**NMR Spectroscopy for Chemists and Biologists**

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**Lecture 34**

**Product Operator Formalism continued**

So, we have been discussing about the density operator calculations, density matrix calculations. We introduced last time a specific formalism known as product operator formalism

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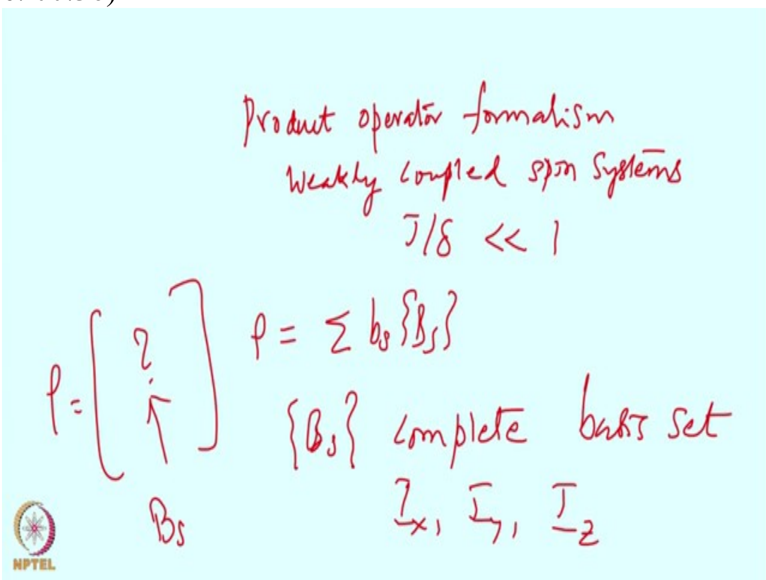


Product operator formalism, which will facilitate the calculation of the density operator at any point in time in a pulse sequence. And this we said this is for weakly coupled spin-systems, weakly coupled spin-systems which is generally valid in most of the modern spectrometers which have very high fields.

So, for this means condition was $\frac{J}{\delta} \ll 1$. So, in this formalism the density operator is written $\rho = \sum b_s \{B_s\}$. So, this $B_s$ set constitutes a complete basis set. This is a complete basis set so, that any density operator can be expressed as a linear combination of the elements of this complete basis. Okay. So, then we started looking at what these individual basis operators mean. We said these are generally described in terms of the angular momentum operators because a very natural thing to do.

There are many ways of doing it. And we considered the Cartesian angular momentum operators $I_x$, $I_y$ and $I_z$ for individual spins. Then we can make combinations of these to generate products of two spins, three spins and things like that which will generate a complete basis set, using which we can express the density operator.

Now, when we define the basis operators, we also must know what these individual basis operators mean, what does it encode. So, if we want to take the complete matrix, the rho as a complete matrix as some huge matrix n by n matrix or whatever that this thing is and which elements are occupied by the particular basis operator.

So, if I want to take a basis operator Bs, one particular basis operator, which elements here are occupied by this? So, that actually gives us an information about what is the meaning of a particular basis operator Bs. So, in this context we actually looked at one-spin, two-spin, three spin, defined the basis set of operators.

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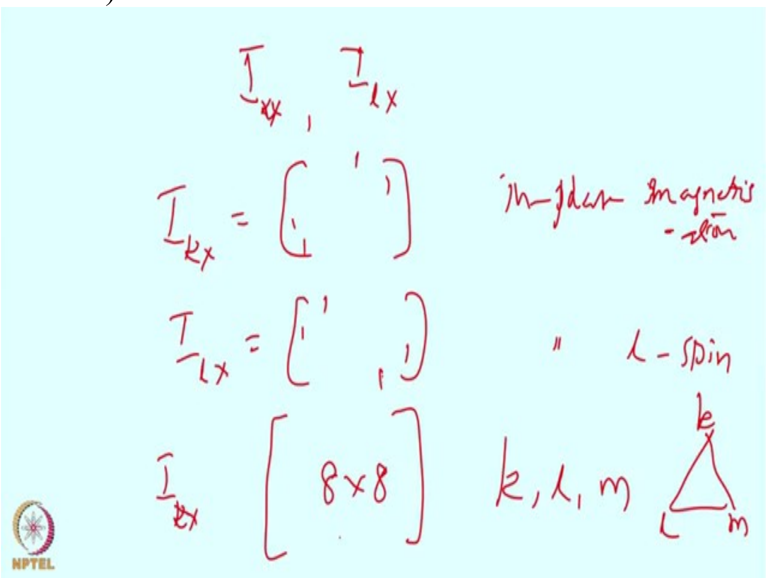


And we also looked at last time particular operators like $I_{kx}$, okay and $I_{lx}$ for one spin system and also for a two-spin system. And what does it represent? What does $I_{kx}$ represent in this density matrix? So, we said okay, this will represent in-phase magnetization of $k$ spin, in-phase magnetization of $k$ spin. Likewise, it is this if you look at the elements here, so we have this 1, 1 here, 1, 1 here, this side 1, 1 here and 1, 1 here.

