Advanced NMR Techniques in Solution and Solid - State
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Module-19
RF pulses and their phrases
Lecture - 19

Welcome back, in the last couple of classes we extensively discussed varieties of topics connected with this course, right from spin physics, chemical shifts, coupling constants and quantum mechanical analysis of NMR spectra, varieties of spin systems 2 spin, 3 spin, weakly coupled, strongly coupled. We discuss about the spin system nomenclature. We also analysed simple 1D spectra of varieties of nuclei.

We discussed the Fourier transformation and arrived at varieties of functions, how to do the Fourier transformation, how they are utilized in NMR spectroscopy, we discussed a lot. And in the last couple of classes especially, we did the quantum mechanical analysis of various spin systems, what are the eigenvalues, Eigen functions, transition frequencies, the type of spectrum we get for weakly coupled, strongly coupled. In this class, we slightly change the topic, because, in a short while from now, you have to discuss more about product operators, more about how the chemical shift couplings will evolve in different pulse sequences, we need to understand the pulse sequence especially, if you have to introduce polarization transfer techniques, varieties of other things.

So, in all these things, 1 important point which we need to understand is, we commonly use what is called a pulse phase and a receiver phase. This of course, I should have introduced, when I discussed the 1D NMR spectrum. I did not want to discuss at that time because this the relevance of this is going to be seen in next couple of classes. And of course, regarding the pulse phase and the receiver phase not though in detail, a little bit we discussed in the previous class, previous course also.

But nevertheless, you must know what is the receiver phase, you must know what is it a pulse phase, which are very often used both for understanding the behaviour of the magnetization by the vectorial diagram or we have to use it for understanding the operators, where we have to show when you apply different phases along different axes, how it behaves. So, I will today discuss more about pulse phase and receiver phase.

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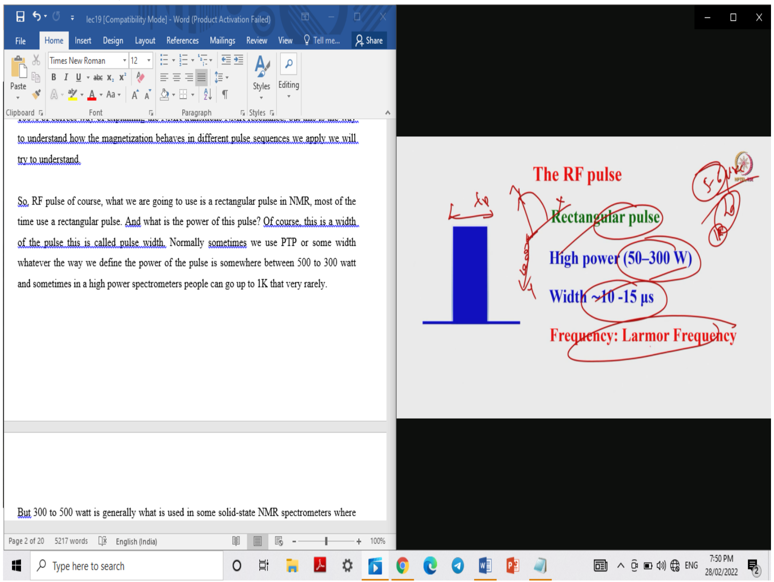

Let me start with, what is an RF pulse? Of course, it is a pulse NMR. We are going to apply RF pulse and then in the very first class I told you the magnetization which is in thermal equilibrium is going to be disturbed. It creates a non-equilibrium situation, bring it to X axis or Y axis and the magnetization goes back to Z axis by decaying in the XY plane, inducing an emf in the receiver coil, which we are going to collect as a function of time.

And do the Fourier transformation to get the spectrum. This is in short, we discussed at stretch long back. So, when we applied RF pulse, but of course, we discuss about the transitions from different energy levels, there is only a layman way of discussing, but in principle it is not very 100% of correct way of explaining the NMR transitions, NMR resonance. But there is the way to understand how the magnetization behaves in different pulse sequences we apply, we will try to understand.

RF pulse, of course, what we are going to use is a rectangular pulse in NMR; most of the time use a rectangular pulse. And what is the power of this pulse? Of course, this is a width of the pulse this is called pulse width. Normally sometimes we use tp or some width; whatever the way we define the power of the pulse, it is somewhere between 50 to 300 watt and sometimes in a high power spectrometers power can go up to 1K, that is very rarely.

But 300 to 500 watt is generally what is used in some solid-state NMR spectrometers; where you want to get broadband spectrum; we want to get broadband spectrum with high power decoupling etcetera. And the width of this policy is about 10 to 15 microsecond. Remember, the 90-degree pulse, in the previous course we discussed a lot, the 90 degree pulse in proton for example, is anywhere between 5 to 6 microseconds. Approximately, it can be little lower or very high depending upon the type of probe you are using. So, 180 pulse is double of this, 270 pulse is triple of this, 360 pulse is 4 times this. Like this the width of the pulse can be utilized and then we say what is a 90 pulse? What is 180 pulse? What is it 360, 270 pulse everything we discussed. Now, we have to understand something more about this thing; about the phase of the pulse.

And of course, another important thing you know when I am applying the pulse in a direction perpendicular magnetic field, this is the magnetization, here X axis and here is let us say a Y axis, magnetization is here and I tilt it, by applying a radio frequency pulse in the X axis. What is the pulse frequency if you are going to apply; the frequency of the pulse? it should be in the Larmor frequency to create nonequilibrium situation to tilt the magnetization from Z axis, to X axis or Y axis, it is very important.

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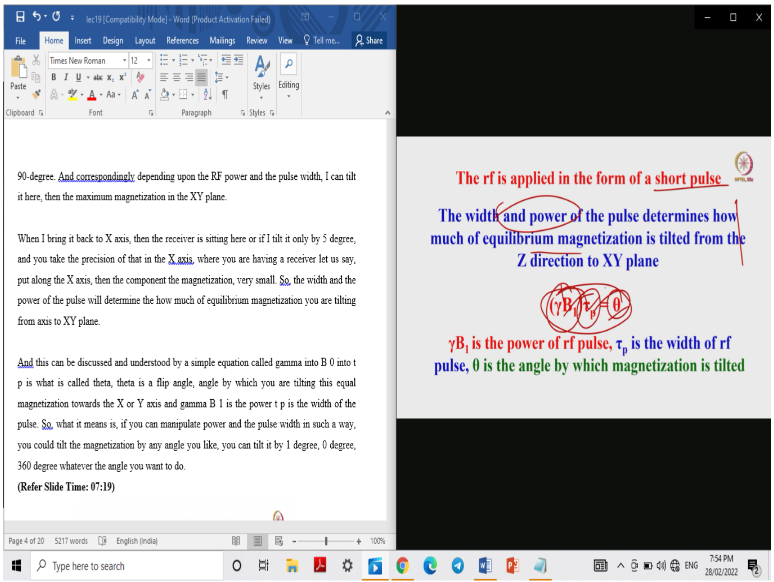

