Introductory Quantum Chemistry

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Lecture – 10

Particle in a Box - Time Dependent States – Expectations Values and Time Dependent States

So, we were thinking of exposing butadiene to electromagnetic radiation and then what happens is that the molecule will interact with the radiation as the result of which an electron gets excited. So, specifically we are saying ok, this is the electron that is going to go up. Why do we think of just that transition? The reason is actually quite simple.

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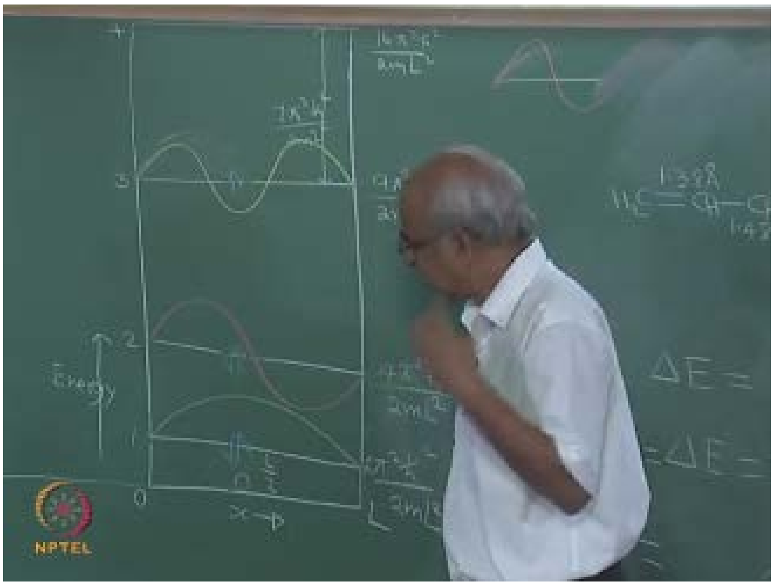

This is the transition that will need the least amount of energy. If the electron went from here to there then obviously, it will need much more energy or if an electron from here is promoted there again that will need more energy. So, this is the transition that will require the minimum amount of energy, right, and so exponentially we can determine that particular transition which will need the minimum amount of energy.

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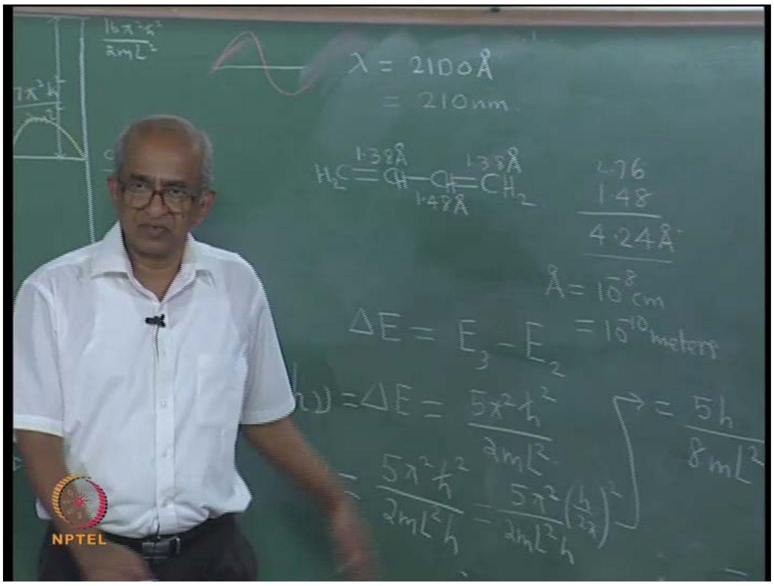

And in fact in the case of butadiene if you do the experiment you will find that transition occurs at the wavelength lambda which is equal to 2100 Angstroms or 210 nanometers. But from our simple model we can calculate the frequency; frequency is found to be how much, well h nu frequency is such that h nu is equal to delta e which is equal to so much. So, that means nu must be equals to 5 pi square h cross square divided by 2 m l square into h, and this is how much? I mean I can actually simplifying, because h cross if you remember is h divided by 2 pi. So, this actually will be 5 pi square h divided by 2 pi the whole square divided by 2 m l square h, right.

You can simplify a little bit. Please check it and tell me if I have made a mistake; five is there? Yes, answer is fine, right. Now this will be the frequency; I mean suppose this expression is correct, you have no problem told me there is not any mistakes, so five. So, nu is given by this, and then if nu is the frequency then you see frequency is related to the wavelength, and so knowing the frequency I can calculate the wavelength, or I can do the following. This is the wavelength. So, this must be equal to the velocity of light which we normally denote by the symbol c. So, c by lambda must be equal to nu. So, let me collect everything together, remove all these things.

