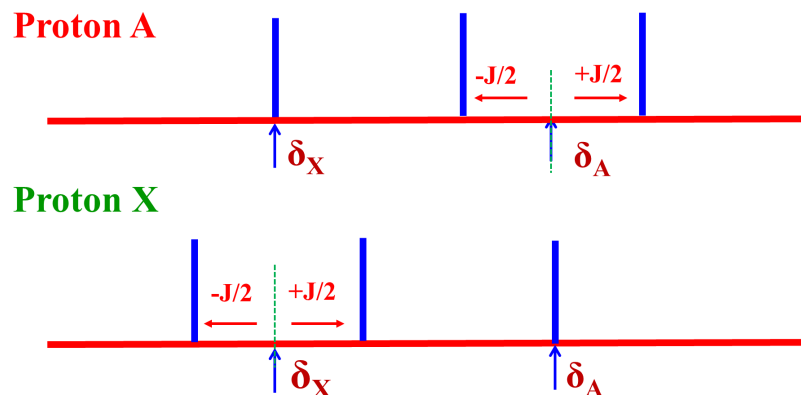
Since the mutual interaction is mutual, as I said, if this is J_{AX} this also has to be J_{AX}. there is no difference because interaction strength should be same because they are interacting equally. So this how when we have two protons and if there is a non-zero J coupling, each of them will give a doublet. Please remember center this doublet correspond to respective chemical shift. If the center of this correspond to chemical shift of X. If this doublet corresponds to A center of this doublet corresponds to chemical shift of A. That is how, you have to see one peak split into two with equal intensity 50: 50. Rhis is equal intensity, so total intensity should remain same. That is what I said so one peak split into two; now the intensity has come down by half for both of them. Pictorially pictorially you can understand this. The proton A and proton X, each is a doublet, with two lines one goes to the right other goes to the left by equidistance. This is called J/2 this is called J/2 where J is the interaction strength between A and X, and exactly center is the chemical shift of A. Same way if I look for the X will have two peaks one more to the left one move to the right with identical strength. I am showing for individual protons but in reality both will be simultaneously present. As a consequence you are going to get two doublets when two protons are coupled to each other. you are going to get two doublets two non-equivalent spins when they are coupled, each proton will split into a doublet with identical separation and intensity is equally divided into by into two peaks 50 50 percent will be intensity and the separation of this doublet is the measure of your coupling strength J_{AX} that is the thing which you should remember. okay
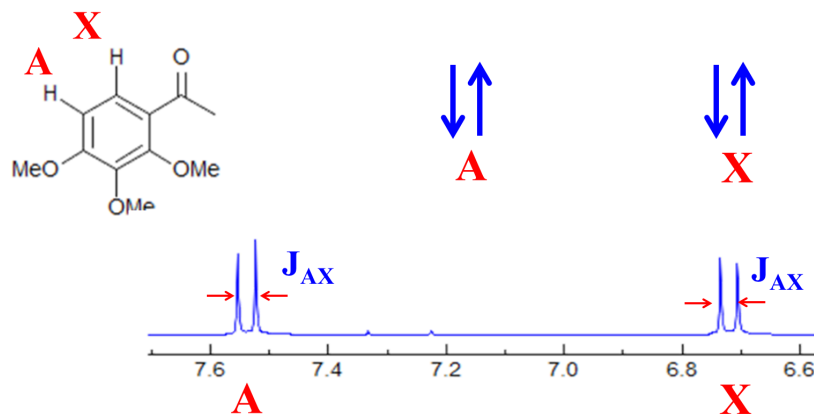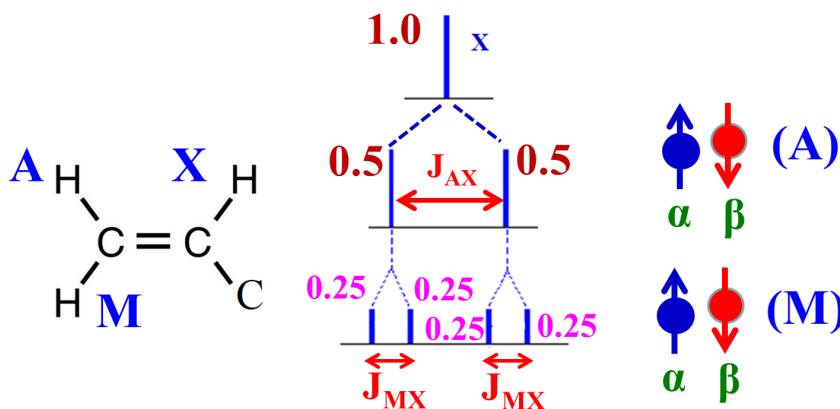

