Fundamentals of Spectroscopy
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Lecture - 29
Harmonic Oscillator Eigenvalues and Eigenfunctions - I

In the study of vibrational spectroscopy, one of the most important ideas that you will need is that of the harmonic oscillator. Now, the harmonic oscillator system is that of a particle moving in a harmonic potential, which I will tell you about and we want to study how this particle behaves by using the laws of quantum mechanics. So, let us start at the beginning let us first understand what is a harmonic oscillator, in other words, what is this harmonic potential?

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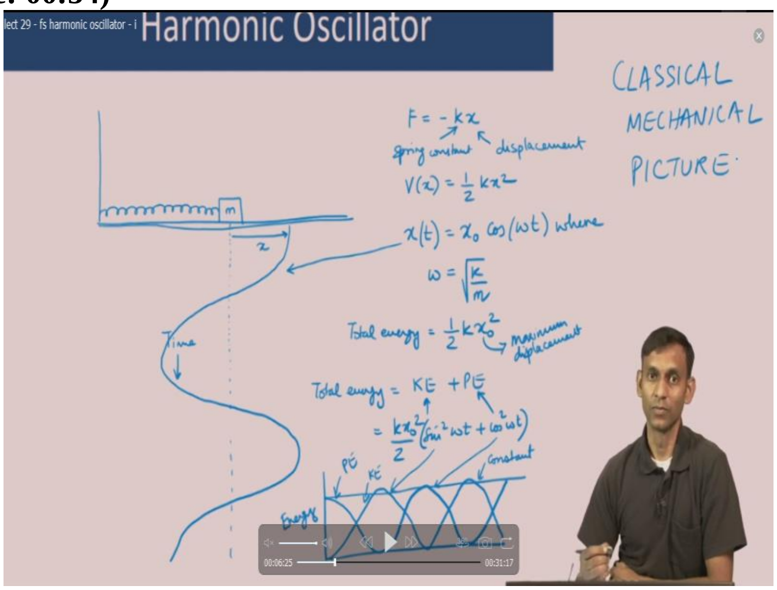

So, for that, consider a system like this where you have a small mass which is free to move on a frictionless surface that is this surface here and it is attached to a wall via spring like this. Now, if you take this mass and make displace it by x, about its equilibrium position. So by including position, I mean this position when the spring is not stretched or compressed and then if I stretch the mass by a distance x and leave it, then the mass begins to oscillate back and forth.

And this oscillation is what is called harmonic motion now if you plot the motion of this particle as a function of time, so, I am going to plot time in this direction and the amplitude of the motion, then the particle initially has an amplitude like that, then it comes down it has an amplitude in this direction it goes up and it oscillates back and forth like this, about this equilibrium position this motion is what is called harmonic motion.

And the force that the spring exerts on the mass F = - k times x that is the force is proportional to the displacement that the particle is has with respect to the un displaced position of the spring. The corresponding potential energy is v x is = 1 / 2 k x square and the classical motion of this particle is given by x as a function of t is = x 0 cosine of omega t, where omega which is the frequency of the oscillation is related to the spring constant.

So, k is called the spring constant and omega is related to the spring constant as square root of k over m. So, the classical motion is given by this x as a function of time and the graph of that is what you see here, the total classical energy of the spring, total energy is half k x 0 squared, where x 0 is the maximum displacement of the spring the total energy is a constant and is a sum of kinetic energy and potential energy.

So, when the particle is moving fast the energy is primarily kinetic energy and when the particle is turning around and it is slowing down, then the energy is primarily potential energy. So this total energy can be written as a sum of kinetic energy and potential energy and classically, this is k x 0 square by 2 sine squared omega t. This is the kinetic energy plus cosine squared omega by 2, which is the potential energy.

If we graph the potential energy as a function of time the graph looks something like this. Initially it is all potential energy and then it decreases eigen its potential energy and decreases. So, this is potential energy and the kinetic energy is initially 0 and then that increases when the potential energy becomes 0 and then it oscillates like this. So, this is the kinetic energy and the graphs are here for the kinetic energy and here for the potential energy.

And you see that the total energy which is the sum of the potential and kinetic energy, that is constant, this is the classical picture of the motion of the particle in a harmonic potential. So what we have in this page is the classical mechanical picture. Our goal is to understand the quantum mechanical description of the harmonic oscillator and that is what we are going to look at in very great detail.

