Introductory Quantum Chemistry
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Lecture - 7
Separating Variables and Particle in a Box

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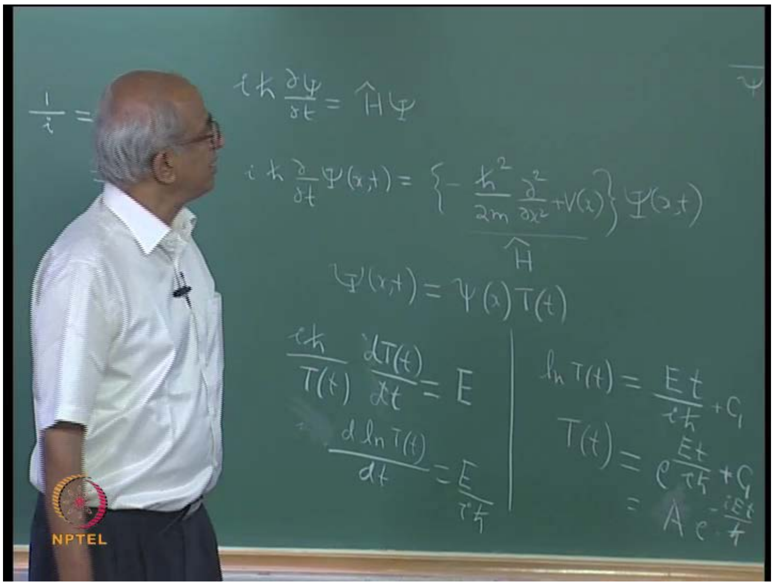

So, we were actually discussing the time dependent Schrodinger equation, which is the basic equation. This is the equation and in fact, this equation can describe all the phenomena, that one is interested in chemistry. In fact, forms the complete description of chemical phenomena unless of course, you are interested in relativistic effects, which normally chemists are not interested in, ok.

Now, we wanted to solve this. In fact, we were thinking of one-dimensional example where we wrote this equation in this fashion. Well, in general, V, the potential will depend upon time also and I told you in the morning, that that is what happens in stereoscopy. If you are doing stereoscopy experiment and if you allow electromagnetic radiation to interact with your molecule, the potential energy, I mean, Hamiltonian will contain ((Refer Time: 01:48)) that are dependent upon time, which will change with time.

But if you are not taking up such situations, then Hamiltonian, this is the Hamiltonian operator and it is independent of time and in such a situation we were trying to find special solutions. Why were they special? They were special because the time dependents and the possession dependents could be written separately and then multiplied together to get the total function. And we made this assumption, put it back into this equation and arrived at two ordinary differential equations. Let me just write them also. The first one said that i h cross 1 by capital T of t dou capital T of t by dou t should be equal to a constant.

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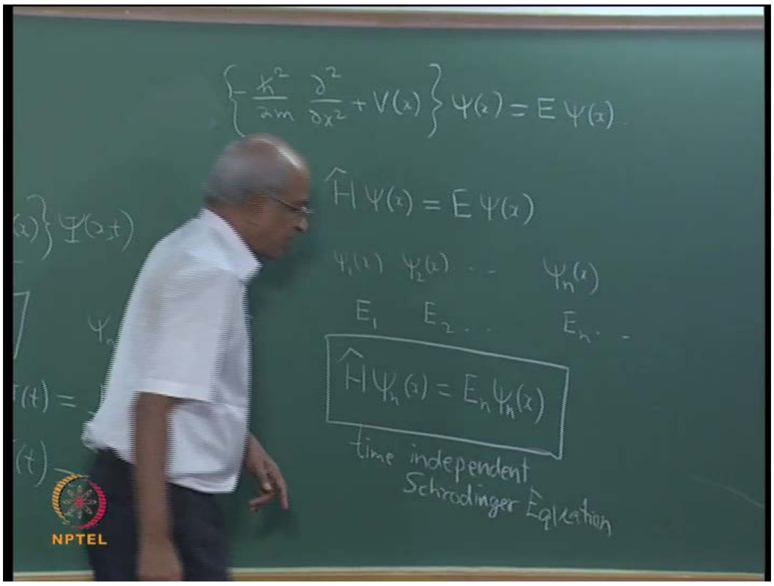

And the other one said, should be equal to the same constant. Now, let us look at this equation. This is an ordinary differential equation and I may also point out, that even though I have put partial derivative notation here, this is something that operates upon capital T. Capital T is a function of small t alone, so there is no other variable that has to be kept constant in this partial differentiation. And therefore, it is not really necessary for me to use partial derivative notation because capital T, after all, is a function only of small t. So, I will just replace it by d capital T by dt, which will be the usual notation for the differentiation, right.

