Advanced NMR Techniques in Solution and Solid-State

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Module-42
Productor Operator Analysis of Pulse Sequences
Lecture-42

Welcome back all of you. In the last class or last 2 classes we started discussing about product operators and how we can utilize to understand the pulse sequences. I told you it is one of the ways to understand pulse sequences and it is based on density operator theory. It is a density operator and we wanted to know how this will evolving in a given pulse sequence and this is defined as rho of 0 and rho of t, rho of 0 is initial density operator and rho of t is the density operator at a time t.

And if you want to evaluate rho of t it is given as e to the power of -iH of T rho of 0 e to the power of iH of t, where H is the Hamiltonian and rho 0 is initial density operator. And for working out these things, of course I also discussed a lot about these things, there are some norms which are followed; what happened to the product operators, rotations like when there is a pi by 2 pulse which is acting an IX, IY, IZ operators, how it will undergo rotation. All those things we discussed.

And then we came to a general conclusion, there are certain set rules; for example I gave you a table where we said what happens if there is rotation of magnetization by applying a pulse on a particular axis, how to evaluate that? So, in this connection, we also understood what is the free precession and what is the Hamiltonian for the pulse, when it is applied on X-axis or Y-axis.

We said when the pulse is applied along the X axis, I said IX is the Hamiltonian, IX is for the rotation along the X axis and IY is for rotation about Y axis; and for free precession Hamiltonian we said it is omega t of IZ. Omega t is nothing but the offset or in other words you have a chemical shift. We also worked out free precession Hamiltonian. And the another important thing we concluded was, in a given pulse sequence, the evolution of the density operator depends upon the time ordering of the pulse sequences.

You have to go in a sequence from the pulse delay and another pulse delay like tha,t the way the pulses sequence is designed, has to be followed. And I said when we apply radio frequency pulse RF pulse; the chemical shift and couplings can be ignored. At that time, you can imagine as if they are switched off. And then you find the effect of RF pulse on spins. If I have let us say 2 spins, you can consider these RF pulses as a cascade of 2 pulses, applied independently on spin 1 and spin 2; that is the way you could evaluate.

And during the delay there is a free precession. The free precession is always the rotation about Z axis, that is what I said. And during this free precession, there is always evolution of chemical shifts and couplings, if any. And these things can be evaluated in any order, it is immaterial. You can take the evaluation of first spin that is a free precession evolution, then chemical shift or J coupling, any other order does not matter. So, this is what we discussed. And I said the rotation is generally given by an expression. All the rotations are in 3 dimension.

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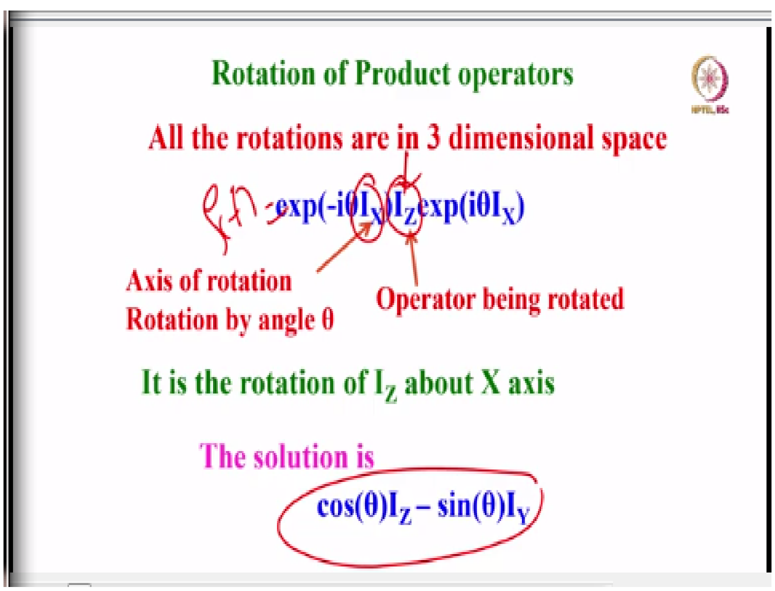

Now we will start with this. I want to discuss the product operators today, we will continue further with this. If I take the rotation of product operators, all the rotations are always defined in 3 dimensional space; that is what we should understand. And this is given by the simple expression, which we have been discussing; for example, now this is the operator IZ and this axis of rotation.

See when an equation of this type is given, you should always understand one thing. When an equation of this thing is given, this is the axis of rotation, what is there in the exponential term is an axis of rotation. And this is the density operator, that is being rotated, this one. This is a convention, you remember when we want to evaluate rho of t which is equal to this thing, of course, IZ = rho 0, this is given by exponential -i theta IX into IZ into exponential I theta IX. Here IZ is the operator being rotated and IX is the axis of rotation by an angle theta because theta is given.

Theta can be any angle, pi by 2 or anything that we can decide. But we have chosen theta some angle. So, rotation by angle theta about X axis for the operator IZ is given by this expression. So, conventionally you should understand it is a rotation of IZ about X axis. And for this solution, we have worked out from the table which was shown earlier. For this type of solution there is a trignometrical identity, about 7 or 8 identities I gave you. And using that you have to understand this solution for this equation is cosine of theta into IZ -sine of theta into IY, this is solution for this rotation of IZ about X axis.

