NMR Spectroscopy For
Chemists and Biologists
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Lecture No. 37
Observable and Non observable Basis Operators, Spin Echo

So far we have discussed extensively the basis operators, the evolution of the basis operators, which forms the basis for calculating the evolution of the density operator, through a given pulse sequence. Now, we will just take a summary of all of this time evolutions.

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And, I have listed here a few illustrative evolutions and by enlarge we will be using these only, most of the time we will be using these many equations for calculating the evolution of the basis operators. Here, I_{kx} is supposed to represent the in face magnetization of the k spin. And, it evolves under the influence of the chemical shift Hamiltonian H_z for a time t. And, then it gives you

$$I_{kx} \xrightarrow{\mathcal{H}_z} I_{kx}\cos \omega_k t + I_{ky}\sin \omega_k t$$

I_{ky} under the same Hamiltonian for the time t gives you

$$I_{ky} \xrightarrow{\mathcal{H}_z} I_{ky}\cos \omega_k t - I_{kx}\sin \omega_k t$$

Notice, here the change in the sign, depending upon what your basis operator is, you have to be careful with regards to what sign you will get here. This I have written for here k spin, but it can be for any other spin, l spin, m spin, whatever. So, in your density operator expression you may combination of all of this, and then each one of them will evolve with its own characteristic frequencies as are indicated here. Now, Ikx again under the influence of the coupling Hamiltonian for a time t gives you

$$I_{kx} \xrightarrow{\mathcal{H}_J} I_{kx} \cos \pi J_{kl}t + 2I_{ky}I_{lz}\sin \pi J_{kl}t$$

Here, we consider the coupling between the spins k and l, and therefore, we have the coupling constant kl here. If it were a coupling of some other spin k to m, then it will have it coupling constant here as J_{km}. And, here it will be accordingly I_{mz}. So, therefore, depending upon what is coupling one is looking at, then you will have such kind of expressions. If you have multiple couplings, then you have to evolve this step wise.

First under one coupling and second time under the second coupling, but the same equations will be applicable, each term will not be evaluated again for another coupling and so on. So, I_{ky} under the influence of the coupling J_{kl} it gives you

$$I_{ky} \xrightarrow{\mathcal{H}_J} I_{ky} \cos \pi J_{kl}t - 2I_{kx}I_{lz} \sin \pi J_{kl}t$$

Once, again note is the change in the sign here. If, you are starting with kx you get plus here so, starting the ky you get a minus here. This is basically due to the convention you have used of a particular times of rotation, the sense of rotation in your group.

Now, if I had, for example, all these were in phase magnetization of the k spin. We have also treated anti phase magnetization of the k spin. We have the basis operators such as this $2I_{kx}I_{lz}$. Under the influence of coupling Hamiltonian it gives you

$$2I_{kx}I_{lz} \xrightarrow{\mathcal{H}_J} 2I_{kx}I_{lz} \cos \pi J_{kl}t + I_{ky}\sin \pi J_{kl}t$$

We do not need to consider a chemical shift evolution because it will simply similar to what we have here. Wherever there is I_{kx} you are evolving you write, put this equation with other things remains the same. So, we do not need to explicitly write the chemical shift evolution of such a term.

Important thing is the coupling evolution of this. Likewise, $2I_{ky}I_{lz}$ under the influence of the H_J Hamiltonian for time t gives you

$$2I_{ky}I_{lz} \xrightarrow{\mathcal{H}_J} 2I_{ky}I_{lz} \cos \pi J_{kl}t - I_{kx}\sin \pi J_{kl}t$$

Once again, notice the change in the sign. So, in summary essentially it is these set up of equations. By and large we will be using for calculating the evolution of density operator and the corresponding basis operators in any given pulse sequence. Therefore, it simplifies your calculation quite substantially.

And, it is important to remember this equations pretty well, so that we can easily write the evolution of the density operator through a given pulse sequence. Now, so let us move forward. The next thing to see is when you actually calculated the evolution of the density operator, obviously you will be getting a mixture of various basis operators adding together in the summation. Now, we have also seen earlier in the density operator depending upon what sort of elements that are present there when you actually make a measurement some of those ones appearance some of those do not appear.