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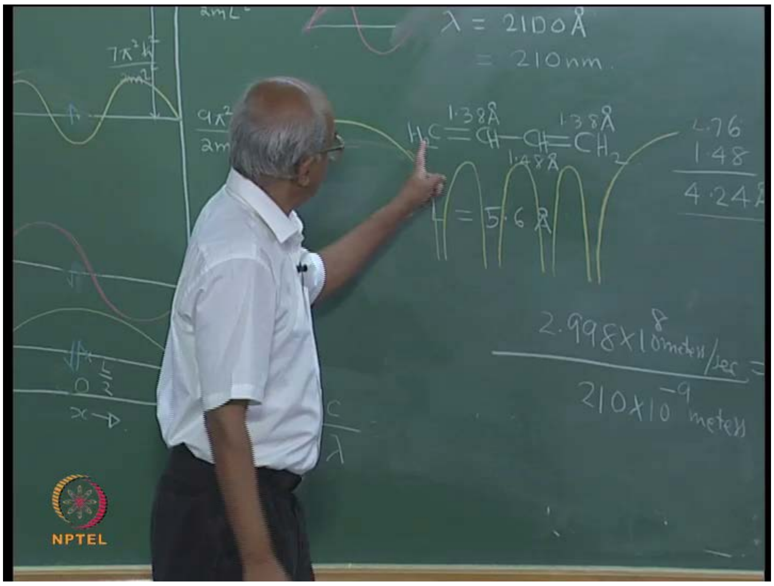

And what we have this is actually c divided by lambda; c divided by lambda is actually the value of c if you remember 2.998 into 10 to the power of 8 meters per second divided by lambda, we have calculated 210 or we know we have not calculated; we have determined experiential its value is 210 nanometers, but one nanometers is 10 to the power of minus 9 meters. And now you can substitute the values for h; h is how much? 6.6 34 Joules second; you can also substitute the value of mass. Remember mass is that appropriate for the electron because the particle is actually electron in this case. So, the value is 9.1093 into 10 to the power of minus 31 kilograms. So, you can substitute these values.

So, h is known, m is known, everything else also known. So, therefore, you can determine the value of l. So, if you did the calculation which is a simple calculation, if you have a calculator, the answer that you get is found to be 5.6 Angstroms; I mean which does make sense I mean because we look at the approximation that we have made. So, many approximations have been made, what are the approximations let me remind you. Actually if your electron is moving along this molecule the potential energy is not a constant; it actually is varying. How does it vary? I have drawn it yesterday; as it nears each carbon nucleus the potential energy goes down. If this is the molecule and if you think of the potential energy it actually goes down like that, okay, and remember I mean drawing if you see that I had drawn it yesterday near the molecules so that it is clear to you.

So, this is how the potential energy; as you are going along this molecule this is how the potential energy is going to change and the distance from this carbon to that carbon we have calculated it is 4.24 Armstrong. The experimental frequency or experimental wavelength actually leads to an answer of 5.6 which is quite sensible, because you see you do not expect an electron when it is moving to stop at this point. So, you do not expect it to stop at that point; you would expect that it will move a little bit more before it turns around, and therefore, this answer that we have obtained using this extremely simple model is reasonable and it makes sense and it is a very nice thing.

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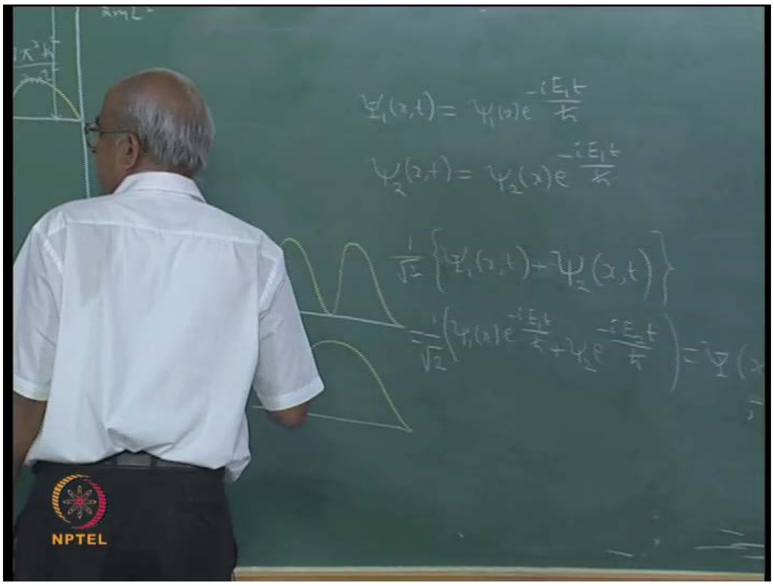

So, another thing that I did mention yesterday is this; imagine I take my ground state, what is my wave function for the ground state? It is actually psi 1 of x t; this is the total wave function that I am writing equal to psi 1 of x e to the power of minus i E 1 by h cross, the full wave function is this. And remember this function actually will obey that equation; it will obey that equation. You just have to put an equal to 1; it is going to obey. Similarly psi 2 of x t will be equal to psi 2 of x, we know expressions for it e to the power of minus i E 1 t by h cross.

And if it is sat if I had an electron sitting in this state then its wave function actually would have this possession dependence, and the probability would have roughly the same kind of appearance, the probability, density will not change when time passes, right. Similarly if it was sitting in this state maybe I should draw this probability distribution we may make a picture here; this is the probability, and that is the probability for the second stage.

So, for the first one the probability density will look like this. Well, for the second one how would be the probability density look like? It would look like this, and as time passes you see this probability distribution does not change; it remains unchanged, that is what I have told you just now. But now suppose I think of a combination of these two, suppose I multiply this by c 1, this by c 2, and add that two, just make things simple I will say c 1 is 1, c 2 is also 1 so that I can just add with that. Actually it will be more correct; I mean correct if I said that they are just added with the same amount of importance, but I always have to ensure that wave functions are normalized, and in this case what happens is that if I put a factor of 1 by square root of this kind of thing we will be working out later.

