NMR Spectroscopy for Chemists and Biologists
Doctor Ashutosh Kumar
Professor Ramkrishna Hosur
Department of Biosciences & Bioengineering
Indian Institute of Technology Bombay
Lecture 31
Density Matrix Description of NMR – 4

So, we are going to continue the discussion of the density matrix, for the description of the NMR experiments.

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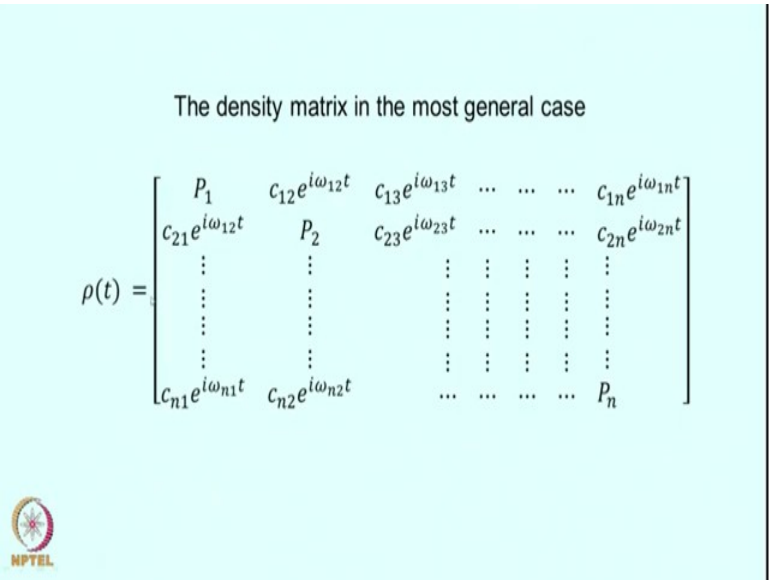

The density matrix in the most general case

$$\rho(t) = \begin{bmatrix} P_1 & c_{12}e^{i\omega_{12}t} & c_{13}e^{i\omega_{13}t} & \cdots & \cdots & \cdots & c_{1n}e^{i\omega_{1n}t} \\ c_{21}e^{i\omega_{12}t} & P_2 & c_{23}e^{i\omega_{23}t} & \cdots & \cdots & \cdots & c_{2n}e^{i\omega_{2n}t} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ c_{n1}e^{i\omega_{n1}t} & c_{n2}e^{i\omega_{n2}t} & \cdots & \cdots & \cdots & \cdots & P_n \end{bmatrix}$$

As a recap I have put here the generalized form of the density matrix for an n level system. So, you have this n, the small n, there are n level system, and if you recall, all the diagonal elements in the density matrix represent the populations of the individual levels, so these ones I have represented as P_1, P_2, P_3, P_4 and P_n like that. The off diagonal elements represent the phase coherences between the spins in the individual states.

For example, if I take this the energy levels are labeled 1 to n, this term represents a phase coherence between the spins in the states 1 and 2. The extent of phase coherence is represented by this coefficient here, C_{12} and this shows the time dependence of this phase coherence, and that goes with this frequency ω_{12}. So, this is an oscillating function, this is phase coherent, this is the degree of phase coherence and that is oscillating with frequency ω_{12}.

And this will be the phase coherence between the states, between the spins in the states 1 and 3 and this is the extent of phase coherences with the magnitude amplitude and this is the phase. How does the phase change between the two spins? So, it is oscillating with the, with time and like that for every pair of states you have a phase coherence between the individual states. And so therefore, in principle you can have phase coherences between any two states, and therefore, here nothing is assumed to be 0.

However, in reality, of course, all of these terms will not be non-zero, there will be some terms which will be zero, or which some terms which will not be zero and that will explicitly consider when we take specific examples.

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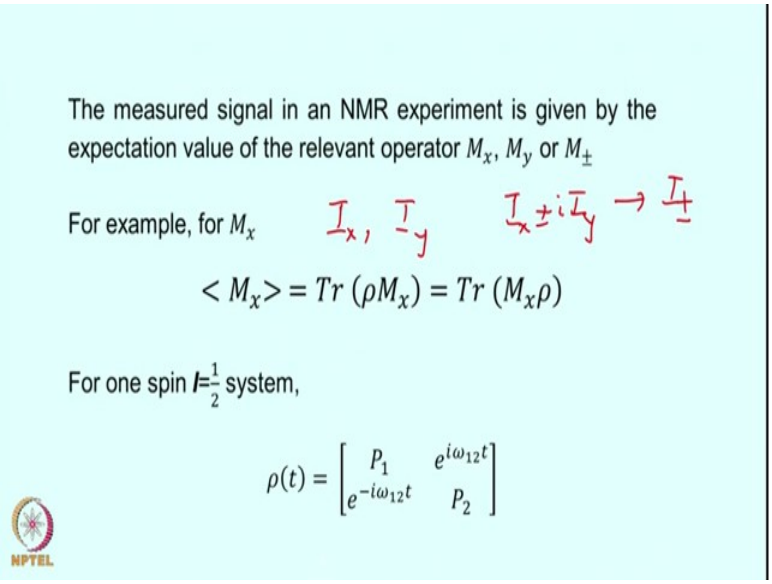

The measured signal in an NMR experiment is given by the expectation value of the relevant operator M_x, M_y or $M_\pm$

For example, for M_x I_x, I_y $I_x \pm i I_y \rightarrow I_\pm$

$$< M_x > = Tr\,(\rho M_x) = Tr\,(M_x \rho)$$

For one spin $I=\frac{1}{2}$ system,

$$\rho(t) = \begin{bmatrix} P_1 & e^{i\omega_{12}t} \\ e^{-i\omega_{12}t} & P_2 \end{bmatrix}$$

Now, having seen what the density operator is, the density matrix is, and we must also see what is a measurement, in fact, we have discussed this earlier also. When we measure a signal in NMR experiment, what we are actually measuring is the so called expectation value of the relevant operator.

M_x or M_y or $M \pm$, $M \pm$ these are called as raising and lowering operators, this is called M_x + I M_y, but remember here, earlier I used symbol, here I used the symbol I_x to measure X magnetization or Iy for measuring Y magnetization and you can also measure in between the two, then that is called as $I_x \pm i I_y \rightarrow I \pm$.

So, for convenience I have used here M_x to say it is magnetization, but this earlier I have used the nomenclature I_x and I_y, these are the operators I_x and I_y, which represent the transverse magnetization components, X and the Y components. The expectation value is given by this, which is the trace of the density matrix with the M_x matrix. And notice here it is the symmetry, the trace of $\rho M_x$is the same as the trace of $M_x \rho$, so it does not matter here, which way you, which order you multiply it, but the trace is invariant to that.

So, this is a kind of a principle which is generally valid and one can easily verify it by taking different kinds of $\rho's$ and M_x's and whatever, then you will find that this equation is actually valid. Now, let us take an example, we take an example for a one spin system, $I=\frac{1}{2}$. So, it has two energy levels, I is equal to half as two energy levels, therefore, the $\rho(t)$ will be a 2 by 2 matrix.

So, we have two populations here, and there is a coherence, one coherence between the two energy levels. So,

$$\rho(t) = \begin{bmatrix} P_1 & e^{i\omega_{12}t} \\ e^{-i\omega_{12}t} & P_2 \end{bmatrix}$$

essentially looks like a complex conjugate of this, this was the same as in the generalized case. If we have such a kind of a one spin system which is clearly not the equilibrium density matrix, right?

