Advanced NMR Techniques in Solution and Solid State
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Lecture - 28
Pulse Field Gradients - II

Welcome all of you. We have been discussing about phase cycling coherence pathway selection etcetera since last 2 or 3 classes. In the last class, I introduced what is called pulse field gradients, we discussed a lot about what is the pulse field gradient, what happens if we apply a pulse field gradient to the static magnetic field, we understood it linearly varies across the entire sample volume along Z axis, it is a Z gradient pulse we are applying.

Gradient means the magnetic field keeps on changing at different parts of the sample. Conventionally it is assumed; it is 0 at the centre and increases above the upper half and decreases below the lower half. And we also understood the precession will be faster in the upper half and slower in the lower half. And you can think of this entire sample as different slices, thickness of different slices and then from slice to slice, what is happening is the process frequency keeps varying.

But within this slice all the spins will experience the same frequency. By increasing the stronger gradient you can reduced the slice thickness, in which case eventually you can see that everything can completely get dephased. And you are going to get a broad signal because over entire sample the spins experience different Larmor frequencies, and the detected signals will be very, very broad. Then, I also said we can apply a pulse and I can even select the coherent order by applying gradient. Coherence pathway I can select by applying gradients also.

We took an 90 degree pulse before the application the pulse, we applied a gradient called G1 with a duration t1 and then applying 90 degree pulse and after you apply another gradient G2 with duration t2. And then our coherent pathway selection also we found out; what should be coherent pathway. Before it was P1 after 90 pulse it was P2. The phase that is acquired by the coherent order P1 during G1 was given a -P into gamma phi z into t; that is -P into phi Z into gamma into G z into t.

Of course G is the gradient into t. Same way we can get the phase for the coherent order after the pulse; and we both of them are negative when it comes to the -P1 into phi into all those things. What happens if the complete phase, if we take totally, if it is nonzero what is going to happen?

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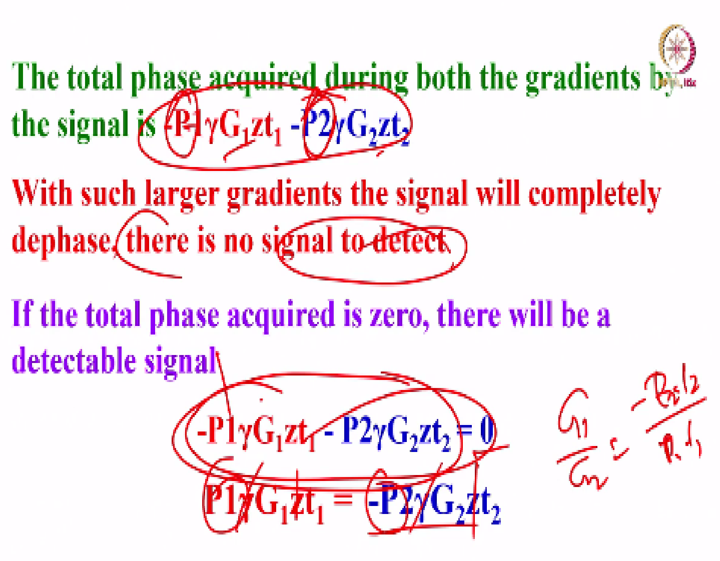

We saw that if it is nonzero then what happens is complete signal will be decaying; the phase acquired is P1 into gamma into G1 z into t for P1 and then for it is P2 is similar; both are negative. If you take the sum, if it is nonzero, there is a complete dephasing.

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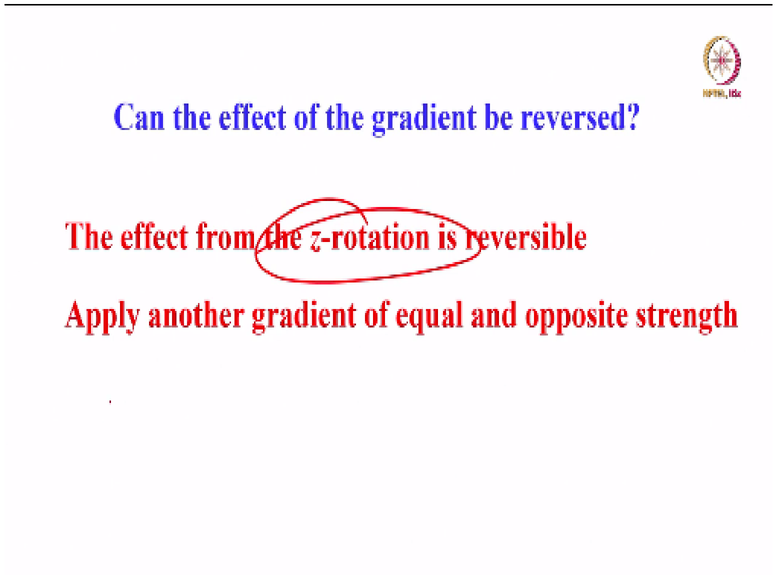

On the other hand, if somehow the sum of the total phase acquired by P1 and P2 during G1 and G2 is 0, then what is going to happen is whatever has dephased can be completely rephased. That is what we discussed. How do you do the reversing? Can we do the reverse gradient effect completely, so that z rotation if you reverse it, then what is going to happen is, whatever is dephased can be rephased also. That means what we understood is the G1 and G should have the opposite signs.

