Advanced NMR Technique in Solution and Solid-State
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Module-40
Product Operators
Lecture – 40

Welcome all of you. In the last couple of classes, we extensively discussed about relaxation phenomena. We understood about spin lattice relaxation, spin spin relaxation, the concepts of what is a relaxation; and what are the sources for such type of relaxation possible in a given system. For example, the spin lattice relaxation if you have to consider the dominant interaction is the dipolar interaction. And that should be local fields that is generate at the site of the nucleus which is undergoing relaxation should also be at the normal frequency. Then only spin can give its energy to the lattices and relax. And we understood the method of determining T1 especially, the spin lattice relaxation time, using what is called inversion recovery technique, where we apply first 180 pulse bring the magnetization to −Z axis. And then see as a function of time how it goes back; fit into the exponential curve, which is known as MZ = M0 into 1 – 2 into e to the power of −t/ T1; and calculate the value to T1. Of course, we understood lot more concepts and principles how the energy is going to lattice and all those things. We will not go more into the details. Of course, spin spin relaxation also we understood and it is the decoherence which is taking place in the xy plane. That is what we understood. Then we switched over to NOE. Of course, the relaxation phenomena is one of the important things for NOE, where we understood if you saturate a particular spin and then if another spin which is close by in space, it need not be j-coupled, in which case we see the change in the intensity of the signal, if there is a spatial proximity by giving energy of this nuclear spin to that. There is a polarization transfer that is taking place.

This change in intensity could be positive or negative. So, this we understood what is the reason for that and we understood the transition probability for a single quantum transition, double quantum transition and 0 quantum transition. We came to know that double quantum and zero quantum transition pathways are the things which are responsible for giving rise to change in the intensity.

And we know, we have calculated the population difference after irradiating one of the spins in a two spins case, and we found out that if the spins undergo preferentially double quantum for relaxation, there is going to be a positive signal intensity, enhancement of the signal by 100%. On the other hand if the spins undergo relaxation through zero quantum pathway, we observed that there is a reduction in the intensity by 50%.

And we understood more about the NOE phenomena. How to measure NOE by doing two experiments, the steady state NOE, once irradiate a particular peak on resonance and then the irradiates somewhere far away, take the difference and find out the change in intensity. This change in the intensity can be correlated to the distance between two spins which goes by one over r power of 6.

As I told you, the NOE depends upon spatial proximity. It goes by inverse of r to the power of 6. That is why if there is a small change, if the distance increases there is a drastic reduction in the intensity of the signal. NOE signal will come down drastically. And we said that most probably if the distance between the two spins is less than 5 angstrom, there is a probability that we will see NOE.

Lot of things we discussed about NOE, and we said we will discuss transient NOE at a later stage. With that we will switcher over to a different topic today. We are going to introduce a little mathematical formulation. It is called product operator formalism. So, this is what is normally used to understand the behaviour of the spin system. In any of the experiment in NMR, be it a simple one pulse experiment or it could be a multiple pulse experiment or a multiple quantum experiment, does that matter. And nowadays, as you see people have designed number of pulse sequences in NMR to determine the information that we require. This experiment is designed in a particular sequence to determine a particular type of information, it can be done. So then how pulse sequences are designed? To understand the spin dynamics or the behaviour of magnetization or in other words in simple terms, the evolution of the magnetization under chemical shift, free precision or j-coupling, how it takes place at different stages of the pulse sequence can be understood. For this a mathematical method, a formalism is there. That is called product operator formalism. We will try to introduce this today. In principle, I wanted to bring this up after discussing 2D. Because we discussed 2D in the previous course also a large. Again, we will to come to 2D in this course also.

But before that, I thought to before we run out of time, we wanted to discuss the product operator formalism. This a new topic which you are discussing in this course. So, I am taking up this. In this, we are applying product operator formalism to understand the behaviour of the spins in a simple one pulse experiment or one dimensional experiment. We are not going to 2D because after introducing 2D, for the benefit of the people who did not credit or attended the course previous course, I will introduce 2D and then take one or two example of how we apply product operator formalism to understand the pulse sequences. We will come to that later. So now, we will start with the product operator formalism and understand simple one pulse experiments.

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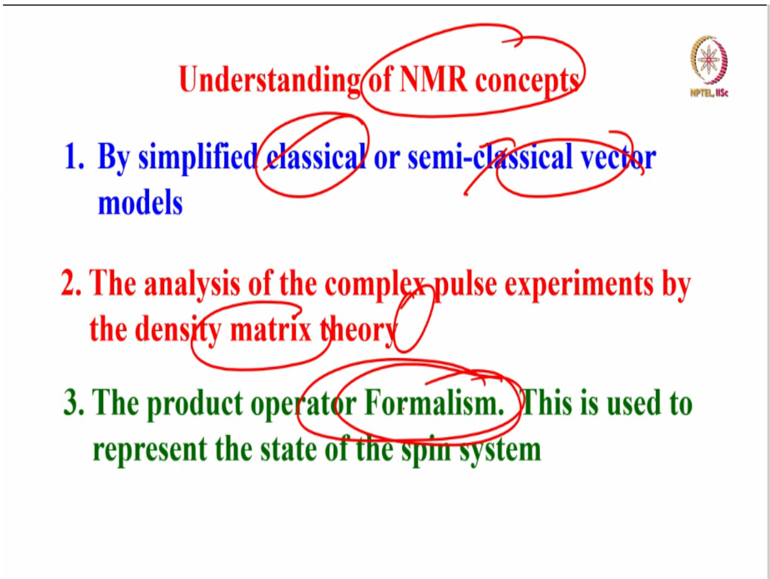

Understanding of the NMR concept, as I said, right from the first class we have been discussing. There are simple approaches. Simple approach is the classical approach or a semi classical approach, where we discuss based on the vector model. We understood magnetization is brought from Z axis to X axis; and how they start dehasing? How they grow back? So, all these things we discussed in a classical approach, by a classical vector model.