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Observable and Non-observable Basis Operators

Transverse magnetization ($M_x + iM_y = M^+$) is measured.

The Corresponding operator is $I^+ = I_x + iI_y$ $Tr\{I^+\rho\}$

$Tr\{B_s I^+\} = Tr\{I^+ B_s\} \neq 0$ for B_s to be observable $\rho = \Sigma b_s B_s$

$Tr\{I^+ B_s\}$

So, therefore, when you have such a kind of situation we have to ask a question as to among the various basis operators which will form the density operator, which of these are observable and which of them are non observable? So, what we measure is the transverse magnetization, so which is represented as $M_x + iM_y$ that is M^+ and this is called M^+. This is

also called as raising operator or ladder operator whatever. So, this is what we measure transverse magnetization is what we measure.

This is the x component with magnetization, this y component with magnetization and this is the complex magnetization we measure. And, we have seen earlier that we have to calculate the expectation value of the corresponding operator for such a kind of observable. If this is our observable, the corresponding operator is I^+ which is $I_x + iI_y$. So, then what we have to do, we have to calculate the trace of this operator with the density operator that you might get at the time of detection.

Just before detection what is the density operator, we have to use the trace of that one. So, what we have to calculate for measurement is $Tr\{I^{+}\rho\}$. And, ρ is the density operator just at the time of the detection of your signal. Now, since, $\rho = \sum b_s B_s$. So, we will have to calculate the trace of individual basis operators. To see what basis operators contribute to observable signal and which ones do not. So, that is what is indicated here.

So, you calculate $Tr\{B_s I^{+}\}$. or I notice that this actually is quite symmetric $B_s I^{+}$ is same as $Tr\{I^{+}B_s\}$. It does not matter in which order you put them in. And, then this should be non-zero for B s to be observable. So, these are the condition we have derived earlier. The expectation value has to be non-zero for it to be observable. So, this is the condition. So we are going to be therefore, calculate the traces of this individual basis operators with this I plus operators.

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(i) $B_s = I_{kx}$ (In-phase basis operator)

$Tr\{I_k^+ I_{kx}\} = Tr\{I_{kx}+iI_{ky}\}I_{kx} = Tr\{I_{kx}^2\} + iTr\{I_{ky}I_{kx}\}$

$= Tr\left\{\frac{1}{4}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\right\} + iTr\left\{\frac{1}{4}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\right\}$

$= Tr\left\{\frac{1}{4}\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}\right\} + iTr\left\{\frac{1}{4}\begin{bmatrix}-i & 0\\0 & i\end{bmatrix}\right\}$

$= \frac{1}{2} + 0;$ observable

Let us take few examples here. So, let us first consider $B_s = I_{kx}$. This is the in phase basis operator whose evolution we saw earlier. And, $Tr\{I_k^{+i\,I_{kx}\}i}$. I have taken it k for magnetization here. And, if it were l magnetization we will put l here and so on so of course. So, it is a sum of various spins you will have to take the sum of all of those spins and calculate the trace. But this is enough to demonstrate what sort of the things we are going to get for all the individual spins.

So, $I_k^{+i\,i}$ if write here this is $I_{kx} + iI_{ky}$ that is $I_k^{+i\,i}$. Then I have the I_{kx} here. So, therefore, if I make multiplication here, trace of I_{kx} square that is this and this the first term gives you I_{kx} square and the second term gives you plus I trace of $I_{ky}\,I_{kx}$. So, how do we calculate this since, both are the operators of the same spin. So, what we will do is I will take the individual spin operators here and take a multiplication. So, the trace I_{kx} is half 0 1 1 0. And, therefore, I take square of this I get 1 by 4 here 0 1 1 0 0 1 1 0 plus I trace of 1 by 4 this I_{ky} half 0 minus I 0 is I_{ky} and I_{kx} is again half 0 1 1 0.

So, trace 1 by 4 0 minus I, I 0 0 1 1 0. So, what is this 1 the trace of this what is the trace? Trace is the sum of the diagonal elements. So, therefore, this gives me half, this is 1 plus 1 2. Therefore, this the first term gives me half and the second term gives me 0. Therefore, this is observable because this is non-zero. Therefore, this term this basis operator is observable.