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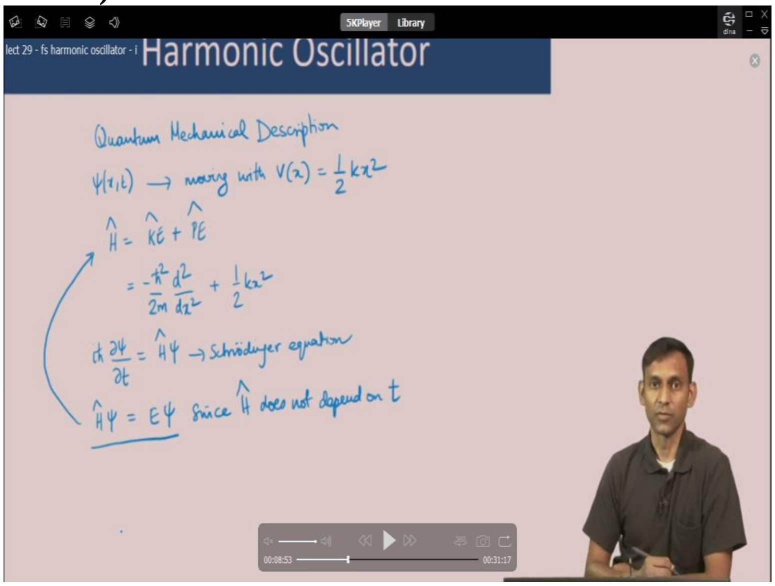

Now, our goal is to obtain a quantum mechanical description of a particle moving in a harmonic potential. More precisely, we want to find the wave function of a particle so, psi of x, t which is moving in the harmonic potential that is moving with potential V of x is = half k x square. So, for this, we have to write the Hamiltonian for this system and then solve its Schrodinger equation the Hamiltonian for the system each is the kinetic energy operator plus the potential energy operator the kinetic energy is simply the one dimensional kinetic energy operator.

Which is - h bar square by 2m d square by dx square and the potential energy is half k x square. Now, our goal is to find a psi x, t which satisfies the Schrodinger equation ih bar del psi by del t is equal H of psi this is the Schrodinger equation. We have seen in the lectures on the basics of quantum mechanics, that if the Hamiltonian does not depend on time which is the case here, then solving the Schrodinger equation is equivalent to solving the eigen value equation of the Hamiltonian H psi is = E psi since, h does not depend on time.

So, let us look at the solution of this equation H psi is = E psi where h is this Hamiltonian H bar squared by 2m d square by dx square + half k squared and let us go and derive what are the actual eigen functions and eigen values of this Schrodinger equation.

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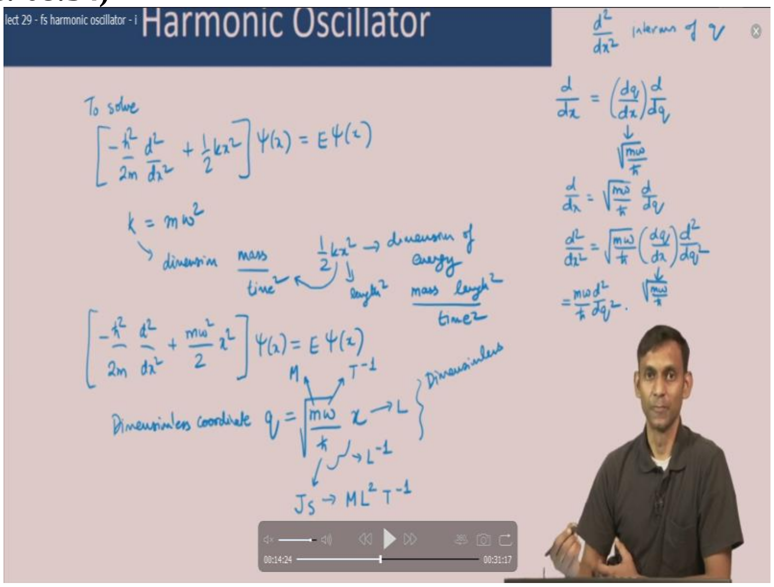

Our goal is to solve the following Schrodinger equation -h bar square by 2m d square by dx square + half kx square psi of x is = E times psi of x. We note that k is = m omega square from the classical solution of the harmonic oscillator. We also see that this is consistent with key having dimensions of mass by time square. Because half kx squared has dimension of energy which is mass length square divided by time squared.

So since x squared has dimension of length squared, k must have dimension of mass by time squared. So taking k to be m omega squared, we write the Schrodinger equation as -h bar square by 2m d square by dx square + m omega squared by 2 x squared psi x is = E times psi of x, we need to find a psi x, which satisfies this equation to obtain solutions of the Schrodinger equation, that is to obtain the value of Psi of x that satisfies this equation.