Now, RF is a short pulse a short burst of pulse, the width and the power the pulse determine how much of magnetization is tilted from Z direction to XY plane. Please understand magnetization is here, along Z axis. If I were to shift it to X axis or Y axis, I had to shift by 90-degree. And correspondingly depending upon the RF power and the pulse width, I can tilt it here, then the maximum magnetization in the XY plane when I bring it to X axis, then the receiver is sitting here. Or if I tilt it only by 5 degree, and you take the projection of that in the X axis, where you are having a receiver, let us say, put along the X axis, then the component the magnetization is very small. So, the width and the power of the pulse will determine the how much of equilibrium magnetization you are tilting from Z axis to XY plane.

And this can be discussed and understood by a simple equation called gamma into B0 into tp is what is called theta. Theta is a flip angle, angle by which you are tilting the equilibrium magnetization towards the X or Y axis; and gamma B1 is the power ; Tp is the width of the pulse. So, what it means is, if you can manipulate power and the pulse width in such a way, you could tilt the magnetization by any angle you like, you can tilt it by 1 degree, 0 degree, 360 degree; whatever the angle you want to do, you can just manipulating the RF power and the pulse width,

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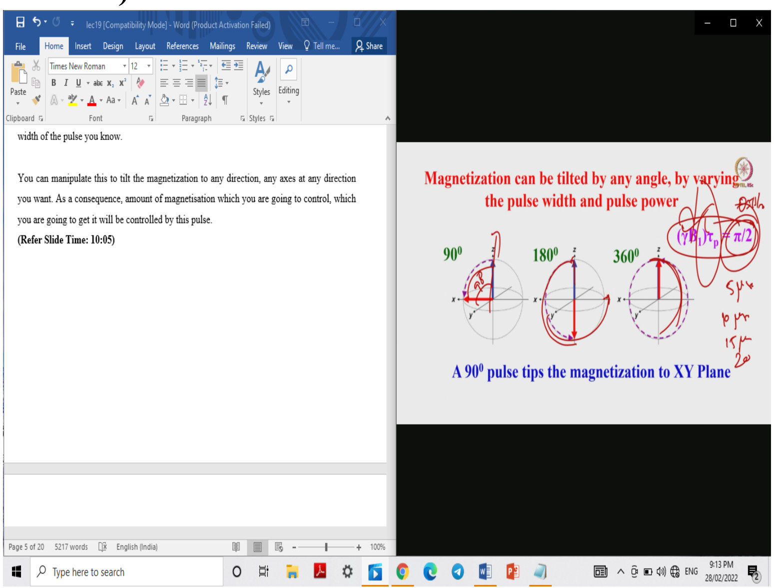

This a very important thing you can do that. Now I will take an example, I have the gamma B1 Tp is equal to pi/2. The magnetisation initially is along Z axis. I am going to apply a 90-degree pulse, what it means is I manipulate in such a way the power and the pulse width that theta becomes 90; pi / 2. That means the magnetization which was along Z axis, I can shift it to one of the axes, how I shift which axis I will discuss later. Let us say, I shift to the X axis, the difference is 90 degree. So, I have shifted the magnetization from Z axis to X axis, the pulse and the width of the power which we use to tilt this magnetization by 90-degree is called a 90-degree pulse. The 90-degree pulse is the one, which tilts the thermal equilibrium magnetization which is along Z axis, either to X axis or to Y axis. It is called a 90-degree pulse. I can determine the 90-degree pulse; I did in the previous course we discussed how to find out the 90 degree pulse. Let us say I know the 90-degree pulse; I double it, what is going to happen? Let us say 90-degree pulse width is 5 microseconds, I will make it 10 microsecond then what is going to happen? The thermal magnetization just along Z axis will go further down, it will take it to minus Z axis; that is called 180 pulse. From here Z axis you tilt it to minus Z axis; that is the 180 pulse.

You can take it further; you can bring it here, this is 270 pulse. Take it further, instead of 10 microsecond, 15 microsecond, bring it here, use 20 microseconds then you take it back to Z axis. What did you do? The magnetization which is along Z axis we tilted, tilted, tilted, tilted like this, brought it back and then took it back to Z axis.

We made the magnetization to go around. Let us apply the pulse along Y axis you are rotating and along this XZ plane. It goes round and round. You do not have to stop at 360 you can apply 720, make it undergo 2 rotations. So, you can make the magnetization dance to our tunes. All you require is the RF power you should know and the width of the pulse you know, You can manipulate this to tilt the magnetization to any direction, any axes to any direction you want. As a consequence, amount of magnetisation which you are going to get will be controlled by this pulse.

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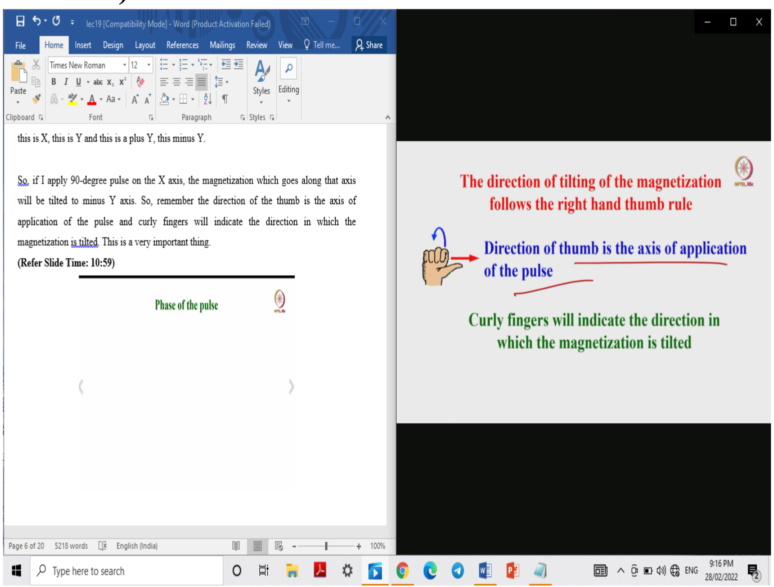

So, direction of tilting with magnetization always follows a right-hand thumb rule. This is a very important rule we should remember. The direction of thumb is the axis of application of the pulse. For example, I consider that let us say magnetization is along Z axis. Now I am going to apply a pulse on the X axis; from Z axis the magnetization is tilted towards Y, this is X, this is Y and this is a plus Y, this minus Y. So, if I apply 90-degree pulse on the X axis, the magnetization which goes along Z axis will be tilted to minus Y axis. So, remember the direction of the thumb is the axis of application of the pulse and the curly fingers will indicate the direction in which the magnetization is tilted, this is a very important thing.

