Advanced NMR Techniques in Solution and Solid State
Prof. N. Suryaprakash
Professor and Chairman (Retd)
NMR Research Centre
Indian Institute of Science – Bengaluru

Module-27
Pulse Field Gradients - I
Lecture - 27

Welcome back all of you, in the last class we discussed about phase cycling. In the sense we discussed a lot about coherent order, and how we can choose a particular coherent pathway; that is coherent pathway selection we understood. For which we discussed a lot about pulse phase and the receiver phase; depending upon which pathway we are going to select, accordingly we can get the receiver phase provided we know what is our starting pulse phase that was given by minus delta P into phi.

But delta P is the chosen pathway which is P2 - P1 and accordingly we found out for various examples how we could choose the particular coherent pathway and took the example of homo-nuclear case and then we selected for example 3P - 3P; + 2P etcetera, and we found out how if I select a coherent pathway delta phi = -3 it selects only particular that one. And when of course when we found out for delta P = 2 we also worked out what is the receiver phase and then we found out the receiver phase; although it matches with that of the minus 3P, but then when you acquired the data it was nullifying. So the receiver phase which was chosen for minus 3P was rejecting that for phase 2P. So we took several such examples also and we discussed a lot about how we can utilize the receiver phase. Also we discussed what happens is there are 2 pulses present; not only 1 pulse; if there are 2 pulses present what can happen?

Of course you can define the pulse phase and the receiver phase for first one, first pulse let us say; we can work out whether delta P = 1 2 3 minus 2 whatever we want. Similarly, we can work out what is the pulse phase for the second one. But then it is a combination; if I a take let us say, the first pulse. In the first pulse, let us say in the phase cycling, I will know what is the receiver phase; keep that receiver phase first second third, all the 4 step cycle or 8 step cycle what we choose.

We have chosen example of a 4 step; take the 4 step cycle, for each of these 4 step, you keep the receiver phase of the second one constant. Let us say that is also 4 step; first is 0, 90, 180, 270 consider. Here also 0, 90, 180, 270; for the receiver phase of this value go through one cycle; and then keep the receiver phase of the second one constant, then again vary these 4 now, change it to the second pulse receiver phase, to be the second one; like that you have to take the combination.

So, if you have a 4 step cycle 4 into 4 there are 16 step cycles will be there. And also we found out we have worked out and saw when delta P = -3 and we calculated what is delta P = + 1 and it was also selecting that. So, we also worked out a general formula for any phase cycling; any delta P which is coherent pathway what you select; depending upon the number of cycles you have for the phase cycling; 360 / N; note it is the capital N; if you consider then there is a general rule which I said minus delta P + n times capital N. N is multiples of small n, where N capital is this a steps of the phase cycle. We found out that is also possible and that can repeat the N number of times; there is a cycle of repetition of the phase cycle. So, this is what we understood everything; and some examples we took and did the coherent pathway selection. Of course when we complete 2D introduction and analysis of 2D spectra everything, we take 1 or 2 simple examples of using this selection of the coherent pathway for 1 or 2 simple 2D experiment like maybe COSY 2D or DQF-COSY like that. And we will see how we can utilize that where we have 2 pulse sequence, 3 pulse sequence; how we can utilize this phase cycling. How we can select the coherent pathway; with that today we will go further what we have to discuss the same thing, which we can do in a different way, called pulse field gradient; PFG.

We can utilize the pulse field gradient and achieve or select particular coherent pathway what you want, like we did with phase cycling using the pulses. One advantage here in the case of the pulse sequence, if you consider using pathway selection by phase cycling using pulses, we have to have N number of repetitions like 4 steps, if there are 2 pulses; 4 into 4, 16 steps like that, it is time consuming.

On the other hand by using what is called the pulse field gradient, you can do it faster; in a single experiment, in one experiment, in one scan you can choose the right pathway; that is possible. So, we can see, we can discuss about pulse field gradient today; and workout and see how we can choose the pathway.

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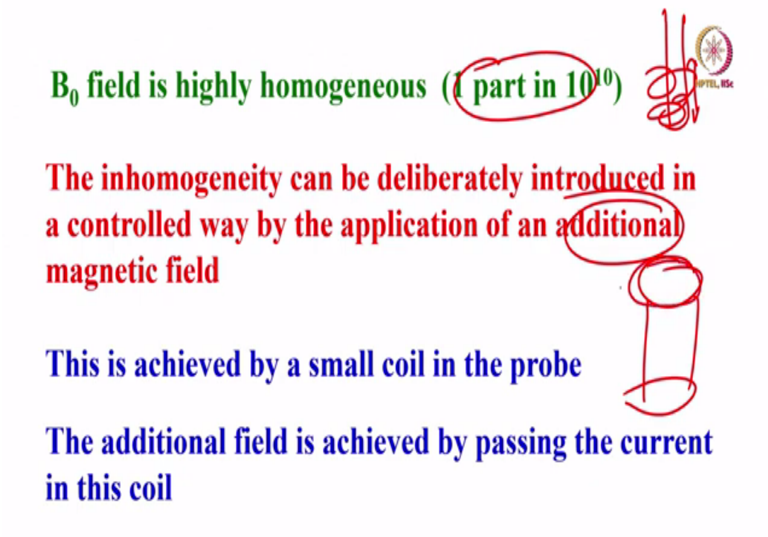

Of course, B0 is the highly homogeneous magnetic field that we know; the external magnetic field what we use for detecting NMR signal is highly homogeneous. That is over a sample area, this is my sample; over a sample area my entire RF coil is here, my entire RF coil area of the sample magnetic field will be perfectly homogeneous. That means each nuclear spin experiences the same magnetic field; there is no difference in the magnetic field at all.

And the homogeneity is so much; it is 1 part in 10 to the power of 10; that means, in a 300 or 500 or 800 megahertz spectrometer, I must be able to distinguish any 2 frequencies that are separated by even 0.1 hertz are less than that. That is the amount of homogeneity or the resolution we get. So a highly homogeneous magnetic field is required. So B0 field is highly homogeneous, but now can I make it an inhomogeneous?

Of course, you do not have to worry naturally if there is inhomogeneity we do need to make it homogeneous by shim coils; that we discussed in the first course itself. If there is a time left at the end, I will tell you some experimental titbits about data acquisition and processing once again for the benefit of those who did not attend that previous course; that will come at the end.