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(ii) $B_s = I_{ky}$ (In-phase basis operator)

$$Tr\{I_k^+ I_{ky}\} = Tr\{I_{kx}+ iI_{ky}\}I_{ky} = i\,Tr\{I_{ky}^2\} + Tr\{I_{kx}I_{ky}\}$$

$$= i\,Tr\left\{\frac{1}{4}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\right\} + Tr\left\{\frac{1}{4}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\right\}$$

$$= i\,Tr\left\{\frac{1}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\right\} + Tr\left\{\frac{1}{4}\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}\right\}$$

$$= \frac{i}{2} + 0;\ \text{observable}$$

Let us look at the second one I_{ky}. So, it do the same thing here $I_k^{+i\,i}$ with I_{ky}. So, $I_{kx} + iI_{ky}\,I_{ky}$. And, therefore, this is i trace I_{ky} square this one here I_{ky} square plus trace $I_{kx}\,I_{ky}$, this one here $I_{kx}\,I_{ky}$. So, use the matrixes again here for I_{ky}, I put here 0 - i, i 0 and for this 1 by 4 0 1 1 0, 0 -

i 0 and we take a multiplication of this. So, here I get I is here and this gives me 1 by 4 I_{ky} square of this obviously is 1.

So, therefore, this is 1 0 0 1 plus trace 1 by 4 *i* 0 0 -*i*.(3) So, again gives me half but, there is a factor *i* is there therefore used $\frac{i}{2}$ and this one gives me 0. None the less it is non-zero and therefore this is observable.

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(iii) $B_s = 2I_{kx}I_{lz}$ (Anti-phase basis operator)

$$\text{Tr}\{I_k^+ 2I_{kx}I_{lz}\} = 2\text{Tr}\{I_{kx}+ iI_{ky}\}I_{kx}I_{lz} = 2\text{Tr}\{I_{kx}^2 I_{lz}\} + 2i\text{Tr}\{I_{ky}I_{kx}I_{lz}\}$$

$$= 2\,\text{Tr}\left\{\frac{1}{8}\begin{bmatrix}1 & 0 \\ 0 & 1\end{bmatrix} \otimes \begin{bmatrix}1 & 0 \\ 0 & -1\end{bmatrix}\right\} + 2i\,Tr\left\{\frac{1}{8}\begin{bmatrix}-i & 0 \\ 0 & i\end{bmatrix} \otimes \begin{bmatrix}1 & 0 \\ 0 & -1\end{bmatrix}\right\}$$

$$= 2\,\text{Tr}\left\{\frac{1}{8}\begin{bmatrix}1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1\end{bmatrix}\right\} + 2i\,Tr\left\{\frac{1}{8}\begin{bmatrix}-i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i\end{bmatrix}\right\}$$

= 0; Non-observable

Now, let us look at this, this is ones again *k* magnetization. But, now it is anti phase with respect to the *l* spin. So, take this Bs is equal *2 I_{kx} I_{lz}* this is anti phase basis operator. Now, doing the same trick so $I_k^{+\ i i}$ here, I have *2 I_{kx} I_{lz}* so therefore I here get 2 trace I_{kx} + iI_{ky} and I_{kx} I_{lz} is here and there 2 I have taken it out. So, then what i get so this gives me I_{kx} square I_{lz} this remains as it is. And this gives me *2 iI_{ky} I_{kx} I_{lz}*. This two are of same spin and this of the different spin notice here.

Therefore, what I have to do calculate this *i* actually have to take the metrics represent of the individual operators here and then take a direct product. So, therefore to evaluate this so, I have here 2 trace and this gives me 1 by 8 because, there are 3 terms here half half half gives me 1 by 8. So, then I_{kx} square is 1 0 0 1 therefore i have here 1 0 0 1. And then I_{lz} is 1 0 0 -1 this is for a different spin notice here. So, let me write that. So, that it becomes clear to you so this is for the *k* spin and this is of the *l* spin.

