Advanced NMR Techniques in Solution and Solid-State

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Module-41
Product Operator Analysis
Lecture-41

Welcome back all of you, in the last class we started discussing about the product operator formalism. It is an approach we use to understand the behaviour of the magnetization, how the magnetization is evolving at different time periods of a given pulse sequence. So, for this we started introducing what is product operator and I said it is based on the density operator theory.

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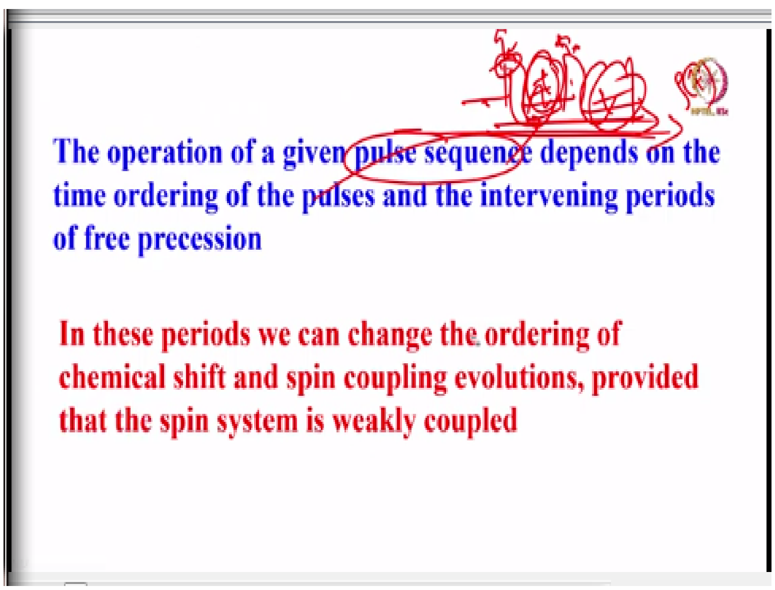

And it is given by rho of t at any given instant of time t. And when I know rho of t, I know how the magnetization is evolving. The rho is nothing but a combination of IX, IY and IZ, 3 components of the angular momentum operator. It is a combination and also because of the coefficients are also there, rho of t at any given instant of time t is given by aX of t into IX + aY of t into IY+ aZ of t into IZ; it is a linear combination of these things. aX, aY and aZ are just the coefficients; they are just the numbers. It defines the amount of IX, IY and IZ which is present for the rho t when you calculate. And this you know we correlated directly; it is nothing but aX of t is nothing but MX of t. Similarly MY of t = AY of t and MZ of t = AZ of t. That is what I said. And I said if I know rho of 0 that is the initial state of the density operator, then I can find out what is the density operator at the time t. For that we have to follow certain norms. And I also said that everything in NMR we can treat as rotations, I take a simple pulse sequence.

Apply a radio frequency pulse. The pulse is a rotation and do not do anything after the pulse keep quiet, there is a free precession and the free precession is a rotation. The chemical shifts evolve in a delay, so delay is a free precession. And during the delay, of course, chemical shifts can evolve, that is a rotation, couplings can evolve that is the rotation. All these things can be treated as rotations for analyzing the pulse sequence. So, I gave an expression rho of t if I want to find out at any given instant of time t = e to the power of -i H of t where H is the Hamiltonian, t is time into rho of 0 into e to the power of i Hamilton H into t.

So, what it means is we have to construct a Hamiltonian. If I know the Hamiltonian, if I know rho 0 I can calculate rho of t. And I said if I apply a pulse along x axis, it is the rotation about X axis. If I apply a pulse about y axis it is a rotation about Y axis, similarly applying pulse along about z axis is the rotation about Z axis or if you do not do anything, the free precession is the rotation about Z axis.

And I also said for the Hamiltonian that if you apply a pulse along X axis Hamiltonian can be written as IX. And if you apply RF pulse of power omega 1; the Hamiltonian for the X-pulse is nothing but I said omega 1 into IX, omega 1 is in the offset or the chemical shift. Similarly for IY it is your omega1 into I Y, Hamiltonian is omega 1 into IY. For free precession Hamiltonian omega is equal to we said IZ into omega 1, omega into IZ, omega is again the offset, this is what we understood.

So, we will go further and see how magnetization can evolve, how we can understand the product operators to find out the evolution of magnetization in different time periods of the sequence. First you must understand, now it can be continuing further here. The operation of any given pulse sequence depends upon the time ordering of the pulses and the intervening periods of free precession, that is very important.

Suppose if I have a true pulse sequence and there is a time delay here, time delay here and apply 90 pulse here and a 90 pulse here. First I have to see what happens to the density operator, what are the rotations that is happening by application of 90 pulse, whether it is X-pulse or Y-pulse and during this delay how the magnetization is evolving, what is happening to the free precession, whether the chemical shift is evolving or J-coupling is evolving, etcetera.

Then you have to go, you cannot go in the random order, it is a time ordering. But one important thing I want to say is during the intervening period between these, for example during this delay if I want to find out how the chemical shift is changing, how it is evolving or how spin coupling is evolving? That can be interchanged, you can work out first chemical shift evolution and then J coupling evolution, no problem.

But the time ordering of the pulse sequences have to be maintained between each of these blocks. Then we can work it out, the evolution of chemical shift, couplings everything can be interchanged, and you can work out independently. It can be free precession, J couplings or chemical shift in any order you can do, in this given block. But the entire sequence the way in which you are operating should remain same.

You cannot start first here and then come back here, You should start from a sequence, but within this period for example when you apply here, in this period whether J coupling evolves you take first or chemical shift evolution you take first, does not matter; that order is immaterial. But sequence of the pulses the time ordering has to be maintained; that is very important.

So, this is what I just wanted to tell you, with this idea life becomes very simple for us, so that we can start understanding what is happening. And you can do this only when this spin system is weakly coupled. As I said initially itself product operator formalism is applicable to weakly coupled spin system, so it does not matter here. So, it is always weakly coupled, so it does not matter whether you take chemical shift or coupling evolution first or second.

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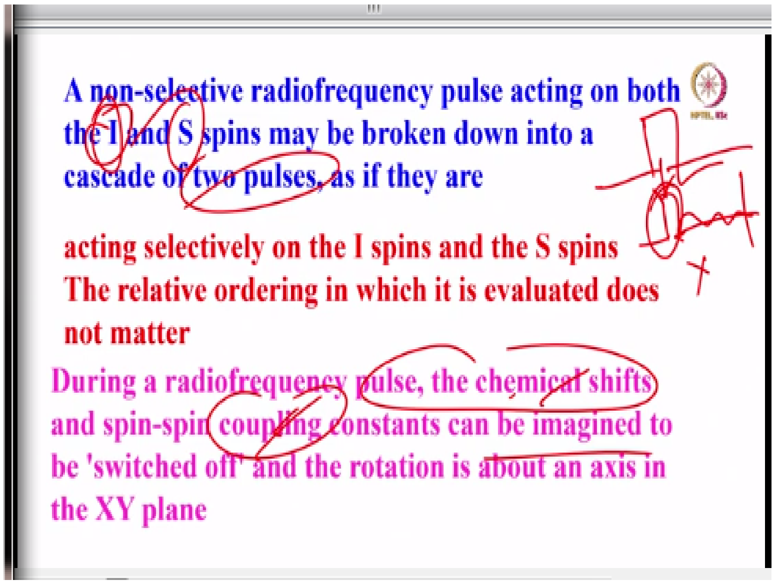

Another interesting thing you should understand; if I am applying a non-selective radiofrequency pulse, hard pulse. Hard pulse for a given system, let us I have two spins, I and S, which are coupled or not coupled, no problem, let us say they are coupled. If I take two spins which are coupled, I and S, then I can break this into 2 cascades of pulses. As if I am applying the pulse selectively once on I spin and once on S spin system.

