One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture - 25
Coupling Among Equivalent Spins - 2

Welcome back, we will continue with our discussion about the appearance of the multiplicity pattern when the group of equivalent spins are coupled to a different spin. You may please remember in the last class, I showed you what happened to a CH2 proton coupled to a CH proton.

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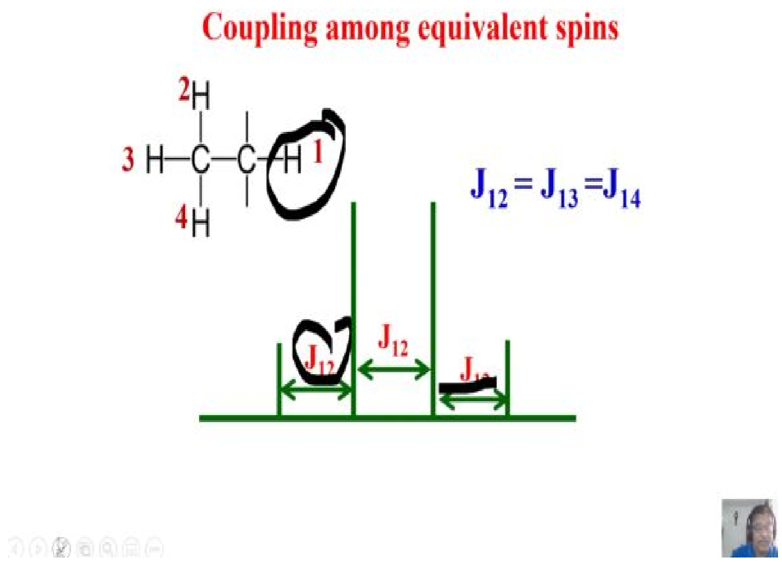

In this case, these two CH2 protons are equivalent, and splits the CH proton into a triplet. I showed you diagrammatically by a stic plot, how do we get a triplet for CH proton. With this 2 couplings of CH2 protons coupled to the third proton CH proton, because the couplings are identical, 2 central lines overlap and we get 1 : 2 : 1 triplet for CH proton. On the other hand, if you look at the CH2 group, it is coupled to CH proton that will be a doublet. So, the total spectrum of a CH group coupled to CH2 group in a NMR spectrum, will be a doublet and a triplet. Triplet is for CH proton, doublet is for CH2 proton coming because of interaction.

Let us now continue further. Let us see what is going to happen if you look at 1 CH proton coupled to 3 chemically equivalent protons, we will looked into 1 coupled to 2 protons; CH2. Now this CH is coupled to CH3 protons, now, let us see what happens.

Now, in this case coupling 12, 13 and 14, they are all same. This is magnetically equivalent spin. All these 3 protons have same chemical shift, coupling to all other coupled protons is same. That is what our definition was. Interestingly here we are going to get a quartet for this proton, here we are going to get a quartet. something interesting. Now let us understand how that quartet will come; see this triplet I am sorry how this quartet will come?

For this proton, how this quartet will come to it. And this separation between adjacent transitions gives you coupling here. Similarly, in the triplet case you get 3 lines, adjacent transitions if we select we can measure the coupling. That will give you a coupling between CH and CH2. Similarly here, if we take adjacent transitions, this is the coupling strength between CH3 and CH. You can take any of the adjacent transitions, this also, does not matter all the 3 are fine, any of them you want you can take it, there is no problem. It will give you coupling strength.

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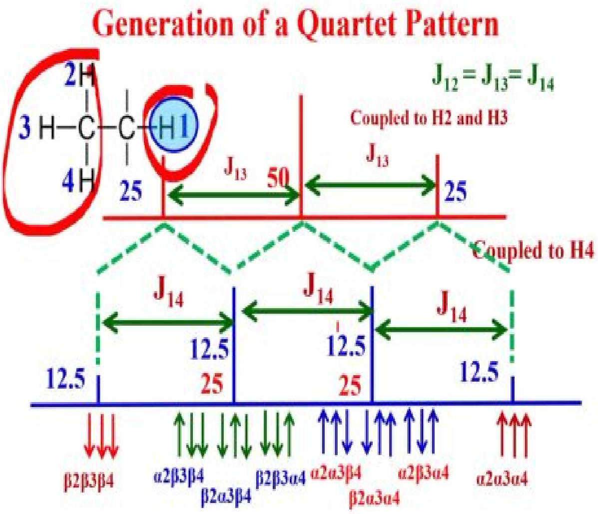

Now, how do you get this quartet? We have developed triplet. Similarly, let us develop the quartet now; see how we get and what is the intensity pattern? Remember, now, I take single proton, up to this coupled to 2 protons we knew, in the one of the previous example, we got triplet 1 : 2 : 1 triplet, up to this we have already done. So don't need to repeat this. We will see what happens when it is coupled to third spin of equal strength.

This was the intensity ratio when CH2 is coupled to CH, 1 : 2 : 1; 25, 50, 25. Now, when it is coupled to this proton, we have to see that each of them will split into a doublet, this will split into a doublet, this will split into a doublet. This in 25 intensity what happens? splits into a doublet, this will become 12.5. This was this splits into 2 it will be 25 and 25. And of course, for this what will happen? splits into 2, 12.5, 12.5, this splits into 2.

So, now what happens? Intensity is 12.5 here, this adds up 25 + 12.5 is going to be 37.5. This is 37.5, 12.5. Now, what is the ratio of intensity? If we consider the ratio of the intensity between this and this together, this is 1 : 3. If you consider this as 1, this is 3 times. So, 1 : 3 : 3: 1. So, the quartet you get intensity ratio as 1 : 3 : 3: 1. Remember, when 3 equivalent protons are coupled to other proton, this proton will become a quartet of intensity ratio 1 : 3 : 3: 1. Any adjacent peak if we take, measure that separation, this corresponds to J coupling, That is the J coupling. Now, why this quartet comes, if you understand? There are 3 possible orientations; 3 spins you consider; now we are dealing with 3 spins. This is all 3 beta, beta, beta or all 3 alpha, alpha, alpha. Now, there are 2 situations.