That is one way, but all the time it is not possible to do that. It does not always gives you the complete information and it is going to be difficult also. The analysis of the complex pulse sequence can also be understood by another theory called density matrix theory. This is an extensive calculation one has to do. The analysis is really very complex, and then it takes enormous amount of time and a lot of involvement is there.

And the other thing is a new approach, not new approach a third approach I would say. This approach has already been there in the literature for more than two and half decades. So, another approach is what is called the product operators formalism. This is a method used to represent the state of spin system in different pulse sequences. So there are several methods.

But by and large, nowadays, people do not use this type of thing for a complicated pulse sequences to understand the spin dynamics or the same classical picture and vector picture is also difficult. So, product operator formalism is commonly employed to understand the pulse sequence.

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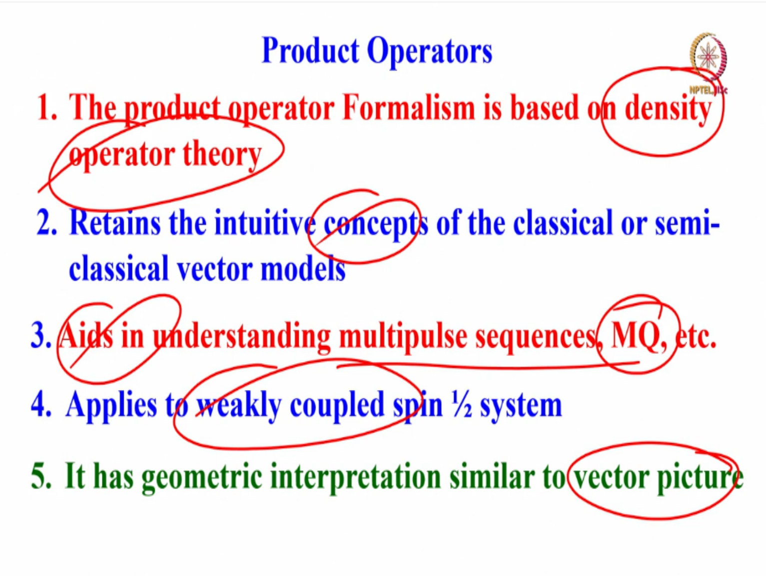

Now we can further go into the product operator. What are these product operators? What is this product operator formalism? Or what is the basis of this one? First thing, as I said, there is a density matrix approach, this also depends the upon density operator theory. Product operator is based on density operator theory. One thing is it retains intuitive concepts of the classical or semi classical vector models.

It retains the concept, not that it completely gets rid of this thing. It is there. But mathematically it is applicable to complex spin system. One interesting thing is it aids in understanding multiple sequences not only single one pulse experiment or a simple 1D experiment, multi pulse experiment, it could be 1D or it could be 2D. Even multiple quantum NMR can be understood by this.

We, have not even introduced what is multiple quantum NMR. I will come to that at a later stage. Maybe after the after introducing 2D. Then we will see how if there is a possibility, we can see how product operators can be utilized to understand multiple quantum sequences also. One important caution I wanted to give you, remember, it is applicable to weekly coupled spin half system.

And it has also geometrical interpretation, similar to vector picture. Easiest way to understand this thing. So, these are the important concepts before we jump into detailed analysis of the product operators. You must remember

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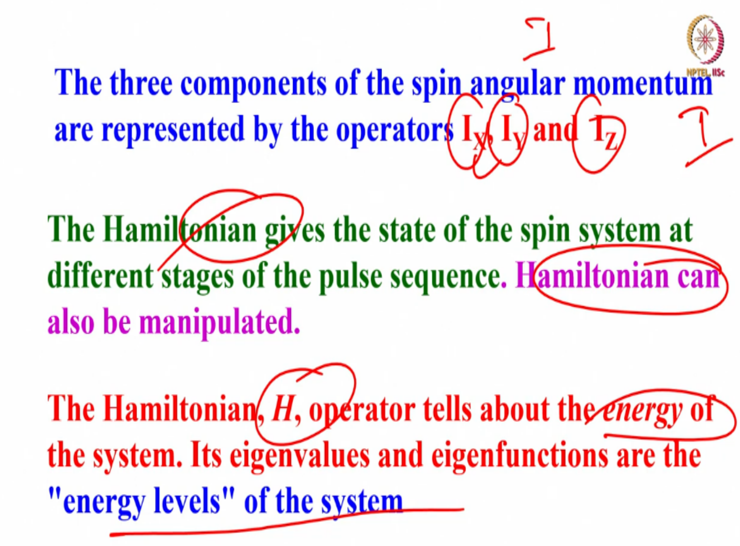

Now we will start by going into to spin angular momentum, which we discussed in the very first class. Spin angular momentum is given as I. It is a vector and it has three components Ix Iy and Iz. All the three components are there. So, the three components of spin angular momentum I is given by Ix; Iy and Iz. That is the first point we discussed already, I am just repeating it.

Now, if I have to analyse the spin system, in the quantum mechanical analysis, we discussed for a couple two spin system; case both weakly coupled and strongly coupled. We analysed, as I said first, we had to find out what is the wave function. And then build the Hamiltonian and then find out the Eigenvalues and get the transition frequencies and wave functions and intensities everything we can find out.

So that is what we discussed. When you analyse it,the quantum mechanical analysis of the two spin case, we discussed these things. So, the Hamiltonian of the system is important. It uses state of the spin system, at different stages of the pulse sequence. We can understand and this Hamiltonian can be manipulated depending upon the type of pulses you apply, the type of interactions you bring in between the pulses. All those things are very important.

