One and Two Dimensional NMR Spectroscopy for chemists
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Lecture - 07
Signal Detection and Rotating Frame Concept

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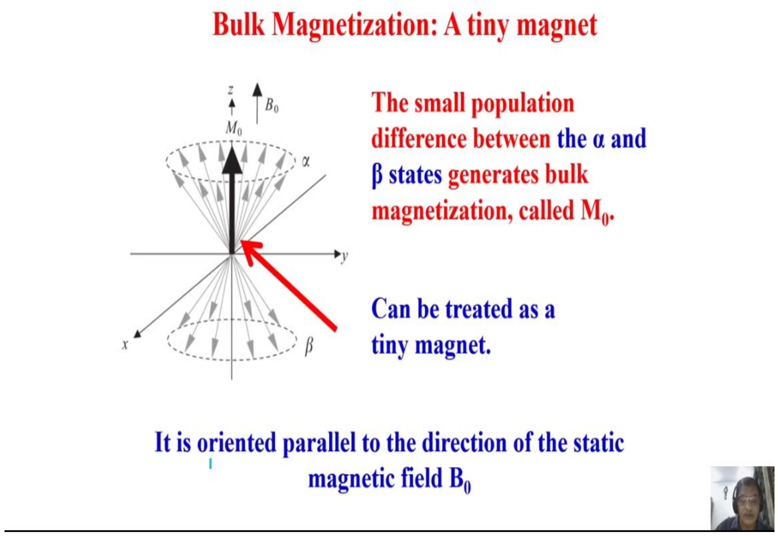

Welcome back in the last class I introduced the term called bulk magnetization, which I said is the population difference between the alpha and beta spin states, due to random phase approximation where the components of this, each individual magnetic moments in the x and y direction then the xy plane, that the Mx and My components of these individual magnetic moments gets averaged out. All these gets averaged out. As a consequence, there is no magnetization in the xy plane.

Because of random phase approximation, finally, what we are going to be left with is the vector addition of the magnetic moments, all the magnetic moments oriented in this direction, in the direction at the field and vector addition of all the magnetic moments oriented in the direction opposite to that of the magnetic field, and because of the Boltzmann distribution, because of the population excess of spins in the direction of the magnetic field. The vector addition of these 2 orientations, along the z and minus z directions will be giving a net polarization or net magnetization or net vector in this direction, this was called bulk magnetization which is represented as M0. It is a nomenclature. M0 is the bulk magnetization which is along the z axis. We can treat it like a small tiny magnet, bulk magnetization, you can treat as a small tiny magnet.

Remember, when we are dealing with the individual spin, we used the term magnetic moment. When I am taking the vector addition of all of them, I am talking about what is called bulk magnetization, which is a tiny magnet. Now, let us understand, what happened to this bulk magnetization. How it is oriented. Look at it, even in thermal equilibrium; we are talking about thermal equilibrium. In thermal equilibrium, because of the random phase approximation and all the vector addition we did. We have got the magnetization along z axis. This bulk magnetization is parallel to the static field and is also static.

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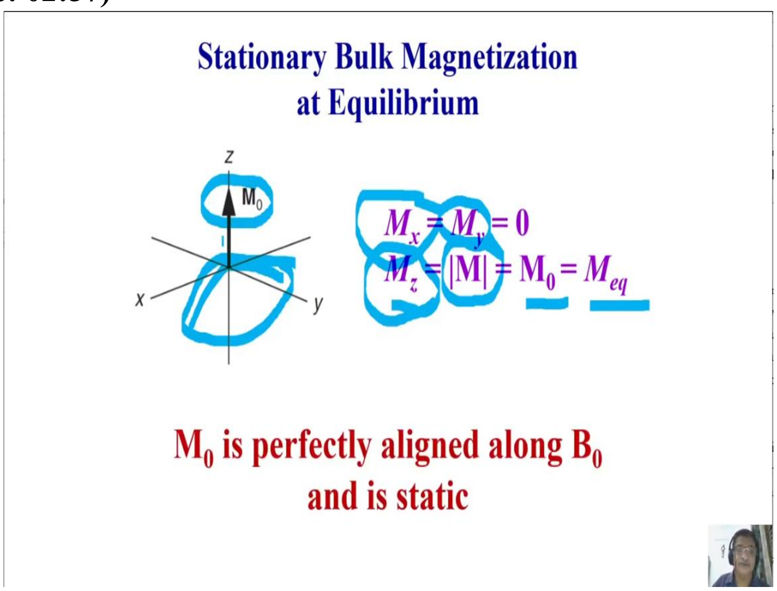

This bulk magnetization is stationary even in thermal equilibrium. At thermal equilibrium M x component that the bulk magnetization and My components are 0. This is bulk magnetization, now I can resolve it into X and Y components. Now Mx and MY components are 0, only we have M0 and it is stationary. So, this is called also called Mz magnetization, because X and Y components are 0. And this is nothing but the magnitude of this magnetization, which is called the M0 are also called equilibrium magnetization.

All these are nomenclatures, terminologies. So the bulk magnetization is called M or equilibrium magnetization M0 are also sometimes they call Meq. M eq or M0 or Mz, does not matter all are same. In thermal equilibrium, one point you must remember is, even in thermal equilibrium, this bulk magnetization is static and aligned along the Z axis, perfectly aligned along the Z axis.