In the equilibrium density matrix we had the populations non-zero, and these ones were 0. So, therefore, this is clearly a non-equilibrium state created somehow, so we will not go into that one now, we will come to that later, when we discuss the multiples experiments. So, we will assume that we have somehow created, these coherences between the two energy levels 1 and 2 and we also assume that the amplitudes here are the same.

So, this is a particular amplitude here, and of course, the same amplitude is present here, we assume it is the same. So, this is my initial density operator to start with, we do not ask, how I created this at this point, and we will see what is the consequence of this. How we created it comes later, and that will that also we will see in due course.

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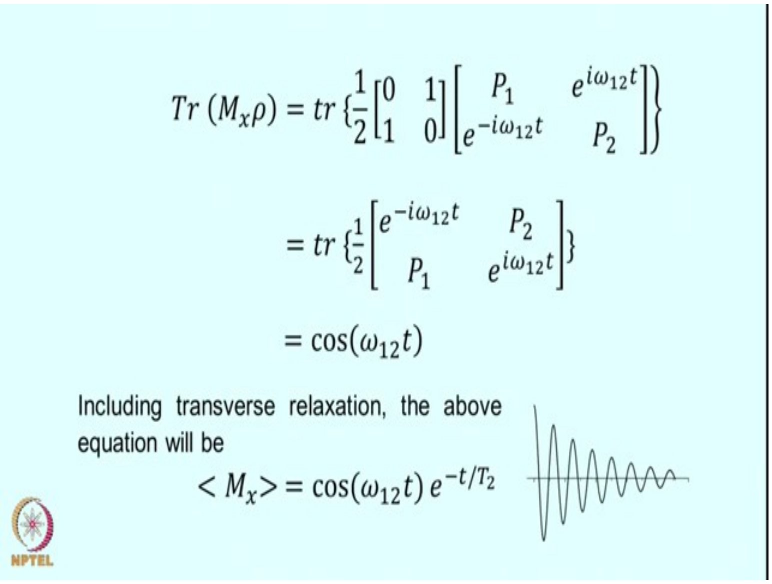

$$Tr\,(M_x\rho) = tr\,\{\frac{1}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}P_1 & e^{i\omega_{12}t}\\ e^{-i\omega_{12}t} & P_2\end{bmatrix}\}$$

$$= tr\,\{\frac{1}{2}\begin{bmatrix}e^{-i\omega_{12}t} & P_2\\ P_1 & e^{i\omega_{12}t}\end{bmatrix}\}$$

$$= \cos(\omega_{12}t)$$

Including transverse relaxation, the above equation will be

$$< M_x > = \cos(\omega_{12}t)\, e^{-t/T_2}$$

So, let us exactly calculate it now. Earlier you remember we calculated the matrix representations of the I_x operator.

$$Tr\,(M_x\rho) = tr\,\{\frac{1}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}P_1 & e^{i\omega_{12}t}\\ e^{-i\omega_{12}t} & P_2\end{bmatrix}\}$$

Likewise, for this multiplication 1 into P_1 + 0 into this and therefore, this will be equal to P_1 and the fourth one will be 1 into $e^{i\omega_{12}t}$ and 0 into P 2, therefore you have this. So, now what is the trace of this? You remember the definition of the trace, the trace is the sum of the diagonal elements of the matrix, so if I add these terms and you have

$$= tr\,\{\frac{1}{2}\begin{bmatrix}e^{-i\omega_{12}t} & P_2\\ P_1 & e^{i\omega_{12}t}\end{bmatrix}\}$$

and that is the cosine function, so the ¿$\cos(\omega_{12}t$¿$)$¿.

Therefore, what I measure is therefore this coherence, I measure the time dependence of this coherence here and so including, now if I include the transverse relaxation which has not been included here in any of these, we only included the time dependence and the frequency dependence of the phase coherences here, and the relaxation is not included. So, if I include the relaxation I have to multiply this whole, this is the transverse magnetization, right?

$$< M_x > = \cos(\omega_{12} t)\, e^{-t/T_2}$$

So, the transverse magnetization has to be multiplied by e^{-t/T_2}, where T_2 is the transverse relaxation time. So, if you plot it, what do I get, I get this function, which is basically my FID, right? So, therefore, I am actually, if I create the density operator which has off diagonal element which is non-zero, that reflects itself in the measurement of the magnetization and what we measure is the FID as a function of time, what we are measuring is free induction decay, this is the FID.

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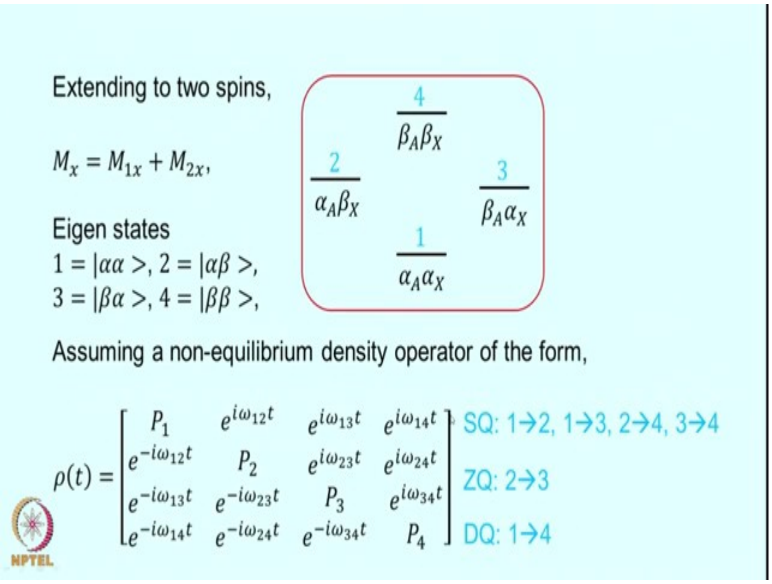

Extending to two spins,

$M_x = M_{1x} + M_{2x}$,

Eigen states

$1 = |\alpha\alpha>$, $2 = |\alpha\beta>$,

$3 = |\beta\alpha>$, $4 = |\beta\beta>$,

Assuming a non-equilibrium density operator of the form,

$$\rho(t) = \begin{bmatrix} P_1 & e^{i\omega_{12}t} & e^{i\omega_{13}t} & e^{i\omega_{14}t} \\ e^{-i\omega_{12}t} & P_2 & e^{i\omega_{23}t} & e^{i\omega_{24}t} \\ e^{-i\omega_{13}t} & e^{-i\omega_{23}t} & P_3 & e^{i\omega_{34}t} \\ e^{-i\omega_{14}t} & e^{-i\omega_{24}t} & e^{-i\omega_{34}t} & P_4 \end{bmatrix}$$

SQ: 1→2, 1→3, 2→4, 3→4

ZQ: 2→3

DQ: 1→4

Let us extent to two spins, that was one spin. Now, $M_x = M_{1x} + M_{2x}$, or otherwise one could have taken $I_{1x} + I_{2x}$, but let us keep the same nomenclature $M_{1x} + M_{2x}$. Now, for the two spins both are spin half systems, the two spins both are spin half, so then I will have, for the two spin system I will have four energy levels here, where and these ones are represented as $\alpha_A \alpha_X$.

