NMR Spectroscopy for Chemists and Biologists

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Lecture No. 32

Evolution of Density Operator in the presence of RF

Welcome. Let us continue the discussion of the effects of the RF pulses. How does the density operator transform in the presence of RF? Because we need to know all such things, how does a density operator transform under the influence of different kinds of Hamiltonians. So the RF constitutes also have Hamiltonian and we actually saw last time how to calculate the evolution of the density operator in the presence of the RF.

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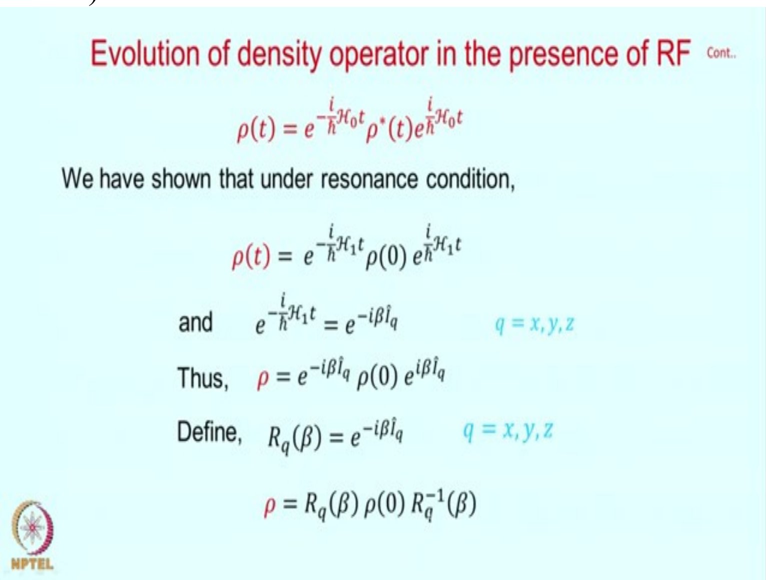

So we had this solution here. We started off with the Liouville equation and we represented a solution like this:

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\rho^*(t)e^{\frac{i}{\hbar}\mathcal{H}_0 t}$$

And H_1, there was the RF Hamiltonian was represented by H_1. And this represent to the interaction representation and we also show after detailed calculation that under the resonance condition we have the

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}_1 t}\rho(0)\, e^{\frac{i}{\hbar}\mathcal{H}_1 t}$$

and this H_1 represents the Hamiltonian of the RF.

And we also demonstrated that

$$e^{-\frac{i}{\hbar}\mathcal{H}_1 t} = e^{-i\beta \hat{I}_q}$$

We will explicitly demonstrate that further, how this will represent a rotation. And therefore having said this, we will say

$$\rho = e^{-i\beta \hat{I}_q}\, \rho(0)\, e^{i\beta \hat{I}_q}$$

Notice here, q can be x, y or z. Generally z is only rotation around the Z axis; therefore it is not kind of an effect of the RF pulse. But general rotation along the Z axis can be represented in the same manner if the rotation is about a particular angle β.

