NMR Spectroscopy for Chemists and Biologists
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Lecture 33
Product Operator Formalism

So, let us continue our discussion with the density operator treatment of NMR experiments. We have described previously the formal definitions of the density operator, the time evolution of the density operator and we have shown what kind of an equation governs the time evolution of the density operator. We have also seen what kind of solutions exist in the presence of the RF and in the absence of the RF. So, a generalized NMR experiment which will consist of several pulses with interleaving evolutions under the influence of different Hamiltonians.

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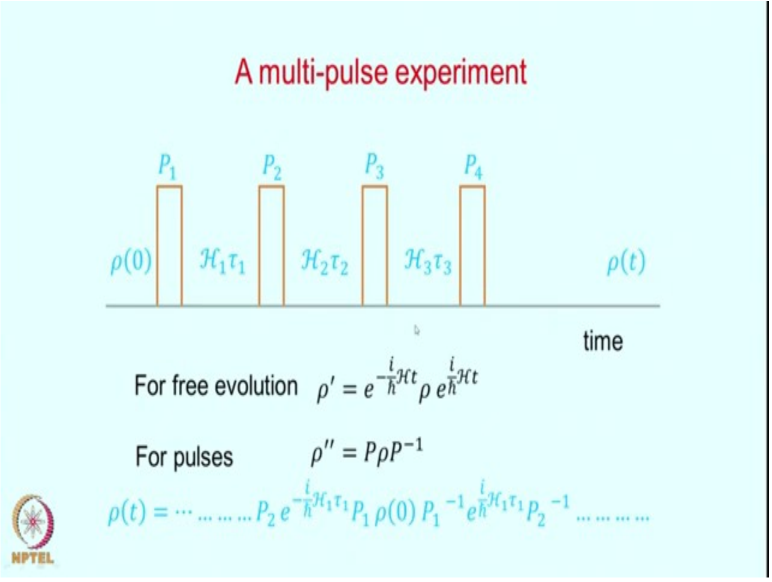

A multi-pulse experiment

For free evolution $\rho' = e^{-\frac{i}{\hbar}\mathcal{H}t}\rho\, e^{\frac{i}{\hbar}\mathcal{H}t}$

For pulses $\rho'' = P\rho P^{-1}$

$\rho(t) = \cdots\ldots\ldots\ldots P_2\, e^{-\frac{i}{\hbar}\mathcal{H}_1\tau_1} P_1\, \rho(0)\, P_1^{\ -1} e^{\frac{i}{\hbar}\mathcal{H}_1\tau_1} P_2^{\ -1} \ldots\ldots\ldots\ldots$

And this is as indicated here in this; this is the repetition from the previous and for continuity, so you have, you start an experiment here with when density operator represent as $\rho(0)$ and then you apply a pulse P_1. It may be any kind of a pulse, it may be a 90 degree pulse, 180 pulse, 45 degree pulse and whatever, that is up to one's choice. Then this is followed by an evolution period, free precision period which is under the influence of the Hamiltonian H_1 and this happens for the time τ_1.

Then this is followed by another pulse, we call it as P_2. And once again it is followed by evolution under the influence of a different Hamiltonian H_2. And that happens for a time τ_2.

And likewise you continue for the P_3 pulse, then you have the evolution $H_3\,\tau_3$; P_4 pulse and so and so forth, till you complete all your pulses and you collect the data some time here and that is where the information is analyzed subsequently.

So, you start from some particular time point here which we call it as 0. And you collect the data here with various kinds of manipulations happening in the various time periods here. The data you collect will carry all the information about that has happened in these previous times. And therefore, we have to calculate this. So, we must know how to calculate the evolution of the spin system under the influence of all of this.

And we have already shown that such a generalized pulse sequence can be represented by a time evolution of the density operator in this manner. You start with $\rho(0)$ and you apply a pulse P_1, the transformation happens as $P_1 \rho P_1^{-1}$ and this density operator now becomes the time $t=0$ for this portion of the evolution and then it continues here. And that is represented by $e^{-¿¿}$and $e^{¿¿}$. Now, this whole thing becomes the time t is equal to 0, so far as the pulse P2 is concerned.

And this is how it continues. So, you see here as you are progressing in the calculation, we go from the laboratory frame here to the interaction representation here, normal representation, interaction representation, back to the laboratory representation, again interaction representation here, back to the normal representation and so on. So, you keep switching between the two representations for the calculation purposes. And these two representations are generally separated out in this way. You see this whole calculation consists of these two kinds of evolutions. One is the $e^{-¿¿}\, e^{¿¿}$.

This is free evolution, this will apply to this period, this period, this period and so on. And for the pulses we have this sort of a transformation, $P_1 \rho P_1^{-1}$. And this will apply to this, this one, this one, this one, this one and so on.

