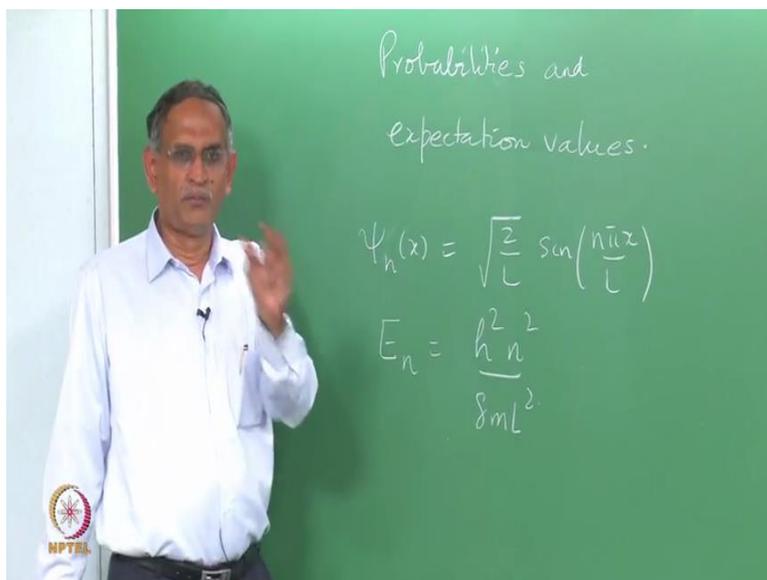**Chemistry I – CY1001**
**Introductory Quantum Mechanics and Spectroscopy**
**Prof. Mangala Sunder Krishnan**
**Department of Chemistry**
**Indian Institute of Technology, Madras**

**Lecture – 04**
**Lecture 3: Part II - Probabilities and expectation values**

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So, let us continue from where we left; namely the wave function psi n of x as root 2 by L sin n pi x by L and the energy E n as h square n square by 8mL square. Since psi star psi is the probability density at any point x and psi star psi at the small interval d x around x gives you the probability that the particle is in that small region.
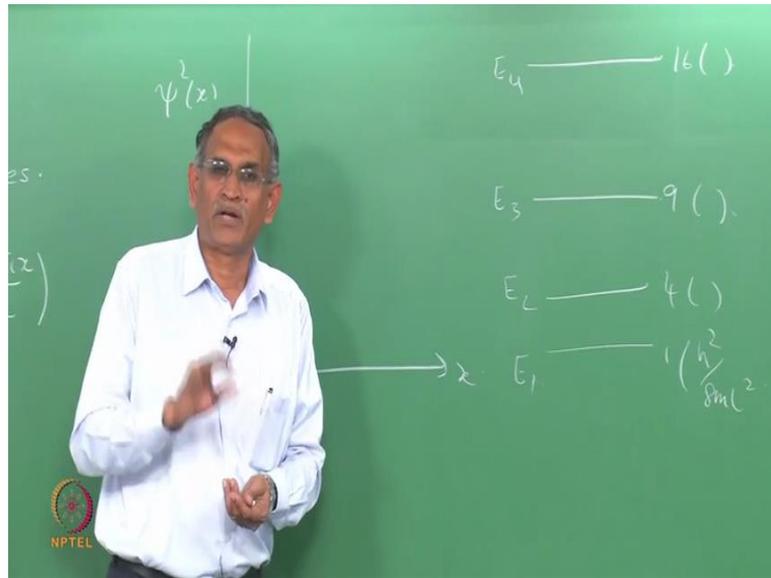
If you plot psi square of x as a function of x, you get some ideas about what these probabilities mean.
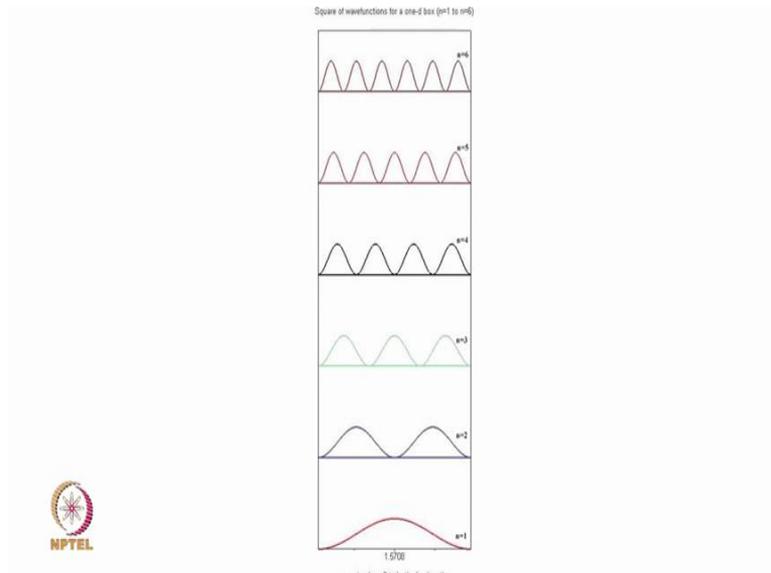
So, let me show this graph for some value of the box length L and we have a root 2 by L which is a pre-factor for the wave function. So the wave function has a dimension, it has