In reality consider a molecule like this, a real molecule there are only two protons of course Ome is there, methoxy groups. We will not look at that spectrum; only spectrum corresponding to two protons of the phenyl ring if I consider, you get two peaks one here one here. one for a proton A and one for X proton. If the coupling was not there each would have been stringlet at the center, but now because of the coupling it is becoming a doublet. Okay.

A will see X into two spin states X will split into two spin states and this separation gives you J AX the real spectrum. Not a hypothetical spectrum or the stick plot which I

did earlier. This is a real spectrum of a molecule now. There will be more complex multiplicity patterns in reality, you are not going to see only this type of simple doublets. Very very complex multiplicity pattern will come. We will see what are the more complex multiplicity pattern. Before that I want to tell you what is the splitting pattern we get by using what is called a family tree approach. When one proton is coupled to n other protons and each of them should be chemically non-equivalent, one proton let us say proton one, is there it is coupled to other protons two three and four etc. Then what will happen is each is split into two, because of its coupling with other one with different strengths.

You can generate this multiplicity pattern by using what is called a family tree approach. That is what I will show you now. let us say one proton is coupled to two protons I consider these protons as A,M and X. Let us look at the proton X, which is highlighted here. The colored one this is the singlet assuming there is no coupling between A and M. It has to be singlet with intensity of hundred percent or take it one intensity. This X can couple with A. The three bond coupling is there. Cis- coupling and because A can have two possible orientations individually, then X will split into doublets. Now what is the intensity of the doublet? this total intensity has been divided into two. So it will become half half; 0.5, 0.5. And the separation is coupling between A and X. What is happening

to the third proton M? It is not sitting idle. That can also couple with X, okay. Now bring the coupling of X with M. The M has again two possible orientations alpha and beta. What will happen now? each of these doublet lines split further into two two lines. One became two now, two became four. What will happen to the intensity now? Again it has to get distributed. So now the intensity become this. The separation of course is coupling between M and X. This is the coupling between A and X and this separation between M and X. The intensity now is 0.25, 0.25, 0.25 and 0.25. But as I told you the total intensity should always match with the uncoupled proton. This is how you can generate the multiplicity pattern using the family tree approach.

You may ask me a question I saw only proton X here ,what happens if I look at this signal for proton A and proton M? It is also possible right! And when I see a proton A it will couple to X and it will couple to M. When I see proton M it will couple to A and it will couple to X. Identically what is happening at X. The similar pattern is going to be observed at the chemical shifts of protons A and M. Now at the chemical shift of proton X we saw four lines, because of its coupling with A and M. But now if I go to the chemical shift of A, at the chemical shift of A we have again four lines because of A coupling with M and X. At the chemical shift of M again you get four lines because of M coupling with A and X. And the similar pattern you are going to get. That is how when three protons are coupled to each other, each proton will give four lines. So three protons together will give rise to twelve lines, twelve peaks you are going to get.