So, Hamiltonian can be different. We can manipulate the Hamiltonian. that is one thing. And then, as I said, the Hamiltonian operator tells about the energy of the system, the spin system. So, it is eigenvalues and eigen functions, if you know, they are nothing but the energy of the the spin system. So, this is important point, which you are already familiar with, we discussed this at stretch in couple of classes about general introduction to NMR and also on quantum mechanical analysis of the coupled spin system.

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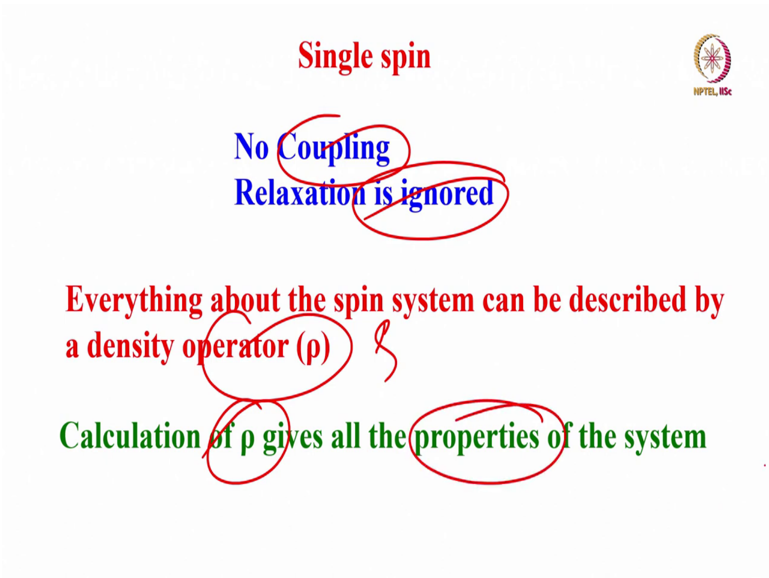

Now, let us start with a single spin, only one spin. Basic assumption, of course, I do not have to tell you anything. If I say single spin, it is understood that J coupling is not there. Atleast to have the interaction there must be two spins, because of the J coupling interaction; or more than two. Since I am considering only single spin case; J coupling is absent, no, J coupling.

Further there could be relaxation going on in different pulse sequences; during the pulse and during the delays you are applying, between the pulses. Spins will undergo relaxation which we discussed, a lot of things we discussed. So that also is there. But what we do is for our calculation purposes, we ignore that. So, the point is, since I am considering, a single spin, the coupling is ignored or not there at all; and also relaxation is ignored.

This is to make our life simple to understand the product operators. So, with this idea what we will do is, if I want to understand about the spin system, everything about this spin system can be described by what is called density operator, which is given as a rho. Rho is a density operator. If I know density operator then I can describe all about the spin system of interest. So, calculation of rho is very important. If I know rho is 0, I can find out what is rho T is the function of T in different pulse sequences. If I know rho I can get the properties of the spin system. So, the calculation of rho gives me all the properties of the spin system.

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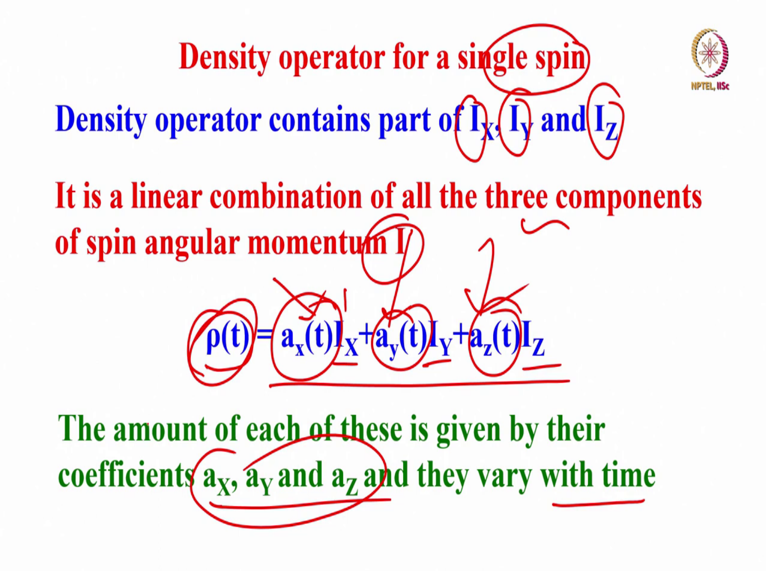

With this no, I know that density operator is needed to understand this spin system. How do you write the density operator for a single spin? We will write down, first for a single spin what is the density operator. Density operator contains part of Ix, Iy and Iz. As I said initially itself, the spin angular momentum, three components are there. So, density operator contains all these terms in different type of parts. It may not be fully Ix, Iy, Iz. It depends, it can be a linear combination of all the three of them. So, the linear combination of all the three components of this spin angular momentum is there in the density operator. That is another thing. So, I can write mathematically, if I want to understand how the density operator is changing with the time. I can give like this, rho of t, which is equal to Ix + Iy + Iz. In each of the term, multiply by the coefficient ax of t; ay of t and az of t. These are the coefficients. So, the total density matrix, if I want to find out or calculate at a given time t for any time t, I can represent as ax of t into Ix + ay of t into Iy + az of t into Iz. So, these are the three terms. All the three are present in linear combination; one may be present; one may be more and one maybe less; or two be present; or two may be not represent only one may be present.

So, all possible combination are there. It depends upon the coefficients ax, ay and az. So, amount of each of these is given by their coefficients and these coefficients can vary with time within a pulse sequence. At some stage, you may have Ix; at different stage of the pulse sequence you may have Iy or you may have something else, it can happen. So, all these coefficients of the ax and ay vary with the time. As a consequence, the rho t is also different, and vary with time.