So, this actually give the in-phase magnetization of the $l$ spin, so for, for the two-spin system. And this is the 4 by 4 matrix. In the individual case of 1 spin system there will be 2 by 2 matrices. For a 2 spin case it will be 4 by 4 matrices. But we can represent the individual $k$

magnetization or the *l* magnetization in the 4 by 4 matrix itself to draw a meaning out of that one. And similarly for a 3spin system also we wrote what does *kx* would mean in a 3spin system of *k, l, m*. And this will be 8 by 8 matrix and obviously it will occupy 4 elements here because the *kx*. If I have *k, l, m* which are coupled like this, *k* here, *l* here and *m* here, if all of them are coupled then each one of them is a doublet of a doublet.

So, there will be 4 lines for each one of those and these 4 lines will occupy 4 elements in this complete density operator. And we saw that they will all have the same signs and we will have for the each *kx, lx* and *mx*. There will be 4 different positions occupied, 4 different positions on this side and 4 positions on this side occupied to represent the in-phase magnetizations of the *k, l* and *m* spins. So, now we go forward from this, so, for we are considering only one spin elements in multiple spin systems.

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$$2I_{kx}I_{lz} = \frac{1}{2}\underset{k}{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}} \otimes \underset{l}{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

x-magnetization of k, anti-phase wrt l

$$2I_{ky}I_{lz} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix}$$

y-magnetization of k, anti-phase wrt l

Now, we look at the products, products of the operators. So, how do we do that? And that is what we are going to do today. So, let us consider the particular element which we represent as 2 $I_{kx}$ $I_{lz}$. So, what it means? I have two, this is now a two-spin product, so of $I_{kx}$ and $I_{lz}$. *k* and *l* refer to the two spins. How do we calculate the matrix representation of this? So, we take the matrix of *kx* here and remember these are for the individual spins.

So, therefore these are, since these are two independent and separate spins, we have to take the direct product. If this is *k* spin and this is the *l* spin and we have the direct product of the *k* spin and the l spin. The x is 0, 1, 1, 0 and the *z* operator for those single spin is 1, 0, 0, -1. So, now to generate a 4 by 4 matrix, we have to take the direct products of these two matrices. So, therefore at the place where there is 1, I get this entire matrix here, 1, 0, 0, minus 1. Here again where there is 1, I get 1, 0, 0, -1. And the other four elements will be 0 because we have 0 here and 0 here.

You multiply 0 by 0 this entire matrix, we get 0 here and 0 there. Now, we notice here these ones represent the single quantum coherences. So, if you recall the energy level diagram, the that will tell you, we will see that on the next slide. And we will exactly know, how these ones mean single quantum coherences. So, these ones are for the two-spin system. We have 4 energy levels as we have mentioned and these ones must correspond to those four energy levels.

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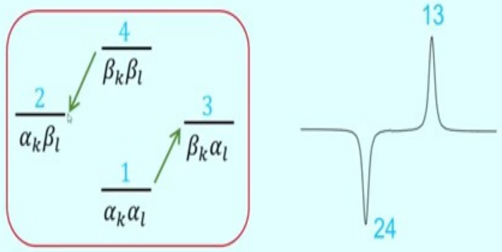
$$2I_{kx}I_{lz} = \frac{1}{2}\begin{array}{c} \begin{array}{cccc} \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \end{array} \\ \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \end{array} \begin{array}{c} \alpha\alpha \\ \alpha\beta \\ \beta\alpha \\ \beta\beta \end{array}$$

x-magnetization of k, anti-phase wrt l




This is indicated here explicitly. So, we have here the two $I_{kx}$ $I_{lz}$, the same matrix represented here. And the four energy levels of the two-spin system are $\alpha_k\alpha_l$, $\alpha_k\beta_l$, $\beta_k\alpha_l$and $\beta_k\beta_l$. These are the four states. And for these four states are 1, 2, 3, 4 on this side and 1, 2, 3, 4 here and therefore I can write these four energy states on the top here. This is $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$and $\beta\beta$. And here also $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$and $\beta\beta$.

