Advanced NMR Techniques in Solution and Solid - State

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Lecture - 26
Examples of Coherence Pathway Selection

Welcome all of you. In the last class, we discussed a lot about the coherent transfer pathway selection. First of all, we discussed what is the coherent order, how initial 90 degree pulse which brings the magnetization from thermal equilibrium to XY plane, I said, it creates coherent orders +1 and -1. And for the magnetization in XY plane, any pulse if you apply on that will create higher quantum coherent orders, that is what we discussed. And also as I said, we can choose a particular pathway for a coherence.

For example, if in the one pulse experiment the 90 degree pulse on the magnetization which is along z axis brings it to the XY plane. We have +1 and -1 coherent orders. I can choose only -1 coherent order. We discussed that how to do that; and then this depends upon your pulse phase and the receiver phase, which is very important. Depending upon what the pulse phase you want, to choose a particular coherent pathway, you have to choose the receiver phase accordingly; but then the question is how do you know what is the receiver phase?

For that I gave an expression; the receiver phase is minus of delta p into phi, delta p is the change in the coherence pathway from initial state to final state. You find out what is the initial state; that is P1 and the final state is P2 and difference between these two is delta p. And if you know what is delta p, then you can select a particular coherence pathway. For that you can find out what is the receiver phase, once you know what are your pulse phases. For that we took the example of a simple one pulse experiment, and showed how we can select -1 pathway.

And we saw that the receiver phase and pulse phase are exactly identical for that. If they were different, we also saw signal gets nullified, that was not a right choice. So, we can use the right phase cycling to select the right coherence pathway. We chose for -1 in one pulse

experiment. You may ask me question what about +1 ? how do I choose +1, the same way we can do that.

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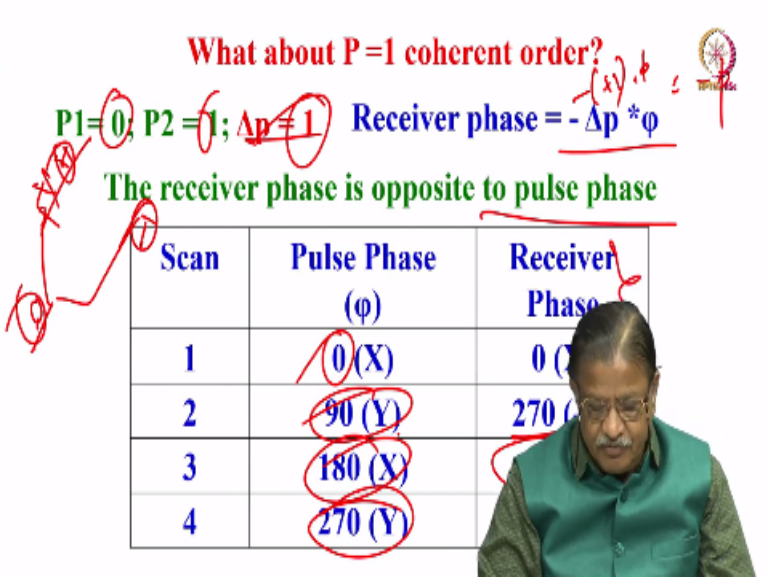

Now, if I want to select the +1 now, 0 and this is +1 and this is -1 state. Now 0 to +1 I take, the initial state is 0 and P2 is +1; now the delta p; is what is my delta p? P2 - P 1 it is +1. So, the receiver phase if you put it minus of minus into +1 into phi; So, it is minus phi. So, the receiver phase is opposite to the pulse phase, if I were to choose +1 coherence pathway, then the receiver phase has to be opposite to the pulse phase, very important thing you should remember.

Now, if my receiver is here, if a pulse is here, the receiver has to be opposite. Then only we can select +1. Earlier for -1 receiver and pulse phase both were going together simultaneously; if receiver was here pulse was here. Here I changed the pulse phase; here receiver also changed here; like that I was doing for -1 coherence pathway selection. It was for -1 coherence pathway of selection. For +1 they have to be opposite. So, let us say I choose for the first time 0 X then this also 0 X in principle, it should go back and come, no it should be a completely opposite. We will see more about it later. If it is 90 then it has to be 270, if it is 180 it has to be -180. There I am just taking the opposite phases, if it is 270 this is 90. What is 0 90 180 you know we have already discussed, what is the pulse phase 0, what is 90, what is 180, what is 270. So, then the receiver phases have to be exactly opposite. Now if I do this, will I select +1 or – 1. Let us see now.

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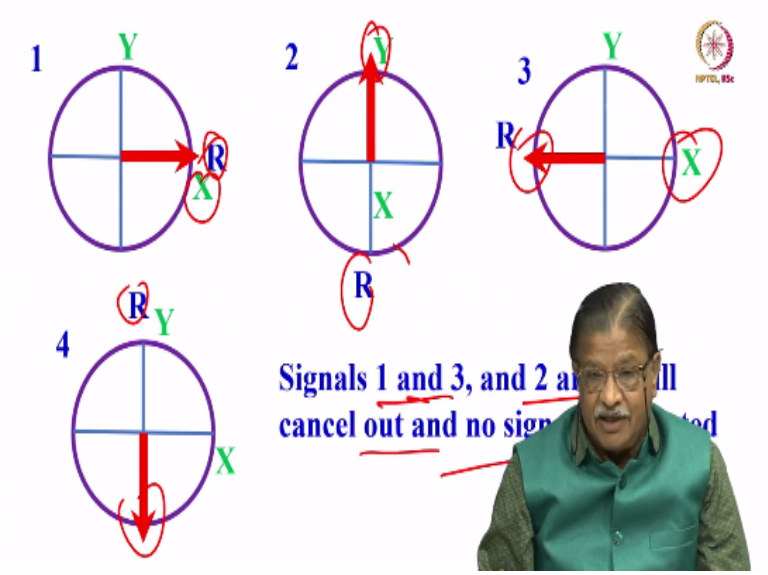

This is the situation, this is the receiver here, pulse is here, receiver is here. Now, pulse is here receiver, they are in the opposite phase; here pulse is here receiver is here. I am sorry pulse and receiver both are here; here receiver is here pulse is here. Now, what is going to happen? signals 1 and 3 and signal 2 and 4 will cancel out, and you do not see any signal at all. So, if you use this 1, we can nullify this 1. We will completely eliminate the signal if we take opposite.

