Advanced NMR Techniques in Solution and Solid-State
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Module-44
Spin echo sequences

Lecture-44

Welcome all of you. In the last class, we started discussing about product operators, where coupling term was introduced; earlier we were considering a single spin, we understood the evolution or the effect of RF pulse and free precession, evolution of magnetization under free precession. When you are taking coupling into account a new term is introduced, in addition, the evolution of pulses and the effect of free precession, you also have to consider the effective coupling; all the three are to be evaluated.

And of course sequence of the pulse sequence remain same; start with the RF pulse delay, RF like that; the sequence has to be maintained, but between the pulses during delay, let us say during the free precession, if you want to find out the evolution of let us say, offset, J coupling, or chemical shift you can individually take it. no problem. Offset and J coupling you can take first or later either of them, there is no order, the order is immaterial for that.

So, we worked out for J coupled spin, especially, we took I 1X tern where X detection in-phase term, I told you what are in-phase terms and what are anti-phase terms. In-phase term are I 1 X, I 2X, I 1Y and I 2Y, anti-phase terms are I 1X I 2Z, I 1Y I 2Z or I 2X I 1Z, I 2Y I 1Z like that. These are all in-phase terms. We also saw what are MQ terms, that is multiple quantum terms, where both spin 1 and 2, X and Y components will be present, they are anti phase. For example, I 1X I 2X, I 1Y, I 2Y like both components of the spin vectors are anti phase each.

These terms diagrammatically also we saw and we tried to understand about the evolution of of magnetization under J coupling; and 2 spins were taken into account; the evolution of offset of spin 1, evolution of the offset of spin 2 and J coupling we calculated; very interesting thing we observed; exactly tau is equal to our delay, you know when you give a delay equal to 1 over 2J we found out that in-phase term I1 x become completely anti phase, This is true if we consider the spin 2 also.

So, very interesting thing happens with the pulse sequences, what is happening? The in-phase term when it becomes anti-phase, the term which is responsible for this is J coupling. J coupling is the one which converts in-phase term into anti-phase term; and this is the one which helps in the transfer of magnetization in polarization transfer experiments.

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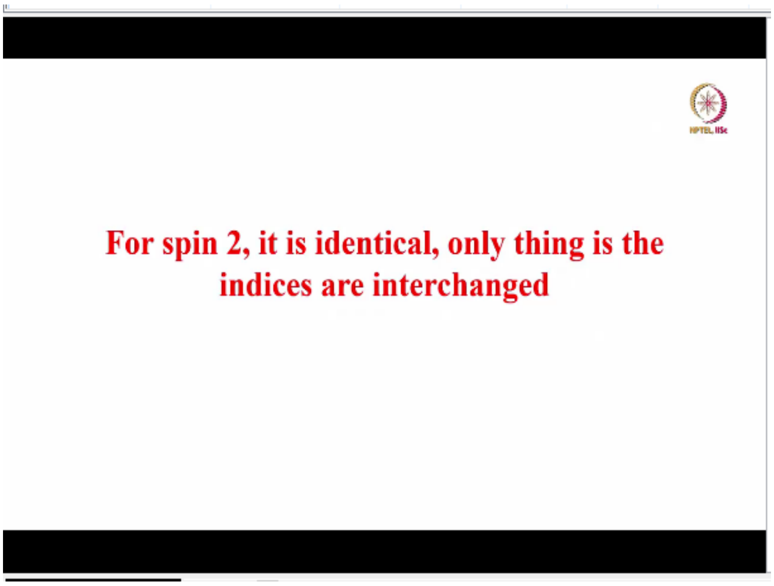

With this we understood same thing is true for spin 2, only thing is whatever we worked out for spin 1 remain same, the indices 1 and 2 get interchanged. That is all.

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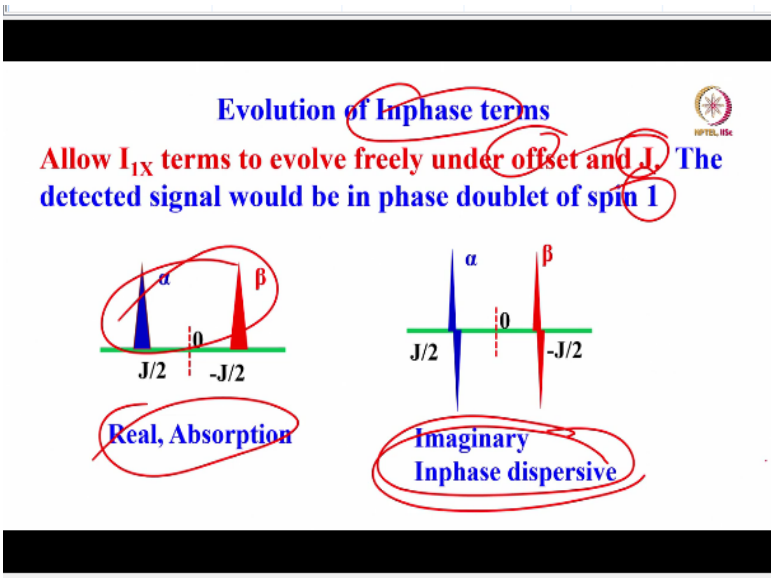

And also remember one thing, we introduced a diagram I 1Z and I 2Z rotation; we will also worked out. So, that is another thing which we can utilize instead of two trignometric identities. The diagram also helps in understanding about rotation, or evolution of J coupling; how J couplings are rotated in different axis. So, that is another important thing we have to use. With that now we will go on diagrammatically and we will see how evolution of in-phase terms can be viewed.

Allow I 1x term to evolve freely under offset and J coupling and the chemical shift and J coupling. Now what is going to be observed? the detected signal will be in-phase doublet for spin 1, spin 1 it will become in-phase doublet. This is a real part absorption, X detection. If see Y detection what happens, it is an imaginary part. It is in-phase dispersive, it is called. I am diagrammatically showing in-phase terms; in-phase real and imaginary terms for spin 1. When you allow I 1x evolution under J coupling you are going to get real absorption and imaginary in-phase dispersive.

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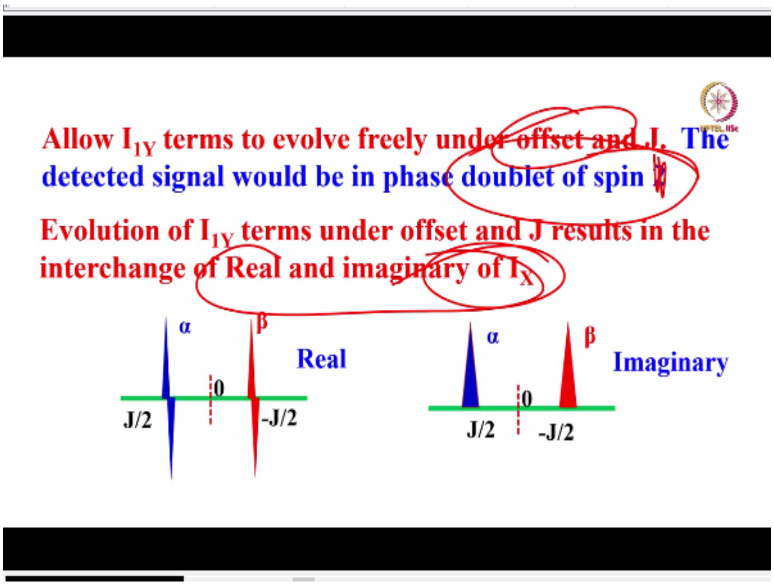

Similarly instead of I 1X, I 1Y is allowed to evolve freely under offset and J coupling. Now it is a Y detection; the detected signal would be in-phase doublet of spin 1. Evolution of I 1Y and I 2 terms under offset and J results in the interchange of real and imaginary of I X, real becomes imaginary, imaginary becomes real, both are in-phase doublets.