And we define now this as the rotation operator, call it as $R_q(\beta)$,

$$R_q(\beta) = e^{-i\beta \hat{I}_q}$$

and q can be x, y or z. So therefore my

$$\rho = R_q(\beta)\, \rho(0)\, R_q^{-1}(\beta)$$

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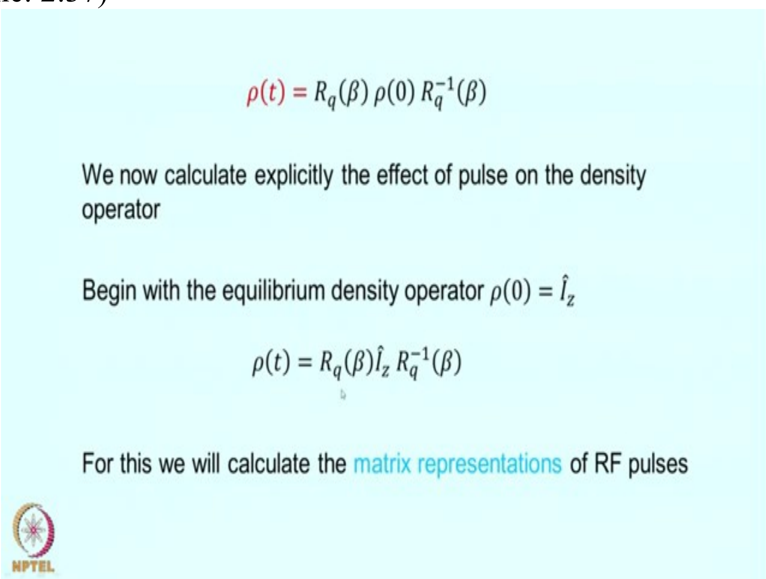

And that is the same equation here. We now calculate explicitly the effect of the pulse on the density operator. So to begin with, let us take the equilibrium density operator I_z. Okay, $\rho(0)$, I_z. Of course, if the $\rho(0)$ has these other entities but operator part is the I_z only. Therefore, we will pick up only the I_z part of the density operator, equilibrium density operator and put that here. So the rho of t for $\rho(0)$put here I_z, $R_q(\beta)$ $R_q^{-1}(\beta)$. So in order to do this, I need to get matrix representations of these operators.

These were in the form of exponential operator whereas I_z I knew is in the matrix operator. Therefore, I have to put this also in the form of matrices. So for this, we will calculate the matrix representation of the RF pulses. We have to get explicit matrix representations for these terms. So how do we do it?

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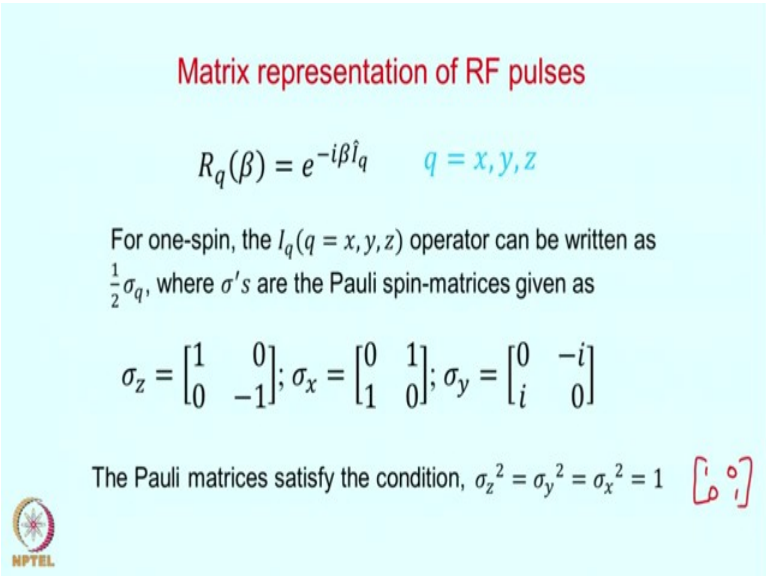

So let us write here again,

$$R_q(\beta) = e^{-i\beta\hat{I}_q}$$

Where, q can be x, y or z. Now, we have earlier seen matrix representations of the operators, I_x, I_y, and I_z and these ones we have calculated matrix representations of the operators, I_x, I_y, and I_z. And those ones were simply are given in this except for the factor half. So therefore, this can be represented as $\frac{1}{2}\sigma_q$ where σ's are the Pauli spin-matrices.

Basically

$$I_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, I_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, I_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

Now we take away ½ , you have this matrix as $\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$. And this is represented as σ_z and likewise

$$\sigma_z = \begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix};\ \sigma_x = \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix};\ \sigma_y = \begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}$$

These are called as spin matrices. For a single spin half, these are called as Pauli spin-matrices. You can easily verify that the Pauli matrices satisfy this condition,

$$\sigma_z{}^2 = \sigma_y{}^2 = \sigma_x{}^2 = 1$$

But one notice here, this 1 is a unit matrix. It is not just number 1. This is unit matrix, $\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$ 1. So this will be useful for us to calculate the matrix representations of the individual operators.