And if you look at this equation, this is the simple differential equation, which can be easily integrated. Remember, E is a constant, it does not depend upon possession, it does not depend upon time, so it is just a constant. So, what you, what you do is you would integrate this. In fact you can write this as i h cross d ln capital T by dt equals to E. Or I can take this i h cross to the other side and put it here and this you can integrate after multiplying by dt. If you integrate it you are going to get ln T of t equals to E into t divided by i h cross plus a constant of integration. That is what happens. I mean, this is a sort of simple differential equation. If you multiplied by dt and integrate, this is what you are going to get and taking an exponential of both the side you are going to get capital T of t to be equal to exponential of E t divided by i h cross plus C 1.

Now, I am going to do two things here. One, you have E to the power of C 1, C 1 is a constant, so E to the power of C 1 itself is a constant. So, I will write this as E to the power of C 1, which as I said, is a constant. And then I will have E to the power of E t by i h cross, but 1 by i. You know, that 1 may be written as minus 1 into minus 1, but minus 1 is actually i square. So, therefore, we can easily see, that one i and other i may be cancelled, you will get minus i. So, 1 by i is easy to write it as minus I, so I am going to use that and therefore, this part will become E to the power of minus i E t by h cross. And as I said, E to the power of C 1 is a constant, so why I take the trouble as I has been saying since morning, I am lazy, so I do not want to write unnecessary things. So, this is just a constant, maybe I can denote it as some capital A, which itself is a constant.

So, what is it that I have done? I have solved and found what capital T should be. It has very simple appearance, it is just a constant multiplied by E to the power of minus i E t by h cross; that is all. Very simple function and having solved that we will look at the second other differential equation written here.

If it is clear, that if you multiply by 1 by psi of x throughout, I can remove this 1 by psi of x. Let me just remove it here and I am going to put it here and this is, say, simple, ordinary differential equation. In addition to being a simple, ordinary differential equation, there is something that you should notice. What is in here is nothing but the Hamiltonian operator. So, this actually is saying, that H, let it operate upon psi of x. What is it that you have on the right hand side? You are getting psi back, right. You are getting the same function, but multiplied by the constant E. So, that is what is happening. You are getting psi back or I can say, I mean, the effect of H operating psi is equivalent to multiplying psi by the constant E. That is what this equation says.

So, what is it? It means, that psi has to be an Eigen function of the Hamiltonian operator; that is the meaning of this equation, right. So, therefore, if you if you find an Eigen function of psi, sorry, if you find an Eigen function of H, then you have determined a possible psi.

As I was telling you in the morning, any given operator can have an infinite number of different Eigen functions and each would have its own associated Eigen value, right. So, therefore, let me say, that it is a very different Eigen function, so H. So, what will I do? I will write them as psi 1 of x, psi 2 of x, etcetera. I may have several different Eigen functions, in principle, normally you have infinite number of them and you will, each one will have its own associated Eigen value, with, right, the Eigen value will usually be different. So, let us say, psi 1 has an Eigen function, Eigen value E 1; psi 2 has an Eigen value E 2, etcetera. If you say psi n of x, that it has an Eigen value E n, and what is going to happen? Imagine, I allow H to operate upon psi n of x, what will be the answer? I shall get E n multiplied by psi n of x, correct. So, this function psi n of x is a potential choice for me as far as my product is concerned. Where is my product? This is my product.

See, what is our ultimate aim? Ultimately, I want to determine capital psi because the basic equation that we have is the timetable and Schrodinger equation, which is third one on the screen, right. It is there on the screen and I have written it here. This is the equation that we want to solve, but then we are looking for special solutions of the form capital psi is equal to small psi into capital T and capital T we have already determined. The functional form is written here.

Now, what about the small psi has? The answer is that the small psi has to be only condition, that small psi has to be an Eigen function of H. If there are several possible Eigen functions, then each one of them are going to give me is a solution of the original time difference Schrodinger equation. So, therefore, if I now took psi n of x, I take psi n of x, I will have to multiply by capital T of t. What will be expression for capital T of t? The answer is it is going to be the constant A, right, E to the power of minus i. I will have to put in the value of E, but for the nth Eigen function, the value of E is going to be E n; the value of E is going to be E n. So, E n t by h cross would be my solution. So, this will give me solution of the time dependent Schrodinger equation, right.

But in order to find the solution is it is not really necessary for me now to worry about this equation? It is enough if I can solve this equation, right. If I can solve this equation and find all the possible Eigen functions and Eigen values of the Hamiltonian, then what

I can, I do is I can take any one of them. For example, is n multiplied by a constant, then E to the power of minus i n t by h cross, I would have solution of the original time dependent Schrodinger equation. That is how it is.