This *A* and *X* represent the spins, one spin is called *A* other one is called as *X*, this is capital *X* not to be confused with this coordinates *x*, $\alpha_A \alpha_X$, and then I have the energy level 2 $\alpha_A \beta_X$, energy level 3 $\beta_A \alpha_X$, and energy level four is $\beta_A \beta_X$. So, these are called as product functions, these are the Eigen functions of the Hamiltonian and for the weakly couple situation as we have seen in the lectures on analysis of NMR spectra.

So, for weakly coupled Hamiltonian this the spin system these ones are Eigen functions of the Hamiltonian and they represent the energy levels in this order. So, we call it $\alpha_A \alpha_X$, $\alpha_A \beta_X$ as number 2, $\beta_A \alpha_X$ as number 3, $\beta_A \beta_X$ as number 4. And we will maintain this same convention in defining the energy levels and their spin states. Now, so here for this spin state, what is the azimuthal quantum number, this is +1, *n* here it is 0, here it is 0, here it is -1 because $\alpha = \frac{1}{2}$ and $\beta = \frac{-1}{2}$.

And it is true for both, therefore this adds to plus 1, this adds to 0, this also adds to 0, this adds to minus 1. Simply, dropping these A and X subscripts here, we can simply write these states as $1 = ¿\alpha\alpha >, 2 = ¿\alpha\beta >, 3 = ¿\beta\alpha >, 4 = ¿\beta\beta > ¿$. Now, once again I will assume a non-equilibrium density operator of this form. Notice here, this was again from the generalized statement of the density operator or the density matrix.

So, I have here the four populations of the four states here *P₁, P₂, P₃, P₄* and I have the coherences between the states 1 and 2, spins in the states 1 and 2, spins in the states 1 and 3, and this represents the spins in the states 1 and 4 and this represents the spins in the states 2 and 3 and this represents 2 and 4. Likewise, so I will also have 3 4 here, and these are their complex conjugates, complex conjugates in the sense, these are actually supposed to be ω_{21}, ω_{31}, ω_{41}, but $\omega_{21}\, is - \omega_{12}$.

$$\rho(t) = \begin{bmatrix} P_1 & e^{i\omega_{12}t} & e^{i\omega_{13}t} & e^{i\omega_{14}t} \\ e^{-i\omega_{12}t} & P_2 & e^{i\omega_{23}t} & e^{i\omega_{24}t} \\ e^{-i\omega_{13}t} & e^{-i\omega_{23}t} & P_3 & e^{i\omega_{34}t} \\ e^{-i\omega_{14}t} & e^{-i\omega_{24}t} & e^{-i\omega_{34}t} & P_4 \end{bmatrix}$$

Now, notice here, the spins in the states 1 and 2, so what is this phase coherence, what are, what is this coherence here, what is this frequency? This frequency is basically the transition frequency of the spin *X*, right? So, it is this transition $\alpha \rightarrow \beta$, therefore, this represent, this single quantum, single quantum coherence here.

We call it as the single quantum coherence because what is the spin state, I mean the azimuthal quantum number change, this is plus 1 here and 0, therefore, this is one transition, or the coherence single called, is called as single quantum coherence. This re-corresponds to the spin *X*. Likewise, this also represents the spin *X*, the single quantum coherence, $\alpha_X \rightarrow \beta_X$ here, the *A* spin is in the β state here, *A* spin is in the Alpha state here, and that is the difference because of this there could be changes in the frequencies and this we have seen earlier.

The interesting thing is here, ω_{14}, if there is a coherence between the spin states here and here, and this is double quantum coherence, right? Because this is plus one here and this is minus one here, therefore, the separation between them is 2, and therefore, we call this as the double quantum coherence. These 4 are single quantum coherences, SQ 1 2, 1 3, 2 4, 3 4 are single quantum coherences and 2 3, what is 2 3, 2 3 is from here to here, right?

And this is zero quantum coherence because there is no change in azimuthal quantum number here. So, it is zero here and zero there, in both the states it is zero and therefore, it is zero quantum coherence. So, let us assume that we have a density operator which looks like this or the density matrix which looks like this and what are we going to get if we calculate the trace of M_x with such a kind of a density operator.

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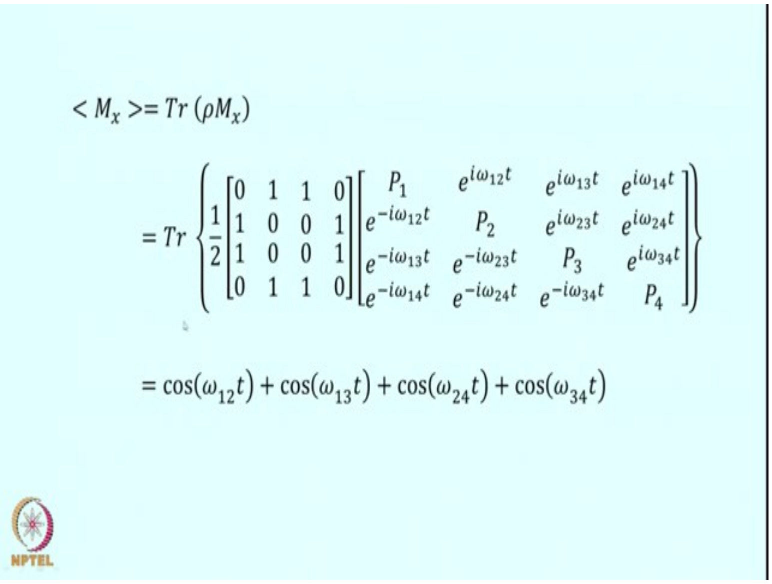

$$< M_x >= Tr\,(\rho M_x)$$

$$= Tr\left\{\frac{1}{2}\begin{bmatrix}0 & 1 & 1 & 0\\ 1 & 0 & 0 & 1\\ 1 & 0 & 0 & 1\\ 0 & 1 & 1 & 0\end{bmatrix}\begin{bmatrix}P_1 & e^{i\omega_{12}t} & e^{i\omega_{13}t} & e^{i\omega_{14}t}\\ e^{-i\omega_{12}t} & P_2 & e^{i\omega_{23}t} & e^{i\omega_{24}t}\\ e^{-i\omega_{13}t} & e^{-i\omega_{23}t} & P_3 & e^{i\omega_{34}t}\\ e^{-i\omega_{14}t} & e^{-i\omega_{24}t} & e^{-i\omega_{34}t} & P_4\end{bmatrix}\right\}$$

$$= \cos(\omega_{12}t) + \cos(\omega_{13}t) + \cos(\omega_{24}t) + \cos(\omega_{34}t)$$

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Now, once again you recall back, what was the I_x operator or the M_x operator here for a 2 spin case, 2 spin case this M_x operator was

$$= Tr\left\{\frac{1}{2}\begin{bmatrix}0 & 1 & 1 & 0\\ 1 & 0 & 0 & 1\\ 1 & 0 & 0 & 1\\ 0 & 1 & 1 & 0\end{bmatrix}\begin{bmatrix}P_1 & e^{i\omega_{12}t} & e^{i\omega_{13}t} & e^{i\omega_{14}t}\\ e^{-i\omega_{12}t} & P_2 & e^{i\omega_{23}t} & e^{i\omega_{24}t}\\ e^{-i\omega_{13}t} & e^{-i\omega_{23}t} & P_3 & e^{i\omega_{34}t}\\ e^{-i\omega_{14}t} & e^{-i\omega_{24}t} & e^{-i\omega_{34}t} & P_4\end{bmatrix}\right\}$$

and if recall here these ones represent the single quantum conferences. These represent the single quantum coherences 1 2, 1 3, 2 4, 3 4 and these are the, their respective symmetrical elements. So, now we multiply this with this density operator. I created a density of matrix like this with all these elements as nonzero and I have the measurement by the M_x operator.

