Introductory Quantum Chemistry
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Lecture - 9
Particle in a Box - Part III

Good morning and thank you for being here. Now, if you remember I was talking about the particle in a 1 dimensional box we solved this equation for the particle. We found the so called the stationary stare which I mentioned which as I mentioned where just the standing wave patterns that you would expect in the one dimensional system.

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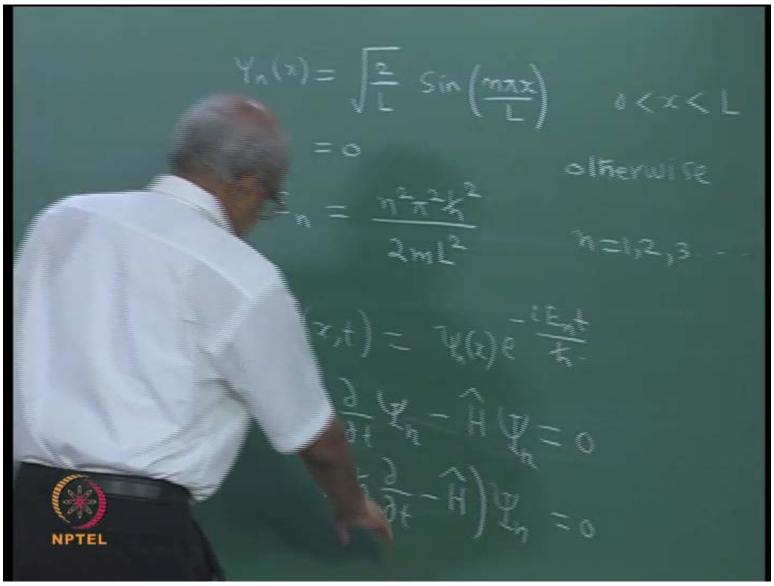

And, let me just write the wave functions and their loud energy levels; we found that the wave functions were given by these were the wave function if x was between 0 and L. And the wave function would be equal to 0 if x is south side and these functions had an energy and the n could take the value as 1, 2, 3 etc. And if you remember n equal to 0 is not allowed because then the wave functions would identically vanish everywhere. And further this function will give me a total wave function; when I say total wave function it is a function of x as well as t, which we have seen would be given by the sine of (x) into a to the power minus i E n t by h cross that is what it is.

So, this is the time dependent wave function for the stationary stare. And this given by such an expression each value of n will give me a different possible stationary stare characterized by a different function capital psi. And what about this capital psi to this equation i, h cross doe psi by doe t is equal to H psi or maybe I will write this equation in a slightly different fashion I will take this to the left hand side. So that I shall get a negative sign and the answer must be equal to 0 right.

So, any side that you have of this form maybe I can put a subscription to n here because I itself never depends upon n. And that psi n will actually obey this equation correct that is how it is this you does not matter what the value of n is it will always obey that equation. And maybe I can even write it in as slightly better form by removing this psi n outside. So, I will have i h cross doe by doe t minus H operating psi n would be equal to 0.

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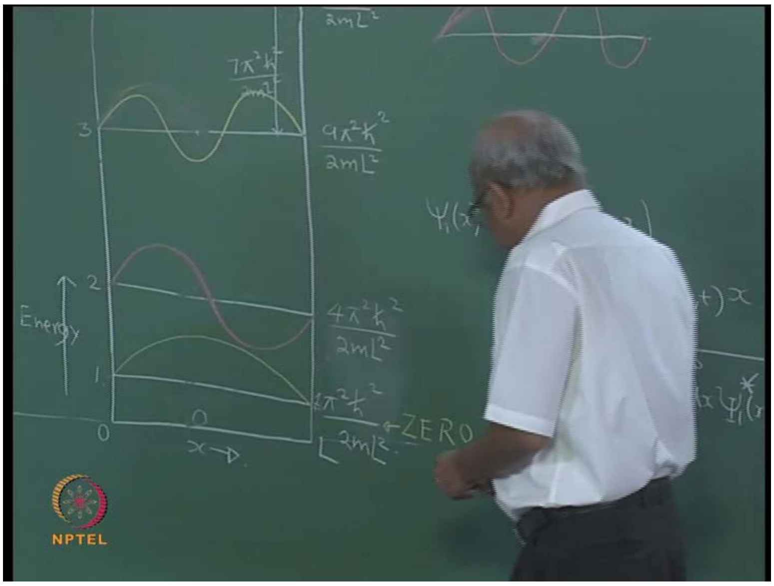

Let me remove that. So, these are the equations that we have. I will also represent the allowed energy levels of the system this is my box extending from 0 to L. And along this axis actually we are going to represent energy. And if you are thinking of potential there remember while we do it actually like this. See in this region the potential of the infinity in that reason also potential energy is infinity well inside the box a potential is 0. And then we look at the loud energy levels you can put n equal to 1 L equal to 0 is not possible as I said you can put n equal to 1 what is going to happen is you we are going to get energy; which may be somewhere pi square, h cross square divided by 2 m L square can represent that in this picture may be much well; maybe I should write little bit lower.

