NMR Spectroscopy for Chemists and Biologists

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Lecture 29
Density matrix description of NMR – 3

In the last class we started with a rigorous description of NMR, a quantum mechanical description which is called as density matrix description of NMR. We tried to derive an expression for the density operator starting from the basic principles of quantum mechanics, that how we make a measurement and what is the meaning of measurement in quantum mechanical terms, that is when we measure the expectation value, calculate the expectation value, it represents a measurement. And we also said that we have to take an ensemble average to represent the measurement.

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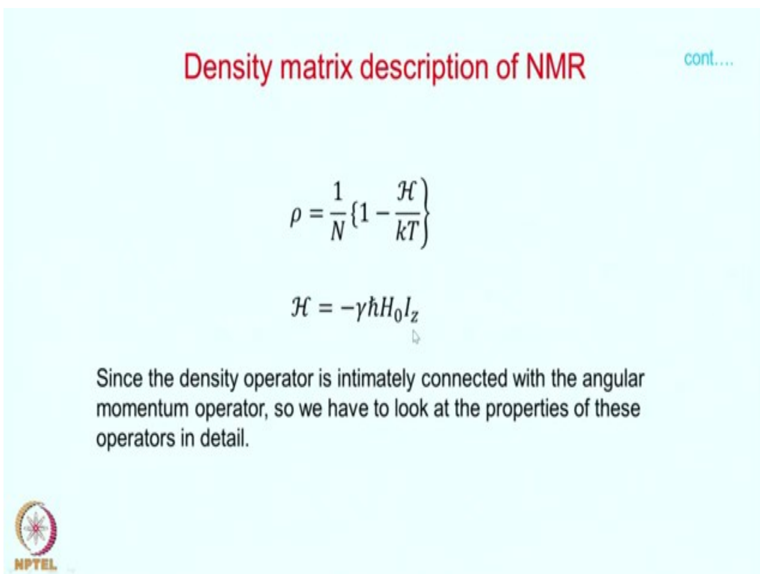

So, as in the end we came up with this expression for the so called density operator,

$$\rho = \frac{1}{N}\left\{1 - \frac{\mathcal{H}}{kT}\right\}$$

and this is an operator here. So, rho is an operator and this represents the total number of states, the eigen states. And that depends upon the spin system, what we might have, whether it is 1 spin system or 2 spin system or 3 spin systems and so on.

And what is the value of the I? For most purposes, we will be dealing with $I = \frac{1}{2}$ systems. And we also said we will represent the Hamiltonian by the interactions and by and large it is represented by this simple expression here,

$$\mathcal{H} = -\gamma \hbar H_0 I_z$$

this is the z component of the angular momentum, this is I_z operator.

Now, since the density operator is intimately connected with the angular momentum operator, so we have to look at the properties of these operators in some details. Now, here, I would like to mention that, since this chapter is going to be quite intensive with regard to the operators and matrices, matrix representations, angular momentum and things like that.

It may be a good idea to take a small digression and spend sometime on the properties of the spin spades for the benefit of those who did not have sufficient exposure with quantum mechanics, operators and so on and so forth. Therefore, we will go slow here and try and calculate this individual, will introduce these concepts clearly and explain from the first principle, how one can calculate these various elements.

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$$\Psi(t) = \sum C_m(t) U_{m,I} = \sum C_m |m>$$

The spin-states satisfy the identity

$$\sum |m>< m| = 1$$

$$|m>< m|\ \Psi(t) = |m>< m| \sum C_n |n>$$

$$= \sum_n C_n |m>< m|n>$$

$$= \sum C_n |m> \delta_{nm} = C_m |m>$$

So, now this is the same equation which we wrote earlier in the first class, that any state is represented by wave function, the wave function is written as super position of the various states, these are so called basis states, they are for my basis set, all the U_m's are the eigenstates or form a basis set and this is the super position of all the basis sets and you have the $C_m(t)$'s, these are the coefficients which contribute to the super position.

In a simpler notation, we simply write it as summation Cmm and this summation goes over all the states of the spin system.

$$\sum |m>< m| = 1$$

So, if as I said this goes from, m goes from 1 to n. The spin-states satisfy this identity. This identity also we used last time. However, let us come back to this identity and try and show how this comes and try and prove this. So, we used this identity in the previous class and this m is the one of the eigen states or the element of the basis set and with this summation runs over all this m's.

Let us take one of these elements, this one which is written here, I take this here and I will show you that this is the actually an operator. So, this if I operate on the wave function

$$\Psi(t) = \sum C_m(t) U_{m,I} = \sum C_m |\mathrm{m}>$$

This operator as it is and then for the $\psi(t)$, I write this. Now, just instead of m here, as a index of summation, I use n, it does not matter, it just runs over all the states.

Whatever index *I* use here, it runs over the all the states. So,

$$|m>< m|\, \Psi(t) = |m>< m| \sum C_n |\mathrm{n}>$$

Now, this C_n's are numbers, so then C_n's are numbers, these are now operators, therefore, I can take this entire part outside of this operator term and then I put the summation here, instead of putting it here, then I say then the C_n comes here, then I put the same thing back, this m, m, this is the ket, this is the bra and this takes an element with the another ket here n.

