NMR Spectroscopy for Chemists and Biologists
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Lecture 38
Spin echo Continued

We have been discussing spin echo as an example and trying to calculate explicitly the density operator evolution through the pulse sequence, so we did that last time for a particular case of two spins with coupling and without coupling, without coupling first and then with coupling later and we are considered the spins echo sequence which was 90 degree x pulse followed by time tau then a 180 degree x pulse followed by time tau and then the evolution was calculated until this point, so we are now going to make a slight variation in this in this sequence to see what difference does it make.

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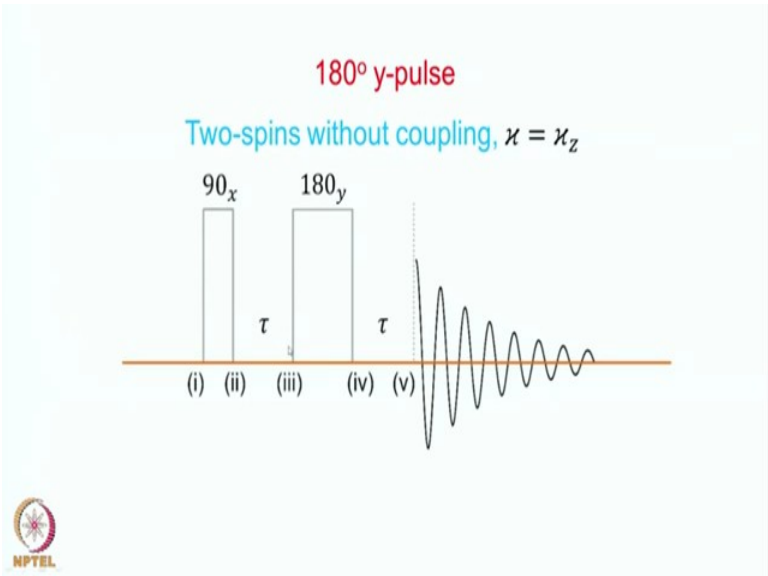

Weather the phase of the RF pulse does it make a difference and if it does in what way does it make a difference, so that is the question we are going to ask and therefore we will simply change the phase of this pulse instead of 180 degree x pulse we will apply the pulse along the Y axis and see what happens, so as before we will first consider two spins without coupling which means the Hamiltonian is simply H_z which is a Zeeman Hamiltonian the evolution happens in the same manner here under the influence of the Zeeman Hamiltonian.

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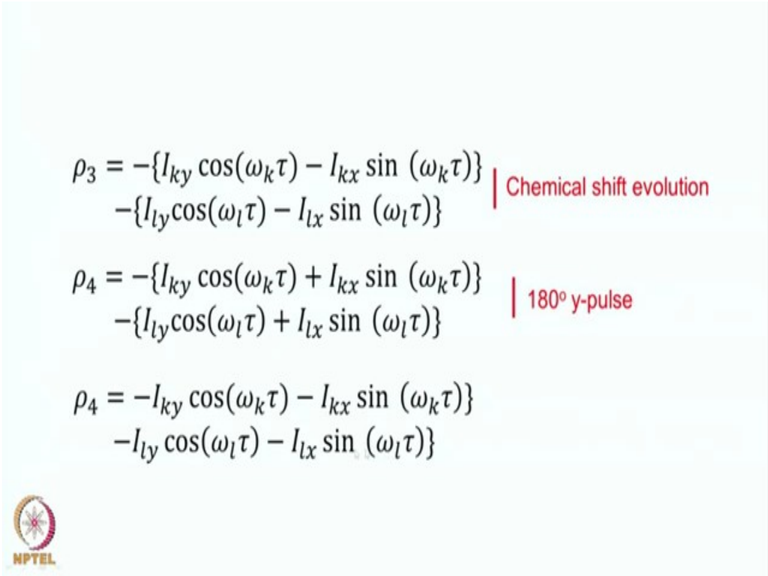

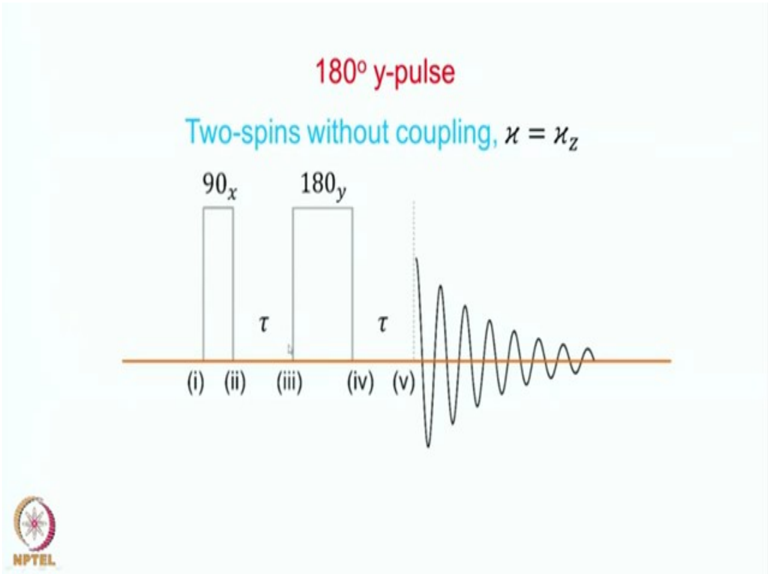

Now, we have calculated the explicitly the density operator in the previous case and the difference here is only at this points so up till here the calculation is the same, therefore we will not repeat that calculation here but simply take what was the density operator from the previous class at this point and that is ρ_3,

$$\rho_3 = -\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin\ (\omega_k\tau)\}$$
$$-\{I_{ly}\cos(\omega_l\tau) - I_{lx}\sin\ (\omega_l\tau)\}$$

this was the result of chemical shift evolution from ρ_2 to ρ_3.

