

NMR Spectroscopy for Chemists and Biologists.
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Lecture 36

Time evolution of basis operators

So let us continue the discussion of the evolution of the basis operators when we will consider various kind of pulse sequences. So we have to know how the individual basis operators evolve under the influence of the Hamiltonians. Basically there are two components of the Hamiltonian we are dealing with. There will be a Zeeman Hamiltonian and the coupling Hamiltonian and last class we looked at the evolution of a particular base operator: base operator I_{kx} under the influence of the chemical shift Hamiltonian. Today we will discuss the evolution of that same operator I_{kx} under the influence of the scalar coupling Hamiltonian. So to remind you as to what is the scalar coupling Hamiltonian. Let me just write here.

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Scalar coupling evolution

$\chi_j = 2\pi J_{kl} I_{kz} I_{lz}$

$e^{-i\chi_j t} I_{kx} e^{i\chi_j t}$

For the basis operator I_{kx} the evolution can be written as

$$B_S'' = e^{-i2\pi J_{kl} I_{kz} I_{lz} t} I_{kx} e^{i2\pi J_{kl} I_{kz} I_{lz} t}$$

$$e^{-i2\pi J_{kl} I_{kz} I_{lz} t} = \cos\left(\frac{\pi J_{kl} t}{2}\right) - 4i \sin\left(\frac{\pi J_{kl} t}{2}\right) I_{kz} I_{lz}$$

$$B_S'' = I_{kx} \cos(\pi J_{kl} t) + 2I_{ky} I_{lz} \sin(\pi J_{kl} t)$$

$I_{kz} I_{lz} = \frac{1}{4} \sigma_{kz} \sigma_{lz}$
 $\sigma_{kz} \sigma_{lz} = 1$
 $-i\sigma_{ky}$

The scalar coupling Hamiltonian is written as

$$H_J = 2\pi J_{kl} I_{kx} I_{lz} e^{-iH_J t} I_{kx} e^{iH_J t}$$

J_{kl} is the coupling constant between two spins k and l and we have this operator I_{kz} and I_{lz} . So this is the for the to spin case this is the coupling Hamiltonian. So for the evolution what we need to

calculate is we have to calculate $e^{-iH_J t}$.

And we're using the same bases operators $e^{iH_J t}$. If explicitly write here, so I have this B_s'' so this is the operator that we get as a result of basis evolution. Here we have

$$B_S'' = e^{-i2\pi J_{kl} I_{kz} I_{lz} t} I_{kx} e^{i2\pi J_{kl} I_{kz} I_{lz} t}$$

Now this individual operator can be expanded or written in a simpler form like this:

$$e^{-i2\pi J_{kl} I_{kz} I_{lz} t} = \cos\left(\frac{\pi J_{kl} t}{2}\right) - 4i \sin\left(\frac{\pi J_{kl} t}{2}\right) I_{kz} I_{lz}$$

This can be proved along the same lines as we derived the expressions for e^{Ibx} for example. When we took the expressions for e to the let me write here so we will write here $e^{-i\beta I_{kz}}$. So we wrote

in a particular manner here $\cos\frac{\beta}{2} - \sin\frac{\beta}{2}$ and things like that. So this was x here. If you are applying it for pulse, this was x here β is a flip angle then we wrote this is

$$i \cos\frac{\beta}{2} - 2I \sin\frac{\beta}{2} I_x$$

So that was how it was written. So in the same manner we right this here except we make note of

the fact that $I_{kz} I_{lz}$ can be written as in terms of poly-spin matrices $\frac{1}{4} \sigma_{kz} \sigma_{lz}$. So this will help us in deriving this equation. And polyspin matrices satisfied this condition this $\sigma_{kz}^2 = \sigma_{lz}^2 = 1$. So this is the property which you should remember and we can prove this equation.

So therefore I am not going to explicitly prove this. This can be a kind of an exercise for students who can practice this and prove this equation. So we will actually use this equation as it is and calculate the evolution of the kx operator under the influence of this. So in this place we will have to put this and on this place what we shall do, I_{kx} and this will be a plus sign. Then you write for $i2\pi J_{kl} I_{kz} I_{lz} t$ then this will be the same as this except we will have a plus sign here.

And then you do the multiplication of this part I_{kx} and the other part which is with the plus sign. Then you arrive at this equation $I_{kx} \cos \pi J_{kl} t + 2I_{ky} I_{lz} \sin \pi J_{kl} t$. So this will be the kind of equation that will come. You notice here that I_{kx} has evolved into a in phase I_{kx} turn and it has generated what we make call as your anti phase term. It is k magnetization which is anti phase with respect to the spin l .

