Chemistry Atomic Structure and Chemical Bonding
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Lecture - 12
Problems and Solutions for Particle in One and Two Dimensional Boxes

Welcome to the lectures in Chemistry on the topic of Atomic Structure and Chemical Bonding.

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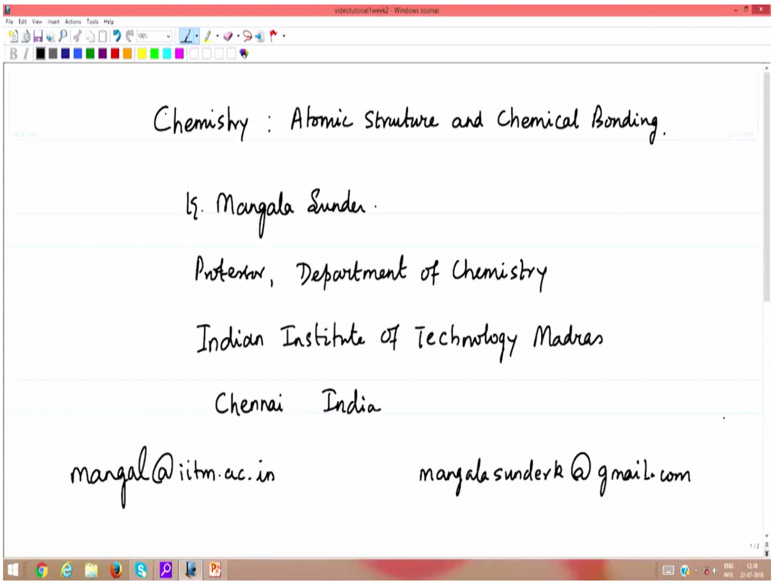

My name is Mangala Sunder, I am I am a professor in the Department of Chemistry, Indian Institute of Technology, Madras and my email coordinates are given here mangal at iitm dot ac dot in, and mangalasunderk at gmail com.

So, this is a video tutorial, problem solving is an extremely important exercise for any area in engineering and science and more so in quantum mechanics. And so we have already have some experience with the tutorials and the online submissions and so on, but these are some of the problems which require a bit of elaboration, and some of the more direct application of the formulae. The others additional concepts are provided and so on. Therefore, I request all of you who are listening to the quantum mechanics course for the first time, to go through all these problems by yourself without having to necessarily do it, with my help attempt to these problems by ourselves and then you come back to the video help in case you have some doubts ok.

So, let me start with the problem. Since there are 10 problems in this tutorial and the video tutorial has problems on one and two dimensional box problems, based on the lectures which were made available to you. The first part contains about 6 problems of numerical as well as simple algebraic exercises. In one dimensional model and the remaining 4 problems are in the two dimensional box model ok.

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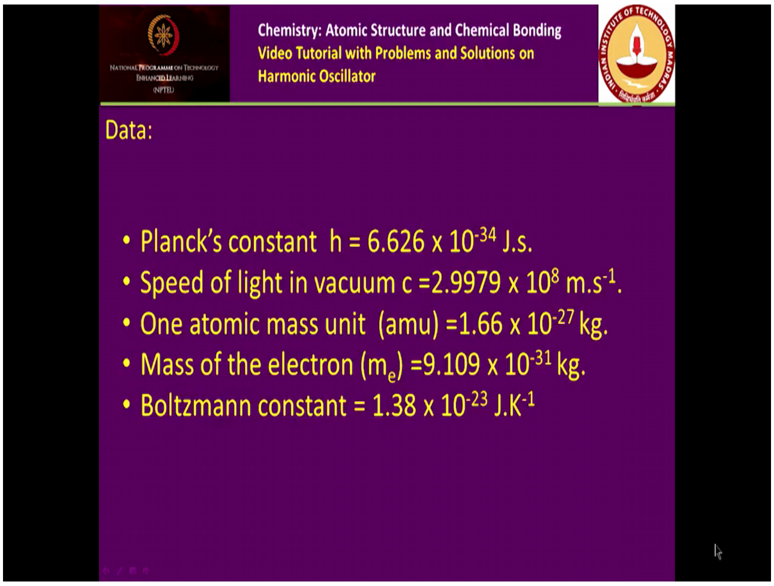

Some of the constants that I would like the students in chemistry and physics to have in memory. This is I mean these are fundamental constants and it is important to have them in memory. The Planck's constant as for example, as 6.626 times 10 to the minus 34 joule second. And then the other constants are also given here speed up light in vacuum, the atomic mass unit, the mass of the electron and the Boltzmann constant these are constants which would be used throughout this exercise.

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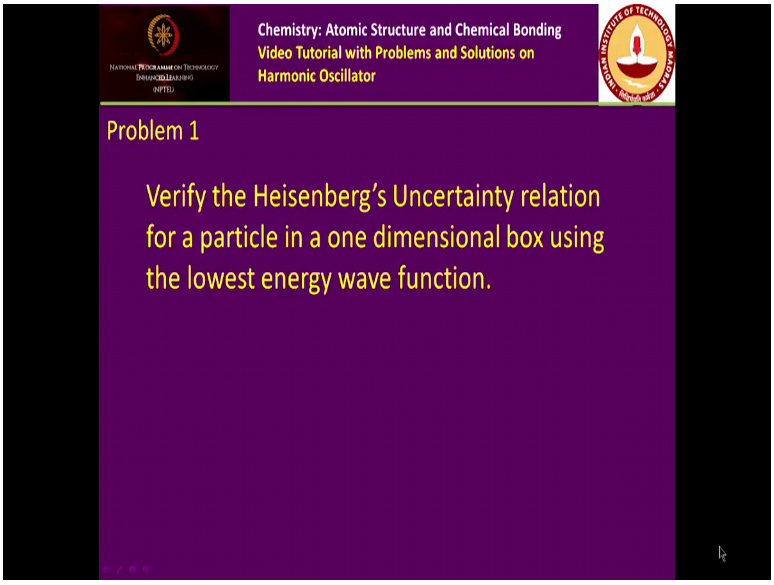

The first problem is on the application of the model the particle in a one dimensional box model to understand the Heisenberg's Uncertainty relation. So, it says that verify the Heisenberg's Uncertainty relation for a particle in a one dimensional box using the lowest energy wave function. We will find out that the lowest energy wave function itself.

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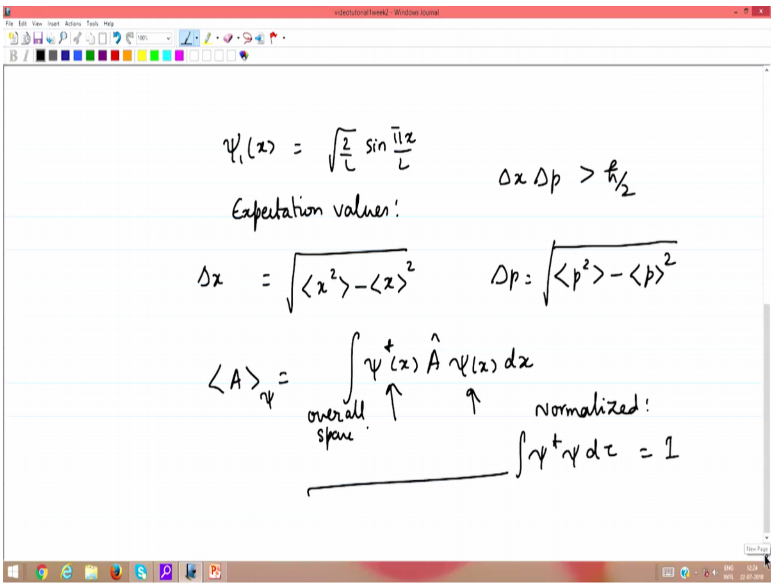

The psi 1 of x which is root 2 by L sin n pi x for the sin pi x by L sin pi x by L sin pi x by L; we can see that this itself will give you the result for the uncertainty in the measurement opposition and the measurement of momentum uncertainty is the product of which would be greater than h bar by 2. We will see that and this involves the calculation of the expectation values and the first definition that, you must remember or recall is the uncertainty in the position is given by this formula. That it is a square root of the difference between the difference between the average of the square and the square of the average and delta p. Likewise, is given by the square root of the average of the square of momentum and the square of the average of the momentum ok.

And the average values are calculated in quantum mechanics. As you recall from the formula that, if you have the wave function psi the average values are psi star of x in one dimension. For example, the operator A associated with the measured value a psi of x dx over all space available to the system assuming that these are normalized to unity. So, psi star psi d tau is 1 assuming that. So, we have to calculate the expectation values of the position.

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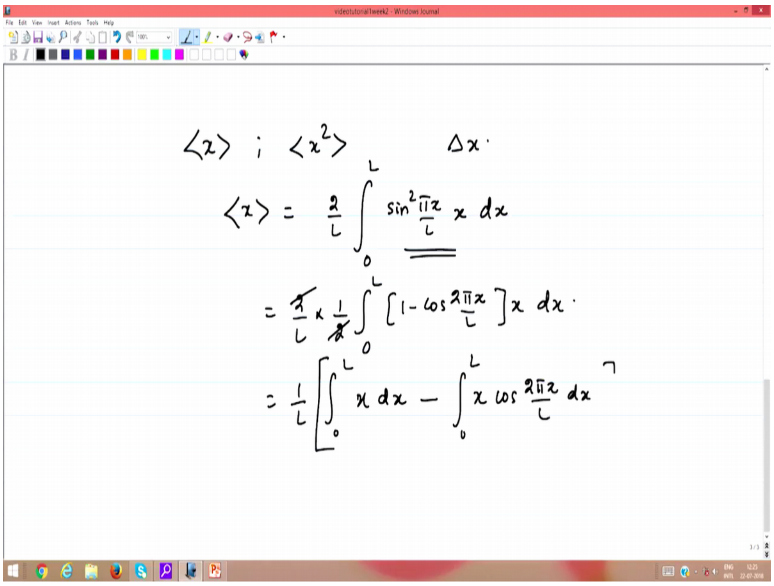

First and the expectation value of the square of the position in order to calculate the delta x; I think this exercise of calculating the average value for x is something you already know. It is 2 by L because, the wave functions are root 2 by L sin pi x by L and the square. So, you have sin square pi x by L x dx x does not operate on sin square sin pi x by L except to give you a product. And therefore, it does not matter whether you put the x between the 2 sins or the sin square and so on and the box length is 0 to L ok.

So, this integral is a standard it is a fairly simple integral to do it is 2 by L into L by 2. You express the sin square using the double angle formula 0 to L 1 minus cos 2 pi x by L x dx and the 2 goes away to give you 1 by L. And there are 2 integrals here between 0 to L x dx and the other integral is between 0 to L x cos 2 pi x by L dx ok.

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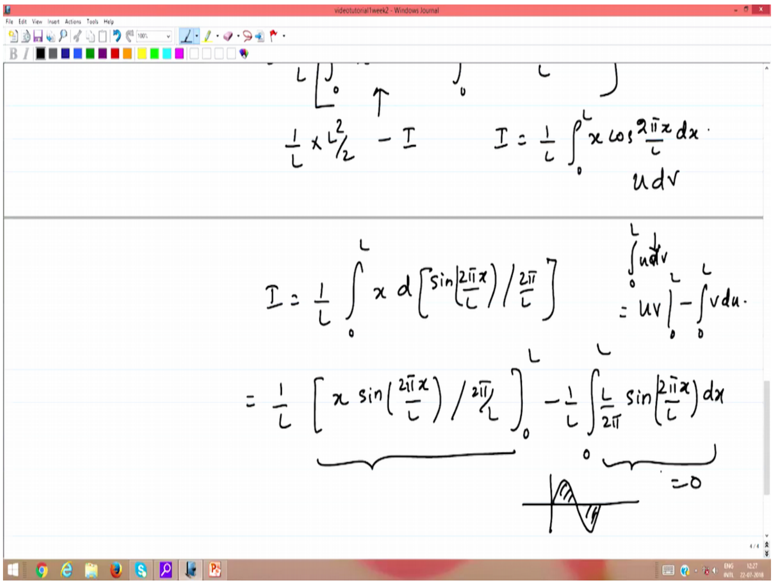

This is well known it is x square by 2 and between the limits 0 and L it gives you L square by 2 ok. The second integral is 1 by L we call it as I and I is 1 by L 0 to L x cos 2 pi x by L dx ok.

Now, calculate to this integral using the udv formula process for udv process for solving the integral. So, we will write this I as 1 by L times 0 to L x d sin 2 pi x by L divided by 2 pi by L ok. That is the udv formula and that is if you recall integral udv between the limits 0 to L is uv between the limits 0 to L, and then the integral 0 to L v vu. So, the same thing that you have to do here which is 1 by L which gives you this 1 by L 0 to L it is not the integral. It is the limit, it is not the integral, it is the limit. X sin 2 pi x by L divided by 2 pi L between the limits 0 and L. And then the other part of this integral is 1 by L integral 2 pi by L sorry L by 2 pi L by 2 pi sin 2 pi x by L dx between 0 and L.

It is easy to see that, this is 0 for x is equal to 0 and also for x is equal to L, because for x is equal to L. It is a sin 2 pi which is 0 and this integral is 0 because, it is an integral of a sin function over the entire cycle. For example, the sin function over the entire cycle between 0 and L. Therefore, the areas cancel each other for this integral is 0 this integral is 0.