And then the individual frequencies are here the ω_k and ω_l for the two spins. Now the difference comes, we are now applying a pulse along the Y axis and not along the X axis, so what does it do, so if it along the Y axis this term does not change this is in variant so this remains as I_{ky} whereas this one goes from I_{kx} to $-I_{kx}$ and therefore this becomes plus here, so this becomes

$$\rho_4 = -I_{ky}\cos(\omega_k\tau) - I_{kx}\sin\ (\omega_k\tau)\}$$
$$-I_{ly}\cos(\omega_l\tau) - I_{lx}\sin\ (\omega_l\tau)\}$$

This is a time point 4.

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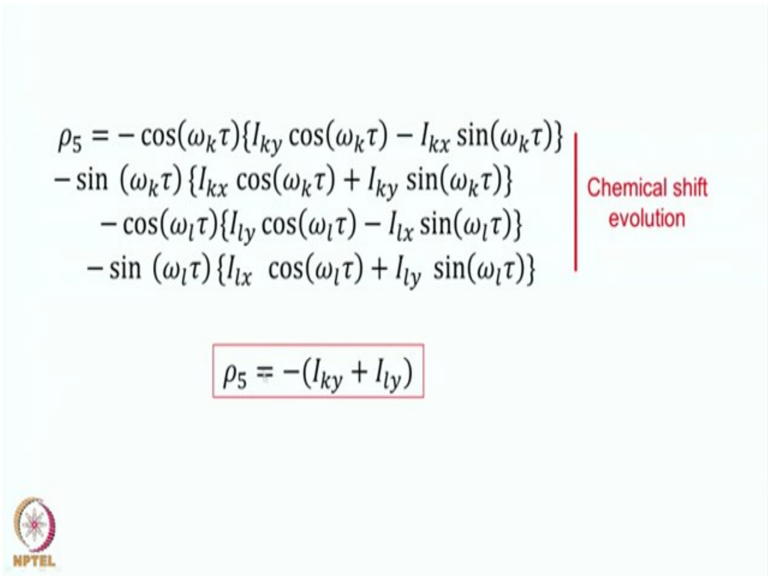

Next we have to evolve under chemical shift once more for the next τ period, now there are four terms and each one of this has to be explicitly evolved, so this is the first term I_{ky} so this gives me here $-\cos\omega_k\tau$ and I_{ky} evolves as under the chemical shift once more like this, $I_{ky}\cos\omega_k\tau - I_{kx}\sin\omega_k\tau$ and the second term which involve I_{kx} will give me this

$$\rho_5 = -\cos(\omega_k\tau)\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\}$$
$$-\sin\ (\omega_k\tau)\ \{I_{kx}\cos(\omega_k\tau) + I_{ky}\sin(\omega_k\tau)\}$$
$$-\cos(\omega_l\tau)\{I_{ly}\cos(\omega_l\tau) - I_{lx}\sin(\omega_l\tau)\}$$
$$-\sin\ (\omega_l\tau)\ \{I_{lx}\ \cos(\omega_l\tau) + I_{ly}\ \sin(\omega_l\tau)\}$$

Now, you notice what happens here so rearrange the terms this is $-\cos^2\omega_k\tau$ and then we have the other I_{ky} term is here and this is $-\sin^2\omega_k\tau I_{ky}$ if you put I_{ky} take I_{ky} take -I_{ky} inside bracket you will have $\cos^2\omega_k\tau+\sin^2\omega_k\tau$ and so therefore what is in the bracket is 1 and therefore you get a - I_{ky}

And what happens to this term, so this is plus $I_{kx}\sin\omega_k\tau\cos\omega_k\tau$and here it is $-\sin\omega_k\tau\cos\omega_k\tau$ this will cancel, so from this two we retain only this, this part and now similarly if you see here we retain this part this two terms will be remaining this is $\cos^2\omega_k\tau I_{ly}$ and this is $\sin^2\omega_k\tau I_{ly}$ and therefore this two terms will remain and we get a I_{ly} here and this two terms will cancel and we therefore in the end for ρ_5 I get

$$\rho_5 = -(I_{ky} + I_{ly})$$

this is exactly equal to ρ_2 so therefore what is happened if you recall here let us see what rho 2 in the previous class $-I_{ky}+I_{ly}$ this is what we start it off with.

Now, in the previous class at ρ_5 we had here plus sign it became $\rho_5=I_{ky}+I_{ly}$, so the effect of changing the phrase of the 180 degree pulse is that this sign has changed and it is remained as $\rho_2=-I_{ky}+I_{ly}$ the chemical shift is completely refocused that effect is the same, there is no change in that one except that we had a change the sign is now becomes minus instead of the plus in that case.

This also we had seen in the vectorial picture when we discussed this spin echo earlier, so this provides the mathematical rationale as to what is happening in the sequence.

