One and Two Dimensional NMR Spectroscopy for Chemists
Prof. N. Suryaprakash
NMR Research Centre
Indian Institute of Science - Bengaluru

Lecture - 22
Multiplicity Pattern of Coupled Spins

Welcome all of you. Since last couple of classes we have been discussing about scalar coupling. In the last class, I introduced to you about the coupling between 2 spins and 3 spins. And I also introduced the concept of spin system, and also what is strongly coupled and what is the weakly coupled spin system. And we worked out for a multiplicity pattern for 2 coupled spin system, and I told you how we got the intensity pattern, how we got the splitting pattern.

We started with the simple 1 spin system. For example, in CHCL3 we are going to get a single peak, that we observed. And then I took the example of two weakly coupled systems, and I showed that we can get 2 peaks each for A and each for X. And they have equal intensity. I also showed that centre of the doublet corresponds to respective chemical shifts, centre of the doublet of A corresponds to chemical shift of A, centre of the doublet of X corresponds to chemical shift of X, this is what I said.

And also, I showed what happens if there is a splitting of energy levels, how the intensity comes down by a factor of 2. So with this, what we will do is, we will continue further today. And let us see how far we can go together with further introduction or further discussion about scalar couplings, the very, very important parameter in NMR. So, you must concentrate and try to listen, try to understand, as much as possible.

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Interaction among spins in NMR are always mutual

If proton A is coupled to proton X

Proton X is also coupled to proton A

If peak of proton A is split into doublet because of its coupling with proton X

Doublet with Identical splitting is also seen for proton X

The center of this doublet corresponds to chemicals shift of X, the center of this doublet corresponds to chemical shift of A, and this separation corresponds to coupling constant between A and X. I said JAX. If you measure simply the frequency separation between these 2 peaks, what you are going to measure is the coupling between A and X. Now another interesting thing you should understand, I said when I was introducing to the salient points of coupling, I said if one proton is coupled to another proton, and there is a coupling which is nonzero, I showed one peak splits into 2, 2 will split into 4, 4 is split into 8.

Remember I showed in one of the slides, what was happening to the intensity. The total intensity of the uncoupled spin and the totally intensity of the multiplicity, that is the area of this all the peaks put together, will not be different. So, what happens? when one spin splits into a doublet, the intensity comes down by half. Now, it is half, half intensity. Although it appears to be equal, together, it is 1 : 1 ratio, but compared to the one without coupling, it has reduced by 50%. Same way intensities of this A peaks also are reduced by half. So that is why we are going to get 2 peaks for this and 2 peaks for this.

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Two Coupled non-equivalent spins, $J_{AX} \neq 0$

Each proton gives a doublet with identical separation. Intensity is equally divided between the two peaks.

The separation of each doublet gives J_{AX}

Centre of each of these doublet gives corresponding chemical shifts

Now 2 coupled nonequivalent spins JAX ≠ 0, I said each proton is a doublet with identical separation; the intensities is equally divided between the 2 peaks; equally divided between 2 peaks. The asymmetric intensity pattern is not seen in NMR. Please remember this asymmetric intensity pattern, because interactions are always mutual and a separation, I said is JAX. I am repeating this point just to make sure you understand. If the separation of each gives JAX, the center of each of these doublet gives you the corresponding chemicals shifts. This is the salient point, which I said when 2 couple spins systems are there with J coupling nonzero.