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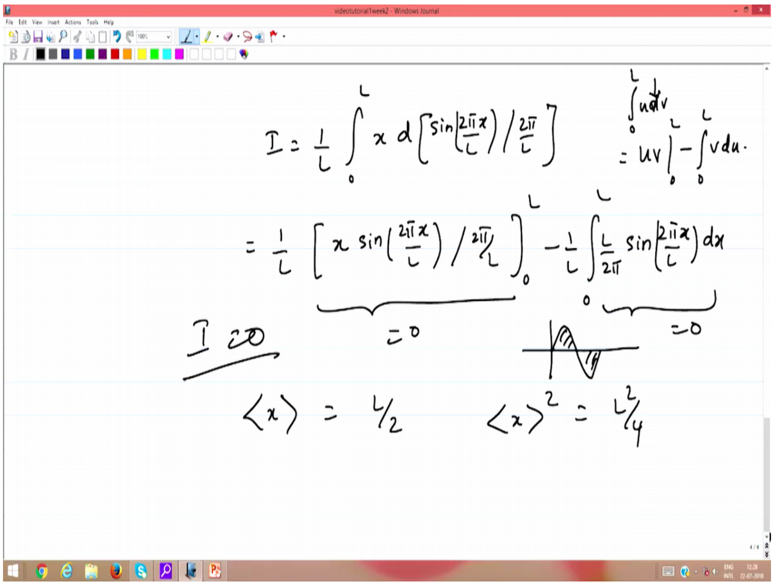

Therefore, the average value of x is L by 2. Since, I is 0 this is easy, therefore the square of the average which is one element for delta x is L square by 4 ok.

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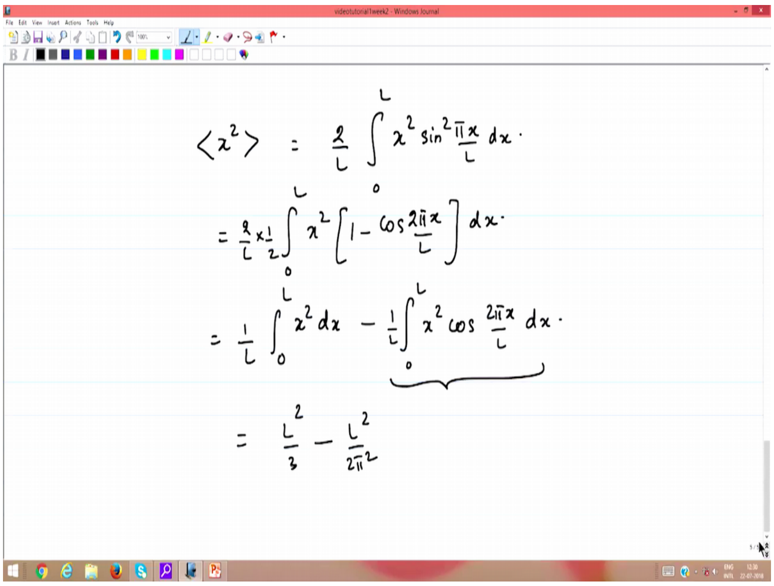

Now, in exactly the same way you have to do the integral x square average. And it requires the evaluation of this integral 2 by L 0 to L x square sin square pi x by L dx. And again, this can be written using the u db formula 2 by L into L by 2 x square into 1 minus cos 2 pi x by L dx and this is sum of 2 integrals.

So, it is 1 by L the first one is 0 to L x squared dx and the second integral is 0 to L 1 by L x square cos 2 pi x by L dx ok. Now, in the lecture notes that you find on the website the details of calculating this are given they are the same as the details for calculating the x. And you would see what the final answer is for this calculation it will be L square by 3 minus L square by 2 pi square there are 4 the delta x value that you want to calculate.

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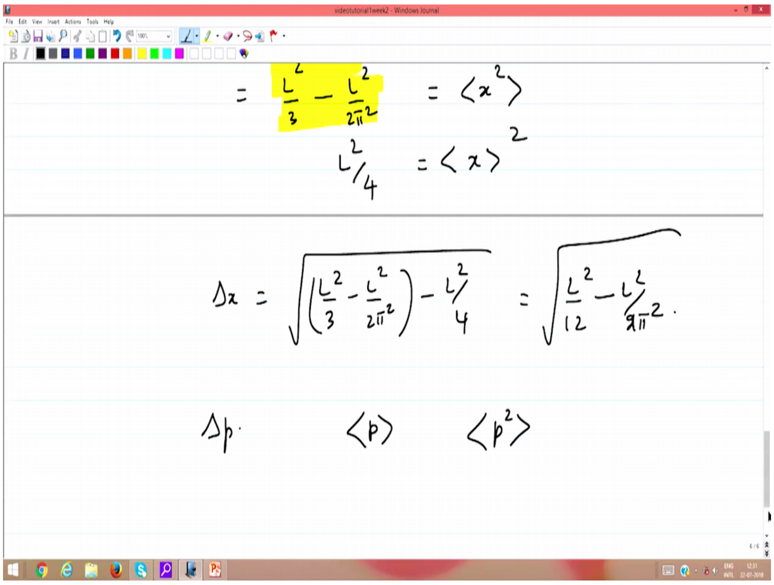

So, let us highlight these 2 things. This is the average value x square and the average value x square is L square by 4.

Therefore, you see delta x delta x square root of L square by 3 minus L square by 2 pi square minus L square by 4, which gives you square root of L square by 12 minus L square by 2 pi square ok. Square root this is the average value delta x I think we should technically use, but I have not been using the brackets of this leave it like that. Now, in a similar way you want to calculate delta p and for that you have to calculate,

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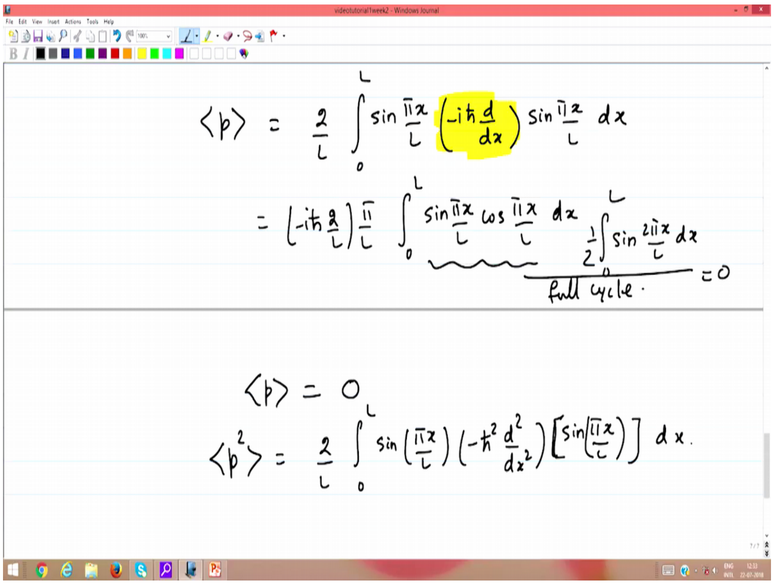

The average value for p and the average value for p square. So, let us do that very quickly the average value for p. Now, you have to be careful about placing the operator between the wave functions as is the requirement. In the calculation of the averages namely it is 2 by L the integral 0 to L and it is sin pi x by L and the operator for p is minus i h bar d by dx. And the wave function on the right hand side is also sin pi x by L dx this is important.

In the case of position, you did not worry about putting the x in between because it is anyway it is just a product, whereas, the differential operator acts on the sin to give you something else. And therefore, you have to ensure that this is the precisely how the expectation values are defined by placing the operator between the 2 wave functions. And so, you have to make sure that you do not miss that now this is also easy to evaluate because the answer is minus i h bar 2 by L pi by L integral 0 to L sin pi x by L cos pi x by L after taking the derivative dx. And this is the integral sin 2 pi x by L dx 1 by 2 between 0 to L again over the full cycle ok.

Therefore, p is the expectation value of p is 0 this is 0 ok. Now, what is the expectation value of p square should be obvious from the way p square operator is used to get this wave function. But, anyway let us write that out it is 2 by L 0 to L sin pi x by L minus h bar square d square by d x square acting on sin pi x by L dx and this you know.

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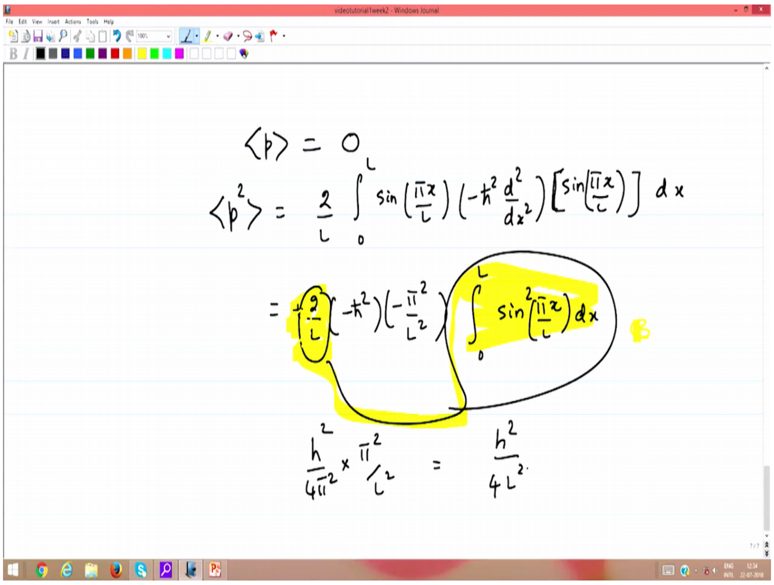

Is, essentially the same sin pi x by L you get except with the minus pi square by L square. Therefore, what you get is plus it is a 2 by L into minus h bar square into minus pi square by L square integral 0 to L. Sin square pi x by L dx and 2 by L times all of this is the normalization of the wave function the answer is one ok.

All of this is the normalized wave function property. And therefore, this gives you therefore, this gives you h bar h square by 4 pi square h bar square into pi square by L square, which is h square by 4 L square therefore.

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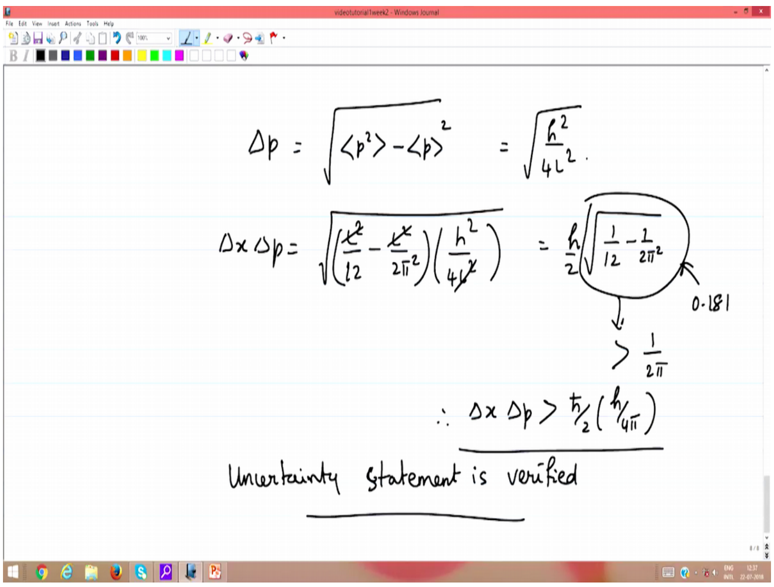

Delta p which is given as the square root of the average of p square minus the p average square is the square root of h square by 4 L square. Therefore, delta x delta p now becomes square root of L square by 12 minus L square by 2 pi square from the delta x and this becomes h square by 4 L square. So, the ls cancel off and h square becomes h and what you have inside the square root is h by 2 here and inside the square root you have 1 by 12 minus 1 by 2 pi square.

And you can show that this is greater than 1 by 2 pi greater than 1 by 2 pi. Therefore, delta x delta p is equal to or is greater than h bar by 2 or h by 4 pi ok. The numerical value if you calculate this turns out to be 0.81. And, that is obviously greater than the h by 4 pi. And therefore, the uncertainty principle is verified uncertainty statement is verified. This is an important problem and similar uncertainty statements have to be verified for every such model; namely, the model for the harmonic oscillator, the model for the particle in a ring particle.

On a ring the model for the hydrogen atom and any other experiment and uncertainty principle never fails in any of these models. And therefore, it is a fundamental principle and the project the problem is chosen to tell you something about, how to calculate the expectation values and how to take the averages and then how to compute the differences and so on ok. So, this is an important problem.

