Mathematics for Chemistry
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Lecture - 21

So, we have studied the power series method of solving differential equations. We noticed that in the power series method of solving differential equations, we often got solutions that had certain properties. This property that will focus on the next in this lecture and lecture section is the orthogonality property.

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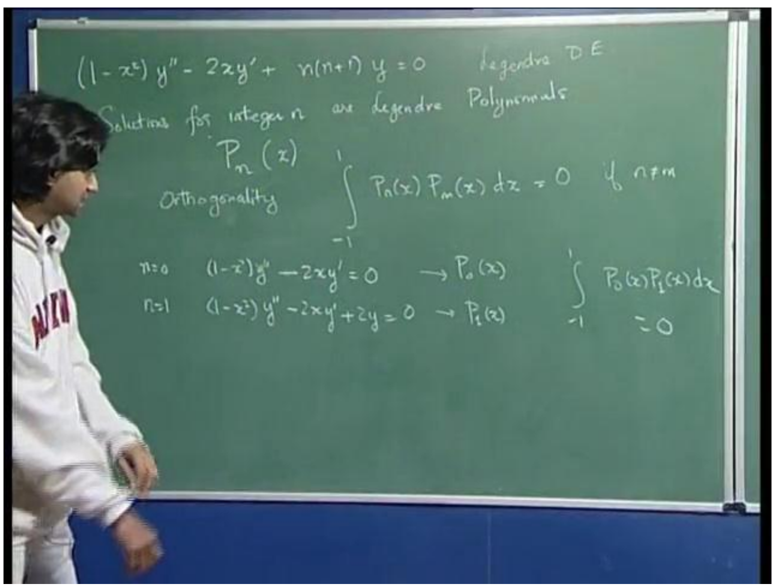

So, suppose we start with Legendre differential equation. This 1 minus x square y double prime minus 2 x y prime plus n, n plus 1 y equal to 0. Now, when n is an integer, the solutions are what are called as Legendre polynomials. So, they go from infinite series to polynomial. They are denoted by P n of x. These are so P n of x is a polynomial of degree n. Now, it turns out that these Legendre polynomials are orthogonal. In the following sense, they are orthogonal.

Orthogonal in this sense at minus 1 integral from minus 1 to 1 P n of x P n of x d x equal to 0, if n is not equal to m. Now, notice that when n and m is for n, you have one differential equation for m. You have another differential equation. Notice that the form of the differential equation changes. Assume change the value of n n or m, whether you say n or is say m. You will get the completely different differential equation, but the solutions are still denoted by this Legendre polynomial.

For example, if n equal to 0, then the differential equation becomes y double prime plus minus 2 x y prime equal to 0 n equal to 1. It becomes prime plus 2 y equal to 0. So, we not is there are 2 different differential equations. They are both homogeneous equations. The nature of the solutions in both cases is different. This is a polynomial. This solution of this P 0 of x, the solution of this is P 1 of x. This is a solution that is obtained.

So, this is one of the series which converges easier than P 1 of x. So, according to this rule, we have that integral P 0 of x P 1 of x d x from minus 1 to 1 equal 0. So, the question they are asking is the following. Is there some way to understand when the solutions of differential equations will give you orthogonal functions? So, is there something varied in the differential equation that tells you when the solution will be orthogonal? Also, mention this that the Bessel functions are also orthogonal in a slightly different sense.

Similarly, the Harney polynomial is obtained when you solve. The Harney differential equation which is the solution of the harmony castigated problem in quantum mechanics. There are also orthogonal. They are orthogonal in the slightly difference sense. We will see that when we come to that. So, this theory of differential equations and orthogonal functions was given by two people called Sturm and Liouville.