So, now you see, so what these elements are? So, we have this transition, this is the 1, 3 transition which means this is 1, 2, 3. This is 1 is here and that is the 1, 3 transition here and this is the $k$ transition, $k$ is flipping from $\alpha$ to $\beta$ and l is remaining the same as $\alpha$. So, this is the $k$ transition. So, therefore we say it is one of the components of the $x$ magnetization of $k$. And this one is the other transition of the element which of the density operator which is occupied is 2, 4. And the 2, 4 is this.

And this again is $\alpha_k$ to $\beta_k$ and so we have here element minus 1 here. But notice one thing that these two have opposite signs. This one is +1 and this one is -1. So, to represent that we put arrows in this manner. If I put 1 to 3 as positive arrow here to represent positive signal here, then the 2, 4 represent by a negative sign. This is only a representation to convey the meaning as to what we are trying to say.

When we actually measure the magnetizations of these coherences in an NMR experiment, when I get the spectrum, I will get these two lines in this manner. 1, 3 line will be positive because it is the +1 here and the 2, 4 line will be negative and that is because of the minus sign here and this is going down.

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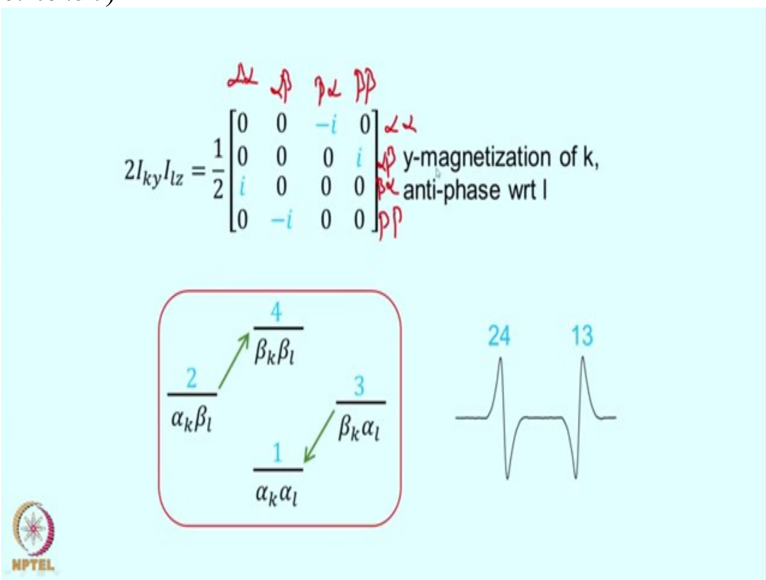


So, similarly for the *ky*, *lz* I have here the same four states. But again once again it is the *k* spin. *lz*, *l* spin in the *z* direction and *ky*, transverse magnetization is of the *k* spin. Previously the transverse magnetization was of the k spin but it was x component. So, here we have the *y* component.

This product is *ky lz*. Now, what we see here? We see *-i* and i. And this one is represented in the same manner here. Now, once again you see this you have opposite signs. What is the meaning of opposite sign? First of all, these are imaginary numbers. The imaginary numbers meaning we have a dispersive component.

This is 90 degrees out of phase. So, if I call *x* to *y*, it is a 90 degrees out of phase and this is represented here in the by an imaginary number here. So, we get an *i* here, so therefore if I have 1, 3 as a particular way, if it is in this manner, then the 2, 4 will be opposite to that and therefore this goes in this manner here.

So, you notice here, if this is positive going like this, then this has to be negative which is going in this manner. So, accordingly you could have chosen either this way, you could have chosen this way as particular sign and this as a particular as an opposite sign. It does not matter. So, you will have the opposite signs for these two signals but they will be dispersive line shapes. Okay, *y* magnetization means these are dispersive line shapes.

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$$2I_{kx}I_{ly} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}_k \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}_l = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \quad \text{DQ+ZQ}$$

$$2I_{ky}I_{lx} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \quad \text{DQ-ZQ}$$

Now, let us look at a product which is *kx ly*. Now, both these components are transverse components of the *k* and the *l* spins. This is *x* component of the *k* spin and the y component of the *l* spin. So, now what we do? So, we have to add here the, this again I will put *k* and this is l. So, for *k* I have the matrix for the *x* and that is 0, 1, 1, 0. And for the *y* I have 0, *-i, i*, 0. This is for the *l* spin. Now, I have to take the direct product of these and then I get here 0, 0, 0, -*i*, 0, 0, *i*, 0, 0, -*i*, 0, 0, *i*, 0, 0, 0.

