One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis

Prof. N. Suryaprakash

CSIR Emeritus Scientist, Solid State and Structural Chemistry Unit
Indian Institute of Science – Bengaluru

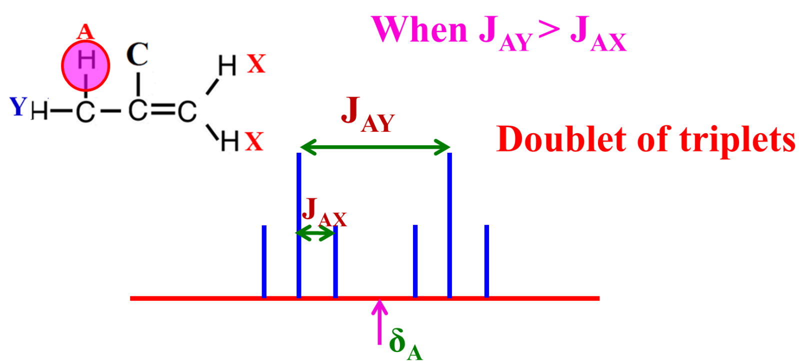
Lecture 14: Multiplicity patterns

Welcome all of you and in the last one or two classes, we have been discussing about one of the interaction parameters, that is scalar coupling. I discussed a lot about the features of scalar coupling, specially some of the important parameters, important thing we must remember. For example, scalar coupling is a covalent bond mediated coupling and it is just a number, it can be positive, negative or 0. And also I said when one spin is coupled to another spin through covalent bond mediated coupling, then there will be a multiplicity of the transitions which comes because of one spin sees the other spin in different possible orientations. When I took the example of two spins, I said if I have a spin A, it can coupled to spin X with just two spin orientations alpha and beta. As a consequence, spin A will see spin X in either alpha and beta states and split into two energy states. Similarly, X will see A in two spin states and give rise totally four transitions. And of course, I also said the sign of the coupling could be positive, negative or 0. And the sign of this coupling has no bearing as far as the appearance of the spectrum is concerned. I said when I have a positive sign, let us say two spins coupled will give four lines.

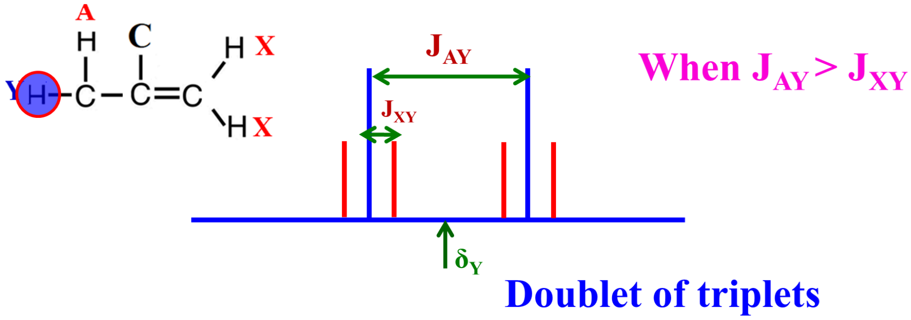
When it means negative sign of the coupling, it is just that transitions appears reversed, that is all. As far as the total appearance of the spectrum is concerned, there is no effect at all. Then I further continued and explained about multiplicity pattern that we are going to get, when one spin is coupled to chemically inequality different spins, then by applying the family tree approach, I said when one spin coupled to N spins, 2^N possible transitions are there. For example, one spin is coupled to three spins, it will give eight lines, it gives rise to eight lines.

And if there are four spins like that, 8 into 4, there will be 32 transitions. That is what I said. Then we have groups of equivalent spins, we get into what is called 2NI+1 rule in which number of transitions that we can get when one spin is coupled to chemically equivalent other spins. How many transitions we are going to get, that also we discussed. And I said intensity of the transitions when among the group of chemically equivalent spins coupled is given by what is called a Pascal triangle. That is what I said. Pascal triangle is also nothing but co-efficient of the binomial expansion. That is what I showed. And then we took several examples to show how the spectrum comes if let us say CH is coupled to CH2, CH3 etcetera. And I arrived at different multiplicity patterns like pentets, sextet, septet etcetera, varieties of multiplicity pattern. What happens if one proton is coupled two different protons with different couplings also, we worked out. We continue further with that discussion today. And I want to show you what will happen to the splitting of particular proton or group of protons when it is coupled to several other spins. It could be single spin or multiple spin which are chemically equivalent. In which case how do we get the multiplicity pattern and what is the nomenclature adapted for that that we are going to discuss today.