So, in the delta p case what is going to happen is, we can see; if I want to set for delta p, p = 1 coherent order, then we calculate the receiver phase; it is just exactly opposite to that. Then, we saw that in this case, signal 1 and 3 and 2 and 4 will cancel out, or no signal will be detected, depending upon the pulse phases. If the signal is detected in the other channel Y, the same behaviour is expected. That is another important point you should remember.

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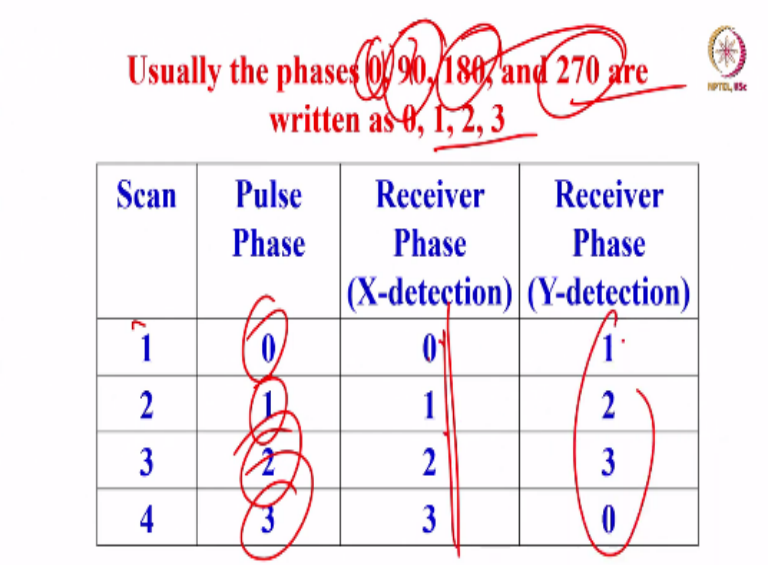

Now usually the phases 0, 90, 180 and 270 are written as 0, 1, 2 and 3; that is what is going to be chosen, that is the way the instrument spectrometer vendors are writing. If I say pulse phase is 0, it is as good as telling 0 degree; if I say pulse phase is 1; it is 90 degree, if pulse phase is 2, it is 180; if it is 3 it is 270. Similarly, the receiver phases 0, 1, 2, 3. Now, the receiver phase if it is the X detection, what if it is detected on the Y axis? what will happen? that is other channel; Two channels are there. I can detect along the X axis or I can detect along Y axis. If I detect Y signal, then exactly they are out of phase at 90 degree, then this will be become 1, this will become 2 this is 3 and this 0, they just undergo phase difference of 90 degrees.

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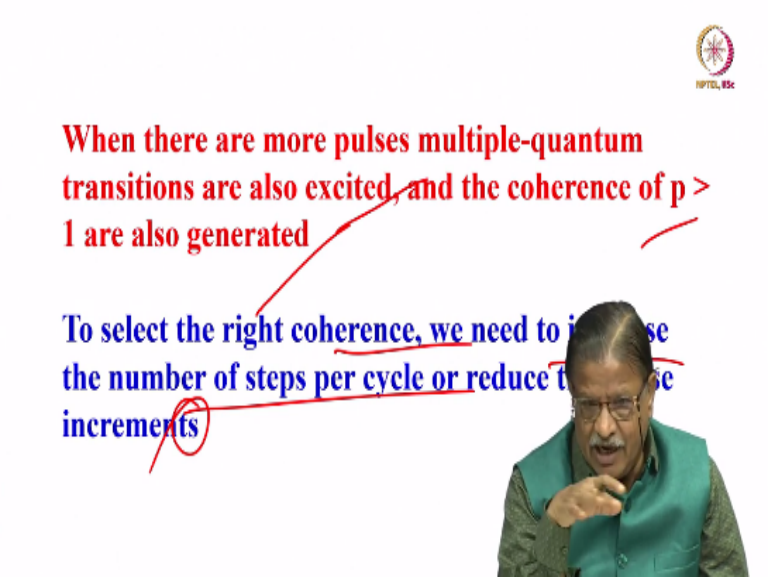

So, when there are more pulses, multiple quanta are also excited and the coherence of p greater than 1 are also generated. To select the right coherence, we need to increase the number of steps per cycle, to reduce the phase increments. That is very important point. When there are more pulses, multiple quantum transitions are excited and of course, signals will be already on the XY plane magnetization already in the XY plane and you apply another pulse then you create higher quantum coherence.

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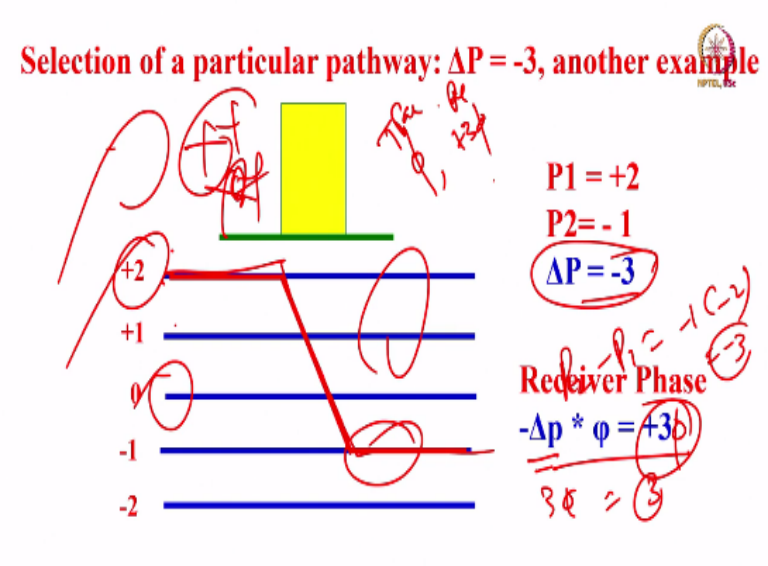

So, a selection of a particular pathway for example, how do I do? I will take an example delta P = -3. I want to see how I can choose this one, like we can choose a particular thing -1, we showed. We can also choose delta P = -3; how do we do that? This is a situation you come across like this, apply an 90 degree pulse. Now, I have several coherent orders; the coherent orders can be -2 to +2 and before it is Z, so the coherent order is 0, I start with 0.

