One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture - 19

Scalar Couplings - 2

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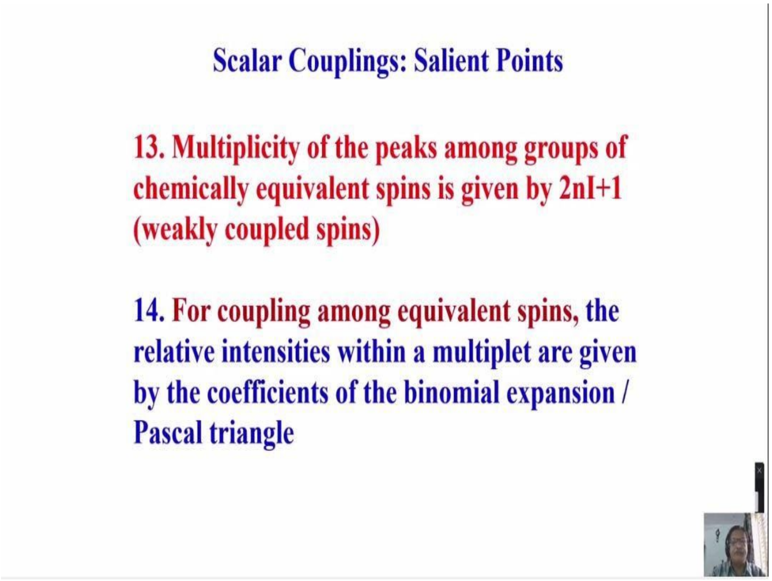

Scalar Couplings: Salient Points

13. Multiplicity of the peaks among groups of chemically equivalent spins is given by 2nI+1 (weakly coupled spins)

14. For coupling among equivalent spins, the relative intensities within a multiplet are given by the coefficients of the binomial expansion / Pascal triangle

Welcome back, so in the last class, we started discussing about scalar couplings. I introduced to you about the mechanism of scalar coupling without going more into the detail theory, mechanism. And afterwards, I started telling you various salient points that you must remember as for this scalar couplings are concerned. The several points I have mentioned. Of course, when I came to this point, almost things were getting late, so I had to go in a hurry. Let me repeat it here, especially these 2 points.

I said when 1 spin or one proton is coupled to other chemically inequivalent nuclear spins, there is going to be multiplicity of the peaks. I said in the previous slide, if you remember I said, here 1 peak can become 2, 2 can become 4, 4 can become 8. This what I said. This is because, multiplicity is arising because 1 spin can interact with this and makes it to 2, another will make this to 4 like this. We will understand this splitting pattern later. A lot more are there to discuss about these things, We will come to that later.

But what I wanted to tell you is, especially when we have chemically equivalent spin there can be multiplicity, but we can give that by a simple expression called, 2nI + 1. When is a number of protons or the number of spins, which are in the equivalent group. For example, if I take CH3, all the 3 protons are equivalent in the group of CH3. Then I take n as 3, what is proton spin, I is equal to half, then you just plug in the value of spin and the number of protons in that group of equivalent spins, For example, if it is CH2, n is 2, like that, whereas for CH4, n is 4, like that.

This is the simple formula to understand the multiplicity. We will discuss that later. Another important point for coupling among the equivalent spins if I see this coupling, here in the previous example, I showed you implicitly 1 becomes 2, 2 becomes 4, 4 become 8 like that. Then what is happening? every time intensity same, 1 : 1, it becomes half, again 1 : 1 again half. So, like that, whatever is a splitting pattern, but each time you have the same intensity, first it is 1, it will become half of equal intensity. Again 4 of equal intensity then 8 of equal intensity\

That is when they are chemically inequivalent spins, that is they are individual spins. Now, for the chemically equivalent group of spins, this is the formula for multiplicity. And for the intensities of them, it is not just 1 is to 1, it goes by what is called Pascal triangle, or the coefficients of binomial expansion. This is the point which we will discuss today mostly, I will teach you what it is, why it is happening, and everything. So, before we proceed further, we have to talk about J split energy states. It is very important to understand the multiplicity pattern.

When 2 spins are interacting. I said one peak will become 2 peaks, why? Because the coupled spin will ensure that this energy level is split. Similarly, this coupled spin will ensure this spin its energy level is split. How it is splitting is another important point you should understand. The energy states have split because of the J coupling, and we can understand the transitions how it is coming, why multiplicity is coming? They are very classically, very easily you can understand these things. We will now go into these.