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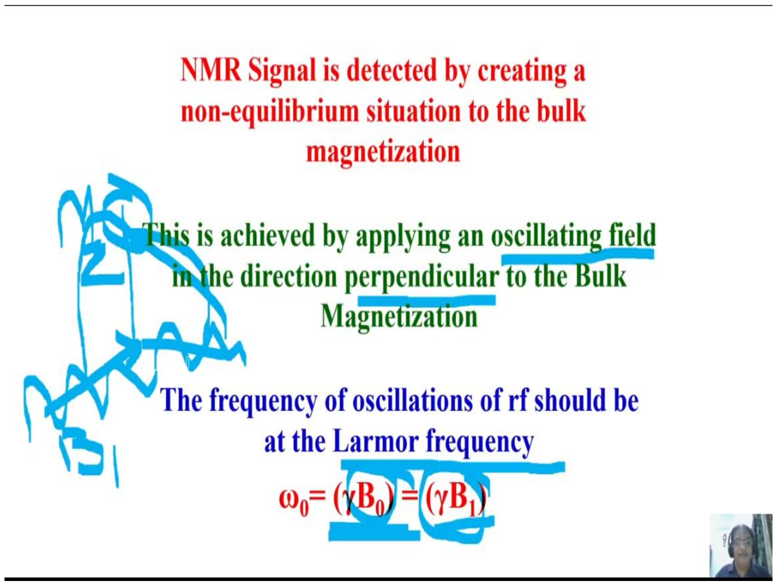

Now, we have to do one small trick, what is the small trick? I have to detect the NMR signal. Now it is a static thing. Unless I perturb this magnetization, bulk magnetization I cannot see the signal. I need to perturb this bulk magnetization, how do I do that? So, this you can achieve by applying the oscillating field in the direction of the bulk magnetization in the direction, sorry not direction of the bulk, in a direction perpendicular to the bulk magnetization. Please remember you have to apply in the direction perpendicular to the bulk magnetization.

What does it mean? Bulk magnetization is along Z axis. So, you have to apply the oscillating field in a direction either the X axis or Y axis, because magnetization M0, Mz is along Z axis. That is what you have to do. And what is this oscillating field, what should be the oscillating field, remember we said about inducing resonance, we have to apply the radio frequency field at the Larmor frequency, right? for getting the resonance.

Exactly the frequency of the oscillations of the oscillating field, you are having oscillating field, its frequency should match with the Larmor frequency. Larmor frequency is what? precession frequency of the spins. So, that one should match with the oscillating frequency which you are going to apply here. You are going to apply like this, when it matches then we are going to get a resonance. In other words, gamma into B0 should be equal to gamma into B1, B0 is what is called the strong magnetic field, which is the resonance condition what we got here.

So, now, when you apply radiofrequency pulse, this is called a B1 field ,and this frequency is gamma into B1. So, gamma into B1 must be equal gamma into B0, this is the resonance condition. And when this condition is met, what we are going to do is, we will tilt the bulk magnetization from Z axis to X or Y axis. Of course you are applying in this axis, you will tilt it in this axis, you are applying in this direction, you will tilt it in this axis.

We will worry about this, by using what is called the right hand thumb rule, how it is tilted later. But just remember, when you apply a radiofrequency pulse, the radio frequency which is oscillating at the Larmor frequency, you are perturbing the Z magnetization which is in thermal equilibrium, and then you are tilting the magnetization to other axis, if you are applying along X axis, you will take it Y axis or vice versa. And then we can start detecting the signal. This is how we detect this NMR signal. This is in the bulk magnetization concept of explanation.

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Important

A stationary magnetic field perpendicular to B_0 CANNOT interact with the precessing magnetization.

It must be oscillating

Most important point to remember a stationary magnetic field if you apply in a direction perpendicular to B0, it will not interact with the bulk magnetization, stationary field will not interact. the rf you are going to apply in a perpendicular direction must be oscillating. If it is not oscillating, it will not perturb the magnetization, perturb the spin system at all. So, when it does not perturb, you will not be able to see any signal at all.

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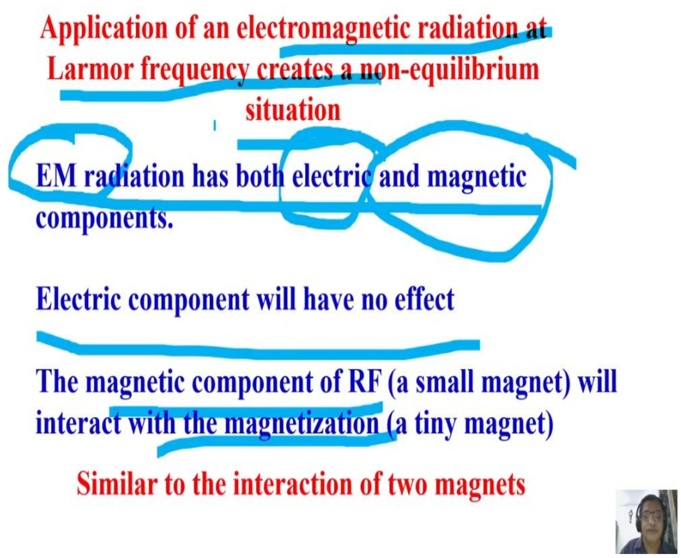

So, what we understand now is the application of an electromagnetic radiation at the Larmor frequency creates a non-equilibrium situation, The spins which were in thermal equilibrium or bulk magnetization which was in thermal equilibrium is disturbed, you are creating a non-equilibrium situation. OK. Now what is going to happen? when you send the radio frequency signal, it has an interaction, how does it interact? Your electromagnetic radiation, rf at the Larmor frequency when you apply, Remember, electromagnetic radiation has both electric component magnetic components. Electric component has no effect at all; it does not disturb the spins. On the other hand, the magnetic component of radio frequency interacts with the magnetization. Because remember, rf when you apply it like a small magnet, it has a magnetic component. We are discussing all about magnetism, now it is like bringing in another magnet, near the tiny magnet, which is the bulk magnetization.