So, it does not matter, I can break it into 2 operations that means the effect of the pulse on I spin can be evaluated individually and the effect of the pulse on the S spin can be evaluated individually. So, I can break down into a cascade of 2 pulses; and this can be independently acting on I spin and S spin. Then how do you evaluate whether I spin first or S spin first? Does not matter, ordering does not matter, that is immaterial.

But it can be broken into as if there are cascade of 2 pulses one on I spin and one on S spin. And during the radiofrequency pulse the chemical shifts, coupling constant everything you can assume to be switched off. That means you are applying RF pulse then you are not talking about chemical shift and coupling evolution. That you consider as if it is switched off nothing is happening to that. And you have to treat only about the rotation about a particular axis. That means I am applying RF pulse and then delay and collect the signal. As when you are applying the RF pulse all you have to worry about is rotation about a particular axis in which you are applying the pulse, X-pulse or Y-pulse; and the rotation about the plane we have to consider, that is all. During that time do not worry about, chemical shift or spin coupling constant. They can be assumed to be switched off or not right now you can imagine to be not there.

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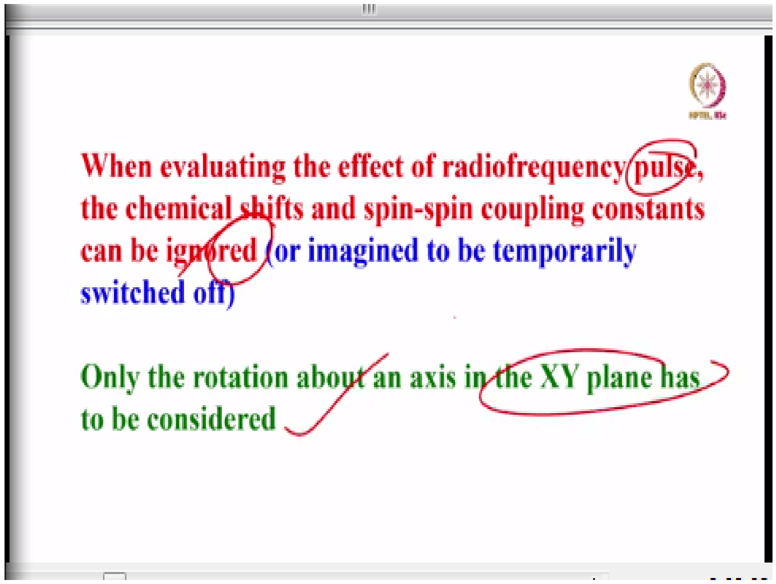

So, when we are evaluating the effect of radio frequency pulse, that means you can ignore, temporarily you can think of as it is switched off. And only the rotation of XY plane has to be considered; that is what I wanted to repeat.

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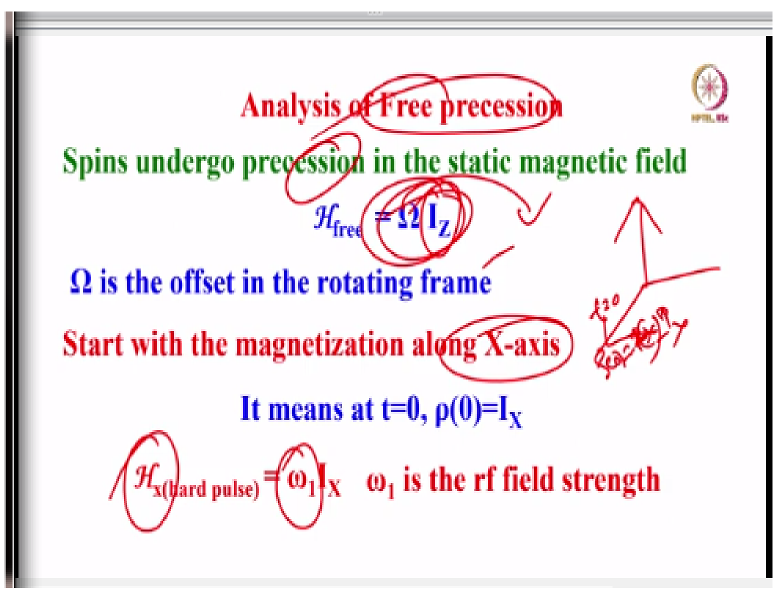

Now with this knowledge what we gained, let us understand or analyze what happens or how the magnetization evolves under free precision. What is free precision? during a delay. Just give a delay and there is a rotation going on about Z axis, spins are undergoing rotation about Z axis. Now let us see when the magnetization is along Z axis, rotation is along Z axis, how we can understand the evolution of the magnetization in the sequence?

Now the spins undergo precession in a static magnetic field. Simply put the sample in a magnetic field, spins undergo precession. What is that precession? It is free precession, and the rotation is about Z axis as I said omega is the offset, that is the chemical shift about Z axis and IZ is the operator for that, ok. Now omega is offset I said, start with the magnetization along Z axis; initially you have put the sample there is a free precession Hamiltonian, which is omega in to IZ.

Now start with the magnetization along X-axis, assume now magnetization is along X-axis, ok. So, that means you have brought the magnetization to X-axis somehow. That means, at time t = 0 we have only IX. The rho 0 = IX is my initial Hamilton, beginning Hamiltonian; rho 0 = IX. And let us say I am applying a hard pulse along X, hard pulse I said, as I said omega 1 is the rf power and the X pulse Hamiltonian can be written as omega 1 into I of X, omega 1 is the rf field strength.