But if I do not refine it just put a square root of 1 by root 2; it is a wrong thing, 1 by square root of 2 if I put there then it is guaranteed that it will be normalized; it is absolutely no problem. If you think of this kind of thing let me write it in a little bit more detail; you would have psi 1 x e to the power of minus i e 1 t by h cross plus psi 2 e to the power of minus i e 2 t by h cross. That is the function. Now very very interestingly this obeys the time-dependent Schrodinger equation. You can easily prove that; all that you need to do is you take this operator take this whole thing. You take that operator; allow it to operate upon this combination. When it operates what will happen? You see you look at this operator it is linear operator, right; that is h is linear, this also a differentiation. It is a linear operator the whole thing.

So, when it to operates upon the sum what will happen? The operator will go and operate here, what will happen? The answer will be 0, and it will operator there, right. If it operates on the first one, right, the answer is 0, because that is what that equation says, and if it operates upon the second one again what is going to happen? The answer is going to be 0. So, the sum is going to be 0. Even if I had a constant c 1 here and a constant c 2 it is completely unaffected, because these constants are not affected by these operators. So, therefore, I can take any linear combination like c 1 psi 1 this is referred to as a linear combination c 1 psi 1 plus c 2 psi 2.

You can take a combination like that; it will obey the Schrodinger equation time-dependent Schrodinger equation, but this is not a stationary state. It is not a stationary state; why is it not a stationary state? Reason is if you took this particular function, if you tool this particular function say that this is your psi, this is your psi. Then you can actually calculate psi star psi. Suppose you had calculated psi star psi what will be the answer?

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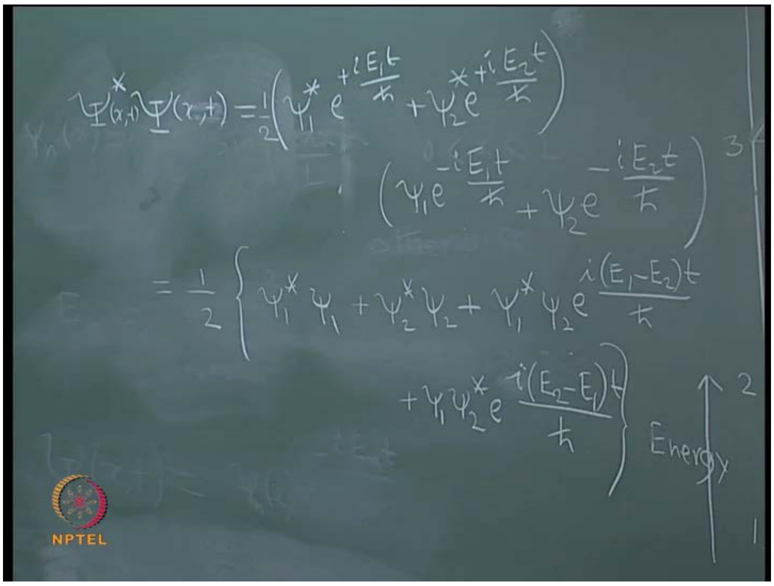

$$\Psi^*(r,t)\Psi(r,t) = \frac{1}{2}\left(\psi_1^* e^{+\frac{iE_1t}{\hbar}} + \psi_2^* e^{+\frac{iE_2t}{\hbar}}\right)\left(\psi_1 e^{-\frac{iE_1t}{\hbar}} + \psi_2 e^{-\frac{iE_2t}{\hbar}}\right)$$

$$= \frac{1}{2}\left\{\psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_1^*\psi_2 e^{\frac{i(E_1-E_2)t}{\hbar}} + \psi_1\psi_2^* e^{\frac{i(E_2-E_1)t}{\hbar}}\right\}$$

Strictly speaking I should write this also. Well it is tedious to write these possession dependences everywhere. So, I will just not write it, but it has to be there. So, psi 1 is dependent on possession, but what you are going to get is this plus psi 2 e to the power of minus i E 2 t by h cross. You will have to take the complex conjugate of that multiplied by this object and of course, the way I have defined it there is this factor of 1 by square root of 2 which is actually a normalization factor, I should put that also. So, there will be no such factors which will make it a half. Think of what is going to happen if you multiplied this? You are going to get half; well, you see this star has the following effects.

You are going to get a star here; if you took the star inside you are going to get a star here. You can remove that, put a plus sign here, put a star here and put a plus sign there; that is all. And imagine what will happen if you multiplied the two things? The answer is going to be the first time this into that, what is there? It is actually psi 1 star psi 1, correct, and if you multiplied this with that, what is going to happen? You are going to get psi 2 star psi 2, right; psi 1 star psi 1 is actually shown here it is like this. It is like this and psi 2 star psi 2 also is shown here, but that is not all.

You get additional terms; what are the additional terms? You are going to get psi 1 star psi 2 e to the power of i e 1 minus e 2 t by h cross; that is one term that you will get, correct. And you are going to get one more term, what would that be? You are going to get psi 1 psi 2 star e to the power of minus; may be I will write like this, right. This is the fourth time that you will get, and you can see that the probability density is not independent of time. In a stationary state it is independent of time, but in this state it is not independent of time. So, as time passes what will happen? The probability density will keep on changing. In fact, I have a demonstration where I made a plot of this probability.