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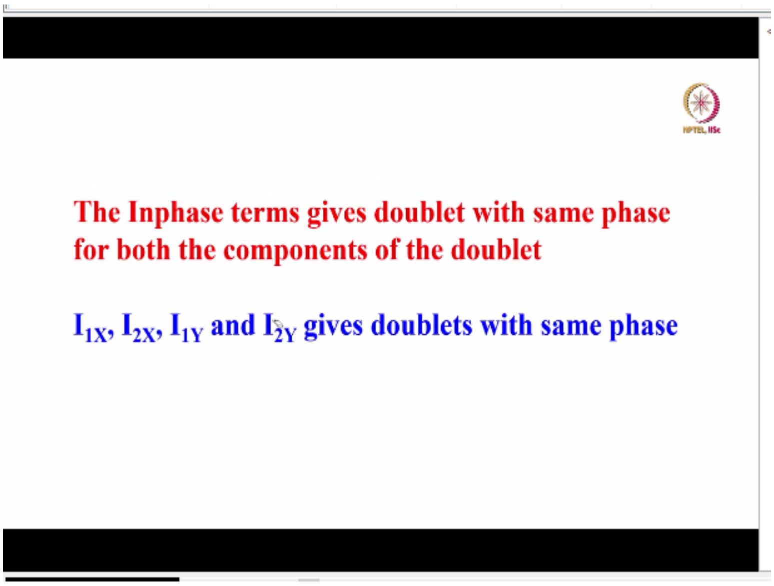

In-phase terms gives doublet with the same phase for both the components of the doublet for I 1X, I 2Y, I 1Y and I 2Y, they all give doublets in-phase doublets, in-phase terms; the doublets of the same phase, that is why they are called in-phase doublets. So, if you detect I 1X it is in-phase doublet like this, for spin 2 is like this for I 1Y it is in-phase dispersive like this. Similarly, for I 2Y it is in-phase dispersive like this. So, the in-phase and anti-phase dispersive and absorptive is represented like this. I 1X and I 2X gives in-phase absorptive, I 1Y and I 2Y is Y detection is in-phase dispersive signal; you are going to get under J evolution; both are doublets.

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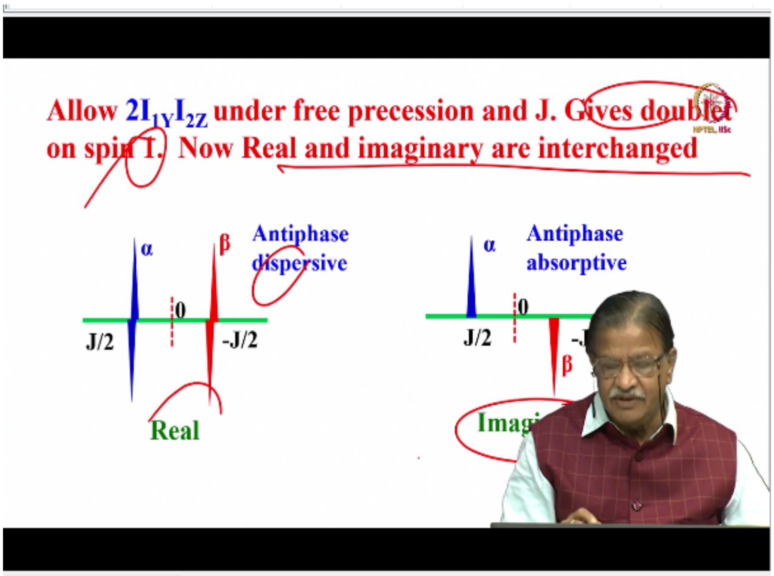

Now, evolution of antiphase terms under free precession and J coupling. Now allow 2 I 1X I 2Z to evolve under free precession and J coupling. It gives antiphase doublet on spin 1 and antiphase dispersive component is imaginary, it becomes antiphase. You see imaginary part this is antiphase doublet. See in the earlier case both were in-phase doublets and were in the same phase.

So, real and imaginary you imagine, we discussed about in-phase absorption, in-phase dispersive and antiphase absorption, antiphase dispersive, all those things we discussed long back. Allow I 1Y I 2Z under free precession again gives doublet on spin 1. Now real and imaginary are interchanged like this, this is a real antiphase dispersive and it is antiphase absorptive.

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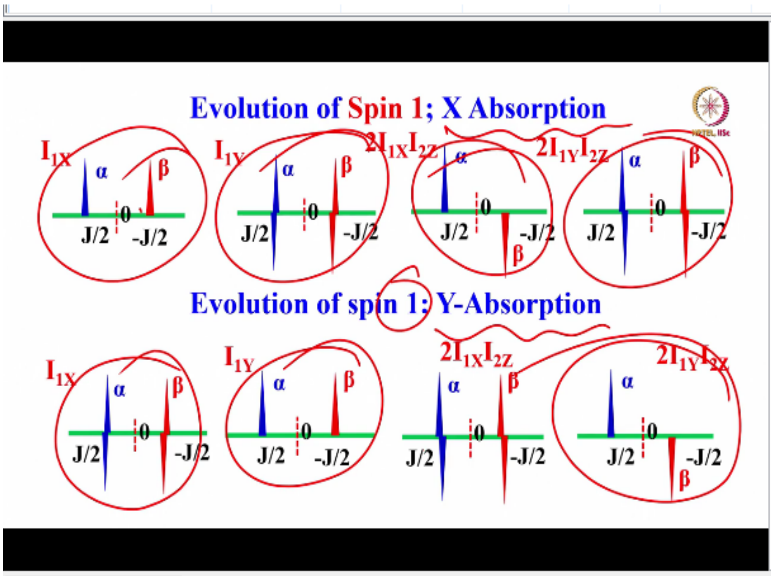

So, evolution of spin 1, if I look for X absorption, I look at the X, then you are going to get I 1X like this. And I 1Y is in-phase dispersive, the in-phase absorptive and 2I 1X I 2Z if I see, it is antiphase doublet. And 2I 1Y I 2Z if I see, it is going to be antiphase dispersive. So, that is the difference. This is for spin 1; I am observing X detection. My receiver is along the X axis. If I observe the evolution of spin 1, where I am going to see the Y absorption what is going to happen? You know it has rotated by 90 degree, all these terms get moved by a 90 degree. So, now I 1X becomes in-phase dispersive and I 1Y becomes in-phase absorptive. Similarly, 2I 1X I 2Z becomes antiphase dispersive, this becomes in-phase dispersive. This is what is going to happen. Diagrammatical I am showing you, what happens if we have a spin 1, X absorption or Y absorption.

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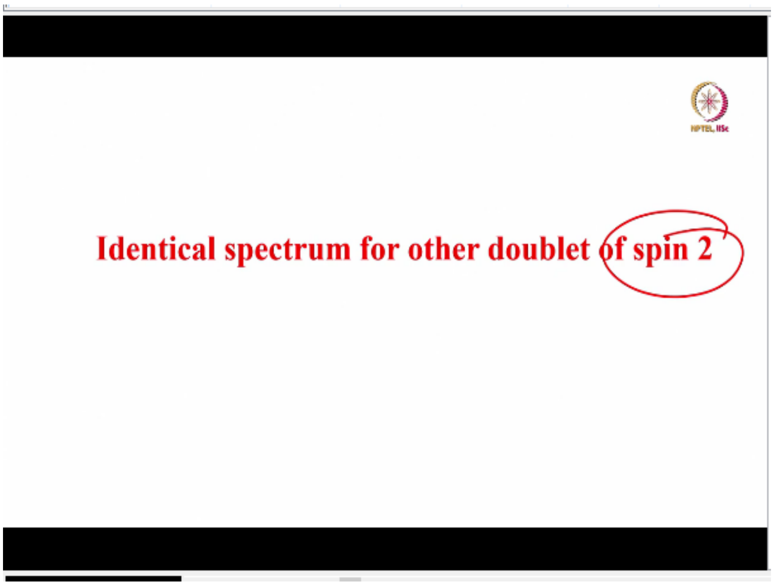

So, if consider spin 2 exactly identical doublet you will see; identical doublet for spin 2; same pattern you are going to see. Depending upon the X absorption and Y absorption, pattern remain same, both in-phase doublet, both in-phase dispersive component or absorptive, dispersive all, whatever we discussed for spin 1 will be identical for spin 2 also.

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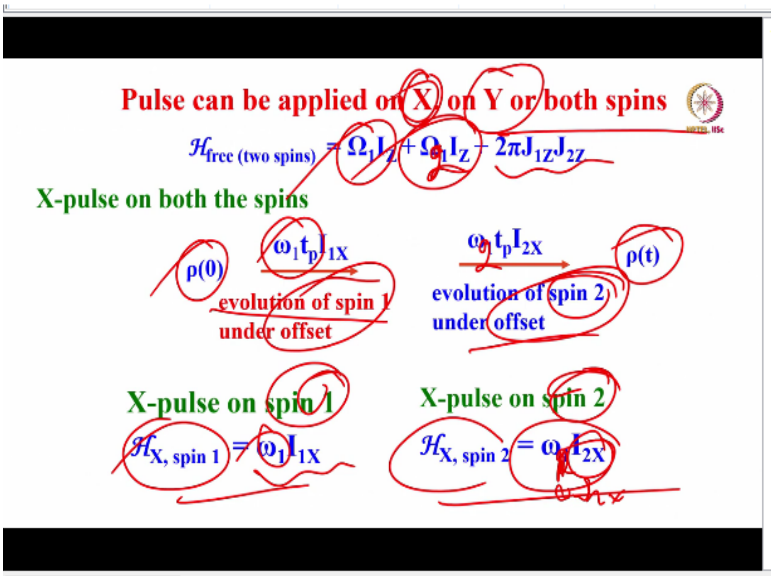

Now you can apply pulse on X axis or Y axis, on both the spins simultaneously, you can apply selective pulse, on the X axis, on spin 1 or spin 2 or and X axis or Y axis or hard pulse, everything is possible, pulse can be applied on X or Y axis. Now we consider the free precession of 2 spins; we will try to evaluate it now. First, we will consider omega 1 Z, this is should be omega 2 IZ.