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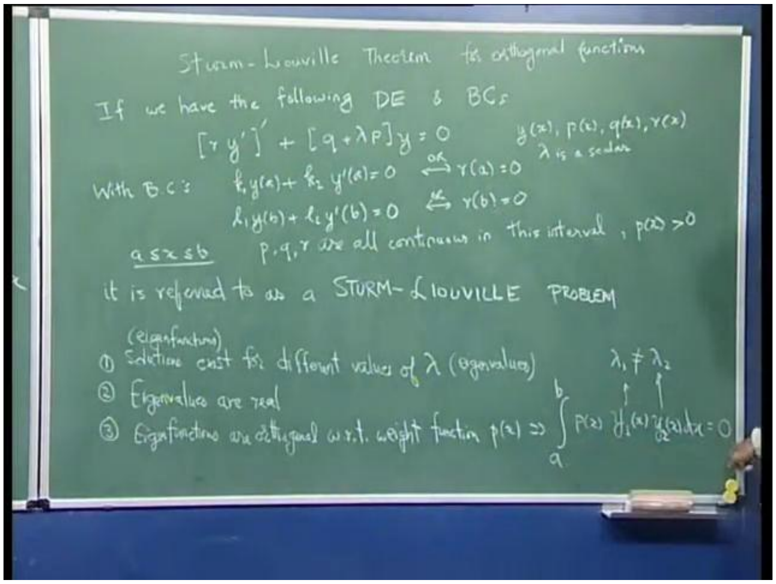

They come up by the theorem called as Sturm and Liouville theorem. This is a theorem for orthogonal functions now. According to Sturm and Liouville theorem, we have the following differential equation and boundary conditions. The differential equation and boundary conditions are given by it is r y whole prime plus q plus lambda p y is equal to 0. Now, here y is a function of x. p is function of x. q is function x. r is a function of x. lambda is a constant.

So, y prime reflected to the derivative of y with respect to x. This is so. r into y prime the whole prime. So, if have differential equation this form with boundary conditions and the boundary conditions for the following form; this plus k 2 plus prime of k equal to 0, 1 equal to 0. This differential equation is valid for a less than equal to x less than equal to b. That is the domain of x. These are the boundary conditions. So, these are differential equations with these boundary conditions and a less than x less than b. So, b, q, r are all continuous in this interval. So, if we have such a problem, then it is referred to as Sturm and Liouville problem.

It is called a Sturm and Liouville problem. p of x is greater than 0. p of x as to strictly greater than 0. Now, let us look what this is trying to say. This is saying that this is basically second order differential equation. So, I can write this as sum of two terms r prime y prime. The second term is r y double prime. So, the point is the co-efficient of y double prime is r co-efficient of y prime is r prime.

So, that is the first thing. You have some scalar. Multiply some positive number plus some other function. The whole thing multiplies by y. So, if you can write differential equation in this form with this kind of boundary condition, then it is satisfied for this problem. So, this Sturm and Liouville problem, if you have Sturm and Liouville problem, then the Sturm and Liouville theorem tells you certain properties of this of solutions. It says that solutions exists or and different values of lambda. So, the solution exists for different values of lambda. Different values of lambda are called Eigen value. The solutions are called Eigen functions.

So, the solutions which are called the Eigen functions, they exist for different values of lambda, which are called the Eigen values. Second point is that Eigen values are all real. So, the values of lambda that are allowed are all real numbers. So, third property is Eigen functions of orthogonal with respect to weight function p of x. So, what this means is that integral from a to b p of x. Now, if the Eigen functions of y 1 of x and y 2 of x, the x, so that you can write it in this form. This quantity y 1 and y 2 equal to 0.

So, if 1 and 2 different Eigen values, these are Eigen functions corresponding to different Eigen values. So, this correspondence to lambda 1 and this correspondence to lambda 2 and lambda 1 and lambda 2 are not equal to each other. Now, notice the orthogonality relation. It states with respect to this weight function p of x that then, we have to have p of x greater than 0. Secondly, it specifies the elements a to b. So, these are the points to note. So, this is the basic of the Sturm and Liouville problem.

Now, there are some more very interesting theorems. This theorem itself is quite powerful. But, this theorem is made even more powerful because of some interesting cases. So, I write them. Suppose, we have r of a equal to 0. Suppose, we have r of a equal to 0. So, this r is function of x value of this function at x is a goes to 0. Then, you do not need these boundary conditions. You either need this or you need that condition. Similarly, if you have r of b equal to 0, then you do not need these boundary conditions. So, these are both r statements.

Either you can have such a boundary condition where the value and slope are linearly related or you can have this of boundary condition. So, the point is that you should have one of this boundary condition and of these bounds. In order to satisfy your Sturm and Liouville problem, you have both r of a and r of b is equal to 0. Then, you do not need any these boundary conditions.