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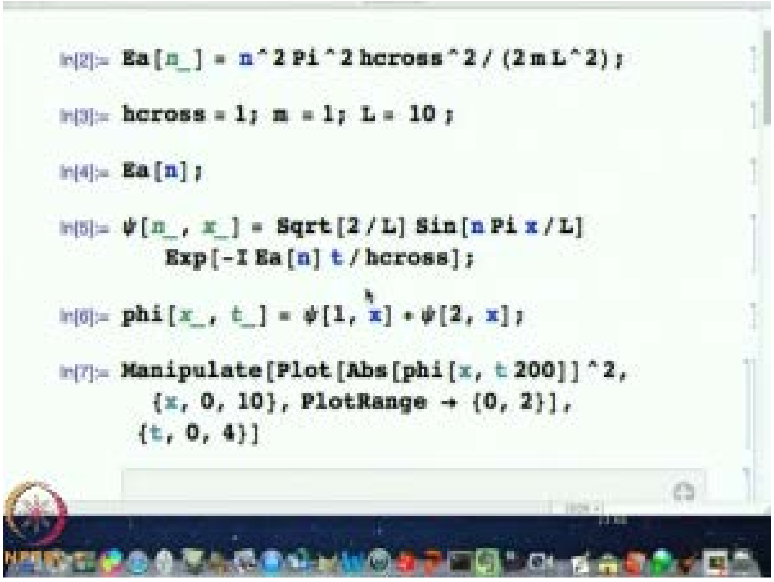

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In[2]:= Ea[n_] = n^2 Pi^2 hcross^2 / (2 m L^2);

In[3]:= hcross = 1; m = 1; L = 10 ;

In[4]:= Ea[n];

In[5]:= ψ[n_, x_] = Sqrt[2 / L] Sin[n Pi x / L]
           Exp[-I Ea[n] t / hcross];

In[6]:= phi[x_, t_] = ψ[1, x] + ψ[2, x];

In[7]:= Manipulate[Plot[Abs[phi[x, t 200]] ^2,
          {x, 0, 10}, PlotRange → {0, 2}],
         {t, 0, 4}]
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Well, I do not really know whether you people are familiar with this software called Mathematica. Mathematica is very useful software which can be used to make this kind of simple plots or even more complex plots. I shall not go in to tell you details of how it is done, but let me just show you the plot.

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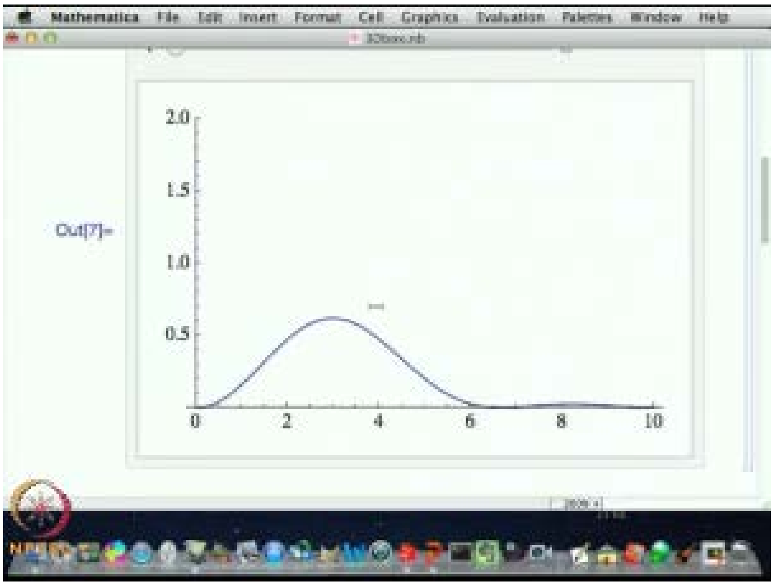

Okay, you look at this figure; what I have done is I have plotted psi star psi. I had plotted psi star psi as a function of x for t equal to 0. This is the plot for t equal to 0 that is the initial time, right, and you see that the way the probability density is it is the particle is actually localized on one side of the box. The box extends from here to there, and you can see that the particle is if you look at this figure you will see that the particle is actually localized to the left hand side of the box, right, and it is not on the other side. This is at the initial time t equal to zero but now look at what is going to happen when I change the time u.

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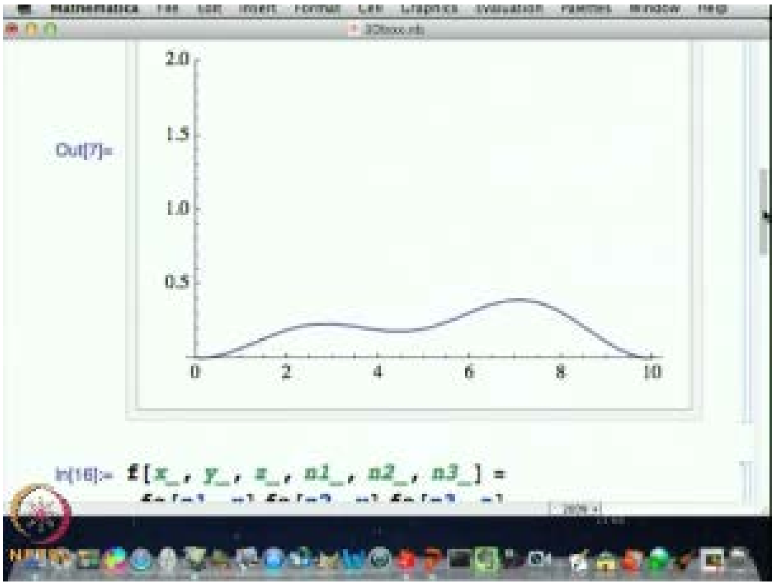

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In[16]:= f[x_, y_, z_, n1_, n2_, n3_] =
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So, this is actually what happens. What has been done is that this function psi star psi is plotted against x but as time passes the shape of the psi star psi goes on changing, and if you look at the figure you would realize that I had actually started with the particle on the left hand side, but then it goes to the right hand side, and then what does it do, it comes back. So, it is as if the particle is actually oscillating back and forth. Again I would like to remind you of the way I started my discussion of a stretched string. Remember I had made a disturbance which was shown one side and then that disturbance was moving back and forth in the string if you remember.

