

Introductory Quantum Chemistry
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Lecture - 36
Perturbation Theory

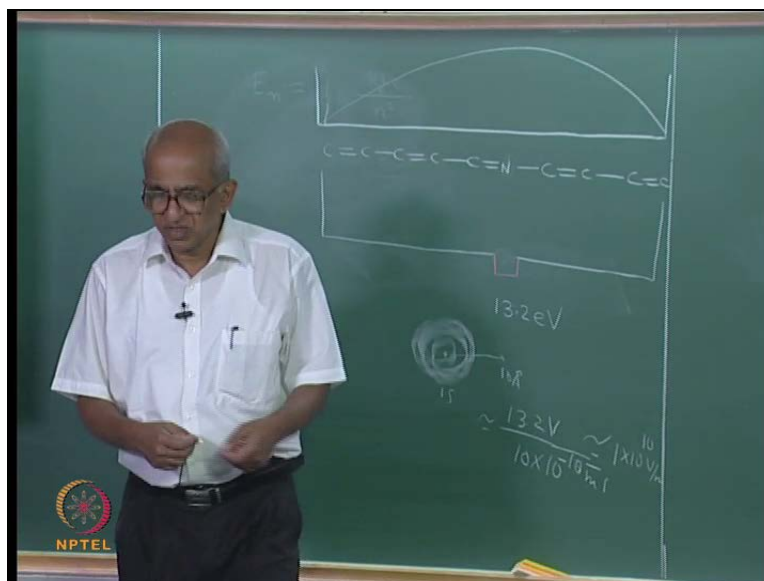
Stressing cases where the Schrodinger equation can be solved exactly, we discussed particle in a box, we discussed the harmonic oscillator, we discussed the hydrogen atom, and now very quickly I have told you the results for the rigid rotator now. So, therefore, you may be under impression that the Schrodinger equation can be solved for any problem, but that is not the way it is. Like there are only very few problems for which you can find the analytic solutions of the Schrodinger equation; these days of course, you have very powerful computers and therefore you can actually solve the Schrodinger equation numerically on the computer, right. But suppose you do not want to do that, because we see numerical solutions many a times do not give you physical ideas; physical concepts are not very transparent if you have a numerical solution.

So, and also there are problems in which you are not terribly interested in finding the exact solution. You would be happy if you can get some kind of estimates and understand the phenomenon. So, there have been approximate procedures of analyzing the solutions of the Schrodinger equation. For example imagine that I have a diatomic molecule like the one that I was describing to you now, and what I am going to do is I am going to subject it to an electric field. The molecule was freely rotating, but the moment I see okay, I will subject it to an electric field may be in the z direction. Then what happens is that the space is no longer isotropic. Earlier it was rotating freely, but the moment you say there is an electric field I think in the upward direction what will happen? The molecule, you see molecule has usually molecules have dipole moments, right, which means that one end is positively charged then the other end is negatively charged.

So, if the molecule has a dipole moment, what will happen? You see the electric field will interact with dipole and so the rotation will no longer be completely free, right. So, therefore, you are externally acting on the molecule essentially. If the moment as it shown an electric field I am affecting the motion of the molecule, right, and so what will

happen is that the Schrodinger equation that I would have will no longer be the simple one. It will have an additional term coming from the interaction of the molecule with the externally applied electric field. And many a times this external influence that you make on the molecule it is not large; it is only a small disturbance, right. And therefore, I can give you other examples you see.

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Suppose I talked about a conjugated system maybe something like this; there are hydrogen atoms I am not showing them, okay. There are hydrogen atoms as many as you want to satisfy the valences of these carbon atoms, and then the simplest thing is to say okay, I would have a particle in a one dimensional box which looks probably like that, right, and they have to say okay, if I am interested in the pi electrons of the system they may be assumed to be contained in a box of appropriate length, and they cannot go outside, and then you will calculate the allowed energy levels such a system, right. This is something that I have already told you, but now suppose I have as a chemist you see I can always replace this one of the carbons with nitrogen.

