Advanced NMR Techniques in Solution and Solid - State

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Module-29
Selective Excitation, Selective Inversion
Lecture - 29

Welcome backs all of you. In the last class, we discussed about pulse field gradients. In fact, last 2 classes we discussed a lot about pulse field gradients. And we discussed how the field gradient is generated, what the gradient does, what happens to the spins in the gradient coil above the center 0; and below what will happen, how the spin precess? And finally, how completely they get dephased without giving any signal.

And then we also discussed that there is a way we can rephase this, because the Z rotation can be reversed by applying the counteracting gradient exactly equal opposite phase. And we also discussed a lot about how we can use this gradient to choose a particular coherent pathway; and took the example of homonuclear case; when I have a gradient pulse just before 90 degree pulse called G1 and I have a gradient pulse just after 90 degree pulse called it G2.

Then we calculated what is the phase acquired during G1 by the spins, the phase acquired; that is given by a simple expression minus p into gamma into the all the G's that we knew. And then worked out the phase acquired the during the gradient G2 also. Of course, both of them come with a negative sign, phase acquired minus of those terms. Similarly, phase acquired during G2 also minus P2 into those gamma into etcetera, etcetera those terms.

I said the refocusing condition to make sure that the signals are detectable, total phase acquired phi 1 + phi 2 that is during gradient one and gradient 2 should be equal to 0. We equated that and did some mathematical jugglery and found out what is the ratio of G1 and G2. For example G2 T2 over G1 T1 or vice versa and what is the ratio of gammas we get. Based on the ratios gammas we could even calculate what is the G1/G2 ratio we require. Keeping T1 = T2 that is the duration of the gradient exactly same, we can get G1 / G2 because we know gamma.

So, very simple; and when you are worked out for the homonuclear case, it is 1 over 1 minus some number which we worked out, especially when you have heteronuclear case also, we worked out what is the ratio. For heteronuclear of course only differences is, coherence you have to consider for both the spins during both the gradients. For example for gradient one what is a pathway selected for spin I, what is the pathway selected for spin S during G1; use that calculate the total phase for that for both. Similar operation you do for calculation, what is the phase acquired during G2 by I spin and also by S spin.

Again for refocusing condition take the total phase equate it to 0; and do simple mathematical jugglery we can find out what is the ratio of G1 and G2 required to select the particular pathway. But in this case it is slightly different because gammas are different for heteronuclear case. IN the homonuclear case, gamma was same and the equation turned out to be very simple one, and we got some number, like G1 is equal to minus of 1 is to 2 or 1 is to -2 like that. Here we get some fraction because gammas are different.

With that we can go further, little bit one or 2 more applications of gradient we discuss quickly without going into the more details, because it is taking a lot of time, because I come back to gradient little bit after 2D, to find out how we can apply a gradient to select the particular pathway. We can discuss a little bit more also. So hence, quickly I will go through some simple applications of gradients. What we can do using gradients? Gradients can be used with refocusing pulses.

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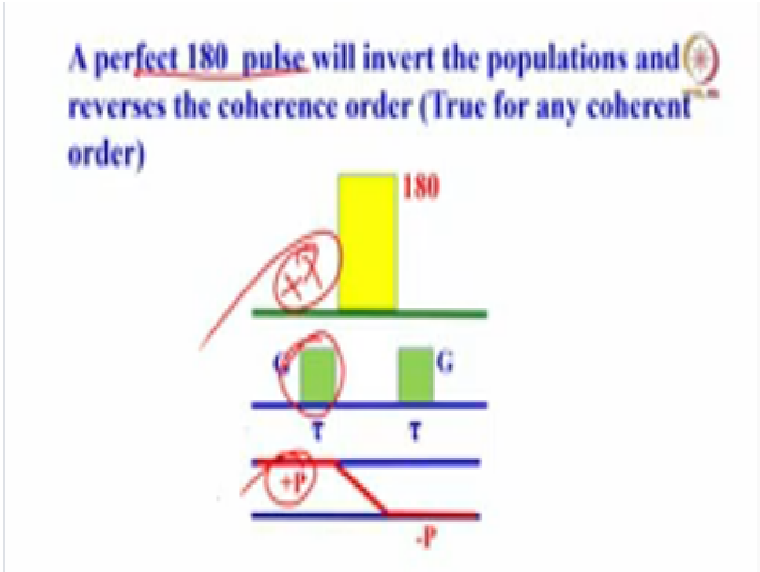