What happens if I extend this molecule let us say we have three protons one two and three now I have added one more P, AMX was there I added P. How does the spectrum come now? extend the logic $\qquad$ same way X will couple to A becomes doublet, it will $\Sigma= N * 2^{N-1}$ couple to M become doublet of doublet, this separation is $\qquad$ J_{AM} this is J_{AX}. It is coupled to P, each time you further split into half half, then this becomes J_{PX}. This is the intensity, one become 0.5 0.5, then 0.25 0.25, 0.25 and 0.25. Here half of that, 0.125. Eight lines. So eight into 0.125, again we will get same intensity. This is the pattern you get when one proton is coupled to three other protons, which are non equivalent chemically. So eight lines you get. This is for the proton X. What happens if I look for the proton A, M and P? Extend the logic identically. At the chemical shift of A, A will couple to M, P and X. At the chemical shift of M, M will couple to A,P and X. And P will couple to A, M and X. So at the respective chemical shift you are going to get 8 lines each. When one spin is coupled to three other spins you get eight peaks for each of them. There are four such protons. Totally you are going to get 32 peaks. What is the type of pattern you are going to get now. Let us see the multiplicity when N non-equivalent protons are coupled. This is the summary. One proton coupled to another single proton gives doublet of equal intensity. When one proton is coupled to two different protons you get four lines of equal intensity. When it is coupled to three protons of different chemical shifts, you get eight

lines of equal intensity. So simply you can generate a formula one will split into two. It is two to the power of one. This is two to the power of two. This is two to the power of three. Two to the power of one is two lines, this is four lines, this is eight lines. So the number of peaks which you are going to get when one proton is coupled to other protons is given by 2^N. The splitting generates two to the power of n lines. So if N is four, two to the power of four is 16. If N is three you get eight lines. Like this that is how when one proton is coupled to N chemical non-equivalent protons, the total number of lines at the set of the each individual proton is 2^N. This is what I said for the example of A, M and X. A gives four peaks, M gives four peaks and X gives four peaks. okay this is for N chemical in equivalent coupled protons. In general you write down the formula. The number of lines at the site of one of the observed protons is given by 2^N-1. And the total number of peaks in the entire spectrum is given by this equation

Simple logic, if I have four protons each proton will have two to the power of four minus one; two cube eight peaks eight into four 32 peaks. N is four so totally that you can 32 for using this formula you can find out how many peaks you are going to see at the chemical site of individual protons; and how many peaks totally you get in the entire spectrum can be understood by this equation

And this is a simple pattern, and it is the realistic spectrum; it is not a strict plot.
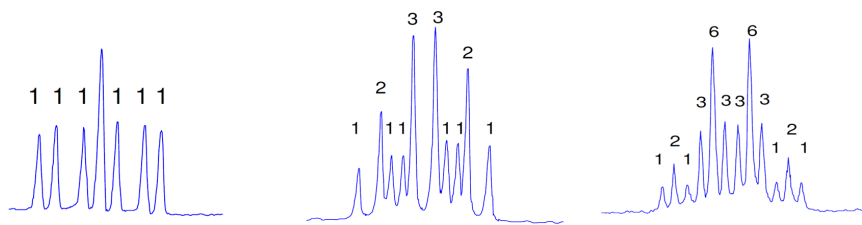

A single proton is coupled to 3 protons **A single proton is coupled to 4 protons** **A single proton is coupled to 5 protons**

For example here one proton is coupled to three other protons how many peaks we should expect I told you one proton is coupled to three other proton two cube eight lines you see, you can count here. There are eight lines here, two are overlapped, so it will be eight lines. When one is coupled to four protons it should be 16 peaks see some are overlapped I have written the intensity here, one, 2, one, one, etcetera. Add up all the intensity you can see number of peaks. You can count the number of peaks. Each peak is one intensity. So if there are three peaks here, three here, two here. If you add up everything you are going to see 16 peaks. If one is coupled to five protons you are going to get 32 peaks. Here that is a reality. Okay, this is a real spectrum. How you get this is at

the site one proton. then entire spectrum. For example 32 there are five protons one is coupled to five there are six protons, then 32 into 6 is the total number of peaks you get in the entire spectrum. This is the simple formula we should understand, Hope you understood now the simple multiplicity pattern, how we generate using the family tree approach and the formula you obtained about getting the number of peaks at each chemical site of proton and total lines in the spectrum here.