And then after applying the pulse several coherent orders are there; I have created let us say; this is not Z this is already XY, Z means you can create only +1 -1. Since I have created +2 -2 etcetera. The magnetizations is here already in XY plane, there is another pulse behind do not worry. So, now I have created higher quantum coherent orders; I want to select delta P = -3. How do I do that? Now P1 = +2 and P2 = -1; if I take that now, what is my P2 - P1? P 2 - P 1 = -1 minus of 2 = -3, then I can select delta P = -3.

So, I have to choose this pathway see +2 to -1 is the pathway, this coherence pathway if I choose I will get delta P = -3 only. All other things will be rejected; not all I will come to that some multiples of that will come back at that, I let tell you at the end; but anyway if some other thing unwanted will go. Let us put it like that; delta P minus 3 will be selected; for example 2, 1 and other orders will completely get rejected. Now, how do you get the receiver phase now? Delta P = -3.

Now, we put -3 here, minus into – of + 3 into phi = 3. So, 3 phi; so, I know what is the receiver phase, my receiver phase; the transmitter phase is phi and my receiver phase has to be 3 times phi; that is all I have to do. Very simple. Let me clarify to you; in a simple way. See, I am going to choose this pathway.

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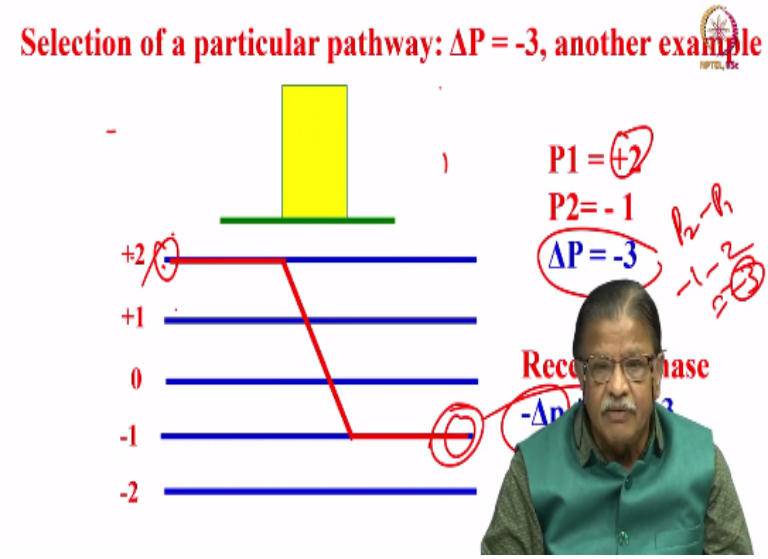

I am going to choose the pathway from +2 to -1. Already this pulse has created, let us say, higher quantum coherent orders, like +2, -2 by up to + 2 to -2, everything is there. When I want to select delta P = -3, I can select from +2 to – 1, + 2 is the initial state P1, and -1 is the final state P2, so P2 – P1 you have to take, then it is -1 minus of 2 = -3. So, delta P = -3 I have chosen. My receiver phase is minus delta P into phi, which is equal to + of 3.

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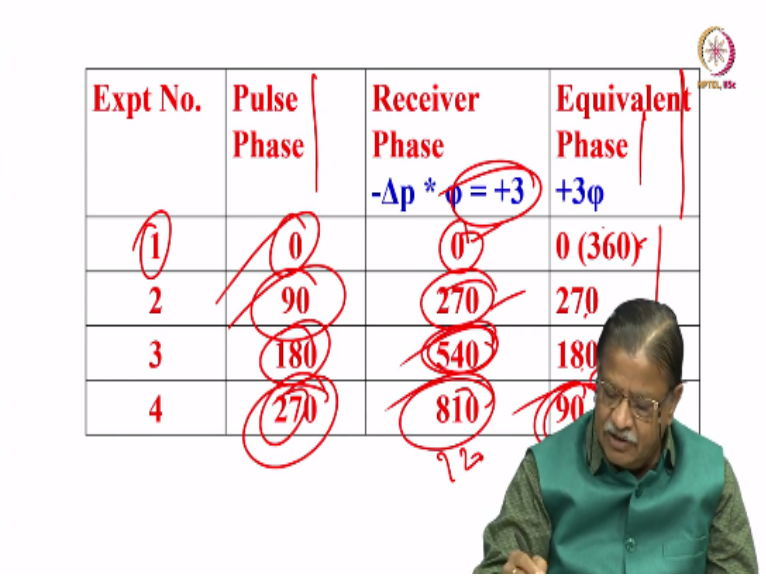

So, now, I choose my pulse phase, that is my choice; first scan, I will choose it as 0. Second scan, I choose it as 90, then 180 and 270. What should be my receiver phase? It should be 3 times that 0, 3 times to 90, 270, then 540 and 270 is 810. What do you mean by telling 810 receiver phase, we have only 360 degree, we can go to +X -X +Y -Y. What do you mean by receiver phase 810? So, simply anything above 360, you are to scale it down to within 360. For example, 0 is okay, 270 is okay. 540 subtract 360 from that; it is going to be 180. 810 subtract 360 + 360= 720 from that, you are going to get 90. So that is all, simple, it is a equivalent phase, although it is 3 times the equivalent phase is 90 only. That is what you have to do. So, now I know the pulse phase, I know the receiver phase which is equivalent of that 0, 270, 180, 90. 0 is nothing but 360 I have taken as 0 is nothing but this thing. So, I did this 3 times of that and it is equivalent phase, and the receiver phase goes in the opposite direction now.

