

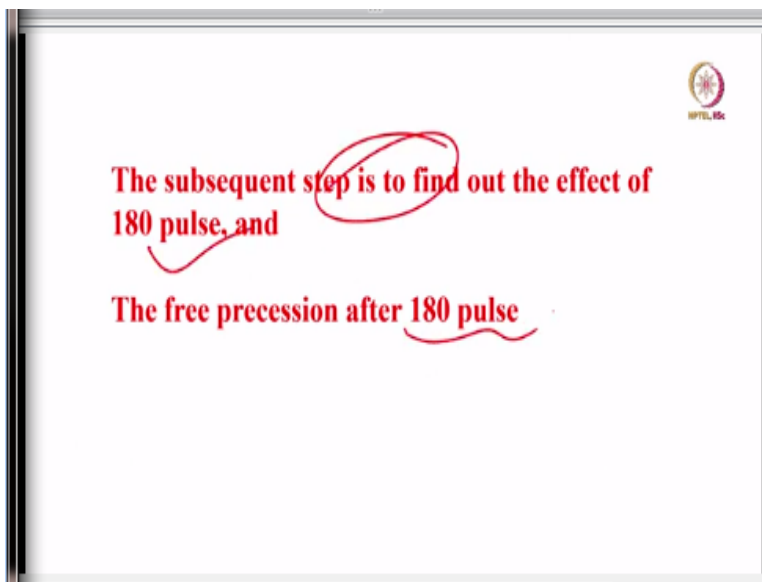
Advanced NMR Techniques in Solution and Solid-State
Prof. N. Suryaprakash
Professor and Chairman (Retd)
NMR Research Centre
Indian Institute of Science-Bengaluru

Module-43
Product Operators for Two J Coupled Spins
Lecture-43

Welcome all of you, now we have been discussing quite a bit about product operators since last 2 or 3 classes. In the last class we discussed a lot about rotations and rotation of particular operator about a particular axis and what is the type of solution we are going to get? The general solution I said is the cosine of the old operator plus sine of the new operator. With the three diagrams which was given to show about rotation of each of the operators at about X axis, Y axis and Z axis we could get a solution very quickly without going to explicit calculation of the density operator ρ of t which is the e to the power $-iH$ of t ρ of 0 into e to the power of iH of t . We do not have to go through all this rigorous maths and use trigonometric identities, everything is clearly available. We worked out for the one pulse sequence; wherein we applied 90 degree X-pulse and started collecting the signal; and we saw that by product operator analysis applying 90 pulse for the Z magnetization which is in thermal equilibrium the magnetization was brought to -Y axis. And then with the time t , when we saw the free precession during the time delay, during acquisition time, we found it generates cosine and sine components. That means the spin vector start fanning out in the XY plane and exactly when $\alpha = 90$ degree it comes to -Y axis. At $t = 0$ immediately after the pulse, the magnetization is -IY that is on -Y axis and then with time it creates MX and MY components; that is cosine and sine components.

And then we wanted to extend this further for spin echo analysis, spin echo is nothing but 90 pulse τ , 180 pulse τ . So, with 90 pulse τ what happens? After 90 pulse and free precession we already understood. Next, the effect is we have to see what happens if you apply 180 pulse, how we are going to refocus the offsets, we are not worried about couplings here as we are taking uncoupled spins; in which case we do not have to worry about coupling at all. If there is a refocusing it has to be offset or chemical shift. So, now we will continue further from that with 180 pulse.

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Now we wanted to find out in the second step effect of 180 pulse, and free precession after 180 pulse.

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$-\cos(\Omega t)I_Y + \sin(\Omega t)I_X$

Pulse along X does not affect I_X . Hence only I_Y term is to be evaluated

$-\cos(\Omega t)I_Y$

Hamiltonian for π rotation about X

$\Omega_1 t_\pi = \pi$ (Pulse Width)

$\cos\pi = -1$ $\sin\pi = 0$

πI_X

$-\cos(\Omega t)[-1.I_Y + 0.I_Z]$

$= \cos(\Omega t)I_Y$

The effect of π pulse is to simply invert the term in I_Y

(a)

So, this is the solution we have got up to time t after the 90 pulse and first τ during free precession. Pulse along X does not affect X, so we do not have to worry about I_X , hence we have to consider only I_Y term, I told you I_X pulse about X, I_Z pulse about Z, all those have no effect at all, Z pulse along Z, X pulse along X, Y pulse along Y, has no effect. So, now we are considering only $-\cosine\ \omega\ of\ t$ and how it evolves with the 180 pulse. Of course, we have to

see the figure, go back to the drawing, you have to see what is, now is the rotation of IY about IX.

So, IY term is there, you are rotating about X axis because you are applying a 180 pulse along X axis. So, this is the term you are going to get, if you see the figure $-\cos(\Omega t)$ is there and IY is rotated and we are going to get $\cos(\Omega t)$ into IY + $\sin(\Omega t)$ into IZ. And this is the Hamiltonian for pi rotation, 180 pulse about X axis. Same Ωt but now t is 180 degree, so it is $\Omega t = \pi$. So, use this diagram $\Omega t = \pi$; pulse width, $\cos(\pi) = -1$ $\sin(\pi) = 0$, substitute it there. Then in arrow rotation we can say the application of pi pulse along Y axis gives you $-\cos(\Omega t)$ of t , this is -1 and this is $\sin(\pi) = 0$, this term will go and we are going to get only -1 into IY, -1 into IY. This will finally minus into minus, it will turn out to be $\cos(\Omega t)$ into IY. This is what we are going to get. This is the application of 180 pulse after the first delay, ok. What does it do? The pi pulse has simply inverted the IY. From -IY it became +IY; that is all.

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The effect of π pulse ;

The term remained unaffected

$\cos(\Omega t)I_Y + \sin(\Omega t)I_X$

Next step is to calculate the free precession after the 180 pulse, the effect of delay on the above two terms

First term $\cos(\Omega t)I_Y$

Rotation of I_Y about Z

$= \cos(\Omega t)I_Y - \sin(\Omega t)I_X$

$I_Y \xrightarrow{\Omega t I_Z} \cos(\Omega t)I_Y - \sin(\Omega t)I_X$

$\cos(\Omega t)I_Y \xrightarrow{\Omega t I_Z} \cos(\Omega t)[\cos(\Omega t)I_Y - \sin(\Omega t)I_X]$

(c)

Diagram (c) shows a 3D coordinate system with axes X, Y, and Z. A vector is shown rotating around the Z-axis. The rotation is indicated by a curved arrow around the Z-axis, with labels X, Y, and -Y. The text "ROTATION ABOUT Z" is written below the diagram.

Now the effect of pi pulse, we have seen this term remained unaffected, we have to now consider that. Next step is to calculate the free precession after the 180 pulse; this is what we got with the 180 pulse. Now this term which remain unaffected we consider because you cannot ignore that. Now the total precession during free precession, ie. during second time we have to consider the free precession for both the terms you have to take.

First term will take cosine of omega t into IY, again that means rotation of IY. IY is rotated about Z axis rotation of IY about Z axis you write cosine omega t into IY - sine omega t into IX by using this formula. Cosine of the original operator IY and sine omega t of IX. IX when it is rotated about Z axis which goes to -X, so it will become minus of IX.

So, this is what we are going to get, IY when it is rotated during free precession about omega t IZ about Z axis, omega t is the offset, t is the time; you are going to get cos omega of t into IY - sine omega t into IX; this is the first term. All we did is rotate to IY about Z axis. So, this is what cosine omega t into IY, now I will take cosine omega t, multiplication still there, we cannot ignore that.

Now you only saw rotation of IY, now it turns out to be, this is the solution of rotation of IY with cosine of omega t you are going to get cosine omega t into IY - sine omega t into I X this is what the solution you are going to get. So, this is what for the first term.