Now, these are the expression gets simplified into this. Now, you remember we also said that these states, the elements of the basis set, these are orthonormal. So, what is the meaning of orthonormal? That this bracket here, this element is either 0 or 1, depending upon whether $m=n$ or $m \neq n$.

$$= \sum C_n\, |m>\, \delta_{nm}$$

This $\delta_{mn}=1, n=¿$or it is equal to 0 if $n \neq m$. Therefore, this summation, once again running on various N's here, C and m, δ_{nm}, this will simply become equal to $C_m\,|m$, because for all other n's which are not equal to m, this is 0, so only 1 element of this survives and therefore, you have here $C_m\,|m$.

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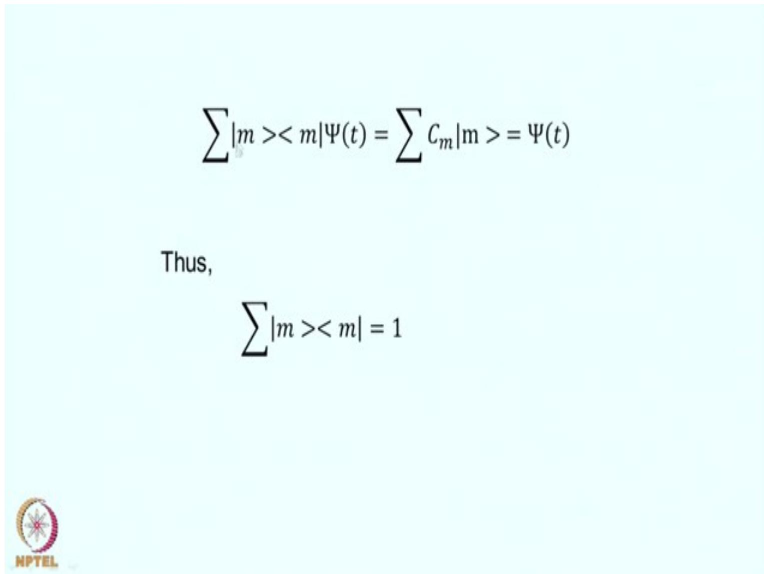

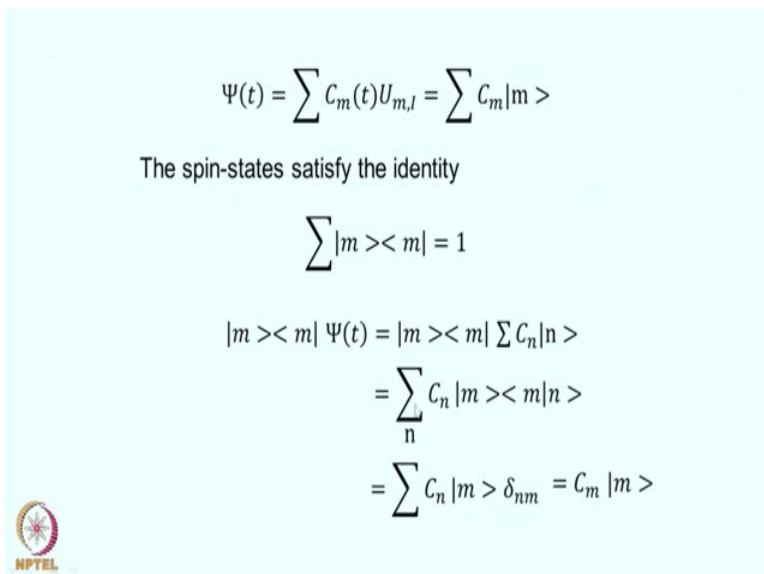

Now, I take instead of this only particular element which I took last time, I take the whole summation. I take the whole summation of all this, so either for you notice, you notice here that this is essentially projecting out one particular state here from the entire way of function, right? This was $\psi(t)$, here, and eventually I have got here only one state with its coefficient $C_m|m$.

Therefore, this operator, this is now, you understand this is an operator, this operates on the way of function psi of t and gives me only one particular state, therefore, this is called as a projection operator, this projects out the particular state m out of this psi of t.

So, now I am taking the entire summation of all these operators, m and m, all the operators, m going from 1 to n, so this is the same here. And this operator giving on $\psi(t)$, give $C_m |m$ and this summation is basically psi of t again, we have seen that this is in the definition.

Therefore, this equation if you see, if I take out psi of t from both sides here, then it simply reduces to this equation, this is the identity which we actually used earlier and we have proved it explicitly here for the benefit of those who are not familiar with this principles. But these are generally used routinely in or various kinds of calculations in quantum mechanics and quantum chemistry, and therefore, it is very important to understand how these things come.

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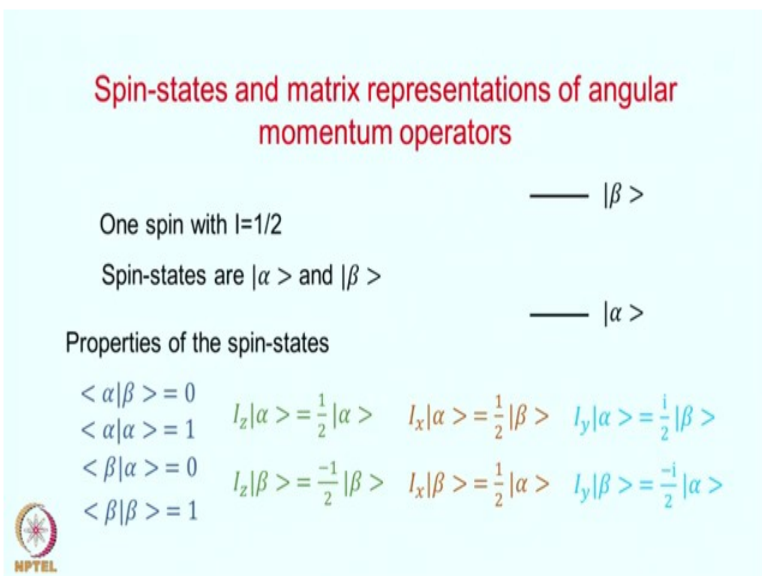

Now, let us do explicit calculations with regard to the angular momentum operators. We said the density matrix is very intimately connected with angular momentum operator I_z and we will also deal with other angular momentum operators in due course, therefore, it is important to describe the spin-states and the representation, matrix representations of the angular momentum operators.