Now, you notice that the energy this is actually the stare that has the lowest energy but it is energy is not 0. Now, if you are thinking of about this system classically; suppose, I have a classical particle which is trapped in a in a box. And what can happen is the particle can be just sitting in the box without moving. I have a particle which is just inside the box without moving. So, it will be sitting somewhere where there is no absolutely no kinetic energy because it is not moving right. And the potential are inside the box you see therefore, the total energy classical energy can be 0.

So, the particle maybe just sitting here like that if it was obeying classical mechanics. And then it can have n as a 0 or in fact, it may be moving. So, suppose it is moving which is going in this direction then it will hit the wall and be reflected. And I can give it any energy I like. So, therefore classically speaking the particle can have any energy which is starting from 0 to any large value right. But that is not possible in quantum mechanics what is just happening in quantum mechanics was first of all you find that energy cannot be 0; not only that energy can have only certain values. So, we say that only certain discrete energy levels are possible for the particle.

So, these stationary stares have only certain discrete while release for their energies. And what are their lowest possible one; we have found is so much pi square, h cross square by 2 m L square. And you mean you can actually as why is it that the particle cannot be simply be sitting at one location why is why is not that this is possible in quantum mechanics? The answer is actually quite simple; imagine that you have a particle just sitting at a particular location then I know where exactly the particle is therefore, it is uncertainty in procession will be 0. Because if it is sitting somewhere precisely then uncertainty momentum; so that an uncertain procession will be 0.

And, if it is not moving it has no momentum. So, you essentially means that momentum is 0. So, therefore there is no uncertainty in procession and there is no uncertainty in the momentum. And delta x is 0, delta p is also 0 which means that I would have a situation; where the uncertainty principle would be wile average right. That is the reason why energy equal to 0 is not possible for this particle which is confined within a box; because it would simply violate the uncertainty principle. So, the lowest way possible energy level for the particle is this one.

The next one is how much you put n equal to into 2. So, you are going to get energy which may be somewhere here; that will be 4 pi square h cross by 2 m L square. So, this has n equal to let me, write the value of n here this is n equal to 1, this is n equal to 2 and then you will have n equal to 3 somewhere here; notice the way I draw this picture. This is the next aloud energy level it is value will be 9 pi square h cross square upon 2 m L square. And notice you see the this gap is only pi square h cross square by 2 m L square; while that gap it will be 4 minus 1; here, you have a 4 there you can say there is a 1.

So, this gap is actually 3 times that gap; that is important to notice this while you think of this gap how much it will be it will 9 minus 4; which is actually going to be 5 times pi square h cross square by 2 m L square. And this will go on happening if you go. If you looked at the next level actually may be I can just draw it here. But it may not be accurate actually the spacing I mean it is difficult for me to show it now. But you know that spacing in going to be how much? This is n equal to 4 it would have an energy of 16 pi square, h cross square by 2 m L square. And this gap will be how much it is going to be 7 times pi square, h cross square divided by 2 m L square.

So, therefore this is another interesting thing this spacing between successive energy levels actually increase as you go up. And further what I will do is I will also represent the wave function in this same picture, so that whatever wave length is there in this picture. So, the wave functions the way I am going to draw them is a percentage here; as well as, this function is concerned that will be the wave function it is 0 there, it is 0 there and the maximum value is right in the middle.

The next stage I will represent with the different color the wave function will be looking like this it has a node in the middle so it would like that. Now, while the lowest one the wave function is positive everywhere so that there is no node. The next one has actually 1 node right in the middle of the box. So, there the function is 0 to this side function is positive, while to the other side right the function is negative. What about the next one it would have 2 nodes and it would look like this. Well, the way I have drawn this figure you see it is not easy; you see it is not possible for me to draw the fourth wave functions.

