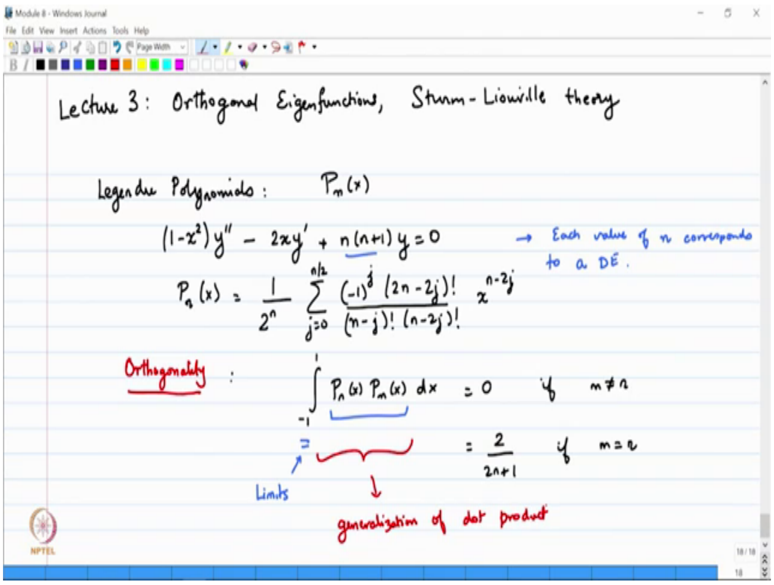
Advanced Mathematical Methods for Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Module - 08
Lecture - 03
Orthogonal Eigenfunctions, Sturm-Liouville Theory

So, now this will be the third lecture of this module, and because the last lecture was a little long. So, this will be; we will have only 4 lectures in this module. So, the third lecture we will have the third lecture now and then the fourth lecture will be some practice problems.

So, in this lecture I want to generalize the idea of the Fourier series and talk about orthogonal Eigen functions. So, in the Fourier series we used sins and cosines and we expanded functions in terms of sins and cosines, but it turns out that you can expand in terms of any orthogonal Eigen function. The Fourier series is a very useful series, but there are also other series that are useful in some cases. So, I want to talk about orthogonal Eigen functions and then I want to talk about the general theory of orthogonal Eigen functions, which is referred to as a Sturm Liouville theory.

(Refer Slide Time: 01:17)



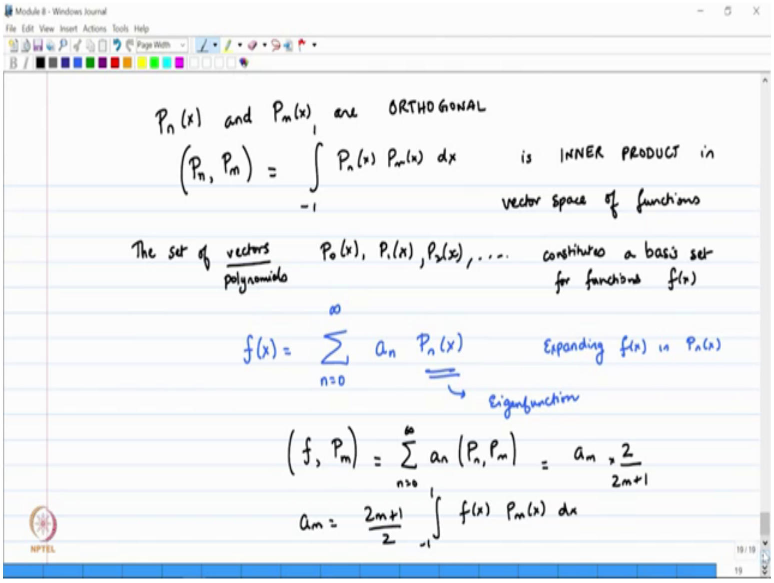
So, to motivate this lets first talk about Legendre polynomials and these are we denoted them as P n of x and these are polynomials and these satisfy the Legendre differential equation which we wrote as. So, this is the Legendre differential equation whose solutions are these polynomials. So, for different value of n you get you get these solutions. Importantly see each value of n of an corresponds to a differential equation and basically when you change your n you get a new differential equation. But the nice thing is that the solutions of all these differential equations they look very similar and they can be express in terms of these Legendre polynomials, and we will just I will just write the expression. So, I mean this is derived in books we are not going to bother with this too much, but I will just say that the Legendre polynomials they have this form by 2 and you have some big expression.

