One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture - 08
Pulse Phase and Signal Phase

Welcome back all of you, see in the last class we discussed about the concept of rotating frame, where I mentioned to you before the applications radio frequency pulse the spins are rotating were precessing around the static magnetic field B naught. B naught was static. When you apply a radio frequency pulse with gamma B naught equal to gamma B 1 exactly, which I said is an on resonance condition. You are bringing the magnetization from Z axis to X axis or Y axis and they start precessing in this plane.

You understand? Now I also introduced that in the on resonance condition, what happens the spins feel that B1 field is static and B naught is 0. So it starts precessing around B1 and the B naught field is of the order of the Tesla. And if you calculate in frequency it is of the order of several megahertz 100s of megahertz. Whereas the rf pulse you apply is much smaller in magnitude compared to B naught field, whose frequency if you calculate is of the order of 20 to 30 kilohertz.

Where is megahertz and where is kilohertz. It is several orders of magnitude smaller we are applying small power and small magnetic field and made the spins to precess along the B field which is assumed to be static in the rotating frame. This is the condition I explained to you, if gamma B naught is not equal to gamma B1, I said you are entering into an off resonance condition where the effective field will be the combination of B naught plus B1, which is instead of being here, it will be somewhere here.

The amount of magnetization that is tilted, if it is on resonance condition then it is a complete magnetization. When it is off resonance it will be somewhere here, the effective field will be somewhere here, the magnetization is seen here. If you can resolve into the 2 components you see the bulk magnetization is not complete. You are not seeing the entire magnetization. The amount of magnetization tiled is much less. So you can manipulate the amount of magnetization that you tilt in different directions and different axis by applying radio frequency pulses in different directions. We will discuss about the pulse phases and pulse signal phases later. But this is the basic concept.

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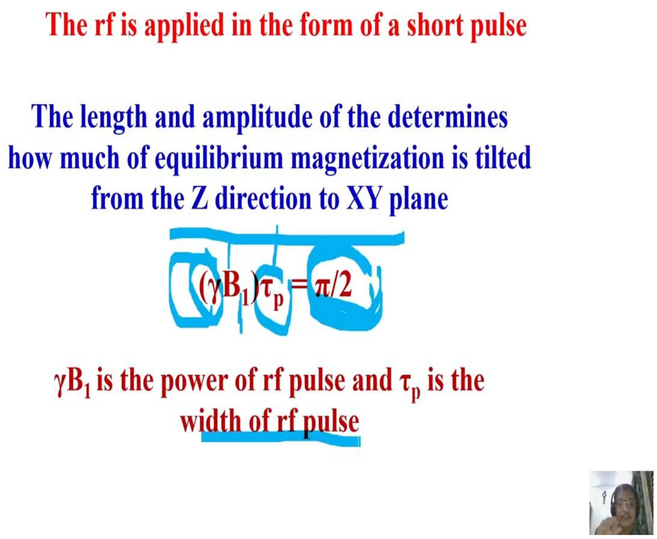

And I said a pulse is applied in the form of a short rf pulse, I discussed and you can manipulate the rf power and the pulse to get the desired angle, desired flip angle. Flip angle is the angle at which you are going to flip the magnetization. So gamma B1 is the power of the pulse. We know gamma, we know pulse width, we know pi / 2. If you want 5 microseconds adjust the power accordingly. In other words, I know gamma, I know pi / 2, I can play with rf power and rf pulse to choose the angle of tilting of the magnetization, the amount I want. So you can manipulate to tilt the magnetization to the desired value.

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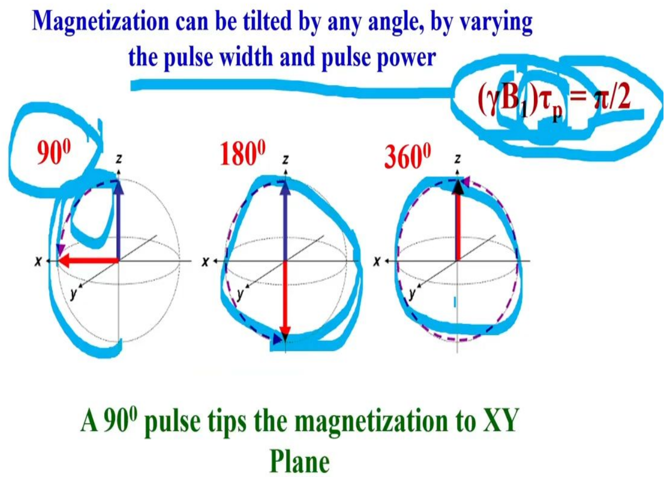

Let us look at this thing how the magnetization is going to be tilted by any angle, by varying the pulse width and the pulse power. In the first situation I gave this equation earlier, consider 90 degree pulse. I am tilting the magnetization from Z axis and bring it to exactly X axis, the power and the pulse you require, let us say, if I keep the power constant, the pulse width which you require can be adjusted. The flip angle, which is of course the combination of power and pulse width, to flip the magnetization from Z axis to X axis is called a 90 degree pulse.

