NMR Spectroscopy for Chemists and Biologists
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Lecture-30
Time evolution of density operator

In the last class we have seen how to calculate the matrix representations of the angular momentum operators in the basis of the eigen states of the individual spin systems.

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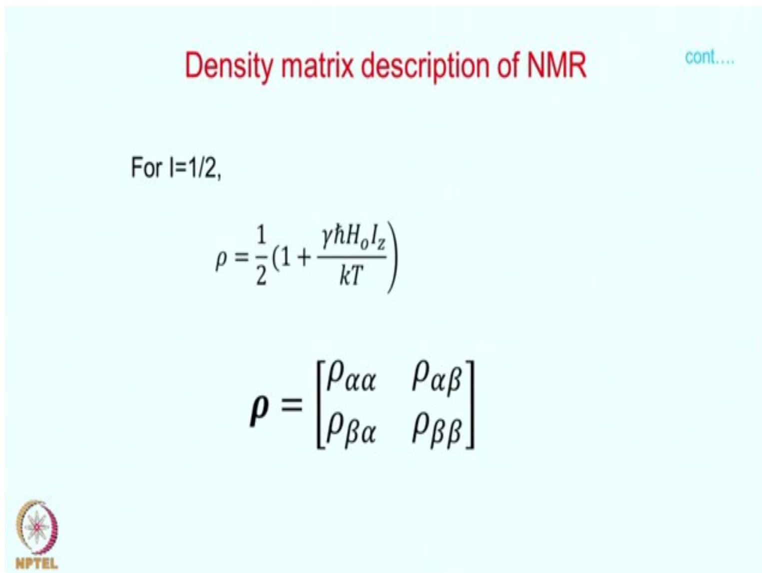

We considered explicitly one spin system with $I = \frac{1}{2}$, and two spin systems both with $I = \frac{1}{2}$, two spins labeled as A and X and we calculated the matrix representations of the operators I_z I_x and I_y. And we also talked about the general properties of the individual spin states, what does the orthonormality mean and how it is used in the calculation of the matrix representations of the angular momentum operators.

We went through step by step and now we will continue this exercise and try and calculate the matrix representation of the density operator, which is of crucial value for us in the description of the NMR experiments. So, we had derived the expression for the density operator ρ for a single spin $I = \frac{1}{2}$, we had calculated that the density operator can be represented in this manner, which is

$$\rho = \frac{1}{2}\left(1 + \frac{\gamma \hbar H_0 I_z}{kT}\right)$$

where H_0 is the magnetic field.

In fact, this is how we actually started calculating the matrix representation of the angular momentum operators, plus we discovered here and we showed here that angular momentum operators were intimately connected with the density operator and that is the one which is actually going to tell us about the response of the spin system to various kinds of perturbations in your NMR experiments.

So, for the single spin we will write this density operator as in this manner, is it will be a two by two matrix because the two spin states for a single spin are alpha and alpha and therefore, I will have here $\rho_{\alpha\alpha}$, $\rho_{\alpha\beta}$, $\rho_{\beta\alpha}$, $\rho_{\beta\beta}$. The states here are the ket states and the states here will be the bra states and I will care to calculate the matrix representations, the matrix elements $\rho_{\alpha\alpha}$, $\rho_{\alpha\beta}$, $\rho_{\beta\alpha}$, $\rho_{\beta\beta}$.

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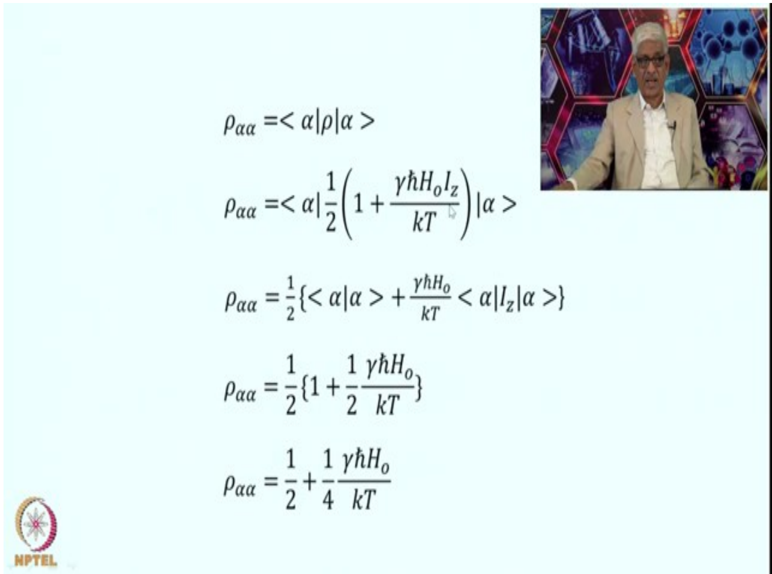

Let us do that. So, $\rho_{\alpha\alpha}$, explicitly, you write it as alpha here,

$$\rho_{\alpha\alpha} =< \alpha|\rho|\alpha >$$

and that is equal to, now,

$$\rho_{\alpha\alpha} =< \alpha|\frac{1}{2}\left(1 + \frac{\gamma\hbar H_o I_z}{kT}\right)|\alpha >$$

So, now, this one does not give us anything, so I will have, I take out the α completely from here, and then I will have alpha 1 alpha and that is simply $\alpha\alpha$.