But right now, I want to tell you in addition to that we can deliberately introduce inhomogeneity for the magnetic field, in a controlled way. How do we do it? By putting additional magnetic field. This additional magnetic field is generated by a small coil which is kept in the probe; which is called a gradient coil. This additional magnetic field you generate by passing the current into this coil. When you pass the current into a coil like this, it will be there you pass the current here, it generates a magnetic field.

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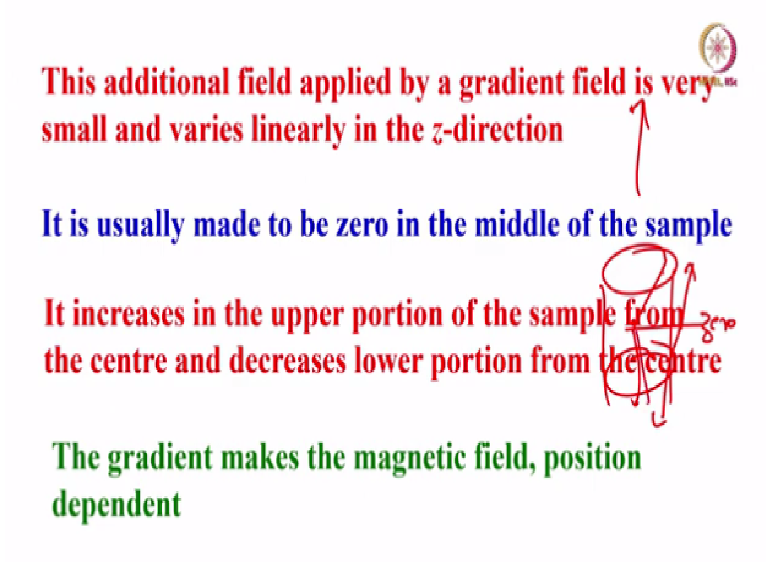

And this how do you control this magnetic field, I am going to tell you; we can do that. The additional field applied by the gradient is very, very small. And we can vary it linearly; in fact designed to vary linearly along the Z direction. We have a Z coil, Z gradient. Of course we have gradients coil for X, Y etcetera. But for our interest, we do not have to worry about X and Y gradients; Z gradient we can select. When the additional field is applied by gradient coil, the magnetic field varies linearly in the Z direction.

Now, how do we design this coil is like this. A crude drawing I am writing; the this is made to be uniform; it is 0 at the centre. The field which is generated by this coil is made to be 0 at the centre, and then it increases in the portion above, the upper portion of this coil. From the centre if you go up the field increases linearly; if you come down the field decreases linearly it comes down from the centre of this coil. So the gradient field, of course, it varies as you go up and down, but it is position dependent now.

So because spatially I can vary it as you go from centre towards top of the sample, sample tube. Or come down in the RF coil, in the gradient coil, the field keeps on increasing this way; here keeps on decreasing, the gradient field.

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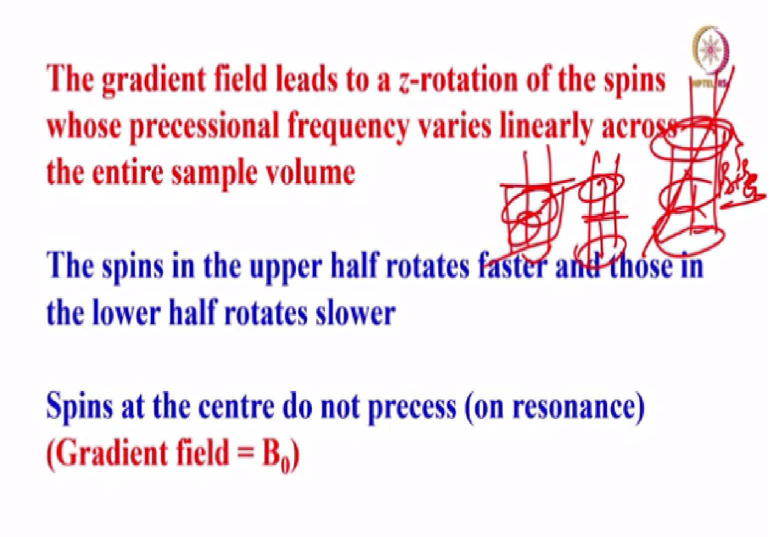

So that is another one point which you should know. The gradient field also leads to Z rotation of the spins, because it is nothing but adding to the B0 field, because the additional field you are applying adds to the B0 static field. That means the precession frequency in the entire sample varies linearly. I take the sample in a tube; here NMR tube and I have a gradient coil here; and then in addition to B0 field, the field is varied here linearly.

So, at every stage, at every point in the space; as you keep on going up what happens? the magnetic field keeps on changing. When the magnetic field keeps on changing what is going to happen? B0 plus addition of the magnetic field because of the gradient; I call it let us say BZ or BG that will keep adding up here, it keeps coming down. So, as a consequence, what happens, different parts of the sample experiences different precessional frequency.

So, that is another important thing; and here what happened, B0 + delta additional magnetic field because of the gradients, here it is added up, here it will be subtracted. As a consequence what happens, the spins in the upper half of the sample rotates faster than the spins in the lower half. Please remember I have the sample tube here; and this is the coil. And of course, I have a gradient coil added here, and I take this one as the centre. All the spins here above the centre rotate faster and one which is below rotate slower.

And what happened to the spin at exactly centre? it is considered as on resonance; that means if the gradient field is exactly at the B0 field. There is no variation; the spins will not precess at all. Spins at the centre which is on resonance do not precess, but the spins in the upper half rotates faster under the lower half rotates slower.