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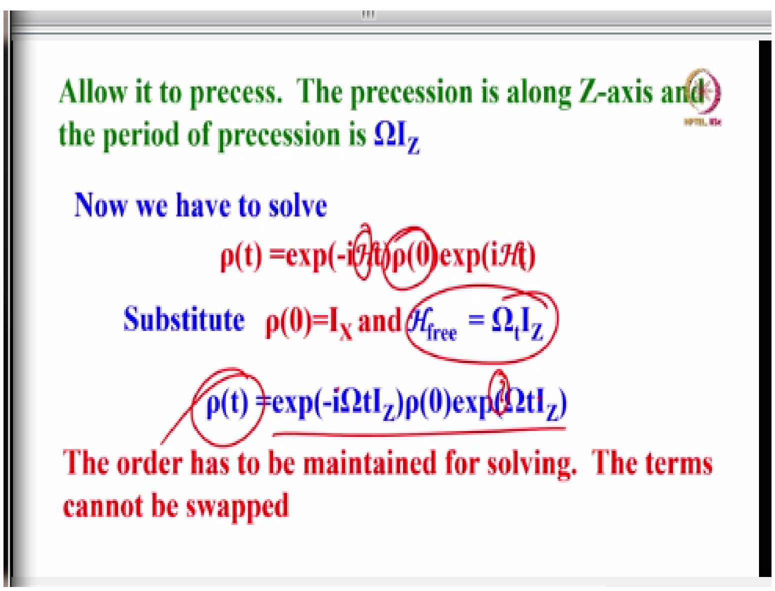

So, with this idea, let us see what is going to happen. Allow the spins to precess. As I told you the precession is along Z axis for which Hamiltonian is omega 1 into IZ. Now what do you have to do? We have to solve the equation rho of t to get what is the final density operator at time t, we should know what is rho 0. We should know e to the power of what is the Hamiltonian H and of course t is the time. We know what is the rho of 0; rho of 0 as I said is IX. We are applying the pulse along X axis.

When you are applying the pulse along X axis what is the free precession Hamiltonian? rho of t into IZ. So, I know H now, I know rho of 0, simply plug it in, substitute and then you have to evaluate it. If you substitute, it turns out to be rho of t = exponential - i omega t into IZ rho of 0 exponential omega t IZ. Sorry I have missed i here, i should be there. Please remember i should be there, it is typo, there is a typo i should be there. So, exponential - i omega t IZ rho 0 exponential i omega t IZ. This is what I have to evaluate now, so that I can get rho of t. How easy or difficult to evaluate this? But one thing when you are evaluating you have to evaluate in the same order, you cannot bring this one here or this one here, not allowed. You cannot swap the terms, you cannot interchange the terms, the order has to be maintained while solving.

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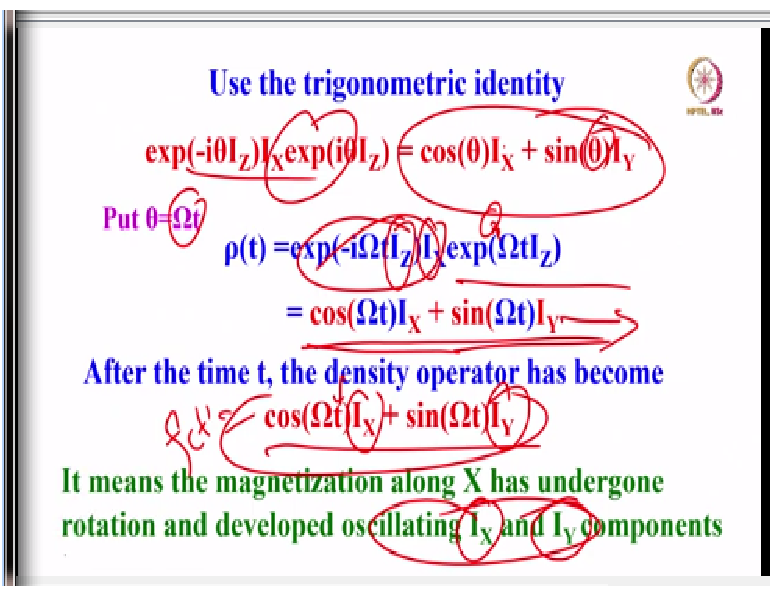

And how do you solve that type of equations? And good part of it is many, many researchers who have done this, many stalwarts of NMR, already they have worked out. And of course solution for such type of equations is known right from the beginning, we do not have to worry. We have to simply use a trigonometric identity, what is the trigonometric identity for such type of equation?

Exponential i e the power of - i theta IZ into IX into exponential I theta IZ. If I use this trigonometry this can be broken down into cos theta of IX + sine theta of IY, it is a simple trigonometric identity. It is already known, you do not have to worry about it. Now knowing this one, put theta = sigma t. Now instead of theta I have to put sigma t, again i is missing I am sorry while cutting and pasting this will happen.

So, now rho of t = exponential - i omega t IZ into IX exponential i into omega t IZ. This can be equated using this identity as cos of omega t IX + sine of omega t IY. We just use this trigonometrical identity for this type of equation. So, that means you do not have to go through elaborate analysis of such type of equation to find the solution. It is very well known, simply use the well known trigonometric identity.

You remember e to the power of -i theta or i omega t IZ into IX into exponential i omega t IZ can be written as cos omega t into IX + sine omega t into IY. I have to simply plugged in the trigonometric identity, that is all. Now after the time t the density operator has become this now, so this is nothing but rho of t now. This is what we have to solve, we knew our rho 0, we knew what is Hamiltonian, we substitute it and then the solution for this by using the trigonometric identity we got this one.

So, after the time t the density operator has now become cos omega of t into IX + sine omega of t into IY. So, we know what is the percentage of IX, what is the percentage of amount of IX and IY present here. It means what is happening is, the magnetization which was along X axis, with the time has undergone a rotation with the time t. As time is increasing or time is changing the magnetization has undergone rotation in the XY plane and developed IX and IY components which is oscillating.

The cosine and sine function they are oscillatory functions, so it has developed oscillating IX and IY components. This is what it means the free precession. What we understood is what is the free precession Hamiltonian, we understood. It is nothing but IZ into omega, what is omega, it is the offset and of course we applied a pulse along X axis and then you know that is what is rho of 0, rho of 0 = IX now because pulse is applied along X axis.

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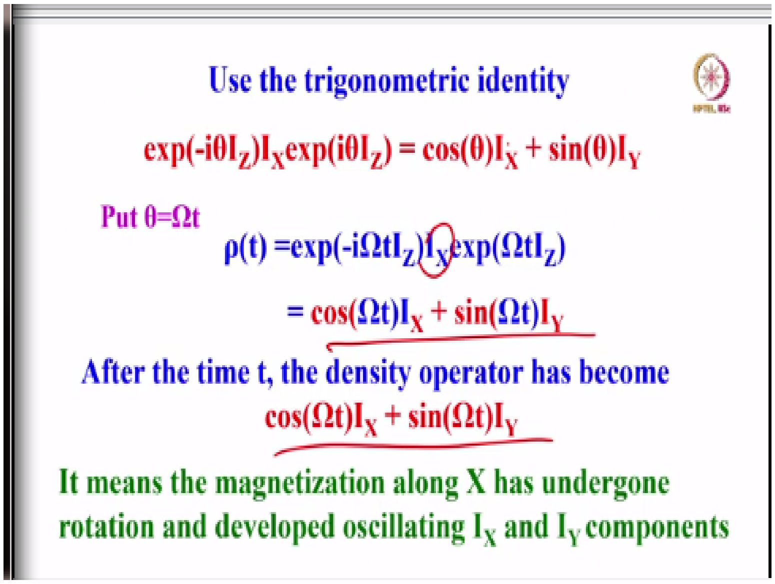

And then we know the Hamiltonian, we just plugged in, used the trigonometrical identity, we found out what is rho of t as a function of time. And we know the magnetization which was along X axis, as a function of time has undergone rotation and developed oscillating IX and IY components.