Remember you worked out once, which is 1 up 2 down, 2 down 1 up. This is the situation 2 down and 1up, this is the situation 2 up and 1 down. So, there are 3 possibilities of equal strength, equal intensity. As a consequence, this is 3 times intensity, as a consequence, this is 3 times intensity. So, what are we going to get? We get a quartet of intensity 1, 3, 3 and 1. You understood how I got a quartet. Simple, you understand. This is 3 possibilities of equal intensity, this is 3 possibilities of equal intensity of orientations of the spins. So, it is only one possibility, it is one possibility, as a consequence 1, 3, 3, 1 is the intensity pattern for a quartet. These are very important when you want to analyze the NMR spectrum later. You must remember it is very important triplet, quartet, triplet pattern, quartet pattern, doublet all of this should be in your finger tips to analyze, Now we understood. let us now look at this proton. If I look at this proton coupled to this, what is the pattern you should get? It is coupled to only single proton, it means it will be a doublet because all are equivalent and this methyl group gives only a single peak and it is coupled to this proton and become a doublet. So, for the entire molecule if you consider, now what is a splitting pattern? It is a quartet and this is a doublet. That is the splitting pattern of this molecule; and then intensity ratio is 1 : 3 : 3: 1; and the adjacent split separations gives you J coupling.

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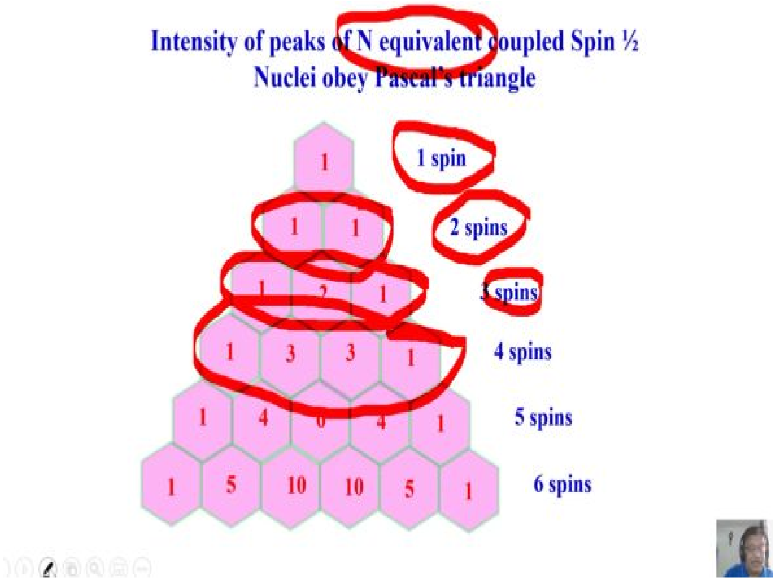

Very simple, now the intensity every time I do not want to draw this family tree diagram and start understanding how the intensity comes. For this, the intensity of the peaks, when equivalent spins are coupled to other spin, it obeys what is called Pascal's triangle. This is a Pascal's triangle, let us say I have a one single spin system, how many peaks I get, for example CHCl3 if I see proton. I have already told you, we will get single peak.

If I take 2 spins coupled, 1 spin coupled to another spin each spin will be a doublet. So, the observing spin will be a doublet like this. When 1 spin is coupled to 2 equivalent spins, N = 2 then we are going to get, there is totally 3 spins are there, one is coupled to 2 equivalent spins we will get 1 : 2 : 1, intensity.

Consider 4 spins, one is coupled to 3 equivalent spins, just now we worked out. It is going to be at 1 : 3 : 3: 1 quartet. Similarly if you work out like this, this is called Pascal's triangle. dPascal's triangle simply gives you the intensity of the couple proton when it is coupled to a group of equivalent spins. Remember, group of equivalent spins will split the other proton, not that, that will split.

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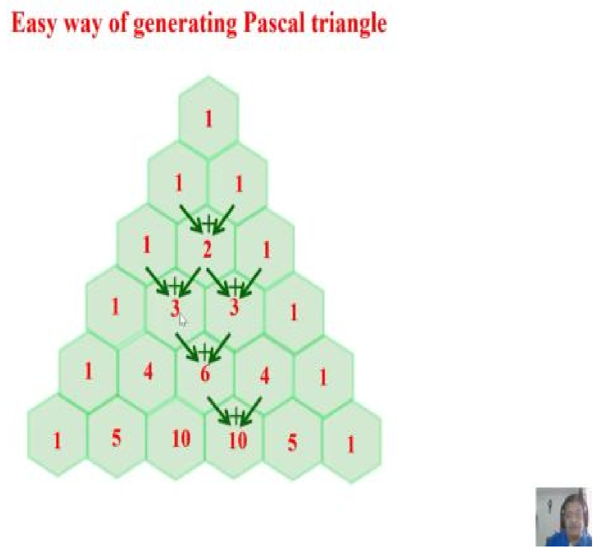

So how do you generate this Pascal's triangle? Very easy, you do not need to worry about anything. It is simple, first you write 1 below this, you write 1, 1, exactly, just 1 at the center. On either side, you write 1, 1. What do you do is, again write 1 here, take the sum of these 2, 1 + 1, add here 2, then write the other 1 here. So now come here, write 1 here, add sum of these 2, 1 + 2, write 3, 1 + 2, 3 and 1. So what you should do is, it always goes by this sum here 1, these 2 together will be 4 these 3 + 3 is 6 and 1 + 3 is 4 like that it goes.

The splitting pattern, the way of generating this Pascal's triangle is simply all you have to do is you have to go back, and then see what you have to do, just add the numbers just above it, to a number and then write this sum here. This is the way you generate Pascal's triangle, 1 + 1 is 2, 2 + 1 is 3, 3, 3 + 3 is 6, 6 + 4 is 10 like that you can generate.