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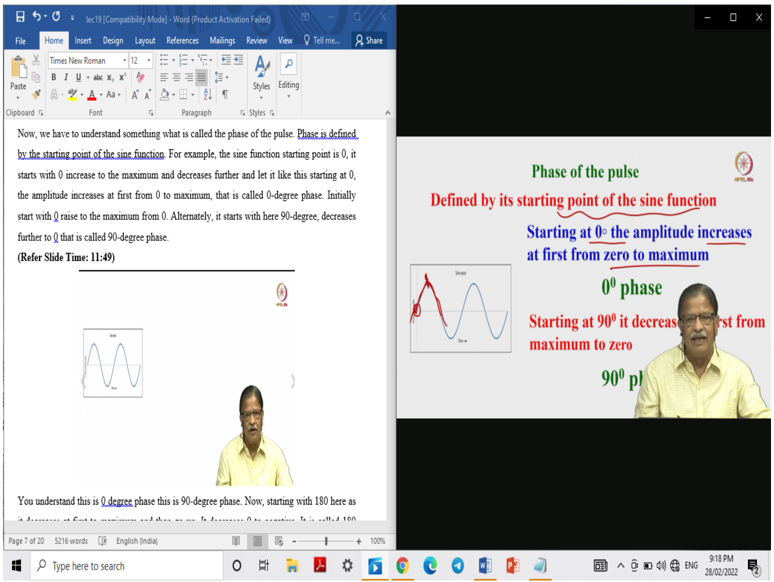

Now, we have to understand something about what is called the phase of the pulse. Phase is defined by the starting point of the sine function. For example, this is a sine function, whose starting point is 0. It starts with 0 increase to the maximum and decreases further; and it like this; starting at 0, the amplitude increases at first from 0 to maximum, that is called 0-degree phase. Initially start with 0 raise to the maximum from 0. Alternately, it starts from here 90-degree, decreases further to 0 that is called 90-degree phase. You understand this is 0-degree phase this is 90-degree phase.

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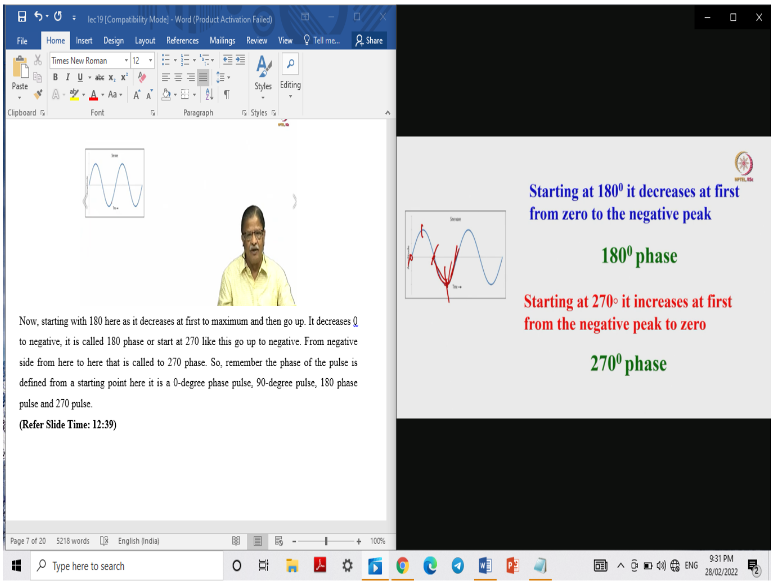

Now, starting with 180 here, it decreases first to maximum and then go up. It decreases 0 to negative, it is called 180 phase or start at 270 like this go up to negative. From negative side from here to here, that is called to 270 phase. So, remember the phase of the pulse is defined from a starting point. Here it is a 0-degree phase pulse, 90-degree pulse, 180 phase pulse and 270 pulse.

So, here afterwards we will be talking about the phase of the pulse 0-degree, 90-degree, 180 degree, 270 phase. Diagrammatically it depends upon the starting point of the sine wave.

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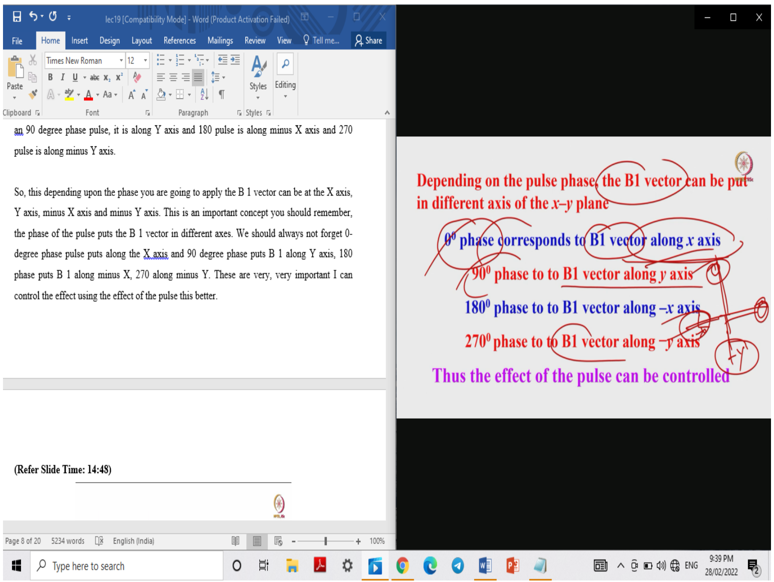

And depending upon the pulse phase, you can put the magnetization vector ton any axis you want. The B1 vector, the rf RF power which are going to apply can be along the X axis, along

Y axis; along any axis; minus X, minus Y, plus X, plus Y or any axis, I can put the RF pulse which are going to apply. I can apply along this axis, this axis, any axis I can apply.

I can put the magnetization vector, main magnetization vector to any of the axes. I can play with it. For example, if I place 0-degree phase pulse that means, I will say the B1 vector is along the X axis; pulse is along the X axis; 0 degree phase pulse is along the X axis. 90 degree phase B1 vector is along Y axis; that means, initially 0 phase pulse is here, 90 degree phase is here; and then 180 phase is here, minus X and 270 pulse is here minus Y.