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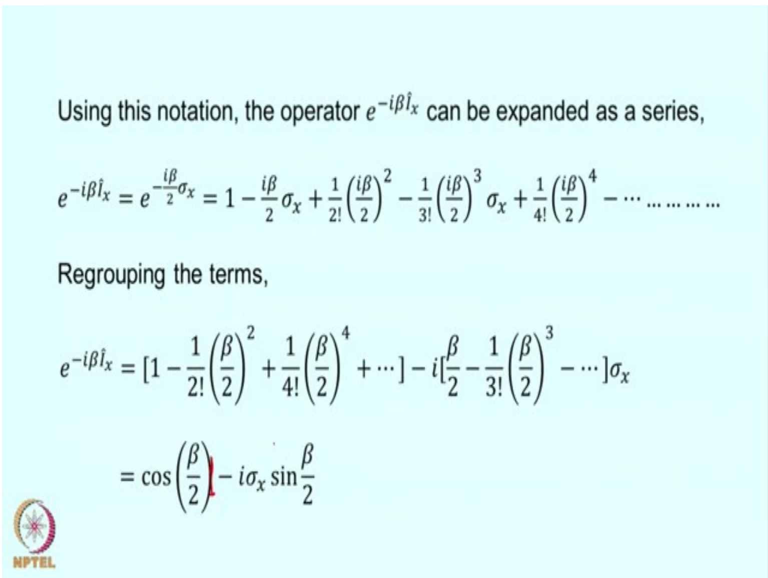

So here I expand this exponential function as a series. This is a typical expansion of the exponential function,

$$e^{-i\beta\hat{I}_x} = e^{-\frac{i\beta}{2}\sigma_x} = 1 - \frac{i\beta}{2}\sigma_x + \frac{1}{2!}\left(\frac{i\beta}{2}\right)^2 - \frac{1}{3!}\left(\frac{i\beta}{2}\right)^3\sigma_x + \frac{1}{4!}\left(\frac{i\beta}{2}\right)^4 - \cdots \ldots \ldots \ldots \ldots$$

Although the explicit unit matrix is not yet written here, but it is there. Remember this. Okay, and likewise $\frac{1}{4!}\left(\frac{i\beta}{2}\right)^4$ and this is $\sigma_x 4$. $\sigma_x 4$ is again 1. Therefore you will get this infinite series. There are terms which depend on σ_x and there are terms which do not depend on σ_x.

Now we regroup these terms and we say put all these terms which do not depend upon

$$e^{-i\beta \hat{I}_x} = [1 - \frac{1}{2!}\left(\frac{\beta}{2}\right)^2 + \frac{1}{4!}\left(\frac{\beta}{2}\right)^4 + \cdots] - i[\frac{\beta}{2} - \frac{1}{3!}\left(\frac{\beta}{2}\right)^3 - \cdots]\sigma_x$$

And all of these then have multiplication with σ_x. So therefore this will be, what is this? This first bracket is actually an expansion of the $\cos\left(\frac{\beta}{2}\right)$

This is the series expansion of the term of the function

$$= \cos\left(\frac{\beta}{2}\right) - i\sigma_x \sin\frac{\beta}{2}$$

Therefore I had here $\cos\left(\frac{\beta}{2}\right)$ multiplied by the unit matrix. And this is, we can write this unit matrix here. So and the $-i\sigma_x \sin\left(\frac{\beta}{2}\right)$. So what does this give me?