And suppose I want to think of this system what is happening is that while you can say at least roughly speaking the potential is the same in these regions, but when it approaches the nitrogen, nitrogen is more electronegative and therefore, in that region may be the potential energy is not the same as 1 square , but it is going to be less. So, therefore, if I had such a molecule, what will I do? I will say okay, the box is not exactly like the one

previously, but what it would have is in the vicinity of the nitrogen the potential is lower which I can perhaps draw in this fashion. So, you see if it is in this region I say the potential is lower while if it is outside the potential is the same as before.

This is very a crude model I have admitted, but then you can say what is happening is that there is a slight modification of the potential in a small region, and that what will it do? You see originally if you were thinking of this system the ground state the lowest possible state would look something like that you know that, because we have discussed this, and then what was the question that I would ask is suppose you make this slight change in the potential, what will happen to the wave function? How much would it get modified; not only how much would get modified, how much would its energy change? You know definitely that the energy of the system has to change. So, how much would it change? And this is only a small disturbance, right.

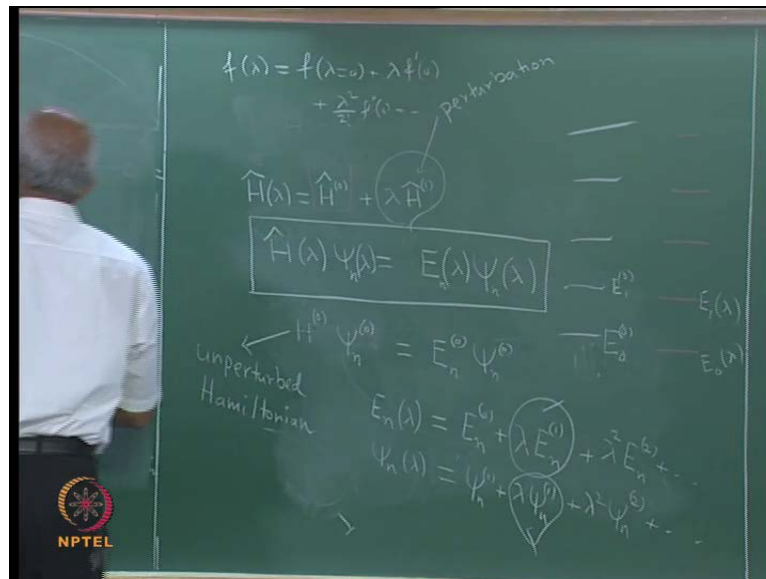
Now I can also give you another example. Imagine that I have a hydrogen atom. So, here is my hydrogen atom, and you know that the electron may be sitting in the 1 s if the hydrogen atom is in the ground state, or may be it may be sitting in 2 s or 2 p whichever state you want, okay, and well, let me just depend up n your previous knowledge. You have to give an energy of 13.2 electron volts, if you want to remove the electron from the ground state of the hydrogen atom, 13.2 electron volts are required; that means if you wanted to remove the electron roughly speaking from here to maybe 10 Angstroms a way you have to spend you have to supply a roughly; I mean this is only a rough because strictly speaking this is the energy required to take it to infinity, but I mean once it is 10 Angstroms a way the expense of the proton is negligible.

So, roughly if you have to take it to a distance of 10 Angstroms you have to spend that much energy and I mean this is only a kind of estimate that a physicist would make. This means that approximately speaking you have an electric field that the electron is experiencing. You see the proton is charged and therefore, what will happen? Anything around it will feel an electric field, and I want to know how much is the magnitude of the electric field? So, from this information typically I can calculate the electric field; what I would find is that it will be something like 13.2 divided by 10 Angstroms is how much? 10 into 10 to the power of minus 10 meters correct. So, approximately what will happen is that were electric field of course, I mean I should say 13.2 volts divided by that and therefore, what happens is that you will estimate roughly speaking there should be

something of the order of 10 to the power of volts per meter the electric field, I mean this is a very good estimate to give you an idea.

The electron near the proton actually fills an electric field of the order of roughly 10 to the power of 10 volts per meter. Now suppose in my lab I am doing an experiment in which I apply an electric field; the electric field that I apply may be 100 volts over a large distance not a small distance of the order of the Angstroms, right. So, the electric fields that we normally apply but of course I can have specialized experiments where the electric fields are very large, but normally if the electric fields that we would apply would be very small in comparison with the electric field that the electron experiences with in the atom.

