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

Module-11
Fourier Transformation
Lecture - 11

Welcome all of you for this class. In the last previous classes we discussed at stretch a lot of things, right from fundamentals of NMR, right from internal interaction parameters, we understood what is chemical shift, we understood what is the coupling constant and then using the coupling constant when one spin is coupled to N number of other spins we understood what is the multiplicity pattern. And we understood also the nomenclature of the multiplicity pattern like doublet, triplet, quartet varieties of things we understood. And we understood what happens for different nuclei? how the multiplicity comes taking for examples, the carbon 13 which is 1% abundant how we can get the carbon 13 spectrum for the molecule containing N number of different chemical inequivalent carbons.

And how to interpret the carbon 13 spectrum; how to interpret the spectrum of proton in addition to other hetero nuclei. What happens in the proton spectrum, if protons are coupled to not only proton but also to some of the heteronuclei, how the coupling comes; when there are 2 other heteronuclei coupled to proton, why we do not see the heteronuclei coupling of passive spins; that also we understood; and we analyzed the spectrum of many interesting molecules.

For example we took the spectrum of carbon 13, carbon 13 coupled to fluorine we understood; carbon 13 coupled to proton and fluorine simultaneously also we understood. And in the heteronuclei examples phosphors is coupled to proton; and proton coupled to phosphors and fluorine we observed; we also saw proton coupled to boron, boron 10, boron 11 mercury coupled carbon and proton. And many such examples. I have even discussed about the tetramethylsilane how tetramethylsilane spectrum will come; all those examples we understood. So that was only to train you as to how to analyze the spectrum from fundamentals of NMR which I discussed. Now you have come to the level of analyzing the spectrum of any given nuclei. All you require is the chemical shift information.

All you require is also the coupling information; some information about the molecule of our interest; nuclei which are coupled to that; its abundance, its presence how far they are situated; the couplings strength depending upon 1 bond and 2 bond, etc. All this information if you have in your hand or if you are familiar with that, remember the spectra are very simple. If they are called first order spectrum which I tell you what are the first order spectrum when we go at further, they are very easy to analyze; all you need is little practice.

So that is why I brought you up to the level of making you to analyze the spectrum. Now today what we are going to discuss some mathematical tool. I do not want to scare all of you with mathematics; without mathematics there is no NMR, you require mathematics; for NMR that is necessary. But in all the classes, especially in the previous course, I did not touch up on any mathematics. I avoided everything because it was mentioned that courses only for the chemists, I did not want to frighten them.

So, I used only as much as possible conceptual understanding without going into the deeper mathematics. No quantum mechanics was discussed; No Fourier transmission, No product operators, nothing was discussed. But remember in the very first class I told you, you apply radiofrequency pulse; collect the NMR signal; you are going to collect the signal in time domain, and instantaneously you create a phase coherence.

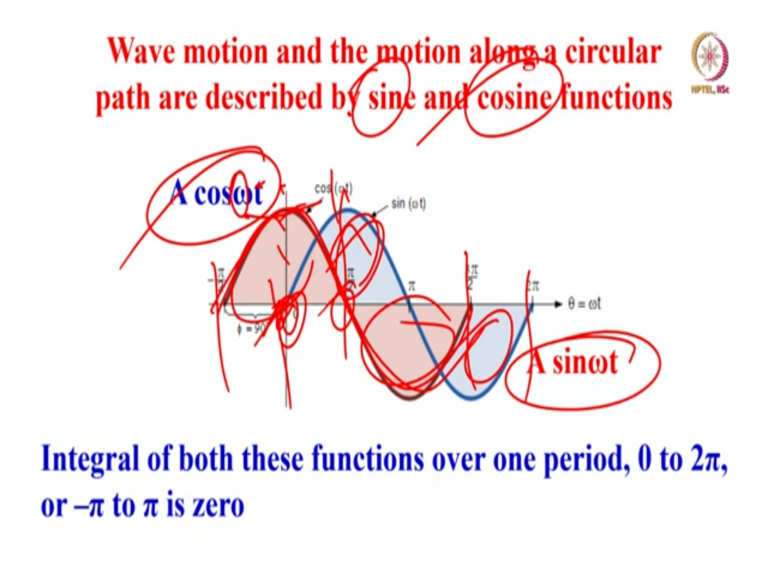
And then there is a decoherence taking place. Simultaneous the spins will go back; while going back it induces the emf in the receiver coil and then emf were going to collect as a function of time; we digitize the data, collect the signal. And then the time domain signal can be converted into frequency domain by a mathematical operation called Fourier transformation. This what I said and I gave an equation; but we did not discuss anything more.

Remember Fourier transformation is one of the important concepts, it is required in NMR. So, we should understand something about Fourier transformation. Many of the concepts of

Fourier transform, many of the laws of Fourier transformation you are using every day. Daily when you are taking NMR spectrum and analyzing without your knowledge you will be using it, and we will try to get the idea, because this being a little advanced course.

I want to give you some brief information about the Fourier transformation, the laws of Fourier transformation, Fourier series etc. But in this case the mathematics is more involved. Remember I could not make the powerpoint of all mathematic equations that involves too much of work. So, I have written the equations by my hand, solved the equations, integrals everything by my hand. So, as a consequence if you have any readability issues, we can discuss nothing to worry. But I hope you bear with my handwriting; we will start with the Fourier transformation right now.