And therefore, if I do this calculation here you see this row multiplies this column, so that gives me only these two terms, first row, I mean first element here multiplication this to this, gives me once again these two terms, we have to see only these two are nonzero, only these two will survive in this second element and the third element in the multiple product will contain these two and the fourth will contain these two.

So, likewise you can do for the second row as well and that one will contain elements in the first position and the fourth position. So, if I multiply here this will contain P_1 and 1 4 and this will contain this one and this one, and this one contain this one and this one, likewise, this one and so you can calculate this and after that you regroup those elements which are present in the total matrix and then you take the trace.

When you take the trace you have to add the elements of the density, the diagonal elements of the density matrix, just as earlier you got only

$$= \cos(\omega_{12}t) + \cos(\omega_{13}t) + \cos(\omega_{24}t) + \cos(\omega_{34}t)$$

Notice none of the populations appear here, in the trace the populations are not appearing nor or the double quantum and the zero quantum coherence is appearing here, right, that is interesting.

Therefore, when you measure the M_x, you are only measuring the single quantum coherence, that is what is the measurable magnetization. So, the populations are not measurable magnetization because M_x is the magnetization in the transverse plane, this is X component of the magnetization and the populations, therefore, cannot be contributing to the measurable magnetization.

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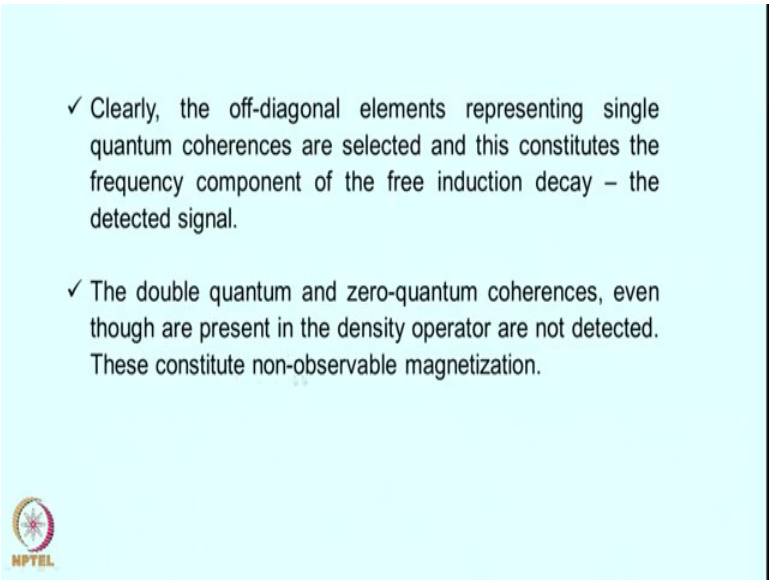

✓ Clearly, the off-diagonal elements representing single quantum coherences are selected and this constitutes the frequency component of the free induction decay – the detected signal.

✓ The double quantum and zero-quantum coherences, even though are present in the density operator are not detected. These constitute non-observable magnetization.

And interesting thing is the double quantum and the zero quantum coherences even though they are present in the density operator are not detected, this constitute non-observable magnetization. So, if we have to observe this, you will have to convert this into observable magnetization by some tricks and this, of course, one will do all the time when we actually do multiple experiments. So, this is, the take-home message here is, when you want to measure the *X* component or the *Y* component of the magnetization, you will only collect the single quantum coherences.

You will not collect zero quantum coherences or double quantum coherences or even the populations. Now, let us see how the various conditions are created of the density operator. So, obviously one has to do some perturbations and in a multiple experiment we have lots of RF pulses, we must also know, we must also know, how to calculate the effect of the pulses on the density operator and because the density operator is supposed to be containing all the information about the spin system which includes the populations and the various coherences and how these ones get transformed under the influence of the RF pulses.

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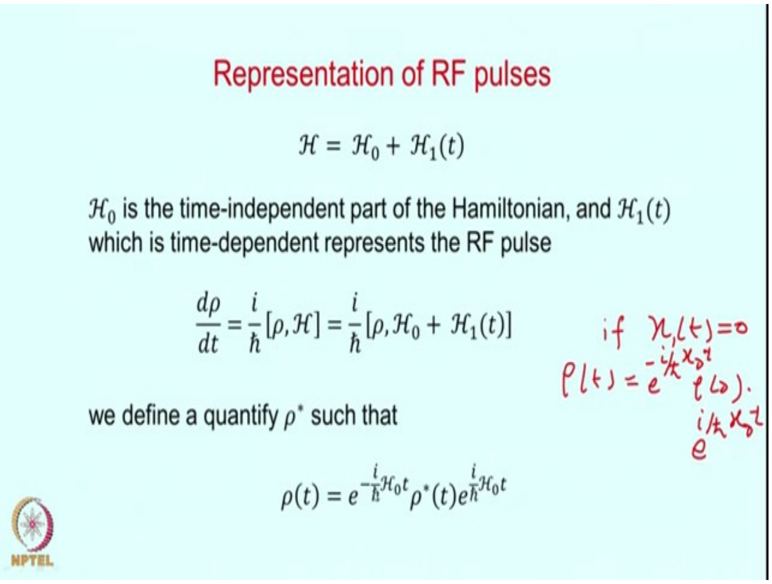

Representation of RF pulses

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$$

$\mathcal{H}_0$ is the time-independent part of the Hamiltonian, and $\mathcal{H}_1(t)$ which is time-dependent represents the RF pulse

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, \mathcal{H}] = \frac{i}{\hbar}[\rho, \mathcal{H}_0 + \mathcal{H}_1(t)]$$

if $\mathcal{H}_1(t) = 0$

$\rho(t) = e^{-i/\hbar \mathcal{H}_0 t} \rho(0) . e^{i/\hbar \mathcal{H}_0 t}$

we define a quantify ρ^* such that

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

So, to do that we must actually go through this calculation once more and how does the density operator transform in the presence of the RF pulse. So, now we have to define a Hamiltonian appropriately. So, the Hamiltonian now consists of this original Hamiltonian which

$$H = H_Z + H_J$$

is your main interaction with the Zeeman Hamiltonian plus the coupling, the *J* coupling which are present, which is time independent.

Earlier we saw that it is the, the main Hamiltonian is time independent and this is the portion which is a time dependent part because of the RF pulse is the time dependent, where you apply it for a short time, this generally one applies for extremely short time, but there is a general thinking that one can treat this as a δ function but nonetheless there is a time dependence here, the RF is applied for a certain is zero and then it goes up and then comes down.

So, the frequency is applied for a short time τ, therefore in this Hamiltonian there is a time dependence, this time, of course, is extremely short, this may be of the order of 1 or 2 microseconds and sometimes tens of microseconds, but not too long. So, H_0 is a time independent part of the Hamiltonian and $H_1(t)$ which is time dependent represents the RF pulse.

