Chemistry Atomic Structure and Chemical Bonding

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Lecture - 48

First Order Time Independent perturbation Theory for Non-Degenerate states

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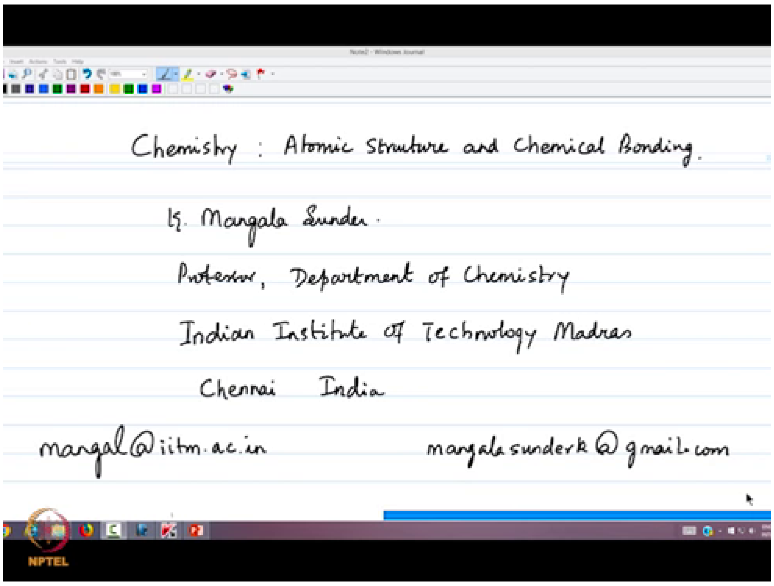

Chemistry : Atomic Structure and Chemical Bonding.

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Welcome back to the lectures in Chemistry and or the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder and I am in the Department of Chemistry, Indian Institute of Technology Madras.

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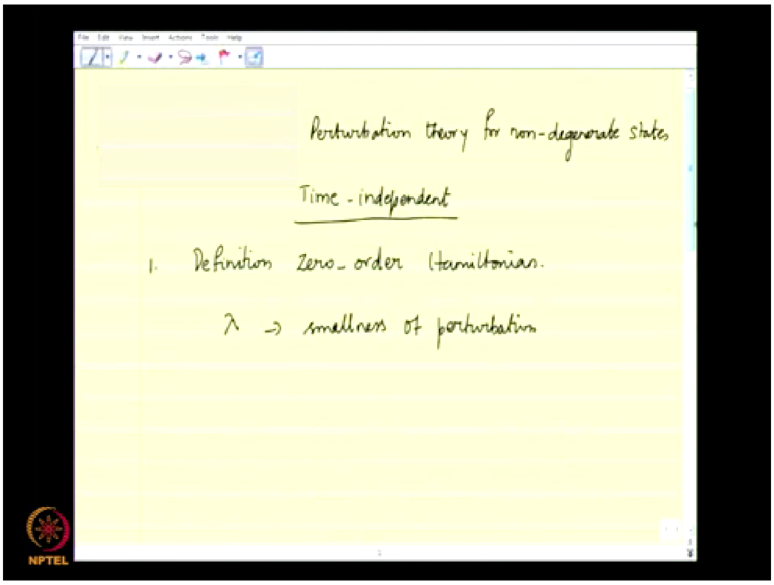

Perturbation theory for non-degenerate states

Time - independent

1. Definition zero-order Hamiltonian.

$\lambda \rightarrow$ smallness of perturbation

Definition of what is known as the perturbation free Hamiltonian or in the language of quantum chemistry and physics it is perturbation or the definition of zero-order Hamiltonian. Recall of the very last part of the last lecture I introduced a parameter called lambda, the lambda referring to the smallness of perturbation.

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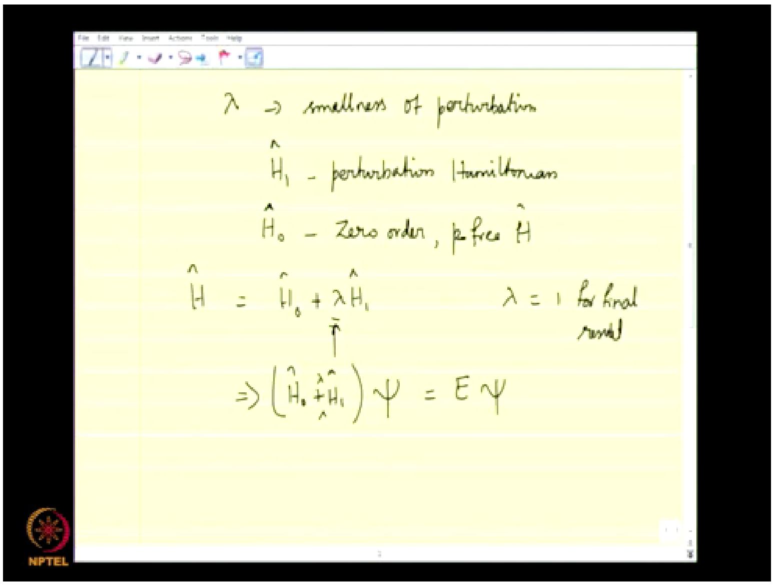