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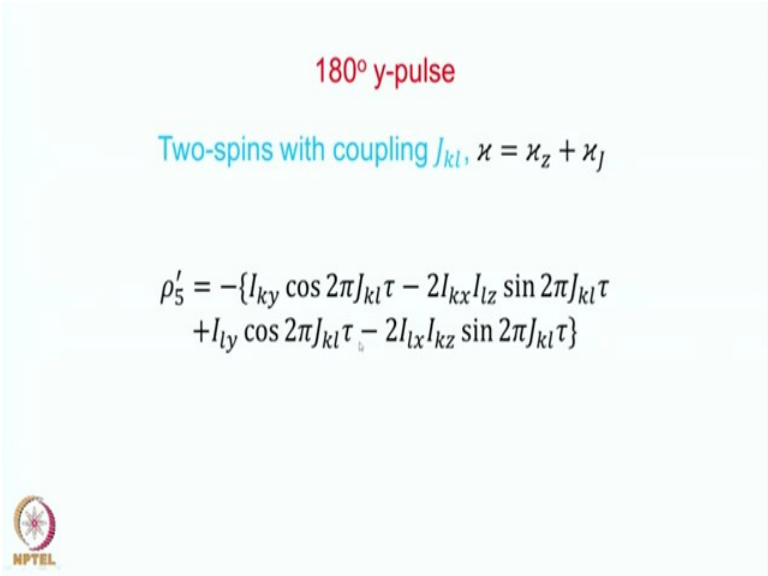

Now let us consider the next case where you have two spins with coupling J_{kl}, now we have $H_Z + H_J$ then is the Hamiltonian now, now we have seen before that the chemical shift is completely refocused at timepoint 5, so therefore we need not calculate the chemical shift evolution once more here because you remember we said evolution under the H_Z and $H_J$can be calculated independently it does not matter which one will calculate first which one will calculate second it does not matter at all.

Now we have assume, that we have already calculated the chemical shift evolution under the chemical shift the influence of the Zeeman Hamiltonian therefore we do not need to calculate that once more we straight away take that result here the$\rho_5 = -(I_{ky} + I_{ly})$, therefore we start from there and now we calculate the evolution under the coupling Hamiltonian.

So, this is the first term there gives me

$$\rho_5' = -\{I_{ky}\cos 2\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin 2\pi J_{kl}\tau + I_{ly}\cos 2\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin 2\pi J_{kl}\tau\}$$

why do we take $2\pi J_{kl}\tau$ now because I am evolving for the whole time period to τ, so I did not evolve under the coupling before therefore I am now evolving for the whole period 2τ. therefore, I get here

$$\rho_5' = -\{I_{ky}\cos 2\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin 2\pi J_{kl}\tau + I_{ly}\cos 2\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin 2\pi J_{kl}\tau\}$$

So, therefore that was the simplest case we could calculate the evolution under the coupling in a simplified manner we do not need to calculate the coupling the chemical shift evolution once more we can assume that we have already calculated and simply calculate the evolution under the coupling, the 180 pulse is applied to both the spins.

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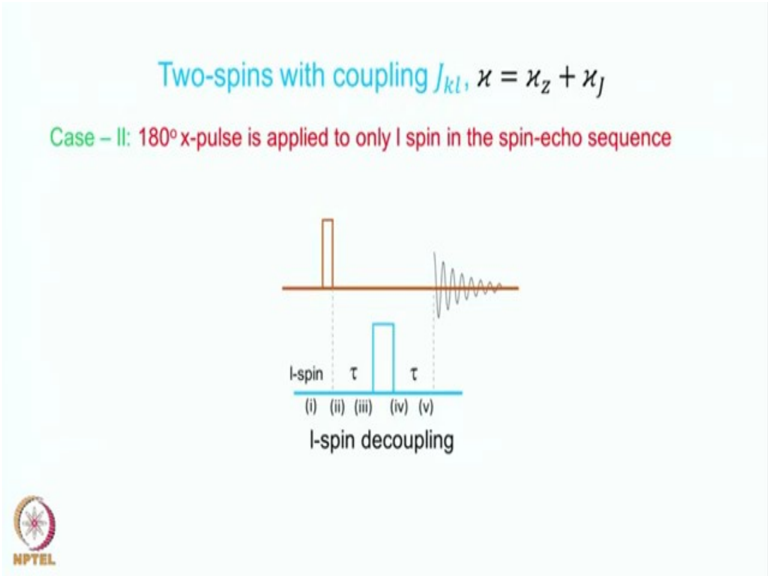

Now we consider the next case which is case 2, here the 180 degree pulse is applied only to the *l* spin noticed the pulse sequence here we have the *l* spin channel here and here is the *k* spin well this is also this is the *k* spin however this is the hard pulse which may be applied to both the channels but to the *l* spin we apply only the 180 degree pulse.

So if you consider this as applying only to the *k* spin then of course we have this nut we are applying the first pulse to both the spins then we will of course also will have a 90 degree pulse here when we say 180 pulse is applied only exclusively to this, so we could in principle say that in this calculation we have calculated it assuming that we have applied the initial 90 degree pulse to both the spins.

So we can add that here that so the first 90 degree pulse is applied to both the spins therefore both are exited and then we have the evolution going on under the influence of the coupling Hamiltonian, we could have done this experiment this way as well in which case of course we apply the pulse only to the *k* spin we need not calculate the evolution of the *l* spin magnetization here because *l* spin magnetization does it exist here, so if we have this pulse also then we have generated both then we can have the evolution of the *l* spin as well going on. So, therefore both are correct in you can choose which over way you want to do it,