So, now we rewrite your Lioville equation,

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, \mathcal{H}] = \frac{i}{\hbar}[\rho, \mathcal{H}_0 + \ \mathcal{H}_1(t)]$$

Now, so what was the solution when this was not present, you recall that

$\rho(t) = e^{-iH_0 t}, \rho(0) = e^{\frac{i}{\hbar}H_0 t}$

That was the solution in the absence of the H1t, right? So, maybe I shall write here for quick reference,

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

So, this was the solution we had. In the presence of the RF, now we would like to seek a solution, which looks like this, instead of this$\rho(0)$ here, we put in here an entity defined as $\rho(t)$¿.

This is the same, this we keep the same and we call this as $\rho(t)$¿. I will explain to you a little bit later and this is actually called as the interaction representation because we are now going into a frame of reference when the interaction is present between the RF and your spin system. And this is also, this is the Zeeman interaction and this represents the going into the rotating frame under conditions of resonance, we will see that very soon.

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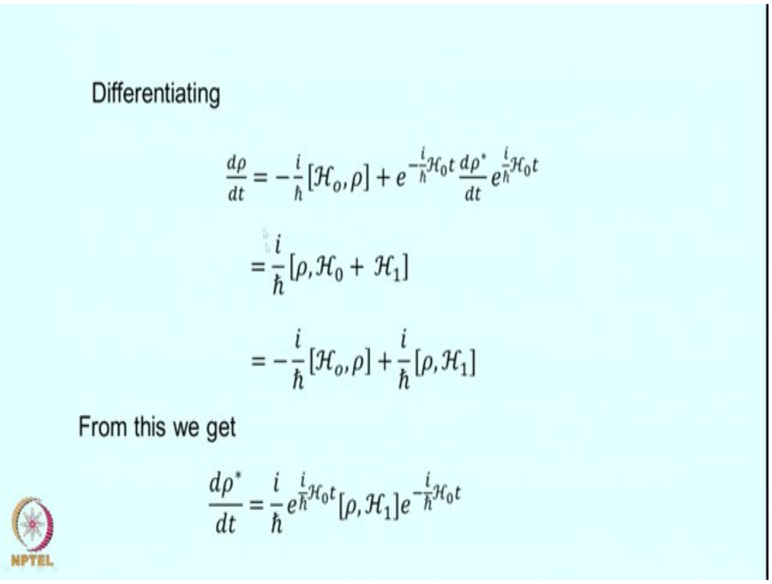

Differentiating

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\mathcal{H}_o, \rho] + e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\frac{d\rho^*}{dt}e^{\frac{i}{\hbar}\mathcal{H}_0 t}$$

$$= \frac{i}{\hbar}[\rho, \mathcal{H}_0 + \mathcal{H}_1]$$

$$= -\frac{i}{\hbar}[\mathcal{H}_o, \rho] + \frac{i}{\hbar}[\rho, \mathcal{H}_1]$$

From this we get

$$\frac{d\rho^*}{dt} = \frac{i}{\hbar}e^{\frac{i}{\hbar}\mathcal{H}_0 t}[\rho, \mathcal{H}_1]e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

So, now what they do, I is substituted there and do a little bit of mathematics here, do the algebra, differentiate this

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\mathcal{H}_o, \rho] + e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\frac{d\rho^*}{dt}e^{\frac{i}{\hbar}\mathcal{H}_0 t}$$

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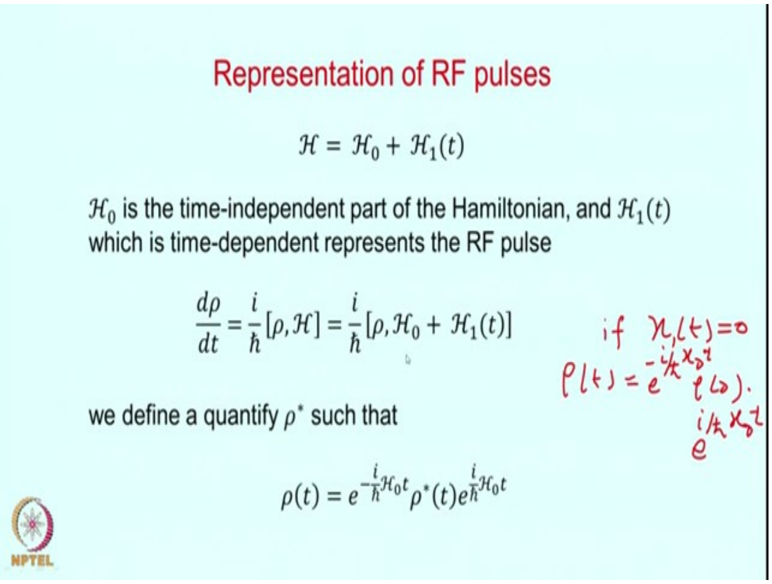

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if $\mathcal{H}_1(t) = 0$

$\rho(t) = e^{-i/\hbar \mathcal{H}_0 t} \rho(0) . e^{i/\hbar \mathcal{H}_0 t}$

we define a quantify ρ^* such that

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

So, this was there. So, if I differentiate it here, what I will have, I will have two quantities here. This is one commutator ρ with $H_0$and the other commutator row with $H_1(t)$, right? So, this is $\frac{i}{\hbar}$ commutator of ρ with H_0 and another commutator rho with $H_1(t)$.

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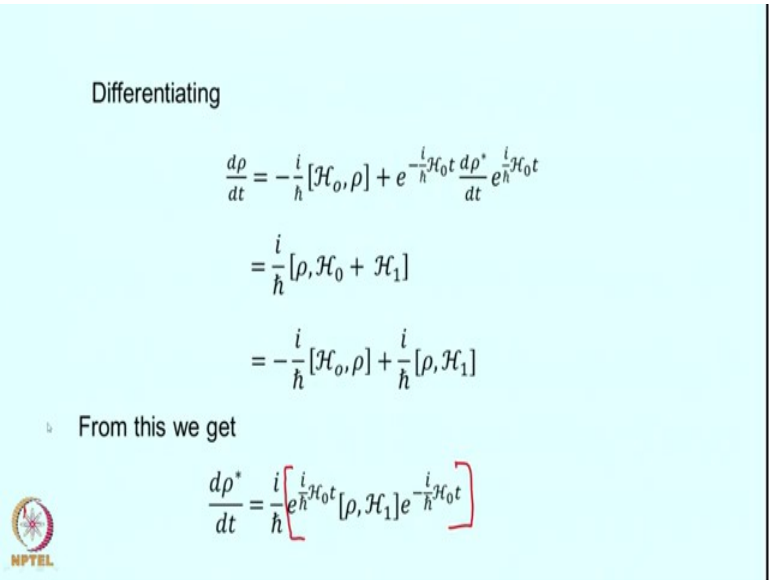

Differentiating

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\mathcal{H}_o,\rho] + e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\frac{d\rho^*}{dt}e^{\frac{i}{\hbar}\mathcal{H}_0 t}$$

$$= \frac{i}{\hbar}[\rho,\mathcal{H}_0 + \mathcal{H}_1]$$

$$= -\frac{i}{\hbar}[\mathcal{H}_o,\rho] + \frac{i}{\hbar}[\rho,\mathcal{H}_1]$$

From this we get

$$\frac{d\rho^*}{dt} = \frac{i}{\hbar}\left[e^{\frac{i}{\hbar}\mathcal{H}_0 t}[\rho,\mathcal{H}_1]e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\right]$$

So, that is put there and this is

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\mathcal{H}_o,\rho] + e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\frac{d\rho^*}{dt}e^{\frac{i}{\hbar}\mathcal{H}_0 t}$$

So, this little bit of algebra is there here when we do the differentiation, you will get the terms which will pull them together it will give you this, and this term will stand out separately, because here is the differentiation with respect to the $\rho *$¿, because earlier this was not there and this was $\rho(0)$.