What is the meaning of a refocusing pulse? A perfect 180 degree pulse what it does? I told you even earlier we discussed, the 180 pulse will invert the population; when it inverts the population means it reverses the coherence order. For example, if this is the +P before 180 pulse, before 180 pulse; I have a coherent order P chosen here. And then I have a gradient G before 180 then after applying 180 pulse then the coherent order immediately after that will become minus P. That is what we have known to us, because 180 pulse always invert the populations. When it inverts the population it reverses the coherence order, P will be come -P; if this were to be -P here it becomes +P, gets reversed. So, it inverses the coherence order; but what will happen if 180 pulse is not perfect? Let us say it is not exact 180, it is 178 degree or 182 degree or 181 degree, like that then what is going to happen?

There is no perfect reversing, there is imperfection left because of a 180 degree pulse being not perfect; there will be some artifacts coming into the picture. So, how do you eliminate that? this is a very easy thing. What you can do is, you can use this for nullifying all the artifacts or pulse imperfections which are coming because of this one. So, what you have to do simply is you apply a gradient pulse before 180 and exactly identical gradient after 180.

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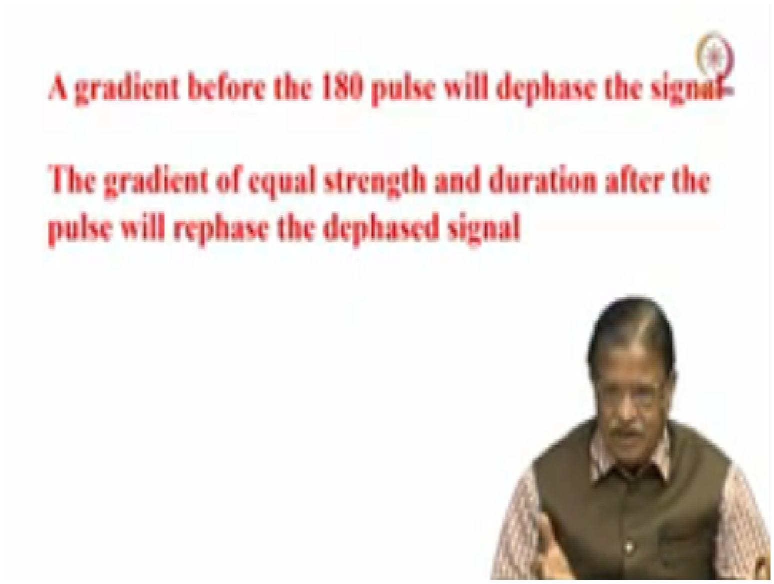

So, what is going to happen? gradient before 180 what we will do? It will diphase; that is what we understood the gradient will completely dephase all the signals because over the entire sample volume different slices will experience different fields. So, it will become broad signal or you will not detect any signal; it completely dephases the signal, depending upon the strength of the field gradient. If the gradient strength is very high then you will make sure that you do not get any signal.

And after the 180 pulse you apply gradient of equal strength and duration then what it is going to do? It will rephase the dephased signal; already dephased, it is going to rephased this one. Then what is going to happen? This eliminates the unwanted signal due to pulse imperfection, whatever is dephased will rephase now and delete all the unwanted signal due to180 degree pulse imperfection, then only the refocused pathway is retained.

If you apply 180 pulses in between like this, what is going to happen is; if you applying 180 pulse, apply a gradient before and after equal strength of the gradient and equal duration then the dephase will be such that then what is going to happen only wanted signal will be refocused, all unwanted signals will be completely dephased and all pulse imperfections will be removed. And we can also do what is called the refocusing in heteronuclear systems, you can use them refocusing pulses. I tell you what.