We will use the method of ladder operators and for that, let me begin by defining dimensionless coordinate q which is related to x in the following manner so, q is equal to square root of m omega by h bar times x. Let us verify that this q is indeed dimensionless. So, if you take the dimensions of all the other quantities, M has dimensions of mass, omega has dimensions of inverse of time, h has dimensions off so, this is units of Joule second.

So, dimensions are mass length squared time inverse so, you see that inside the square root the mass in the numerator and denominator cancel and the time inverse in the numerator and denominator cancel and you are left with one over L squared square root, which is one over L. So the dimension of this entire square root is L inverse and the dimension of the X is L. So the dimension of this entire Q is dimensionless.

We will now write the Schrodinger equation in terms of Q and to do that, we need to write d squared by dx squared in terms of q. Let us start by writing d by dx in terms of q so d by dx is = d by dq and dq by dx and we know that dq by dx is = square root of m omega by h bar. So d by dx is = square root of m omega h bar d by dq d squared by dx squared is another derivative with respect to x which gives dq by dx and then a another derivative with respect to q and again we write the expression of dq by dx as square root of m omega by h bar.

So finally, we have d squared x by d squared by dx squared is equal to m omega h bar d squared by dq squared using this expression we will now write the Hamiltonian in terms of the dimensionless coordinate q and solve the Schrodinger equation for the dimensionless coordinate and in the end, you can always come back to the coordinate x by using the conversion factor. The reason we use the dimensionless coordinate is to simplify the math, which will follow in the ladder operator approach and we will understand this in detail as we proceed

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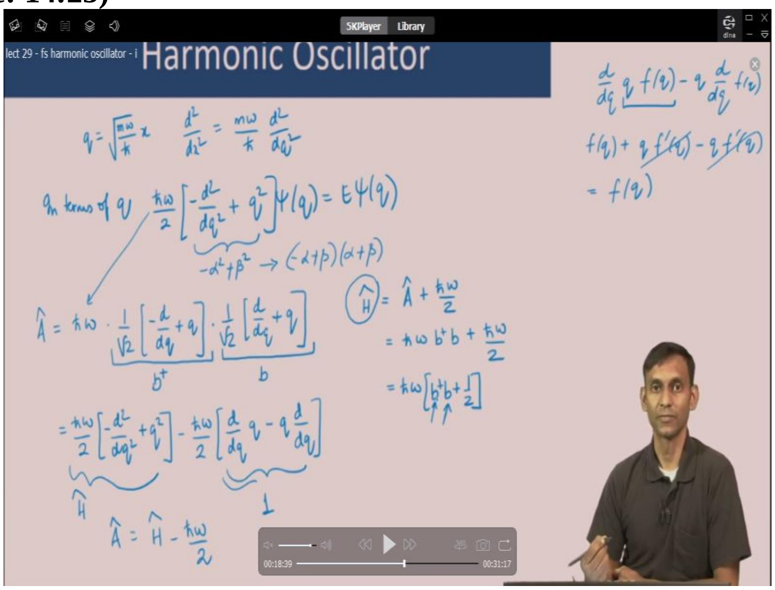

Using the relation of q and x, which is m omega by h bar x and d squared by dx squared, which is m omega h bar d squared by dq squared in terms of q the Schrodinger equation becomes h bar omega by 2 - d squared by dq squared + q squared psi of q is equal to E of psi of q. We notice that in the Schrodinger equation, this operator has the form minus alpha squared plus beta squared, which as you know, can be factorized as minus alpha plus beta and alpha plus beta.

So, just as an experiment, let us write an operator, which is h bar omega, this h bar omega here and whatever is in the brackets as 1 over square root of 2 - d by dq + q multiplied by 1 over square root of 2 d by dq + q. Now, if we expand this out, we get h bar omega by 2 - d squared by dq squared + q squared and the additional terms - h bar omega by 2 d by d2 q times q multiplied by q times d by dq. So, here we have the operator like in the Hamiltonian and additionally we have operator which we see here.

So, the question is what is the value of this operator? Let us try to determine this d by dq n q operating on f of q - q d by dq operating on f of q gives and you have to use the chain rule here f of q + q times f prime of q - q f prime of q now, these 2 will cancel and you get this to be simply f of q. So, the operator here is nothing but just one and this entire operator he had that we have written here is effectively h the Hamiltonian - h bar omega by 2.

Now, if we give some special names to the operators here and here so, we call the first one as the b dagger and this other operator as b, then we can see that the Hamiltonian which is the operator A + h bar omega by 2 is = h bar omega b dagger b + h bar omega by 2 that is h bar omega b dagger b + half. So, effectively, we have written the Hamiltonian operator in terms of 2 new operators which we have defined, which are b dagger and b and we will see how this will help us actually solve the Schrodinger equation H psi = E psi.