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So, therefore, if you are thinking of the hydrogen atom you can say okay, I have my Hamiltonian for the hydrogen atom; I am not going to write down the Hamiltonian, but you know what the Hamiltonian is for the internal motion of the hydrogen atom, and if you say that you are going to apply a standard electric field which you may denote by what we got. So, notation should I use is a question? Well, let me denote it by capital E, and if you apply it in the z direction then what will happen is that there is an additional term because of the interaction of the electric field with the charges, and that additional term would look like this minus E into capital E; capital E is the externally applied electric field and E z is the z coordinate of the electron. Why z coordinate because I am

applying the electric field in the z direction. If you had applied it in the y direction they you would have had y there.

So, effectively I mean the details are not very important at this point of time. Then effectively what is happening is that I have a Hamiltonian, right, like may be the harmonic oscillator or the hydrogen atom. What I am doing is I am modifying that Hamiltonian by a small amount changing the Hamiltonian by a tiny amount. By applying an external electric field or by replacing one of the carbons with hydrogen; again I am modifying my potential there. So, there I can now generalize this, and say okay, I have a Hamiltonian which I will denote as H_0 . Now this notation can be confusing because this may mean H to the power of 0; I mean you may interpret this as H to the power of 0. I do not want that to happen. So, I will put this 0 within a bracket to indicate that this is my Hamiltonian.

For example, this may be the Hamiltonian for the hydrogen atom without any electric field, or it may be the Hamiltonian for the harmonic oscillator; one of these things for which we actually know the solution of the Schrodinger equation or may be the rigid rotator. We know precisely; today we have seen the Hamiltonian. So, it is one of them, and then what am I going to do? I am going to have a perturbation; perturbation means disturbance, right. How you apply may be an electric field or something you do, right; you replace a carbon with nitrogen. So, therefore, I have a disturbance, and that disturbance I am going to write as λH_1 . Why did I introduce a lambda? Well, if you want to have a physical example you can think of lambda as the electric field if you feel like; it is not necessary to think of it as an electric field.

So, there is a parameter lambda may be the electric field. When I change the value of lambda, what will happen? The disturbance that I cause is going to change; I mean I increase the electric field. So, the disturbance will increase, and this is my total Hamiltonian of the system, okay. Well, maybe I should put hat everywhere, and this actually is H is now a function formally of lambda, but as I have told you the effect of this term I would extract will be small in comparison with the effect of that. This is huge; I mean for example, hydrogen atom example I have showed you electric fields that exist in the hydrogen atom could be of the order of 10^{10} volts per meter when the electric fields that I obtain may be perhaps 100 volts per meter or much smaller essential.

So, what is it that I want to do? I want to find solutions of this equation $H \psi = E \psi$, but because your H is dependent upon the parameter λ , what would you expect? The energy also has to depend upon the value of λ ; I mean if I have an electric field applied then naturally the energy of the system will change when I change the electric field. So, therefore, this has to be a function of λ ; not only that the wave function when I change the electric field the wave function also should change. Therefore, this is going to be everything is going to depend upon λ . That is actually obvious, and further you say the way things are I know exactly the solution of the Schrodinger equation for this Hamiltonian, because you see this is for example, the hydrogen atom; I know precisely what the solutions of the Schrodinger equation are, correct.

Your Hamiltonian is such that I know I am assuming that I know the solutions of the Schrodinger equation if this was the Hamiltonian; that means if λ was equal to 0, suppose λ was equal to 0 then my Hamiltonian will be that and I know what the solutions are. So, therefore, let me say that imagine H_0 operates up on something. I will need a notation for that; that will be equal to some $E \psi$, correct. Well, here effectively what is happening is that I put λ equal to 0, right. And then what will happen? Here I would have ψ when λ is actually equal to ψ by λ is equal to 0, and how many ψ 's can I find? I can solve this exactly; therefore, I would have found all possible solutions. So, in a large number of in principle infinite number of Eigen functions and Eigen values. So, therefore, I would have different possible states of the system which I made invert to the subscript n .