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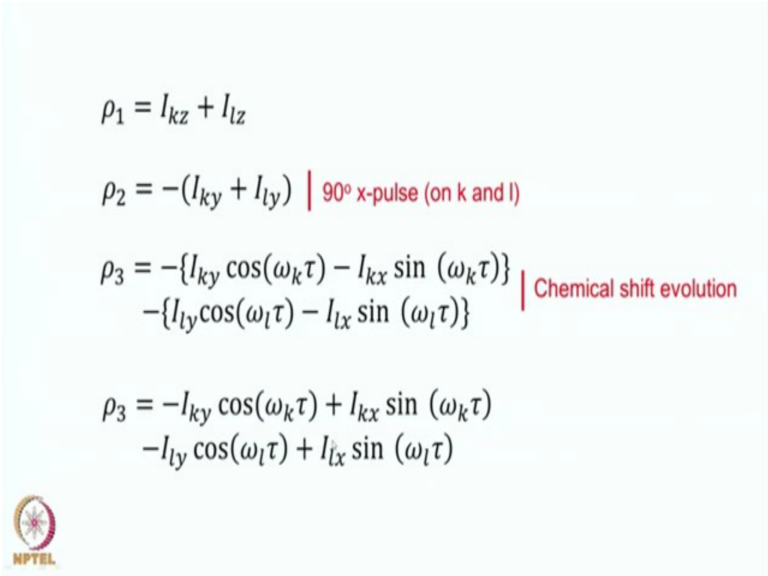

So here we have considered both the spins and therefore we said the

$$\rho_2 = -(I_{ky} + I_{ly})$$

the first 90 degree pulse is applied to both the spins and on *k* and *l* therefore we have this one now. Now what is ρ_3, is minus the evolution now under the chemical shift

$$\rho_3 = -\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\}$$
$$-\{I_{ly}\cos(\omega_l\tau) - I_{lx}\sin(\omega_l\tau)\}$$

So put it expand it and rearrange it properly and we have

$$\rho_3 = -I_{ky}\cos(\omega_k\tau) + I_{kx}\sin(\omega_k\tau)$$
$$-I_{ly}\cos(\omega_l\tau) + I_{lx}\sin(\omega_l\tau)$$

so then now you see here there four terms this ρ_3 has four terms now each on them we will have to evolve under the coupling.

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$$\rho_3' = -\cos(\omega_k\tau)\{I_{ky}\cos\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\}$$
$$+\sin\ (\omega_k\tau)\ \{I_{kx}\cos\pi J_{kl}\tau + 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\}$$
$$-\cos(\omega_l\tau)\ \{I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\}$$
$$+\sin\ (\omega_l\tau)\{I_{lx}\cos\pi J_{kl}\tau + 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}$$

$$\rho_4 = -\cos(\omega_k\tau)\{I_{ky}\cos\pi J_{kl}\tau + 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\}$$
$$+\sin\ (\omega_k\tau)\ \{I_{kx}\cos\pi J_{kl}\tau - 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\}$$
$$-\cos(\omega_l\tau)\ \{-I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\}$$
$$+\sin\ (\omega_l\tau)\{I_{lx}\cos\pi J_{kl}\tau - 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}$$

180° x-pulse (on l only)

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So, therefore ρ_3' will now evolve under the coupling to ρ_3' gives the result after the coupling evolution, so the first term here gives you this coefficient remains the same, so we have here

$$\rho_3' = -\cos(\omega_k\tau)\{I_{ky}\cos\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\}$$
$$+\sin\ (\omega_k\tau)\ \{I_{kx}\cos\pi J_{kl}\tau + 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\}$$
$$-\cos(\omega_l\tau)\ \{I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\}$$
$$+\sin\ (\omega_l\tau)\{I_{lx}\cos\pi J_{kl}\tau + 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}$$

So, therefore the result is now we have a total of 8 terms here, let us rewrite this in a making some rearrangements so the ρ_3 is now after 180 degree *x* pulse now that is after the on the *l* spin only, so ρ_3' was after the coupling evolution 8 terms are there and now we apply 180 degree *x* pulse only on *l*.

So therefore what happens there is no pulse applied here so this remains the same this term remains the same and here again I_{kx} nothing happens *k* spin but the *l* spin 180 degree pulse is applied so therefore this I_{lz} goes to -I_{lz} and therefore this becomes plus here, so this gives you $2I_{kx}I_{lx}\sin\pi J_{kl}\tau$ that remains the put in different colour for that reason.

Now, once again here nothing happens to this term on this term I_{lz} goes to -I_{lz} and therefore this gives me

$$
\begin{aligned}
\rho_4 = &-\cos(\omega_k\tau)\{I_{ky}\cos\pi J_{kl}\tau + 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\} \\
&+\sin\ (\omega_k\tau)\{I_{kx}\cos\pi J_{kl}\tau - 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\} \\
&-\cos(\omega_l\tau)\{-I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\} \\
&+\sin\ (\omega_l\tau)\{I_{lx}\cos\pi J_{kl}\tau - 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}
\end{aligned}
$$

Now therefore you rewrite this as 8 different terms right we have now 8 terms here each one them we have expand it we have 8 terms.

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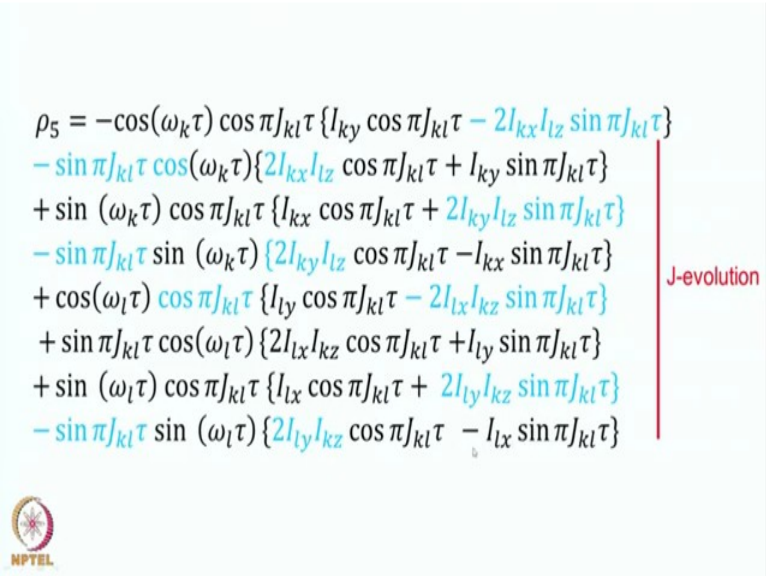