Let us start with 1 spin with $I=\frac{1}{2}$. In 1 spin, how many states do we have in the presence of the magnetic field? Well there are anyway 2 states, in the presence of the magnetic field they are non-degenerate, they have separate energy levels. In the absence of the magnetic field they will degenerate, but nonetheless the two states are present. And because, we said I_z is the quantized state and we have only two possibilities there, therefore, we have 2 states alpha and beta and these are the spin-states.

And these are also the Eigen functions of the I_z operator as we see here. Now, what does the properties of these states that is indicated here, in this matrix element $\alpha\beta$ goes to 0, whenever I say $\alpha\beta$ actually in the conventional nomenclature, those who have used quantum mechanics the integral forms actually this ket, this is called the ket, this is actually wave function ψ and this side which is there which is the bra, this is the complex conjugate.

So, therefore, when I write like this, it is essentially the integral psi star psi. So therefore, in the case of the spin states, we simply write this as the bra here and the ket here, and therefore, this is orthogonal and therefore this is 0. All these basis, elements of the basis set are orthogonal in nature and if I do that with the similar states, $\alpha\alpha=1$

$\beta\alpha=0$, $\beta\beta=1$. Therefore, we say these states are orthonormal because this is normalized to unity and this individual matrix element, these are 1 here and their crossed terms are 0, and therefore, these are orthonormal basis sets. There are only two states, right? These two states are orthonormal.

Now, we also saw earlier that I_z which is operating on the state alpha if it is m, and this is the m value is, this we define in the very early stages of this course, that this is the m value, this gives me half. $I_z\left|\alpha=\frac{1}{2}\right|\alpha$, $I_z\vee\beta=\frac{-1}{2}\vee\alpha$, because these are the *m* values.

For the β the $m=\frac{-1}{2}\alpha$ and for the α the $m=\frac{1}{2}\alpha$, therefore, this gives me ½ and - ½ , and you see the same state is back here, therefore, these are the eigenvalue equations and alpha is eigen state of the I_z operator and beta is also an eigen state of the I_z operator with the eigen values ½ and - ½.

Now, this $I_x \vee \alpha$, this we can take it for granted, although this can be proved later. This $I_x \vee \alpha=\frac{1}{2}\vee\beta$. So, $I_x \vee \alpha=\frac{1}{2}\vee\beta$, $I_x \vee \beta=\frac{1}{2}\vee\alpha$. Notice here, the α's I_x operator converts the α state into the β state, and it converts the β state into the α state. In fact, this is what was used when we described the selection rules for energy absorption by the *RF*.

The *RF* was applied along the *X* axis and the I_x operator was coming as a perturbation by interaction of the *RF* field with the magnetic moment and then the I_x or the I_y operators coming there and because of the change in the state here, then $\Delta m=\pm 1$ selection rule was derived as a result of this, and that becomes conspicuous again, when we will actually try to calculate this matrix representation of this, I_x and I_y operator.

Likewise, if I do $I_y \vee \alpha=\frac{i}{2}\vee\beta$ and $I_y \vee \beta=\frac{-i}{2}\vee\alpha$. Once again this α state is converted into the β state here, and the β state is converted into the α state and therefore, these are not eigen value equations, because the Eigen function is not written. There is a change of state and but with a certain kind of a result here as a coefficient.

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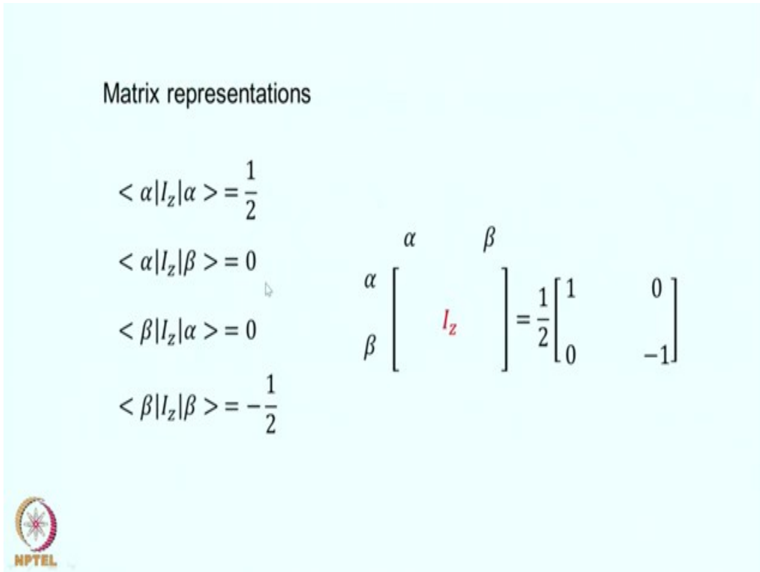

Now, I calculate the matrix elements of the I_z operator. The matrix elements of the I_z operator meaning what, so I have this sort of calculations I have to perform. I_z in the middle, α here α here, α here β here, β here α there, β here and β a is there, so this 4 elements represent a 2 by 2 matrix of the I_z operator. So, this is called as a matrix representation of the I_z operator in the basis set of the two states aα and β.