So it is expressed in few microseconds. The pulse width for a pi / 2 flip angle could be of the order of 5 to 10 microseconds for proton. You can calculate easily, it is easy to calculate. If I double the pulse width what happens, keeping all the other things constant. I can keep the power constant. This any way I can handle. If I double pulse width what will happen? This magnetization goes further, it comes to minus Z axis. Interesting right? I am just increasing the pulse width.

I took the magnetization from Z to X, X to minus Z. Now I am going to increase further, make it 3 times this value, what is used for 90 degree, then it will come to 270. From here we started, this is called a 270 degree pulse. you have tilted the magnetization by 270 degrees starting with Z brought to X, minus Z and took to minus X axis. Increase further make it 4 times the value of this 90 degree pulse width. Then it will bring it back to 360 degree, go here come back and complete rotation is done.

What did you do? You make the magnetization to rotate one complete precession. It goes one complete rotation from Z to X; X to minus Z, minus Z to X, so it is rotating. So you brought the magnetization by 90 degree here, brought here, brought here, brought here, you took it like this. Keep on making it, you can make it rotate the way you want, Z to X, X to minus X, minus Z to plus Z, you can make the magnetization to rotate in the XZ plane.

Remember, from Z came to X, minus Z minus X and Z. So you can make the magnetization to rotate in the XZ plane. In this way when you bring the magnetization initially to plus X axis take it into minus X and Z, you make to rotate 360 degree. Of course you do not have to stop there. You can continue further. Keep on applying 360, 720 degree pulse, you can make it go around 1 rotation, 2 rotations, you can continuously make the spins to undergo rotation.

You understand the beauty of it. You can play with the nuclear spins the way you want. You can make nuclear spins dance according to your tunes. You apply a 90 degree pulse like this and bring 180, whatever you want, it will listen to what you want to do. You can bring here if you want, ask it to come here, come here, like this. So this way, in this example I have shown, I made the magnetization to rotate in the X, Y, Z sorry X Z plane.

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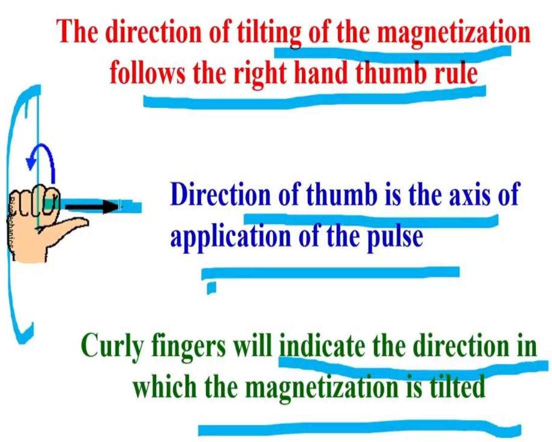

And the direction of tilting, I initially said I tilted to X axis ,but I cannot tilt, I cannot apply the pulse wherever I want and tilt it to particular axis. There is a rule which has to be obeyed, which is followed. The direction of tilting of the magnetization follows the right-hand thumb rule.

Please understand this. It follows the right-hand thumb rule, the direction of the thumb is the axis of application of the pulse. The direction of thumb is the axis of application of the pulse and the curly fingers here tells you, which gives indication, the direction in which the magnetization is going to be tilted. Please understand, now let us say this is Z, X and Y axis. Now I am going to apply a pulse on this axis, the magnetization is along Z axis. So what will happen, if my thumb is in the X axis, from Z axis it will tilt to this axis curly finger is pointing towards Y. So if I apply a pulse along this axis, the magnetization which is here tilts like this, to the Y axis, you understand? So the curly fingers tell you the axis in which the magnetization is going to be tilted. And your thumb tells you that the axis in which you are going to apply the rf pulse. This is the right-hand thumb rule which you must understand to see where the magnetization is tilting. Let us understand. From this I will give you some ideas about pulse phase and signal phase,Which we will discuss later when you go to some sophisticated discussion.