So, with these conditions, we can show that means that if you take a differential equation and r of a equal to r of b equal to 0. Then, automatically this orthogonality condition is satisfied. So now, let us look at this. Let us compare with the Legendre differential equation. So, the Legendre differential equation is in that form. So, if you just look at this Legendre differential equation, we conclude what is so p q and r differential equation. So now, notice that is nothing but the 1 minus x square.

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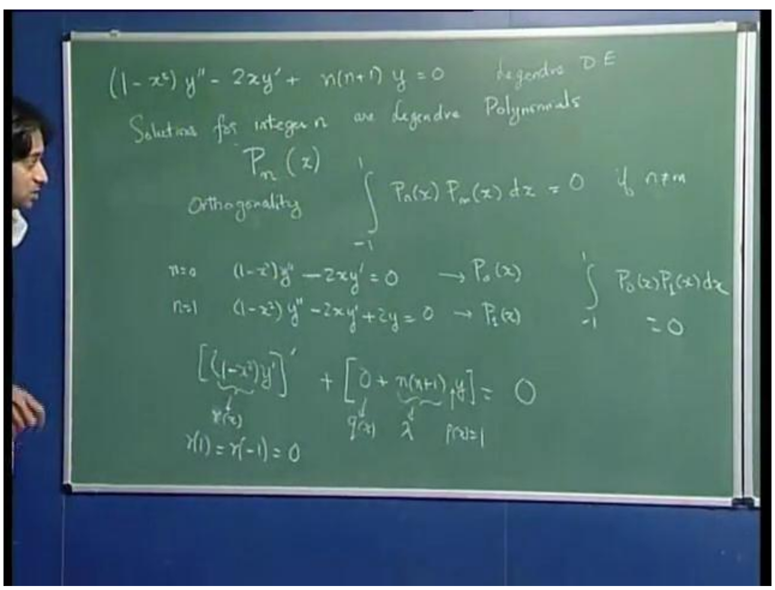

So, I can write this as 1 minus x square the whole prime. So, if take the derivate of this thing, first term will give you x square y double prime. Second term will be minus 2 x into y prime. So, these two can be combined in this from. The next term I can write it as s a 0 plus n n plus 1 y equal to 0. So, immediately say that p of x this 1 minus x square q of x is 0. r of x sorry, of x, sorry, this is r of x; r of x is this p of x is 0 t of x is 1 and lambda equal to n n plus 1. So, now I take different values of lambda corresponding to take different values. If I take different values of n, I get the different polynomials. So, p will correspond to value of n. m will correspond to n equal n.

Notice that r of x has this, so, r of x is 1 equal to r of minus 1, 0. So, what you do is equal to 0 x is equal to plus or minus 1 minus 1 equal to 0 equal to minus 1, 0. So, r of 1 is equal to this 1 equal to 0. Therefore, you can write this Sturm and Liouville problem in this value. So, you can immediately by just looking in the equation, you can write this orthogonality condition. So, P n of x, P n of x from minus 1 to 1 should be a 0. So, this theorem, Sturm and Liouville theorem for orthogonal functions is very powerful theorem. It immediately just by inspecting of differential equation, we can identify such orthogonality relations.

It is actually at the very heart of the entire quantum mechanics. So, quantum mechanics, in quantum mechanics are postulate is that theorem observably corresponds to operators. The observed values correspond to an Eigen values. Now, you can easily see that if I take this lambda P y to the right that looks like an Eigen value equation. So, it looks like some operator time operating on y lambda P times y. So, the whole terms out that the entire quantum mechanics. The existence of real Eigen functions is the consequence of more general version of Sturm and Liouville theorem. These can be complex functions. So, this Sturm and Liouville problem is really at the core of all of quantum mechanics. There is one more situation. So, we saw that when r of b equal to r of a, we need the boundary condition.