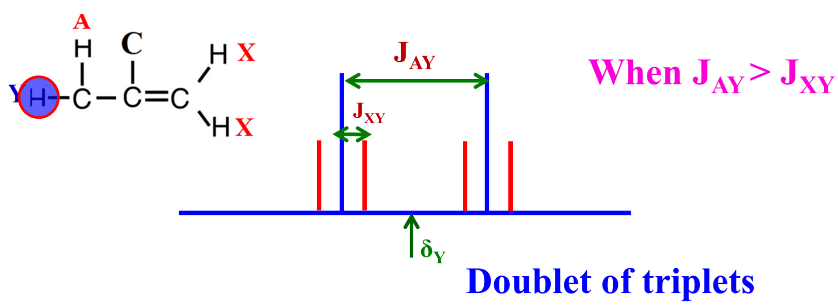
For example, I will consider a CH proton which is marked here which is split, let us say, by CH and CH2. Now we have to put some condition about the coupling here. What is the strength of the coupling? If A is coupled to Y, A is also coupled to X. I am looking at A, of course, I can look at X and Y also, that is a different question. But I am looking at A, A has a coupling with Y and also with X. And I put a condition J_{AY} is greater than J_{AX}.



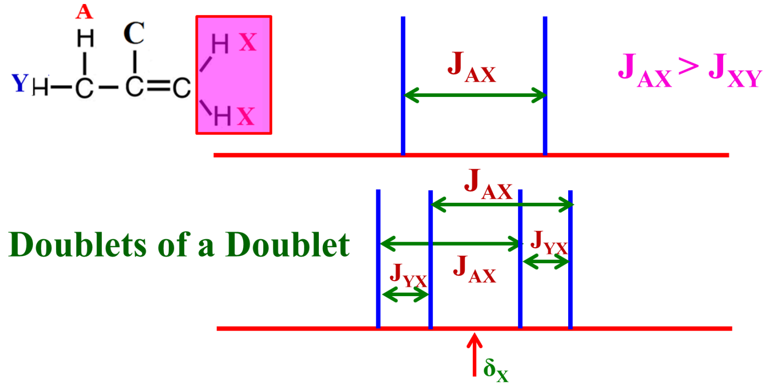
That means the coupling between A and Y, J_{AY} is greater than J_{AX}. In which case what is the type of splitting we are going to see? We will work it out. For example, the CH proton when it is coupled to another CH proton, proton Y, it is a single proton gives us a doublet and the doublet separation correspond to J_{AY} coupling. This one proton splits into two lines of equal intensity 50, 50 half half intensity. Now further what happens this also splits into triplet. Each line of the doublet will become a triplet because of coupling with two chemically equivalent protons CH2. As a consequence it is going to be doublet of triplet. This pattern is called doublet of triplets. And this triplet separation consider the lines of the triplet gives the coupling between A and X. And from the center of this triplet to center of this triplet separation if you measure, you are going to get the coupling between A and Y. This is a condition I have taken. AY coupling is larger than AX coupling. The splitting pattern for A appears to be what is called doublet of triplets. Remember this is because the triplet coupling is smaller. Always when you are putting the nomenclature like this we have to mention the largest coupling first. First largest coupling is doublet. This one is larger and then each line is split further into triplets. So this nomenclature, remember how do you mention this nomenclature, it is called doublet of triplets. And the center of this correspond to chemical shift of this proton A.



Now what is this pattern for Y? I was looking at A proton earlier. Now I look for Y proton. What will happen? Remember the same condition I have put J_{AY} is larger than J_{AX}. What will happen? JAY again gives a doublet because of coupling AY is larger it is a doublet. And each line of this doublet is further split into triplet. This triplet comes because of coupling of Y with X and YX coupling is smaller because it is separated by several bonds. I have deliberately taken J_{AY} is larger than J_{XY}. In the previous case it was J_{AX} and in this J_{AY} is even larger than J_{XY}. As a consequence again the pattern you are going to see is doublet of triplets. And only thing is this appearance of this pattern remain same, but the triplet separation is smaller. That is all because the coupling J_{YX} is smaller compared to J_{AY}. Again this pattern is called doublet of triplets because the larger coupling is a doublet.

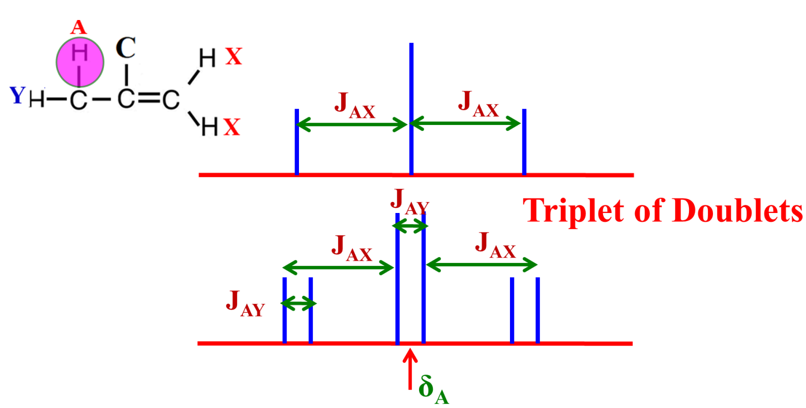


We will go further in the same molecule now I am going to see X proton. What will happen now? Let us put a condition J_{AX} is larger than J_{YX} or J_{XY}, both are same because interactions in NMR are always mutual. Now what is the pattern we expect? J_{AX} is larger A spin will split this X into a doublet, it will be a doublet. But it also sees Y proton again the single proton. So, this is the doublet then what will happen? Each line of this doublet is going to be further split into another doublet. And this separation correspond to AX coupling, the larger doublet and each line is split into another doublet the smaller doublet correspond to YX coupling. So, what do you call this pattern? Of course, center of this is nothing but chemical shift of this X. So, what is this pattern called?