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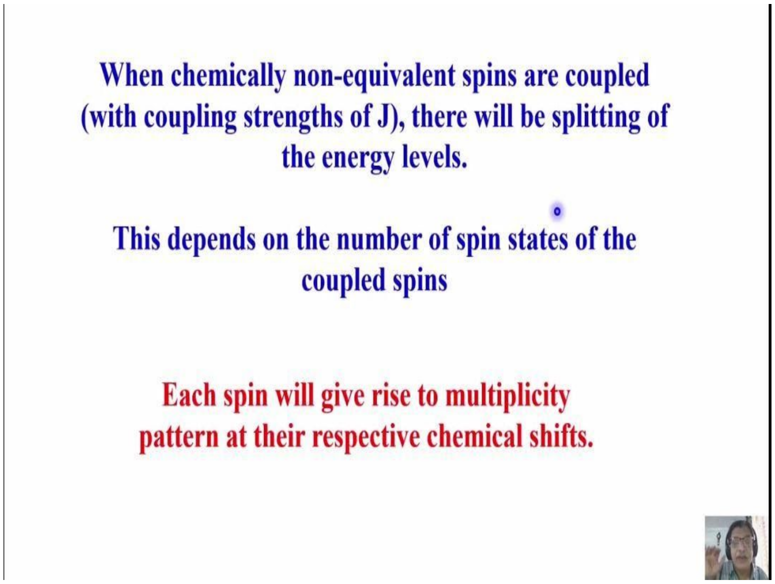

When chemically non-equivalent spins are coupled (with coupling strengths of J), there will be splitting of the energy levels.

This depends on the number of spin states of the coupled spins

Each spin will give rise to multiplicity pattern at their respective chemical shifts.

Now, consider a situation when there are chemically non-equivalent spins with this coupling strength of J, the splitting of energy levels, always. How does energy levels split, we will come to that later. This depends upon the number of spins it is coupled to. Remember, if it is coupled to 1 it is 2 lines, if it is couple to 3, 4, more peaks. We take all those examples and see how the multiplicity pattern comes at respective chemical shifts.

This is a point, please remember, the energy level is going to be split between 2 coupled spins. That number number of splittings depend upon how many spins it is coupled to, and we can understand the multiplicity pattern.

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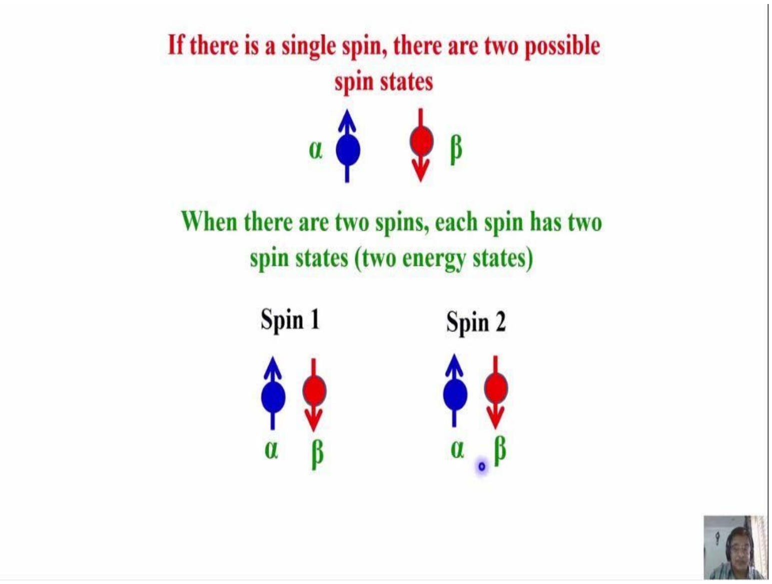

If there is a single spin, there are two possible spin states

When there are two spins, each spin has two spin states (two energy states)

Start with a simple example. Now, if there is a single spin, how many possible orientations of magnetic moments are there? You all know, we have been discussing, there are only 2 possible orientations of spin, upstate or down state, alpha state, or beat state that is what we have been discussing. From the day one I have been discussed this. There are 2 possible spin states for spin half nuclei. Now, let us say, this is for 1 spin. I have 2 spins, let us say, for interaction to take place, there must be 2 spins. One spin cannot be interact with itself. Since it cannot interact with itself, so we will have 2 spins.

Considered spin 1, what are the possible states for this spin 1? 2 states alpha and beta. Take spin 2, what are the possible states? again 2, alpha and beta. Spin 1 has alpha and beta. But is it just simple 2 spin here, 2 states here and 2 states here?

When there are 2 spins, each spins has 2 spin states.

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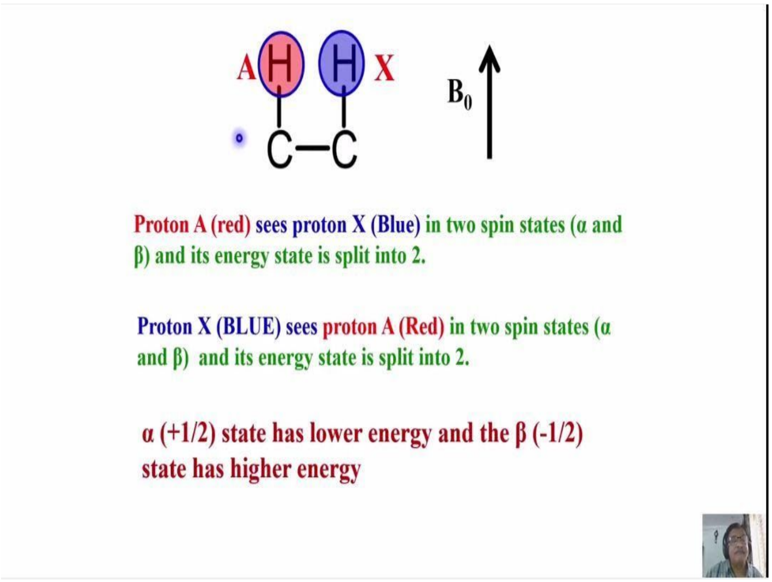

Proton A (red) sees proton X (Blue) in two spin states (α and β) and its energy state is split into 2.