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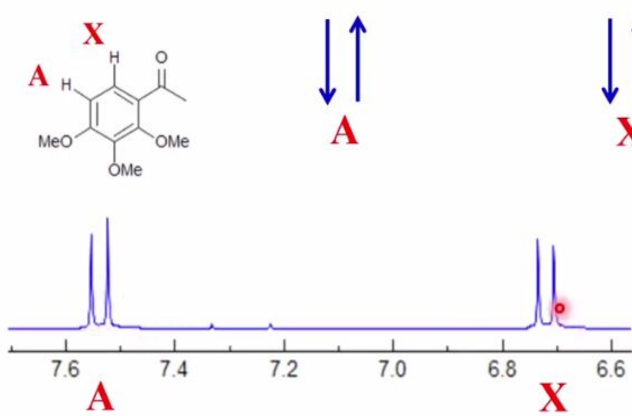
The realistic situation where two spins are coupled



We have a realistic situation where 2 spins are coupled, I show you the spectrum, now. Look at this molecule, there is some substitution here, we have 3 methoxy groups and these are the 2 protons which are separated by 3 covalent bonds. Now, if I take the proton NMR spectrum of it, it looks like this. Look at it. Now, what is happening is, A has 2 orientations, X has 2 orientations, which so far we were discussing, as a consequence, you see A is a doublet, X is a doublet. A is coupled to X and becomes doublet, X is coupled A and becomes a doublet.

You understand? This is a spectrum of 2 couple spin system. And I was telling you about strong and weak coupling, I introduced the term strong and weak coupling. I said when the chemical shift separation is larger than the separation, this coupling constant, then it is weakly coupled. Look at this chemical shift here, it is about 6.7 ppm here, it is about 7.5 approximately. So, 7.5 and 6.7, it is is 0.8 ppm difference. Remember 0.8 ppm is a huge value. At 500 megahertz 0.8 X500 = 400 hertz. Coupling constant may be of the order of 10 hertz. 10/400 is nearly 40. So, this is a weakly coupled spin system. That is why I called it as A and X. We will talk more about Pople spin nomenclature, weak and strongly coupled in subsequent classes. A detailed discussion will be there, I will discuss with you all these things. But one interesting thing you must understand, in a weakly coupled system like this AX or AMX, whatever you take, the intensity pattern should be always equal, they must be of equal intensity.

Here, look there is some sort of intensity anomaly. Intensities are not equal. Strictly speaking, even at a particular spectrometer where it is recorded, although chemical shifts are far away separated, the intensities are not equal. So, there is a minute strong coupling character present in this. But nevertheless, for the purpose of analysis, this chemical shift of A and X can be obtained. This separation gives the J coupling. so, this is the realistic situation, this separation gives J, this separation gives J.

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Coupling of a proton with "n" Chemically inequivalent protons

Splitting Pattern is obtained by a Family tree approach

And now we will go to more complex multiplicity patterns. Remember one important point, coupling of a proton with chemically inequivalent protons, chemically inequivalent, in which case we can obtain this splitting pattern by what is called a family tree approach. What is the family tree approach? Husband and wife, now if they have 3 children, each of them get married, each of them may get 3 or 4 children. 1 will become 2, 2 will become 4, 4 will become 8, like a chain reaction it keeps going on. This approach is called a family tree approach. So, when one proton is coupled to n chemically inequivalent protons, we can go by what is called a family tree approach to understand the splitting pattern.

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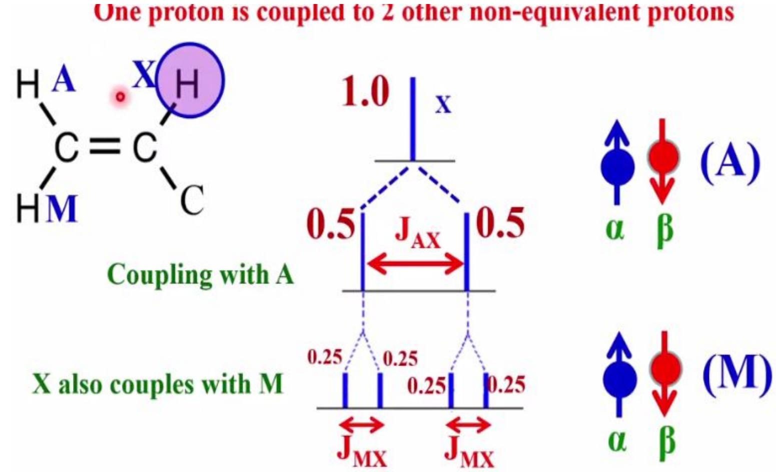
One proton is coupled to 2 other non-equivalent protons