Therefore, you see, starting from here we have derived the simpler equation, which small psi has to obey and this equation is known as the time independent Schrodinger equation. And look at what has happened? I have derived the time independent Schrodinger equation starting from time dependent one. So, therefore the time dependence one is more basic and time independent one can be obtained only if your potential energy has no dependence on time. So, only in such cases will you be able to derive such equation. But once you derive the equation, you see, I do not have really have to worry about this equation because I can get solution of this equation simply by solving this equation and then taking the solution and multiplying it by the constant E to the power of i n t by minus h cross.

Yesterday I was telling you, that the wave function, eventually, I will have to normalize the wave function. If it does not satisfy the normalization condition, I shall have to normalize it. So, any constant that is occurring here is, it is relevant because eventually what I will do is I will normalize my function.

So, therefore, what I will do is, this A, I am going to absorb it into my psi n because after all, eventually, you will have to multiply psi n by a suitable constant, which will be done. So, this constant, we can just say it is observed as the part of this psi n and therefore, from now on we will write the solution as psi n into E to the power i E n t by minus h cross. Now, let us, having found this solution let us look at properties of this solution. So, this is what we have found.

Let us imagine, that I am thinking of the probability density. What is the definition of probability density? Well, if you remember, we have defined it as psi of x t star multiplied by psi of x t. And what is the use of this? Well, if you are interested in an interval dx, starting from x to x plus dx, then the probability of finding of particle in that small interval will be equal to psi star psi dx, correct. This is the part of our postulates, the first postulate actually.

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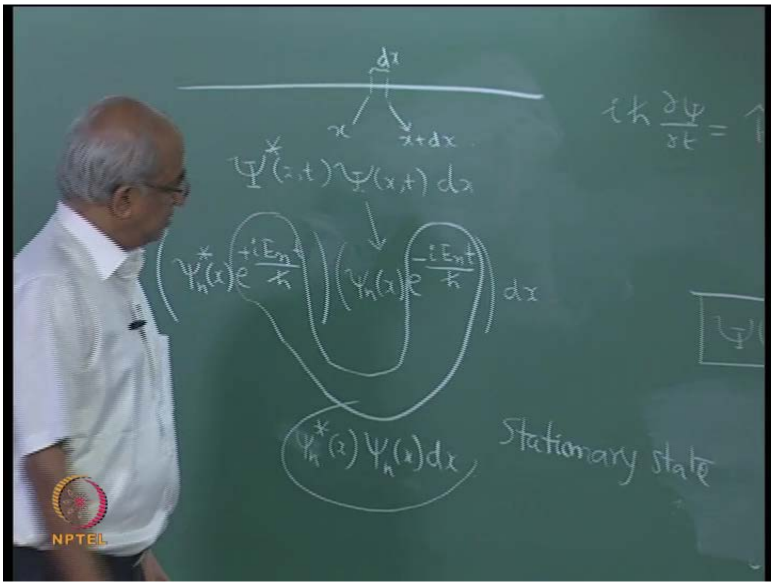

So, what is happening is that I have the particle moving in one dimension, then this is the small length dx lying between the point x and point x plus dx. The probability that your system will be found in this small interval is given by that expression. And you know, that psi is a function of time, so therefore naturally you would expect, that psi star psi also be a function of time. And therefore, the probability of finding the system in this interval, we would expect will change with time that is the general situation.

In general, most general situation will be, that the probability of finding system in the small interval will go on changing as time passes because a state function, we expect, is changing. But let us imagine that the state function is given by this particular expression, what will happen if you had this particular expression? Let us look at that by substituting this expression in here.

So, psi of x going to be psi n of x E to the power of minus i E n t divided by h cross, correct. This is psi of x and you have to multiply it by dx and you have to multiply it by complex conjugated of this, which will be equal to the psi n of x E to the power of minus i E n t by h cross with a star written. And what does this star mean? It means take the complex conjugates and I hope you remember how to take complex conjugates. The way to do that is, you see, look at the expression, wherever square root of minus 1 that is i. It is, you have to replace i with minus i.

So, if you look at this expression, well, there is minus i sitting obviously here, you have to replace with minus I, that means, this is going to become a plus. I can remove this star, but then I do not have the full detailed expression for psi n, may be, it will content an i in which case I will have to replace the i with minus i. So, the result is actually nothing but the complex conjugate of psi n, right. This is what happens.

Then, you look at this expression and you look at this term and that term together, right. One have E to the power of plus, the other has E to the power of minus and you would see, that the two things combine and give you the answer, answer is unity. So, therefore, what is the net result? The net result is that I get the answer, which is, which is psi n star of x psi n of x dx.

So, even though originally you see time was there in our expressions, it was there originally in this expression time is there. But if it so happens, that the state function is given by such an expression, then what has happened? The answer you get is independent of time. So, the probability that your system or your particle may be in a small interval of length dx, it does not change even though your state function.