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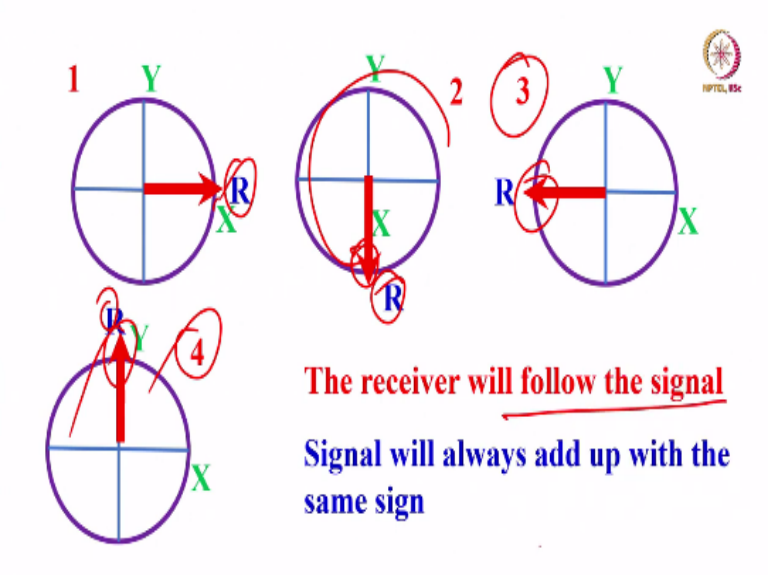

Now, how it goes in the opposite direction? We will see, let us say, this is the receiver phase here, and also my signal is here. Now, when I move this by 3 times my signal comes here and receiver comes here, it is going like this already. Now, I put my signal here in the third case, what happened first it was 0, 270, 540, 0, 90, 180, 270; I am changing the pulse phase only by 90 degrees, but this one I am changing in 3 times that one. So, what is going to happen? the third phase is like this; in the fourth scan receiver is here pulse is also here.

So, what is going to happen? the receiver follows the signal. The signal always add up with the same sign; you are rotating along with this. So, the receiver always will add up along with the signal with the same sign.

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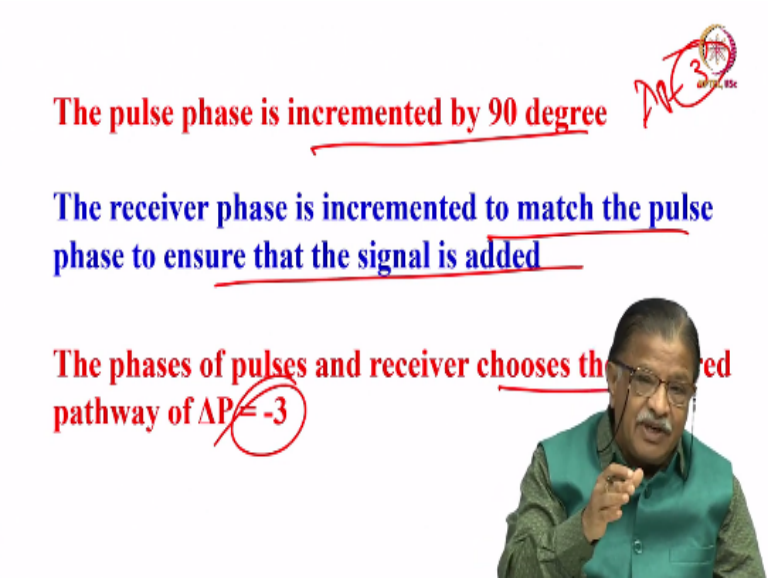

So, the pulse phase is incremented by 90 degree, the receiver phase is also incremented to match the pulse phase to ensure the signal is added up. The phase of the pulses and the receiver chooses the required pathway of delta P = -3; my delta P was -3. Now I have chosen the transmitted pulse phase in such a way and the receiver phase is also 3 times that; and it is it goes in such a way that pulse phase and receiver phase go together. As a consequence, signal gets added up here.

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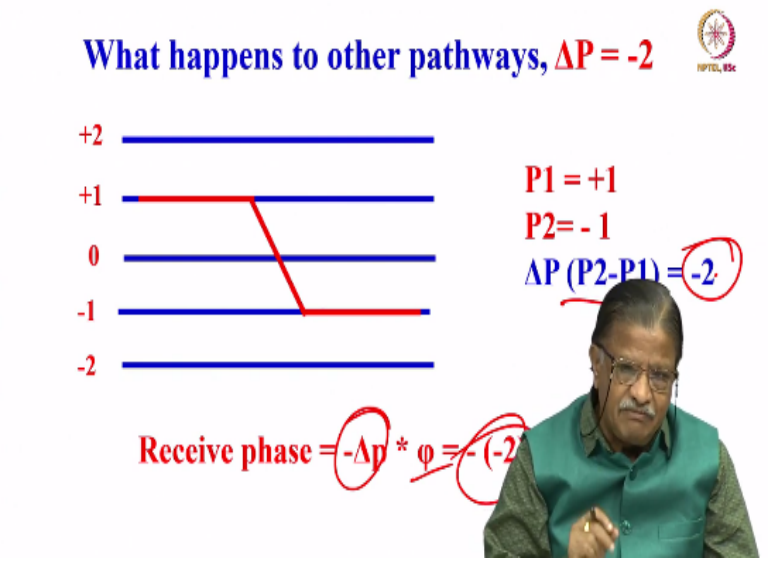

Now what happens to other pathways delta P = -2 will it come through? we will go through with the same phase cycle and let us see. I have the same coherent orders; I want to select -2, -2 is you have to take P1 = +1, P2 = -1, delta P = P2 – P1 which is -2. That is correct. Now, what is my

receiver phase - delta P into phi, - delta P is minus of -2, it is +2 into phi it is 2 phi. I have to select receiver phase twice of the transmitter phase, pulse phase.

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Receive phase = $-\Delta p * \varphi = -(-2) * \varphi = 2\varphi$

Expt No.	Pulse Phase (φ)	Receiver Phase $-\Delta p * \varphi = +2\varphi$	Equivalent Phase $+2\varphi$
1	0	0	0
2	90	180	180
3	180	360	0
4	270	540	180

My pulse phase, if it is 0, receiver phase is 0, 90 180; 180 360; 270 540. Of course, 360 is one full rotation it is nothing but 0; 540 subtract with this it is 180. So, if this is your transmitter pulse phase and the equivalent receiver phase is this 0 180 0 180.