So, bring in one more magnet close by, then what would happen? These two will interact. This is exactly what happens when you apply radio frequency signal, rf pulse, in the direction perpendicular to the bulk magnetization, the magnetic component of rf interacts with it and causes disturbance that creates a non-equilibrium situation.

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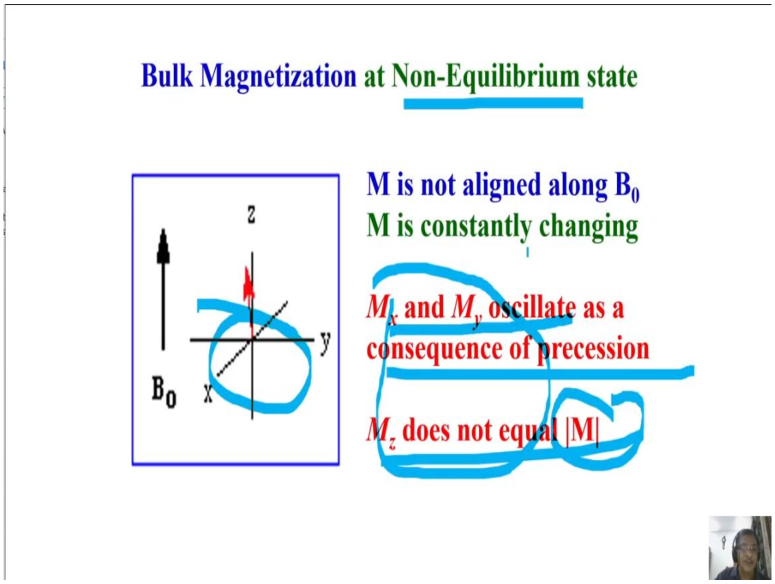

Now, what happens to the bulk magnetization at non equilibrium state? At non equilibrium remember, bulk magnetization and is undergoing precession like this. At equilibrium it was static, Mz = M0. So, now M is not aligned along B0, M is constantly changing. So, Mx and My oscillate as a consequence of precession. Now, Mx and My components I would say is nonzero, in the earlier situation in thermal equilibrium it was in the equilibrium condition.

The bulk magnetization was along the Z axis it was along Z axis and Mx, My components was 0, but in the non-equilibrium situation, these 2 are non-zero because of the constant rotation of bulk magnetization. Mx and My also oscillate, and Mz is no more aligned along Z and it is not equilibrium magnetization. Because Mz has a different component now. Mz is not equal to M0, they are different. So you have you understood the trick, what we did.

We understood what is the bulk magnetization. We know it is static at thermal equilibrium, you disturb it by radiofrequency pulse at Larmor frequency, then what happens in the non-equilibrium condition, we resolved this bulk magnetization M into 3 components Mx, My and Mz. Now, Mx and My is oscillating, because it is changing, it is in the non-equilibrium situation and the Mz is not equal to M0.

With that now, I want to introduce a concept of rotating frame very mildly, because I am not going to the extensive mathematic, you require that to understand. But in a simple way, let us try to understand. This is required to many, many experimental conditions we talked about, like rotating frame, rotating frame overhauser effect, etc. you should have some idea about what is a rotating frame and how it is used. The concept of rotating frame in NMR.

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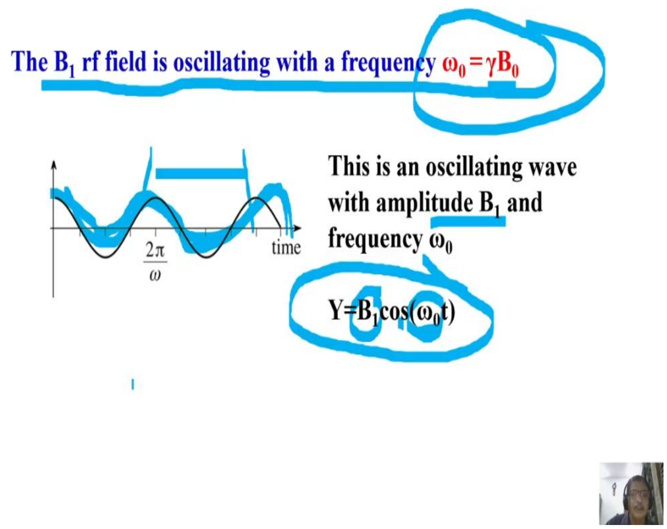

Now, consider the situation B1 rf field is oscillating with the frequency omega 0 = gamma into B0. We are applying a radio frequency pulse, which is oscillating with a frequency which is equal to a omega frequency, that is what we said to induce resonance. Now, let us see what is an oscillating field? Now oscillating wave is like this, you know that. What is the oscillating wave, it is represented mathematically by this equation. Y component is this, Y has a B1 cos omega 0 t, what is a B1?