You look at the state function; the state function actually depends upon time. There is time dependence here, but this dependence is very special. It is very special in the sense, that if you actually calculate the probability density, probability density is this product or if you calculate the probability, which include the dx also, then you find, that it does not, it is independent of time.

So, if the system is sitting in the state the probability, that the, that the system may be found in a small interval of length, dx does not change with time. Even though the system itself is evolving with time, probability does not change and this is reason why such a state is referred to as a stationary state because state is stationary. As far as time evolution is concerned, the probability does not change. So, such a state is referred to as a stationary state.

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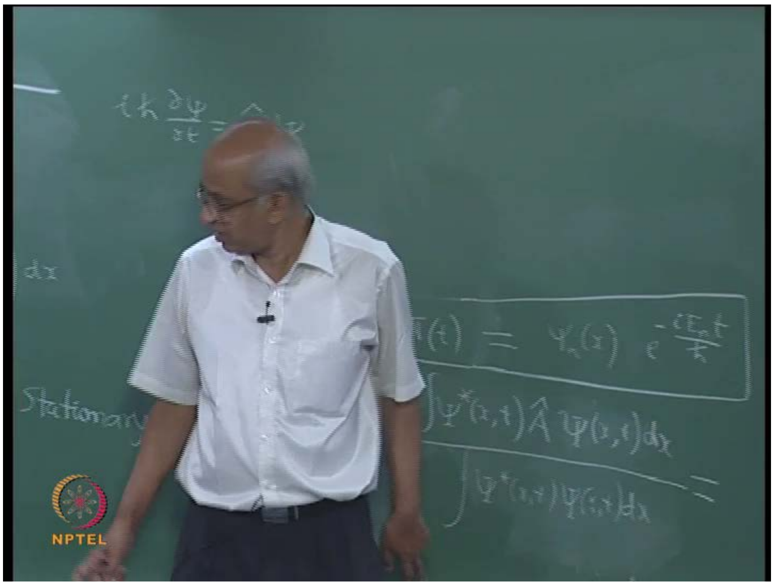

Now, in addition to this, suppose I have any operator A, you think of any operator A. For example, you can, you can think of any different operator, may be the Hamiltonian operator or may be the momentum operator corresponding to momentum or may be operator for possession. These are the simple things that you can think of. You think of, you think of any operator and I want to think of the expectation value of A, which is something that we have defined today. Expectation value is defined as integral of…, right. I am writing the expression that is appropriate for the one-dimensional system. So, integral of psi star is psi dx divided by integral of psi star psi. This is what it is.

Now, just the way we have done in this case, you see, I can proceed to evaluate this also. Well, as far as the new denominator is concerned, it is obvious, psi star psi, these are capital psis. But then you substituted which expression, where is the expression? This expression in, here this product is going to be independent of time, this product is going to be independent of time, so the integral of it over the entire space will independent of time. Ok, I need space.

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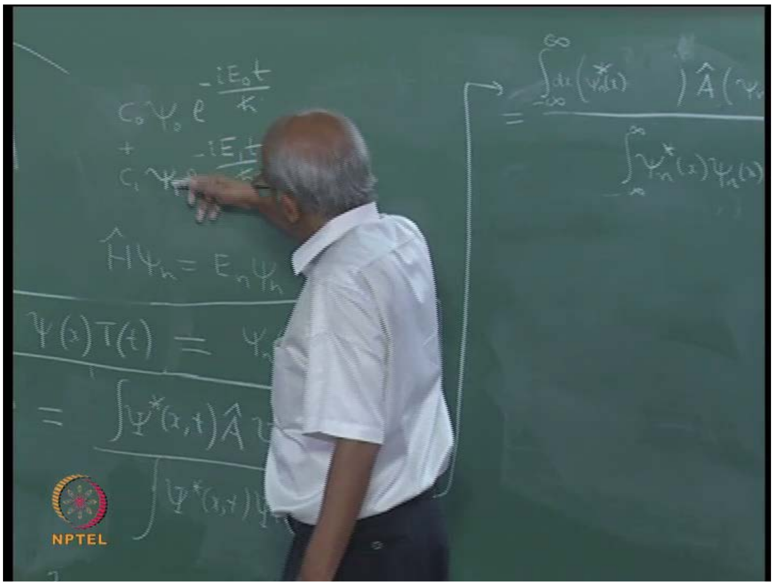

So, this is equal to, you can see the denominator, it is nothing but integral of psi star n x psi n x dx over the entire space is simple. Even though I have not put the limits, it is over the entire space actually. If you want to put the limits there from minus infinity to plus infinity, maybe I will do it, so that there is absolutely no confusion.