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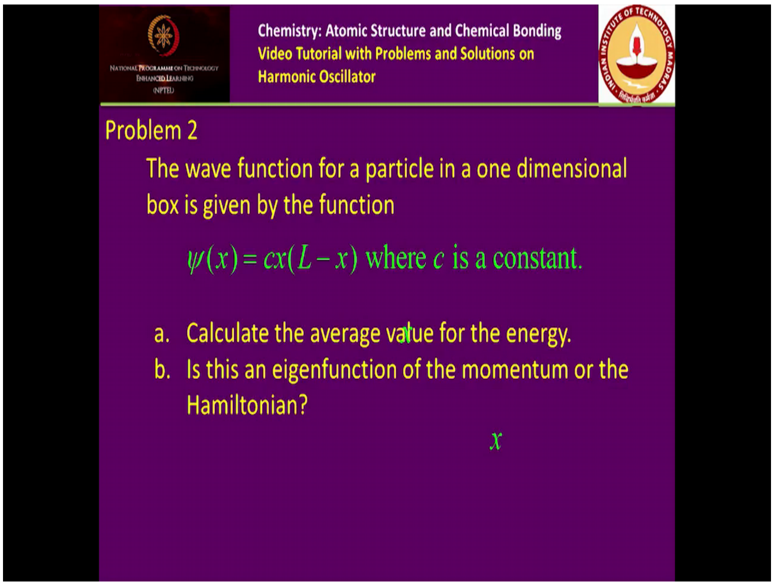

Now, the second problem this is problem 2. So, the second problem gives you a different wave function. The wave function for a particle in a one dimensional box is given by this function psi of x is equal to c x times L minus x. Where, L is the length of the box and c is a constant. Therefore, is asking you to calculate the average value ignore these 2 x's these are errors calculate the average value for the energy and the second is this an Eigen function of the momentum or the Hamiltonian ok. The second one should be obvious that it is not an Eigen function. So, that is the first thing we will do.

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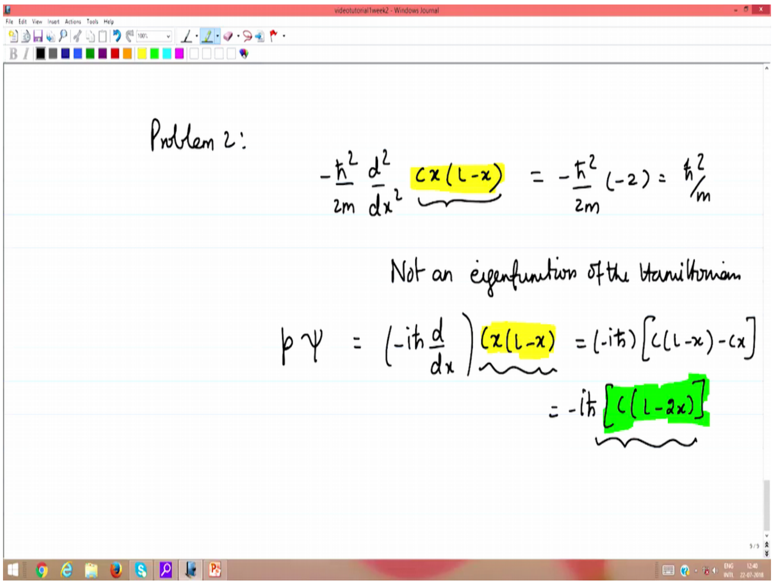

Problem 2 minus h bar square by 2 md square by d x square psi is equal to e psi is the equation that we solved.

Now, if you are given the psi as c x into L minus x c is the normalization constant does it give you this function back it does not. In fact, what you get out of this is minus h bar square by 2 m and there is only 1 minus x square term and that gives you minus 2. So, it gives you h bar square by m the function is not recovered. Therefore, it is not an Eigen function of the Hamiltonian. Likewise, if you think about the momentum operator acting on this function the momentum is minus given by the operator minus ih bar d by dx.

Again, acting on cx into L minus x gives you the answer minus i h bar times c into L minus x. If you differentiate dx and if you differentiate L minus x you get a minus 1 then you get a minus cx. Therefore, the answer you get is minus i h bar c into L minus 2 x this is not the same as c x into L minus x. It is different it is a different function. Therefore, this function that is given in this problem is not an Eigen function of the momentum operator as well as the energy operator. Why do we have to worry about it, I mean if you just ask the question if an arbitrary function is given when it if you do not know what the Eigen functions of a Hamiltonian.

One should be worry about arbitrary function because that is quantum mechanics, we never know in except for the elementary model problems the exact Eigen function of any problem. In fact, the search for the solution of the Schrodinger equation is the search for the exact Eigen function. Therefore, what we do is to express the Eigen for the supposed Eigen function. In terms of some arbitrary functions with specific properties and then we try to extract from that a relation to the Eigen function.

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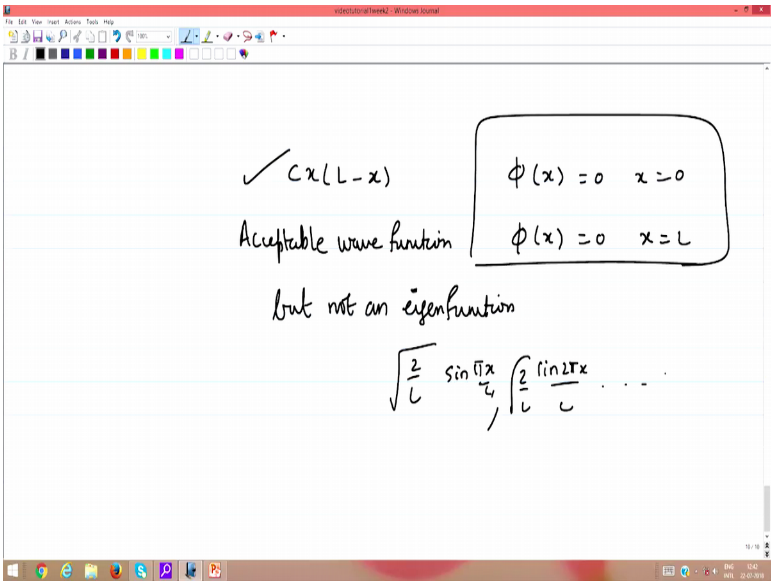

So, the fact that the function is given cx into L minus x as an arbitrary function is not entirely arbitrary, because it also satisfies the boundary condition that you require. Namely, phi of x is 0 at x is equal to 0, phi of x is 0 at x is equal to L. I think the boundary conditions cannot be violated by any of the arbitrary functions because if they are violated, then they have not even solutions of that particular problem. So, it is important that when you see arbitrary basis functions or arbitrary wave functions it is important to study their properties. First, verify that they satisfy all the boundary conditions for the solution in this case of course, it is 0 and therefore, it is an acceptable wave function, but it is not an Eigen function.

In the case of particle in a one dimensional box we already know all the Eigen functions and they are given by the formula root 2 by L sin pi x by L sin 2 pi x by L 2 by L, and likewise infinite number of Eigen functions are already known. Therefore, why do we need to worry about the c x into L minus x, because we do not know; what is the state of a system until we measure it and quantum mechanics tells you that when we measure it the result is one of the Eigen functions, and if the measurement is on the measurement of the energy.

The result is one of the eigenvalues until we measure we do not really know, what is the state of the system is or what the energy is. And therefore, we can only calculate an average value for the particle the energy an average value for the particle position the average being the average of many measurements. And the formula in quantum mechanics tells you that is the average of infinitely large measurements given by that integral formula. Namely, the expectation value of a is the psi star integral a psi of x dx for one dimension ok.

Therefore, the quite a lot of these concepts in the very early stages is I mean they can be exemplified by simple problems and it might take a while for you to get into it. But, it is important to solve these problems now the second question.

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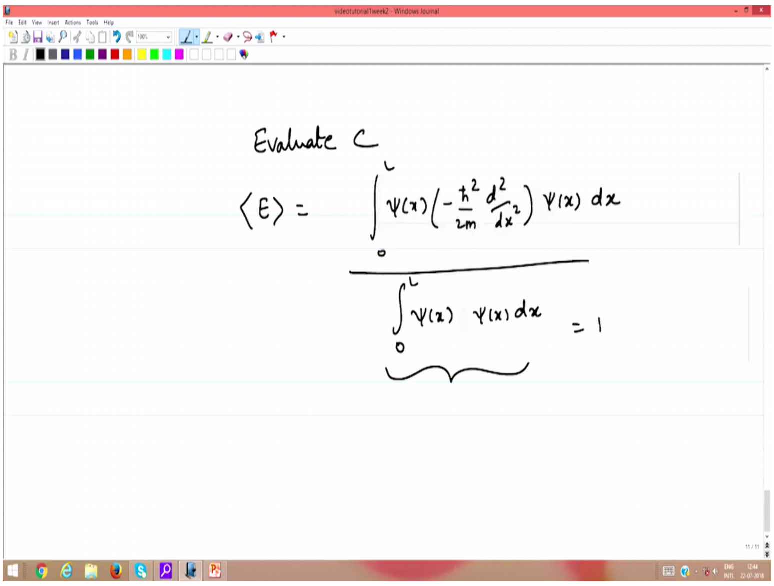

Second part of this question or the first part of this question is evaluate C. If I remember calculate the average value for the energy. Of course, we need to know what C is in order to do the energy calculation ok. So, that is one way of doing it namely if you want to calculate the average without evaluating c you can do it. Namely, you write to the wave function psi of x and the energy operator is minus h bar square by 2 m d square by dx square. For the particle in a one dimensional box, write psi of x dx between 0 to l, but since you know that the wave function is not normalized you have to ensure that the wave function is written psi of x psi of x dx 0 to L.

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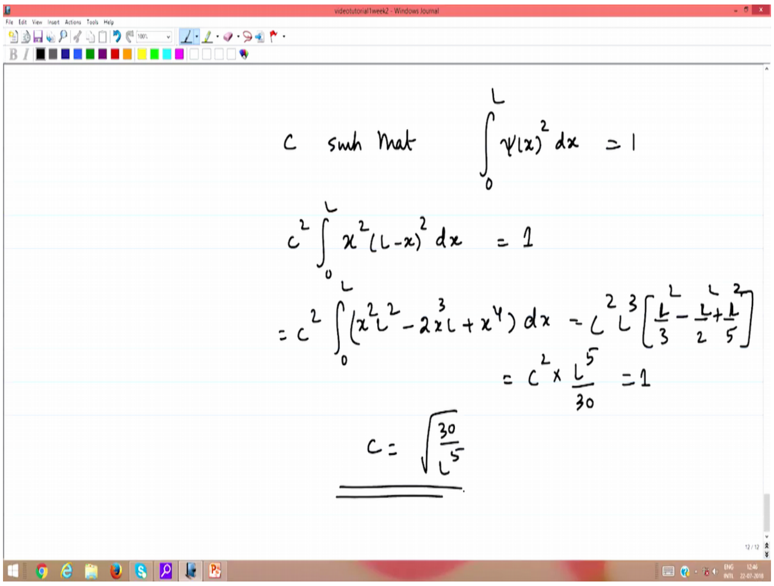

So, if we set this equal to 1 if not, the C square will cancel out and the lower integral needs to be calculated. So, let us do the following let us first evaluate C such that the integral psi of x square dx 0 to L is 1 ok. And in this case it is 0 to L C square x square into L minus x square. Dx is equal to 1 that is what we want for the wave function to be normalized. Therefore, it is easy to do this integral it is 0 to L it is x square L square minus 2 x L cube 2 x cube L plus x raise to 4 dx and between the limits 0 to L the x square gives you the integral gives you x cube by 3 and that gives you L cube by 3.

So, we can write to this straight away as L cube into 1 by 3 minus 1 by 2. This will give you x cube x 4 by 4. And therefore, will be L 4 by 4 with a 2 it is 1 by 2 and the other will give you 1 by 5.

So, the answer is and will also be an L square in each of them L square in each of them, because there is an L square here that is this is L raise to 4 and this is L raise to 5. So, what you have is c square into L to the 5 by 30 that should be equal to 1. And therefore, c is root 30 by L raised to 5. So, once you know this normalization constant

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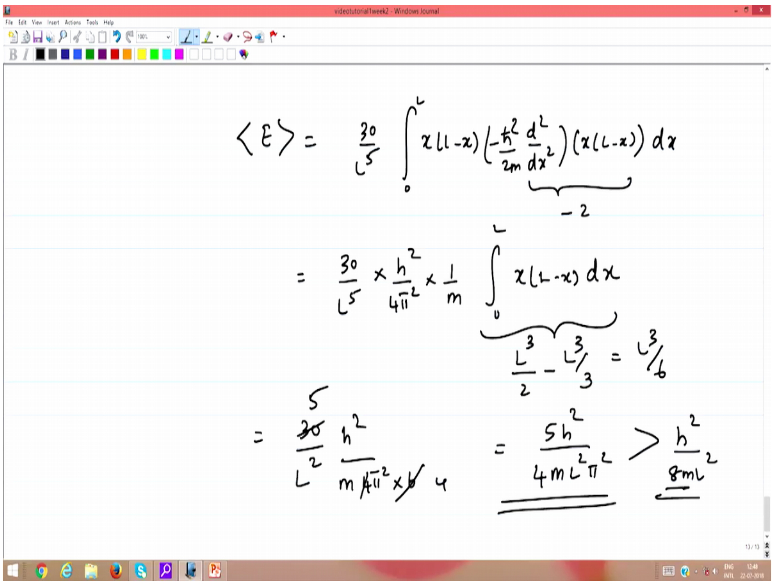

Then the energy average value it has to be average, because it is not like energy operator this function is not an Eigen function of the energy operator. And now you write 30 by L raise to 5, because of psi square and then you write x into L minus x to the operator minus ih bar minus h bar square; sorry minus h bar square by 2 m d square by dx square on x into L minus x dx and this gives you the answer minus 2. And therefore, you get plus.