And here also I would have to put the subscript n , here also I would have to put subscript n , because the energy will depend up on that subscript, right, and then what will happen is that you see that these are actually Eigen functions of your unperturbed Hamiltonian, and this term, also this H_0 is referred to as the unperturbed Hamiltonian while this one is referred to as the perturbation. This whole thing is my perturbation; that is why disturb my system, and when you look at this equation you say the ψ_n 's here are Eigen functions of H_0 the unperturbed Hamiltonian. So, therefore, because we are going to have several ψ 's sitting in different places it is best that I put a superscript 0 here also, because these are solutions corresponding to that Hamiltonian which means that I should put a 0 here or here as well as a 0 there.

It is necessary; I mean we should not get confused when we say different ψ . So, the moment you see this ψ_0 there you will realize that this is actually an Eigen function of H_0 , okay, and further this ψ_n ; well, one more thing I want to say your unperturbed system had several energy levels, correct. So, if I can draw the allowed energy levels this is probably something like allowed energy level which are having energy E_n . We can have the ground state with n equal to 1, next state with n equal to 2, or ground state I should not say n equal to 1; n equal to 0 is the usual notation for the ground state, and then what will happen? As I increase my electric field or as I increase my disturbance what will happen is that these energy levels are going to change. So, therefore, let me say what is going to happen is that I will have a new ground state, then another new first excited state, another new second excited state, third, fourth, etcetera. So, the energy levels are no longer coinciding with this.

So, this is the ground state. This actually this one is the ground state in the absence of any disturbance, and this is the first excited state in the absence of any disturbance; first excited state with disturbance and so on. So, therefore, you see this Hamiltonian itself has several different Eigen functions and their corresponding Eigen values. So, it is only natural that I should put a subscript n here, a subscript n here and the subscript n there, and further I actually know that $E_n(\lambda)$. As I change the value of λ , what will happen? $E_1(\lambda)$ is going to change, correct, and if I had λ various nodes λ close to 0, what will happen? $E_n(\lambda)$ will actually be equal to the unperturbed energy level and therefore, I would say that $E_n(0)$ will be if λ is 0 this is actually true, but if λ is not true, sorry λ is not zero then this will not be true.

But if λ is very small then what I can say is okay, there will be corrections to this energy, and those corrections will be, well, we can say linear; these small corrections that you would have will be linearly dependent upon λ . So, therefore, I would have to say okay, λ times the correction, right; it will be linear, but now you can imagine that when λ is very small this E_n is a function of λ . So, you can imagine that you are going to do a Taylor expansion of $E_n(\lambda)$ about λ equal to 0. If I did a Taylor expansion what will happen? You will get I mean may be if you want I can remind you of $E_n(\lambda)$ if you do Taylor expansion what is going to happen you will

get f at λ equal to 0 plus λ times f' at the 0 plus λ^2 by 2 factorial f'' at 0 plus etcetera; that is what is going to happen.

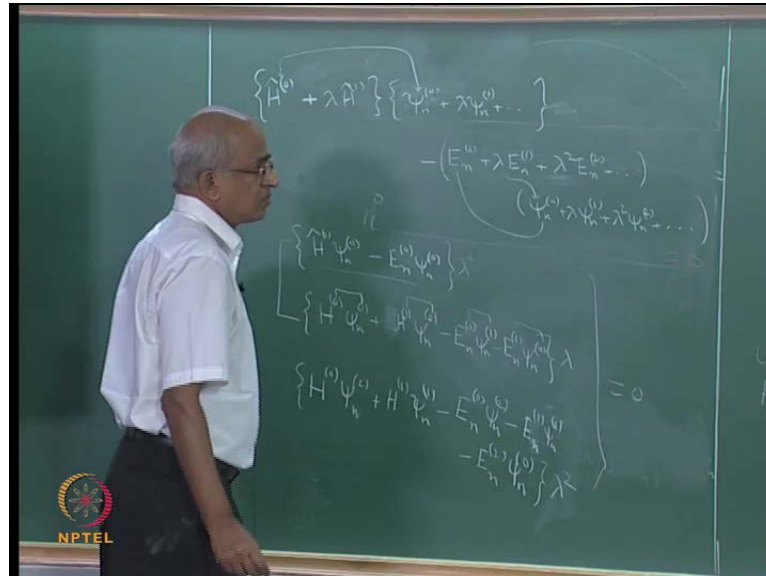
So, what is important for us is actually it is possible for me to imagine expanding E_n λ as a series in λ , and the first term the unperturbed term will be E_{n0} and the next time will be λ times E_{n1} ; this is not my notation. This whole thing is my correction to the energy, and then if I wanted the next correction, what will happen is that it is going to be equal to λ^2 into E_{n2} plus etcetera. So, that is the way I write the expression, and now I will use the following words. This is my unperturbed energy unperturbed energy; this is my first order correction to the energy. That is my second order correction, then I can think of third order, fourth order, fifth order, okay if I want. In a similar fashion I can think of the wave function, what will happen with my wave functions? $\Psi_n \lambda$ I can imagine.