And then you look at the numerator, what has happened? You have the operator A and you have operator A operating upon psi n of x E to the power of minus i E n t divided by h cross and this is going to be multiplied by the complex conjugate of that. So, I am going to get psi n of x E to the power of minus psi E n t by h cross. It is the star here and then I will have dx and I will have integrated from minus infinity to plus infinity. So, this is what happens.

And now imagine, you see, you think of an operator like Hamiltonian operator or the momentum operator, these are things that normally do not dependent upon time, right. I have assumed that for this problem Hamiltonian is independent of time. So, Hamiltonial does not depend on time. Hamiltonian operator is simple operator, there is no time dependence. Possession, again is independent of, operator is independent of time.

So, if you are thinking of your situation where this A does not depend upon time, definitely this A will not affect this step; it will not affect that. So, you can move this term to the left side of A. And on the left side of A what is it that you have? You have the complex conjugate. So, this star can be taken inside, this minus sign will become a plus.

So, once you move this outside, this and that are going to cancel and you are going to get once I can safely remove this term as well as that term and you look at the result. You find that the result has no time anywhere, it is independent of time. So, therefore for the stationary state, the expectation value of any operator is independent of time.

And remember, we talked about yesterday the importance of expectation values. The importance is that you think of making a measurement and if you took average of all the answers that you get, that average is just equal to this expectation value, right.

So if the system is stationary state what happens? All the properties that you expect or all the things, all the properties that you measure and find out, they all are independent of time. Whether you measure the system now or may be, may be tomorrow or may be one year later, if it is, if it was on the stationary state, you are going to get the same answer. So, that is what it means and that is again the reason why this particular, this kinds of states are referred to as stationary states.

But then is that the most general solution of this equation? After all what is that we wanted? We wanted to solve this equation, but what we have found is actually certain special solutions, right, for which the time dependence and the possession dependence can be separated out, right. So, that is, those are the solution that we have found.

But can I have more complex solutions? The answer is yes. For example, let me say, that I have one stationary state, which I shall denote as psi 0, it has an energy E 0. So, therefore, the total time dependent wave function for this will be psi 0 into E to the power of minus i E 0 t by h cross, right. So, let me imagine what I am saying is I have the state i 0 having Eigen value E 0 and then I know, that psi 0 into E to the power of minus i E 0 t by h cross actually obeys this equation, correct. And similarly, if I have another Eigen function, which I shall denote as psi 1, this time having a different energy, right. Then what will happen is that I will have E to the power of minus i E 1 t by h cross.

Now, I measure i. I refer to this as the energy of the system. Why did I do that? The answer is actually extremely simple. If you look at the time independent Schrodinger equation, which I seem to have removed, If you look at the time independent Schrodinger equation, it is said that h psi n is equal to E n psi n. This is what I said. This means, that E n is an Eigen value of the Hamiltonian operator and remember, Hamiltonian operator is the operator associated with energy.

And therefore, if you make a measurement of energy, according to one of our postulates you make the measurement of energy, what would be the answer? It will be an Eigen value of the corresponding operators. So, therefore, these are nothing but answer that you are going to get if you make a measurement of energy of the system and that is reason why I will refer to E n as the energy of the system. Because if you make a measurement, this is going to be the answer, measurement of the energy, this is going to be an answer.

So, now, suppose I have one Eigen function, which I shall call I 0 having Eigen value E 0 and another one having the Eigen value, sorry, having another Eigen function, which is i 1 having the Eigen value E 1. Now, it is actually possible for me to multiply the first by some constant C 0, the second by other constant C 1 and add the two together. You take the first solution, multiply it by any constant; you like take the second solution, multiply it by some other constant. Add the two together. It is very, very easy to prove that. This also satisfies the original time dependent Schrodinger equation, right. This is the property of the time dependent Schrodinger equation. If you have a two solution you can just add them together and that the sum will also be a solution of the same equation, right.

So, having found special solutions these are, these are actually special solutions i 0 into E to the power of minus i E 0 t by h cross is a special solution. This one also is a special solution. Why are they special? Because they are products of two functions, which are multiplied together; one is dependent only upon x and other is dependent only on t. So, having found such a solution it is possible for you to add them linearly. You add the two of them linearly and get the new solution, right. It is, it is not difficult to show, that this sum actually satisfies the original equation.

Very, very, very easy to show an equation of, taking the equation and substituting it there and then you will see this is the solution, right. The question is automatically satisfied by this sum and further, you see, if you, if you think of such a state, you can actually calculate, may be, I shall leave that as an exercise. You can actually calculate psi star psi, the probability density and you can find that for such a solution psi star psi is dependent upon time. It will change as time passes, so that it is not a stationary state. Such a state does not represent the stationary state; it represents the state in which the probability density will change with time, ok. If you have question, of course, I shall be happy to answer them. Now, we have all the machinery that we need to look at chemical examples and that is what I am going to do. I am going to look at the simplest possible examples.