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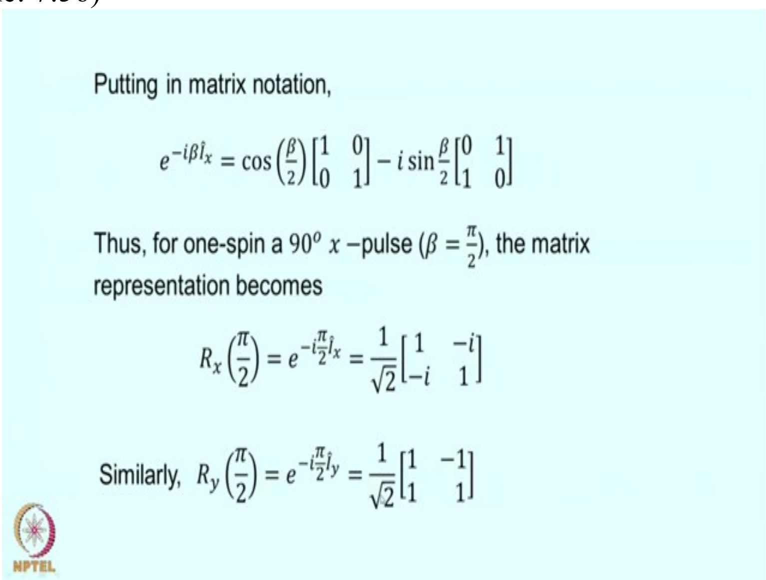

Put this in the matrices, matrix form explicitly,

$$e^{-i\beta\hat{I}_x} = \cos\left(\frac{\beta}{2}\right)\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} - i\sin\frac{\beta}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$$

Therefore, now if I put $\beta=\frac{\pi}{2}$, if I put $\beta=\frac{\pi}{2}$, then what do I get? I get cosine 45 here and sine 45 here and both of them are ¿ $1/\sqrt{2}$. Therefore,

$$R_x\left(\frac{\pi}{2}\right) = e^{-i\frac{\pi}{2}\hat{I}_x} = \frac{1}{\sqrt{2}}\begin{bmatrix}1 & -i\\-i & 1\end{bmatrix}$$

So this is 1 and this gives me -*i*, this gives me -*i*, this gives me 1 and $1/\sqrt{2}$. factor comes out here.

So similarly, for

$$R_y\left(\frac{\pi}{2}\right) = e^{-i\frac{\pi}{2}\hat{I}_y} = \frac{1}{\sqrt{2}}\begin{bmatrix}1 & -1\\1 & 1\end{bmatrix}$$

pulse applied along the *X* axis. RF is applied *x*, this is again now a $\frac{\pi}{2}$ pulse applied along the *Y* axis. So this gives me

$$\frac{1}{\sqrt{2}}\begin{bmatrix}1 & -1\\1 & 1\end{bmatrix}$$

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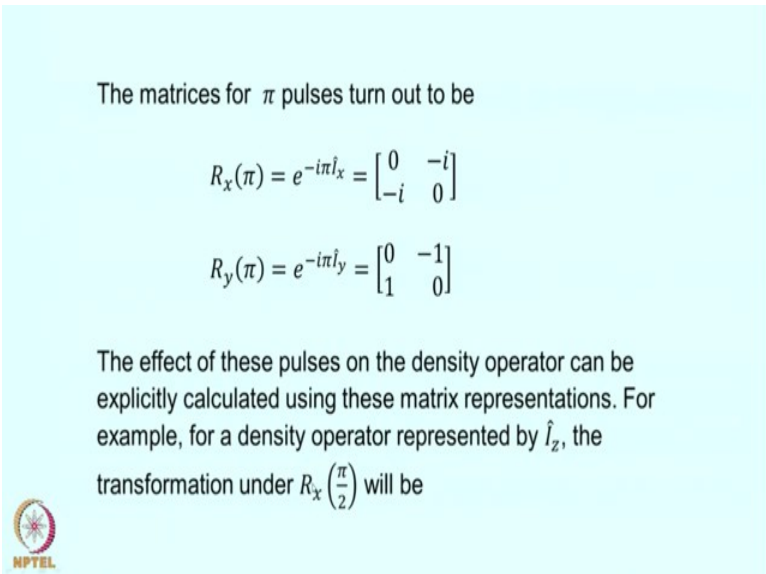

So similarly, we can calculate matrices for the π pulses. If I choose $\beta=\pi$, then

$$R_x(\pi) = e^{-i\pi\hat{I}_x} = \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$$

And

$$R_y(\pi) = e^{-i\pi\hat{I}_y} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

The effect of these pulses on the density operator can be explicitly calculated using these matrix representations. So for example, for a density operator represented by I_z, so this is easiest example to take. So we take the equilibrium density operator represented by I_z.