a dimension of L by square root of the length and then you see that psi star psi d L takes care of the probability being a number.

Now if you plot the psi star sin for the first wave function namely n equal to 1 you see that this is nothing but the half sin wave with a little bit of tapering on the edges. When it is n equal 2, please remember that the expression if you look at the wave function, where is the wave function itself. If you look at the wave function n equal to 1 is a half sin wave, n equal to 2 is a full sin wave, this is a 3 half sin wave and so on. Therefore, if you take the square of this wave; obviously, the picture that you get is the picture that I showed you now.

So, this is the square of the n equal to 2 wave and this is the square of the n equal to 3; sin 3 pi x by L, since it is 0 to L you have that shape and also the shapes for n equal to 4. And as you see that as n increases, these oscillations become so close to each other that for very very large n, it looks like that the probability density is uniform. What does that mean? If we have to do this exercise for a classical system, let us assume that the particle is moving in the box in somewhere and let us not ask the question how does it get deflected from one end to the other end. There are questions for which we do not have any answers and questions which are also meaningless.

Let us assume that we are looking at the particle at a given instant of time and using a small window. If the particle is moving at constant speed because its kinetic energy is a constant; energy E and if it is a constant then the probability of locating the particle in every small region of the same size is uniform, it is a same value. That is what is meant by this particular flash movie telling you that the probability P 1 for an interval of delta X, if you are locating the particle in that interval across this, it is uniform.

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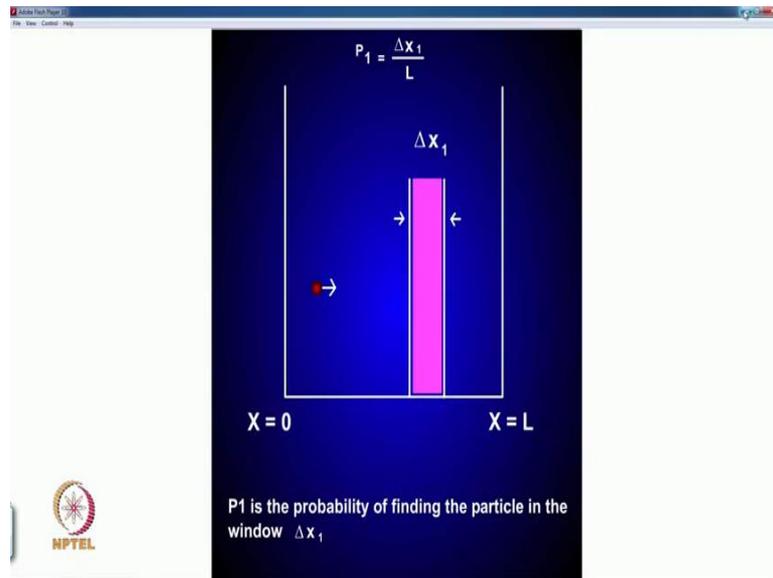


Now if the delta X is different, it is going to be different by that corresponding ratio namely delta X 2 by L. This is what we expect the particles position and its probability to be associated with, but in quantum mechanics, we do not see that. In this particular case, we see a slightly different result see that, the probability is not uniform and the probability is also not the same for different energies at any given location. So, let us look at this particular graph here; let us look at this region right in the middle for n equal to 1; the red line, you see that near the middle if you are looking at a probability of this kind, the way to represent this is using this simple picture.