It is very interesting. You see which elements are occupied here, remember this was the $\beta\beta$ state. And this side is the $\alpha\alpha$ state, so $\alpha\alpha$to $\beta\beta$ that is actually double quantum coherence. So, therefore this element represents a double quantum coherence. So, therefore this is the 1, 4 element of the energy level diagram. And this will be double quantum coherence. And this has a minus sign and it has it is *i* here. Now, you also have a non-zero element here and this is *i*, and this represents 2, 3 state, 2, 3 coherence, right?

This is energy level 2 and this side is energy level 3 and therefore I have a 2, 3 here and the 2, 3 state is actually zero quantum coherence because they are both alpha beta and beta alpha, their m values are zero and therefore we have a zero quantum coherence here. Therefore, and similarly and these are the corresponding complex conjugates in this area. So, therefore this matrix represents a combination of double quantum plus zero quantum coherences. This was *kx*, *ly* and now, if we look at *ky lx* let us look at *ky lx*, so what I have to do is simply I have to interchange these two.

For *k* I will put 0, -*i*, *i*, 0 and for *l* I put here 0, 1, 1, 0. So, now if I take this direct product, so I get here 0, 0, 0, -*i*; 0, 0, -*i*, 0; 0, *i*, 0, 0; *i*, 0, 0, 0. Now, it is the same four elements which are populated which are non-zero here. The difference however is that these are -*i*, -*i*, here and these are correspondingly *i*, *i*. So, therefore there is a sign difference between these two.

If this way to represent *DQ* + *ZQ*, then this will represent one of the elements is changed to minus sign, so we call it as *DQ* - *ZQ*. So, double quantum minus zero quantum coherence for this element. So, 2 *ky lx* is represents *DQ* - *ZQ*, both of them of course are combinations of double quantum and zero quantum coherences. But they have different signs and therefore in this case I have *DQ* + *ZQ*. Here I will have *DQ* - *ZQ*.

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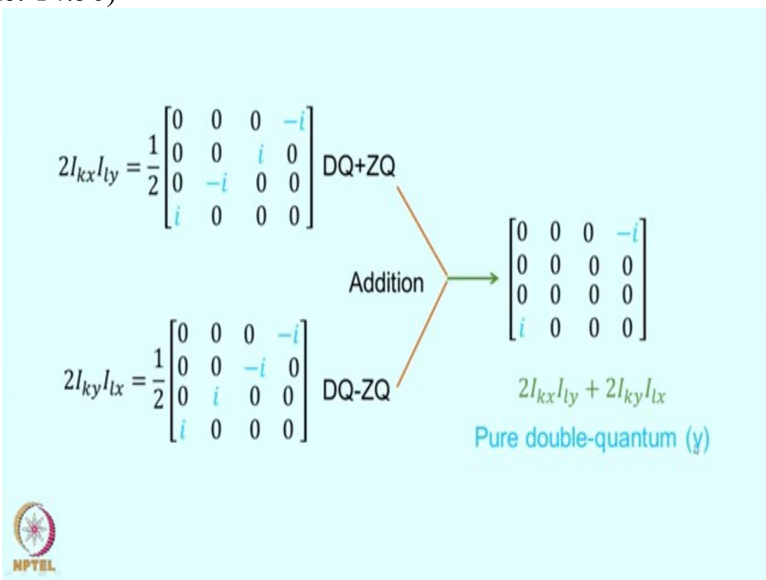


So, now what I do? So, I have here the same elements represented here. $2I_{kx}\, I_{ly}$, put the same matrices here. So, I have 0, 0, -*i*; 0, 0, *i*, 0; 0, -*i*, 0, 0; i, 0, 0, 0. This is *DQ* + *ZQ*. And I put here *DQ* - *ZQ*. Now, I take an addition of these two. I take a sum of these because in a density operator when we are doing, it may be that we will have combinations of basis operators. It cannot be that we will only have one of them as your density operator.

So, your density operator, remember is a summation of the various basis operators. So, if I take a combination of these two, *kx ly* and *ky lx*, add it over here, then what do I get? I get here -*i*, I get here *i* and all the others are 0. That means I get pure double quantum coherence. So, this is the unique way of getting pure double quantum coherence.