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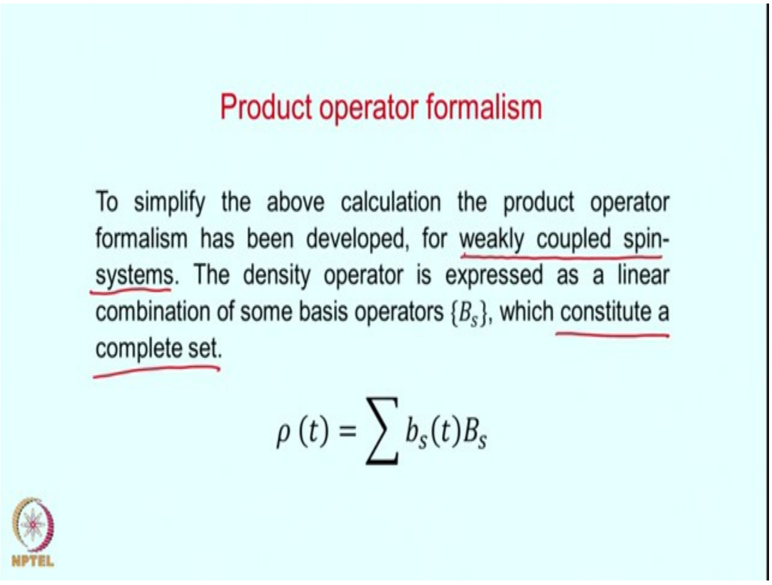

Product operator formalism

To simplify the above calculation the product operator formalism has been developed, for weakly coupled spin-systems. The density operator is expressed as a linear combination of some basis operators $\{B_s\}$, which constitute a complete set.

$$\rho(t) = \sum b_s(t) B_s$$

So, this is the quite involved calculation as we could, as we saw earlier because each one of these operators will have to be represented as a matrix and the matrices become larger and larger as we go to larger and larger spin systems and different kinds of flip angles of the pulses, different phases of the pulses. All of that will complicate the matter quite substantially. So, therefore a simplification was developed and that is called as the Product Operator Formalism.

To simplify the above calculation, the product operator formalism has been developed for weakly coupled spin systems. Notice here the key elements, key points here I want to underline here. One is this weakly coupled spin-systems you have to highlight this point. This is applicable to weakly spin-systems. The density operator is expressed as a linear combination of some basis operators which are represented as B_s. And this constitute a complete set.

So, these are important terms here which one has to understand. You have already studied these situations earlier but let me try and recap this to some extent. What is a weakly coupled spin system?

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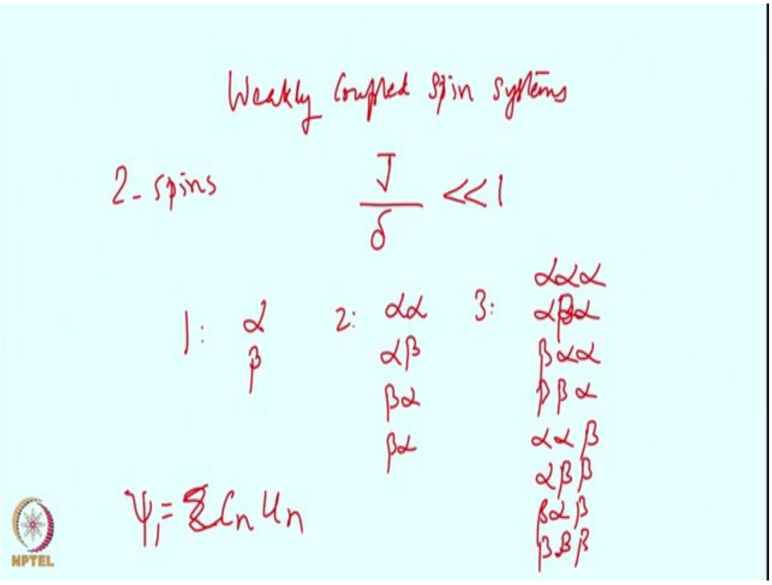

Weakly Coupled Spin Systems

2-spins $\frac{J}{\delta} << 1$

1: α
β

2: $\alpha\alpha$
$\alpha\beta$
$\beta\alpha$
$\beta\alpha$

3: $\alpha\alpha\alpha$
$\alpha\beta\alpha$
$\beta\alpha\alpha$
$\beta\beta\alpha$
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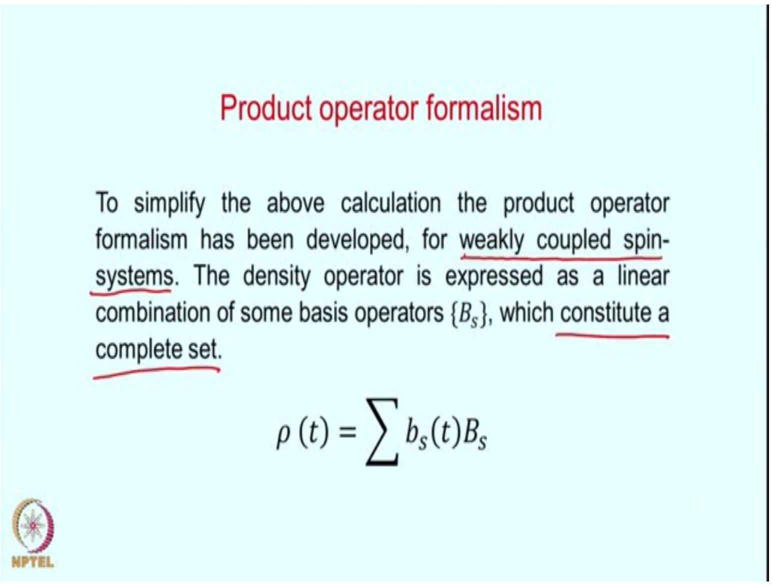
$\Psi_1 = \Sigma C_n U_n$



Product operator formalism

To simplify the above calculation the product operator formalism has been developed, for weakly coupled spin-systems. The density operator is expressed as a linear combination of some basis operators $\{B_s\}$, which constitute a complete set.

$$\rho(t) = \sum b_s(t) B_s$$

So, weakly coupled spin system, this was an important thing to remember. So, if we had two spins, both are spin half and if we have a coupling constant between them J and there a chemical sheet separation between them is δ, then $\frac{J}{\delta} \ll 1$, then we say it is a weakly coupled spin system. And this has been studied earlier when we actually went through the analysis of NMR spectra, how the spectra get complicated when this condition is not satisfied.