So, it is exactly the same kind of thing that it is happening here, and these are actually time-dependent states, and you may ask I mean are they of physical relevance? The answer is yes. These days we have lasers and we can manipulate systems using lasers. So, what we can do is we can allow your system to interact with laser pulse. What will happen is that the laser pulse will interact and will go away. After it has gone away the system will be left in this kind of states which are linear combinations so as your stationary states. After the laser pulse has gone the system will be in that and then the probability density everything will be changing as a function of time, whereas if the system was in a stationary state this will not happen. The probability density will not change. Okay, this actually, well there are one or two more things that I would like to tell you.

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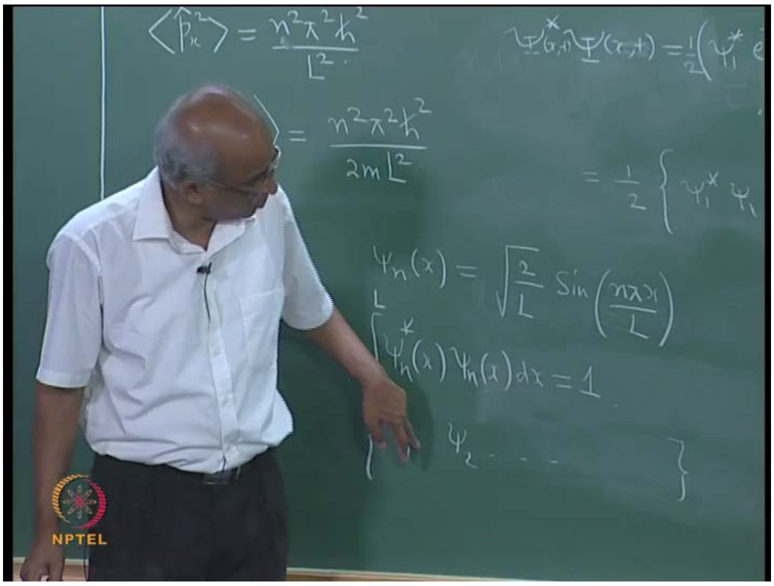

If you look at the wave functions for the stationary states they are having this form; I had it, but unfortunately I removed it. So, this is the form of your wave function for the nth stage, and this function actually is normalized, okay. It is normalized and in addition this set of functions; when I say set of functions what I am saying is you see you could think of all possible values of n. N equal to 1 is one possible function, n equal to 2, n equal to three and so on. So, I have an infinite set of functions, right. In that infinite set of functions each function is normalized.

Then if you took the first function multiplied by the complex conjugate of the second and integrated over the entire space, right; that means I will take psi 1 of x multiplied by the complex conjugated psi 2 of x and integrate from 0 to l actually after multiplying by d x. This is a simple integral not difficult to evaluate. You can easily find if you evaluate the integral; you can easily show that this is zero, okay. There is no specialty as far as this two and one are concerned we can take the m th stage function multiplied by the nth one. As long as m is not equal to n these are simple functions; integrals are not very difficult to perform, and if you perform that you will find that this integral is always 0 as long as m and n are different.

If m is equal to n, what will happen? The answer will be one, okay. So, therefore, this set of functions psi 1, psi 2, psi 3, psi 4, etcetera, they have the property that they are all normalized. Each one of them obeys the normalization condition, and each one of them I am going to say is orthogonal to all the others. So, what do I mean by saying that it is orthogonal? Well, I say that the nth function is orthogonal to m, because this integral is 0. So, if this integral is 0 then I say that two functions are orthogonal. So, if you had made this list psi 1, psi 2, psi 3, etcetera, and this is a set, the set has a nice property that each one of them is normalized; each one of them is orthogonal to all the others.

And this you will find it is going to occur in all the problems that we will study, and in fact, it is a property of Hermitian operators. You remember psi 1, psi 2, psi 3, they are Eigen function. So, if the Hamiltonian which itself is a Hermitian operator, okay. These are all psi 1, psi 2, psi 3, they are all Eigen functions of the Hamiltonian operator; Hamiltonian operator is a Hermitian operators. So, Hermitian operator has this nice property that all its Eigen functions are orthogonal to one other which is something that we will prove later. But this is an example of that property of the Hamiltonian. In addition to that these functions also have very nice property which is little bit mathematical and therefore, we will not worry too much about it.

They have a property which is referred to as completeness. I will explain only what is meant by this. See these functions are actually nonzero in this interval, right, from 0 to l. Now you give me any function in that interval; you can choose any function in that interval any arbitrary function. It is possible to express that arbitrary function in terms of these functions