$\lambda \rightarrow$ smallness of perturbation

$\hat{H}_1$ - perturbation Hamiltonian

$\hat{H}_0$ - Zero order, p. free $\hat{H}$

$$\hat{H} = \hat{H}_0 + \underset{\uparrow}{\lambda \hat{H}_1} \qquad \lambda = 1 \text{ for final result}$$

$$\Rightarrow \left(\hat{H}_0 + \hat{H}_1\right)\psi = E\psi$$

So, that if the perturbing interaction is expressed by H1 the Hamiltonian H1 as the perturbing or perturbation Hamiltonian to a perturbation free Hamiltonian of the molecular system called H0 which is zero-order perturbation free Hamiltonian. Then we write the total Hamiltonian as H naught plus lambda H1 keeping the parameter lambda as a parameter that helps us to order the contributions in a series. You recall that I have been saying that the perturbation theory provides you solutions in the form of infinite series.

And therefore, we need to find out what is the most important correction, what is a less important correction to the total energy and what is and so on. So, to keep that ordering clear we use a parameter lambda and of course, then we need the fine result we can always set lambda is equal to 1 for getting the energies. So, in a sense it is also like the convergence parameter. The smallness of the electric field, the smallness of the magnetic field, the smallness of the external electromagnetic radiation, if you have a time dependent perturbation and so on, all those things are represented by this mathematical parameter lambda which of course, is set to 1 at the end. So, that this goes to H naught plus H1 which is the solution that we are looking for acting on some psi giving you and E times psi. To do that we keep this lambda in between and then obtain the solutions in the form of lambda, lambda square, a power series in terms of various powers of lambda. And then we can order these perturbation corrections.

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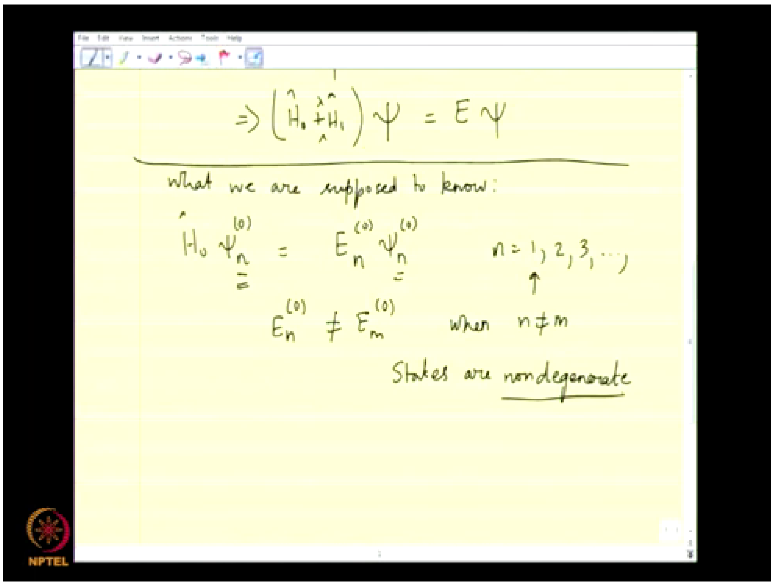

$$\Rightarrow \left(\hat{H}_0 \overset{\lambda}{+} \hat{H}_1\right)\psi = E\psi$$

What we are supposed to know:

$$\hat{H}_0 \psi_{\underline{\underline{n}}}^{(0)} = E_n^{(0)} \psi_{\underline{\underline{n}}}^{(0)} \qquad n = 1, 2, 3, \ldots,$$

$$E_n^{(0)} \neq E_m^{(0)} \quad \text{when} \quad n \neq m$$

States are <u>nondegenerate</u>

So, let us do that by first writing down what we are supposed to know before we proceed towards solving the problem ok. We are supposed to know the H naught; that is the feel free, the perturbation free Hamiltonian and it is solutions; psi n 0 to indicate that this is the solution of the field free Hamiltonian or the perturbation free Hamiltonian and the energies are E n 0 psi n 0 ok. Please remember that there are many solutions n can be 1 2 3 etcetera like in the case of a particle in the box; n can be 0 1 2 3 in the case of a harmonic oscillator or asses in the case of hydrogen atom n can be 1 2 3 etcetera.

So, this is a quantum number we will generally represent by the lowest value for harmonic oscillator this will be 0. But it does not matter we are only doing a notation we are only representing it by a notation. So, we have many solutions and many energies and the requirement is that E n 0 is not equal to E m 0, when n is not equal to m ok. That is it is as states are non degenerate. The problem of degeneracy comes in when you remember particle in a two dimensional box where the first time you come across the degeneracy. That you have two quantum numbers n 1 and n 2 and the wave functions are associated with the 2 degrees of freedom x and y. And if you interchange n 1 and n 2 you still have the same solution, but the wave functions are different.