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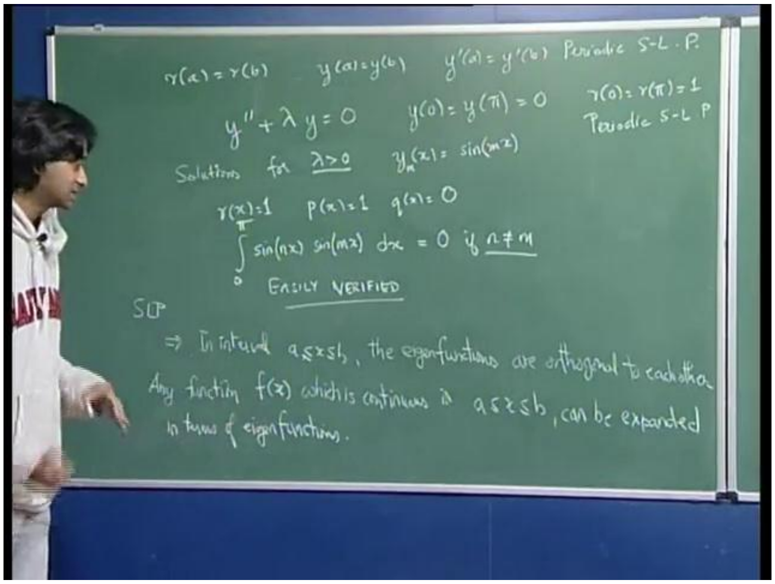

There is another condition. When r of a equal to r of b and y of a equal to y of b, y prime of equal to y prime of b, this is called periodic Sturm and Liouville problem. So, it is a periodic Sturm and Liouville problem. In this case also, we can use the Sturm and Liouville theorem. So, the Sturm and Liouville theorem needs either or r b equal to 0 or r a equal to 0 r b equal to y a y b equal to y prime equal to y prime b. So, there you do not need those boundary condition concern the form that we are mention. So, let us look at some example now. We look at simple differential equation whose solution now so suppose, I have y double prime plus lambda y is equal to 0. So, this is a simple Sturm and Liouville form.

Now, with the condition that y of 0 equal to y of pi equal to 0, 0. So, if you have that boundary condition so in this case, we can immediately say that the solutions for lambda greater than 0. So, let us take lambda greater than 0. So, if you take lambda greater than 0, then the solutions are sin m x. So, y m of x sin of m x. You can put some constants if you want. But, I will just look at this. So, sin m x will ensure that it satisfies both these boundary conditions. Now, if you take this, according to the Sturm and Liouville problem, what this says is that r of x equal to 1.

So, 1 times y prime whole prime is just y double prime P of x equal to 1 q of x equal to 0. So, this you can verify with the Sturm and Liouville problem that this is the case. So, according to

Sturm and Liouville problem, you will say that 0 to pi. So, 0 equal to y of pi equal to 0. So, this can be that of either of periodic or will you are given the boundary condition at any case. Notice that, r of r of 0 equal to r of pi equal to 1.

So, this can be thought of as periodic Sturm and Liouville problem. So, you can also think of this as this is actually periodically Sturm and Liouville problem. So we take integral 0 to pi d x. So, the solutions sine n x sine m x p of x is 1. So, this should be equal to 0 if n not equal to m. This is obviously true because you take sine of n x sine m of x sine of m x. This if you integrate, then from 0 to pi if n not equal to m, you can show that this should sine n plus m x sine n minus m x and those two terms will each of them will be 0. This is easily verified, so easily verified.

So, what we saw is that coming, I mean you can think of this in terms of Sturm and Liouville problem. The orthogonality relation in this case is easily verified. In more complicated case, it is not that easy to verify this. But so, having theorem actually helps. So, furthermore, we saw that what this implies is that Sturm and Liouville problem implies that in integral a to b, the Eigen functions are orthogonal. So, in this interval a less than equal b less than equal b, the Eigen functions are orthogonal to each other. Now, we can say that any function f of x which is continuous in a less than equal to x less than equal to b, can be expanded in terms of Eigen functions.

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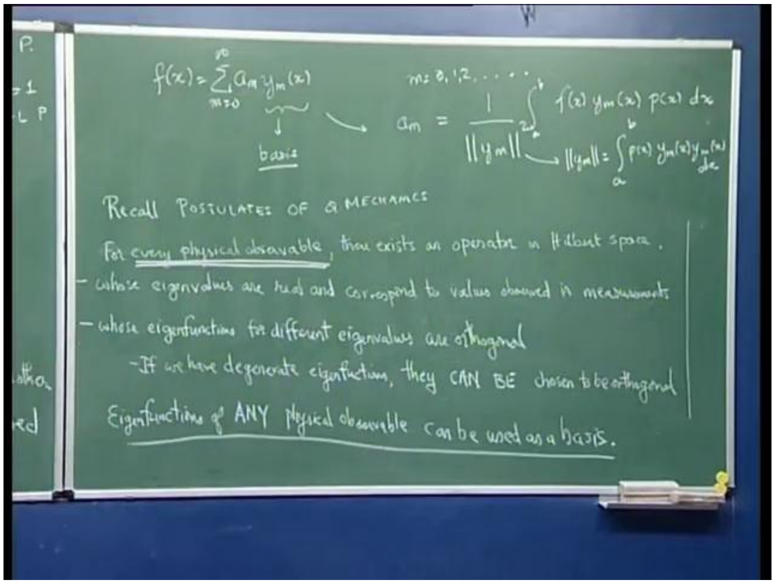