You have the two states α and β here, this form the ket individually and this form the bra individually, once α and once β. And here the ket once α once β, therefore, I have a 2 by 2 matrix here. Now, you notice $I_z \left| \alpha = \frac{1}{2} \right| \alpha$, right? So, the $\frac{1}{2} \vee \alpha$ and α, thus $\alpha\alpha = 1$, this is what we saw in the previous slide and therefore, this results, it gives me ½ .

Now, $I_z \vee \beta = \frac{-1}{2} \vee \beta$, as we saw in the previous slide. So, if I take -½ out then I have the $\alpha\beta = 0$ here, and that $\alpha\beta = 0$, because these are orthonormal. Similarly,$\beta \vee I_z \vee \alpha$, $I_z \left| \alpha = \frac{1}{2} \right| \alpha$, therefore, the matrix relevant will be ½ $\beta\alpha = 0$. So, and here, , $I_z \vee \beta = \frac{-1}{2} \vee \beta$, so therefore, I will have -½ outside, then I allow the $\beta\beta$ and the $\beta\beta = 1$, therefore, this is equal to -½ .

So, if I put this 4 elements in the matrix, then I will get here

$$\begin{array}{cc} & \begin{array}{cc}\alpha & \beta\end{array} \\ \begin{array}{c}\alpha \\ \beta\end{array} & \begin{bmatrix} & I_z & \end{bmatrix} \end{array} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

So, basically this will become the matrix representation of the Iz operator for a single spin I is equal to half.

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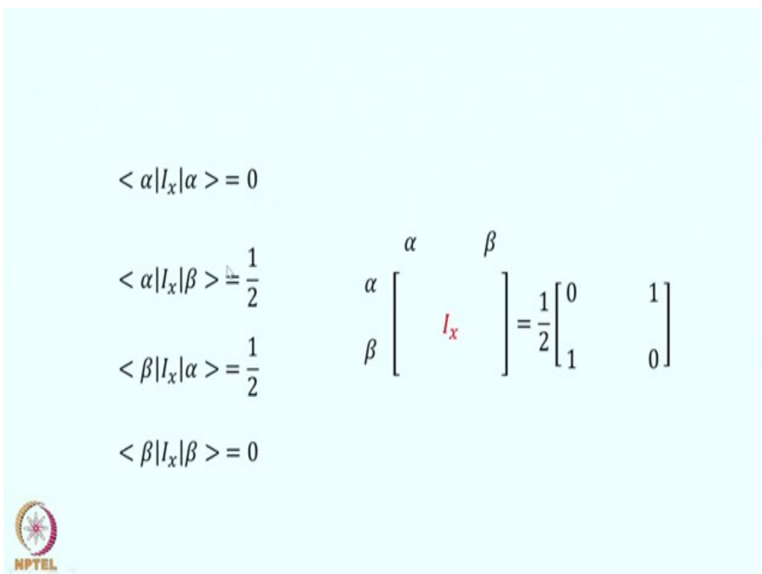

Similarly, we can do that for I_x operator. Now, I_x operator, if you remember, I_x converts $\alpha \rightarrow \beta$, it gives me $\frac{1}{2}\beta$. So, the $\frac{1}{2}\beta$ means I take away ½ out, then I have the $\alpha\beta = 0$. So, therefore, I know if you see I_x β, so I_x β gives me I_x $\frac{1}{2}\alpha$, then $\alpha\alpha = 1$, therefore, I have here half. This was exactly the same thing what we used when we were actually calculating the selection rules with the perturbation magnetic moment interaction with the *RF* field and the operator part was I_x there.

So, you see the difference of $\Delta m = \pm 1$, right? So, therefore, that is how we get an selection rule of $\pm 1$for RF induced transitions, basically it comes from this sort of a calculation. Similarly, $\beta \vee I_x \vee \alpha$ if I do, the $I_x \vee \alpha$ converts α into the β state, I get a $\frac{1}{2}\beta$, so $\beta\beta = 1$, so I get a ½ here. So, here $I_x| \beta$ goes your $\frac{1}{2}\alpha$, and therefore, $\beta\alpha = 0$.

So, therefore, if I write it in the same manner here, so $\alpha\beta$ here, $\alpha\beta$ here, these are the two kets and these are the two bras, so I_x is in the middle so I will have 4 elements here,

$$\begin{array}{c} \\ \alpha \\ \beta \end{array} \begin{array}{c} \alpha \qquad \beta \\ \left[\quad I_x \quad \right] \end{array} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

so therefore, this becomes the matrix representation of the I_x operator.

So, similarly, if I do for I_y, $I_y \vee \alpha$, $I_y \vee \beta$ and these was now, notice here, I have a I coming here, these are imaginary, so, I will have

$$\begin{array}{c} \\ \alpha \\ \beta \end{array} \begin{array}{c} \alpha \qquad \beta \\ \left[\quad I_y \quad \right] \end{array} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

So, this will be the matrix representation of the I_y operator for a single spin ½ . Now, if we eliminate this ½ , we remove this half, the matrices which are present for the I_z, I_x and I_y, so they are simply 2 by 2 matrices.

In

$$I_z=\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$$

For

$$I_x=\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$$

for

$$I_y=\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$$

and these three 2 by 2 matrices are called Pauli-spin matrices. For, single spin and these are the ones which you actually calculated and these are called as Pauli-spin matrices. Okay.