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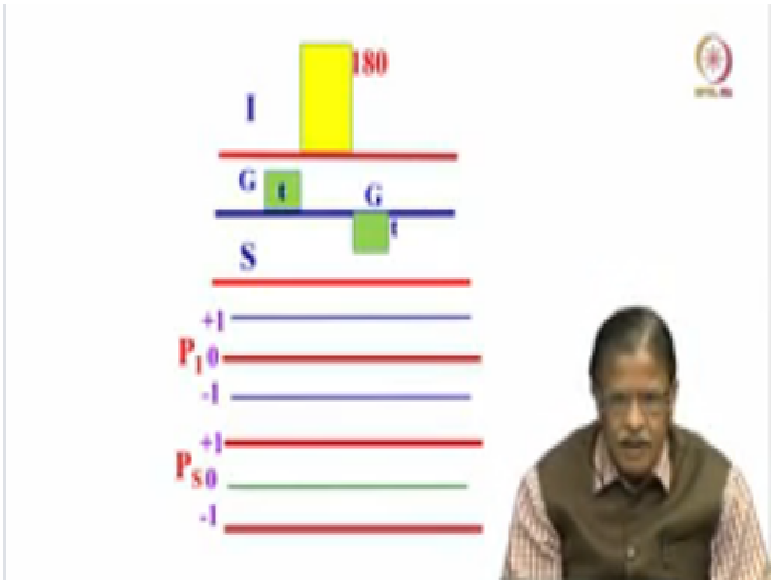

Consider a sequence like this I have a 180 pulse on I channel, I spin; and I have a gradient G of equal and opposite, not the same phase, equal to opposite; before and after the pulse. What does 180 pulse will do? it will reverse the coherent order. Now, let us say I do not choose any coherent order in PI case, it is 0.

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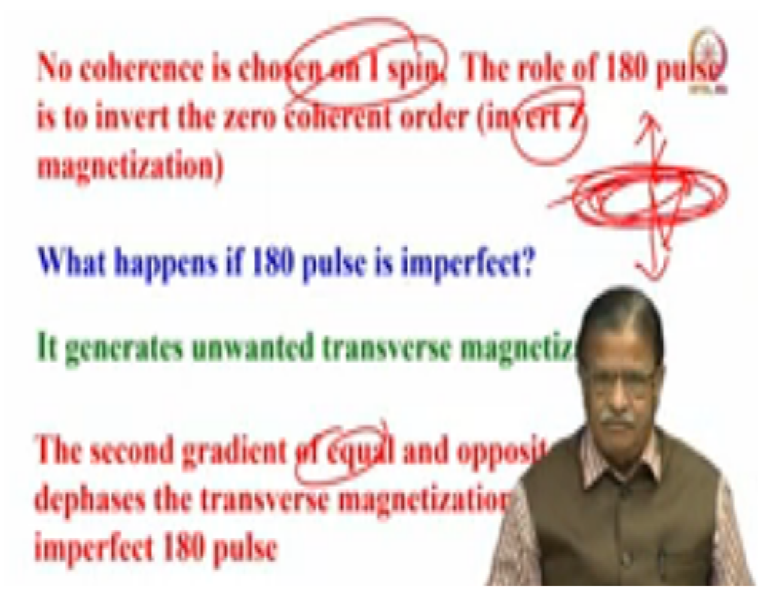

In the PS case, I can choose coherent order different. When no coherence order is chosen on I spin field, what is the role of 180? It will simply invert, when it is 0 order what is the meaning of 0 here? 0 means it is magnetization again along Z axis, it is Z magnetization +Z, so what is 180 does, the magnetization it was along Z it will reverse it, it will make it –Z; Z magnetization become -Z because of 180. Although there was no coherent order chosen, the coherent order P = 0 pertains to Z magnetization. That is what I was telling you.

So, it will invert this Z magnetization. What if the pulse is imperfect? 180 pulse imperfect, it is correct. Then entire Z magnetization here will not come exactly to -Z. There will be some residual transverse magnetization left, some magnetization some component of the magnetization will be there, and then you can get some components here, then it generates unwanted transverse magnetization. If the 180 pulses not exactly perfect, the inversion is not 100% proper, then you will generate transverse components.

But now, there is advantage of the second gradient of equal and opposite phase; opposite strength which is equal, what it will do? It will again dephase the transverse magnetization, you understood it will dephase the transverse magnetization, then all the transverse components which were present will become 0; you will not detect at all, they become unobservable or undetectable magnetization.

So, if there is 180 pulse which is imperfect, the magnetization which is tilted from + Z to -Z is not proper, because of imperfect 180 pulse, then the application of gradient like this just before and after of equal strength; equal and opposite strength; will nullify the transverse components and remove all the pulse imperfections. What did we do here? We have chosen P = 0 for I spin, but some different orders are also present here. There are, P = +1 and different orders are present here for S spin.