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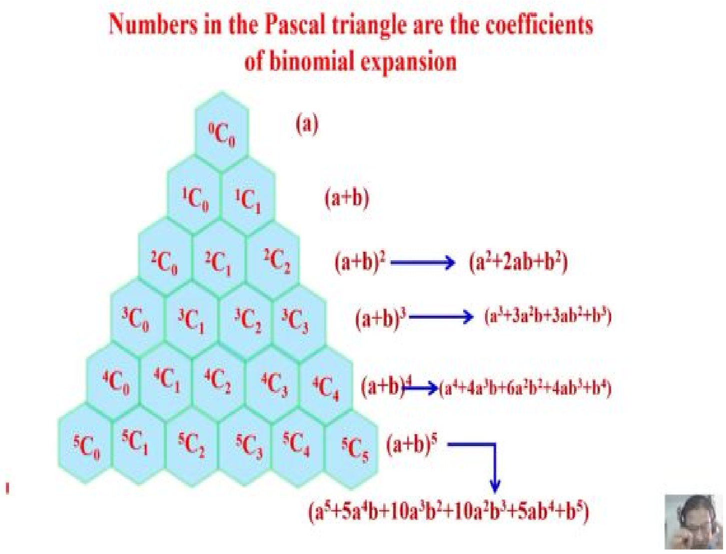

In principle, that is a simple easiest way school way of doing, but you should have already understood binomial expansion. What is this Pascal's triangle number? It is nothing but coefficients of the binomial expansion. Remember, you can write like combination, this is 0 C0. What is 0C0? It is 1. It is nothing but a, write simply a here. It is simply we write a here.

Now, when next one can write 2 hexagons, hexagons I wrote here. It is just a hexagon for writing, otherwise you can write without that also. So, now 1C0, 1C1 both are same. So, now I will take 2C0, 2C1 and 2C2.
1C0 and 1C1 is nothing but the coefficients, both are 1; it is like coefficient of a is 1, coefficient of b is 1
2C0; what is 2C0? Coefficient is 1, this coefficient is 1 and center coefficient is 2. It is nothing but a + b whole square.

When take a + b whole square, $a^2 + 2\ ab + b^2$, so the intensity is coefficients of this expansion 1 is to 2 is to 1. Remember, this is easy to understand by looking at the coefficient

come to this one this is 3C0, 3C1, 3C2, 3C3; this is simple logic you can keep on extending by the logic what is adopted here. This is 1, 3C1 is 3, 3C2 is 3; this is 1. So what does it mean? This is a + b whole cube; a cube + 3 a square b + 3 a b square + b cube. What is the coefficient 1, 3, 3 and 1 so, this is a situation in a quartet.

Like that this is a + b whole power of 4, a + b whole to the power of 5 and you get the intensity here, I showed you 1, 5, 10, 10, 5, 1 so, this is how intensities are generated in the Pascal's triangle. So, what I showed in the previous slide was simply addition; adding 2 numbers above, but mathematically they are the coefficients of binomial expansion, please remember that.

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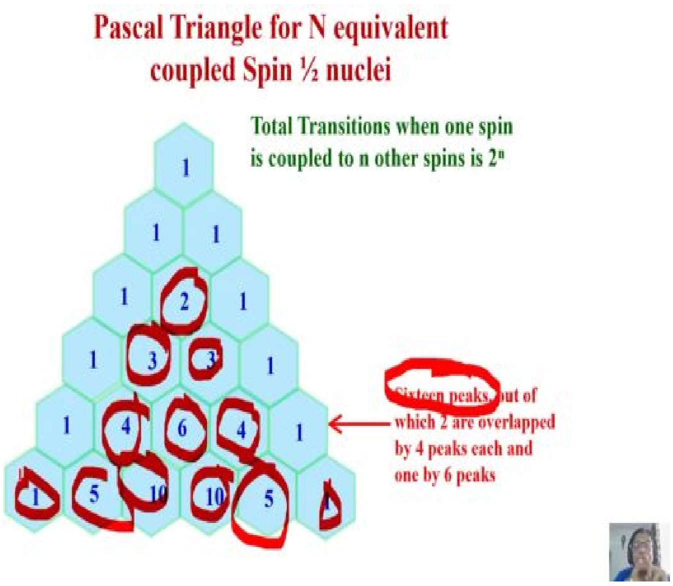

Now, let us understand more as far as a NMR is concerned, when Pascal's triangle for N equivalent couple spins represent the spin of nuclei, how many transitions you should get? but whatever you do, when 1 spin is coupled to n other spins, you must get 2 the power of n transitions. Remember, this is what you understood, when we understood family tree approach; when 1 is coupled to 2 other protons 2 to the power of 2 you will get 4 lines.

When 1 is coupled 3 protons, 2 cube 8 lines. So, we understood you know A, AB, AX and AMX systems like that. So, the total number of lines will not change it is always 2 to the power of n. But, because some lines will overlap at the center, like they became a triplet. Actually how many lines are there, there were 4 lines. When 2 spins are coupled, 1 is coupled to 2 other spins, there must be 4 lines. There are 4 lines only thing is 2 lines are overlap at the center.

Similarly, if we see here 1 is coupled to 3 other things, how much you should get? 2 cube, 2 cube is 8, there must be 8 lines. But what happens, you get intensity 1, 3, 3, 1. Three lines here are overlapped, 3 lines here overlapped and 3 + 3, 1 + 1. There are 8 lines. So the number of lines do not change. The patterns appear as a triplet and quartet etcetera, because some lines are overlapped because they have the same coupling and it appears as if we are observing less number of lines. In reality, these are the 8 lines. so do not get confused. Now we will understand this one. This gives you 2 peaks of equal intensity. This has 4 peaks out of which 2 are overlapped. This gives you 6 peaks, I am sorry 8 peaks, this is 3 and this 3 are overlapped

And what about this one? This will give you 16 peaks; remember, this will give rise to 16 peaks and out of which 4 peaks of this are overlapped, 6 are overlapped and 4 of these are overlapped. In reality, it has 16 peaks. So now you should tell me what happens here. This has 32 peaks; this 10 peaks are overlapped here 10 are overlapped here, 5 are overlapped here, 5 are overlapped here that is 32, 10, 10, 20 + 10, 30 + 2 so it is 32.

So, the number remains always as 2 to the power of n, do not get confused. The pattern appears as triplet, quartet, etcetera, just because some of the lines overlap because of equal coupling strengths. This is what I wanted to tell you, please remember this. Now we will go further.