Proton X (BLUE) sees proton A (Red) in two spin states (α and β) and its energy state is split into 2.

α (+1/2) state has lower energy and the β (-1/2) state has higher energy

Now the point comes like this. I am qualitatively giving you idea about the splitting mechanism. Please understand this. I am discussing about the splitting mechanism now. Consider this proton A. And I am not worried about the molecule, it is an hypothetical molecule. I am not worried about what are attached here and about the different valency of carbon, it could be X Y Z, different attachments.

But as far as my understanding of this splitting is concerned, I consider only 2 protons separated by 3 covalent bonds. Consider the proton A which is highlighted in red color in the circle, which is couple to, through covalent bond, proton X. This spin highlighted in blue color in the circle. Now it is in a magnetic field B0. Now you have taken the sample, put your sample in a magnetic field, external magnetic field, huge magnetic field and observe NMR. What is going to happen? I said in the previous slide, each spin has 2 orientations, alpha and beta.

Now, proton A sees proton blue in 2 spin states, alpha and beta. What about proton X? that also will see proton A in 2 spin states. So, each of them has 2 spin states, alpha state with lower energy and beta state which is minus half, which has a higher energy. Each spin sees the other spin in 2 energy states, plus half and minus half, alpha and beta, 2 different energy states. One has higher energy and one has lower energy. So, it sees in 2 energy states. So, that means it is not seeing one magnetic field, It is seeing 2 different fields. Similarly, this one also split this into 2 energy states.

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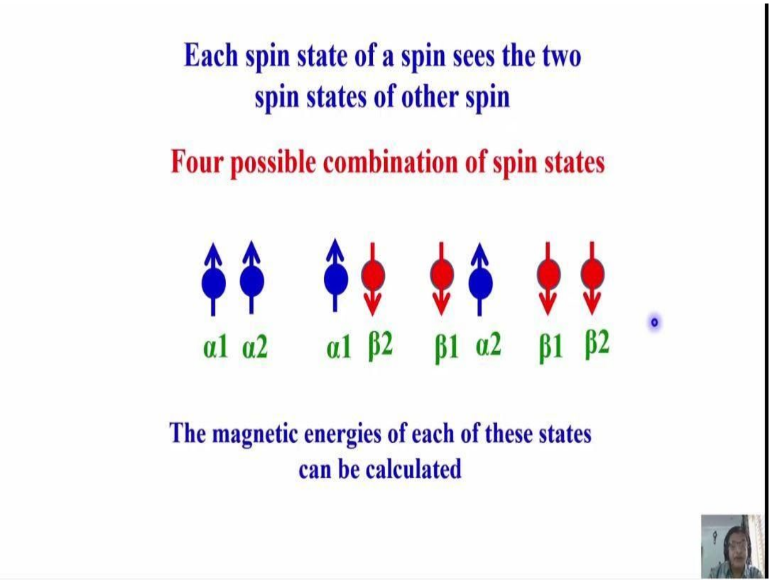

Each spin state of a spin sees the two spin states of other spin

Four possible combination of spin states

The magnetic energies of each of these states can be calculated

So how many you have? Each spins sees the 2 spin states of other spins. Then what are the possible combinations? why 4 states will come, each one will see 2. So, in principle, if I have 2 spins, this spin will see this spin in 2 energy states. This spin we see this spin 2 in energy states. Totally how many energy states are there? There are 4, but, what is the energy of each of the states? when it is 1 spin, you know it is half and minus half. And this spin when it is seeing this that it is plus half or minus half, then both are combining together, it is not just half and half.

There is a different way to calculate. Let us consider 4 possible combination of all these spin states, to define the energy of each of these 4 magnetic states. please follow me. Now, let us understand spin state, to discuss the energy for all the 4 possible energy states. What are the 4 possible combinations of the spins. First, both the spins alpha 1 and alpha 2, 1 and 2 spins both can be up. That is one combination. Remember both can be up, this is one combination. Spin 1 can be up spin 2 can be down. It is like this. That is possible, that is another energy state. Spin 1 can be down spin 2 can be up, that is another possibility. One more possibility is both can be down like this. So, there are 4 possible combinations. Each spin when they see other spin in plus half or minus half states, when you take the combination of all these 4, there are 4 different energy states, alpha alpha, alpha beta, beta alpha and beta beta. Four possible energy states. Now, this magnetic energy of these states can be calculated, how do you calculate.