Before the applications the pulse I apply gradient G1, identical gradient with the opposite sign if I apply after the pulse, what is going to happen? before it will dephase; immediately after the pulse, if I apply equal and opposite gradient, then it will rephase. The signal would not get nullified, it is a very interesting concept. So, the effect of this z rotation is reversible.

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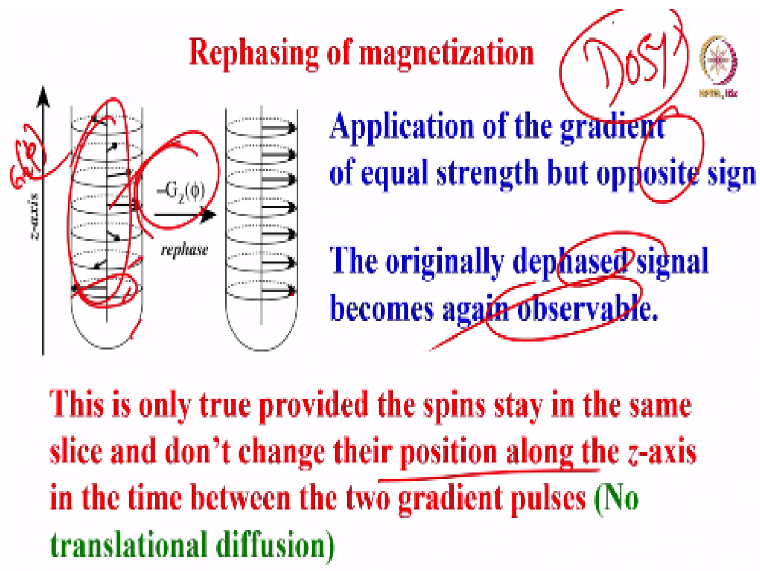

So, how do you do the rephasing; now it is already dephased here , in homogeneous has already been created and as you see in different slices the spin vectors are rotating or precessing at different frequencies, the phases are different in different slices. Now, this is after applying gradient Gz of phi. Now, I am applying gradient -Gz of phi, equal and opposite. What should happen? It is like a spin echo; exactly what happens is, wherever the spins have started, it will go back to the same place.

We started like this earlier and it comes back to the same place again. This is what is called rephasing. So, the spins were completely homogeneous and were in precessing in particular frequency, you created inhomogeneity at different slices of the sample, they all now precessing at different frequencies, their phases are different. And after some time, you apply equal and opposite gradient, the opposite sign, then spins will start going backwards. It reverses the rotation, the z rotational along z axis is reversed and the spins start going back.

So that means it will rephase, exactly where they were before the application of gradient pulse. And this is what happens when you apply equal and opposite strength of the gradient; the originally dephased signals become observable. Now, the question is, is it true always? Are the nuclear spins of the molecules constrained to a particular place? No, they will be undergoing translational motion, they will be undergoing diffusion.

There is a translational diffusion going on. This rephasing is true only when the spins do not change their position along the z axis, between 2 gradients. That is a very important point. But supposing you apply a pulse gradient and then start dephasing, when you apply a rephasing gradient, it is assumed that spins have not moved from its original place. If they have moved because of translational diffusion then the rephasing would not be proper. And in fact, this is the idea used to measure diffusion coefficients in NMR, when you are doing an experiment called DOSY, which we are going to discuss if there is time at the end.

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So, as I said, we can select a particular coherent pathway using gradients, it is possible. Like we used the pulses and using phase cycling, you can also use gradients and select it.

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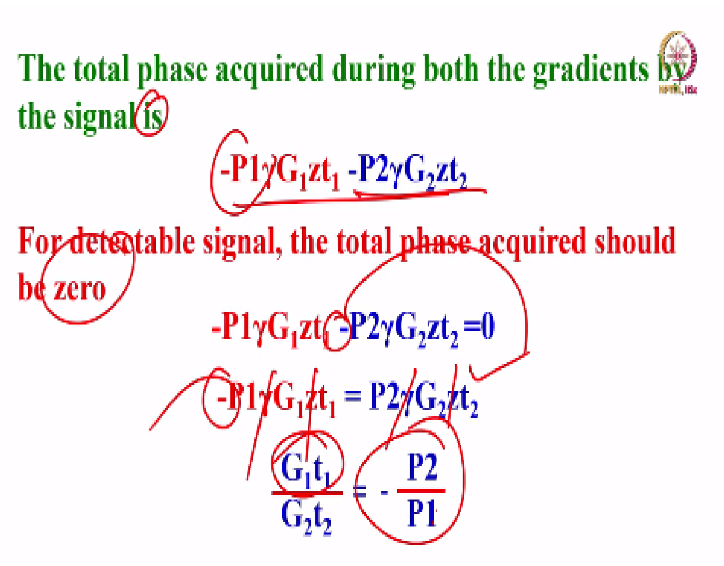

Now, we know what is the total phase acquired during both the gradients; that we worked out, which is -P1 into gamma into G1 z into t1. Similarly, for P2, this is the total phase acquired. Now, for the detectable signal, I told you this has to be equal; which will become 0. The total phase I made it 0. Now, I equated this; simple arithmetic which I did earlier. Now, this turn out to be this. So, if you do that arithmetic what it says, this gets cancelled, this gets cancelled out.

Now, G1 t1 over G2 t2 becomes minus of P2 over P1. This is what it is, because this minus when it comes to this side it became plus, but this still remains minus; so, it is minus of P2 over 1. So, G1 t1 over G2 t2 equal to minus of P2 / P1.