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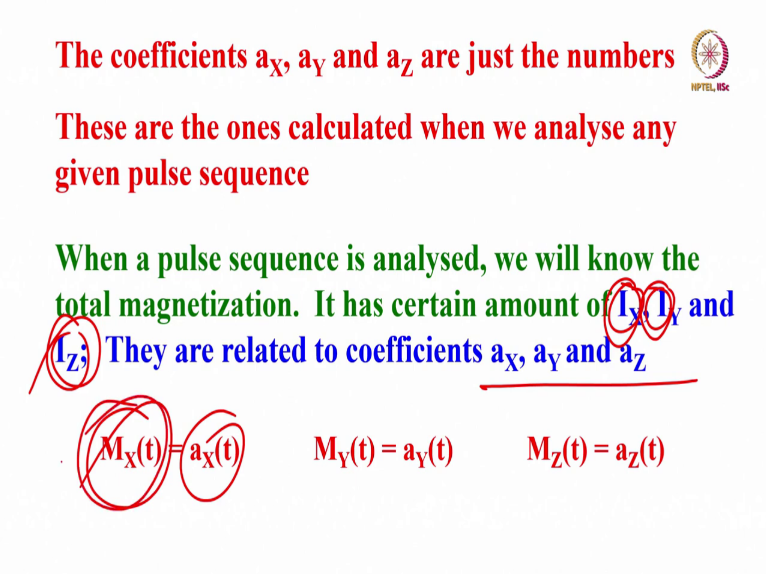

Now, what are these ax, ay and az? when they say it defines part of the Ix is present, Iy is present, Iz is present in rho t. It is based on the coefficient ax, ay and az. What are these coefficients? These are just the numbers, nothing else. And these are calculated. When you analyze any given pulse sequence. Take a pulse sequence and keep analyzing that and eventually you are going to calculate the ax, ay and az; some numbers.

So, when a pulse sequence is analyzed we will know the total magnetization. You take any given pulse sequence. Let us say I have two pulse sequence with some delay here and here here and see what is the state of the magnetization after two pulses. That is I apply 90 pulse and here the spins are in thermal equilibrium; apply 90 pulse and here they will evolve, spins will evolve under the influence of chemicals shift or coupling, if there are more than one spin or and after again I apply 90 pulse on X-axis, Y-axis. And again they will evolve under a free precession and see what is going to happen. What is they behaviour of the magnetization at the end, when you are trying to detect. So that's what we will have to understand. So, if I analyze any pulse sequence, then I will know what is the total magnetization in the pulse sequence. So, it has certain amount of Ix, Iy and z that all are present and they are related to coefficient ax, ay and az, That is what I mentioned.

So, all I want to tell you in summary is; take a pulse sequence and analyze it. We will know what is the total magnetization? The total magnetization consists of Ix, Iy and Iz so that a density matrix what we calculate; the density operator at the end is, only the component Ix, Iy and Iz with different coefficients ax, ay and az.

Now with this, I say when I have the components of Ix, Iy and Iz, I can immediately directly correlate to magnetization on x axis y axis and Z axis. So simply Mx of t is nothing but ax of t. So, ax coefficient is nothing but the magnetization along the x axis. And My of t is ay of t and Mz is az of t; these are the coefficient. They directly related to each other.

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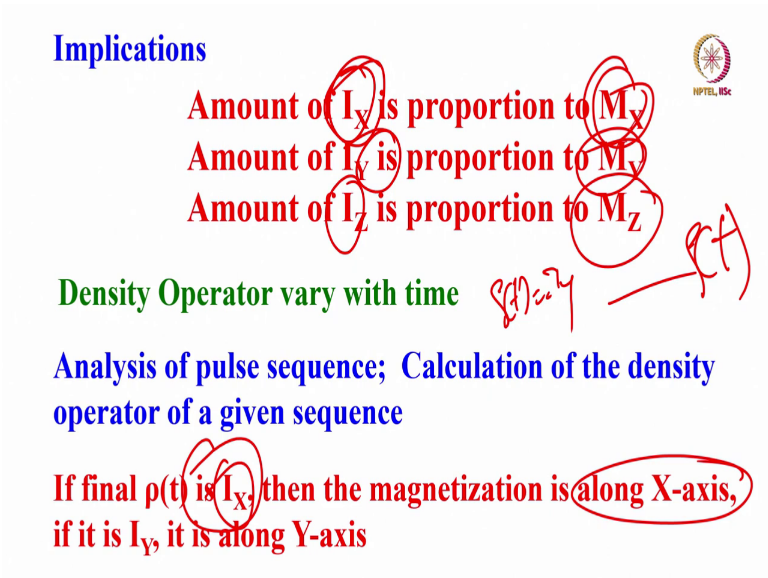

With this what are the implications? What does it mean if I say Mx of t is ax of t, My of t is ay of t and Mz of t is az of t; when I say that, magnetization is directly correlated into the coefficients. What does it imply? What it implies is the amount of Ix magnetization is present at any stage of the pulse sequence, if I calculate, it is proportional Mx. Similarly, the amount of Iy is proportional to My and Iz is proportional to Mz.

It is a simple correlation, simple relation. When I say that Mx is proportional to ax, My is proportional to ay and Mz is equal to az t. It means the coefficient, I am telling, is correlated Mx My and Mz it means Ix is proportional to Mx. Iy is proportional to My and Iz is proportional to Mz. This is what it implies from my expression, which I gave you before. So, I know density operator, varies with the time. That is what I said in a different pulse sequence. Depending upon at what stage of the pulse sequence you are calculating, the density operator, vary the time. So, analysis of the sequence, if I want to do. I want to do the calculation of the density operator of the given sequence, at any time. Let us say the final density operator is after a time t is rho t. If I want to know what is the final rho t and I calculated this somehow, that I say with all this product operator which we understand now. If final rho t is Ix. What does it mean? That means, finally, if it is only the rho t, the magnetization is along the x axis, rho t if it is Ix it is the magnetization that is along the x axis. If I rho of t it turns out to be Iy then my conclusion is the magnetization is along y axis. Please understand the rho of t, when it finally worked out, if it turns out to be a Ix or Iy then your conclusion is; if rho of t is Ix the magnetization is along the x axis. If a rho of t is Iy; the magnetization is along the y axis. This is the interpretation of this thing.