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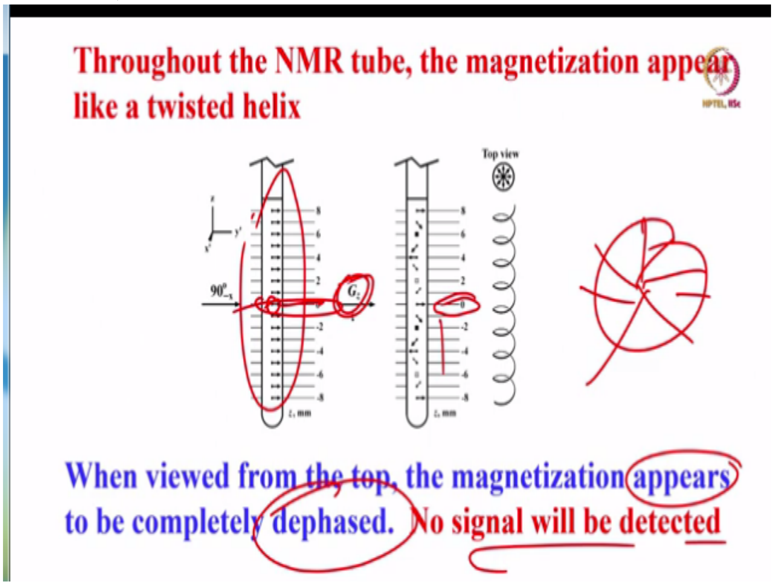

This is the one which is diagrammatically shown here. Throughout the NMR tube the magnetization appears as if it is appearing as a twisted coil. See this is the centre of the NMR tube, at which it is 0, there is no change. Let us say the gradient field along Z axis is 0 at this point; all the spins here are at on resonance, it does not change at all. But the ones here, before application of the field everything is actually having the same precessional frequency across the entire sample tube. Now I am going to apply GZ exactly matching with the 0, at the centre of the tube. But this one; the spins aligned at 0 will not precess, because they are on resonance. But look at this, there spins which are above and below they start rotating one is faster here, and the other is slower here. And when you view from the top; from the top of the magnet, top view is like this, as if it is rotate like this.

For the entire tube of the sample it is going like this; that means when viewed from the top the magnetization appears to be completely dephased, and no signal will be detected that is important. Please remember, when I am seeing the signal from the top the spiral is going like this, it is a helix not spiral, helix is going like this. And then when you view from the top it appears as if the spins are completely dephased. When there is completely dephasing in the XY plane, you will not get any signal and that is what the gradient does, it dephases the signal.

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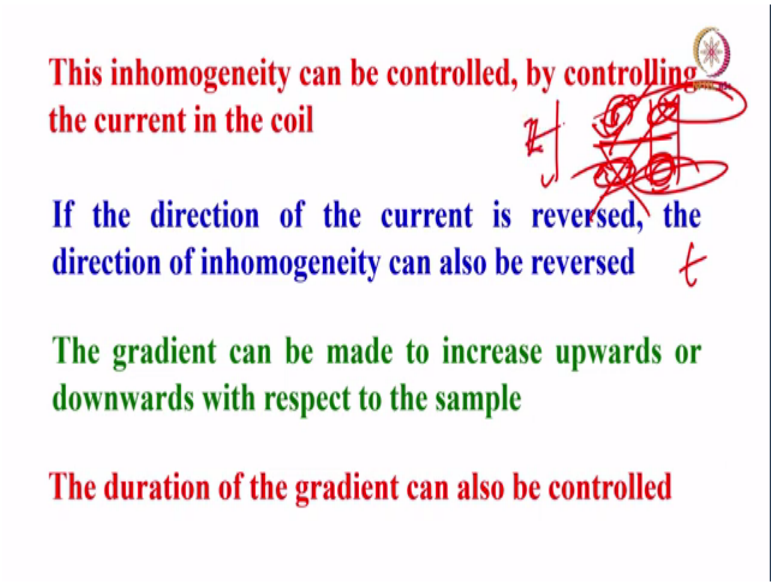

And this inhomogeneity of what you are going to create by gradient you can control it, by controlling the current in the coil. And what happens now? I take an example like this; the spins here are rotating faster, the spins here are rotating faster when I apply the gradient current. Now, here current is flowing in this direction, from the centre go to the bottom current is put in the opposite direction. That is why I just told you this moves faster, this moves slower. And the centre is 0 and here it increases here it decreases.

Now, what will happen if I reverse the current instead of applying current in this direction if I reverse it now, what will happen? Remember, Z rotation can be completely reversed; this sample starts precessing in the opposite way; in the sense the spins which are moving faster here starts moving slower; and the spins which are moving slower here, starts moving faster. In the sense centre the precession of the spins here now becomes faster, precession of the spins here now become slower; so that is another important thing.

Next question is, you may apply a gradient pulse, in the gradient coil ; again it is controlled by application of a pulse. What is the duration of this gradient? How long you have to apply? that can be given by a time t, you can control that. And if it is along Z axis, sometimes we call it as duration time is Z, we can also control that. So duration of the gradient can be completely controlled.

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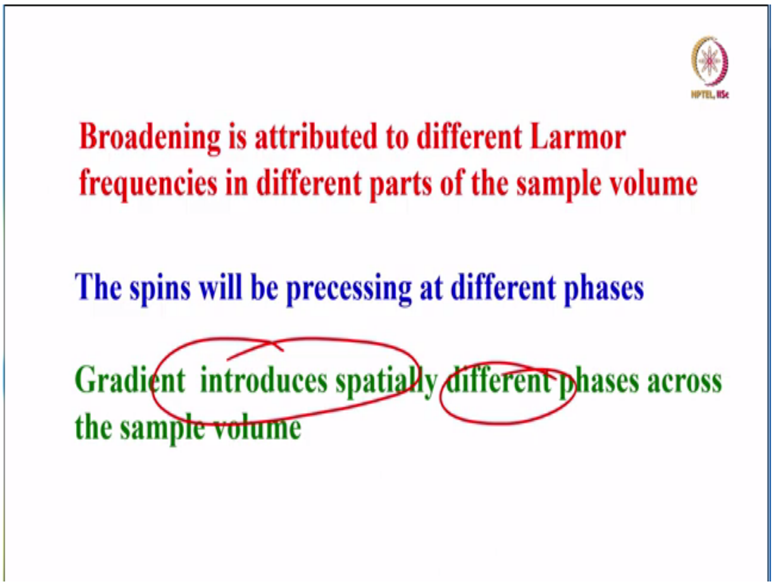

Now you might ask me the question what happens if I take the spectrum which is generally you can get in the static magnetic field being highly homogeneous, you will get a very, very sharp signal. But with the Larmor frequency getting changed all across the sample, when the different parts of the sample experiencing different magnetic fields, the Larmor frequency will differ then; what we are going to get?