So, you get 30 by L raised to 5 into h square by 4 pi square into 1 by m and then the integral between 0 and L x into L minus x dx. This is a very simple integral to do it is x square by 2. So, it is L cube by 2 and this is x cube by 3 and therefore, this is minus L cube by 3 and the answer is L cube by 6. And so, the final answer is 30 by L square h square by m into 4 pi square that is also a 6. So, this is 5 by 4. So, the answer is 5 h square by 4 m L square pi square and this is clearly greater than the lowest possible energy h square by 8 ml square.

Later, when you study the atomic structure you will realize that any arbitrary function will always give the Eigen. They will give you the average value greater than the exact ground state Eigen function it is called variational theorem. And we will see that, but you can immediately notice that an arbitrary function gives you values which are greater than the lowest eigenvalue ok. So, there are quite a few things which are exemplified by solving this problem. So, the next problem is to use the wave function.

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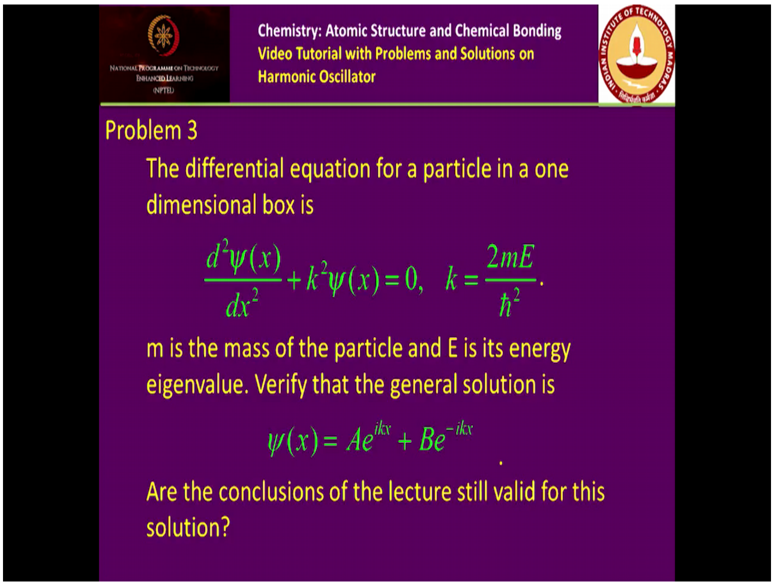

In a slightly different way, the complex form the particle in a one dimensional box the differential equation is given by obviously d square psi by dx square plus k square psi is equal to 0. Where, k is given by the parameter the 2 m by 2 m times E by h bar square.

M is the mass of the particle and d is it is energy eigenvalue the question is whether the following solution is also the right solution. Verify that the general solution is A exponential ikx plus b exponential minus ikx. Where, A and A are arbitrary constants are the conclusions of the lecture still valid for the solution.

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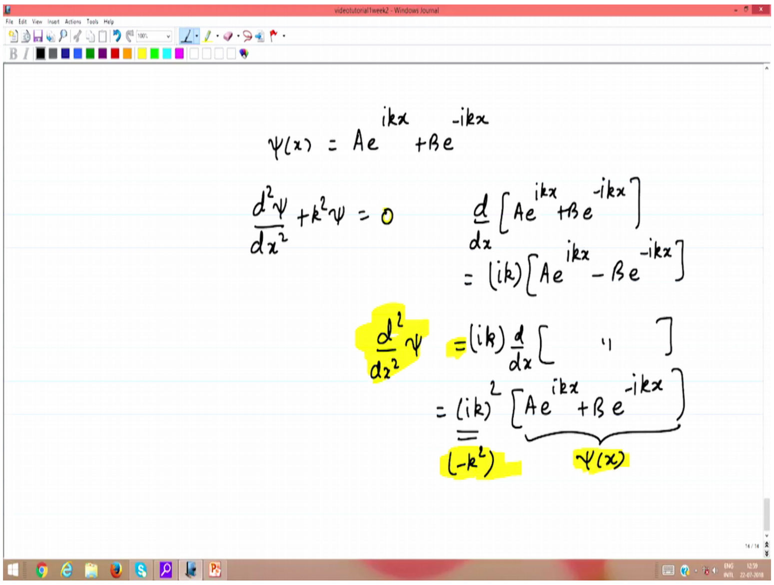

So, the wave function is psi of x is equal to A e to the ikx plus B e to the minus ikx. And the differential equation that we want to do check with is d square psi by dx square plus k square psi, what does it give you ok.

So, the first is to take the derivative d by d x of A e to the ikx plus B e to the minus ikx. The derivative gives you I k times A e to the ikx minus B e to the minus ikx and the second derivative d square by dx square on psi is one more derivative on this; i k d by dx on this whole function again the answer is I k whole square A e to the ikx again. But now the sin of b will change it becomes B e to the minus ikx and now you see that this is nothing but psi of x.

Therefore, I k square is obviously, minus k square. So, the differential equation that we have is d square psi by dx square and that is equal to minus k square times psi. So, that is the same thing as that therefore, this wave function gives you the answer that that it satisfies the differential equation d square psi by dx square plus k square psi 0 ok.

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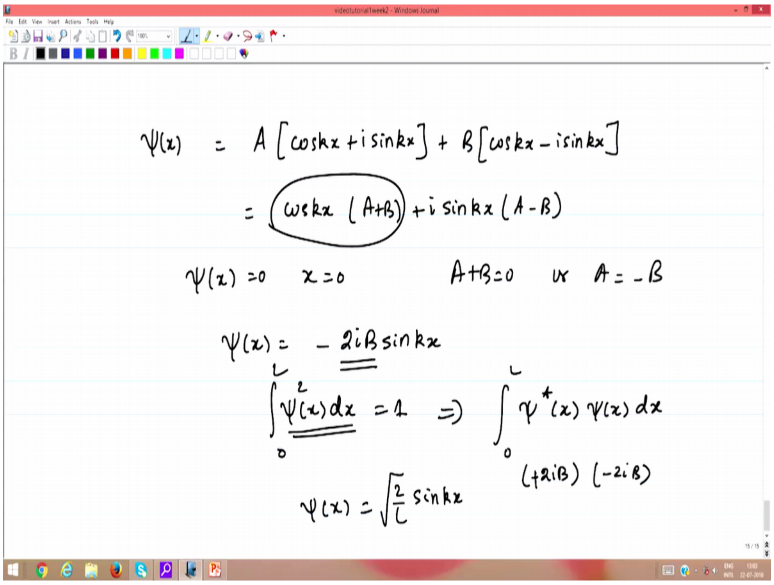

So, no problem it is also an Eigen function the and that should be obvious because, when you write a e to the ikx using trigonometric forms. It is cos kx plus i sin kx psi of x is equal to plus b cos kx minus i sin kx ok.

We want to find out whether the conclusions of the previous lecture using the cosine and sins are they valid using these functions ok. So, let us go back to the form and see if that is true. So, what you have is this is cos kx times a plus B plus i sin kx times a minus b now the conclusion is that psi of x should be 0 at x is equal to 0 which implies that when x is 0 cos kx is 1. Therefore, this gives you a plus B and this is 0 therefore, a plus b is 0 or a is equal to minus B when you substitute this into your equations psi of x when A is minus B you are getting psi of x is equal to minus 2 i B sin kx, because this term will go to 0 when A is equal to minus B.

So, you have that the only thing we have is minus 2 i B instead of B. In the lecture, but remember when you normalize the wave function psi of x square into dx is equal to 1 between 0 to L this integral. This, the 2 is irrelevant it will get cancelled out and the i now please remember this is true for the real functions. Whereas, the normalization integral in general for complex function is psi star of x psi of x dx between 0 to L. Therefore, if we have the wave function psi of x is minus 2 I B then psi star will be plus 2 I B. And the psi will be minus 2 I B and then the rest of it will be sin square kx and you will see that the complex number goes away. And we will be such that this whole thing will give you exactly the same result namely root 2 by L sin kx.

So, all the conclusions that we have by using the exponential formula are reproduced and they are no different from the functions. The trigonometric functions, because they are anyway linear combinations of the trigonometric functions 2 things are important one no matter.

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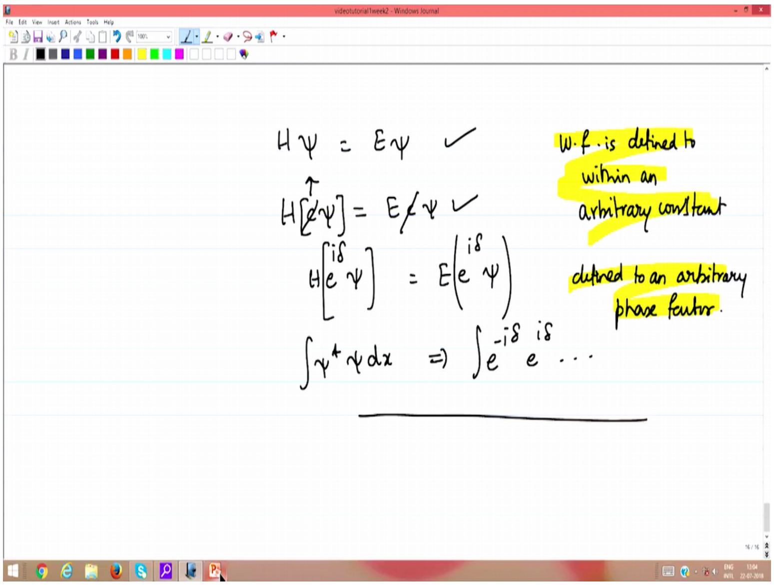

What constant you put in when you say H psi is equal to E psi if psi is multiplied by a constant c. Then H on c psi is e on c psi and therefore, the equation is still valid. So, psi is defined only with respect to a numerical constant the second thing is H psi if psi is multiplied by a complex number E to the i delta ok. And if you multiply on the right hand side also by E to the i delta psi. This is no different because when you write this psi star psi dx for normalization the complex number will go away E to the minus i delta E to the i delta times all the other things E psi ok.

Therefore, the wave function is defined to within a an arbitrary constant to be the same. And the wave function is also defined with respect to an arbitrary face the complex phase factor is irrelevant. For the wave function overall all right the purpose of bringing. In this problem, is to highlight these 2 conclusions; namely, the arbitrary constant and the arbitrary phase factor.

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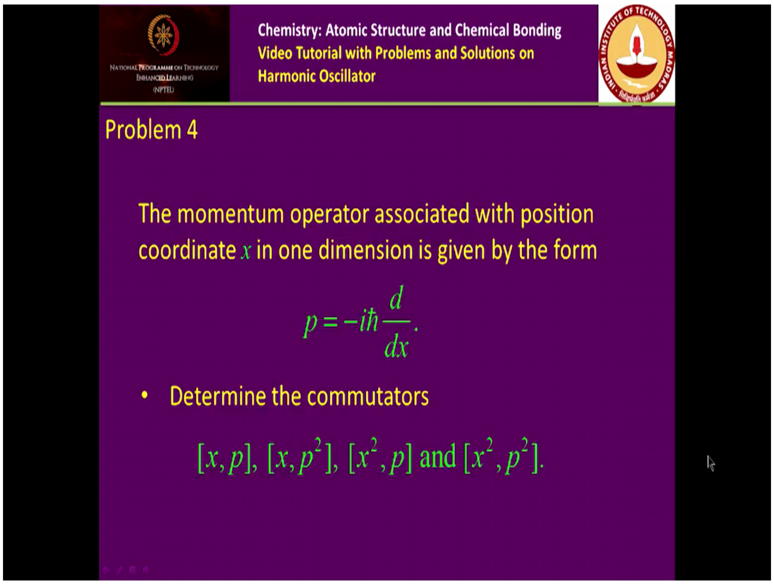

Let us go to the next problem: problem 4 is an algebraic computation for a calculation for you the momentum operator associated with the position coordinate x. In one dimension is given by, the form p is equal to minus i h bar d by dx. And therefore, you want us to compute. Calculate the commutators: commutators are important and commutator essentially I think it has been defined in the lecture if not let me do that now.