So, now this will appear separately because we have a time dependence here as well. So therefore, and this must be equal to this

$$= \frac{i}{\hbar}[\rho, \mathcal{H}_0 + \ \mathcal{H}_1]$$

So, put it separately out, the two commutators are put out separately here, so therefore, this right-hand sides of the two have to be the same. This must be equal to this, since this and this are the same, therefore, this will become equal to this.

So, now what we do, I want to get an equation for

$$= -\frac{i}{\hbar}[\mathcal{H}_o, \rho] + \frac{i}{\hbar}[\rho, \mathcal{H}_1]$$

So, this will become 1 and multiply from the right,

$$\frac{d\rho^*}{dt} = \left(\frac{i}{\hbar} e^{\frac{i}{\hbar}\mathcal{H}_0 t} [\rho, \mathcal{H}_1] e^{-\frac{i}{\hbar}\mathcal{H}_0 t} \right)$$

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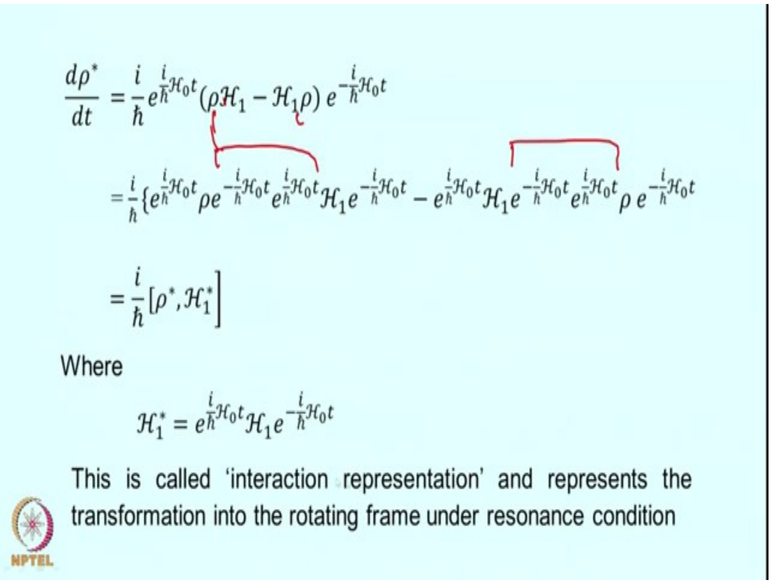

$$\frac{d\rho^*}{dt} = \frac{i}{\hbar} e^{\frac{i}{\hbar}\mathcal{H}_0 t}(\rho\mathcal{H}_1 - \mathcal{H}_1\rho)\, e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

$$= \frac{i}{\hbar}\{e^{\frac{i}{\hbar}\mathcal{H}_0 t}\rho \overbrace{e^{-\frac{i}{\hbar}\mathcal{H}_0 t} e^{\frac{i}{\hbar}\mathcal{H}_0 t}}\mathcal{H}_1 e^{-\frac{i}{\hbar}\mathcal{H}_0 t} - e^{\frac{i}{\hbar}\mathcal{H}_0 t}\mathcal{H}_1 \overbrace{e^{-\frac{i}{\hbar}\mathcal{H}_0 t} e^{\frac{i}{\hbar}\mathcal{H}_0 t}}\rho\, e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

$$= \frac{i}{\hbar}[\rho^*, \mathcal{H}_1^*]$$

Where

$$\mathcal{H}_1^* = e^{\frac{i}{\hbar}\mathcal{H}_0 t}\mathcal{H}_1 e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

This is called 'interaction representation' and represents the transformation into the rotating frame under resonance condition

So, then we take this calculation further, and

$$\frac{d\rho^*}{dt} = \frac{i}{\hbar} e^{\frac{i}{\hbar}\mathcal{H}_0 t}(\rho\mathcal{H}_1 - \mathcal{H}_1\rho)\, e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

Once again there is a bracket here, this bracket I by H cross multiplies the whole thing. Anyway, so that is since this is all inside the bracket here, it does not matter. So, what they do now, $\frac{i}{\hbar} e^{\frac{i}{\hbar}H_0 t\rho}$.

Now, here I introduce this. At this point, I introduce this. So, in between $\rho\, H_1$, I put in this e^{-i} by and I do the same thing here as well. At this point also I will introduce this, what is that, that is basically one only no, so here is the ρ, this is 1 so, therefore, $\rho\, H_1$ is not perturbed, so I put this in between and then this $H_1$and this is $e^{\frac{i}{\hbar}H_0 t}$

And similarly, for this I have this $e^{\frac{i}{\hbar}H_0 t}$ that comes from here, this term then H 1, then again in the middle I introduced this 1. It taken as the product of these two quantities which is actually 1 and $\rho e^{\frac{i}{\hbar}H_0 t}$. Now, we notice something very interesting happening. So, this portion, this portion is similar to is my $\rho^{¿} e^{\frac{i}{\hbar}H_0 t}$, $\rho e^{\frac{-i}{\hbar}H_0 t}$ this is my $\rho^{¿}$.

Now, this one from here to here is a similar transformation with H_1, therefore, I call this as $H_1^{¿}$ and likewise here, from here to here, from here to here, this is

$$= \frac{i}{\hbar}\left[\rho^*, \mathcal{H}_1^*\right]$$

$$\mathcal{H}_1^* = e^{\frac{i}{\hbar}\mathcal{H}_0 t}\mathcal{H}_1 e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

So, that is basically my commutator $\rho^{¿} H_1^{¿}$. Therefore,

$$\frac{d\rho^*}{dt} = \frac{i}{\hbar} e^{\frac{i}{\hbar}\mathcal{H}_0 t}(\rho\mathcal{H}_1 - \mathcal{H}_1\rho)\, e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$$

Now, this is called as interaction representation, this represents the interaction between the RF and your spin system and in the rotating frame this becomes equivalent to the rotating frame under resonance condition, under resonance condition this one is actually is 0 and we will see what is the consequence of that.