We are going to get a broad hump because different samples are undergoing precession at different frequencies or otherwise spins are under having precessions with the different phases. So, what it means is the gradient introduces spatially different phases across the entire sample volume. The phase and frequency are related; that in the very first course, in the beginning itself we have discussed, The phase and frequency, you can correlate them.

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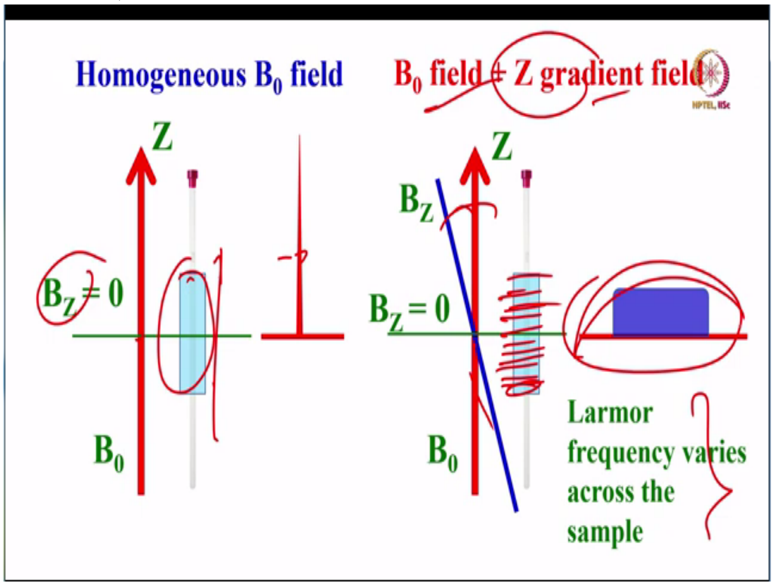

In a homogeneous magnetic field this is what happens. I take a NMR tube take the sample and put it; this is my RF coil area. The magnetic field is along this axis, BZ it is 0 here; does not matter whether it is 0 or what, because the entire sample volume the magnetic field is highly homogeneous, perfectly homogeneous. So what we are going to get? Homogeneous magnetic field with each sample, every nuclear spin which are detecting for a particular nucleus experience the same magnetic field.

As a consequence, you are good to get a single sharp peak. Of course, this is the natural line width here, that also we know. What we are going to do, we are going to get now. Now I am applying with gradient field along with B0, field of course B0 field still is homogeneous, but we are making it inhomogeneous by applying a gradient coil, like this. Now, what is going to happen? We apply a gradient, we discussed what happens to the spins above 0 and below 0.

Now, the Larmor frequency keeps on varying across entire sample. As a consequence, you are going to get a broad signal; you can consider there are thin slices of the samples here. And in each slice actually what happens, the spins have different frequencies, but within this slice they have the same frequency. But from slice to slice the precession frequencies are different. As a consequence, you are going to get unresolved number of precessional frequencies which are going to give a broad hump like this.

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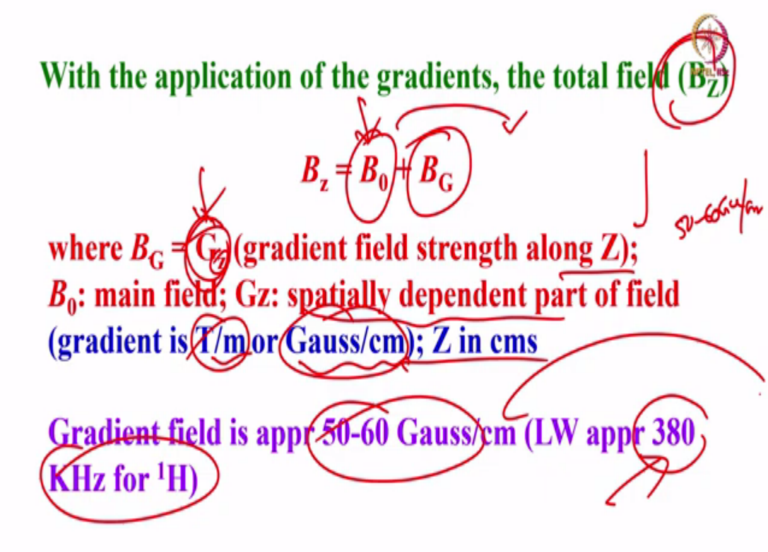

Now you will ask me a question; what happens if the slice thickness becomes narrow, I increase the gradient; manipulate the gradient in such a way here, that the slice thickness I can make it narrow, becomes very, very narrow; then what happens? Then the entire sample volume, you can consider the continuous distribution of slices, in which case not only the broad signal, you do not get any signal, because there is a complete dephasing that is what happens. So with the application of the gradient, the total B0 we can work out like this.

Now, B0 is magnetic field, what is the magnetic field generated or total magnetic field now with the application of the gradient field BG. Now BG = GZ, it is because it is a gradient that is applied along Z axis; G is the strength of the gradient; G is always given us a strength of the gradient. The subscripts tells me that we are applying along Z axis. Of course, what is B naught, you know the main magnetic field; and GZ if I calculate BG = GZ it is a spatially dependent part of the magnetic field.

So we know B0, B0 is of the order of several tesla; 5 tesla, 10 tesla, 20 tesla, like that. What is the gradient field? it is very, very small. It is few Gauss per centimetre or tesla per meter. Or in other words, if you say Z is the centimetres, we can say over the approximately 50 gauss per centimetre or 50 to 60 is the strength of the gradient field that we are applying. So gradient field is reasonably quite large, it may not be as large as B0, but reasonably quite large to create complete in a broadening of the signal and completely make sure that no signal will be detected when the slice separation becomes very, very small. So gradient field is approximate 50 to 60 gauss per centimetre, which if we calculate line-width turns out to be about 380 kilo hertz proton; 380 kilo hertz remember; our spectral width is only about 10 ppm in 500 megahertz, it is 5000 hertz; 5 kilohertz, but it is 380 kilohertz, that is the reason why when you apply a gradient, the inhomogeneity is so much; in principle, there is a complete dephasing and you do not see any signal.

