Principles and Applications of NMR spectroscopy
Professor Hanudatta S. Atreya
NMR Research Centre
Indian Institute of Science Bangalore
Module 2
Lecture No 9

welcome back, so in the last class we looked at how the chemical shifts arise, what are the different factors which affects the chemical shift values such as inductive effect, mesomeric effect, hydrogen bond effect and so on. in this class today we will look at the another para very important parameter in NMR which is called as J-coupling. so, that j-coupling has a very rich history and what basically wase observed early on is that when you record NMR spectrum, for let us say ethanol let us say to the mol ethanol CH3CH2OH what happens is CH3 we said we saw in the last class that is 3 protons they act as a chemically equivalent so they act as single entity.

So, CH3 you expect one peak. For CH2 the hydrogen C of CH2 you expect another peak because both the hydrogens are chemical equivalent and for the OH group the H hydrogen attached to the OH there also you expect one particular peak. So, basically in a ethanol spectrum if I record theoretically or logically you expect three three peaks in a spectrum. However, what we actually see in a spectrum is not three but some many peaks more.

Basically, what happens is each of the peak is split in to smaller peaks and this is why this is what was seen early on in NMR spectrum and it was took it was took a long time to understand what from where this originates and there was then it was understood that this is because of interaction between two nucleus nearby nucleus, for example, two hydrogens mediated means carried out through the intermediate electrons in the bond. So this is the is basic origin we will look at more detail aspects of the J-coupling as we move on.

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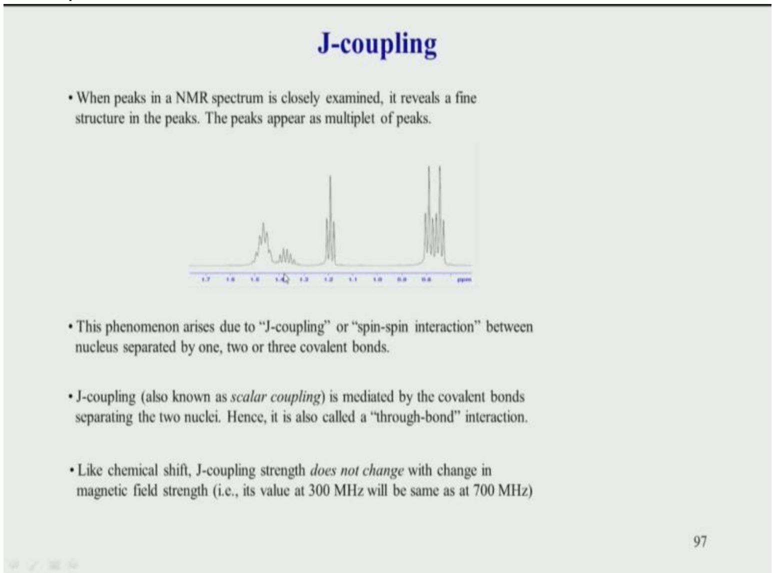

So, if you look at this spectrum here, you can see here this is what is shown, what is meant by the multiplet structure. So, we can see each of this peak here is not a single peak. It is split into smaller peaks. So, this for example, looks like a triplet, means three peaks, here it looks like a more complicated peak structure and similarly, here you can see there are many peaks which are within this particular peak envelop.

you can see in a similar manner here that there are multiple peaks here. So, this is what a was very intriguing in the beginning of NMR spectroscopy and this was then discovered that this is because of what is called as j-coupling. So, what is j-coupling? J-coupling basically is a interaction between two spins and therefore, we also use the word spin- spin interaction. So, it is interaction between two spins, we will look at theoretical theoretically how where does it come and because of this interaction the peaks of each of the spins is resolved or splits split into more lines.