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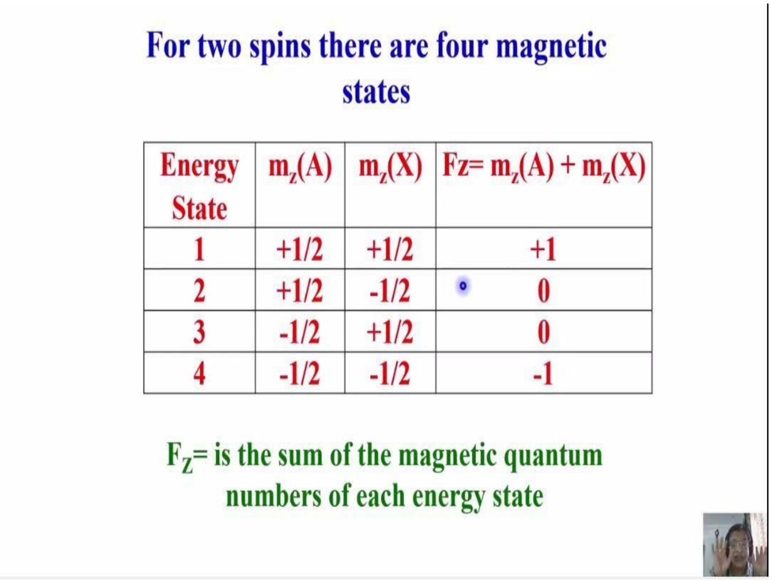

For two spins there are four magnetic states

Energy State	$m_z(A)$	$m_z(X)$	$Fz = m_z(A) + m_z(X)$
1	+1/2	+1/2	+1
2	+1/2	-1/2	0
3	-1/2	+1/2	0
4	-1/2	-1/2	-1

F_Z= is the sum of the magnetic quantum numbers of each energy state

Very simple in this case, this is plus half this is plus half, a simple addition. Why does it total this thing, first state 1 energy state both are half, half. That is alpha, alpha. This is the magnetic state of A spin, plus half, for X spin plus half. both half half. Like this both are up, up then you have to add for the total magnetic quantum number of this energy state, total m. if you want to find out you would add m of A, and m of X. Half plus half, you add up what are we getting? 1.

So far 1 energy state, the total energy total magnetic quantum number, or total magnetic energy for this is plus half plus half. Take another energy state, second one, plus half and minus half. If you add up these 2, it is 0. Take the other energy state 3, this is minus half this is a plus half. So total magnetic energy 0. Fz, that is sum of mzA + mzX. Total magnetic moment along Z axis for this A spin, and for this spin if you take, the total it is 0.

Now, for the energy state 4, the magnetic moment of this is also minus half, this is also minus half. Take the sum of this. it is minus 1, minus half plus minus half is minus 1. So, in the last column I am writing Fz. Fz is nothing but the sum of the magnetic quantum numbers of each energy states, here plus half plus half, plus half minus half, minus half plus half, minus half minus half. So, this is the energy now, you should not consider individually plus half minus half plus half, minus half, etc. take the combination.

Now, there are 4 different energy states for 2 coupled spins. very interesting is it not, how we arrived at four energy states. Now, we will write down the energy level diagram, how it comes. This is all essential to understand, so that you know how the transition occurs, how the peaks come when 2 protons are coupled. You must know. For this you must know how the energy levels come. So, I will write down the energy levels for the homo and heteronuclear spins now.

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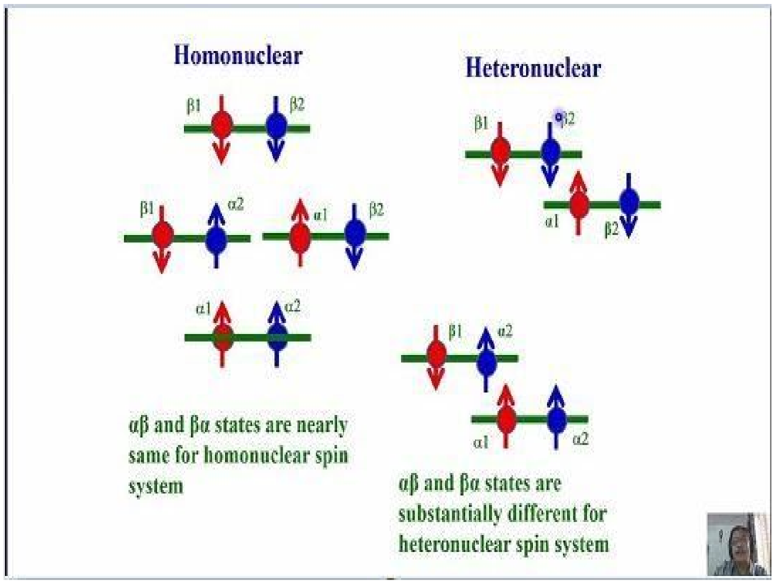

Homonuclear

Heteronuclear

αβ and βα states are nearly same for homonuclear spin system

αβ and βα states are substantially different for heteronuclear spin system

By homonuclear spin these are the energy levels. very interesting, why, look at this, both are down -1 it is a higher energy, because E= - μ0.B0. In this case both are negative. So, it will be minus 1 into B0 that is why this is higher energy. So, that is why this spin down states is always higher energy according to the energy level diagram. So, it is written here what is the magnetic energy state what is mz here. Total minus half minus half, - 1. This state has total magnetic moment of - 1.

What about this state, it is 0, mz total; mzA + mzX is 0. similarly, mz1 and mz2, total of m is again 0. Here, half plus half; this total mz is 1. This is the energy level diagram each energy level is separated by 1 quantum of energy. Of course, if you go more into the detail there is slight difference between these two. We will not worry, we say it is 0. For our understanding it is enough to say they are equal.

