Advanced NMR Techniques in Solution and Solid-State

Prof. N. Suryaprakash
Professor and Chairman (Retd)
NMR Research Centre
Indian Institute of Science – Bengaluru

Module - 14
Fourier transformation in NMR
Lecture - 14

Welcome back, in the last class, we understood lots about the Fourier transformation, theorems of Fourier transformation, what is the Fourier transformation, what is the band limited function and what are the theorems, like Shift theorem, Linearity theorem, Additive theorem, Nyquist theorem, Sampling theorem, all very important theorems in Fourier transformation.

We understood in the last class and also we just worked out especially for the Gaussian function and showed that the Fourier transmission of a Gaussian is a Gaussian. But I did not work out for other functions, of course, for the rectangular function, we worked out in the beginning itself and showed it as sinc function, while we explicitly introduced Fourier transformation. We worked it out and we thought of working out other functions, as I mentioned to you, the Fourier transformation of Gaussian is a Gaussian.

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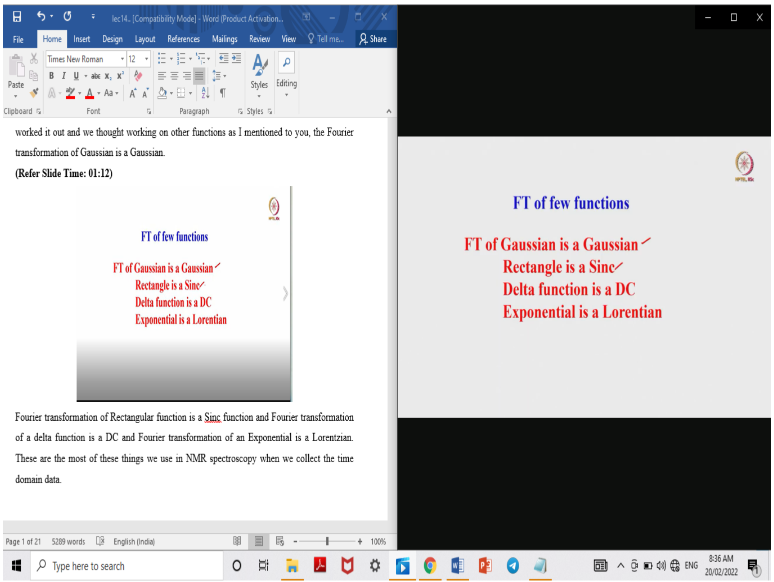

Fourier transformation of rectangular function is a sinc function and Fourier transformation of a delta function is a DC and Fourier transformation of an exponential is a Lorentzian.

These are most of these things we use in NMR spectroscopy when we collect the time domain data.

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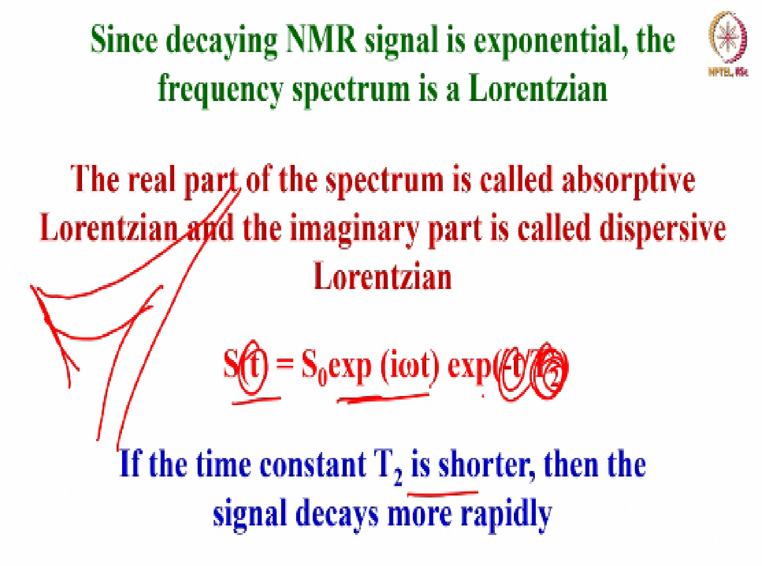

So, now, where do we use this in NMR, where do we come across this thing to understand Fourier transformation so much? First of all, remember, when we discussed NMR in the beginning itself, I said we apply radio frequency pulse and collect the signal in time domain, it is a decaying exponential. And then for converting the exponential time domain function we do the Fourier transformation to get the spectrum.

Since it is the exponential function, when you do the Fourier transformation, you are going to get a Lorentzian. That is why NMR spectrum is a Lorentzian spectrum, and when you do the Fourier transformation you get real and imaginary parts; and we call the real part as absorptive Lorentzian, and the imaginary part is called dispersive Lorentzian; and this is a general expression, we use for Fourier transformation. Remember Fourier transformation, if you want to get the time domain this is what the function you have to use; S of 0 exponental, i omega t into exponential minus t / T2. Time constant T2 is very, very short, then the signal decays more rapidly, if it becomes shorter and shorter, then this becomes larger and larger in the numerator. The exponential becomes quite big, as a consequence it decays very fast, just this is what you should understand, in the NMR spectrum what is going to happen? if the signal is decaying very slowly like this; that means, your spectrum is very, very sharp is a Lorentzian like this, width is very small. On the other hand, if the T2 is larger, which is in the denominator of this exponential, then what will happen? this becomes larger value, so, signal decays very fast like this. The similar expressions we are going to discuss for a T 2 and T 1 and as we go for relaxation studies, you will see that the T1 and T2 which comes in the denominator, you can see that there also you will find out that the signal decay is very fast in the xy plane, you are going to get a broad signal. So, this is where you understand, the Lorentzian and Gaussian will come into the picture.

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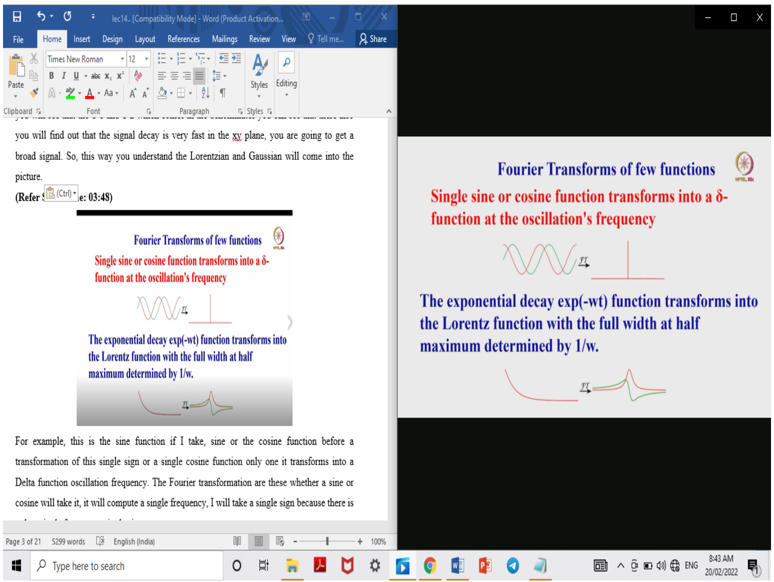

For example, this is the sine function if I take, sine or the cosine function; the Fourier transformation of this single sine or a single cosine function, only one; it transforms into a delta function, this is the oscillation frequency. The Fourier transformation of this whether a sine or cosine will take it, I will compute as a single frequency, I will take a single sine because there is only a single frequency, single sine. If I take from here to here is the frequency, only 1 frequency. Similarly cosine here to here is the single frequency, because you can measure it. So, then it gives rise to a single line. Whereas, if I take the exponentially decaying function, then it transforms the Lorentzian function like this, I take this exponential decay, this is the FID of the NMR spectrum, you do the Fourier transformation. This is what you are going to get. And this is called real part and this is called the imaginary part; the real part is absorptive like this, and imaginary part is dispersive like this. So, this is an absorptive part which is nothing but the real part of the Fourier transformation, this is the imaginary part which is the dispersive component of the Fourier transformation.