So, j-coupling is also known by the word scalar coupling or through bond interaction and so on and like chemical shift j-coupling also does not change with change in the magnetic field. So, example if I measure the j-coupling of between two atoms as a 3 at 300MHz spectrum let us say say 10Hz that value will be the same if I go to higher magnetic field. So, that value does not depend on the magnetic field.So, let us now look at the theoretically from where does this j-coupling come about.

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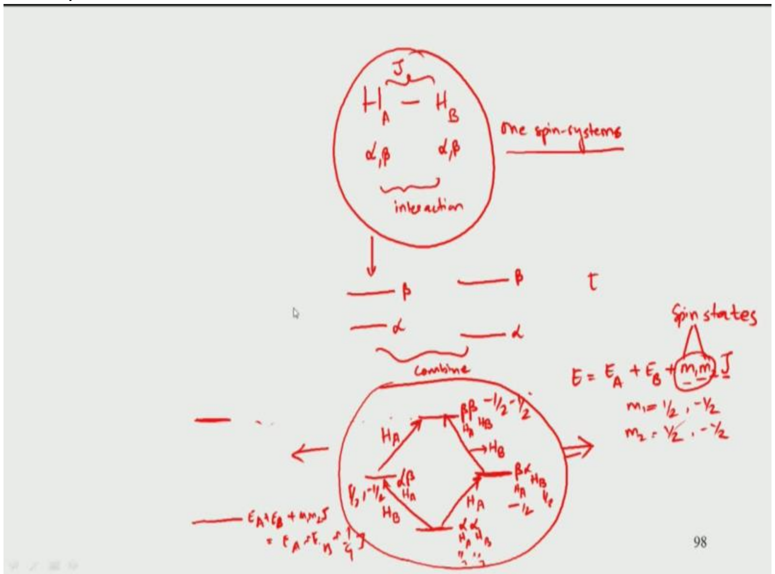

So, I will take an example, of two hydrogen atoms. So, we will call it HA and HB. Okay. So, now this hydrogen atom can exist in two spin states which we saw alpha, beta. Similarly, this hydrogen can exist in two states, alpha, beta. Now, if there is an interaction between these two spins then what happens is? We considered this whole thing as one spin system. We do not consider the two spins separately we call this together as one spin system.

So, we can write the now because there are two spin system now if the HA has energy levels alpha, beta. Similarly, HB has energy levels alpha, beta but we do not consider now this as separate we will combine these two and this results in four energy levels. We can call it as alpha-alpha, alpha-beta, beta-alpha and beta-beta. So, we can say this particular the first letter (corres) the alpha state correspond to HA and the second will be HB. That means if you look at this particular transition what is happening is the H alpha the alpha state of hydrogen is same or HA is same but the beta is undergoing from alpha to beta.

So, this is a transition corresponding to H beta. Similarly, if you look at this particular transition that is molecules when they get excited from this energy level to this energy level again the HA is constant that is both beta state but the HB is going from alpha to beta. So, therefore, this particular transition also corresponds to Hbeta. So, this is basically this whole drawing which is shown here this particular (sys) this is one particular system and there are four energy levels now, because there are two alpha beta for each and therefore, two into two makes it four energy levels for a spin system which contains two hydrogen atoms.

Now, this particular energy transition from this energy level to this energy level now, we will corresponds to A because in this particular case alpha of A is changing to beta but alpha of B is remains alpha. Similarly, if we go from here to here this corresponds to transition for A because hydrogen atom A is going from alpha to beta but the hydrogen atom of B remains in the beta state. So, this is that particularscenario scenario when we say that these two together form a two spin system that is combined system.

However, now suppose there is a j-coupling between the two. So, let us say now that they are there is a j-coupling between the two because of this j-coupling this whole picture now changes. What happens is we say that the energy at any for any given spin system energy is equal to EA + EB. This is the total energy of the system if you consider A hydrogen and B but in case of j-coupling we have to add one more term which we write it as m1m2j where j is the j-coupling value between the two atoms.