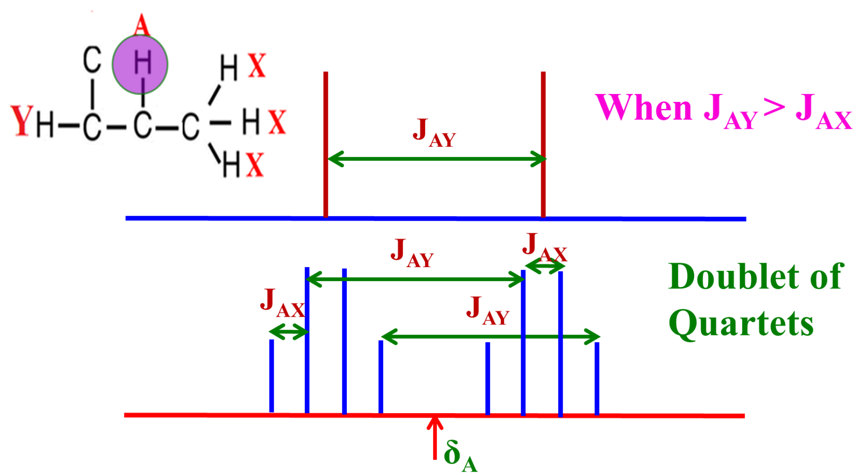
This is again called doublet of doublets. Remember the pattern when we observed A it was doublet of triplets when I observed Y it was doublet of triplets. But whereas, I am observing X here, the pattern is doublet of doublets this larger separation from any of the doublet line of doublet to other line of this doublets exactly identical. If you take the right most line here and take right most right most line of this doublet and measure the separation that gives AX coupling. It exactly corresponds to this, because the second splitting of the doublet is from the center of this at equidistance. There are two lines, one line each for this side and one line from this side. So, hat means, you are going to get a doublet exactly center of this peak. So, that means, you can measure from this peak to this or this peak to this, does not matter, it gives J_{AX} coupling. Measure this separation it gives you J_{XY} coupling. This is what is called doublets of a doublet.

Now, I will consider a situation J_{AX} is larger than $J_{AY;}$ this is larger than AY. This is the condition. When J_{AX} is larger I am looking at A now. Remember earlier I was considering a different situation J_{AY} was larger than J_{AX}. Now in this hypothetical example I am taking J_{AX} larger than J_{AY}.

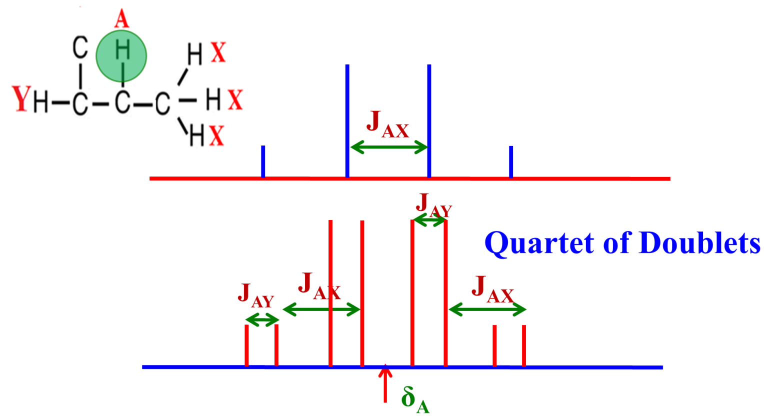


So, A will split into a triplet because of this two equivalent protons, it is a triplet and separation between two adjacent lines of the triplet gives you coupling between the proton X and proton A, and the center always correspond to chemical shift of X, fine. Now each line of this triplet is further split into a doublet because of proton Y and this doublet separation is J_{YX}. So, this is the situation we are going to consider, this separation correspond to J_{AY}, because I am looking for A correct, this is AY coupling. So, this A is split into triplet because of this, and each line of the triplet is split into doublet because of J_{AY} coupling and this is the pattern you are going to get. This is the J_{AY} separation and any line of this triplet you take from left most line, essentially this one or from this to this or this to this or this to this you take, it gives rise to J_{AX} coupling. What do we call this multiplet? The larger coupling here is triplet, and the smaller coupling is doublet. So, it is called triplet of doublets. And this is the pattern we call triplet of doublets and a center of this multiplicity pattern corresponds to chemical shift of proton A, that is what it is.