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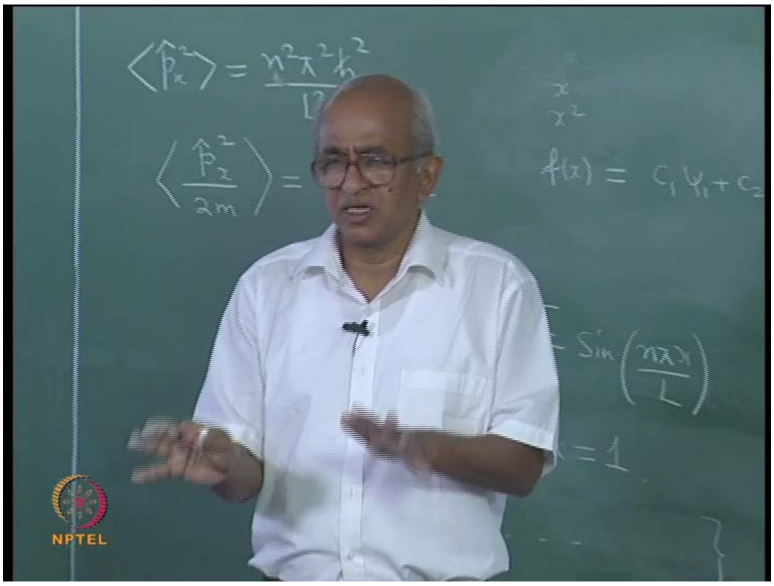

That means if I had a function like you can choose your function may be x or may be x square or in general a function f of x. Now this set is complete which essentially means that I can express this as any function of x as c 1 into psi 1 plus c 2 into psi 2 plus c 3 into psi 3 and so on. Any function that you have can be expressed in terms of these functions, right, and the set for which this is satisfied is refer to as a complete set. So, these functions actually mathematically speaking they can be shown to form a complete set, okay. Another thing that I would like to mention is this. You look at the way the figures that are drawn here the wave functions.

Now the way I have put my coordinate system is such that the x is equal to 0 is at the boundary of the box, right, and x is equal to l is here. But suppose I change my origin; origin of my coordinate system is equal. Coordinate system is something that we use; the system does not know about any coordinate system. Coordinate system is for our convenience. So, what I am going to do is I am going to shift my coordinate system, and I am going to say that okay the origin is going to be taken right in the middle of the box.

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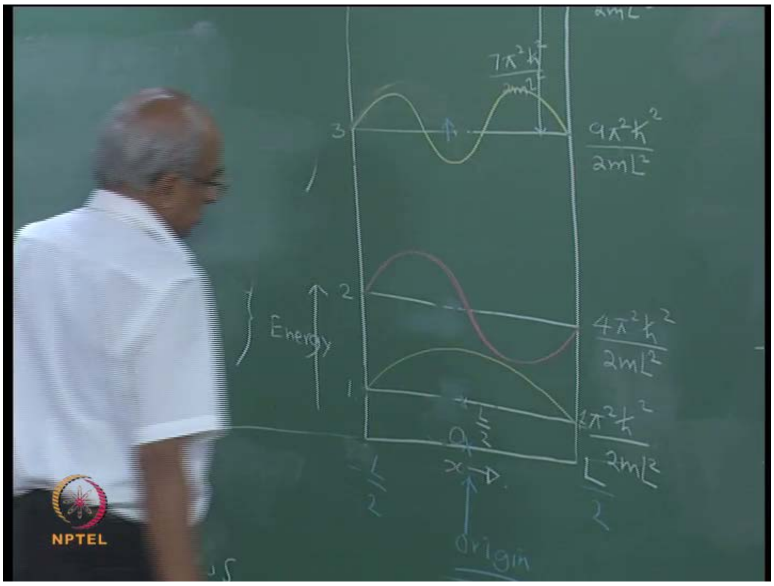

This is my new origin, right, and then what will happen? This boundary will be at minus l by 2 and that boundary will be at plus l by 2, right, but then of course you see the wave functions has their appearance, nothing is going to change; the wave functions would have still the same appearance, the energies also would have the same appearance. See those things cannot depend upon where I put my origin, right. Now why do I want to do that? Let me remove these two electrons, because we do not need. So, if you put the origin right in the middle then what I can see is the following.

The potential energy of the system which is v of x is symmetric about the origin; that is obvious. The potential energy of the system is symmetric about the origin; that is the advantage of putting the origin right in the middle. So, therefore, I can say that for this problem potential energy is symmetric; how can I state that mathematically? Well, the way I can state that is if I evaluated the potential energy at minus x for any x if I evaluated the potential energy at minus x the answer will be equal to the potential energy evaluated at plus x. So, v of x will be equal to or v of minus x will be equal to v of x. So, this means potential energy is symmetric function of x. So, if you change the x to minus x potential energy does not change; that is the meaning of saying that it is symmetric, or mathematicians would say it is an even function of x.

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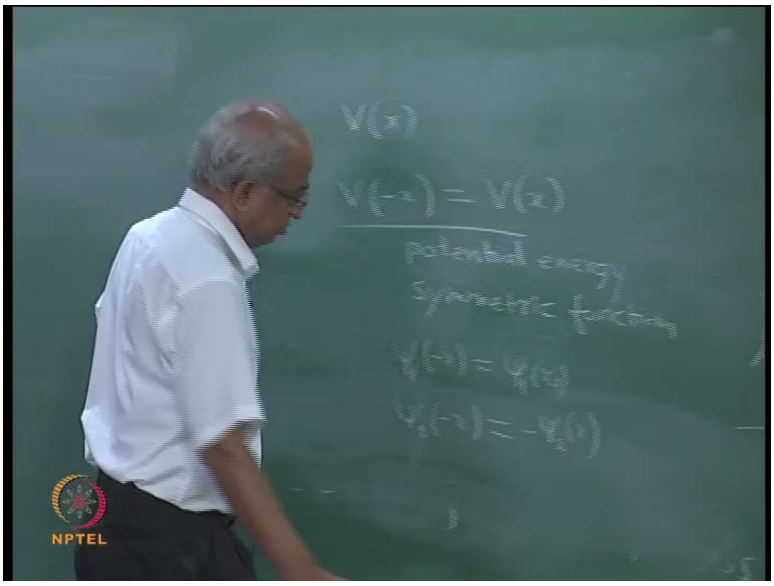

Potential energy is an even function of x; that means if you change the value of x to minus x the function does not change. Now you look at the wave functions that we have in the picture. What happens with them? I mean if for example you see you think of a point let us say at this distance may be that distance is one Angstrom on the positive side and again the editions of one Angstrom on the negative side. What about the wave function at these two points? As far as this yellow curve is concerned this should be obvious to you that the wave function is actually same at valuate at plus x as well as at minus x they are the same.