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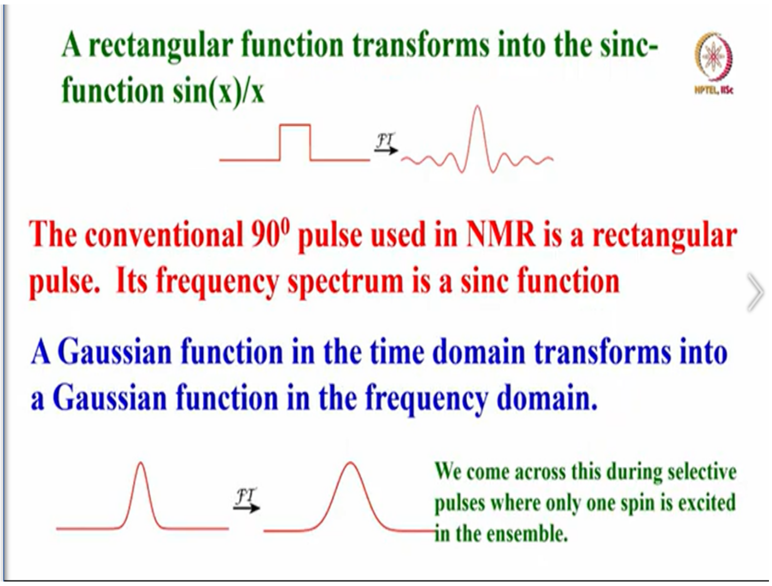

And of course, rectangular function we discussed; it comes as a sinc function. So, sinc/c function, you will come across these and some of that, when you are trying to do the NMR experiment. Let us say I am going to collect the signal very fast like this. It is an exponentially decaying function, somehow the gain of a receiver is huge, I use lot of gain of receiver, the initial portion of the FID gets amplified like this, then the FID would not be smooth decaying FID, it will be like this; then what does it mean?

This portion behaves more like a square pulse or a rectangular pulse, then if you do the Fourier transformation such type of free induction decay. You are going to get in each spectrum, at each frequency if there is especially when you have a stronger signal present in your spectrum. Near the strong signal, you get wiggles like this, on either side of this. These wiggles are nothing but the sinc function peaks. Please remember in the Fourier transmission and when you do the NMR spectrum. Collect the free induction and do the Fourier transformation, if the FID is cut in the initial portion, you are going to get the wiggles like this, and they are because of sinc function. You will understand, all these things when you understand Fourier transformation, you go back to the NMR spectrum and you see all these problems, you can immediately reason out why it is happening?

That is why the understanding of this Fourier transformation is very, important for you. The conventional 90 degree pulse which you use in NMR is a rectangular pulse like this. So obviously, we are going to use rectangular pulse, the output has to be a sinc function. That is the reason why we use this type of pulse and a Gaussian function in the time domain. Of course, I already showed you it transforms itself into Gaussian.

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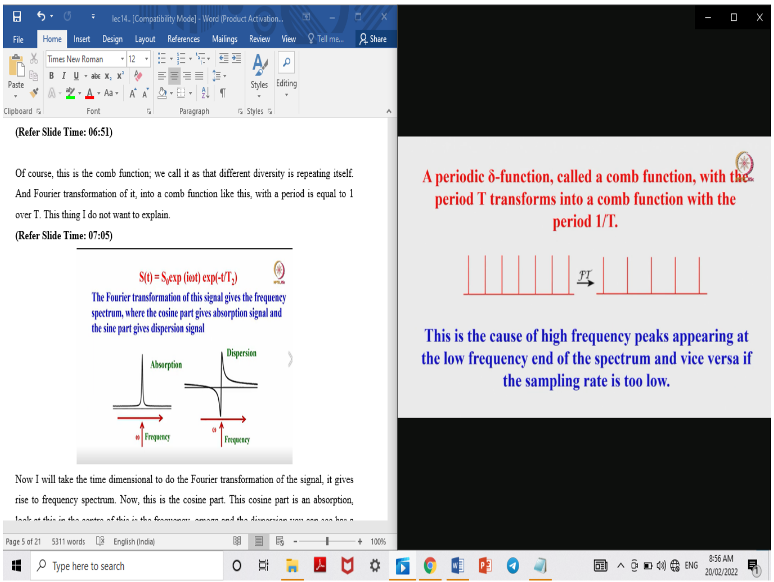

Of course, this is the comb function; we call it as that different times it is repeating itself. And Fourier transformation of it, a comb function like this, with a period is equal to 1 over T. Ok this thing I do not want to explain.

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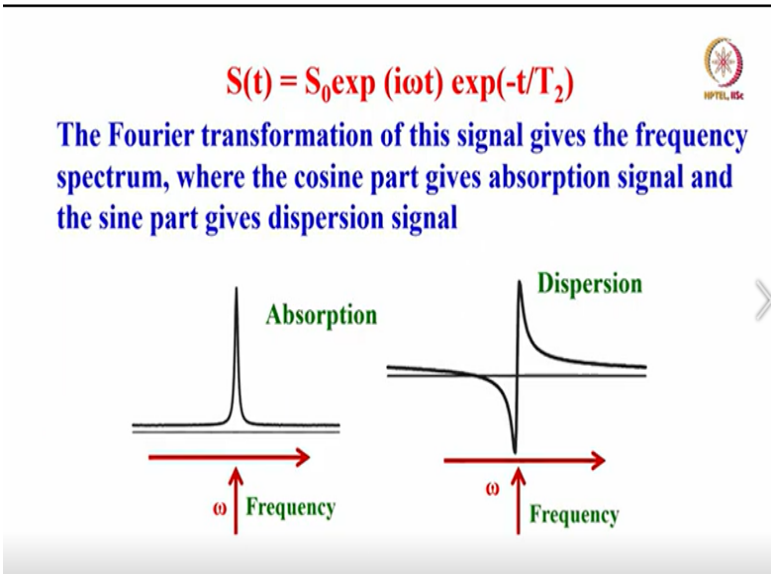

Now I will take the time domain signal and do the Fourier transformation of the signal, it gives rise to frequency spectrum. Now, this is the cosine part, this cosine part is an absorption, look at this; in the centre of this is the frequency, omega. And the dispersion you can see, has a phase shift in line by 90 degree. The absorptive and dispersive component has a phase shift by 90 degree.