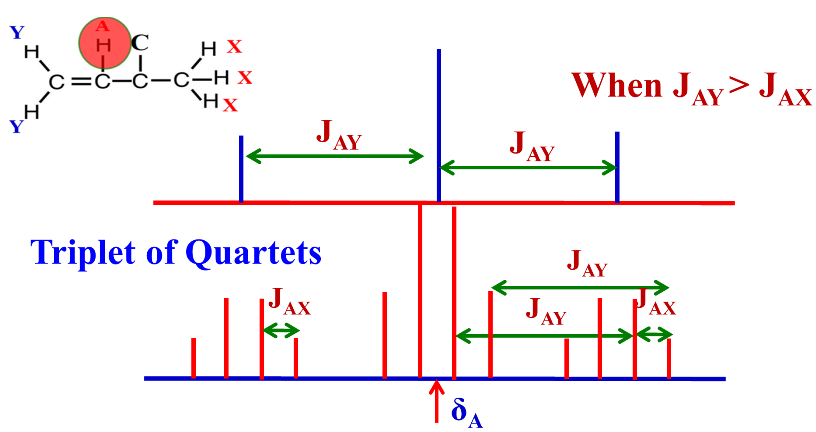
Let us continue further we will take few more examples now I am considering single proton coupled to CH and CH3 protons. What will happen? we extend the logic. Now, we are looking at proton A. I am putting a condition J_{AY} is larger than J_{AX} like in the previous example, let us extend the logic.



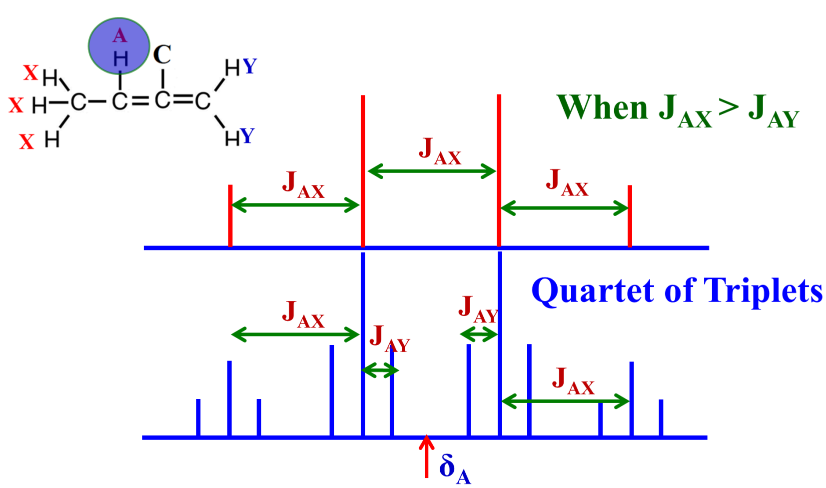
Proton A, because of coupling with proton Y has to be a doublet, that coupling is larger and it is a doublet. And each line of the doublet is split because of 3 equivalent protons of CH3 group; 3 are chemically and magnetically equivalent protons makes the each of this line into a quartet. What do we call this pattern? The larger separation is doublet and smaller separation is quartet. So, this pattern is called doublet of quartets. Again the center of this multiplicity corresponds to chemical shift of A. And take any 2 adjacent lines of the quartet that gives you coupling between A and X; and any similar lines you take, leftmost to leftmost here, this line to this line, third line to third line, fourth line to fourth line, if you consider between the quartets, measure the separation that correspond to J_{AY}. So, this pattern is called doublet of quartets.



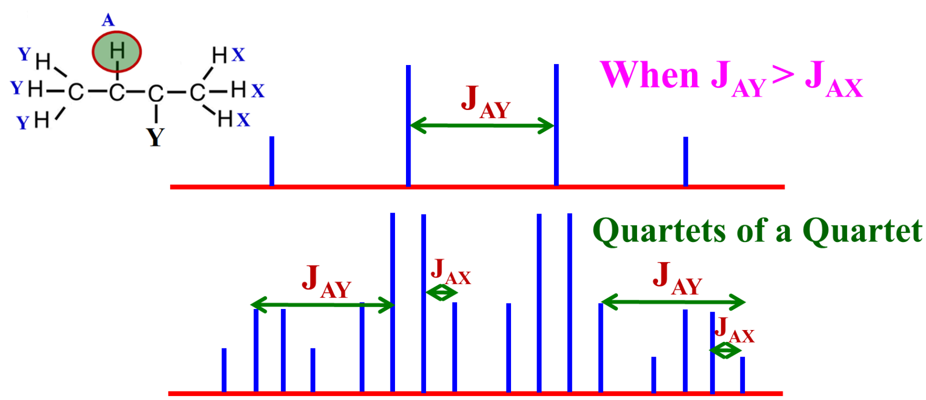
What happens to this splitting pattern? If J_{AX} is larger than J_{AY}. Here, this is larger. In the earlier case I took the example JAY was larger, the doublet coupling was larger. Now, I am considering quartet coupling is larger. What is going to happen? The proton A is split into quartet because of CH3 protons. All the 3 protons are equivalent. It will become a quartet. Of course, by the Pascal triangle we have already understood the intensity ratio is 1 3 3 1. So, A will become a quartet because of this, and then what will happen? A is also coupled to this Y; this proton. Then what is going to happen? This is single proton when it is coupled, each line of this quartet is going to become a doublet. This is how the pattern comes now. And the separation of any adjacent line if you consider it gives the coupling between A and X; Any of these 2 lines of the quartet if you consider, the adjacent lines of this quartet, this gives rise to AY coupling. And from center of this to this, or this to this, or this to this, whatever you consider; that gives rise to AX coupling. So, this how it is and the center of this multiplicity correspond to chemical shift of A. What do we call this pattern? this largest coupling is a quartet. So, it is called quartet of doublets. Remember earlier it was doublet of quartets. But now it is quartet of doublets. So, you have to find out which coupling is larger and that should be named first. In this case quartet coupling is larger. So, we call it as quartet of doublets.