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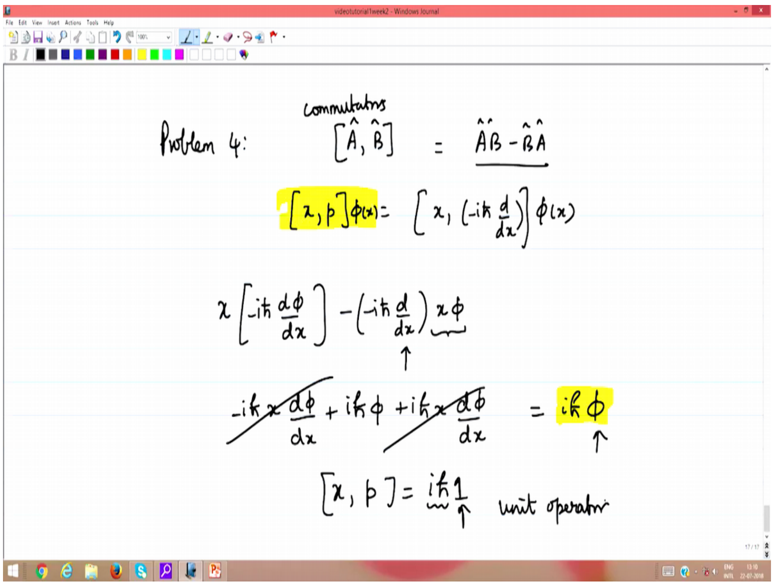

Let us go to problem 4: you have seen this in matrices in the mathematics earlier. The commutator of 2 operator 2, operators A and B is A B minus B A ok. These are operators therefore, sometimes I use the hats and sometimes I do not, but remember that in the context therefore, if you are asked to calculate the commutator x and p. It is the commutator of x and minus ih bar d by dx to evaluate this. It is easier for us to calculate this for an arbitrary function phi of x and then see how phi of x is the results are the same independent of what phi of x is. So, let us do that therefore, it is x into minus ih bar d phi by dx that is A B and then minus B A is minus ih bar d by dx on a phi.

Now, the operator d by dx acts on both A and phi and A is also a function of x and in this case what. So, the derivative here is minus ih bar x d phi by dx plus ih bar d by dx on x is 1. And therefore, you have ih bar phi and then the other thing is that d by dx operating on the phi which gives you plus ih bar x d phi by dx and these 2 cancel out. And so, the answer is ih bar phi, now phi is an arbitrary function for the commutator xp acting on and the commutator xp acting on that function is therefore, equivalent to multiplying that function by ih bar.

Therefore, the commutator equivalence is x comma p is equivalent to ih bar. Usually some textbooks write the unit operator in order to say that this is the left hand side is an operator in. Therefore, the right hand side should also be an operator, but remember the context the context says should be multiplied by ih bar and A unit operator ok.

So, given this the remaining commutators in the problem that you have in the problem that you have is the commutator x comma p square x square comma p and x square comma p square to be calculated. Let me do that very quickly also. And these are illustrative of the algebraic methods which are important in quantum mechanics let us go to.

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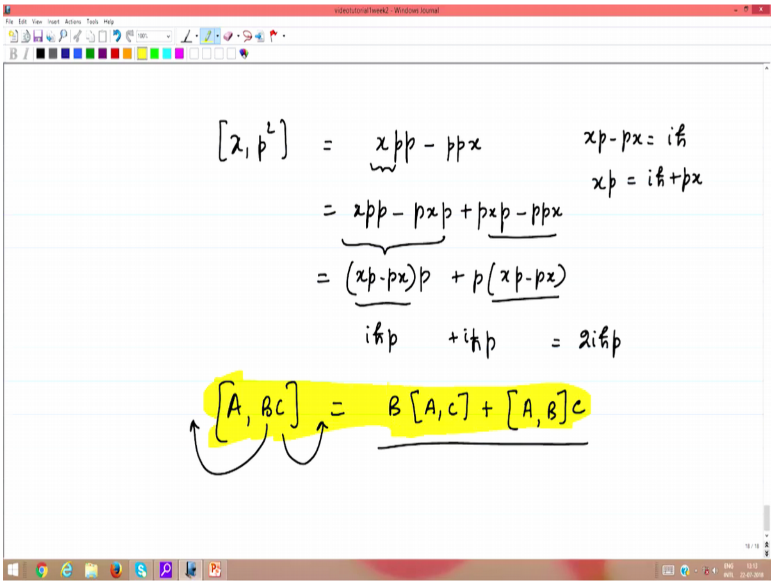

X comma p square ok. So, x comma p square if you recall the derivative the definition of the commutator it is x p p minus p p x. So, let me keep this x p in mind because we know the answer x p minus p x is ih bar. Therefore, we can write x p is equal to ih bar plus p x to solve that what we can do is to write x p p minus p x p and let us add p x p again and do minus p p x ok.

Now, look at this and this is x p minus p x on p and look at this is p on the left hand side x p minus px. Therefore, you know the answer this is ih bar p and you know the answer this is ih bar p. So, the answer is 2 ih bar p ok. In fact, if you have an operator A BC it is easy to remember the mnemonic that this operator commutator is given by the left goes to the left the right goes to the right and whatever remains as a commutator. So, if the left goes to the left it is B and the commutator is AC and if the right goes to the right the left over is the commutator A B and C is on the right side. This is the mnemonic this is how the rule should be remembered for operator commutations is exactly the same thing.

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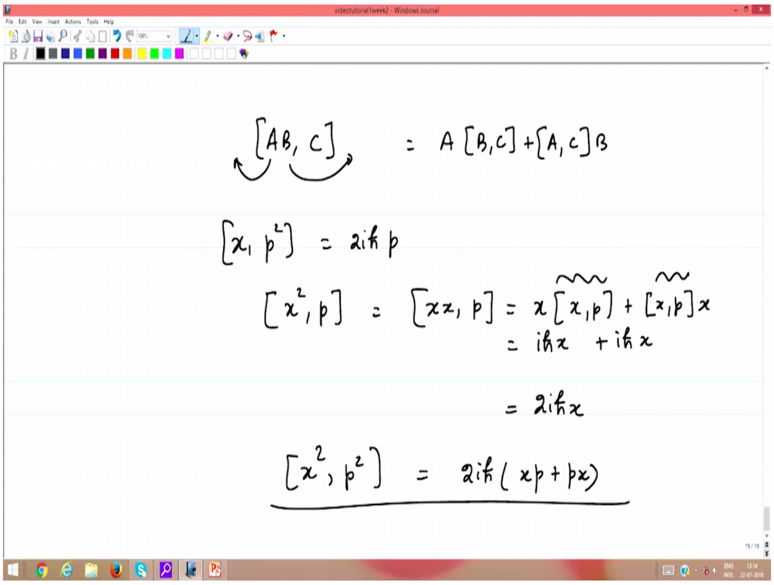

You can easily verify that if you have a b on the left hand side as a committed as an operator with the c commutator. Again the left goes to the left to the right goes to the right you will get the answer it is a times B comma C plus A comma C times B. Therefore, the operator x comma p square we have already done as 2 ih bar p what about x square comma p. Again, that is easy it is x x comma p. So, if you recall our rule of left and right A left is x with the now x comma p and the right is also x comma p with an x. And what you have is ih bar x plus ih bar x because, the commutator is ih bar times a number unit operator unit operator. Of course, commute with then the number goes away number commutes with all these operators. So, you have to ih bar x.

Now, I would leave it to you to show using the similar form that x square comma p square is 2 ih bar x p plus p x. Exactly the same way ok. So, this is to give you some handle on operator manipulations which are important because. In fact, very often many physicists believe that quantum mechanics is also stated in one line as the commutator between x and p being equal to ih bar that is a fundamental statement that was first identified by Werner Heisenberg and Max born and. In fact, the tombstone of max born is supposed to have this inscribed in the symmetry where max born is buried it is a fundamental statement ok.

So, commutators will become important as you go more as you read more and more in quantum mechanics let us go to problem 5.

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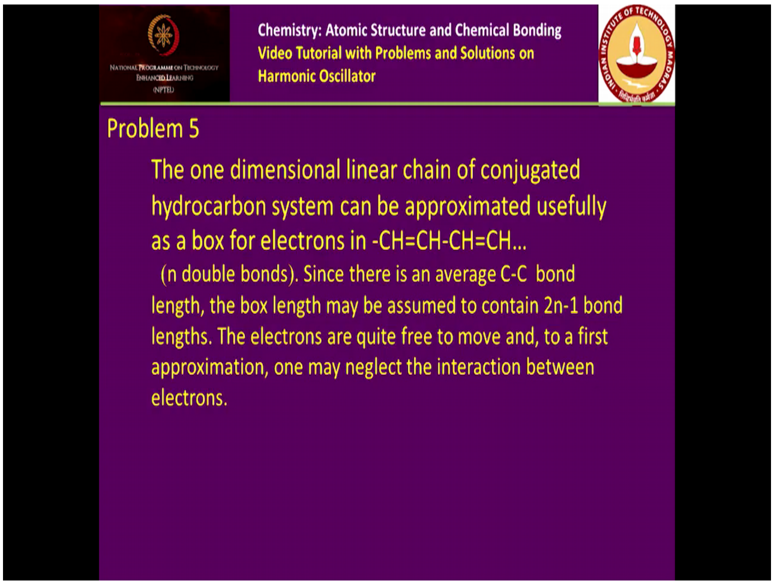

The next problem is a simple application of the one dimensional particle in a box to is a linear molecular systems. This is a standard example that you find in many books how to approximate the electronic states and also the transition between the different electronic states using the particle in the box for the specific case.

So, the problem reads like this the one dimensional linear chain of conjugated hydrocarbon system can be approximated usefully as a box for electrons. In this is the conjugated system CH double bond CH single bond CH double bond CH and so on. If there are n double bonds, then you can see that the chain has a certain length. And since that is the bond length is average bond length for C C the box length may be calculated and you can see that leaving adjust out there are 2 n minus 1 bond lengths.

The electrons are quite free to move and to a first approximation we neglect the interaction between the electrons. So, this is a statement what is a problem.

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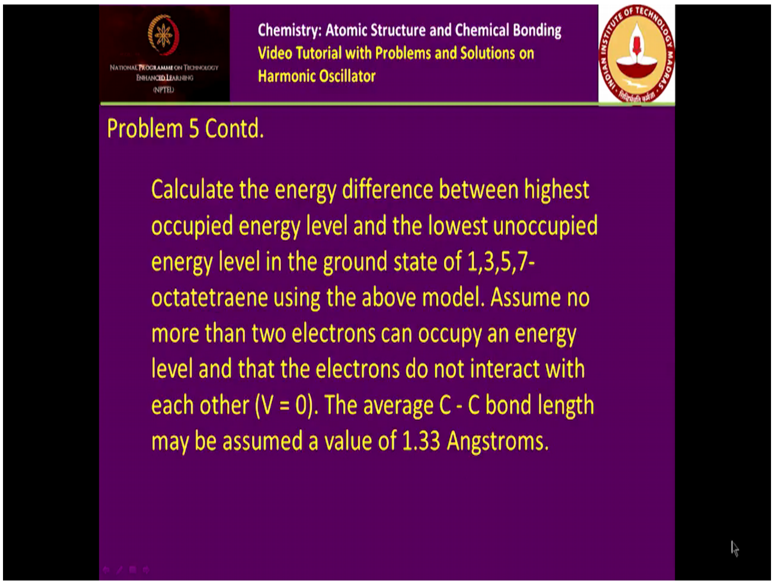

But that is a background now you calculate the energy difference between the highest occupied energy level, and the lowest unoccupied energy level in the ground state of one such conjugated system 1 3 5 7 octatetraene using this model. Now, in order to do this of course, there are other requirements; namely in each energy level of the particle in a box model that the electrons are supposed to be part of no more than 2 electrons can occupy an energy level. Recall the Pauli principle that that no 2 electrons will have all the quantum numbers identical.

So, keep that in mind that in any given energy level there are only 2 electrons and that the electrons also do not interact with each other. Therefore, the potential inside the box is 0 using the bond length of the C C 1.33 angstroms calculate the delta e between the highest n up to which the electrons are there and the lowest n in which there is no electron.

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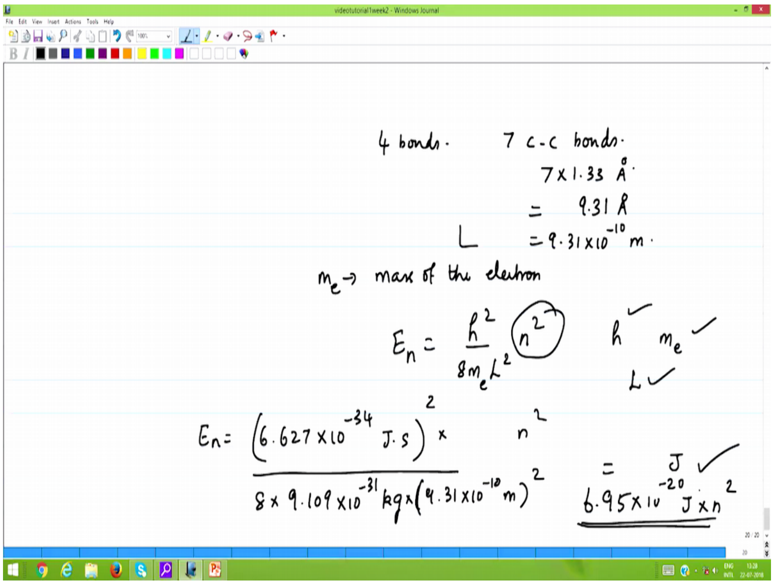

There are 4 bonds, the box length is about 7 C C bonds average. Therefore, the one dimensional box length is 7 into 1.33 angstroms. So, that gives you 9.31 angstroms or 9.31 into 10 raise to minus 10 meters in SI units. So, this is the L and the m is the mass of the electron single electron even though there are 8 electrons they do not interact with each other. Therefore, there are no other effective masses each electron behaves independently. So, the system is a particle in a one dimensional box with n electrons, but each electron is by itself therefore, the m is the mass of the electron.