It is an amplitude and the oscillating frequency is given by omega 0. Any frequency you can take, I have just chosen some number. This is oscillating frequency, you can calculate from the lambda what is frequency, fine. This is the concept of a oscillating wave.

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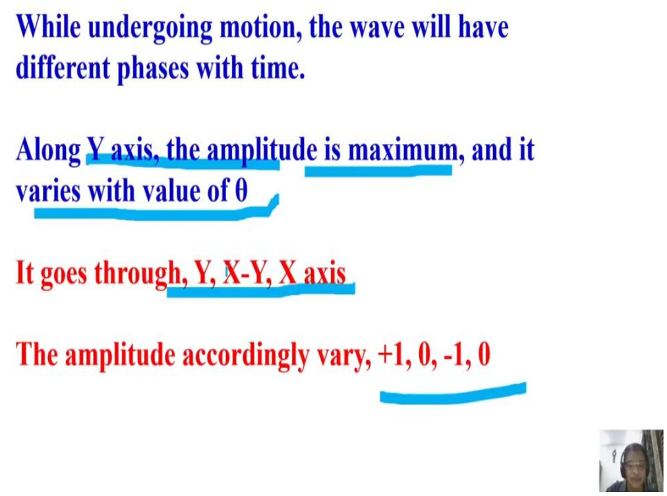

Now, what happens while he says undergoing motion, the way will have different phases with time, what happens remember it starts along Y axis when it is along Y axis, the amplitude is maximum, its value varies with the value of theta, let us see what it is, it starts let us say along Y axis, it is a maximum value, amplitude is maximum, at theta = 0, cos 0 let us say this omega t 0, we are talking about time now, at time t is = 0, it is cosine of 0, it is 1. So, Y is maximum amplitude B1.

Now, as it keeps moving what happens? It comes here, it is a situation it is this is pi / 4, pi / 2, 2 pi and 3 pi / 2 ,and then like finally it becomes 2 pi. It is an oscillating like this. So, what happens the Y component is 1 becomes 0, -1, 0, +1. What is happening, the Y component is going through Y, X - Y and X axis. See, this curve going through Y, then you look at this one, I have to show you the circular one, the Y component as a function of theta, what happens, it will be Y, comes to X, minus Y, minus X and go back to Y. The same thing you can see, represented in the form of a wave as a function of theta.

And amplitude is varying from 1, 0, -1 and 0. So, the wave is oscillating and going through all the amplitude values 1, 0, -1, 0 in 1 cycle, and in 1 cycle, it goes through starting with plus Y axis, goes to the X - Y and X.

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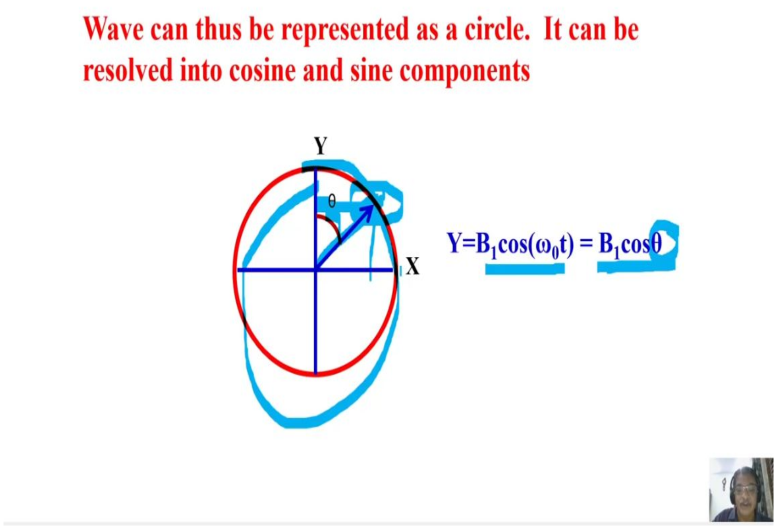

That means, we can represent this oscillating wave is a circle. That is what we said in the conceptual understanding it is maximum amplitude is here for theta = 0, when theta = pi / 2, theta = 90 degree, these values here, Y component is 0, but it is along X axis, when Y = - 1 along minus, Y axis and when Y could take again 0 at 270, it is minus X, go back. So I am representing the wave in the form of a circle.

Let us say, at any given instant of time, this is the place we are looking at this this point. I know this angle theta, then I can resolve this into 2 components X and Y. This is a cosine component, it is the sine component, I can resolve it. So this amplitude is maximum here at Y component 0, maximum like this you can fully work out what happens as a function of theta, what we have written is the same, the amplitude equation Y, wave equation in the form in terms of amplitude and this frequency is represented as B1 cos theta, let us say. Now what is happening to this one as a function of theta, when theta = 0, it is here, when theta is = 90 it is here. Now, you can find out the components. When theta = 45 degree it is here, it is a vector it is resolved to this component and this component.