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second term $\sin(\Omega t)I_X$ Rotation of I_X about Z

$$I_X \xrightarrow{\Omega t I_Z} \cos(\Omega t)I_X + \sin(\Omega t)I_Y$$

$\sin(\Omega t)I_X \xrightarrow{\Omega t I_Z} \sin(\Omega t)[\cos(\Omega t)I_X + \sin(\Omega t)I_Y]$

The first and the second terms together

$$\begin{aligned} & \cos(\Omega t)\cos(\Omega t)I_Y - \cancel{\cos(\Omega t)\sin(\Omega t)I_X} + \cancel{\sin(\Omega t)\cos(\Omega t)I_X} + \sin(\Omega t)\sin(\Omega t)I_Y \\ &= \cos(\Omega t)\cos(\Omega t)I_Y + \sin(\Omega t)\sin(\Omega t)I_Y \\ &= [\cos(\Omega t)]^2 I_Y + [\sin(\Omega t)]^2 I_Y \end{aligned}$$

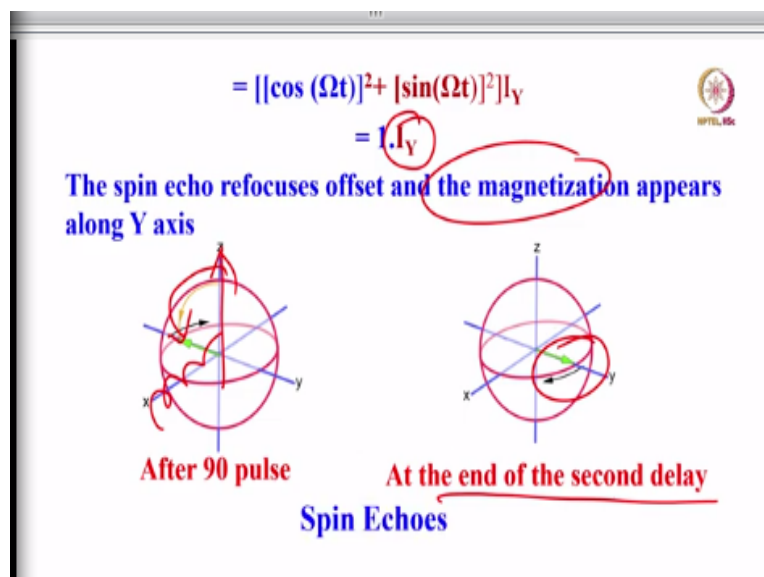
Now let us see second term, second term is sine omega t into IX, what is happening here? You are rotating IX about Z axis, now the rotation is about Z axis during free precession. IX is rotated about Z axis, this is drawing you have to use, this figure. Now you are rotating IX about Z axis it should go to IY; that is a solution. So, IX when you rotate about IZ with omega into t is the

offset. See, now cosine of omega of t into old operator plus sine omega t to new operator into IY, this is the solution for it. So, now sine omega t into IX if you take that product was also there sine omega t which you cannot ignore. Now during free precession this turns out to be sine omega t into cosine of omega t into IX + sine of omega t into IY, this is what you are going to get.

Now we have to bring both these terms together. We have evaluated individually each of these terms, now combine both of them you have to see what is the effect of that. Now bring both the terms together this is the term which you obtained from the first one, this is the term you have obtained in the second one. Sine omega t into cos omega t + sine omega t into sine omega t into IY, this is what the term you are going to get.

But interestingly you can see this term and this term will cancel out, plus and minus. So, what you are going to left with is, cosine omega t into cosine omega t into IY, sine omega t into sine omega t into IY, so what is this? Cosine omega t into cosine omega t is cosine square omega t, this is sine square omega t.

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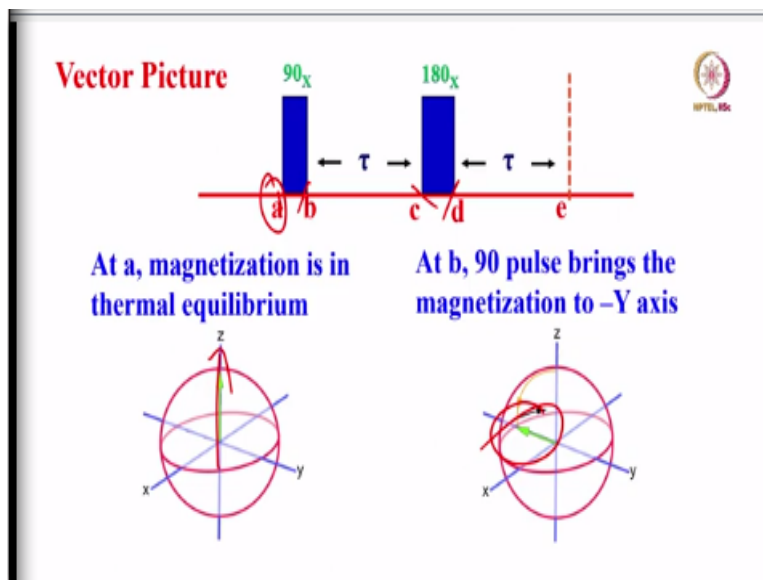


Now take out IY as a common factor, what are you going to get? cosine omega square + sine omega square, what is cos square theta + sine square theta, it is 1. So, this term turns out to be 1 and solution is going to be 1 into IY, that is IY, so what happened now? See, what happened is

when you applied 180 pulse and allow to evolve for equal amount of time another time period t and in a workout during free precession what happened? The magnetization remained as IY , what happened? The spin echo refocuses the offset and the magnetization appears along Y axis, the chemical shift term will go, it is not there, offset term is not there, it is removed, only the magnetization which is along $-Y$ axis you brought to Y axis. This is called refocusing of the offset or chemical shift, please remember this. Now we are considering the homonuclear case, now in the spin echo sequence that is 90° tau, 180° tau sequence, it refocuses the offsets or chemical shifts and make sure that the magnetization which is along $-Y$ will go to $+Y$ axis, that is the spin echo sequence.

Diagrammatically you can understand like this, look at it what is happening? The magnetization which is along Z axis is brought to $-Y$ axis by applying an RF pulse along X axis, that is what we did. And then at the end of the second delay this is what happens, the magnetization has come back to $+Y$ axis. This is what is called in an echo, how it works out? You can see vectorially like this, there is a vectorial picture.

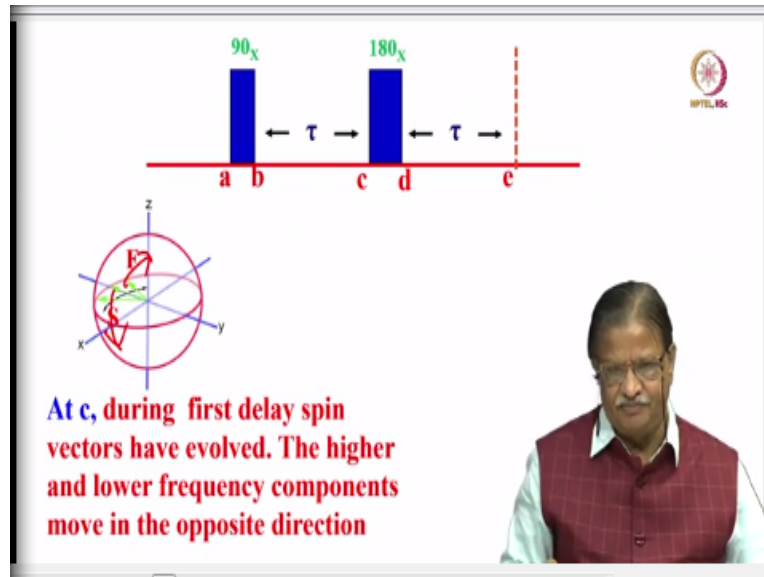
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We have worked out by product operators for different sequences. Vectorially also we can understand to get a picture. But we cannot do this for all pulse sequences, especially for the complicated sequence easily; it is a very complex thing. But just for this I will show you, we start with different time periods a , b , c , d etcetera, I call these a , b , c , d , I call this as e .

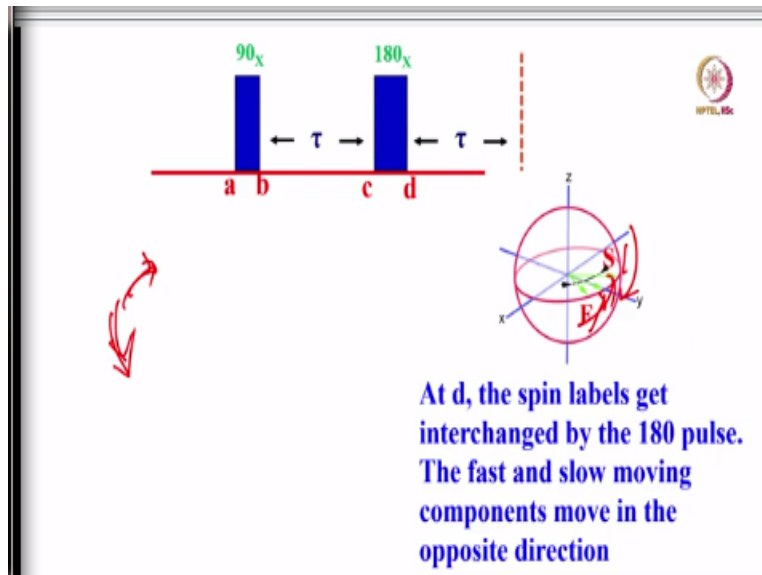
What is the state of magnetization at a? It is in thermal equilibrium along Z axis, at a the situation is the magnetization is along Z axis in thermal equilibrium. At b, what is happening? You are applying a 90 degree pulse; you brought the magnetization to -Y axis; that is the state of magnetization at b.