So, I will just draw it here the important thing is that you see here there is 3 nodes. So, let me put the nodes 1, 2 this nodes you see these are the nodes. So, the function would be like this. So, these are my wave functions. But then let us imagine that it is sitting in the particle is sitting in the ground stare; then the wave function would be square root of 2 by L, sine pi x by L this is the lowest of possible stage. The lowest possible stage is actually referred to as the ground stage of the system. The next possible one is referred to as first excited stage, second excited stage, third excited stage right.

And, imagine that you have a prepared system, imagine that it is in contacts I mean, this my system is a particle. But imagine that this interacting with the surroundings. And the surroundings is at a temperature of t; that may be a room temperature. Then what will happen is that I mean I suppose, you know a little bit about these you will have a Boltzmann distribution of the particle right. When, the particle may be in this stare or may be in that stare or may be in that stare with what is refer as a Boltzmann distribution; which will depend exponentially upon the aloud the energy of the particle. But suppose your surroundings is a 0 Kelvin which is an idealized situation. And if the surroundings is at 0 Kelvin what will happen is that your particle will be in the lowest possible stage.

But even in that lowest possible stage the particle has an energy. So, even if the system is at 0, even if the surroundings are at 0 Kelvin, even when it is in the lowest possible stage the system has an energy. And so therefore, this energy that is processed by the particle even at 0 Kelvin is referred to as 0 point energy; where, I can did may be here 0 point energy why do you say that this is the pseudo code energy. Because even in the lowest possible stage the system has a non 0 energy; that is why you say it is pseudo code energy. I mean, I have considered 0 leave this system of ((Refer Time: 16:25)).

Actually, classical mechanics what will happen is that it will not do anything it will not move it will be just sitting there and the energy would be actually 0; but quantum mechanics does not allow that right. And that even at absolute 0 this system would have that much energy. And we have seen the reason for this the reason is simply your uncertainty principle. If the particle just sat there without moving that will violate the uncertainty principle would. So, it has been moving.

Now, let us look at this particular function; this is the function that we refer to us as psi 1 of(x) remember this is only the time in independent part; that means, it is only the position dependent part of the wave function and the function has this form. In fact, yesterday I had drawn the value of psi 1 square; how it would look like. And the maximum or the most probable position I showed that these are the middle of the box. But now suppose, I can do some experiment where I will measure the position of the particle right. Then what do you find? Most of the time you will find that the particle is right in the middle but then of course, other procession are also probable.

And, therefore, what will happen is that when I do the experiments remember our process number 3; each time you may get the different answer. And suppose I make an average of all this measurements what will be the answer? As you remember the average of large number measurements would be given by the expectation value of x which I can calculate from my knowledge of the wave function.

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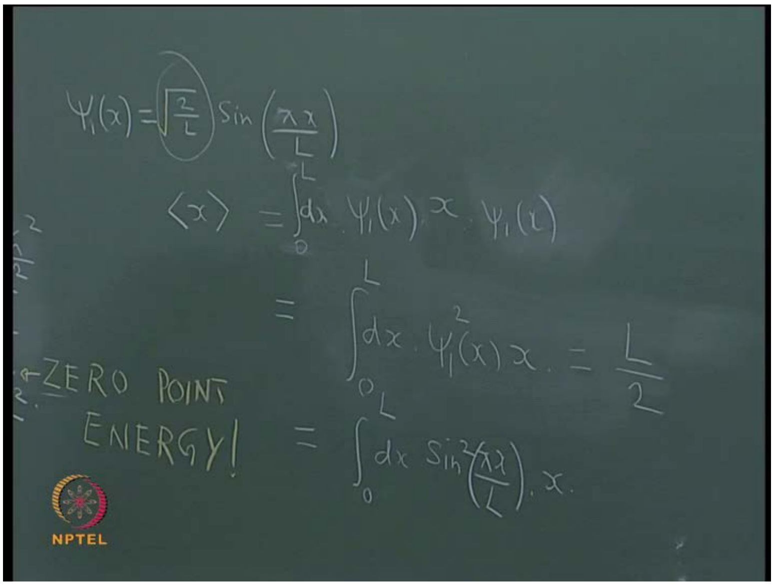

How would I calculate that? Well, actually the way I would have to calculate this I would have to have the operate associated with procession which is just x itself. I will have to allow that to operate upon in principle I should say psi 1(x, t) and psi 1 star (x, t). And then multiply it by d x integrate from minus x infinity to plus infinity. And divide this by integral minus infinity to plus infinity d x psi 1 (x, t) star, psi 1(x, t) d x this is our more very detail expression. But you would realize from old discussion yesterday that there is a time dependency here, there is a time dependency there. But stationary stages are such that the time dependence from here will become exactly cancelled by the time dependence from there. And what happens is that this psi 1; this is not really necessary to you use that capital psi 1. But it is enough if you just use this psi 1 right.