You remember earlier we have discussed what this individual what these basis operators represent. Therefore here we have said under the influence of coupling Hamiltonian the I_{kx} operator will be e into this $I_{kx} \cos \pi J_{kl} t + 2I_{ky} I_{lz} \sin \pi J_{kl} t$. So this is the anti phase term. So such evolutions will keep happening and we will look at them as we go along.

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For the basis operator I_{ky} the evolution under \mathcal{H}_z and \mathcal{H}_j can be written as

$$B'_S = \cos(\omega_k t) I_{ky} - \sin(\omega_k t) I_{kx}$$

$$B''_S = I_{ky} \cos(\pi J_{kl} t) - 2I_{kx} I_{lz} \sin(\pi J_{kl} t)$$

For the basis operator $2I_{kx} I_{lz}$ the evolution under \mathcal{H}_z and \mathcal{H}_j can be written as

$$B'_S = 2\{I_{kx} \cos(\omega_k t) + I_{ky} \sin(\omega_k t)\} I_{lz}$$

$$B''_S = \cos(\pi J_{kl} t) 2I_{kx} I_{lz} + \sin(\pi J_{kl} t) I_{ky}$$


Now similarly you can calculate for the basis operator I_{ky} evolution under the Zeeman Hamiltonian. This is the chemical shift Hamiltonian and the coupling Hamiltonian H_j and they can be represented in this manner. We will not prove this, basically they can be derived in the same manner and we will just write it down here and we will use them later. So the

$$B'_S = \cos(\omega_k t) I_{ky} - \sin(\omega_k t) I_{kx}$$

So because here we have considered the evolution have the kx operator.

So the ky operator ky operator evolves with I_{ky} here and $-\sin \omega_k t I_{ky}$. Similarly, the coupling Hamiltonian generates this sort of evolution.

$$B_S'' = I_{ky} \cos(\pi J_{kl} t) - 2I_{kx} I_{lz} \sin(\pi J_{kl} t)$$

Similarly, in this case also even when you had I_{kx} evolution it was

$$B_S' = 2\{I_{kx} \cos(\omega_k t) + I_{ky} \sin(\omega_k t)\} I_{lz}$$

Therefore, this indicates in some way a kind of a rotation in the transverse plane and you can pictorially represent them very soon. I have already indicated this to you in the evolution shifts early that such kind of a representation can be used for calculating the evolutions of any of this operators.

Whether it is I_{ky} or I_{kx} , $-I_{ky}$ or $-I_{kx}$ and things like that. Now similarly we can do this exercise for the basis operator $2I_{kx} I_{lz}$. Evolution under the H_z and H_J . Now H_z works on individual spins therefore if I consider $2I_{kx} I_{lz}$, which is the transverse term here. The transverse term is I_{kx} therefore chemical shift evolution will happen only for I_{kx} part. I_{lz} part will not contribute to the chemical shift evolution therefore if I consider the B_S' here.

$$B_S' = 2\{I_{kx} \cos(\omega_k t) + I_{ky} \sin(\omega_k t)\} I_{lz}$$

So even if it is in this form the two product operator the chemical shift works on the individual operator because we have the I_{lz} here and I_{lz} coming here I_{kx} evolves in the usual way as it is for the individual single spin. Now the coupling Hamiltonian that causes this sort of a transformation here it gives you $\cos \pi J_{kl} t 2I_{kx} I_{lz}$.

So the antiphase term which remains as amplitude modulated by this expression $\cos \pi J_{kl} t$ and you generate here $I_{ky} \sin \pi J_{kl} t$. Notice here that when you consider I_{ky} rotation you got

$I_{ky} \cos \pi J_{kl} t - \sin \pi J_{kl} t$. Now you are considering this you are generating the same term once more. So this appears in the positive sign then you have plus $\sin \pi J_{kl} t I_{ky}$.

So this indicates you that this kind of terms form some sort of a group. They transform within themselves. The Hamiltonian here is I_{kz} and I_{lz} and, the basis operator is $2 I_{kx} I_{lz}$ and we have also another basis operator $2 I_{ky}$. So $2 I_{kz} I_{lz}$, $2 I_{kx} I_{lz}$ and I_{ky} they somehow form a kind of a group and similarly for the I_{kx} as well.