(Refer Slide Time: 05:36)

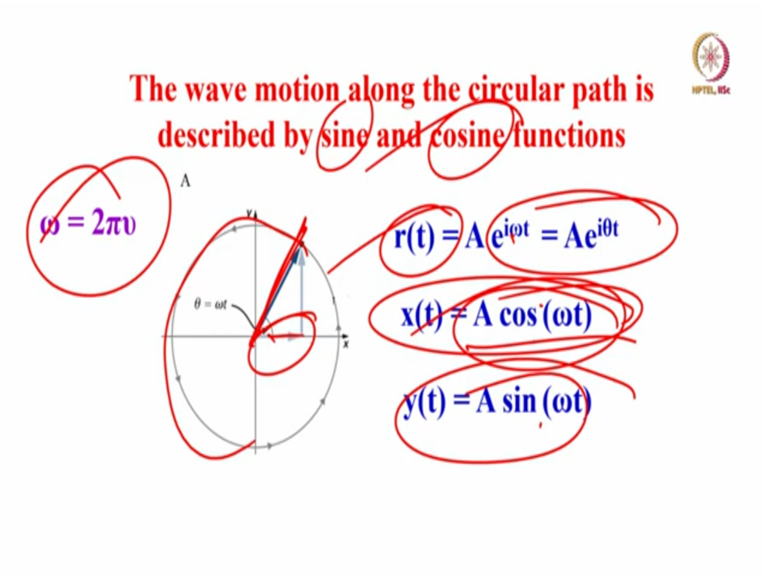


For Fourier transformation we will start first with a wave motion. If you consider any wave motion and a motion along a circular path we can always describe this by 2 functions; it is 2 trigonometrical functions. One is a sine function and the other is the cosine function; these are 2 functions if we have we can define the wave motion; and motion of any particle or anything in a circular path. For example this is a function which is the cosine function, because at zero origins its value is 1; as you know cos 0 is 1. And there is a phase difference of 90 degrees between cosine function and sine function. That is why the sine function starts with an origin, origin it is 0, there is a phase difference of 90 degrees. And this is a function which can be described by an equation A cosine of omega t. A is the amplitude and omega is the frequency as a function of time; this is sine omega t.

That is the way we have to represent a wave motion in cosine and sine; only difference between these 2 is a phase difference of 90 degrees, that is all you remember. And remember at different intervals of pi, pi/2 it is marked at cos 0 is 1; and then at cos pi / 2 it is 0; cos 90 is 0. And then similarly sine 0 is 0; of course sine pi / 2 is 1, like that, it is very easy with a phase shift of 90 degree to plot this graph.

So, what happens if I take 1 full cycle from here to here I consider 1 cycle; from here to here I consider 1 cycle, 1 cycle means 0 to 2pi or minus pi to pi, whatever you want to take. And if I take this function and integrate over the volume entire A; integrate over this entire region 0 to 2 pi, what is going to happen? Remember this if you take this area, this and this, it is nullified; similarly this and this get nullified. So, integral of these 2 functions over 1 period; 0 to 2pi or minus pi to pi is 0 this is a point we should remember.

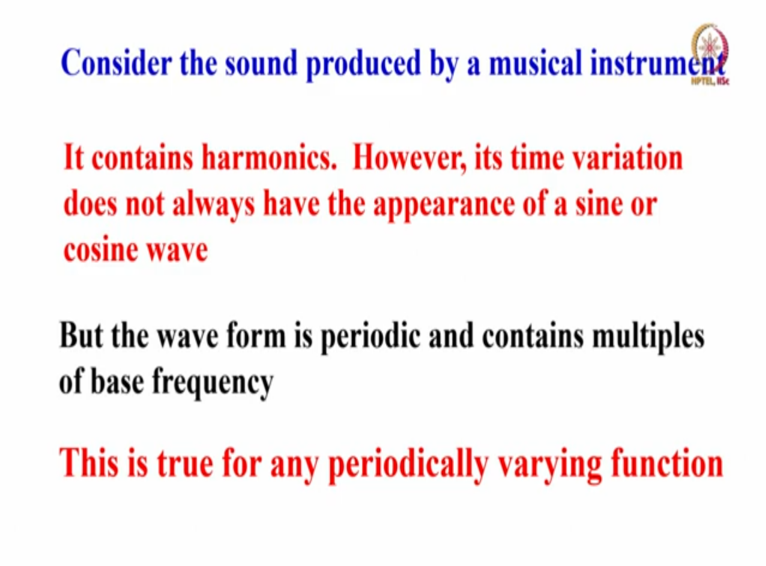
(Refer Slide Time: 07:33)



Now we will go to a circular path; motion in a circular path. It is described by a sine function and cosine function again; of course the x component is again a cosine function, x component of it. This is let us say the object which is undergoing circular motion. And this hypotenuse is called r(t). I am going to call it can be express by an exponential function e i to the power i omega t. This can be resolved into cosine and sine functions.

And the x component of this as cosine omega t and y component is sine omega t. And omega is the frequency; it is given the 2πv, the circular frequency. So, this a wave motion along a circular path. So, what I am trying to say is; in the previous case wave motion and also having the circular path, all these things we can simply represent by trigonometrical functions of sine and cosine. These 2 functions are enough to describe motion of all these things.