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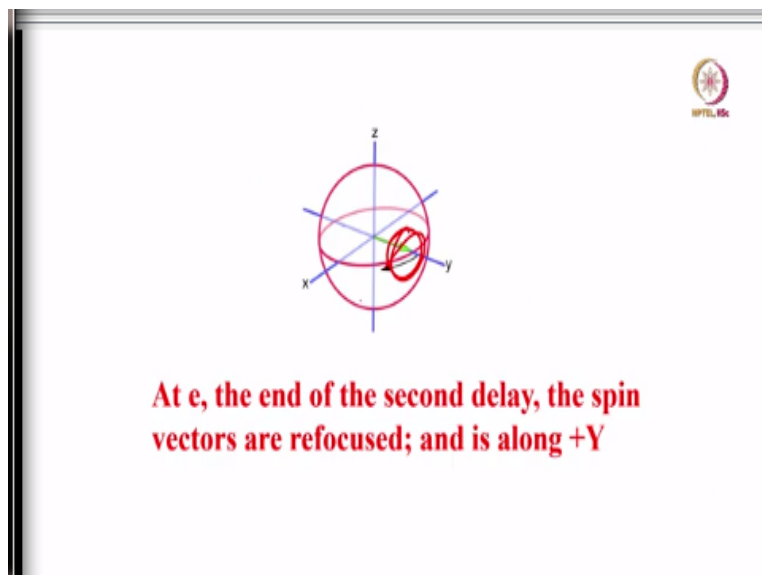
At c, what is happening? During the time period there is a dephasing, we said you know magnetization starts fanning out; it creates cosine and sine components; oscillating components will be produced as a function of time, as time evolves. So, now magnetization vectors start moving on either side. First this one which move this side, other which moves other side, we call them as fast moving and slow moving components; one is at higher frequency other is at lower frequency; they start moving in the opposite directions. This we call it as fast moving and slow moving components.

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Now after a certain time, now we are going to apply 180 pulse. With the 180 pulse what you are going to do? You simply invert the magnetization from $+\pi$ to $-\pi$, the entire vectors which were here it is like turning, turning a pancake you completely turn it on other side, from $-Y$ axis to $+Y$ axis. Then what is happening is the fast moving and slow moving components interchange the directions of motion, they start moving in the opposite direction now. Fast moving earlier it was going like this, slow was moving like this, now fast starts moving like this, slow starts moving in the opposite direction. Then what is going to happen?

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After the exactly same amount of time they will come back, refocus along Y axis. So, the vectors get refocused under +Y. Started with -Y for a given time they start dephasing and created cosine and sine components; and apply 180 pulse, invert the magnetization from -Y axis to +Y axis. Fast and slow moving components start moving the opposite direction and after exactly same amount of delay, they refocus along Y axis.

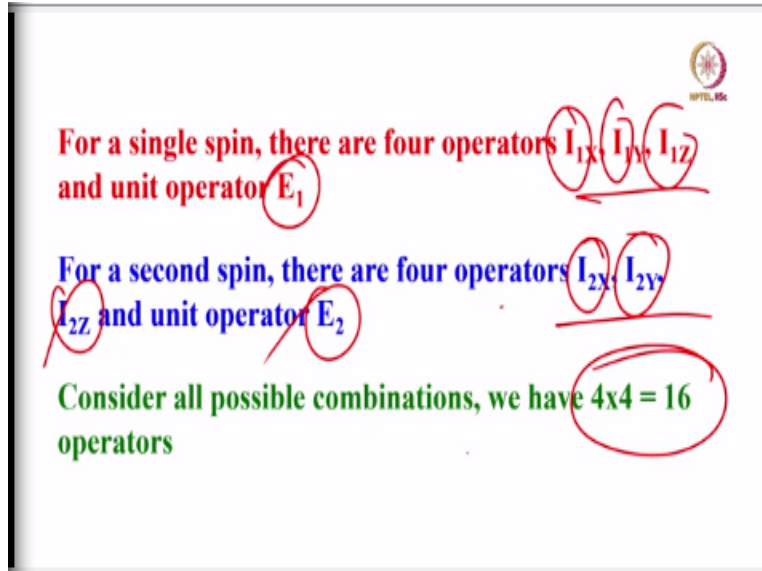
This way, this is the diagrammatically how it works can be seen like this animation of a spin echo; it is like this; you see like this. Now magnetization is along Z axis 90 pulse brought like this and then rotated by 180 pulse and they can go back and assemble, fantastic, this is what is called spin echo sequence.

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Now we got some hang of how to analyze the pulse sequence using product operators. But remember till now we have taken a single spin or more spins without any J coupling; there is no interaction between the spins. You are only concentrating on evolution the magnetization under free precession or under offset. Now consider the case of a coupled spin system, take example of two couple spin system. Again weakly coupled I and X spin or we call it 1 and 2, does not matter, this is a weakly coupled case.

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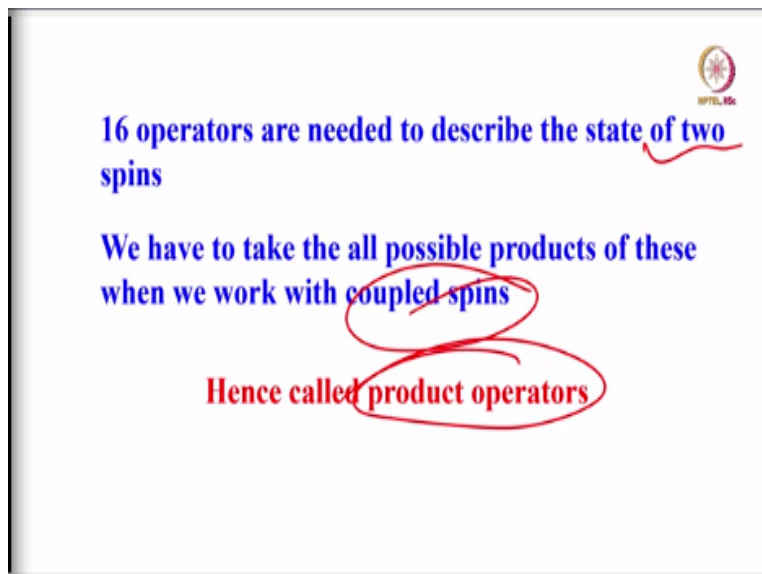
For a single spin, there are four operators I_{1x}, I_{1y}, I_{1z} and unit operator E_1

For a second spin, there are four operators I_{2x}, I_{2y}, I_{2z} and unit operator E_2

Consider all possible combinations, we have $4 \times 4 = 16$ operators

Now for a single spin, there are 4 operators. Of course, you know I_{1x} , I_{1y} and I_{1z} , there is also called the unity operator E_1 . Of course practically it does nothing, it only helps in mathematical operation. For a second spin, there are 4 operators, again I_{2x} , I_{2y} and I_{2z} and a unit operator E_2 . So, for a second spin, there are 4 operators like this, now when 2 spins are interacting, we consider all possible combinations. We have 4 operator for spin 1, 4 for spin 2, 4 into 4; we have 16 operators. There are 16 operators.