And this is 2 pi J I 1Z I 2Z. This is omega 2, remember this omega 2. This is the free precession Hamiltonian for two spins. Now X-pulse on both the spins. Firstly you apply X pulse. Now evolution under free precession omega 1 t p I 1X. This I 1X is evolving under offset. So, spin 1 under offset, this is what we have to consider. Evolution of spin 2 under offset we have to consider. Then you are going to get rho of t.

If I apply X pulse on spin 1, the Hamiltonian for spin 1 is omega 1 I 1x and X plus on spin 2 Hamiltonian is omega 2, omega 1 I 2X; omega w I 2X or if you want omega 2 we can write no problem, that need be same as omega 1; to avoid confusion you can put omega 2 I 2X, you can put no problem. So, X pulse on both the spins if you have to consider evolution of spin 1 under offset, evolution of spin 2 under offset, X pulse on spin 1, this is X pulse and spin 2 you can consider this one. So, these are the Hamiltonians under free precession; different Hamiltonians if you want to evaluate.

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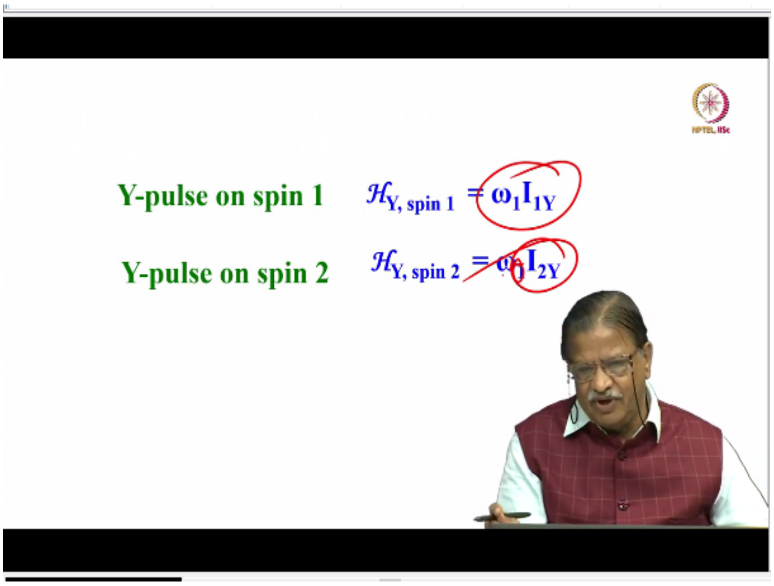

If you apply Y-pulse on spin 1, of course, this is Y-pulse, Y-pulse on spin 2 is this one; you are applying Y-pulse. This can be again omega 1 or if you want to change it omega 2 you can make it, to make it very clear to show that power is not same as spin 1, you can make it omega 2.

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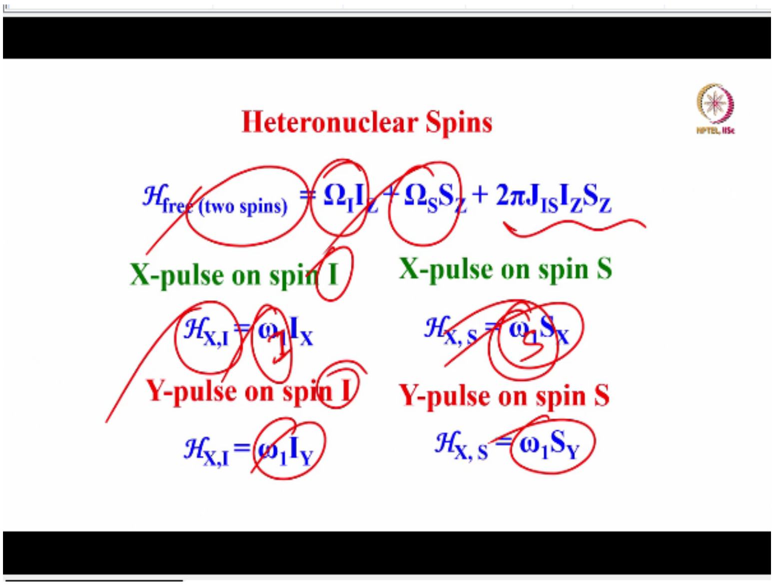

So, now with this we will go to the heteronuclear spin; that is very interesting. So, far we are considering the homonuclear spins. In the case of the homonuclear spins, we took spin echo what did we observe? Offset gets refocused, chemical shift refocused, but not J coupling. So, J coupling we observed, chemical shift completely got refocused, we did not consider the J coupling at that time.

So, now, we will consider heteronuclear spin, and how spin echo comes, from product operators we understand which term gets refocused, when you have spin I and spin S, instead 1 and 2 we call spins I and S in the heteronuclear case and the coupling between heteronuclear spin is I Z S Z. This is the free precession Hamiltonian for 2 spins. Now how it evolves? we will understand and then also we look at the example of a spin echo in heteronuclear case. Now I am applying X-pulse and spin 1.

This is the Hamiltonian; omega 1 into I X, X-pulse on spin 1 omega 1 into S X. So, this is for X-pulse on spin ; on spin I and spin S. In principle I can make it as S and I. This is to be precise for you. Since omega 1 is for normally used for power, I put omega 1, if you want to make it explicitly make it omega into I X plus omega into S X, omega I is the RF power for spin I, omega S is the RF power for spin S, does not matter to avoid confusion you could do this as well, otherwise omega 1 I 1X itself is okay.

Similarly for Y-pulse on spin 1 put omega 1 IY. This is the omega 1 S Y, Y-pulse on spin S. These are the Hamiltonians when you apply pulse selectively on I spin or S spin along the X or Y; these are the 4 free precession Hamiltonians we should know to evaluate the heteronuclear spins and to find out the density operator for that.

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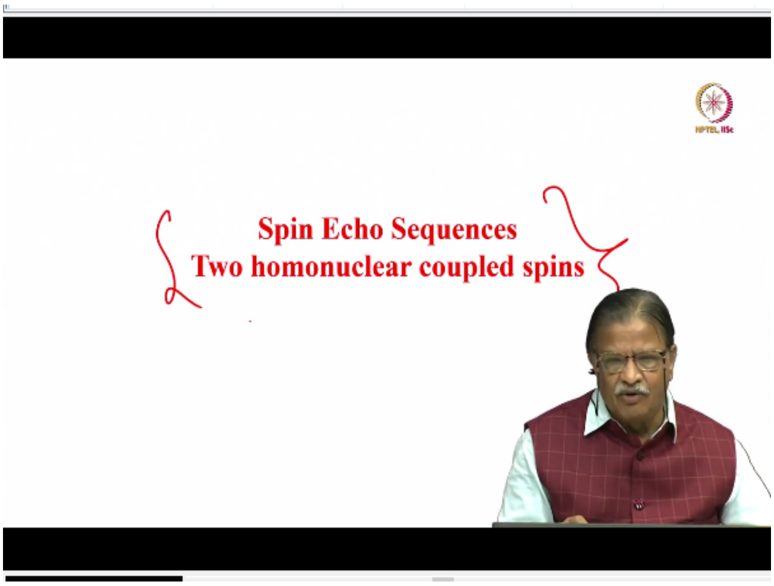

Now, we consider the spin echo sequence. We know the Hamiltonian how to write for homonuclear case, we know how to write the Hamiltonian for the heteronuclear case also; both we know. Now we understand in the earlier case without J coupling, we understood after get refocused in the homonuclear case, we saw that; from – IY the magnetisation went to + IY under spin echo. Now with the J coupling taken into account whether J coupling is refocused or not, we do not know.