So, therefore, this is again for the *k* spin and this is of the *l* spin. So, when I do that I take a direct product of this and direct product here. So, I get here 2 trace 1 by 8 1 minus 1 1 -1 all

other terms are 0. And here I have 2 i trace this gives me -i i -i and all other terms are 0. So, therefore, what we get? If I take the trace it is the sum of all the diagonal elements. This is 0 and so also it is 0 here and there the whole thing is 0. So, therefore, notice there is anti-phase magnetization here is not observable. $2 I_{kx} I_{lz}$ is not observable.

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(iv) $B_s = 2I_{ky}I_{lz}$ (Anti-phase basis operator)

$$2\text{Tr}\{I_k^+ I_{ky}I_{lz}\} = 2\text{Tr}\{I_{kx}+iI_{ky}\}I_{ky}I_{lz} = 2i\ \text{Tr}\{I_{ky}^2 I_{lz}\} + 2\text{Tr}\{I_{kx}I_{ky}I_{lz}\}$$

$$= 2i\ \text{Tr}\left\{\frac{1}{8}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\otimes\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\right\} + 2\ Tr\left\{\frac{1}{8}\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}\otimes\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\right\}$$

$$= 2i\ \text{Tr}\left\{\frac{1}{8}\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\end{bmatrix}\right\} + 2\ Tr\left\{\frac{1}{8}\begin{bmatrix}i & 0 & 0 & 0\\ 0 & -i & 0 & 0\\ 0 & 0 & -i & 0\\ 0 & 0 & 0 & i\end{bmatrix}\right\}$$

= 0; Non-observable

Similarly, DQ and ZQ basis operators are non observable. Anti-phase basis operators evolve under J-coupling into observable terms.

Similarly, if i take $2I_{ky}I_{lz}$ which is again anti-phase basis operator of the *k* spin anti phase respect to *l*, so substitute here I_{ky} I_{lz} so, same calculation and you have I_{ky} I_{lz} here so it gives you 2 i trace I_{ky} square I_{lz} plus 2 trace I_{kx} I_{ky} I_{lz}. So, once again we do the same thing here and this is for the *k* spin and this is for the *l* spin and here it is again for the *k* spin and this is for the *l* spin. And, then we take a direct product, take a direct product of these two matrices.

So, I get here1 -1, 1 -1 and here again I get *i -i i -i* and you the trace of this is 0 and the trace of this is also 0. Therefore, this is non observable. So, therefore, I have illustrated here how to calculate whether, particular basis operator is an observable or not. When you have some of various kinds of operator terms in your density operator not all of them contribute your observation. When you make a measurement some terms will gone make contribute to the measurement and some will not.

And those which do not contribute to the measurement you can simply ignore them so for as your signal is concern. Now, if you do a similar exercise for the various operators representing the double quantum and the zero quantum. Then, you will find that they are also non observable. So, however, anti phase basis operators evolve under *J* coupling into observable terms. Now, if you are doing an experiment where at the beginning of detection,

so you have the anti-phase magnetization. And, the anti phase magnetization evolves under coupling as you have seen evolves under coupling into an in phase magnetization here.

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Summary of time evolutions

$$I_{kx} \xrightarrow{\mathcal{H}_z} I_{kx}\cos\omega_k t + I_{ky}\sin\omega_k t$$

$$I_{ky} \xrightarrow{\mathcal{H}_z} I_{ky}\cos\omega_k t - I_{kx}\sin\omega_k t$$

$$I_{kx} \xrightarrow{\mathcal{H}_J} I_{kx}\cos\pi J_{kl}t + 2I_{ky}I_{lz}\sin\pi J_{kl}t$$

$$I_{ky} \xrightarrow{\mathcal{H}_J} I_{ky}\cos\pi J_{kl}t - 2I_{kx}I_{lz}\sin\pi J_{kl}t$$

$$2I_{kx}I_{lz} \xrightarrow{\mathcal{H}_J} 2I_{kx}I_{lz}\cos\pi J_{kl}t + I_{ky}\sin\pi J_{kl}t$$

$$2I_{ky}I_{lz} \xrightarrow{\mathcal{H}_J} 2I_{ky}I_{lz}\cos\pi J_{kl}t - I_{kx}\sin\pi J_{kl}t$$

For example, if you took $2I_{kx}I_{kz}$ it evolves into I_{ky} term here and similarly, $2I_{ky}I_{lz}$ evolves into I_{kx} term here. So, after that evolution is done if you consider the evolution during the detection period and during the signal collection. And, therefore, this will, these terms will then contribute to observable magnetization. This themselves are not observable but, this ones evolves under the coupling into observable magnetization as I_{ky} or I_{kx}. So, therefore, anti-phase of basis operator evolve under J coupling to observable terms.