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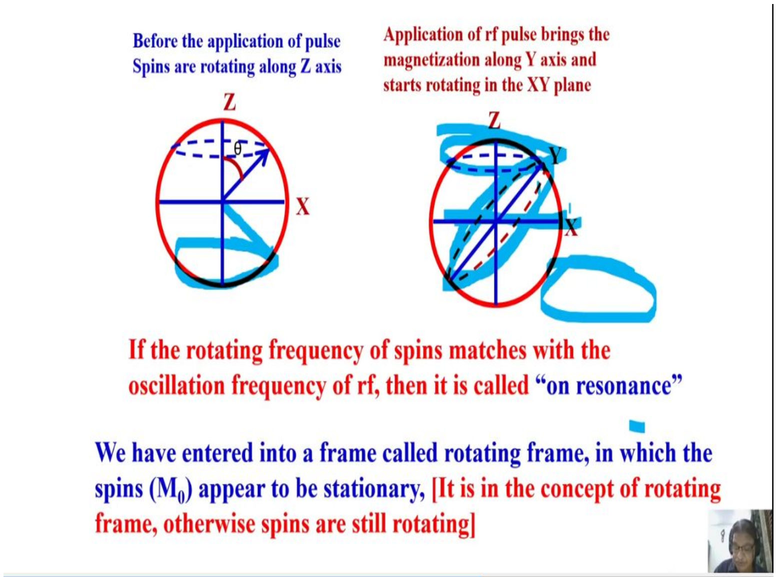

So, you can have cosine component and sine component both like here. I did not mention that, ok does not matter, you can resolve them into cosine and sine components. Now, before the application of pulse, let us understand what is happening to spins, spins are rotating along Z axis. Remember, this is how the spins are rotating. That is what the precession you are talking, individual magnetic moments are possessing along Z axis making an angle theta, this theta I know for 2 orientations of spin half nuclei, along this axis and also it rotates along this axis.

Keeps rotating like this. Now, when you apply radiofrequency pulse, you bring the magnetization along Y axis, that as I am applying along the X axis being the magnetization along Y axis, then it starts rotating in the XY plane. Imagine it is along Z axis here. You bring to let us say X axis, and it starts rotating in this XY plane. That is what is happening. And if the rotating frequency of the spin matches with the oscillating frequency of the radio frequency which we apply, we call it on resonance.

See now in the XY plane, the spins are rotating. This frequency when it matches exactly with the applied frequency of, that is rf pulse, external radiation which apply in a direction perpendicular, when it matches it is on resonance, then you are in the XY plane, understand. This is a situation where we say we have entered in a frame called rotating frame. In the rotating frame, we always see the spins appear stationary. What does it mean? It means, if you are in this laboratory frame along the Z axis the spin are precessing.

But when I go to the X, Y axis, it is in the spins which are rotating in this XY plane that I sit in that plane, the XY axis and look at the spins, it appears stationary. That means, from the laboratory frame you move to a frame where the spins are rotating, this rotating frame of reference. When you move to that frame of reference for you, the spins are stationary, they are not moving. It is only conceptual understanding, but do not be under the impression the spins are not spinning, they are spinning, but it is consumption mathematically can understand. When you are sitting here you would not feel it as moving.

Whereas when you are here you can see the motion. For example, let us see a merry go round. In merry go round if you are standing outside the merry go round. You can say merry go round is going, but you go yourself into the merry go round, you will not see a merry go round rotating because you are rotating with the merry go round. As far as you are concerned, you do not see merry go round rotating it is stationary. You do not see rotation with the merry go round similar to that when you are in the rotating frame of reference, you will not see spins rotating, you will see spins are not precessing, they are stationary.

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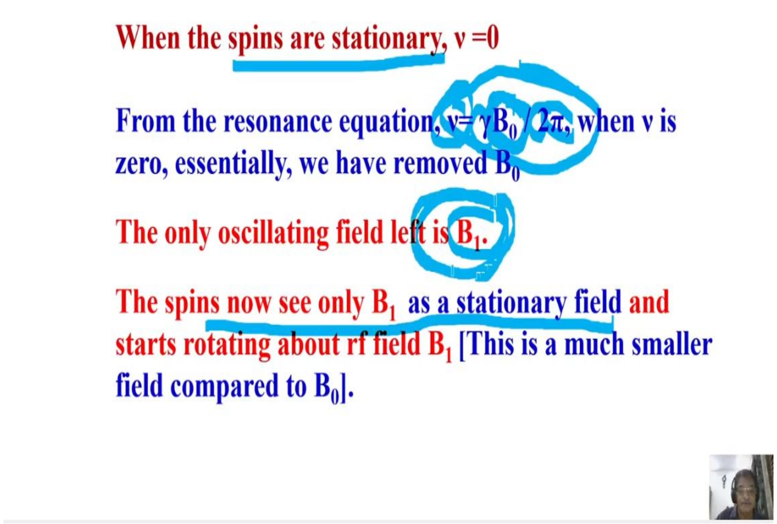

Now what do you mean by spins are stationary? It is precession frequency is 0. So I put $\nu = 0$. What is my resonance condition? Resonance condition is ν= gamma into B0 / 2 pi. I am going to put ν as 0. I am assuming this is my condition, because the spins are stationary. When this is 0, this is a constant. I do not deal with that. This is constant, this is constant, I cannot play with these numbers, these 3 parameters, then what does it mean, when ν is 0, you are making B0 as 0.