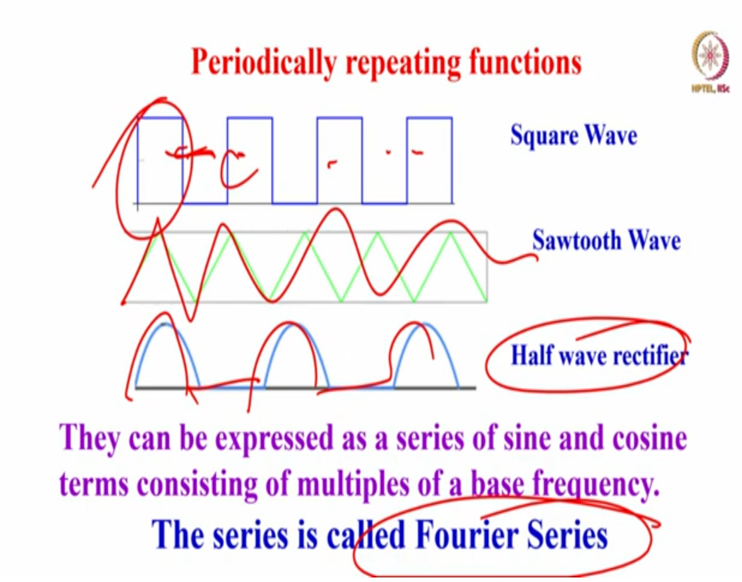
(Refer Slide Time: 08:34)



Now let us consider another example; you would have heard of sounds produced by a musical instrument like tabla, veena, something. It contains harmonics but its time variation always do not appear as a sine or a cosine. It does not have a sine wave pattern the cosine wave pattern, but is harmonics, keeps repeating at different intervals, no problem; but it does not follow a sine wave or a cosine wave.

But the wave form is periodic; as I said it repeats at regular intervals. What is the repetition frequency? There is a base frequency with which it gets repeated. At the multiple intervals of base frequency both these functions, not both, this sound which is produced by any musical instrument gets repeated. That is why it is called periodic; and it can be for any other varying function. It may be true not only for the sound produced by a musical instrument, but also for any other of the functions. Many periodically varying functions need not always you know reproduced by sine and cosine. It is not always possible to represent by sines and cosines, but it may contain harmonics and multiples with the base frequency.

(Refer Slide Time: 09:53)

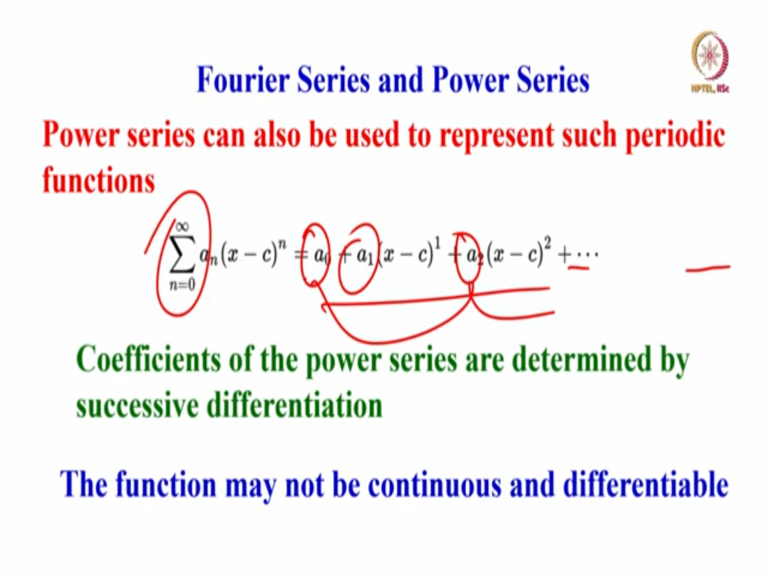


So, let us see what are the periodically repeating functions; can we represent by sine and cosine, we will try to understand. One of the things you can see is a square wave; is it periodic? Of course, yes, this is the base function, you know with some interval it keeps on repeating N number of times. It is a periodically repeating function; it is square wave. Now consider this one, it is a sawtooth wave; again keeps on repeating N number of times, is also a periodic function.

Take this, it is the output of a half wave rectifier; you know that in electronics you would have studied, it is the output of a halfway rectifier, you have a function here ,0 function, 0 function; it repeats. It is again a periodic function; this output of a half wave rectifier; this is also periodic. So, all these can be represented by what is called series of sines and cosines which consists of multiples of a base frequency, that is the point you should remember.

They are periodic functions; but they are represented by the multiples of a base frequency. So, then such type of series which you can represent these periodic functions as sines and cosines with a base frequency is called Fourier series. Remember I am not talking about Fourier transformation, I am introducing only Fourier series. Fourier series are the representation of the periodic functions as sines and cosines with multiples of a base frequency. That is all the definition I am giving you broadly for Fourier series.

(Refer Slide Time: 11:29)

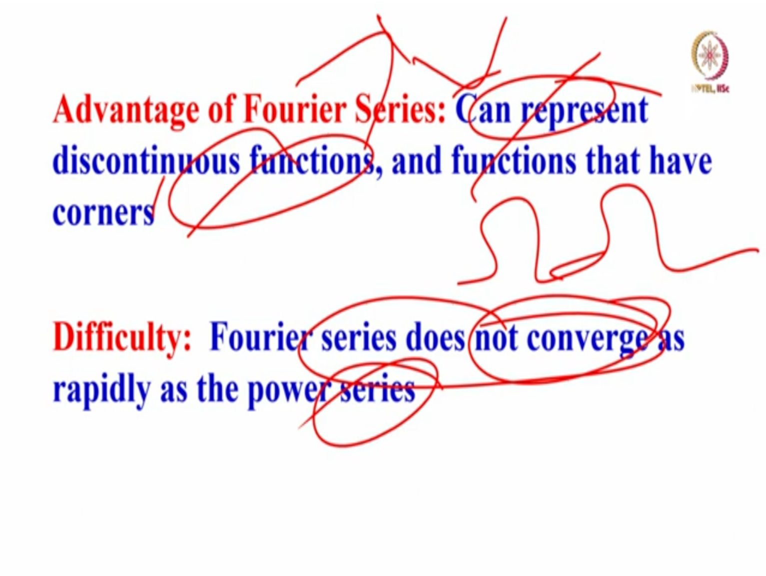


Now I want to give you one distinction between a power series and a Fourier series. Of course, power series are also there, which can also be used to represent periodic functions. It is possible; for example this is a power series. For a given periodic function one can generate the power series to represent that; it need not be sines and cosines. It need not be trigonometric functions; you can have a power series like this.