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For the basis operator $2I_{ky}I_{lz}$ the evolution under \mathcal{H}_Z and \mathcal{H}_J can be written as

$$B'_S = 2\{I_{ky} \cos(\omega_k t) - I_{kx} \sin(\omega_k t)\} I_{lz}$$

$$B''_S = \cos(\pi J_{kl} t) 2I_{ky} I_{lz} - \sin(\pi J_{kl} t) I_{kx}$$

This can be represented in a pictorial manner like this. So similarly I can write this same kind of expressions for $2I_{ky} I_{lz}$ under the influence of H_Z and H_J . So B'_s gives me the same here evolution of I_{ky} as individual chemical shift evolution and I_{lz} remains here. And B''_s which is a result of evolution under coupling we had $\cos \pi J_{kl} t 2I_{ky} I_{lz}$ same here and it generates the I_{kx} term. So as I said these indicate some sort of rotation in a particular plane.

Pictorially we can represent it like this. So we put the Hamiltonian this is from the coupling similarly we wrote earlier for the chemical shift so the coupling Hamiltonian is written from this axis here. So $I_{kz} I_{lz}$ this is the coupling Hamiltonian and if I take the particular base operator I_{kx} . Here then it under the influence of this rotation evolution under this the circle indicate the evolution under this Hamiltonian.

It generally rotates in this manner so you get rotates like this you generate components of I_{kx} and $2I_{ky} I_{lz}$. Suppose it has rotated up till here then you generate the $I_{kx} \cos \pi J_{kl} \tau$ and $I_{ky} I_{lz} \sin \pi J_{kl} \tau I_{kx}$. And if you were to continue this rotation under the influence of the same Hamiltonian like this so what you will get. So this vector has moved over here so you get $I_{ky} I_{ly} \cos \pi J_{kl} \tau$ as it is.

Suppose it has moved until this once you draw a vector as well here. If I wish to draw vector here so then if this rotation has happened for a particular angle this angle and this will be the $\pi J_{kl} \tau$. You will write the $\cos \pi J_{kl} \tau$. So if this is $\pi J_{kl} \tau$ here then you will have $2I_{ky} I_{ly} \cos \pi J_{kl} \tau$ and this component will be $-I_{kx} \sin \pi J_{kl} t$. So and similarly if you continue this if you were to start here your you will move here.

If you want to study you will move here and things like that. Therefore, these actually transform within themselves. These I_{kx} , $2I_{ky} I_{lz}$ and $I_{kz} I_{lx}$. This form a group which transform within themselves. Go from here to here, you get this and this you can go from here to here again you get this and this under the influence of the same Hamiltonian. So if I were to write in the similar manner here $2I_{kx} I_{lz}$. So I get here $I_{kx} I_{kz}$ going to I_{ky} and I_{ky} going to $-I_{ky} I_{lz}$ here.

And so and this continues to generate this portion here and the $-I_{ky}$ here. So like that. So this whole set of operators which are represent here $2I_{kx} I_{lz} I_{ky}$ and this coupling operator here this $I_{kz} I_{lx}$. These form kind of a rotation group. When I said group they transform themselves so under the influence of one thing the one operator transforms into the other. So that is the meaning of the rotation group. So this is a very, these are the very useful operations calculating the evolution of any density operator as we get along.

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Rotation by pulses

This is represented by the transformation,

$$R_q B_S R_q^{-1} \quad q = x, y$$

(i) $B_S = I_z$

For a 90_x pulse the transformation will be

$$\begin{aligned} R_x \left(\frac{\pi}{2} \right) I_z R_x^{-1} \left(\frac{\pi}{2} \right) &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -I_y \end{aligned}$$



Now that is so much for the evolution of the basis operators. So though the illustrative examples which I gave you but there will be; we have to do this exercise for every other rotation basis operators. This will be this can be easily done because we already indicated what sort of principles are involved what sort of rotation groups are formed and therefore it is easy to write down the expressions for all of those.

Now we turn to the evolution under the influence of pulses. What do the pulses do? And we have seen earlier the particular basis operator gets transformed by this sort of a transformation. If this represents rotation, this represents pulse here and this is a basis operator. This is the pulse $P_1 \rho P_1^{-1}$ and the pulse can be applied along X or the Y axis and therefore I write here R_q the rotation operator R_q and R_q^{-1} .

$$R_q B_S R_q^{-1} \quad q = x, y$$

So these represent pulses and q can be x or y . Now let us actually calculate the influence of this on some basis operators. We take as an illustration, $B_S = I_z$. This is the simplest all of those and for a 90 degree x pulse the transformation will be, we have to write the individual matrices for this pulses. We have here suppose we have here R_x , suppose we apply it along X axis at 90_x pulse.

