One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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Lecture 13: NMR Spectral Splitting patterns

So, in the last two or three classes, we discussed at stretch about coupling interaction, varieties of factors, varieties of information I gave you right from the different features of coupling constant. And in the last class especially, we discussed about sign of the coupling, where I explained to you about how the spectrum changes, appearance spectrum changes, if there is a change in the sign of the coupling. Because the sign of the coupling could be either positive, negative or 0, we do not know. Why the sign is important? I will come to that later, because sign of the coupling is extremely important, especially when in dealing with some of the structures of the molecule by using what is called RDCs concerning heteronuclei. If the sign of the coupling is not known, we make mistake in getting the geometry of the molecule. So, the sign of the coupling is very important. And I also told you about the relative signs of the coupling, how do we get by using Dirac model. I showed you the situation when both the spins are unpaired, it is a stable state and we said $^1J_{CH}$ is positive, $^2J_{CH}$ is negative and $^3J_{CH}$ is positive. That is oK. That is about the sign of the coupling.

How the appearance of the spectrum changes, when the sign of the coupling is changed. In the AX example, there are four peaks of equal intensity, like this. When, let us say, this is for positive J coupling, and for the negative J coupling, this will get reversed like this and this gets reversed. As far as we are concerned, spectrum remains unaltered. You will not know whether the transitions have got interchanged or not. But in reality it has happened. So, the one-dimensional NMR spectrum is not be able to give us the sign of the coupling. It is not possible to get it, because the spectrum remains invariant. And I also showed you, I told you about magnetic equivalence. Magnetic equivalence is the situation where in a coupled spin system, all these chemical shifts of the spins, coupled spins should be identical. They must be chemically equivalent because of symmetry operation or whatever it is. But at the same time, when they are coupled to each other, coupling among each of the spin to other coupled partner should be identical. If I take the example, three protons, 1, 2, and 3, the chemical shifts of 1, 2, and 3 should be identical. They are chemically equivalent. And the J coupling between 1, 2, 1, 3 and 2, 3 should
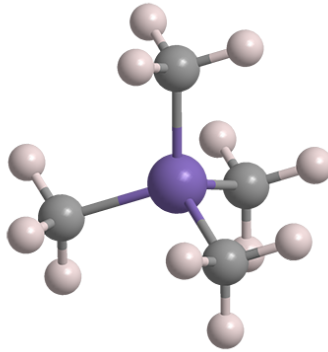
also be identical. Then in such a situation, these spins 1, 2, 3 are called magnetically equivalent spins. Magnetically equivalent spins gives at a single peak. Even though there are couplings among them, they will not get reflected. So, you will get only a single peak. And this magnetic equivalence need not be because of one coupling. If a particular spin experiences three different couplings, take for example, benzene. Each proton of the benzene has an ortho coupling, meta coupling and the para coupling. Each proton experiences three different couplings with different strengths. But nevertheless, benzene gives a single peak because all the protons are magnetically equivalent. Similarly, I took the example of ethylene also. And at the same time, I also mentioned to you, all chemically equivalent spins are not magnetically equivalent. But all magnetically equivalent nuclei are invariably chemically equivalent. This is a term which you people should understand.

With this, we will go continue further today and discuss more about what is called complex multiplicity pattern. I already told you about multiplicity pattern. But how do you get complex multiplicity pattern, we will try to understand today. Among chemically equivalent spins and among chemically different spins, etc. If there are chemically equivalent spins, which we already discussed, if one proton is coupled to other group of proton like CH2, where two protons are chemically equivalent, it could be a single proton or it could be CH2, which may be coupled to CH3. These are also equivalent protons, these are also group of equivalent protons. When it is coupled to group of equivalent protons, how does the multiplicity come? It obeys what is called 2NI+1 rule, where N is the number of protons in a group and I is the spin and plus 1. So, for example, if N is equal to 2, let us say 2 protons of CH2. When one proton is coupled to CH2, 2 into 2 into half plus 1, it will become 3. When one proton is coupled to CH2, it will become a triplet, three lines pattern. When one is coupled to 3, it will become, 2 into 3 into half plus 1, that will become 4. So, we get four lines pattern. One proton is coupled to CH3, we have four lines pattern. When one is coupled to CH2, it will be a three line pattern and the intensity of the multiplicity is given by what is called Pascal triangle. We will now go by this thing. But there are exceptions for this 2NI+1 rule.
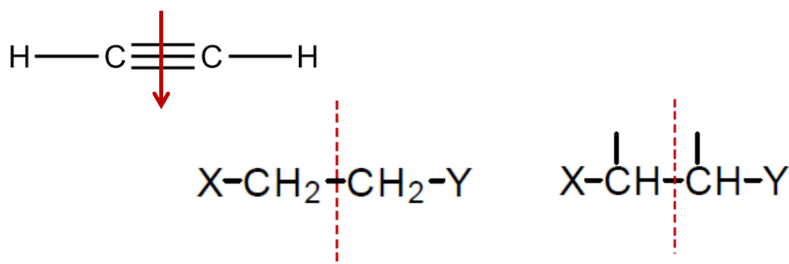