Now, if you take m1, so these are basically the spin states. These are the spin states. Okay? So, now if m1 can be equal to half it can be m1 can be equal to half or it can be - half, m2 can be equal to half or it can be - half. So, there are four possibilities half-half combination, half-- half combination, - half - half combination and - half + half.

So, this is what is shown here. Here it is half-half in this particular case it is it is - half + half and in this case it is - half - half and this is case it is + half-- half.

So, the four different possibilities four different the spin states are captured in this particular diagram but now the energy levels will also start changing. What happens is if you look at this picture in this slide what will happen is, this particular energy level if I draw a line here and look at these energy level if I draw a line here. Now, what happen this is EA + EB, now + m1m2j but m1 and m2 both of them are + half and therefore, this total adds upa value j by four. Half into half into j. So, this basically becomes EA + EB + 1 by 4 j.

So, what basically is happening is this particular energy (lev), this particular energy value where you can see the red dot here, this particular down below So, let me so, if you look at this particular here so, where the pointer is you can see this energy level which is a ground state energy level. This is another excited state and this is a also excited state. Now you can see the energy levels of these states are modified because of an additional term which is shown here.

So, you can see because of this m1 into m2j which is adding to the total energy based on what is the value of m1 and m2 the energy levels starts changing. So, now these energy levels shown here earlier it was in the absence of j-coupling but because of the j-coupling now the energy levels of this states start changing and it basically what happens is you introduce extra energy. So, we will see that in this next slide.

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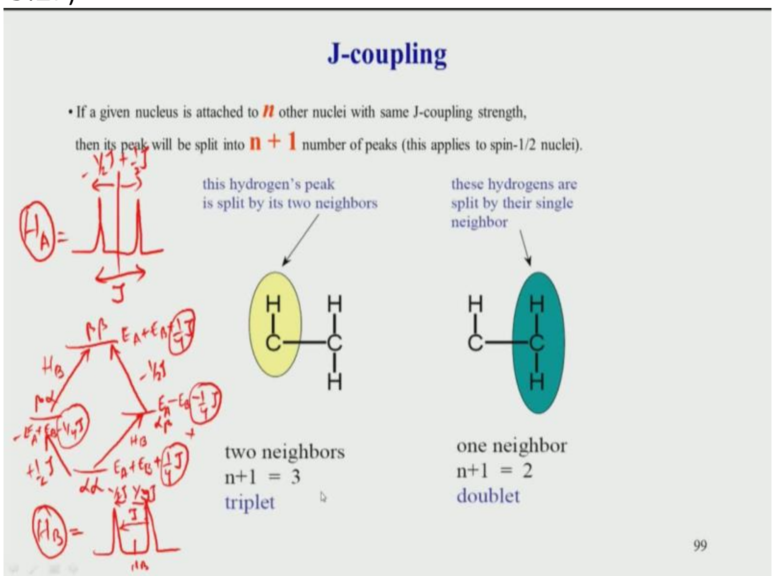

So, we can see here particularly in this particular slide. So, we can see that suppose I draw a two energy level here. Now, what happens is this energy gap is now EA + EB + 1 by 4 j because m1 into m2 makes it 1 by 4. Now, this one is EA - EA - EB - 1 by 41 by 4j and this is EA - - EA + EB - 1 by 41 by 4j and this is one is basically EA + EB + 1 by 41 by 4j. So, what has the happened? If you now look at the transition this transition which was corresponding to Hbeta HB this is alpha-alpha, this is alpha-beta, this is beta-beta and this is beta-alpha.

So, this one which we saw in the previous case that this corresponds to the transition of HB in this particular case, the energy is now earlier the energy value of this you can see this - this there is a additional contribution of + 1 by 4 j. So, if you add these two, basically what is happened is these two energy levels now if you look at this transition here, this is another transition corresponding to again Hbeta because Halpha is constant Hbeta is taking a change transition and because of this what happens is the two energy levels.