So, let us do that let me remove make that simplification remove this with psi 1 of (x) and that with psi 1 star of (x). Because there is time dependency but that time dependency gets exactly cancelled. Time dependence of one is cancelled by the time dependence of the other that is what we saw yesterday. And not only that it is necessary to integrate from minus infinity to plus infinity but it is enough if it integrates from 0 to L. Because it is only in that region that psi 1 of (x) is non 0. And you can do this same kind of thing below down here; you can say well you would have psi 1 star f(x) and psi 1 of (x).

And, again you do not need to integrate from 0 to sorry, minus infinity to plus infinity. But it is enough if you integrate from 0 to L and to do this. But then of course the wave we have taken this function remember we did calculate this. And how did we calculate that we arrived at this expression; this square root of 2 by L by usineg the normalization condition by imposineg the condition that this integral is when evaluated the answer is 1; that is how this is square root of 2 by L was done. Therefore, if I am usineg that function actually this integral I do not have to perform because I already know what the answer is, it is 1.

So, this is the object that we have to evaluate and even here you can make simplification. Because if you look at psi 1 there is no effect of star operation taking the complex of integrate does not effect it; because it does not contain square root of minus 1. So, even that can be removed. And therefore effectively what is it that I have after all these simplifications; what I have is integral d x of psi 1 of (x) is actually referring 2 times. So, psi 1 square x into x is the integral that I have; I mean, of course I can calculate this I will do that.

But let us just think about the problem physically. I have a particle which I know is somewhere between 0, x equal to 0 and x is equal to L. And further if I look at the most improbable position; which is this point L by 2. If you look at the wave function you will find that this wave function is actually symmetric about that point. And if you look at the square of the wave function you will find that the even this square of the wave function is symmetric about that point; which means, that when I make a measurement it may be to the particle may be found to the left of this point or to the right of the point with equal chance.

And, therefore what would you expect the average to be? Obviously, the average has to be equal to L by 2. Because the particle may be to the left of that point or may be to the right of that point with equal likelihood. And therefore even without doing this calculation I can make a prediction that it has to be equal to L by 2. And this is exactly what happens? I will not do the complete integral because the integrals are not that difficult. But I will tell you how it comes ((Refer Time: 23:41)). If you integrate from 0 I mean, the integrals that you have to perform is integral 0 to L, d x, sine square (pi x divided by L) into x.

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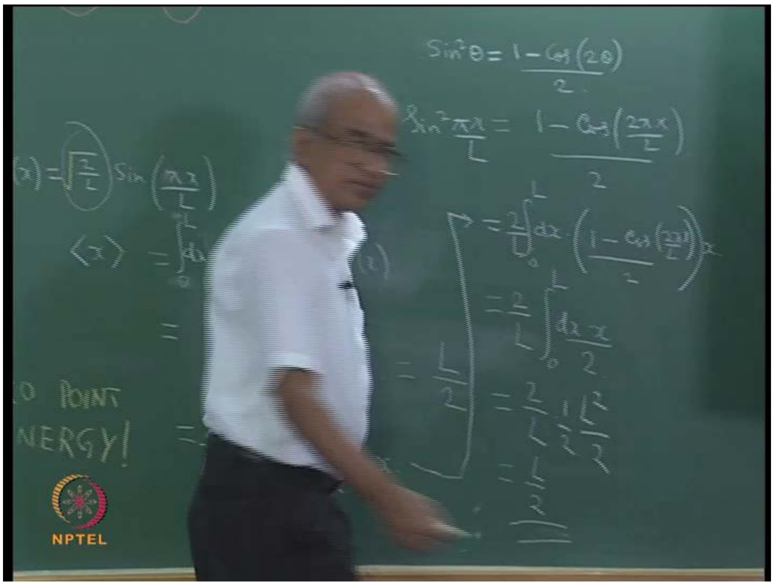

So, here you see you have sine square. But there is a trigonometry identity that you can use sine square theta is actually equal to 1 minus cos 2 theta divided by. So, you can use this trigonometry identity. So, instead of that sine square by x, by L you can actually write sine square pi x by L; may be written as 1 minus cos (2 pi x by L) divided by 2. Now, what you can do is; we can substitute that in here then you will see that there are 2 times correct there are 2 times in the integral; what happens is that the first time is non 0 value; where at the second time you will find that the second time is identically equal to 0.