Therefore, if you are at the beginning detection if he has this anti-phase term and during detection if you do a decoupling of 2 spins then those terms will not be observable. But, if you do not decouple, you allow them to evolve during the detection period under the influence of J coupling then they will contribute to observable magnetization. So, we are now prepared the ground for calculating the evolution of the density operator through any given pulse sequence. What we are now going to do is consider a simple example?
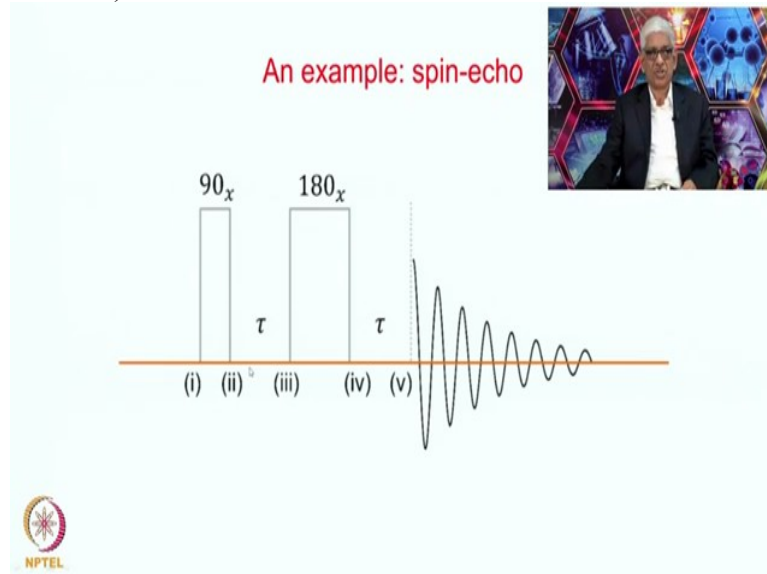
The first example this is the spin echo. This is considered to be one of most crucial and fundamental pulse sequence, which is used in many of the multiple experiments. And, we will now explicitly calculate the evolution of the density operator for this particular pulse sequence, the namely the spin echo. Now, you recall the previous lectures, what is the spin echo sequence? It starts with a 90 degree pulse. And, then there is a tau period, then you have a 180 pulse here and again the same τ period.

And, we said that the magnetization which was decaying here, now it rebuilds and then causes an echo at this point. So, and all the field inhomogenity will be refocused, chemical shifts will be refocused. This is what we said and we are now actually going to explicitly calculate that using the density operator formalism. Now, notice here this phases I have chosen arbitrarily, they can be anything. You can use x or y combination of those and we will take some illustrations of those as well.

We keep for simplicity, for illustration we keep the pulse as $90x$ and we as various time point indicated here. This is time point 1 2 3 4 5, so this is the beginning of the detection period we will do our calculation until this point. We are not going to do a further evolution here this will be normal FID and the data collection happens here. So, we will see the effect of this pulse sequence until this point. Therefore, we evolve the density operator through this steps and reach up to this point.

So, now we consider two spins k and l and without coupling assume to the first case that there is no coupling between there slow spins. So, at time point 1 arrow as ρ_1, what is the density operator is just the sum of the two I_z operators. Because, if you remember the equilibrium density operator was the I_z operator, which is the sum of the magnetization of the two spins.

$$\rho_1 = I_{kz} + I_{lz}$$

Now, if I apply the 90 degree x pulse, then I get the density operator time point 2. This gives me

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

Now, during the next period tau this period evolves under the influence of the chemical shift because there is no coupling. So, we need to consider only chemical shift evolution, so I consider the evolution of the individual these operators here. So, I_{ky} gives me

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

For ready reference I also put that here those if you can see this is the small picture. But, this I hope some of you can see it with good eyes. So you have the x here y here -x here -y here and this is z. ρ_3

So, there is a rotation around the z which is the chemical shift evolution, so I_y goes to $\cos\omega_k\tau$ here, this is this component and this component will be $-I_{kx}\sin\omega_k\tau$ minus. Similarly, for the l spin, so this will be $-I_{ly}\cos\omega_k\tau - I_{lx}\sin\omega_k\tau$. So, this will be the density operated at the time point 3. Now, what I do at this time point, I apply one at a 180 degree x pulse to both the spins. So, 180 degree x pulse what does it do?