By and large in the modern spectrometers when you have very high magnetic fields, this condition is usually satisfied for most systems and therefore it is convenient to work with the theories which are developed for weakly coupled spin-systems. And what is a consequence of this? So, if you look at the spin-systems and you want to calculate the various eigen states and the energy levels of this, it turns out that the product functions are the Eigen functions.

If for example, one spin the states are α and β, this is one spin. For two spins, each one of them is α, beta, then we say we have the product functions $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$. These are the Eigen functions of the spin system. For three spin-systems then we will have product of three functions. We will have $\alpha\alpha\alpha$, $\alpha\beta\alpha$, $\beta\alpha\alpha$, $\beta\beta\alpha$. And then $\alpha\alpha\beta$, $\alpha\beta\beta$, $\beta\alpha\beta$, $\beta\beta\beta$. So, we have 8 Eigen functions here.

So, the reason why I am saying is the product functions are the basis set. So, here all these functions represent the complete spin system. Any situation can be expressed as the linear combination of these wave functions. So, that takes me to the next point there. Just as you are able to write a basis set and able to describe the complete wave function for a given spin system, as the linear combination of these various functions if I call this as U_n's, each one of them is called U_n, then we wrote psi is equal to summation C_n U_n. We wrote like that earlier. So, these U_n's are these various basis functions. And one can write a generalized wave function as the linear combination of these basis functions.

The same principle will be used for the product operator formalism where we will represent the density operator as a linear combination of some basis operators. So, this so therefore we write

$$\rho\ (t) = \sum b_s(t) B_s$$

this capital Bs. This constitute what are called as the basis operators. And these are the coefficients which will contribute to the summation here and that whatever are the ones which are contributing here that will determine the nature of the density operator at any point in time.

So, what are these basis operators? And this must form a complete set. Just as we talked about the Eigen functions forming a complete basis so far as the wave function is concerned, here these operators must form a complete basis set so that we can represent any density operator as a linear combination of this.

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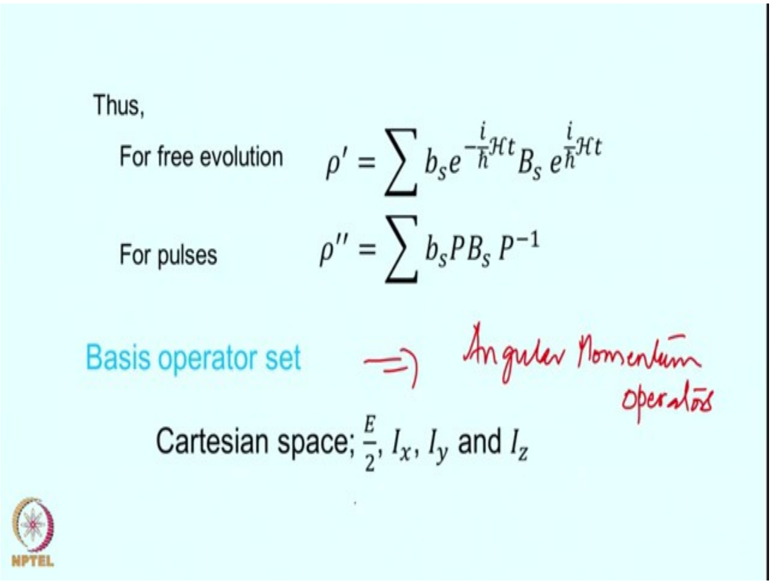

Thus,

For free evolution $\rho' = \sum b_s e^{-\frac{i}{\hbar}\mathcal{H}t} B_s \, e^{\frac{i}{\hbar}\mathcal{H}t}$

For pulses $\rho'' = \sum b_s P B_s \, P^{-1}$

Basis operator set $\Rightarrow$ Angular Momentum operators

Cartesian space; $\frac{E}{2}$, I_x, I_y and I_z

Now, having said that, now let us try and calculate what is the transformation that happens for these density operators. For the ρ' now we introduce the $\rho(t)$ here, the $\rho(t)$ was here. So, therefore now it becomes

$$\rho' = \sum b_s e^{-\frac{i}{\hbar}\mathcal{H}t} B_s \, e^{\frac{i}{\hbar}\mathcal{H}t}$$

And similarly, for the pulses we have the

$$\rho'' = \sum b_s P B_s \, P^{-1}$$

Now, how do we choose these basis operators? There can be, there are many ways of choosing these basis operators. And we will take only one of those examples which is the one which is most commonly used for various calculations. For certain situation some other kinds of basis operator sets are also used. But we will use the one particular one which is most commonly used. In every case however these are formed from what are, what we know already as angular momentum operators.

These are formed from angular momentum operators which is a very natural choice to make because your Hamiltonians consist of the angular momentum operators. Therefore, there will be kind of operationally easier things to do when you have the basis operators also expressing in terms of angular momentum operators which do satisfy the condition of completeness and therefore the calculations also become relatively easy.

Now, what are angular momentum operators? Typically, we have in the Cartesian space this is the unit matrix and we have the three angular momentum operators, I_x, I_y, and I_z. So, we build on this, we build using this. So, for a single spin if it is, then I will have one I_x, I_y, and I_z and E is the unit operator. And this is the normalization factor half, which is there in every case.