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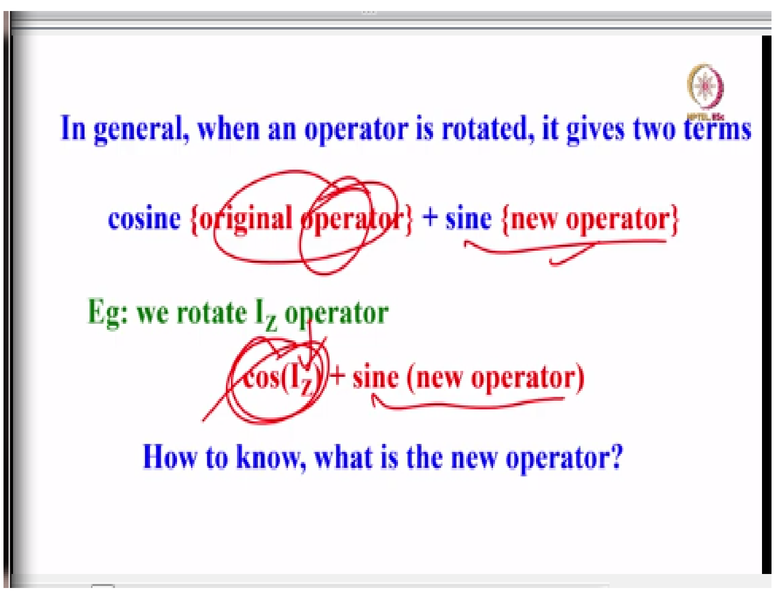

So, in general, if you say when an operator is rotated it always gives 2 terms, you should understand. Now if remember here I rotated IZ about X axis, I got 2 times, cosine of IZ and sine of IY. Remember one thing what is IZ. IZ is the previous operator, original operator. After I rotated that, I got a new operator IY. So, generally what happens is when an operator is rotated, it gives 2 terms. One is the cosine of the original operator plus sine of the new operator. What is this new operator? We can find out from the table, solution was given.

For example, I want to rotate IZ operator then what I am going to get? Cosine of IZ + sine of a new operator; that is what we got in the previous this thing, which I showed you when IZ was rotated about IX. So, this is general formula; in any rotation of an product operator, if you consider, you always get 2 terms about any axis we rotate. One is the cosine of the original operator and second the sine of the new operator. Now you may ask me the question correct, I know what is the old operator, I know cosine of the old operator what about the new operator, how do I know what is the new operator, how do I know?

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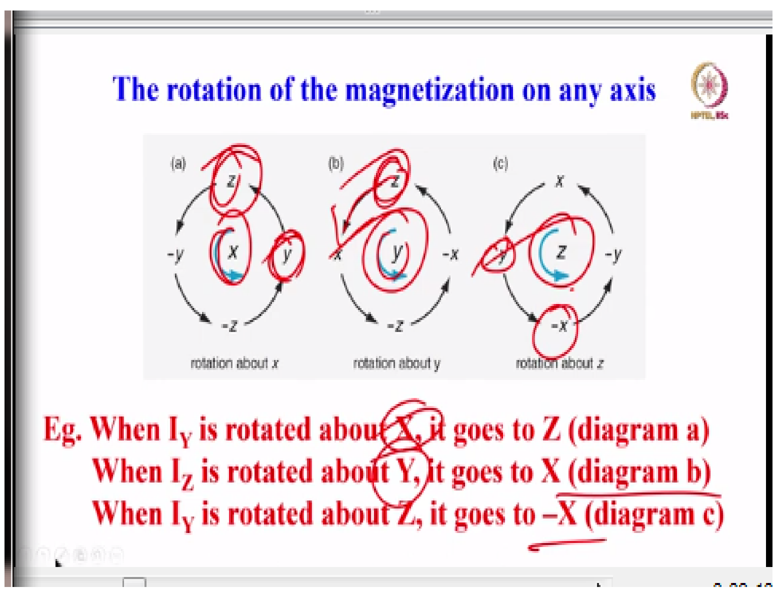

So, there is a way to understand this. This is a figure which is given by a James Keeler in his book, it is very interesting, fantastic book and fantastic way to understand, atleast once you should read this. The rotation of the magnetization on any given axis is given simply by these 3 pictures, which is a, b and c, these are the 3 pictures. This is about the rotation of the X axis, rotation about Y axis, and rotation about Z axis. How do you interpret this? I will take this one.

For example, I am going to consider a situation, where now IY is rotated about X axis. From this I understand now I am rotating about X axis. What is the product operator I am rotating? Y. So, Y when is rotated about X axis, it goes to Z, that is it. You see from this diagram, you can easily understand. So, what is my new operator? Old operator is Z, rotated about X axis it goes to Y, that is exactly what we got; cosine of IZ - sine of IY, that is what we got in the previous expression.

Take for example here rotation about Y axis, I am going to rotate IZ let us say, I am going to rotate IZ about Y axis. When I rotate IZ about Y axis, now you look at this is axis, this is arrow which is going from Z to X. About Y axis when I rotate IZ, it goes to X. This is what the diagram says. Now we go to the rotation of the Z axis, when IY is rotated about Z axis what happens, what is IY here? This one. IY when is rotated about Z axis it goes to -X. So, this is a very simple diagram, you must remember this. With this we can understand rotation of any product operator about any of the three X, Y and Z axis. So let me repeat please understand, if I have to rotate Y operator about X axis it goes to Z, simple. So, this is a diagram you have to understand.

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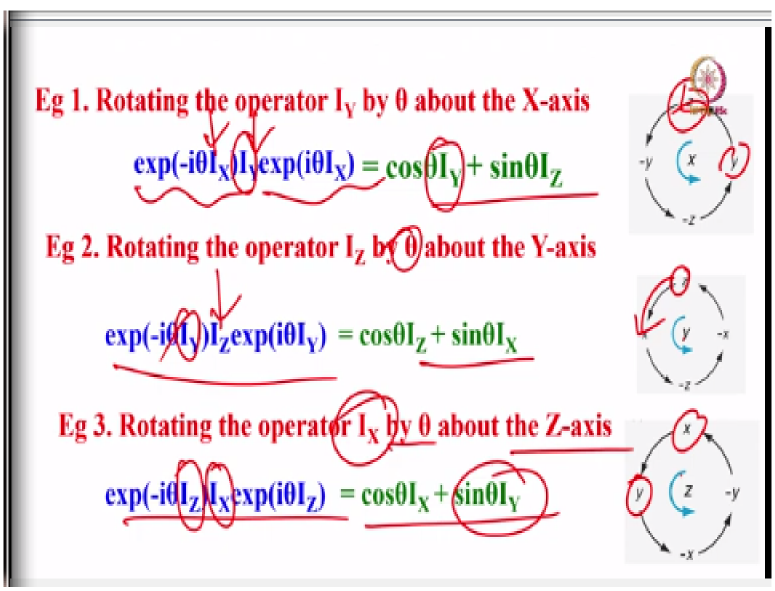

Now we take some examples, 1 or 2, rotating the operator IY by theta about an axis. How much do you rotate? You can rotate by 90 degree, 180 degree or any angle theta, does not matter. So, now a general formula is exponential i theta of IX into IY into exponential of i theta IX; if I consider this expression, what does it mean? It means the IY operator is rotated about the X axis.