I do not expressed x expect you to remember this expression, but you should know that it is actually possible to write such expressions. So, there are a bunch of factorial this 2 n. So, j goes from 0 to n by 2. So, n minus 2 j will always be greater than or equal to 0 similarly n minus j and 2 n minus 2 j will also be greater than or equal to 0 and then you have x raise to n minus 2 j. So, in this term there are n by 2 terms. So, if n is odd then you will have x raise to all the odd powers if you if n is even you will have only even powers.

So, you will have a polynomial that contains either odd terms or even terms. Now what is interesting about this Legendre polynomials is a very very interesting fact about these Legendre polynomials is they orthogonality, and what this orthogonality says is that integral P n of x P m of x dx from minus 1 to 1 equal to 0, if m is not equal to n very very interesting relation. So, if I take 2 polynomials and I take the product and I integrated from minus 1 to 1 then you get 0. And if n is equal to m this is just 2 over 2 n plus one equal to n. Now there are a few things to note first is this limits. So, limits are from minus 1 to 1, second thing is that you just took a product of the polynomials and you did this and you and you said it is equal to 0. Now what is interesting is that we just took the product we did not multiply by any factor. Now we go back to our ideas of vector space and what we say is that this looks like a dot product, it is the generalization of a dot product.

So, what we are seeing here this whole thing is like a generalization of a dot product.

(Refer Slide Time: 05:45)



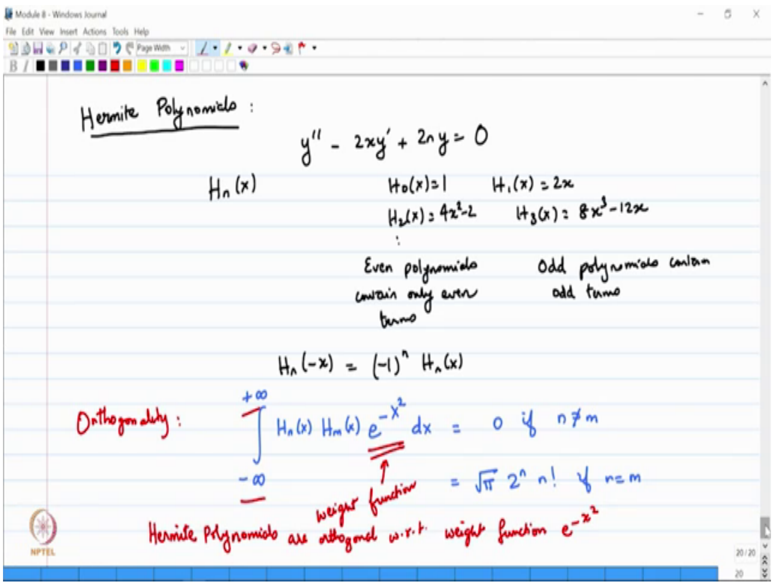
So, we use a terminology that P n of x and P n of x are orthogonal in other words the inner product if you if I imagine these as vectors then this if I imagine them as vectors this inner product is defined as minus 1 to 1 P n of x P m of x dx. So, this is inner product. So, basically you can think that in this space of functions in vector space of functions. So, in this space of functions these are vectors these are like vectors that are orthogonal. So, this is like a dot product. Now what you can do is you can write any. So, since these are orthogonal vectors the set of vectors or in you can use polynomials P 0 of x P 1 of x P 2 of x constitutes a basis set for functions of x. So, for all functions f of x you can use this as a basis and you can write you can do a basis function expansion.