Therefore, they represent two different quantum states with the same energy we preclude we do not include such states in our calculation at the moment; so this is for non degenerate states. Likewise in the case of hydrogen atom, if we have to look at the degenerate states like the 2 s and 2 p the 3 2 p states or the 3s 3p and the 5 3 d states. We will have to do it slightly differently, so we will not worry about such problems of the moment. We will consider only states which are non degenerate.

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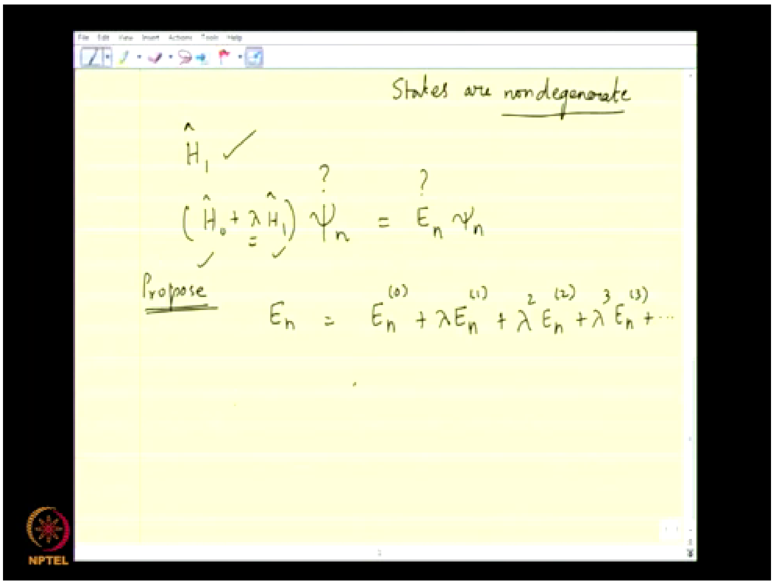

States are <u>nondegenerate</u>

$\hat{H}_1$ ✓

$$\left(\underset{\checkmark}{\hat{H}_0} + \underset{=}{\lambda}\,\underset{\checkmark}{\hat{H}_1}\right) \overset{?}{\psi_n} = \overset{?}{E_n}\,\psi_n$$

Propose

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \cdots$$

Therefore we are supposed to know the zero-order Hamiltonian, the solution to the zero-order Hamiltonian the wave functions and the solution the energies, the Eigen values to the zero-order Hamiltonian. Now, we are also supposed to know the perturbing Hamiltonian, we must know what is the disturbance new term and the form of the disturbance. Our objective is to calculate the effect of this disturbance on the wave functions that we already know and then obtain corrections to the energy.

So, we know this and therefore, the question that we are asking is H naught plus lambda H1 on some wave function psi n because there also you expect many solutions to the total Hamiltonian, but the psi n is not the same as the other psi n zeros that I have written down except when lambda is equal to 0 because at that point you have only the zero-order solutions. So, we have E n this E is again different from the E 0 and psi n. So, this is the solution that we are looking at. We want to know the psi n we want to know the E n. We now sorry let me not put a tick mark because it is not something that we know already we want to know the psi n and we want to know the E n.

This is known H naught is known H1 is known and therefore, we are looking at the solutions. What are the steps? First propose, ok I am going to be non quantitative in the sense I want to prove mathematically certain results which are needed for this purpose namely the convergence of the perturbing series and so on. I will not do any of those things, but let me propose based on some simple logical argument; that E n can be expanded in the form of a power series in terms of the parameter lambda ok.

So, that we will write E n as E n 0 when lambda is 0 times lambda times the corrected quantity E n 1. This 1 refers to the fact that this is to the power lambda associated with to the power lambda. To first order in lambda it is lambda square E n 2 meaning that this correction E n 2 is the second order correction to the total energy because it is associated with lambda square. Ultimately this lambda will have no meaning I mean no significance, but now we have a way of finding out the most significant correction, the less significant and so on. So, we will keep this as a parameter; lambda cube E n 3 plus and so on. In general if you need to calculate beyond E n 3, E n 4, E n 5 etcetera my first reaction would be why use perturbation theory, why not think about some other method to more direct method to obtain the energy.

Because if you have to obtain many correction terms the perturbation series then it is probably that it is probable that the perturbation series is not a very effective method; but that is my personal opinion ok. People do obtain several orders of corrections to this and there are programs which would calculate some 10th order perturbation correction, 13th order perturbation correction, I mean I do not understand the significance, but that is because I do not understand it.