And, the first time so let me just look at the first time what is the first time? Integral into L, d x. The first time is simply well I did make a mistake did not I? At this point I did make a mistake. Because psi 1 of (x) actually condemns where is it? Square root of 2 by

L as I did not write this; square root of L I just wrote the sine square there. So, therefore I have to correct for that mistake; there will be a 2 by L sitting here correct. So, therefore I should have written that I would have 2 by L. And then I would of course have this sine square which is actually going to give me 1 minus cos 2 pi x by L divided by 2 into x.

So, that is what integral lies. But then obviously as I told you there are 2 times the first time will come from here, the second time will come from there. But that second time I am not actually going to evaluate other than ((Refer Time: 26:47)). If you did evaluate the contribution from that time it is going to be 0; maybe you can do this as an exercise. And then what will happen to the other time I will get 2 by L, integral 0 to L, d x into x is what you are going to get from the first term.

And, there this is a half. And this is pretty straight forward integral what will happen is that you will get 2 by L into L square by 2 as there is a result of doing the integral there is a half already there. So, therefore, this is what will happen. And if you cancelled all these things properly what is the answer. The answer is going to be L by 2 this is which I would have expected physically any way. Now, interestingly you see I have done this calculations for the first the lowest possible stage. But I can do the calculation for the any stage.

But do I need to do this calculation you can use your physical argument; whatever, be the stage you take sine coir effect you see you will find that it is symmetric around the middle point. And therefore it does not really matter what the stage is; what I would expect is that the average value of the procession should be L by 2. And that you can easily calculate and show but it is not necessary, because the physical intuition tells me that has to be equal to L by 2, because simply because it does not matter what the value of n is psi n square is going to be symmetric about the matrix of the box. So, having completed that calculation let me look at the expectation value of momentum the particle is moving only in one direction. So, any momentum that I would like to think off would be denoted as p x.

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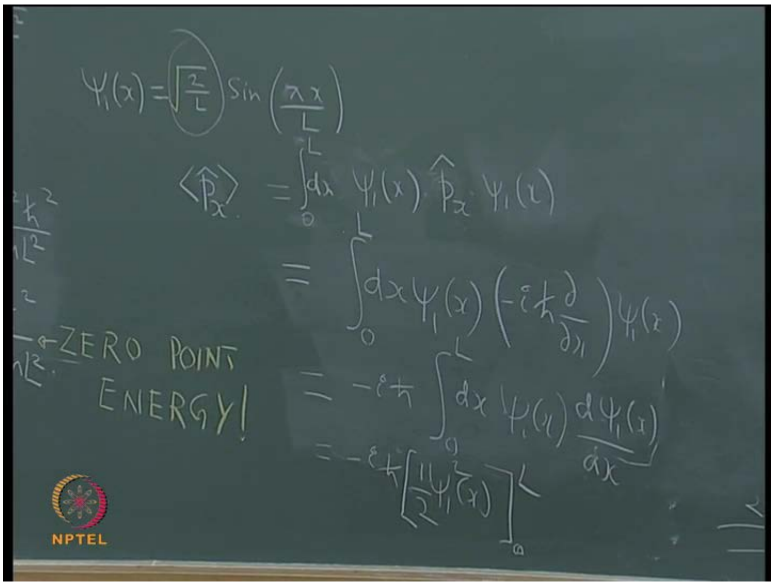

Say, if you wanted to calculate the expectation value of p x actually to be very precise. I should say the operate associate with momentum that is the expectation value what is it that? I am trying to calculate the particle is within the box. I want to calculate the average value of momentum; if I can make it large number of measurements of momentum. And take it is average what would be the answer. The answer is going to be this with of course p x of ((Refer Time: 29:40)).

So, what is actually p x? Well, actually I should start from the beginning where I would start with the time dependent wave functions and did exactly what I had done earlier, but because we already done it in the case of procession I not going to do that. The experiment is going to simply simple because you will have for this the same kind of simplifications as earlier. So, be the operate will be minus x cross doe by doe x; that is the momentum operator and it is going to operate 1 psi of x.

So, that is the object that I have to evaluate. But then again I mean, we can think about physically you see the box is here let me say the particle is inside; what is going to happen basically, the particle will be maybe it is moving in this direction at one instant. But then of course you have to heat the wall; let us, the physical way to think of about it than deflect. So, therefore the particle may be moving in this direction or may be going in the opposite direction with equal latitude right. If it is moving in this direction you would expect momentum is 0; while, if it is moving in the opposite direction you would expect that sorry, made a another mistake point out my mistakes it may.