Now the question is the coefficients of the power series how do you determine? like a0, a1, a2, a3; these are all the coefficients of this power series; it keeps going, the series continues. It is 0 to infinity is there, of course, we have some limiting values of the data; that I am not going into the details of mathematics; but there are coefficients a0, a1, a2, a3, etc. We have to determine the coefficients of this power series. How do you determine that?

Normally it is done by successive differentiation; you have to differentiate once; further differentiation; further differentiate like that; successive differentiation you have to do to get these coefficients. Now the question is what happens if the function is not continuous? If it is not continuous; if there is a break or if there are turns you cannot differentiate. One of the conditions of differentiable function, for for being differentiable, it must be continuous. If it is not continuous, you cannot differentiate, that is the one problem you see in the power series. That is why Fourier series is a very useful thing, which we can always use.

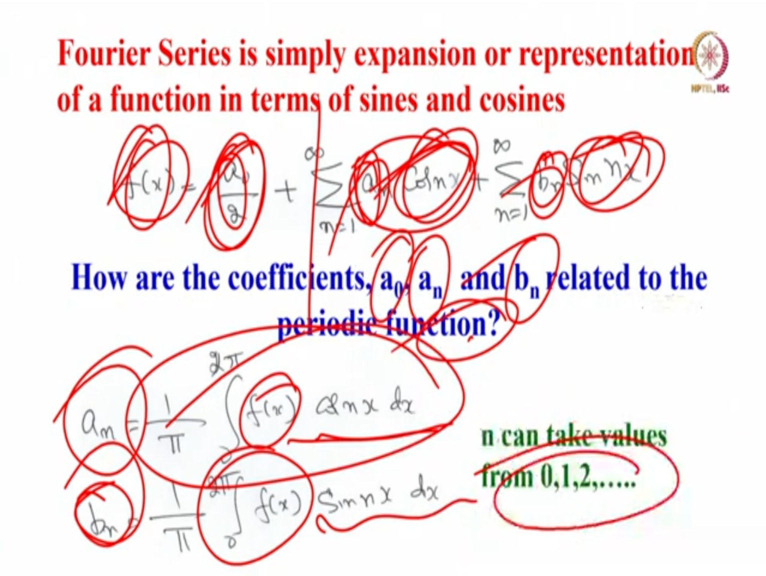
(Refer Slide Time: 13:02)



And there is an advantage for that, it can represent discontinuous functions also. For example we saw with there are several functions which are periodically coming; there could be discontinuous, no problem. And it can represent the function that have corners like this, like this. So, advantage is there for the Fourier series. But there is some difficulty; Fourier series compared to power series, will not converge as rapidly as the power series.

You would have understood you know, I do not want to go to the much basics of mathematics; you can find out whether the series is converging or diverging. If we want to converge this thing; see the Fourier series, if you want to converge it; it does not converge as fast as rapidly as the power series; the Fourier series do not converge rapidly. This is one difficulty, but of course advantages are it can represent discontinuous functions and functions that have corners.

(Refer Slide Time: 14:01)



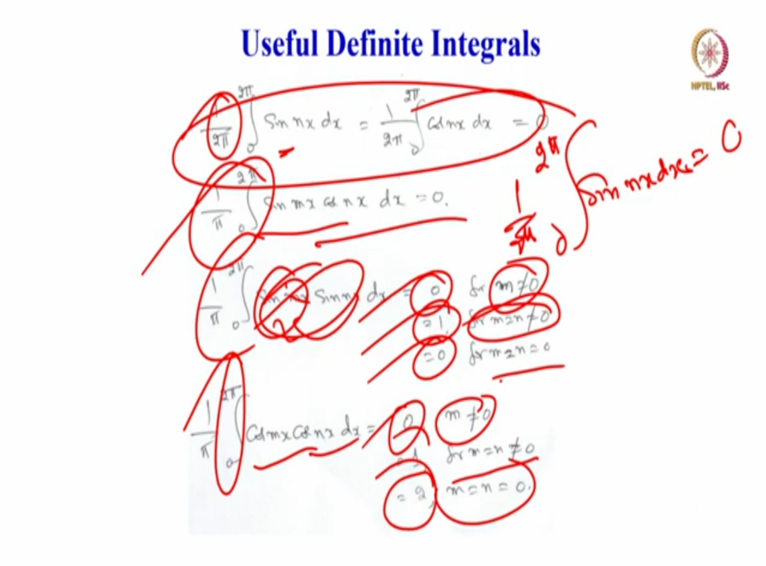
Now this is a simple Fourier series; it is simply an expansion of representation of terms in sines and cosine. I am giving a function f of x, it is given by a series, of course the coefficient is a0/2; some number. And then it can be represented by a series of cosines and sines, and each of them have coefficients an and bn. The coefficients of the cosine functions are an, coefficient of the sines functions are bn. Now, of course, the summation is n = 1 to infinity.