That means, this is a cosine part and this is the sine part of the Fourier transform signal, when you do the Fourier transformation, you get real and imaginary part. One is a cosine part correspond to real part, which gives rise to the absorption signal and the sine part is the imaginary part which gives rise to dispersive signal. So, this is what we are going to get, this the dispersive signal.

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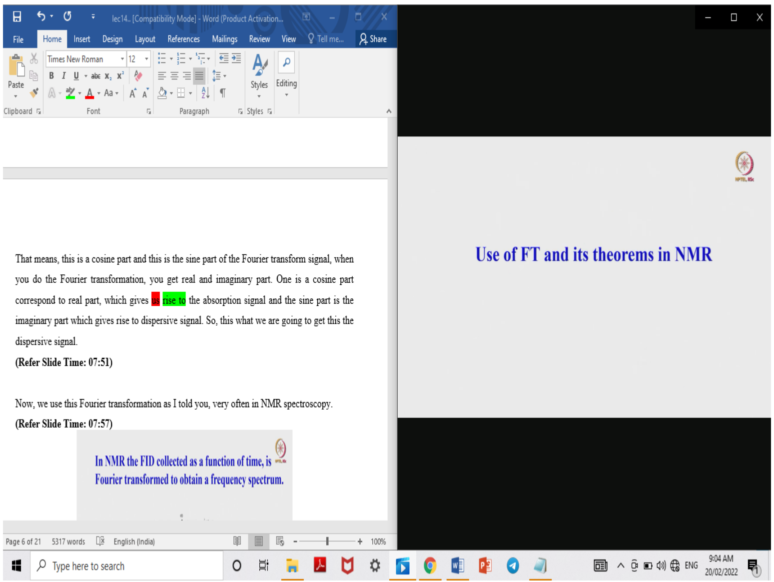

Now, we use this Fourier transformation as I told you, very often in NMR spectroscopy.

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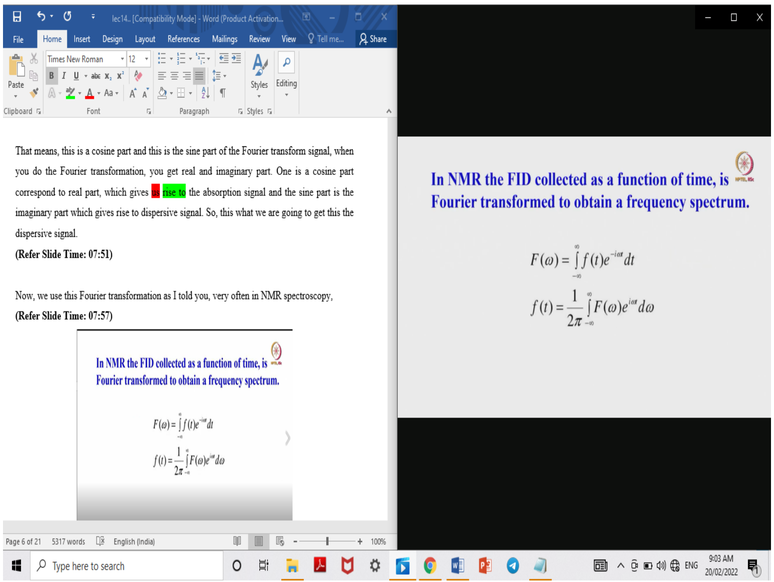

Like I collect the time signal in the time domain and do the Fourier transformation like this, and this is the time domain signal collected. I do the Fourier transformation to get the frequency. I can go back; I have the frequency spectrum, do the inverse Fourier transformation of it, then I will get back time domain signal. I can interchange between these two, this is normally collected.

We collect the signal as a function of time, this is the equation, F of omega is equal to integral of minus infinity to plus infinity f of t e to the power of minus i omega t dt. This is a famous important equation of Fourier transformation of time domain in NMR. Remember that. Of course, the inverse of that where you remove the negative part here, it is e power i omega t dt, if you take it, then you can do the Fourier transformation of this frequency domain, you go back to time domain signal.

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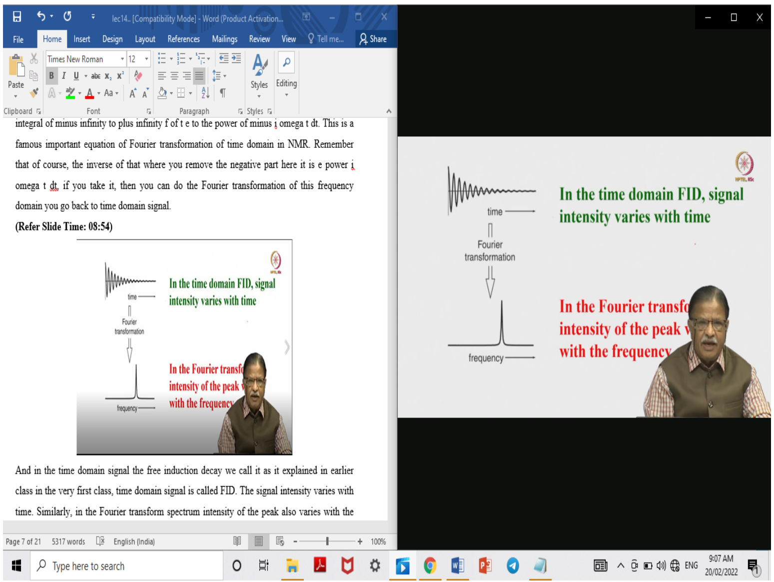

And in the time domain signal the free induction decay we call it, as I explained in earlier class in the very first class, time domain signal is called FID. The signal intensity varies with time. Similarly, in the Fourier transformed spectrum the intensity of the peak also varies with the time, very easy to understand this. Let us say I have 2 frequencies present in your NMR spectrum, 1 intensity is very large, huge free induction decay is there, signal intensity is very large; other is very weak intensity like this, both are present. Do the Fourier transformation of it, we will have frequency one is bigger intensity, and other is smaller intensity. The frequencies are different and the intensities of time domain varies; correspondingly the intensity should be also different in the frequency domain spectrum. This is what you come across in the NMR spectrum; all peaks are not of equal intensity, different peaks have different intensities. As a consequence, you do the Fourier transformation the frequency spectrum also will have different intensities. So, like the time domain FID have the different intensities, different amplitudes when the signal is collected. Similarly, here also the frequency will be different in the Fourier transform spectrum.