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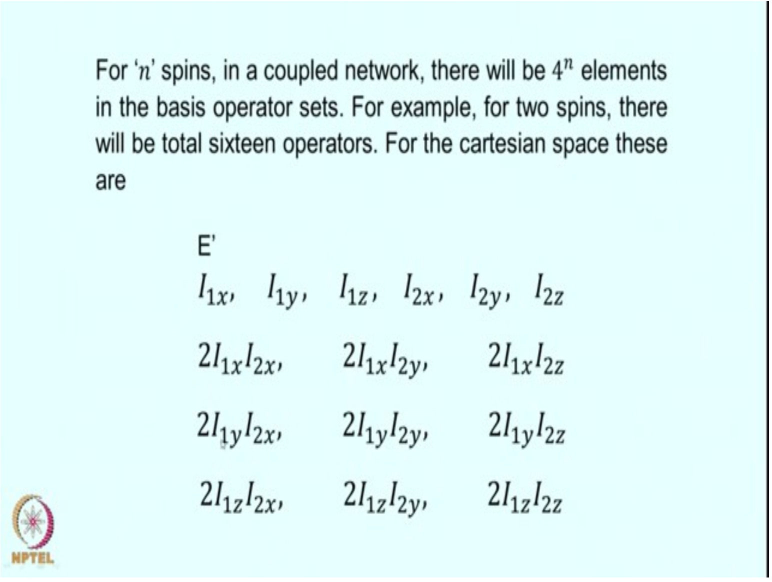

For '*n*' spins, in a coupled network, there will be 4^n elements in the basis operator sets. For example, for two spins, there will be total sixteen operators. For the cartesian space these are

E'

$I_{1x}, \quad I_{1y}, \quad I_{1z}, \quad I_{2x}, \quad I_{2y}, \quad I_{2z}$

$2I_{1x}I_{2x}, \quad 2I_{1x}I_{2y}, \quad 2I_{1x}I_{2z}$

$2I_{1y}I_{2x}, \quad 2I_{1y}I_{2y}, \quad 2I_{1y}I_{2z}$

$2I_{1z}I_{2x}, \quad 2I_{1z}I_{2y}, \quad 2I_{1z}I_{2z}$

Now, if I have *n* spins, so we said for one spin, we have four operators. One was a unit matrix, and then you have I_x, I_y and I_z. So, if I have n spins, I must I will have how many, how many combinations I can make from each one of those? Each one of them has possibilities and therefore I can create 4 to the power n combinations of these.

Various kinds of products I can take, because I should not be missing any portion of the density operator. So, all the spins must be represented. All situations of all the spins must be represented. Therefore, all the operators of the individual spins must find a representation in your basis set.

Therefore, if I have n spins in a coupled network, there will be total of 4 to the power n elements in the basis operator sets. So for example, for two spins there will be total of 16 operators. So, Cartesian space these are, we have this *E'*, this is basically related to the unit matrix.

We have this one half, that we will explicitly see what those ones are. Then you have the *x, y, z* of one spin and then the *x, y, z* of the second spin. Then I take individual products of each one of these with the other spin. And this is again a normalization factor here too. I will have

$$E'$$

$$I_{1x},\quad I_{1y},\quad I_{1z},\quad I_{2x},\quad I_{2y},\quad I_{2z}$$

$$2I_{1x}I_{2x},\qquad 2I_{1x}I_{2y},\qquad 2I_{1x}I_{2z}$$

$$2I_{1y}I_{2x},\qquad 2I_{1y}I_{2y},\qquad 2I_{1y}I_{2z}$$

$$2I_{1z}I_{2x},\qquad 2I_{1z}I_{2y},\qquad 2I_{1z}I_{2z}$$

And these are the normalization factors in each of these cases.

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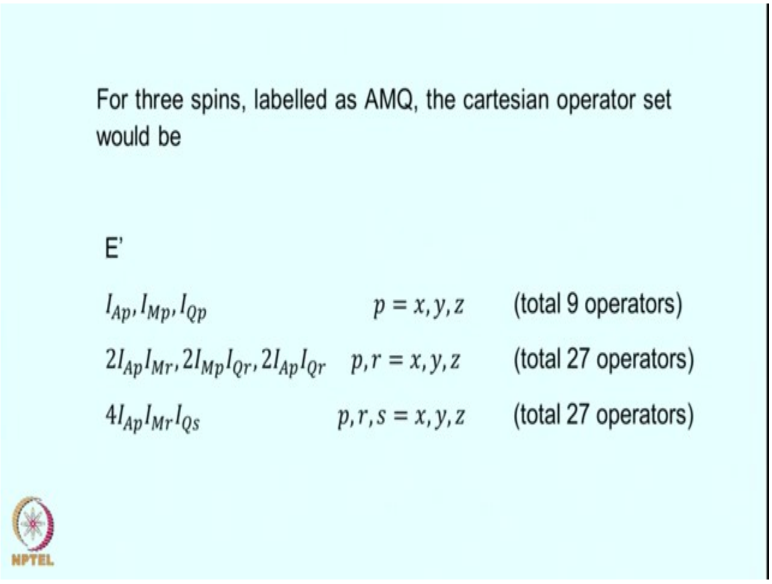

For three spins, labelled as AMQ, the cartesian operator set would be

E'

I_{Ap}, I_{Mp}, I_{Qp} $\quad p = x,y,z$ $\quad$ (total 9 operators)

$2I_{Ap}I_{Mr}, 2I_{Mp}I_{Qr}, 2I_{Ap}I_{Qr}$ $\quad p,r = x,y,z$ $\quad$ (total 27 operators)

$4I_{Ap}I_{Mr}I_{Qs}$ $\quad p,r,s = x,y,z$ $\quad$ (total 27 operators)

So likewise, if you go for 3 spins, how many operators you will have? Notice the previous case we had a total of 16, 4 to the power 2. Now, here how many we should have? If you have three spins, I should have 4 to the power 3, so that means 64 operators. So, here it is the unit matrix once more and then I will have here I_{Ap}, I_{Mp}, I_{Qp} where *p* goes from *x, y, z*. So, there will be total of 9 operators. *A, M* and *Q* are the three spin symbols and *p* goes from *x, y, z*. This represents the Cartesian index.