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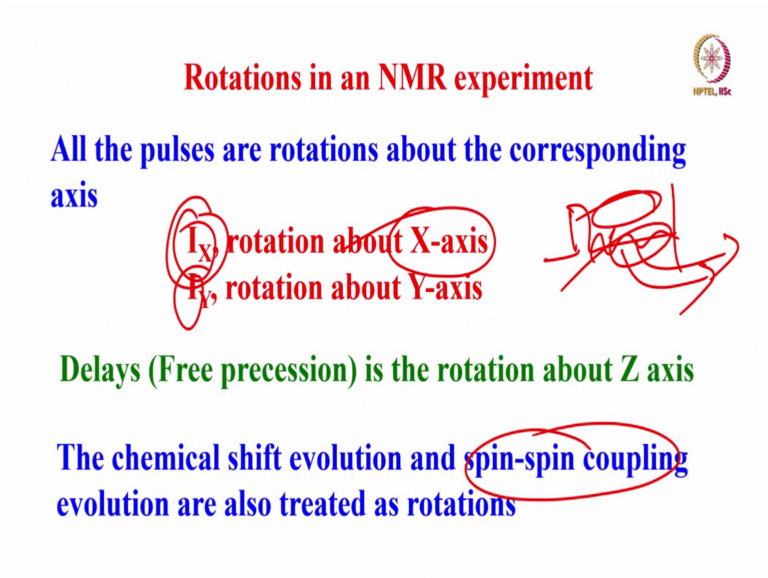

And before we proceed further with product operators, we need to introduce few rotations. Of course, we all know, rotations in NMR. Everything in NMR is rotation. We can understand those things. First all the pulses are rotations about a corresponding axis you apply. Suppose, I am going to apply a pulse along the x axis, it is a rotation about the x axis; then Ix.

If I say Ix, I am applying pulse along the x axis; then angular momentum operator component is Ix; then it is a rotation about X axis. Similarly, Iy is a rotation about y axis. This is what we know, right from day one we have been discussing. All the pulses you apply in different axis can be treated like a rotation. You are applying pulse means you are rotating; you are rotating these you are making these spins to undergo rotation.

So, these are all rotations; pulses are rotations. I will apply a pulse let us say and then keep quite, and then start collecting the signal after some time. During this time between the pulse and the time at which I am acquiring the signal, I am not going to do anything. I will simply keep quiet it is called free precession. After you apply the 90 degree pulse bring the magnetization to xy plane and then do not do anything.

But in this time till you acquire signal, spins are not simply keeping quiet, they are undergoing precession, the precision is along Z axis. Now, you do not do anything you brought the magnetization the xy plane but the spins are undergoing precession along Z axis. It is the rotation about Z axis. So, the delays in between the pulses are called free precision and that defines the rotation about Z axis.

Now, what about chemical shifts? if there is chemical shift and spin spin coupling, they are also rotations; chemical shift can also be treated as rotation. How the chemical shift evolves after applying an 90 pulse or during the delay. Just let us say I apply a pulse and give a delay and then when I apply a pulse and give a delay; it does not mean that chemical shifts are not evolving.

I apply a pulse and keep quiet here chemical pulse can evolve during this delay; J coupling can evolve; and there is a free precession. There is a rotation over that Z axis. See evolution of the chemical shiftt here is called a rotation and the evolution of J coupling is also another rotation. So, all these can be treated as rotations. please understand pulses, delays, chemical shifts and coupling all the four are treated as rotations.

The evolution of chemical shift, evolution of J coupling and free preession and application r f pulse are all rotations.

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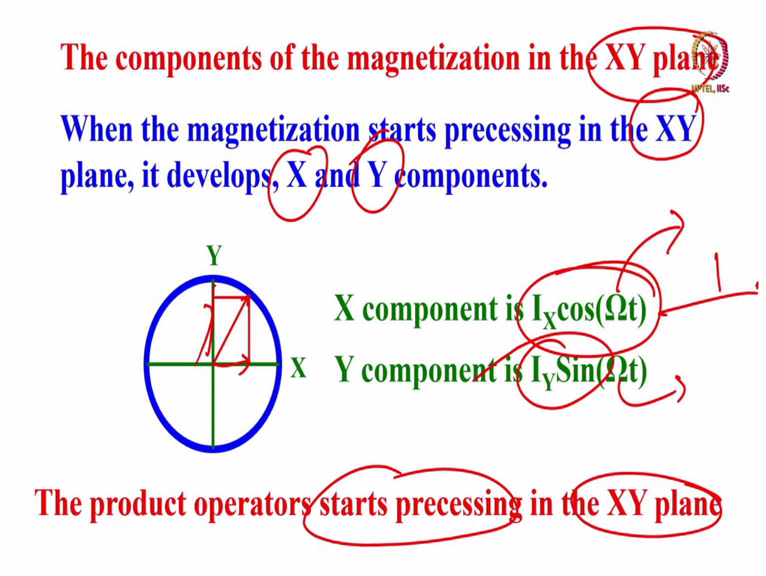

Now, before we understand the rotations in the x y plane; this part we almost discussed this when we were discussing about the pulse space and receiver phase etc. But just for recapitulation, just remember this thing, the component of the magnetization in the xy plane, we know how to resolve into 2 components, when the magnetization is brought to the xy plane.