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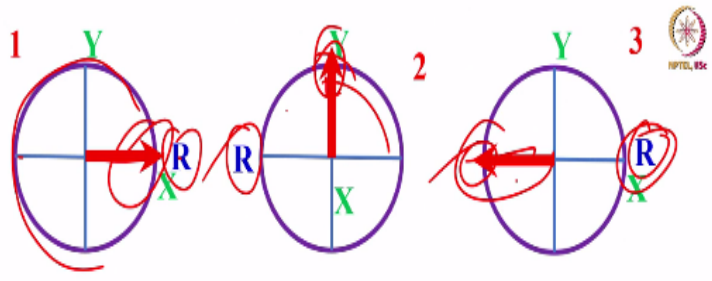

The signal 1 and 3 and 2 and 4 gets cancelled

The phase cycling chosen for $\Delta P = -3$ rejects the signal for $\Delta P = -2$

Now let us see what is happening. In the first case receiver is here. Signal is here. The second case the receiver is here. You shifted. You know it is going like, 0 180 0 180. So, receiver, from

here I moved the receiver here, the signal moved only by 90 degree, transmitter phase, pulse phase is moved by only 90 degree. And now, I move another by 90 degree, but receiver moved by 180 degree. And now, this again moved by 90 degree, but the receiver again came back here.

The receiver I am alternating from 0 180 0 180, that is if it is +X -X +X -X. I am alternately doing that. Whereas, pulse phase I am incrementing in steps of 90 degree regularly. Correct, that is what I have to done. So, what is going to happen now? signal 1 and 3, look at it 1 and 3, they are opposite. If the receiver is here, in this case, the receiver is here, but one signal is here, one signal is opposite. So, you get positive absorption negative absorption whatever you get, signal will get completely nullified, gets cancelled out.

Take this one, 2 and 4, again you get signal once positive here was negative here; they get cancelled. So, in this situation for delta P = 2 if you select delta P = 2, the phase cycling for delta P =-3, will reject this one. It will not take that one; it is the phase cycling for delta P =2 is different than phase cycling for delta P =-3. So, delta P = -3 phase cycling will not choose this because it is different. So, it rejects this signal.

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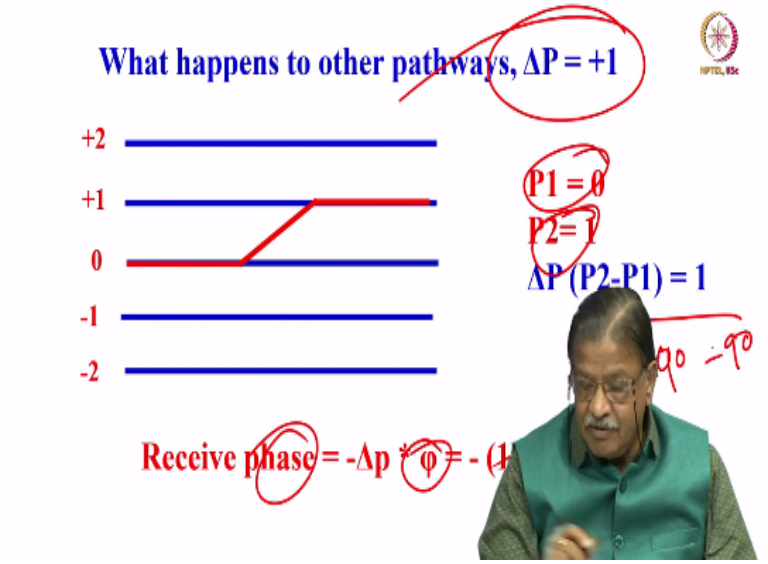

So, that is what is happening. Now, what happens to other pathways there, let us say delta P = +1. If I see delta P = +1, what is going to happen? if it takes 0 to +1, P1 = 0, P2 = +1. So, delta P

= 1. So, pulse phase is exactly opposite, this receiver phase is exactly opposite of the pulse phase. From this equation I calculate if I have my pulse phase is 90 receiver phase is -90.

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For the pathways, $\Delta P = +1$; P2=1, P1=0

Receive phase = $-\Delta p * \varphi = -(1)*\varphi = -\varphi$

Expt No.	Pulse Phase (φ)	Receiver Phase $-\Delta p * \varphi = -\varphi$	Equivalent Phase Rec phase + 360
1	0	0	0 (360)
2	90	-90	270
3	180	-180	180
4	270	-270	90

So, do like that 0, 90, 180, 270 pulse phase, receiver phases this one, the equivalent phase is 0 270 180 90.

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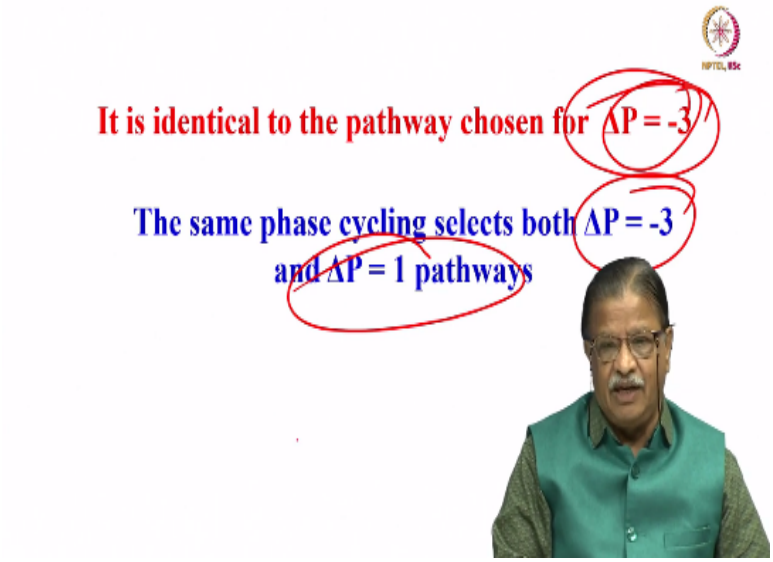

Now, it is identical delta P = -3; something different right. See delta P = 2 it rejects; delta P = -3 is selects that phase cycling. Whereas, now, if I want to see the same phase cycling, if I want to select but delta P = 1 is identical to delta P = -3. This phase cycling is identical to that. So that

means this phase cycling also we will select delta P = 1. So, the phase cycling what we choose for delta P = -3 will also sell the select delta P = 1 both are identical.