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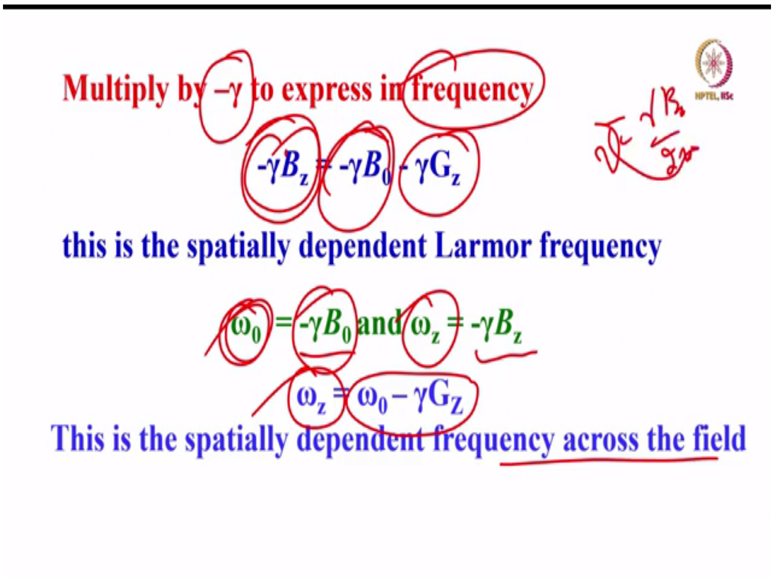

Now, the same equation here, BZ = B0 + BG. Now I am going to multiply this equation by minus gamma, gamma is my gyromagnetic ratio. Why did I do that, because I want to express this in frequency for some unit conversion. There is not any magic we are doing; simply we are multiplying this minus gamma to express in frequency. So, this becomes minus gamma BZ - gamma B0 and minus gamma GZ. This is a spatially dependent Larmor frequency.

We calculated Larmor frequency just by multiplying by minus gamma. We know what is gamma B0; it is a precessional frequency; Larmor frequency; you can express in omega 2 phi nu or omega. This is similarly, now WZ I can call it a gamma BZ. So, if I put this gamma Z as WZ then what is my equation? this becomes WZ equal to this is omega 0 - gamma GZ this is my equation.

This is spatially dependent frequency across the entire magnetic field, entire sample we are taking. This what it is; I did not do anything except simply multiply this equation by minus gamma. And I know the Larmor frequency or precessional frequency is omega = - gamma into B naught. You know that; do not have to get confused nu = gamma B0 over 2 phi. So, this 2 phi when it goes here just can be called as omega0. That is all is done, nothing else and then this is the spatial dependent frequency across the field.

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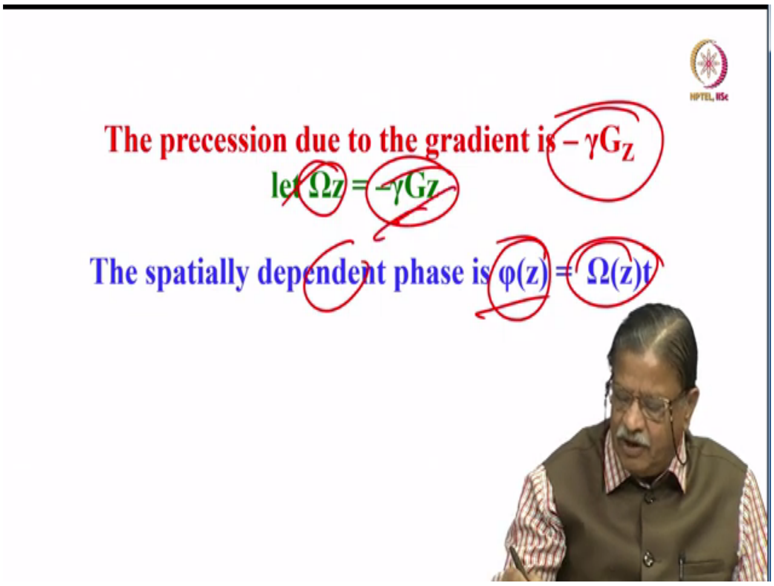

The precession due to the gradient is minus gamma into GZ, because of the gradient. Now what I am going to do this; let the capital omega Z as minus gamma into GZ; I am going to call it like that, just to make my mathematical writing very simpler. Then the spatially dependent phase I defined as phi of Z, across the direction Z. you could do omega Z into t from the previous equation. So that is what the spatially independent phase, which is equal to gamma Z, gamma Z is going to B0 into t, t is duration for which you are going to apply the gradient.

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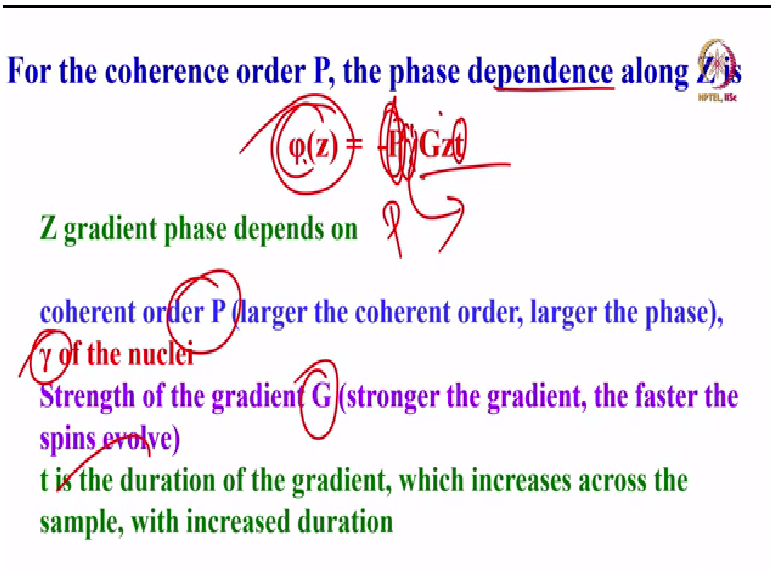

So now we can define one thing for the coherence order, which we know. For the coherence order P, we can also find out what is the phase dependence along Z; like we have coherence order we knew, we have worked out the coherence transfer pathway. If I have a coherence order P then this phase of that is dependent along Z axis; that phase can be given by phi of Z is equal to coherent order P into gamma into GZ of t. GZ is we know, the t is a duration; G is gamma and P is the coherent order.