This minds remains the same, it shifts I_{ky} to $-I_{ky}$ rotates by 180 degrees. So, it is a rotation from here to here. So, is $-I_{ly}\cos\omega_k t$, this remains the same and it has no effect on I_{kx} and therefore, this remains as $I_{lx}\sin\omega_1\tau$. Similarly, for this I_{ly} goes to $-I_{ly} - I_{ly}\cos\omega_1\tau - I_{lx}\sin\omega_1\tau$, so this is the result of 180 degree pulse. There we now got the density of operator at time point 4 in the pulse sequence.

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

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

Chemical shift evolution

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

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

Chemical shifts are refocused

So, rearranging those terms removes the signs I rewrite this ρ_4 as

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

So, during the next τ period I will have to evolve under the chemical shifts ones more. Again there is no coupling, therefore, evolve under the chemical shifts only. Now, there will be how many terms, each one of this produces one term here. So, it evolves under the chemical shift and so therefore, I will have total of 4 terms. Here there are 4 terms each one I will have to evolve under chemical shift.

So, therefore, $\cos\omega_k\tau$ this remains here, now for this I_{ky} I write here $I_{ky}\cos\omega_k\tau - I_{kx}\sin\omega_k\tau$ plus for this term now, $\sin\omega_k\tau$. And, I will have I_{kx} term here $I_{kx}\cos\omega_k\tau + I_{ky}\sin\omega_k\tau$. Notice the change sign here. So, you have to be careful with that, these are very important. Similarly, now for the l spin this is $\cos\omega_l\tau$ evolve I_{ly} $I_{kx}\cos\omega_l\tau - I_{lx}\sin\omega_l\tau$ and I_{lx} term gives you $\sin\omega_l\tau$ into $I_{lx}\cos\omega_l\tau + I_{ly}\sin\omega_l\tau$

These ones are put in different colours the reason is these ones you cancel out, see here I_{kx} what is these product here $\cos\omega_k\tau\,\sin\omega_k\tau$. And, here it is $\sin\omega_k\tau\,\cos\omega_k\tau$ and the same I_{kx} term. Therefore, this will cancel this term, so maybe I can just indicate that you by explicitly writing at there so this we will cancel this. Similarly, for the I_{ly}, so this will cancel this one. So, then what we are left with. So, we are left with $I_{ky}\cos\omega_l\tau$.

And, this will give me $\sin^2 I_{ky}, I_{ky}\sin^2\omega_k\tau$. That is this here and similarly, for $I_{ly}\cos^2\omega_l\tau + \sin\omega_l\tau$ and obviously this is one and this is also one. And, therefore, I got here ρ_5 this is the density operator timepoint 5, this is $I_{ky} + I_{ly}$ so everything is vanished. All this time dependence is vanished, the frequency dependence is vanished we started with the density operator ρ_1 as $I_{kz} + I_{kx}$.

And after the first 90 degree pulse at - $I_{ky} + I_{ly}$ and I got back $I_{ky} + I_{ly}$. So, the chemical shift evolution is been refocused. Except for the change in the sign here and that of course depend upon what of the sign of the 180 degree pulse. And, accordingly we put at another different minus sign here as well we will also see that later. So, therefore, the chemical shift information is completely refocused we got a back the basic operator as we had in the beginning.