Imagine a 3 dimensional space, I am going to apply a 90 degree pulse along here, X axis, it is a 0 degree phase pulse. Here it is a 90 degree phase pulse, it is along Y axis and 180 pulse is along minus X axis and 270 pulse is along minus Y axis. So, this depending upon the phase you are going to apply; the B1 vector can be at the X axis, Y axis, minus X axis and minus Y axis.

This is an important concept you should remember, the phase of the pulse puts the B1 vector in different axes. We should always not forget 0-degree phase pulse puts along the X axis and 90 degree phase puts B1 along Y axis, 180 phase puts B1 along minus X, 270 along minus Y. These are very, very important; I can control the effect of the pulse this vector.

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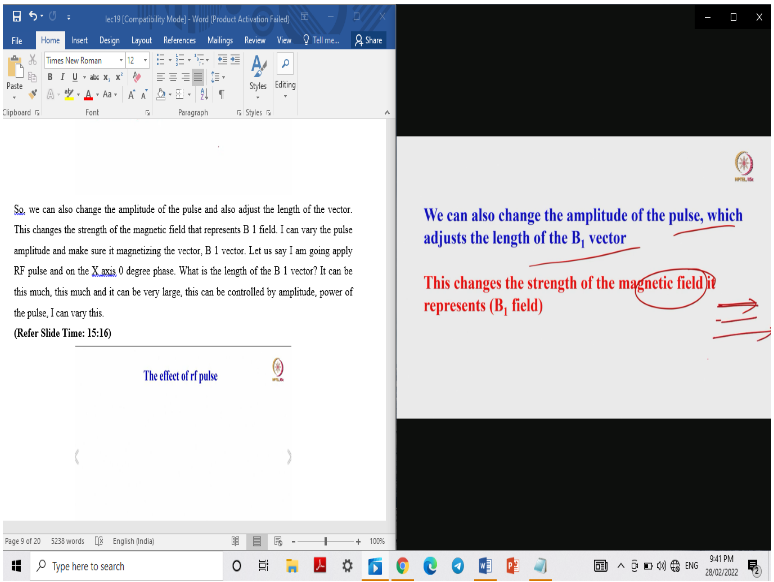

So, we can also change the amplitude of the pulse and also adjust the length of the vector. This changes the strength of the magnetic field that represents B1 field. I can vary the pulse amplitude and make sure the magnetization vector, B1 vector; let us say I am going apply RF pulse and on the X axis 0 degree phase. What is the length of the B1 vector? It can be this much, this much and it can be very large. This can be controlled by amplitude and power of the pulse, I can vary this.

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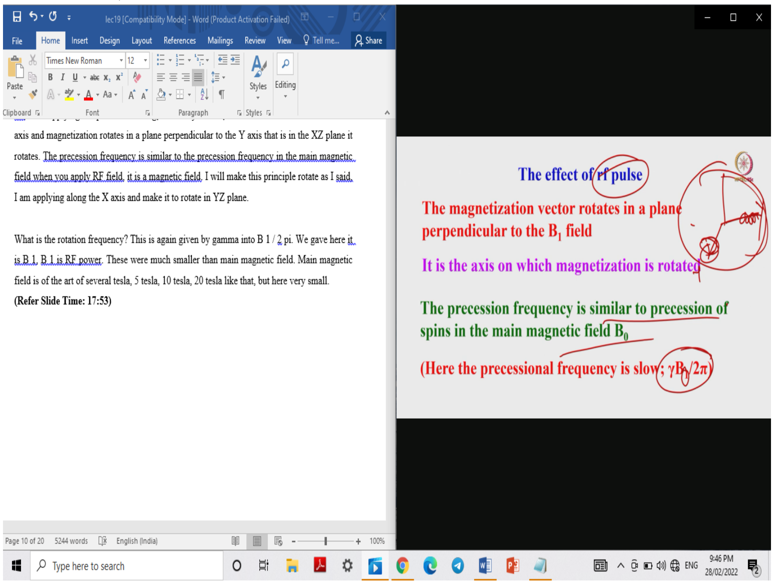

So, the effect of the RF pulse, we will try to understand. What is the RF pulse effect? The magnetization vector rotates in a plane perpendicular to the B1 field. Remember, the magnetization vector rotates in a plane perpendicular to the B1 field. For example, imagine this is the X axis, this is Y axis, this is Z axis. I am going to apply a pulse along X axis in a direction perpendicular to this means, YZ plane, the magnetization rotates in the YZ plane.

If I am going to apply a pulse along the X axis; direction perpendicular to this is X, this is Z so that means the magnetization rotates in the XZ plane. So, magnetization vector rotates in a plane perpendicular the RF pulse you are going to apply. The RF pulse, B1 field, I am going to apply in one direction, in a plane perpendicular to that, the vector keeps rotating. We will understand this thing as we go ahead further.

So, it is the axis on which we are going to see the magnetization rotates. That is the important thing. I am going to apply a pulse along Z axis means, I am rotating the magnetization along, let us say, I consider here. I am going to apply RF pulse along this axis means I am rotating along this axis and the rotation in the plane perpendicular to the RF pulse axis. This concept should be very clear then only you will understand more as we go ahead about the pulse sequences.

So, I am applying RF pulse here along, let us say Y axis, that means the rotation is about Y axis and magnetization rotates in a plane perpendicular to the Y axis; that is in the XZ plane it rotates. The precession frequency is similar to the precession frequency in the main magnetic field. When you apply RF field, it is a magnetic field; I will make this principle rotate as I said, I am applying along the X axis and make it to rotate in YZ plane.

What is the rotation frequency? This is again given by gamma into B0/2pi. Here it is B1, B1 is RF power. This is much, much smaller than main magnetic field. Main magnetic field is of the art of several tesla, 5 tesla, 10 tesla, 20 tesla like that, but here it is very, very small.