So, I use this formula, IY is rotated about X axis, I must go to Z. So, use this thing for general formula which I gave you, cosine of the old operator IY and the sine of the new operator is IZ; that is what you are going to get. So, very easy, now you do not have to work out in detail. Thanks for the people who have already worked out and the stalwarts have already made our life simple by defining these things using trignometrical identities.

So, now let us understand rotating the operator IZ by theta about Y axis. Now this is the expression for that, I am rotating the operator IZ about IY. Now what is that? Rotating IZ about IY, it should go to X; so what is my solution? Cosine of the original operator IZ + sine of IX, see this is what you are going to get, that is a solution.

Similarly, now rotation about Z axis we took another example rotating operator IX by theta about the Z axis and this is the expression for it. I am rotating IX about Z axis and this is what it is and when I rotate IX, I will go to IY, exactly what is happening; the cosine of theta into IX which is the old operator + sine of IY the new operator, this is what you get. Simple if you remember these 3 diagrams you can work out the rotation of any product operator, on any 3 axis, not only one particular axis you can also go the other way clockwise, anti-clockwise, everything you can understand. So, now that is the solution for that.

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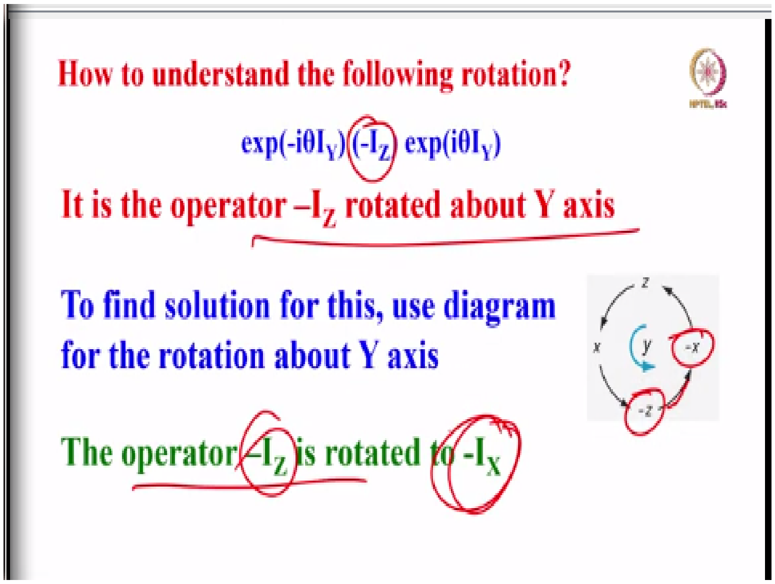

Now if I give you this thing, how do you understand the following rotation? The following rotation is -IZ is rotated about Y axis. That means you have to consider -IZ is rotated about Y axis, so this is the direction of rotation it goes to -X. To find the solution for this one, now the rotation of IZ is taking to -IX.

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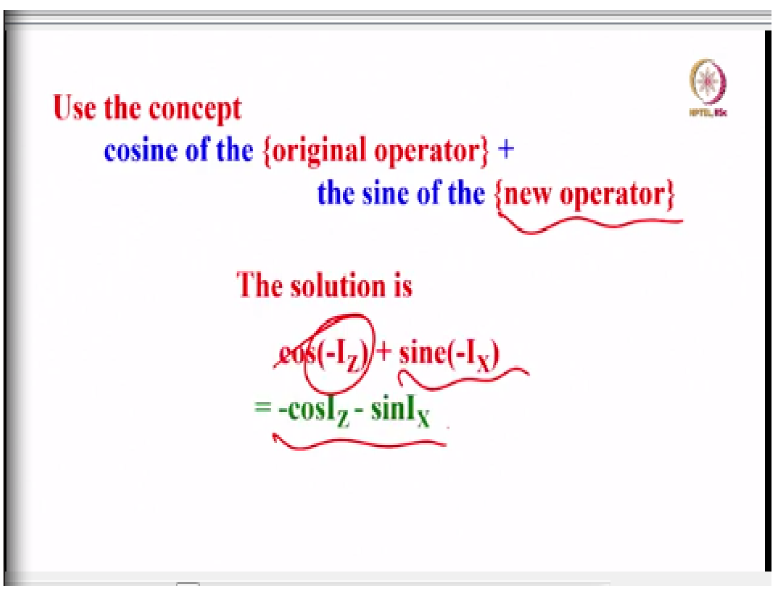

Again use the concept cosine of the original operator plus sine of the new operator; it is the general expression to understand the rotation of any product operator. Now what is the solution? Cosine of -IZ + sine of -IX. What is sine of -IX it is nothing but minus of sine IX. So, this is the final solution, the solution for the expression which I gave you. How do you understand, that is this one, this is rotation of -IZ about IX.