So, if the Eigen functions are denoted by y m of x for different values of m. So, m equal, we just denote this varies Eigen function in this way. Then, you can write any function f of x 0 to infinity, some constants time y m of x. So, what it says that any continuous function can be expanded in terms of these orthogonal Eigen functions. In other words, these orthogonal functions are also form of basis. So, we can go back to the language of vector. We can say that these are linearly independent in the form of basis. Any function that is continuous in this range can be expressed as a linear combination of these Eigen functions. So, what we done is we have gone from language of differential equation to language of vectors and basis.

We could do this because of this Sturm and Liouville theorem for existence of orthogonal Eigen functions. Now, if you recall the postulates of quantum mechanics, one of the postulates of quantum mechanics states that; so, just we recall postulates of quantum mechanics. One of the postulate states that for every physical observable, there exists an operator better in Hilbert space. So, for every physical, there is operator in Hilbert space whose Eigen functions, Eigen values are real and correspond to values observed in measurements. So, they exist in operator in Hilbert space whose Eigen values are real and correspond to values observed in measurements.

Eigen vectors for different Eigen values are orthogonal. So, if you take two different Eigen values, the corresponding Eigen vectors or Eigen functions are orthogonal. I show, I should say

Eigen functions; so, whose Eigen functions for different Eigen values are orthogonal to each other. There is another statement. There is another part of this if we have degenerate Eigen functions. So, if you have one Eigen value, we have multiple Eigen functions. They can be chosen to be orthogonal. Then, this is very powerful statement. It says that if I take any physical observable; I see that it has degenerate Eigen values. Then, I can choose these degenerate Eigen functions. I can choose the Eigen functions to be orthogonal.

So, this is very powerful statement. This fact is true for every physical observable. So, for each and every physical observable, you can do this. This postulate of quantum mechanics was finally arrived at by Derek, but he used some of the properties of this Sturm and Liouville problem in order to arrive to these postulate. What I want to appreciate is that the idea of orthogonal Eigen functions. Some this that is very central trues all of quantum mechanics. So, this is one of the most fundamental postulates of quantum mechanics. It tells you what the measure in quantum mechanics are and what does it correspond to.

So, when we do such a basis functions expansion, then what is the value of a m of x? What is the value of a m? You show this that a m equal to integral f of x y m of x, p of x d x divided by 1 over y m whole square. This is from a to b. It would be where y m is equal to integral p of x y m of x y m of x d x from a to b. So, this completes the basis function expansion. What we have seen is that if you have orthogonal Eigen function, they can be chosen as a basis. So, you can expand any function that is continuous in this limit from a to b in terms of this basis.

This is connected to one of the fundamental postulates of quantum mechanics. It is that for every physical observable, there exists an operator in Hilbert space whose Eigen values is real and corresponds to values observed in measurement. The Eigen functions for different Eigen values are orthogonal. If we have degenerate Eigen functions, that means many Eigen functions corresponding to the same Eigen values. Then, you can choose them to be orthogonal to each other.

That means in other words, you can say that Eigen function of any physical observable. When I say any physical observable, I mean Eigen function of operator corresponding to any physical observable can be used as a basis. This is one of most important theorems in quantum mechanics where it is actually postulate of quantum mechanics that you can any physical observable as basis. So, you can write here general function of as linear combination of Eigen functions of Hamilton operator or the momentum operator or the positions operator; whichever operator you want.

This is generally true. So, we have seen Sturm and Liouville problem. We have seen how the nature of differential equation can tell you whether you can have orthogonal Eigen functions solutions. Now, very important and now, very widely used example of this. This is Fourier series, the function and that will be two topics of this lecture and the next lectures.