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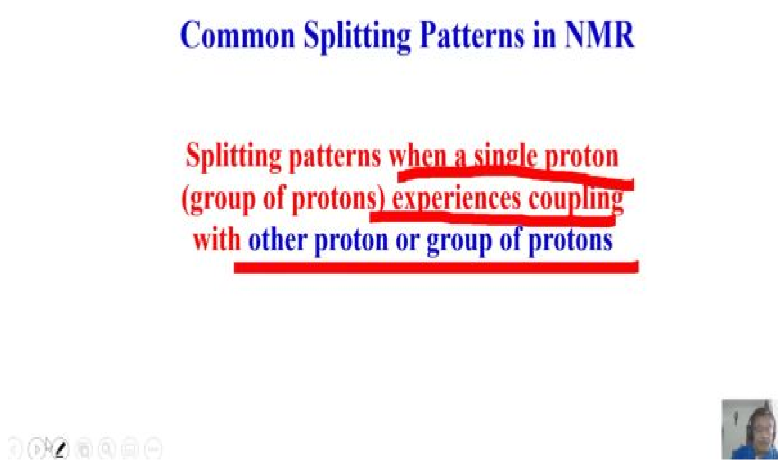

So this I already explained to you. The common splitting patterns in NMR we will analyze now. Very interesting thing. Splitting pattern when a single proton is coupled to a group of protons experiencing coupling with other protons or group of patterns gives a complex pattern. We will try to analyze, how we do that? We will go ahead.

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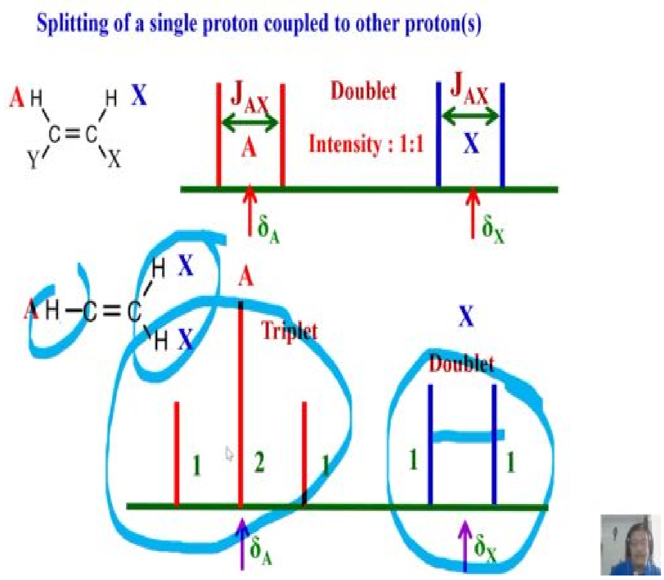

Now, splitting of a single proton coupled to other protons, we know that when A is coupled X it is a doublet, we started with the simplest, then intensity 1 is to 1. Now 1 is coupled to 2 equivalent protons, CH is coupled to CH2 protons, then CH will be a triplet, this is CH is a triplet and CH2 will be a doublet, because CH2 comes at high field, remember that, and this is a doublet because of this CH. Whereas this CH comes down field, is a triplet because of CH 2, understand the pattern, in this group of the hypothetical molecule that I have taken here; CH2 will be a doublet CH will be a triplet, this is 1 : 1, this is called doublet and a triplet. Of course, central triplet gives you the chemical shift of this A and center of this doublet gives you the chemical shift of X, and the separation between these, or any separation between these adjacent lines gives you J coupling.

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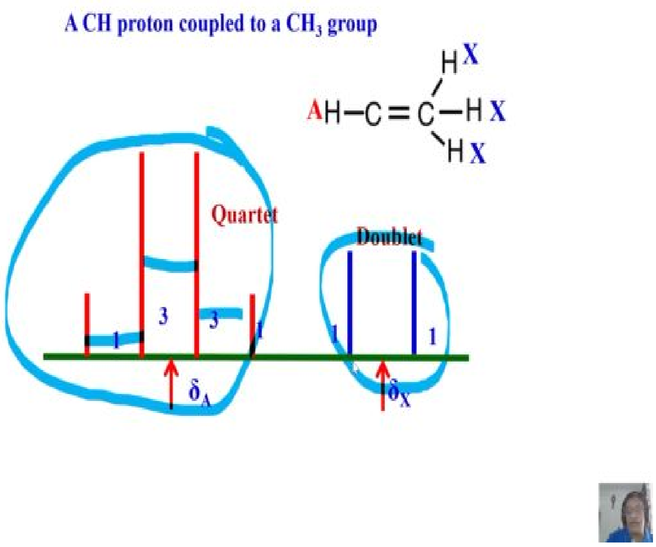

Now, CH proton is coupled to CH3. How does this spectrum come? CH3 comes in the high field region. So, this is CH3, this CH3 will be a doublet because for the CH. Now this CH, if you consider, this is going to be a quartet with the intensity 1, 3, 3, 1. Remember this one, CH will be a doublet, I am sorry CH3 will be a doublet here, and CH3 is quartet, in this coupling spin system. This is called doublet and the quartet, again center this quartet, gives you chemical shift, the adjacent lines gives you J coupling, and center of this doublet gives you chemical shift of X and the adjacent separation gives you J coupling.