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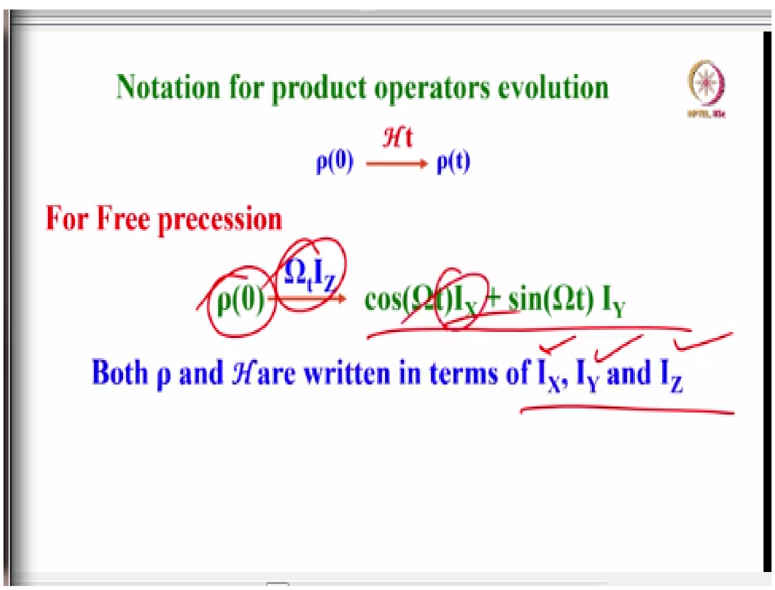

So, all these operations can be represented by simple notation, what is that notation? it is called a arrow notation. In all the books you see and when you try to understand product operators in various books and the literature, you will see it is represented by arrow like this. That means if rho of 0 is there; that is the beginning of my density operator, my Hamiltonian is Ht. During the period when there is a Hamilton Ht, when this is operated on this rho 0 and the final density operator is rho of t.

What it means is if I know rho of 0 if have I Ht, which is written on the arrow means this is my Hamiltonian and which is operating on this rho of 0; and finally I get rho of t, that is what it should be understood. So, for free precession if I want to write it, I know rho 0 that was my beginning Hamiltonian, beginning density operator. Now my rho t into IZ is my Hamiltonian for free precession, so this is acting on that.

In the free precession rotation what is going on? the rotation about Z axis is going on and this is what is rho 0 and finally using the trignometrical identity we got cos omega t into IX + sine omega t into IY. Now both rho and H are written in terms of IX, IY and IZ; that is what we are going to do. Hamiltonian both rho and H is always written in terms of IX, IY and IZ which tells you the amount of IX present, IY present, IZ present is represent for rho of t.

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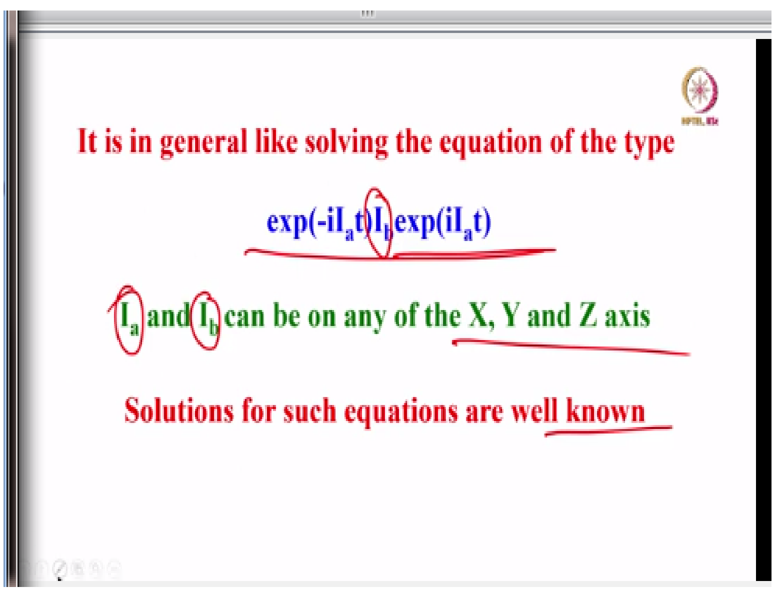

So, in general what it means is if you want to solve equations of this type, for let us say, rho of 0 if H of omega t IZ is operating on rho of 0 to get rho of t, this is an expression which is generally given like this is, whose exponential -i of Ia t, Ib exponential i of Ia of t. Now what does it mean?

Ia and Ib can be on any axis, X, Y and Z, no problem and solution for such equations are well known. In general it is solving a equation of the type in the product operator analysis.

If you are try to do either for the free precession when you apply RF pulse or chemical shift evolution or J evolution you always come across an equation of this type, for which you have to find a solution. The solution in general for equation can be written like this exponential -i of Ia into t into Ib into exponential i of Ia into t. So, solution we got for IX and IZ, you know during free precession we know. We worked out and by using trigonometrical identity, we wrote it as cos of omega t + sine of omega t; we worked that out; that you remember here.

Cos omega t IX + sine omega t IY, IX and IY components are generated. But it is not all the time like this. It depends upon in which axis you are applying the pulse and which is your Hamiltonian; it depends upon what is your Hamiltonian and what is the axis in which you are rotating, that is very important. So, it is a general equation for all such equations the solutions are very well known. You do not need to make explicit calculations, using trigonometrical identities they have been tabulated.

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Rotation about the axis	Operator	Identity	Written as
X	I_Y	$\exp(-i\theta I_X)\, I_Y \exp(i\theta I_X)$	$\cos\theta I_Y + \sin\theta I_Z$
X	I_Z	$\exp(-i\theta I_X)\, I_Z \exp(i\theta I_X)$	$\cos\theta I_Z - \sin\theta I_Y$
Y	I_X	$\exp(-i\theta I_Y)\, I_X \exp(i\theta I_Y)$	$\cos\theta I_X - \sin\theta I_Z$
Y	I_Z	$\exp(-i\theta I_Y)\, I_Z \exp(i\theta I_Y)$	$\cos\theta I_Z + \sin\theta I_X$
Z	I_X	$\exp(-i\theta I_Z)\, I_X \exp(i\theta I_Z)$	$\cos\theta I_X + \sin\theta I_Y$
Z	I_Y	$\exp(-i\theta I_Z)\, I_Y \exp(i\theta I_Z)$	$\cos\theta I_Y - \sin\theta I_X$

2nd Row: It is the rotation of operator I_Y along X by an amount θ

3rd Row: It is the rotation of operator I_Z along X by an amount θ

And this is a simple table which tells you what is the rotation about an axis, what is an operator and what is your identity, what is the final solution for such type of things. Only couple of them is needed for you because let us say you have an operator IY or an operator IZ, what can happen for IY and IZ? You have your rotation of about X axis or rotation about this, you can have rotation of IZ about X axis, you can rotate IY about X axis.

You can take IX, IX is an operator that can rotate about Y axis, IZ is an operator that can rotate about Y axis. Similarly IX and IY operators can be rotated about Z axis; there are various combinations you can think of. So, for all these things identities are very well known. For example I will take the first one. For an operator IY which is rotated about axis X, this what is written, this is operator IY and it is rotated about an axis.