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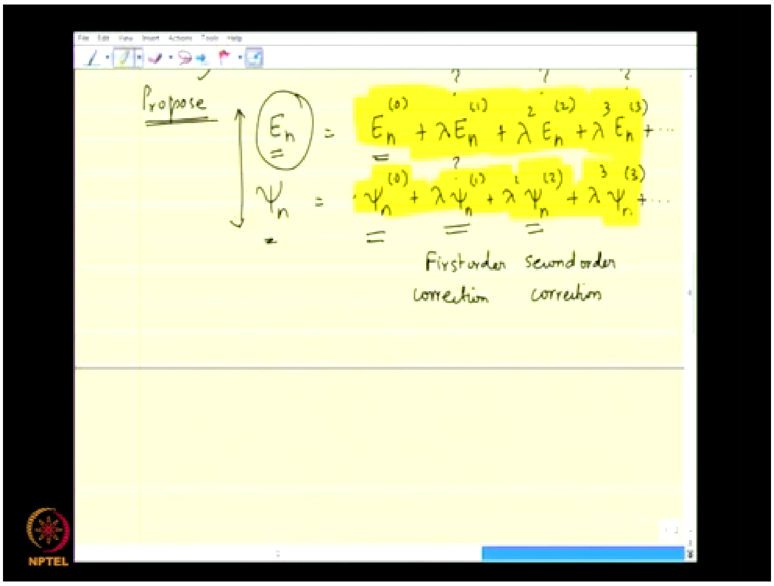

Propose

$$\boxed{E_n} = E_n^{(0)} + \lambda \overset{?}{E_n^{(1)}} + \lambda^2 \overset{?}{E_n^{(2)}} + \lambda^3 \overset{?}{E_n^{(3)}} + \cdots$$

$$\psi_n = \psi_n^{(0)} + \lambda \overset{?}{\psi_n^{(1)}} + \lambda^2 \psi_n^{(2)} + \lambda^3 \psi_n^{(3)} + \cdots$$

First order correction

Second order correction

What about the wave function psi n? That also we will write in the form of psi n 0, the in the absence of perturbation the solution plus lambda psi n 1 plus lambda square psi n 2; these are corrections to the wave function this is called the first order correction; this is called the second order correction, first order correction, second order correction plus third order if you wish psi n 3 plus so on. You see that the values of E n and psi n or E n 0 and psi n 0 if the perturbing Hamiltonian is not there which make sense because that is what we have assumed.

Therefore, we are adding correct and correctional quantities, correction to the exact value in the form of these. And our objective is therefore, to obtain this 1 sorry E n 1 E n 2 may be E n 3, but I will not do it in this course in this I will probably give it as an assignment. Obtain possibly psi n 1 we may not even need to do psi n 2.

So, you see that I would only explain the method to determine the first few terms and then of course, you can carry out the analysis yourself for other terms. So, we have a proposal for E n in the form of let me highlight this, we have a proposal for E n in the form of this. We have a proposal for psi n in the form of this expansion and what other properties do we need to know in order to make use of this proposal?

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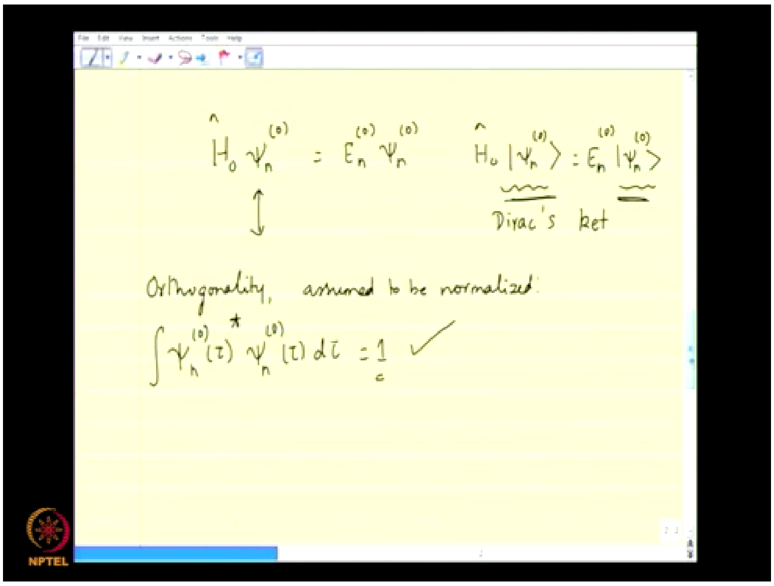

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \qquad \hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$$

$\updownarrow$

Dirac's ket

Orthogonality, assumed to be normalized:

$$\int \psi_n^{(0)*}(\tau)\, \psi_n^{(0)}(\tau)\, d\tau = 1 \quad ✓$$

Let us look at the solution in the absence of perturbation in the H naught psi n 0 is equal to E n 0, psi n 0 ok. Now these are wave functions, but if I have to use this in a formal way I would rather write H naught using the ket notation psi n 0 giving you E n 0 times psi n 0 ok, this is the Dirac's ket notation ket.