This is general representation of the Fourier series where we are expressing the terms in sines and cosines; with a0/2 as the first term. So, the summation starts from n = 1 to infinity. Now question you may ask me, I can represent by sines and cosines; what are these coefficients? how do we determine that? how these coefficients are related to the periodic function? it depends upon the periodic function.

If I know the function and its periodicity, I can find out a0, an, bn etc. All the 3 series we can find out. So, if I want to find out these coefficients, I should know the periodicity, the period of the function. For example, if I want to find out an, I integrate the function from 0 to 2 pi; or this function f of x into cos of nx into dx. This is the cosine of nx. I will integrate from 0 to 2 pi, the function f multiple cos nx dx; for the coefficients bn I multiply these integrate this function again from 0 to 2 pi; this function fx multiple by sinx dx.

Remember if I multiple cosx and dx this function, and integrate over 0 to 2 pi, I can determine a_n coefficients. If I do the same thing by multiplying sin x dx integrating 0 to 2 pi, I am going to get coefficients b_n. So these are the things which we need to find out; and how do you calculate n, what are the values of n; it can take values 0, 1 to n, any number; n can take values 0, 1, 2, 3 etcetera.

(Refer Slide Time: 16:22)

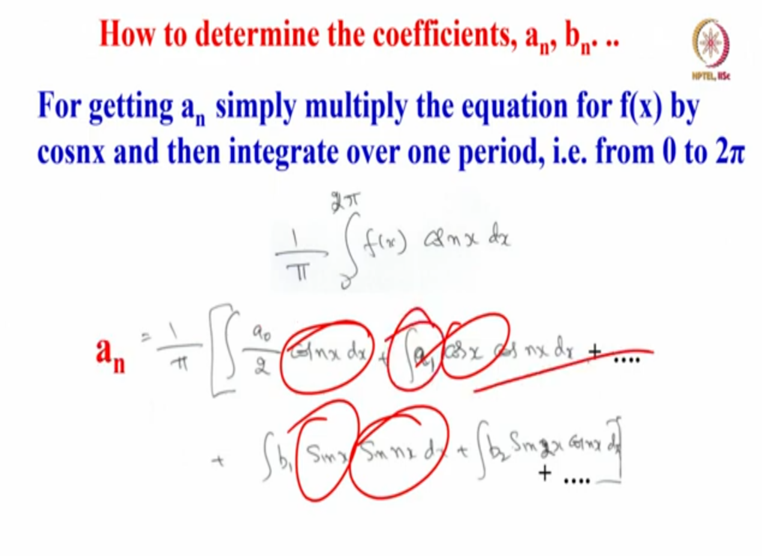


I am sorry about my handwriting since I cannot write equations by powerpoint, it is too time consuming, I have written by my hand. So, very simple; these are definite integrals. Why I am giving this thing is, these are the integrals we do not need to do anything. You do not have to integrate this function; you do not have to go for deeper mathematics. Very easily if I consider the function here; 0 to 2 pi integral sin of nx dx. If I take it, of course 1 over 2pi, if you want you can take it or not; it does not matter and it will be 0. This is a well known definite integral.

So, these are the integrals, for example 1 over pi; 0 to 2pi; integral sin mx into cosnx dx. That is also 0; whereas 0 to 2pi sin mx into sin nx dx if you take; that has different values. For m 0 ≠ 0. If sin mx is present, this function is 0; whereas m = n both are not equal to 0, this is equal to 1; whereas for m = n both equal to 0; this function becomes 0. So, these are some useful definite integrals.

Similarly, this is for sin function; what about for the cosine function? do the same thing; 0 to 2 pi cos nx dx if you take the same way for m not equal to 0 it is 0. For m not equal to 0, it is 1. But the only difference is for m = n = 0, unless for this sin function which is equal to 0 here its value is 2. These are all well known in the book of integration; go to any book on integral calculus, this is very easily available you can see. You would not have to think too much, you do not have to work out, you have to remember this. I am giving this to you because I am going to use this very often in future, in this class.

(Refer Slide Time: 18:22)

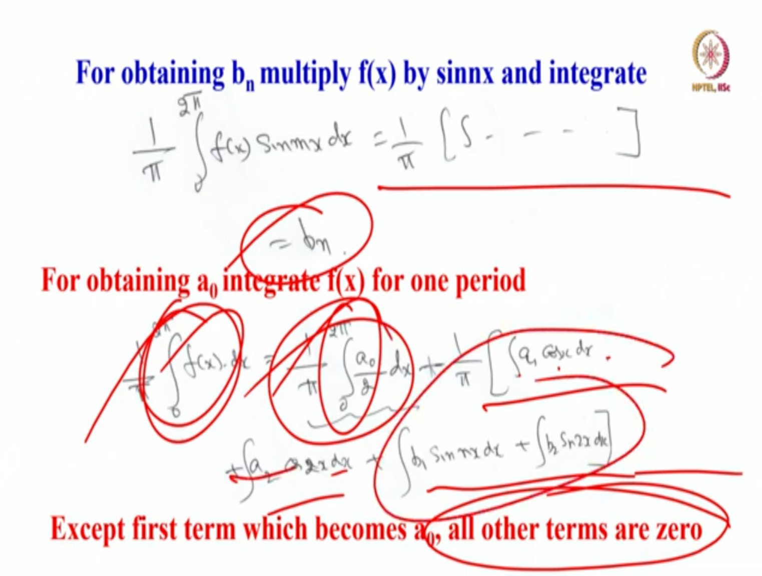


Now the question I ask you is how do you determine an, bn, a0 etcetera? How do we do that? For getting an simply what you have to do with the function, I told you already, multiply by cosine of x and integrate from 0 to 2pi. In the previous 2 slides I showed you that; For getting bn I said multiply by sin nx and integrate from 0 to 2pi, that is what I said. So, now we will do that; 0 to 2pi I will take; this function f(x) multiply by cos nx and dx.