And then I will have here this part the α,

$$\rho_{\alpha\alpha} = \frac{1}{2}\{< \alpha|\alpha > + \frac{\gamma\hbar H_o}{kT} < \alpha|I_z|\alpha >\}$$

then I will have this matrix element coming $\alpha \vee I_z \vee \alpha$ because I_z is an operator, I cannot take that out, so this is the constant here. So, this I can take it out, so then I will have $\alpha \vee I_z \vee \alpha$. So, this gives me one because of the orthonormality.

So, therefore,

$$\rho_{\alpha\alpha} = \frac{1}{2}\{1 + \frac{1}{2}\frac{\gamma\hbar H_o}{kT}\}$$

So, totally, Rho alpha alpha will become

$$\rho_{\alpha\alpha} = \frac{1}{2} + \frac{1}{4}\frac{\gamma\hbar H_o}{kT}$$

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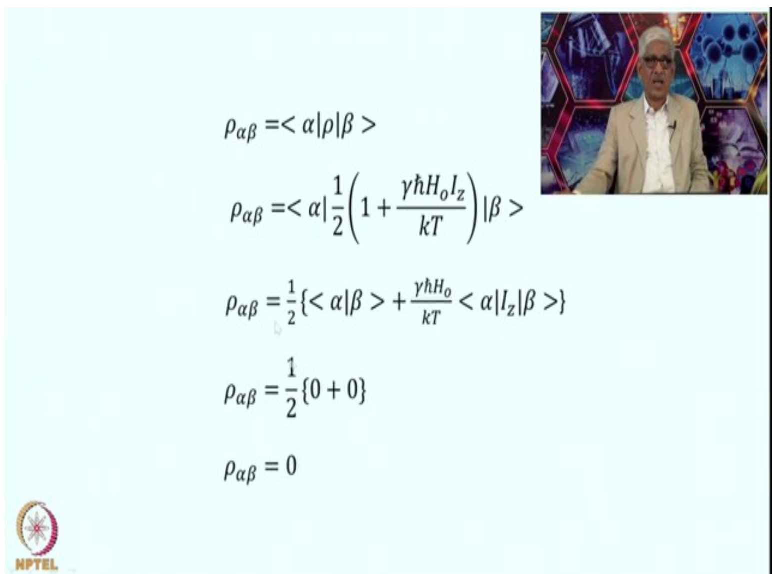

Now, $\rho_{\alpha\beta}$, so it is the same way,

$$\rho_{\alpha\beta} =< \alpha|\rho|\beta >$$

$$\rho_{\alpha\beta} =< \alpha|\frac{1}{2}\left(1 + \frac{\gamma\hbar H_o I_z}{kT}\right)|\beta >$$

So, this now gives me

$$\rho_{\alpha\beta} = \frac{1}{2}\{< \alpha|\beta > + \frac{\gamma\hbar H_o}{kT} < \alpha|I_z|\beta >\}$$

$$\rho_{\alpha\beta} = \frac{1}{2}\{0 + 0\}$$

And similarly, here this gives me$\alpha \vee I_z \vee \beta$, $I_z \vee \beta$ gives me $-\beta$, therefore, I will have $\alpha\beta$here and once again this will be 0. So, therefore, this total element will be 0.

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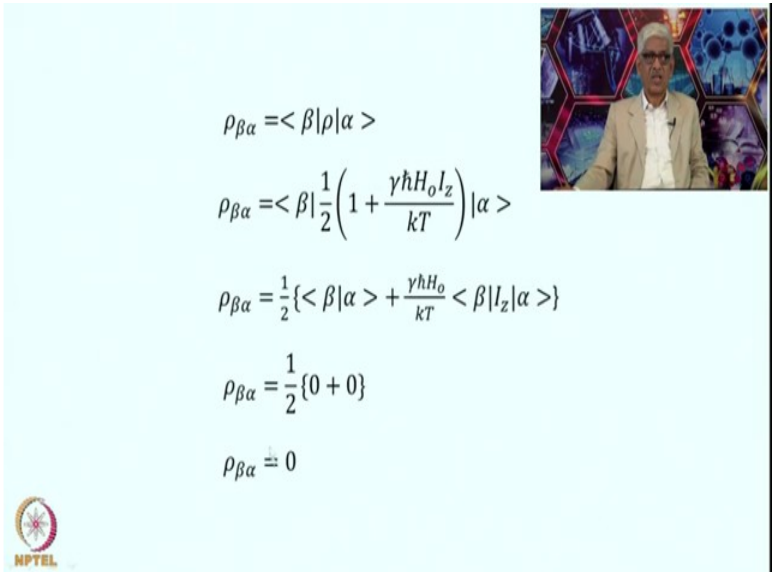