It is homonuclear, both are protons I am taking. What happens if I take heteronuclear, If the interacting 2 spins here, 1 and 2; if it is instead of protons; one is proton and the other is carbon, then what is going to happen? Let us understand that, and this is the energy level; something very interesting. Why it change so much? Look at this energy level, look at this energy level. Everything is same, as far as the orientation of nuclear spin magnetic moments are concerned. In this energy state both are down, both are down up and down, down and, up and up.

Everything is same, but why do I write like this? Why not like this? What is so special about the heteronuclear spin? You must remember one thing, in this case, alpha beta and beta alpha states are nearly same, and they are separated by one quantum of energy, it is fine. But in this case alpha beta and beta alpha states are substantially different, why, because remember, this to this is is homonuclear this very large, this to this is homonuclear. Whereas this energy separation is the heteronuclear, like carbon.

What is the gyromagnetic ratio of carbon when compared to proton, it is 4 times less. Remember I have been teaching you, this is 4 times less. If this separation, let us it is 8, some unit, for proton; This carbon separation has to be 2, four times less. That is the reason, why this clearly tells me this is the energy separation for carbon 13 spins, this is the energy separation for carbon 13 and these 2 are for proton transitions. This gives you proton transitions, this gives you carbon transition. Energy separation deliberately I wrote much smaller than this one, because this energy separation of carbon spin carbon, between 2 states is much less compared to proton; 4 times smaller. That is how I represented this heteronuclear energy level, the 2 energy levels corresponding to protons transitions are larger; the 2 energy levels which are corresponding to carbon are smaller. What do you understand by this? We will come to that later.

This tells me about a lot about intensity. We will come to that later. But this is just to give you an idea. When you want to write down the homonuclear state energy states we write like this. f\For heteronuclear we write like this. When I discuss NOE, all these things are important, please remember. When one of the classes I will come to NOE, I will have to teach you all those things.

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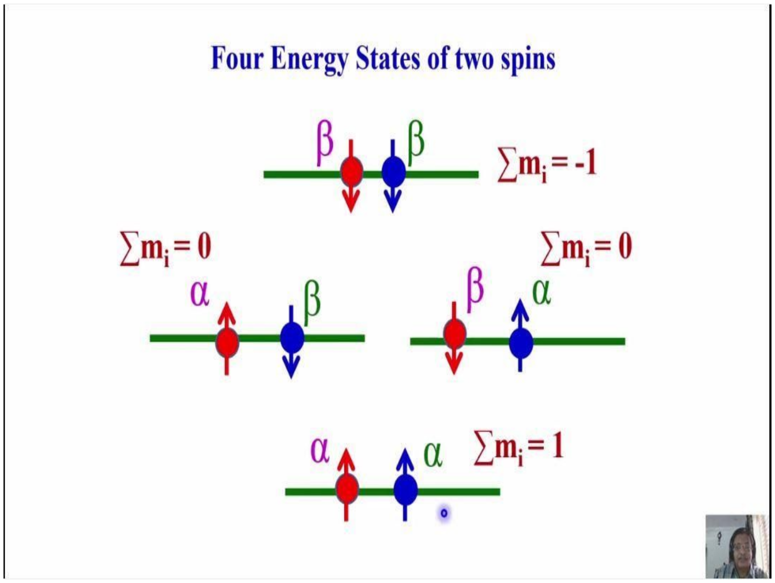

Four Energy States of two spins

Now, the 4 energy states of 2 spins will start with. Let us see what will happen if I see this. So these are the 4 energy states of 2 spins exactly, delta sigma of mi; mz for this one, z for this one, for A and B, this is 0, this is 0, 1, - 1 and + 1. This you should never forget, I keep on using this 4 energy states for 2 coupled spins very often in my talks, if not now after some time. So this 4 energy states for 2 coupled spins are very important. Remember always, 2 up, 2 down, up, down, down, up; this is – 1, 0, 0, + 1. These energy states and spin orientations are important.

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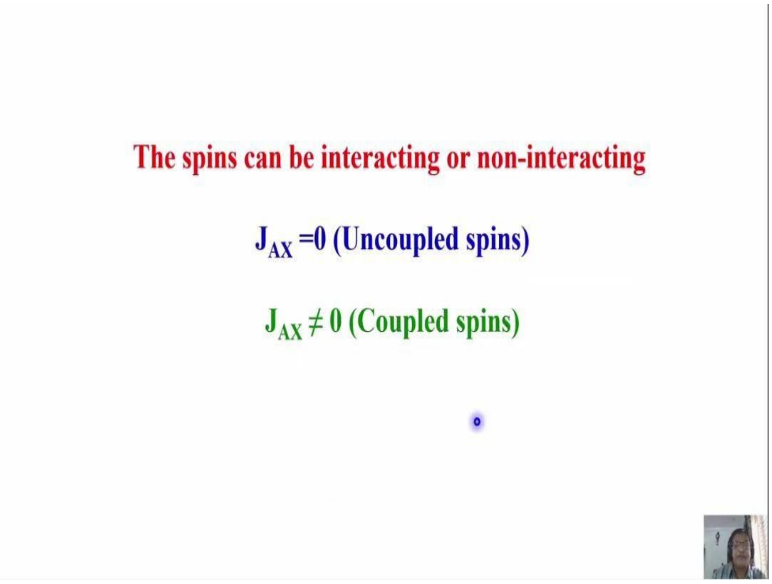