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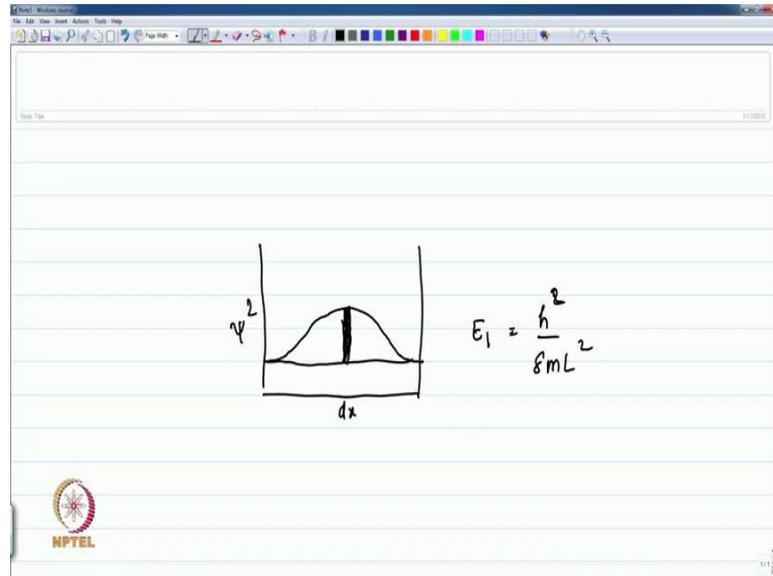


Then if we have the function in this finite region, the probability in the middle region for a small interval dx you are looking at; it is the area here dx. Such small this size square, calculated right at the middle value of the interval and likewise if you have a particle with a slightly different energy, this energy is E 1 and that is h square by 8mL square.

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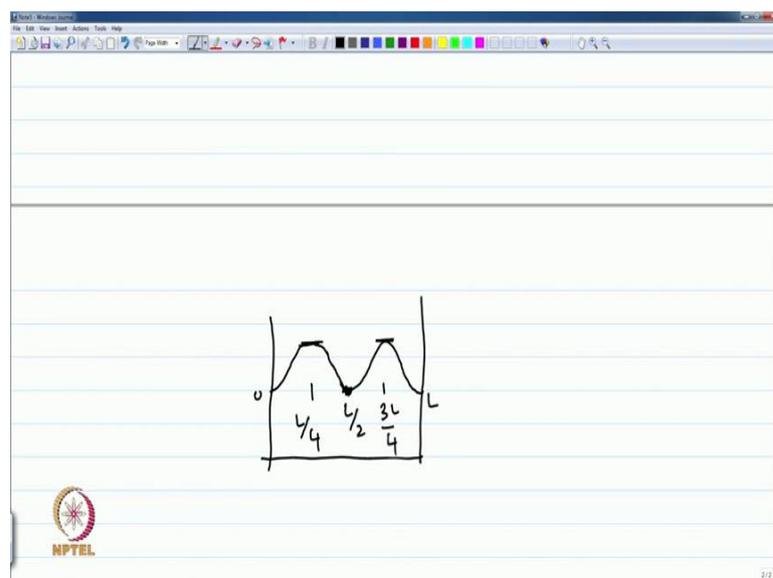
If the particle has energy E 2, now you say that the sin wave gives you for the same thing two components, a maximum at this point and again a maximum; this is L by 4; this is L by 2, this is 3L by 4 and this is L and this is 0. So, you see that the probability maximizes in the intermediate regions; L by 4 and 3 L by 4, but its minimum in the middle and also the probability is not uniform. The probability of locating the particle in a certain region is dependent on what that region is and also what the energy associated with that particular wave function is of that particle. So, this is something very unique and very special with quantum mechanics and it is not something that we can immediately accept; I mean something that makes sense that is the way it is.

If you write the Schrodinger equation and if the interpretation of Max Born has the most meaningful interpretation for the wave function is to be accepted then this are consequences with that accepting those what are called the quantum stores and the probability varies depending on what the energy is as you see in this particular graph. You see that the probability is according to the square of the wave function plot that you have here. For example, in the one-fourth length of the box or the three-fourth length of the box is different and you have a little bit of a different energy then you see that at that point it is is actually very nearly 0 and then it varies, but what happens when n becomes extremely large.

To see that all these things become more or less uniform I mean so many oscillations that if you take any particular small region, if the n is extremely large; the probability of locating the particle in that region is nearly the same as locating the particle in any other or the same extent of that region. Therefore, the classical idea gets closer and closer to the reality of a quantum equation, when the energies of the particles become extremely large.

Now there are two conditions; namely in the energy expression that you have here, you remember h square and n square; the mass of the particle is m and the length of the box L, both of them determined what is the spread between different energy. So, if you plot E 1, it is 1 times by h square by 8mL square, E 2 is 4 times that unit, E 3 is 9 times that unit, E 4 is 16 times that unit and as you increase this energy, you see that the gap between the energy is increased, but you can also see the following namely as you

increases energies, the probabilities of finding the particle in a given region more or less approaches a constant value; which is proportional to the extent of that region divided by the total length of that region for very very large values of n; that is a classical limit. And that classical limit can be obtained by doing some manipulations here by choosing heavy particles so that the gaps are smaller and therefore, the larger energies are reached very quickly or the length of the box is very large.