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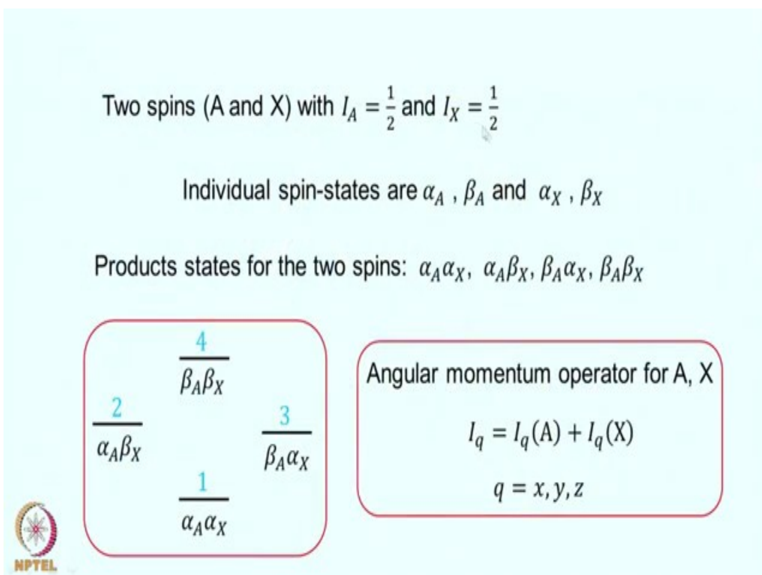

Now, let us turn to 2 spins. So, two spins consider A and X, $I_A=\frac{1}{2}$, $I_X=\frac{1}{2}$. Now, the individual spin states of these two spins are α_A, β_A and α_X, β_X. Now, for generating the basis set for the two states, we take the products of this individual spin states. This was done in the second chapter when analysis of spectra was described, when you wrote the

Hamiltonian, you tried to calculate NMR spectra using the quantum mechanical principles, this also was done in a very generalized way.

So, for the two spins we calculate the product states for the two spins. These will be $\alpha_A\alpha_X$, $\alpha_A\beta_X$, $\beta_A\alpha_X$, and $\beta_A\beta_X$. These are the 4 states which constitute the basis set. So, 2 by 2, two states for this and two states for this, so therefore, I will have here 4 states. I represent this 4 states in the energy level diagram like this, I have, I have labelled this $\alpha_A\alpha_X$ state number 1, $\alpha_A\beta_X$ as state number 2, $\beta_A\alpha_X$ as state number 3, $\beta_A\beta_X$ as state number 4.

And now, the angular momentum operator, consolidated angular operator for the two spin system if the I_z or the I_q or I_x or the I_y will be the sum of individual operators. So, I_z here for 2 spins, will be $I_z = I_z(A) + I_z(X)$, I_x for the 2 spins will be $I_x = I_x(A) + I_x(X)$ and I_y for the two spins will be $I_y = I_y(A) + I_y(X)$. So, therefore, in abbreviated notation we write like this, $I_q = I_q(A) + I_q(X)$where $q = x, y, z$.

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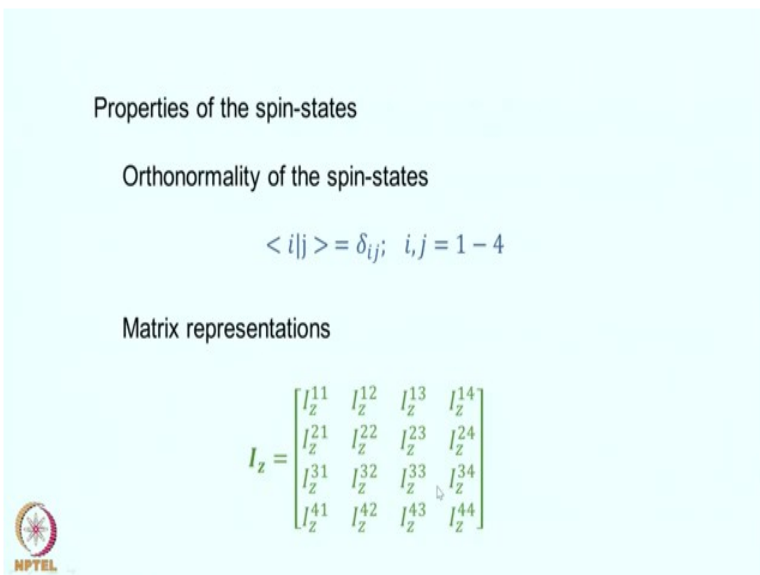

$$I_z = \begin{bmatrix} I_z^{11} & I_z^{12} & I_z^{13} & I_z^{14} \\ I_z^{21} & I_z^{22} & I_z^{23} & I_z^{24} \\ I_z^{31} & I_z^{32} & I_z^{33} & I_z^{34} \\ I_z^{41} & I_z^{42} & I_z^{43} & I_z^{44} \end{bmatrix}$$

Now, what are the properties of the spin-states? So, this will follow from the general properties of the alpha and the beta states. If I label this now, I labelled with my 4 states as 1 to 4, so here therefore, I take the products of the individual states, *ij*, then this is

$$< i|j > = \delta_{ij}; \quad i,j = 1-4$$

So, the 4 states which are there, so these are orthonormal states of the two spin system.

ij is called the δ_{ij}. So, therefore, how many matrix elements will be there for the two spin-states? Since, there are 4 states, so 4 ket states and 4 bra states and therefore, this will be 4 by 4 matrix for the I_z operator and likewise, for the I_x and the I_y operator. So, it will consist of these elements,

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

and these are the matrix elements we have to calculate.