And this is because it is -*i* here, we call it as *y*. Although you cannot represent a double quantum coherence as *x*, as along the any of the Cartesian coordinates as *x, y, z*, we simply say by convention for the sake of ease of representation, we call this as y component and this is represented by *i* here, this is basically imaginary.

And one could have called them as real and imaginary as well. But for convenience or some convention which has been used, so we call it as pure double quantum *y*.

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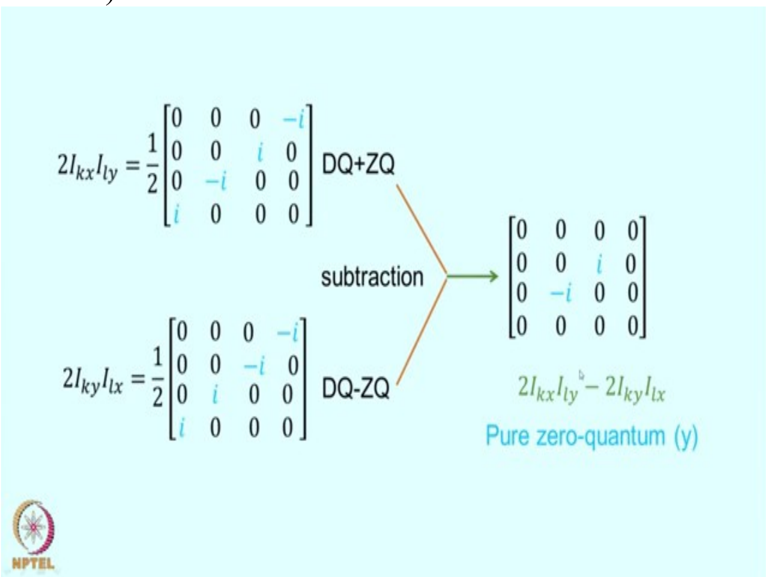


Now, suppose I do a subtraction of the same two elements, $I_{kx}$ $I_{ly}$ here, $I_{ky}$ $I_{lx}$ here and make a subtraction. If we do a subtraction, I will get *i* and -*i* here and all other elements are 0. So, what that means? I get pure zero quantum *y*. This is y coherence, pure zero quantum. And this remains as -*i*, *i* and therefore it is called as *y*.

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$$2I_{kx}I_{lx} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}_k \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}_l = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \quad \text{DQ+ZQ}$$

$$2I_{ky}I_{ly} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}_k \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}_l = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} \quad \text{DQ-ZQ}$$

So, now let us look at the other product here. $2I_{kx}$ $I_{lx}$. Now, in this case I have the *x* components for both *k* and *l* spins. So, let me write here once more, these are for the individual spins. This is for k and this is for l. So, once again it is for k and this is for l. So, here these direct products now will have real numbers. You see, this product gives me 0, 0, 0, 1; 0, 0, 1, 0; 0, 1, 0, 0; 1, 0, 0, 0. Once again this is a mixture of double quantum and zero quantum coherences.

Because this is the double quantum, this is zero quantum. This is the mixture of the two and they have the same sign. So, I represent as mixture of double quantum plus zero quantum here. Now, if I take *ky ly*, then now I have 0, -*i*, *i*, 0, direct product is 0, -*i*, *i*, 0 and this gives me once again real numbers here. In the 4 by 4 matrix I get here minus 1, 1, 1, minus 1 and all other elements are 0. So, therefore because of the opposite signs of these two, so this will be represented as double quantum minus zero quantum.

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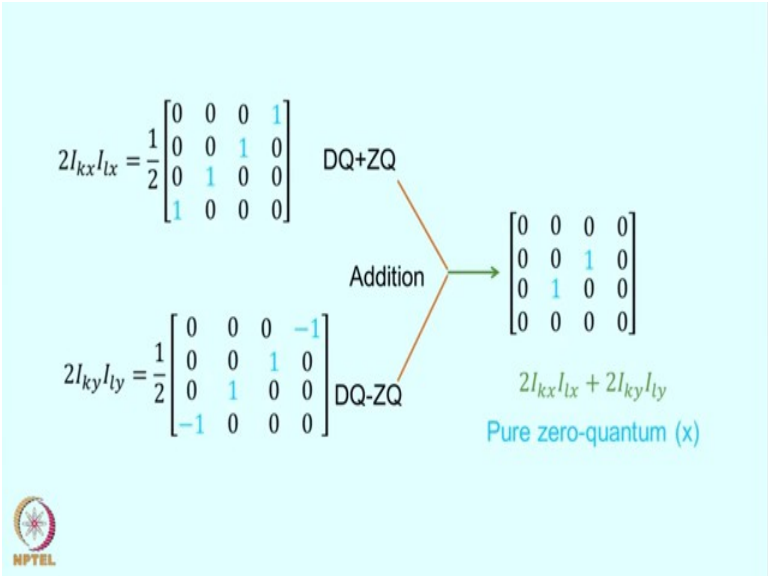