We will identify, we will understand that now. Same thing we will do for heteronuclear case also and see how the spin echo sequences play with dominant or really interesting roles in the spin echo sequence, in the homonuclear and heteronuclear case, selectively you can do this type of experiment to refocus particular parameter, chemical shift or J coupling or retains particularly J coupling, like that. So, all those things we can understand. We will understand spin echo sequences, simple example start with a two homonuclear coupled spin.

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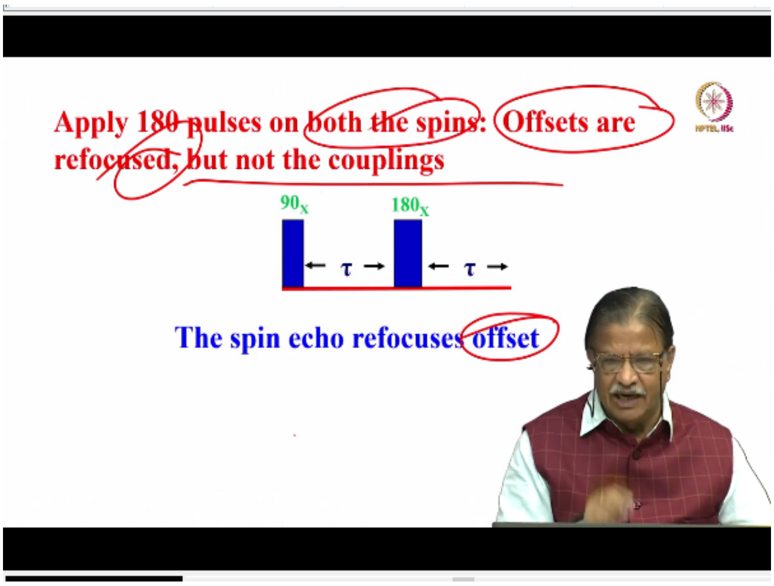

What is the offset? Apply 180 pulse on both the spins; offsets are refocused, but not the coupling. This is one of the important terms. Remember, in the spin echo sequence, I apply 180 pulses and both the spins I and S. Homonuclear case we have only 90 tau 180 tau, that was there. But now in heteronuclear case this is I, I can have S. Here also I can have 180 pulse here, on both I can apply 180 pulse. That is also possible; or I can apply 180 pulse only on this not on this. I apply 180 pulse only on this not on this; all possible combinations you can think of. Now apply both the 180 pulses for I and S spins. Interesting thing what is going to happen here is offsets are refocused, but couplings are not. Very interesting thing. Apply 180 pulse on both the spins I and S, or in our case homonuclear, you can consider 1 and 2. In the homonuclear case we are considering apply 180 pulse on both the spins offsets are refocused, but not the couplings.

This is what we have to understand, this 90 tau 180 tau sequence, for homonuclear case, spin echo refocus the offset, this is the term which everybody uses in the books. Let us understand how it happens.

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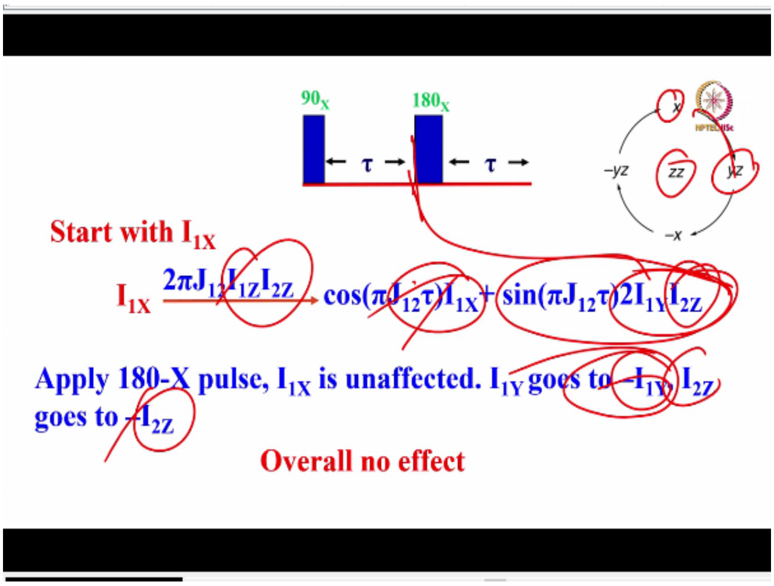

We know it refocuses offset; what about the J coupling we will see. We will start with I 1X. Now, we apply 90 degree pulse and then I 1X we have to see how it is going to evolve under J coupling. This we already discussed; I 1X when it evolves under I 1Z I 2Z it goes to YZ. This is what it is. So, we observe that in-phase magnetization becomes antiphase magnetization, that is what we observed. Now it turns out to be antiphase magnetization and the magnetization will be like this I 1Y I 2Z.

This is when you started with I 1X. This is up to this point, this is up to this point is what happening; 190 pulse plus evolution during tau under offset and J coupling. That is what is happening up to here. Now simultaneously we apply 180 pulse. So, when I apply 180 pulse, I am applying 180 X-pulse, when I apply X-pulse what happens? X does not get affected, rotation about X will not affect at all, will not change, has no effect. So we can ignore this. We have to consider the effect of 180 pulse only on this term, on I IY I 2Z term.

So, what does 180 X-pulse does? I 1X does not get affected, but I 1Y it takes it to - I 1Y. That is what we saw the rotation of various product operators under pi by 2 pulse and pi pulse. We showed in one of the slide in last class or previous to that, we saw that I 1Y with the 180 pulse goes to – I 1Y. Similarly, I 2Z goes to – I 2Z with 180 pulse. So, overall, there is no effect.

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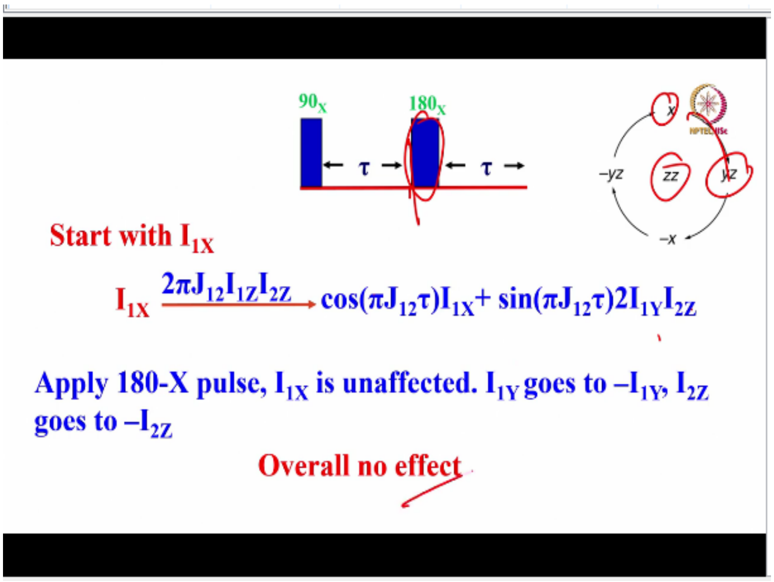

That means what is going to happen. Both the terms are allowed to evolve for another period tau here, after 180 pulse neither this term, I 1X term not I 1Y I 2Z term has no effect at all, because I 1Y beccomes – I 1Y and I 2Z because – I 2Z; minus into minus because plus. So, this term will continue to remain same. Similarly, this term continue to remain same. So, this in-phase term and antiphase term both will not get affected at all by 180 pulse; on homonuclear spins. That is a thing, overall no effect.