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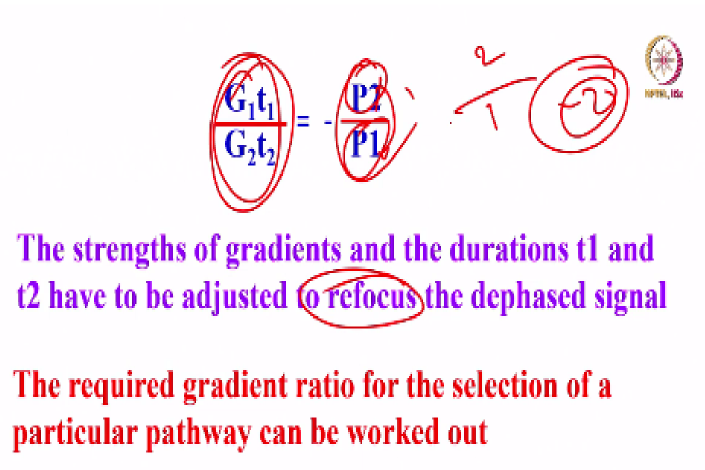

So, what do you understand from this, the strength of the gradient and the duration t1, have to be adjusted properly to refocus the dephased signal, that is what we can adjust. That means, if I adjust this G1 and G2 properly then I can find out the ratio of P1 and P2. I can select the particular pathway. Thus the require gradient ratio for a selection of particular pathway can be worked out. Let us say I have P2 is 2 and P1 is 1. Now, P2 / P1 is -2. So, you have to adjust G1, G2 and t1, t2 in such a way that ratio should become -2; then you can select this pathway.

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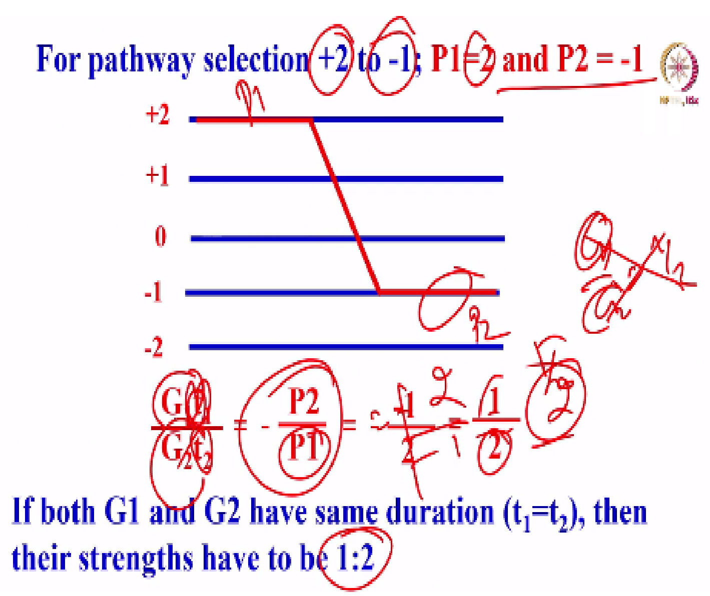

I will show you taking one example. I want to select the pathway +2 to -1; this is a pathway I am choosing. This is my pathway +2 and then I want to select this one; this is my P1, this is my P2, P1 = 2 and P2 = -1. I want to choose this according to my formula, G1 t1 over G2 t2 is equal to minus of P2 / P1. What is P1 here? P1 = 2; substitute here; what is P1 here -1 minus of -1. So, it will become 2. So, the G1 t1 or G2 t2 should be equal to 2. If this becomes 2, then 1 is to 2 ratio, I am sorry, it is 2 is in the denominator, I am sorry it is half.

So, G1 and G2 have the same duration if you make it, now, let us say t1 = t2 I adjust it, then G1 / G2 has to be in the ratio of 1 is to 2, because G1/ G2 ratio = half; as a consequence, what you have to do is G1 or G2, if you take G2 should be equal to 2 times G1. So, if I adjust the ratio of G1 / G2 keeping the duration t1 and t2 identical for both, you can choose this particular pathway for P1 = 2 and P2 = -1.

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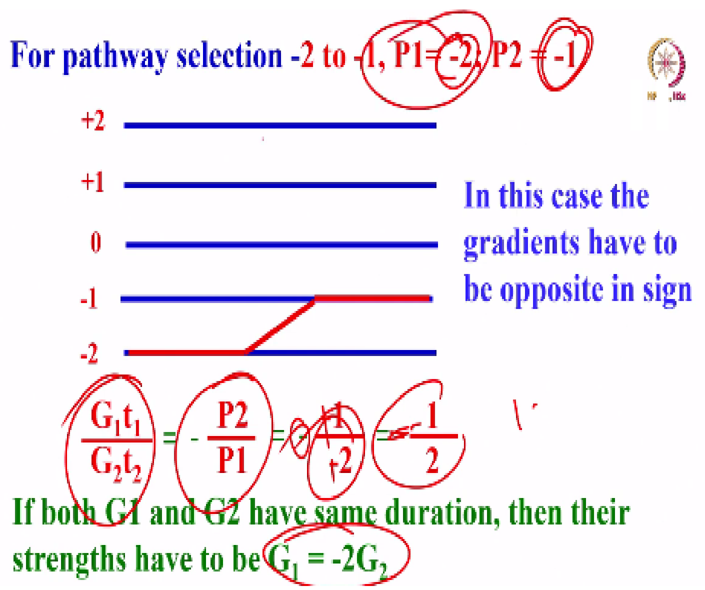

For the pathway I want to select -2 to -1, let us say. how do I do that? P1 is -2 and P2 is -1. So, now, we know the simple formula G1 t1 divided by G2 t2 is equal to minus of P2 / P1. You see again P2 is –2, P1 is -1. So, it turns out to be minus, because this minus is still there. So, this minus, this minus you may cancel it, but this minus is still there. So, this is minus half. Now in this case G1 / G2 have the same duration, but their strengths have to be opposite in sign, they have to be opposite.