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16 operators are needed to describe the state of two spins

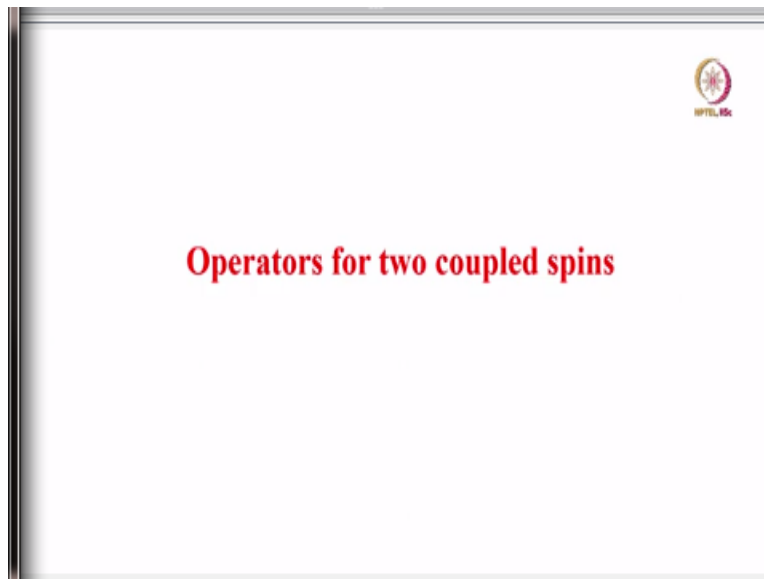
We have to take the all possible products of these when we work with coupled spins

Hence called product operators

The 16 operators are needed to describe the state of 2 spins completely. So, we have to take all the possible products of these when we work with coupled spins. All 16 operators we have to

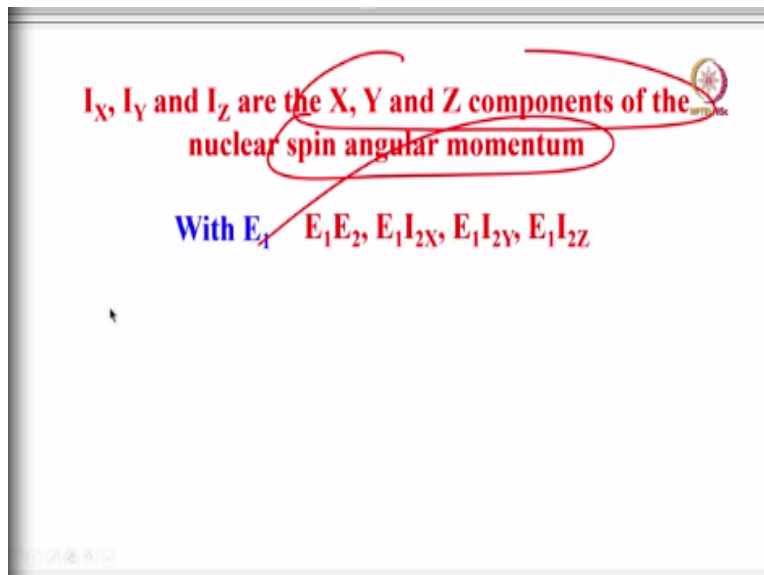
consider. That is the reason since we get product of all these things, these are called product operators, why product operator name comes? Because when you consider multiple spins, for example 2 spins here, each spin has 4 operators we have to take the combination of all the 4 with all remaining for the other spin, so we will have 16 operators; that is why they are called product operators.

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Now what are the operators we require for 2 coupled spins?

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One thing is I_X , I_Y and I_Z are the X, Y and Z components of the nuclear spin angular momentum, that we know I_X , I_Y and I_Z . And with E_1 , considering E_1 also, E_1 is a unity operator.

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I_X, I_Y and I_Z are the X, Y and Z components of the nuclear spin angular momentum

With E_1 $E_1 E_2, E_1 I_{2X}, E_1 I_{2Y}, E_1 I_{2Z}$

With I_{1X} $I_{1X} E_2, 2I_{1X} I_{2X}, 2I_{1X} I_{2Y}, 2I_{1X} I_{2Z}$

With I_{1Y} $I_{1Y} E_2, 2I_{1Y} I_{2X}, 2I_{1Y} I_{2Y}, 2I_{1Y} I_{2Z}$

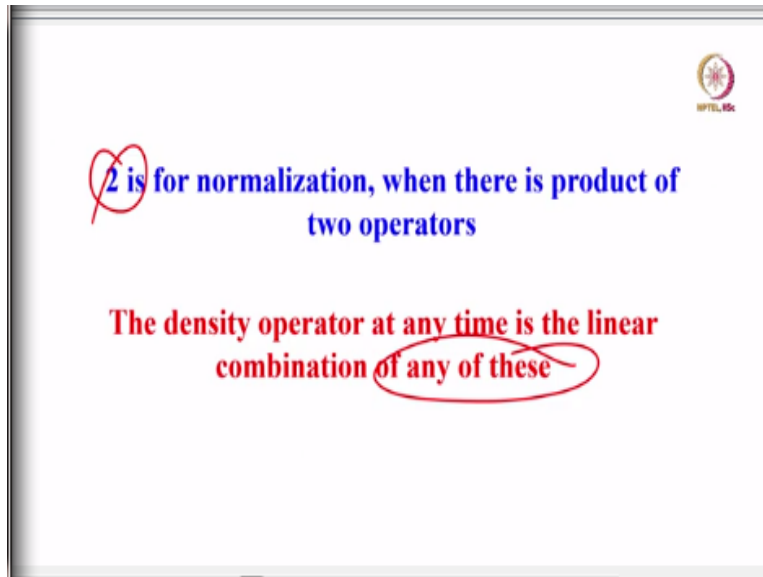
With I_{1Z} $I_{1Z} E_2, 2I_{1Z} I_{2X}, 2I_{1Z} I_{2Y}, 2I_{1Z} I_{2Z}$

The Unit operator E does nothing. Helps in mathematical operation

As I told you it is E_1 is only to simplify the mathematical operation. Unity operator is there for easing the maths. With E_1 now what are the 4 possible product operators E_1 into E_2 for the second spin, E_1 into E_2 , E_1 into E_{2X} , E_{2Y} and E_{2Z} . Because now I am considering for the second spin $E_2 I_{2X}$, I_{2Y} , I_{2Z} are the 3 operators angular momentum operators, when it combines with E_1 we get 4 possibilities E_1 into E_2 , E_1 into I_{2X} , E_1 into I_{2Y} , E_1 into I_{2Z} .

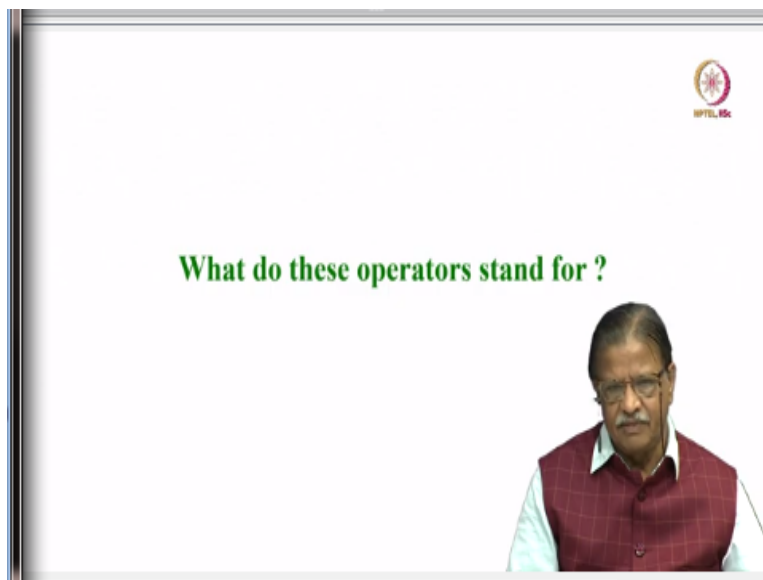
With I_{1X} of the first spin, first X component of the angular moment of the first spin, again 4 combinations $I_{1X} E_2$ etcetera like this, I_{1X} , 2 times I_{1X} , I_{2X} . Now the question here why 2 comes, it is only for normalization, do not worry, that is a number. Similarly, with I_{1Y} we have 4 operators, I_{1Z} we have 4 operators, so 4, 4, 4, 4 there are 16 operators we have generated together for 2 spins. The unit operator E nothing is only helps in mathematical operation.