The spins can be interacting or non-interacting

$J_{AX} = 0$ (Uncoupled spins)

$J_{AX} \neq 0$ (Coupled spins)

Now, we considered 2 important situations, very important situations. I said 2 spins are interacting, that is also correct. Interacting means there is a way, I explained to you when I gave this salient points of couplings. When 2 spins are coupled, I expressed its coupling strength in terms of Hertz, I used the notation J. So, between 2 protons A and X here, let us say this is A and this is X. When I have to calculate the J coupling, I represent this as JAX; coupling between A and X.

When 2 protons are coupled there are 2 possibilities. The coupling can be 0. Who says coupling should always be there. They might have coupled, but coupling may be very small, negligible or 0. It is called uncoupled spins, coupling is 0, in case of 2 spins; or coupling can be nonzero. Remember the point, coupling can be 0 or nonzero, nonzero means it could be some number either minus or plus, I do not care. I just take magnitude. The coupling in this case one possibility is, they may be uncoupled, they need not be coupled, they can be simply there without interaction; or they can interact with the coupling strength of JAX which is nonzero, you are all with me, I hope.

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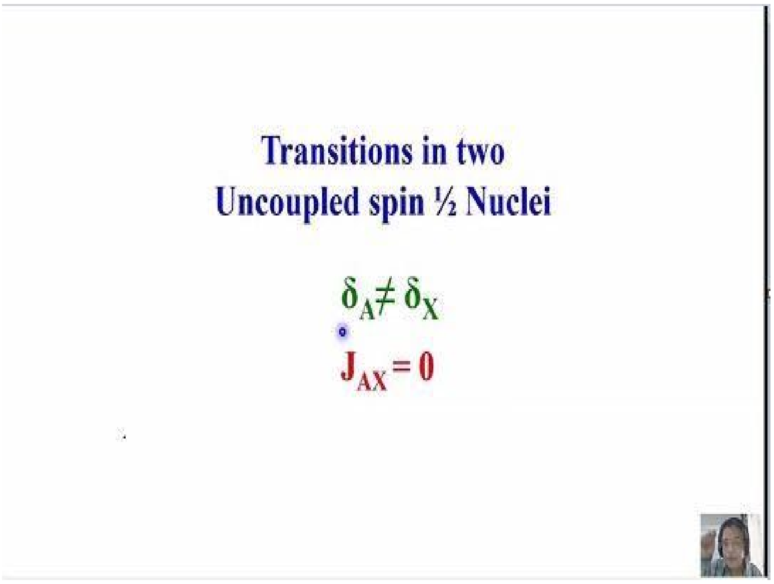

Transitions in two Uncoupled spin ½ Nuclei

$\delta_A \neq \delta_X$

$J_{AX} = 0$

Now, consider a situation of one possibility. How many transitions you get in 2 uncoupled spin half nuclei. You please understand this point, I am considering 2 spins which are coupled for which we wrote the energy level diagram. Now I will put a condition JAX = 0; remember, JAX is 0, and they are non-equivalent nuclei, they are different chemically. They are different chemically inequivalent spins; means chemical shift of one proton and other proton are not same. That this is a condition I am putting here.

They are chemically inequivalent spins, at the same time, the coupling is 0. It is one of my conditions. Let us see, in this situation, how many peaks I expect. It is very interesting. From the energy level diagram, you can get information about the possible transitions, like, how many transitions you get in 2 spins, 3 spins like that. Of course, you do not go and do for 4 spins, 10 spins like that, after some time it will become cumbersome. OK. It is not easy to go beyond 2 or 3 spins. So, you can get analytical solution up to maximum 2 spins or 3 spins. Beyond that, it is very difficult. But now from the energy level diagram, let us try to understand and see how many peaks we are going to get. You are all with me, I hope.

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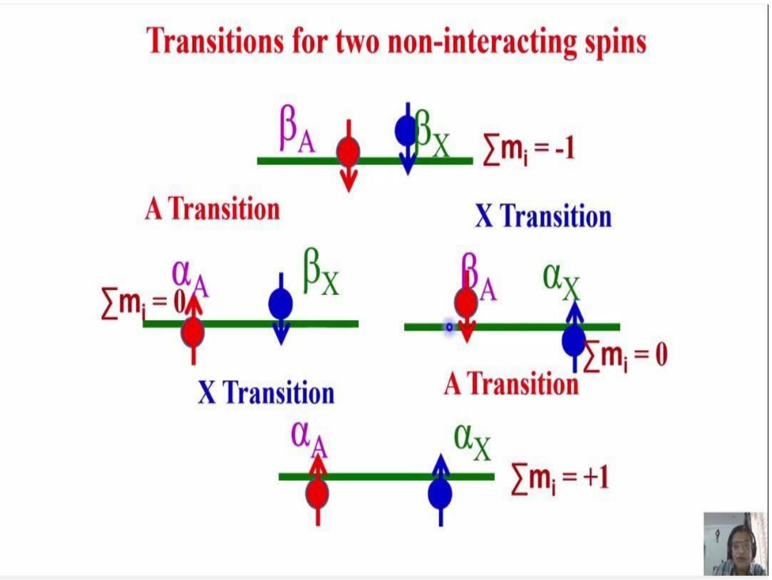