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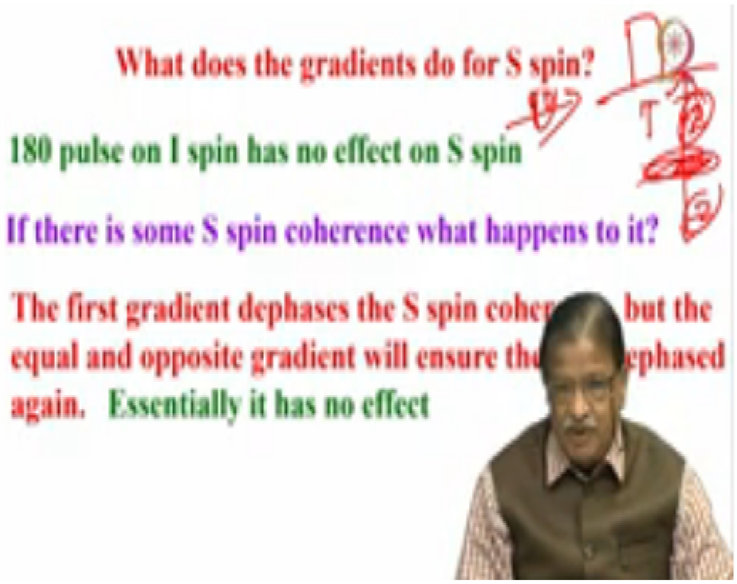

Now question is what will happen to S spin? the gradient before and after what it is doing for S spin. 180 pulse on I spin has no effect on S spin, remember pulse applied is on I spin that is what I explicitly I asked you to see that here pulse is only on I spin, there is no pulse on S spin here, absolutely no pulse at all. So, as a consequence, since there is no pulse, if there is some coherence present; there is no pulse I agree, if there is some S spin coherence present it what will happen?

The first gradient dephases that S spin coherence, but equal and opposite will again rephase it. Eventually what is going to happen is S spin will remain unaltered, it will be undisturbed. Understand what I am telling? You apply a 180 pulse on the proton channel. Now the coherent order chosen is P0, the P0 is the Z magnetization, Z magnetization gets inverted with 180 pulse it will become -Z. Now, if it is not exactly 180 pulse, there will be some transverse component of the magnetization created.

But what you are going to do is, you are applying this another gradient of equal strength; the gradient after 180 pulse, then it is going to complete the dephase it. That is what it does. We will remove that. But the S spin whatever may be the coherent order present, that is not matter? The reason is we are not still applying the pulse on S spin, we are applying only on I spin that will not disturb S spin at all. There is no effect on the S spin. But nevertheless, the gradient is applied to both, even though I do not apply the pulse on S spin.

So, the gradient dephase also S spin magnetization, it will dephase S spin magnetization before 180 but then after 180 equal and opposite gradient is applied, then what is going to happen? That is what we understood the dephasing will gets rephased; with equal and opposite gradient, a gradient of equal duration and equal strength with opposite sign, if you apply, whatever is dephased will get rephased.

And essentially, this has no gradient has no effect on S spin. It effects only and I spin to remove the transverse components which is created because of pulse imperfection. So, this is what the important concept of effect gradient; it cleans up the signals due to 180 degree pulse imperfection. This is the important thing for 180 pulse imperfection, how do we remove 180 pulse imperfections, and this is where gradient useful. Can you remove the phase errors also how do we remove the phase errors?

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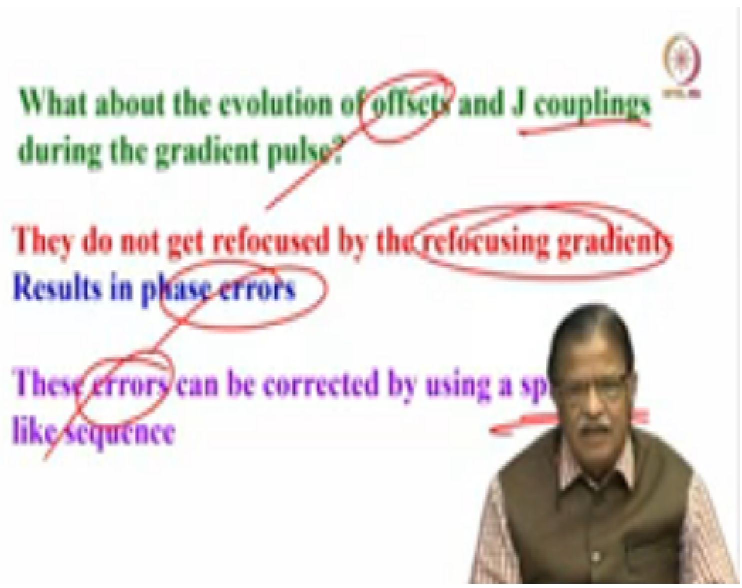

See we have been discussing about the coherence order, coherence pathway. What about the evolution of chemical shifts or offset what you call, and J couplings during the gradient pulse. When the gradient pulse is applied, at that time also chemical shifts and J couplings can evolve, then what happens to that; that gives rise to some errors. They do not get refocused by the refocusing gradients. Onlyin spin-echo sequence they refocused, but not just like that on all the gradients.