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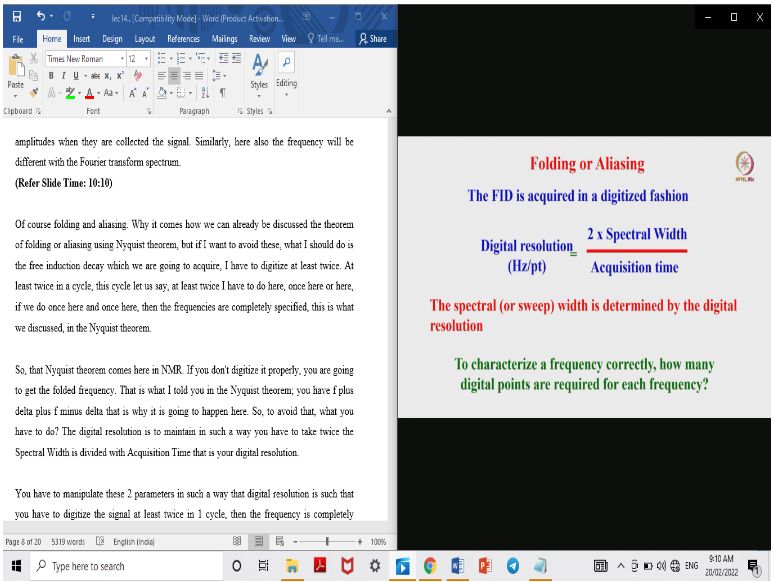

Of course folding and aliasing, why it comes we have already discussed; the theorem of folding or aliasing using Nyquist theorem, but if I want to avoid these, what I should do is, the free induction decay which I am going to acquire, I have to digitize at least twice. At least twice in a cycle, this is a cycle, let us say, at least twice I have to do here, one here or here, if we do once here and once here, then the frequencies are completely specified, this is what we discussed, in the Nyquist theorem. So, that Nyquist theorem comes here in NMR. If you do not digitize it properly, you are going to get the folded frequency. That is what I told you in the Nyquist theorem; f + delta appears as f - delta that is what is going to happen here. So, to avoid that, what you have to do? The digital resolution you have to maintain in such a way you have to take twice the spectral width divided by the acquisition time; that is your digital resolution. You have to manipulate these 2 parameters in such a way your digital resolution is such that you have to digitize the signal at least twice in 1 cycle; then the frequency is completely specified. So, to characterize the frequency correctly, I have to digitize at least twice.

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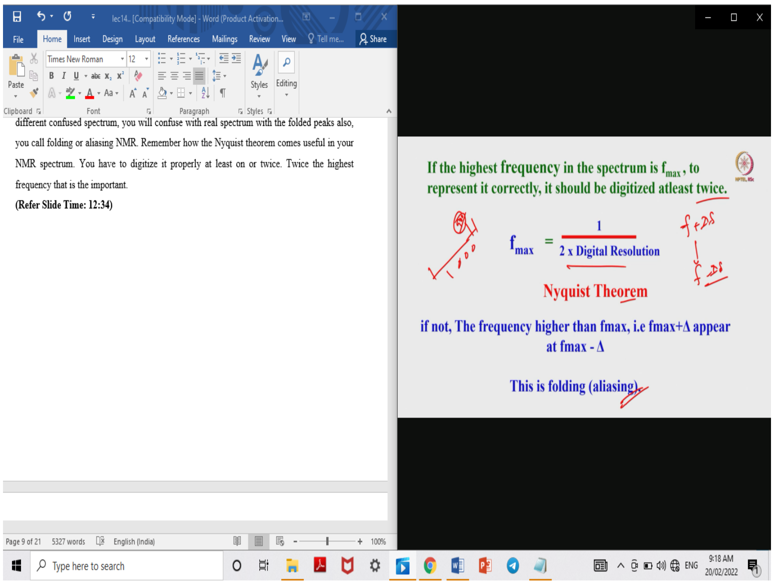

And this is what it is Nyquist theorem. So, highest frequency in the spectrum you find out take the highest frequency of that is what is called like band limit. I told you, whenever I see, it should be digitized at least twice of the highest frequency, I take this spectrum with some at least 0 to 1000 I will take and my highest frequency is about 900 at least one or twice of that you have to digitize it twice of that. That is very important, the highest frequency you have to take it, represent it correctly by digitizing at least twice of its frequency.

So, now come to Nyquist theorem, if you do not digitize it properly, what happens I told you f + delta come appears as f - delta in the frequency domain spectrum, you get different confused spectrum, you will confuse with real spectrum with the folded peaks also; you call folding or aliasing in NMR. Remember how the Nyquist theorem comes useful in your NMR spectrum. You have to digitize it properly at least twice. Twice the highest frequency that is very important.

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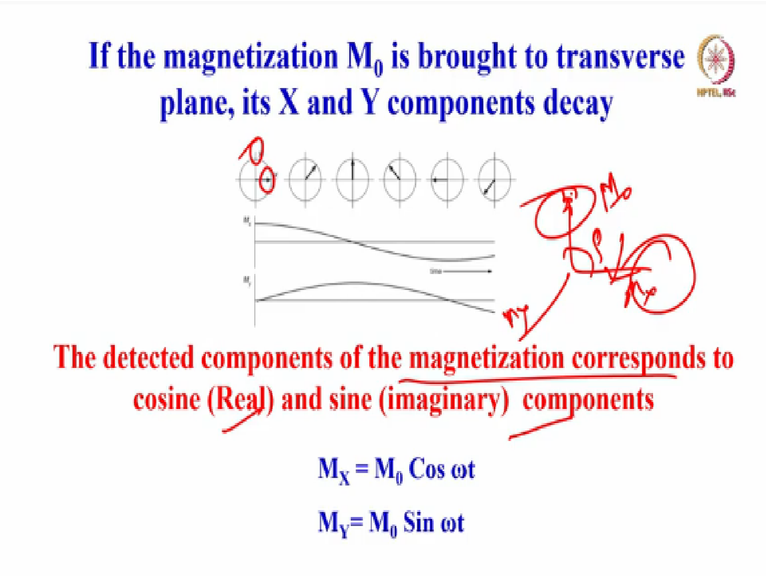

The magnetization M0 is brought to transverse plane and it decays into XY components; you will have an X component here and Y component here, the detected components of the magnetization correspond to cosine and sine because of Fourier transformation, when we express in the complex form. We have cosine component and sine component, both are present. So, when you take your time domain signal like this and do Fourier transformation, you will get M0 as the magnetization. In NMR, I can resolve this into 2 components; MX and MY. MX is the X component, MY is the Y component. The X and Y are opposite you know, they are phase shifted by 90 degree. If I have my receiver here, I get a real component here, then this is phase shift by 90 degree, this signal will be dispersive signal. So, I am going to get the absorptive peak here and dispersive peak here. So, this is what I was telling that you come across this absorption and dispersion, absorptive component and dispersive component. All those things very often we will discuss that. So, this MX component is nothing but the cosine omega t and MY is the sine omega t.