In the previous example, remember G1 = G2, see here 1 is to 2 ratio, but here the same 1 is to 2 ratio, but they should be opposite; 1 is to -2 see G1 should be equal to minus of 2G so, G1 should be equal to 2 times G2 then I can select this particular pathway from P1 = -2 to P2 which is equal to minus 1. So, here it is very easy; and in the homonuclear case gamma gets cancelled out z gets cancelled out all you have to deal with G1, t1, G1 into t1 over G2 into t2 = –P2 / P1.

All you have to know if you keep the delays identical t1 and t2 durations, keep it identical, G1 / G2 ratio you can find out for a particular pathway you want. So, that is easy. But in the case of heteronulear case, it is not so simple. It is slightly different, because as you know gammas are different. When the gammas are different, you cannot consider just like that, not so simple. So, we had to work it out in a slightly different way. How do we select the pathway for hetero nuclear spins? Now I will take one is I spin, and the other is S spin; earlier I did not bother as both were homonuclear.

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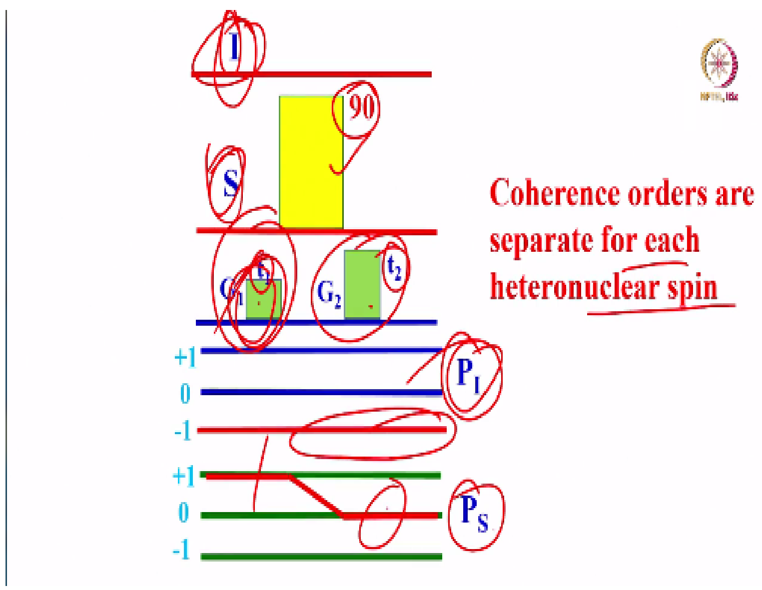

Now I am going to put a diagram like this, this is I spin; notice, I have not applied any pulse on I spin, No need to apply pulse on I spin, but they are coupled; coupling is there. And this is S spin, on the S spin I apply 90 degree pulse. The gradient before the pulse is G1 duration is t1, gradient after the pulse is G2 for the duration t2. Please understand, pulse is not applied only on I spin, but the gradient is applied on both, gradient is general, it is not on a particular spin.

So, gradient is applied here; pulse can be applied on a particular nuclei, gradient is applied just like that for everything. Now, coherent orders are separate for each heteronuclear spin. The coherent order for this is different and the coherent order for S are different. They are not same. coherent orders for I and coherent order for S are totally different. In this case, I deliberately take, since I have not applied any pulse on I spin; I want only -1 path, that is what my detection, I want to detect let us say -1. Finally what if I detect I spin, I look for -1 pathway.

So, this is my pathway let us say, and for the S spin my pathway is +1 to 0. Please understand for the I spin the pathway is -1 throughout, for S spin the pathway is +1 during G1 and pathway is -1 during G2. See the difference for both nuclear spins the pathways are different. For one of the nucleus PI which I have taken, I will take -1 as the pathway for my detection, and it is same for both G1 and G2. During the both the gradient times the pathway for this is -1. As far as S spin is concerned during G1 the pathway is +1, during G2 pathway is 0.

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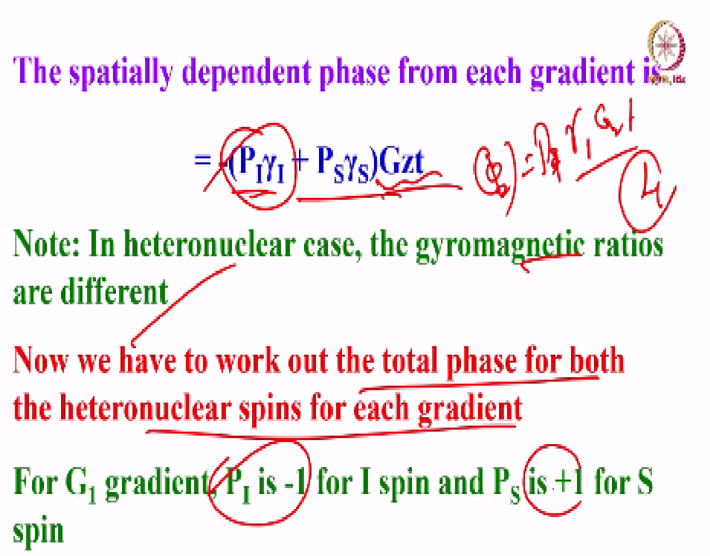

This all the logic I we have to understand. Now, we calculate the spatially dependent phase for each of these gradients. We know how to calculate the phase; that is already given. earlier gammas are same, the gammas are different now, now PI gamma is multiplication factor, this is Gz into t. So, earlier you did P1 gamma Gzt; we wrote. This is phi z; this was the phase acquired for a particular coherent order that we knew.