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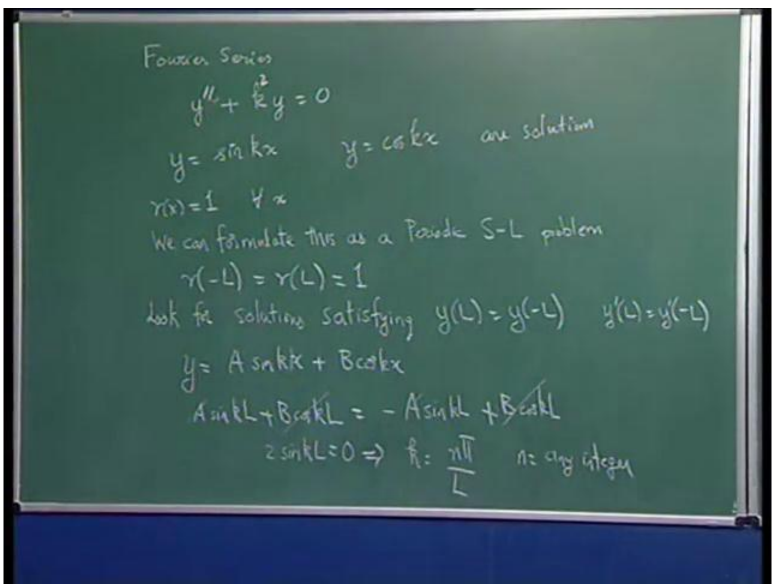

So, first we start with the Fourier series. In this, I will try to motivate from the postulate of Sturm and Liouville problem of differential equation. So, suppose you have differential equation y square y y double prime plus k y equal to 0. If you want, which is as k square so, k square, ensure that the coefficient of that can of y is positive. So, suppose you had such a differential equation then, you can easily show that y equal to sine k x.

These are example of solutions. So, these are example of solutions of this differential equation. Now, if you think the Sturm and Liouville problem then, what you will say? That f x is equal to 1 because when r of x equal to 1 for all x. So, r of x is 1, for all x. So, we can formulate this as a periodic Sturm and Liouville problem. We can take any periodic and we can found terminated as an appropriate Sturm and Liouville problem. But, we will do is we will take is formulated as a periodic Sturm and Liouville problem r of minus L equal to r of L equal to 1.

So, what we will do? We formulated as the periodic Sturm and Liouville problem between minus L and 1. So, we look for solutions satisfying y of L equal to y of minus L. Same with that derivates since, r of minus L equal to r of L. We can choose solutions that can satisfy. Now, if you choose solutions then, you can easily show that if you want to satisfy these boundary conditions, the general solution as a sin k x plus B cos k x.

If we want to y of L equal to y of minus L, when you will get that, you will get A sine k L plus B cos k L equal to minus A sine k L plus B cos k l. So, sine of minus L sine of minus k L is minus sine k L cos of minus k L is cos of k L. So, you get this and immediately see is that 2 sine k L equal to 0. This implies k equal to n pi by L; where n equal to n is any integer. So, mathematically this is satisfied Sturm and Liouville problem. So, that satisfies the Sturm and Liouville equation. So then, you can say that you can write the general solution.

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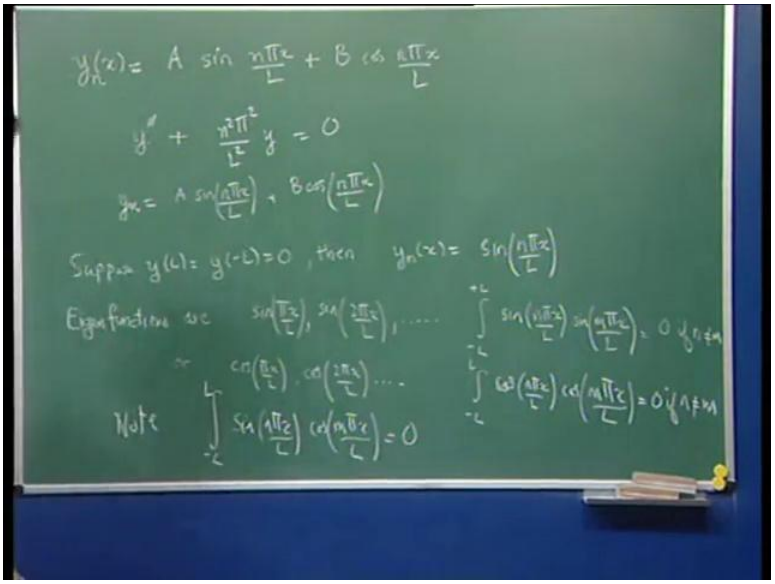