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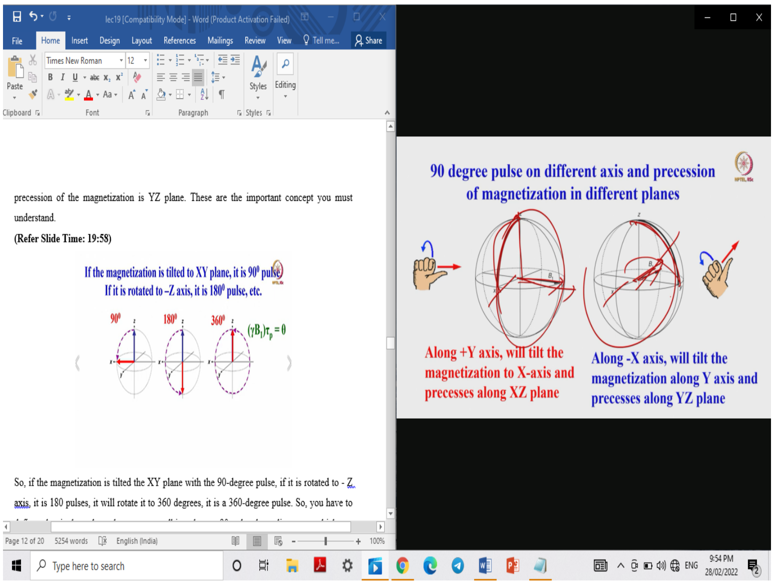

Now we will go to the 90 degree pulse on different axes and the precession, I am going to apply an 90 degree pulse. Let us say on plus Y axis. This is my axis plus Y and this is X axis in a direction perpendicular; they are orthogonal to each other. What do you mean by telling apply along plus Y axis, when I apply this axis my pulse is along plus Y. Put the thumb in this direction plus Y, magnetization was along Z axis. The curly finger shows the direction of tilting. So, you apply RF pulse along Y, magnetization which was along Z, will be tilted to the X axis, it will be tilted towards the X axis? Then what will happen? It starts rotating in the XZ plane, it starts precessing in the XZ plane. This concept should be very clear, because these are all very, very important to understand the behaviour of magnetization in different pulse sequences.

So, in the simple logic, now I will take the other example here. For example, I would apply radio frequency pulse on minus X, of course this is the X axis towards me. And opposite to me other direction is minus X. I am applying along this axis. So put the curly finger that side then magnetization which was along Z, it has to move towards the right side. So, from here, it moved toward the Y axis. The curly finger is telling me if you put along minus X axis, the curly finger tells me magnetization should move towards plus Y axis.

Because this is my X and that is minus X. Along minus X if you apply you bring it to + Y axis; then what will happen? Because you are applying RF pulse along the X axis that means rotation is about the X axis, but the plane of rotation of the magnetization, the plane of precession of the magnetization is YZ plane. These are the important concepts you must understand.

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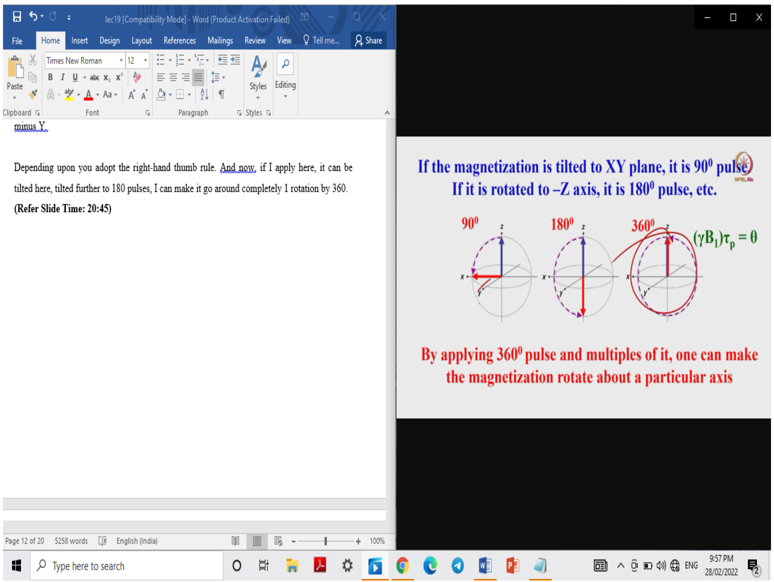

So, if the magnetization is tilted to XY plane with the 90 degree pulse, if it is rotated to minus Z axis, it is 180 pulses, if it is rotated to 360 degrees, it is a 360 degree pulse. So, you have to define what is the pulse, when we start talking about a 90 pulse depending upon whichever the direction you are going to apply with X axis or Y axis, minus X axis, minus Y axis, you are tilting in a direction, if I am applying on an X axis it may be tilted to Y axis or minus X, minus Y; you adopt the right-hand thumb rule. And now, if I apply here, it can be tilted here, tilted further to 180 pulses, I can make it go around completely by one rotation by 360.

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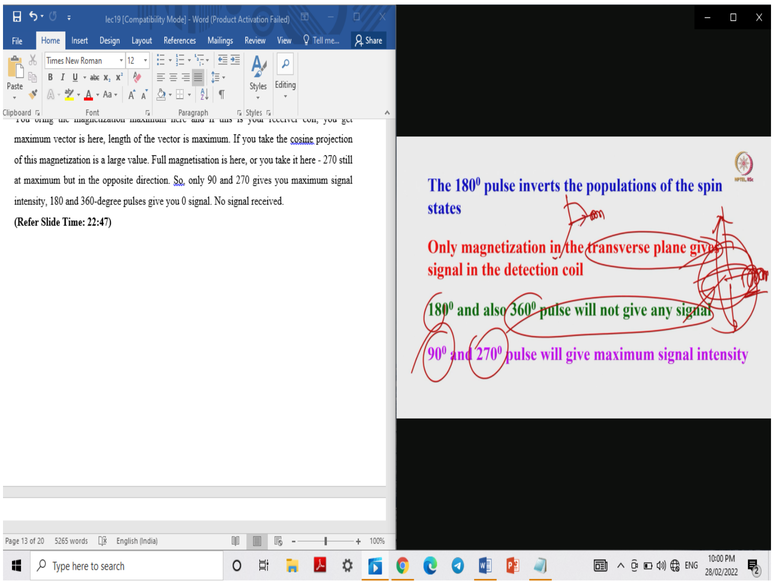

So, 180-degree pulse inverts the population of the spin states. If I am going here, 180 pulse bring the magnetization from Z axis to minus Z axis. It will invert the populations and remember, 180 degree pulse and 360-degree pulse will not give any signal. Only a magnetization in the transverse plane gives the signal, that will only induce the signal in the receiver coil, see, I am having a receiver coil kept here.

Remember in the very first class and in the previous course, we explained this is the direction of magnetization direction which applies RF field, your receiver is in a direction perpendicular to it, all the 3 are orthogonal to each other. That is what we have been discussing, please understand. So now you have got a receiver here, you bring the magnetization from plus Z to minus Z here, you do not see any signal.