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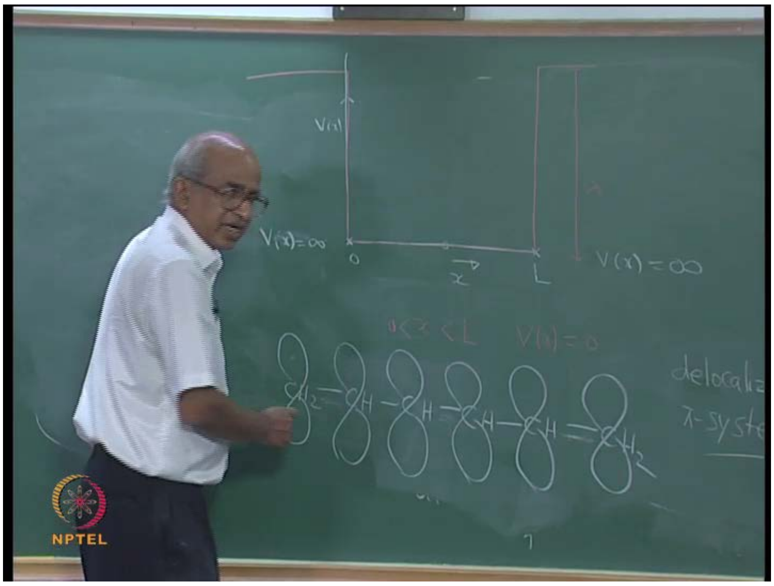

So, the simplest example is this. I, imagine that I have a particle, which is moving in one dimension, ok. And I shall further put the condition that it can move only in the certain length of that line. So, here is x equals to 0 and there is x is equal to L and I will say, that the particle is allowed to move only in that range, why? Because beyond this point, beyond that point I will say, that a particle will experience the potential that is infinitely large. So, here I will say the potential is infinity large in this region. I will also say that in this region the potential is infinitely large.

If you are, think I will tell you physical motivation for doing this in a few seconds, but suppose I am going to represent the potential energy along the vertical axis, right. I am going to represent potential energy along the vertical axis and this is my horizontal axis, which is actually x, then what will happen is that I am going to assume, that the potential energy is 0 if the particle is in this region within the box. That means, x is between 0 and the length of box, right. If x is between 0 and l, v of x is assumed to be 0. Well, if the particle is outside the box what will happen? The potential energy will jump to very large value.

So, suddenly, when I go from inside box to the outside potential energy, it jumps very rapidly to very high value, which actually will be taken to be infinity. This height, of course, I cannot represent infinity on the blackboard, but that is how the potential changes and similarly on the other side also. The potential energy actually jumps to infinity as you go out of box.

Now, before I go on to describe this model I want to tell you why think of such a model, which obviously, is not physically realizable, but it is very, very useful model. I mean, you all know, for a conjugated system, right, you have a conjugated molecule like C H 2, CH, CH, C H 2. Well, why stop it there. I will think of a more longer system. This is hexatriene; there are six carbon atoms and three double bonds.

Now, I suppose you would know, that this as a pi system is, well, I do have to assume some knowledge of orbitals and hybridization and so on, you would know any. If you ask any organic chemist he will tell you, that each of this carbons are s p 2 hybridized that will leave p orbital perpendicular to the plain of the molecule. So, therefore, I can represent them. I would have p orbitals in this fashion taking out one each, one of the carbons and the p orbitals are actually overlap and leads to what is referred to as the delocalized system into conjugated molecule. And each carbon actually contributes one electron to the, to this delocalized system, which is referred to as the pi system of the molecule.

So, you, in this case what happens is that because there are six carbons, each carbon contributes one electron. So, we say that pi system contains six electrons. So, if you think of any one of the pi electrons, that is, an electron is sitting here, but you say this orbital and that orbital overlap and therefore, what happens is that the electron can move from here to there to there to there, etcetera. That is the meaning saying that this system is delocalized, the electron can actually move from one end of the molecule to the other edge. So, you think of any one of the six electrons, they are free to move from here to the other.

And suppose, one electron is moving in this direction, what is the potential energy that the electron will feel? Let me draw a systematic appearance of the potential energy that the electron will feel. If it is moving along the molecule, see if it is moving along the molecule, right, let us say start starts somewhere here or may be it starts somewhere

here, at this end there, it is not very close to the nucleus, it is not very close to the carbons, so therefore, your potential energy will be relativity high. While if it is moving in this direction somewhere here, in the energy it is going to be someone close to the nucleus and therefore, what will happen? The potential energy will start decreasing.