One is a molecule like this, if you consider, there is a symmetry along this axis and this proton will not couple to this. Now, there is no coupling at all, no J coupling. Consider this one, if X and Y are different, then this will couple to this, 2NI+1 rule, this will couple to these two protons, this will give three line pattern. When this is coupled to this, again it

will see 2 into half plus 1, they will get three peaks here, if X and Y are different, If X and Y are identical, you will not see the coupling. So, there are exceptions for 2NI+1 rule. So, this is what I simple example is know, I told you TMS is proton, silicon and carbon There is no splitting of with this, this with this or example of exception of wanted to tell you. The tetramethylsilane. We all used as the reference for 13 NMR. It has 12 protons. these three protons, CH3 anything. So, it is a classic 2NI+1 rule.

Now, we will look at the multiplicity due to coupling among equivalent spins. Consider one proton, you will get single peak, that is what we have been discussing. Consider one proton coupled to another proton, how many peaks we expect? We expect two peaks, that is clear, fine. And it is this gives you coupling between 1 and 2, this separation gives 1 and 2 coupling. Now, we have equivalent couplings, equivalent spins. Consider equivalent spins such that not only these chemical shifts are same, coupling to this and this are same.
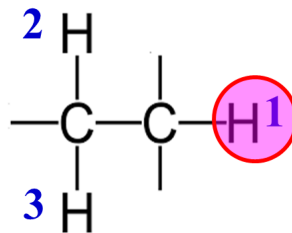
For example, I look at one proton, one proton when is coupled to two other protons, J12 is equal to J13. This coupling and this coupling are same; and I am looking at proton 1. Please understand this, I am looking at proton 1, proton 1 is coupled to 2, proton 1 is coupled to 3, J12 equal
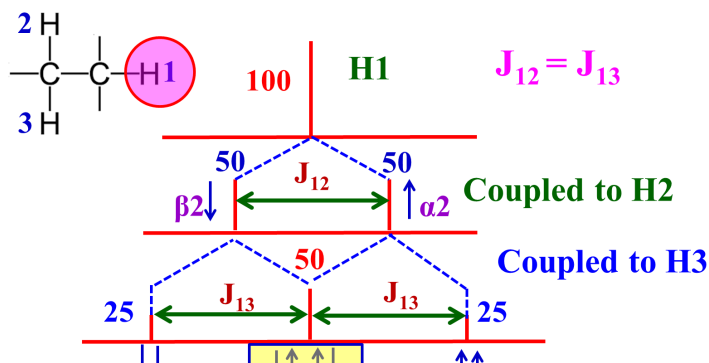
to J13, couplings are identical. Then this will become a triplet because of 2NI+1 rule, N is equal to 2, 2 into 2, the spin of proton is half plus 1, it is going to be three line pattern, exactly what you are going to get. But this is called triplet in NMR. Intensity ratio is 1 : 2 : 1, we will come to that later. And this separation gives you J12. Now, how does this triplet arise? I told you any proton coupled to other protons, with one proton coupled to two, we should get 2^N transitions. The 2 to the power of N; M is equal to 2, you must get four lines, but why we got three lines? That is because two of the lines are overlapped. How does that triplet arise? We will see now.

Consider one proton, it is a single peak, it is coupled to one of the protons H2, it will become doublet of equal intensity. Now 100 intensity became 50-50 because when it divides intensity comes down. Further it is coupled to proton 3, what will happen? Exactly because coupling is identical, this will split into two, this will also split into two. But these lines will overlap because of exactly equal coupling. So, 100 intensity become 50, 50, then 25, 25, 25 and 25. These two 25 intensity lines are overlapped. So, this is 1-2 coupling and this is 1-3 coupling. So, 1-2 and 1-3 couplings are identical. As a consequence what is going to happen is, two lines of these peaks overlap and it appears as three lines with an intensity of 1:2:1. This is how we get triplet. This is for a simple way of understanding, but quantum mechanically if you try to understand NMR, the reason why we say is, it is because this is a beta-beta state, this is beta-alpha, alpha-beta and this is alpha-alpha states and these two are identical states, indistinguishable, That is the reason why two peaks are overlapped and we get triplet. Clear now, how we got triplet. Now, instead of two protons, let us say it is coupled to three equivalent protons, instead of CH2, I made it CH3, again I put the same condition, coupling 1-2 is equal to 1-3, is equal to 1-4. The chemical shifts are also same. Now, I am looking at the proton 1, what is the pattern I expect? Four lines, how did I get four lines? This is called a quartet. In NMR quartet is 1:3:3:1 intensity pattern and this separation gives me couplings.How did this quartet come? we will generate it. Up to this thing we understood triplet, because up to this we knew early in the previous that I explained to you; how we got