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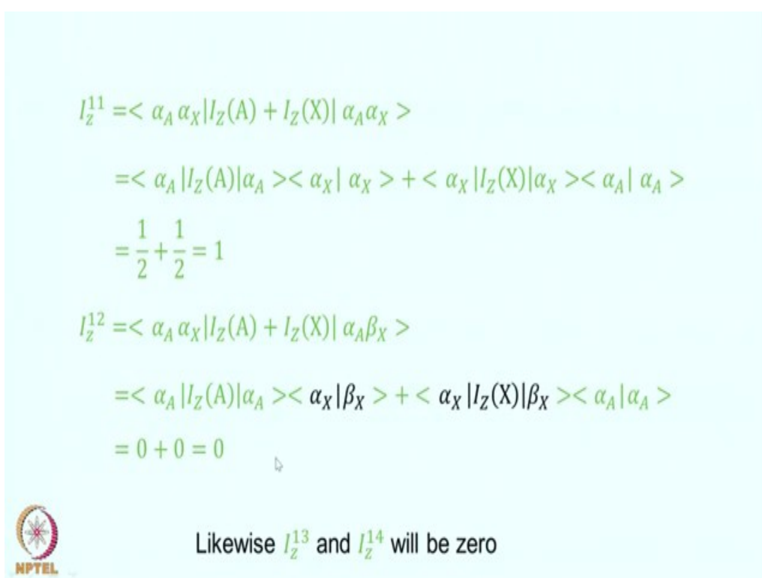

Let us illustrate this, how this can be calculated. So, let us calculate I_z^{11}. I_z^{11} is the one state is $\alpha_A \alpha_X$, right? So, therefore, in the bra here I have the $\alpha_A \alpha_X$, and the I_z operator here is ¿$I_z(A)+I_z(X)\vee$¿ and the ket again is the 1 1, 1 state and that is $\alpha_A \alpha_X$. Notice, each of these operator operates only on its own spin-state and it does not operate on the other spin-state.

For example, $I_z(A)$ will operate only on the α_A, it will not operate on α_X. So, therefore, if I am calculating the matrix element with the respect to $I_z(A)$, I can take out the α_X state. So, this is what we shall do. Now, if I have this two states here, now α_X, I can take a note if I am calculating $I_z(A)$ here, so I separate out these 2 into separate calculations, so in one case I have the $I_z(A)$, in the other case I have the $I_z(X)$ here.

So, if I have $I_z(A)$ here, I keep this α_A here, then the $I_z(A)$ and keep this α_A here, and this α_X, this α_X come out here as a separate entity, α_X, α_X. Similarly, plus α_X, $I_z(X)$, α_X, that is if I am looking at this operator, then $\alpha_X \alpha_X$ these two are taken here and these $\alpha_A \alpha_A$ come out separately here. Now, because of the orthonormality of this, this is equal to 1 and likewise, this is also equal to 1.

And what does $I_z(A)$ give me or operating on α_A? It gives me $\frac{1}{2}\alpha_A$. Now, therefore, $\frac{1}{2}\alpha_A$, half we take it out, $\alpha_A \alpha_A$, that gives me 1 again and therefore, I have a ½ here coming from this term. This is 1 and this gives me half. Similarly, this gives me half and this gives me 1. Therefore, ½ + ½ this gives me 1. Let us do it for I_z^{12}. I_z^{12} is $\alpha_A \alpha_X$, here, this I_z remains the same and here I have the state number 2 which is $\alpha_A \alpha_X$.

So, I do the same as I did here before, so I have here $\alpha_A \vee I_z(A) \vee \alpha_A$ those are this, these states are taken, α states and α_X and β_X come out here. That because I_z operator does not operate on the *X* spin-sates, therefore, this $\alpha_X \beta_X$ come here. For the second one, when I am putting $I_z(X)$ here, I have to use the X spin-states only, therefore, I have here I_x, α_X and then you have the β_X here, and the $2\alpha_A \alpha_A$ come out.

Now, notice here because of the orthogonality this term gives me 0 here, $\alpha_X \beta_X$ is 0 whereas this gives me half, on the other hand here this gives me 1 and this gives me 0 again, because this is $\frac{1}{2} - \beta_X$ and $\alpha_X \beta_X$ gives me 0. Therefore, both these terms actually become 0 and we vanish. And likewise, I_z^{13} and I_z^{14} will be 0.

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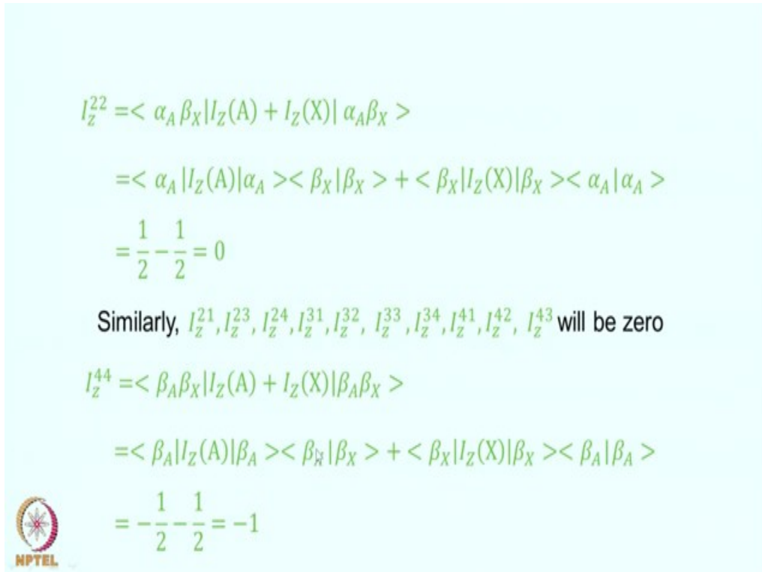