See remember general expression which we wrote in the form of Ia and Ib, please understand this is an operator that is to be rotated. That is the operator which undergoes rotation; and the axis of rotation is given by this. This is all what is there in all these things about what we do in the product operator formalism when we try to work out. This is what you have to understand. An expression of this type you have to understand like this, if I consider this thing, this is an operator that is undergoing rotation. And this axis of rotation that means IZ is rotated about X axis that is what it implies. If I consider an example of this, it is already written here. See for example if I consider second row and third row, what is the second row here? Second row says this thing rotation of IZ about X axis; third row third row is rotation of IX about Y axis. Here rotation of IY about X axis, that is all you have to understand.

Finally you write a big equation like this, physically it means it is a rotation of an operator about a particular axis. Simply in this case, example, this is the rotation of the operator IY about the axis Z. Snd for all these operations 5 or 6 which are there, the solutions are easily written like this. For rotation of IY about X it is the solution cosine of theta IY + sine theta of IZ. Similarly for rotation of IX about Y axis it is cosine of IX - sine of IZ. Similarly take IX, rotation of IX about Z axis is given by cosine of theta of IX, the amount by which it is rotated is given by theta; that is what it is.

So, simply theta is the amount by which you are rotating and this is the axis of rotation, this is the operator that you are rotating, that is all you have to understand. For 6 of them these equations are very well known, solution is known, you must remember these things. If you know these things you can understand the operation and the rotation of any operator on any axis in any pulse sequence given, you can easily do these things.

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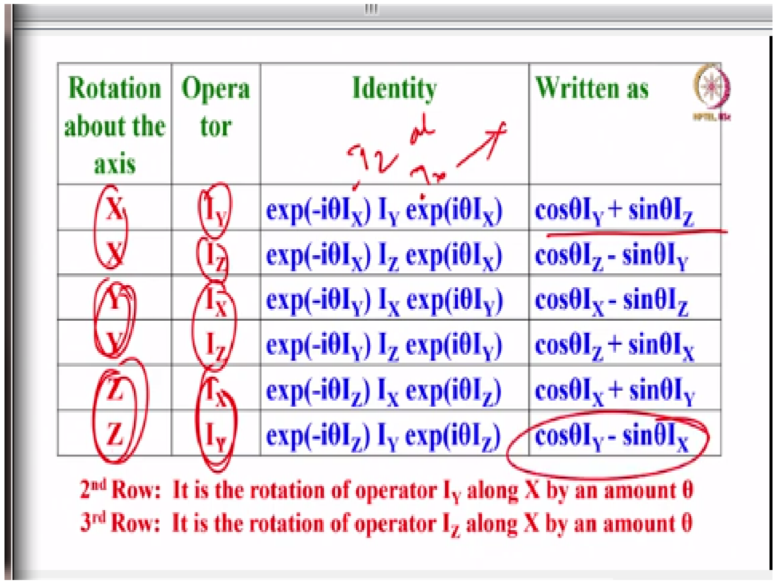

Rotation about the axis	Operator	Identity	Written as
X	I_Y	$\exp(-i\theta I_X)\, I_Y\, \exp(i\theta I_X)$	$\cos\theta I_Y + \sin\theta I_Z$
X	I_Z	$\exp(-i\theta I_X)\, I_Z\, \exp(i\theta I_X)$	$\cos\theta I_Z - \sin\theta I_Y$
Y	I_X	$\exp(-i\theta I_Y)\, I_X\, \exp(i\theta I_Y)$	$\cos\theta I_X - \sin\theta I_Z$
Y	I_Z	$\exp(-i\theta I_Y)\, I_Z\, \exp(i\theta I_Y)$	$\cos\theta I_Z + \sin\theta I_X$
Z	I_X	$\exp(-i\theta I_Z)\, I_X\, \exp(i\theta I_Z)$	$\cos\theta I_X + \sin\theta I_Y$
Z	I_Y	$\exp(-i\theta I_Z)\, I_Y\, \exp(i\theta I_Z)$	$\cos\theta I_Y - \sin\theta I_X$

Now you may ask me here when we discussed these things; one interesting thing you notice. We always started writing about rotation of IX, IY, see for example IX, IY operators are rotated about X, IX, IZ rotated about Y, IX, IZ, IY rotated about Z. But we never found out what happens about the rotation of IZ about Z, IX about X and IY about Y.

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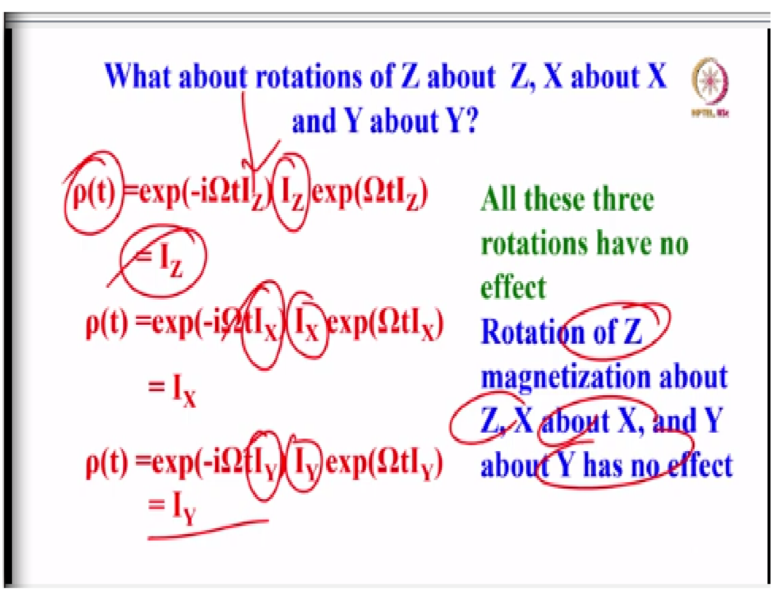

That is also possible. Here you have seen rotation of IY and IZ about X, rotation of IX and IZ about Y, rotation of IX, IY about Z; but we have not written rotation of IZ about Z, rotation of IX about X, and rotation of IY about Y. What happens to those rotations? Other rotations have been given, solutions are known in the table. Simply you write like this, rho of t is rotation of IZ about Z; that is what it implies, that is what we were trying to understand. This is exactly equal to IZ if you work out.

Similarly, you work out I will come to that what it is, similarly you work out for rho of t rotation of IX about IX is equal to IX, rotation of IY about IY = IY, what does it mean? It means all these 3 rotations have no effect; this has no influence when you are making the analysis. That means rotation of Z magnetization about Z, rotation of X magnetization about X and rotation of Y magnetization about Y has no effect at all, please understand.

Rotation of Z about Z, X about X and Y about Y has no effect. Only rotation of Z about X and Y, rotation of X about other things Y and Z and rotation of Y about X and Z are important, not about rotation of the same operator IZ about Z, IX about X, IY about Y. They have no effect and you do not have to worry about those things when you are analyzing any pulse sequence.