Okay, so now what we do? We take, we do the same trick as we did before. So, we take a summation of these two elements. $I_{kx}$ $I_{lx}$, $I_{ky}$ $I_{ly}$, remember these two elements is always as the normalization factor. So, I get *DQ* + *ZQ* addition, *DQ* - *ZQ*. I get here 0,0,0,0; 0, 0, 1, 0; 0, 1, 0, 0; 0, 0, 0, 0. So, therefore if I take this addition, I have only these elements non-zero. Therefore, this will be pure zero quantum and I call it as *x* because this is the real number. This is not imaginary.

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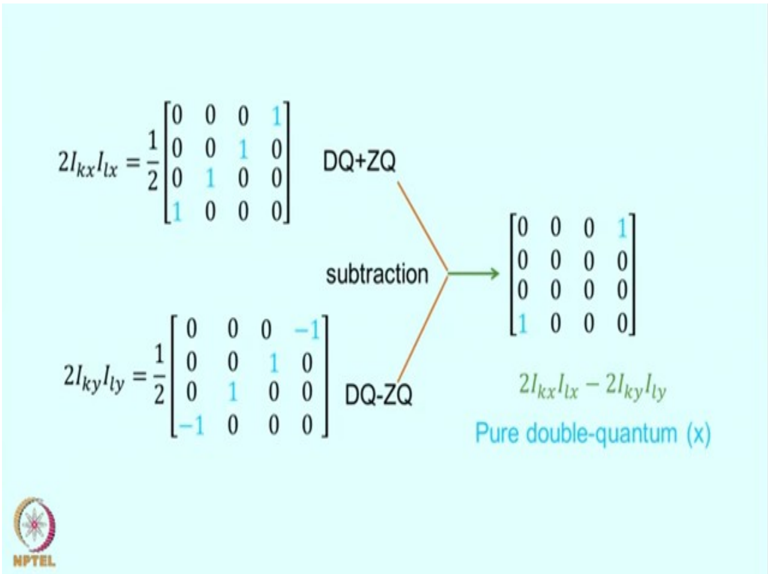


Let me now take the difference. If I take the difference, then what do I get? The same matrices here, I take the subtraction here. I get here 1, I get here 1 and all other elements are

0. So, what do I get here? Therefore, I get pure double quantum *x* coherence. So, therefore we have seen from this matrices for single quantum coherences and double quantum coherences, how we can get the representation in the density operator. So, these different elements occupy different places in the total density operator and whenever they are present, we know we have created these elements.

And often when we write the total density operator, there will be mixtures of such elements and they will all be present. By looking at what elements are present in our density operator, you can say which coherences you have created and which coherences are observable. And all of that will become helpful in analyzing the results of your NMR experiments.

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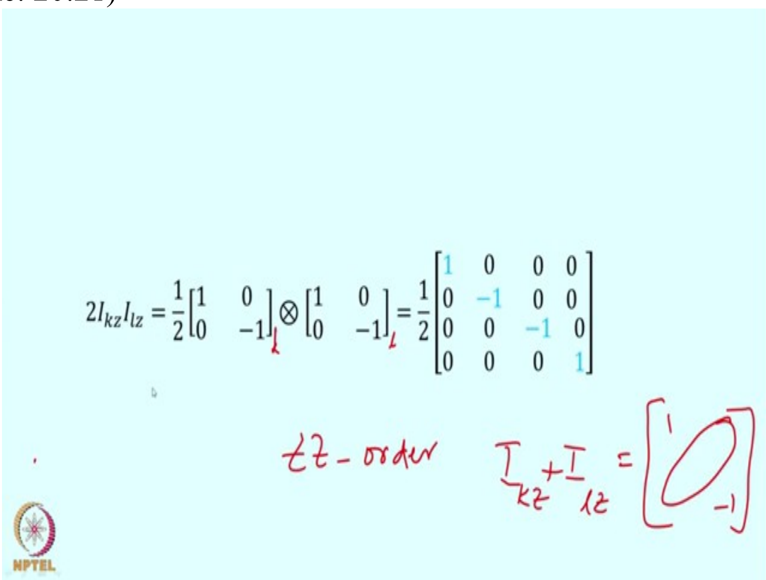