If the particle is moving in this direction its momentum will be positive; while, if it is moving in opposite direction the momentum will be negative So, what do you expect on an average to happen the answer is there has to be pseudo; without doing any calculation I could have said that the answer had to be 0. But here this integral is actually fairly easy see this minus h cross I can take out. I would have integrals 0 to L d x psi 1 of x and I have doe by doe x operating upon psi 1 of (x). But that is nothing but the derivative psi 1 of x with respect to x correct that it what it is.

And, what would that be; well, it is actually minus x cross well you have sine 1 effect it is multiplied by the derivatives f 1 of (x) very easy to do in this integral. It is nothing but integral ray is nothing but psi 1 square divided by 2. Because the derivatives of this is nothing but psi 1 of x into d psi 1 by d x; in this integral is nothing but 1 by 2 psi 1 by x square. But then you have to substitute the limits. The limits are from 0 to l. But you have the nice thing when x is equal to 0 psi 1 I know it must be 0. And when x is equal to L psi 1 again must be 0.

So, therefore at the boundary at these are the boundaries; at the boundary the function is 0. So, that the function at boundary there is psi 1 of (x) is 0. So, therefore you get that answer to be 0. And you would realize that it does not matter whether it is the lowest possible stage or the first x stage; you can have any value for the quantum number n same derivation can be done. And you will find that for all the stage the average value of the momentum has to be 0.

But what about I mean that is all fine what about; suppose, I am going to think of this square of the momentum; while, momentum may be positive or negative. But this square is guaranteed to be positive. So, if I was going to calculate the average of the square of the momentum. Let me, just modify what is here d x is square let me remove the other parts. So, I want to calculate the x square so how can I do that? You will have to put d x square here.

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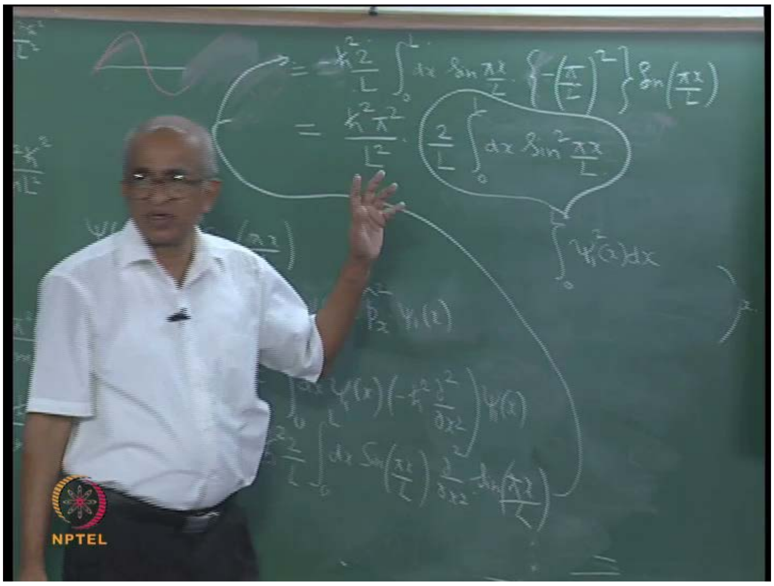

And, what is going to happen is integral 0 to L, d x, psi 1 of x, square of p x I know it is just minus h cross square, doe square upon doe x square, psi 1 of x; remember discussion of the in which we did calculate the square the operator corresponding to the square momentum. And it is just h cross square minus h cross by 2 sorry, minus h cross square doe square up on doe x square that is what it is. But then what is going to happen is I am going to substitute for psi 1 as I will get this 2 by L square, integral 0 to L, d x, sine pi x by L, doe square upon doe x square, sine pi x by L.

So, you have to take this second derivatives of this sine function. If you remember how to calculate derivatives the first time you differentiate psi you will get different sine. And the next time you differentiate you are going to you are going to get the sine pack. So, doe square upon doe x square operating upon sine what will it give me? Let me continue from here on to here or may be somewhere up it would be equal to 2 by L, integral 0 to L, d x sine pi x by L. And carry 2 differentiations the answer is going to be minus pi by L the whole square. Because the each time you differentiate the factor of pi by L is going to come out.

So, you are going to get minus x pi by L square sine pi x by L and this object is just a constant. So, again another mistake I will you please point out when I make mistakes this negative sign should have a forgotten to write, h cross also I have forgotten to write this keeps on happening to me. So, I that means I shall have to modify my equations this minus h cross I will have to put it outside. So, I should not forget that which means that I shall have to put a minus h cross square here also.