That is the only thing you can vary. You cannot vary, these constant terms. That means, in this rotating frame, when the spins are stationary, you feel main magnetic field B0 is removed. It is 0, you feel as if you have not applied the field, the spins feel as if you have not applied the external magnetic field in the rotating frame. So, what does it mean? Earlier the spins were precessing along Z axis, precessing in the direction of main magnetic field. Now that is absent, but they are processing along the oscillating field, that is the oscillating rf, which you have applied in the direction perpendicular to the magnetic field. That field is called B1, what is this B1 field, this is not the magnetic field of several Tesla. We have not applied that much, it is a small rf, small pulse we apply and this field if we calculate, this is much, much smaller, that if I want to express in frequency it is about 25 to 30 kilohertz will be there.

Whereas, the same thing in B0, if we express in a frequency it is 500 megahertz to 1000 megahertz, remember 500 megahertz and 30 kilohertz, the difference here is very small. B1 field is several orders of magnitude, at least 10 to the power of 6 smaller than that of main magnetic field. Spins now see only B1 as a stationary field. This spins see as if you the external field you applied is B1 as a stationary field and start rotating around B1.

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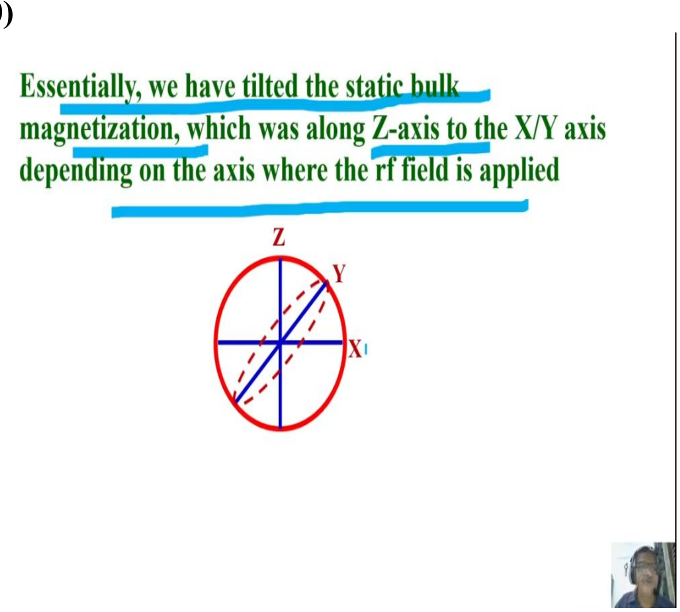

This value so small, much, much smaller compared to B0. You have a concept of the field which are going to apply, the rf pulse and wif e calculate the frequency it is of the order of 20 to 30 kilohertz. Whereas the same thing if you express in B0, it is 500 to 1000 megahertz. It is the resonant frequency for fields in Tesla. This is few to kilohertz 20, 25 and 30 kilohertz. So that is a very small field we apply. So what we did is essentially, we have tilted the static field, with static bulk magnetization from Z axis to the XY axis, and depending upon which direction you are applying the pulse.

So if you are applying along X axis, you can bring it along Y axis. If you are applying along Y axis, you can bring the magnetization to X axis, the exact directions we will discuss when we talk about the phases of the pulses and the NMR signal. OK, are you understanding. Is it clear for you? so it means in the B1 magnetic field, we are worried about the precessional frequency around B1, then we are not worried about the frequency of the order of megahertz, we are worried about the rotational frequency or the precession frequency of the order of few kilohertz.

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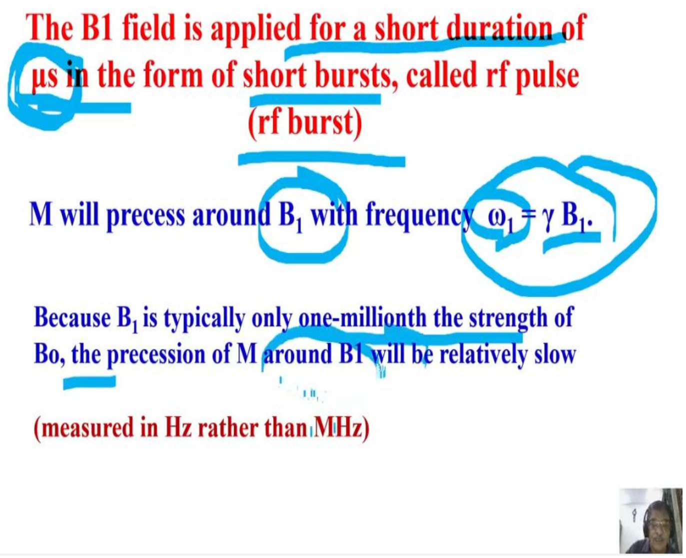

So B1 field when you apply, this is for a short duration of microseconds to milliseconds very, very small value, 5 microseconds, 10 microseconds. In some special examples, we apply 1 millisecond like that, do not worry. But we consider most of the time for excitation pulse, for the excitation of spins, we apply only 5 microseconds to disturb spins from equilibrium situation to non-equilibrium situation. We apply only microsecond pulse, and this is called short burst of rf, also called as rf pulse.

rf pulse is nothing but a burst of rf. Short bursts, for a microsecond we apply, like you are giving a picture like you will send on pulse for a microsecond and keep quiet. That is all you do. Like you flash, the flashing the rf pulse for a microsecond or 5 microseconds once and keep quiet.

After some time, you can apply once again and keep quiet. That is like flashing, sending the burst of rf in flashes. That is what is we do, then magnetization is precessing around B1. Now the precession frequency is gamma B1 not gamma B0.