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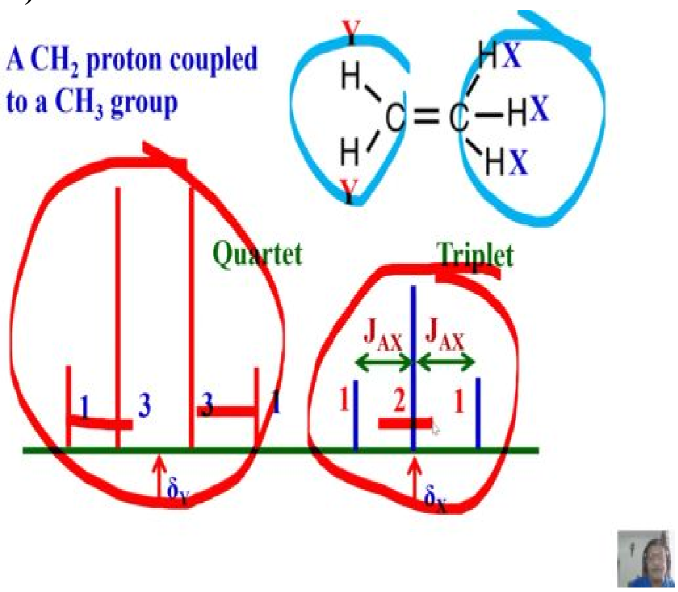

Now we will come to a situation what happens when CH2 proton is coupled to a CH3 group, hypothetical molecule I am writing. Now CH2 is coupled to CH3. What type of coupling we are going to expect now? What is the pattern? we will think carefully, there is no need to worry too much. Already we have worked out this, CH2 splits this into a triplet, this CH3 is split into a quartet, spectrum should be like this CH3 has to be a triplet and CH2 has to be quartet. Very easily you understand. CH2 is a quartet because of CH3 and CH3 is a triplet because of CH2; this is understandable. Again how to measure the chemical shift, how to measure the J coupling? Is very well known, I already discussed many times.

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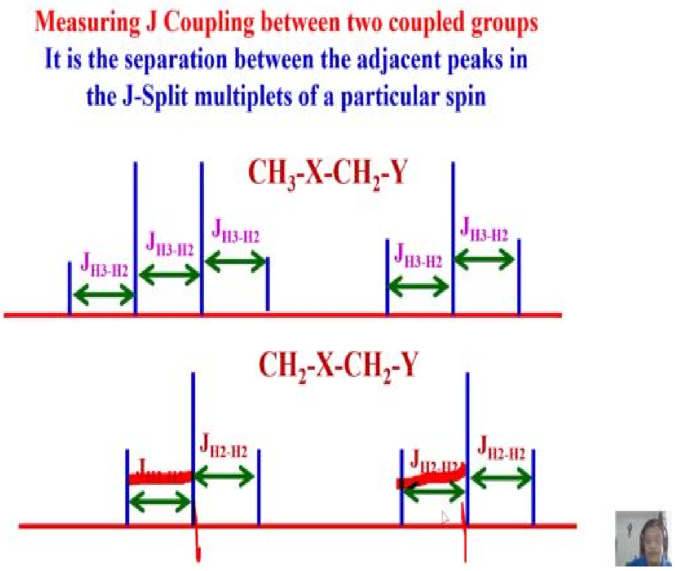

Now how do you measure, as already said, in the example like this, if you have taken separation between adjacent peaks, always gives you J coupling.

If I take CH2, coupled to CH2 what is the type of pattern I expect? Here X and Y are different, let us say there is no symmetry, then this will be a triplet because of this, and this will be a triplet because of this; very interesting thing. So this is what happens; you get a triplet and a triplet in this molecule; this will give you J coupling; this will give you J coupling and this gives you chemical sheet of one; this will give chemical sheet of the other.

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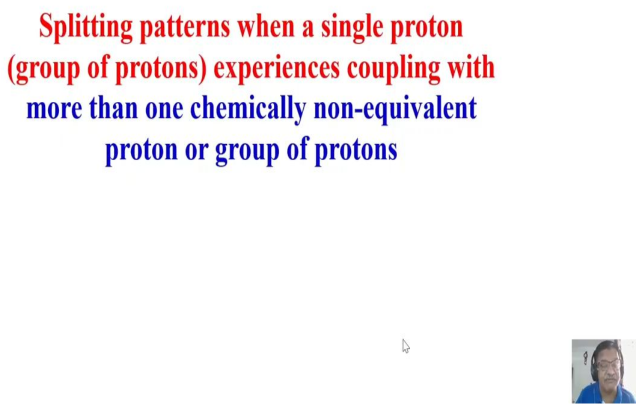

Now we will go further and understand what happens to the splitting patterns when a single proton experience coupling to many other chemical equivalent spins, not one; many let us say, many groups of protons, group of equivalent protons, if it couples how does the splitting pattern come? You understand

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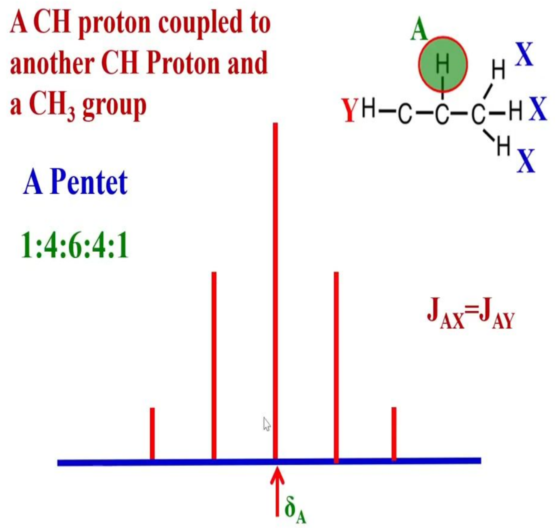

Now let us take a hypothetical molecule a CH proton is coupled to CH proton sorry; a CH proton here is coupled another CH proton and the CH3 group. That means each group is experiencing coupling with 2 other groups. This is coupled to this, and this, this is coupled to this and this, this is coupled to this and this. Let us see how this spectrum comes. This is hypothetical molecule.

And I am looking at this CH highlighted one, because this is my problem. Remember my problem is this CH proton coupled to other two; CH and CH3. Now let us see how the pattern comes. We should immediately look at it and say first you have to find out what is the condition? to look at the pattern; whether JAX and JAY are equal; if they are equal there is one pattern, if they are different there is another pattern.

Now let us generate the situation for JAX equal to JAY; that means this coupling and this coupling are same. How does this spectrum come? Look at this pattern of proton. First it is going to be a singlet, this singlet will be split into a quartet of because of CH3 and each line of this quartet will split into a doublet because of this; As I told you in one of the earlier slides, there multiple couplings can be experienced by a single proton.