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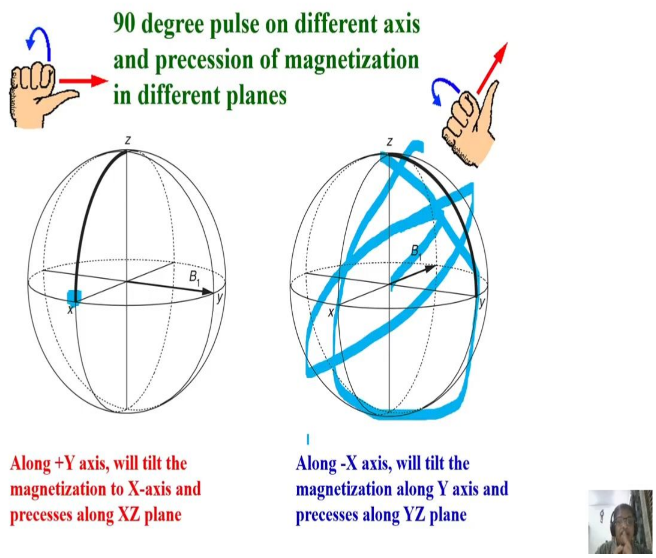

Now let us take the example of 90 degree pulse applied on different axis and see what happens to the precession of magnetization in different planes. Apply 90 degree Y pulse. Of course this is Y, Y is taken along this axis, this is Y, this is the X, see remember this is Z, this is Y, and this is X, towards you the axis is X, this is a convention followed in this diagram.

So now you are applying the pulse along Y axis, what will happen? The magnetization along Z comes to the X axis, remember the previous scene, I said this is X, and but only I change the nomenclature in this diagram that is all. Now you are applying the rf along Y axis, the magnetization from Z axis is tilting to X axis. So this is a curly finger, my thumb says I am applying the magnetization along Y axis and the curly finger says it is shifting to, or tilting towards X axis.

So then continue further it goes here go to minus Z, minus X and Z. So this is the axis it rotates, you can make the magnetization to rotate along the XZ plane it rotates the XZ plane. Understand, see here it comes from here to X, goes to minus Z, goes to minus X and Z. So imagine now XZ axis is here keeps rotating in this XZ axis. What happens if I apply instead of on Y axis, along this axis? If this is my positive X axis this I consider as negative X axis.

What happens if I apply pulse along this axis here? What is going to happen? Now see this is the axis, you have to think my thumb is in the negative X, X was here, minus X is here. So my thumb is in the minus X axis, the magnetization is along Z axis, the curly finger is here. That means it comes to Y axis, that is what happens. So now if I apply the pulse along minus X axis we are bringing the magnetization to plus Y, and then keep on increasing the pulse width, make it 180 degree pulse, it comes to minus Z, then go to minus Y and then goes here.

So what is happening here, see this one, you can make this magnetization to come to Y, minus Z and it keeps rotating in the YZ plane? Very interesting right? I can make the magnetization to rotate in any plane, in any direction I want. Need not be 90 degrees, I can take along this axis, I can make it to rotate in this plane, in a plane where contributions from all other things are there. I can make it rotate here. It is possible.

So I can decide the pulse angle and pulse power in such a way I can tilt the magnetization to any axis, I can make it a rotate it in any plane. This is the important rule called right hand thumb rule. You must understand, please do not forget this point, thumb shows you the direction of application and the pulse. The curly finger shows you which direction the magnetization is going to be tilted.

You understood here, let us say you are brought the magnetization from Z to X axis, it is already here. We are applying the pulse again along Y axis. Further it goes down. So you can keep tracing the path like that. OK. This you can practice what happens if apply the pulse in a different axis like this. You can practice. Now I will tell you something about the pulse phase and signal phase.

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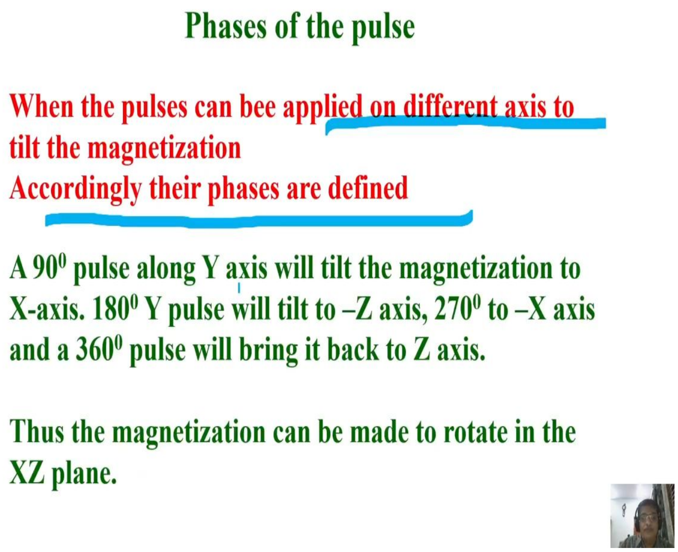

This what I was telling you was signal phase. Now phases of the pulses, what is the phase of the pulse? When the pulses can be applied on different axis to the tilt the magnetization accordingly you can define the phases. What does it mean? Go back to here, this drawing, I applied a pulse, 90 degree pulse to bring the magnetization to the X axis, where did I apply the pulse, applied 90 pulse Y. The applications the pulse here is called a 90Y pulse.