We will calculate what is the effect of $R_x = \frac{\pi}{2}$. Is it actually a rotation? Now we will actually demonstrate that this pulse does make a rotation.

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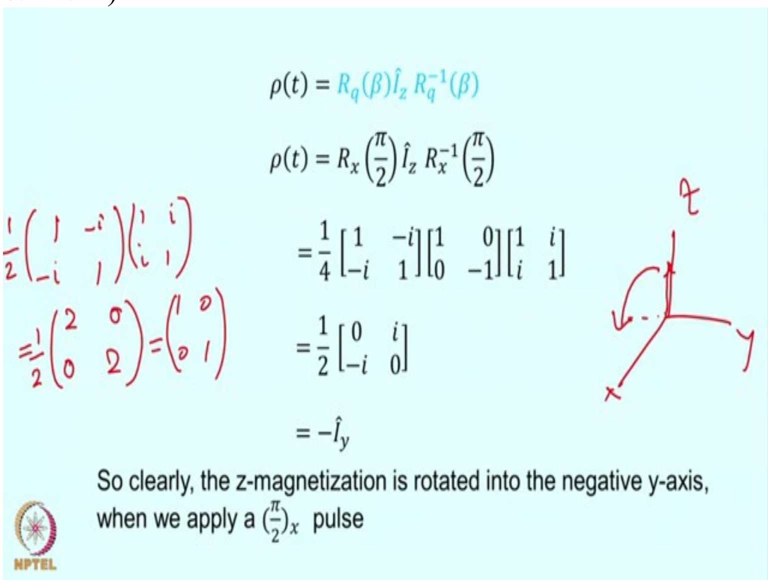

Okay, how do we show that? So the density operator here

$$\rho(t) = R_q(\beta)\hat{I}_z R_q^{-1}(\beta)$$

and therefore I put here

$$\rho(t) = R_x\left(\frac{\pi}{2}\right)\hat{I}_z R_x^{-1}\left(\frac{\pi}{2}\right)$$

So now we calculated what is $R_x = \frac{\pi}{2}$. That was this. And now I get here a $\frac{1}{\sqrt{2}}$ from here, $\frac{1}{\sqrt{2}}$ from here and this gives me $\frac{1}{2}$ in the matrix. Therefore, I have $\frac{1}{4}$. And this gives me

$$= \frac{1}{4} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}$$

Half factor we have already taken away here and the inverse of this R_x inverse, inverse of this matrix is this: 1, i, i, 1. How do I say this? Because now you see if you multiply this matrix with this matrix, you will get 1.

So this product you take 1, 1 here and this gives me 1. And $-i^2$so $-i^2 = 1$. So therefore, $1 + 1 = 2$. We can actually do that. Let me do here the $1, -i - i$, 1 and multiply by 1, i, i, 1. So this gives me, this is equal to 1, $-i^2$, this is 2 and this is i, $-i$ this is 0. And $-i + i = 0$. And this is $-i^2 = 1$, +1, this gives me 2. And therefore, if I take this $\frac{1}{\sqrt{2}}$, $\frac{1}{\sqrt{2}}$, I will have 1 by 2 here. Therefore, this is equal to 1, 0, 0, 1. So therefore, what I have got? Therefore this is the inverse, this is demonstrated that this matrix is the inverse of this matrix.

$$¿ \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -I_y$$

So what I have got? As a result of this $I_z \rightarrow -I_y$. Therefore there is a rotation, 90 degrees rotation. Therefore we have explicitly demonstrated that the *z* magnetization is rotated onto the, so if I had the *z* magnetization here and if I apply the *x*, this is *X, Y, Z* the axis, and this rotates, it transfers magnetization along this. So I get here magnetization rotation to $-I_y$. So for clearly this *z* magnetization is rotated onto the negative *Y* axis.