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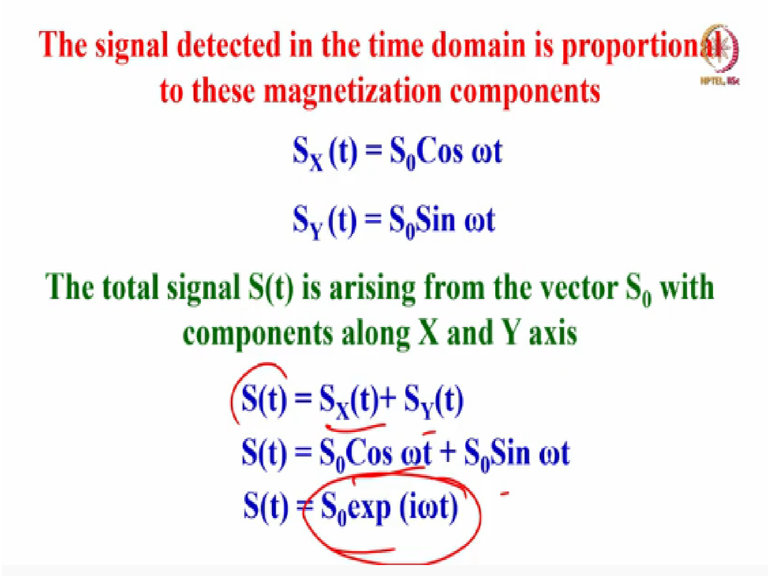

The signal detected in the time domain is proportional to these two constants, the total signal comes because of sum of these things. So, for example, if I have total signal, it is a sum of SX of t and SY of t; that is the sum of cosine component and sine component. That is why we can write this formula as S of exponential i omega t; sum of these two.

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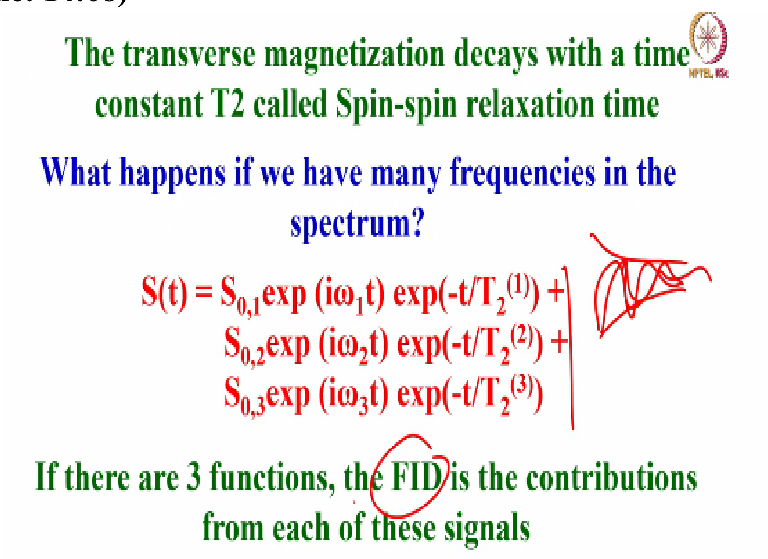

Now, what happens if there are many frequencies present in this spectrum. Let us say I have 3 frequencies, omega 1, omega 2, omega 3. Now, what I am going to do is individually I can do the Fourier transformation, they are all added up. That is what I told you about the linearity theorem. There are 3 different functions, the FID contributions from each of them are overlapped, one FID is like this, other FID is like this, other FID is like this. They are all overlapped, and you do the Fourier transformation individually; they are Fourier transforms.

That is where you are going to get 3 different frequencies. So, if there are many frequencies present in the spectrum, in the time domain there are many free induction decays overlapped. It is an interferogram and do the Fourier transformation. You are going to get that many number of frequencies present. I took the example here with 3 frequencies, in the time domain we have 3 free induction decays and in the frequency domain after doing the Fourier transformation we are going to get 3 frequencies.

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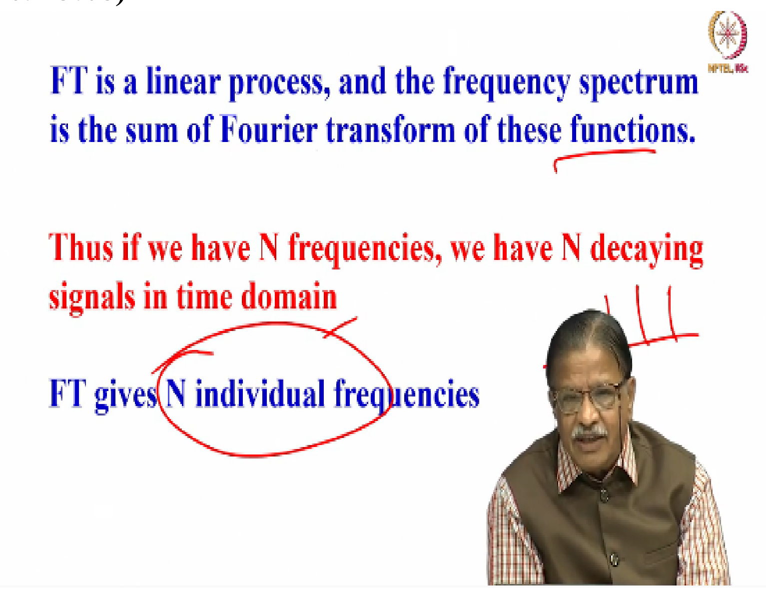

Of course, this is what I said, FT is a linear process and because of this sum of the Fourier transform of this function is sum of the frequencies you see in the frequency domain also. If you have N frequencies, we have N decaying signals in the time domain. Let us say in the NMR spectrum there are 10 peaks. Each peak is different; 10 different frequencies are present, that we see the time domain signal has 10 FIDs; they are overlapped and each frequency correspond to 1 decaying signal and the Fourier transformation gives N individual frequencies.

This is what is the linearity theorem I explained; you to understood the Fourier transformation so many theorems I discussed; all these theorems are used in your routine analysis of the NMR spectrum, or while recording the spectrum; you will come across these things. Only thing you should know what are these things; so that you know how to interpret these things at the right time.

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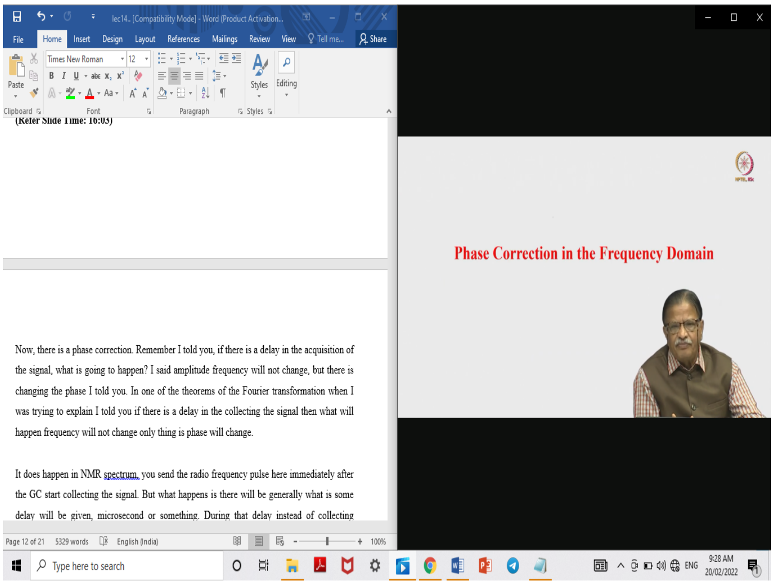

Now, there is a phase correction, remember I told you, if there is a delay in the acquisition of the signal, what is going to happen? I said amplitude and the frequency will not change, but there is change in the phase, I told you. In one of the theorems of the Fourier transformation when I was trying to explain I told you, if there is a delay in the collecting the signal then what will happen? Frequency will not change only thing is phase will change.