So, they do not get refocused by refocusing gradients; what it will do? It will result in what are called the phase errors. These gradients, because of evolution of offsets or chemical shifts and J couplings give rise to what are called phase errors. What to do with these errors, how do you correct it? You can correct these phase errors by what is called a spin-echo sequence. You can do that, that is what I said. The spin-echo you can utilize to correct all these type of errors.

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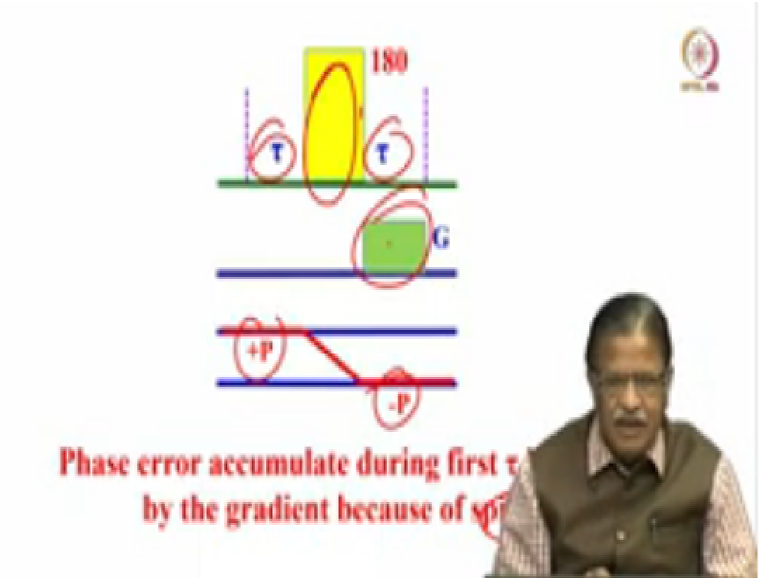

And this is what it is, you look at the simple pulse sequence, it is a 180 pulse, it is like an echo there is a tau before and tau after. And then there is a gradient only after 180 here and before the gradient coherent order is +P; we know 180 pulse will reverses it and become coherent order -P. Now, what I am expecting is the error because of this gradient, phase errors will come, phase errors will accumulate during this gradient, during the first tau and it has to be refocused by the gradient, by the spin echo. By now, whatever the phases that are acquired here, during this time, this gradient it completely refocus this one.

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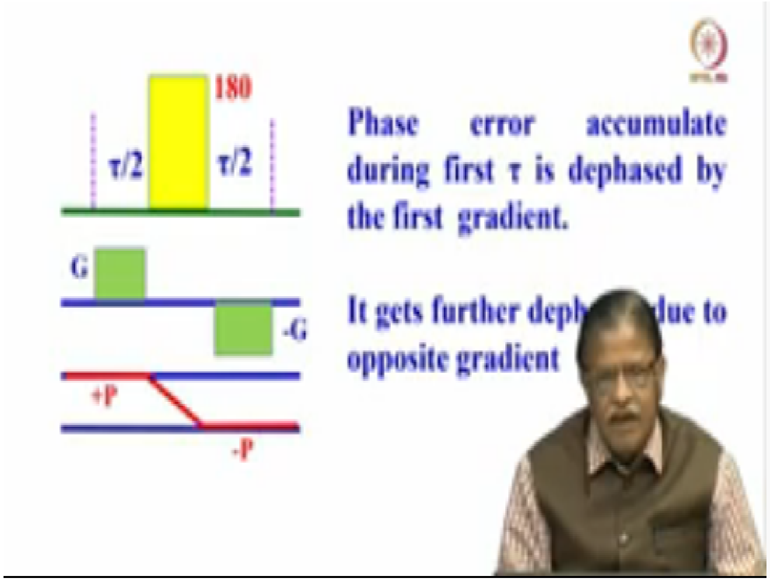

And that way or any phase error if it is present that will be completely removed. Now, another thing; phase error accumulated during first tau is dephased with gradient, it gets further dephased if you apply another pulse of equal and opposite gradient after the 180 pulse; does not matter, we are allowing it to dephase further; nothing is going to happen. So, what is going to happen? All the phase errors which are present because of the evolution of J couplings and offsets during the gradient pulse, will be completely removed.