So this proton experiences 2 types of couplings; one with this CH3 group and the other with the CH group. So you understand now and you get a pattern like this, it is called a Pentet. 5 lines are there, it is a pentet. What is the intensity pattern? They are 1: 4 : 6 : 4 :1, interesting. How do we know this intensity is 1: 4 : 6 : 4 :1? we have to understand this. Let us generate the intensity pattern. Again Of course I do not have to repeat again and again central peak gives a chemical shift.

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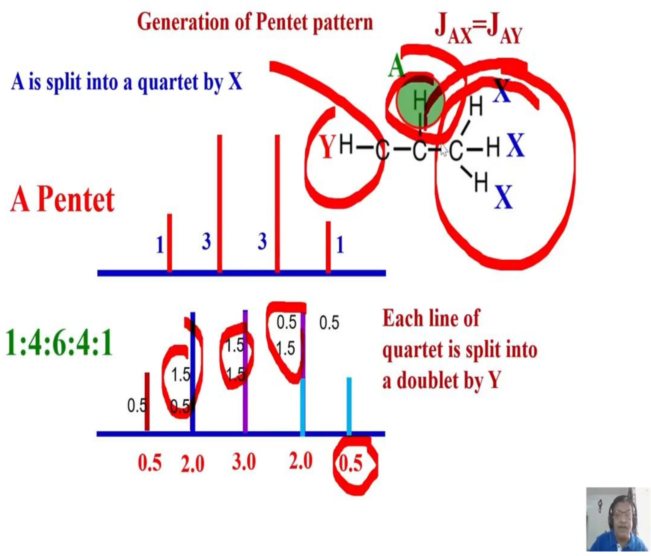

And the separation of the adjacent peaks will give you J coupling. Okay, now will generate the pentet pattern for you. How we get 1, 4, 6, 4, 1 intensity; very interesting. Let us see first A is going to spilt into a quartet because of CH3 that I already explained to you I do not have to repeat that. So 1 3 3 1 intensity, it is a quartet when one is CH is coupled to CH3, it is a quartet. Now this CH2 is coupled to this also; that means each line has to be a doublet, each line. So now we will work out intensity 1 3 3 1, each will be a doublet. This will be a doublet what is the intensity now? 1 become 0.5, 0.5 What is this intensity? 3; Intensity should be 1.5 + 1.5; because the couplings are the same 2 lines here overlap. Okay, this line overlap with this. Now this one, again intensity 1.5 + 1.5 here; these 2 lines overlap. What about this one? this is intensity 0.5 and 0.5 because of this. We did not do any magic. We simply split the lines based on the splitting pattern CH is quartet and is split into each with doublet; because of this we just divided each of the intensity by 2. Wherever is overlapping, now we have to add up. What you will be doing in add up what is the total intensity you will get? This is 0.5, this will be 2, this will be 3, this will be 2 and this will be 0.5. What is the ratio? 1 : 4 : 6: 4: 1, it is a pentet.

You understand, when you get the pentet in the spectrum, please understand there is a possibility one of the proton of this your interest, may be coupled to CH3 and also CH with equal coupling strengths. As a consequence lines will overlap; it is quartet of doublet; lines will overlap and you get pentet of 1: 4 : 6 : 4 :1, remember this point very clearly.

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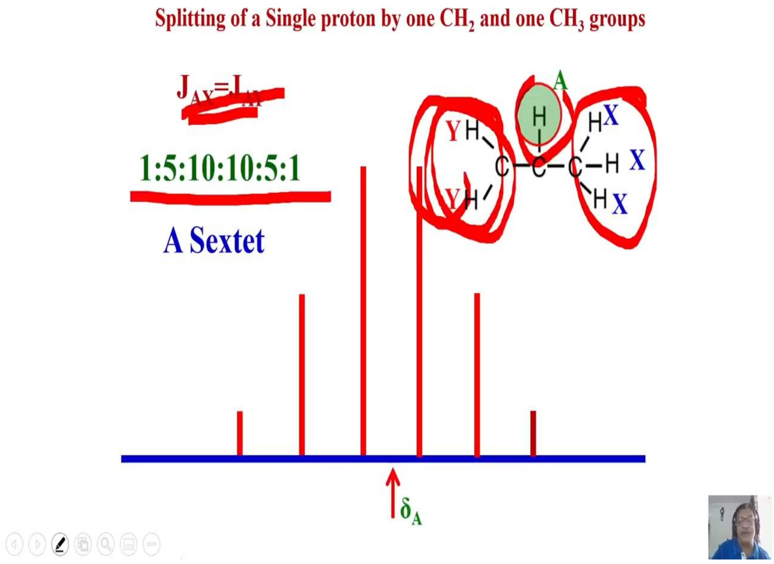

Now if you consider another situation. Here we had a CH before in the previous molecule, you see here we had a CH. Now I will introduce; instead of CH, I will make it a CH2. Remember here it was CH, now we want to make it CH2. Again JAX = JAY. What is the pattern I expect? of course first one you know, this is split this by a quartet and each line of the quartet splits into a triplet because of this and you are going to get a Sextet.

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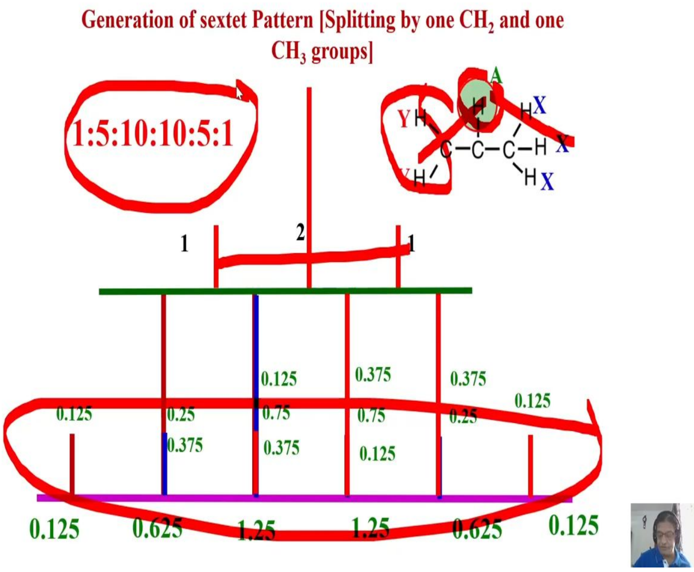

Sextet of the intensity ratio 1 : 5 : 10 : 10: 5 :1. How do I know this? very easy, work out; you know this splits this into a triplet and each line of the triplet becomes a quartet and because of the equal coupling strengths, some lines here overlap. So now go back here. Let us say intensity is 1, and it split into a triplet, I made all intensity such that the that total becomes 1 this is 0.125, 0.375, 0.375, and 0.125; so the total is 1.