So, now if you look at this difference here, this - this what is happened is it has because of this additional term, it has gone down by - 1 by 4 j this - this. Similarly, if you look at alpha-alpha or - alpha-beta what has hapended? It has gone up by 1 by 2 j. So, basically if you look at the Hbeta peak, it has got split in to two now. This is original HBeta peak where it should have come but because of this splitting it has become 1 by 2 j 1 by 4 j this side one ba sorry , 1 by 2 j this side 1 by 2 j this side and the total difference which has become j.

So, because of this presence because of the presence of the j coupling. So, Because of the presence of the j-coupling between Hbeta and HA, the Hbeta peaks now gets split into two peaks. It no longer becomes is no longer as a single peak. It has got split in to two peaks because of this change in the energy of the transition and where this is the energy of transition change coming from? It is coming because of this term here. That each of this term adds some energy level to the lower state, subtracts some energy from the upper state.

So, because of this, these two energy levels have come closer by 1 by 2 j and these two levels have gone further away because of 1 by 2 j.So, therefore this is how we can explain that these two transitions earlier weret they were of the same energy level. So, they were one peak. Now, because of this addition of j-coupling value it has got split into two different peaks. The same situation will happen for A. In the case of A your peak will now be not one single peak; it will ge t split into two because of this transition here. Now, it has got sub - 1 by 2 j this side and here it is + 1 by 2 j this side.

So, compared to the earliest scenario it gets split into two. One goes to + 1 by 2 j - 1 by 2 j this side another goes to + 1 by 2 j this side and the total difference becomes j. So, HA has got split into two, HB also has got split into two. So, this is the basically the explanation of how the j coupling comes from. J-coupling comes basically because of this (sin) situation that the energy levels of A which was earlier a single peak because of the there is no coupling, because of the presence of coupling with another spin B it get split into two halfs and this is exactly the half in the sense initially if the signal was hundred percent here, it becomes fifty-fifty.

So, the whole signal has come down by fifty percent and split into two peaks instead of one peak. So, this is called a multiplet. It is called a doublet in this particular case. Similarly, here in the H case of HB, itthas also got split into two and it has become a doublet. So, this is how and the j-coupling comes about soone important thing to understand is j-coupling is now we can see if HA it splits Hbeta into two peaks, Hbeta is also splitting is Halpha HA into two peaks.

So, we can see that both the hydrogens they split each other. So, this is a very important point to keep in mind that when one spin splits the other peak into two because of j the other peak also splits the original one into two. So, it is a mutual, equal and opposite kind of effect. And if you see one more thing this j value is is measure of the coupling. If j is very high we say the coupling is good. If the j is very low we say coupling is very very weak.

So, therefore this j value is the strength of the coupling. It depends on the strength of the coupling and therefore, it matters whether it is hetroneuclear coupling will be different hydrogen-hydrogen coupling, Hydrogen-proton coupling and so on. Now if you can extend this picture more, let us say that we take a molecule which is shown here that I have one hydrogen on one side but now, I have two hydrogens here.

So, instead of Halpha let us say this is HA, this is HB but here, there are two HBs. There are two equivalent HBs.So, then it is not similar to this picture because this picture was only for one hydrogen atom interacting with another hydrogen but here one hydrogen atom which is shown in the yellow shade is now interacting with two hydrogen atoms. So, this is through bond coupling. So, remember j-coupling is always through bond which means that these three bonds this hydrogen is shown in the yellow shade is now interacting with this hydrogen via 1, 2 and 3 bonds.

Similarly, this hydrogen is interacting with this hydrogen here also via 1, 2 and 3 bonds. Now, let us suppose this is an assumption now, let us suppose that these two hydrogens are equivalent. Please remember this is not always the case. It is not always possible to say that the two hydrogens like this are chemically equivalent, they may be chemically equivalent or they may not be chemically equivalent.