So, let me keep this in parallel, the wave functions are the Eigen functions of the Hamiltonian H naught satisfying orthogonality properties and are also assumed to be normalized ok. What it means is that in some coordinate system in which it is expressed psi n 0 tau the coordinate can be x or x y z or r theta phi in the case of hydrogen atom, whatever is that it is represented collectively by this symbol tau psi n 0 start tau psi n 0 tau, d tau is equal to 1. This is the normal normalization property if we want to interpret to the wave function squares as probabilities of finding the system in certain coordinate space and so on; therefore this is assumed ok. If it is not we can always find a normalization constant and make sure that we use only the normalized wave functions.

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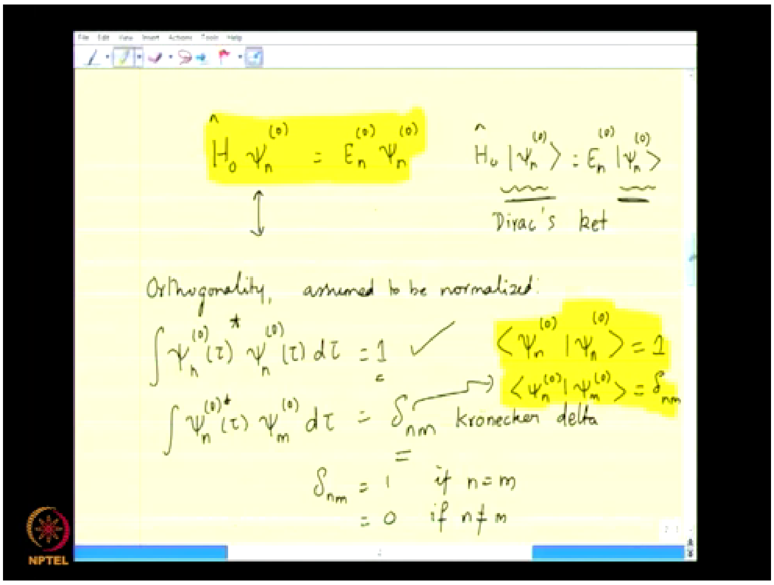

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \qquad \hat{H}_0 \underbrace{|\psi_n^{(0)}\rangle}_{\text{Dirac's}} = E_n^{(0)} \underbrace{|\psi_n^{(0)}\rangle}_{\text{ket}}$$

$$\updownarrow$$

Orthogonality, assumed to be normalized:

$$\int \psi_n^{(0)*}(\tau)\, \psi_n^{(0)}(\tau)\, d\tau = 1 \ \checkmark \qquad \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$$

$$\int \psi_n^{(0)*}(\tau)\, \psi_m^{(0)}\, d\tau = \delta_{nm} \text{ kronecker delta} \qquad \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}$$

$$\delta_{nm} = 1 \quad \text{if } n = m$$
$$= 0 \quad \text{if } n \neq m$$

The other property is the orthogonal property namely psi n 0 star tau psi m 0 d tau is delta n m. This is kronecker delta which means delta n m is equal to 1 if n is equal to m is equal to 0 if n is not equal to n ok. Therefore, the wave functions are orthogonal to each other they are normalized they are orthogonal to each other and these examples are already known to you from particle in a box. That the wave functions psi n and psi m, if you calculate the integral d x between 0 and l the length of the box if you calculate that you see that these wave functions are they cancel each other. And likewise the wave functions have been normalized and therefore, that is how you got the normalization constant that root two by l, where l is the box length as the quantity preceding the wave function.

So, we will use these properties and the corresponding ket notation for these is psi n 0 psi n 0, the bracket is 1 and for this one it is psi n 0 psi m 0 is delta n m. So, let me highlight that this is the bracket notation for normalization and this is the one for the orthogonality of the wave functions ok. So, keep this in mind and these things are needed when we use this proposal for the energy E n that you have highlighted here we have it highlighted here and the proposal for psi n when we substitute that in the Hamiltonian and start solving the Schrödinger equation ok.

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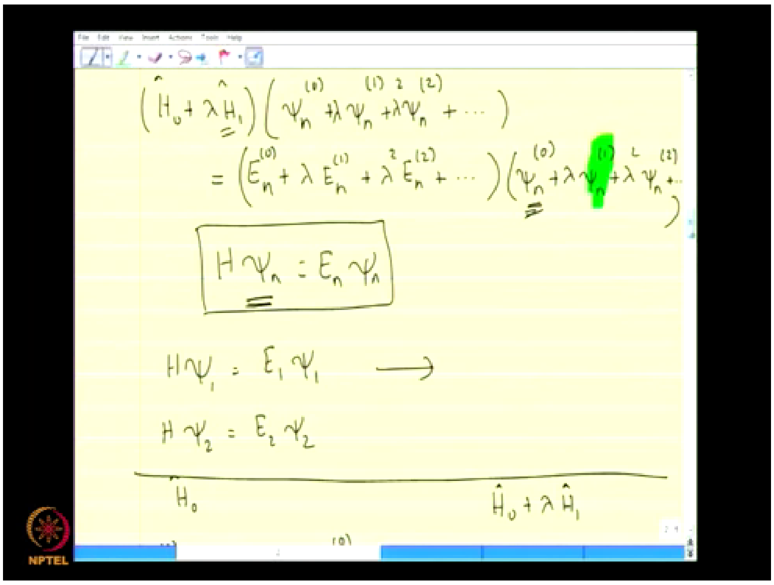