If you plot on the potential energy as the function of the possession of the electron what is going to happen is, the potential energy will start decreasing. At the nucleus itself, it will reach a very large, but negative value, right, the potential energy. And then as it moves further what will happen is, the potential energy will actually increase, right. This is the possession of the nucleus. But as the electron is moving away from the nucleus, the potential energy will increase, reach maximum and then decreases to a very large negative value when it is near the second nucleus. And as it moves further what will happen? The same kinds of thing go on repeating again and again and again.

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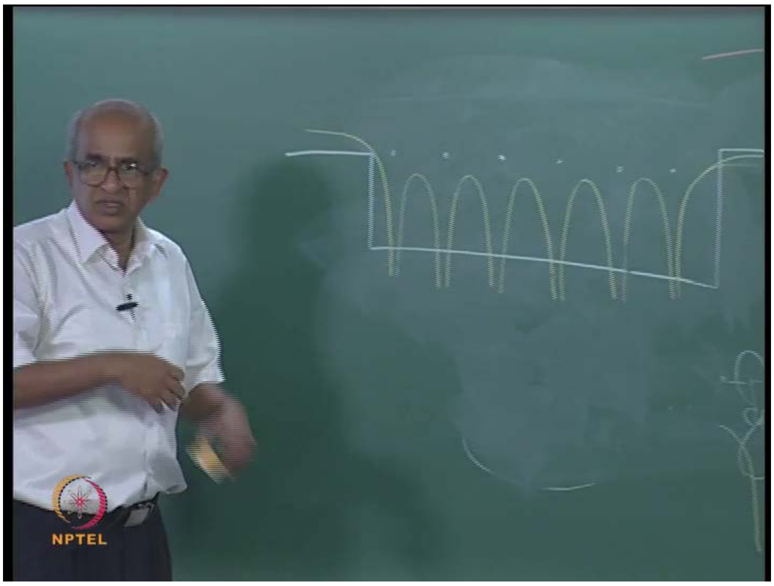

Well, maybe I will draw it better in here. This is how the potential energy will change. So, how many such? You will have six of them, right, no, five bonds, right; 1, 2, 3, 4, 5. Oh, actually I have drawn one too many. So, here is carbon atom 1, that is carbon atom 2, carbon atom 3, 4, 5, 6. And then what will happen is the potential energy, it actually will increase, ok. So, this is how the potential energy will be changing as the, as the electron moves along the molecule.

See, if you wanted to construct a model for the motion of this electron, actually what I should do is, I should think of having a potential energy, which has this kind of variance with the distance and then try to analyze that part. This is, obviously, very, very difficult. It is, such potential, solving the Schrödinger equation for the potential is extremely difficult.

So, therefore, what people have done is, they said ok, let us not worry about the fact, that there are variation inside the molecule. What is important is that if the electron is within the molecule, its potential energy is low because it feels the presence of the nuclei. Well, if you take the electron outside the molecule it does not feel the presence of nuclei and therefore, its potential energy has to be high or large right.

So, therefore, what is simplest thing that you can do? You can say ok, the simplest thing is that imagine I have certain length, within that length the potential energy is same everywhere, that only is an assumption. And outside the potential energy is large, right. It is actually large, but not infinitely large. But as an idealization we say, outside it is infinitely large because that makes things extremely simple. In fact, later on I will tell you what happens if you did not assume this. If you can assume that potential outside is not infinitely large, then what will happen, that I will tell you may be tomorrow.

But let us look at this model. What is the model? I have already given you this. See here, you are saying now that the potential energy is the same everywhere, so the potential energy of this curve, this curves are replaced by a flat potential energy. But then outside of curves you see what I should have done is, I should have the potential, which has this kind of appearance. That is what I should have actually done because outside of potential energy is not infinitely large, but to make the things simple I shall just say, that this height is infinity large and that what I have done in the description, that I have already given you, ok.

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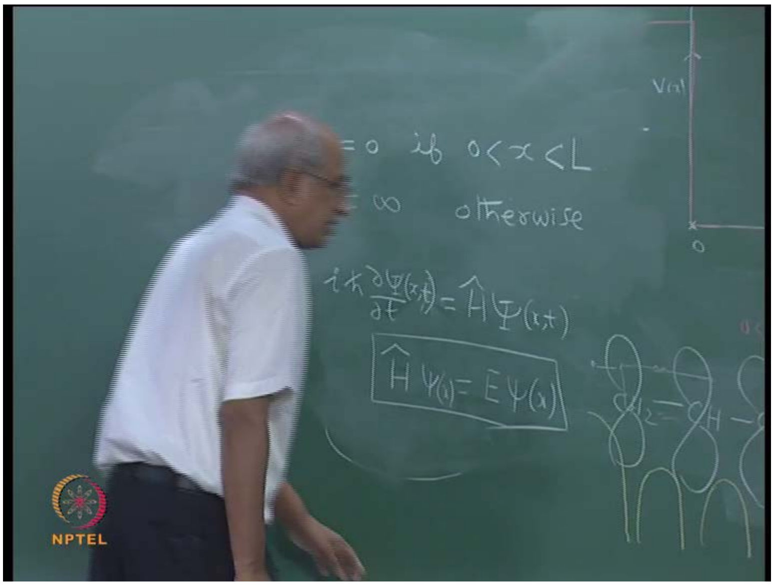