Similar pattern is observed at the chemical shifts of protons A and M

Let me once again explain to you. Let us consider the example of one proton coupled 2 other non-equivalent protons. Just now we discussed 2 protons coupling. One is coupled to other one single proton, that is fine. That is a 2 spin case. Now I am considering 3 spin example. One proton is coupled to 2 other non-equivalent protons. Let us see what it is. I am taking example of a hypothetical molecule like this, there is some other substitution X. So that all is, 3 protons are chemically inequivalent. I have deliberately taken this. It is just a hypothetical molecule not a realistic situation. I am trying to tell you for a realistic molecule. I am looking at the proton X which is highlighted with a light pink color here. Look at this proton X. What is the multiplicity of this proton X when it is coupled to A? and it is coupled to M?; that is what we will understand now. Now, assuming there is no coupling with proton A, and there is no coupling with proton M, X we will be singlet. Correct ! Like we understood the single spin situation. CHCl3 we saw right? When only 1 spin is there, no other coupling, we get the single peak. It is an isolated spin system. Assuming couplings are 0 with the X, we get a single peak for X; fantastic and call this intensity as 1, 100%; full intensity is there. Now, what I will do is, I will bring in the coupling of this with proton A. What are the possible orientations of proton A? alpha and beta, spin states. Proton X sees proton A in 2 possible states, 2 possible orientations. You see the magnetic moment of proton A is alpha and beta 3 in the magnetic field. So, this is 2 different energy states. As a consequence, when it interacts, we understood it has 2 different energy states, splits into doublet. See, we understood the mechanism of coupling you know. So, as a consequence, there is polarization transfer taking place between A and X, through covalent bond and this peak splits into a doublet. Now what is the intensity of this doublet, this is 0.5 and 0.5; 1 has been divided into 2, like a family tree approach I said; the family property of home 1, divided into 2 children; 50-50. So the intensity is divided into half. As I said in the earlier case, this separation tells you the interaction strength between this proton and this proton. It is $J_{AX;}$ is it clear? We understood that. Now we will extend the logic further. Now, I bring in the coupling of proton X with also proton M. Now when I bring this, what is going to happen? further each of these lines splits into doublet, because M is coupled to X again. So one was splitting into 2 now. because of course, I have taken some coupling strength here I do not know what it is, this M is coupled to X and split each of this line into a doublet. Please remember each of this line is split into a doublet, and what happened to intensity? it was 0.5, 0.5, now came down to 0.25, 0.25. Again it is the divided into half. The property of one family was full, 100% was there. It was divided between 2 children, it become 0.5 0.5; and each of the children had further 2 children. And it was further divided and became 0.25, 0.25. Like a family tree approach, it was a division. The intensity got divided like this, and again this is 0.25 0.25.

So this is the interaction strength between A and X. This is the interaction strength between M and X. So what does it mean? One spin X, when coupled to 2 other spins, you will get doublet of doublet. A will split X into 2, M will split further into 2, you are going to get 4 peaks of equally intensity. Remember, it is intensity might have come down by 1 fourth compared to uncoupled proton, but the intensity pattern, if you see, all are equal. It means 1 : 1 : 1 : 1 ratio. You understand? this is the coupling pattern of 1 proton when it is coupled to other 2 protons.

And this pattern depends upon what is called the coupling strength. That is fine. Whether this is larger or this is larger, depending on that the pattern can be worked out; which is the coupling and everything. I am just giving you an example of splitting pattern here. We will go more into extraction of the coupling from the spectrum, at that time we will try to understand all those things. But one point remember, in the salient points when I discussed about interaction strength of the about the scalar coupling one of the important point I said, each nuclear spin can experience coupling with all NMR active spins, which are chemically equivalent, simultaneously. So, I am giving an example first X coupled A, and then to M, no matter how to go. It can be any order, only thing is simultaneously this is interacting with this, also interacting with this. At the same time this proton experiences coupling with these 2. Tomorrow do not come and tell me, first it has to interact with this and then with this. No, there is no sequential operation like that.