So, then I will have two spin products. So, 2 $I_{Ap} I_{Mr}$, 2 $I_{Mp} I_{Qr}$ and then $2I_{Ap} I_{Qr}$. And here notice I am varying *A, M, P* and *r* both. So, there are three spins, *A, M, Q*. So, I will have product *A* to *M*, *M* to *Q*, *A* to *Q*. These three products will be there. And for each case I will have the *p* and *r* varying as *x, y, z*. So, there will be total how many? Total of 27 operators. So, this is there are 3 here, *p* takes three values, *r* takes three values.

So, therefore, 3 into 3 into 3, so we will have total of 27 operators. And then we will have the three spin products because all the 3 spins combinations can be present. So, you have three spin products, so here again we have a normalization factor 4. Now, the products of all the three spin operators here corresponding to each of the three spins. So *A, M, Q* and then I will have the here indices *p, r, s*; all the three *p, r, s* can go from *x, y, z*.

So, therefore this is 3 to the power 3 and I will have again 27 operators here. So, total of 64 operators I get for the three spin system. So, likewise I will get many more as I go to larger and larger spin systems. However, by and large we generally do not come across operators which are more than 3 or 4.

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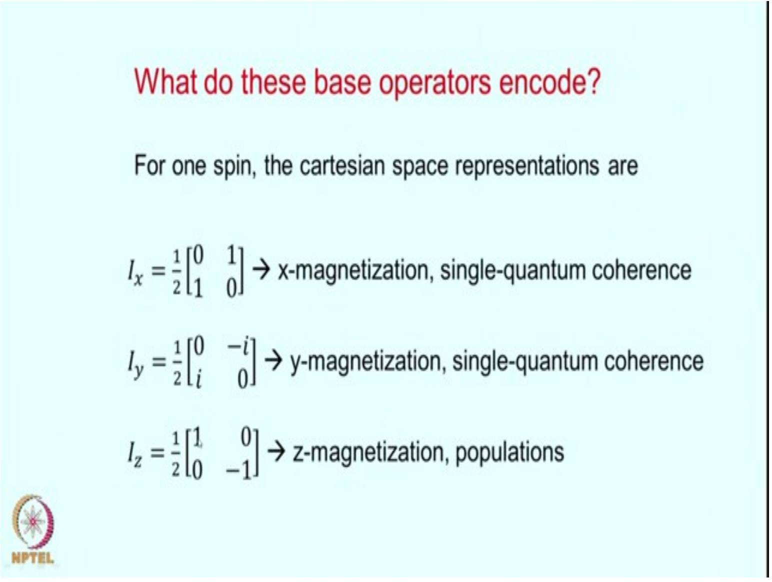

What do these base operators encode?

For one spin, the cartesian space representations are

$I_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ → x-magnetization, single-quantum coherence

$I_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$ → y-magnetization, single-quantum coherence

$I_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ → z-magnetization, populations

Now, let us see what do these operators encode. Okay, we created the various basis operators and we said they represent the density operator and we have seen the density operator contains various kinds of populations, single-quantum coherences, double-quantum coherences, zero-quantum, multiple quantum, various kinds of coherences are present. Now, what do these basis operators represent? Which base operators, this is basis operators, okay.

Which basis operator represents what sort of information, what kind of information does it contain? So, now for one spin, the Cartesian representations in the turn of matrices are as you have seen here $I = 1/¿$. So, there are two states, alpha beta, alpha beta, so therefore this is an off-diagonal element in the if you want to take this matrix.

And if you put this in the density operator, this off-diagonal element will imply a single quantum coherence and that means it is x-magnetization of a particular spin. This is one spin, so therefore in our case of one spin it is the x-magnetization of that spin. Now,

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

This is once again a single quantum coherence because this is off-diagonal element here, states α, $\alpha\beta$, α and β, α and β. So, this is the transition from α to β.

Therefore, single quantum coherence here but this is a y-magnetization because you have imaginary quantity here. The I_z here is the diagonal elements are non-zero, off-diagonal elements are zero. Therefore, this represents the populations and the populations will indicate to you the z-magnetization.

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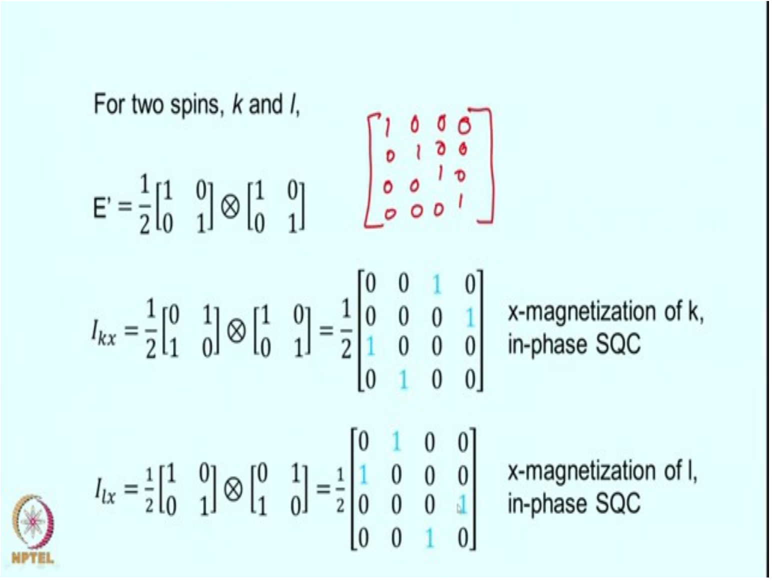