Only thing we saw phase cycling for delta P = 2 is different. That is why phase cycling chosen for -3 will not accept that, it will reject that, you will not get that through. To select that delta P = 2 you should have a different phase cycling, you cannot have that. So, as a consequence delta P = -3 will not select that, whereas delta P = -3 phase cycling will also select delta P = +1.

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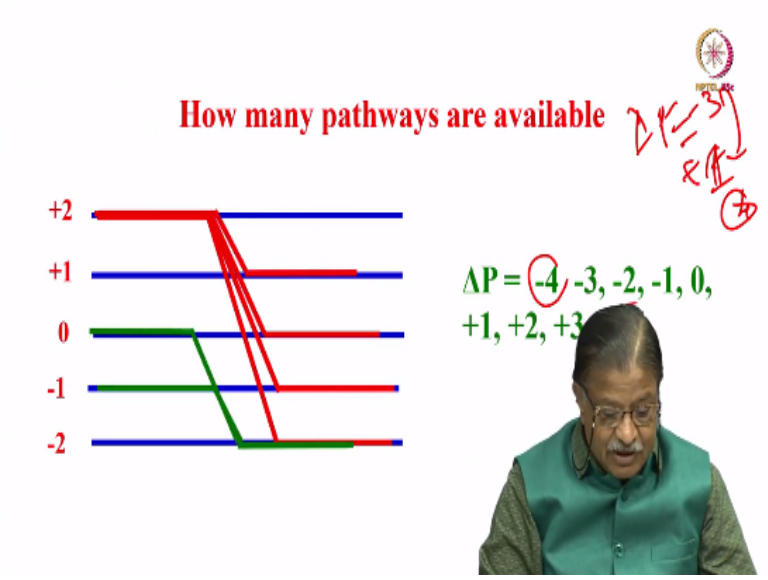

So, now, if I ask you a question, how many such thing I can select? Can I select several pathways, if available? For example, let us say I have + 4 to –4, different coherent orders. delta P = -4 -3 -2 are everything is there, up to +4. Now what are the pathways I can select with the same phase cycling? For the same phase cycling with equal delta P = -3, I also could select delta P = +1. What is the difference between these two? Four, keep this in mind. I will come back to that.

Now, delta P is +2 to -2 is one pathway, delta P is +2 to -1 is one pathway, this is one pathway, this is one pathway and this is one pathway, this is another pathway and like that, several path ways we can see.

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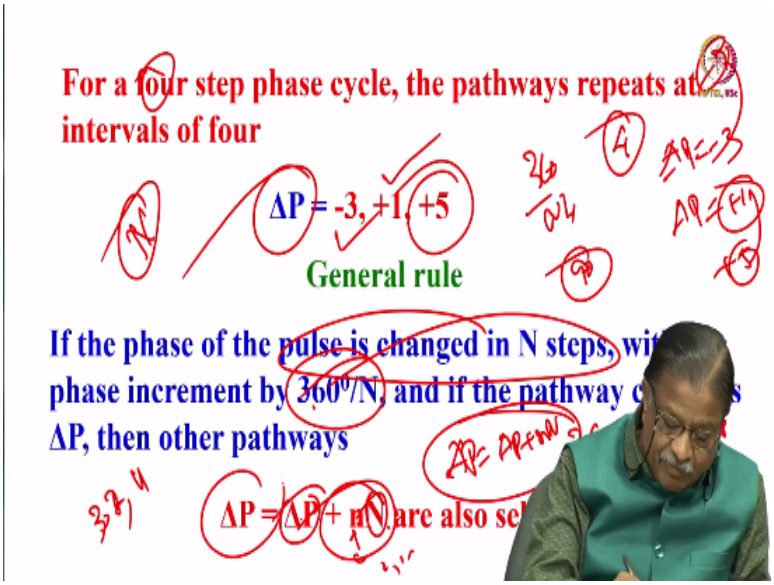

Now, for the first 4 step phase cycling we took, remember, 0. 90, 180, 270, for the pulse phase, 4 steps you took that is called 4 step phase cycling. Now pathway always repeats at intervals of 4; remember, it is a 4 step phase cycling. That is why when I took delta P = -3, I was able to select delta P = +1 also. That is interesting, because in steps of 4, in intervals of 4, it can select all the pathways. Supposing you go to be +5, It would have selected that also because, now, this difference is 4. If there was to be -7, it would have selected that also.

So, for a 4 step phase cycling, the pathway repeats at the intervals of 4, you get this point is very clear. So, now, delta P = -3 is chosen, +1 is chosen and +5 is also, it can select, if there is a coherent order of that +5 or -5 whatever it is; if there is a +5 coherent order you are going to get that. Now, with this we can form a general rule, what is the general rule? If the phase of the pulse is changed in any N steps, that is here we took 4 steps, we take N steps, then with the incremental 360 / N, in my case 360 / N, was N was 4.

So, I changed at the interval of 90 degree, we took as 0, 90, 180, 270 like that, intervals of 90 we change, because 360 is the maximum one cycle you can think of. If I would have N steps of phase cycling at the interval of 360 / N, then the pathway chosen delta P always repeats a delta P + n times N. Meaning now, I will take an example, I have taken a four step for phase cycling. Now, N = 4. Now, delta P if I choose, whatever the value I want, if I take delta P = 3, let us say I choose something like delta P = 3, N = 4.

So, n times 4 that means, n can take value from 0, 1, 2, 3 including minus also. So, n times 4; 1 to 4, 1 into 4. So, that means 3 + 4 is 7 and n = 2, 2 into 4 8, 8 + 3= 11 like that, all other pathways which obey this formula, delta P = delta P + n into N are also chosen. This is the important point; if you want to select the phase cycling; with the N step phase cycling the N steps correspond to 360 / N; let us say N = 2; then here N = 2 then delta P = n into 2. So, you can select N number of , such as, 2, 4, 8, 6 everything it will select.