But remember now, we also have hetero nuclear spin present; what I am going to do I write a simple equation PI gamma I + PS gamma S; both in brackets multipled by Gzt. Of course, you can write individually, I have taken G z out because that comes as a product for both terms here; and therefore negative sign continues. Now, note in the hetero nuclear case gyromagnetic ratios are not identical, they are different. Gamma for carbon is 4 times less than that of proton, you know that. So, that is why you have to explicitly calculate now.

Now, we have to work out the total phase of both the heteronuclear spins for each gradient, that for each gradient you have to work out what is the total phase. For G1 gradient PI = -1 for I spin; and PS is +1 for S spin.

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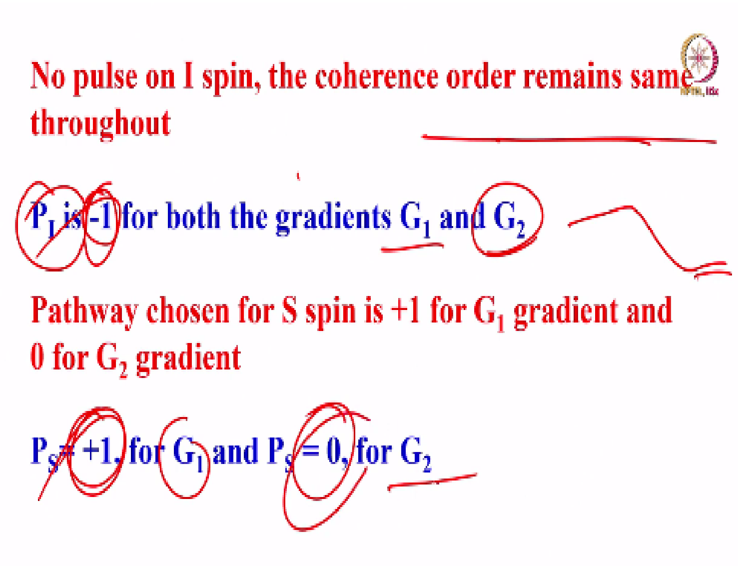

Or in other words, we write like this, simple, there is no pulse on I spin. Since there is no pulse on I spin, the coherence order remains same throughout. It is because I have not appled anything and I have chosen -1 pathway. So, PI is -1 for gradient G1 and is also -1 for gradient G2. I have not changed it, it continuous and I have taken only 1 pathway. What about PS? For the PS I took the pathway 1 to 0. So, for PS for G1 pathway, this PS is 1 and it is 0 for G2, because during G1 the pathway was +1, the coherent order was +1; and then during G2 the coherent order was 0.

So, remember, the coherent order was -1 for PI all through both during G1 and G2; whereas for S spin the coherent order is +1 during the gradient G1. And it is 0 to for a gradient G2.

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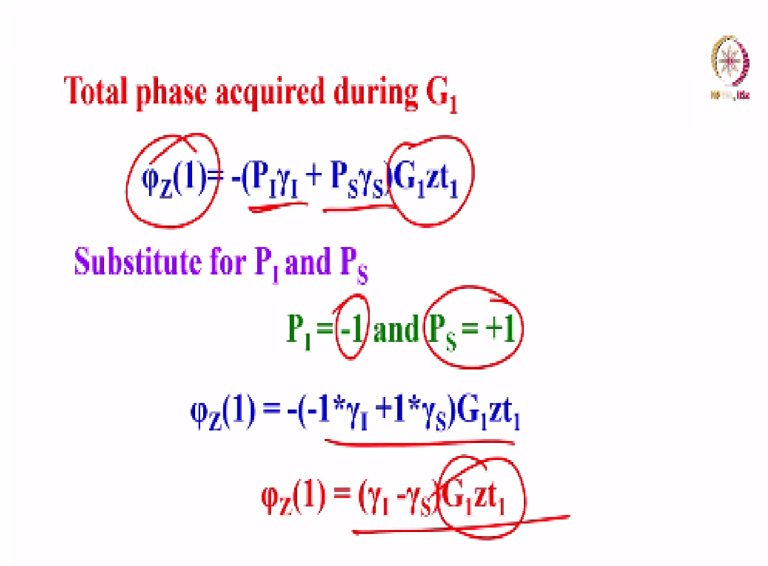

With this now, total phase acquired you calculate. For now you know for the phi z1, first time for the gradient 1, what is the phase acquired? For the gradient 1 phase acquired is PI gamma I plus PS gamma S. Now PI is -1 here PS is +1, add it up. Now make the simple calculation phi z for the gradient 1 turns out to be minus of 1 into gamma I1 in to gamma S, this 1. This boils down to simple phi z1 for the gradient 1 the phase acquired is gamma I - gamma S into G 1 zt 1 that is for the first this thing we worked out first gradient, because both these spins are there now, both heteronuclear there. Similarly worked out for Phi z 2 for the gradient 2,