For two spins, *k* and *l*,

$$E' = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$I_{kx} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

x-magnetization of k, in-phase SQC

$$I_{lx} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

x-magnetization of l, in-phase SQC

Okay, now when we go to two-spins, we calculate the matrix representations of the two spin operators in the following manner. We follow the same trick as we did for the pulses. You notice here, I have here the unit operator as *E'* and *E'* is calculated simply as this is the unit matrix here and this is again an unit matrix. You take a direct product. Because for two spins *k* and l, it will be a 4 by 4 matrix and what does this represent?

So, I take a direct product here 1 0 0 1 into 1 0 0 1, so I will get here, is not written here but this will be only diagonal elements will be present, we can write that explicitly. We can write here.

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

If we take *kx*, now in a two-spin system, I am trying to represent the x-magnetization of the k spin alone. So, therefore my operator for *k* spin is 0, 1, 1, 0 x-magnetization. Then I take a direct product with a unit matrix here.

So, that is how I get a 4 by 4 matrix. So, if I take this direct product here, 0 into this matrix give me this 0 matrix here. And 1 into this matrix give me the same matrix, 1, 0, 0, 1 and similarly here this 0 into this 1 into this matrix give me 1, 0, 0, 1 and 0 into this gives me 0, 0, 0, 0. So, therefore now what do I get here?

Now, this is the, if this way the density operator, you see what this represents. This represents the 1, 3 coherence. We will show the explicitly energy level diagram in a slide. This is the 1, 3 coherence, this is the 2, 4 coherence and these are the other corresponding elements on the other side.

Okay, so therefore this represents x-magnetization, take it as the case spin. And these are in-phase single quantum coherences, in-phase because these two coherences have the same sign. If I do I_{lx}, now this has to be, this is another spin. So, how do I get this? To get this, I will have to simply reverse this order. Unit matrix I put it here, and the x operator I put it here. So, therefore unit matrix comes 1, 0, 0, 1 and 0, 1, 1, 0.

If I now take the direct product of this, you see I get these elements which are non-zero. In this case we have these elements non-zero, here I will get these elements non-zero and all other elements will be zero. So, this will be now 1 2, 2 1, 1 2 and 3 4. Again, two coherences, this obviously belong to the different spin. And that we will see in the next slide here.

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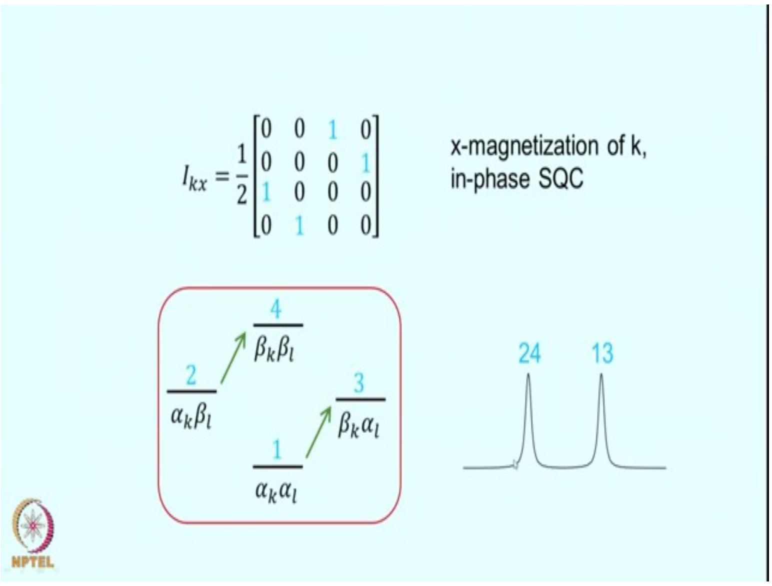

$$I_{kx} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

x-magnetization of k,
in-phase SQC

So, if I take *kx*, I put the same matrix here and you see this is the 1, 3 coherence and these are the energy levels of the two spins, 1, 2, 3, 4, this is 1 3 transition. So, 1 3 transition is this, 1 3 coherence is this and here it is the *k* spin which is flipping. *l* spin is the same, $\alpha_l$and it is the *k* spin which is going from α to the β. And similarly here in the 2 4 transition it is the k spin which is going from α to the β. l spin remains the same.

Therefore, these two are positive, therefore this represent *k* spin coherences and therefore that represent a *k* spin magnetization *x* spin. Now, if I were to draw this in terms of the coherence as NMR spectrum, because the coherence will appear as magnetization which is observable in NMR spectrum. So therefore, these two transitions will be represented as 1, 3, 2, 4 and both have the same sign because these coherences have the same sign.