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Two-spins with coupling J_{kl}, $\varkappa = \varkappa_z + \varkappa_J$

Case – I: 180° x-pulse is applied to both k and l spins in the spin-echo sequence

Evolution under $\varkappa_z$ and $\varkappa_J$ can be considered independently

$$\rho_1 = I_{kz} + I_{lz}$$

$$\rho_2 = -(I_{ky} + I_{ly}) \quad \bigg| \; 90° \text{ x-pulse}$$

Since evolution under chemical shift is refocused at the end of the spin-echo, we will calculate only evolution under $\varkappa_J$ through the spin-echo
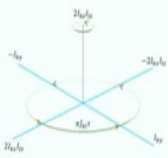
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Now, let us consider a situation when we have the coupling as well. Now, the coupling means when you have to coupling your total Hamiltonian will be $H_Z + H_J$, this is the chemical shift Hamiltonian and this is the chemical Hamiltonian. So, we will consider k is two cases here, case I 180x pulse is applied to both k and l spins in the spin echo sequence. So, therefore evolution under H_Z H_J can be considered independently. And now as before your

$$\rho_1 = I_{kz} + I_{lz}$$

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

Since, evolution under chemical shift is refocused at the end of the spin echo, we will calculate only evolution under H_J through the spin echo. Because, we already shown that chemical shift is refocused, so there we do not need to calculate under the chemical shift again. Therefore, we only calculate the evolution under the coupling constant.

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$$\rho_3' = -(I_{ky} \cos \pi J_{kl}\tau - 2I_{kx}I_{lz} \sin \pi J_{kl}\tau)$$
$$-(I_{ly} \cos \pi J_{kl}\tau - 2I_{lx}I_{kz} \sin \pi J_{kl}\tau) \quad | \text{ J-evolution}$$

$$\rho_4' = -(-I_{ky} \cos \pi J_{kl}\tau + 2I_{kx}I_{lz} \sin \pi J_{kl}\tau)$$
$$-(-I_{ly} \cos \pi J_{kl}\tau + 2I_{lx}I_{kz} \sin \pi J_{kl}\tau) \quad | \begin{array}{l} 180° \text{ x-pulse} \\ \text{on both k and l} \end{array}$$

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

So, therefore, J evolution I put here pictured ones more here $2I_{ky} I_{lz}$ and this is also if you can see clear then you have that indication here as to what terms will you get. So, ρ_3' is the 1 this is the result of J evolution and I kept here I have $-I_{ky} + I_{ly}$. So, the first term gives me

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

this is under the influence of coupling J_{kl} J evolution.

So, now I apply a $180x$ pulse on both k and l. So, this sign minus is same so $180x$ pulse takes me I_{ky} to $-I_{ky}$ so, this remains this and what happens here, I_{kx} does not change l spin is applied it takes I_{lz} to $-I_{lz}$, therefore, this gives me plus here so, therefore, $2 I_{kx} I_{lz} \sin \pi J_{kl}\tau$. And, ones again here $- I_{ly} \cos \pi J_{kl}\tau + 2 I_{lx} I_{kz} \sin \pi J_{kl}\tau$. When, I apply the pulse both spins and this is what I will get. So, simplifying this ρ_4' is

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

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So, now, you will have to evolve under the J evolution evolve ones more after the 180 degree pulse. So, now, each one, each of this term will has to be evolved. So, there are 4 terms here, there will be 4 evolutions therefore. So, therefore, the first term I take away the

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

Now, I am evolving this anti phase term you remember the summary.

So, now, we regroup these terms. So, what I get here I_{ky} cosine cosine gives me cosine square that is the first term here. And then where else is I_{ky}, I_{ky} is present here and this gives me sine and sine, this is sine square $\pi J_{kl}\,\tau$.

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

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

Scalar coupling evolution is not refocused
at the time of spin-echo

Now, what is this inside the bracket? That is

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

Notice therefore, each of the individual spins have the tau dependence in the end. And, the two magnetization components would have separated out in face by this amount, the $2\pi J_{kl}\tau$. Depending upon what the value of tau is, the face separation between the two components of the k spin will be given by this.

And, it also generates here an anti-phase magnetization so this we see. And, this we may not, this is not observable if you, of course, it is over under the coupling later in terms of magnetization. But, if we you are looking at the end of this spin echo. It is just this term which is observable and this is term which is observable. So, scalar coupling evolution is not refocused at the time of spin echo. So, we saw that chemical shift evolution is refocused and the coupling evolution is not refocused.

This is what we also derived by vector picture earlier in our previous classes, very early in the course we had actually derived this. So, we stop here and continue with this discussion in the next class.