Now, what we do each one those 8 terms we have to evolved under the *J* coupling, because the *J* coupling is present during the next tau period so this each one those we now evolve so this is

$$
\begin{aligned}
\rho_5 = &-\cos(\omega_k\tau)\cos\pi J_{kl}\tau\{I_{ky}\cos\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\cos(\omega_k\tau)\{2I_{kx}I_{lz}\cos\pi J_{kl}\tau + I_{ky}\sin\pi J_{kl}\tau\} \\
&+\sin\ (\omega_k\tau)\cos\pi J_{kl}\tau\{I_{kx}\cos\pi J_{kl}\tau + 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\sin\ (\omega_k\tau)\{2I_{ky}I_{lz}\cos\pi J_{kl}\tau - I_{kx}\sin\pi J_{kl}\tau\} \\
&+\cos(\omega_l\tau)\cos\pi J_{kl}\tau\{I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\} \\
&+\sin\pi J_{kl}\tau\cos(\omega_l\tau)\{2I_{lx}I_{kz}\cos\pi J_{kl}\tau + I_{ly}\sin\pi J_{kl}\tau\} \\
&+\sin\ (\omega_l\tau)\cos\pi J_{kl}\tau\{I_{lx}\cos\pi J_{kl}\tau + 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\sin\ (\omega_l\tau)\{2I_{ly}I_{kz}\cos\pi J_{kl}\tau - I_{lx}\sin\pi J_{kl}\tau\}
\end{aligned}
$$

In these cases, you should remember that summary of the evolution which I had given earlier because it is all what I am using here those summary equations which are there for the evolution under the coupling and evolution under chemical shift is what is being used. The third term gives you

$$
\begin{aligned}
\rho_5 = & -\cos(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{ky}\cos\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\} \\
& - \sin\pi J_{kl}\tau\cos(\omega_k\tau)\{2I_{kx}I_{lz}\cos\pi J_{kl}\tau + I_{ky}\sin\pi J_{kl}\tau\} \\
& + \sin\ (\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{kx}\cos\pi J_{kl}\tau + 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\} \\
& - \sin\pi J_{kl}\tau\sin\ (\omega_k\tau)\,\{2I_{ky}I_{lz}\cos\pi J_{kl}\tau - I_{kx}\sin\pi J_{kl}\tau\} \\
& + \cos(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\} \\
& + \sin\pi J_{kl}\tau\cos(\omega_l\tau)\,\{2I_{lx}I_{kz}\cos\pi J_{kl}\tau + I_{ly}\sin\pi J_{kl}\tau\} \\
& + \sin\ (\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{lx}\cos\pi J_{kl}\tau + 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\} \\
& - \sin\pi J_{kl}\tau\sin\ (\omega_l\tau)\,\{2I_{ly}I_{kz}\cos\pi J_{kl}\tau - I_{lx}\sin\pi J_{kl}\tau\}
\end{aligned}
$$

This is at the end of *J* evolution from the after the 180 degree pulse, so this is adjust before the spin echo at the time of the spin echo.

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$$
\begin{aligned}
\rho_5 = & -\cos(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{ky}\cos\pi J_{kl}\tau - \cancel{2I_{kx}I_{lz}\sin\pi J_{kl}\tau}\} \\
& - \sin\pi J_{kl}\tau\cos(\omega_k\tau)\{\cancel{2I_{kx}I_{lz}\cos\pi J_{kl}\tau} + I_{ky}\sin\pi J_{kl}\tau\} \\
& + \sin\ (\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{kx}\cos\pi J_{kl}\tau + \cancel{2I_{ky}I_{lz}\sin\pi J_{kl}\tau}\} \\
& - \sin\pi J_{kl}\tau\sin\ (\omega_k\tau)\,\{\cancel{2I_{ky}I_{lz}\cos\pi J_{kl}\tau} - I_{kx}\sin\pi J_{kl}\tau\} \\
& + \cos(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{ly}\cos\pi J_{kl}\tau - \cancel{2I_{lx}I_{kz}\sin\pi J_{kl}\tau}\} \\
& + \sin\pi J_{kl}\tau\cos(\omega_l\tau)\,\{\cancel{2I_{lx}I_{kz}\cos\pi J_{kl}\tau} + I_{ly}\sin\pi J_{kl}\tau\} \\
& + \sin\ (\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{lx}\cos\pi J_{kl}\tau + \cancel{2I_{ly}I_{kz}\sin\pi J_{kl}\tau}\} \\
& - \sin\pi J_{kl}\tau\sin\ (\omega_l\tau)\,\{\cancel{2I_{ly}I_{kz}\cos\pi J_{kl}\tau} - I_{lx}\sin\pi J_{kl}\tau\}
\end{aligned}
$$