Similarly, $\beta\alpha$ if I calculate, this will again give me ½ , this is β here and α there, therefore, this is $\frac{1}{2}\beta\alpha$ will be 0. And here once again this constant being the same, I_z on α gives me $\frac{1}{2}\alpha$, therefore, they have $\beta\alpha$, the $\beta\alpha$ also gives me 0, therefore, this will also be 0.

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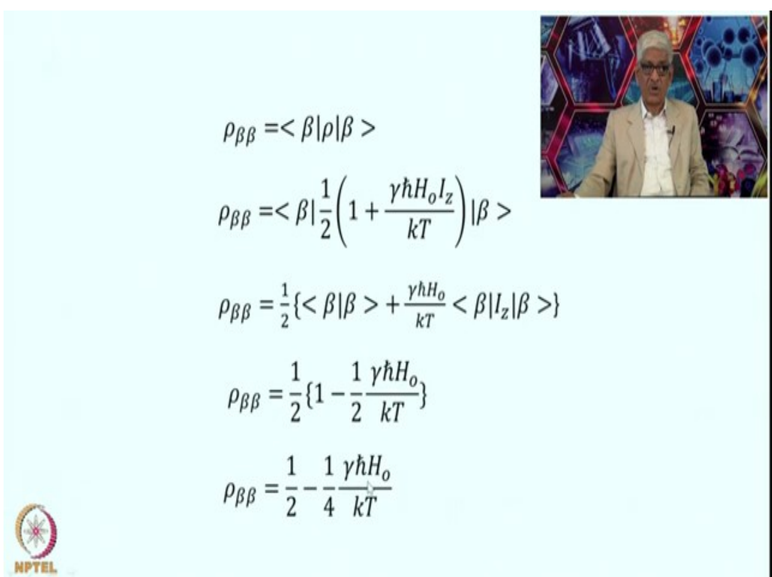

Now, $\beta\beta$ will yield some non-zero value because as in the same way as the $\alpha\alpha$ yielded, so $\beta\frac{1}{2}$ half here and this gives me

$$\rho_{\beta\beta} = <\beta|\frac{1}{2}\left(1 + \frac{\gamma\hbar H_o I_z}{kT}\right)|\beta>$$

$$\rho_{\beta\beta} = \frac{1}{2}\{1 - \frac{1}{2}\frac{\gamma\hbar H_o}{kT}\}$$

therefore, this total will be

$$\rho_{\beta\beta} = \frac{1}{2} - \frac{1}{4}\frac{\gamma\hbar H_o}{kT}$$

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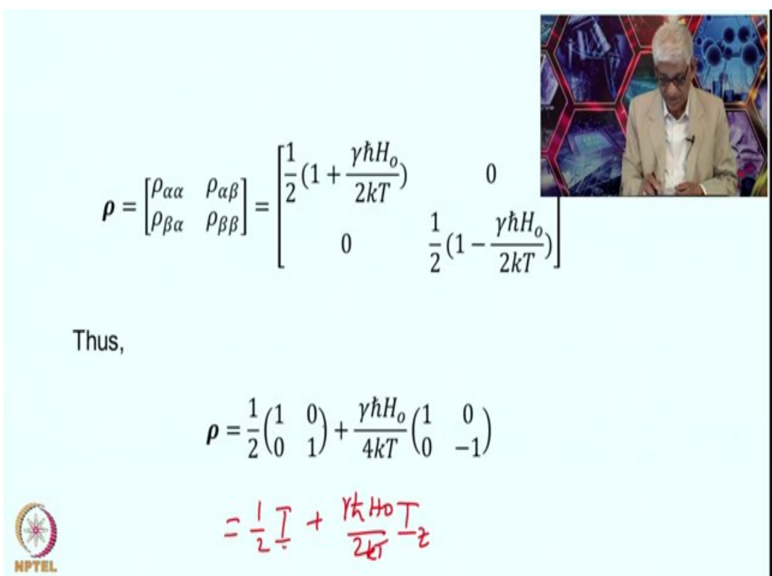

So, put it all together so the matrix representation of the density operator is explicitly here the diagonal elements, these are the diagonal elements, this will be non-zero and off diagonal elements are 0. Now, these diagonal elements are the same what we calculated on $\rho_{\alpha\alpha}$ and $\rho_{\beta\beta}$a and that is I can take this, separate it into 2 matrices here, so therefore,

$$\boldsymbol{\rho} = \begin{bmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(1 + \frac{\gamma\hbar H_o}{2kT}) & 0 \\ 0 & \frac{1}{2}(1 - \frac{\gamma\hbar H_o}{2kT}) \end{bmatrix}$$

You recall the previous class that this was actually I_z operator for the single spin system and this is the unit operator. So therefore,

$$\boldsymbol{\rho} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\gamma\hbar H_o}{4kT}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

because if I take away the 1, one more 2 *I* have to take it out, then it will be I_z. So, therefore, they simply once we know the matrix representations of the individual operators, one can straight away this write these matrix elements in for the total density operator as well.