Now consider this situation same A proton I am considering, instead of CH, I made it CH2. What is the pattern we expect? very easy to understand. Since I again put a condition this is larger than this, this coupling J_{AY} is larger than J_{AX}; that is the condition I have put. So, what is the pattern we are going to get? Proton A will split because of CH2 protons into a triplet. Of course, you can take CH3 coupling also first. I told you in the previous class the order in which you take the coupling to generate the multiplicity does not matter. The pattern remains invariant whether you take this coupling to this first; or coupling of this to this. It does not matter. You can take this first take this second or you take this first and take this second pattern remains same. So, does not matter we will consider first coupling of this proton A with proton Y which is CH2 proton what is the pattern we get? this is CH2 proton it will split with this into a triplet. Now the intensity ratio 1:2:1. Further this proton is also coupled to CH3 group; there are 3 protons, equivalent. So, what is the pattern we expect? Each line of this triplet is going to be split into quartet, because of this. So, now, the pattern we are going to get is this. The larger separation correspond to AY coupling and in the quartet take the adjacent lines of this quartet, that gives rise to AX coupling. So, any line of this quartet to this; or this to this; this to this; or this to this you consider, this gives rise to AY coupling. You see here we measure AY coupling very easily, but actually this is not the only thing; we have other couplings also. So, when the pattern comes like this you should know how to measure the coupling. So, this center of this gives you the chemical shape and this separation gives you JAY coupling. Any peak of this quartet you consider, the identical peak in the other quartet you consider like left most peak to left most peak, second peak to second; third to third; fourth to fourth; similarly this group to this group you consider, in the same manner that separation gives you AY coupling. So, you understood how do you measure coupling from this multiplet pattern. Then what do you call this pattern? this is called triplets of triplet of quartets. Remember doublet of doublet; doublet of triplet; triplet of doublet; triplet of quartet, everything we have understood now.

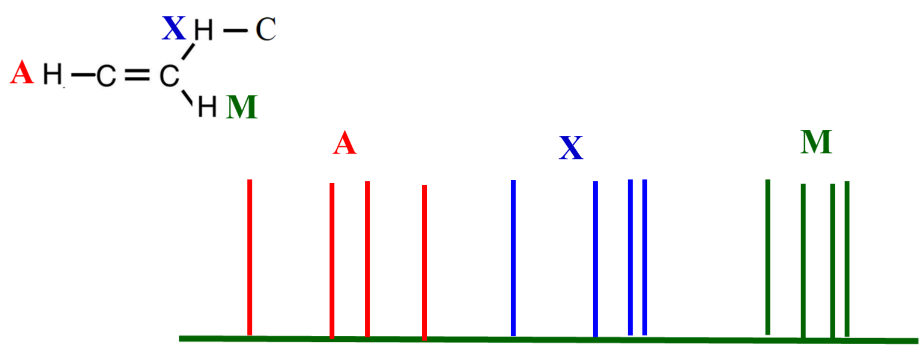


This is the situation. Now I have put AX coupling is larger. See these are all subtle points you should understand about the multiplicity. To understand and explain the multiplicity pattern you must know how the coupling comes, which coupling is larger, how the splitting pattern arises depending upon the coupling, etc. I have put a condition this coupling is larger now J_{AX} is larger than $J_{AY.}$ In the previous example, CH2 coupling with proton was larger. So, this is going to be a quartet now, first coupling is large quartet I have taken and each line of the quartet, ofcourse, adjacent lines gives you AX coupling. The center of this gives you chemical shift of A. The each line of this quartet is split because of this Y proton, CH2 into a triplet. This is 1 3 3 1 intensity and this is 1 2 1 intensity. So, each line of the quartet will be a triplet, and this separation between any adjacent lines of the triplet gives you coupling between A and Y and this separation to this separation, this to this, whatever the order you take, you take any of the multiplet and then exactly identical lines you have to identify. if it is right most line take the right most line here, if the middle line here take the middle line, if it is the left most take the left most line, and measure the separation between them. That corresponds to AX coupling and between the triplet if you measure the separation between adjacent lines that gives rise to AX coupling. So, this pattern is called quartets of triplets; quartet of triplets. The centre will give you chemical shift.