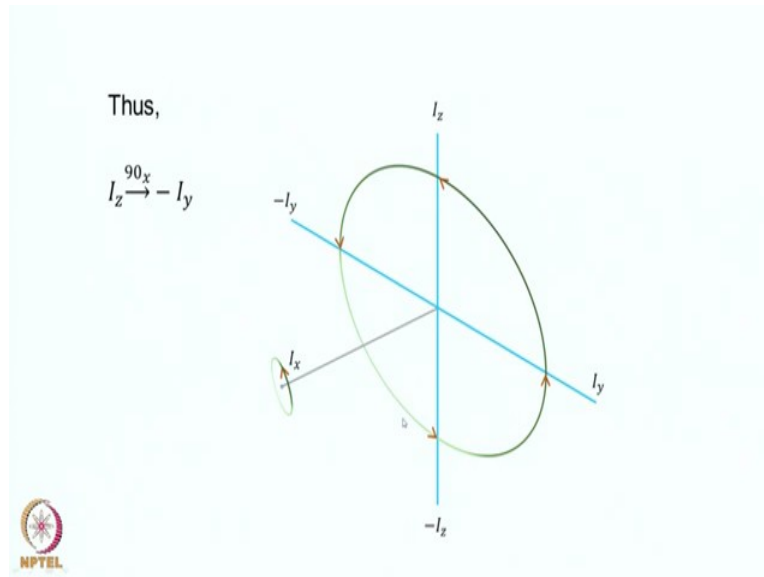
Therefore, this is

$$\begin{aligned}
 R_x\left(\frac{\pi}{2}\right) I_z R_x^{-1}\left(\frac{\pi}{2}\right) &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \\
 &= \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -I_y
 \end{aligned}$$

So one can calculate inverse of this matrix, take a product of this matrix and this matrix you will get 1.

So that indicates that this is the inverse of this. Now when you all this multiplications you will get $\frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}$. And this is equal to $-I_y$. So what this has told us that 90 degree x pulse rotates the I_z into $-I_y$. So this is also what we have said earlier in discussion with the derivation of the pulses and that was we can write is, so this is the X, Y, Z and if I have a vector here; I_z here, this gets transformed into $-Y$. So it goes here $X Y Z$ goes into $-Y$ gets rotated here to $-I_y$. I_z goes to $-I_y$. If I apply a pulse along the X axis. So that is the calculation what we got from this 90 degree x pulse.

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So I_z operator, 90_x this indicated in the figure here. This figure is already there. So if I here write rotation around X this is the Y this is the Z . So rotation operator is along this I_x and Z magnetization is rotated into the $-I_y$.

So from the same, we could also see what if your magnetization was along the $-Z$ axis, it will go to Y . If it were along the Y axis it will go to $+Z$. So if you are considering this initial operator here as I_y then you can imagine that this I_y will go to I_z . We said I_z will come to $-I_y$. This is what we had in the explicit calculation. Now if you were to start with I_y , the same rotation will take I_y to I_z . And I_x will of course be invariant nothing will happen we will show that explicitly show that also and if you were to have $-I_y$ then $-I_y$ will go to $-I_z$ under the influence of this rotation.

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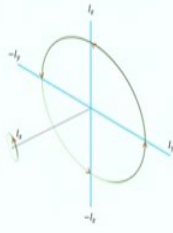
(ii) $B_s = I_y$

For a 90_x pulse the transformation will be

$$R_x\left(\frac{\pi}{2}\right) I_y R_x^{-1}\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}$$

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

Thus,
 $I_y \xrightarrow{90_x} I_z$



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Now that is explicitly calculated here, if $B_s = I_z$ then what I have to say here

$$R_x\left(\frac{\pi}{2}\right) I_y R_x^{-1}\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}$$

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

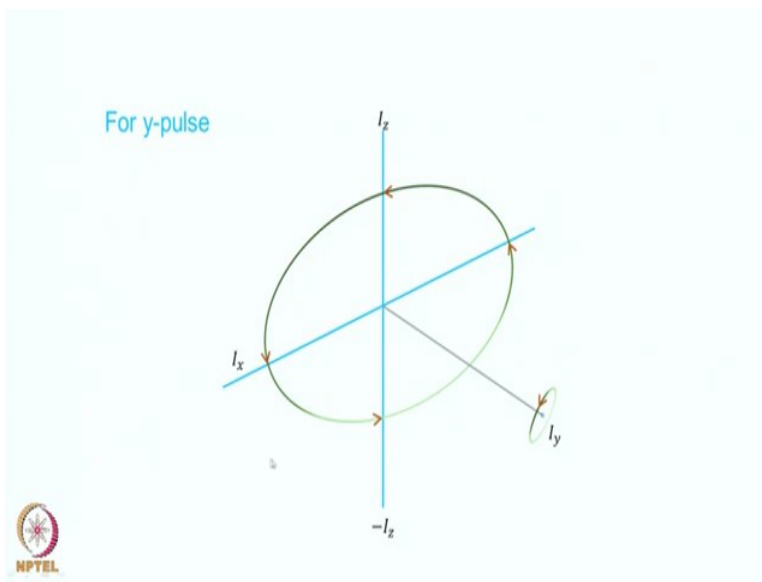
So this is the same which told you before that under the same rotation the I_y is going to I_z . So therefore these again form the rotation groups X , Y and Z these form rotation groups. They transform within themselves, if there is in sign that is not considered different. It is the same rotation group.