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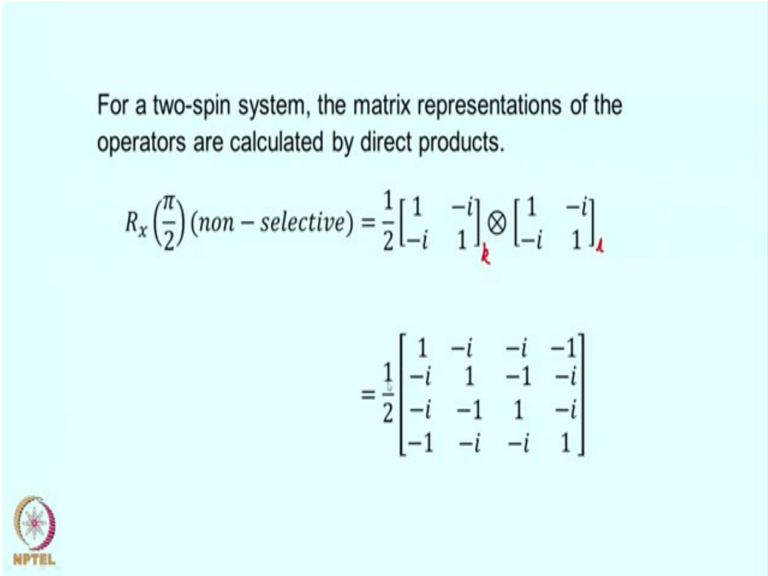

Now for two-spin system, that was simple for one-spin system. For two-spin system, of course it is also simple but we have little bit more calculation here. Now there are two spins, both are independent. Now I want to calculate the matrix representation of the pulse for two-spins. So both are, $I=\frac{1}{2}$, so they have this one spin here and the second spin here. So let me call them as spins *k* and *l*, so if I call this as spin *k* and this spin as *l*, and each one of them is independent. Therefore, if I want to represent a matrix, it represents both of them.

I have to, when I take the product, the product means I cannot take a simple matrix multiplication here. I have to take what is called as the direct product. So direct product means each of these element, when I take the multiplication of the direct product means if I take this and multiply, I put the entire matrix here. Multiply the entire matrix with this element, therefore I get here 1, $-i$, $-i$, 1. Now so far as this element is concerned, I multiply minus i with this entire matrix. Therefore, I get $-i$ here and $-i$ into $-i$ this gives me $+i^2$, that is minus 1 here.

$$= \frac{1}{2}\begin{bmatrix} 1 & -i & -i & -1 \\ -i & 1 & -1 & -i \\ -i & -1 & 1 & -i \\ -1 & -i & -i & 1 \end{bmatrix}$$

So now you see this is the 4 by 4 matrix. So I should get a 4 by 4 matrix, that the I x operator for a two-spin system is a 4 by 4 matrix. So we get that by doing this direct product of the individual spins because the two spins are independent and they can be multiplied by this direct product method.

So therefore, I get a 4 by 4 matrix and my operators I_x, I_y, I_z, they will also be 4 by 4 matrices. And this is the way we calculate the matrix representations of operator for RF pulses.