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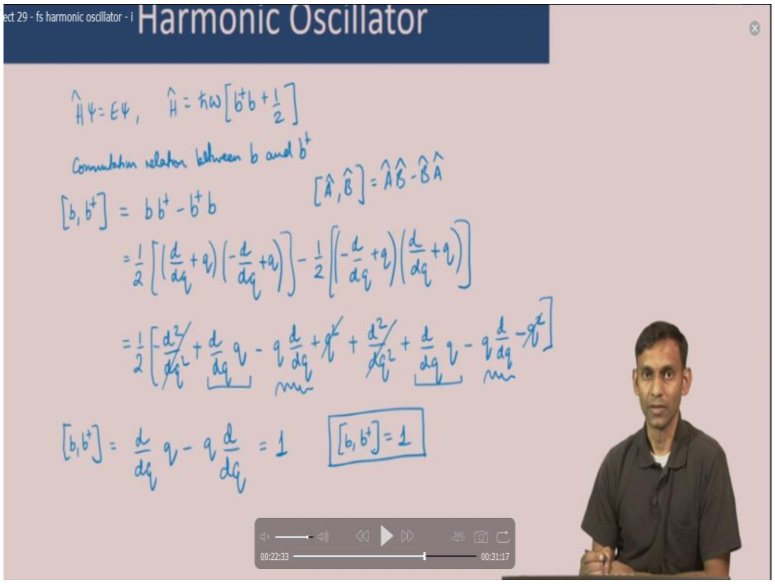

Our goal now is to solve H psi = E psi, where h is written in terms of the 2 new operators which we have defined b dagger and b. So, this is h bar omega b dagger b plus half do this, it is helpful to derive a commutation relation between these 2 new operators b dagger and b. So, we want a commutation relation between b and b dagger. By commutation relation, the mean what is the value of the commutator b b dagger?

So, this is the symbol of a commutator the square brackets and the commentator simply means, b b dagger - b dagger b. In general the commutation operator between 2 operators A and B is AB - BA. So, in our case, the commutation between BB dagger is written out here and if you write this explicitly in terms of the q this becomes b is d by dq + q and this one over square root of 2 has been taken out as half outside and d dagger is - d by dq + q and we have minus half b dagger is minus d by dq + q multiplied by d by dq + q.

When we expand this out, this becomes half - d squared by dq squared + dy by dq q - q d by dq + q squared and + d squared by dq squared and + d by dq of q - q d by the q and - q squared. Several terms here cancel so for example, this first term cancels with this term, and the q squared term cancels the - q squared term and furthermore, this term dq d by dq times q, and d by d q times q appears twice and similarly this term here appears twice.

So, we can write this b the dagger commutator as the by dq q - q d by dq and this operator we have seen is simply equal to what we have just derived this in the previous slide. So, the final result we get is the commutator of BB dagger is equal to one which we will use in our derivation going ahead.

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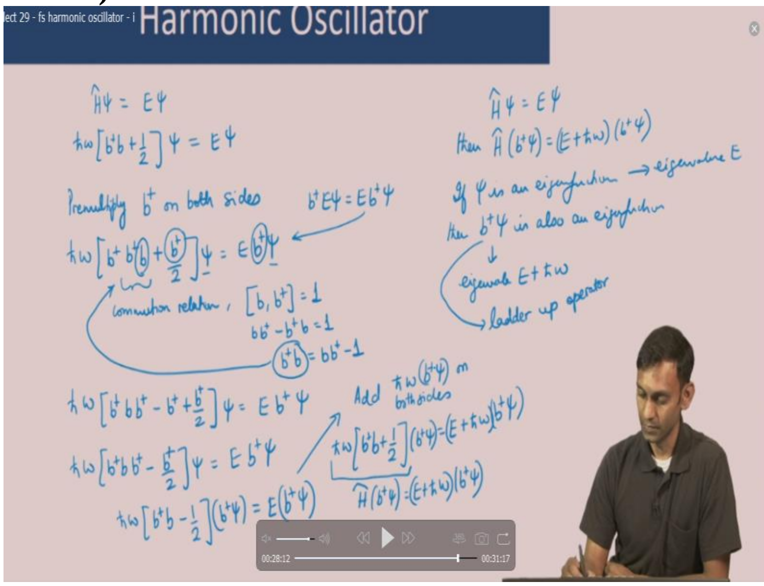

Let is eigen write the eigen value equation for the Hamiltonian H psi is = E psi so, h bar omega b dagger b + half times psi is = E psi and we want to find what Psi satisfies this equation. So, let us pre multiply or multiply from the left by b dagger on both sides of the equation that gives h bar omega b dagger b dagger b + b dagger by 2 psi is = E times b dagger of psi b dagger is a linear operator and so, I could write b dagger E of psi as E times b dagger of psi, which is what I have here.