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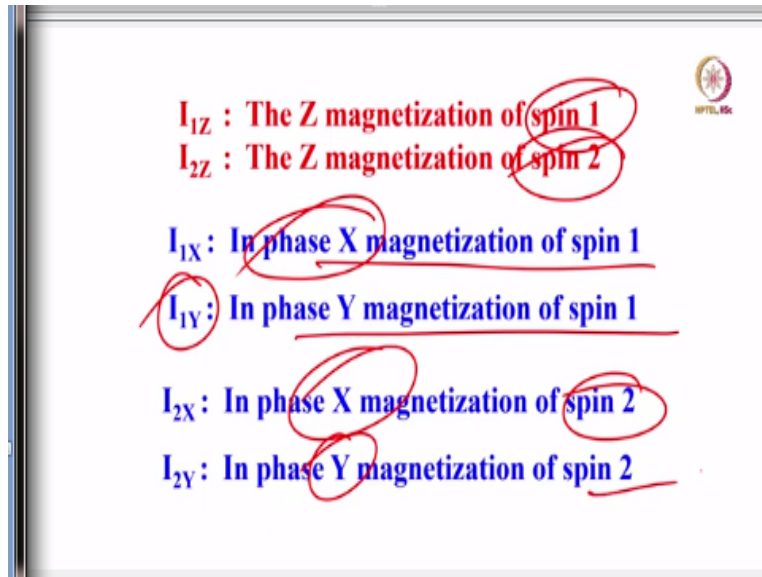
What is the 2? I showed you for normalization when there is product of 2 operators 2 comes, we use it for normalization. So, now if I have to consider the density operator at any time when the 2 spins are interacting including J coupling. It is a linear combination of any of these, all the 16 operators; it is a linear combination of any of these together.

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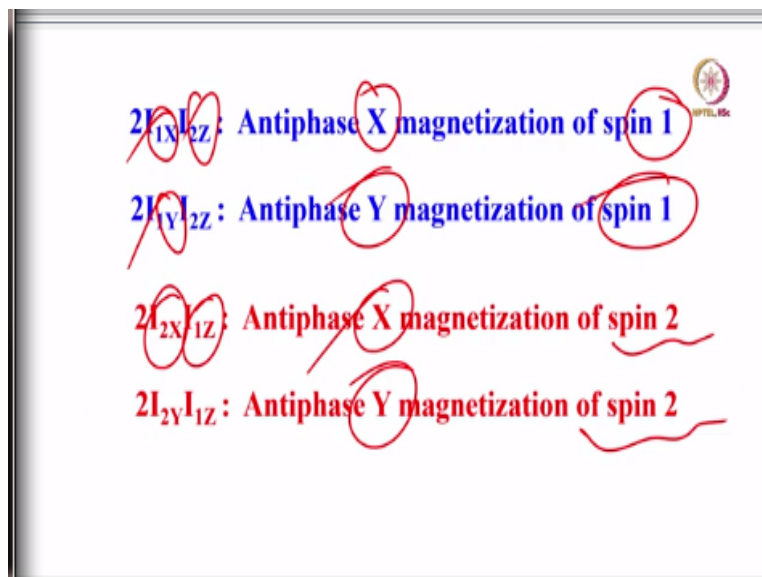
What do these operators stand for, how do you understand these operators?

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See I_{1Z} is a Z magnetization of spin 1, I_{2Z} is called Z magnetization of spin 2, I_{1X} is called in phase X magnetization, please remember I_{1X} is the in phase that is the word I am stressing; an in phase X magnetization of spin 1. Similarly, I_{1Y} is in phase Y magnetization of spin 1, I_{2X} is in phase X magnetization of spin 2 and I_{2Y} is in phase Y magnetization of spin 2.

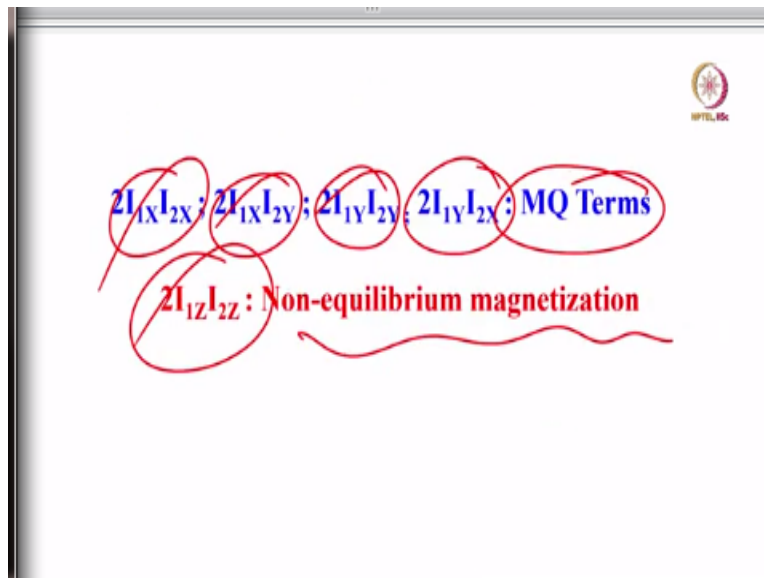
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$2I_{1X}I_{2Z}$, for this product if you consider it is an antiphase X magnetization of spin 1, you look at this spin 1. For spin 2 it is along Z axis here, spin 1 is along X axis, this is called antiphase X magnetization. Same thing along Y axis it is called antiphase Y magnetization of spin 1, you understand. Similarly if I consider $I_{2X}I_{1Z}$ for the second spin also we have antiphase X

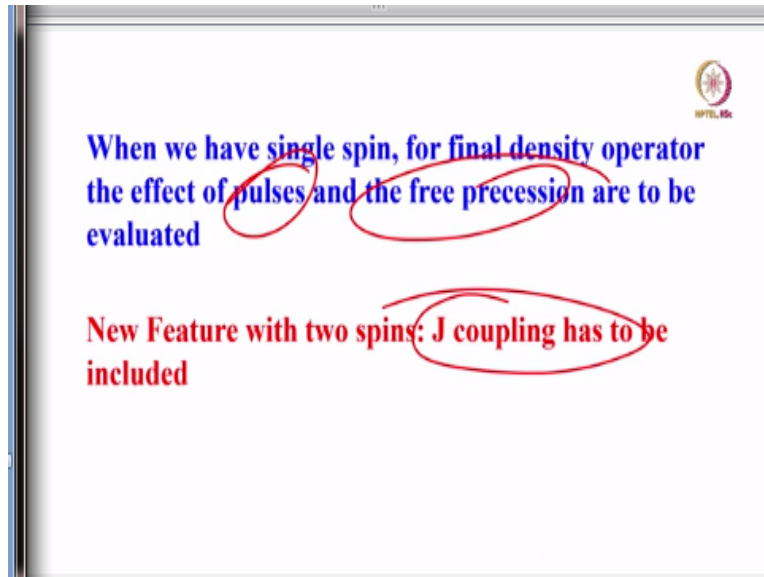
magnetization of spin 2 and antiphase Y magnetization of spin 2, this is what each of these operator mean.

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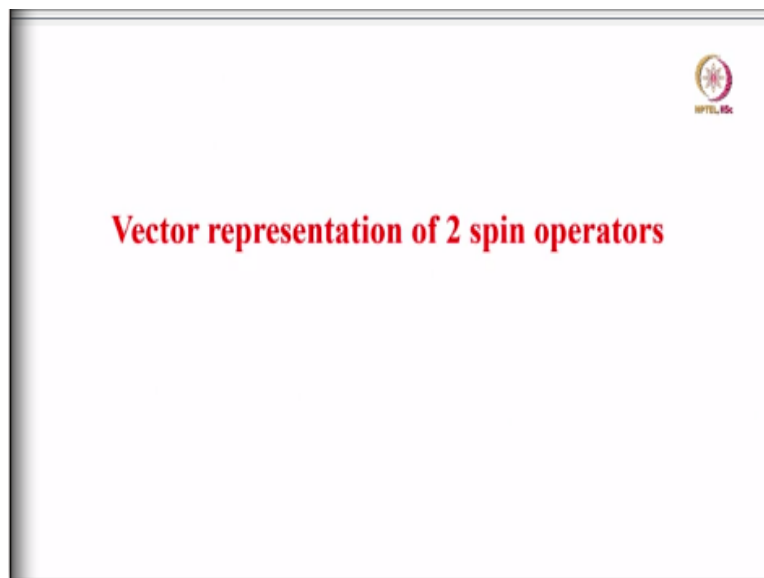
Now there are also combination of other operators like this I_X into $2I_X$, I_{1X} into I_{2Y} , I_{1Y} into I_{2Y} , I_{1Y} into I_{2X} . Here both the X and Y operators of both spins are present in the XY plane; these products are called multiple quantum terms. Since there are 2 spin operators, these are called as double quantum terms. And the product $2I_{1Z}$ and $2I_{2Z}$ is called a non-equilibrium magnetization along Z axis, it is a non-equilibrium magnetization, that is all, you do not have to worry about it. That will not generate any observable magnetization, this what it is.