When applying the pulse along the particular direction, you can define the direction and the degree. So I call it as a 90Y pulse. If I apply along this axis, I call it a 90 minus X pulse, if I apply along this axis, I call it 90 minus Y pulse. If I bring the magnetization, apply here such that this magnetization comes from here to here is a 180 degree flip, then it is called 180 Y pulse. You understand, I am applying pulse along Y axis and tilted the magnetization by 180 degree, please understand this point.

Supposing I apply a pulse along minus X axis, and bring the magnetization to this axis, this is minus X, 90 degree X, 90 minus X, I bring it further to minus Z axis in the same direction I apply. It is 180 minus X, pulse phases you can mention like this. Remember a 90 degree pulse brings along Y axis, 180 will continue further to minus Z, 270 to minus X. I can make it to rotate along XZ plane.

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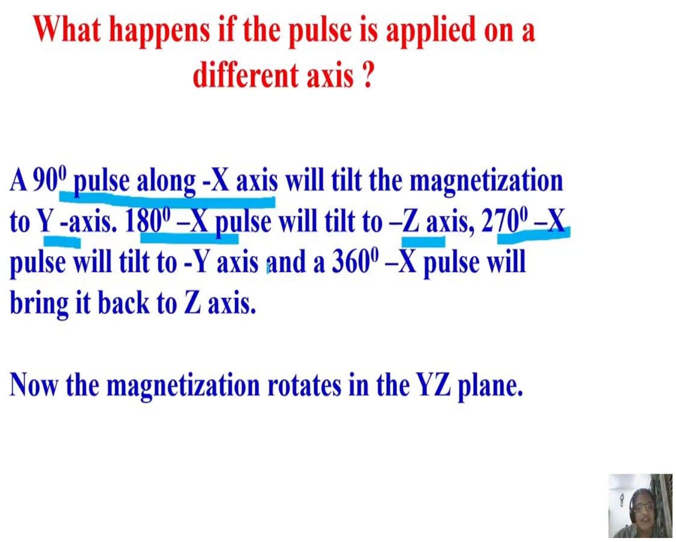

Then I can define the pulse on the basis of the axis, 90 pulse along X axis, 90 pulse along Y axis, 270 along X axis all those things I can decide depending upon the pulse. So a 90 degree pulse first I apply along and minus X axis bring to Y axis, apply 180 pulse along minus X axis it comes to minus Z, it keeps rotating. Apply 270 pulse along minus X bring the magnetization minus Y, apply 360 pulse take it back to the Z axis. So this way the pulse phases or the nomenclature is defined.

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Thus the pulses are defined by their phases,

E.g. 90^0 X pulse, 90^0 Y pulse, 180^0 X pulse, 180^0Y pulse, etc.

The magnetization trajectory can be traced depending on the degree of the pulse and axis in which it is applied

What is the type of pulse, it is called a 90 X pulse, 90 Y pulse, 180 X pulse, and 180 Y pulse like that. These are the nomenclatures. If I say in one of the coming classes, I am applying 90 X pulse what does it mean? I am applying 90 degree pulse along the X axis, if this is my X axis and this is Y axis I am bringing in the magnetization to Y axis, that is all, you have to imagine that way.

Of course this thing you can understand in a better way by using what is called product operators, which I do not think we are discussing, we will see later, but this is the nomenclature. So magnetization trajectory can be traced depending upon the degree of the pulse and the axis in which we are going to apply it.

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It can also be applied along negative axis.
E.g. 90^0 (-X) pulse, 90^0 (-Y) pulse, 180^0 (-X) pulse, 180^0 (-Y) pulse, etc.

The magnetization trajectory can accordingly be traced

You can also apply on the negative axis, that you can call as 90 minus X, 90 minus Y, 180 X, 180 minus X, 180 minus Y, etcetera.

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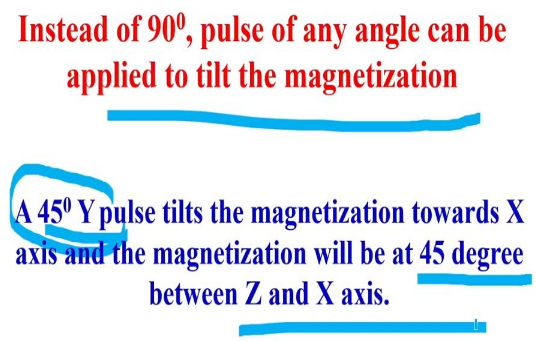

So this is about the phases of the pulses. As I said you do not need to apply only 90 pulse. You can also apply any angle you like, tilt the magnetization by any degree. For example, I can apply 45 degree Y pulse, 45 degree X pulse, 45 –X ,45 - Y whatever it is, If we apply 45 degree y pulse I can bring the magnetization to 45 degree between Z and X axis, you understand.