It does happen in NMR spectrum, you send the radio frequency pulse here; immediately the receiver start collecting the signal. But what happens is, there will be generally some delay will be given, few microsecond or something. During that delay instead of collecting signals from this point, in principle, you have to start collecting from this point or sometimes from this point; its no problem. But then if there is a delay, you start collecting from this point then what will happen? this is not exactly you are starting at 0, there is a phase error. Phase errors will invariably be present; you need to correct this in the frequency domain.

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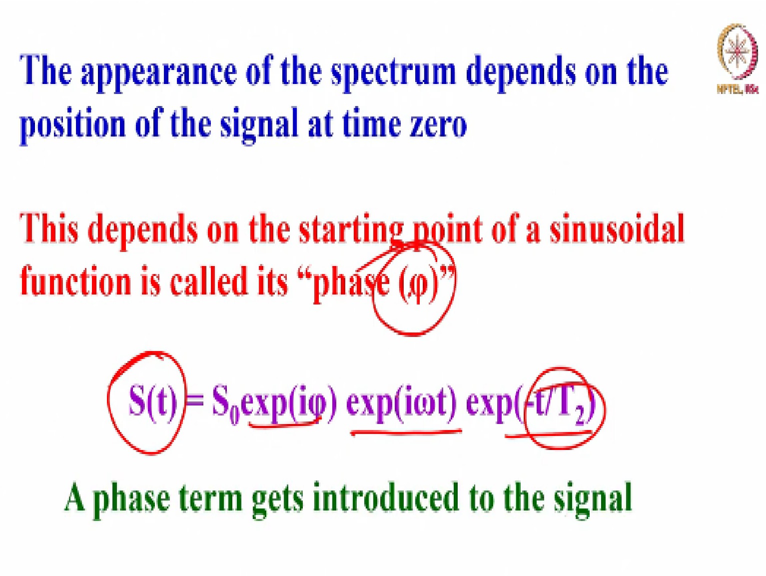

So, how do you correct this, see the appearance of the spectrum depends upon where do you collect the signal; it is at the point of time t = 0 you have to collect; immediately after the pulse. If the starting point is not exactly at t = 0, you have a phase, that is called phi. So, now I can incorporate this phase error like this, this was the exponential i omega t it is for exponential minus t by T2; I wrote this earlier. The time domain signal is decaying because of this. But now, there is a phase error, which also I can incorporate like this; exponential i phi multiply by this function. So, a phase term gets introduced with the signal now, because there is a delay in the acquisition of the signal.

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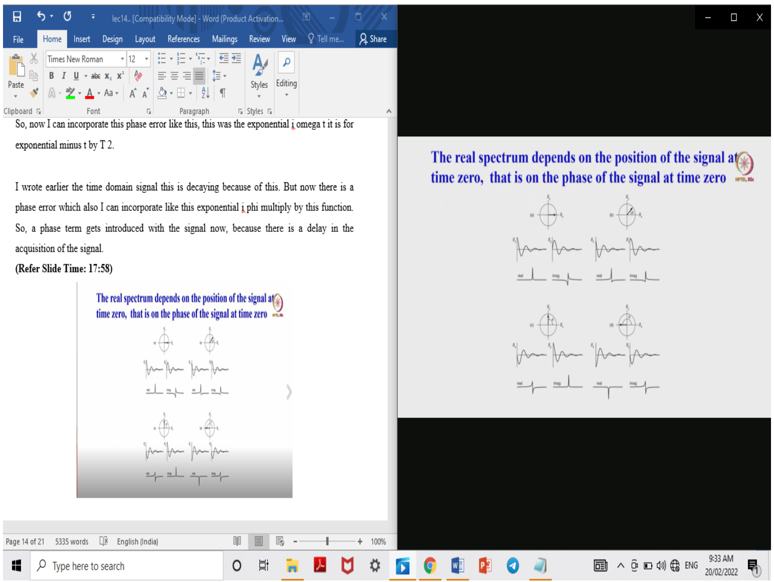

So, what happens if there is more delay? for example, if I have a receiver here, I will discuss about this receiver phase and pulse phase in 1 or 2 classes later; we will come back and discuss. If I have a signal here, receiver is here, you are going to get the real part here like this, but the signal here is out of phase by 90 degrees, it is imaginary part. If on the other hand, my receiver is here and the signal is somewhere here what will happen? It has components of both X and Y, cosine part and sine part present with the mixed phase. The real part is pure absorptive and imaginary part is pure dispersive. Both are mixed up, it can happen; but then it is a clumsy spectrum, you need to do the phase correction. What do you do for that? You have to make sure the phase difference between the real and imaginary part is exactly 90 degrees; that is what is called the phase correction.

If you try to do that, then you can make this, like this, I am sorry other one like this or like this. So, phase corrections if you want to do you have to make the real and imaginary part exactly out of phase by 90 degrees.

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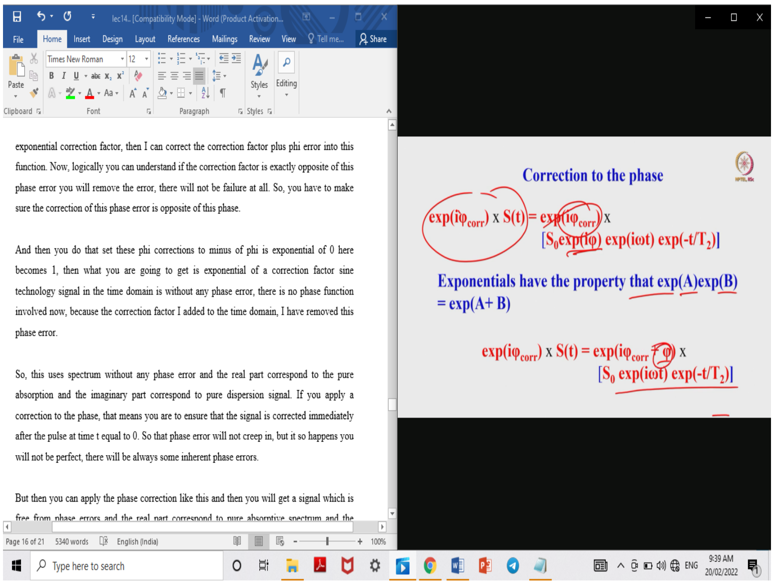

How do you do the correction to the phase? You can do it in the time domain or also in the frequency domain. In the time domain what you will do is take this frequency into the correction factor, exponential, I call it as a correction factor, this is the phase error, a phase error I call it exponential i phi. Correction, I put it like this, and then multiply these two functions, these two functions can be multiplied. Now, exponential have the property that exponential A and exponential B, you could write as exponentially A + B. Now, I am going to do this, if I take this function, multiply by the exponential correction factor, then I can incorporate the correction factor plus phi error into this function. Now, logically you can understand, if the correction factor is exactly opposite of this phase error you will remove the error, there will not be phase error at all. So, you have to make sure the correction of this phase error is opposite of this phase.