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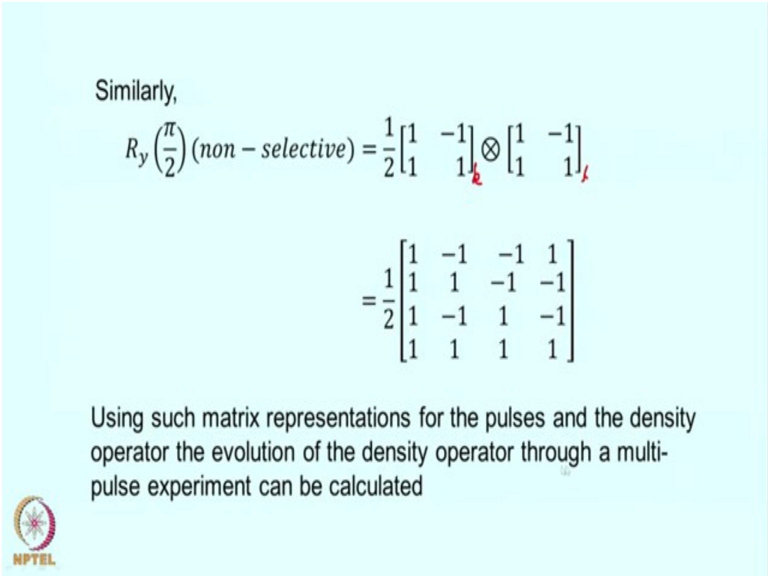

So similarly, we calculate for

$$R_y\left(\frac{\pi}{2}\right)(non-selective)=\frac{1}{2}\begin{bmatrix}1 & -1\\1 & 1\end{bmatrix}_k \times \begin{bmatrix}1 & -1\\1 & 1\end{bmatrix}_l$$

I take the direct product. So if I take the direct product, I get here 1, minus 1, 1, 1, that is the same. And then this is basically multiplying with minus 1, this whole thing, so I get here minus 1, 1, minus 1, minus 1 here. And this will be 1, minus 1, 1, 1. And this will be 1, minus 1, 1, 1. Because all these are 1's here.

So therefore this will be except this, this term will be different. So this $R_y\left(\frac{\pi}{2}\right)$ now consists of all real numbers. Whereas R_x contain all imaginary i's also. Using such matrix representations for the pulses and the density operator, the evolution of the density operator through a multi-pulse experiment can be calculated.

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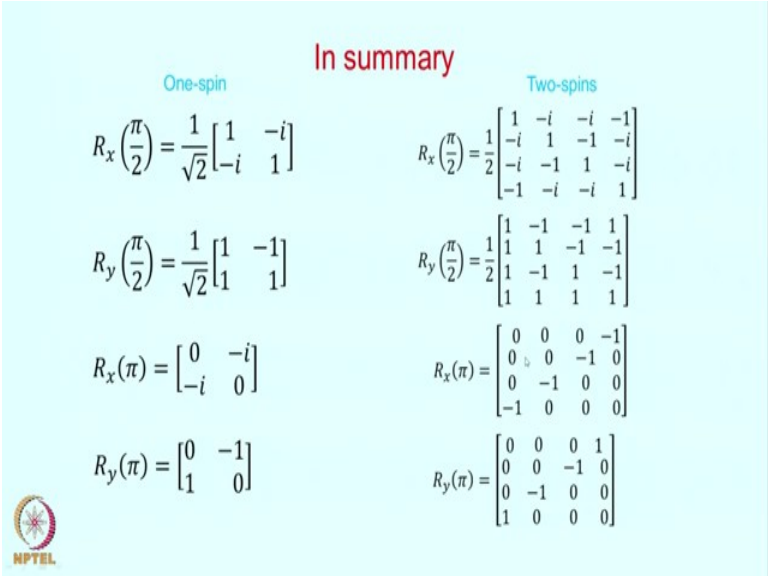

So put this all in summary. I have for one spin,

$$R_x\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix}$$

$$R_y\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$$

$$R_x(\pi) = \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$$

$$R_y(\pi) = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

And similarly, for the two-spins you have 4 by 4 matrices and you have calculated here

$$R_x\left(\frac{\pi}{2}\right) = \frac{1}{2}\begin{bmatrix} 1 & -i & -i & -1 \\ -i & 1 & -1 & -i \\ -i & -1 & 1 & -i \\ -1 & -i & -i & 1 \end{bmatrix}$$

$$R_y\left(\frac{\pi}{2}\right) = \frac{1}{2}\begin{bmatrix} 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

which will contain only anti-diagonal elements. Notice here, of course here also they contain anti-diagonal elements. This is the diagonal and this is anti-diagonal. So I have only anti-diagonal elements here and here also I have only anti-diagonal elements,

$$R_x(\pi) = \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}$$

And this indicates how, this shows how the calculations have to be performed.