One proton, simply understand, simultaneously experiences coupling with all the other NMR active spins, so long as there is interaction among them. Now I was concentrating on this proton X, forget it. Now I look at the proton A, and when I see proton A what is the type of splitting I am going to get. Remember this proton A again, similar to X, experiences coupling with this; what happens? it will become doublet, further this proton A also experiences coupling with this proton M. So simultaneously this also experiences 2 couplings. So proton A, start looking at it again, the proton A here split into 2 because of AX coupling and then split further into 2 because

AM coupling. So what happens? Again we get 4 lines pattern of equal intensity. Remember I said 4 line pattern, but I did not say identical pattern, the pattern can be different, please understand, pattern can be different, because here this coupling and this coupling, there are 2 different couplings and this coupling may be larger, and this coupling may be relatively less.

But when I look at this, this is one coupling and this coupling may be smaller. I will tell you when you go further about cis, trans and geminal couplings, etc. So, coupling strengths will be different. This proton experienced 2 different couplings. Similarly, this proton experiences this coupling may be same, but this coupling is different. So, you got 4 lines of equal intensity, but the pattern may not be same. I have written here as if, 4 well separated lines. It may so happen that these lines may come closer, or these 2 layers may come closer, because this coupling is smaller; it can happen. But remember the pattern is identical. I mean splitting pattern, but the separations can be different. Now, what happens if I observe M? I will get the same pattern, do remember, this M experiences coupling with the X, it is a 3 bond coupling and in addition to that this experiences coupling with the A, it is a 2 bond coupling. So, this coupling is quite large and then this coupling is quite small so, it is a large doublet and the each of this doublet into split into smaller doublets. So, this pattern again you get 4 lines of equal intensity but the pattern is different from this and this, different from this. Very interesting. Is it not? It is a 3 spin coupled system, if I take 1 proton coupled to 2 other non-equivalent protons, it so happens each proton gives rise to 4 peaks of identical intensity, 1 : 1 : 1 : 1 ratio. But the separations between the peaks may not be identical, because the coupling strengths are different.

In this example, I will give you further, please understand, this proton coupling is 3 bond trans, and 3 bond cis. This proton experiences 3 bond cis and 2 bond germinal. This experiences 3 bond trans and 2 bond germinal. All the couplings may not be same. So the pattern you get, 4 4 4 lines of equally intensity, with a different separations due to different coupling strengths.

Remember, when we understood the 3 spin AMX, I observed a transitions, and saw what are the allow transitions and we observed that you know, through the energy level diagram, we observed twelve peaks of equal intensity 4 for A, 4 for M and 4 for X, Remember, exactly this is realistic situation now. You get 4 for X, 4 for M and 4 for A. So, we are going to get 12 line pattern. This is an example, when 1 proton is coupled to 2 other protons of different strengths of chemical inequivalent protons.

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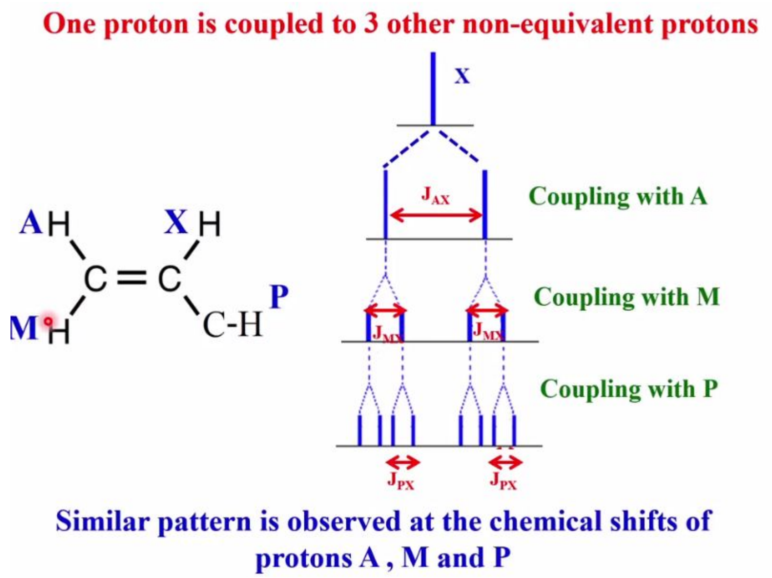