Except that the coefficient will be different. So this rotates Y into Z , rotates Z into $-Y$ and Z rotates $-Y$ into $-Z$ and so on. So this forms a rotation group. You remember if I had the rotation around the Z axis; rotation around the Z axis is what that is a chemical shift evolution. When I had the chemical shift evolution my operator going from here to here. I_x was going a part of it was rotating in this plane X to Y , Y to $-X$, $-X$ to $-Y$ and so on so forth.

Therefore, these three operators from a rotation group and one of them can be the basis operator

other one can be your Hamiltonian. In this case operator is the I_x , the rotation is around this axis therefore and we have the basis operator is I_z or I_y . In the chemical shift case this was the Hamiltonian and this was the operator and the basis was here and therefore one could go from I_x to I_y and $-I_y$ to I_x and so on so forth. So this is the way we can look at all of this in a comprehensive manner. So thus I_y goes to I_z .

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So for a y pulse, earlier I wrote as x pulse. So what does the y pulse do? y pulse take this rotation here; you can do the same calculation here. So it goes I_z goes to I_x . Notice you have a left handed rotation here I_z will go to I_x and I_x will go to $-I_z$ and $-I_z$ will go minus I_x and so on. So this is the way describe the rotation groups. Rotation under the influence of various pulses.

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(iii) $B_S = I_x$

For a 90_x pulse the transformation will be

$$\begin{aligned} R_x\left(\frac{\pi}{2}\right) I_x R_x^{-1}\left(\frac{\pi}{2}\right) &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = I_x \end{aligned}$$

Thus, I_x is invariant under R_x pulse.



Now what about I_x itself? Suppose your base operator is I_x and apply a 90 degree x pulse. Intuitively you would think that nothing happened to it but let us also prove it. So we put

$$\begin{aligned} R_x\left(\frac{\pi}{2}\right) I_x R_x^{-1}\left(\frac{\pi}{2}\right) &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = I_x \end{aligned}$$

So therefore, the I_x is invariant under R_x pulse. So that is intuitively one would have imagined that. You have put the magnetization along the same axis and you are applying rotation around that axis and you should not move the principle.

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For multi-spin basis operators, the effects of pulses can be applied on individual spins.

For example,

$$2I_{kx}I_{lz} \xrightarrow{90_x(k)+90_x(l)} -2I_{kx}I_{ly}$$

SQ
DQ+ZQ

This represents conversion of anti-phase x-magnetization of k spin into mixture of zero and double quantum coherences.



Now let us consider multi spin basis operators. So far we looked at the individual spin operators and we now turn to multi spin operators. The effects of pulses can be applied on individual spins. Now the pulses can be applied on all the screens for or an individual spin.

So the effects will be different. Now here we consider the case we consider the, this operator $2I_{kx}I_{lz}$ and we have seen this operator represents the k magnetization which is anti phase with respect to l . This is the single quantum coherence because this is kx , $kx lz$ is the single quantum coherence x magnetization of k anti phase with respect to l . Now we apply a pulse on both the spins anti x (k) plus $90_x(l)$.

So this is called as a non selective pulse. This is applied to both spins k and l . So now what happens when I apply kx pulse nothing happens to kx because we said this is invariant the x magnetization invariant under the x pulse. Therefore, nothing happens to the kx operator. And what happens to lz ? Now lz goes to $-ly$. This is calculated. Z goes to minus y so therefore x pulse on l spin take this I_{lz} to $-I_{ly}$. Therefore, I get here $-2I_{kx}I_{ly}$.

So what is this? Now here we got a mixture of double quantum zero quantum coherence. This we had explicitly calculated earlier that this represents a mixture of double quantum and zero quantum coherence. So what we have done here is by applying nonselective 90 degree pulse on anti phase magnetization of one spin we have converted that into a mixture of double quantum and zero quantum coherences. So these are called as coherence transfers and various types of experiments will make use of such kind of transformation.