So, you can write f of x is equal to sum over n equal to 0 to infinity, an P n of x this is expanding f of x in P n of x. This is you can call this an orthogonal Eigen function expansion. So, this is like an Eigen function again, this idea we already saw this when we were doing the Fourier series in the Fourier series we took a very particular form of this P n means would a we took sins and cosines, but this is sort of a generalization of that now what is an given by. So, I can use the orthogonality relation to say that if I take f as a vector and or let me write an, then I take the inner product with P m. So, if I just take this inner product, now this will be equal to. Now what will happen is that I will have I will have some over n equal to 0 to infinity, an and I have P n P m.

But using the orthogonality I will see that this term is equal to 0 if n is not equal to m. So, all the terms in the sum where n is not equal to 0 will be 0. So, the only term that will be non-zero is when n equal to m and when n equal to m, P m P m will be 2 over 2 m plus 1. So, what we will get is am that will be the term where n equal to m times 2 over 2 m plus 1. So, therefore, I can write am as 2 m plus 1 over 2 and I can write I will just write out this f of x P m of x dx from minus 1 to 1. So, this is what these are this is how you calculate the coefficients of this expansion. So, now, this is very powerful method and we showed this for the Legendre polynomials, now there are now the Legendre polynomials are solutions of the Legendre differential equation there are solutions of this differential equation.

Now, you could have other polynomials that satisfy other differential equations, and they could also be orthogonal. For example, you could have let us say the Hermite polynomials.

(Refer Slide Time: 10:18)

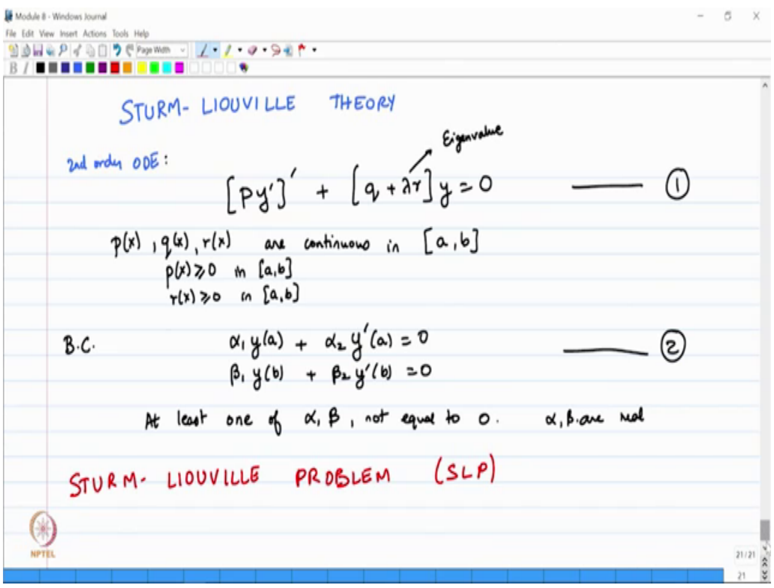


So, incidentally the Legendre polynomials appear in the rotational states rotational degrees of freedom of a particle, the Hermite polynomial appear of a molecule Hermite polynomial is used to describe the vibrational degrees of freedom of a molecule. So, that is a harmonic oscillator. So, they appear in the solutions of the quantum harmonic oscillator, where as Legendre polynomials appear in the solution of the quantum rigid rotor. So, the Hermite polynomials now these satisfy the differential equation y double prime minus 2 xy prime plus 2 ny equal to 0. So, they satisfy this differential equation and these are written as Hn of x is a solution of this differential equation. You have a H 0 of x equal to 1, H1 of x equal to 2 x, H 2 of x equal to 4 x square minus 2, H 3 of x equal to 8 x cube minus 12 x and so on.