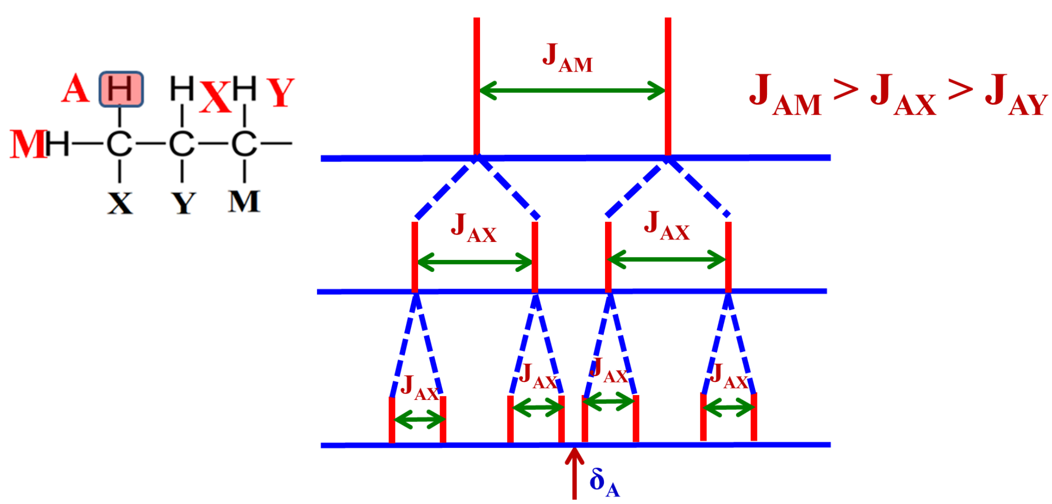


Instead of CH2, I will make CH3 now. Obviously we can extend the logic, very easy whatever the pattern you take whether this is larger or this is larger does not matter. So, if I consider, of course this is some X or something which is not coupled to. I have named this proton as Y. This is another substituent, nothing to do with proton. Y means there is some other substituent. When A is coupled to any one of this proton I have taken AY to be larger does not matter, you can take AX also. It will be a quartet because both are CH3, does not matter you can take whatever you want. I have taken this and it is a quartet and each line of this quartet is further split into quartet because of this CH3 group. There are two CH3 protons coupled to a single proton with different coupling strengths. As a consequence it is going to be quartet of quartets. This is what you are going to get.

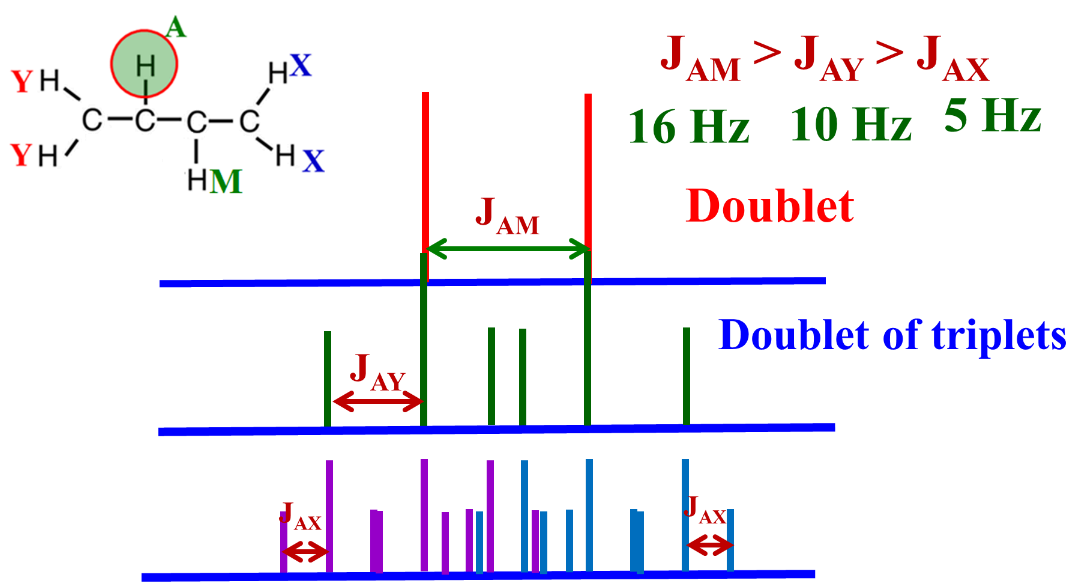
Of course, similarly you can measure any of these lines you consider, identical line in the other quartet you consider, measure the separation this gives you AY splitting. And measure the adjacent lines of the quartet that gives you AX coupling. So, this is called quartets of quartet, and you can get the coupling information and the center of the multiplicity is the chemical shift. So, these are the common first order splittings we always get when we are looking at different protons coupled among different groups. The different protons could be a single proton a group of protons.