They start processing in the xy plane; immediately apply an 90 pulse bring it to x axis then it starts processing the x y plane. So, it develops x and y components. Magnetization develops x and y components, this we know; we have already discussed. Let us say this is the x component, this is the y component; the x component is cosine of Ix into cosine of omega t, what is omega? in the rotating frame it is an offset or you can call it as a chemical shift. It depends upon how far it is from the center of this spectral width are chosen. So, that is called offset. We discussed this, when we were discussing about the evolution of chemical shift and coupling constants. And Y component is Iy sin omega t. Again omega is a offset or chemical shift, you can call it. Let us when I say bring the magnetization to x y plane. We have x component, the product operator starts processing in the xy plane. I would simply say the product operator starts processing in the xy plane; it means Ix and Iy starts processing.

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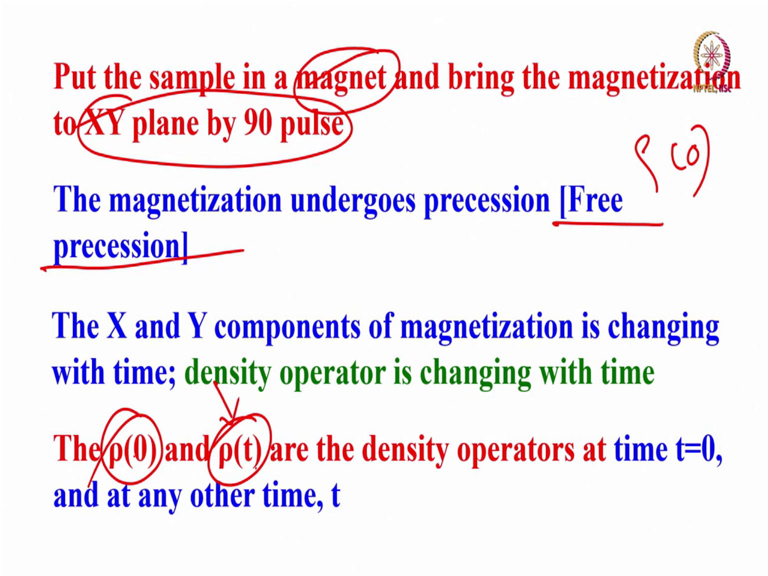

With this idea, we will start understanding more about the product operators. First, you put the sample in a magnet and bring the magnetization to the xy plane by a 90 degree pulse. That is what in the previous lesson slide I said. This, what we will do? Now, this is called free precision; After you apply the 90 pulse bring the magnetization the xy plane. Now we have to think of what is called free precision. That means as I told you, the free precision is a rotation about Z axis.

That is what is going to happen now. So, it means the x and y components of the magnetization keeps on changing with time and this magnetization is undergoing rotation; the x component y component also keeps changing with time. What does it mean? The density operator rho is also changing with the time; that is the conclusion. Simply do not do anything, bring in magnetization from Z axis to xy plane by 90 pulse.

Then the xy components magnetization start changing with time that means density operators changing with the time; that is the conclusion. So, now to understand the rho t, rho of t is the final density operator at the time t. If I want to find out what is rho of t? I must definitely know what is rho of 0? What is rho of 0? It is the density operator at time t equal to 0. So, I should know rho 0; both rho of 0 and rho of t.

So, I defined rho of 0 as the density operator at time t equal to 0 and rho of t is a density operator at the time t. So, these are the 2 things; rho 0 and rho t we are defining.

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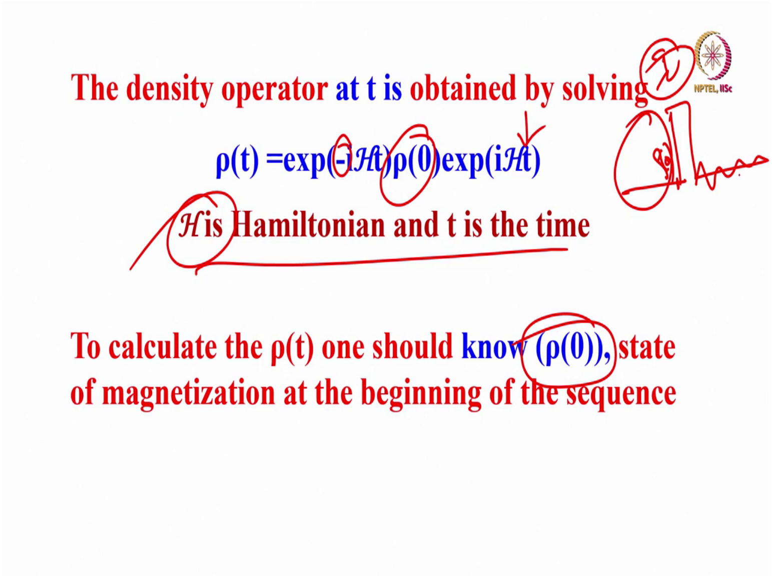

And if I want to calculate density operator at time t, that is rho of t, the magnetization would have evolved with time. So, in the beginning I must know what is initial rho 0, that is initial density operator. This is the one which evolves with time under pulses, delays etc. So, if I know what is rho 0 then I can find out what is the rho t by a simple expression like this. This expression is e to the power of minus iHt rho of 0 into e to the power of iHt.

So, this is what is the equation that we have to use if we have to calculate rho of t, in any given sequence. Now, you might ask me, what is H here? Of course, t is time, i and all those things you know. The rho 0 is my initial density operator, what is H? H is Hamiltonian, and t is the time at which Hamiltonian is getting changed as a function of time; what is happening to this Hamiltonian? That is what you have to study. So, t is the time; H is the Hamiltonian.