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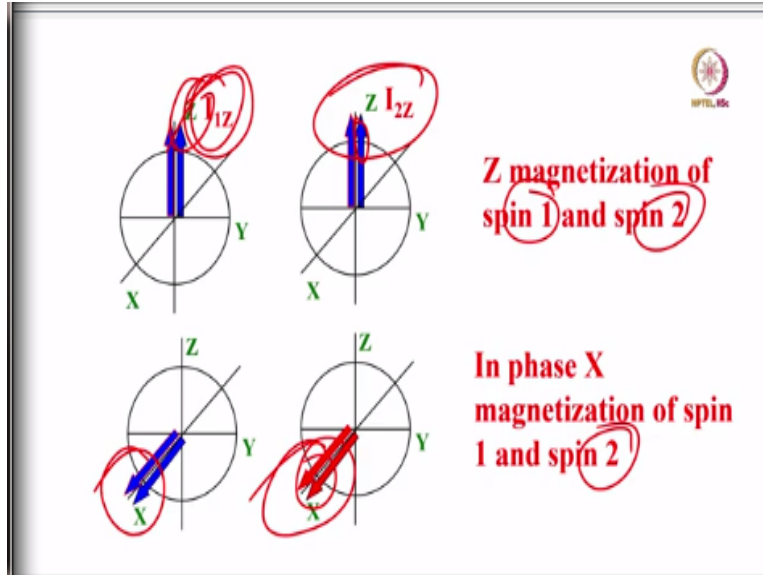
And when we have a single spin, for final density operator we have to consider the effect of pulses and free precession. But when we have 2 spins the new feature is, we need to consider J coupling also, that has to be included.

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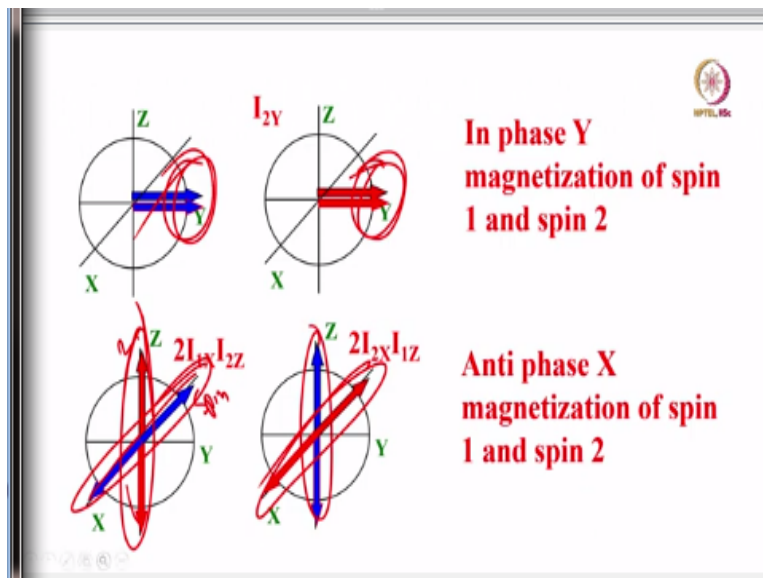
So, now vector representation of all these 2 spin operators can be made, this is what we said; I_{1Z} , I_{2Z} what are the I_{1X} , I_{2X} etcetera. Graphically also we can see how are they. So, we can represent vectorially these 2 spin operators.

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For example if I write like this, this is I_{1Z} , the 2 J split multiplets are along Z axis, it is I_{1Z} , the Z magnetization of spin 1; This is called Z magnetization of spin 2 both along Z axis. Here in phase X magnetization of spin 1, let us say, both along X; this is in phase X magnetization of spin 2. I have given you different colours. Of course this should have been red, I have given red colour for spin two. Of course does not matter the colour code is only to make you understand clearly, this is for spin 2.

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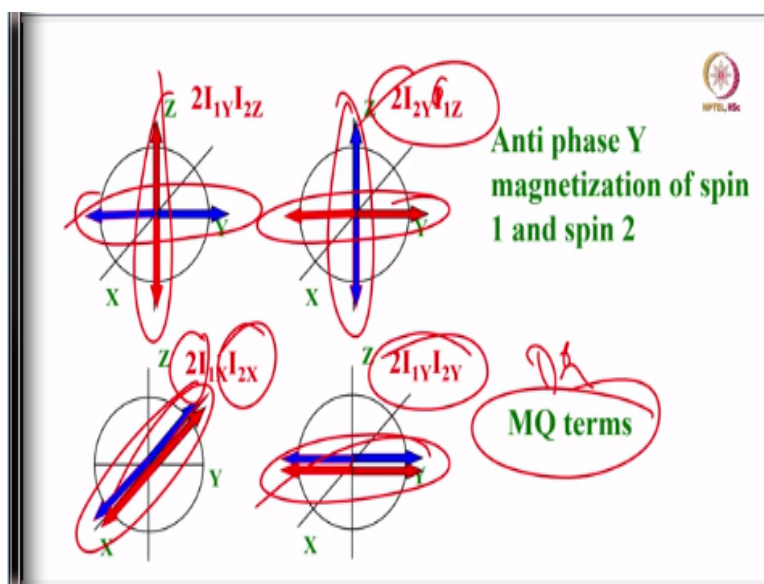


Now this is I_{2Y} , this is I_{1Y} and this is I_{2Y} the in phase Y magnetization of spin 1, this is in phase Y magnetization of spin 2. And this is important; X magnetization and Z magnetization

here $2I_1I_X$ and I_2I_Z , this is for spin 2, this is for spin 1. This is anti phase X magnetization of spin 1, remember spin 1 has X magnetization in the antiphase and this is Z magnetization of spin 2. Similarly for spin 2, X magnetization is antiphase like this and for spin 1, Z magnetization is antiphase along Z axis.

Remember, one thing you should clearly understand these antiphase terms are very, very important, especially for transferring the spin polarization in experiments involving polarization transfer. Please understand, $2I_1I_XI_2I_Z$ means it is antiphase X magnetization, see X components are antiphase along X axis and for spin 2 it is along Z axis. Spin 1 along Z axis, spin 2 along Z axis both are antiphase. For the spin 2, X components are anti phase and for spin 1, Z components is antiphase like this.

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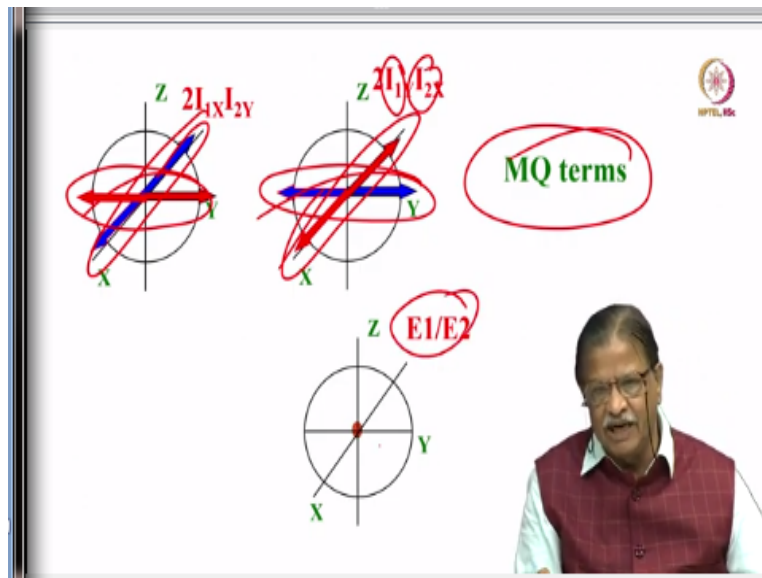


Similarly anti phase Y magnetization of spin 1 and 2. Now spin 1, both the vectors are anti phase along Y, The spin two is anti phase along Z. Similarly I_2I_Y and I_1I_Z it is for second spin, Y magnetization is anti phase, for spin 1 Z magnetization is anti phase. And here $2I_1I_X$ and $2I_2I_X$ both X components of both spin 1 and spin 2 are anti phase.

Please understand, X components of both spin 1 and spin 2 are anti phase, that is $2I_1I_XI_2I_X$. Similarly $2I_1I_YI_2I_Y$ for spin 1 and spin 2, both the Y components are anti phase like this. These

are called multiple quantum terms or in our case it is a DQ term, double quantum term, because both these spins are either along Y axis or X axis anti phase with each other.