You can play with the magnetization the way you want, this is the beauty of NMR. That is why I introduced the concept of bulk magnetization. The magnetization can be made to take, or you can take it in any direction in a 3 dimensional sphere, if you take. That type of the diagram what I showed you is called a grapefruit diagram. In the grapefruit diagram we saw, we can take the magnetization to any plane, and make it rotate in any plane, and you can tilt by any axis by applying pulse in some direction and this is the beauty. Now I will tell you something about what is called the signal phase.

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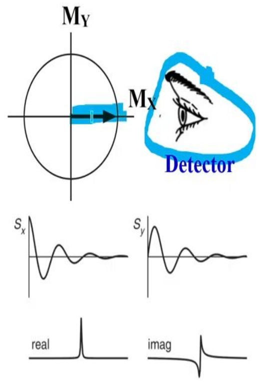

Signal phase depends upon where we are putting the detector. When I apply a radiofrequency pulse I must detect the signal. Let us say, I am applying the radiofrequency pulse and I am inducing the resonance. That is what I said induction of resonance. How you induce resonance, by applying a radio frequency pulse in a direction perpendicular. I said we can bring the magnetization at the XY plane, that is tilt it and detect the signal. Now let us say my detector is here along the X axis. I am sitting here to see the signal.

Somehow ,we have done something and brought the magnetization to the X axis. What is going to happen now. I am seeing here, but of course you should understand in mathematics, which I have not told you, when I do the Fourier transformation. I will tell you more about it later. When the magnetization is along this axis, it is the time domain signal.

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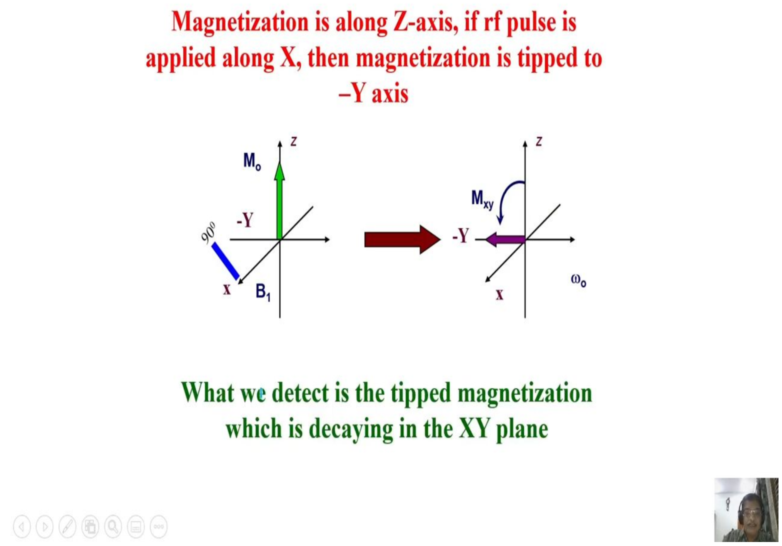

What I am going to do is, the signal Phase, I will introduced to you after the Fourier transformation Otherwise you will not know what is real and imaginary. I will come to that signal phase. You understood the pulse phase, the signal phase will depend on how would detect the signal. I will come to that later, please wait for that. Right now do not get confused, but you understood the pulse phase. Now magnetization is along Z axis, we are applying rf pulse along the X axis, bring like this. Now what we detect is a tipped magnetization. How much magnetization is flipped here, that is what we are going to see.

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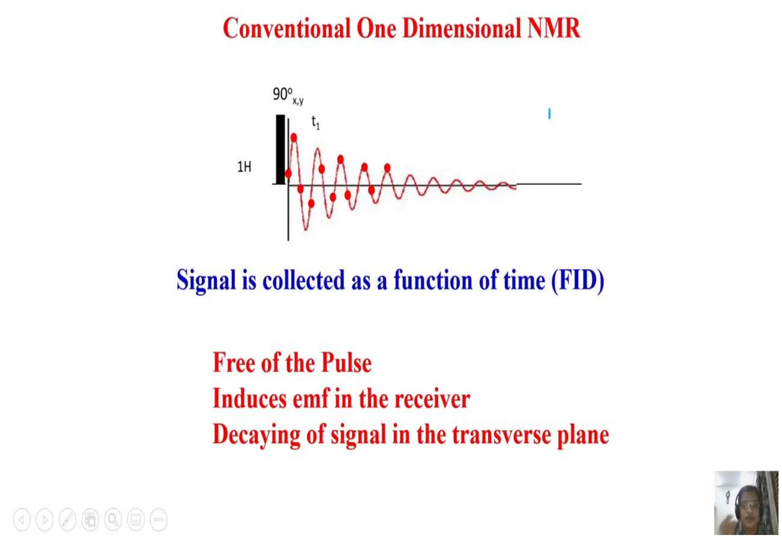