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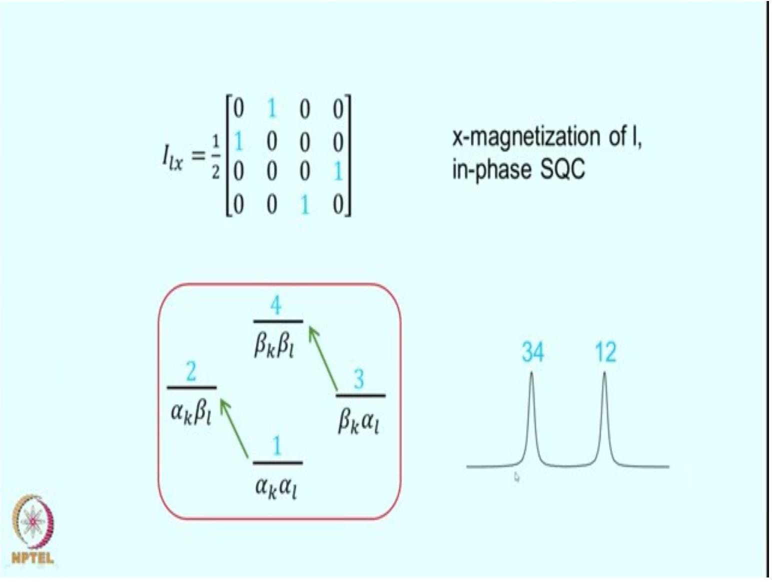

$$I_{lx} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

x-magnetization of l,
in-phase SQC

Now, if I take the other one, I_{lx}, these elements are non-zero. Now, what are these? This is 1 2; 1 2 is this and 3 4 is this. Now, here it is the l spin which is flipping. The k spin is constant. That is why these are the l spin coherences. So, once again therefore this implies *x*-magnetization of the *l* spin which is in-phase single quantum coherence. What it means in-phase? They have the same sign. Therefore, we call them as in-phase and these two transitions are in the NMR spectrum will appear in this manner, 1 2, and 3 4.

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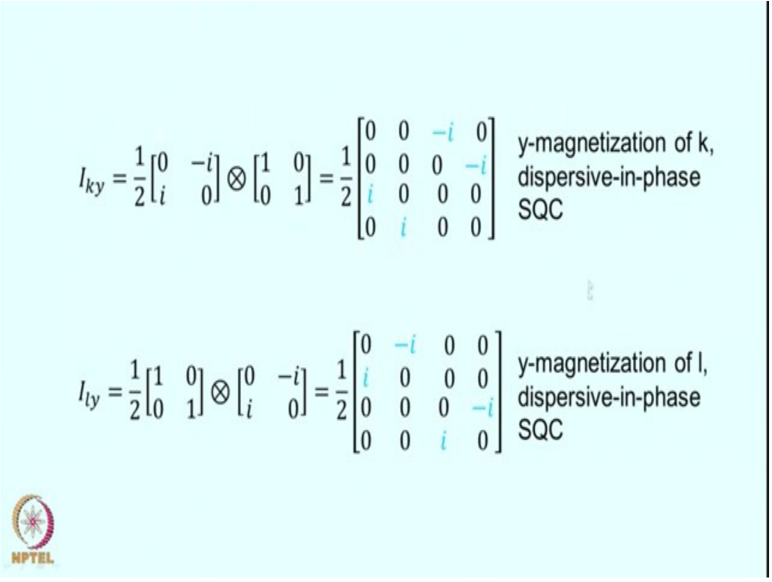

$$I_{ky} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}$$

y-magnetization of k,
dispersive-in-phase
SQC

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

y-magnetization of l,
dispersive-in-phase
SQC

Now, I_{ky}, I do the same thing, I have this *ky* operator here and the unit matrix here. And therefore I get here, the *y* may get the same elements except that I get here *-i*, *-i*, *i, i,* and similarly for l, I get here *-i*, *i*, here and *-i*, *i* here. So, this represents the *l* spin magnetization. This represents k magnetization. But what about this i? i means it is imaginary.

So, this is 90 degrees out of phase and that we call as the dispersive line shape. This represent a dispersive line shape. Because if I were to measure the x-magnetization as in-phase then the y-magnetization will be the 90 degree out of phase. The 90 degree out of phase is the dispersive line shape. So, and how does that look?

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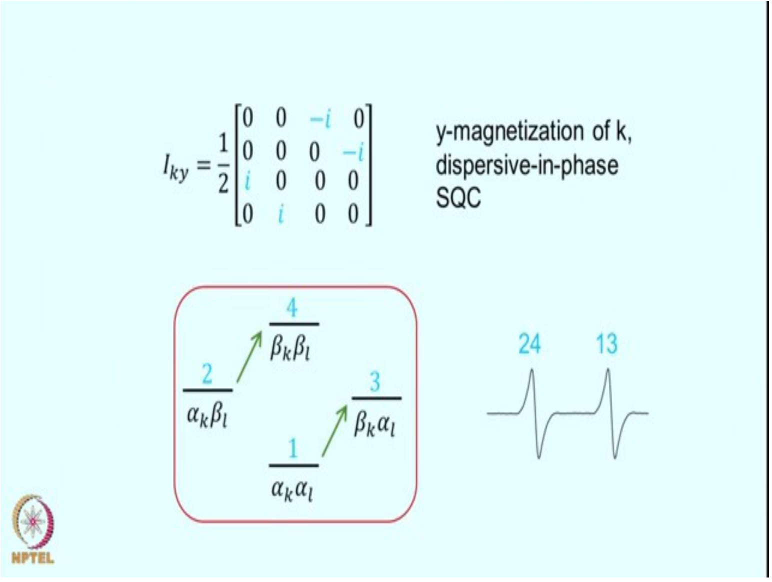

$$I_{ky} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}$$

y-magnetization of k,
dispersive-in-phase
SQC

So, here we have here, the I_{ky} these are the two transitions here, the same here, 1, 3, 2, 4 but in NMR spectrum we look at the 90 degrees phase shift. This will be dispersive line shape but these are in-phase. In-phase meaning this goes up and down here. And this also goes up and down in this manner. So, therefore these two transitions are in-phase. These are dispersive in-phase transitions.