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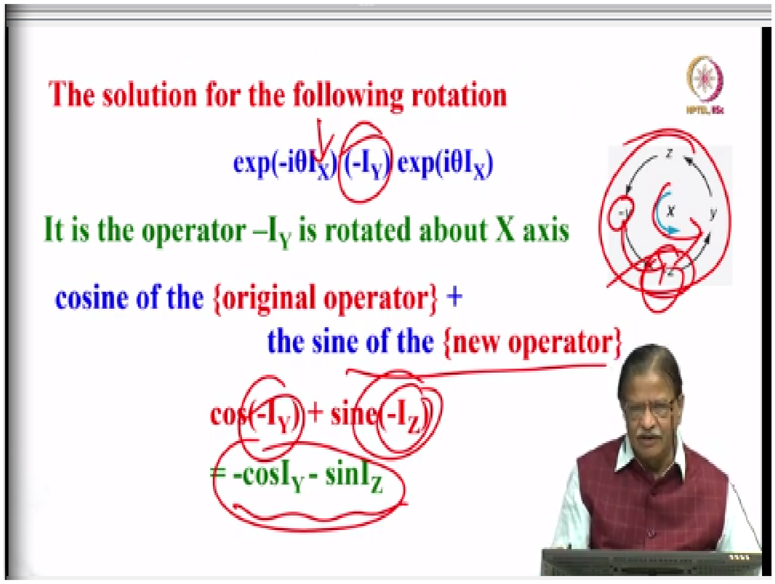

So, now the solution for the following equation if I want to get it, just give you another example. I want to get a solution for this, how do you get the solution for this? What is the operator being rotated - IY, correct. About which axis you are rotating? You are rotating about X axis. So, this is the operator -IY rotated about X axis. Now this is a diagram you have to use; now this is axis of rotation in this direction.

Now -IY when you rotate in this direction goes to -Z. So, cosine of original operator + sine of the new operator. Again adopt the same formula. Now cosine of -IY, the original operator and new operator is -IZ, so the sine of -IZ = minus of sine IZ, so this is the solution. The solution for the following equation is rotation of -IY about X axis is turning out to be minus of cosine IY minus of sine IZ.

Of course, we can define the angle theta and everything. In principle, you can write cosine of theta and all those things, I should have written clearly cosine of theta here. So, that clearly you can understand I wrote cosine of minus sign it is angle theta is also there.

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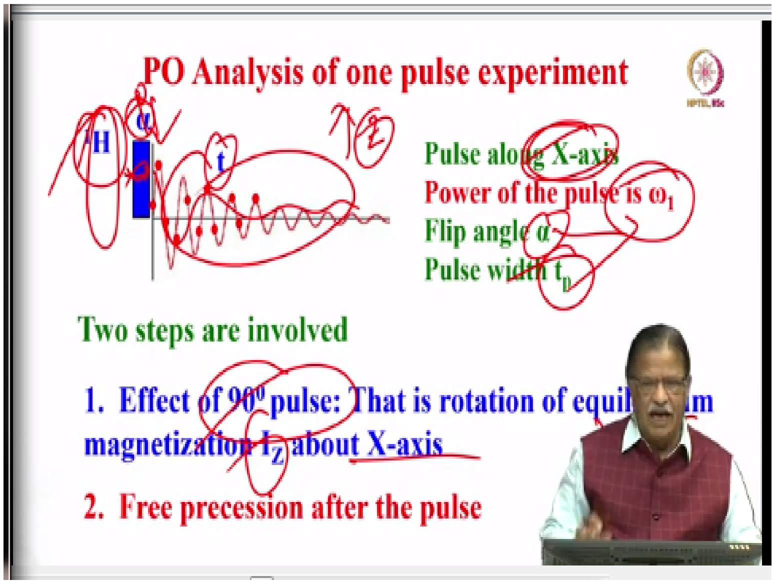

Now PO analysis of one pulse experiment we will do. What is the product operator analysis of the one pulse experiment? What is the one pulse experiment? We have been discussing that, just send the RF pulse and then start acquiring the signal, that is all, it is a simple conventional one pulse experiment, which is commonly adapted in any NMR, one dimension experiment.

This is what it is, I am going to apply a pulse of an angle alpha or theta whatever it is and then FID is going to be collected like this. FID is collected for a time t and this is on proton channel, I am collecting the 1H signal. So, the pulse is along the X axis, power of the pulse is omega 1, flip angle of the pulse is alpha, alpha can be any angle it could be any angle of up to 90 or 180 also you can utilize whatever angle you want, you can define it.

And pulse width this tp, tp is the pulse width, this width is tp. There are 2 steps are involved in analyzing this using product operators. What are the 2 steps? First thing effect of 90 pulse, of course, you are applying the pulse; you have to understand the effect of 90 pulse on this. What is 90 pulse? Now the thermal magnetization initially is along Z-axis, so it is a rotation of the equilibrium magnetization IZ about X axis, you are applying a X pulse, that is what I said.

You are applying pulses along X axis, that means you are rotating Z magnetization about X axis. That means IZ is rotated about X axis, what is your expression? Rho of t if you want to write, e to the power of -i X theta into iX rho of 0, rho of 0 is nothing but IZ into e to the power of iH t, H is again IX, so this is what the expression. Now what is the solution for this, we will work it out?

So, first thing is effect the RF pulse, rotation of equilibrium magnetization IZ about X axis. After that what happens during this time? It is a free precession time, nothing is happening, no pulse is there but still the spins are undergoing precession; it is a free precession after the pulse, what is free precession? It is rotation about Z axis. We also discuss the free precession Hamiltonian; it is omega of IZ, what is omega? It is offset or in other words offset in the rotating frame or you can say as the chemical shift.

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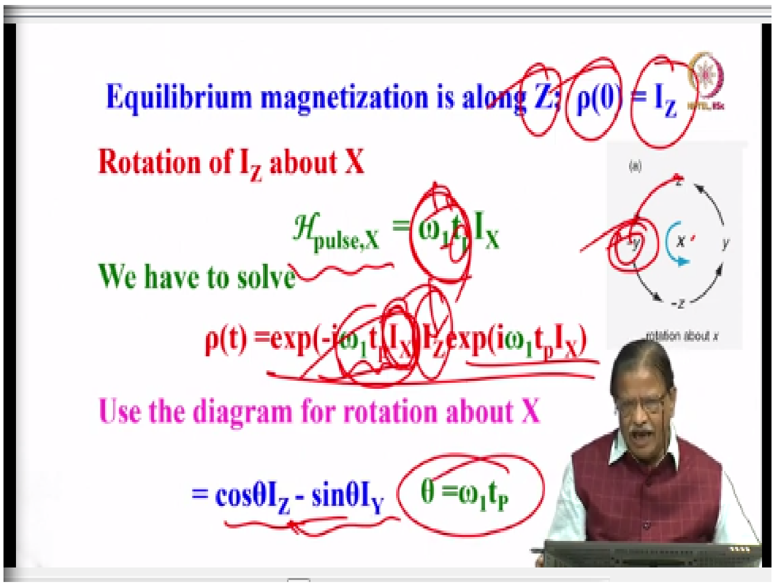

So, now with this we will work it out using product operator formalism, how we can understand this one pulse experiment? Equilibrium magnetization is along Z axis, so the rho of 0, initial magnetization, the initial product operator is IZ. Now I am rotating about X axis, because I am applying an X-pulse. So, Z is rotated about X it should go to -Y. So, my solution, we will work it out, H pulse, Hamiltonian of the pulse along X axis is given by omega of tp into IX omega into tp is the RF power.