So, then all other pathways which are available, coherent orders if present, if the pathways are available, it will select all the pathways which are equal to delta P = delta P + n into N, they also will be chosen. That is a general rule.

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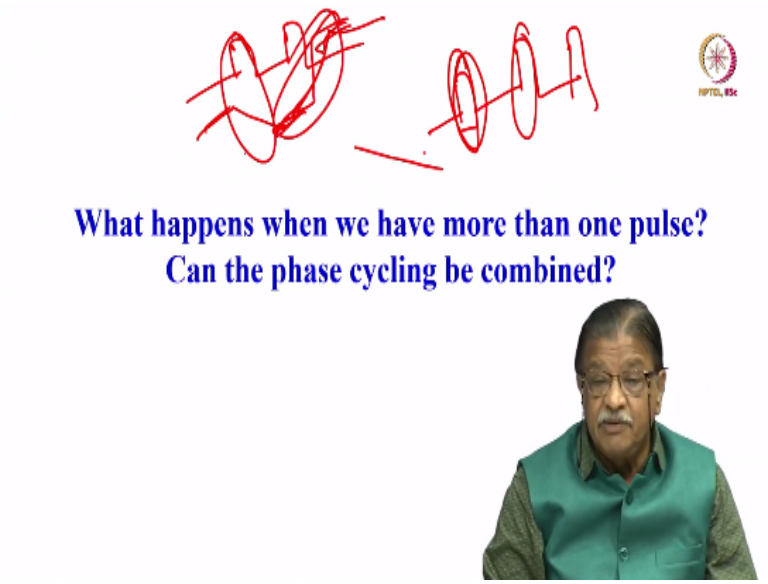

What happens when you have a more than one pulse? That is the next question. See, we were talking about only single pulse phase cycling. But in multi pulse experiments, you can have 2 pulses one 90 Pulse followed by another 180 pulse, another 90 pulse like that. Suppose, if I want to change the phase cycling of this one, and if I have to change the phase cycling of this one simultaneously, is it possible? Can I have the phase cycling? if implement the phase cycling and choose a particular pathway.

If I have the sequence with more than 1 pulse, 2 pulse sequence, 3 pulse sequence like that, can I have a phase cycling implemented? can I combine? If I choose a phase cycling? Let us say from here to here, I will put 2 pulses like this; here to here; I will select one pathway, from here to here, I might select another pathway, I can select different pathways. Then, I need a phase cycling to select this particular pathway from here to here. From here to go here, I have to select another particular pathway. Is it possible to combine 2 pathways of selection when you have 2 pulses?

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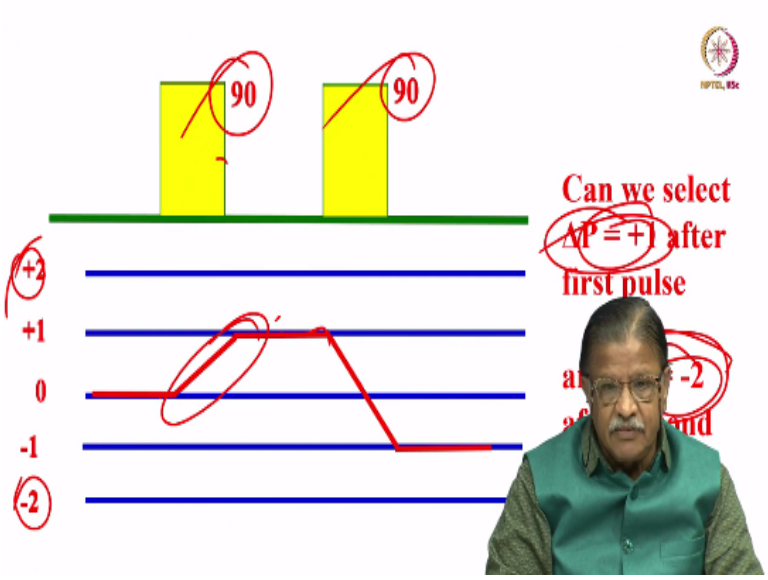

Yes, the answer is yes, you can do that; it is possible to combine the phases when you have multiple pulses. Take for example, you have 2 pulse sequence 90 and 90. And we have different coherent orders, -2 to +2, different coherent orders are there. Now, I want to select this coherent pathway; after the first pulse 0 to +1, this is a coherent pathway I am going to select. So, 0 to +1, so this is +1 pathway, that is fine, here this is +1 because P2 - P1 is +1.

Now after the second pulse, I want to select this pathway, this pathway is +1 to -1. So, P2 - P1 is -2; that means, in a 2 pulse sequence after the first pulse I want to select delta P = +1 pathway, after the second pulse, I want to select delta P = -2 pathway. Both I want to do simultaneously because my experiment is like that I have 2 pulse sequence can I do that?

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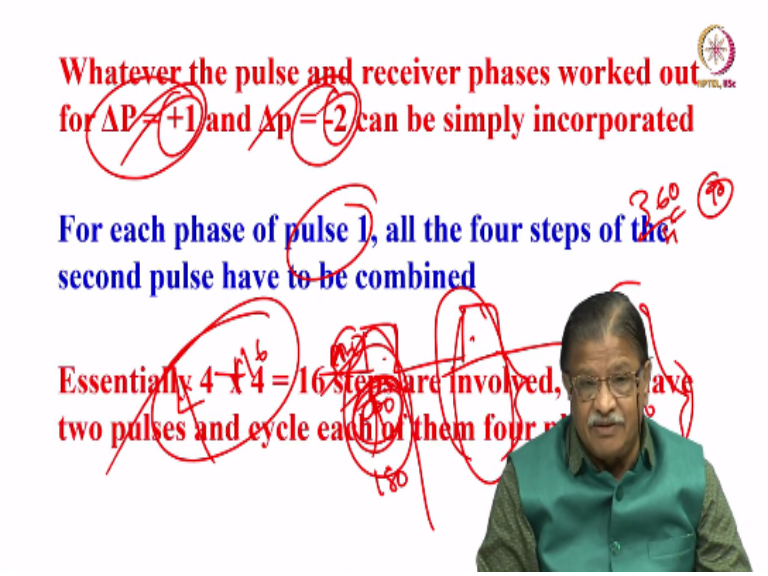

Yes, whatever the pulse phase we chose for delta P = +1 with let us say I have chosen N = 4, when N = 4, for what is it delta P = +1 we know that, 360 divided by 4; which is in a 4 step phase cycle 90, 180, 270, 360, we can select for delta P = +1. Accordingly you calculate what is the receiver phase, but we have done that for delta P = +1. Now, for delta P = -2 same 4 phase cycling you can have; but now what is the receiver phase now, same 4 phase cycling the receiver phase for delta P - 2 we calculate, that also we calculated. Now, it is easy to combine both.