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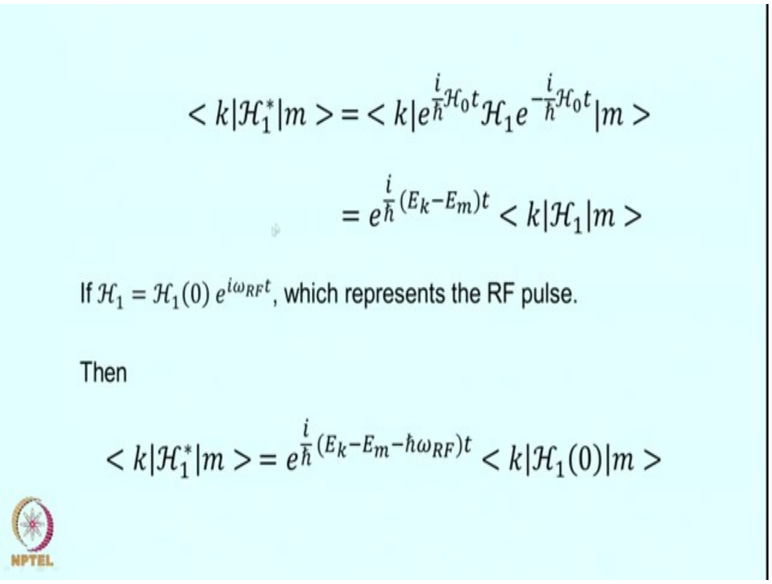

$$< k|\mathcal{H}_1^*|m > = < k|e^{\frac{i}{\hbar}\mathcal{H}_0 t}\mathcal{H}_1 e^{-\frac{i}{\hbar}\mathcal{H}_0 t}|m >$$

$$= e^{\frac{i}{\hbar}(E_k-E_m)t} < k|\mathcal{H}_1|m >$$

If $\mathcal{H}_1 = \mathcal{H}_1(0)\, e^{i\omega_{RF}t}$, which represents the RF pulse.

Then

$$< k|\mathcal{H}_1^*|m > = e^{\frac{i}{\hbar}(E_k-E_m-\hbar\omega_{RF})t} < k|\mathcal{H}_1(0)|m >$$

Let us try and calculate the matrix element of this

$$< k|\mathcal{H}_1^*|m > = < k|e^{\frac{i}{\hbar}\mathcal{H}_0 t}\mathcal{H}_1 e^{-\frac{i}{\hbar}\mathcal{H}_0 t}|m >$$

and I explicitly put here for

$$= e^{\frac{i}{\hbar}(E_k-E_m)t} < k|\mathcal{H}_1|m >$$

What does this give me? This give me

E_k, because this is an Eigen function of this, of the Hamiltonian H_0, right. So therefore, H_0 operating on the state k gives me E_k.

Therefore, this being in the exponential, so I have here $e^{\frac{i}{\hbar}(E_k-E_m)}$, this is operating on the state m, so this view with the energy E_m and I have here, therefore, and the matrix element of k|H_1 |m. So, this being numbers this can be taken out therefore I have here So, this is a matrix element and this is the time dependency, the time dependence has come here and the time dependence from this, will we will see how this will slowly can be removed.

Now, notice this is the energy difference between the two states k and m.

$$< k|\mathcal{H}_1^*|m > = e^{\frac{i}{\hbar}(E_k - E_m - \hbar\omega_{RF})t} < k|\mathcal{H}_1(0)|m >$$

So, time dependence is completely taken out. It comes in this term and this one is time independent and this represents the amplitude of the RF at time t is equal to 0 and during the pulse also the amplitude will not vary if this term is non-zero, if the term is 0.

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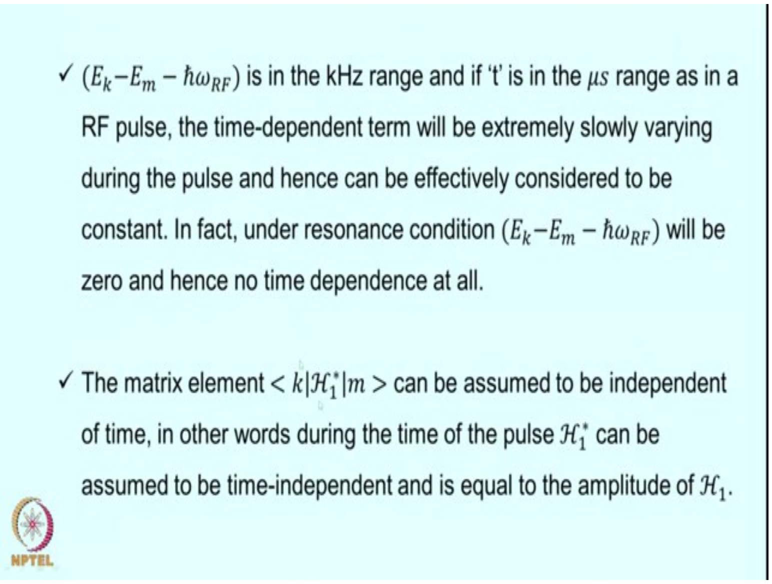

✓ $(E_k - E_m - \hbar\omega_{RF})$ is in the kHz range and if 't' is in the μs range as in a RF pulse, the time-dependent term will be extremely slowly varying during the pulse and hence can be effectively considered to be constant. In fact, under resonance condition $(E_k - E_m - \hbar\omega_{RF})$ will be zero and hence no time dependence at all.

✓ The matrix element $< k|\mathcal{H}_1^*|m >$ can be assumed to be independent of time, in other words during the time of the pulse $\mathcal{H}_1^*$ can be assumed to be time-independent and is equal to the amplitude of $\mathcal{H}_1$.

So, what happens now, look at this $E_k - E_m$is the energy difference between the two levels, right? And what is the order of this, this is typically in megahertz, this is also in megahertz ω_{RF}, therefore this difference is typically of the order of your spectral range which is in kilohertz range, and therefore, this is an extreme and if your time is in in microseconds t, the duration of the pulse, if it is in microsecond this will be extremely small number.

Therefore, the time independent term will be extremely slowly varying during the pulse and can be effectively considered to be constant, in fact, under resonance condition this is ideally, identically zero, right? So, this is the resonance condition, when you have the resonance condition this is identically 0 then there is no time dependence at all. Because you know all hertz per experiments you notice our H_1 is so large, the amplitude of H_1 is so large that the resonance condition is actually satisfied for all the spins at the same time.

Because the effective field is along the H_1field, the field along the Z axis the 0 field is 0 and therefore, the resonance condition is satisfied for all of them at the same time. Therefore, typically for a hard pulse which is of the order from one microsecond or even sometimes you can effectively treat as the delta function, when it is zero, then this term will be completely independent of time. In that case the matrix element this can be assumed to be independent of time, in other words during the time of the pulse $H_1^{¿}$ star can be assumed to be time independent and is equal to the amplitude of H_1. And what will be the amplitude of H_1, this is not varying, therefore it must be equal to $H_1(0)$, so what was in the beginning that is what is going to be there.

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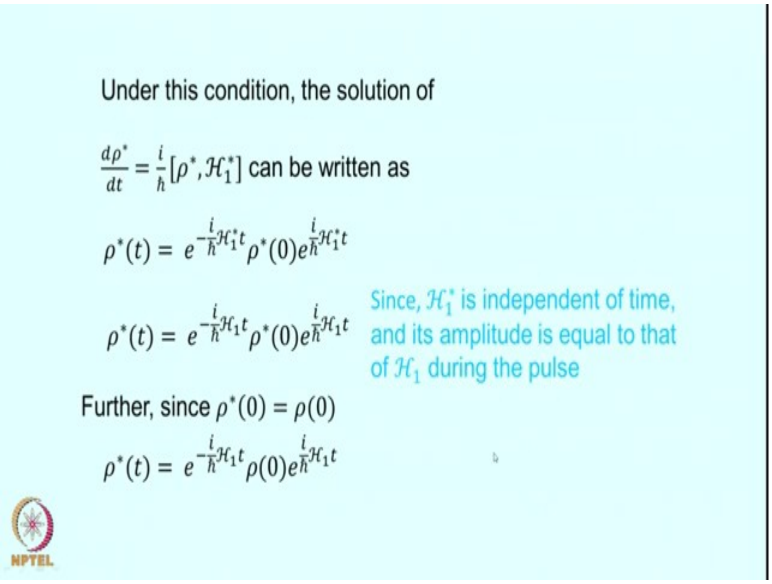

Under this condition, the solution of

$\frac{d\rho^*}{dt} = \frac{i}{\hbar}[\rho^*, \mathcal{H}_1^*]$ can be written as

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

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

Since, $\mathcal{H}_1^*$ is independent of time, and its amplitude is equal to that of $\mathcal{H}_1$ during the pulse

Further, since $\rho^*(0) = \rho(0)$

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

Therefore, when if it is time independent then I can write the solution of this equation as

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

Now, I can replace this

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

And now, $\rho^{¿}(0)=\rho(0)$ and therefore, I can also replace this as $\rho(0)$.