So, for this state I can definitely say that psi the wave function, let me be very precise psi 1 at minus x must be equal to psi 1 at plus x. So, what does it mean? This means that the wave function actually is symmetric, symmetric function of x or an even function of x, correct. What about this one? You think of one Angstrom distance here and one Angstrom distance there while you have the wave function at this point is negative while the value of the wave function at that point is positive. So, this is an odd function, correct; no, it is not an even function. So, therefore, I can say that as far as that function is concerned with psi two, psi two of minus x actually is how much minus psi 2 of x. So, now it is fairly easy actually; this is even function, that is an odd function, what about this one? It is even; the next one I would expect is odd and so on, right. This is something that is quite useful, and now I want to prove to you the general result.

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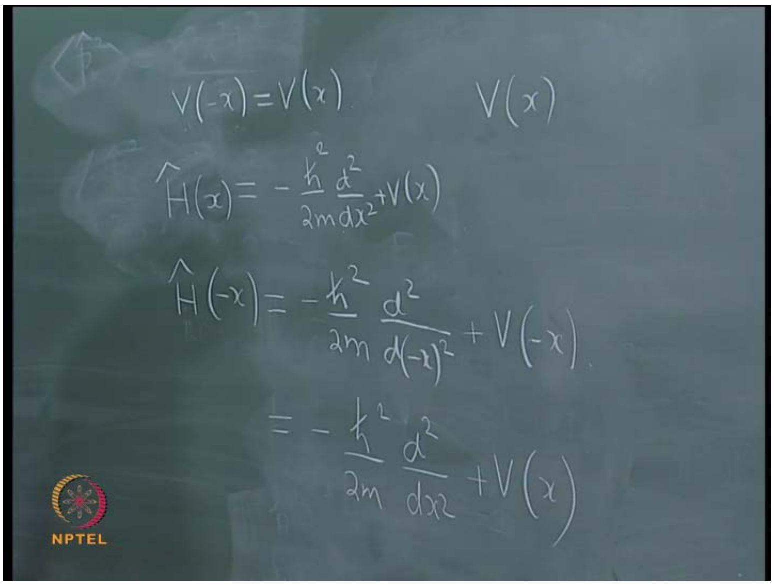

$$V(-x) = V(x) \qquad V(x)$$

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$\hat{H}(-x) = -\frac{\hbar^2}{2m}\frac{d^2}{d(-x)^2} + V(-x)$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

See as far as this particular situation is concerned v of minus x is actually equal to v of x okay. So, let us imagine that I have a situation where this is satisfied. It does not have to be this particle in a box but any problem for which v of minus x is equal to v of plus x; potential is symmetric, right. Then what would you expect? I mean you see whether you can guess what the answer is going to be. Then what will happen is that your wave function can be either symmetric which means that when you change the value of x it does not change or it can be antisymmetric which means that when you change the value of x its sign changes.

This is the general result which I will prove. So, v of minus x is actually equal to v of x which assumes that the potential is symmetric. Now if you think of the Hamiltonian, what is it? I mean for a one dimensional system the Hamiltonian is actually to minus h cross squared by 2 m d square by d x square plus v of x. But of course you see I am going to change x to minus x so I will better say that, okay, Hamiltonian after all depends upon the variable x. It of course involves differentiation with respect to x and to set as v of x, but it depends upon x. So, suppose you think of h of minus x; that means I am taking this x and replacing it with minus x. What will happen to the Hamiltonian? Wherever x is occurring I am going to put minus x; that is all I am doing

So, what will happen is your this term will become minus h cross square by 2 m d square upon d; instead of x I will have to put just minus x, correct. That is what is going to happen, and this is going to be plus v of minus x, and if you look at this what is happening is that this is going to be minus h cross squared divided by 2 m d square by d x square, because you see if you think of d minus x square it is going to be just d x square plus v of minus x, but v of minus x I am assuming that the potential is symmetric. So, that v of minus x is v of x itself. So, therefore, this is just v of x. And what is the whole point? Well, the whole point is that this is nothing but my h of x. So, what does this mean? This means that my Hamiltonian operator does not change if I replaced x with minus x; that is what it means, okay.

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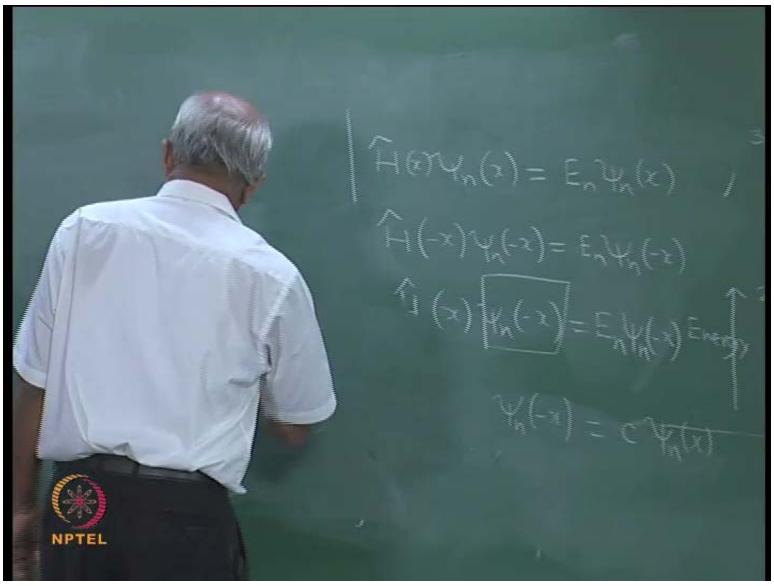