So, what is important is that the even terms even polynomials they contain even terms and odd polynomials contain odd terms, that are odd powers of x. So, therefore, therefore, you can say that Hn of minus x is equal to minus 1 raise to n Hn of x. So, these Hermite polynomials are odd if n is odd, then you then Hn of minus x is minus Hn of x. So, they are odd functions if they are even they if n is even then it is an even function. So, now, these Hermite polynomials they satisfy an orthogonality. So, their orthogonality is slightly different, this is slightly different this satisfies this is written as integral minus infinity to plus infinity, Hn of x of x, e to the minus x square dx equal to 0 if n is not equal to m, and equal to root pi into 2 raised to n n factorial if n equal to n.

So, now in this case you notice that the limits go from minus infinity to infinity, and there is this function here this is referred to as a weight function. So, we say that Hermite polynomials are orthogonal with respect to this weight function. So, Hermite polynomials are orthogonal with respect to weight function e to the minus x square. So, these are the 2 these are this is another kind of orthogonality that takes that is there now the; we can generalize this.

(Refer Slide Time: 14:11)



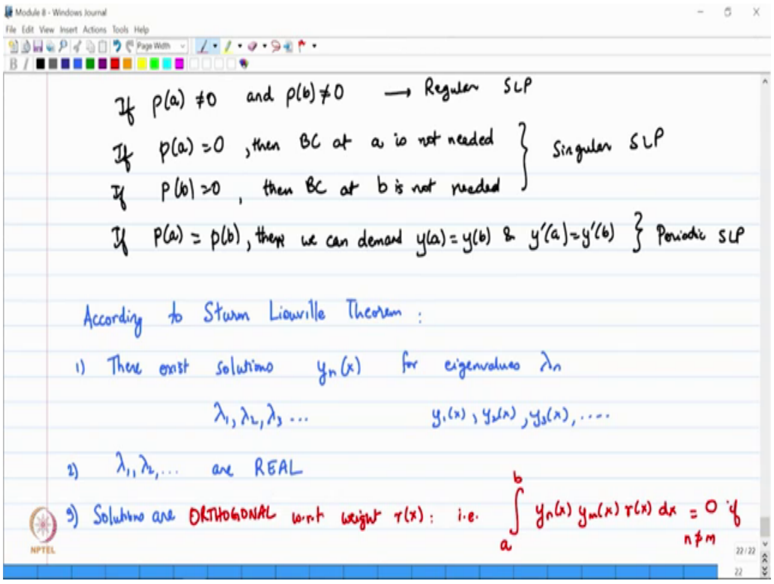
So, the general description of orthogonal functions is called as Sturm Liouville theory. So, this is the theory that will help you understand what should be the limits, what should be the weight function and so on. So, here what is done is you write at second order ODE in the following form you write it as P y prime the whole prime plus q plus lambda r y equal to 0.

So, P is a function of x, and q is a function of x, r is a function of x lambda is a scalar, lambda is a real, lambda is a scalar are continuous in some interval you take some interval ab. So, a b is some interval in x. So, and what else some other conditions we will demand that P of x is greater than or equal to 0 in a b, and r of x is greater than equal to 0 in ab. So, this is a differential equation. So, it takes this differential equation I will call it equation 1. Now I wrote it this way I mean basically this is a general second order linear differential equation. Second order linear homogeneous differential equation can be written in this form and now the. So, suppose you have this differential equation and you have and you have the boundary conditions. So, the boundary conditions at a. So, a and b are this a and b are the is a range of x is the allowed values of x.

So, the boundary condition I will write as alpha 1 y of a, plus alpha 2 y prime of a equal to 0. So, this is the boundary condition at a, and you have beta one y of b plus beta 2 y prime of b equal to 0. So, these 2 are the boundary conditions boundary condition at a and b. So, a and b are the boundaries and we want at least one of alpha beta not e not equal to 0. So, one of these for alpha one alpha 2 beta 1 beta 2 one of those should not be equal to 0, and we will assume that alpha is alphas and betas and real. So, lambda is referred to as an Eigen value and lambda should be a scalar it, it can be a real or a complex number. Now this is called a Sturm Liouville problem. So, suppose you have this differential equation with this boundary conditions, this constitutes what is called a Sturm Liouville problem. We will we will refer to it as a SLP the Sturm Liouville Problem.