So, therefore what is going happen this factor and that factor I can combine what would I get? h cross square there is a negative sign there, another negative sign there; with this I can forget the 2 negatives sign h cross square, pi square divided by L square this is what you are going to get. And then you will have of course this 2 by L. And you are going to get integral 0 t L, d x sine pi by x, another sine pi by x. So, you will get sine square pi x by L this is what you are going to get.

And, if you look at this integral is nothing but pi 1 square of (x), d x integral 0 t L this whole this you can say psi 1 of (x) square d x. And what is that your function remembers is normalized. And therefore that integral you do not have to actually perform. Because you know what it is; it is equal to 1. And hence this is equal to 1. And therefore this object which actually is equal to this integral that we were trying to evaluate; this object is nothing but h cross square pi square by L square. So, we have evaluated the expectation value of d x square the average value of this square of the momentum.

Now, I have done it for the ground stage n equal to 1. But suppose, I had done it for a general stage with an arbitrary what would you expect? The thing that is going to happen is that you will have an n pi here and an n pi is going to occur everywhere. But then when you carry out the differentiation with respect to x; you see in this case it is a pi by x that is coming here out. But if I had sine n by x by L; then what will happen an n pi will come out each differentiations 1 n pi will come out. So, therefore if the final answer in such a situation would be not just pi square, h cross square by L square. But n square, pi square, h cross square by L square. So, for a general stage what would the value of p x square average? It would be simply n square, pi square, h cross, pi square by L square.

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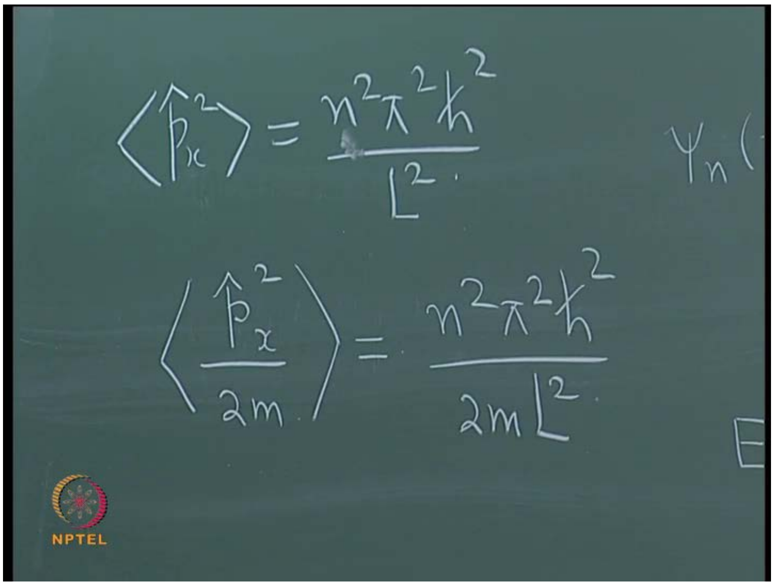

Now, it is very simply straight forward to calculate average value of kinetic energy what is kinetic energy? Operator it is going to be p x square divided by 2 m; this is the kinetic energy operator shall we calculate the average value of this what will happen while you see 1 by 2 m is the step constant. So, you will have the average value of p x square by 2 m. And the we have already calculated the average value of p x square it is going to be; n square, pi square, h cross square divided by 2 m L square. If you want if you calculated the average value of kinetic energy in the n stage; this is going to be the answer.

And, what is this actually if you look at this expression; this is nothing but the expression for the energy level well. So, if you just calculate the average value of left kinetic energy you are getting the total energy of the system is that surprising? No, it is not because the particle has 0 potential energy. So, there is no contribution for the potential energy the energy is purely kinetic that is why this happens. Now, I want to illustrate a simple a chemical application of this model.

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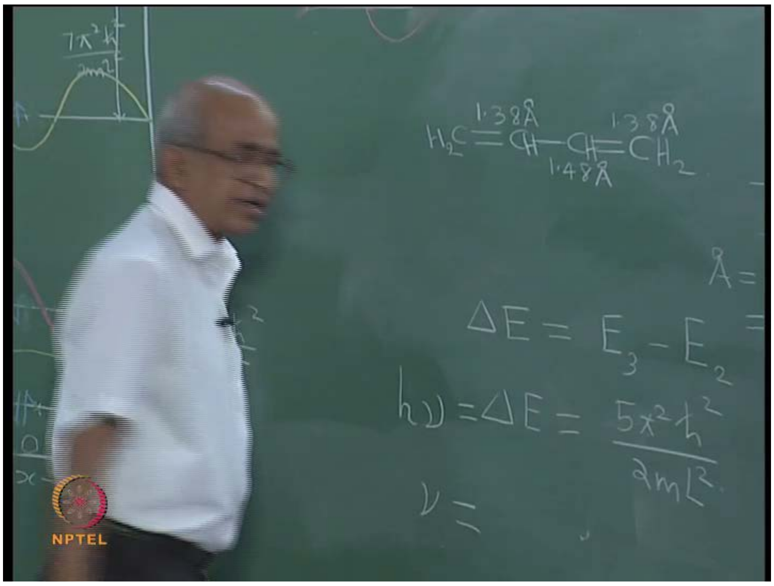