Now, extend the logic. Now I will take 4 couple spin system. Simple logic, how many peaks I must expect? start extending the logic. When 1 proton was there, you get 1 line, and 2 protons were there, you got 4 lines, when 3 protons were there, for each proton you got 4 lines. So 1 proton single line, for 2 protons 2 lines each, and when 3 protons are coupled, for each one you got 4 lines.

Now we will see what happens when 4 protons that are coupled, one is coupled to chemically non equivalent to 3 other protons. So, now this is a hypothetical molecule, again consider proton X. You understood coupling with A, this in the previous example, we understood this also, X will couple to A doublet, and X couple M doublet of doublet, Now what is the new thing we have brought? another proton, third proton P, what will happen? Each of them will further split into two half.

So, what is intensity now, this was intensity 1, became 0.5, 0.5, further became 0.25, 0.25, 0.25, 0.25. Again further divided into 0.125, 0.125, 0.125, 0.125, 0.125, 0.125, 0.125, 0.125; all 8 lines are of equal intensity with 0.125 intensity. Add up all these things 0.125, 0.125, 0.125, 0.125, 0.125, 0.125, 0.125, 0.125. So, the total intensity is 1. What is this intensity? The total is 1, this is what I was explaining to you under the salient features of the coupling pattern. I said the total area of the peak of uncoupled proton or uncoupled spin is same as the total area of the multiplicity pattern.

When they split, take the total area of this and this remains same. You understood now. Very nicely this gives JAX coupling, this I brought another coupling with the M, give JMX; this separation gives JAP coupling. so now how many peaks you got? When one proton is coupled with 3 other protons, you got 8 peaks. Now what is the pattern you are going to get for other protons? I observed X here. What happens if I observe A. A gain is coupled to 3 protons. Similarly work out the family tree diagram for proton A, A is coupled to X, A is coupled to M and A coupled to P. So you will get 8 lines of equal intensity for A. Similarly, for M, M is coupled to A, M is couple to X and M is coupled to P. You get again 8 line of equal intensity for M. What about P? exactly same 8 lines of equal intensity. But, like I said in the previous example, the separations are not same. When I took this one, this had a cis coupling and trans coupling and other long range coupling.

When I took this one, it has a cis coupling and germinal coupling, it does not have a trans coupling. But when I took this one, it has a trans and germinal, but does not have a cis coupling. So the couplings are different because protons experience different types of coupling, but the pattern of 8 line remains the same although the separations are different, you understand. So this is the logic. Now let us go by the logic. What is the simple logic now.

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Multiplicity when N non-equivalent protons are coupled

One proton coupled to another proton gives a Doublet of equal intensity

One proton coupled to two different protons gives four lines of equal intensity

One proton coupled to three different protons gives eight lines of equal intensity

When N non-equivalent protons are coupled, how many peaks we expect? go by the logic now. When 1 proton, 1 isolated proton was there we get a single peak, when 2 protons were coupled, and was observing any 1 proton, at that site of that 1 proton at the, at the chemical shift of that proton how many likes we get? 2. When 1 proton is coupled 2 other protons, how many we got? 4 lines, and when 1 proton is coupled to 3 other protons, how many lines we got? 8. what is the logic?