So, let me now go ahead then define things quantitatively. So, precisely speaking, what I have is v of x, I am going to say it is equal to 0. If x is between 0 and capital L, where L is the length of the box and particularly, we have a molecule like the hexatriene.

What is the typical length of the, of the molecule? Well, you know, that carbon-carbon double bond roughly is of your 1.4 or 1.5 Angstroms. If you have such five such bonds, roughly the bonds will need the length of how much? 5 bonds, 5 into 1.5, so roughly 7 Angstroms, 7.5 Angstroms, is the size of the bonds. I am telling you this so that you have an idea, that how big the box is.

So, what I am thinking of essentially? I am thinking of an electron, which confines to a one-dimensional box. It is assumed to move only in one direction and that box as a size of may be 7 or 7.5 Angstrom. So, if you have a longer molecule, let us say, if you have a conjugated system of 12 carbon atoms, then it will be twice as long. So, it may be about 15 Angstroms long. So, this L is of the order of, I mean, few Angstroms, let us say.

Let us say this is the system that I am interested in. So, if v of x, if x is between 0 and L, v of x is equal to 0 while if x is outside v of x is actually infinitely large, that is the nature of the potential. And what is it that I wanted to do? I want to look at my time dependent Schrödinger equation. What is the equation it is going to be? i h cross dou psi by dou t is equals to H psi. This is my time dependent Schrodinger equation.

Now, this obviously is an example where the potential energy does not depend on time, it does not change with time. So, therefore, it is possible for me to find what are referred to as stationary state, right. And in order to find the stationary state what should I do? Answer is very simple, I just have to solve. I do not need to solve this equation, but it is enough.

If I can solve this equation, H operating upon psi is equal to E psi that is enough. If you can solve this equation, then you can be happy because once you have solved this equation, you can take that psi and multiply that psi by E to the power of minus i E t by h cross, you will get the solution of the first equitation.

So, now I have to solve this equation and what is this equation? Now, let me write this in little bit detail. What this equation says is minus h cross square by 2 m dou square upon dou x square because that is our operator for kinetic energy Hamiltonial contents kinetic and potential energies, so minus h cross square by 2 m dou square upon dou x square plus v of x is my Hamiltonian operator. So, this is the equation that I should solve. This is the Eigen value equation that I should solve. Well, I think I will stop here and continue in the next lecture.

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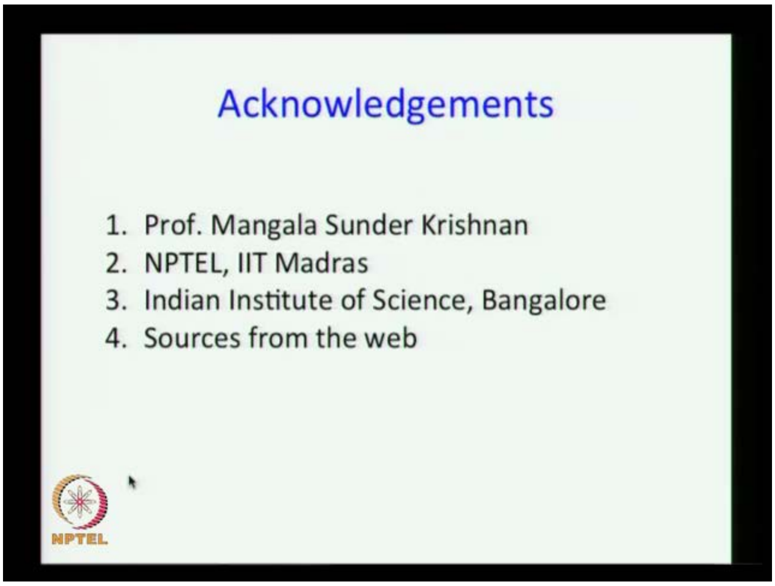

Acknowledgements

1. Prof. Mangala Sunder Krishnan
2. NPTEL, IIT Madras
3. Indian Institute of Science, Bangalore
4. Sources from the web

Thank you for listening.