What is going to happen is that I would have Ψ_{n0} plus λ times Ψ_{n1} . So, this is actually this whole thing is my first order correction to the wave function, then λ^2 times Ψ_{n2} to second order this whole thing again is my second order correction to the wave function and so on. So, what is it that I would like to do? I would like to estimate the first order correction to the energy; I have applied an electric field that I want to know, what is the modification of the energy level? So, this I would like to calculate; if possible I would like to calculate that and so on, but already as I told you the disturbance is usually small. So, maybe it is enough if I just calculated the first term, because I would expect that the second term will not be that much important, because you look at this it involves λ^2 . Suppose if λ was identified with the electric field and electric field as I said is very small in comparison with the electric field that exists in the atom.

So, therefore, this is a term that is linear in the electric field; this will be a term that will be a second order square of the electric field. So, you would expect that this correction to the energy will be much smaller than this correction, unless of course, you have a large electric fields, right. So, therefore, we would be happy if we can estimate this and perhaps that. In fact, you can derive expressions for those also, but we will not go into those expressions, right. So, what am I going to do? I want to determine these things, and of course, you see what do I have? I have the Schrodinger equation; this is the Schrodinger equation that I have of course, this is the term independent Schrodinger

equation. So, let me write that equation once more; I know that H lambda is given by this expression.

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So, therefore, I am going to say I would H_0 plus lambda times H_1 operating upon ψ_n , where is ψ_n ? ψ_n is sitting here, and ψ_n lambda I am going to write as ψ_n^0 plus lambda times ψ_n^1 , etcetera is equal to. So, this is what happens to the equation. Now even though you would not have realized it; I have made a very strong assumption in whatever I have done. Let me tell you what that assumption is. This says that if I put lambda is equal to 0 my perturbed wave function actually will become equal to ψ_n^0 ; that is what it assumes. This is true in general provided your energy level is non degenerate, okay. If your energy level is degenerate let us say it is doubly degenerates then when lambda is equal to 0 you see I mean you do not have a unique state, because there are two states there, right. So, what would this be? Can I think of a unique state or may be it can be a linear combination of the two states that are already there.

It may be the first state, it may be the second state, or perhaps it may be a combination of the two; I do not know. So, this expansion actually assumes that I know uniquely what this ψ_n^0 is, and that I can do only if my energy level is non-degenerate, and therefore, whatever I am actually developing is applicable only for non-degenerate levels; it is not applicable for degenerate levels. Actually strictly speaking I should make a discussion of degenerate levels, but I am not planning to do that, because we will discuss the other

method which is referred to as the variation method and it is fairly straight forward to make use of that method even for cases where we have degeneracy; that is absolutely no problem. So, whatever I am doing is valid for a non-degenerate level; this actually means that if you are thinking of the harmonic oscillator then things are fine, because for the harmonic oscillator everything is non-degenerate.

If you think of the particle in a box also everything is fine, because they are all the allowed energy levels of the particle in a box are non-degenerate, but if you think of the hydrogen atom then you have to be careful the theory that I am developing. It will be definitely applicable for the ground state, because ground state is non-degenerate; it is the 1 s stage, but if you are going to apply if you want to apply perturbation theory to the other states then you have to be careful, okay. Now what I want to do is so therefore, I have already told you that this equation is constrained in that ψ_n or this energy level E_n is assumed to have only one stage; it is non-degenerate. Now what I am going to do is you see I know that this equation the left hand side should be equal to the right hand side for any value of λ . If you look at this you have a power series in λ actually; you can say okay, remove this equal sign and make it negative, and then what will happen this has to be equal to 0.