triplet, because two lines of this are overlapped. Now, I have brought in the third proton, this third proton is also coupled to this with identical coupling strength. So, what will happen, it was 1:2:1, intensity; 100 became 50, you know 50: 50 and then it will overlap 25:25, these two 25s overlap, it become 25-50-25, 1:2:1, intensity. Now, what I am going to do is, I will bring in one more coupling, that is to H4, when H4 coupling is brought in, again this will split into two peaks, this will split into two peaks, this 25 intensity become 12.5, here 12.5, this 50 became 25 here, 25 here and then this will again become 12.5 and 12.5; here three lines are overlapped, three lines of intensity 12.5, two from here, one from here, here two lines from here, one from here overlapped. Now, what is the total intensity, this is 12.5, this is 37.5, 37.5 and 12.5. Qhat is the ratio now? 1:3:3:1. You got a quartet. This is the intensity pattern you are going to see.
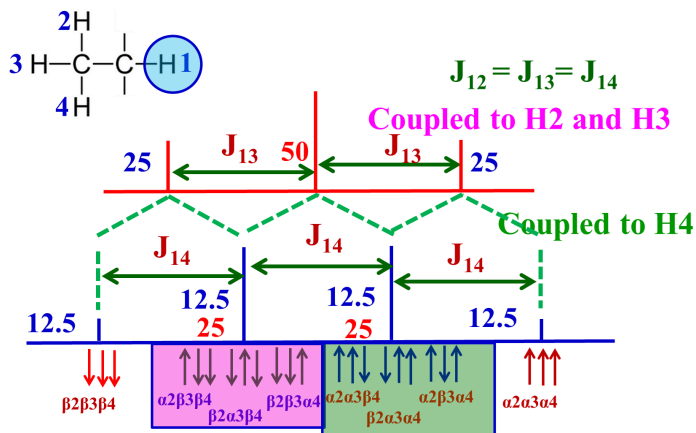

So, in reality, the four lines of this, four lines are called quartet and this separation gives me J14 and J12; all are identical, does not matter. So, now the four lines comes because this is the beta beta beta state of three spins, alpha alpha alpha state, this is what the way you have to understand. Here there are three possibilities, alpha beta beta, this is beta alpha beta, this is beta beta alpha. There are three possibilities, here alpha alpha beta, beta alpha alpha, alpha beta alpha. These three such possibilities are there and they are indistinguishable, that is why three intensity, that is why here also three intensity, this is the way you have to understand NMR. But if you are worried about mathematics and quantum mechanics; you do not have to worry, there is a way to understand this, this is called a Pascal triangle.

How do you understand by a Pascal triangle? Let us say, I have N coupled spins, spin half nuclei. First, when there is only one spin, you have only one line, when you have two spins, each will become equal intensity half half, 1 : 1 intensity ratio. When there are three spins, we get 1 ,3, 3. 1 intensity and we have four spins, 1 4 6 4 1. Like that we can

start getting intensity patterns, they obey what is called Pascal triangle. How do you arrive at this intensity? There is easy way of generating the intensity in a Pascal triangle, First you put one single spin, not coupled to anything, it is coupled to another spin, one spin, each become 2 2. When you bring in two other spins, two spins are there, one spin plus another spin, two spins, how do you generate the intensity? Add one one intensity at the top of that, one plus one you add it is two. This one you retain here, this one you retain here, only these two you add up and it will become 2.
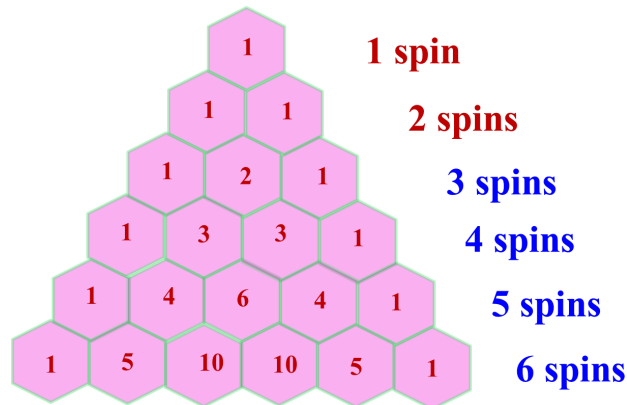