Logic is very, very simple. Number of transitions, when 1 proton is coupled to N chemically non-equivalent protons, it is simply given by 2 to the power of N. I will come to that later, there is some other thing which I want to tell you. When one proton is coupled to another proton gives a doublet of equal intensity, that is what I explained. When one proton is coupled 2 different protons gives 4 lines of equal intensity, when one proton is coupled 3 different protons, gives 8 lines of equal intensity. This is a summary of what I was telling you; I have written explicitly here.

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Example of 3 coupled Spins; A, M and X

A gives four lines due to its coupling with M and X

M gives four lines due to its coupling with A and X

X gives four lines due to its coupling with A and M

Now coming to the logic; when 1 proton A is coupled to M and X, A gave 4 lines. Similarly M gave 4 lines, X gave 4 lines. So, totally we got 12 lines; fantastic.

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For N different protons coupled Protons

The number of lines at the site of one observed proton is

$$\Sigma = 2^{N-1}$$

The TOTAL number of peaks in the spectrum is

$$\Sigma = N * 2^{N-1}$$

Now, we come to a general formula. For N different protons coupled among themselves. Now, what is the logic? The number of lines at the site of one observed proton is joined by 2 to the power of N - 1. What is this formula I am writing? you understand. At the site of one of the observed proton, let us consider, we look at this thing now. I have 4 protons, 1, 2, 3 and 4. I am looking at this proton. At the site of this proton, I will take 3 other protons coupled, how many peaks I expect?

It is totally there are 4 couple spin system, N - 1 is 3. Leave this proton we are looking at. How many are there that are coupled to it, 3. So what is 2 cube? Here 2 to the power of N - 1 is 2 to the power 4 – 1, what is 2 cube? It is equal to 8. So that is what we observed. When 4 coupled spins are there, when you observe 1 proton, it is coupled to 3 other protons. As a consequence, it gave rise to 8 lines, at this position. Now I am going to take, let us say, other protons this and this.

Now I am looking at this proton what happened to this proton? Again it is coupled to remaining 1 2 or 3. So, 2 to the power of 4 – 1; there are 4 protons, you have to – 1, because this is what you are observing, you have to consider only the remaining 3 spins. These are the remaining 3 spins. So, 4 – 1, 2 cube so, this also gives 8 peaks. What about this one? now I am going to observe this spi.n what will happen? This we observing; there are 3 remaining protons here. Again 2 to the power 4 - 1, this also gives you 8 lines. Look at this one. This proton, this is observed, it is coupled to remaining 3. This also should give you 8 peaks. So, what do you see in the formula I am telling you now, remember, simple N protons are coupled, at the site of any of the protons, if you can see, at the site of any of these protons the number of observed transitions are given by 2 to the power of N – 1. Understand the logic, and 4 protons are coupled 2 to the power 4 – 1; 8 peaks you get. 2 cube at each proton. Now, how many protons are there? 4 protons.

So, totally how many lines you get in the entire spectrum, at the site of 1 proton, 1 spin. Now 4 are coupled, so totally you will get you N star 2 to the power of N - 1. Now, plug in the parameters here. Start with a 2 spin. When N = 2, 2 - 1 is 1, so it is 2 spin and N is to 2; 2 into 2 4 lines, exactly. That is what we observed when 2 protons are coupled.

We will go even one level lower. What happens when N is equal to only 1, isolated proton, like CHCl3 we took example, when N = 1, 1 - 1 is 0; 2 to the power of 0 is 1, so we get 1.

So, in an isolated single proton spin system like CHCl3, without any coupling to other carbon 13, etc. you get the single peak. Now I took the example of 2 spins, when N = 2; 2 - 1 into 2; the N = 2 - 1 is one, 2 to the power of 1 is 2. So when 2 protons are coupled, totally you get 4 lines. 2 for A, 2 for X. Now take the example of 3 spins. When N = 3, 3 - 1 is 2, what is 2 square 4, 4 into 3 12. So when 3 protons are coupled, you can 12 lines. 4 for A, 4 for M, and 4 for X. That is what we observe.