Now let us think of anyone of the different possible states of the system. Let me call I have a state which is denoted by the symbol psi n of x, particular state of the system which is denoted as psi n of x. I will assume that this has an energy which may be referred to as E n and that there is only one stage which just that energy which is what happened in the case that we have discussed in the case of the particle in a box. For any given energy that is only one stage, right; for any given energy there is only one stage, right. I will assume that the cases where there are more states are there with the same energy that is not included in this description.

So, let us confine ourselves to the situation where there is only one state which has that energy, okay. Then what it means is if I allowed my Hamiltonian operator to operate upon this psi n of x, what will be the answer? It is going to be e n times psi n of x, right.

And there is only one state which satisfies this equation; that is there are no other states. Now suppose I take this equation I know that this equation is obeyed, and there is only one state that satisfies or one wave function which satisfies this equation. And imagine now that I am going to replace x with minus x in this equation throughout; that has to be valid because this equation is valid for all x.

So, therefore, even If I replaced x with minus x this equation has to be valid. So, h of minus x psi n of minus x must be equal to E n times psi n of minus x, correct. It has to be correct, because you see this first equation is valid for all x. So, it should be valid for minus x also, but I know that I have a situation where h of minus x is h of x itself you know that; that is what we are thinking of. So, therefore, h of x operating upon psi n of minus x is equal to e n psi n of minus x; that is the result that I am getting now. So, what does this mean? This means that psi n of minus x obeys the same Schrodinger equation with precisely the same Eigen value, right. If psi n of x is obeying if this is obeying the Schrodinger equation with that Eigen value then psi n of minus x also obeys exactly the same equation with same Eigen value.

But I know that there is only one state which obeys the Schrodinger equation with that Eigen value and therefore, what is the result? This psi n of minus x must be psi n of x itself, right, but it may be multiplied by some constant. So, this is possible only if psi n of minus x is actually equal to the original stage psi n of x but perhaps multiplied by a constant which we will denote as c. That is the meaning; that is how the equation can be satisfied. Why does this happen because there is only one state that satisfies the Schrodinger equation; there are no two states. So, if that is the way it is I can do the following. Let me remove everything else; I do not need anything else now.

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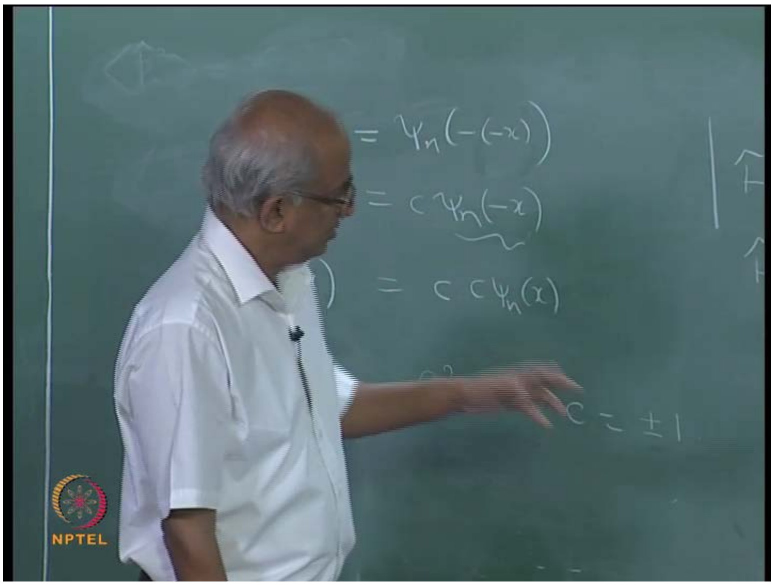

Let me now think of psi n of x but actually if you like I can write as psi on of minus minus of x, correct, this is only a trick, psi n x must be equal to psi n of minus minus of x, but then there is a negative sign here; think of this as one unit. So, this is actually psi n of minus of something. That we can say okay, it is actually c into psi n of that something, correct, and now what do we have here psi n of minus of x, but that must be equal to this much be equal to c times psi n of x itself. So, therefore, effectively what happens? I will have two c's and therefore, psi n of x actually is equal to c into c into psi n of x. This implies that c square must be equal to unity, right.

So, c square must be equal to unity which implies that c must be c square is equal to plus one then c can be either plus one or minus one, right. So, we have rigorously proved that when I change or when I put minus x here what happens? My original function gets multiplied by c. If c is positive; that means the function is symmetric, and if c is the negative what does it mean? It means that the function is antisymmetric, or if c is positive then the function is an even function, while if c is negative the function is an odd function. And that is what has happened in the case of particle in a box. This is just an example, but what I have shown to you is very general, right. It does not matter what the potential is as long as the potential is symmetric it is possible for it to classify the Eigen functions as being either symmetric or antisymmetric, and this is extremely useful when we discuss problems of this nature later. I think I will stop here. Thank you for listening.