The general equation is equal to some constant plus another constant term. So, what we did was we wrote in this. So, that it becomes very clear what the conditions are. Now, k equal to n pi by L. so, if k is n pi by L, we can think of this as y of n. So, I can write my differential equation as y double square plus n square pi square by L square y equal to 0. This is a differential equation. Lambda here is your Eigen value and y n equal to A. So, corresponding to any n, you have either solutions of sine or you can have solution of cos, of course, sine Eigen function.

This is because sine or cos related by the simple shifting. So, we can choose either one of sine Eigen function. So, depending on your choice of condition, you can choose either of these as the boundary conditions. Suppose, want that your wave function is 0. So, your y suppose, y of L is equal to y of minus L equal to 0. Then, y of x so, when you put x equal to L, this term will give 0. This term will not give me 0. In general, will not give me 0. So then, it is a best choose y n of x is sine n pi x by r.

So, if you have this y of x goes to 0 at these boundaries then, you choose sine n pi by x. This is exactly what is done in the particle in one dimension Sturm and Liouville problem in quantum mechanics. On the other hand, if you had some conditions on that derivative of y at the boundaries but then, we choose cosine functions. So, now either of these can used as infinite series. You can use is combination of this as n as this general solution.

Now, so then, the Eigen functions are sine pi x by L sine 2 pi x by L and so on or cosine pi x by L and so on. So, either of these cases works equally well; we can choose this Eigen functions. Then, the Sturm and Liouville problem theorem says that integral from minus L to f plus L sine n pi x by L sine n pi x by L equal to 0 m and not equal to m. Similarly, for the cosine; similarly, one can write for cosine.

Now, interestingly, you notice that we take mix interestingly. Note that integral minus L to L sine n pi x by L cosine of n pi x by L equal to 0; equal to 0 irrespective of whether you take n and m or same or different. Whether it takes them as same or it takes them as different, this integral will go to 0. So, in a sense, we can take this entire set as a set of orthogonal functions. So, sines and cosines are orthogonal to each other. We do not need to choose. Only orthogonal functions are cosines. They can choose combinations and this is what is done. In the typical Fourier, represent Fourier series.

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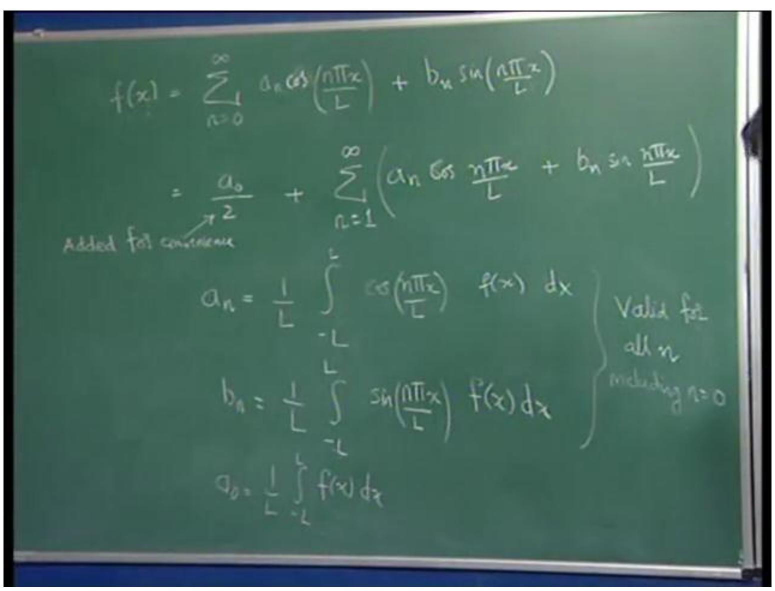

Any function as f of x linear combination of sines and cosines, n equal to plus or a n cosine a n. The typical notation is a n is used for the cosine series. b n is used for the sine series. So, n goes from 0 to infinity. We deliberately, in negative values of n because it turns out at those when you take negative is just a simple multiple of this. So, cos of minus n pi of x is same as cos of n pi of x by L sine of n pi of x by L minus sin, linearly depended function. So, we do not need to take in this basis expansion.