So, it is easy to calculate this quantity the energy n in terms of h square by 8 m e mass of the electron L square n square h is norm m e is norm. L is now norm. And therefore, this number you can calculate as a function of m square ok. So, the answer turns out to be when you do these calculations ensure that you put the units carefully. So, that you do not make mistakes in algebra in numerical calculations. So, if you write the e n h square is 6.627 into 10 raise to minus 34 joule second. Whole square into n square divided by 8 into 9.109 into 10 raise to minus 31 kilograms for the mass of the electron. And then multiplied by 9.31 into 10 raise to minus 10 meter square into square.

So, you can see that the joule second will give you a kilogram meter squared per second will give you that per second. And then the units will give you joules when you cancel the units the numbers are fairly straightforward to calculate. I would not do this the actual calculation of these numbers I think from what I have done the answer turns out to be 6.95 into 10 raised to minus 20 joules in to n square if you think it is verified it is if it is wrong let me know. And I will correct to that, but this is the number I have this is n square.

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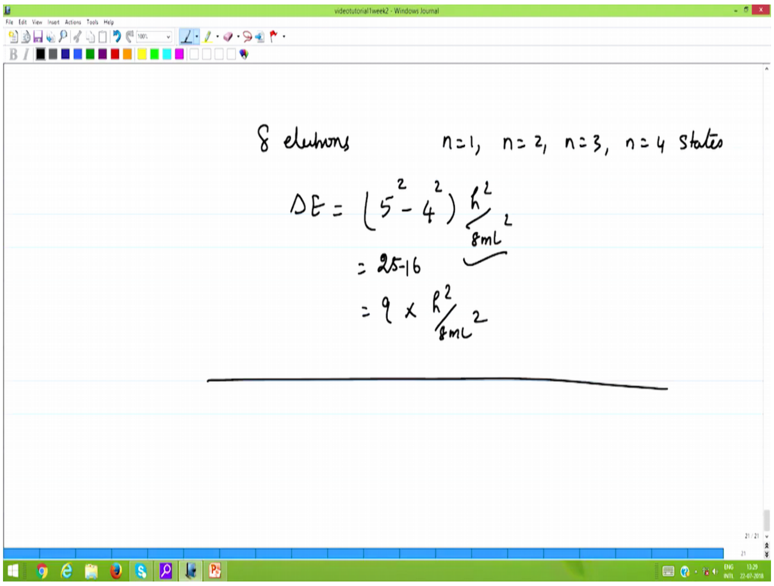

Now, you are 8 electrons conjugated each double bond has 2 electrons which are mobile. And therefore, the 8 electrons will occupy n equal to 1 n equal to 2 n equal to 3 and n equal to 4 quantum states. Now, for the delta e is the highest the difference between the energy of the lowest unoccupied level which is n equal to 5, 5 square minus the highest occupied level 4 square times h square by 8 m L square. This you already know and this is nothing but 25 minus 16. So, this is about 9 times h square by 8 m L square. So, it is fairly simple problem.

But this is important to give an approximate estimate of the energy of transition for the electronic states in a linear system. And likewise you can calculate it for other systems using elementary models ok.

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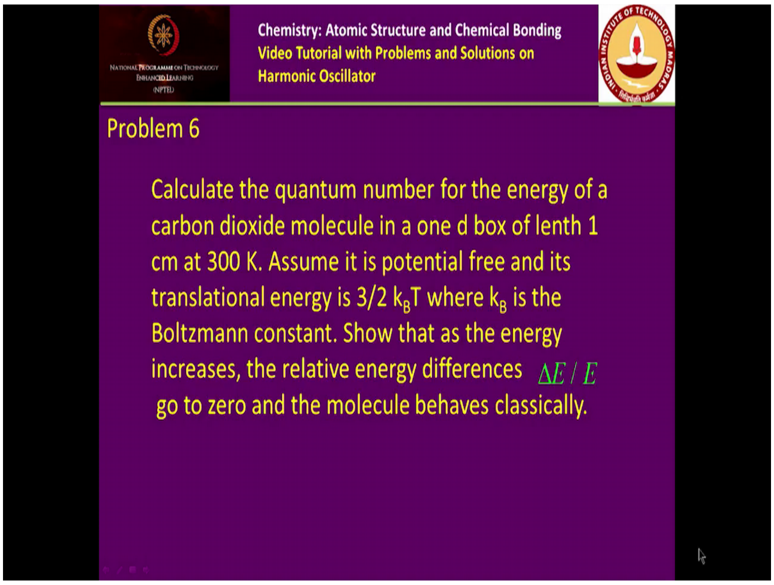

Let us go to the next problem, problem 6 is the calculation of the quantum number for the energy of carbon dioxide molecule in a one d box of length: l e n g t h, there is a spelling mistake, but anyway one centimeter at 300 Kelvin. Assume it is potential free that is the carbon dioxide moves in a box which is potential free and carbon dioxides translational energy is 3 by 2 kb t where kb is the Boltzmann constant.

So, one has to calculate the n given the energy E and one also notices that as the energy increases the relative energy differences between the energies delta E by E they go to 0. And therefore, the molecule behaves classically as e becomes very large now the important point for this for this problem is that the length is given us 1 centimeter. This is a macroscopic dimension and for microscopic dimensions quantum conditions are not really important. And you would see that the quantum number corresponding to this value of energy 3 by 2 kb t or the electron in a box of one centimeter is ridiculously high the quantum number.

Therefore, you would see that it is not a quantum state it is almost like a classical state; let us see.

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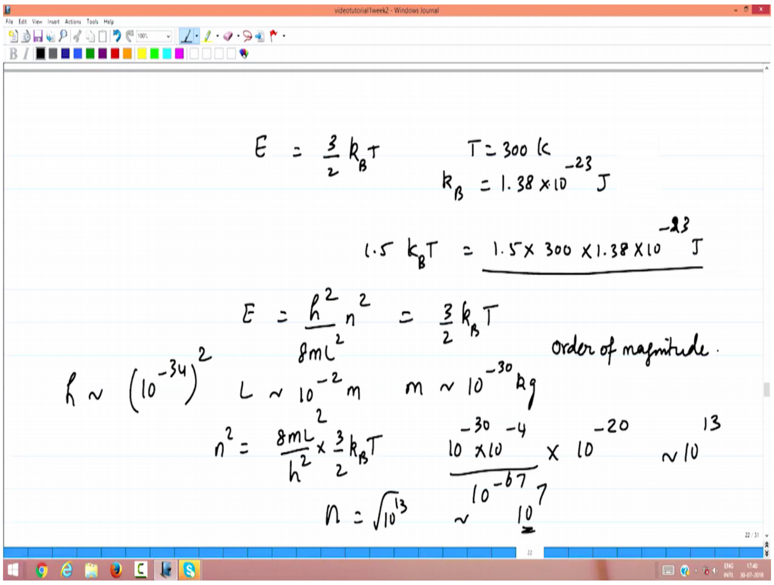

Quickly what that is all about so when you say that the energy E is 3 by 2 K BT and T is 300 Kelvin and K B is 1.38 times 10 to the minus 23 joules. So, you know what kbt is and 1.5 it is 1.5 times 300 into 1.38 into 10 raise to minus 23 joules. This is the E and this E is given by h square by 8 m L square n square and that is the K BT 3 by 2 K BT.

Therefore, to evaluate the n let us do what is called the order of magnitude I do not want to do exact computation, but I will simply give you the orders h is of the order of 10 to the minus 34 joule second.

So, h there is a 6 point something let us not worry about it the square and L is of the order of a centimeter. So, it is 10 raise to minus 2 meters and the mass of the electron is approximately 10 to the minus 30 kilograms is 9 point something 9.1 into 10 to the minus 31 which is 10 to the minus 30 kilograms. Therefore, if you want to calculate the n square it will be 8 m L square by h square into 3 by 2 kb t.

So, K BT we have approximately 10 to the minus 21 into 3 into 1.5. So, we can put it approximately as 10 to the minus 20 and the mass is 10 raised to minus 30 and the L square is 10 raised to minus 4 and the h square is 10 raise to minus 68 6 into 63 points. So, it is 10 raised to minus 67, now if you look at this number this is minus 30 4 minus 20 and this is n square let me see the numbers are right m is 10 to the minus 30 L is 10 to the minus L square is 10 to the minus 4 h is 10 h square is that. So, into 10 raise to minus 20. So, the order is 30 4 20 50 4 and 10 to the minus 67. So, this is 10 raised to 13 therefore, n is a square root of 10 raised to 13 of the order of 10 raise to 7 is a ridiculously large number.

But the point to be made is that for a macroscopic dimension for a thermal energy which is like 300 Kelvin, which is very high a temperature for a molecular system you see that the quantum numbers are ridiculously very very large. And therefore, quantum mechanics is not very relevant for microscopic system that was the whole purpose of this exercise the second thing that you have to do is remember.

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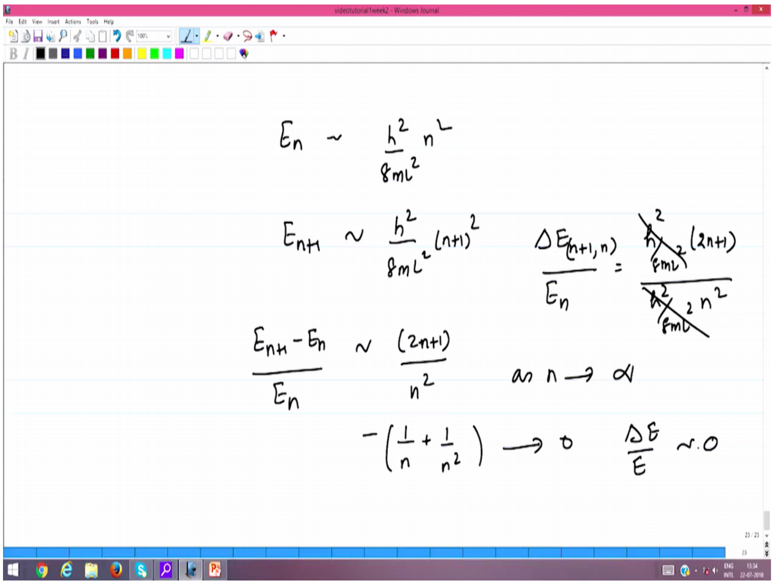

When E n is given as h square by 8 m L square times n square E n plus 1 which is the next level is; obviously, h square by 8 m L square into n plus 1 whole square. Therefore, delta E n plus 1 minus comma n I would say delta E is between these 2 levels divided by E n. If you calculate, you see the answer is h square by 8 m L square into n plus 1 whole square minus m square gives you 2 n plus 1 divided by h square by 8 m L square n square.

So, this goes away. So, what you have is essentially E n plus 1 minus E n divided by E n is 2 n plus 1 by n square as n goes to infinity this goes as 1 by n plus 1 by n square. And therefore it goes to 0, therefore delta E by E goes to 0 for very large values of E which means that the energy levels are too dense and they are.

So, continuous that the quantum description of energy discretization is not no longer relevant that was again the purpose for giving this problem to see; what is the classical limit? Or what is the correspondence? What is called the Bohr's correspondence problem limit? Namely the masses are very large the energies are very high or the box dimension is the macroscopic dimensional boxes all these things give rise to classical results. Next problem please which is now for a particle.

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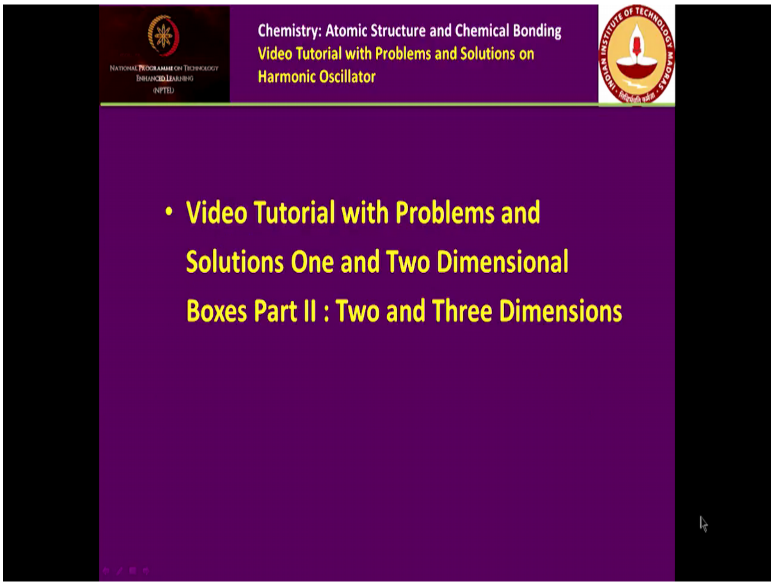

In a two dimensional box, I mean it is a two and two dimensions, but I think I am only having some examples of 2 dimensional problems ok.