Now, for each of the pulse, each phase of the pulse for delta P = +1, 4 different pulses we have to see ensure that the receiver phase of pulse 2 has to be incremented. For example, let us say, this is delta P = +1. I have chosen 1 phase cycling, for the receiver phase that says 90. And now, for this receiver phase is chosen in such a way it is 90, 270, 180 or 270 something like that I chosen. This is my receiver phase; For the first pulse, all the 4 should be changed here you should undergo one cycle.

Now increment the second time the phase of this pulse to 180, again all the 4 should be done; the phase cycling has to go sequentially like this. First for this, for the first pulse, the phase of the first pulse all the 4 receiver phase have to go through; for the second one, then the second pulse phase of this first pulse. Again all the 4 has yo undergo all the 4 receiver phases; they have to undergo like that. That means we have 4 phase cycling, for the 4 pulse phases for the first one and for the 4 pulse for the second one; and that means 4 into 4 you have 16 cycles.

For each time for 1 receiver phase here 4 receiver phase of this has to be changed, second receiver phase here all 4 has to be changed, you have to go sequentially like that, then it is possible to combine both the phase cycling for both the phases. So that is what is going to happen.

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Step	Phase of pulse 1	Phase for δP = +1	Equivalent Phase	Phase of pulse 2	Phase for δP = +2	Equivalent Phase	Total phase
1	0	0	0	0	0	0	0
2	90	-90	270	0	0	0	270
3	180	-180	180	0	0	0	180
4	270	-270	90	0	0	0	90
5	0	0	0	90	180	180	180
6	90	-90	270	90	180	180	90
7	180	-180	180	90	180	180	0
8	270	-270	90	90	180	180	270
9	0	0	0	180	360	0	0
10	90	-90	270	180	360	0	270

You can combine that, for example, we have worked ou;t for this is going to be 16 step; I did not write complete and I stopped, I got fed up after writing this table. Remember phase of pulse one 0, 90, 180, 270 we chose. For delta P = +1; 0, 90, 180 with opposite phase we saw that; and equivalent phase is this. So, first it is 0, this phase of the pulse should be 0; start with that. For delta P = + 2 it is 0. So, equivalent phase is 0 that; now the total phase is 0, it starts with that 0, 270, 180, 90.

Second one, you come to 5 6 7 8; again now order is going, now second one is for the 0, 90, 180 is over; 0 equivalent phase is 0, 270; this remains the same. this order or we do not have to go here we start this itself. First of all, let understand this itself. Now for the 90 you have to undergo all the 4 again; For 90, similarly 180 all the 4 you have to undergo. So, pulse phase for each of these things all this 4 you have to undergo. You have to combine in such a way that the entire phase cycling for both of them can go through.

So, 4 into 4 16 possible steps you have to choose and each phase what is the total phase you can work out total phase combining both pulse 1 and the pulse 2. So, if you have more number of pulses is a bit complicated to workout. See this is the have we had to go for 16 steps while working out up to half of that I got fed up imagine if you have more pulses is going to be very difficult, but it is possible people have been doing you can keep doing that.

So, we will work it out for each of these things. First you undergo 4 cycle; keep the receiver phases the second one 0. Now go through all the 4 keep the receiver phases the second one as 90. Now go through all the 4 keep it as the 180; again go through all the 4 keep it as 270 like that, each time first pulse undergo all the 4 phases, second one sequentially increment 0, 90, 180. Each time for first 4 pulses this should remains constant, then the second 4 pulses increment this 180 degree, and keep it constant like that, this is the procedure you have to follow.

It is possible to combine both receiver phases; both the pulses in multiple sequences. We took the example of 2 pulse sequences, so, this is what I wanted to tell you about the phase cycling, how do we use the coherence selection, how do you get the coherent transfer pathway; for a defined coherent transfer pathway what you want to choose? You can select it by using a particular receiver phase; the particular receiver phases you obtained by minus delta P into phi - delta P is delta P2 - P1. P2 is the final pathway, P1 is the initial pathway.

And depending upon the number of coherent orders we have choose a particular pathway; once you choose a particular path way find out the receiver phase and the pulse phase defined, how many number of pulses phases you want, this is 360 / N. If you want 4 pulse phases 360 / N is 4; then you have 0, 90, 180, 270 like that. So, similarly, then you can find out what is the receiver phase depending upon the coherent order you want, you have chosen and the corresponding coherent pathway.

If you have 2 pulses, it is possible, you have 4 receiver phases are there, each time we have the receiver phase for the second pulse. And for first 4 receiver phases, keep first 1 constant, then for a second 4 receiver phases, keep the second pulse phase constant for all the 4 like that. So, it

is a very complex thing. If you have 4 step phase cycling for first one, 4 step phase cycling for the second one, have 4 into 4 16 step phase cycling combined together for 2 pulses.

Like that you can work out for any pulse sequences. If you know the coherent order, and the coherence pathway, all you have to do is to simply calculate the number of cycles you require. And what is the receiver phase and which is this coherent path way you are interested in selecting. That is all we have to do. So, with this I will stop for the coherence selection and everything. Next the same thing we can do by what is called gradients. Tomorrow I am going to discuss about gradients, how we can use gradient to do the selection, select this pathway also.

Whatever you did by phase cycling, you can do to by gradients. Then what are these gradients? I will introduce that tomorrow. So, thank you very much I stop it for today.