Now, to calculate rho t, I must know what is rho 0, then that means I must know the state of the magnetization at the beginning of the sequence. What is the magnetization at the beginning of the sequence? I must know. For example, I have to simply apply a pulse and start collecting the signal. If I want to understand this by density operator; before applying the pulse, I call this as rho 0.

What is the rho 0 here, it is in the thermal equilibrium, rho 0 is just the Iz component, that is all. So, we must know what is the state of the magnetization at the beginning of the sequence. If we know that then of course, how that evolves as a function time in different pulses and time we can understand. So, if I know rho 0, I can calculate rho of t; see very important thing.

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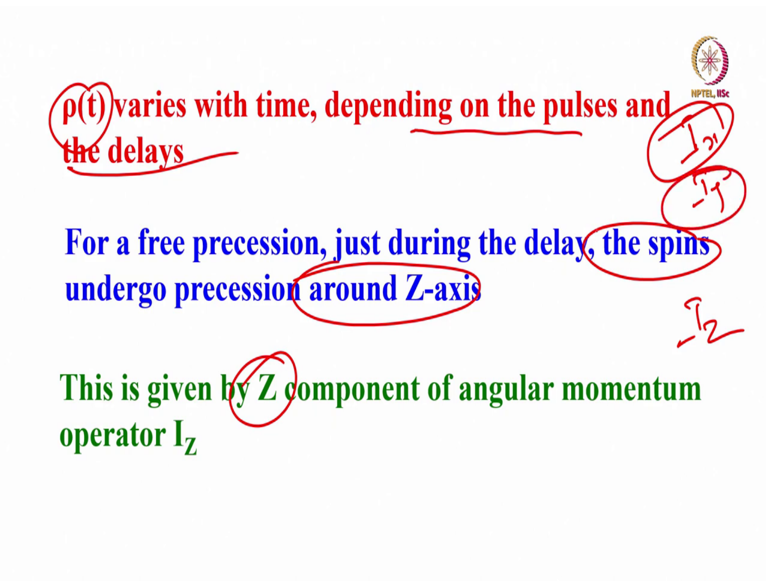

As I said rho t varies with time depending upon the pulses and the delays. It is not same for all the pulse sequences; it is different, depends upon the pulse you apply. Depends upon the delay you give, depends upon sequence of pulses you apply, one pulse, two pulse and what type of pulse, whether it is 90 pulse, whether it is on x axis y axis; all those things. So, it depends upon the type of pulses, the phases, the pulses you apply and the delays; all are important.

So, the rho t varies with time. So, as I said, when I am considering a free precession that is just during the delay. I always have to consider the spins undergoing precession along Z axis. I repeated this; I said the sometime back I am repeating it again, in the free precession there is a rotation around Z axis. And this is given by Z component, a rotation about z component as I said is Iz.

Remember I told you Ix and Iy components, Ix rotation about x axis. Iy is the rotation about y axis. Similarly, if I have to consider the rotation about Z axis, it is simply Iz. Iz is the rotation about Z axis.

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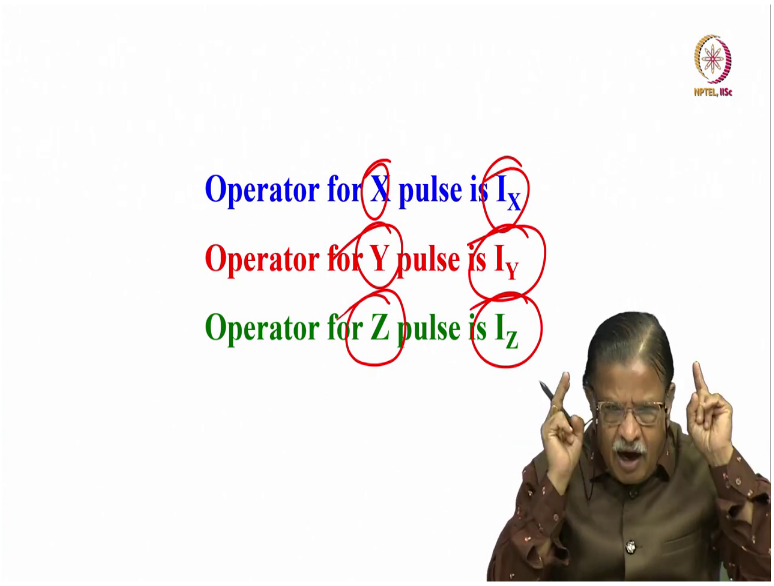

So, now with this, we can define operators for different pulses. For example, operator for X pulse is Ix; if I apply Y pulse, the operator for Y pulse I have to start with Iy. If I want to consider the operator for Z pulse I have to take Iz. These are the operators for X Y and Z pulses. Please note operator for the X pulse is Ix, operator for the Y pulse Iy and the operator for the Z pulse is Iz.

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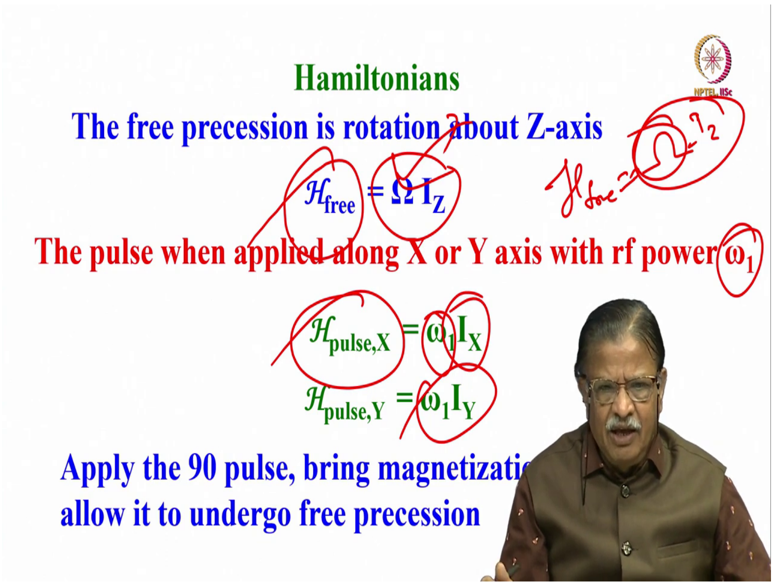