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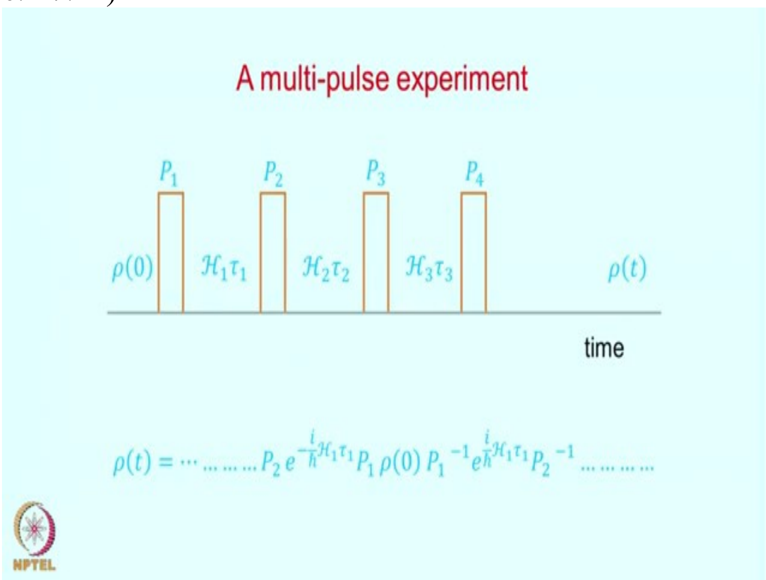

Okay. So for now we can, now we are ready to calculate any kind of a matrix representation, any kind of evolution of a multiple-pulse experiment. So if I have multiple pulse experiment, so I start with initial density operator $\rho(0)$. Start with this, apply a pulse P_1 here and then allow the spin system to evolve under the influence of the Hamiltonian H_1 for the period τ_1. Then apply a pulse P_2, then apply and then allow this system to evolve the influence of the Hamiltonian H_2 for a period τ_2 and continue like this.

Therefore, any number of pulses what we might have here, I can continue to calculate the evolution of this, of the density operator through the pulse sequence and finally I will get density operator here which is what I actually measured. And then that contains entire information about the evolution of the spin system through the pulse sequence. Okay, how do we actually do it? So therefore we start with the $\rho(0)$, this is my initial density operator.

So if I put the density operator here, the first thing that is coming here is the P_1. That is the pulse. Therefore, when I have the pulse, I have P_1 and P_1 *-1*. So this is the what I get after the first pulse. That means for this part of the evolution, the density operator here becomes the $\rho(0)$. This is the new $\rho(0)$. So for the beginning of this one, this becomes my $\rho(0)$. So therefore this is my rho0 for the next operation and that is the evolution under the Hamiltonian H_1 for the period τ_1.

So e to the power minus i by h cross H1 tau1 and on this side you have $e^{\frac{i}{\hbar}H_1\tau_1}$. So now, where I am? I have reached here at the end of this. Now apply the pulse again. If I apply the pulse, therefore once again I multiply by P_2 here and P_2 *- 1* here. Now if I, then I reach here, then of course I will have to multiply by $e^{\frac{-i}{\hbar}H_2\tau_2}$. And on this side, $e^{\frac{i}{\hbar}H_2\tau_2}$and so on. So this is the way one can actually calculate the matrix representations of the density operators and evolutions of the density operator through the multi-pulse experiment.

And that is way one has to calculate it and I think we can take it forward in the next classes and with the explicit calculation and see what is the physics and what is the science that comes out of these calculations. So we will stop here.