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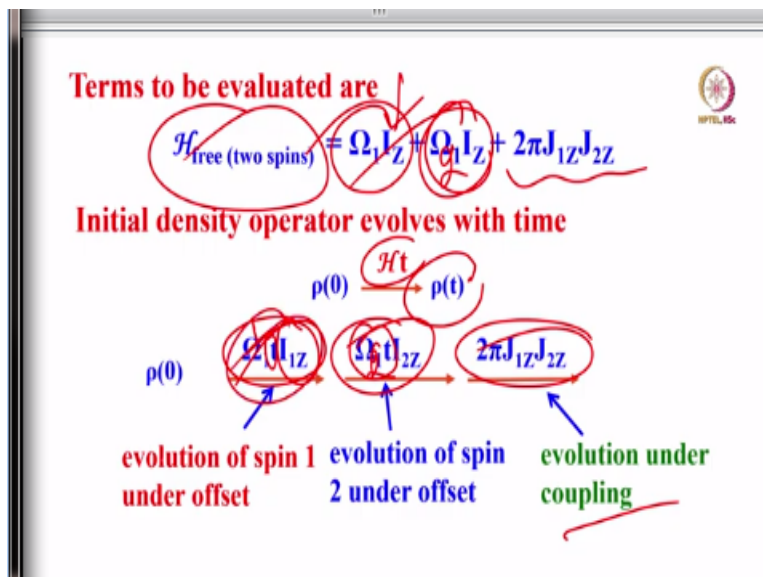
So, now continuing further I can write $2I_{1X}I_{2Y}$ and $2I_{1Y}I_{2X}$, that means spin 1 both X vectors are opposite, anti phase. whereas spin 2 they are in Y axis anti phase. Similarly $2I_{1Y}I_{2X}$ spin 1 is anti phase along Y axis, spin 2 is anti phase along X axis, all these are called MQ terms. E_1 and E_2 is nothing but just a vector representation for mathematical operation, this is diagrammatically represented like this.

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So, the free precession Hamiltonian for 2 couple spins we have to consider now.


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Terms to be evaluated are free precession of 2 spins. Now when I consider first free precession of spin 1 that is rotation about Z axis $\omega_1 I_Z$. And then this should be $\omega_2 I_Z$, $\omega_2 I_Z$ that is our spin 2 and then J coupling $2\pi J_{1Z} J_{2Z}$. These are the terms which you need to evaluate. So, initial density operator now evolves with time, initial density operator $\rho(0)$ when it evolves with time finally what we have to evaluate is $\rho(t)$.

Now $\rho(0)$ first evolution of spin 1 under offset $\omega_1 t I_{1Z}$, ω_1 is the offset with time t , how it is evolving we know. And this is for the spin 1, that is first one evolution of spin 1 under offset. Now evolution of spin 2 under offset is again should be $\omega_2 t I_{2Z}$. This evolution has spin 2 under offset; it need not be same for both ω_1 and ω_2 , they could be different. And also third term is evolution of J coupling, $J_{1Z} J_{2Z}$, so this is the evolution of the coupling term, this is the evolution of offset under spin 2, evolution of offset under spin 1.

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Evolution of each of these terms can be considered
individually and sequentially, under pulses and free
evolution

The rotations have to be applied to each spin
individually

As I said evolution of each of these terms can be considered individually and sequentially under pulses and free precession, both. Applying pulse individually you can take evolution of spin 1 and spin 2. There is no correlation between 2. When you are considering spin 1, spin 2 can be ignored, when you are considering spin 2, spin 1 you do not have to worry. Similarly when evaluating evolution a chemical shift you do not have to worry about J coupling. When you are evaluating J coupling evolution you do not have to worry about chemical shifts. So, all these rotations have to applied to each spin individually.

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Points to remember

The order in which it is evaluated is immaterial

The rotation of spin 1 does not affect spin 2 and
viceversa

And the order in which it is evaluated is immaterial that is not very important. And when you consider the rotation as spin 1, it does not affect the rotation of spin 2. Similarly when you are considering rotation of spin 2 does not affect spin 1. So, both are important points in order to evaluate whether chemical shift first or J coupling first, free precession, all those things does not matter. Individually spin 1, spin 2, chemical shift, and J coupling anything you can do in any order. And another important thing rotation of spin 1 does not affect the rotation of spin 2 and vice versa.

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Consider the evolution of I_{1X} under offset of spin 1, offset of spin 2 and J_{12}


Step 1: Evolution of I_{1X} under offset of spin 1

$$I_{1X} \xrightarrow{\Omega_1 t I_{1Z}} \cos(\omega_1 t) I_{1X} + \sin(\omega_1 t) I_{1Y}$$

Step 2: Now allow this term to evolve under offset of spin 2

$$\cos(\omega_1 t) I_{1X} + \sin(\omega_1 t) I_{1Y} \xrightarrow{\Omega_2 t I_{2Z}} \text{No Change}$$

The operator of spin 2 does not affect the spin 1



Now let us consider the evolution of I_{1X} . what is I_{1X} ? Under offset of spin 1 and offset of spin 2, and J_{12} . What is I_{1X} ? It is in phase X magnetization of spin 1, I told you, in phase X magnetization, diagrammatically I showed you. I_{1X} is for first spin, spin 1 in phase X magnetization. Now let us see how does it evolve under offset. So, now what is that evolving rotation is about Z axis, evolution of I_{1X} rotation about Z axis. So, I_{1X} when you rotate about Z axis, it goes to Y.

So, cosine of the old operator it becomes cosine $\omega_1 t I_{1X} + \sin \omega_1 t I_{1Y}$, this is I_{1X} I am considering. Now allow this term to evolve under the offset of spin 2, now these 2 both have to be evaluated under offset of spin 2. Now what is going to happen? Absolutely no change you will see, the reason is as I told you, when you are considering rotation of spin 1, it has no effect on spin 2, and vice versa. So, now you are considering rotation of spin 1 and it is effect

and spin 2 is not there at all, it is ignored. So, that is why no change is there, you can ignore, it does not affect spin 1.

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The overall evolution under both the offsets is

$$I_{1X} \xrightarrow{\Omega_1 I_{1Z} \text{ and } \Omega_2 I_{2Z}} \cos(\omega_1 t) I_{1X} + \sin(\omega_1 t) I_{1Y}$$

Step 3: evolution of I_{1X} under J coupling


Two new identities are introduced

$$\begin{aligned} \exp(-i\theta I_{1Z} I_{2Z}) I_{1X} \exp(-i\theta I_{1Z} I_{2Z}) &= \cos(\theta/2) I_{1X} + \sin(\theta/2) I_{1Y} I_{2Z} \\ \exp(-i\theta I_{1Z} I_{2Z}) I_{1Y} \exp(-i\theta I_{1Z} I_{2Z}) &= \cos(\theta/2) I_{1Y} - \sin(\theta/2) I_{1X} I_{2Z} \end{aligned}$$

Now overall evolution under both the offsets is given as $\omega_1 t I_{1Z}$ and $\omega_2 t I_{2Z}$ should be equal to this, $t I_{2Z}$. Now it should be like this $\sin \omega_1 t I_{1X} + \sin \omega_1 t I_{1Y}$ because this has no effect. Step 3: evolution of I_{1X} under J coupling we have to see, there are now 2 new identities introduced in phase term, we have considered evolution of I_{1X} under $\omega_1 t I_{1Z}$ $\omega_2 t I_{2Z}$ that we have considered. Now evolution of the same term under J coupling, so that means these 2 terms should be considered under J coupling evolution.

So, in this case the 2 new identities are introduced like it was introduced for the single spin case. Remember, 3 drawings were given finally to summarize this thing. Exactly these 2 terms, new identities are introduced, this is cosine of $-\theta$ into $I_{1Z} I_{2Z}$ into I_{1X} is into this one is given as cosine of θ by 2 into $I_{1X} + \sin \theta$ by 2 into $I_{1Y} I_{2Z}$. Similarly, the rotation about Y axis this is what it is, so this is for the rotation of I_{1X} and this is rotation of I_{1Y} , these are the things we have to consider.

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I_Y evolves into $I_{1Y}I_{2Z}$
 I_X evolves into $I_{1X}I_{2Z}$

In phase magnetization evolves into antiphase magnetization

Evolution of I_X under J_{12} Hamiltonian

$$\exp(-i\theta I_{1Z}I_{2Z})I_X\exp(-i\theta I_{1Z}I_{2Z}) = \cos(\theta/2)I_{1X} + \sin(\theta/2)I_{1Y}I_{2Z}$$

$\theta = 2\pi J_{12}\tau$, τ is the period for which the spin vectors evolve

Now I_X what do you understand from this? When I_X is evolving under J coupling, remember it evolves into this one. I_X when it evolves the in phase term evolves into $I_{1Y}I_{2Z}$, what is $I_{1Y}I_{2Z}$? I told you it is an anti phase term. I_X evolves into $I_{1Y}I_{2Z}$, similarly I_Y evolves into $I_{1X}I_{2Z}$; both are anti phase terms. What it means under J coupling? In phase terms evolves into anti phase terms.