Now I am going to introduce another term called active and passive couplings what is an active coupling and wha[   ]ber of protons I have written here. There are [   ] inequivalent. I have numbered it as, one two t[
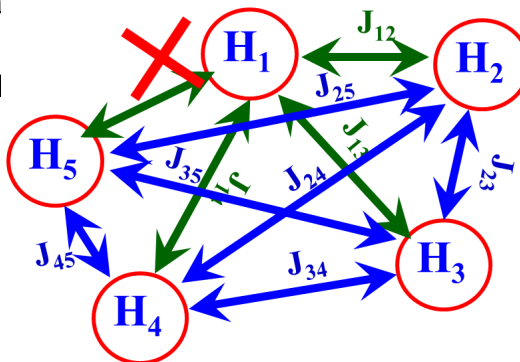
I am sitting at the chemical shift of proton one, the chemical shift of the particular proton which I am seeing is called an active spin. Remember this proton, which I am observing is an active spin. And the remaining are passive spins. if I go to the chemical shift of the proton two, then that is active spin, the remaining are passive spins. Now let us see I go back to this I look at the proton one, that is an active spin to me; all the remaining four are passive spins. What will happen one can couple to two, one can couple to three, four and they are called active couplings. For the active site at the proton one which you are detecting, for the active spin all the remaining passive spins are coupled that is called active couplings. Remember the statement coupling of active spin with all the passive spins are called active couplings, which you are going to see at the site of this proton one. And for that matter the one coupling may be zero it may not exist, doesn't matter. But these type of interactions, the couplings of one with two, one with three and one with four gives multiplicity at the site of proton one. How many multiplicity you get now? because it is coupled to this becomes doublet, then doublet of doublet, then doublet of doublet of doublet. Totally eight lengths you get, because one coupling is absent. At the proton chemical shift of one, you get three couplings; they are called active couplings. Now what will happen to other coupling? There are other couplings. There is a coupling of two and five, three and five, two and three, all other couplings are there, many other couplings are there. They are called passive couplings. please remember there are called passive couplings. These passive coupling are not shown at the chemical site of proton one. At the chemical site of proton one these passive couplings are not seen, you please understand. The active coupling is the one where at the particular site of the proton, that is active proton. With respect to that all other couplings of the passive spins is seen. That

is called active coupling. Whereas, all other couplings apart from this proton, remaining other passive couplings among the passive protons are not seen at the chemical shift of proton 1. This is a simple logic you should understand. You may extend this logic what happens instead of proton, I detect proton 3.
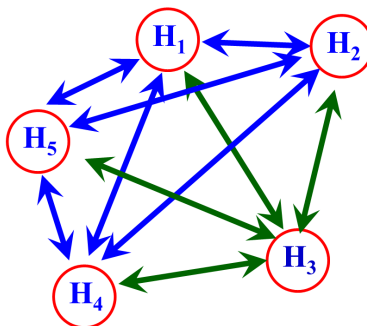

Now, what is my active spin? My active spin is proton 3. And 3 can couple to 2, 1, 5 and 4. So, there are 4 active spins, of coupling strengths different. These are all called active spins. And these couplings will be seen at the chemical shoot of proton 3. So, proton 3 when you analyze that spectrum, multiplicity you get is due to 2, 3 coupling, 1, 3 coupling, 5, 3 coupling and 4, 3 coupling. What about the other things like this 2, 5 the all other remaining proton couplings? They are called passive couplings and these passive couplings are not seen at the chemical site of proton 3. Now, you understood what is the difference between active spin and passive spin.

Active spin is the one which is detected or at the chemical shift of the particular proton and that proton when it is coupled to remaining protons, they are called passive protons that coupling is seen at that particular chemical shift. Whereas, coupling among the remaining spins are not seen there. So, for that you have to go to particular chemical shift of other passive spin. That is the important concept. This concept has to be very clear for you, if you have to analyze your proton NMR spectrum or any NMR spectrum. The active and passive coupling is important. So, if I look at the chemical shift of proton 1 and if I want to see the coupling 3, 4 you will not see that.   You cannot get it because that is a passive coupling.