Now, there is one more here and this is $2I_{kz} I_{lz}$. Ok now, both are *z* here, *z* component, okay. So, this is *k, l* and *z* and this is 1, -1 here and for each of these once more I have to put here *k* and *l*, *k* and *l*. This represents a different kind of a situation. We have 1, 0, 0, 0; 0, minus 1, 0, 0; 0, 0, -1, 0; and 0, 0, 0, 1.

And notice that all the diagonal elements are occupied here. All the diagonal elements are occupied all off-diagonal elements are zero, which means this operator does not represent transverse magnetization or it does not represent coherences between the spins in the individual states. What does it represent?

So, this represent what is called as *zz* order. Notice, while this has to do with populations, this is not the *z* magnetization of the any of the particular spins. If you remember, for the *z* magnetization for a two-spin system, if you were to write $I_{kz} + I_{lz}$, this was the representation for the total $z$ magnetization of the two-spin system. And this was simply 1 and -1 here and all other relevance were 0.

So, this was $I_{kz} + I_{lz}$ representing the total magnetization, total population difference between the two for the two spins and that was contributing to the total magnetization. But here there is some sort of a correlation between the populations of the $k$ and $l$ spins. And therefore we call it as $zz$ order. It must be distinguished from the $z$ magnetization of the two-spin system.

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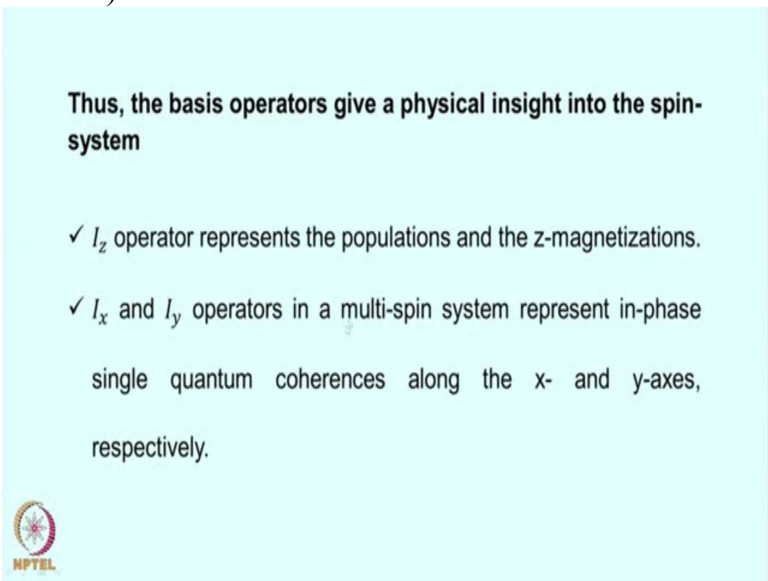


So now to summarize all of these, so what we have is thus the basis operators give a physical insight into the spin-system. Because we have seen what the individual operators are, how they are represented in the density, density operator, which elements do they represent and that gives us an indication into what these individual basis operators represent and which is easy to calculate. $I_z$ operator represents the populations in the $z$ magnetizations, $I_x$ and $I_y$ operators in a multi spin system represent in-phase single quantum coherences along the $X$ and $Y$ axis respectively.

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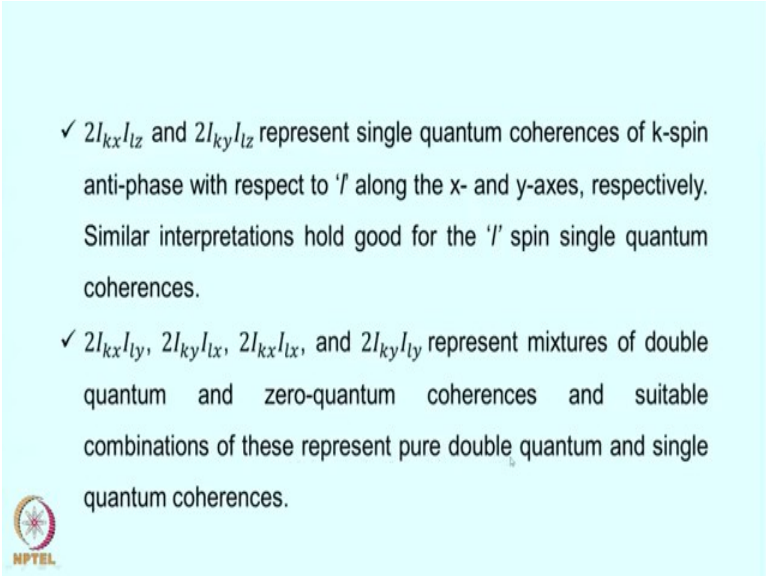