But here, we actually from the first principles we calculated and demonstrated, how this expressions are obtained. So, this will be in a simpler form

$$\rho = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\gamma\hbar}{2kT} I_z$$

So, therefore, if I want to write explicitly in a similar form, I can also write this as

$$\rho = \frac{1}{2} I + \frac{\gamma\hbar H_0}{2kT} I_z$$

Here, I am actually representing the matrices of I_z and the matrix *I*.

The *I*,

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

this *I* is a unit matrix 1 0 0 1 and this is the I_z of the single spin 1 0 0 minus 1, right? So, this is the way also one can write once you know the basic matrix representations of the individual operators one can write the density operator also in that manner.

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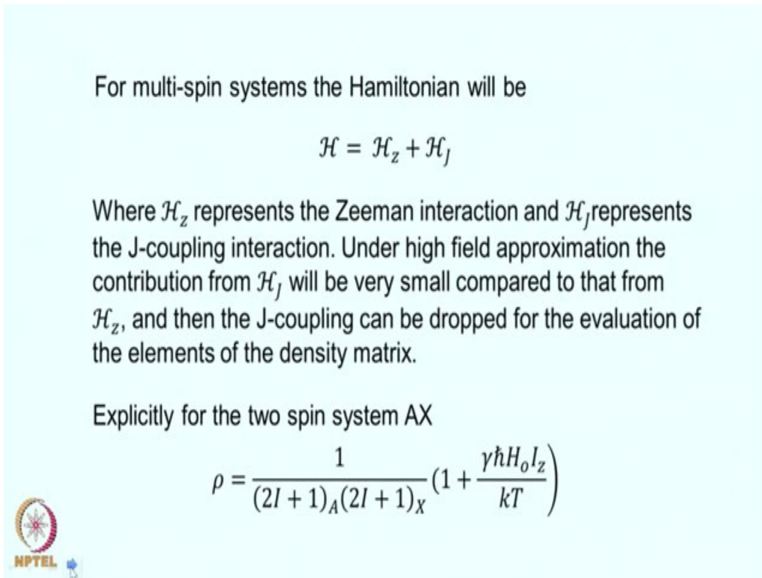

Now, that was for the single spin system. Now, let us do it for a multi spin system, you go a little bit more because we always have to deal with multiple spin systems. So, if I have multi spin systems, then I will have to consider the Hamiltonian in a more generalized form that it has the

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_J$$

Hamiltonian is $\mathfrak{H}_Z$, this is a Zeeman part of the interaction and this is the coupling interaction which is the $\mathfrak{H}_J$.

So, $\mathfrak{H}_Z$ represents the Zeeman interaction and $\mathfrak{H}_J$ represents the *J* coupling interactions. However, under high field approximation that is because your magnetic field is of the order of several Tesla's, right? So, therefore hundreds of kilowatts, so that is a huge magnetic field and this $\mathfrak{H}_J$, this is in few hertz, okay. So, this is about coupling constant, this is about 10 hertz, 20 hertz and things like that and this is in megahertz.

Several megahertz is the total interaction here it is in megahertz, and this is in several hertz, therefore, this is a very small quantity and often one can neglect this for the purpose of the calculation of the density matrix. So, therefore, explicitly for the two spin system *AX*, we will write in this manner, this is 1 by, now n is the total number of states, right, the total number of states are

$$\frac{1}{N}=\frac{1}{(2I+1)_A(2I+1)_X}$$

So, therefore, the total number of states will be the product of this. For example, in the case of 2 spin $I=\frac{1}{2}$, we had 2 states here and 2 states there, so therefore, it became 4 states. Therefore, in that case it will be, it will 4 for the two spin system I is equal to half, this will be 4. and I_z again will be the sum of the two operators for the individual spin states.