So, we are in the rotating frame, now precession frequencies omega1 which is equal to gamma into B1. And this is typically one millionth of the strength of B0. As a consequence, precession frequency you can talk now in terms of kilohertz or Hertz rather than megahertz then it is easier to handle and understand the things much better.

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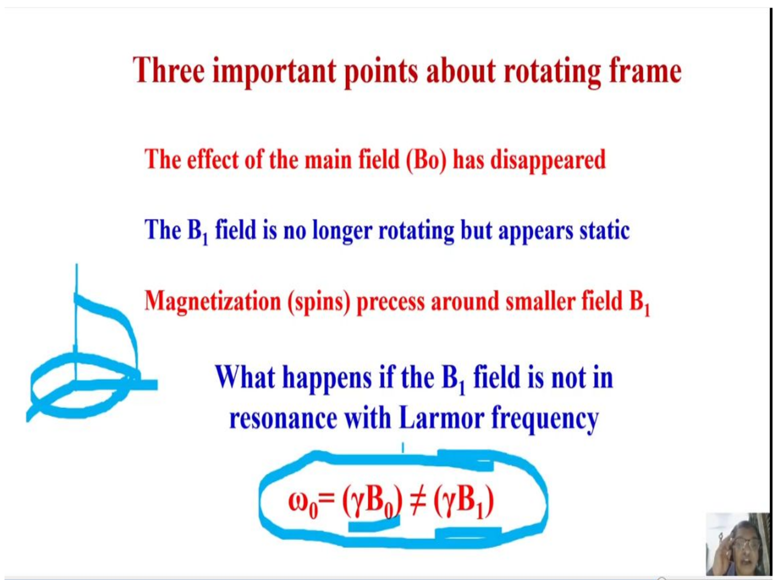

This is how the concept of rotating frame is introducing, and it is very useful in NMR. Now, understand 3 important points about the rotating frame. First point, the effect of the main magnetic field is disappeared in the rotating frame, the spins feel as if B0 is absent, and B1 field is no longer rotating and appear static as far as the spins are concerned, understand.

Earlier the spins were rotating or processing along B0, before the application of the pulse. After application of the pulse, you bring the B0 magnetization to the XY plane, in this case the spins starts rotating in this XY plane. So, this is small field compared to the main field. When spins were rotating along this axis, this was a static field. Now, it is rotating along this axis and this is a static field. It is called B1 field, it is a B0 field and this is of the order of several Tesla, this is the order of few kilohertz, very small value.

So magnetization, or the spins precess around the smaller field B1, instead of bigger field B0. So to it precesses around smaller field B1 instead of bigger field B0.

So what happens if the B1 field is not exactly on resonance? When this one matches with this, it is exactly on resonance, you understand, in which case we are bringing the magnetization exactly from here to XY plane and start rotating like this. In case, if gamma B0 or the rf you applied is not exactly matching with this one, what will happen? when it matches it is on resonance, when it is not matching, it is called off resonance condition.

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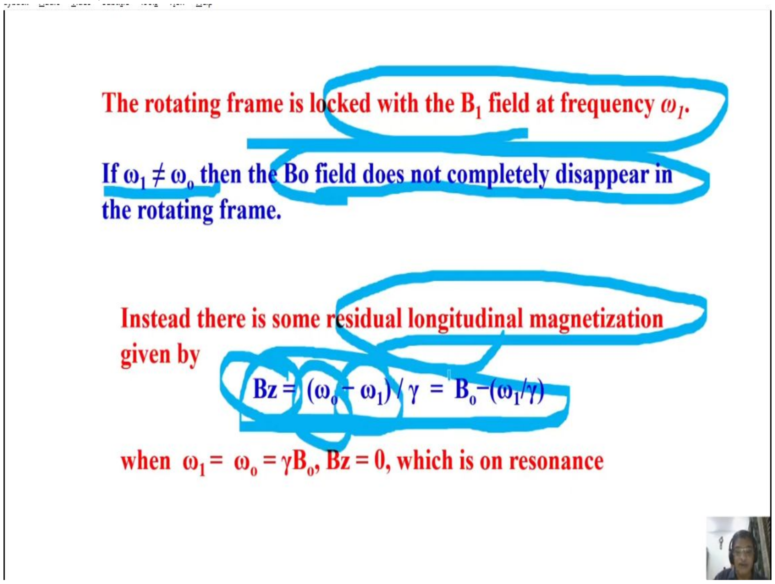

Off resonance condition is the one, where the rotating frame is locked now along with the B1 field at different frequency. omega1 is not equal to omega0. Then what happens? B0 field does not completely disappear in the rotating frame. Earlier when it is exact on resonance, I said the spins freely only B1field for which B0 main field is 0. The main field is assumed to be absent for the spins, which are processing in the XY plane.

But when this condition is not matched, it also says B0. Now it sees in addition to B1, it is also going to see B0. So, there is some residual longitudinal magnetization will also be present. This is given by this equation, which is an equation you put in, to work out the frequency in off resonance, i.e. when it is not in on resonance. So, what will be the Z component of this thing, if you find out the B, then it is omega 0 - omega 1 divided / gamma. So, when omega 1 = omega 0 then it is equal to exactly B0, that is on resonance, otherwise it is off resonance.