So, these are all important things. How do you eliminate the phase error like a echo like sequence. Of course, you can have the gradient pulse only one before and after; either of them, or both methods can be adapted. We have what is called a purge gradient, also called homospoil gradient, this is something which is very often used in many experiments.

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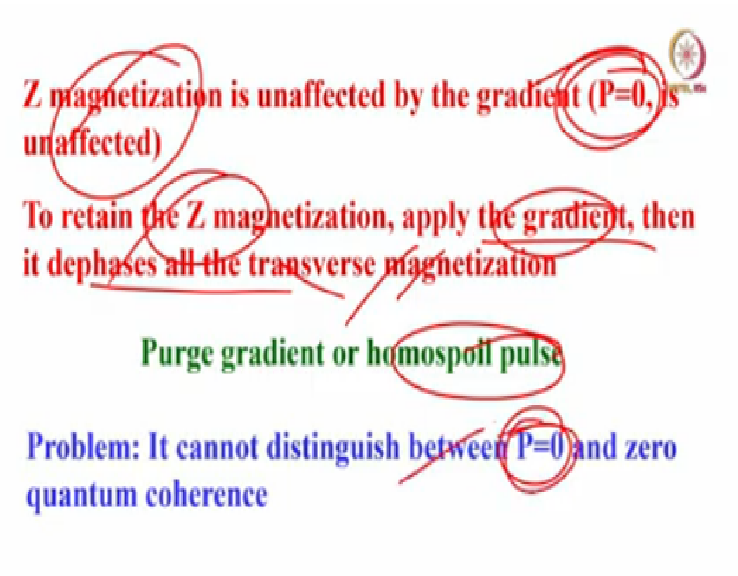

When you come to that will understand when we take an example. As I told you Z magnetization is nothing but order P = 0, is always unaffected, it is not good order P = 0, it will not be affected by anything. To retain Z magnetization what we have do, is to apply the gradient then it dephases all the transverse magnetization. You apply a gradient pulse P = 0 is unaffected, P = 0 will not be affected with the gradient at all. But if I want to retain only Z magnetization, and dephase all the transverse magnetization. what I have to do? Apply the gradient now, simply apply a gradient then all the transverse magnetization gets rephased; then Z magnetization alone will be retained. So, in many experiments in between, suppose you have a doubt that the transverse magnetization is generated for various reasons because of the imperfect 90 pulse or imperfect 180 pulse or anything; let us say there is a transverse magnetization created, but also you have brought back the magnetization to Z axis; you want to retain that, at the same time we want to nullify the transverse components, you can use this type of purge gradient. This is called homospoil pulse, homospoil gradient or purge gradient. This is also often used in many experiments. Of course, one problem if you do that, it would not distinguish between P = 0, which is also for 0 quantum order. We know P0 is also Z magnetization is also for zero quantum coherence.

In many coupled spin system, more than one 2 or 3 and above. You also have 0 quantum coherence. But this may not be able to distinguish these two, but there is a way to select that. So, zero quantum coherence can never be selected with gradients; you have to use phase cycling. So, when we come to multiple quantum, if there is time we will discuss that. But right now remember, this problem will be there. For P = 0, especially it cannot distinguish, P= 0 coherent order and 0 quantum coherence.