So, 180 and 360 pulse, same way it goes back to Z axis, you do not see any signal. So, 180 degree and 360 degree pulse will not give signal, will not induce emf in the receiver coil. Only the transverse magnetization here induces emf, that is what is detected. So, if you have receiver in the X axis or Y axis or minus X, minus Y, the magnetization should be in the XY plane, it should be brought to XY that is transverse plane and maximum intensity you get for 90 degree and 270 degree, that also we discussed.

You bring the magnetization maximum here and if this is your receiver coil, you get maximum vector here, length of the vector is maximum. If you take the cosine projection of this, the magnetization is a very large value. Full magnetisation is here, or you take it here minus 270 still at maximum but in the opposite direction. So, only 90 and 270 gives you maximum signal intensity, 180 and 360-degree pulses give you 0 signal no signal received.

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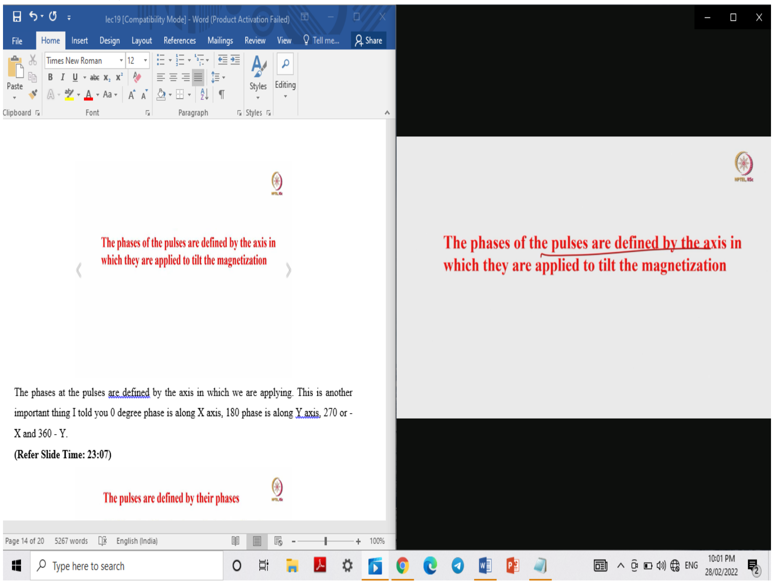

The phases at the pulses are defined by the axis in which we are applying. This is another important thing I told you 0 degree phase is along X axis, 180 phase is along Y axis, 270 along minus X and 360 along minus Y.

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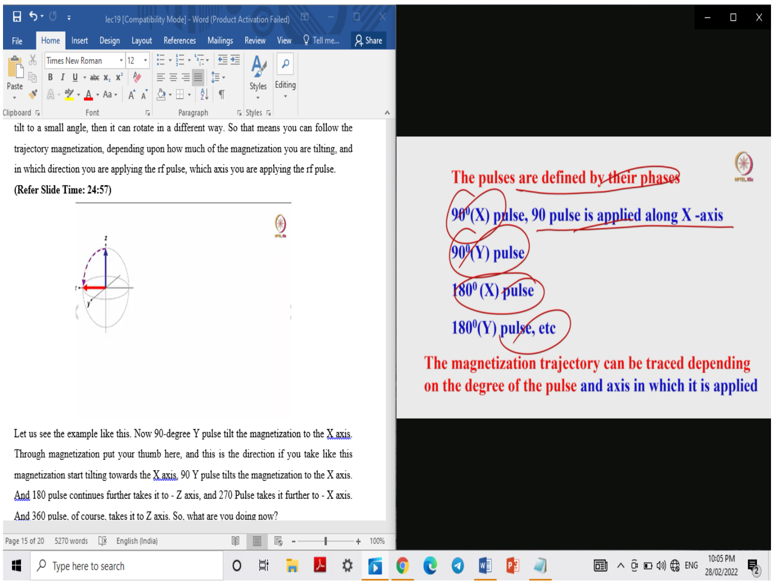

But we can define pulses and phases like this, the pulses are defined by their phases. If I apply 90X pulse means, I am applying a 90 degree pulse along the X axis that is the convention. If I say I have a 90X pulse, it means in the direction of X axis I am applying 90 degree pulse. What I am trying to do now, I am rotating the magnetization along the X axis; the rotation of the magnetization is in the X axis, but in the direction perpendicular to it, in the YZ plane.

That is what you should remember. So now 90 degree Y pulse means 90 degree pulse applied along Y axis. Similarly, I can apply 180 X pulse 180 pulse along the X axis; and 180 pulse along Y axis. And you can follow the magnetization trajectory depending upon where you are applying the pulse. And what is the degree of pulse you are applying. That means how much magnetization you are tilting with that you will follow the trajectory of magnetization.

I told you already, magnetization is along the Z axis; apply 90 degree pulse along the X axis. Then you are tilting it in the transverse plane since the rotation is along the X axis is the magnetization, rotate in the YZ plane, in a direction perpendicular rate. Instead of 90 degree I tilt by a small angle, then it can rotate in a different way. So that means you can follow the trajectory of magnetization, depending upon how much of the magnetization you are tilting, and in which direction you are applying the RF pulse, which axis you are applying the RF pulse.

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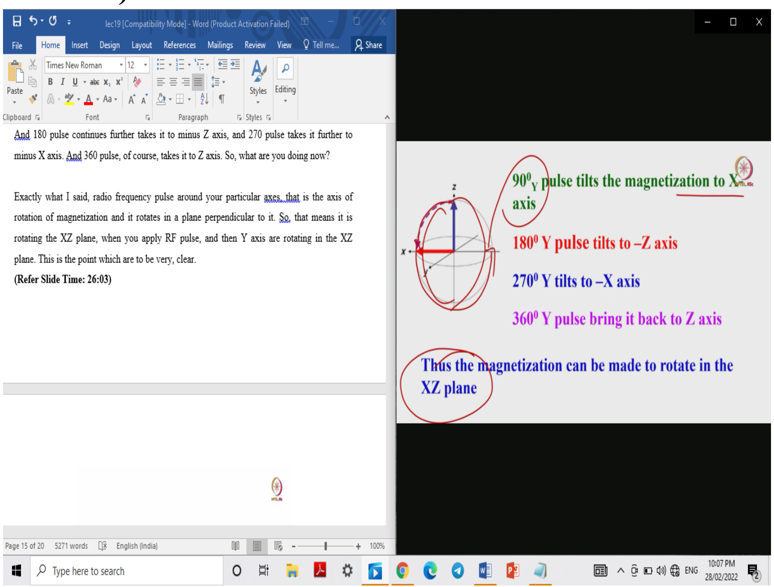

Let us see the example like this. Now 90 degree Y pulse tilt the magnetization to the X axis. True you know, the magnetization is here, put your thumb here, and this is the direction if you take like this magnetization start tilting towards the X axis; 90Y pulse tilts the magnetization to the X axis. And 180 pulse continues further; takes it to minus Z axis, and 270 pulse takes it further to minus X axis. And 360 pulse of course, takes it to Z axis. So, what are you doing now?