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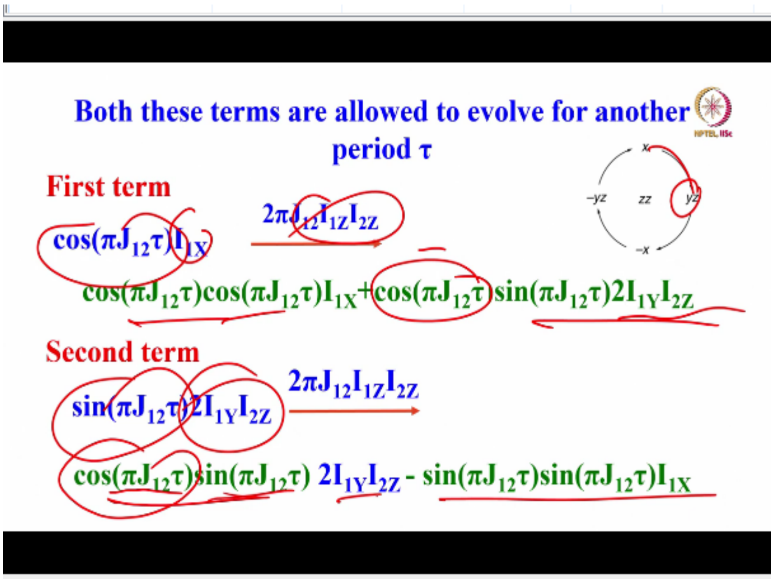

Now, both of them we allow to evolve for a second period tau. Now with a free precession under rotation about Z axis. Let us see, we will consider the evolution undee J coupling now; we are worried about J coupling now. So, during the second period after 180 pulse evolution under J coupling if you consider; the first term we consider that is in-phase term. Now, I 1X is rotated about Z axis, this comes to YZ. So, it becomes I 1Y I 2Z that is fine, everything remains same, cosine of this term remain same and I 1X becomes this. So, we are multiplied these 2 terms. So, this is a common factor but it is multiplied. That is all change, no other change is there. Second term, what is the second term? Second term is sine pi J 12 tau into antiphase term. This again evolves under J Coupling and then this becomes cosine pi J tau sine pi J tau into this one 2 I1Y I 2Z and this term. So, this turns out to be I IY I 2Z, you can find out if it rotates what is going to happen to the J coupling term. So, if you work it out, you will get it. This is nothing but cos pi J tau sine pi J tau into 2 I1Y I 2Z under this.

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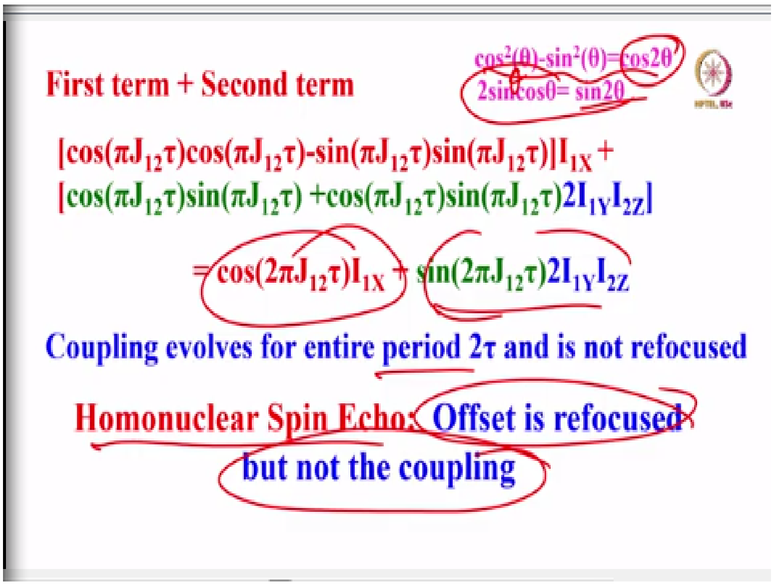

And now we have to consider both first term and the second term together. You have to add up. The first term cosine pi J term evolves under J coupling like this, second term antiphase term under J coupling. This is what happens. First term plus second term together that is our total evolution of magnetization. Now, if I add up these two very interesting thing will happen. I did some jugglery of rearranging the terms.

Then we know that cos square theta - sine square theta = cos 2 theta, 2 sine theta cos theta = sine 2 theta, that is important thing you should know. So, using those three things, we have written like this, this is cosine of 2 pi J tau I 1X + sine 2pi J 12 I 1Y I 2Z. Now coupling evolve for the entire period 2 tau, second period also coupling is there, it has evolved, it has not refocused at all, what does it mean?

In the homonuclear spin echo case the couplings does not evolve as it is not refocused, whereas offsets are refocused. In the homonuclear case important term you remember, offset is refocused but not the coupling, coupling continue to evolve, that is the homonuclear spin echo case.

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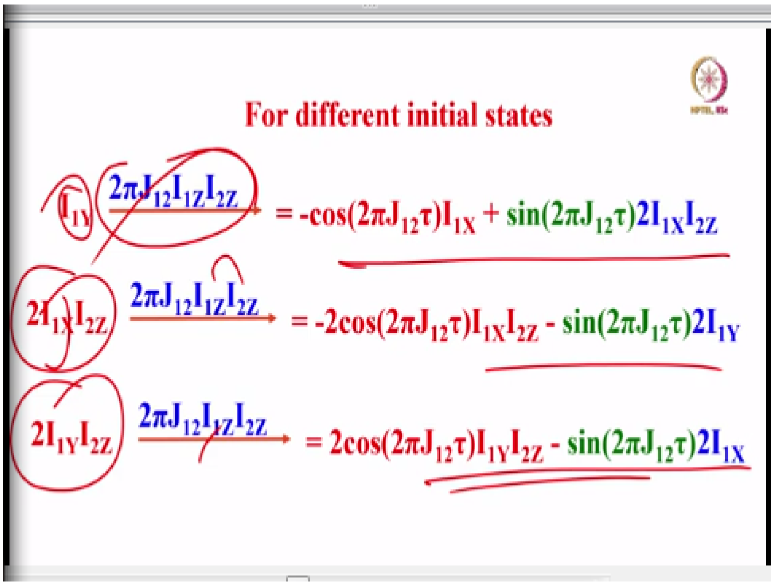

Now you may ask me I started with I 1X, why not I started with I 1Y; or any other product operator term? If I start with I 1Y also, work it out, when it evolves under J coupling this turns out to be like this. That means the J coupling continue to evolve and it will not get refocused. Same way if we consider this term, allow to evolve under J, this what happened.

Take this anti-phase term, allow it to evolve, it is like this. Then you take two in-phase terms I 1X or I 1Y or I 1X I 2Z or I 1Y I 2Z, I am considering spin 1. So, now if you consider this thing evolve under J coupling the term remain same, there is no change at all. So, that means this spin echo whether you start with I 1X or I 1Y; in-phase or anti-phase term, the coupling will not get refocused, only chemical shifts or offset get refocus in the homonuclear case.

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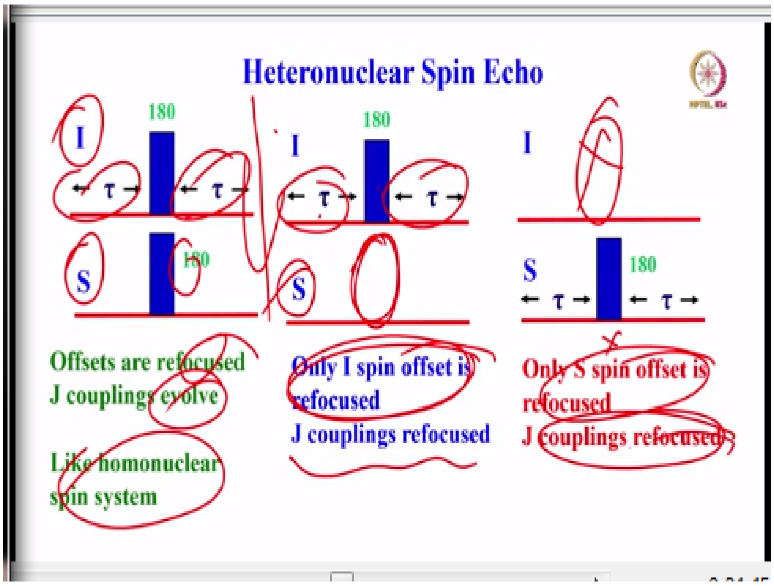

Now we go to the example of a heteronuclear spin case, I am quickly going through because I have to finish faster. If I go to heteronuclear spin case, heteronuclear I consider this I, this is S. Of course, this is the delay between these two, this identical after 180 pulse, before and after. I can apply 180 pulse on S and I also; both proton and X nuclei; simultaneous I can apply 180 pulse during the spin echo sequence.

The very interesting thing when both 180 pulses are applied on I and S spins, offsets are refocused and J coupling evolve, similar to the homonuclear case. In homonuclear spin echo what happens? Offsets are refocused, couplings evolve, exactly similar to homonuclear case if I have a spin echo sequence, 180 pulses are applied on both I and S, offset get refocused, J couplings evolve, ok.

Now go to a situation like this. I have S spin and I am not applying 180 pulse at all. I have echo sequence, tau here, tau here; part of the echo sequence I am taking only 180 pulse I am applying. We are not worried about 90 and all those things, we are interested only in echo part, the tau 180 tau part only we are considering for understanding purpose. Do not be under the impression that is nothing, we are applying only 180 pulse that means we are just inverting the magnetization, we are just applying 180 pulse, no.