$$(\hat{H}_0 + \lambda \hat{H}_1)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots)$$

$$\boxed{H\psi_n = E_n\psi_n}$$

$$H\psi_1 = E_1\psi_1 \longrightarrow$$

$$H\psi_2 = E_2\psi_2$$

$\hat{H}_0$ $\quad$ $\hat{H}_0 + \lambda \hat{H}_1$

So, what I am going to do is to write down the two equations that we need sorry the 1 equation that we need to write namely H naught plus lambda H1. And now we shall write the wave function as we had proposed namely psi n 0 plus psi n 1 plus psi n 2 there is a lambda here it is a lambda square here plus so on. And we shall write this using the energy expression that we have proposed E n 0 plus lambda E n 1 plus lambda square E n 2 plus acting on or multiplying the wave functions psi n 0 plus lambda psi n 1 plus lambda square psi n 2 plus so on ok.

So, this is nothing other than the equation H psi n is equal to E n psi n. So, what does this mean in English; in words? What it means is that you are obtaining the wave function psi n one of them which is a correction to the zero-order wave function psi n 0 again one of them in the presence of the perturbation by including all the other terms and looking for their explicit expressions. So, the perturbation correction that we obtain we are obtaining sequentially correction to each and every zero-order wave function and to each and every zero-order Eigen value though this is symbolically n.

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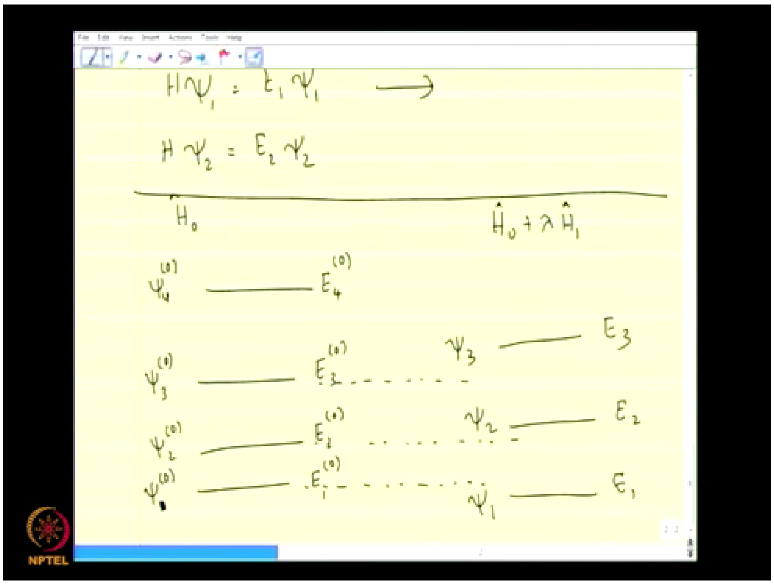

$H\psi_1 = E_1\psi_1 \longrightarrow$

$H\psi_2 = E_2\psi_2$

This is essentially H psi 1 is equal to E 1 psi 1. So, we have to solve the set of equations for psi 1 and obtain E 1 again many terms H of psi 2 is equal to E 2 of psi 2. Therefore, if we have pictorially if we have for example, for a Hamiltonian H naught we have a whole series of energy levels given by E 1 0, E 2 0, E 3 0, E 4 0 these are all zero-order corrections, zero-order I mean Eigen values not correction zero-order Eigen values and the corresponding wave functions are psi n, psi 1 0, psi 2 0, psi 3 0, psi 4 0 and so on.

Now, how do these things change when we have a Hamiltonian H naught plus lambda H1. How do these energies does this energy go up or go down, does this energy change again go up or go down draw this. We do not know, we have to find out. In the presence of H1 these energy levels are altered. What about the wave functions themselves which you call know as psi 1, you call as psi 2 and psi 3?

And this is E 1 this is E 2 this is E 3. This equation that we have H psi n is equal to E psi n is to obtain all these things generally by proposing a general series, but you remember that we are obtaining the corrections to each and every Eigen value when we change n from 1 to 2 we get the second the correction to the second Eigen function when we change n from 1 to say 5 we get the corrections to the fifth wave function and so on and like ways for the energies. So, this is a symbolic way of writing the equation and obtaining the solutions.