So, if you look at this it is a power series in λ and the power series has to be identically equal to 0 for all values of λ starting from 0 to some value. And if that is to happen what is the condition? We already know what the condition is you can think of it as a power series in λ , the coefficient of each power of λ should be equal to zero. So, let us do that. The other thing that you should remember is that these are all there are operators. So, therefore, I mean I have forgotten to put the hat sign, right; so better that I put the hat sign. So, what is the coefficient of λ to the power of 0? From here you are going to get, right, this into that is going to be giving me a term that does not depend upon λ . So, H_0 operating upon ψ_n is one term, and from here you see this; this is occurring with the negative sign, because I should not forget the negative sign; let me put it here.

So, this into that is going to give me a term that is independent of λ . So, therefore, the first term will be $H_0 \psi_n$ minus $E_n \psi_n$. This is the coefficient of λ to the power of 0, the term independent of λ and then I would have a term that is linear in λ ; what is that? H_0 operating upon this one; remember λ has no

position dependence; λ is like your electric field which is the same everywhere. So, therefore, H_0 operating on λ , λ is unaffected, right; it is just a number. So, it is unaffected by H_0 . So, what you are going to get is H_0 operating upon ψ_n , is that all? No, because there is a λ here that λ has an H_1 and that can go and operate up on ψ_n . So, this λ is there, and I have already taken into account of λ because I put a λ outside minus what will happen? You will have E_n multiplying that, and then you will have this term multiplying that.

So, that is going to be minus $E_{n+1} \psi_n$. I will continue in my next lecture; what I shall do then is to write the term that depends upon λ^2 , and then you will have λ^3 , etcetera, perhaps the series actually continues, and everything together is equal to 0. But because this is a power series in λ which is identically equal to 0 what will happen is that the coefficient of each power of λ must be 0. So, therefore, I will have many many equations to work with. So, we have this power series, and do we say that the power series has to be equal to 0; I will just fill in the coefficient of λ^2 . It is not actually very difficult to write it down, because you see if you look at the one that corresponds to λ . If you look at this coefficient you will see that the sum of this 0 and that one; if you just added these two up answer is 1, if you added these two answer is 1, those two add 1, add those to 1.

So, naturally if you add a λ^2 what you would expect is that if you added those things you should get through that is all. So, remembering that you can easily write down. So, $x_0 \psi_n^2$ plus $H_1 \psi_n$; there is no H_2 that you have to remember H with superscript 2 is not there, because this is the perturbation minus $E_{n+2} \psi_n^2$ minus $E_{n+1} \psi_n$ minus $E_{n+2} \psi_n$. This will be the coefficient of λ^2 . Similarly if you wanted to write the coefficient of λ^3 or λ^4 it is not difficult, easily you can write it. But anyway we are not going to be worried about the higher terms involving λ^2 or λ^3 ; we will only be interested in these two equations, why? Because I am interested in first order correction to energy and first order correction to the wave function, right. So, let us look at these two equations what do they tell us? It tells me that this must be equal to 0. That is the first thing.

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$$H^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

$$H^{(0)} \psi_n^{(1)} + H^{(1)} \psi_n^{(0)} - E_n^{(0)} \psi_n^{(1)} - E_n^{(1)} \psi_n^{(0)} = 0$$

$$H^{(1)} \psi_n^{(0)} - E_n^{(0)} \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} - H^{(0)} \psi_n^{(1)}$$

$$\int \psi_n^{(0)*} (H^{(1)} \psi_n^{(1)} - E_n^{(1)} \psi_n^{(0)}) = E_n^{(1)} \int \psi_n^{(0)*} \psi_n^{(0)}$$

$$0 = E_n^{(1)} - \frac{\int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)}}{\int \psi_n^{(0)*} \psi_n^{(0)}}$$