So, let us do the same thing for I_z^{22}. I_z^{22} is, now we have the two state here and the two state here, $\alpha_A\beta_X$, $\alpha_A\beta_X$, and ¿ $I_z(A)+I_z(X)\vee$¿. So, this is $\alpha_A \vee I_Z(A) \vee \alpha_A$ which is easily followed from here. Then I have this $\beta_X\beta_X$X. Here, $\beta_X \vee I_z(X) \vee \beta_X$ and $\alpha_A\alpha_A$. Now, what do I get from here. $I_z(A)$ and α_A gives me half and therefore, and this is 1, $\alpha_A\alpha_A$ is 1 and therefore, I get a half here. Now, what do I get here, $I_z(X)$ operating on β_X gives me $\frac{-1}{2}\beta_X$.

And therefore, $\frac{-1}{2}\beta_X\beta_X=1$, $\alpha_A\alpha_A=1$, therefore, I get a -½ , these two terms will then cancel, I will have a 0 here. So, therefore, this the second term I_z^{22} will be 0. Now, similarly, we can do this calculation for all the other elements of the matrix, and we will find that in the second row, I_z^{21}, I_z^{23}, I_z^{24} and in the third row I_z^{31}, I_z^{32}, I_z^{33}, I_z^{34}, that means all the 4 terms and in the fourth row I_z^{41}, I_z^{42}, I_z^{43}, these will all be 0.

So, therefore, in the first row also we said $I_z^{11}$was non-zero and other three terms were 0, so earlier. Now, I_z^{44} also we can calculate and this is in the same manner when we calculate it, this is β_A, β_X, $\beta_A\ \beta_X$ here and $I_z(A)\, I_z(X)$ and this terms, so this will turn out to be -½ , -½ and this will be -1 because $I_z(A)$ on β_A gives me -½ and $I_z(X)$ and β_X also gives me -½, so therefore, both will be minus half, minus half and this will be -1.

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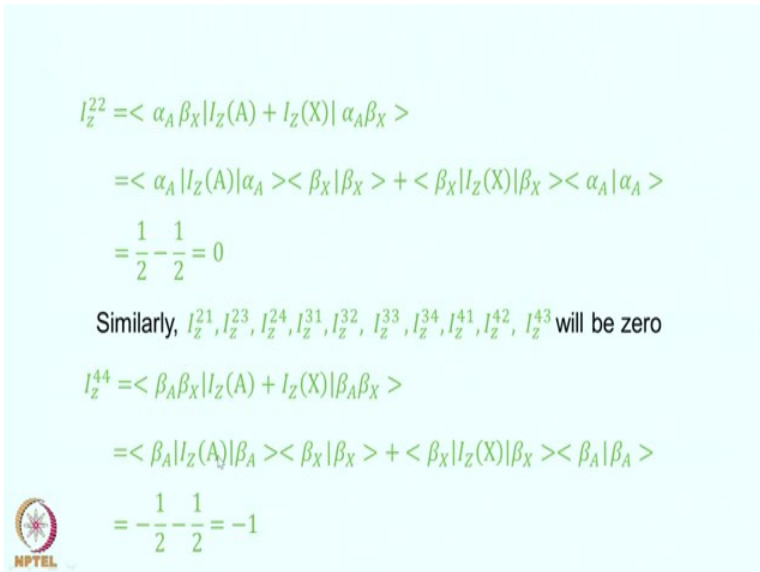

So, totally therefore, if I see, list all of these elements here, you can see that in this I_z matrix I have only these two elements which are non-zero and all the other elements are 0. Therefore, for the two spin-states, the two individual, $I = \frac{1}{2}$ spins, the I_z matrix representation will be simply this.

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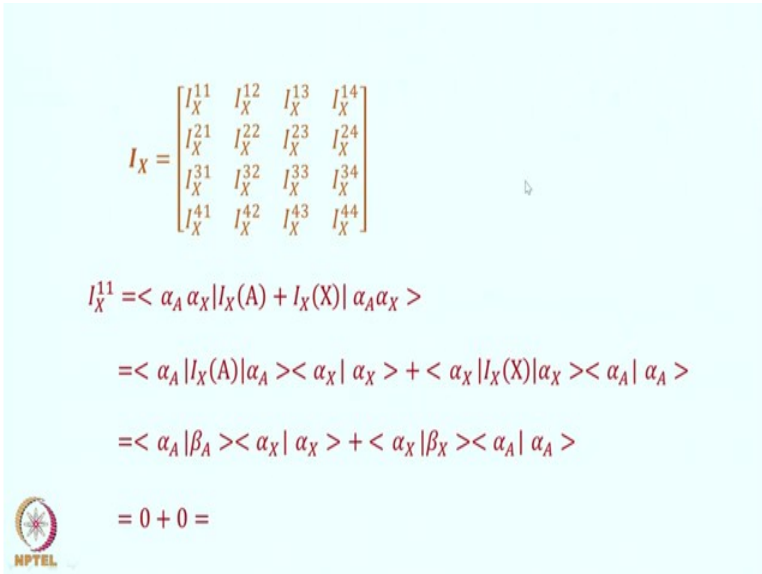

Now, for the I_x, we can do the same thing. I_x also will have these 4 elements here and now let us try and calculate for some of those. So, if I_x^{11}, this is $\alpha_A \alpha_X$, $I_x(A) + I_x(X)$, and $\alpha_A \alpha_X$ here. So, we do the trick as before, so $\alpha_A \vee I_x(A) \vee \alpha_A$ and $\alpha_X \alpha_X$and this is $\alpha_X \vee I_x(X) \vee \alpha_X$ $\alpha_A \alpha_A$. Now, notice here I_x operating on alpha gives me β, that is this here, whereas this remains the same.