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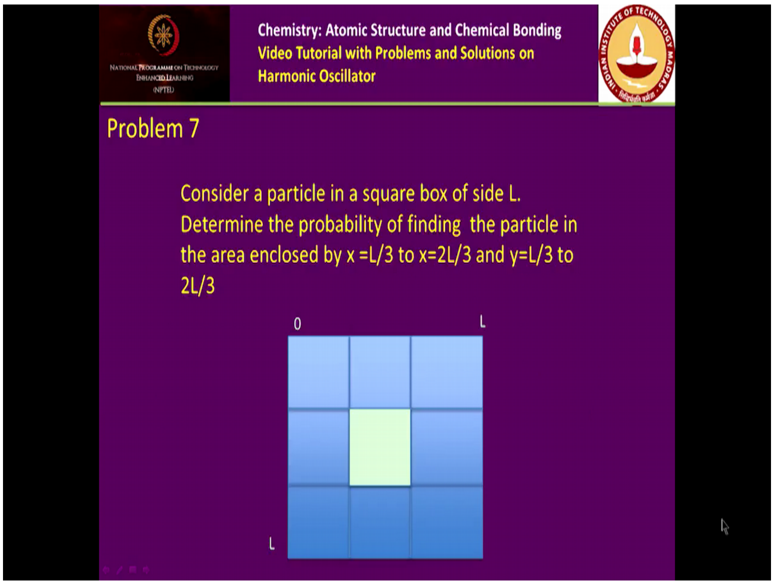

Some examples of two dimensional problems ok: so here it is a very simple algebraic exercise to calculate the particles probability. So, consider a particle in a square box of side L determine the probability of finding the particle in the area enclosed by x is equal to L by 3 to 2 L by 3 here, and likewise y is equal to L by 3 to 2 L by 3. So, this is the highlighted area what is the probability of finding the particle in that area it is just an simple formula which you have to remember psi x of y for any arbitrary quantum number n1 n2.

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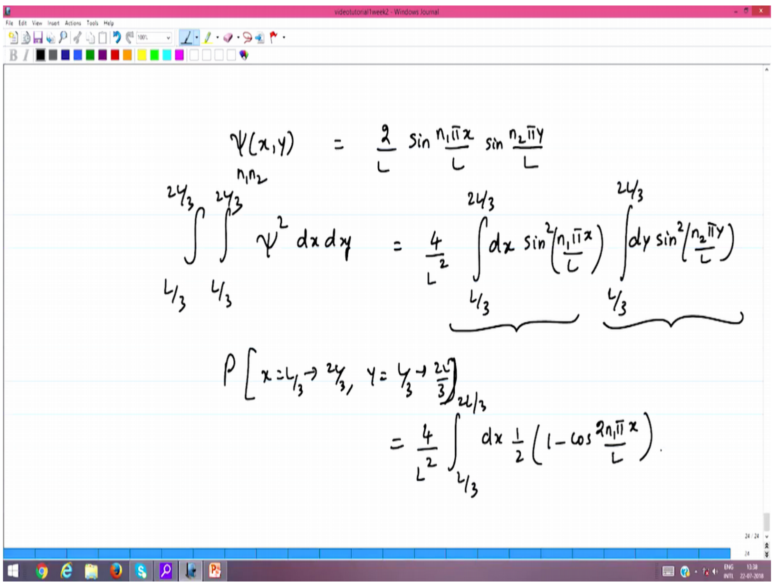

You remember particle in a two dimensional box has 2 quantum numbers this is given by the formula 2 by L sin n1 pi x by L sin n 2 pi y by L. Therefore, psi square dx dy between the limits L by 3 to 2 L by 3 L by 3 to 2 L by 3 is what we are asked to calculate. And that is given as 4 by L square between the limits L by 3 to 2 L by 3 dx sin square n 1 pi x by L times the integral L by 3 to 2 L by 3 limits dy sin square n 2 pi y by L.

So, these are the 2 integrals that give you the probability of finding the particle between x is equal to L by 3 to 2 L by 3 y is equal to L by 3 to 2 L by 3 ok. This integral is fairly simple for you to evaluate. And therefore, I am not going to write the answer, but will just write the next step namely it is 4 by L square integral L by 3 to 2 L by 3 dx into 1 by 2 1 minus cos 2 n1 pi x by L times the corresponding integral for the y.

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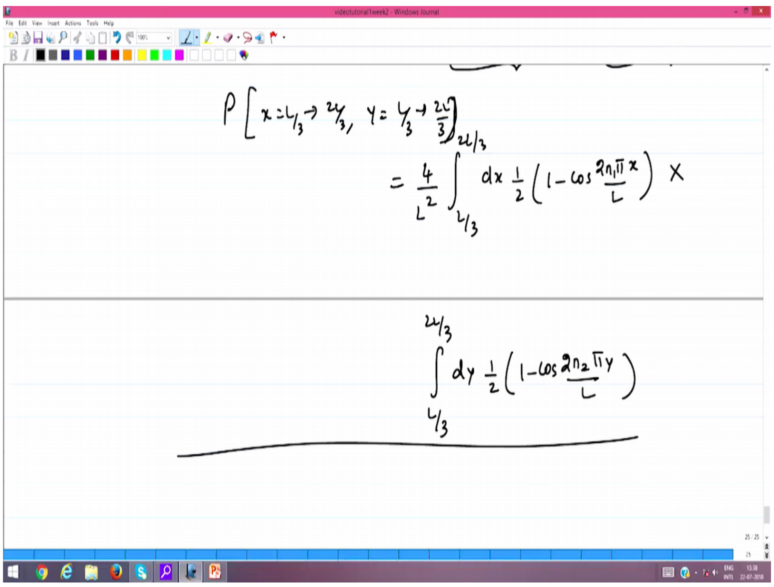

Integral between the limits L by 3 and 2 L by 3 dy 1 by 2 1 minus cos 2 n 2 pi y by L. This is easy to evaluate and I will not worry about giving you the final results you can calculate them.

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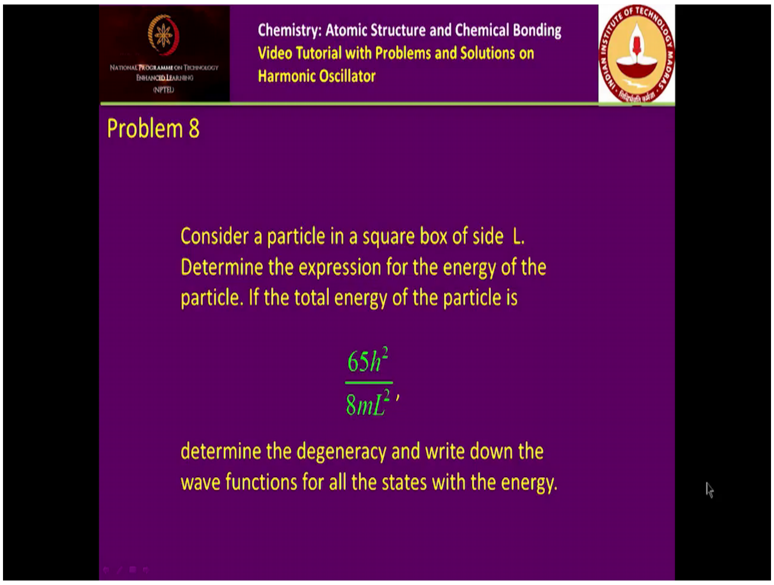

The next problem is on understanding the degeneracy consider a particle in a square box of side L. Determine the expression for the energy of the particle it is a textbook, it is there in the lecture if the total energy of the particle is 6 65 h square by 8 m L square. I mean this number was chosen to illustrate the degeneracy determine the degeneracy and write down the wave functions for all the states with the energy ok.

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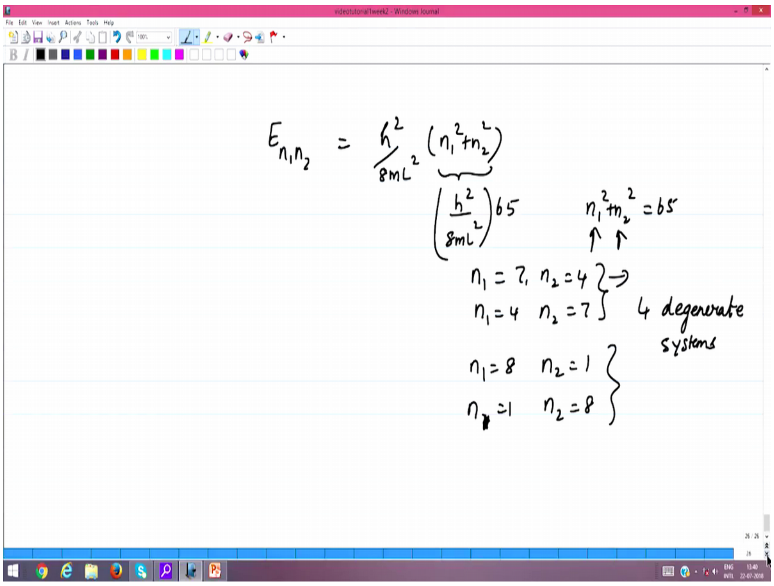

Now, the first one is the expression for the energy of a particle in a two dimensional box and that all of you gone through the lecture know that, it is h square by 8 m L square for a square box it is n 1 square plus n 2 square ok.

Now, the sum total is given as 65 and you can see the rest of it is the unit for the energy h square 8 m L square. And so, you have n 1 square plus n 2 square giving you 65. So, find the n 1 and n 2 what are all the choices that you have obviously n 1 is equal to 7 n 2 is equal to 4 is one possible choice, and then the degeneracy implies that the n 1 is equal to 4 and n 2 is equal to 7 is also the degenerate state. But these are not the only 2 states here. N 1 is equal to 8 and n 2 is equal to 1 will also give you 8 square plus 165. Here, it is 7 square plus 4 6 4 square which is 65 and likewise n 1 is equal to 1 n 2 is equal to 8. So, there are 4 degenerate states.

Now, what will come to you as a surprise and you will see that in the future.

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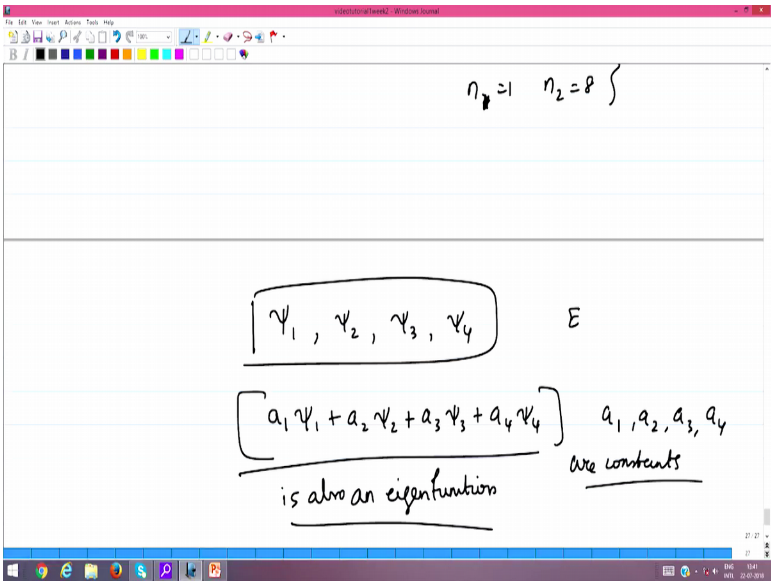

When you do more quantum mechanics is that when there are degenerate states psi 1 psi 2 psi 3. For example, here psi 4 there are 4 degenerate states not only that these have all the same energy, but any linear combination of these 4 states a 1 psi 1 plus a 2 psi 2 plus a 3 psi 3 plus a 4 psi 4. Any linear combination where a 1 a 2 a 3 a 4 are constants they can be real or complex numbers any such state is also an Eigen function.

Therefore, when you talk about degeneracy the linear combination of degenerate states themselves are Eigen functions of the Hamiltonian if the states are Eigen functions of the Hamiltonian. And there are infinite combinations, but linearly independent number of eigenstates for degenerate systems will be the same as the number of degenerate states. So, in this case there are 4. So, you may choose infinitely many choices for a 1 a 2 a 3 and a 4, but only 4 out of them will be linearly independent of each other. Everything else can be expressed as a linear combination of these 4.

So, the dimensionality of the degenerate states is given by the simple exercise that you see and writing these states is fairly straightforward for you namely; I will write this for one.

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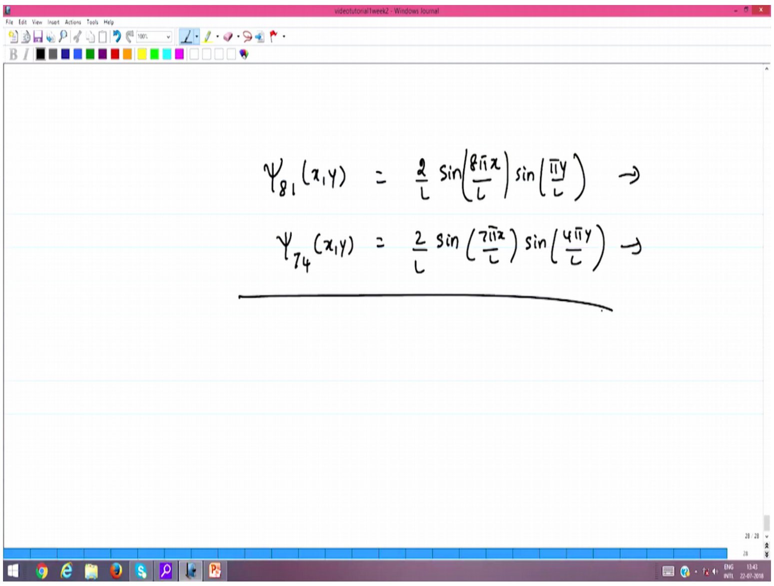

State psi 8 1 x comma y is in our notation it is 2 by L sin 8 pi x by L sin pi y by L quite obviously the other psi 7 4 x comma y is written as 2 by L sin 7 pi x by L and sin 4 pi y by L. And there are 2 more states for each one of them with the 8 and one interchanged and 7 and 4 interchanged. So, these are the 4 states that you have. I think that is what this problem is asking you to do if the determine the degeneracy and write down the wave functions ok.