So, you should know the difference between active coupling and the passive coupling. Active and passive coupling is a homonuclear coupled spins I will show you. For example, this is a molecule A M and X, a realistic spectrum we will take. I will give you an example now. What is happening for active coupling and passive coupling.
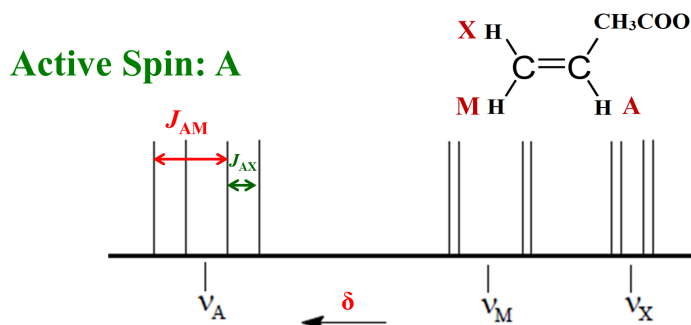
I am looking at proton A, this is chemical shift of proton A, that is an active spin. So, what are the couplings you get here? You get the coupling between proton A with M and X. So, you get coupling AM and AX they are active couplings. What is the coupling between M and X? See we are detecting A coupling. Between this M and X it is a passive coupling. That passive coupling you will not see at the chemical shift of the proton A, which is active spin passive. The coupling MX is not seen. The other 2 couplings are seen. They are active couplings. This is how we can measure.
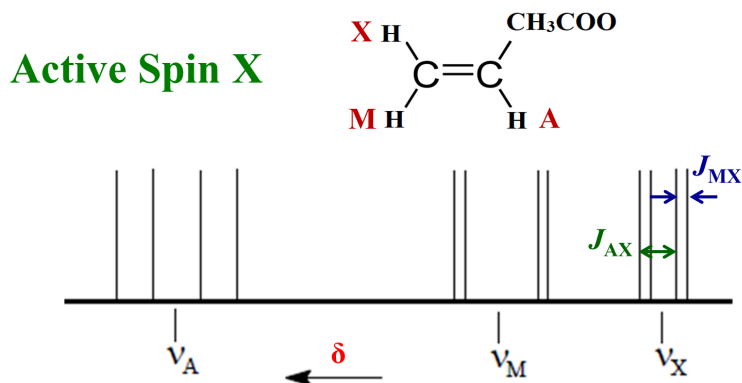
Now let us go to the M, now this is the chemical shift of M.
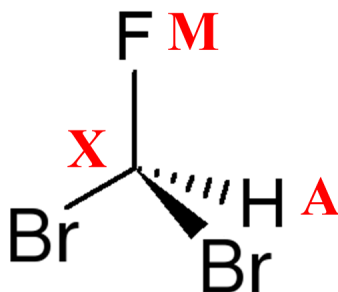
Active Spin M
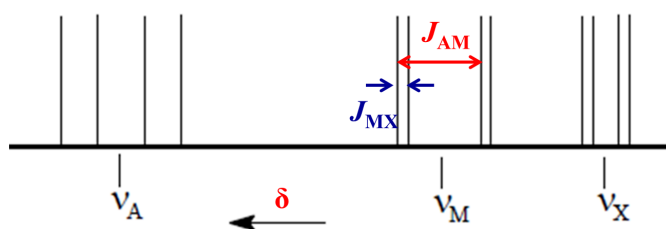
What are we seeing here at the chemical shift of M? we are going to see active couplings AM and MX, they are the active couplings. What about the coupling between A and X? They are passive spins. That passive coupling is not seen at all.