Therefore, it is very important not to assume things but let us say for this particular example that these two hydrogens are equivalent.Then, we have a very famous rule known as the n + 1 rule which is shown written here. It says that if a given nucleus there is hydrogen example in this yellow color is attached to n other nuclei with the same j-coupling value means suppose this hydrogen is having a j-coupling with this hydrogen where the value let us say some jx value and if the same x value is for this coupling then this particular yellow colored hydrogen shown in the yellow color shade will be split into three peaks because it has two neighbors.

So, whenever there are n neighbors then it is called n + 1 rule. This n + 1 rule remember applies very very specifically only to a particular case and what is that particular case and condition which should be satisfie?. Number one, it should be coupling to the same hydrogen i mean it should be having a same value to two different hydrogen. These two different hydrogens may be chemically equivalent, may not be need not be chemical equivalent. Okay? but the value of coupling of this hydrogen to this hydrogen and the value of coupling of this hydrogen to this hydrogen should be same.

Typically this happens when these two hydrogens are chemically equivalent. So, this n + 1 rule is very specifically applied only in the case where there are chemically equivalent hydrogens and an hydrogen atom is coupled equally to both these hydrogens. So, this is what is shown particularly here that in this particular case the yellow colored hydrogen gets split into three peaks because of two neighbors here. So, n + 1 is equal to three.

So, this yellow color hydrogen that is also hydrogen shown in yellow color shade will appear as a triplet. Now, triplet means what is a triplet? Is it three peaks and what is the relative intensity? We will see that in the coming next few slide. Look at this example here now. Here what is shown in this shade has two hydrogens and now, let us assume as we saw here that there are they are chemically equivalent.

So, if they are chemically equivalent then these two are considered as one entity or one hydrogen. So, now these two hydrogens considered together as one. Okay, they are together as one. Now, these two together are coupled only to one hydrogen here. So if you considere these two hydrogens as one unitthen, this one unit is coupled by j-coupling to another only one hydrogen that means this unit has one neighbor and according to the n + 1 rule this unit together will be split into two. So, because this unit is chemically equivalent unit for us it is giving you if there is no coupling it will give me only one proton means one peak.

One type of proton, two proton but both are equivalent. So, they will give you one peak but now because they are coupled to this hydrogen that peak will splits split into two and that is called a doublet. So, doublet basically the as the word sounds it is basically it means two peaks, as the word sounds here it means three peaks. So, like that you can actually look at the different types of coupling which is shown here in different examples.

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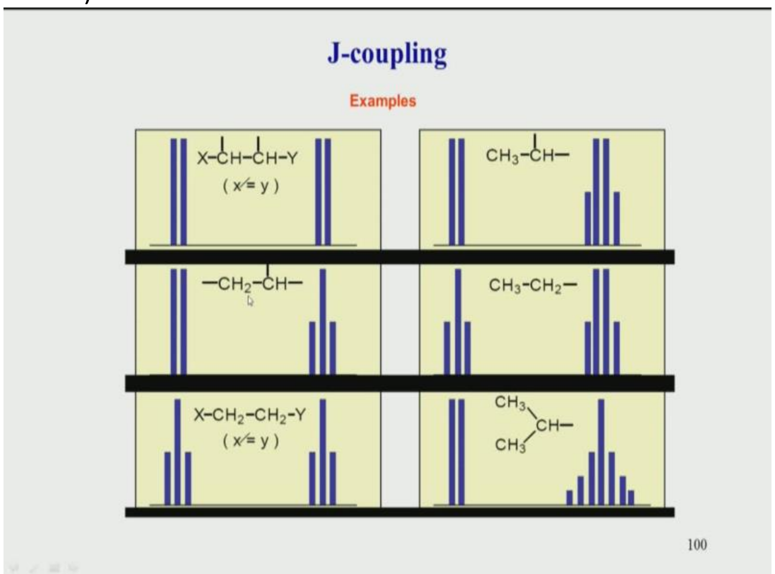

So, we can see here this particular hydrogen which is shown in this arrow and this particular hydrogen. Now, what happens is this x and y are not same. Suppose x and y are not same which means that this these two hydrogens are not equivalent. So, therefore this hydrogen will split this hydrogen peak in to two and this hydrogen will split this hydrogen peak into the two. This what example what we saw in the previous slide if you have HA and HB then each will split each other and this is what we shown here that both of them give a doublet peak. The both the hydrogens are got split into two two each.