So for a particular coherent order I can find out what is the phase. That is given by phiZ. Simply remember phi Z = - P into gamma into GZ into t. The Z gradient phase depends upon various factors; that is what it means, the phase of the Z gradient depends upon various factors. First it depends upon the coherent order P, it depends upon gamma of the nuclei because different nuclei, if I want to have a hetero-nuclear pulse sequence for which I want to select the coherent order for proton coherent order for x nuclei, then accordingly we have to calculate differently because gamma will be different. And it also depends upon strength of the magnetic field I am sorry gradient field G. And stronger the gradient faster the spins will evolve, and t is the duration of the sample. So, these are the things which are important parameters on which the phase of the pulse, the phase dependence of the particular coherent order P along Z can be defined. So simply remember if I have a coherence order P, the phase dependence of that along Z axis is given by phi of Z = - P into gamma into GZ of t; that is all you have to remember.

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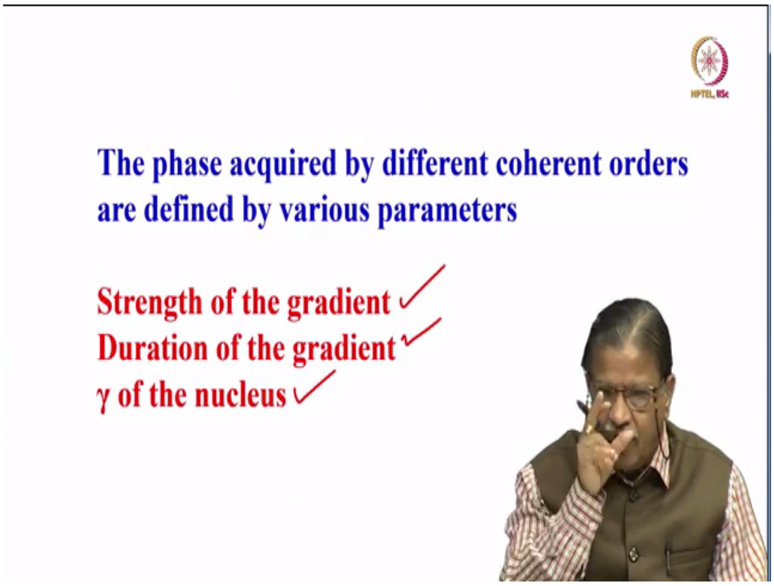

So, the phase acquired by different coherent orders, now are defined by various parameters. I can define by strength, I can define by duration, I can define by the gamma of the nucleus. These are the parameters, which control the phase of the different coherent orders.

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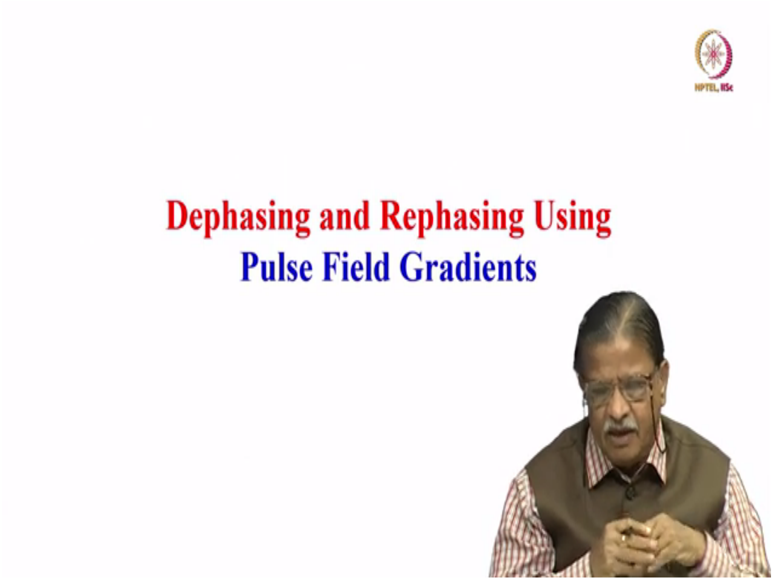

Now I will introduce something what is called dephasing and rephasing using pulse field gradients. We understood something about pulse field gradients, already I told you about rotation and everything.

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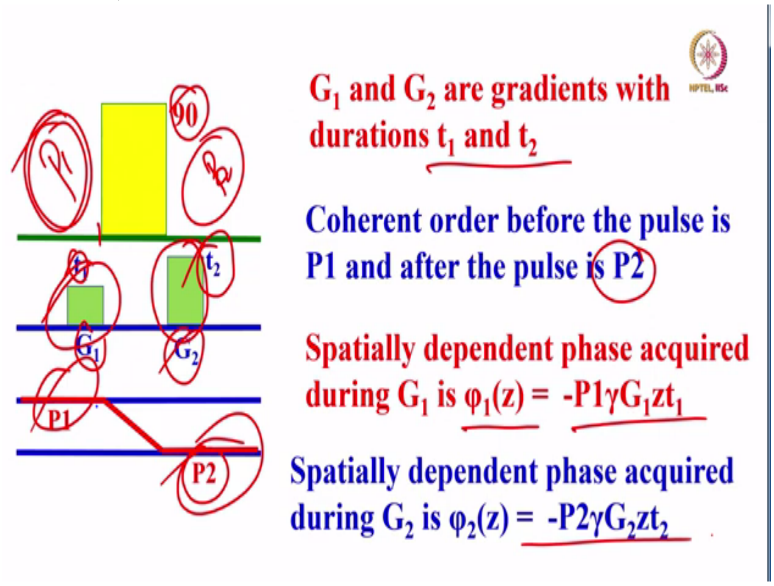

Now, I consider a situation; I am going to apply a 90 degree pulse on some nuclei, proton let us consider. And before the 90 degree pulse, I am applying a gradient which is G1, the strength as the gradient. The duration of the gradient is t1; for the time t1 I apply a G1 gradient just before the application of the 90 degree pulse. After the 90 degree pulse, I am going to apply another gradient pulse, another gradient G2, that is for the duration t2.