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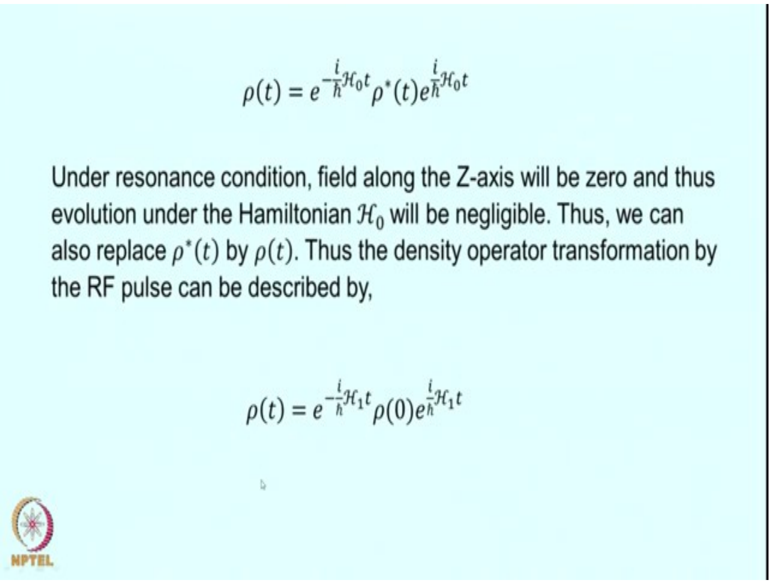

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}_0 t}\rho^*(t)e^{\frac{i}{\hbar}\mathcal{H}_0 t}$$

Under resonance condition, field along the Z-axis will be zero and thus evolution under the Hamiltonian $\mathcal{H}_0$ will be negligible. Thus, we can also replace $\rho^*(t)$ by $\rho(t)$. Thus the density operator transformation by the RF pulse can be described by,

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

And then you will also see that even the $\rho^{¿}$, since this is under the resonance condition this evolution also extremely small, then my $\rho(t)=\rho^{¿}$, therefore, I can write the whole thing as

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

This becomes a very simple calculation now and we can calculate the evolution of the density operator under the effect of the RF pulse in the, so notice this is valid during the pulse.

We should remember this, this is the thing which is during the pulse and we assume we are in the resonance condition and this density operator and the interaction representation becomes equal to what is in the normal case. This density operator transformation by the RF pulse can be described in this manner.

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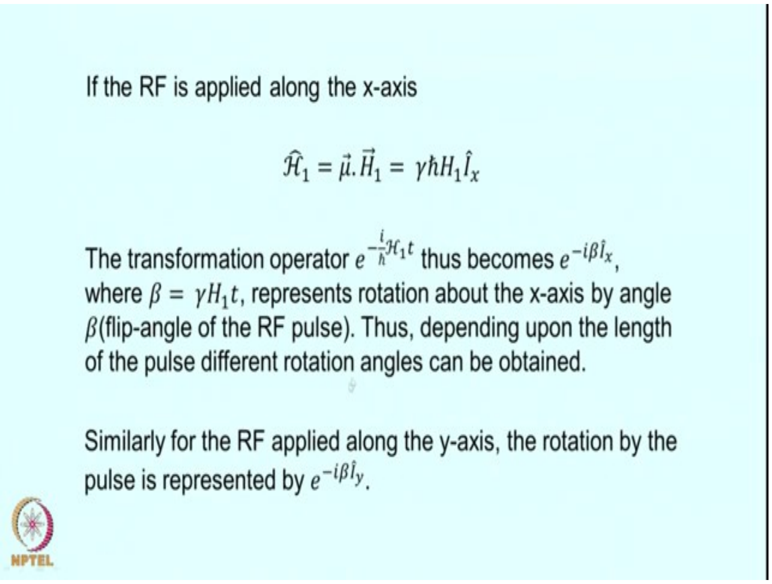

If the RF is applied along the x-axis

$$\hat{\mathcal{H}}_1 = \vec{\mu}.\vec{H}_1 = \gamma\hbar H_1 \hat{I}_x$$

The transformation operator $e^{-\frac{i}{\hbar}\mathcal{H}_1 t}$ thus becomes $e^{-i\beta\hat{I}_x}$, where $\beta = \gamma H_1 t$, represents rotation about the x-axis by angle β(flip-angle of the RF pulse). Thus, depending upon the length of the pulse different rotation angles can be obtained.

Similarly for the RF applied along the y-axis, the rotation by the pulse is represented by $e^{-i\beta\hat{I}_y}$.

So, now we are ready to calculate explicitly the form of the Hamiltonian H_1 in including the interaction between the magnetic moment and the H_1. The effective field is now along the RF axis, right, is equal to the H_1. So,

$$\hat{\mathcal{H}}_1 = \vec{\mu}.\vec{H}_1 = \gamma\hbar H_1 \hat{I}_x$$

if the H_1 RF is assumed to be applied along the Ix axis then the transformation operator it is $e^{\frac{-i}{\hbar}H_1 t}$

Now, what is this interaction, you put here for the H_1 you put $\gamma\hbar H_1$, so the γstays there, $\hbar$ cancels with this $\hbar$and the $\gamma H_1 = \omega_1$, $\omega_1$is the RF you convert the RF amplitude into a frequency that is ω_1, γH_1, $\gamma H_1 t$ and $\gamma H_1 t$ we have seen earlier that it is a flip angle, is a particular angle, this is the frequency and this is time t and therefore, this is the flip angle.

So, the processional frequency, γH_1 of the processional frequency in the rotating frame, in the under the resonance condition and therefore, how much the magnetization is flipped will depend upon this time t, so we have seen that earlier this is you can create a 90 degree rotation or 180 rotation and things like that depending upon what the time what we will have here. So, this represents the rotation of the magnetization about the X axis by angle β and thus depending upon the length of the pulse different rotation angles can be obtained.

Now, we will also explicitly show that putting this equation for the pulse, we will demonstrate that it actually results in rotation of the magnetization from the Z-axis or wherever. So, similarly for the RF applied along the y axis the rotation by the pulse is represented by $e^{-i}\ \beta\ I_y$. So, this can be extended to other kinds of situations wherever you want to apply, if you want to apply somewhere in between, then one has to put in I_x+I_y and things like that so those are called as phase shifted pulses.

And so, we will not discuss about those things right now, we will say, we will take the simpler cases where it is clearly along the X or the Y axis and this will be sufficient to understand the principles that are happening and those involved things can be calculated separately. I think we will stop here and we will continue in the next class with further description of the pulses and their effects on the magnetization.