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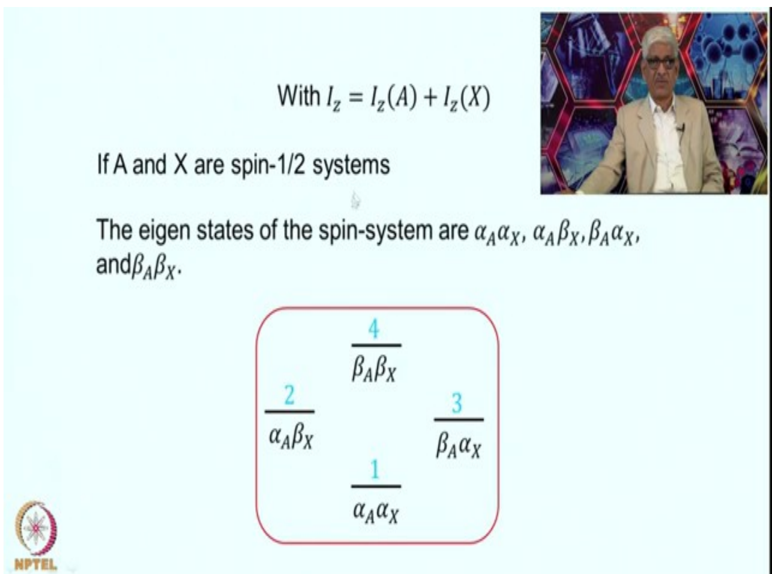

Now, so let us recap that here,

$$\text{With } I_z = I_z(A) + I_z(X)$$

If A and X are spin half systems, I will have this 4 states as individual basis set states $\alpha_A\alpha_X$, $\alpha_A\beta_X$, $\beta_A\alpha_X$and $\beta_A\beta_X$. So, once again I will write them as in the form of energy level diagram here, if these ones are non-degenerate, then I will have these 4 energy levels, then I will have 1 2 3 4 as labels for this 4 individual states.

This is the convenience, we have just labeled them in this manner, one can label it any another manner also, but one has to keep the convention and maintain the same convention all through.

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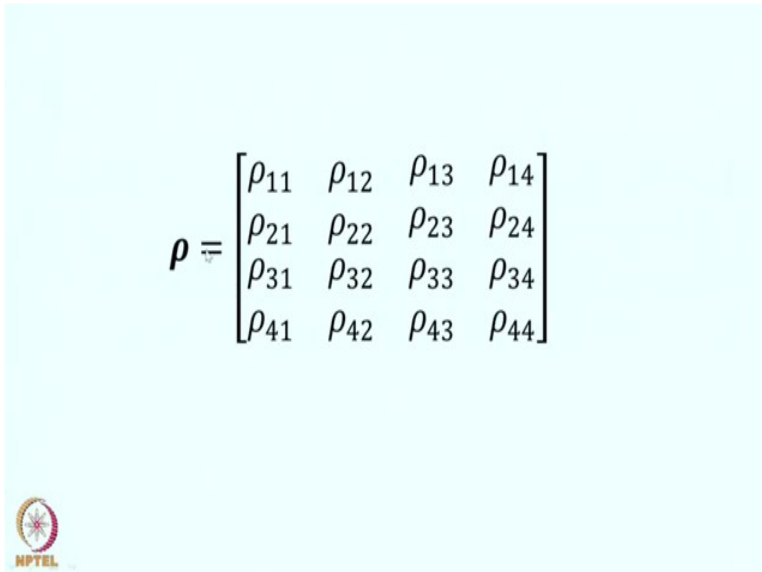

So, now the generalized form of the density operator or the density matrix for will be in this form, matrix representation of the density operator will be

$$\boldsymbol{\rho} = \begin{bmatrix} \rho_{11} & \rho_{12} & \rho_{13} & \rho_{14} \\ \rho_{21} & \rho_{22} & \rho_{23} & \rho_{24} \\ \rho_{31} & \rho_{32} & \rho_{33} & \rho_{34} \\ \rho_{41} & \rho_{42} & \rho_{43} & \rho_{44} \end{bmatrix}$$

So they will have a 4 by 4 matrix for the density operator.

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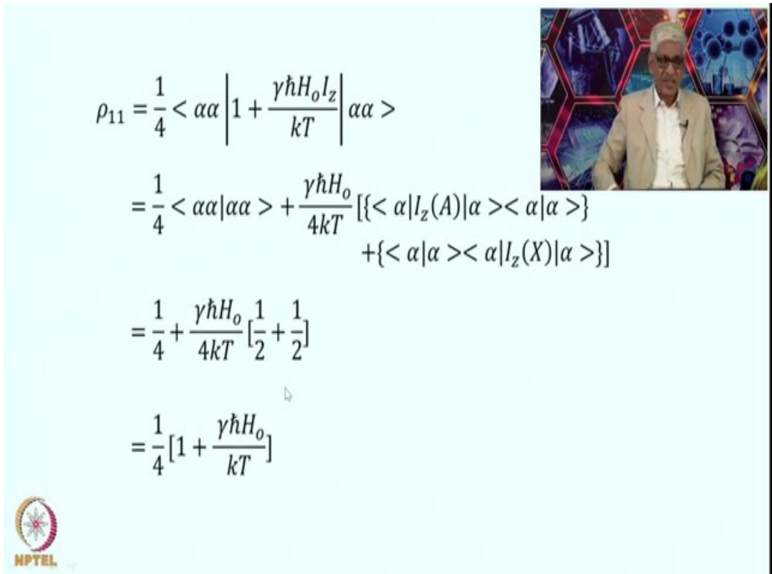