If you have three spins, what you will do, write this 1 here, add up this to 1 plus 2 , 3, add up this 1 plus 2, 3 and this put 1 here. For example, if you have four spins, put 1 here, add here 1 plus 3, 4, 3 plus 3 6, 3 plus 1, 4 and put 1 here. This is the way you generate the intensity pattern by looking at the Pascal triangle. This is how you have to understand. Actually, it is a layman way of understanding, but what is the way to understand the intensity of the Pascal triangle? It is nothing but the coefficients of the binomial expansion.
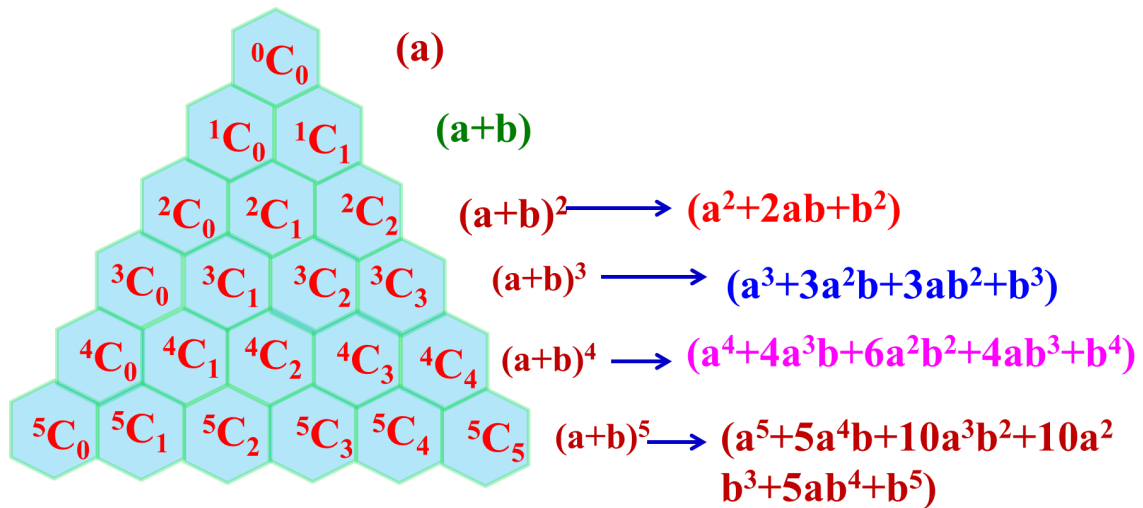
When there is no spin coupled to other, we have only one single spin, let us say A. When you have two spins, A plus B. When you have three spins coupled, make it A plus B whole square, which is nothing but A square plus 2ABB plus B square. What is the intensity? 1: 2 :1, that is the intensity ratio. What about A plus B whole cube? 1 3 3 1, that is intensity ratio 1 3 3 1, but if you want to understand that, there is a way to understand by combination also. These are $^0C_0$, $^1C_0$, $^1C_1$ like that you can understand. This is nothing but the coefficients of the binomial So, Pascal triangle that is how we generate.

Now, the question is total transitions I said, when n spins are coupled, we have 2^N transitions. Where are those? Please remember, here two peaks of equal intensity, one is coupled to other one, that is fine. When it is coupled to two equivalent spins, we get four lines, but remember two of which are overlapped. So, 2 to the power of 2 is 4, there are four peaks, only two are overlapped. Similarly, when you have 2 cube, then we can see there should be 8 peaks here, 2 cube 8, when it is coupled to 3. See, 3 peaks here and here are overlapped, that is why intensity 3 3. So, total it is 8 intensity, 8 intensity is 8, that means there are 8 peaks, 3 of them are overlapped here, 3 of them are overlapped here. Like that you can get here 16 peaks, 4 are overlapped here, 6 overlapped, 4 are overlapped here. Like that there is no violation of the number of peaks that you are seeing. The number of peaks what you are going to see still it is 2^N only, when one proton is coupled to another protons. But because of equivalence of magnetically equivalence or chemical equivalence, j couplings are identical, some of the peaks are overlapped. So, intensity is different, but the total number of peaks, if I take one to one intensity, total number of peaks are 4 only, but two peaks are overlapped, same way for others you have to understand.

So, with this we will go into the common splitting patterns among coupled spins or groups of coupled spins. Let us see how we get this one. I consider one spin coupled to other spin ,then each will be doublet, fine, of intensity 1 is to 1. This is chemical shift and we get j coupling here.
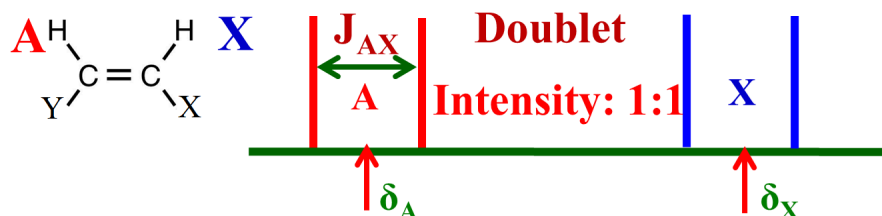
Now, let us say one spin is coupled to two equivalent spins. Here A and X was there, here there was no proton, here I brought proton now.
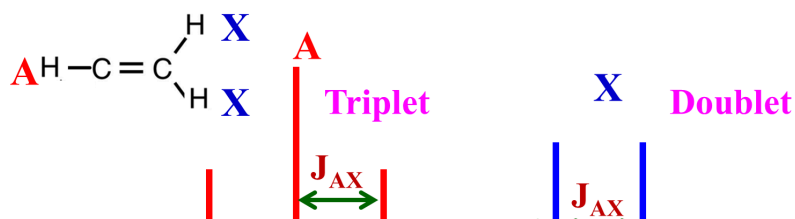
These two are equivalent AX2, we already worked out. When A is coupled to two protons, it will become a triplet, that is what we worked out because of the Pascal triangle. Whereas, if I look at this H, H will be coupled to only single proton, so it will be a doublet. You got the point, when I have CH coupled to CH2, CH is going to be a triplet, whereas CH2 is going to be a doublet. So, that is why X is doublet, whereas CH is going to be a triplet. See this CH is going to be a doublet, this CH2 is going to be a doublet, this is what it is. This is called triplet and this is called a doublet. So, centers of this gives you chemical shift of A and X and the separation gives you j coupling.
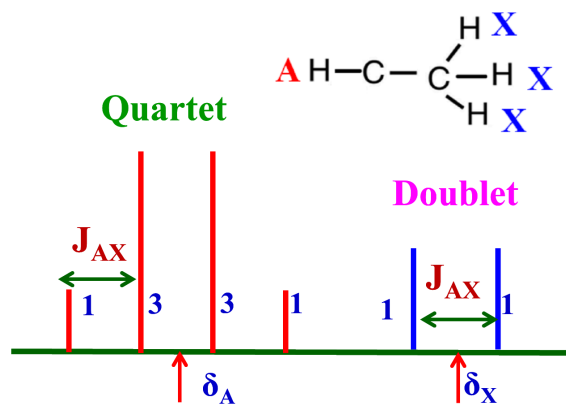
Now, on the other hand, I consider a situation where one CH proton is coupled to CH3 group, just now we worked out. When this is coupled to three chemical equivalent protons, 2NI+1 rule you apply or you can get the intensity by Pascal triangle, n is equal to 3 here, 2 into 3, spin is half, then you get four lines, that is what you get. When one proton is coupled to three equivalent methyl groups, you got four lines, but intensity of the four lines is given by Pascal triangle. But what about these three? If I look at the CH3 group, but this is seeing only the CH, CH has only two states, alpha and beta. So, it will be a doublet. You understand, when CH proton is coupled to CH3, CH is going to be a quartet, CH3 is going to be a doublet and this is center. Again it gives chemical shift of CH, this gives the chemical shift of CH3 and separation gives you j coupling. Easily, you can identify that.