Exactly what I said, you apply a radio frequency pulse around a particular axis; that is the axis of rotation of magnetization and it rotates in a plane perpendicular to it. So, that means it is rotating in the XZ plane. You apply the RF pulse along the Y axis, then you are rotating in the XZ plane. This is the point which you have to be very, very clear. So, now, we can understand the rotation of the magnetization on different axes. How it rotates when you apply different pulses? What is the way it rotates, we will understand.

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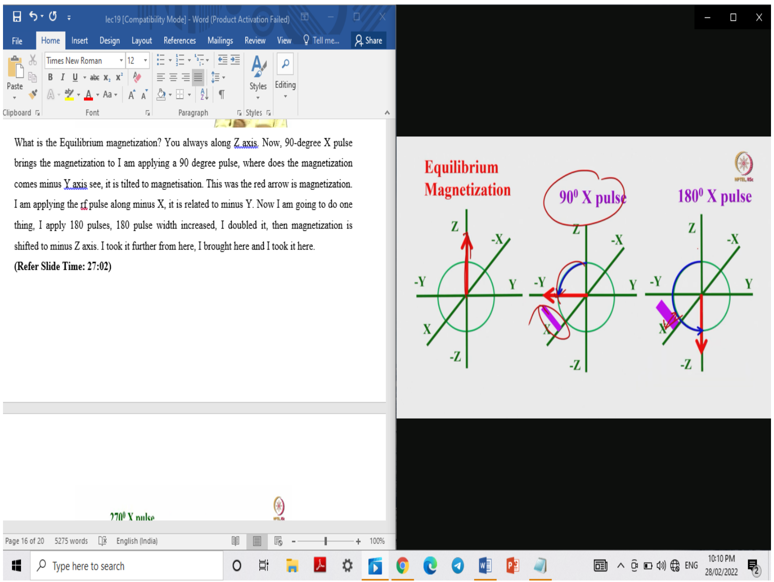

What is the Equilibrium magnetization? It is always along Z axis. Now, 90-degree X pulse brings the magnetization to, I am applying a 90 degree pulse, where does the magnetization come? to minus Y axis, see, it is tilted. This was the red arrow, it is the magnetization. I am applying the RF pulse along minus X, it is tilted to minus Y. Now I am going to do one thing, I apply 180 pulse, 180 pulse width increased, I doubled it; then magnetization is shifted to minus Z axis. I took it further; from here, I brought here and I took it here.

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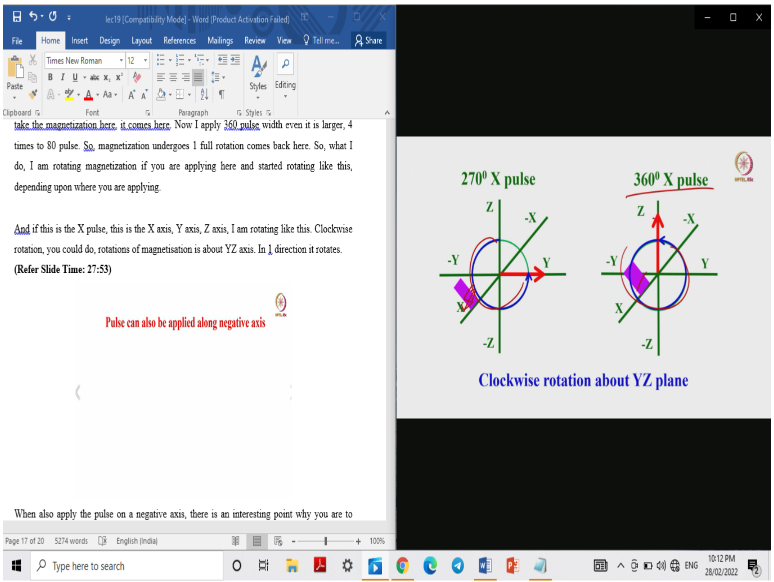

Now I am applying a 270 pulse along X; what I am doing? Increasing the width more, then I take the magnetization here, it comes here. Now I apply 360 pulse; width even larger, 4 times to 80 pulse. So, magnetization undergoes one full rotation and comes back here. So, what I do, I am rotating magnetization. If you are applying here and started rotating like this, depending upon where you are applying. And if this is the X pulse, this is the X axis, Y axis, Z axis, I am rotating like this. Clockwise rotation, you could do, rotations of magnetisation is about YZ axis, in one direction it rotates.

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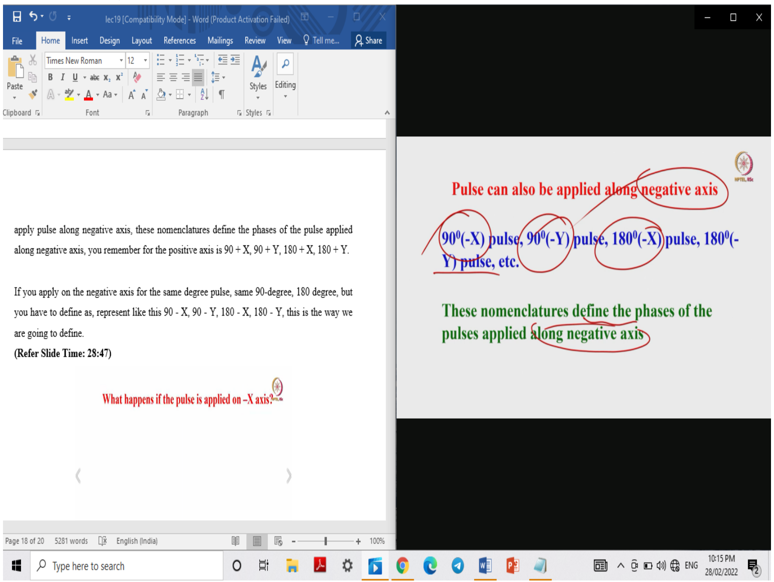

When also apply the pulse along negative axis. It is an interesting point; why you are to apply always only on plus X or plus Y, you can apply along negative axis also; then they are called accordingly 90 -X pulse, 90 -Y pulse, 180 -X pulse, 180 -Y pulse. You can also apply pulse along negative axis, these nomenclatures define the phases of the pulse applied along negative axis. You remember for the positive axis is 90 + X, 90 + Y, 180 + X, 180 + Y.