It is only a part of the sequence I have chosen. On S spin no 180 pulse at all. Interesting thing, what happens here? Only I spin offset is refocused here. Remember, in the earlier case we observed I spin offset gets refocused in homonuclear case with the 180 pulse. Here also

180 pulse is there in the homonuclear case; similar to homonuclear spin echo, I spin offset gets refocused.

But, interestingly J couplings also refocused; heteronuclear J, not homonuclear J, heteronuclear J coupling is refocused. Now on the other hand, I don't apply 180 pulse on I spin, I apply 180 on S spin. Interestingly, only S spin offset is refocused and J coupling is refocused, very interesting thing you know. Here J coupling evolves, here I spin offset is refocused. Here S spin will evolve, J coupling will refocus. Here S spin offset will get refocused, I spin offset gets evolved, and J coupling gets refocusing in both the cases.

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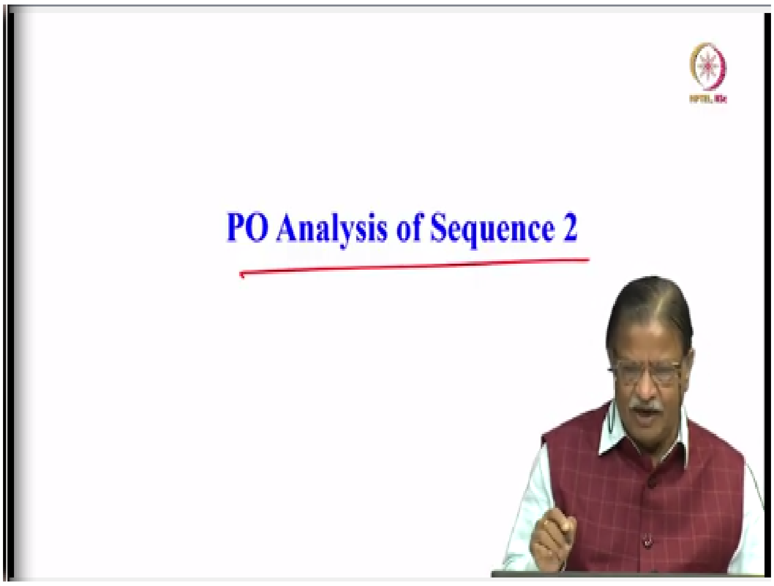

Now we will quickly see the product operator analysis of sequence 2 to understand, that is important. Afterwards, we can generalize this thing for everything and of course each of them systematically you can go step by step, starting with thermal equilibrium magnetization and then apply 180 pulse delay, keep on working out for each term, how it evolves under offset, under J coupling; all the terms. Each term you have to evolve, it is a laborious process. To understand this in a simple way, we will not go into the details.

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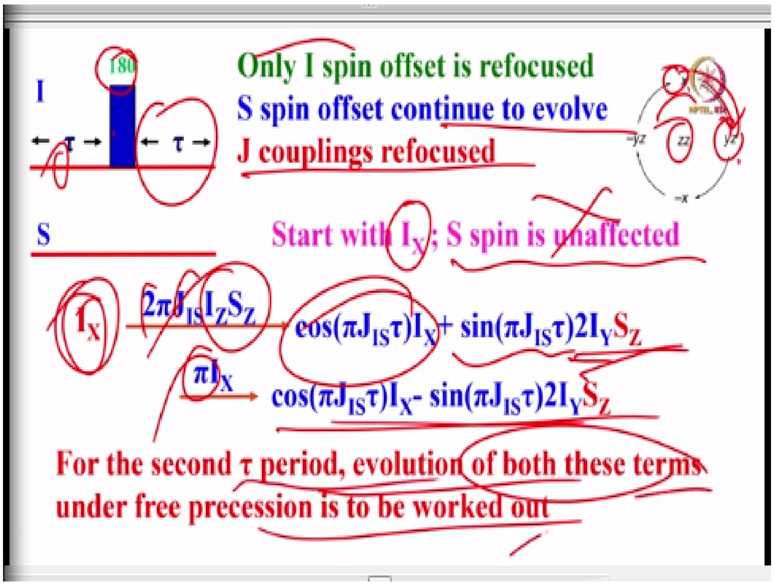

We will consider this sequence, where we are applying only 180 pulse on I spin, what I said? Only I spin offset is refocused, S spin continue to evolve and J coupling gets refocused, there will not be J coupling at all, you understand only S spin will evolve. Now we will start with IX here, what will happen to S spin? I said in the earlier case when spin 1 is considered spin 2 is unaffected, rotation of spin 1 has no bearing on the spin 2, rotation of spin 2 has no effect on spin 1.

So, we start with IX. So, S spin is unaffected, we will not worry about it. Now we go for this rotation diagram. Now IX is rotated under IZ SZ about X axis, when rotated, it turns out to be YZ, it is the direction it goes. So, this is direction of rotation, it is given, arrow is like this. So, X when it is rotated because of J coupling, it becomes YZ.

So, cosine of the original operator plus sine of the second operator, second operator is IY SZ, so that is what happened. In phase magnetization under J coupling evolve into antiphase magnetization. Now this in the arrow notation; and simplifying further you can write like this, there is nothing much has been done, it has been simplified. And for a second period tau evolution of both these terms under free precession has to be worked out.

Now under these things what we have to do is both these terms, we will consider this evolution under free precession during the second period after the 180 pulse. Up to 180 pulse what happens we know, this is the same thing now under pi pulse on X axis what happens is worked out; it is simplified, that is all, nothing much is there. Now for the second period evolution of both these terms under free precession we will work it out.

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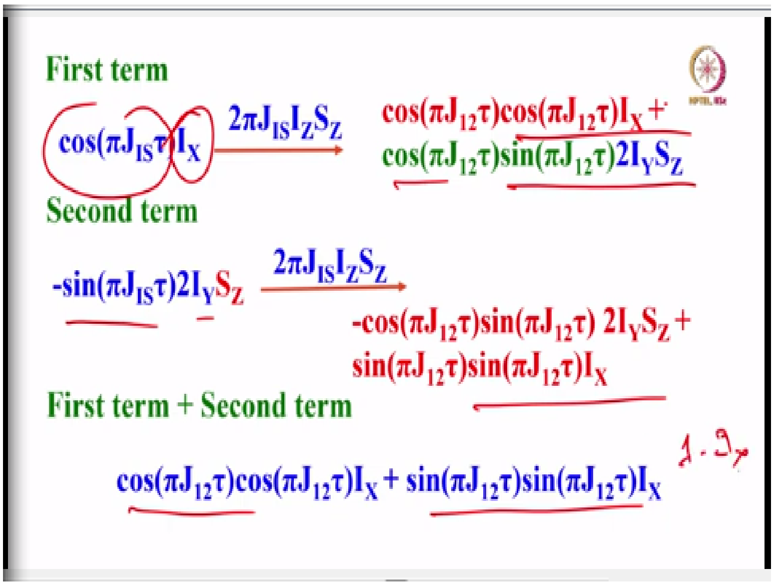

What is the first term? First term is cos pi J tau into IX. If you go by the drawing, you can work it out, this is cos pi J tau into cos this one, cos pi J tau into this one. Of course, this is a common factor we are worried about only IX evolution under IZ SZ, you can see from the diagram IX evolution under IZSZ it become YZ, that is what we are going to get YZ. So, but it is multiplied both the terms together. Second term also now -sine of this one, again when rotated about YZ SZ, it turns out to be this.

Now you have to take the sum of first term and second term together, because finally both the terms how it evolves during second tau period we have to consider. Now you use simple mathematical jugglery, only added up these 2 terms and rearrange something. This is going to be cos squared IX + sine squared IX. What is the meaning of that? You take IX common factor out; this is going to be 1 into IX exactly.