And this I can express as a series; f(x) you know it is a series; which can be written 2 pi a0 /2 of course. Earlier I showed you the sequence, it can be written as sin and cosine. This is a series, Fourier series is a0/2 cos(nx) and integral of a1 cosx. And I multiply by cosnx; remember. If you want I will go back and show you this thing. Here this what I am using, see this is what I am using; see a0/2; this equation I am using and multiplying by this cos of nx and integrate, that is all I am doing here.

So, this what I am now trying to do; here I have take this function, the Fourier series I have put it; multiply by cos of nx each term, both for a1, b1 coefficients are represent. And this is a cosine term; this is a sin term; multiply this and then expand it as a series. That is what I am trying to do. As I said for finding bn we have to multiply by sin nx; for finding an you have to multiply by cos nx; this what the thing which I explained; this is called an.

(Refer Slide Time: 20:30)



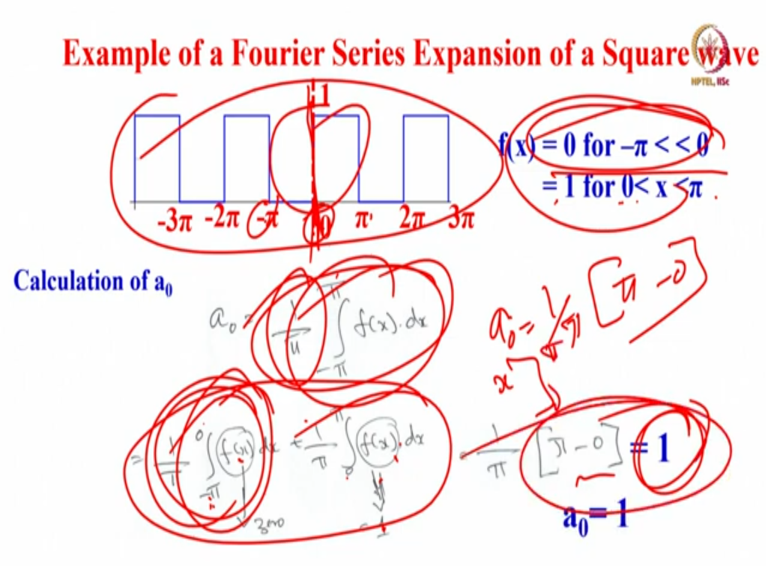
For obtaining bn of course, the same thing you can do; multiply by sin of mx. So, same thing 1 over 2pi integral series you can continue; and then if you solve it you are going to get bn. Now question is you get an, bn fine. Here also you got an by multiplying by cos of nx and integrating, expanding this function integrating over the region. Now the same thing I do for bn; multiply by sin mx fine; I can get bn what about a ? a0 is something different.

There was no cosine or sin function here; if you remember that function a0 if you multiply with a cos of nx and dx to show, but actually it is only a0/2. So, now how do you get a0? For getting a0 you have to integrate the function of f of x for 1 period; what is 1 period? I showed you how, 0 to 2pi, 0 to 2pi of this function f of x if you take I can integrate and then get value of a0; it is very easily done.

F(x) is expanded here; 0 to pi a0/2; again same simple mathematics is done, I have expanded this function f (x) into a1 cosx dx, a2 co2s, b1 sinnx, b2 sin2x; like that keep on writing series. So, a's and b's are present here; I have expanded this integral that f (x) function; only thing is now I am integrating 0 to 2 pi here. This is a0/2, this function is integrated from 0 to 2pi. And then we can expand like this here.

Except for the first term which becomes a0, all the terms are 0; why they are 0? Remember I gave you a few definite integrals, as a sort of a table or a chart for you to use it. I just used those things, that is all. I did not explicitly workout integrals. You can do that it is not difficult at all. Simply I have expanded this, and integrated from 0 to 2pi; but I know after doing this all the steps will go to 0 except a0.

(Refer Slide Time: 22:49)



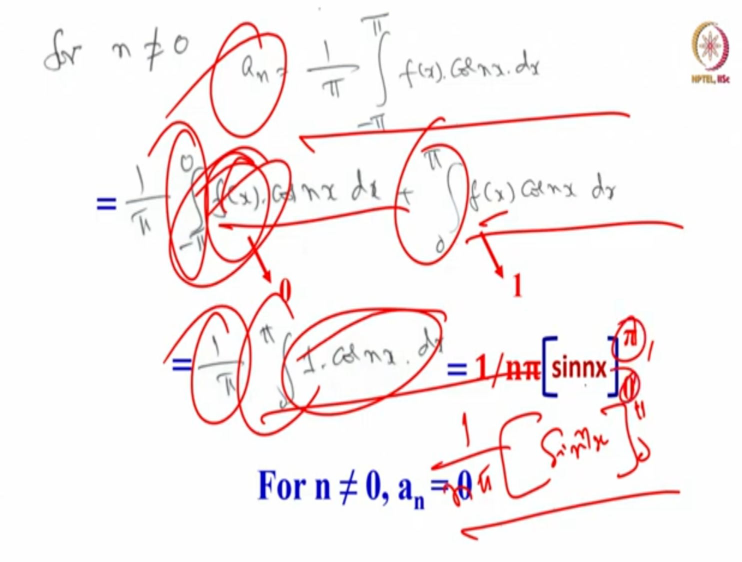
And see for example I will take, how to work it out, how to get a0. It is only theoretically I was explaining to you, can we do it for a real function? Can you work out this Fourier series? Take the example of a square wave, this is a square wave we discussed here. And remember it starts with 0 here, how do you define this function now; it is a function has a value from minus pi to 0, it is 0, and 0 to pi is 1; you can define this function.