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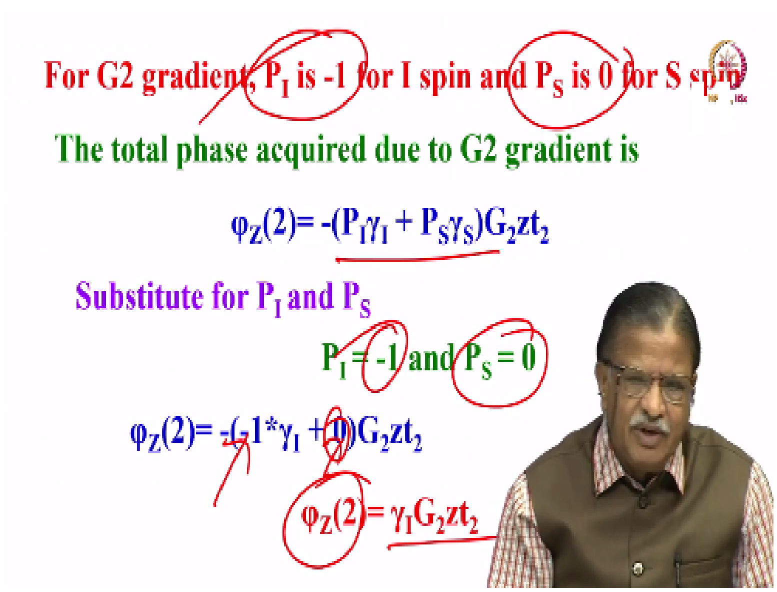

For the gradient 2 we know that P1 continues to be -1 whereas PS you have chosen pathway from +1 to 0. What is the total phase acquired now? For the gradient G2, this is same. Now you have to substitute like these our PI and PS, PI = -1 PS is 0; previously it was +1 for G1. Now for G2 it is 0. Work it out, simple arithmetic, plug in these values here for Phi z2 then it turns out to be phi z2 = gamma I G2 zt2; this is 0. So, gamma S term does not come into the picture here at all. We calculate it now. Phase acquired during G1 and phase acquired during G2 both are known.

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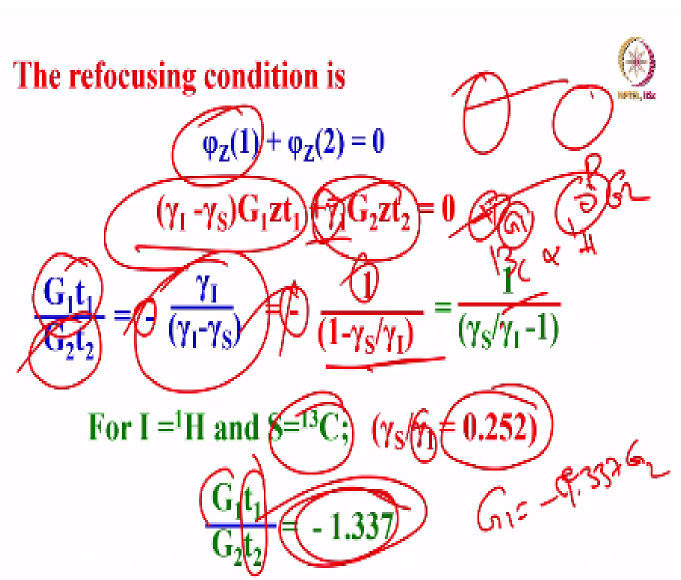

What is the refocusing condition, sum of both the phases should be 0, in which case you can get the detectable signal. So, phi z1 + phi z2 should be equal to 0. Put this condition now, you worked out for phi z1 it is gamma I gamma S into G1 zt1 + gamma I G2 zt2 this is equal to 0. Do this simple jugglery by rearranging the terms. Now, G1 t1 / G2 t2 turns out to be gamma I divided by this term, because both are positive here, this negative sign is carried forward.

This can be further simplified like this, you divide this by gamma I, then this will become 1 over 1 - gamma S into gamma I. What is gamma S and gamma I? Take for example carbon 13 and proton, carbon 13 gamma is 4 times less than that of proton; plug that value here. Of course, to remove the minus sign this was put in the reverse order now. So, instead of 1 - gamma I it is gamma S over gamma I over gamma I - 1 was written. So, this minus sign was taken out.

So, now for I = 1H and the S = carbon 13, these 2 are the hetero nuclei, this ratio turns out to be 0.252, because gamma of protons 4 times nearly larger than that of carbon. So, this ratio turns out to be 0.252. So, put it here. If you maintain the duration t1 exactly equal to t2, you do not change the duration; then what is that you have to calculate G1 should be equal to -1.337 times G2. So, what you did? we know what is the ratio of G1 and G2 to be chosen so that you will select the particular pathway; that is the coherence pathway remains -1 all through for gamma I and +1 to 0 for S spin. So, that what is going to happen is, when you select the pathway during the G1 you are going to have -1 for PI and during G2 also -1 for PI; and for the S spin, it is +1 during G1 it is 0 during G2. So, this is what you have to do; make a simple calculation and then now adjust G1 G2 ratio, this is the coherent pathway are going to select.

Remember exactly analogous to what you do in where by adjusting the pulse phase and receiver phase by doing phase cycling you can get the particular pathway. Same thing you can do by adjusting the gradient ratios between G1 and G2; this is what happens.