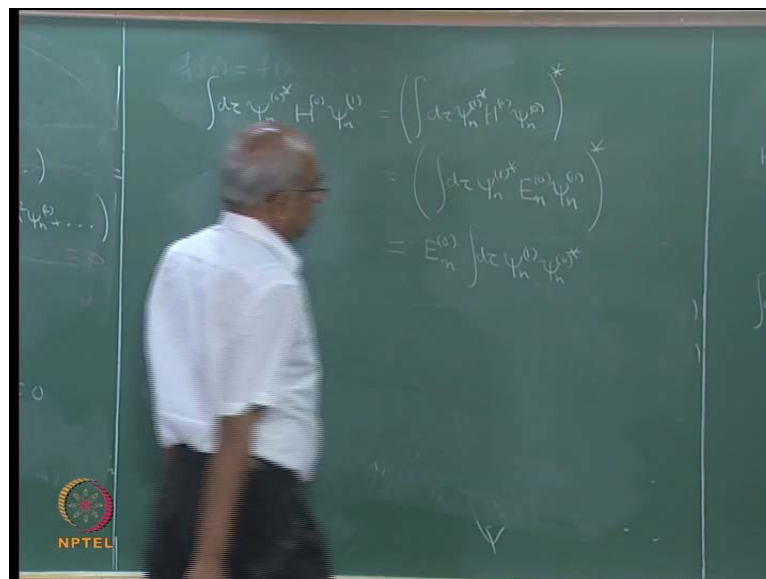
So, what is that equation? Equation says that $H^{(0)} \psi_n^{(0)}$ must be equal to $E_n^{(0)} \psi_n^{(0)}$, but this we already know; I mean this equation satisfies, because this is just the unperturbed Schrodinger equation, Schrodinger equation corresponding to the unperturbed Hamiltonian. So, nothing new; this we already know. Well, if you look at the second equation; what is the second equation? It is the coefficient of lambda, what are you going to get? You are going to get $H^{(0)} \psi_n^{(1)} + H^{(1)} \psi_n^{(0)} - E_n^{(0)} \psi_n^{(1)} - E_n^{(1)} \psi_n^{(0)}$; this is what the equation says, right. I hope I have not made any mistakes on the superscripts. Now among in this equation what is going to happen is that I actually know what $\psi_n^{(0)}$ is. $\psi_n^{(0)}$ is I know because I have solved the Schrodinger equation for the unperturbed problem; I also know, what are the other things that I know? I know this one, I know this term; yeah, that is all that I know, right, but I do not know $E_n^{(1)}$.

So, what I will do is I will take the terms that involves $\psi_n^{(0)}$ to the right hand side. So, I would have $H^{(0)} \psi_n^{(1)} - E_n^{(0)} \psi_n^{(1)}$ is equal to something; what is that something? Well, you please check this; what have I done? I have retained this term as well as that term in the left hand side and removed the other terms and put them on the right hand side, correct. Now I want to find out $E_n^{(1)}$ for example. Now it seems difficult, but actually it is very easy with this equation. All that you need to do is you multiply form the left hand side with $\psi_n^{(0)*}$; this is known to us, $\psi_n^{(0)}$ is known to us. So, therefore, I can multiply throughout by $\psi_n^{(0)*}$, maybe I will write the terms

separately $\int d\tau \psi_n^{(1)} H \psi_n^{(0)}$, that will be the first term minus $E_{n-1} E_n$; sorry not E_{n-1} but E_{n-0} , remember E_{n-0} is a constant. So, it is unaffected by the integral sign.

So, you will get $\int d\tau \psi_n^{(0)} \psi_n^{(1)*}$ with a star here that will be the second term; what happens to the right hand side? I would have $E_{n-1} \int d\tau \psi_n^{(0)*} \psi_n^{(0)}$ minus $\int d\tau \psi_n^{(0)*} H \psi_n^{(0)}$; it does look messy, but it is actually fairly simple to evaluate this because I know that this term, how much is this term? See these are functions Eigen functions, they are all; oh, no no, that I do not know. This is the one that I was talking about this object I know $\int d\tau \psi_n^{(0)} \psi_n^{(0)*}$ integrated over the entire space. Answer is unity, because the function is normalized. So, let me just removed that. So, this is actually unity; this whole thing is equal to unity, and now if you look at this expression, what is it that I have? I am going to look at this expression, where do I write? Maybe I can remove these things.