Transitions for two non-interacting spins

Now go back to my energy states. This is for which spins? homonuclear spins. Now, we have 4 possible energy states, what is the magnetic energy of this state - 1, both the negative half, half minus half minus half. Plus half minus half this is 0. This is 0; minus half plus half; this is plus 1, plus half plus half. So, these are the possible orientations. Now, you remember what was my condition of selection rule. In one of the classes when I was talking about the fundamentals of basics of NMR, when we try to see the signal, I introduced what is called selection rule. What is the selection rule in NMR? They changing the mi, between 2 energy states; change in the magnetic quantum number mi between the energy states, what is the change? if it is + 1 or - 1 it is the allowed transition.

Do not forget the selection rule which I told you. Find out the total magnetic quantum number of each energy state. What is the magnetic quantum number of this state? Find out what is the magnetic quantum number of this state and all the 4 states. Now, find out what are the allowed transitions. The allowed transition is change in the total magnetic quantum number between 2 energy states must be + 1 or – 1, remember this point.

So, now, let us look at the diagram what are allowed transitions? Can we allow this transition from - 1 to 0? Of course it is allowed, because - 1 to 0, the change is only - 1 or if you go from 0 to – 1, it is + 1. So, this is an allowed transition. What about this one? 0 to – 1 or - 1 to 0, allowed transition. What about this one 0 to + 1, of course yes. if it comes this way, it is - 1 if you go this way it is + 1, that is allowed. Same way here, 0 to 1 ,of course it is allowed. This is, if you go this way is 1; if you come this way to – 1; fine.

So, how many transitions we can get? There are 4 possible transitions where the change in the magnetic quantum number if you take between the 2 energy states, it should be + 1 or – 1. Look at this one. Now, let us see what are the transitions. The beauty is, if you identify this magnetic moment of each spin whether it is plus half or minus plus; you can even identify the transitions corresponding to the particular spin. Very interesting is it not? Look at the 4 energy levels, I can say if there is a transition here, here, here, here, allowed as per selection rule then I can say whether it corresponds to spin A transition or corresponding transition for the X spin. It is possible I can say that, how? look at it very carefully. What is this transition, what is happening here? Look at carefully the beta spin of A came to alpha of A; the alpha of A went to beta of A, it is allowed, the change is from the 0 to – 1, it is allowed. The change in spin quantum number where one of the spin is changing it spin state from alpha to beta or beta to alpha is allowed. And which spin is changing its state, alpha A is going to beta of A and beta of A coming to alpha of A. So, this transition must be corresponding to A.

Similarly this cannot undergo, the X cannot undergo, because both are beta, beta minus half minus half; so that cannot take place. So that has to be only alpha spin; A spin is changing its state from alpha to beta. One of the spins has to flip from alpha to beta or beta to alpha. Here both are beta, beta there is no question of X spin flipping between these energy levels.

You understand, between these 2 energy states, beta spin of X will not flip; it is not going from alpha to beta or beta to alpha like here. These are both in beta states it remains like that. Are you all with me? please follow me carefully. In this case the A spin can change from alpha to beta and beta to alpha, it is allowed transition, I will say this is A transition; X is not possible here. you see this is A transition and X is not possible here. Now, that is allowed, there is a A transition. What about this one? Here also, alpha A is going to beta A, beta A came to alpha A. Again + 1 to 0 is allow transition. So, this is what again an A transition. This is an A transition. Now, you identified 2 A transitions.

What are the next allowed transitions? Here 0 to 1 is allowed, but her A is not changing its state; A is still remaining as beta. What happen to X? X is changing from alpha to beta or beta to alpha, you understand. So, what is this transition? This is X transition.

Fantastic you know. We could even identify the transitions. Normally what people do, take the NMR spectrum start interpreting the peaks, which is CH3, which is CH2, which is aromatic, fine; that is one way, but now, you can even identify the transitions coming from particular spin. OK. What is next allowed? think carefully. Now, what about this transition? Now this one, alpha of X can go to beta of X, but alpha remains same here, that will not flip. So, in this transition, A is not flipping, but X is flipping; fantastic.

So, what is this transition? It is X transition. You are all with me; see very carefully understand now. I am going to tell you a transition from this state to this state is allowed, where A is spin is going from alpha to beta and coming from beta to alpha, X spin cannot flip here, because both are in the beta state, that is not allowed. This A transition. What about this one? alpha of A goes to beat of A and beat A is coming to alpha A, there is allowed, that is A transition.