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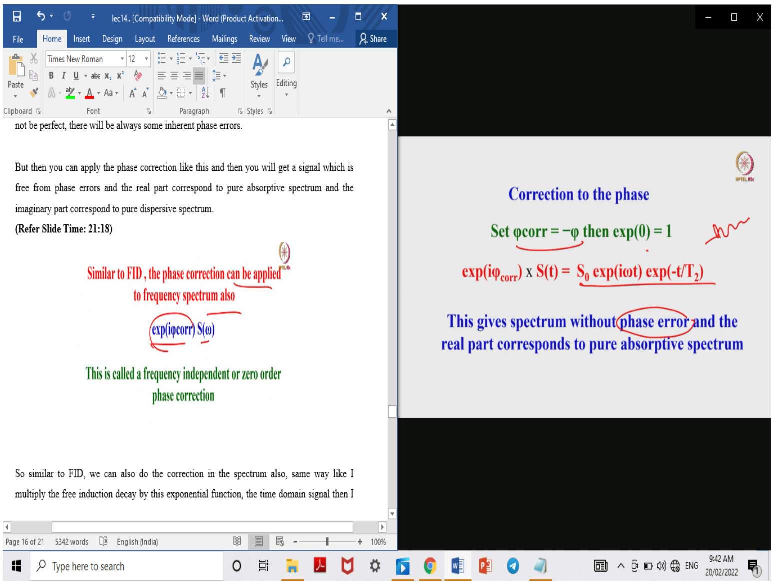

And then you do that, set these phi corrections to minus of phi; the exponential of 0, here becomes 1, then what you are going to get is exponential of a correction factor sine signal in the time domain is without any phase error; there is no phase function involved now, because the correction factor I added to the time domain, I have removed this phase error. So, this gives spectrum without any phase error and the real part corresponds to the pure absorptive and the imaginary part correspond to pure dispersive signal.

If you apply a correction to the phase, that means you have to ensure that the signal is corrected immediately after the pulse at time t = 0. So that phase error will not creep in, but it so happens you will not be perfect, there will be always some inherent phase errors. But then you can apply the phase correction like this, and then you will get a signal which is free from phase errors. And the real part corresponds to pure absorptive spectrum and the imaginary part corresponda to pure dispersive spectrum.

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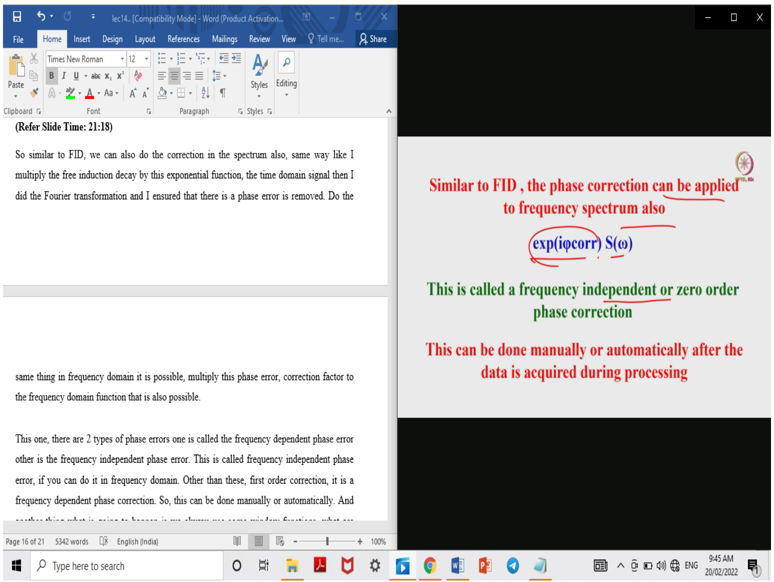

So similar to FID, we can also do the correction in the spectrum also, same way like I multiply the free induction decay by this exponential function, the time domain signal; then I did the Fourier transformation and I ensured that there is a phase error is removed. Do the same thing in frequency domain; it is possible, multiply this phase error, correction factor to the frequency domain function, that is also possible.

This one, there are 2 types of phase errors; one is called the frequency dependent phase error other is the frequency independent phase error. This is called frequency independent phase error. If you can do it in frequency domain. Other than this, first order correction, it is a frequency dependent phase correction, and this can be done manually or automatically.

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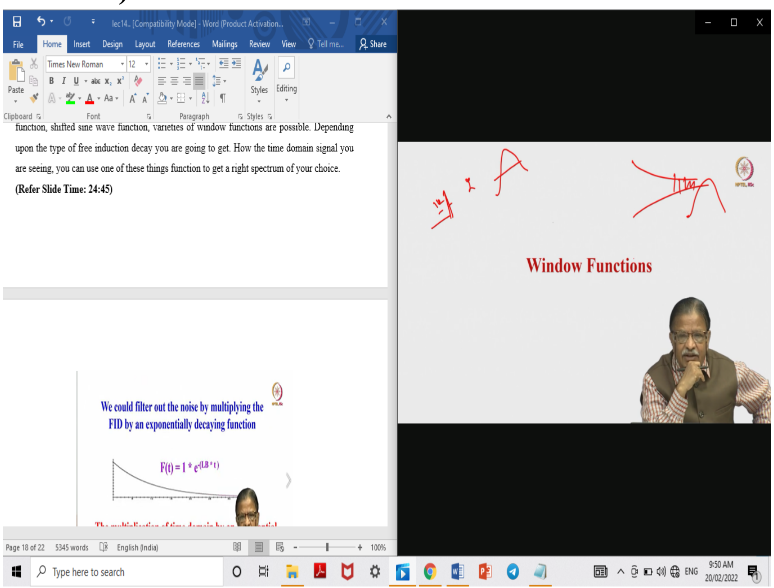

And another thing what is going to happen is we always use some window functions, what are these window functions? Of course, if you have attended my first course, you would know how we manipulate the time domain signal to get this frequency domain spectrum with a larger line width, smaller line width, better resolution, better signal and all those things. For example, I have a time domain signal like this, it is decaying, no problem.

I have the signal, all through. If I have collected the signal for a length of time like this for this much time, and then signal decays like this very fast, rest of the thing is only noise. What is the point in keeping the noise? you will add only noise to the spectrum, what I will do is I will multiply this one by the decaying exponential function like this; and then it will cut off this part of the decaying exponential. So, this portion will become 0; when this portion becomes 0, what you are going to get? you will see when you multiply by that you are going to get less noise, because you are removing the noise by multiplying by an exponentially decaying signal. So, this portion you cut it out. So reduce the noise, but what did you do? You have multiplied by another exponential function which inherently adds up. It is additive theorem I told you know, these two will add up and because of that, the line width becomes larger. For example, the width of the spectrum let us say is 1 Hertz, you multiply this by an exponentially decaying function with 2 Hertz, then what happens? it will add up. The line width will become 1 + 2 hertz. So, you could play with the window functions either to reduce the line width or to increase the line width or to reduce the noise. Like that there are all several window functions which you multiply, which you can do after you acquire the data in the time domain. After acquiring the data and multiply by these window functions and see the type of frequency domain spectrum what you get. It could be highly resolved or less noise and everything and many window functions are available to do that. Some of them are exponential function, Gaussian function, trapezoidal function, sine bell function, shifted sine bell function, varieties of window functions are possible. Depending upon the type of free induction decay you are going to get, how the time domain signal you are seeing, you can use one of these things function to get a right spectrum of your choice.