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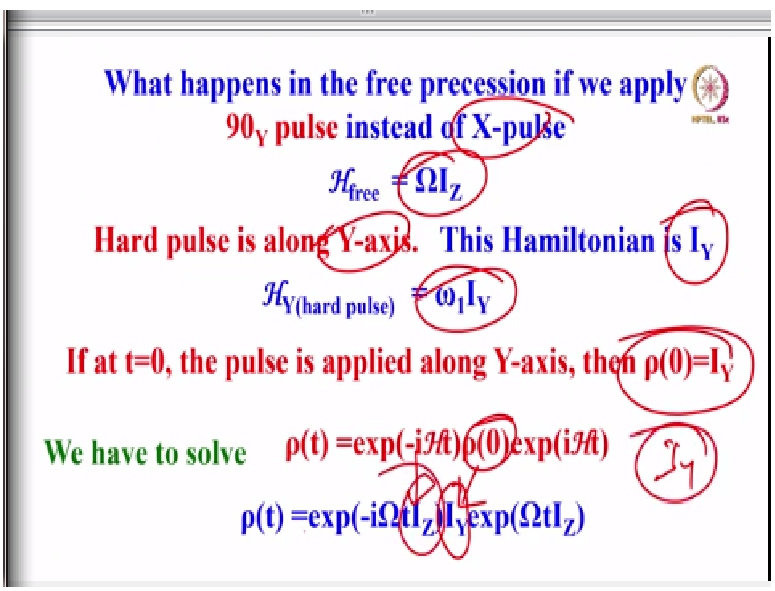

So, what happens in the free precession if you apply 90 degree Y pulse instead of X-pulse? You are understanding; you apply a pulse along X axis, you wrote Hamiltonian as H of X = omega 1 into I of X we wrote. Remember, omega 1 is RF power and IX is the Hamiltonian along IX, that is what we wrote. So, H for the free precession we know omega into I Z and then hard pulse along Y axis we are applying, Hamilton is IY instead of IX it is IY, there is no difference.

So, for the Hamiltonian for a hard pulse you have to write as omega 1 into IY. instead of omega 1 IX it becomse omega 1 into IY. Now at time t = 0, the pulse is applied along Y axis that means rho of 0 = IY. Earlier it is rho of 0 was IX, because pulse was applied along X axis, now we are applying pulse along Y axis, so rho of 0 = IY. So, what you have to do now? You have to solve this equation. Now what is rho 0? What is the operator and what is the axis in which you are rotating?

You should know by now, it is the operator that is rotated about Z axis because of free precession, it is rotation about Z axis, this is the operator that you are rotating. Now IY is rotating because you are applying the pulse along Y, IY operator is rotated about Z axis, so what you have to do? Go back to your table here, IY rotate it about Z axis, simple, this should be the solution. Simply write down those equations for this now.

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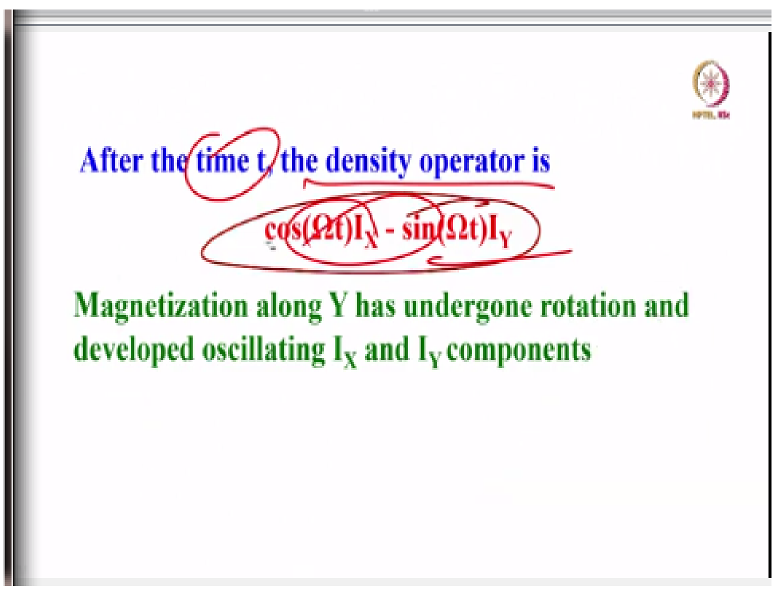

After the time t, the density operator is simply written by this. What I did is I copied from the table, that is all, the solution is known. What you have to understand is the operator at which you are rotating which is the rho 0 or whatever it came at the center of that expression, and e to the power of I into H into t where Hamiltonian was the operator there was the axis in which you are rotating. If you know these 2 then from the table which is given you can simply write the solution without going into any explicit calculations at all.

So, when we apply RF pulse along Y axis for a free precession, we know rho of t turns out to be this one. So, that means the magnetization along Y has undergone rotation and developed oscillating IX and IY components. There was a magnetization along Y axis, it has undergone rotation and developed IX and IY components; that is what it means. Same, when it was magnetization was along X also it started moving and then developed IX and IY oscillatory components. Same thing here also the cosine and sine components will be developed now.

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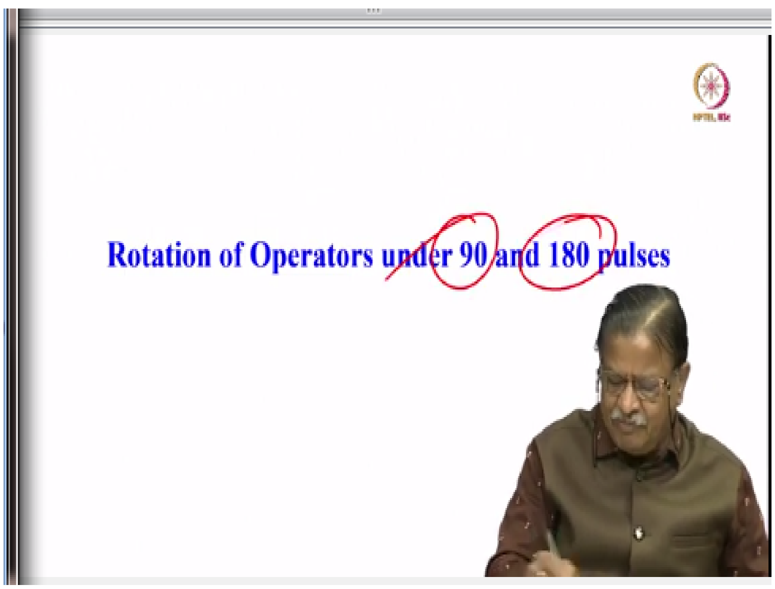

Now with this we have to introduce few other things what is called rotation of operators under 90 and 180 pulses. This is basically very important, all what is written in the table, the solution can be understood by this method also. This is also another same approach; it is in a simple form written there. But to make it clear for you I will tell you all those things which you know already. We have discussed this when we discuss about the evolution of pulse phase, receiver phase and rotation everything, we discussed these things. But again let us see rotation operators under 90 and 180 pulse ,how it happens?