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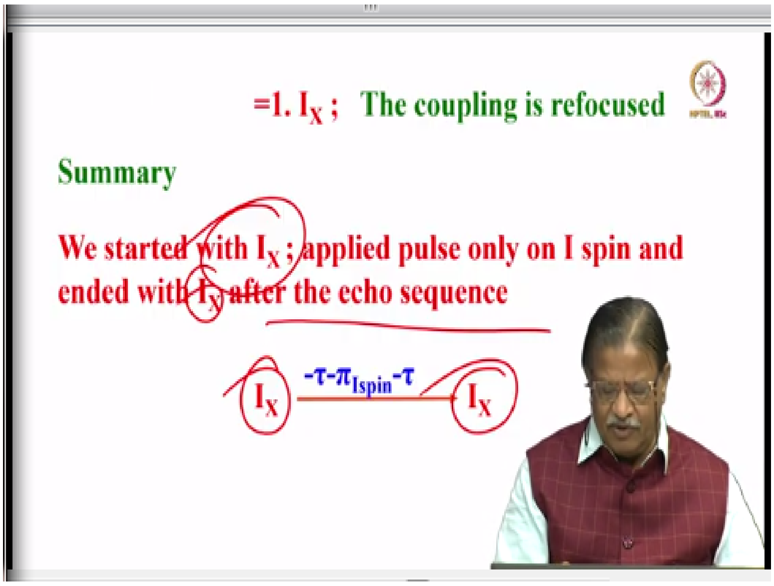

The coupling is refocused, coupling is not there at all, the coupling term is completely gets removed now. That is what I said. In a sequence like this when we wanted to understand only 180 pulse on the I spin, no pulse on the S spin, coupling is refocused. So, summary is we started with an IX spin, applied pulse only an I spin and ended with IX after the echo sequence, no J coupling at all, J coupling is completely refocused.

This is the important point, you please understand; and diagrammatically if you want to represent IX magnetization when it evolves under spin echo remains as IX. No J coupling evolution, only chemical shift. The J coupling is completely refocused here.

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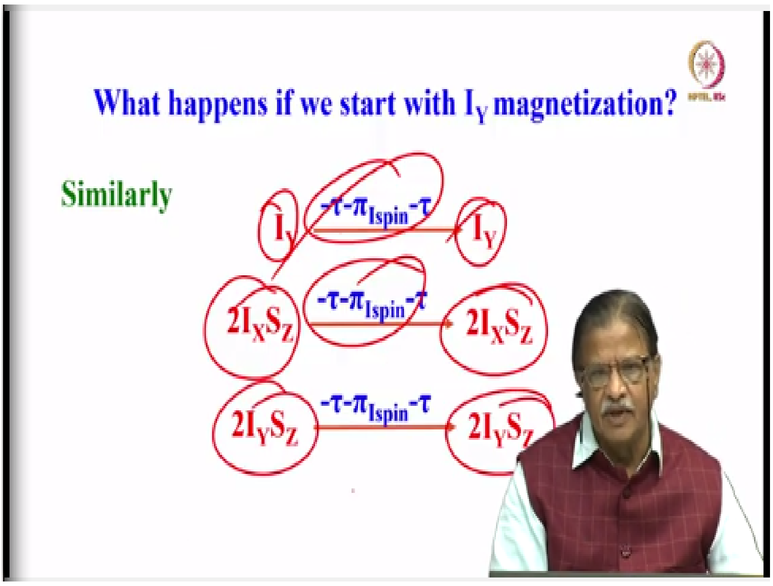

Means no J coupling evolution, this is completely refocused. You may ask me question what happens if we start with IY magnetization it should be same? There is no difference at all.

Similarly you do this for IY evolve under spin echo it remains IY. Start with IX SZ evolve under spin echo it remains IX SZ. Similarly IY SZ start with anti-phase remains anti-phase.

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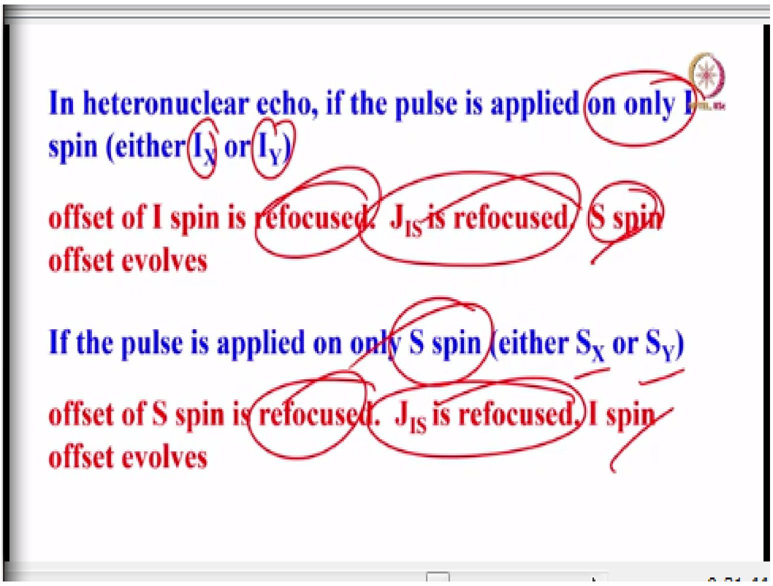

So, in heteronuclear echo when a pulse is applied only on I spin, only one of them, I spin let us say, either IX or IY; you can apply along X-axis or Y-axis, offset of I spin is refocused and J coupling is also refocused, offset is refocused similar to homonuclear case we saw that. Offset is refocused, J coupling is also refocused in heteronuclear case if only pulse is applied on I spin, I spin, chemical shift is refocused, J IS is refocused.

S spin offset what happens? That evolves, you are not touching that; you are disturbing anything. So, S spin offset continuous to evolve. If the pulse is applied only on S spin let us say, either SX pulse or SY pulse, no problem. Offset of S spin is refocused, J is again refocused but I spin offset evolves, simple conclusion. If you apply only 180 pulse, spin echo 180 pulse either on I spin or S spin, no problem. If you apply on only I spin, I spin offset gets refocused, J coupling refocused, but S spin gets unaffected that continues to evolve, that offset evolves.

If we apply on S spin; offset of the S spin gets refocused, J coupling between I and S spins gets refocused whereas I spin continues to evolve. This is what is the case for heteronuclear spin echo. And another interesting thing about heteronuclear case is what is called a coherence transfer, we should understand.

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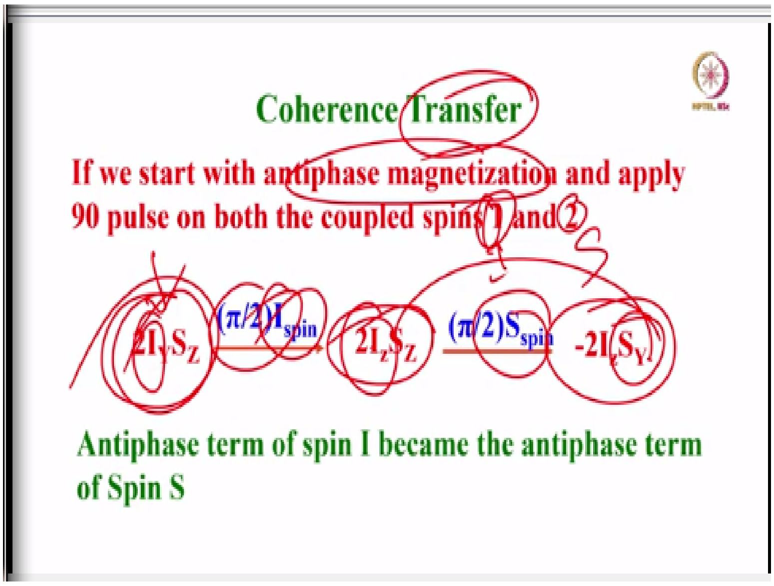

This is what is happening in all the polarization transfer experiments, please understand. This is the where the polarization transfer takes place. If we start with an anti-phase magnetization like this, 2IY SZ and apply 90 pulse on both the coupled spins I and S. Let us say coupled spin 1 and 2 is there or I and S whatever it is, you apply 90 pulse. 2IY SZ it become 2IZ SZ and for S spin also if you apply it will become -2IZ SY, what happened?

Anti-phase term of spin 1 became anti-phase term of spin S. When you apply simultaneously 90 pulses and both the spins, interestingly what happened? Anti-phase term of one spin that is if you consider I spin it gets transferred to S spin. If it is the anti-phase term of S spin, it gets transferred to I spin, the anti-phase term of one gets transferred to others spin, this is what is called coherence transfer; when you apply simultaneously 90 pulse on both coupled spins.

I consider spin I and spin S, now this is anti-phase term of Y; spin I anti-phase term is taken. Now apply 90 pulse on that, it goes to IZ, apply 90 pulse on S spin; it will become SY. So, IY become IZ here, it remains IZ it become -SZ because of 180 pulse whereas I spin here became SZ became S spin. And then IY become IZ here, so what is going to happen is the anti-phase term of spin 1 became anti-phase term of spin S by applying 90 degree pulses simultaneously on both the spins.

This is what is called coherence transfer, this is very important and it does happen in most of the cases, whenever you are doing the polarization transfer experiment. We discuss about INEPT earlier you know, polarization transfer INEPT sequence, DEPT sequence like that. In all these polarization transfer sequences it always happens. And the J coupling term is the one which creates anti-phase magnetization and that is the one which is responsible for coherence transfer between the coupled spins.