Looking at this function you can say that minus pi to 0 this function is 0, because minus pi less than 0 this value is 0; it is 1 for 0 less than x less than pi, so this is 1. So, this is the way we define the function. Now I can calculate a0 how do I do that? As I told you a0 is integral of 1 over pi - pi into pi f (x) dx. Of course minus pi to plus pi or 0 to 2pi, both are same. It is 1 cycle; finally I am trying to tell you have to integrate for one cycle to get this value.

So, this is what; it came earlier itself. so now this is resolved into 2 terms, how? minus pi to plus pi, I wrote from minus pi to 0 f(x) dx and 0 to plus pi f(x) dx. I just resolved into 2 terms. Minus pi to 0 integral of f (x) is what? It is 0; that means this term is 0. 0 to plus pi , what is f(x), it is 1. So, this, integral turns out to be a0 = 1 /r pi into pi - 0. Now I am putting the limit; the limit is 0 to pi.

When you put that, this turns out to be one; for the Fourier series of this square wave a0 is 1. You understood how it worked out? Very simple, all I did is I integrated this function from minus pi to plus pi or 1 cycle; resolved into 2 terms. One term goes from integral of minus pi to 0; and the other integral goes from 0 to pi. And then because the way we have defined the function; from minus pi to 0, this values f(x) is 0 and 0 to pi f (x) = 1 and it is going to be 1/pi f (x) dx is equal to just x. So, it is one. And you are going to substitute from 0 to pi you are going to get 1; this is the value you are going to get. So a0 we worked out to be 1.

(Refer Slide Time: 25:27)

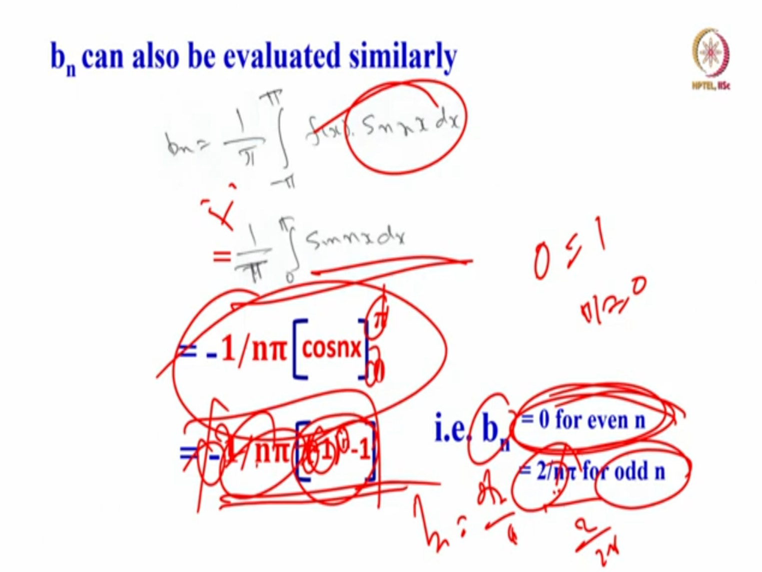


For n not equal to 0 what happens? an I have to calculate; an and bn are other terms; coefficients which we need to work out. For n not equal to 0, I told you we have to multiply by cosine of nx and dx and then integrate over 1 cycle minus pi to plus pi. Now again resolve into 2 terms; minus pi to 0 ,f (x) cos of nx dx; 0 to pi f(x) cos of nx dx. All I did is simply remember, I have multiplied this function by cosine of nx and integrated over 1 cycle.

But again what is this f(x)? minus pi to 0. From from the functions limits which I have shown actually earlier it is 0; f (x) is 0 in the range minus pi to 0, minus pi to 0 in the range f (x) is 0. What is the f(x) in the range 0 to pi; plus 1 this we know. So, now substitute that, then integral is going to become 1 over pi, 0 to pi 1 into cosnx into dx. This simple formula you should know, basic integral I am not going to work out.

Which can be written as 1/ npi into sin of nx; 0 to pi sin nx 0 to pi. This is the formula. So what I did is, I just resolved into 2 terms. This term I know; in the range this term goes to 0 and this term is 1; I substituted the limits and this is what you are going to get. So, for n not equal to 0, an = 0. So, n if not equal to 0 what we will have happen? i sin 1 x; you see you have to put the values of the limit for pi. You know that then what happens for a not equal to 0, an = 0.

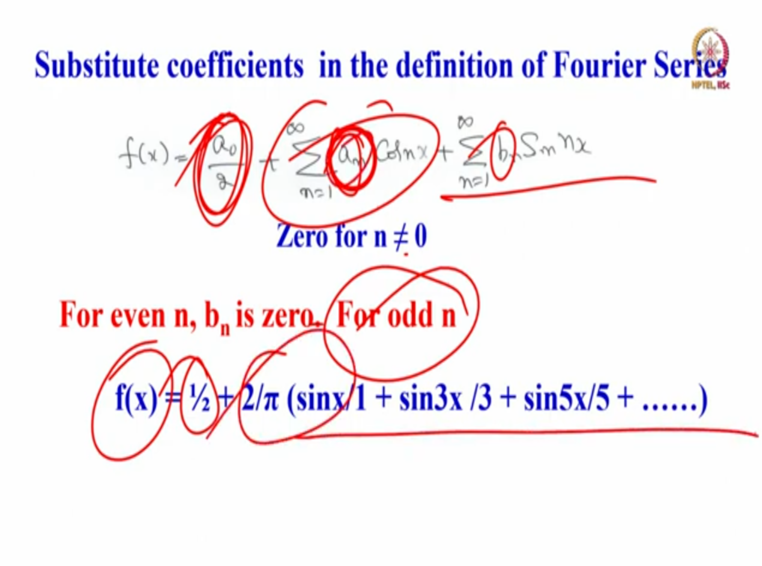
(Refer Slide Time: 27:20)