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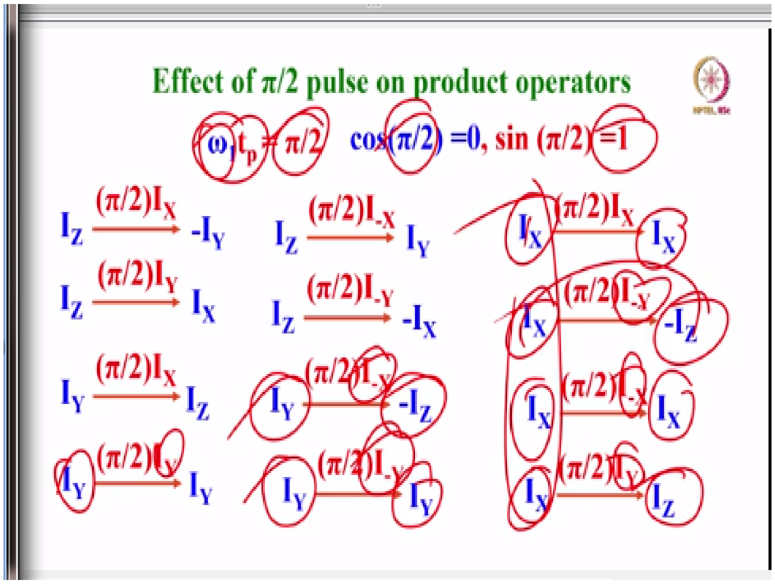

I will see effect of pi by 2 pulse on product operators. What is the pi by 2 pulse? Now it is omega one tp is pi by 2, you know the pulse width, it is always given by gamma H1 into tp; gamma H 1 = omega 1, tp is a pulse width, which is equal to pi by 2. And cos phi by 2 is 0 because cos 90 is 0, similarly sine pi by 2 is 1, you know that one. Now we will understand, when I apply a pi by 2 pulse that is X-pulse on IZ what will happen? It will go to the product operator IZ will become -IY, apply a pi by 2 pulse on X axis, then IZ will become -IY.

Similarly apply +IY pulse IZ will go to IX. You can also apply in the opposite direction other axis instead of +X I apply like -X then IZ will go to IY, here IZ will go to -IX, very simple. This we have been discussing, we understood by vectorial diagram also, about the pulse phase, receiver phase, how it is rotating everything you know; different pulses when you apply how the magnetization is undergoing rotation, we understood that. Similarly IY pulse, IY magnetization let us say, I apply a IX-pulse then the product operator IY will go to IZ. Similarly on IY remains IY, what does it mean? It has no effect. I tell you, you apply a pulse along the same axis you simply rotate along the same axis, this has no effect. So, pulse has to be applied on the other axis different other 2 axis. Now if you want to see effect of IY the pulse has to be on X or Z not on I Y. So, IY pulse applying on IY has no effect; that is what we said. It remains same, it has no effect, what it essentially means is here, it means it is rotation of IY about IY has no effect; similarly rotation of IZ about IZ has no effect.

So, here again apply IY, - IX pulse will take product operator goes to -IZ, similarly IY product operator when you apply minus Y-pulse it goes to IY. So, all these things you know IX operating on I X has no effect and when they apply a -Y pulse on IX it goes to -IZ. The rotation about IY, IX will go to IZ, rotation about -IX, IX will go to IX, this is how you have to understand, rotation about IY, IX will go to IZ.

These are all simple, effect of the pi by 2 pulse on various product operators, all these are product operators. The effect of pi by 2 on all the product operators if you know, if you remember these things, any pulse sequence you can very easily understand by product operators. And you understand they analyze this thing using product operator any pulse sequence and see how the magnetization is evolving at different time periods of the sequence.

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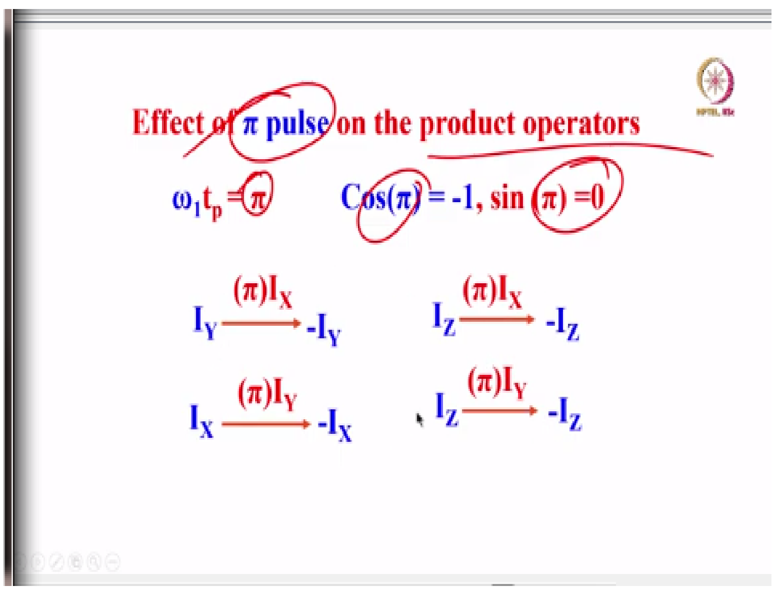

We can also talk about effect of pi pulse on the product operators, so far in the previous slide we saw about the effect of pi by 2 pulse. We can also discuss about the effect of pi pulse. We know that what is omega 1 t p = pi, cos pi = -1 and sine pi = 0, it is very simple, when you rotate about IX apply a pi pulse along X axis then IY will go to -IY, it is simply inverts the magnetization you know that. A 180 pulse will tilt it in the opposite direction, similarly IZ will go to -IZ if you apply X pulse, if you apply Y pulse IX will go to -IX, if you apply Y pulse IZ will go to -IZ; if all these pulses are pi pulses.

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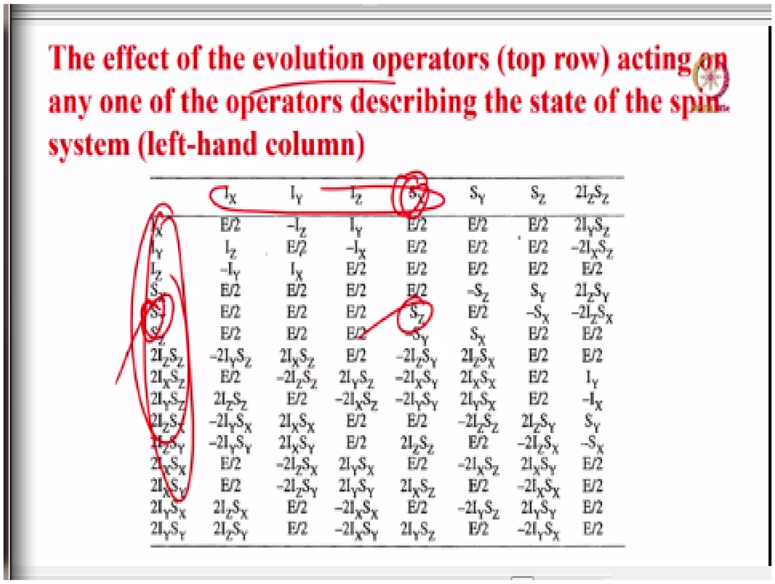