You see omega 1 into a pulse width is the power, it defines the power of the pulse. So, now we have to solve this expression. This is the Hamiltonian; exponential e to the power of -iH of t is nothing but, what is this one? Omega into t1 into IX or tp into IX; that is Hamiltonian which we have to find out; that is the Hamiltonian for the pulse which are applying on an X axis. And IZ is the thermal magnetization which you are rotating. Of course, this is the general expression. It is a general expression which we have been discussing for getting the density operator at any time t. So, we started with the initial density operator IZ which is rho 0, rotated about X axis with an RF power omega 1 into tp applied along the X axis, this is the Hamiltonian for that.

So, now we have to use this diagram, what is a solution for it? Cosine of original operator is IZ and the new operator is, if you will go by this, -Y, so new operator is IY. So, we are rotating by an angle theta, IZ magnetization, the solution is cosine of theta of IZ - sine theta of IY, this is. So, now put the value of theta as omega 1 into t p, it could be any angle.

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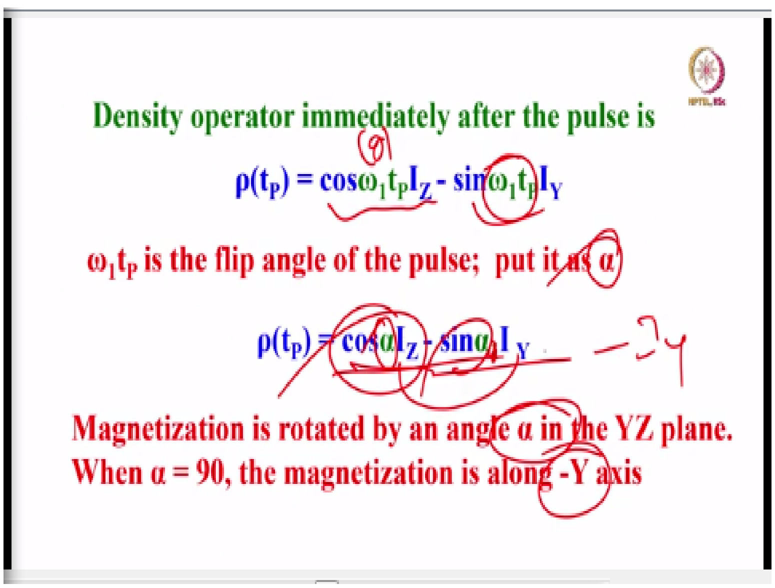

You can work it out, how much you have tilted the magnetization from equilibrium value. So, the density operator now we got it, immediately after the pulse is cosine of omega 1 tp into IZ, this is what I said, theta we could add it to omega 1 tp into IZ - sine of IY where theta = omega 1 into tp, which we have worked out. Omega 1 tp is the flip angle of the pulse; now let us say it is alpha. It is cosine of alpha into IZ - sine alpha into IY. This is what is the solution for it, rho of tp when you apply pulse width tp along X axis, this is a solution, cosine of alpha IZ - sine of alpha IY. What do you understand from this? Magnetization is rotated by an angle alpha in the YZ plane; that is what it is happening.

Now we are in the YZ plane, to apply a pulse along X axis we are tilting the magnetization to YZ plane. Put alpha = 90 degree here, what is happening? When alpha = 90, this is 0, that means this is 1, so this will become minus of IY. It means, when you are applying an 90 degree pulse along X axis, the Z magnetization has shifted to -Y axis. This is what we have been understanding from our right hand thumb rule right from the beginning. So, this is what you can understand a simple one pulse experiment using product operator.

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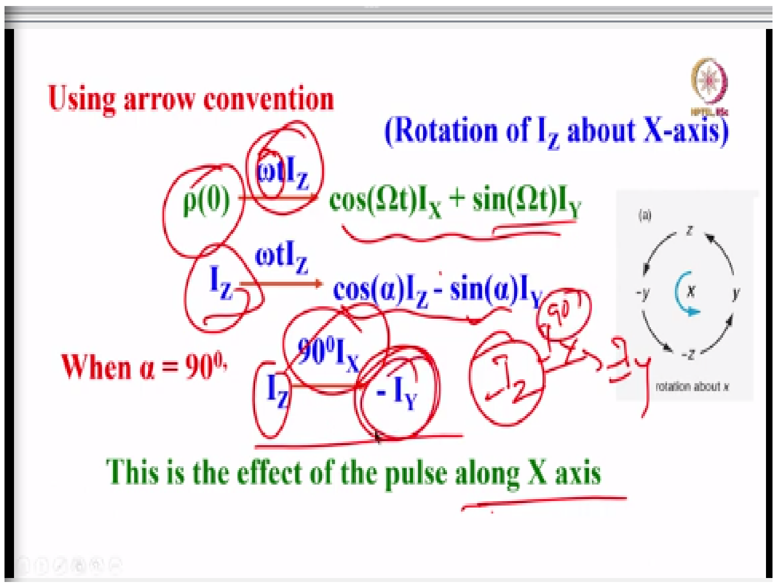

The same thing of course we can represent by a convention by using an arrow. So, what it means is rho of 0 is the initial density operator, that is rotated along IZ axis, omega tp is the pulse width. And then the solution for this is gamma of t into IX + sine of omega t into IY. It is a rotation of IZ about X axis. Now what we wrote as this is rho 0 = IZ omega t into IZ, this is the solution we got, cosine of alpha into IZ - sine of alpha into IY is the solution.