Now, consider this case where this CH3 remember according to chemical equivalence theory, these three will hydrogens are equivalent and they will all be in the same peak, they will be one chemical shift value, they will all be equivalent but three now therefore, you should considered as one unit as far as chemical shift is concerned. So, therefore this unit will be split by this hydrogen into a doublet. So, this is what we shown for a CH3.

So, on the left hand side what you see here is a CH_3 peak which has got split into two because of this hydrogen. Now, if you look at this side here what is happening, this hydrogen is having (four) three hydrogens as neighbor but all the three are equivalent. it does not matter as far as this hydrogen is concerned it sees there are three hydrogen in it is neighbor therefore, an all the three if you because they are equivalent it is having the same coupling to all of the three hydrogens and therefore, this hydrogen will now get split into four peaks by the n + 1 rule.

So, the n + 1 rule says that this hydrogen which is have indicating by the arrow get split because of this CH_3 into four. Now, look at this pattern here it will looks very strange pattern here but how does this pattern come? We will see in a few slides from now, how this pattern can be derived mathematically is a very easy to do that but now one thing we should note you should ignore here which I have not-drawn properly is the intensity.

So, this is just as a schematic to show you the peaks splitting pattern. Therefore, the intensities are not to scale which means these two peaks you would expect three times bigger than this peak. Why? because this is one hydrogen together and these two together are three hydrogens CH_3-CH. So, you expect this unit to be three times stronger than this but for the sake of explanation I have ignored the intensity right now you have to only concern your focus, your attention on the peak pattern.

Now, look at this peak pattern here this is CH_2. So, we are assuming these two are chemically equivalent and therefore, these two together act as one unit both of them are split by because of this hydrogen into two and that is the CH_2 peak what you are seeing in this left side and on the right side this hydrogen now, is coupled to both this equivalent protons. So, there are two protons here. So, n + 1 two means three peaks.

So, this CH gets splits into three peaks and this is the triplet (())(22:2) peak. Again how the intensity is in this manner we will see in the next few slide. Now, consider these three CH_3-CH_2. Now, here CH_3 which is on the left side will gets split because of the two into three peaks. That means all the three hydrogen which are one entity one unit because of chemical equivalence now, they gets split into triplet because of two hydrogens which they are coupled two this is what is on the left side, on the right side these two hydrogens now are equivalent but each both of them are coupled to three hydrogens three on this side.

So, the n + 1 rule says they should get four peaks. So, this is what it is a similar in this case. So, whenever you have any CH or CH2 coupled to three H3, we will get a quadret. This is called a quadretquadret. Quadret means four peaks. Now, you can extend this idea to these two the scenario here, here you can see both are CH2-CH2. So, they will get split by each other into three three peaks because n + 1 is the two + one and three. So, both the CH2s now will show triplet each and and finally in this particular case which is a more complicated structure this an isopropyl group very very common in amino acids in chemistry and so on.

So, very often you will encounter this kind of a moiety. So, here you can see there are three hydrogen there are three hydrogens. Now, what happens is both are CH3 so both are further equivalent. So, what it means is that these six hydrogens these hydrogens together act as one unit. They are basically one unit. So, these three hydrogen six hydrogens are one unit and these six together are coupled down to one hydrogen.

So, these six hydrogens which act as one single hydrogen because they are equivalent they will show a doublet which is shown this side because of one single hydrogen. On the other hand this side hydrogen because now it is coupled to six hydrogens it will become seven peaks. So, you see this is how the x n + 1 rule six + one seven and again remember intensity pattern we will see shortly but the idea in this whole slide is to illustrate how this different splitting happens because of j-couplings.