Now, we notice in this equation that we have a b dagger operating on psi here and a b dagger operating on psi here, but in this term, we have b be operating on Psi. So, let us try to interchange the b dagger and b and for this we can use the commutation relation which we have just derived which is b b dagger is = 1 or in other words b b dagger - b dagger b is = 1 or b dagger b is equal to b b dagger -1.

So, if I substitute this b dagger b here then I will get h bar omega b dagger b b dagger minus one which is simply b dagger + b dagger by 2 psi is = E times b dagger of psi and this gives h bar omega b dagger b b dagger - b dagger by 2 times psi is equal to E b dagger of psi and this gives h bar omega b dagger b - half B dagger of psi is equal to E times b dagger of psi. If we want to make this operator on the left hand side look like the Hamiltonian operator.

Then we had from here you add h bar omega v dagger psi on both sides and this gives h bar omega b dagger b + half B dagger psi is equal to E + h bar omega b dagger psi. Now, this operator on the left hand side here is nothing but the Hamiltonian operator. So, we have Hamiltonian operating on b dagger psi gives E plus h bar omega b dagger of psi. This implies that if h psi is = E psi then each of b dagger psi is = E + h bar omega b dagger psi so, if psi is an eigen function then b dagger psi is also an eigen function.

And if psi has eigen value E then b dagger psi has eigen value E + h bar omega so, if you have an eigen function of the harmonic oscillator Hamiltonian, then operating with b dagger on that eigen function gives another eigen function, but with an eigen value which is increased by h bar omega. So, this operator b dagger is raising the energy of the eigen function and giving another eigen function and this b dagger operator is sometimes called the ladder up operator.

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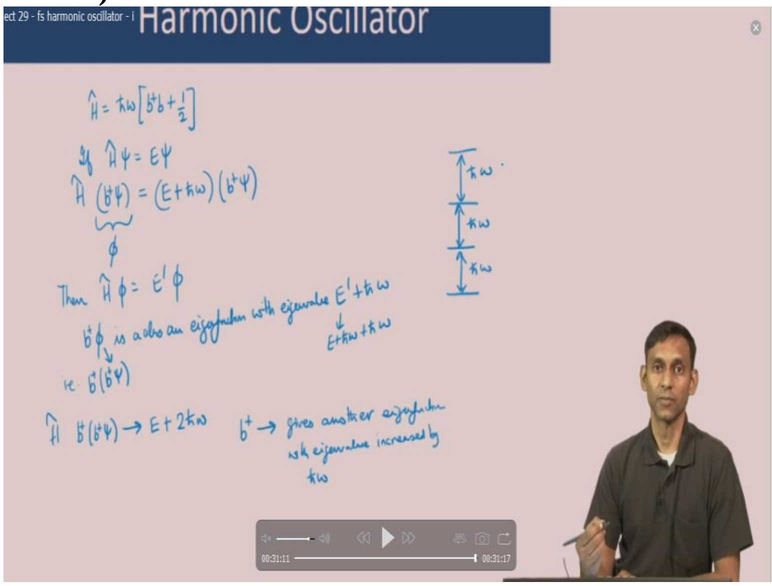

To summer rise up to now we have seen that the Hamiltonian of the harmonic oscillator is h bar omega b dagger b + half and we have seen that if psi is an eigen function with eigen value E, then b dagger psi is also an eigen function with eigen value e + h bar omega. Now, if we consider this b dagger psi to be another eigen function, let us say phi then h phi is = E prime of phi and this implies that b dagger of phi is also an eigen function with eigen value.

E prime + h bar omega that is b dagger of b dagger psi phi is just b dagger psi is also an eigen function with eigen value E prime is E + h bar omega so, the total eigen value is E + h bar omega + h bar omega. So, in summary, b dagger b dagger psi E is an eigen function of the Hamiltonian with eigen values E + 2 h bar omega. We see that the operator b dagger operates on an eigen function and gives another eigen function with eigen value increased by h bar omega.

So, this suggests that the eigen values of the harmonic oscillator Hamiltonian are spaced by equal values and the spacing in each case is h bar omega. So, all of these are eigen values corresponding to different eigen functions and these are all obtained by operating the b dagger operator on one of these eigen functions the question now is what is the lowest eigen value and what are the functional forms of these different eigen functions.