Now what we are doing, simply apply 90 degree pulse before the 90 degree, we apply a gradient G1 for duration t1 and immediately after the 90 degree pulse we apply a gradient pulse for the duration t2 of strength G2. Now G1, G2 are gradients and t1 and t2, I told you are the durations. Now the coherent order before the pulse I call it is P1 here, this P1 is coherent order; and the coherent order after the pulse is P2; this is what I am defining.

If I want to find out what is my coherent order before the pulse I call it P1 and after that I call it P2, this is how I define the coherent pathway now. Just before the pulse this is P1 now after a 90 pulse it is P2. Now you might ask me what is the gradient doing there? what are the gradients doing there? Spatially dependent phase is acquired, we can calculate. The spatially dependent phase acquired during G1; I already told you the phase can be calculated by minus P into gamma into G1 into Zt I told you.

Now for the coherent order P1 which is P1 gamma G1 Z t1, this is the phase is occurred during G1 because coherent before the pulse was P1. That coherence is now I call it P1, it acquires the phase which is P1 gamma G1 z t1; this what the phase it is a acquiring. Now what happened to the phase immediately after the pulse, now it is P2, the coherent order is P2; same way you can calculate the phase acquired after the pulse by G2.

Now the coherent order is P2, gradient is G2 and duration is t2; that is all. Simple 2 equations only. What I did was, I just varied the terminology here, you should remember. I did not do anything here, only what I did was before I calculated the phase of the coherent order P 1 because of the G1 gradient and P2 because of this one. So that I told you a coherent order of the phase can be calculated along Z axis based on these equations. These 2 equations always remember. Now I know what is the phase due to G1 and due to G2.

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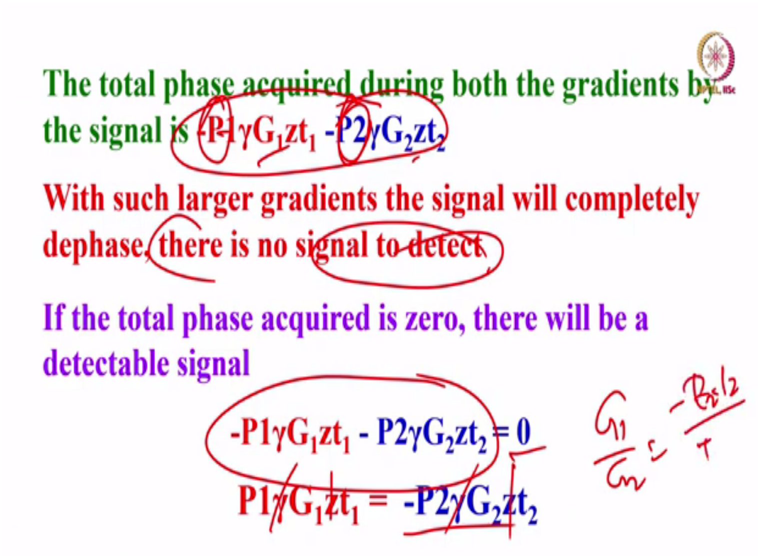

But what is the total phase acquired during both the gradients by the signal. When both the gradients are applied, the signal will experience phases, first because of G1 and secondly, because of G2. Both the phases are there. And the total phase is the sum. The sum is again phase acquired by P1 and the phase acquired by P2 due to G1 and G2, for the duration t1 and t2 respectively. This is the total phase acquired.

Now with such a large gradient the signal completed dephased and there is no signal to detect. Then what is the point in applying the gradient if we cannot detect the signal? You must detect the signal, that is our aim. So, what to do with the total phase somehow make it 0. Instead of total phase is something which is quite different because of sum of these two with a large gradient, then you do not see the signal to detect. I will ensure whatever may be the phase acquired for the coherent order P1 during G1 and for a coherent order P2 during G2 does not matter.

If I take the total phase and make sure that the total phase becomes 0, then I can still detect the signal that is an important condition. So, what we can do is, now I will put a condition that the total phase acquired if I equate it to zero, then I am going to get the signal I will detect the signal, signal will not get nullified. So, now we will do the simple arithmetic then this will become like this, now gamma being the homonuclear get cancels out, Z is you can cancel it out. So what you are going to get G1 / G2 = - P2 into t2 over P1 into t1. This what you are going to get now.

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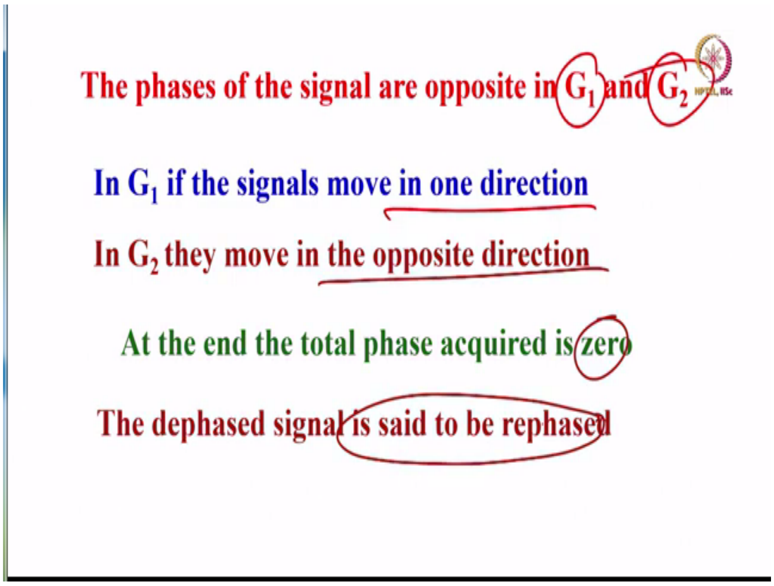

So the phase of the signal is opposite in G1 and G2. So the phase of the signal of what we got are opposite in G1 and G2. In G1 the signal moves in one direction; in G2 they move in the opposite direction, because that is what we saw here; they are opposite now. So, this is what it is; at the end finally it so happened that total phase becomes 0. Now we call this as rephasing.

If the total phase is not 0, then what is going to happen? There is a complete dephasing you do not get the signal, if I ensure the total phase acquired by phase by coherent orders P1 and P2 during G1 and G2; the total phase somehow equal to 0; then I can still get the signal. Then I say the dephased signal is rephased. This is an important point.