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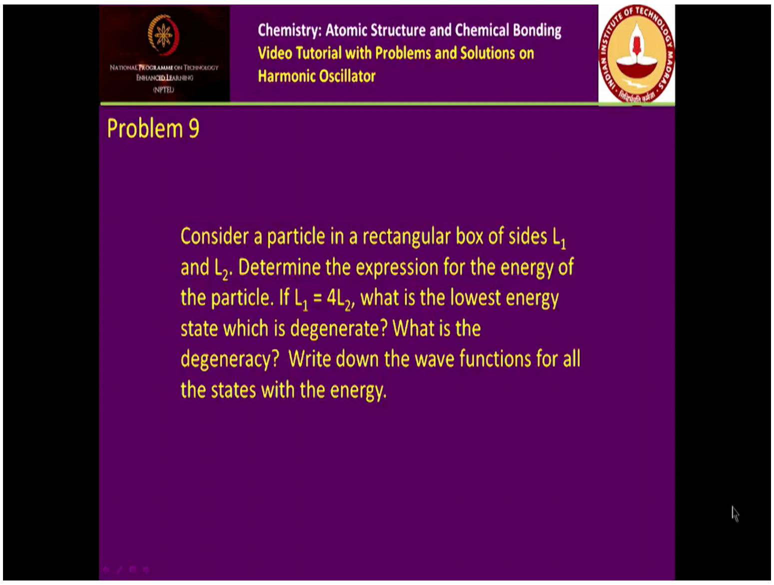

Next problem is a problem of a rectangular box with sides the L 1 and L 2 and the question is to find out the expression for the energy of the particle. And for a specific ratio L 1 is equal to 4 L 2 what is the lowest energy state which is degenerate and what is the degeneracy write down the wave functions for all the states with the energy. Again, I shall indicate the solution not write down the solution verbatim if you need it I will always do that in a piece of paper and put it upon the website. But, understand what it means a square box is one in which L one is equal to L 2 and everything ls is rectangular or any other shape that you have.

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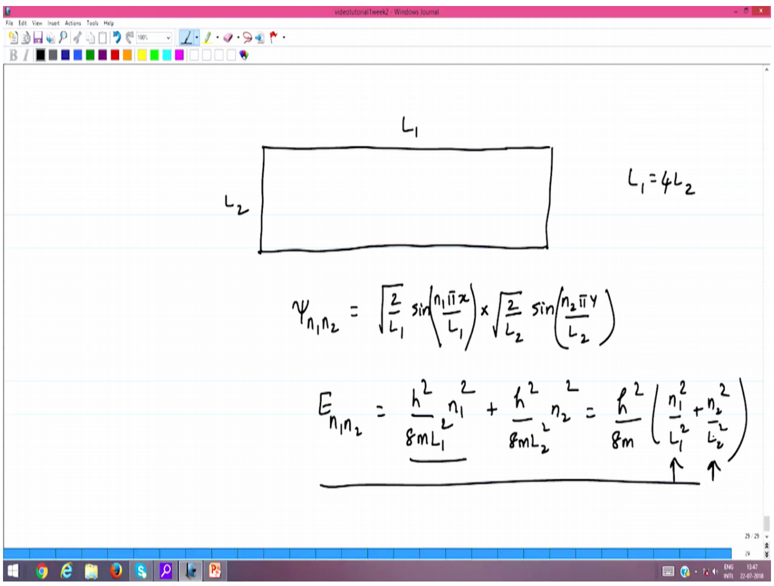

So, if you have this picture should be if this is L 1 this is 1 2 3 about maybe just about this that is L 2.

L 1 is 4 L 2 therefore, this is L 1 and this is L 2 L 1 and L 2. Now, the I mean you can call it x or y what is important is the wave function psi n 1 n 2 is going to be for the one dimension it is root 2 by L 1 sin n 1 pi x by L 1. And for the second dimension if you recall is were 2. One dimensional problems therefore, the second dimension the normalization is 2 by L 2 square root sin n 2 pi y by L 2 in the case of a square box. Since L 1 and L 2 were the same the root 2 by L and root 2 by L came 2 by L and the expressions were very simple.

But this is the rectangular box and therefore, correspondingly the energy e. N 1 n 2 is the sum of the 2; one dimensional energies which is h square by 8 m L 1 square n 1 square. This is the energy in the dimension of L 1 and the other energy is h square by 8 m L 2 square n 2 square. Therefore, to write this in common form it is 8 m n 1 square by L 1 square plus n 2 square by L 2 square this is the expression for the energy. When you have a rectangular box the n 1 and L 1 go together. N 2 and L 2 go together when these 2 are equal we had the simpler expression. So, this is what you have to remember.

Everything else is finding out the corresponding numbers of L 1 and L 2 if L 1 is 4 L 2.

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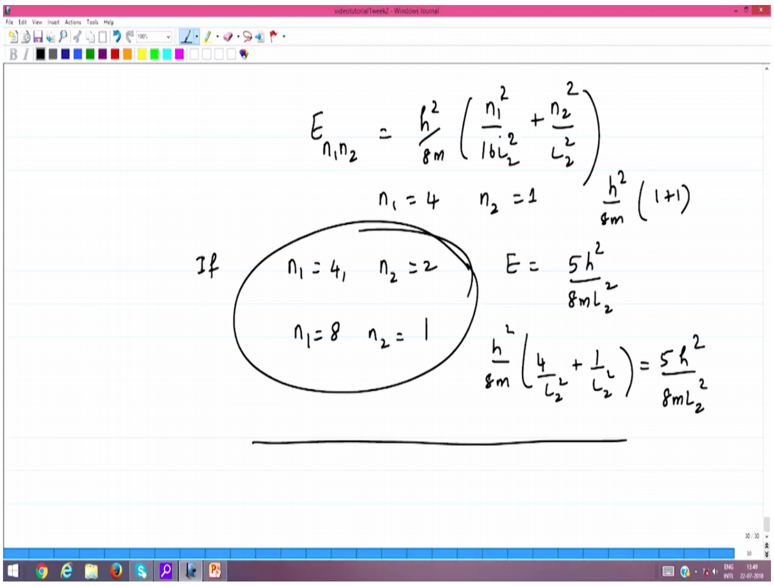

What it means? Is the following we have the energy for the particle in a box given by h square by 8 m L 8 m n 1 square by L 1 square it is 4 L 2. So, it is 16; 16 L 2 square and the other one is n 2 square by L 2 square. Now you have to find degeneracy for n 1 and L 2 I will give you a simple solution if n 1 is equal to. Let me see if the n 1 is 4 and n 2 is 1. What we have we get h square by 8 m 1 plus 1 2 does not do anything.

Now, if n 1 is 4 and n 2 is 2 e give is given by 4 is 4 square is 16 1 and 2 square is 4 this gives you 5 h square by 8 m L 2 square this is L 2 ok. And the other possibility for which you have the same energy is n 1 is 8 and n 2 is one you can calculate this as h square by 8 m if it is 16 it is of course, 64 by 16. So, it is 4 by L 2 square and the other 1 is 1 by L 2 square. So, you also get 5 h square by 8 m L 2 square ok. So, these 2 states n 1 is equal to 4 and n 2 is equal to 2 and n 1 is equal to 8 and n 2 is equal to 1 these are degenerate states.

Now, verify whether this is the lowest degeneracy or not I will leave it to you as the problem ok.

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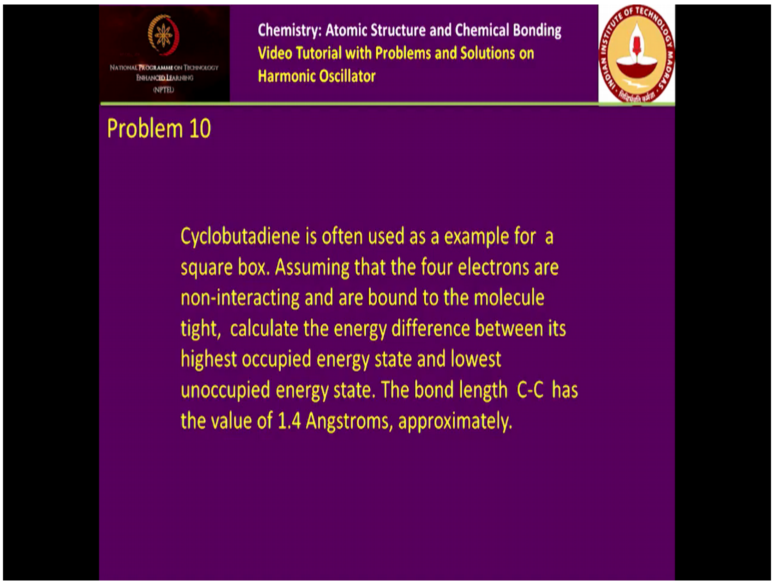

The last problem that, we have for this video tutorial is the model similar to the particle in a 1 dimensional box for a linear chain. Now, we have a square box and the square box is ideally modelled with a cyclobutadiene. As an example, I mean these are approximate models and it is used often as an example for a square box and cyclobutadiene has 4 electrons, which are relatively freer than the others. And assuming that they do not interact I mean these approximations are you have to take them with a little bit of care these are to illustrate what is meant by a model.

So, if the 4 electrons are assumed to be non-interacting and are bound to the molecule tight; you can calculate energy difference between again the highest occupied energy state and the lowest unoccupied energy state. It is a square box and you are given the bond length therefore, you can calculate the sides of the square that is the length of the box. So, let us see the answer.

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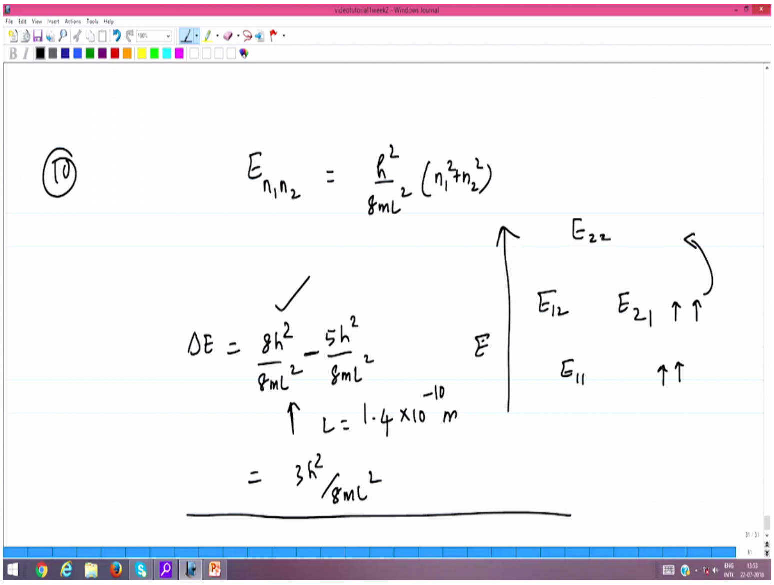

E n 1 n 2 is h square by 8 m L square for the square box is this problem 10. N 1 square plus n 2 square you can write E 11 here E 12 E 21. Here and E 2 2. The energy is now in being standard increasing progression. So, you can put 2 electrons in this and you have 21 electrons in each of these levels.

And so, what is the transition that is happening is one of the electrons going up 2 to 2. So, the delta E that you are calculating is between 1 2 or 2 1 which is 5 h square by 8 m L square. That is the lower energy it is also minus sign and the higher energy is 2 2 which is 8 h square by 8 m L square. L is given as 1.3 what is a number I believe 1.4. So, this is given as 1.4 l. So, you can calculate into 10 raise to minus 10 meters and h is known and mass is the mass of the electron. And therefore, the energy difference between the highest occupied state and the lowest occupied state is 3 h square by 8 m L square ok.

Now, this is the first of the few video tutorials I would like to have for solving problems which are slightly longer than a simple one dimensional quiz with multiple choices ok. Therefore, what is important for the listener is to tell me if such video tutorials are useful and if you would like me to prepare more of them I mean obviously I cannot prepare many more, but at least about 5 or 6 such tutorials for the entire course or even more maybe even up to 10 tutorials.

Because, we have a 12 week course it is possible for me to prepare, but your input and feedback is important for me to continue this process for supporting the lecture materials with problem solving skills and enabling you to look into more and more detailed problems. I hope you will enjoy such tutorials in the future until we make the second tutorial or until we meet next time with the lectures.

Thank you very much.