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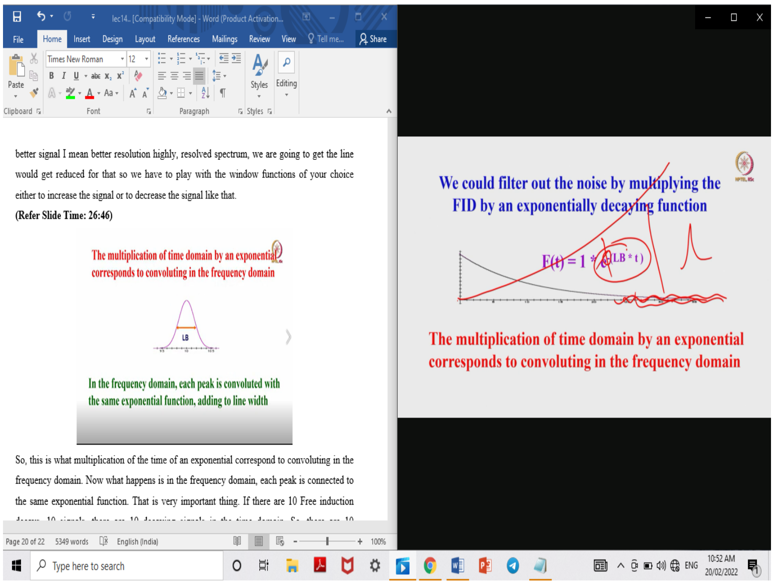

For example, look at this signal, it is a time domain decaying signal; this multiply by an exponential function, LB. We could filter out the noise now; I told you by multiplying by this if there is lot of noise in the later portion of the free induction decay, it gets removed. So multiplication of time domain by an exponential is what? It is nothing but a convolution in the frequency domain, I told you convolution of two functions in 1 domain is the multiplication is other domain.

In the time domain, now I am multiplying two functions, one is an exponentially decaying function for that I am multiplying by another exponentially decaying function, I am multiplying these two functions. That means I am convoluting these two functions in the frequency domain. Now, you found the use of convolution theorem in NMR, which we discussed, this is the convolution theorem.

So, we multiply by this time domain signal and ensure that later part of the free induction decay, noise is cut off and we are going to get the better signal to noise ratio; at the expense of the linewidth that you do not forget. Alternately, you ask me a question instead of exponentially decaying function, what happens if I multiplyby exponentially increasing function; instead of decay like this?

If I multiply like this very interesting thing will happen, then what will happen is, noise you know keeps adding up here, the signal becomes very, very noisy. But there is a price for that.

See, here, you pay the price of linewidth. In this case, there is an advantage; the price you paid was the noise. Lot of noise came but the gain is resolution, you get better signal; I mean better resolution; highly resolved spectrum we are going to get. The line would get reduced for that we have to play with the window functions of your choice either to increase the signal or to decrease the signal like that.

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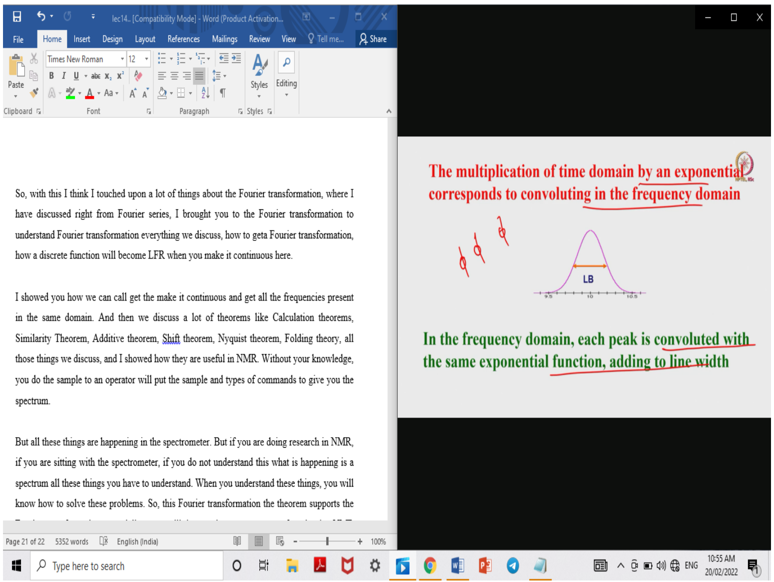

So, this is what is the multiplication of the time domain of an exponential corresponds to convoluting in the frequency domain. Now what happens is in the frequency domain, each peak is convoluted by the same exponential function; that is very important thing. If there are 10 free induction decays, 10 signals, there are 10 decaying signals in the time domain. So, there are 10 frequencies present.

And now when we convolute it in the time domain, we are multiplying by an exponential function in the time domain, then each of these are multiplied by the exponential function; what that means, in the frequency domain, what is happening is each of these peaks is convoluted by the same exponential function, the linewidth will be uniformly added up it is not differential. There are 10 peaks you add up, let us say, I multiply the exponential decay function by 2 Hertz, linewidth will be added by 2 Hertz for this, 2 for this, 2 Hertz for this; each peak in the spectrum will become broader by the same amount. This is what happening when you multiply by the exponentially decaying function, when you do this in time domain, these are called window functions in NMR, which are used very often.

So, with this I think I touched upon a lot of things about the Fourier transformation, where I have discussed right from Fourier series, I brought you to the Fourier transformation to understand Fourier transformation, everything we discussed, how to get the Fourier transformation, how a discrete function will become, when you make it continuous. I showed you how we can make it continuous and get all the frequencies present in the time domain.

And then we discuss a lot of theorems like Convolution theorems, Similarity Theorem, Additive theorem, Shift theorem, Nyquist theorem, Folding theorem, all those things we discussed. And I showed how they are useful in NMR. Without your knowledge, you give the sample to an operator, he will put the sample and type some commands to give you the spectrum. But all these things are happening in the spectrometer.

But if you are doing research in NMR, if you are sitting with the spectrometer, if you want to understand what is happening in a spectrum all these things you have to understand. When you understand these things, you will know how to solve these problems. So, this Fourier transformation theorems you will be coming across very often in the NMR spectrum.

So, with this discussion, I think I have given you a fair amount of information about the Fourier transformation, because this being little like advanced course as compared to the previous course, we discussed that was more elementary and for the beginners. I just wanted to introduce little mathematics, of course without mathematics no NMR; but remember I did not go to many of the steps in detail; because if I had to work out using a chalkboard.

You know, chalk talk I can give; but then it will take ages to work out all these things, using a chalk talk, working out each step would have taken several more hours of my talk. So, many of them I skipped, assuming that because these are basic simple integral functions, simple trignometrical functions, you will use it very often and you will know that. Of course, while working out 1 or 2 if I have made a mistake of sign or something, will find out very easily also, because this is simple integral calculus, which I said you have already studied in high school, PUC like that. So, with this, I am going to stop. Next, I will go to a different topic, and let me see whether I can introduce Quantum Mechanical Analysis, of the NMR spectrum are phase cycling. I will see what are the interesting things, I will discuss that in the next class. Thank you very much.