If you apply on the negative axis for the same degree pulse, same 90 degree, 180 degree, but you have to define as, represent like this; 90 -X, 90 -Y, 180 -X, 180 -Y, this is the way we are going to define.

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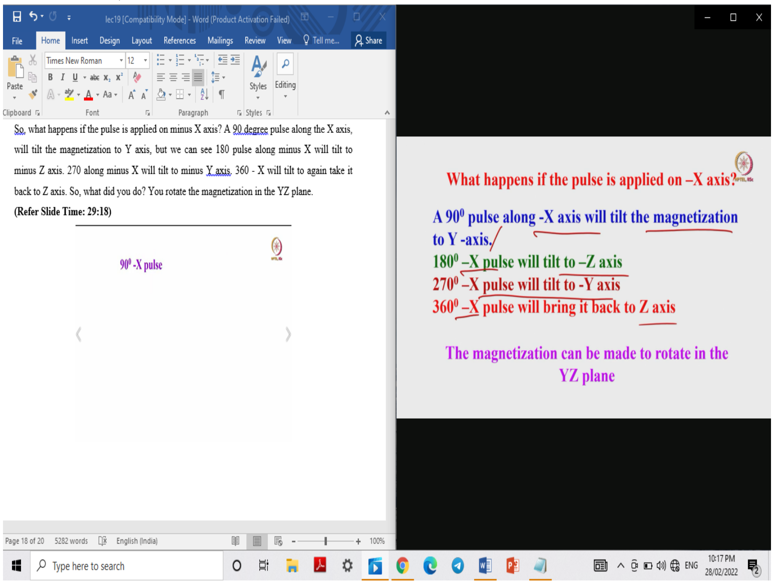

So, what happens if the pulse is applied on minus X axis? A 90 degree pulse along the minus X axis, will tilt the magnetization to Y axis, but we can see 180 pulse along minus X will tilt to minus Z axis. 270 along minus X will tilt to minus Y axis. 360 -X will tilt again and take it back to Z axis. So, what did you do? You rotate the magnetization in the YZ plane.

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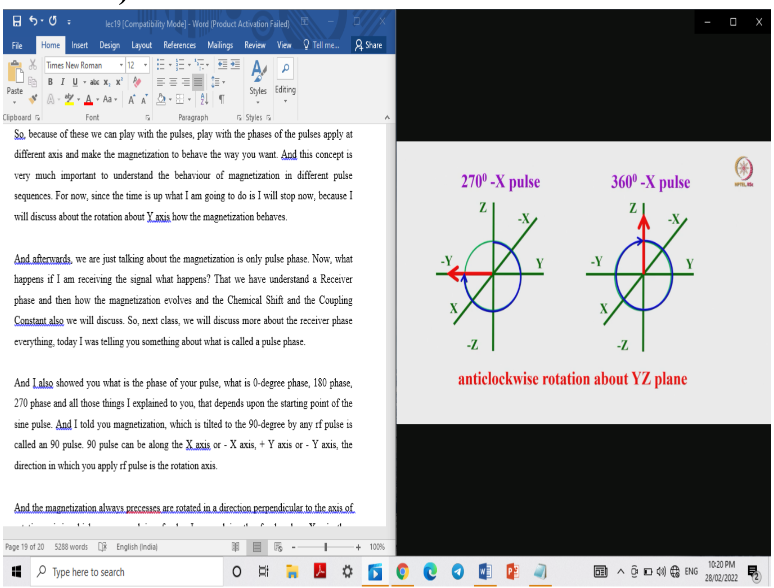

Let us see what is happening 90 -X I am applying. We bring the magnetization to plus Y axis, applying 180 -X, take it to minus X, applying 270 -X take it to minus Y, applying 360 -X, but taking it back to Z axis, what did you do? You created anti clockwise rotation about the YZ plane. You understood the point. Either way you can think of it. You can make the magnetization to go clockwise like this. You can make the magnetization to go anti clockwise like this. Depending upon which direction we are going to apply the pulse. If you know, whether it is X axis or Y axis; like plus X or plus Y, minus X or minus Y, accordingly, you can tilt the magnetization and make magnetization to rotate either 90 degree, 270 degree, 180 to 360, either the clockwise or anti clockwise, this is the beauty.

So, because of these we can play with the pulses, play with the phases of the pulses, apply along different axis and make the magnetization to behave the way you want. And this concept is very much important to understand the behaviour of magnetization in different pulse sequences. For now, since the time is up what I am going to do is I will stop now, because I will have to discuss about the rotation about Y axis and how the magnetization behaves.

Now we are just talking about the magnetization, that is only a pulse phase. What happens if I am receiving the signal? what happens? For that we have to understand the receiver phase and then how the magnetization evolves and the chemical shift and the coupling constant also we will discuss. So, next class, we will discuss more about the receiver phase and everything. Today I was telling you something about what is called a pulse phase.

And I also showed you what is the phase of pulse, what is 0 degree phase, 180 phase, 270 phase and all those things I explained to you, that depends upon the starting point of the sine pulse. And I told you magnetization, which is tilted to the 90 degree by any RF pulse is called an 90 pulse. 90 pulse can be along the X axis or minus X axis, plus Y axis or minus Y axis, the direction in which you apply RF pulse is the rotation axis.

And the magnetization always precesses in a direction perpendicular to the axis of rotation, that is perpendicular axis in which you are applying RF pulse. I am applying the RF pulse along X axis, then you make the magnetization to rotate along YZ plane, I apply the magnetization along Y axis you make the magnetization rotate along XZ plane and again depending upon, whether we are applying plus X or minus X, you can make it rotate clockwise or anti clockwise.

Similarly, whether you apply pulse along plus Y or minus Y you can make it rotate clockwise in the XZ plane, or rotate anti-clockwise. So, these are some of the important concepts which you should be very clear. We have to understand these things, to understand the behaviour of magnetization in different pulse sequences as we go further. So, we do not discuss every pulse sequence at least 1 or 2 especially when you want to understand product operators.

These type of phases of the pulse and receiver pulses especially in understanding phase cycling is very important. So that is why I wanted to introduce this in the next class. We will continue with the pulse phase and receiver case and different rotations and also the evolution of magnetizations and discuss further, I will stop here. Thank you.