So, in phase magnetization became anti phase magnetization because of J coupling evolution. So, under J_{12} Hamiltonian if you write how the evolution of I_X takes place, this is the formula I_X is being rotated under J_{12} in which case this is the identity we have to use. Now I_X component which is in phase turned out to be antiphase. Now exactly at $\theta = 2\pi J$ period for which spin vector τ is the period for which spin vector evolves, we can work it out, what happens if you put this value in this θ and calculate cosine and sine terms.

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Start with I_X and allow it to evolve under the coupling for τ

We have to now use the first identity

$$I_X \xrightarrow{2\pi J_{12} I_{1Z} I_{2Z}} \cos(\pi J_{12} \tau) I_X + \sin(\pi J_{12} \tau) 2I_{1Y} I_{2Z}$$

When $\tau = 1/2J_{12}$ the first term is 0

$$= 2I_{1Y} I_{2Z}$$

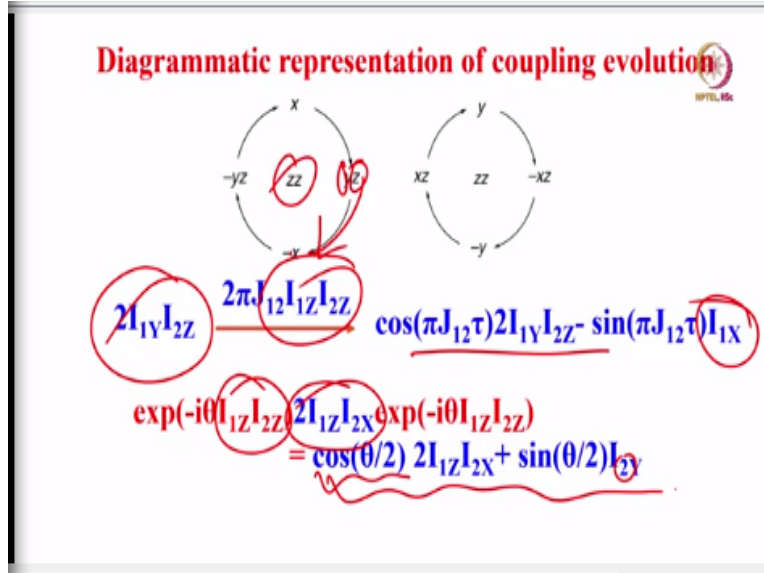
The inphase term became completely anti-phase at $1/2J_{12}$

Now we will start with I_X and allow it to evolve under coupling for τ . I started with I_X and see I_X means it is the first one you have to consider, first identity you have to consider because that is the rotation of I_X . So, now we have first term, we have to consider I am worried about I_X which is rotated under J coupling. So, now with that if I consider, go to the next one, here.

Consider an I_X , allow it to evolve under coupling for a period τ , we are using the first identity, this is a first identity. And now $\theta = \pi J$ into τ J_{12} is between 1 and 2 and that is J , θ by $2 = \pi J$ into τ . So, now I am evolving I_X in phase magnetization of spin 1, in phase X magnetization of spin 1 under J coupling, you get cosine of I_X of this term into sine of this J term into anti phase term, this is what you are going to generate.

Now put $\tau = 1$ over $2J$ here, what happens 1 over $2J$? This gets cancelled out J , it will become π by 2 , what is cosine of π by 2 ? 0 , so we are going to left with only again here $\tau = 1$ by $2J$ if you put this J will cancel out π by 2 you get, $\sin \pi$ by $2 = 1$. So, you are going to left with only this term. Exactly when τ , the delay for which you allow this coupling to evolve is 1 over $2J$ then in phase term became anti phase term, very important point. The in phase term becomes completely anti phase at exactly $\tau = 1$ over $2J$.

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And this is diagrammatically you can represent the coupling evolution, it is like this. For example $I_{1Y} I_{2Z}$ if it is evolving like this $I_{1Y} I_{2Z}$ if you consider, now Y and Z if you consider, Y is the first spin, Z is the second spin. Now I am considering Y and Z which is rotating like this, in this direction. Now when it evolves under J coupling this is going to be $-I_{1X}$, you put it $-I_{1X}$ and now this is a anti phase term.

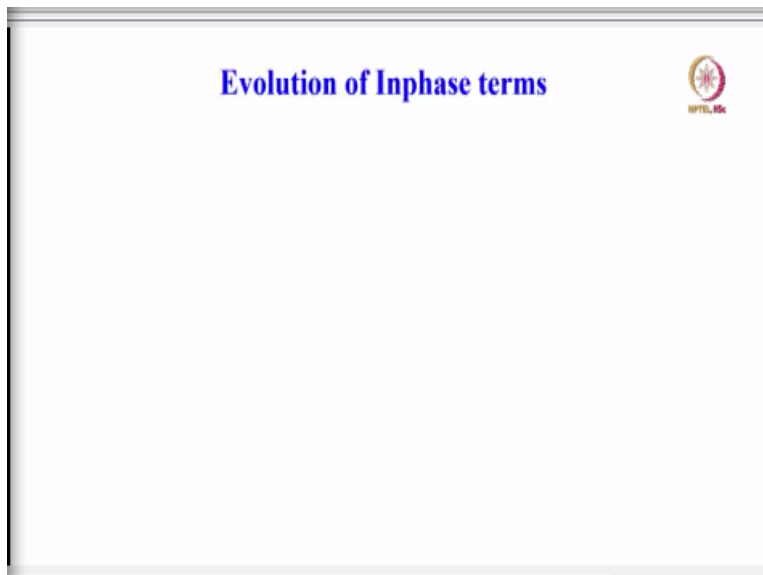
So, exponential of this term if you put it, if you work it out using diagram it turns out to be now what I am doing? This $2I_{1Z} I_{2X}$ is evolving under I_{1Z} and I_{2Z} , the solution is cosine of theta by 2, 2 of $I_{1Z} I_{2X} + \sin \theta$ by 2 into I_{2Y} , very simple.

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So, what we worked out for this spin 1? This is for spin 1 we worked out. We took this spin 1 evolution under offset and then under J coupling. Now what about spin 2? I said both can be individually taken, individually you can calculate, rotation of spin 1 does not affect spin 2, and vice versa I said. Now if what happens if I calculate for spin 2? Identical term you get, only thing is indices which you saw here get interchanged; 1 become 2, 2 become 1, that is all. Here 2 become 1, that is what is going to happen. So, indices get interchange when you work out for spin 2.

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So, now we can work out how does in phase term evolves after this. So, now since the time is getting over what I am going to do is I will stop here. We will come back and continue the evolution of in phase term and then work out how product operators can be applied for heteronuclear case in the case of 2 spins when the J coupling is present. So, right now we have understood quite a bit about product operator, especially when J coupling is taken into account.

We got product operators, diagrammatically represented, we understood $I_{1X} I_{2X}$, $I_{1Y} I_{2Y}$ all those things are called in phase magnetization of X and Y for spin 1 and 2. Similarly we understood what is the anti phase magnetization $I_{1X} I_{2Z}$, $I_{1Y} I_{2Z}$, $I_{2X} I_{1Z}$, $I_{2Y} I_{1Z}$ all those things; they are anti phase term. Similarly $I_{1X} I_{2X}$, $I_{1Y} I_{2Y} I_{2X} I_{1Y}$, all those terms are called multiple quantum terms.

So, altogether there are 16 possible combinations we saw, we could see their product operators when there are 2 spins coupled. With the 2 spins, evolution we have to consider under J coupling also. So, now under J coupling all the 16 operators will be there and how it evolves we understood by taking a simple example of two spins which are coupled; how they evolve under the offset and J coupling.

And then we understood when you consider the evolution of the J coupling the in phase term turned out to be anti phase term, very interesting. When we took I_{1X} term evolution of I_{1X} term, the in phase term of spin 1 and during J coupling we found it turns out to be anti phase term. So, same thing happens to I_{2Y} term also, if you consider for spin 2 also. So, identical things you are going to see.

So, now we are going to understand evolution of in phase terms, so far we understood how in phase term evolved everything, how it become anti phase terms? We will continue further and understand few more concepts that are involved in this. So, I will stop here, I will come back and continue in the next class, thank you.