Let us think of beta dine, 1- 3 beta dine into a precise. This is the molecule it has a 2 conjugated carbon carbon double bonds. And if you do experiments you can measure this distance using x ray techniques these 1 line these 1.38 and that this is 1 point roughly I mean 1 .48. So that the distance between the 2 end carbon items how much would be; you can somehow these things. So, 2 .76 plus 1 .48 will find there it is 4.24 Armstrong well, I wonder whether I mentioned even x these are in Armstrong. So, how much is an Armstrong is again let me remind your memory; it is 10 to the power minus 8 centimeter or it is equal to 10 to the power of minus10 meters.

Now, beta dine has a 4carbon items remember my discussion; yesterday I said that each carbon is being to this will leave the orbit perpendicular the pane of the molecule. And they show there are 4 p orbital which are un hybridize one sitting on each carbon and these 4 p orbital can overlap right. And if you put an electron to this pi system; this system is referred to as the pi system of the molecule. If you put an electron into the pi system electron can be thought as moving from one end of the molecule to the other end. And this model you can try to apply to the system.

So, what is it you think of any particle electron in the pi system; it is moving from 1 end of the molecule to the other end of molecule. And what would you expect? You would expect that the length of the box is perhaps something like 4.24 roughly; I mean, it up the order of 4 or may be 5. So, therefore I say, I have a box which is of a length I mean; let me not worry about the this number that is given. Let me try to estimate the length using experiment. So, I say that I have a box which is of length L. And if you think of these electrons which are confined to that length L; their loud energy levels are given here this is the first energy level, this is second, that is a third and so on.

But remember each carbonate will contribute only 1 electron to the pi system; the other electrons of each carbon is used to form sigma bonds with the hydrogen and with other carbon .So, therefore how many pi electrons should I worry about. Because there are 4 carbon items, there are 4 pi electrons. And how are they going to set; well, these are the loud energy levels. So, the out these 4 pi electrons 2 of them will see here in this energy level; well, I am anticipating your previous knowledge; you would have something previous knowledge.

So, therefore, only 2 electrons can be sitting in anyone particular stage. So, these are 2 electrons there and you have 2 electrons which are sitting here. And that is all there are 4 electrons all of them are accountable; for the first you are sitting in the lowest way possible stage. And the second 2 electrons second stage is sitting in the next stage. So, that I what would what you would expect to happen in the molecule. And the pi electrons are accommodated in the first and the second loud energy levels; just the remember we are thinking only of the pi electrons; we are not worried about the sigma electrons which form the framework of the molecule.

And, now suppose I take this molecule and allow it to interact with electromagnetic radiation; as I was mentioning though it is possible for electromagnetic radiation to make the potential energy time dependent; and as the result of that possible for the wave function to get modified. And effectively what would happen is that quantum may be absorbed as a result of each 1 electron from here may be promoted from that orbit from that stage to this stage ok. So, 1 electron could be promoted from here to there. And you can see how much energy will be required to cause this promotion energy of the initial stage as far as that electron is concerned it was having an energy which is equal to so much. And as the result of the absorption of the radiation it has gone on to that stage.

So, therefore the change in energy which I will denote as delta E, in this case will be actually the energy of these stages with the n equal to 3 minus the energy of the stage with n equal to 2; that is the change in energy. And that will be equal to 5 pi square h cross square divided by 2 m L square. And that should be equal to the change in energy. And if this is brought about by photon of frequency nu; then h nu has to be equal to change in energy and that must be equal to so much, and so it is possible you to calculate nu. And it is possible for you to estimate nu or a or a not estimate nu not can determine nu by studying the absorption of the molecule; you can find out at what frequency the radiation is absorbed; what is the frequency of the radiation that is absorbed by the molecule experimentally you can determine that. And then you use that I think I will stop here.

Thank you for listening.