We will go further. Consider a situation where we have a molecule like this. It has CH2 and CH3, there are two groups, and it is hypothetical molecule.
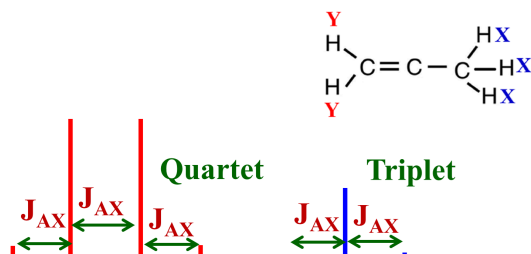
You get a pattern like this. How? Very easy to understand. This CH2, will see three equivalent protons using 2NI+1, it will give four lines. This is is CH2 coupled to CH2. use 2NI+1, 2 into 2 into half plus 1, it will become three. Because they are equivalent groups, you have quartet and a triplet. This is called a quartet and this is called a triplet. Triplet is always intensity ratio 1:2:1, quadrat is 1:3:3:1 intensity ratio. You understand, how we can get the multiplicity pattern when CH2 is coupled to CH3 or CA3 is coupled to CH2, we get patterns like this. And again, center of this gives you chemical shift of CH2, this center gives you chemical shift of CH3. This is called a quartet this is a triplet and separations gives you coupling between CH2 and CH3, very easy.
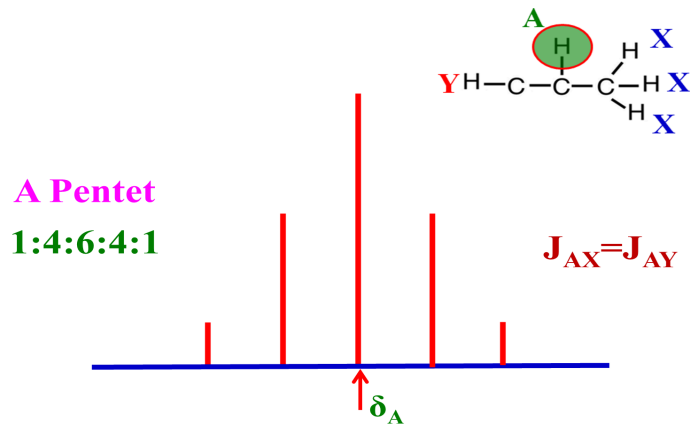
So, how do you measure the J coupling? Already I told you, this is very easy. If I have a pattern like this, adjacent peaks you have to consider.
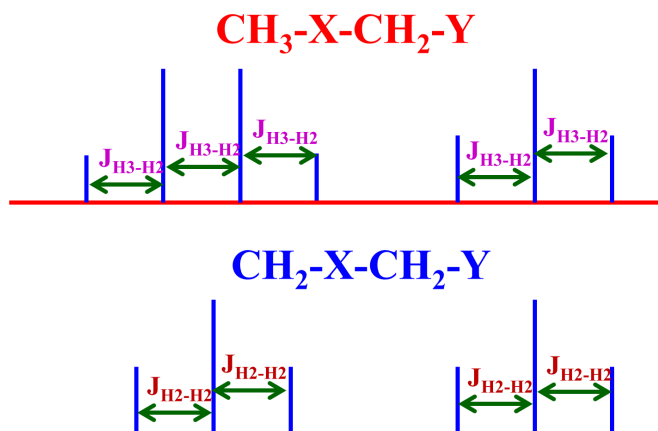
You cannot measure the separation between this and this. Adjacent peaks of the multiplet pattern gives you J coupling. In this molecule, CH3 and CH2 are there and this is coupled to this, and it will be triplet or quaartet, does not matter. This separation will be the adjacent peaks, if you measure, you get coupling constant. You cannot measure peaks which are far away, only adjacent peaks you have to consider. Same way here, there are two CH2s, this will become a triplet because of this, this will become a triplet because of this. And this will give you 2 triplets and separation gives you coupling, very easy.