This alpha X will go to beta X; beta X can come to alpha X, but here A will not be undergo transition, because both are beta. That is X transition. What about this? Alpha X can go to beta X beta X can go to alpha X, but this both are in A; up up; there is no A transition here. This is X transition. How many transitions you got? 4 transitions, but what are the frequencies? This energy is exactly same as this energy. This energy is exactly same as this energy. What does it mean? the frequency of this A and frequency of this A transition are identical. there is no difference at all. They will overlap one over the other. Though there are 2 A transitions, because their frequencies are not different, they overlap and give rise to a single peak. Please understand me. There is no energy separation between this here. Let us say if the energy separation was this much, this was larger like this, difference in energy separations, the frequencies are different, then they come a different places the NMR spectrum, but now, the energy separations are exactly identical. So, the transition frequencies are exactly same.

So, they overlap; both A will overlap and give rise to single peak. Similarly look at the X transition here and X transition here. Exactly both of them have the same energy separation, same frequency, what does it mean? X transitions also will overlap like this. So, please understand, in the non interacting 2 spins, there are 4 energy states, but it so happened there are 2 A transitions and 2 X transitions.

However, the frequencies of 2 transitions of A are identical and give us to only one peak. They overlap. Still there are 4 transitions, but in the spectrum you observe only 2 peaks, because 2 are overlapping in A and 2 are overlapping similarly, in X. The 4 peaks appear as 2 peaks for you because of overlap of 2 A transitions and overlap of 2 X transitions.

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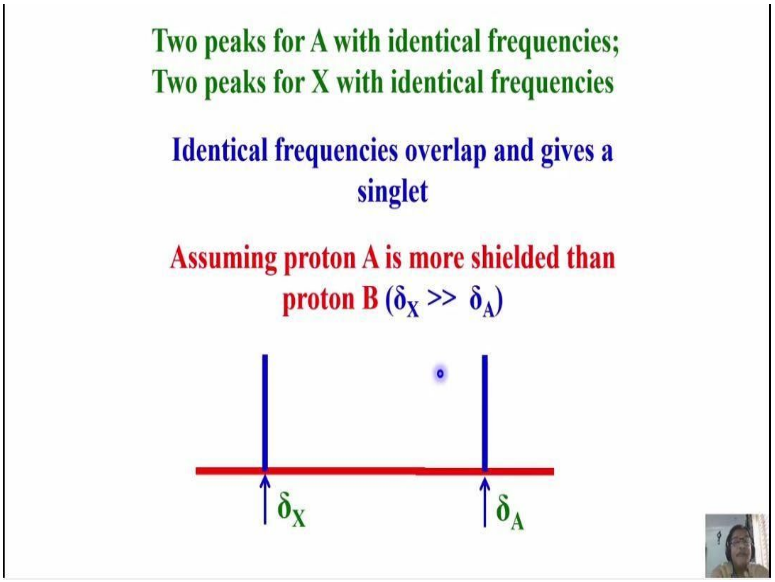

Two peaks for A with identical frequencies;
Two peaks for X with identical frequencies

Identical frequencies overlap and gives a singlet

Assuming proton A is more shielded than proton B ($\delta_X >> \delta_A$)

And this is the type of spectrum you get. Two peaks for A with identical frequency, 2 peaks for X with identical frequency, gives as a singlet for A and singlet for X, 1 peak. Singlet means 1 peak. So, assuming proton A is more shielded than proton X, what do you mean by that? proton A is more shielded means it comes high field and the X is less shielded, so it comes down field so, chemical shift of X is larger than the chemical shift of A, when expressed in ppm.

So, delta of X is larger than delta of A. This is my assumption. It need not be true. I am assuming. It can be other way also. So just for understanding purpose, there are 2 the peaks we are getting at 2 different places, and this is 1 peak for X in reality 2 overlapped peaks for X, and 2 overlap peaks for A; and delta of X, by my assumption is larger than A. So A comes at high field, X come to down field compared to A; fantastic is it not? so beautifully you can understand how the lines are coming when 2 spins are coupled.

It is a simple example I took, to show you that you get 4 peaks; 2 of which are overlapped when the couplings are 0, in two weakly coupled AX spin system. What is weakly coupled, the word I am using, just a jargon do not worry. I will discuss more about strong and weak coupling in one of these classes. Very important to understand this pattern, but I will come to that later. But here for today, I just wanted to tell you what happens when 2 spins are coupled. How the splitting comes, what are the energy states, and what are the what is the magnetic quantum number of each energy state, which you have to add up based on the magnetic quantum number of individual spins and then get the magnetic quantum number for each energy state, apply the selection rule, find out which are the allowed transitions. A classic example which I took where, 2 protons are not coupled or coupled with JAX = 0; non interacting spins; in which case you get 4 transitions are allowed, 2 for A and 2 for X, which are overlapped, and this is the spectrum. So in this spectrum, you will not get information about J coupling, which is 0. If there was a J coupling it should have been split into 2 peaks, which is not happening. So J coupling is 0 here, here also it is 0. But chemical shifts are different, otherwise, it would have been an equivalent spin system. So it is different. So I will get chemical shift information for this spin in this case and a chemical shift information for this spin in this case, but no coupling inforamtion. I hope you are all with me.

Today I try to start with giving you more about the splitting and some examples of how splitting occurs when 2 spins are interacting, everything. So with this, we will stop for today, and we will come back tomorrow where I take an example of the same 2 spins where coupling is nonzero. another interesting example. There how many peaks I get that will understand I will come back tomorrow?