When alpha = 90, we said IZ magnetization, when you apply an 90 degree IX pulse it goes to -IY, that is what it simply means. We always use the arrow representation in future, remember if I say IZ and here I write IX 90 degree, 90 degree IX pulse is applying on IZ and we are going to get -IY, that is what the convention is. So, instead of writing the exponential e to the power of -i H of t e into rho of 0 e to the power of +i H of t, all those things, this the easiest way of representing by an arrow, this is called arrow convention.

We can generally adapt this most of the time, this is the effect of the pulse on the X axis, you understood now. Effect of the RF pulse on the X axis is given by this, in a special case on alpha = 90 degree is -IY, that is it. But that is not the end of it, what will happen next? What is going to happen next is, after the magnetization is brought to XY plane by applying an 90 degree pulse along X axis, the magnetization undergo precession, free precession is there.

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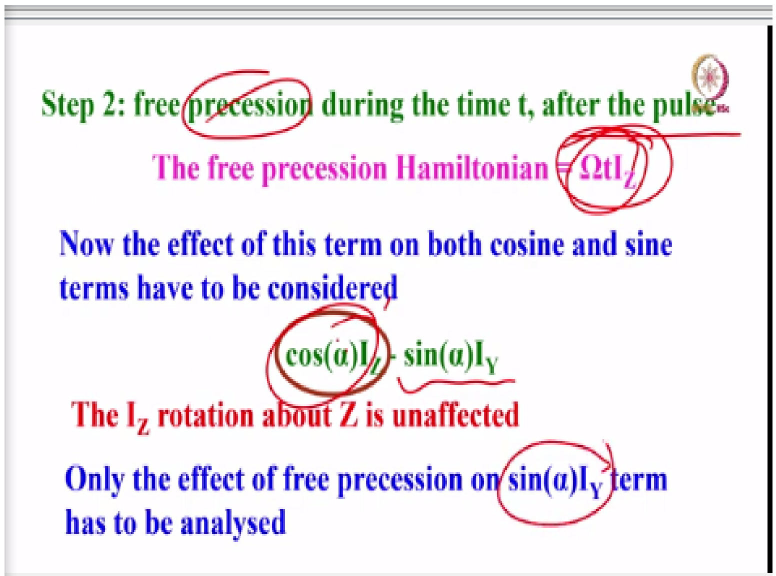

The free precession is along Z axis that is the step 2. You have to understand for analysis further, there is a free precession during the time t when you are acquiring the signal after the pulse, the free precession is about Z axis. So, this is the Hamiltonian for a free precession about Z axis, which we have been discussing right from the beginning. Now the effect of this term on both cosine and sine terms have to be considered, because after the pulse you have created 2 terms, cosine term and sine term.

Now for the free precession we have to evaluate for both the terms, together. And good part of it I told you individually you can evaluate each of these terms. Now what we will do is, first consider the rotation of IZ about Z. Remember, I have been telling you rotation of the density operator IZ about Z axis has no effect. Similarly, IX about X axis, IY about Y axis has no effect. As a consequence rotation IZ about Z axis, this term gets unaffected.

So, we have to evaluate only this term - sine alpha into IY under free precession, what is going to happen? How this term will evolve under free precession, we have to analyze this. We will do that. So, this will keep it as such, because that is getting unaffected, we will evaluate only sine alpha into IY term.

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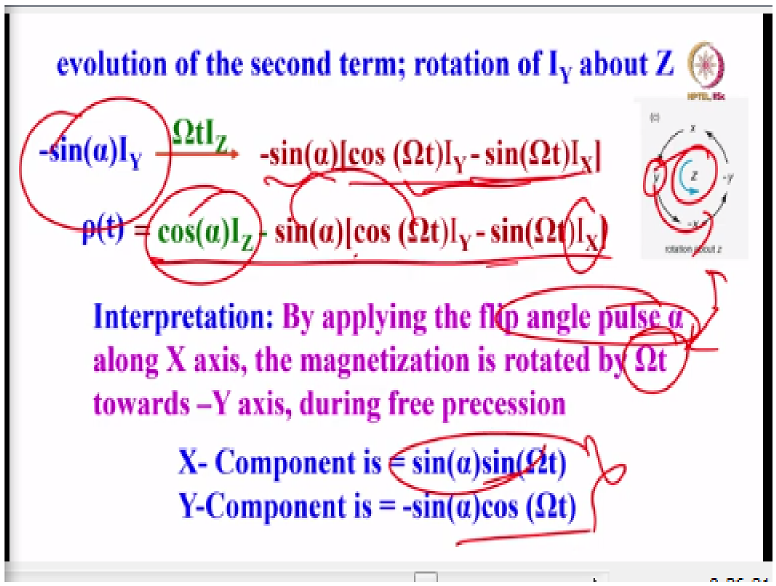

So, how does this evolution term come? Now this is a rotation about Z axis and the magnetization is IY. Now product operator is IY here but rotation, the free precession is about Z axis. So, now we know that your rotation about Z axis you consider and magnetization IY, Y is rotated and it goes to -X. Exactly without going into the details, we can simply write minus of sine alpha of IY, you can write it as minus sine alpha into cosine omega of t into IY - sine omega t into IX, because it is going to -IX, so this is what the term we are going to get.

So, now rho of t in principle, you have to bring the original term which did not get affected IZ rotation about Z axis this will not get affected, but you cannot ignore that. Now you have to bring it back, though during free precession there is no effect on this; but for calculation of final rho t we have to include that. So, we are bringing back rho of t cosine of alpha into IZ - sine of this term; this the solution rho t which you are going to get, final product operator during free precession.

What you understand by this? If you simply understand by applying a flip angle pulse of alpha degree along the X axis, you have brought the magnetization from Z axis towards -Y axis and then during free precession it started fanning out. It has developed oscillatory cosine and sine components, magnetization which was along Z axis by applying the X pulse you brought towards -Y axis. As time evolves, as a function of time it generated cosine and sine components, that is X and Y components.