This is a simple molecule, but in reality you are not going to see only this type of simple molecules. You come across various complex multiplicity patterns. How do we get that?
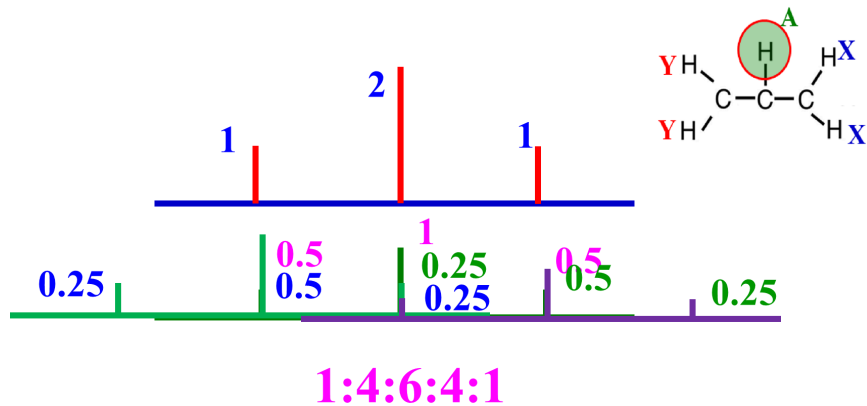
How do you get the splitting patterns when a single proton is coupled to groups of protons or several groups of protons, both chemically equivalent protons or not. And then how the multiplicity comes. Several examples we will take now. I take a hypothetical molecule like this. Where I have considered a proton here, which is highlighted in green, it is coupled to two things now, one CH proton and also CH3 protons. Understand the point, proton A is coupled to proton Y, it is single proton, it is also coupled to CH3 which has 3 protons which is X. So, I call it J_{AY}, this is J_{AX}. The proton A coupled to Y is J_{AY}, proton A coupled to X is J_{AX}. Now, I will put a condition J_{AX} equal to J_{AY} that means the couplings are identical.

A Pentet

1:4:6:4:1

$J_{AX}=J_{AY}$

δ_A

This will experience coupling, identical coupling with this and this. Then what is the pattern you are going to get for proton A? If I observe proton A, what do you get? I get a pentet, very surprising. How did you get this pentaet? Of course, center of this is the chemical shift of this proton and this will give you couplings, separation of adjacent peaks will give

1   2   1

0.25   0.5   1   0.5   0.25
          0.5   0.25
                0.25

1:4:6:4:1

coupling. But how did you generate the pentet? How do you know it is a pentet? Remember, it is because of the equivalent coupling. What I will do is, I have put the condition J_{AX} equal to J_{AY}. Proton A is split into quartet because of X, that is correct, that we have already discussed because of magnetically equivalence according to 2NI+1 rule, this will become a quartet because of 3 protons, of the intensity 1, 3, 3, 1 that we have been discussing today. But simultaneously, this A is also coupled to Y, but it is single proton. As a consequence, A will become a doublet, but is already coupled to this one, become a 4 line pattern, quartet. But now because of the coupling with single proton, each line of this quartet will become a doublet. This is the intensity ratio 1:3:3:1. The each peak will become a doublet of the intensity half half. This intensity again half half, 1.5 and 1.5. Exactly from the center and either side, you will see doublets. Again, from the center, you will get half line, again half of lines. I have put different colors for you to understand. This is one color, another color, another color and another color. Each line is split into two two lines, half half intensity and this intensity is half half, this is 1.5, 1.5, but two lines are overlapped here because of identical J coupling. So, calculate the total intensity now. This become 0.5, 2, 3, 2, 0.5. What is the intensity ratio? Now, it is a pentad, intensity 1, 4, 6, 4, 1. It is called a pentet because you have 5 line pattern. See, you have 5 line pattern here and that is why this is called a pentad of intensity 1, 4, 6, 4, 1. Please remember, when one proton is coupled to CH3 and another CH single proton, if the coupling constants are identical, you will get a pentet. What happens if this proton is coupled to two CH2s? One proton is coupled to two CH2s. That is also interesting. Earlier, I took the example of CH and CH3. If I take the example of both CH2s coupled to this proton A, what will happen? When this is coupled to one of them, again I assume the condition J_{AX} is equal to J_{AY}, couplings are identical. That is my condition.