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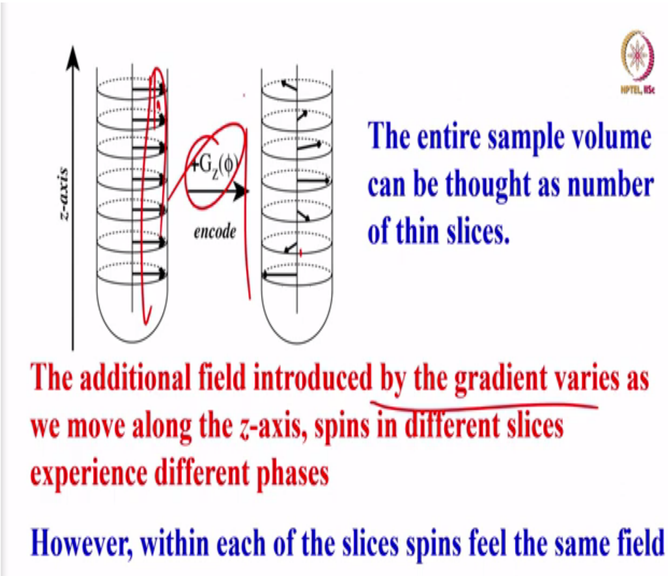

And diagrammatically you can see like this; these are all uniformly aligned, there is a perfect alignment here. And they are in homogeneous phase, there is no change in the frequency; all the frequencies are same; here because of the GZ they are all different. The slices of sample experiences different Larmor frequencies, there are rotating with different precessional frequencies. Now, the additional field introduce with the gradient various along Z axis. However, within each of these slices, all the spins are rotating, and experience the same field.

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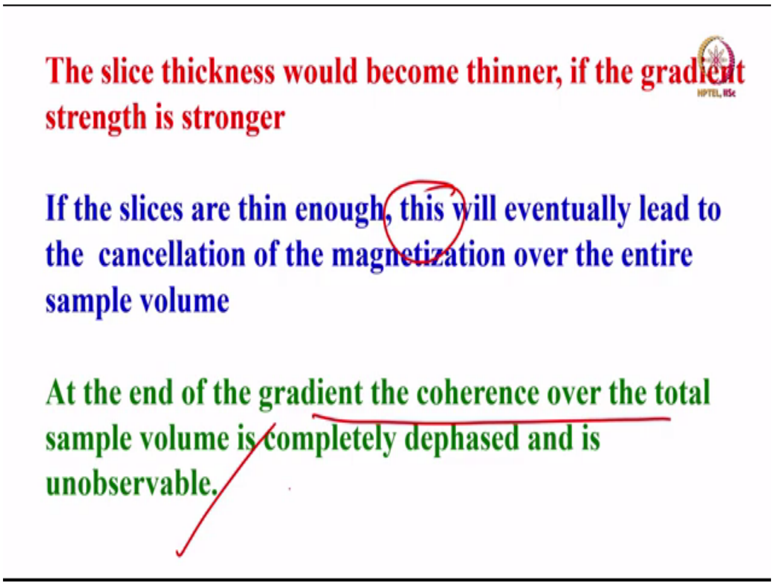

So now what is going to happen? As the slice thickness becomes thinner and thinner, the gradient becomes stronger and stronger. In which case, when the slice thickness becomes very, very thin, eventually there is a complete cancellation of the magnetization over the entire sample volume. At the end of this gradient the coherence over the entire sample is completely dephased and there is no observable signal.

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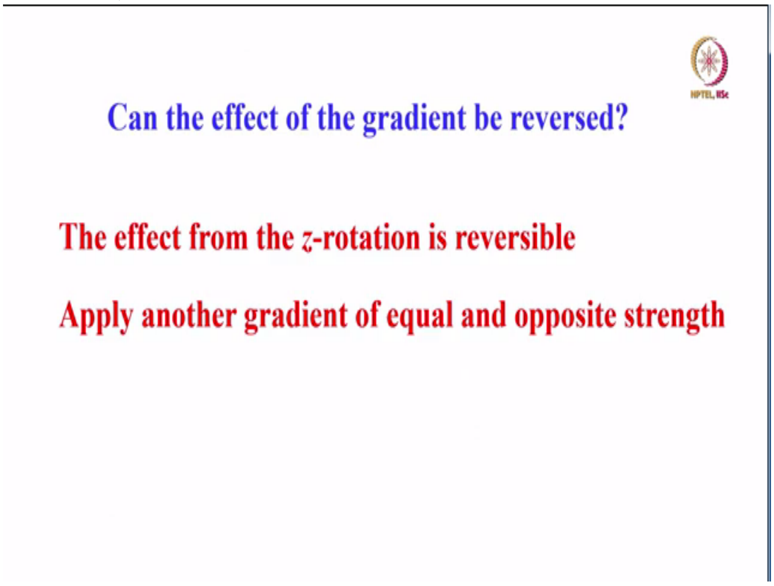

So now what we are going to do is, we can reverse this one. So, how you reverse it; I am going to tell you. Now since the time is getting up, I am going to stop at this point. What I wanted to tell you is in this class; I introduced the gradients, I told you how we generate gradient by a coil, and it is assumed to be 0 at the centre and above if you got top upper half of the coil there it is increasing and the spins are precessing faster and below they are precessing slower.

And the opposite current make spins rotate in the opposite direction below, it decreases, it increases. So in fact, it is strictly analyze, the spins in the upper half goes in one direction precess clockwise, the spins below the centre of the gradient coil, below the centre, precess in the anticlockwise direction. The clockwise and anti clockwise precessions also will be there. I did not discuss more about these things, because these are two fundamentals, conceptually; we can worry about it later.

But what I wanted to tell you is by applying the gradients before the pulse and after the pulse, you can make sure that signal that is completely dephased can be rephased. If G1 is and G2 are the two gradients before and after the pulse; the phase acquired is given by minus P into gamma G Z into t; that is what I said. So, depending upon the coherence order, one can know how much phase is going to be acquired.

Take the total phase, if turns out to be equal to 0; then you will get rephasing. You can still get back the signal. If the total phase acquired is not 0, it is a complete dephasing. You do not get the signal. So how do we get the rephasing? How we can? what we can do? I will come back and tell you later, thank you.