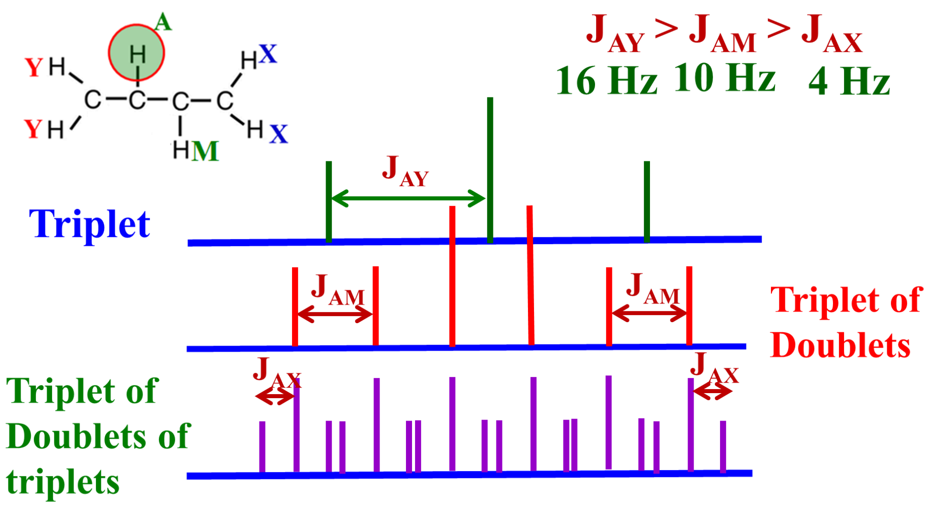
The simple example of a molecule like this. All three protons are independent. There is no CH2 group, no CH3 group. All are coupled among themselves. Let us say this A is coupled to M, A is coupled to X, X is coupled to M. I already explained to you when one proton is coupled to two other protons each line gives rise to four peaks. A will first become a doublet due to couping with X, and each line of the doublet become further doublet, because of this coupling with M. So, A will be four line pattern. Similarly X will be four line pattern, and M will be four line pattern patterns. Identical intensities will be there, but a separations of the multiplicity of different peaks are different, because the couplings are different. So, A will give rise to four peaks, A experience couplings with AX and AM. X gives four peaks, experience couplings AX and MX, M gives four peaks, expericnce couplings with AM and MX. We get four peaks each proton. What is called doublet of a doublet; the each group of protons gives rise to doublet of a doublet and intensity pattern is very easy 1 :1 : 1 : 1.



So, one proton is coupled to two other protons single protons or more number of protons, it is this type pattern we always expect. But always remember the order of coupling is immaterial, but the strength of the coupling matters a lot which is larger. Now, I am considering A, I have put the condition J_{AM} is larger than J_{AX} larger than J_{AY}. One proton is coupled to 3 other individual protons and in this hypothetical molecule I am considering looking at proton A, the spectrum of proton A. First it will split because of M into a doublet, this separation correspond to AM. Now, I will bring the coupling of this with X then each line of this doublet is going to be a further split into a doublet we already worked out long back, you know 1 or 2 classes back how in the family approach comes, Again each line of this is going to be further split into doublet of doublet of doublet. This is called ddd doublet of doublet of doublet. This is an important term used in NMR. So, A will become 8 line pattern; similarly X will become 8; Y will become 8 and M will become 8 depending upon the coupling strength, This how it is; this is pattern. It is called doublet of doublet of a doublet.



And if I have again multiplicity pattern because of chemical equivalent protons, now instead of 1 or 2 protons, I am considering multiplicity due to groups of 2 or 3 protons coupled to single one. The proton A is coupled to this one X, M and Y; very easily you can understand the logic. I have taken AM coupling larger, the large coupling is doublet then each line of the doublet is split into triplet because of Y proton. And each line of this doublet of triplet is further split into triplets because of coupling with other CH2 protons. For example you understand this logic, this is the AM coupling first doublet and each line of the doublet is split into triplet; this is AY couplings. There are 2 triplets. When the adjacent lines of the triplet if you consider you are going to get AY coupling. Further what will happen? it is split because of X, two protons. Each line is going to be triplet now; triplet triplet triplet triplet triplet triplet. See what is happening you are going to get a very very complex pattern, not easy to analyze. But since I knew where I have started. The center is considered to be the chemical shift of A, and the doublet is the largest coupling then second largest coupling is a triplet and another smallest coupling is also a triplet. This pattern is called doublet of triplets of triplets. This is the nomenclature we have to use. So you can use this. What happens if you take the other couplings larger?