Go to the next one proton X. Now this is the chemical shift of proton X.
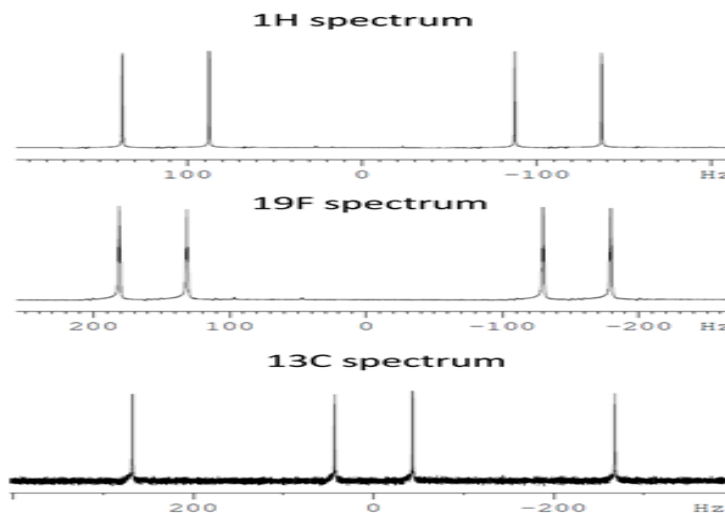
Active Spin X

That means that is the active spin. At the active spin, we get AX coupling and MX coupling, but AM coupling, the passive is not seen. That is how we can start analyzing and we know now what is the active spin what is the passive spin and what are active couplingx and what are passive couplingx. This information is essential. You should understand this. Only then you can interpret the spectrum analyze and extract the couplings.

You cannot look at proton A and start looking for the MX coupling, you will not see. This is a very important concept you must remember. Let us see active and passive couplings in a heteronuclear coupled spins I will show you an example. Let us take the example of ^{13}C labeled dibromofluoromethane this is the molecule. This is the weakly coupled spin system you have A, M and X, 3 spins are there, 3 different heteronuclei are there, and this is proton spectrum, this is a 19F spectrum and this is a carbon 13 spectrum.

If proton is an active spin if this is the proton spectrum, that is the active spin. Fluorine and carbon are passive spins. So at the proton spectrum when you analyze you will get

JCH and JFH, but what you are not going to see JFC. you will not see, that is not possible, you will not see. Similarly go to now fluorine NMR, fluorine is an active spin proton and carbon are passive spins. So when you analyze the fluorine NMR you get JFH and JFC, but you do not get JCH you will not get. Similarly now go to the last one, carbon 13 is an active spin. This is a carbon 13 NMR. What do you get now JHC and JFC you are going to get. What you do not get is JHF you do not get that is a passive spin.

This is how you can understand for the analysis spectrum, whether it is a homonuclear heteronuclear. What is active coupling and passive coupling. Siince the time is getting over, I am going to stop here. So today what we discussed in this class, I started introducing to you about the multiplicity pattern that we are going to see. When one proton is coupled to several other chemically iniquivalent protons. When one is coupled other proton, I said each will be a doublet if I look at both of them. If one is coupled to two each it will be a each of them is going to be four four lines, because three coupled spins are there. If I have four coupled spins each spin will be coupled to the remaining three other spins, will give eight lines each. The total number of lines in the spectrum is given by $N * 2^{N}-1$. T his is the total number of lines in the entire spectrum. At the chemicals of each of them you are going to get $2^{N}-1$ transitions. That is what we understood, how the multiplicity is going to be obtained. And I said one line split into two, two into four, and the intensity keeps drastically coming down in the same ratio. Each of them will be divided by two but the total intensity of the multiplicity remains same as that of the uncoupled proton, it does not change. Total multiplicity a integral area of the multiplicity and that of the uncoupled proton should remain same. This is what we understood and you also understood about active spins and passive spins. What is an active spin and what is a passive spin? Active spin is the one where you are going to detect the particular spin for example, particular proton chemical shift. There are other protons in the molecule, they come at different chemical shifts. Then they are passive that you cannot consider them as active. So, at the side of the active spin you get coupling between this proton the remaining protons and the proton coupling between the remaining protons are passive couplings, is not reflected at the active site. And this is how we know if I analyze a particular group of multiplicity pattern what are the couplings we can extract, what we can get, we can interpret and analyze and interpret the spectrum. So, this is what I summarized today. we will stop here and I will come back and continue with this in the next class. Thank you.