Now this is 2 so it will become 0.25, 0.75, 0.75, 0.25; so that this total will be 2. Now the last one, same it is the quartet with intensity like this. Understand, here 2 lines are overlapped, here 3 line are overlapped, here 3 lines are overlapped, here 2 lines are overlapped and is only single line. Add up the intensity now; what is the intensity are going to get? 0.125, 0.625, 1.25, 1.25, 0.625, 0.125.

Calculate the ratio it is 1 : 5 : 10 : 10: 5 :1; sextet ratio 1 : 5 : 10 : 10: 5 :1. Remember this, is the sextet ratio this is the sextet ratio and this is what we generated here. So these are all cases I have taken example hypothetical molecules, I have drawn the drawing for you to understand in this situation this coupling and this coupling are same. And now I did one trick here, I took proton A and took CH2 as the coupling CH2 first I took the triplet and then worked out coupling with CH3; each of them gave a quartet and worked out the pattern and got a sextet like this.

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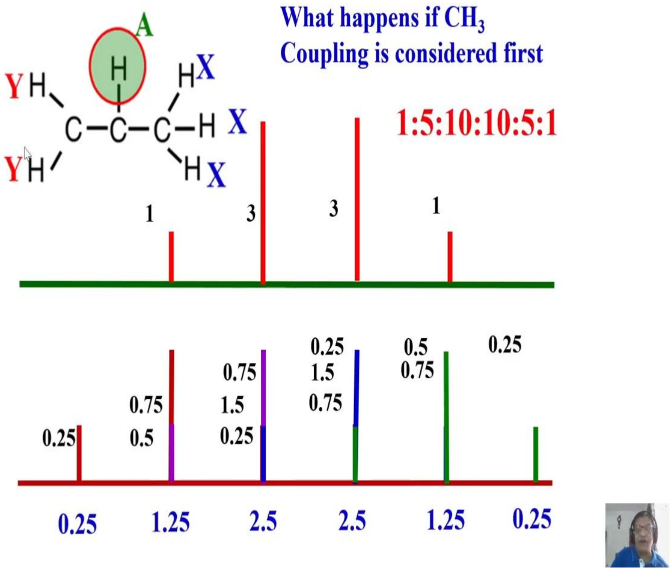

You may ask me a question; why did I take CH2 first, why not, if I take CH3 what will happen? Will the coupling pattern is different? Let us see that. Now I will take CH3 first, it is a quartet; this one. Now what will happen? Each line of the quartet will split into a triplet. Now add up the intensity. Same, there is no difference at all. Again intensity is 1 : 5 : 10 : 10: 5 :1. What does it mean?

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Splitting Pattern is invariant with the order of the coupling chosen for obtaining multiplicity !!!

The splitting pattern is invariant with the order of the coupling chosen in obtaining multiplicity. You keep this is invariant, you take coupling of this 2 this first, and then this later; or coupling to this to this first and then to this later. No problem at all; the order of coupling what you are going to take is immaterial. Your final pattern remains the same. You can work out the splitting pattern taking this coupling first, and coupling to this later; or this coupling first and coupling to this later, does not matter. The pattern of splitting remains invariant.

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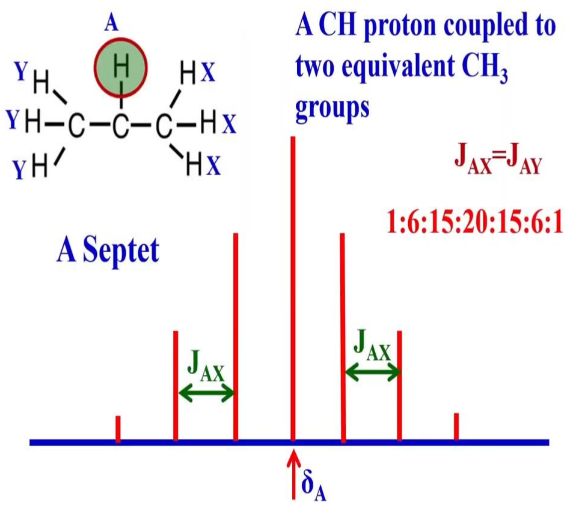

Now I will take another example; here is a beautiful example, again hypothetical molecule. I have taken this proton A coupled two CH3s of equivalent coupling. Understand, 2 CH3s of equivalent coupling. What is the pattern I expect? Does not matter whether you take this first or this first ,both are CH3's. It is going to be septet. first we saw pentet, then sextet now I am working septet for you, 5 line pattern, 6 line pattern, now 7 line pattern. see count it, 1 2 3 4 5 6 7; this 7 lines pattern is a septet. What is the intensity of this? 1 : 6 : 15 : 20 : 15 : 6 : 1. We can work out this one also, the septet in a easy way.