Let us try and calculate these individual elements more explicitly. So, let us do for ρ_{11}, the is, I have, now I have dropped this *A* and *X* here because we have already seen that explicitly, for simplicity I drop the *A* and *X*, but it is understood that they are there, this will be $\alpha_A \alpha_X$, $\alpha_A \alpha_X$, but simplicity I have just dropped the *A* and *X*, we understand that they are there.

So, now if I want to calculate this, so this will be $\frac{1}{4}(2I+1)_A$, there are two states there, and for the *X* also two states, therefore, this total number of states will be

$$= \frac{1}{4} < \alpha\alpha|\alpha\alpha > + \frac{\gamma\hbar H_o}{4kT} [\{< \alpha|I_z(A)|\alpha >< \alpha|\alpha >\} +\{< \alpha|\alpha >< \alpha|I_z(X)|\alpha >\}]$$

Plus and these are now the *A* states $\alpha_A \alpha_A$ and here are the X states, these are $\alpha_X \alpha_X$, I_z *(X)* is coming here. Now, so this gives me 1 and what does this give me, this gives me half, right, this gives me half, this is 1 and this is 1, this also gives me half, therefore, this is half plus half. So,

$$= \frac{1}{4} + \frac{\gamma\hbar H_o}{4kT} [\frac{1}{2} + \frac{1}{2}]$$

Therefore, I will have a total of

$$= \frac{1}{4}[1 + \frac{\gamma\hbar H_o}{kT}]$$

So, this is the first diagonal element of the density matrix.

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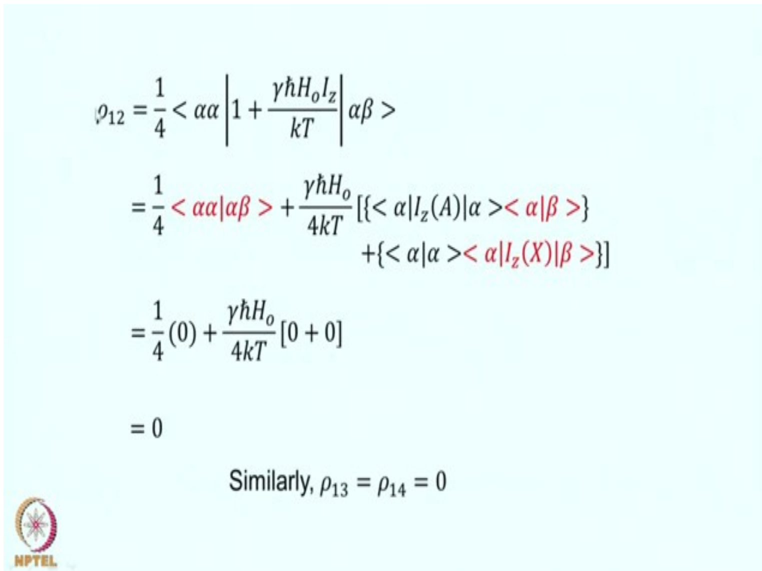

Now, we calculate ρ_{12}, the row 1 2, this is the second element of the first row and this is

$$\rho_{12} = \frac{1}{4} < \alpha\alpha \left| 1 + \frac{\gamma\hbar H_o I_z}{kT} \right| \alpha\beta >$$

$\frac{1}{4}$ here as before and then $\alpha\alpha$, and here I have $\alpha\beta$. So, the first number, this gives me $\alpha\alpha\ \alpha\beta$ here, this obviously goes to 0 because orthogonality of these individual states and this

$$= \frac{1}{4} < \alpha\alpha|\alpha\beta > + \frac{\gamma\hbar H_o}{4kT}[\{< \alpha|I_z(A)|\alpha >< \alpha|\beta >\} + \{< \alpha|\alpha >< \alpha|I_z(X)|\beta >\}]$$

And when I take the *X* of the *Iz*, then I will have alpha alpha, these are the A states, and this is alpha I_z X β. Now, you see this also is 0 and this gives me again $\alpha\beta$, I_z operating on β gives me β only, therefore, this again gives me β, therefore, this also will be 0. So, therefore,

$$= \frac{1}{4}(0) + \frac{\gamma \hbar H_o}{4kT}[0 + 0]$$

so the whole thing is 0.

So, similarly, when we calculate it we will see that ρ_{13} is 0, ρ_{14} is 0 and we have this, the first row, except the first diagonal element, all the three are the three elements are 0.