Microscopic dimension, macroscopic particle you see that the quantum conditions are becoming less and less important, but smaller particles narrow region, the quantization results are somewhat unique and that is where we have to spend a lot of time trying to understand why quantum mechanics is important for atomic particles in atomic dimensions.

When L is very large, when m is very large you see that these quantization energies; the gaps between them are not very important and very large amount of energy that is very high values of the quantum number are easily reached and the particle behaves more or less like classical. So, this is an important what is called the correspondence limit as one would call it.

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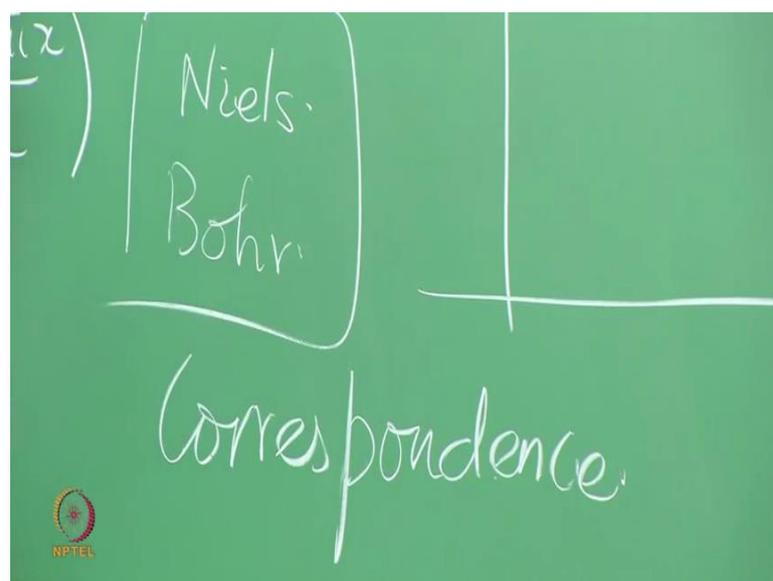
And this was first considered by Niels Bohr, the correspondence principles is that quantum mechanics approaches classical predictions, classical mechanical predictions for very very large values of the quantum number as in this case, very large particles of macroscopic dimensions and particles of microscopic size then quantum is less and less important and that is how we were never able to discover quantum mechanics until we started looking at the atomic details more and more closely.

So, this is the association that I would like you to have with the particle in a box model. We will look at to the particle in a two d box and some other simpler models, before we discuss what are called the expectation values or the average values to be seen or to be calculated using quantum mechanics as we will see in these problems. We will put that for a later lecture, but remember the message that we have here quantization of energies, probability descriptions and the probability descriptions being very different from classical expectations and when the system becomes more and more classical with larger and larger energies. These are the pointers that you have to have in order to understand things better. In the next lecture we will start looking at not one dimension, but motion in a plane that is there are two coordinates X and Y or even three X, Y and Z.

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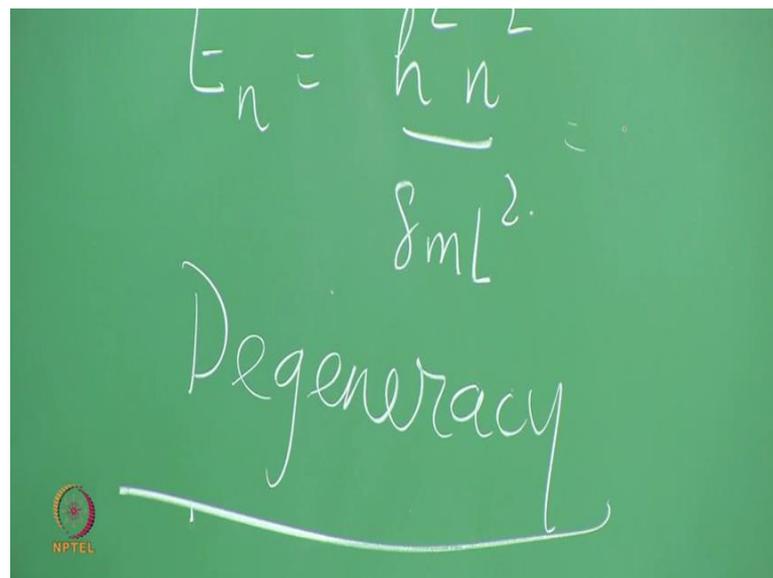
And look at to the particles and we will see one more unique result namely the degeneracy, we will look at that in the next lecture.

Thank you.