And what happens it starts decaying like this, magnetization starts decaying as a function of time. This is a conventional one dimensional NMR. All you understood so far, I am applying the

90 degree pulse along some perpendicular axis, and I know which direction I am tilting the magnetization. Let us say I have a detector in this direction, I will start collecting the signal as a function of time. This is a called a time domain signal and it is an oscillatory signal and damped oscillation.

It is not oscillation of equal amplitude, you see, it is not equal amplitude, amplitude is damping. It is a damped oscillation. This is collected as a function of time, is called free induction decay, FID. Why it is called FID? You apply rf pulse as a short burst, flash of pulse like this. And then you do not do anything. now the signal, or magnetization and spins are free from pulses, while because of this pulse you are tilting and when it goes back it induces EMF in the receiver.

At the same time the signal is decaying in this plane. So from Z axis bring to XY plane. This XY plane is also called transverse plane. This is a longitudinal plane, sorry longitudinal axis. This is a transverse plane. In the transverse plane the signal decays also. So it is free from rf pulses, it induces EMF in the receiver at the same time it is decays with time. That is why it is called free induction decay. Go to NMR laboratory, you see all of our technicians what they will do, they will apply a pulse and collect a signal like this and they will do some mathematical operation to show you the spectrum. This is called free induction decay, FID.

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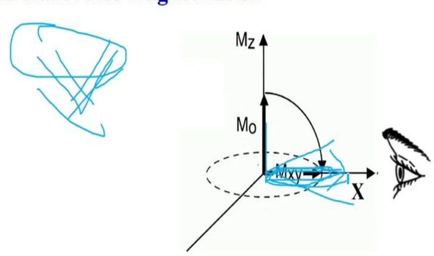
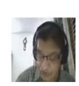
Coherence

Initially the magnetization is in thermal equilibrium and along Z-axis. Also called longitudinal magnetization.

Immediately after the 90^0 pulse, the magnetization is tilted from Z-axis to XY plane. There is temporary statistical phase coherence, called transverse magnetization





So now I will introduce another term called coherence. what is coherence? We have to understand coherence, to get the signal, Fourier transformation, everything I will introduce now.

Initially the magnetization is along Z axis. Apply a pulse bring it to X axis. If this is the magnetization, my bulk concept, what is happening to individual nuclear magnetic moments.

Individual nuclear magnetic moments, are all aligned at a particular angle and precessing in the cone. Remember that concept? I brought the concept of magnetization to understand manythings. But individual magnetic moments if you consider they are all undergoing precession and they are not in phase in the XY plane, because of random phase approximation I said, there is no component of the magnetic moment vectors in the XY plane.

That is what I said, in the transverse plane μX or μY is not there. They are 0. That is what we said. But now what I am going to do is, similarly as soon as you apply 90 degree pulse bring the magnetization to this axis. All the nuclear spins, all the magnetic moment vectors which were rotating like this temporarily you bring them into coherence, statistical coherence. This is called phase coherence. At a time all of them are rotating like this, simultaneous you bring them here.

If you look at this one they were all different spins, they were all rotating like this, now all of them you bring it here simultaneous at a time. And we are in phase coherence, we see temporary statistical phase coherence. This is called transverse magnetization. This is the longitudinal magnetization. This is called transverse magnetization. Immediately after the 90 degree pulse in the transverse magnetization, the components of all those individual magnetic moments are in the phase.

All of them are in phase. That is where you see a single bulk magnetization here, you understand. They are all in phase. And this is called coherence, because there is a phase coherence of all the magnetic moment vectors at a time when they are brought to x axis, this is called coherence. Please remember what do you mean by coherence? Apply 90 degree pulse bring the magnetization to one of the axis, perpendicular axis. Immediately after that you see that when the magnetization is brought to the X or Y axis, all the magnetic moments are in phase. Statistically all of them are in phase. That is called coherence.