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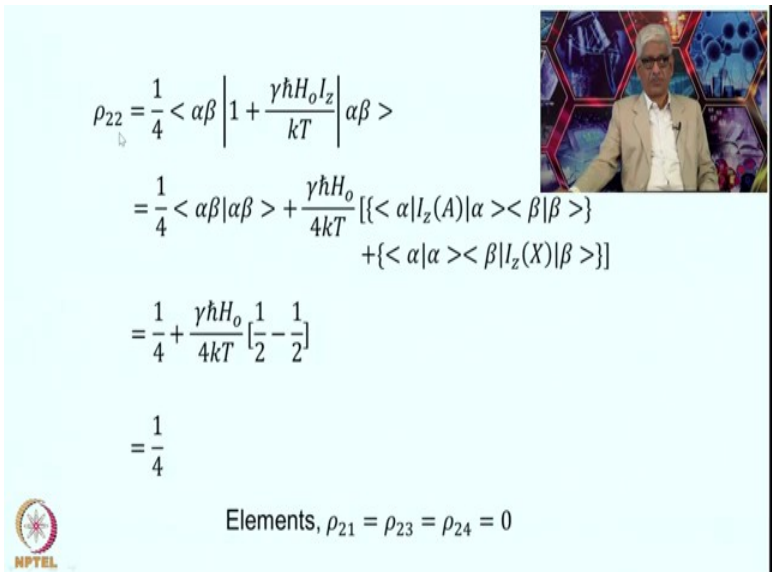

Now, let us calculate for the second row. We will calculate for the ρ_{22}. So, the ρ_{22}this is

$$\rho_{22} = \frac{1}{4} < \alpha\beta \left| 1 + \frac{\gamma \hbar H_o I_z}{kT} \right| \alpha\beta >$$

So,

$$= \frac{1}{4} < \alpha\beta|\alpha\beta > + \frac{\gamma \hbar H_o}{4kT}[\{< \alpha|I_z(A)|\alpha >< \beta|\beta >\}$$
$$+\{< \alpha|\alpha >< \beta|I_z(X)|\beta >\}]$$

So, this gives me 1, this gives me 1, this gives me half and this also gives me minus half. So, therefore, what happens here, this part is

$$= \frac{1}{4} + \frac{\gamma\hbar H_o}{4kT}[\frac{1}{2} - \frac{1}{2}]$$

I will have only this term remaining $\frac{1}{4}$. So, this term goes to 0. So, similarly, if you calculate it, you will see that ρ_{21} in the second row and ρ_{23} and ρ_{24}, will be 0.

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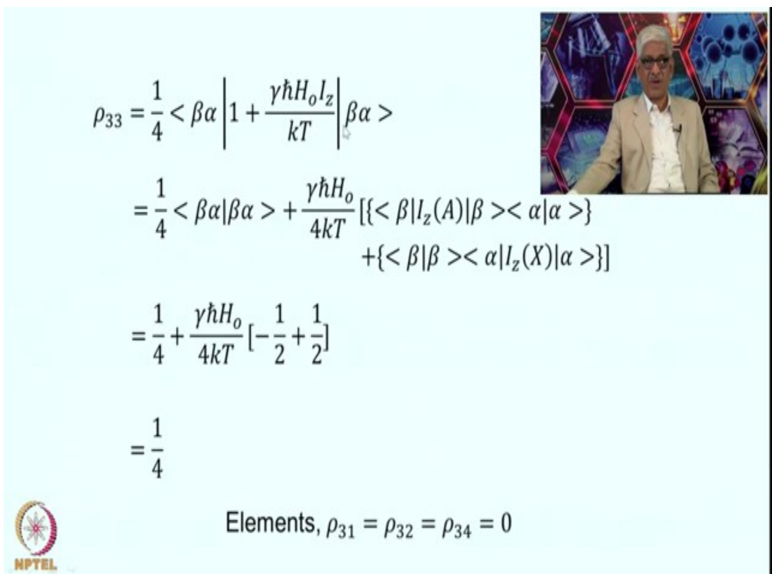

And you do the same exercise for ρ_{33}, now it is $\beta\alpha$ and $\beta\alpha$ here. This one gives me 1 again, and this gives $I_z(A)\beta \rightarrow \frac{1}{2}$, this is 1 1 this is 1 and this is 1, and this gives me half, so this will be minus half, plus half and therefore, this vanishes, I will only have, I am left with only $1/4$. So, other 3 elements in the third row, ρ_{31}, ρ_{32}, ρ_{34}, they will all be 0.