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Now, let us rearrange this and look at this terms which actually tend to cancel, now we notice here that earlier which I put it all inside colour and now I put the same in the red colour, and say this terms cancel, this cancels with this so we have here plus and here it is a minus and therefore this terms cancels this remains and similarly here this terms cancels with this term

$$\begin{aligned}
\rho_5 = &-\cos(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{ky}\cos\pi J_{kl}\tau - \cancel{2I_{kx}I_{lz}\sin\pi J_{kl}\tau}\} \\
&-\sin\pi J_{kl}\tau\cos(\omega_k\tau)\{\cancel{2I_{kx}I_{lz}\cos\pi J_{kl}\tau} + I_{ky}\sin\pi J_{kl}\tau\} \\
&+\sin\,(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{kx}\cos\pi J_{kl}\tau + \cancel{2I_{ky}I_{lz}\sin\pi J_{kl}\tau\}} \\
&-\sin\pi J_{kl}\tau\sin\,(\omega_k\tau)\,\{\cancel{2I_{ky}I_{lz}\cos\pi J_{kl}\tau} - I_{kx}\sin\pi J_{kl}\tau\} \\
&+\cos(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{ly}\cos\pi J_{kl}\tau - \cancel{2I_{lx}I_{kz}\sin\pi J_{kl}\tau\}} \\
&+\sin\pi J_{kl}\tau\cos(\omega_l\tau)\,\{\cancel{2I_{lx}I_{kz}\cos\pi J_{kl}\tau} + I_{ly}\sin\pi J_{kl}\tau\} \\
&+\sin\,(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{lx}\cos\pi J_{kl}\tau + \cancel{2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}} \\
&-\sin\pi J_{kl}\tau\sin\,(\omega_l\tau)\,\{\cancel{2I_{ly}I_{kz}\cos\pi J_{kl}\tau} - I_{lx}\sin\pi J_{kl}\tau\}
\end{aligned}$$

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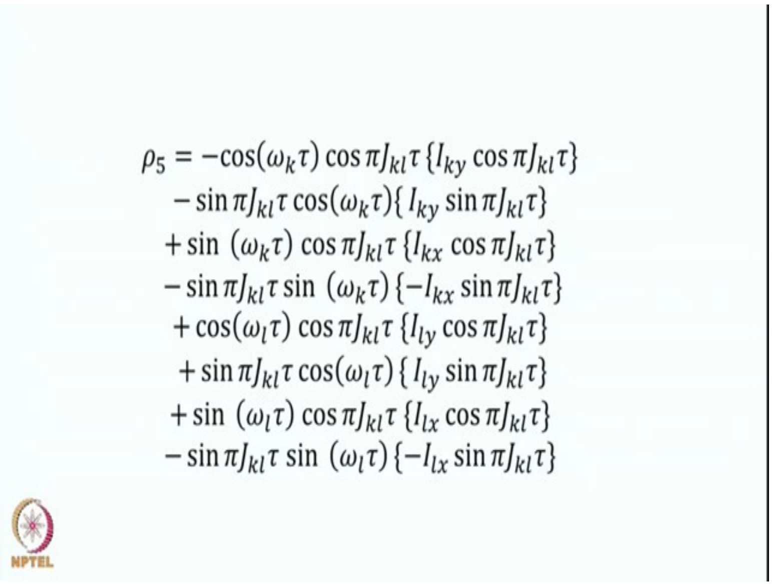

$$\begin{aligned}
\rho_5 = &-\cos(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{ky}\cos\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\cos(\omega_k\tau)\{I_{ky}\sin\pi J_{kl}\tau\} \\
&+\sin\,(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{kx}\cos\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\sin\,(\omega_k\tau)\,\{-I_{kx}\sin\pi J_{kl}\tau\} \\
&+\cos(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{ly}\cos\pi J_{kl}\tau\} \\
&+\sin\pi J_{kl}\tau\cos(\omega_l\tau)\,\{I_{ly}\sin\pi J_{kl}\tau\} \\
&+\sin\,(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{lx}\cos\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\sin\,(\omega_l\tau)\,\{-I_{lx}\sin\pi J_{kl}\tau\}
\end{aligned}$$

So, now therefore half of the terms are canceled. So let us pull together the other terms and we have now the

$$\begin{aligned}
\rho_5 = &-\cos(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{ky}\cos\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\cos(\omega_k\tau)\{I_{ky}\sin\pi J_{kl}\tau\} \\
&+\sin\,(\omega_k\tau)\cos\pi J_{kl}\tau\,\{I_{kx}\cos\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\sin\,(\omega_k\tau)\,\{-I_{kx}\sin\pi J_{kl}\tau\} \\
&+\cos(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{ly}\cos\pi J_{kl}\tau\} \\
&+\sin\pi J_{kl}\tau\cos(\omega_l\tau)\,\{I_{ly}\sin\pi J_{kl}\tau\} \\
&+\sin\,(\omega_l\tau)\cos\pi J_{kl}\tau\,\{I_{lx}\cos\pi J_{kl}\tau\} \\
&-\sin\pi J_{kl}\tau\sin\,(\omega_l\tau)\,\{-I_{lx}\sin\pi J_{kl}\tau\}
\end{aligned}$$

So therefore now you see we have the operator terms are either I_{ky} I_{kx} or I_{ly} I_{lx} and then we have the various coefficients for those, so we pooled together all those which belong to particular operators and then we get this.