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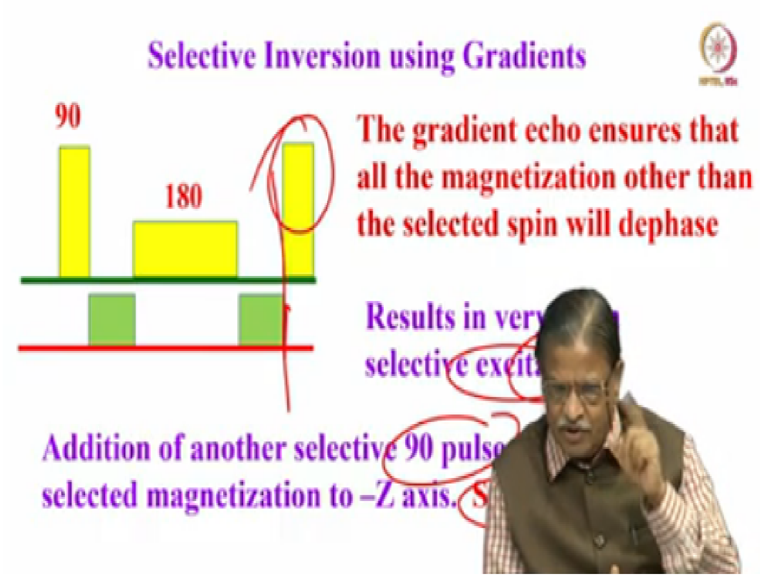

So, another thing what we can do is very interesting. We can do selective excitation and selective inversion, both we can do; these are another one or two applications of gradients; that you must understand. This is the pulse which is going to be applied, it is called the gradient echo sequence, is called a gradient echo. Whatever the gradient applied here, equal and opposite gradient is applied on the opposite side.

It is like 90-180-90 echo sequence. This is like this, a 180 pulse is coming in between. The gradient echo ensure that all the magnetization other than the selected spin will dephase. So, I can select only particular spin, let us say. I can use soft pulse here, then what will happen is, I can select the particular P spin, then I will invert that, or selectively excite that, and make sure that all other components which are present other than the selected spin completely diphase, it is possible. These 2 gradients will dephase all the magnetization other than the selected one. This is better way of selective excitation, the excitation is going to be very clean selective excitation

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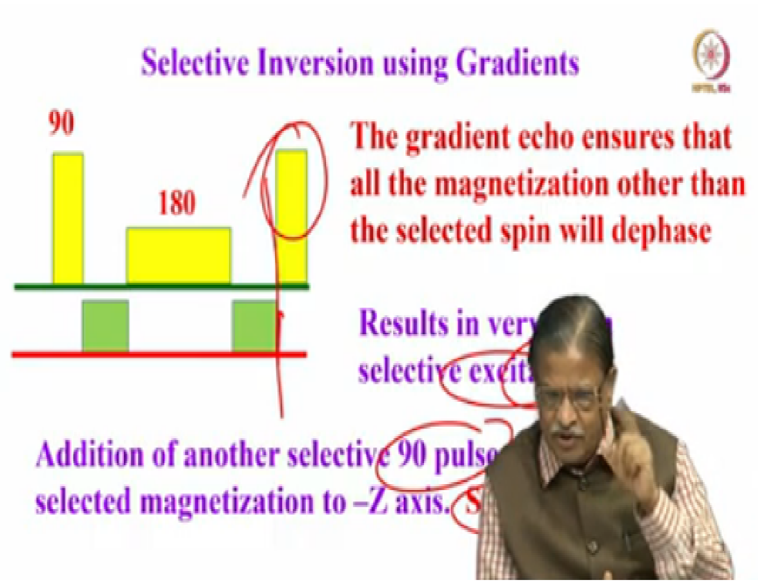

And of course, this is another thing which I wanted to say. You know after this gradient you apply another pulse, what it is going to do? Gradient echo ensures that all magnetization other than the selected one, uptill now you know, it selects only the selected magnetization, selected spin and all other things get completely nullified. After this if I apply another pulse what is going to happen? This result in very clean selective excitation also, plus the additional 90 degree pulse will take the magnetization to –Z axis.

Up to now, up to here we know, that is a very clean selective excitation because other than the selected magnetization of a particular spin, the entire other magnetization gets completely dephased. After that, you apply another 90 pulse, you are taking the magnetization of –Z axis. Then what is going to happen? then you do what is called selective inversion, this is called selective inversion. You can do selective excitation using gradients, very clean selective excitation, at the same time you can do selective inversion that is also very clean.

So, these are all very very useful applications. By applying gradients in many experiments we may have to do, apply for example, selective or refocusing experiments are there; where I want to get the J coupling for a particular selected proton, I need to apply the gradient pulses in such a way only the particular selected coherence are selective spin, only that magnetization will survive, all other I can remove it. I can completely clean up these things, then clean selective excitation I can get.

At the time I can use the gradient; or I want to selectively excite a particular spin and make sure all other spins are inverted, that means there would not be coupling between the excited spin and the inverted spin, I can do that. Then what is going to happen is, that is going to be a very clean experiment for decoupling; selectively we can do that also. We can invert the spins of the selected spin, so that it won't couple to other spins; the couplings can be removed. So, like this lot of experiments can be done.