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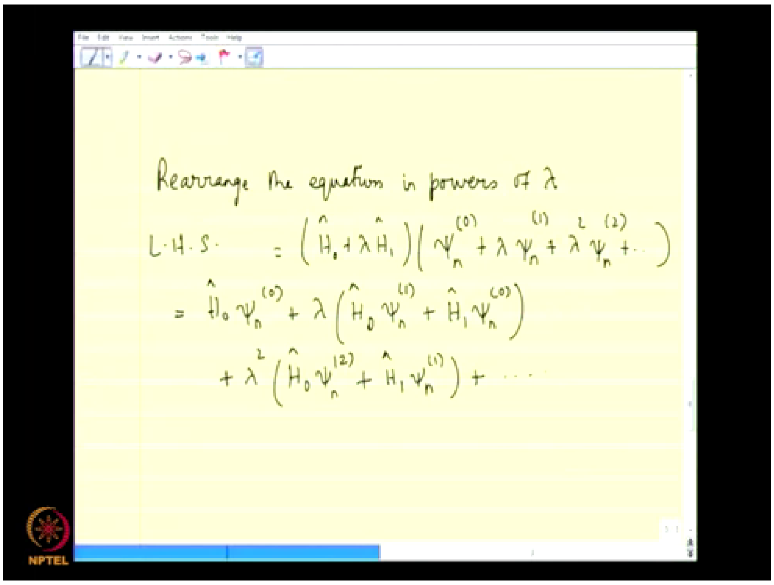

Rearrange the equation in powers of λ

$$L.H.S. = (\hat{H}_0 + \lambda \hat{H}_1)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots)$$

$$= \hat{H}_0 \psi_n^{(0)} + \lambda(\hat{H}_0 \psi_n^{(1)} + \hat{H}_1 \psi_n^{(0)})$$

$$+ \lambda^2 (\hat{H}_0 \psi_n^{(2)} + \hat{H}_1 \psi_n^{(1)}) + \cdots$$

So, we shall now go back and rearrange these things equation in powers of lambda. Powers of lambda left hand sign if you look at is H naught plus lambda H1 acting on psi n 0 plus lambda psi n 1 plus lambda square psi n 2 plus so on. So, if we write this in increasing powers of lambda the first term which does not have any lambda is H naught acting on psi n 0. The next term is a couple of them in lambda namely H naught on psi n 1 plus H1 on psi n 0, you have two terms the zero-order Hamiltonian acting on the first order correction to the wave function which we do not know.

And the first order the perturbing Hamiltonian acting on the zero-order correction. We know the Hamiltonian, we know the wave function, therefore this is in principle something that we can calculate ok. Here unless we know psi n 1, we do not know how to calculate this therefore, that is the objective. The second step is second term is lambda square. Again if you look at lambda square the correction is lambda square term is H naught acting on psi n 2 has the same power and the other one is H1 acting on psi n 1 plus lambda cube terms lambda 4 terms. So, this is the left hand side arranged in the in the increasing powers of lambda.

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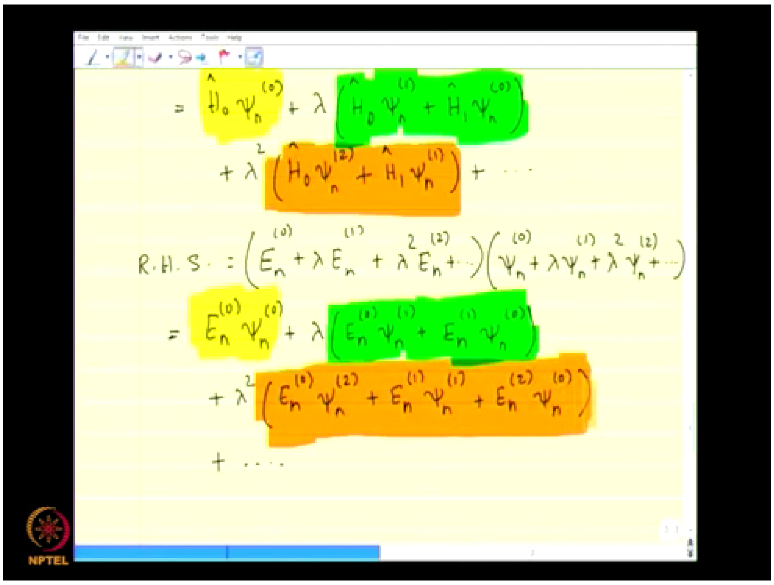

$$= \hat{H}_0 \psi_n^{(0)} + \lambda \left(\hat{H}_0 \psi_n^{(1)} + \hat{H}_1 \psi_n^{(0)} \right)$$
$$+ \lambda^2 \left(\hat{H}_0 \psi_n^{(2)} + \hat{H}_1 \psi_n^{(1)} \right) + \cdots$$

$$\text{R.H.S.} : \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \right) \left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots \right)$$
$$= E_n^{(0)} \psi_n^{(0)} + \lambda \left(E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \right)$$
$$+ \lambda^2 \left(E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)} \right)$$
$$+ \cdots$$

What about the right hand side? Remember it is given by E naught E n 0 plus lambda E n 1; let me take this clearly E n 0 plus lambda E n 1 plus lambda square E n 2 plus etcetera multiplying the wave functions psi n 0 plus lambda psi n 1 plus lambda square psi n 2 plus so on. So, if we write this in increasing powers of lambda the first term is E n 0 psi n 0 plus lambda times remember there is an E n 0 times psi n 1 and there is an E n 1 times psi n 0; two terms psi n 1 plus E n 1 times psi n 0 plus we write that E m plus lambda square.