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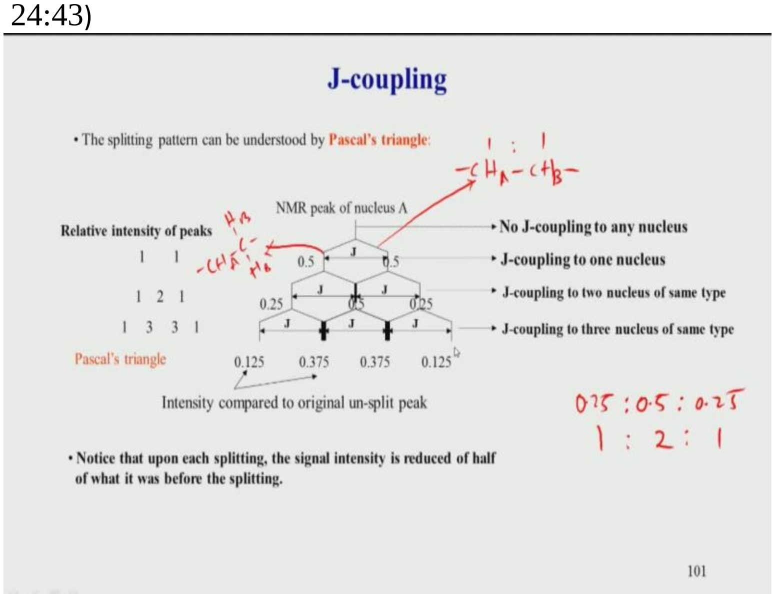

Now, where does this splitting pattern come up about? So, for that we will go like this. So, if you look at this, this is called as a Pascal's triangle, this is a very famous way to obtain the chemical shi the keep coupling pattern. So, let us look at this like this. So, let us say there is no coupling. So, let us take a hypothetical nucleus A which has no coupling. So, when there is no coupling it is obviously only one peak.

Now, because of coupling to any other hydrogen any other nucleus the suppose we are let us we have it has only one hydrogen in the neighbor , in that case it will get split into two this is a doublet. So, this is what is drawing here drawn by this triangle in this pa, sorry these two lines and this is a doublet. Now, what is happening let us say that the intensity of this line which is shown by which I am pointing by this arrow is one then because of the splitting it gets equally divided into half and half.

So, you can see this is called one is to one pattern because the ratio of this to this peak is equal. They are both equal. So, 0.5 is to .05 is 1 is to 1. This is happens when there is j-coupling to one nucleus. Now, I can take now j-coupling to a second nucleus. So, imagine now a situation where we have something like. So, we looked at this particular case is when HA is coupled to one another HB, okay.

So, this is basically one is to one. Now, consider another case where there is now one more so, we can look at this particular case. So, there is one more HC-H and there are two hydrogens. So, there HA, HB, HB two hydrogens. Now, what happens in such scenarios? So, this is what we have to now look at. Now because of this this two hydrogens here what is shown here, these two hydrogen this one gets first split because of this into two. So, this is what you see here. Now, next this hydrogen you consider and that will further split this hydrogen into another two.

So, first this peak is splitting this HB splitting HA into two, then another HB is splitting this that other two peaks into further two peaks. So, you get two into two four peak. So, that is what is shown here but what happens is because (())(27:06) are same that means the j of HA to HB is same as HA to this HB. Therefore, this J is same so the middle line middle line when you draw a line from here and you draw a line from here and the distance between these two is jdistance between these two is also j then what happens is the middle lines they collapse, they join together.