Now this is the last example I took. N = 4, 4 spins are coupled. A,M,P and X I took. Now 4 - 1 is 3, what is 2 cube? 8. So at each proton chemical shift site, you get 8 lines. There are 4 such protons coupled. Then it is 4 into 8, 32. So when 4 protons are coupled, in the entire spectrum there will be 32 lines. When 3 protons are coupled, in the entire spectrum there will be 12 lines, Like this, this formula tells you how many peaks you get when N different chemically non-equivalent protons are coupled.

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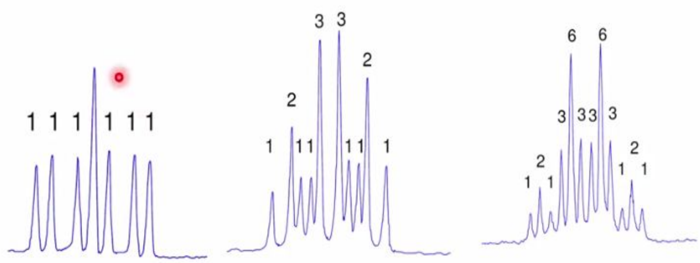
Spectral pattern when one proton is coupled N other protons



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

Is there simple logic? Now, this is taken from one of the websites of Reich, from the university of Wisconsin. I tried to get permission from him by writing emails. Somehow the emails bounced back. I have taken the example. So, I would like to acknowledge him here. So, this is what I want to tell you, a spectral pattern when 1 proton is coupled N other protons. For example, 1 proton is coupled with 3 protons, you get 8 lines 1 1 1 1 1 1 1 1 of equal intensity, but here there are 2 overlapped. So there are 8 lines here. 1 1 1 this is 1 + 1 2 overlapped . So 8 lines, When 1 proton is coupled to 4 other protons, very 2 to the power understand when 1 is coupled to 4 how many usually we expect, 16. Here you see 1, 2, this is 3 4 5 8 11 12 13 15 16 some are overlapped 3 are overlapped here, 2 are overlapped here, 2 are overlapped here. So when 1 is coupled to 5, more interesting, how many should get? 32 peaks. It is not that all the time you get in realistic situation. Just to show you, when 1 proton is coupled to N other protons, for splitting simply you go by the family tree approach and this is how you can understand the multiplicity pattern.

Remember in my formula, now, you are going to get 32 peaks when one is coupled to 5 other protons that means the total number of coupled spins are 6. So, then how many you should get in the entire spectrum N, I wrote the equation sigma N star 2 to the power of N – 1, that is, 32 into 6, 192 lines you get in this spectrum; very complex spectrum like that, you can work out how many lines we get for each of these things.

So, in this taken example here, let me work out and tell you all as you should be in a position to work out now, one single proton is coupled to 4 other protons, how many peaks you got here? 16 for the total number of spins are 5. So, we are observing 1, remaining 4 are coupled. So, there are totally 5 into 16, 80 peaks are there in this? Very, very difficult you know. So 5 into 16, to 16 into 5 ;80 peaks will be there in case entire spectrum.

So, this is what the important thing I wanted to tell you about the multiplicity pattern, when you want to understand how to go ahead and analyze it is a very important thing. Simple in all these things I have taken the example of chemically inequivalent spins, so, please observe what I was taking example. In each of them I was taking 1 proton coupled to another single proton, like H, H, H only are coupled, but in the realistic molecule, it will not go like that. There will be CH proton here, next may be CH2, next may be CH3. They are equivalent spins. So far I have not discussed about the coupling equivalent spins. I am now discussing only the coupling of individual spins, which are chemically inequivalent. And we are arrived at the number of peaks that we can expect at each chemical site of the proton and what is the total peaks you get in the entire spectrum. You understand, This is what I was discussing and I have told you everything today. So, with this I will stop here today, we will come back and continue further and learn more about splitting pattern, analyze the spectrum pattern tomorrow.