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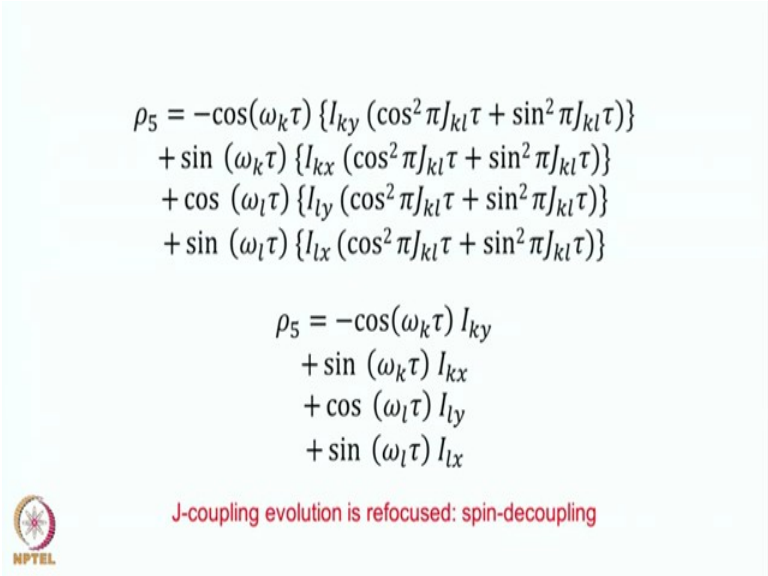

So, here what we have is the coefficient of I_{ky}, so I_{ky} is this operator which was there and we pooled together those terms which have I_{ky}, so here we

$$\begin{aligned}\rho_5 = -\cos(\omega_k\tau)\,\{I_{ky}\,(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}\\ +\sin\,(\omega_k\tau)\,\{I_{kx}\,(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}\\ +\cos\,(\omega_l\tau)\,\{I_{ly}\,(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}\\ +\sin\,(\omega_l\tau)\,\{I_{lx}\,(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}\end{aligned}$$

Now notice everything that is present inside the bracket is on 1 therefore it simply it simply equal to 1, therefore I have only have this terms remaining.

So $\cos\omega_k\tau\, I_{ky} + \sin\omega_k\tau\, I_{kx} + \cos\omega_l\tau\, I_{ly} + \sin\omega_l\tau\, I_{lx}$ now where is the coupling therefore the coupling is all vanished all the terms which contains the coupling information have vanished. So, therefore we say the J coupling evolution is refocused in other words this is called as spin decoupling, so if I apply a 180 degree pulse only on one of the spins then it results in spin decoupling.

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$$\rho_5' = -\cos(\omega_k\tau)\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\}$$
$$+\sin(\omega_k\tau)\{I_{kx}\cos(\omega_k\tau) + I_{ky}\sin(\omega_k\tau)\}$$
$$+\cos(\omega_l\tau)\{I_{ly}\cos(\omega_l\tau) - I_{lx}\sin(\omega_l\tau)\}$$
$$+\sin(\omega_l\tau)\{I_{lx}\cos(\omega_l\tau) + I_{ly}\sin(\omega_l\tau)\}$$

Chemical shift evolution

$$\rho_5' = -\cos(\omega_k\tau)\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\}$$
$$+\sin(\omega_k\tau)\{I_{kx}\cos(\omega_k\tau) + I_{ky}\sin(\omega_k\tau)\}$$
$$+\cos(\omega_l\tau)\{I_{ly}\cos(\cancel{\omega_l}\tau) - \xcancel{I_{lx}\sin(\omega_l\tau)}\}$$
$$+\sin(\omega_l\tau)\{\xcancel{I_{lx}\cos(\omega_l\tau)} + I_{ly}\sin(\cancel{\omega_l}\tau)\}$$

$$\rho_5 = -\cos(\omega_k\tau)\{I_{ky}(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}$$
$$+\sin(\omega_k\tau)\{I_{kx}(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}$$
$$+\cos(\omega_l\tau)\{I_{ly}(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}$$
$$+\sin(\omega_l\tau)\{I_{lx}(\cos^2\pi J_{kl}\tau + \sin^2\pi J_{kl}\tau)\}$$

$$\rho_5 = -\cos(\omega_k\tau)\,I_{ky}$$
$$+\sin(\omega_k\tau)\,I_{kx}$$
$$+\cos(\omega_l\tau)\,I_{ly}$$
$$+\sin(\omega_l\tau)\,I_{lx}$$

J-coupling evolution is refocused: spin-decoupling

$$
\begin{aligned}
\rho_3' = &-\cos(\omega_k\tau)\{I_{ky}\cos\pi J_{kl}\tau - 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\}\\
&+\sin(\omega_k\tau)\{I_{kx}\cos\pi J_{kl}\tau + 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\}\\
&-\cos(\omega_l\tau)\{I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\}\\
&+\sin(\omega_l\tau)\{I_{lx}\cos\pi J_{kl}\tau + 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}
\end{aligned}
$$

$$
\begin{aligned}
\rho_4 = &-\cos(\omega_k\tau)\{I_{ky}\cos\pi J_{kl}\tau + 2I_{kx}I_{lz}\sin\pi J_{kl}\tau\}\\
&+\sin(\omega_k\tau)\{I_{kx}\cos\pi J_{kl}\tau - 2I_{ky}I_{lz}\sin\pi J_{kl}\tau\}\\
&-\cos(\omega_l\tau)\{-I_{ly}\cos\pi J_{kl}\tau - 2I_{lx}I_{kz}\sin\pi J_{kl}\tau\}\\
&+\sin(\omega_l\tau)\{I_{lx}\cos\pi J_{kl}\tau - 2I_{ly}I_{kz}\sin\pi J_{kl}\tau\}
\end{aligned}
$$

180° x-pulse (on I only)

So, we can do this calculation for evolution for with the initial 90 degree pulse applied to 1 spin only then also we can do the same calculation, but we have since we have included both it is actually more general, now we notice one thing in the previous case we after the ρ_4 that is after this point we calculated the *J* evolution, so we switched the order of the evolutions earlier we have calculating the chemical shift evolution first and then the *J* evolution now we have done the *J* evolution and then we are going to do chemical shift evolution now.