So, when they join together they add up in their (())(27:30) intensity. Therefore, this peak which is 0.5 but 0.25, 0.25 in the beginning. Similarly this 0.5 got split into 0.25 and 0.25 but in the middle those 0.25 and 0.25 they add together and they become 0.5. So, therefore after splitting because of these two hydrogen this HA now has three peaks. 1, 2 which are together and 3. So, now what is a relative ratio of the intensity? It is one this .25 is1, .5 is 2, .25 is 3.

So, we can see in this manner that if you look at this you have 0.25 and 0.5 and 0.25. now if you take a mathematical ratio it is 1 is 2 is to 1. So, this is how the triplet comes from because of coupling of this hydrogen with these two hydrogens. Okay. Now, let us say that there is one more hydrogen here. So, there are three hydrogens. So, in that case the third hydrogen will also split this into two. So, then each of these peaks will further get split into two, then further it will half of 0.25.

And again because of the same j value coming repeating everywhere the middle it is one which comes from this side and 1 which comes from this side gets joined and therefore, it (bec) add some together. Similarly, here it will add together. So, if you see if you draw a line like this which is half of this 0.25. So, 0.125, this side 0.125 but here also point from 0.5 this is 0.5 remember.So, half of 0.5 is 0.25. So, 0.25 from this side. 0.125 from this side becomes 0.375. Similarly, the logic here 0.25 contributes half of itself that is 0.125, 0.5 contributes half which is 0.25. So, together it 0.375 and this peak last one is half of 0.25 and which is 0.125.

So, now if you take the relative ratio it becomes 1 is to 3 is to 3 is to 1 and that is the concept of quadrate, that is what is a quadret. So, you see in this manner one can keep on splitting this hydrogen because of any number of hydrogen around itself. So if there is one more hydrogen you can split it further, if you have one more hydrogen here you can split it further and what one has to do is start from initially with no splitting, then start splitting because of the hydrogen into two peaks, half and half and give as because of some j value, then further split because of next j and you can keep on doing this j value as long as you have.

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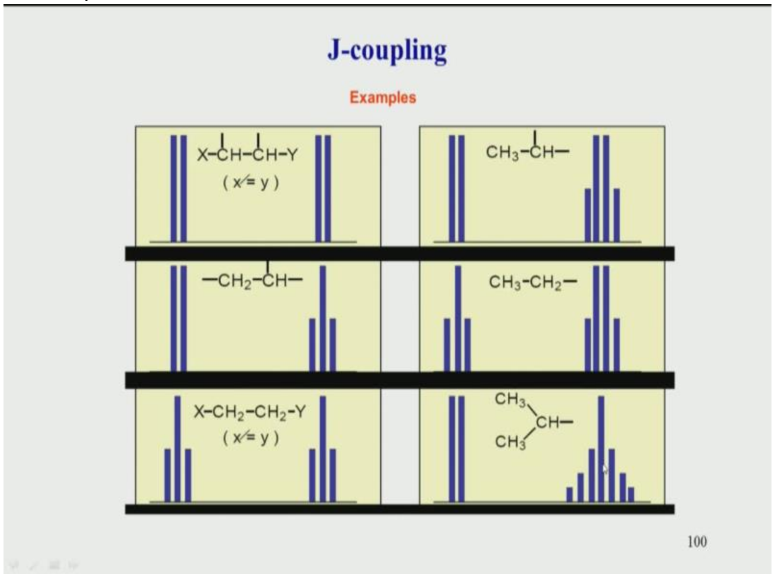

So, for example if you go to the previous slide then we saw here this is what happens that there is now a six peaks. So, here we saw this is a quadret just now we saw how a quadret comes because of this hydrogen is split into four but now here this hydrogen is split into seven because of the six hydrogens here. So, that pattern also can be derived ya using this j coupling and I would suggest you as an exercise to work out that given another hydrogen and like this up to six hydrogen how will this pattern look like and what will be the relative ratios. So, we will continue in the next class with j-coupling and we will see some more interesting features of j-coupling. What are the typical values of j-coupling? How they are useful in structure determination and so on. Thank you.