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$$2I_{kx}I_{lz} \xrightarrow{90_y(k)+90_y(l)} -2I_{kz}I_{lx}$$

SQ
SQ

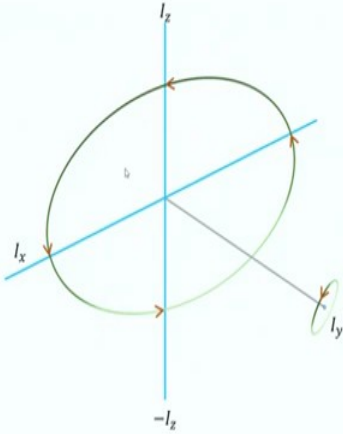

This represents conversion of anti-phase x-magnetization of k spin into anti-phase x-magnetization of 'l' spin: **coherence transfer**

$$2I_{kx}I_{lz} \xrightarrow{90_y(k)} -2I_{kz}I_{lz}$$

SQ
ZZ-order



For y-pulse

Suppose I take the same operator here now apply a pulse not 90_x pulse but I apply 90_y pulse; 90_y pulse on both the phase. So if I take x what happens to x ? So you have to recall when I apply y pulse what happens to x ? So at 90_y on I_z will take me to I_x and this will take me to minus $2I_{kz}$. So you have to go back and look at what happens when I apply y pulse on X magnetization. Let us go back and look at this. So this will be easier to follow if you do that.

So looking at here, so the what happens here apply y pulse on X magnetization, it will go to $-Z$. And y pulse on z will take on to x . So therefore this apply here. So this will go to $-Z$, I_z goes to I_x . Therefore, I get here minus $2I_{kz} I_{lx}$. Now notice here just phase change of the pulse has made a huge difference in the transformation. This was antiphase magnetization of k spin with respect to spin in l . And what we have here? This is X magnetization of l spin anti phase with respect to the k spin.

Now this is single quantum coherent. This was single quantum coherent this was single quantum this is also single quantum. When we apply the 90_x pulse we get got double quantum here from this basis operator. Now when you apply y pulse to the same basis operator I get a single quantum coherence of the l spin. So this is a different kind of a coherence transfer. Single quantum to single quantum to one spin to one spin which are coupled from k spin to l spin get a transfer and this is a single quantum to a single quantum coherence.

Just by changing a phase of this 90 degree pulse. So in the earlier case when the 90 degree pulse was along the Y -axis applied to both the spins so I got a single quantum coherence into a mixture of double quantum and zero quantum coherence. And so this this is an important implications. So this represents conversion of anti phase x magnetization of k spin into antiphase X magnetization of l spin. That is the single quantum coherence term.

Now suppose I apply the again once again with the same operator base operator here. But I apply a pulse only on k spin for example. I will not apply along the l spin at all. That means I apply selective pulse a selective 90 degree pulse on one spin only. I applied to only the k spin. So therefore the l spin remains unaffected because I have not applied any pulse onto them and kx takes me to the $-kz$. Therefore, this will go to $2I_{kx} I_{lz}$ takes me to $-2I_{kz} I_{lx}$.

So it is a completely different transformation. Now this anti-phase magnetization has now got

transformed into zz order. zz order has to do with the order of the populations in the 2 states $\alpha\alpha$ state and the $\beta\beta$ state as we had discussed earlier. So this antiphase magnetization of the k spin is getting transformed into a zz order simply by changing what kind of pulses we apply. We get different kinds of transformations of the basis operators.


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$$2I_{kx}I_{lz} \xrightarrow{90_y(l)} 2I_{kx}I_{lx}$$
SQ DQ+ZQ

Similarly,

$$2I_{ky}I_{lz} \xrightarrow{90_x(k)+90_x(l)} -2I_{kz}I_{ly}$$
SQ SQ

This represents conversion of anti-phase y-magnetization of k spin into anti-phase y-magnetization spin- l . This is referred to as coherence transfer from spin- k to spin- l . In general, it is seen that application of RF pulses to anti-phase magnetization in multi-spin systems causes coherence transfer among the spins. This forms the basis of many multi-pulse experiments in homo and heteronuclear multi-spin systems.



So now if I apply on the other hand the same basis operator once more here but I apply a pulse selective pulse carefully on the l spin not on the k spin. Earlier when I applied on the k spin I got zz order. So now I applied only on the y spin so what I get here. kx remains kx because no pulse applied and lz takes me to lx to $I_{kx} I_{lx}$. Now this is the mixture of double quantum and zero quantum coherences. So therefore you see once again how a single quantum is converted into double quantum plus zero quantum coherence by changing the kinds of pulses we apply.