The effect of the evolution operators (top row) acting on any one of the operators describing the state of the spin system (left-hand column)

	I_X	I_Y	I_Z	S_X	S_Y	S_Z	$2I_ZS_Z$
I_X	E/2	$-I_Z$	I_Y	E/2	E/2	E/2	$2I_YS_Z$
I_Y	I_Z	E/2	$-I_X$	E/2	E/2	E/2	$-2I_XS_Z$
I_Z	$-I_Y$	I_X	E/2	E/2	E/2	E/2	E/2
S_X	E/2	E/2	E/2	E/2	$-S_Z$	S_Y	$2I_ZS_Y$
S_Y	E/2	E/2	E/2	S_Z	E/2	$-S_X$	$-2I_ZS_X$
S_Z	E/2	E/2	E/2	$-S_Y$	S_X	E/2	E/2
$2I_ZS_Z$	$-2I_YS_Z$	$2I_XS_Z$	E/2	$-2I_ZS_Y$	$2I_ZS_X$	E/2	E/2
$2I_XS_Z$	E/2	$-2I_ZS_Z$	$2I_YS_Z$	$-2I_XS_Y$	$2I_XS_X$	E/2	I_Y
$2I_YS_Z$	$2I_ZS_Z$	E/2	$-2I_XS_Z$	$-2I_YS_Y$	$2I_YS_X$	E/2	$-I_X$
$2I_ZS_X$	$-2I_YS_X$	$2I_XS_X$	E/2	E/2	$-2I_ZS_Z$	$2I_ZS_Y$	S_Y
$2I_ZS_Y$	$-2I_YS_Y$	$2I_XS_Y$	E/2	$2I_ZS_Z$	E/2	$-2I_ZS_X$	$-S_X$
$2I_XS_X$	E/2	$-2I_ZS_X$	$2I_YS_X$	E/2	$-2I_XS_Z$	$2I_XS_Y$	E/2
$2I_XS_Y$	E/2	$-2I_ZS_Y$	$2I_YS_Y$	$2I_XS_Z$	E/2	$-2I_XS_X$	E/2
$2I_YS_X$	$2I_ZS_X$	E/2	$-2I_XS_X$	E/2	$-2I_YS_Z$	$2I_YS_Y$	E/2
$2I_YS_Y$	$2I_ZS_Y$	E/2	$-2I_XS_Y$	$2I_YS_Z$	E/2	$-2I_YS_X$	E/2

And the effect of the evolution of operator this is taken from the Ray Freeman's book. It is a very good book and fantastic book to read and understand. The effect of evolution operators acting on any one of the operators describe the state of the spin system can be given like this. So, what it says? Evolution operator is given in the top row and then what is the state of the spin system is given by what is given here, in the column. For example I will say I apply a IX on IY it goes to IZ, now apply IX pulse on IZ it will go to -IY.

For example I will take IY pulse apply on SY another spin, there is no effect, I told you, if you apply pulse on I spin, S spin will not be disturbed. You can independently evaluate application of pulse I spin, the application of pulse on the S spin. So, like this, all these things we can discuss, What are these 2? This is the longitudinal, Z magnetism everything we will discuss when you go further. But this basically tells you evolution of each of the operator and how you discuss the state of the operator when it evolves is given like this. So, when SX operates on SY, it gives rise to SZ, like this the table has to be utilized.

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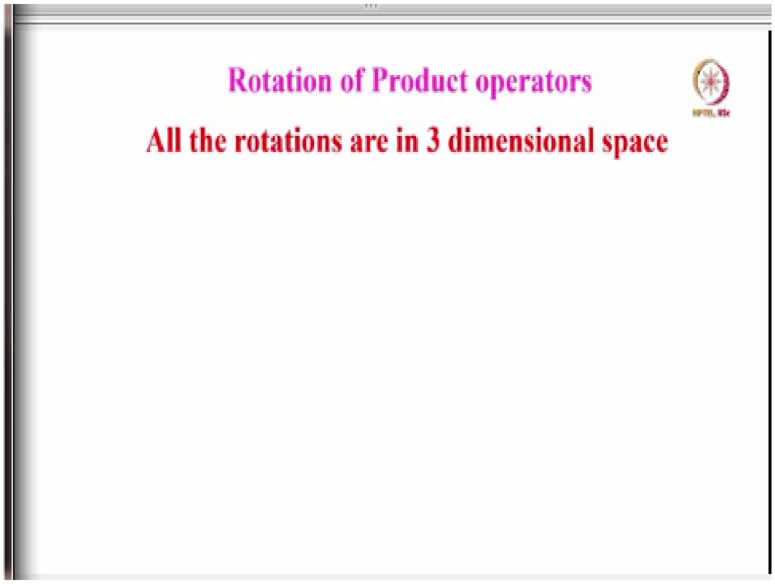

So, with this now we will come back and since the time is up we will discuss about the rotation operators everything later stage in next class. In this what I was trying to say is after understanding something about the product operators some fundamental concepts, we wanted to understand what happens in the free precession, we wrote down the free precession Hamiltonian H of free, Hamiltonian for free precession is omega into IZ, because during free precession which is during the delay, the magnetization rotates about Z axis. So Hamiltonian is omega into IZ, omega is the offset in the rotating frame or the chemical shift what you call. And then apply a pulse about X axis, it is the rotation about Y axis. And then how these things evolve is going to be a simple expression, e to the power of –i H into t into rho of 0 into e to the power of i H t.

The rho of 0 is initial state of the product operator, if you know the initial state of the density operator you know what is the final state of the density operator rho of t. All you have to understand is you have to build the Hamiltonian, you should know rho 0 and then you can find out rho t. So, we gave simple expression rho 0 is nothing but the operator that is to be rotated and then what e to the power i H t when we wrote on the Hamiltonian. They all can be expressed in terms of rho 0 and rho t in terms of IX, IY, IZ components that is what I said. So, if I say rho 0 is IX that is the operator that is being rotated and then in the Hamiltonian you will write IX, IY, IZ whatever it is; and that tells you the axis in which it is going to be rotated. For all these things solutions are well known and then using a simple trigonometric identity they have been tabulated.

You can simply look into the table and write down. Or in other words I also gave you the table where we can say what is the effect of different pi by 2 pulses on different product operators, what will happen if I apply pi by 2 X pulse on IZ, IX, IY and all those things, we discussed that. Similarly effect of pi pulse. So, with all those things now it is very easy for us to analyze any pulse sequence, sequentially we have to go.

First pulse then effect of the pulse and then the delay what will happen whether chemical shift evolves, free precession rotation, J coupling is evolving, everything can be treated as a rotation. And it has to go sequentially in the pulse sequence and in a given block, for example there is a delay, in that chemical shift may be evolving, J coupling also may be evolving. We can operate either first coupling and then chemical shift later, it does not matter, that is immaterial. But the sequence has to be followed; then at the end you can find out what is rho of t, the final density operator at the time t. So, that is how we can understand the state of the magnetization. We will go further, I will stop at this stage, we will come back in the next class, continue further and try to analyze some of the sequences, thank you.