So, X component of this is you can find out, it is nothing but sine alpha into sine omega t and Y component is sine alpha into cos omega t; that is the X component and this is Y component. So, simply what you have done? You applied a 90 degree pulse along X axis, brought the IZ magnetization to Y axis and we have generated 2 terms. And now we have the evolution during the free precession; only IY term.

And then what is happening? You generated again IX and IY terms, it essentially means by applying any flip angle pulse along an X axis, you rotated the magnetization by omega t, omega is the offset and then that is towards Y axis; during free precession it developed 2 components X component and Y component which are fanning out, that is the interpretation of this.

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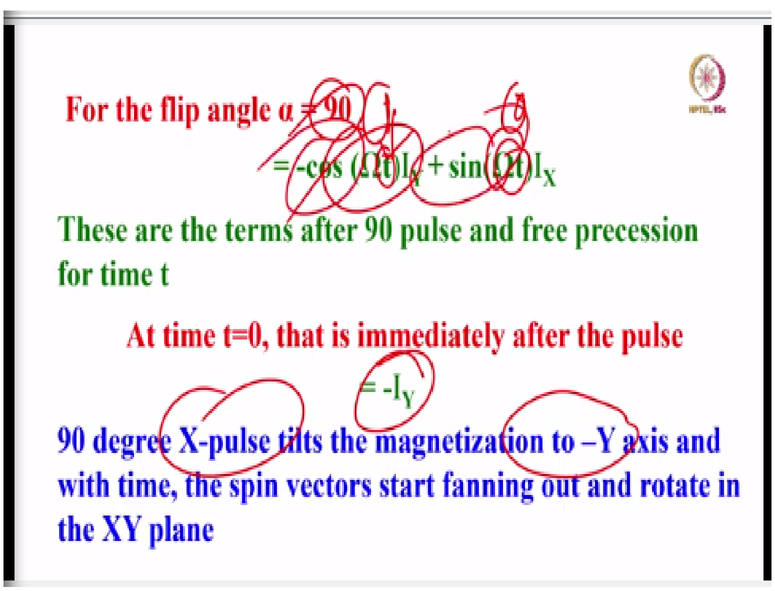

So, now let us see what happens if I put the flip angle as 90 degree? These are the terms after 90 pulse and free precession for time, at time t = 0. If I put flip angle as 90 degree, then what is going to happen? First term goes to 0. Then at time t = 0, this is 0, and this is 1, this is 0. So, you are going to get minus of IY. That is immediately after the application of the pulse, immediately at time t = 0 you have brought the magnetization to -Y axis with 90 degree pulse. And for any theta degree pulse it was towards -Y axis but not exactly an Y axis, it had other components. Now exact 90 degree pulse the pulse along X-axis brought the magnetization -Y axis. But as a function of time what is happening? It is generating cosine and sine components in the XY plane, it is fanning out that is what it means.

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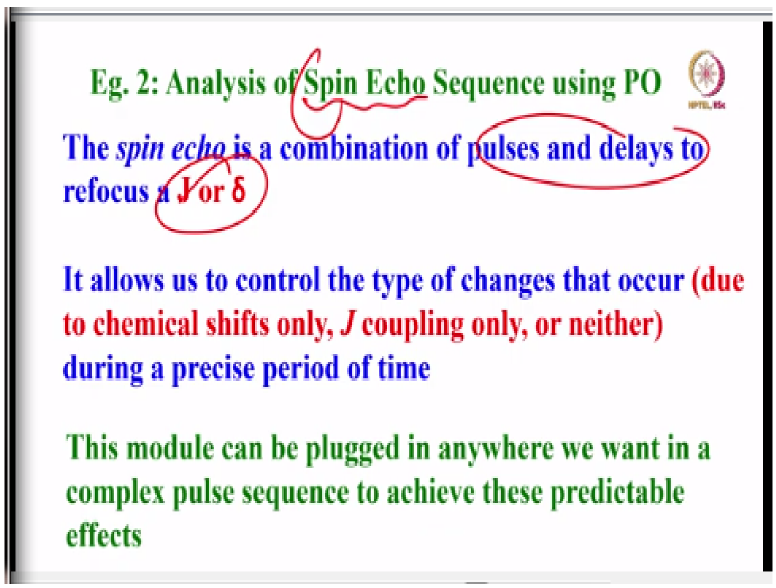

Now we will understand one more important sequence which we come across in most of the NMR pulse sequences; that is called a spin echo sequence. We discussed this spin echo and many applications especially when I was discussing about the polarization transfer techniques, enhancement techniques, we discussed these things. And not only in this course, but in the previous course also we discussed a lot about spin echo.

What is the spin echo? Just for the sake of people who have not taken the previous course, attending this course first time. It is a combination of pulses and delays to ensure to refocus only J coupling or delta. That means this pulse spin echo sequence enables me to control the parameter in such a way I can make sure that only chemical shifts evolve or J coupling evolve after the echo period.

That means the echo period if I precisely define; using spin echo I can control the type of change that I want either, I want only chemical shift evolution or only J coupling evolution. And the interesting thing this module is introduced in lots of experiments, it can be plugged in variety of experiments in complex pulse sequences, so that we can get the predictable results, whatever you want we can get it.