Lot of experiments are possible and gradients can be applied to the various examples and apply gradients at various places in various 1D and 2D experiments. This has become nowadays very very handy compared to phase cycling, phase cycling. Phase cycling, of course in some cases we cannot avoid to use it, but then gradient has become very very useful technique, application of gradients with number of experiments you can do.

So, I think more about gradient we can discuss, but I think we have discussed enough. There is no need to discuss pulse field gradients further, you we can keep on discussing, but what basically I was telling you about the pulse field gradient is that; the pulse field gradient right from the beginning what we discussed, it creates gradient; it creates inhomogeneity along the Z axis and adds to the main magnetic field.

The gradient coil is designed in such a way, from the center the coil, upper half is always increasing in gradient, increasing in field. From bottom half the field decreases and then spins above above the center of the gradient coil, the spin rotates very fast, the spins below rotate slowly; and this Z rotation can be reversed by applying a counteracting gradient of equal and opposite strength. So, another thing what happens when you apply the gradient, the gradient decreases gradient strength is very large.

You can imagine there are several slices of different thickness, and each slice the spins will experience different Larmor frequency. They undergo different Larmor frequency, but within the like given slice, they all have the same frequency. But the gradient strength is huge, sufficiently large then what is going to happen the slice thickness become narrow and narrow. And it is like continuous distribution, in the sense all to the sample volume the different nuclear spins right from bottom to top, in the entire RF coil area will experiment different Larmor frequencies. As a consequence, you are going to get enormously broad signal which cannot be detected, this is what is called dephasing. Z rotation can be reversed by applying a counteracting magnetic field of equal and opposite strength, then you are going to get back the magnetization whatever is dephased you can get back and this is called rephasing of the magnetization. You can use the gradients by applying before and after the pulse to select a particular coherence pathway, you can select the coherence pathway for homonuclear case. And you can select the coherence for the heteronuclear case also. But in the homonuclear case, we took the example it was 1 is to 2, 1 is to 3, -1 is to minus is to 2, where one or two examples we took we could select a particular coherence pathway by looking at the ratio of the gradients. But same thing we did also for heteronuclear case, for heteronuclear case what happens, only thing is gamma is different. But you should not forget one thing in the heteronuclear case the total phase acquired during along Z axis, during the gradient G1 and G2 by both the spins I1 and I2 or I and S spin. Heteronuclear spin we will just call it S, I and S is to be considered; and then found out what is the total phase acquired and this should be equal to 0 for perfect refocusing. And then calculate; what is the ratio of the G1 and G2, keeping the duration t1, t2 identical, you can find out what should be the gradient ratio to select a particular pathway both for I spin and S spin, both during G1 and G2.

And also we saw in addition to that, the gradients can be applied for varieties applications; it is for selective excitation, clean up; we can selectively excite a particular spin, and there is a transverse magnetization created that we can remove also. The 180 pulse inverses and 180 pulse for imperfections can be corrected by applying the gradients before and after. So, it will continuously dephase and make sure that imperfection will be removed.

And selective inversion can also be clean, if there is any imperfection coming because of that, that also can be removed by the gradient. So, like this number of examples, we saw including purge gradient, pulse imperfection removal, selective excitation, selective inversion, everything is possible. But all these things I was trying to give you an example only for the one dimensional experiment, one dimensional NMR spectra; but these gradients are extensively utilized.

And we have number of 2 dimensional experiments; these will come very handy when you use it. And then since I have not introduced 2D, I have not discussed that. I will come back when I introduce 2D we will discuss more about these things, moreor at least one or two examples will take, how we can choose the pathway by using this gradient. For example, for a DQF COSY, NOESY, HSQC, we can do that. So, I will come to that later I will discuss all those things in the subsequent classes.

So, since today, the time is getting oer. I am going to stop here. With this we have covered all about phase cycling. Using pulses, pulse phase and receiver phase we can manipulate and get the chosen pathway, that is coherent pathway selection. You can also do the same thing by using gradients, by gradient dephasing and rephasing, everything we discussed. So, we will stop here, come back and in the next class I will continue with a different topic. No more phase cycling, for that will come back only after 2D. So, next class we will see maybe we can start discussing about NOE or T1, T2 relaxation phenomena. that we will discuss. thank you.