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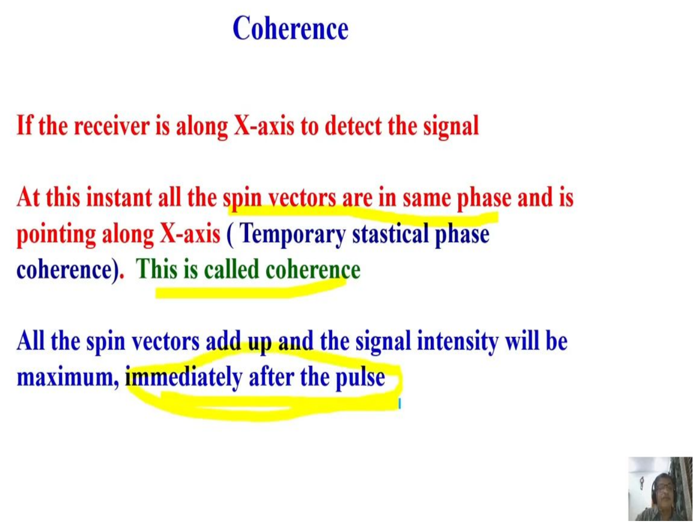

So now if you continue coherence, if the receiver is along the X axis, what happens, I have to detect the signal along the X axis. Let us look at it. I am sitting here. You see my receiver. I am looking at it, so I start collecting the signal here, in this axis. But if I sit somewhere here, if I sit somewhere here, you are not seeing the full signal you are seeing this component. So, of course you do not see the signal here.

I will tell you what happens if the signal is here they receiver is here. That is what is called a signal phase I will discuss later. So now what we are going to do is, the receiver is along the X axis to detect the signal, at a given instant of time what is happening is, all these spin vectors are in same phase. I said this is coherence. Now what is the magnetization?

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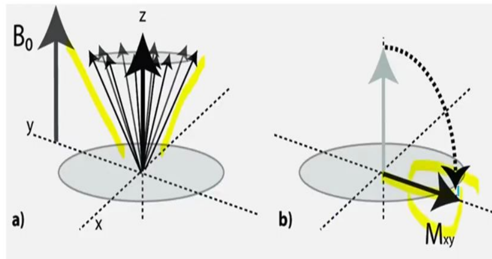
Temporary Statistical Phase Coherence



All the spins are added up, maximum signal is there. All of them are added up. There is a maximum signal, right! So all the spin vectors add up, vector addition is there along the X axis and the signal intensity is maximum immediately after the pulse. You collect the signal in the X axis, you have maximum signal intensity. But what happens to this phase? they will not stay in the same phase for a long time.

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What happens to this coherence with time ?

Spins interact with the surroundings. The spin vectors starts dephasing and keeps rotating in the XY plane.

The signal intensity decays in the XY plane.

The total signal intensity due to addition of all the spin vectors is no more maximum and starts decreasing

Now what will happen to these spins? These spins interact with the surroundings. This what I said is the phase coherence. All different vectors are in different directions, they all come, all of them, at a time along one axis. This is a phase coherence, that is called coherence. Now we will see these spins interact with the surroundings. They are not keeping idle, when the spins interact with the surroundings, the spins vectors start dephasing, they lose their phase coherence.

What it means, those spins which were here, all of a sudden they lose the coherence. If there is no interference from any external thing there is no interference at all. It should remain like this forever but does not happen. What happens is, the surrounding are there with the nuclear spins. Spins would get disturbed, interact with the surroundings. The spin vectors start dephasing all in which were in phase like this, now they will start dephasing like this. Some move faster some move slower, they all completely start dephasing. They start moving out from this axis, some move in this direction and some move in this direction. You understand, see some spins moves in this direction some spins moves in this direction. This we call, with respect to this, omega 0 let us say, on resonance, then all the spins which are moving this side are fast moving component, this is slow moving component.

So we can like resolve vectors into 2 components, one is fast moving component, other is slow moving component, depending upon the direction. So what will happen is spins starts decoherence in the XY plane, the signal intensity decays. When everything was added, the vector addition maximum intensity was there. Now they start moving out like this, what happens now there is a component in different axis, you have to consider. Resolve them into X and Y axis, take the component, the addition is only for those which points in this direction, particular direction. The opposite directions components get nullified, what will happen? Now the vector addition sum is reduced, slowly. So then what will happen, the total signal intensity due to the addition of all the vector components which was maximum, starts reducing.

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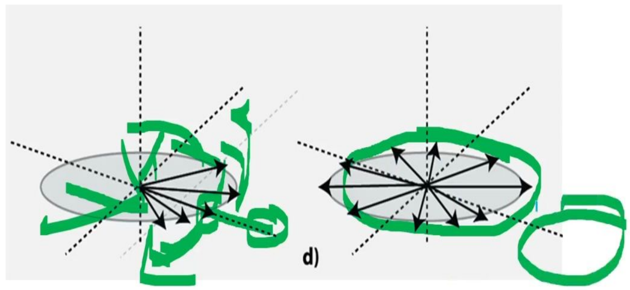
What happens to this coherence with time ?