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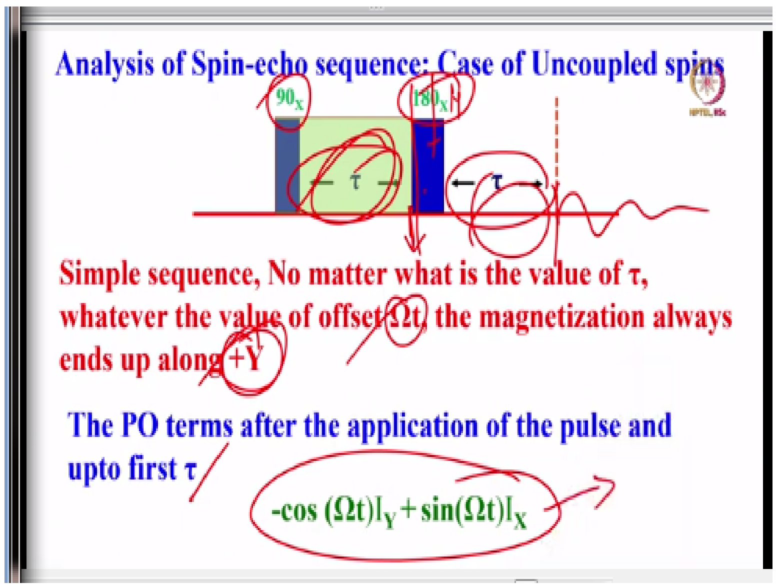

So, using that idea we will analyze the spin echo sequence for a case of uncoupled spins. We have not still introduced J coupling because J coupling means that we have to introduce the lot number of product operators, right now we are considering a single spin, no J coupling and we are ignoring relaxation. So, we consider only 3 product operators IX, IY and IZ and then we worked out various examples.

So, it still considered case of uncouple spins, no coupling at all. So, you can still deal with the only product operator IX, IY and IZ, we do not have to bring in the coupling term. This is a sequence used for spin echo. It consists of an 90 degree X pulse with a tau delay immediately after the pulse and then apply 180 X-pulse you can apply Y also, there is no problem. I have taken X here; and then give equal amount of delay and then start collecting the signal, this sequence is called spin echo sequence.

And up to this we have already understood; that is the one pulse experiment, effect of 90 pulse and the effect of free precession we understood, that it created cosine and sine component, that is what we discussed. So, up to this we know. So, what we have to analyze for the product operators for this sequence? Whatever the term we got up to this we can take that and then see the effect of 180 pulse on that and then effect of that for the another delay, second free precession. And then see what we are going to get.

If analyze that we will come to know what is that is going to happen for the magnetization during the spin echo sequence. No matter whatever the pulse sequence, however the simple sequence you take, whatever maybe the tau value you take ,and whatever value of the chemical shift offset you take omega t; the magnetization always ends up +Y in this case. Because to apply a 90 degree X-pulse; brought the magnetization into -Y axis. Up to this, we know what happened, it is fanning out into cosine and sine components.

By application of 180 degree pulse you are refocusing them in such a way the magnetization vectors, all the spin vectors come back and then reassemble along another axis; that axis is +Y. So, from -IY it goes to +IY; they would always end up in this +Y axis, this is called spin echo sequence, this is called spin echo. So, PO term up to this first sequence and first tau is known. Now this is the solution for that we have got. Now effect of this 180 pulse and these 2 terms we have to understand.

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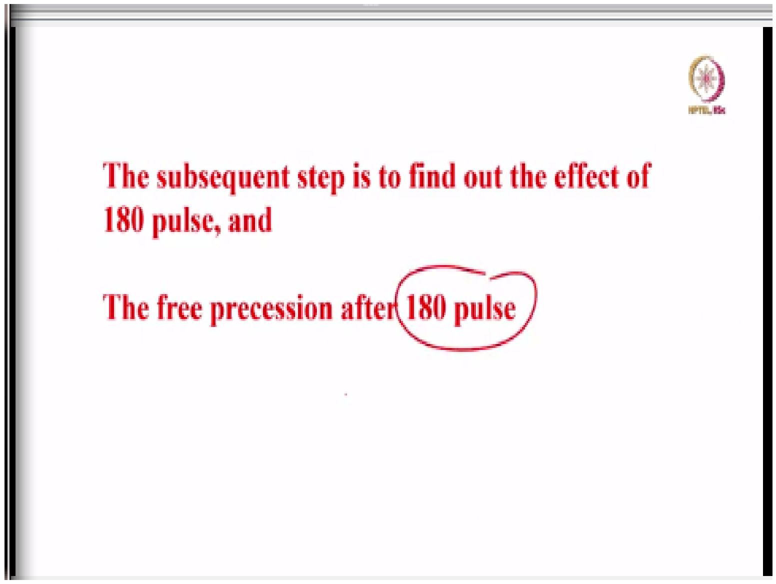

If you understand that we will know what happens with 180 pulse and subsequently during the free precession. So, since now the time is getting up, what I am going to do is I will stop here. In the next class we will see the effect of 180 pulse on this signal up to plus tau what is the evolution of the magnetization cosine and sine components we know. And then apply 180 pulse on that see the effect of that and also the further free precession second tau period and see the how the echo comes.

So, that part we will do later, so as in this class we started discussing about the product operators right from the last 1 or 2 classes we discuss a lot. And we wanted to understand and general formula we know about the rotation of any operator about any axis. It was diagrammatically given over rotation about X axis, Y axis and Z axis. And then generally if I am rotating an operator about a particular axis, the solution will be of the type cosine of the old operator plus + sine of the new operator, that is what you are going to get.

What is this new operator? Depending upon the axis of rotation from the three diagrams which I shown, you can find out what is the new operator and this is a general solution for any rotation of any product operator in any axis for any angle also. So, we took the simple example of a one pulse sequence. One pulse sequence, we have 90 degree pulse applied along X-axis and then we started collecting the signal.

Now 90 degree pulse when it is applied on the X-axis, what is the effect of that? We understood, it brings the magnetization to -IY; exactly it is going to 90 pulse. And then during the free precession there is rotation about Z axis, we found out it generates cosine and sine components oscillatory components it generates ,and spin vectors start fanning out. And then we wanted to extend this further, for extending further we wanted to see how we can understand this spin echo sequence using product operators.

So, up to this we have come and we have spin echo sequence is nothing but a 90 pulse applied along X-axis, give a time delay tau, apply another 180 pulse, either along X-axis or Y-axis, give equal delay and then start collecting the signal. During this echo what happens? The magnetization which was brought to -Y, axis -IY will go back to +IY during the echo sequence. Again, so we have up to first tau we know how the magnetization evolves. The effect of 180 pulse and the subsequent free precession, what happens, we will understand in the next class. So, I am going to stop here, we will discuss this further in the next class, thank you very much.