So, this is what constitutes a problem a Sturm Liouville Problem and you find that you know you can write a whole lot of differential equations in this form. So, this is not a not a very restrictive form, you can easily see that you can write your Legendre differential equation, your Bessel equation your etcetera in this form. Now suppose if so, there are there are various special cases.

(Refer Slide Time: 18:50)



If P of a not equal to 0 and P of b not equal to 0. So, we said that P of x has to be greater than or equal to 0. So, it cannot be negative, but it can be 0, but in case P of a and P of b are not equal to 0 and then this is called a regular straw a Sturm Liouville problem. If P of a equal to 0 then boundary condition at a is not needed.

So, we do not need this boundary condition we know we do not need the first the top boundary condition at a. If P of b equal to 0 then boundary condition at b is not required not needed. So, if these 2 are referred to as singular Sturm Liouville problems and the third case if P of a is equal to P of b then we can demand y of a equal to y of b, and y prime of a equal to y prime of b and with this we considered something called a periodic Sturm Liouville problem. So, we can look for solutions that satisfy this. So, there exist these solutions and this constitutes a periodic Sturm Liouville problem. So, these are the various types of Sturm Liouville problems and for and for each of these the Sturm Liouville theory says that that there exists.

So, according to Sturm Liouville theorem first is that there exist solutions yn of x for Eigen values lambda n. So; that means, you have a you have Eigen values like lambda 1 lambda 2 lambda 3 and you have solutions of y 1 of x, y 2 of x, y 3 of x etcetera. So, there exist these solutions second thing is lambda one lambda 2 etcetera are real, and the third is that corresponding to these lambdas. So, ys are orthogonal. So, solutions are orthogonal with respect to weight r of x that is integral yn of x ym of x from a to b this is a limit r of x and dx equal to 0 if n is not equal to m. So, this is a very powerful theorem and notice that just by looking at the differential equation.

So, just by looking at the differential equation and the boundary conditions we can immediately imply that the solutions the solutions, now notice if you change the value of lambda, you will get a different differential equation. So, and this is exactly what happened in the Legendre polynomials or the Hermite polynomials. For example, in the Legendre polynomials your lambda will look like n n plus 1. So, you have this is what your lambda looks like. So, just by having a differential equation in this form and having suitable boundary conditions you can get orthogonal Eigen functions. So, obviously, obviously we said that if P a equal to 0 then boundary condition at a is not needed if P b equal to 0 boundary condition is it b is not needed, and if both are 0 then boundary then you do not need any boundary conditions and you can just write this orthogonality. Now once you have this orthogonality then you can expand your functions in terms of these orthogonal functions. So, I will conclude this lecture here and what I want to emphasize in this is that there is a very general theory of orthogonal function expansion.

And this is called the Sturm Liouville theory, and this theorem is extremely powerful because you can just look at differential equations and you can identify that the solutions should be orthogonal Eigen functions, and once you have orthogonal Eigen functions you can take any function and expand in those. The place in chemistry where you see this see this really in action is quantum mechanics. In fact, the whole of quantum mechanics; the very postulate of quantum mechanics is related to a kind of operator called a Hermitian operator, this operator has real Eigen functions and it has Eigen value it has real Eigen values.

And it has orthogonal Eigen functions and in fact the important thing about quantum mechanics is that you can almost write you I mean the most common equation that you see is a Schrodinger equation or the Eigen value equation for the energy for the Hamiltonian operator, which is actually a second order differential equation and you can show that its Eigen functions should be orthogonal and its Eigen values should be real. So, the energy is the Eigen value which has to be real. In fact, the whole of quantum mechanics is founded on this Sturm Liouville theorem, it is an extension of Sturm Liouville theorem to complex functions and. So, I will conclude here now in the in the practice problems I will try to show you how to write the various classic problems as

Sturm Liouville problems and how to use the orthogonality to do various simple integrals in quantum mechanics.

Thank you.