So after this term we will now do chemical shift evolution because here I am demonstrating to you that we can actually switch the order of chemical shift evolution and coupling evolution and that is what we have done here. So, now after the ρ_5 I now calculate the chemical shift evolution, chemical shift evolution gives me therefore

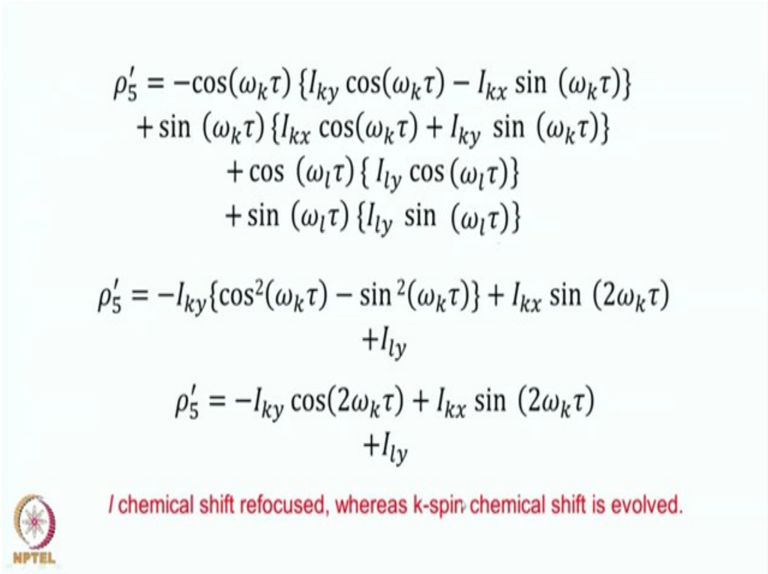
$$
\begin{aligned}
\rho_5' = &-\cos(\omega_k\tau)\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\}\\
&+\sin(\omega_k\tau)\{I_{kx}\cos(\omega_k\tau) + I_{ky}\sin(\omega_k\tau)\}\\
&+\cos(\omega_l\tau)\{I_{ly}\cos(\omega_l\tau) - I_{lx}\sin(\omega_l\tau)\}\\
&+\sin(\omega_l\tau)\{I_{lx}\cos(\omega_l\tau) + I_{ly}\sin(\omega_l\tau)\}
\end{aligned}
$$

So this is for the last τ period this is the after the 180 degree pulse we evolve for the next τ period under the influence of the chemical shift evolution, so now you see what happens you look at the terms once more ρ_5' this part we leave it as it is but notice here there is a cancellation, so this term

$$
\begin{aligned}
\rho_5' = & -\cos(\omega_k\tau)\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\} \\
& + \sin(\omega_k\tau)\{I_{kx}\cos(\omega_k\tau) + I_{ky}\sin(\omega_k\tau)\} \\
& + \cos(\omega_l\tau)\{I_{ly}\cos(\omega_l\tau) - \cancel{I_{lx}\sin(\omega_l\tau)}\} \\
& + \sin(\omega_l\tau)\cancel{\{I_{lx}\cos(\omega_l\tau)} + I_{ly}\sin(\omega_l\tau)\}
\end{aligned}
$$

and this two terms will cancel because this is the chemical shift evolution of the l spin therefore the l spin must have the $\omega_l$as the evolution and then we can see that this terms will cancel and what will happen to this this is cosine ω_l^2square omega square l τ.

(Refer Slide Time: 24:06)



So what we get

$$
\begin{aligned}
\rho_5' = & -\cos(\omega_k\tau)\{I_{ky}\cos(\omega_k\tau) - I_{kx}\sin(\omega_k\tau)\} \\
& + \sin(\omega_k\tau)\{I_{kx}\cos(\omega_k\tau) + I_{ky}\sin(\omega_k\tau)\} \\
& + \cos(\omega_l\tau)\{I_{ly}\cos(\omega_l\tau)\} \\
& + \sin(\omega_l\tau)\{I_{ly}\sin(\omega_l\tau)\}
\end{aligned}
$$

this both have the same sign this minus minus plus and this is also plus.

So therefore your ρ_5' is

$$
\rho_5' = -I_{ky}\{\cos^2(\omega_k\tau) - \sin^2(\omega_k\tau)\} + I_{kx}\sin(2\omega_k\tau) + I_{ly}
$$

So, this is substantially simplified now what we have here this is

$$\rho_5' = -I_{ky}\cos(2\omega_k\tau) + I_{kx}\sin\ (2\omega_k\tau)$$
$$+I_{ly}$$

So the *k* spin has evolve under the chemical shift whereas the *l* spin chemical shift also is refocused you do not see any term remaining here which contains ω_l therefore ω when I apply 180 degree pulse only on the *l* spin the *l* spin chemical shift is refocused but the *k* spin chemical shift continues to evolve for the whole period 2τ. Therefore, I have here starting from I_{ky} because $-I_{ky}$ therefore I have inside $I_{ky}\cos 2\omega_k\tau + I_{kx}\sin 2\omega_k\tau$ so *l* chemical shift is refocused whereas *k* spin chemical shift is evolved.

So, therefore to in summary we have seen the different ways of dealing with the spin echo we have done explicit calculation under different conditions when the in the spin echo the 180 degree pulse is applied along the *X* or the *Y* axis what happens when there is only chemical shift evolution when what happens when the 180 pulse is applied on only 1 spin that leads to spin decoupling.

This is the common technique which is used in all multiple experiments for decoupling during the course of the pulse sequence particularly in along the in direct action periods in multi-dimensional NMR spectra, this we will discuss in the detail but we have demonstrated here the general principle as how these things are working and explicitly show me density operator calculation the various terms that evolve under the influence of different Hamiltonians.