And I_x operating on α gives me β so, therefore, I have α_X and β_X, and notice these ones are 0, this is 0 and therefore, this will be 0.

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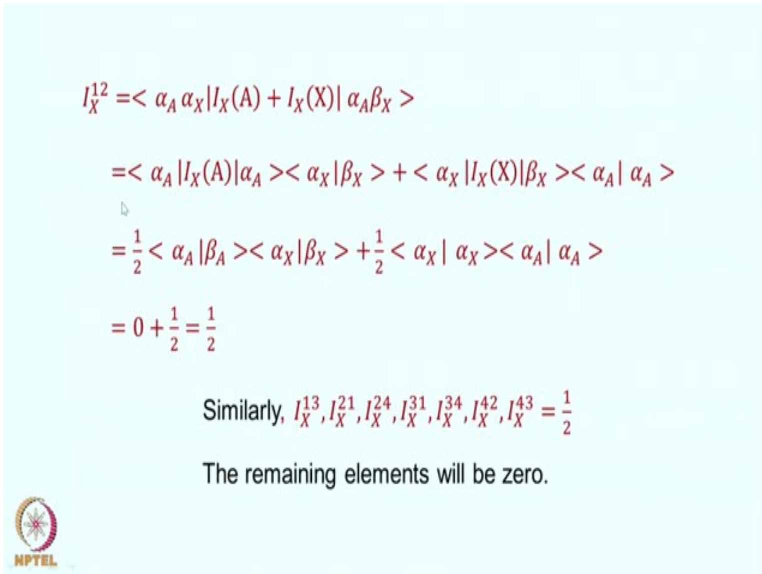

So, similarly, I_x^{12} if I calculate, I have here $\alpha_A \alpha_X$for the 1, and $\alpha_X \beta_X$ for he 2. So, here I have, therefore, the same expansion, $I_X(A)|\alpha_A > ¿ \alpha_X ¿ \beta_X > + ¿ \alpha_X | I_X(X) ¿ \beta_X > ¿ \alpha_A \vee \alpha_A > ¿$ Notice here this fellow actually gives me 0, $\alpha_X \beta_X$ gives me 0, right? And, what about this?

$I_z(X)$ operating on this is equal to 1, I_x operating on β_X gives me $\alpha \frac{1}{2}$alpha half α_X therefore, $\alpha_X \alpha_X = 1$and then I get a ½ therefore, I will get a 0 plus half and that is equal to half. So, similarly, we can calculate for these elements, I_x^{13}, I_x^{21}, I_x^{24}, I_x^{31}, I_x^{34}, I_x^{42}, I_x^{43}, all these will be equal to half and the remaining elements will be 0.

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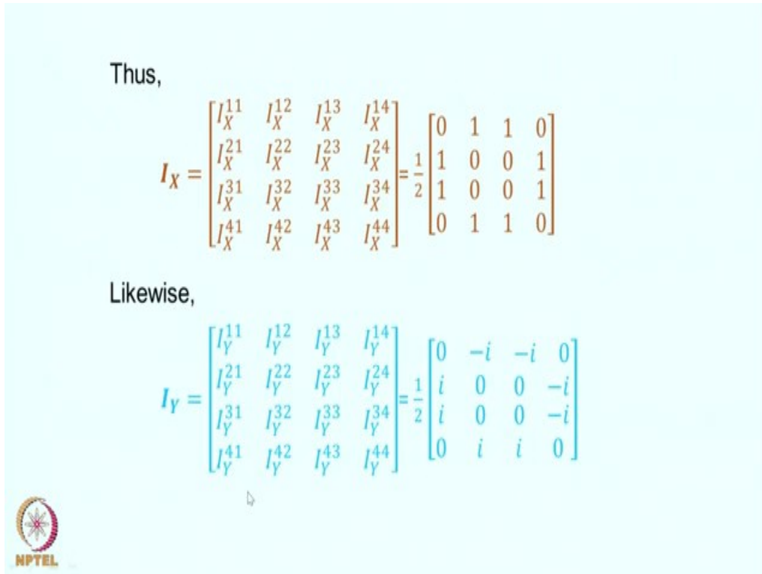

So, thus your I_x representation will look like this, all the 4 elements will have a half here, 1 1 here, 1 1 here, 1 1 here and 1 1 here and all the other elements are 0. You can do the same exercise with I_y and then it will turn out that you have half here, it will be very similar to this, except that instead of 1 you have this I elements.

So, you will have *-i -i*, *-i -i*, here. In the upper triangle you will have the *-i*'s and in the lower triangle you will have *i i* and *i i* here. So, this will be the matrix representation of the I_y operator for the two spin-states. I think we will stop here, thank you, we will continue with this discussion in the next class.