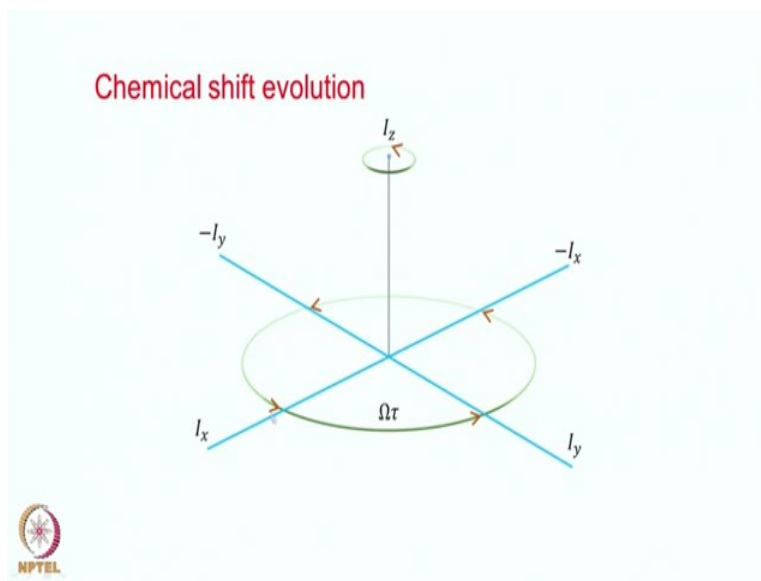
So you notice therefore that a combination of different kinds of pulses with different cases can really be used to create a whole lot of transformations in your density operator and all of these when we will use when you actually calculate various pulse sequences and that will be coming important will be easy to calculate in a simple operator form product operator form. So similarly here $2I_{ky} I_{lz}$, so far I was looking at $2I_{kx} I_{lz}$ and we can calculate similarly for $2I_{ky} I_{lz}$.

So if I start with $2I_{ky} I_{lz}$ apply a non selective pulse x both k and l spin along the X axis then I get this into $2I_{kz} I_{ly}$ this is now the l magnetization antiphase with respect to k . This was k

magnetization antiphase with respect to l and this is l magnetization antiphase with respect to k . So single quantum to single quantum coherence transfer. So these are important results which we will play a very major role in how we calculate the evolution of the density operator through the sequences.

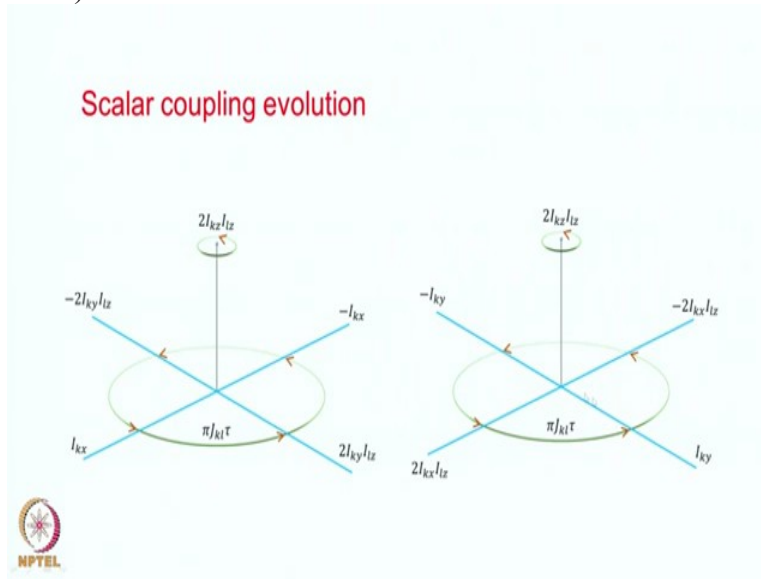
So this is referred to as coherence transfer of spin k to spin l . In general, It is seen in application of RF pulses to antiphase magnetization in multi spin systems causes coherence transfer among the spins. This forms the basis of many multiples experiments in homo and heteronuclear multi spin systems.

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So here is a summary of all of these revolutions what we have indicated here. Once again as a recap so because this will be extremely useful and we have to remember this very well remember this by heart. Which operator turns which bases operator into what? So which Hamiltonian converts what basis operator into what basis operator? So we will have to see all of this. If this is chemical shift evolution your Hamiltonian has the I_z operator here therefore we are writing this manner and your basis operators are I_x and I_y . Therefore, I_x rotates into the I_y and I_y rotates into $-I_x$. $-I_x$ rotates into $-I_y$ and so on so forth. So all transformations happen here. These form rotation group all these 3 operators form a rotation group.

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The scalar coupling evolution once again the same thing is repeated for the benefit of consolidation. So you have this the Hamiltonian is $2I_{kz} I_z$ we put it along the Z axis. This is my axis this is my axis. So this axis is $2I_{kz} I_z$ and I_{kx} is rotated into mixture of I_{kx} and $I_{ky}I_z$ and the same Hamiltonian rotates the basis operator $2I_{ky} I_z$ into mixture of $2I_{kz}$ and $-I_{kx}$.