So, similarly now we can work out bn also; how do you work out bn? Same, bn you have to multiply sin of nx; I told you and again integrate over one cycle now. What you are going to do? resolve into 2 terms; 1 term of course I did not write the other one, minus pi to 0, fx is 0. So, I removed that, directly I removed that term. So, I am concentrating only at this term; so this again turns out to be minus 1/ n pi cos of nx; 0 to pi this is also well known integral, that is why the definite integrals I give you. Now substitute this; when you substitute this limit, 0 to pi; this is the formula you work out. This is minus 1 to the power of n) - 1 because cosine of n; and cos an even function, cos 0 = 1 cos pi / 2 = 0; and then you know the trigonometrical values, you can find out this. When you put this limit, this turns out to be 1/n pi into minus 1 to the power of n) - 1.

So, now what will happen? For even n; when n is equal to even, this will become positive. So, 1 – 1= 0, very simple. So, for n is equal to even bn is 0. For n other than this thing, for 2/npi. for all odd values of n, can we take it as ,let us say n = 1 then what is going to happen? if n = -1 you find out it turns out to be 2 over n pi. So that means for bn there are 2 conditions you can think of, for your even bn is 0 ; for n odd which is equal to 2 over n pi, because this minus and this minus get cancelled out; and you are going to get 2 over n pi. So, the series all bn and now you can keep on varying; for what different values of n 1, 2, 3, 4, 5. If it is b1 you will know 2 over pi; if it is b2, 2 over 2pi; like that you can keep working out all the coefficients. Similarly for an also you can work out; a1, a2, a3 for all values of n. But only thing is for 2, for even number here bn is 0. You can take for n = 1, 3 etcetera. For 2,4, 6 it is 0; so that odd terms will be present and even terms will be absent.

(Refer Slide Time: 29:59)



So, now substitute all these coefficients in the definition of the Fourier series; what is the definition of the Fourier series? This is what I said a0/ 2; an into cos of nx; bn into sin of nx. Now we know what we have worked out an and worked out bn he also worked out a0/2 by integrating over 0 to pi in 1 cycle we integrated; and this one we know for n not equal to 0 we have calculated an = 0.

So, n not equal to 0 means for example any value we take 1, 2, 3 this term is 0. Now for even n what will happen? bn is 0. And for odd n it is equal to, you worked out n over the previous one you remember do not forget that, you got it 2 over n pi. So, we can work it out now for bn is 0 for even n and for odd n it is equal 2 over npi. Now using these, substitute this function f of x is a 0 we worked out to be 1 remember a 0 we should showed it as 1. Now a 0 / 2 this value is half; the coefficient an we worked out. And this we are going to get a series function like the sin function.

(Refer Slide Time: 31:21)

Example 2: What happens if the x is shifted by $\pi/2$ in the above equation?

And cosine function of course you know already, what is the cosine function, what is going to happen for even and odd. Now of course we can go to the second example to work out. Before that I will I think now the time is up, I will take the second example later; but just I wanted to tell you how we got the bn; how we got an and we substituted with this function and it is a series.

So, for n not equal to 0 what happens? For n = 0 what happens? Simply substitute in this basic equation, base equation and you are going to get this series. This is a Fourier series for a square function which is different like this, at this place whose value is 0 from 0 to minus pi; its value is 1 from 0 to pi. This is a function we defined; as a periodic function for a periodic square function which is defined like this, with chose the limits and this is the Fourier series, that is how we work out.

You can take a few more examples later. Another example of Fourier series and what happens if there is an exponential functions; Fourier series can be expressed as exponential also. All those things we discuss in the next class; and then I will introduce Fourier transformation and some theorems of Fourier transformation also we discuss. So, today I want to do tell you is, I wanted to introduce the Fourier transformation is one of the important mathematical tool you need this for NMR, because you use invariably to covert the time domain signal into frequency domain to get the frequency positions in the spectrum, and analyze the frequencies. And then before introducing the Fourier transformation, I explained to you what is the Fourier series by taking a periodic function, and I showed you and sometimes the function may be periodic, but it may not be possible to represent by sines and cosines; it is also possible; so we finally introduced what is the Fourier series which is nothing but function f of x = a0 / 2. The summation n = 1 to infinity, an into cos of mx, + summation of n = 1 to infinity bn in to sin of nx. This is a general form of a Fourier series we worked out. What is coefficient a0? we showed for a square function a0 = 1 and an and bn also we worked out. It is a simple integral, you have to multiply by cosx for an; you have to multiply sinx for bn.

And then integrate over 1 cycle for sin of nx and the integrate for one cycle and then by doing a simple integral calculus, for which integrals are always available in the book, which I did not work out in detail, we could get what have an' s and bn's and finally substitute all this; a0, an and then bn, in this equation for the Fourier series f (x). Then this is what we are going to get. So, with this I am going to stop today we continue with other examples and then Fourier transformation later. Thank you very much.