Instead of doublet for example this coupling if it is larger? First it is going to be a triplet and each line of the triplet is split into a doublet, because of M and each line of the doublet is further split into triplet because of other coupling. Then what do we call this pattern? First it is a triplet, it is triplet of doublets now, it is triplet of doublets of triplets. This is what the nomenclature you have to use. It is called triplet of doublets of triplets. As always I said this separation gives you AX coupling and identify with the particular pattern, if you go by the family tree, this separation gives you AM coupling, and center of this to say any of these lines if you consider will give you AY coupling. So like this you can analyze and get the coupling information. But the pattern what you have to identify is important this is called triplet of doublets of triplets.

This is even more complex; identical molecule I am only changing the groups. Here CH becomes CH2. Again now it becomes CH3. Here what is the pattern we expect? AY coupling is going to be a triplet because of coupling with Y large triplet. I have written coupling strength larger; A-Y is larger. Then each line of this triplet is going to be further split into a triplet because of M. You get three triplets. You got what is going to happen now. Further this also splits because of CH3 group. So it is already triplet it is triplet of triplet. Now each line of the triplet is further split into what is called a quartet. Now you are going to get one quartet, another quartet, another quartet, another quartet.

See so many quartets you are going to get. What do you call this pattern? You see the spectral complexity. Remember it is not easy to analyze, it takes enormous amount of time, you know experience is required to analyze such a spectrum. Nevertheless since I know the coupling pattern I know the molecule what do you call this pattern? This is called triplet of triplets of quartets. This is called triplet of triplets of quartets. So basically remember if you consider the splitting pattern at the active set of any proton coupled to other groups of protons, normal abbreviations what we use in NMR is ee, it means doublet of doublet. When you say doublet of doublet, the largest coupling is a doublet, the second largest coupling, in this case there are only two, is also a doublet. If I consider dt as the nomenclature, I use for the pattern first is the largest coupling is a doublet, the second coupling is a triplet. Instead of dt I write td that means first largest coupling is a triple, thet second coupling is a doublet, the smaller coupling is doublet. The largest coupling is triplet. Like that you can say quartet of triplet, first largest strength is quartet then the smallest strength is a triplet. You can have many couplings like I showed you two or three coupled to each other. You can have ddq that means first coupling is also a largest coupling gives a doublet, the second largest coupling is also a doublet and third is a quartet. So that means one proton is coupled to another proton gives you a doublet. It is coupled to another single proton gives you another doublet. Each line of doublet will become a doublet there is also coupled to CH3 then doublet of doublet, Each line of this doublet of doublet splits into quartet and largest coupling is first doublet then second doublet the smallest coupling is quartet we call it ddq. like that tdq triplet of doublets of quartet, the first coupling is triplet, the largest then second coupling is doublet and the last least coupled one is a quartet. This is the nomenclature we use for analyzing any NMR spectrum of any molecules, when there is multiplicity because of couplings. This we should remember, okay. So now I think you have already got an idea as how we can identify the multiplicity patterns, etcetera. So what I am going to do is I will show some exercises to identify the multiplicity pattern. Since I think the time is getting over already now, our time is up, what I will do is I will stop here. In the next class I will take some of the examples to make you more comfortable to interpret the multiplicity pattern. And then we go into few other things, extend this coupling further. And I would like to finish it and then we will go to interpretation of the NMR spectra and how do you get the Pople nomenclature everything. So what I was trying to tell you is extending from yesterday's discussion I wanted to show you how when one proton is there, a single CH proton or CH2 proton or CH3 proton, and when it is coupled to other two protons or other groups of protons of different coupling strengths what is the pattern we are going to get. I showed we get doublet of doublet doublet of triplet; triplet of triplet. All varieties of combinations. But how did you arrive at this nomenclature? what is the difference between DQ and QD? DQ means first strength is larger that is doublet. Why? because it is coupled a single proton becomes a doublet then each line of the doublet becomes a quartet. That is called doublet of quartets. On the other hand if the coupling strength with respect to CH3 is larger, quartet is larger strength it will become a quartet and then each there is a quartet splits into a doublet because of the smaller coupling strength. We call it as quartet of doublet. Like that we have not only two we can have many protons coupled. One proton can couple to two three, couple to three protons, four protons four groups of protons, three groups, like that n groups of protons. Accordingly the nomenclature is given as DD, DQ, QD, QQD, QTD, TTT, varieties of combinations we can think of. So to make you more comfortable what I am going to do is in the next class I will give some of these examples then we will go ahead further with the other strengths of the couplings in different molecules, and some discussion about Kaplus equation, how do we use coupling to arrive at the conformations of the molecules, etc. So we will see how we go ahead further, so probably with that I will put an end to this, because there is no end for this. NMR is a huge ocean I can keep discussing this for any length of time. So we will , may be in the next class, we will put an end to this scalar coupling and then go into the interpretation of the NMR spectrum, both proton and X nuclei etc Thank you very much. I am going to stop.