These things I must understand, then I can generate the Hamiltonians with this idea and then start calculating the rho of t. Let us say I want to build a Hamiltonian, that is another thing. I must construct the Hamiltonian; for a free precision I said rotation is about Z axis. So, I call this Hamiltonian is a Hfree; Hamiltonian free which is rotation, omega is the offset or the chemical sheet.

It is precession, free precision Hamiltonian is given as H free, which is equal to omega into Iz. It is the offset. that is a free precision Hamiltonian. You should always remember when after the pulse if some delay is given, then this is the Hamiltonian you have to apply, and find out how the product operators are changing under free precision. When the pulse is applied along the x or y axis, let us say, I am going to apply the pulse with an rf power of omega1. It is the power of the rf.

Then Hamiltonian for the x pulse if along the x axis, I call it the omega 1 into Ix. Omega 1 is the rf power which is going to be gamma h1 into pulse width. Similarly for the Y pulse it is omega 1 into Iy. These are the Hamiltonians when you apply a pulse along the x or y axis. So, after the 90 degree pulse, bring the magnetization the x axis and allow it undergo free precession, then you have to use this free precession Hamiltonian.

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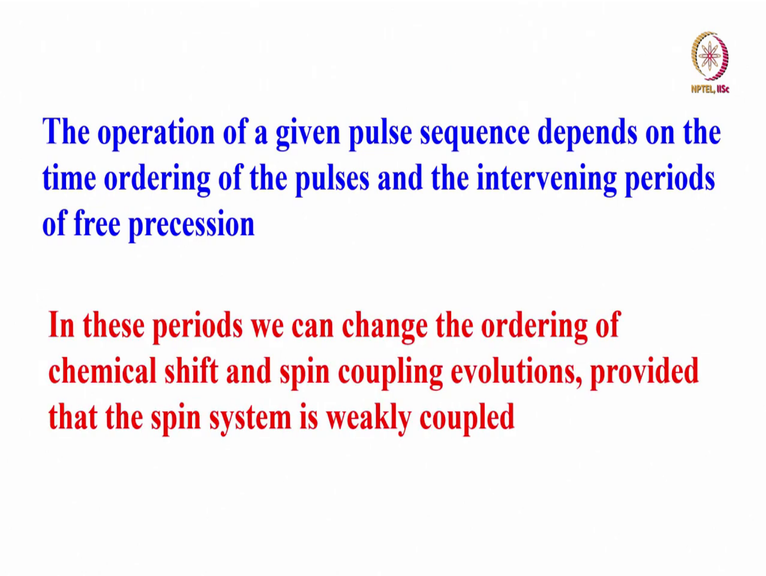

And then start calculating what is going to happen. So, now the operation of the sequence, how it is going to evolve, everything we shoud know. Mow the time is getting over. What I am going to do is I will stop here, we will come back and continue further about the product operators; evaluate about free precession; what happens if under different pulse sequences everything. So, what I wanted to tell you today, in this class, I started introducing the product operators formalism. it is based on the density operator theory.

I told you the product operator contains Ix, Iy and Iz components of angular momentum which is a linear combination. How much is the rho of t at any given instant of time if we want to calculate the density operator rho of t which is given as ax into Ix + ay into Iy + az into Iz. Of course ax of t it is time dependent variable. So, ax and ay and az are the coefficients.

Then finally, we understood that the Mx is nothing but ax of t, Mx of t. My of t is equal to ay My of t like that. We understood what are the coefficients also. Finally, we know the amount of magnetization Mx correspond to Ix. Ix can be correlated to the Mx component of magnetization Mx. We understood Ix; Iy and Iz which are correlated to Mx, My and Mz also.

But also I said if I have to understand the pulse sequences and what is happening to the density operator at different times of the pulse sequences, I must know what is rho 0. That is the beginning of the sequence and where we are applying the pulse, whether the magnetization is along the x axis; y axis or what? If you apply a pulse along x axis, I said it is Ix. If you apply the pulse along y axis it is Iy.

And each of them can be treated as a rotation. I said Ix can be treated as the rotation along x axis; Iy can be treated as a rotation about y axis; Iz is the rotation about Z axis. All the 3 we understood. And then while understanding the product operators how things evolve, I said everything is rotation. If you apply a pulse, rf pulse that is the rotation. And then give a delay, do not do anything. That is a precession. And during the time chemical shift, can evolve J couplings can evolve. They are all rotations; everything can be treated as rotations. So, then you have to consider the Hamiltonian for free precession in different pulse sequences, there are different pulses when you apply, then you can work out the rho of t. I told you the Hamiltonian for a free precession is omega into Iz it because in the free precession, the rotation is a about Z axis.

Now, if I apply a pulse of rf omega 1, rf power omega 1, then Hamiltonian of the pulse, let us say x pulse, it is omega 1 into Ix. If I am applying the pulse along y axis with the power of rf omega 1, then Hamiltonian of the pulse along y axis is omega 1 into Iy. So, this is what we understood and we will continue further we will come back and see how we can calculate rho t for different sequences, with some examples, understand more about product operators. How we can utilize them to understand the evolution of the magnetization in different sequences, different time periods with one or 2 examples of pulse sequences. So, with this, I am going to stop now, we will come back again and continue with this. Thank you.