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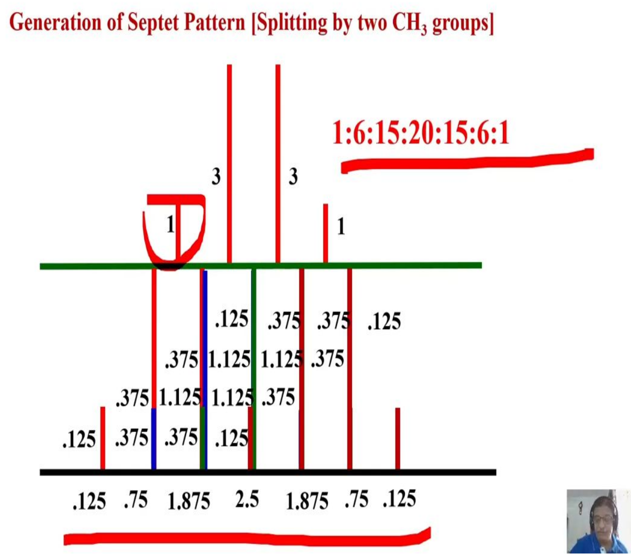

How do we generate a septet? Now we have 2 CH3s; each CH3 will split the CH, first it is this proton which splits into a quartet and each line of the quartet splits into another quartet. So now it is the first quartet, and each line split into quartet, 1quartet here, 1 quartet here, another quartet here, another quartet here, another quartet. I have given different colors and the written the intensity. Now add up all the intensities the way I took it. You know a simple example, I took this one first; the quartet I divided the intensity. So that total become 1. Similarly, next one 3 is the intensity, I divided such the total become one line; that you do and add up all the intensities, this is the intensity ratio. What is this ratio? 1 : 6 : 15 : 20 : 15 : 6 : 1, this is a septet pattern. So when do you get septet? when one of the proton is coupled to equivalent CH3 groups or equal strength; Two CH3s of equal couplings, then you will get septet.

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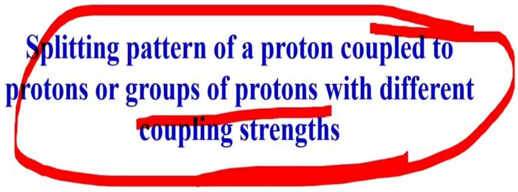

Now so far you understood a lot about coupling, about how do you get the splitting pattern when one proton is coupled to group of equivalent protons. It could be CH2, 1 CH2, 1 CH3 or 2 CH2 or 2 CH3, does not matter. We know how to work out the pattern. And we got several examples a doublet, a triplet, a quartet, a pentet, a sextet and septet. So many things we worked out.

And these patterns you must remember, When analysing the spectrum; soon I am going to start the analysis the spectrum of simple molecules, reasonably complex molecules, where you have to learn the analysis easily. At that time all these things are required, this information. Looking at the pattern you must say, whether it is the pentet or sextet or septet. This helps you, the intensity pattern or multiplicity pattern, So this is what it is.

Next we will take some examples of splitting pattern of a proton coupled to protons or group of protons with the different couplings, very important point. Remember, so far I was taking here for example here JAX =JAY; they weres all equal coupling strength I took, in the other molecules of CH2 and CH3 they were of equal strength. Now what happens when the coupling strengths are different, is it same? how does a pattern change?

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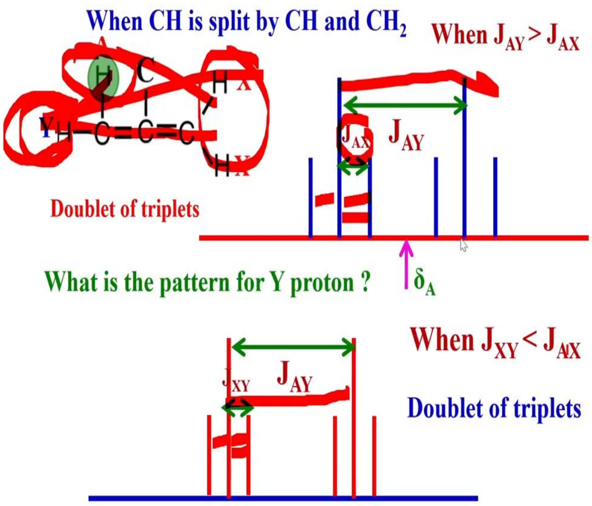

We just start this with a simple example, what happens when CH is split by CH and CH2. This is a hypothetical molecule, a CH is split by CH and another CH2. So now you see JAY is greater than JAX which is close by, only 2 bond coupling. This is 1 2 3 4 bond coupling, is much smaller. So AX is smaller than AY; couplings are not same, they are different couplings. Now see the pattern, when it is split by this proton, A split by Y, this going to be doublet. Now what happens to each line of doublet, it split into triplet by CH2 protons.

You understand, this is what happens. Now I did not write explicitly one below the other. First it was a doublet, first it was a doublet and each line is split into a triplet. I wrote on the same diagram, so that we are going to get a pattern like this. There is a way to name it. Which is the largest strength here JAY is larger than JAX. What do you call this? It is called doublet of triplets. First largest couplings you have to say, the largest coupling is a doublet and each line is a doublet becomes triplets.

What is the triplet separation. Triplet separation is small. So smaller coupling comes second largest coupling comes first. So we should call it as doublet of triplets. That is a nomenclature do not forget that, use the nomenclature, it is a doublet of a triplet. And again center of this give the chemical shift, this largest separation here gives you this coupling and each line of this triplets and the adjacent lines of the separation here gives you this coupling. This large coupling gives you AY coupling.

Now what is the pattern for the Y proton, another interesting thing I looked at A. If we look at Y what will happen now in this case again JXY is very much smaller than JAX. Now it is a doublet for Y proton first, which is largest coupling. one of the coupling AY splits into a doublet. Because this is A it is a large coupling JAY. Then each of them splits with a triplet, which is a small coupling. This is far away 1 2 3 4 bonds away, this coupling YX coupling is small this. Now pattern remains same, only thing is these lines are close by, because this coupling is smaller this one. But what do you call this pattern? This is also doublet of triplets but only thing is, here this triplets separation is larger because this coupling is more, here in this the triplets separation is smaller, because this coupling is small, but the pattern is still called doublet of triplets, understand.

So now in this class we tried to discuss more about the multiplicity pattern. When one proton is coupled spins of equivalent groups of identical couplings, and also we took one or 2 examples of couplings which has spins with the coupling strengths are not equal, and we generated the pattern called doublets of triplets. And if I observe one proton, or other protons, how the spectrum changes we know, and the nomenclature is always largest coupling your have to say first, largest coupling is doublet and then smaller coupling here the triplet. So simply look at this, this coupling is larger and this is smaller, it is called a doublet of triplets. So we can generate like this for few more examples, where the complex multiplicity pattern will be there, then analysis of the spectrum is easy, and I will stop here today. In next class we will discuss much more and we start to analyze few spectra.