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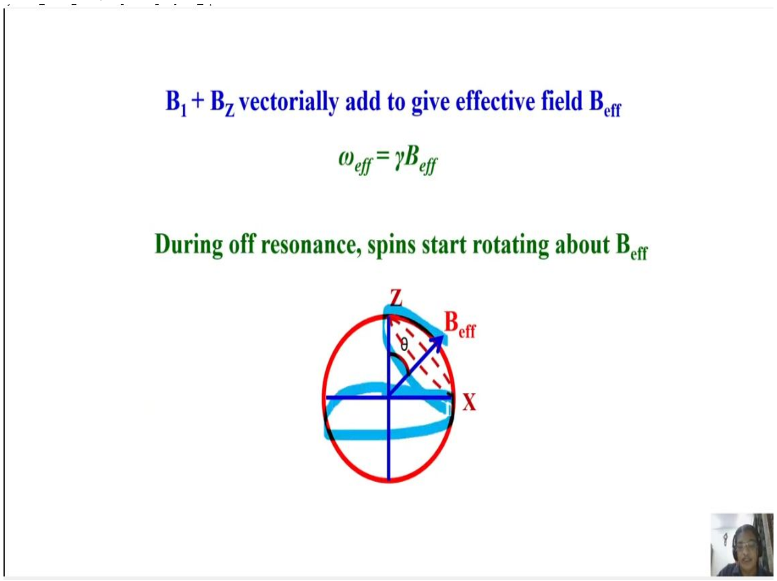

So, in the off resonance vectorially now you take the addition. Now instead of being exactly on the XY axis, now it is somewhere here, now you have a component of this and component of You have to take the vector addition of component on this axis and component along this axis. Then you are going to get an effective field along this axis. So, this is off resonance. when it exactly on resonance, it will be along X axis or Y axis. When it is off resonance, it is away from this axis. And the field will be effective field which is a combination both the main magnetic field and rf field which we apply. So, this is what happens in the case of the off resonance condition, Instead of rotating in the XY plane, you are rotating in a different axis making certain angle with respect to this. This is called B effective.

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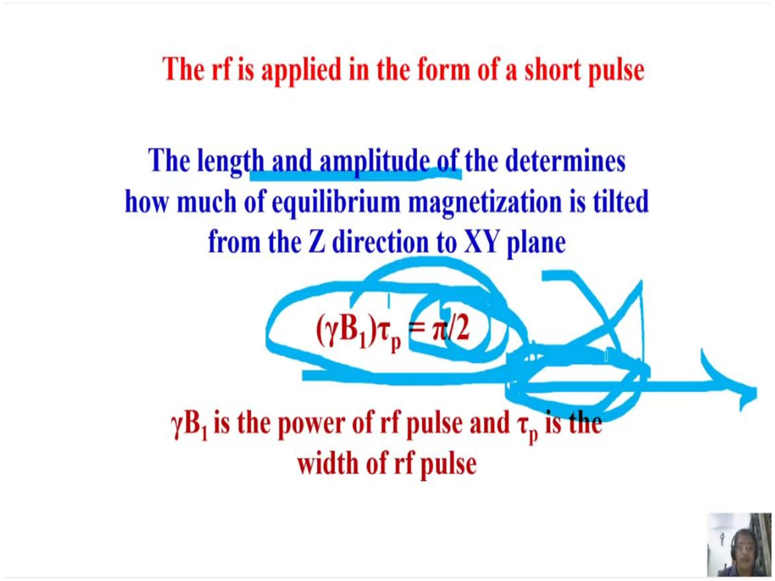

So rf field is applied in the form of a short pulse, I said, the length and amplitude of the pulse determines how much of equilibrium magnetization tilted from Z axis to XY plane. So now, if you want to exactly tilt the magnetization, that is to the X axis and Y axis, that is by a 90 degree from Z axis, this is the condition you have to use. Gamma we know, B1 is rf power, this is a pulse width, this is called the width of the rf pulse. Width and the power put together, you can manipulate to bring the magnetization from Z axis to the X axis or Y axis, you can use this.

So this is what we want, we know this one, and we have to play with these 2 terms, rf power and the pulse width. If I have a radio frequency pulse that I am applying, the power of that pulse and the width of the pulse I can manipulate and bring the magnetization to 90 degrees. If I do not want 90 degree, I can bring it to 180 degree, and I can bring it to 45 degree, any angle I want. So, this equation helped me to calculate the direction of tilting of the magnetization, the direction I want, or for a particular angle I want.

So, please remember this equation, the length and the amplitude of the rf pulse, that is power and width defines how much of equilibrium magnetization is tilted from Z axis to XY plane, whether it is tilted completely or not, because if it is tilted completely the entire magnetization is along this axis. If it is tilted 45 degrees, let us say, you have to resolve the components, then only this much magnetization is tilted. The amount of magnetization tilted from the equilibrium position is defined with this pulse. And because we can resolve into components, we can find out how much is the component in this axis, this is an important point.

Remember, gamma B1 is the power of the pulse, and tau p is the width of the pulse. I can manage this to get the magnetization tilted by any degree, to any axes. Next I will tell you more about tilting of the magnetization and then right hand thumb rule etcetera. I am going to stop here. I will come back and we will continue the next class more about this.

So that now we have got the conceptual idea of rotating frame etcetera. We will start talking more about 90 degree, 180 degree etcetera, how the magnetization undergoes flipping and discuss further. So I will stop today.