And now we saw here today $2I_{kx} I_{lz}$, $2I_{ky} I_{lz}$ represent single quantum coherences of *k* spin anti-phase with respect to *l* along the *X* and *Y* axes. Notice once again, the *kx lz* and *ky lz*, so therefore they are both k magnetizations anti-phase with respect to the spin *l* because that is in the *z* but this represent the real and imaginary component or the *X* and the *Y* axis respectively. Similar interpretations hold good for the *l* spin single quantum coherences. For instance, if I had $I_{lx}$ $I_{kz}$ and $I_{ly}$ $I_{kz}$ then they would represent the *l* spin single quantum coherences.

Then we looked at $2I_{kx}$ $I_{ly}$, two spin products with both transverse components and $2I_{ky}$ $I_{lx}$, $2I_{kx}I_{lx}$, $2I_{ky}I_{ly}$, all of these represent mixtures of double quantum and zero quantum coherences. And suitable combinations of these represent pure double quantum and single quantum coherences. And we can, we have the x components and the y components represented here as well but that is a kind of convention. You cannot actually draw a double quantum or zero quantum coherence on the Cartesian axis.

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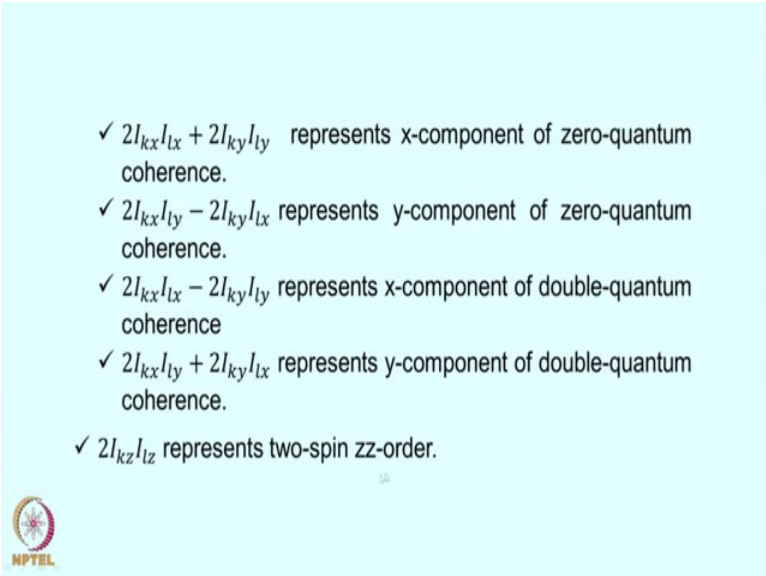


And then we said if we take a $2I_{kx}\, I_{lx} + 2I_{ky}\, I_{ly}$ represents $x$ component of zero quantum coherence. $2I_{kx}\, I_{ly}$ - $2I_{ky}\, I_{lx}$ represents $y$ component of zero-quantum coherence. And then $2I_{kx}\, I_{lx}$ - $2I_{ky}I_{ly}$ represents $x$ component of double quantum coherence. $2I_{kx}I_{ly}$ + $2I_{ky}I_{lx}$ represents $y$ component of double quantum coherence. Then the $2I_{kz}\, I_{lz}$ represents two-spin $zz$ order. This has to be distinguished from the $z$ magnetization as I indicated before.

So, we have now seen the various components of the basis operators, products, what do they physically mean and the interpretation they can give, the insight they can give in the density operator will be useful for understanding the experiments which we will discuss in greater detail, for varieties of experiments that we will discuss in greater detail in later classes. But this forms the basis for understanding all of those experiments.

So, in the next class we have to see how these evolutions, how these basis operators evolve with time because that is what is require to be calculated when you require the response of your spin system through the pulse sequence and that we will stop here and that will be taken care in the future classes.