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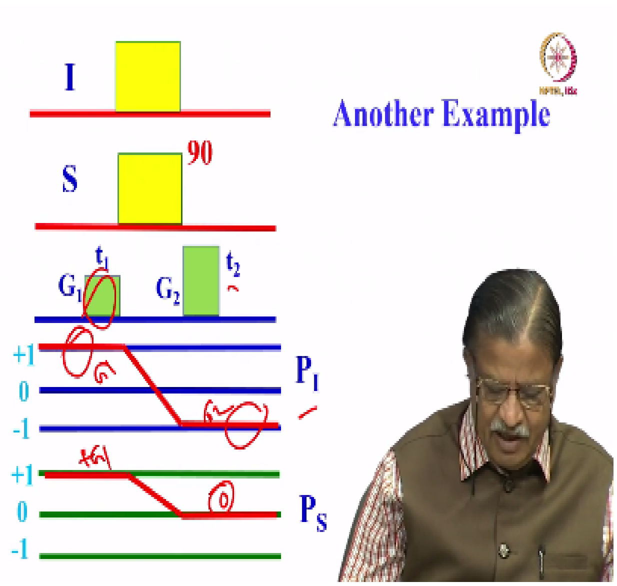

And this is simple example we have chosen. Let us take another simple example now, another simple example is this one; for PI it is +1 during t1 and it is -1 during t2; that is +1 during gradient 1, -1 during gradient 2. This is for gradient 1 this is for gradient 2. What about PS? what is the pathway for S? During the gradient 1, this is +1, during gradient G2 this is 0. Now, unlike in the previous example, where -1 was running continuously for during G1 and G2 for I spin, now I have changed it. G1 and G2 are different for both PI and PS .

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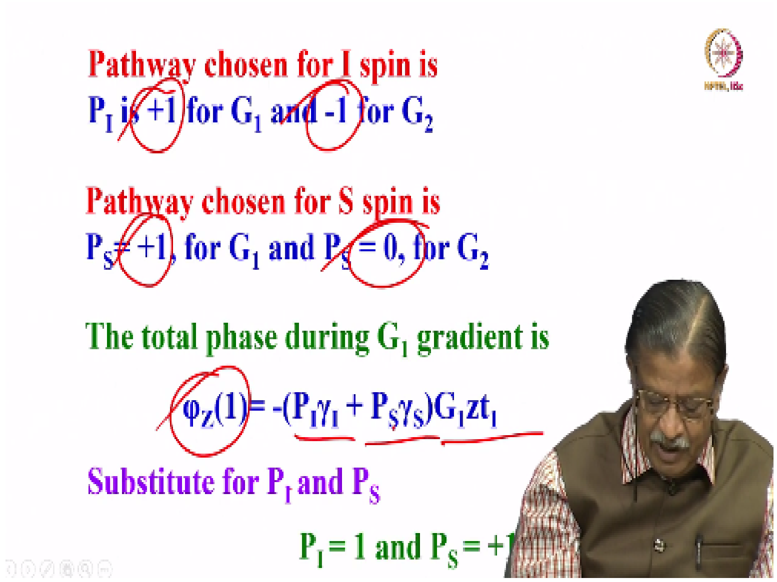

So, now using this one, we will go back and select the pathway. Now pathway chosen for I is what? clearly you see +1 to -1. So, PI is 1 for G1 and -1 for G2. So, what is the pathway chosen for S spin? It is +1 for G1 and 0 for G2. We see very well known now; we have already worked out. What is the total phase during G1? the total phase during this G1 is phi z of I = PI into gamma I minus of +PS gamma S into G1 z t1. Plug in the values now; what is PI for the G1? it is 1 and this one you put it 1. So, this is turning out to be PI = 1 PS = +1; substitute in this equation.

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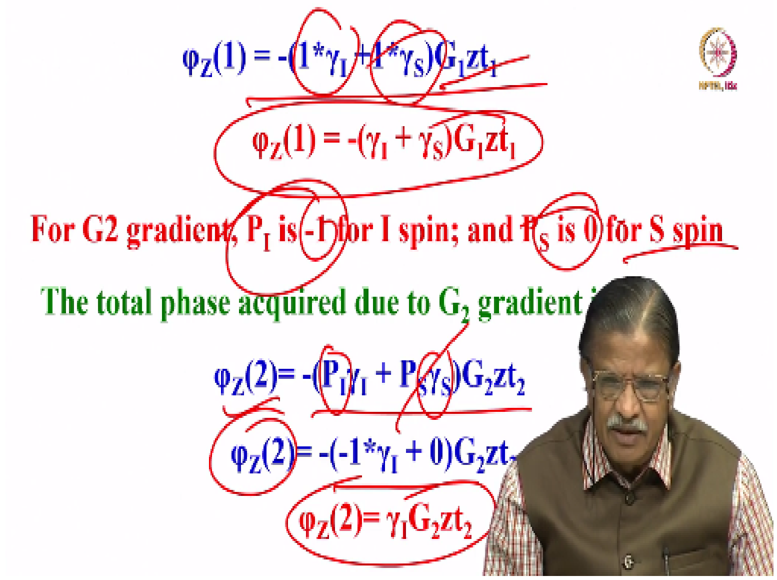

What you are going to get is; minus of 1 star gamma I 1 star gamma S. So, both will remain as minus of gamma I + gamma S over into G1 zt1. This what you are going to get. See this what you are going to get for the phase 1 during the gradient 1, the phase turn out to be minus of gamma I + gamma S into G1 zt1. So, that is what is this. work out similarly, the phase for the gradient G2; for the gradient G2 we know, we have chose the pathway for +1 to -1. So, now, for gradient G2 P I is -1 for I spin and PS is 0, that is for S spin.