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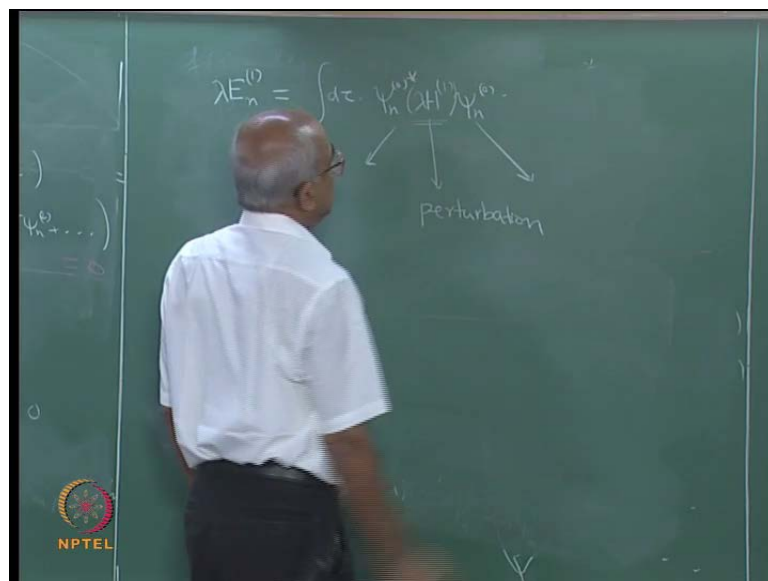
The integral that I have is $\int d\tau \psi_n^{(0)*} H \psi_n^{(1)}$; this is the object that I have, but I know that H is a Hermitian operator. So, I can make use of the properties of the Hermitian operator. So, how will I make use of the properties of a Hermitian operator? It is actually equal to $\int d\tau \psi_n^{(1)} H \psi_n^{(0)*}$. You can allow H to operate upon $\psi_n^{(0)}$ instead of it operating up on $\psi_n^{(1)}$, and you can put $\psi_n^{(1)*}$ on the other side, and from the properties of the Hermitian operator I know that these two have to be complex conjugate. So, therefore, properties of the Hermitian operator imply that this has to be valid, and

that is actually very nice because see here H_0 was operating up on ψ_{n-1} , but there H_0 is operating up on ψ_{n-0} , and this is an Eigen function of H_0 .

So, what will be the answer? You will have $\int d\tau \psi_{n-1}^* E_{n-0}$ will be the answer of this operating upon ψ_{n-0} multiplied of course by ψ_{n-0} ; that is what it is, correct, and I can take the star operation inside, what is going to happen? E_{n-0} is an Eigen value, Eigen values of Hermitian operators they are real. So, this starring will have no effect on this. I can take it out, because it is just like a real constant. Then I would have $\int d\tau$, again take this star inside. So, you will have ψ_{n-1} multiplied by ψ_{n-0}^* , correct. So, we have evaluated this, evaluated this and found that it is equal to that.

And if you look at this equation you would realize that this we have evaluated and we have found that it is exactly equal to; look at that and you look at this you will see that they are the same. So, therefore, this and that are actually equal and therefore, they will cancel each other, right, and hence what is it that I have left with? I have left with 0 equal to E_{n-1} , right. This is actually equal to 1 ; this term we have said it is equal to 1 minus $\int d\tau \psi_{n-0}^* H_1 \psi_{n-0}$ with a star of course. Well, I will rewrite that equation; I mean write that equation once more so that the idea is very clear. There is a 0 here. So, I will take E_n , I will take this to the other side; I mean I can write it as an equality sign.

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What do I find? I find E_{n1} is equal to how much? $\int d\tau \psi_n^* H_1 \psi_n$; now what is our first order correction to energy? First order correction to energy strictly speaking is λ times that. So, what will happen? I will have to put that λ back, and I will get this. So, this is my first order correction to the energy, fine. Now what does it say? You look at the physical content; whenever you have an equation you should be looking at the physical content and understanding that. What it says is here is your perturbation, and what is it that you have here? The unperturbed Eigen functions, right.

So, if you wanted to calculate the first order correction to the energy of the n th stage, what you should do is you should take the perturbing Hamiltonian calculate its expectation value using the unperturbed wave function; that is all very simple. You know the unperturbed wave function, you know what the perturbation is, and therefore, you can easily calculate this. It is not difficult at all.

Thank you for listening.