I put the condition J_{AX} is equal to J_{AY}, because of one of the CH2 groups, when it is coupled, it will become a triplet. That we already discussed. When this proton coupled to CH2 group, 2NI+1 rule, will become a triplet. But now what is happening? It is also coupled to another CH2. What that CH2 will do? It will ensure that each line of this

triplet is further split into a triplet. Each line will become another triplet because of another CH2. So like this. This is a 1:2:1 intensity. Now, because of another CH2, it will split into another triplet, intensity becomes 0.25, 0.5 and 0.25. This will also be like that, and this will also like that. And interestingly because of the coupling is same, these lines here overlap, these lines will overlap, these lines also will overlap. Now, calculate the intensity now. What is the intensity? 1 4 6 4 1 ratio. That is also a pentet. This is where the confusion comes. When you want to analyze NMR spectrum, you will see that a single proton coupled to another proton and CH3 with identical strength also gives pentet. One proton coupled to two CH2 protons with identical strength also gives a pentet. This is where the beauty comes and you have to have the knowledge of unraveling this multiplicity to get the information about the structure of the molecules. This is another way of getting a printed.

Now, we will go to a complex example. A CH proton is coupled to CH2 and CH3. Extend the logic. What is the type of pattern you get for this proton? It is coupled to let us say, CH3. Again, coupling is same. It gives actually a sextet now, not pentet but a sextet. How? We will work it out. Take this one. When this CH is coupled to CH2, will give actually a triplet. What is the intensity? 1:2:1 and each line of the triplet is split into quaartets because of CH3. 2NI+1 rule we apply and now each will become a quartet and again this is a quartet.
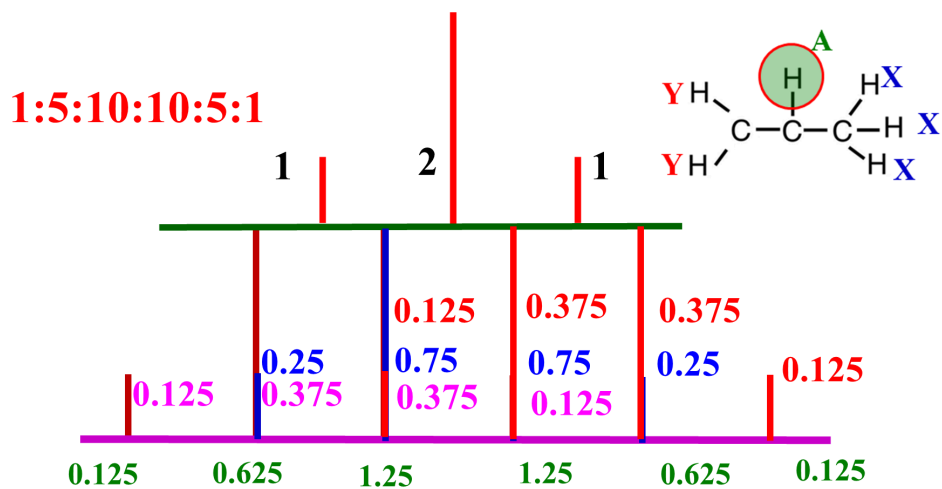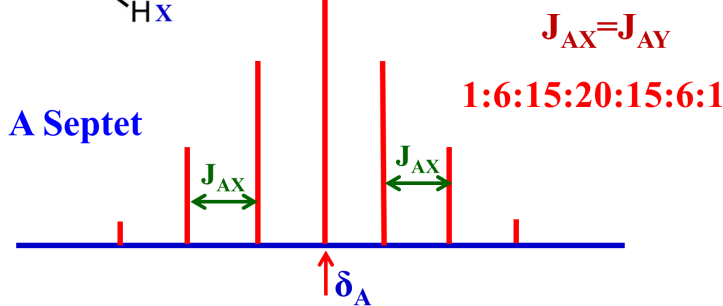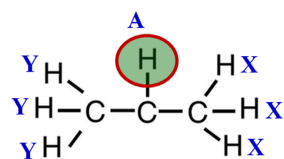

This is again a quartet. You see, I am showing different colors because the coupling is same. Some of the lines overlap here. Now, calculate the intensity. If you put the intensity, this turns out to be like this; and this intensity is 1:5:10:10 : 5 : 1. This is a sextet. Six line pattern. Remember, when one proton is coupled to another CH2 and a CH3 group, you get a sextet pattern. I use this while analyzing the spectrum at a later