Because of this this, see now what is happening. some start moving like this, some moving like this, fast moving and slow moving components. Now this vector has a component here and here. When it was here it was full amount, now the magnetization amount is reduced for this component, again for this. So if we take the vector addition of all these components of resolved into 2 axis, the magnetization component, let us say, along this axis now is reduced, because the spins are undergoing decoherence. The intensity which is maximum immediately after the pulse starts reducing, slowly keep on moving, this is not the end. They keep moving like this, some more will move like this. Finally what happens after sufficient time, all the spin vectors undergo complete decoherence. When they all undergo complete decoherence, what happens? Remember, we discussed about the random phase approximation. Exactly, now if you take vector addition of all these components, there is no signal at all. Here it is 0, total is 0 signal.

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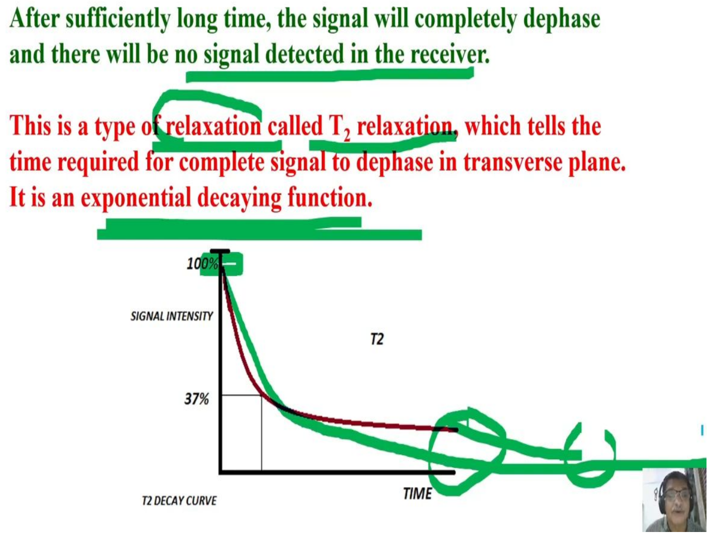

And complete decay will be there, signal will complete de phase and you do not get any signal in the receiver. Why it happens? This is a type of interaction happens and makes the spins to dephase because of their interaction with the surroundings. This is a phenomenon called relaxation, that means the spins are relaxing, you disturb the spin system by giving energy, brought from Z axis to X axis, now they are disturbed, now you have perturbed them. They want to relax.

So it will go back to Z axis to attain thermal equilibrium. That is one time. But before that the spins also start undergoing dephasing due to surroundings. This is another one type of relaxation called T2 relaxation, that is relaxation in the transverse plane, dephasing in the transverse plane. It follows an exponential decaying function, it follows an exponentially decaying function, in the sense it decays like this. 100% maximum immediately after the pulse it slowly goes, goes and goes. It takes infinite time to reach 0. But does not matter we have after a certain time we know if itreduces this much it is enough, we do not have to wait for 5 times T1. This is a one type of relaxation called T2, also called spin, spin relaxation also called transverse relaxation. These are the synonyms which are discussed when I discuss more about relaxation measurements in one of the classes later.

So what happens you apply a pulse, start correcting the signal, signal will not have the same amplitude, it decays, the amplitude of the signal decays and that is precisely what I said in the FID here, remember. This is what the FID, the signal is decaying and it follows an exponential function, that is what I said, decay is an exponential and is oscillating. During this time it is inducing EMF, that is the free induction decay. This phase decoherence is due to a phenomenon called relaxation, called T2 relaxation.

So now what will happen to this? This is dephasing in the XY plane, but our magnetization initially was along Z axis. If I have to send another pulse to collect signal once again the spins should come back to that Z axis, otherwise there is no magnetization, no spins. What do I do? The spins have to come back to thermal equilibrium, that will do, it will happen, that is another type of relaxation I will discussed that in that in the next class.

So you understand in this class I introduced to you about the phases of the pulses, I have not introduces the phases of the signal, which I will do later. And then I discussed with you about the coherence and decoherence, and introduce a phenomenon called T2. As a consequence, the signal intensity in the XY plane decreases while you are detecting the signal. Immediately after the 90 pulse you bring the magnetization to the X axis. The signal is maximum intensity. And slowly decays because it is undergoing decoherence and is an exponential decay. And this decay is what is called a free induction decay which we collect. So we will come back and continue with the other type of relaxation and more about signals collection and we will start really looking at the NMR spectrum and everything is subsequent class.