Substitute in this equation. Now the total phase acquired again for phi z2 is this one. Now, in this case, substitute P1 as -1, PS as 0. So, this term will go, and what you are going to get is minus of gamma I into G2 zt2; this is the phase acquired during G2 together; the total phase acquired. So, phi z2 turns out to be this 1 phi z2 we already calculated; what is phi z1, we know that. So, what you have to do now, for refocusing condition Phi z1 + Phi z2 should be equal to 0.

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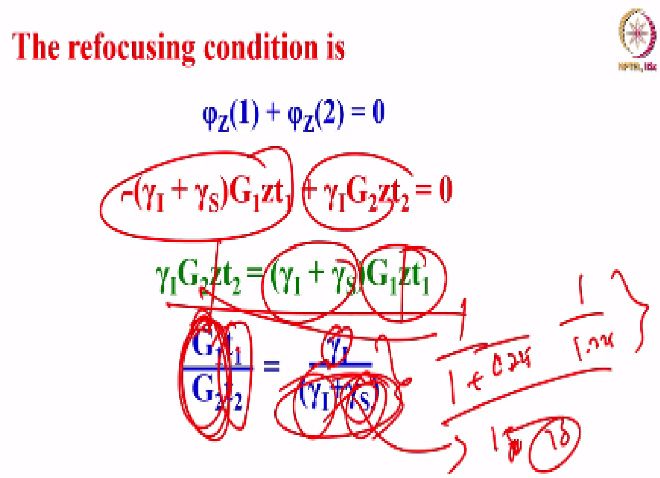

Now, when you put that condition, this is the Phi z1, this is Phi z2 so, now minus is there, take it this side then it turns out to be, a very simple equation, do the simple arithmetic now. Take out z will go but gamma you cannot cancel because they are heteronuclei now. G1 t1 divided by G2 t2 is equal to now gamma I over gamma I plus gamma S, that is a simple arithmetic. So, now, if we know the ratio, if I put again t1 = t2 the duration the gradient if I keep it constant, then G1 / G2 ratio should be equal to this.

Again you know divide this by gamma I 1 over 1 + gamma I / gamma S 0.225 now; you take 1 over 1.225, this is going to be a different number. So, now, this number what you have to choose is entirely different. So, that the pathway chosen for I spin and pathway chosen for S spin are different now, as a consequence, you can find out what is the G1 / G2 ratio. Of course, you can vary t1 and t2 also it is your choice, but the mathematics is going to be clumsy, you need to calculate the numbers.

So, best thing is keep the duration constant of the gradients, if you keep the durations constant, what you are going to get is the ratio of G1 by G2 which is given in terms of gamma of both the nuclei here. And once you know gamma of carbon 13 and proton, we took the example, we worked out and in 2 examples, we could select the particular chosen pathway. Now what will happen if I have a nitrogen instead of a proton, all you have to do is gamma S is different.

Gamma S of 15 N is 10 times smaller, nitrogen 15 gamma approximately 10 times smaller, then it you work it out, then G1/ G2 become smaller, the same pathway you can select now instead of proton and carbon it is going to be proton and nitrogen, that is also possible. So, you do not have to do anything. Let us see how multinuclear system you want to select the pathway for proton and carbon, you worked out you decide to select the same pathway for proton nitrogen, all you have to do is simply know the gamma of the nitrogen, recalculate the value simply adjust the G1 and G2 values. That is all, then automatically you select the identical pathway for proton nitrogen also. So, this is what is the thing which I was trying to tell you. Now the since the time is up, I want to stop here. But what I wanted to tell you is about gradients. You can select the particular pathway. Coherent pathway you can select.

Now, we took the example of the homonuclear spins, we found out how we can select pathway, in the case of the homonuclear spins very easily, you can calculate G1 t1 by whatever G2 t2 and what is the ratio of gammas, that we worked out. But if you keep the duration constant G1 by G2, gamma is same in the case of homonuclear, it was a simple number we worked out, we can select a particular pathway, but in the heteronuclear case it is not similar, because gammas are different.

You have to calculate the phi 1 phase occurred during G1 for both the spins individually like for during gradient G1 phase acquired by I spin, phase acquired by S spin have to be taken together. And then similarly calculate the phase acquired by I spin and the phase acquired by the S spin during the gradient G2. For the refocusing condition, the phase phi z1 during gradient 1 + phi z2 during gradient 2 should be equal to 0.

Now, equate this condition do simple jugglery of arithmetic, not a great thing, then you find out what is the G1 / G2 ratio. Adjust that number, you can select a particular pathway for heteronuclear spin also. And we took the example of proton carbon. And we chose 2 examples one is when there is no pulse at all on I spin. And we chose the pathway -1 and S spin was going from -1 to 0. In another case, I spin was going from +1 to -1 and S spin was going from +1 to 0, like that.

Some examples we took and we worked out and we saw how we can perfectly choose a coherent pathway, even in heteronuclear spin case. So, with this I am going to stop now, we will come back and continue further about this gradients, a little bit I want to tell you. And then of course, we can use this gradients in many multiple experiments to choose the particular pathway. Since I have not introduced 2D, I am not taking the example of 2D pulse sequences.

After that, we will take example of 1 or 2, for example, COSY, DQFCOSY, NOESY like, and then find out a particular pathway selection; how we can do both by phase cycling and also by gradients. We will come to that later. So, right now I am going to stop here, will continue the gradient, little more to I have to discuss in the next class. Afterwards what I will go to another topic; thank you very much.