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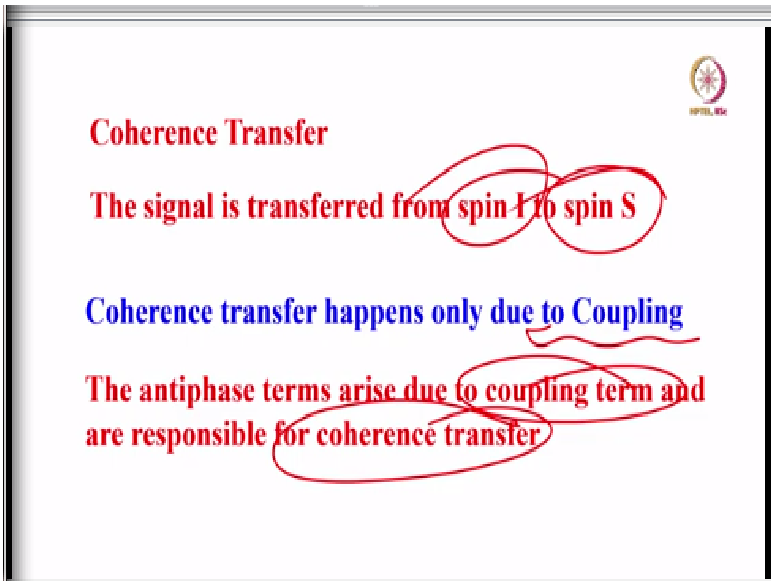

So, now coherence transfer what happens is the signal is transferred from spin I to spin S. Coherence transfer happen only due to coupling, please remember. Coherence transfer happens only due to coupling not because of chemical shift. And anti-phase terms arise due to coupling term and is responsible for the coherence transfer. In-phase term is not responsible for coherence transfer, only anti-phase term is responsible for coherence transfer and it happens; it occurs only due to coupling. In such a case the signal from I spin gets transferred to S spin or vice versa, this is called coherence transfer.

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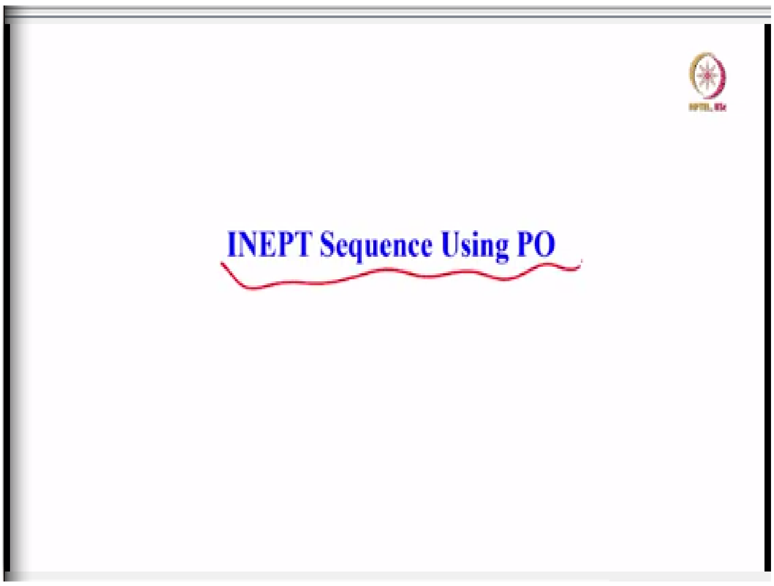

The common experiment which is adapted in most of the polarization ttransfer sequences. Let us look at a simple INEPT sequence using product operators.

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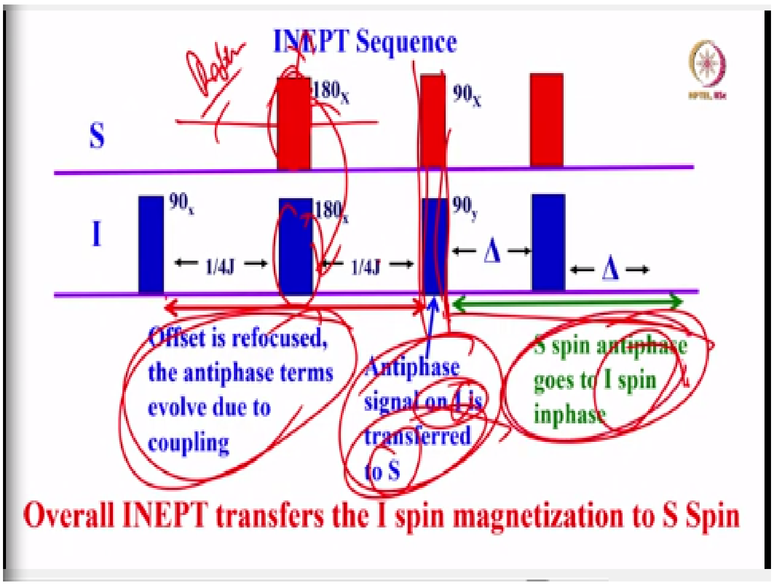

Of course we do not need to do the detailed analysis because spin echo sequence is understood. Up to this we have already discussed. What happens to this spin echo for 1 spin when you apply 90 tau, 180 tau sequence. This is called refocused INEPT, not INEPT it is called refocused INEPT, up to this is INEPT. So, now up to this you consider, you apply 90 pulse simultaneously, this is INEPT.

So, now the INEPT sequence what is happening is upto this offset is refocused, anti-phase term evolve due to coupling, that is what we observed; spin echo term this what happens. And when you apply two 90 pulses simultaneously on both of them, then anti-phase term of let us say I get transferred to S, apply 90 pulse on both S spin and I spin, then anti-phase term of I gets transferred to S.

It could be other way also, it can be anti-phase term of S gets transferred to I spin. And then of course this is for the refocusing INEPT. Here S spin anti-phase goes back to I spin, this is another experiment, this is for refocusing, called a refocused INEPT used for various purposes which we discuss in the earlier class itself. So, up to this what is important you understand? INEPT sequence is like this, here your applied 90 tau, two 180 pulse on both I and S spin and give a tau delay, here offset is refocused, anti-phase term will evolve due to coupling.

When you apply simultaneously two 90 pulses on both I spin and S spin the anti-phase signal of I gets transferred to S spin. So, there is a polarization transfer taking place. For various purposes in refocusing INEPT we bring it back to I spin for detection. So, this is the overall concept of INEPT. In INEPT what we do? We allow the coupling to evolve under spin echo sequence. This can happen only when you apply 180 pulse on both the spins. We saw that if we apply only 180 pulse on one of them, if I apply only on this, J coupling and offset of this gets refocused, only this will evolve, offset of this will evolve. When we apply only on this J coupling is refocused only offset of this will evolve. See we observed that. But only when we apply 180 pulse simultaneously on both I spin and S spin, then we observed that J coupling will evolve, anti-phase term will be there. And then the anti-phase term on I spin gets transferred to S spin. And then finally we will transfer it back then start detecting the signal. So, this is the coherence transfer experiment which I wanted to tell you. Please remember this diagram you should always remember. Here only thing you what J coupling will evolve when you apply both on both this, if you apply only here then J coupling get refocused, S spin offset is refocused. If you apply here I spin offset is refocused, J coupling is refocused. So, this is the sequence which is commonly adopted for INEPT sequences. So, I wanted to tell you how anti-phase magnetization term is very important in getting the polarization transfer taking place between one spin to other spin in heteronuclear case. It is very important concept in all the polarization transfer experiments.

With this I am going to stop here and we discussed a lot about product operators and how to understand the concepts and everything. And we took several examples of homonuclear case, spin echo where you found out what happened to the J coupling and chemical shifts, how it gets refocused. And similarly heteronuclear case what happens if you 180 pulse on one of them or on both these spins.

So, all these examples we took and very simple, by using product operators you can understand that in-phase term becomrd anti-phase exactly at 1 over 2J and when to apply simultaneously 90 pulses on both the spins there is a transfer of spin polarization from one spin to another spin. Anti-phase of 1 gets transferred to anti-phase of the other spin. So, these are all the common experiments we can understand very easily by product operators.

I did not take example for the 2D experiment about analysis of product operators, I have not talked about 2D that is why I am keeping quiet. Maybe when I introduce 2D in next class, I will start discussing about 2D. At that time if there is a time we will understand how in COSY the cross peaks and diagonal peaks come, we can understand by using product operators. So, I stop here, at least from the next class we will go to different topic called 2 dimensional NMR, thank you very much.