Now, what is done typically is that take the n equal to 0. You have a 0 cos of 0 is 1 and b 0 that term will be 0. So, this term is taken out a 0. For convenience, you put a factor of 2. So, this is added for convenience. So, define a 0, this 2 factor. Then, you write plus. So, write your series in this form. So, it becomes. Why we choose to do this? If you write it this way then, the question is what are a n and b n? Given by, you can show that a n equal to; a n is given by 1 by L integral minus L to L. So, this L by L and what you had is cos n pi x by L terms f of x d x and b n d x.

Now, notice that if you put n equal to 0 then, a 0 is just integral minus L to L f of x d x divided by L. If just integral for minus L to L of f of x; that will just be this right hand side from minus L to L. You can show that you need a 0 times L because all other terms will vanish. So, what will be left? It is a 0 by 2 times L. So, that is the reason why we put this 2 factor here. So, if you put the 2 factor here then, a n definition, you have unit definition of a n in plain way.

So, this definition valid is for all n. In this case, you can check. b 0 will be 0. So, this is valid for a n, a equal to 0 also. All these are valid for n then, including n equal to 0. So, another words a equal to 0, a 0 equal to 1 integral minus L to L f of x d x. So, a 0 is area under the function f of x divided by f of x. Now, this is a general basis function in expansion. What we did is you can expand any function that satisfies the boundary condition in terms of this basis and the boundary condition f of L equal to f of minus L.

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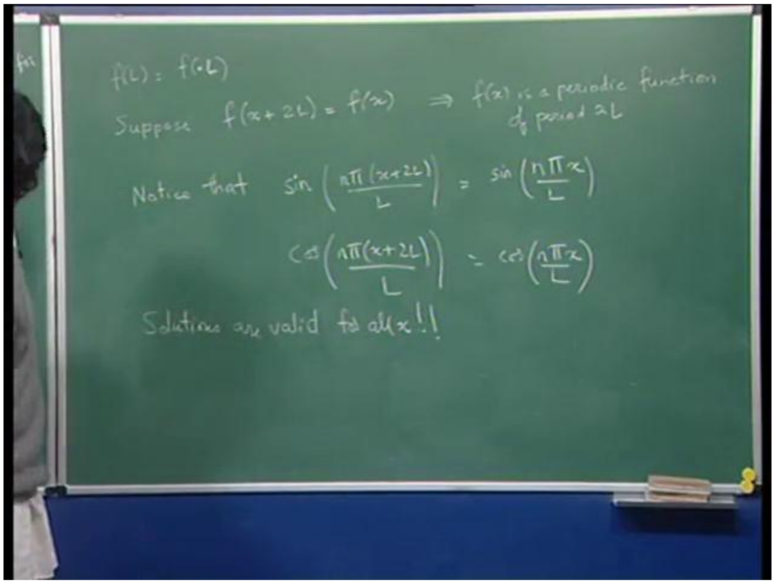

So, f of L should be equal to f of minus L. Any function that satisfies the boundary condition can be written in this basis form. Now, suppose f of x plus 2 L equal to f of x. In other words, f x is the periodic function of period 2 pi. So, if f of x is periodic function with period, sorry, 2 L then, we notice that sine of n pi x plus 2 L divided by L equal to m sine n pi x by L and cos equal to cos of n pi x by L.

So, in other words, this sine n pi by L and cos n pi x by L are also periodic functions. So, that means each of this terms is periodic with period 2 L. Therefore, this function that you are expanding automatically is periodic. So, to come back, what you did that when we wrote this expansion, this was only valid for this. It was only valid for minus L less than equal to x less than equal to L.

So, it is going to be valid in this range because our solutions thoroughly valid in this way. But, if your function is periodic function, if what you are doing is the periodic function then, solution is valid. The solutions are valid for all x. So, the point is we started with this expansion, which is valid for minus L less than equal to L. Then, we said that if our function is periodic, then the solutions are valid for all n if the function is not periodic for this range. But, if your function is periodic function, this valid for all x. This is what to use to motivate the Fourier series. So, this is called Fourier series, the periodic function. You can write if f is a periodic function of period 2 L, write it in the form of this Fourier series.