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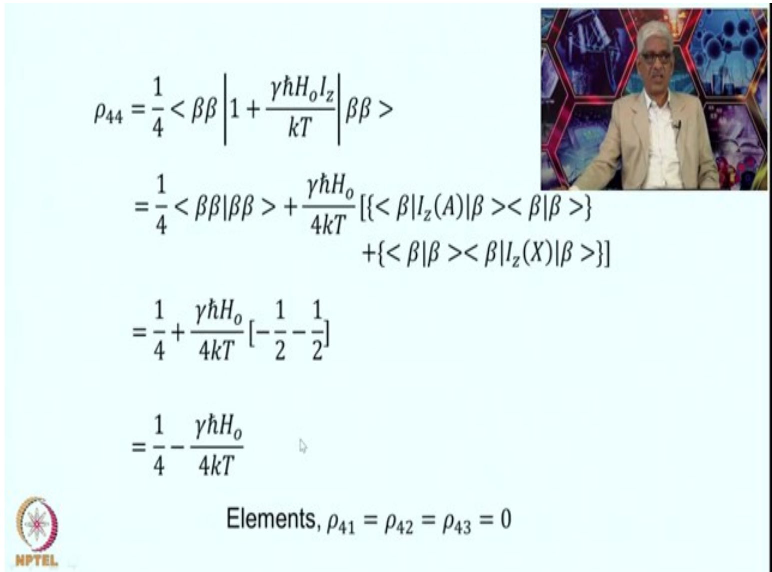

There fourth row, the ρ_{44} states if I do the calculation, I will have a $\beta\beta$, and $\beta\beta$ here, and this

$$= \frac{1}{4} < \beta\beta|\beta\beta > + \frac{\gamma\hbar H_o}{4kT} [\{< \beta|I_z(A)|\beta >< \beta|\beta >\} + \{< \beta|\beta >< \beta|I_z(X)|\beta >\}]$$

$$= \frac{1}{4} - \frac{\gamma\hbar H_o}{4kT}$$

The other elements ρ_{41}, ρ_{42}, ρ_{43} are equal to 0.

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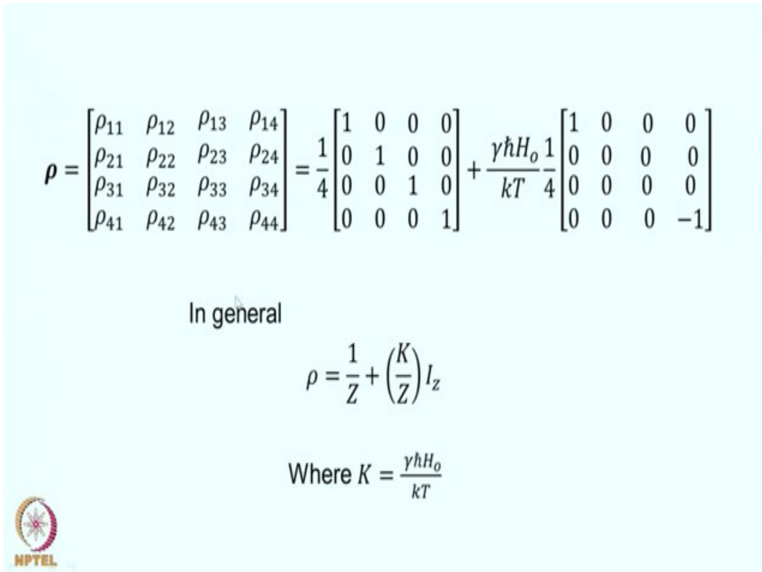

So, therefore, what do I get? So, I have here, the all the elements listed here,

$$\boldsymbol{\rho} = \begin{bmatrix} \rho_{11} & \rho_{12} & \rho_{13} & \rho_{14} \\ \rho_{21} & \rho_{22} & \rho_{23} & \rho_{24} \\ \rho_{31} & \rho_{32} & \rho_{33} & \rho_{34} \\ \rho_{41} & \rho_{42} & \rho_{43} & \rho_{44} \end{bmatrix} = \frac{1}{4}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} + \frac{\gamma\hbar H_o}{kT}\frac{1}{4}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

This actually if you remember, this was the I_z operator for the two spins, right? And this is the unit matrix. This is the unit matrix, unit matrix multiplied by $\frac{1}{4}$, and this is the number of states, this is basically the partition function.

In the generalized manner this is the partition function number of states, which is equal to the number of states and here again it is a number of states and this is a constant, $\frac{\gamma\hbar H_0}{kT}$ that is the constant K here and therefore, I can write this in a simplified manner,

$$\rho = \frac{1}{Z} + \left(\frac{K}{Z}\right) I_z$$

I_z is your matrix for the I_z operator, therefore, rho is simply equal to this. So, if we knew this density of state or the partition function, if we know this number of states here, and I_z operator you know what it is, we can simply write down explicitly the matrix representation of the density operator.

So, I think we can stop here; this is the good time to stop for the calculation of the density operator for the 2 spin-states.