So you to where to start from $-I_{kx}$, I will get $-I_{kx}$ plus cosine component will be $-I_{kx}$ and I will get here minus $2I_{ky} I_z$. Now if I want to put here the antiphase magnetization here it was starting from the in phase magnetization. This is how they transformed if I start with $2I_{kx}I_z$ this antiphase magnetization and this operator remains the same $2I_{kz} I_z$ this rotates into I_{ky} . So this will be the cosine component will be $2I_{kx} I_z$.

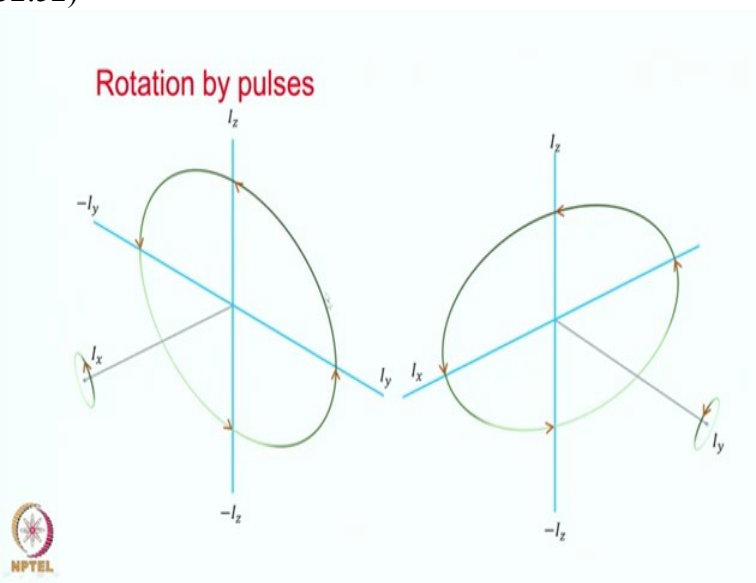
The sine component will be I_{ky} . So if I consider rotation for there, I_{ky} rotates into minus $2I_{kx} I_z$ but it remains as I_{ky} . The cosine part $I_{kl} \tau$ will be I_{ky} and the sine will be $-2I_{kx} I_z - 2I_{kx} I_z \sin \pi k_1 \tau$. So this is the way rotation happens the when you wrote here this is the rotation is happening depending upon the value of tau your vector will be somewhere here or here or here wherever. So if it is equal

to $\frac{\pi}{2}$.

If τ is such that this whole rotation is $\frac{\pi}{2}$. Then you will go entirely from here to here. If it is not $\frac{\pi}{2}$,

if it is this whole thing is equal to 30 degrees or 40 Degrees or something then your vector will be somewhere here so you will have cosine component and a sine component. Similarly, here if you rotate in an angle $\frac{\pi}{2}$ to that depends upon the value of your τ then this goes completely into this but if it is less than that the vector can be somewhere here then and you will have a cosine component here and then sine component. So this is the way we actually calculate the evolutions under the influences of various Hamiltonians.

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So about the rotation by pulses. So if I have x pulse then I_z rotates into $-I_y$. Notice here we consider a 90 degree pulse which goes into this. But if you extend this argument to you say a well I don't want to apply the 90 degree pulse. Suppose I apply 45 degree pulse what happens? It is not very easy to imagine here. Now we understood the principles how the rotations are happening.

If I were to rotate by 45 degrees then the rotation will take the vector from here to here. So this angle will be 45 degrees so I will have a component I_z and a component $I_y -I_y$. So show if any angle can be chosen. So if I have a 90 degree pulse it takes me to $-I_y$ but if I have a β pulse then I will have cosine beta component for the I_z and the sin beta component for the $-I_y$. So similarly if I apply this pulse to the I_y magnetization goes for a 90 degree pulse it will go here but suppose I were to apply I pulse which is not 90 degree, somewhere like 45 degree for something like 30

degree.

Then I will rotate it only up till here then I will have a cosine component here and sine component here. Similarly, if I were to take rotation around the y axis pulse along the y axis the rotations will happen like this: I_z goes to I_x , I_x goes to $-I_z$, $-I_z$ goes to $-I_x$ and again $-I_x$ will take you to I_z . Once again the same arguments applied with regard to the flip angle. Instead of a 90 degree flip angle is you use a different flip angle you will get different components of on the Y and the Z axis. So with that we will stop here and we will continue the discussions in the next class.