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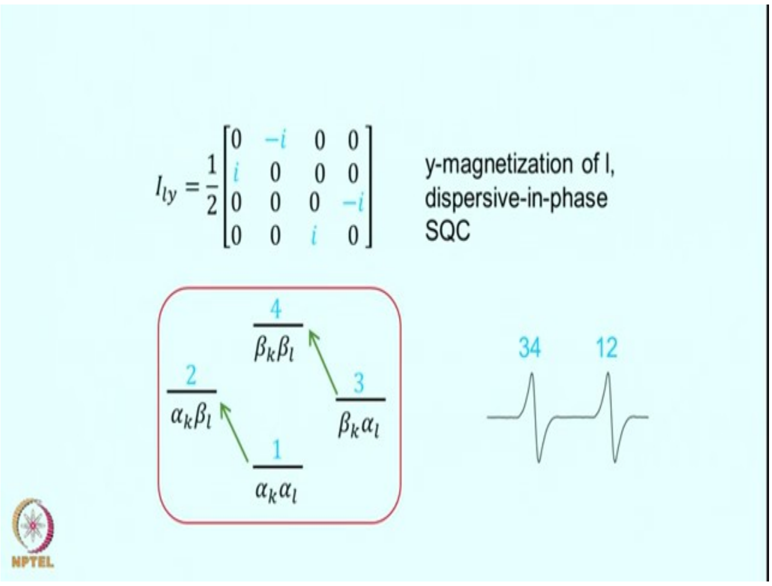

$$I_{ly} = \frac{1}{2}\begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}$$

y-magnetization of I,
dispersive-in-phase
SQC

Similarly, for l_y we have 1, 2 and 3, 4 and these are once again in-phase transitions and 1, 2, 3, 4 and that is because I have the same sign for this and this. So, this is clear about the two-spin system, how the individual elements of the base operators are to be interpreted. What is the information content in the different elements of the base operators?

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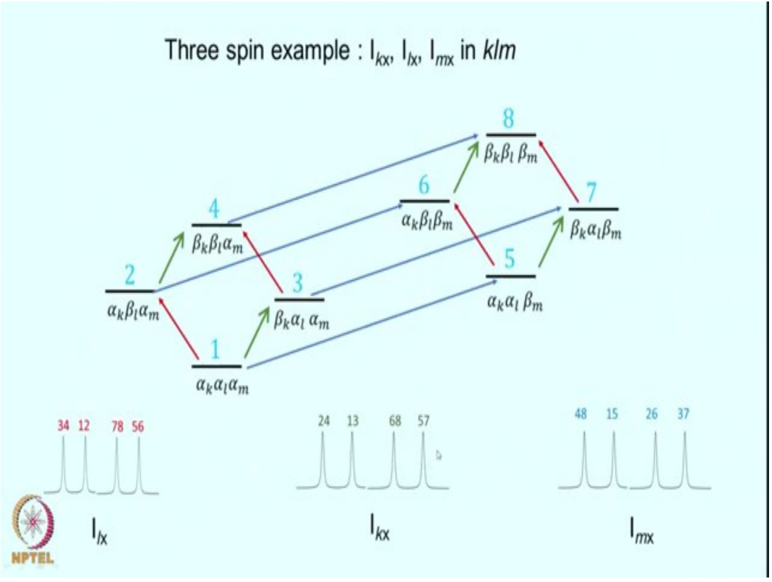

Three spin example : I_{kx}, I_{lx}, I_{mx} in *klm*

What do they represent? Now, extended to three-spin, the three-spin will make a beginning here because we will continue later with more details. Continue take us three spin-system which is *k, l, m*, these are three spins. So now, I said there earlier that there will be total of 64 operators, we will illustrate only some of those. Here we take I_{kx}, I_{lx}, I_{mx} which are supposed to represent the *x*-magnetization of *k, l* and *m*.

Now, each one of them will have how many transitions? Suppose, there is a coupling between k and l and l and m and k and m, all the three spins are coupled. Then I will have four transitions for each one of those because each one of them leads to a splitting into two, therefore I will have four transitions.

Now, the energy level diagram for the three-spin system, there will be 8 energy levels. As I mentioned to you earlier with the case of two-spins here I will have α_k,α_l, I_{lm}, α_m. Essentially 1, 2 spin-system another 2 spin system except now you add the third spin as α here and the β here.

So, you generate a 8-level, energy level diagram. So, now each one of them now there is the duplication happens. These states belong to 1, these transitions belong to 1spin. All the red ones belong to 1spin and these green ones belong to 1spin as before and now we have the third spin transitions happening from here to here, here to here, here to here and here to here. And all of those are represented in this manner. Since all of them are in-phase, I must write them as absorptive line shape for each one of those individual transitions are indicated here for the l-magnetization, the k-magnetization and the m-magnetization.

So, therefore this is the simplest. Here, we are seeing the individual transitions of the k, and l spins. And these we call them as in-phase magnetizations because they are in-phase with respect to the orientation of the other two spins. So, regardless of what the other two spins are, other two spin states are, I have the same positive absorption signal. Therefore, we call them as in-phase. The other things we will see in the next class. We stop here.