stage. That is why I am giving all these examples. Now, you may ask me a question. Here, I took CH2 first and then worked out this multiplicity pattern and get a sextet of intensity, this one. Why I should take CH2 first? Why not CH3 coupling first? This is coupled to both of them. I took sequentially this first and then this one. Why not I take the reverse order? What happens if I consider CH3 first? Then it is a quartet because of 2NI+1 rule. That is correct. But now, each line of the quadrant is split into triplet because of this. We will see what will happen. One triplet, another triplet, another triplet, another triplet. Now, calculate the intensity. Same, there is no difference. This is also a sextet, same intensity ratio. So, what did we understand from this? If you are generating multiplicity pattern, then order in which you take the coupling is immaterial. For this CH proton, you consider this coupling first or this coupling first, does not matter. Totally, both of them are coupled simultaneously. For working out the multiplicity pattern. The splitting pattern is invariant with the order of the coupling chosen for obtaining the multiplicity. How do you get the multiplicity? Whether you take CH2 first or CH3 first or converse of them, does not matter as far as the total spectrum appearance is concerned. Finally, the multiplicity pattern remains identical. So, when you are working out the multiplicity pattern by using this type of Pascal triangle approach, it does not matter which one you take first, which one you take second.
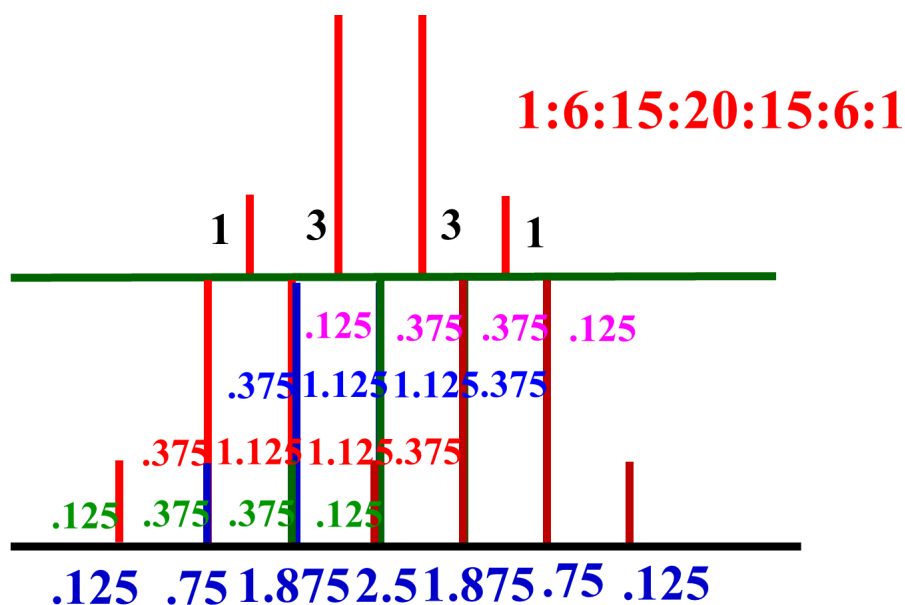
So, we will take the example of another one. A CH proton is coupled to two equivalent CH3 groups. Now, you should understand already you know what is the type of pattern we expect. This CH coupled to this CH3 will be a quartet and each line of the quartet is further split into a quartet because of this and because of the overlap of the the transitions, what is going to happen? We are going to get what is called a septet, a 7-line pattern, if the couplings are equal, J_{AX} and J_{AY} are identical.

This is the intensity ratio 1, 6, 15, 20, 15, 6, 1. And now, we will see how do you generate the septet pattern. We know one proton coupled to CH3 group is going to be a quartet, intensity ratio 1:3:3:1. Now, it is coupled to another CH3. Each line of the quartet becomes another quartet like this, different colors you see, but interestingly these lines here overlap, here overlap, here overlap. Calculate all the intensities what I have written at the top here. And if you put the intensity, calculate the ratio, it is like this, it is a septet 7-line pattern and this is how you get the septet.

1:6:15:20:15:6:1

1   3   3   1

.125 .375 .375 .125

.375 1.125 1.125 .375

.375 1.125 1.125 .375

.125 .375 .375 .125

.125 .75 1.875 2.5 1.875 .75 .125

So, this is how we arrived at the splitting pattern when one proton is coupled to remaining other protons. Now, some complex multiplicity pattern will be there, which I am going to discuss in the next class. Right now, I have given you umpteen number of examples today to obtain the multiplicity pattern. What happens when one proton is coupled to two protons, when one is coupled to three protons, and two CH2s are coupled to single proton, CH2 proton is coupled to CH3, and CH also coupled to CH3 simultaneously. How do you get the multiplicity pattern? I said when one proton is coupled to CH2, it will be just a triplet, when it is coupled to CH3, it is a quartet, when one is a CH2, other is a CH3, we get triplet and quartet in the spectrum. We took the example of one proton coupled to two different groups, when one proton is coupled to

CH2, it is a triplet, it is also coupled to another CH2, it is a triplet, each line of the triplet will become another triplet, which I showed as a pentet. And then similarly, we saw when one is coupled to CH2, one CH3, another CH2, we got sextet, when both are one proton is coupled to two CH3, I showed it is a sextet. And I also showed the multiplicity pattern and the intensity can be easily worked out in a simple way. But then order in which you take the take in arriving at this multiplicity pattern is immaterial, whatever the order you take multiplicity pattern finally, remains invariant. And we took several examples of getting sextet, pentet and septet, everything. We will continue further and few more examples we will take and then we will see, we may become confident enough to analyze 1D spectrum of varieties of molecules in the subsequent classes. Of course, still lot more I have to discuss about the few more multiplicity patterns, what do you call such patterns, when they have many couplings. How do you explain this one, we will come to that in the next class. Thank you very much.