If you look at lambda square there are three terms there is an E n 0 times psi n 2 E n 1 psi n 1 E n 2 psi n 0. There are three terms, psi n 2 plus E n 1 psi n 1 plus E n 2 psi n 0. If you go for lambda cube you will see that there will be more term there will be four terms E n 0 with psi n 3, E n 1 with psi n 2, E n 2 with psi n 1, and E n 3 with psi n 0. And therefore, you see right hand side for each power of lambda the number of terms increases by 1, but let us stay with 1, 2 and 3 we will not worry about other corrections.

First and second order corrections are the most important in elementary quantum chemistry. So, we shall derive expressions for that now left hand side is equal to right hand side so you can take a look at this term ok. So, I think I have the expressions on the screen so you can see that the first term they now we are equating the left hand side with right hand side for term by term according to the powers of lambda. That is the first term is lambda to the power 0 it is independent of lambda left hand side that term is equal to the right hand side lambda is arbitrary we said it is a very small parameter. Therefore, the perturbation theory now gives us a handle to organize terms into groups.

So, that you can see the term H0 psi n 0 which is independent of lambda is equal to E n 0 times psi n 0 which is independent of lambda on the right hand side and this is of course, is what we started with. This is the equation for the Eigen values of the perturbation free zero-order Hamiltonian; that is what this is ok; we started with that. Therefore, it is redundant I mean you are getting the same thing does not help us much ok. But then what we have is a series of the equations that we can write down for the power of lambda there is one equation and for the powers of lambda square there is another equation and so on.

So, if you think about lambda square, let me see if I can use a different color. I guess yes I can use a different color let me use that ok. So, let us take the first order term in lambda; this is H naught acting on psi n 1 plus H1 acting on psi n 0. And that should be equal to the same power of lambda here on the right hand side which is E n 0 psi n 1 and E n 1 psi n 0.

So, that is the second equation which is the first real one that we need to solve because the one in yellow is of course, we already know that is the proposal we started with. What about the third one? Well, the lambda square term if you take care of that say on the left hand side we have H naught on psi n two plus H1 on psi n 1 and on the right hand side we have the three terms on lambda square which is E n 0 at multiplied by psi n two E n 1 multiplied by psi n 1 and E n 2 on psi n 0 ok.

So, now, you understand that there are infinitely many equations if we go on with many powers of lambda infinitely many powers of lambda. And therefore, we have to sequentially solve these equations and what is important is that the first equation the one in green which we have to solve contains psi n 1 and psi n 1 and E n 1; therefore, by solving the first equation it is possible that we will get the solution for E n 1 and psi n 1 by solving the second equation involving psi n 2 and the known thus the previously obtained the solution for psi n 1 it is possible that we will get when we write the lambda square equation we will get a solution for E n 2 and psi n 2 and so on. Therefore, you see perturbation series essentially tells you step by step to obtain the solution.

So, at this point let me take a short break, we will come back and write these equations then use the properties of the orthogolisation and normalization of these wave functions to actually extract the values for E n 1 and psi n 1. In this lecture and in the next lecture we will obtain the values for E n 2 and psi n 1 again ok. We will have a break for about 10 seconds.

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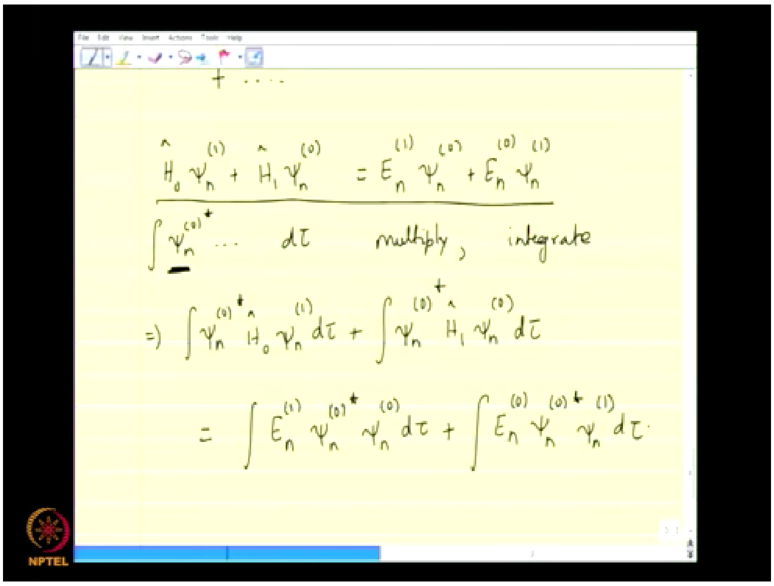

$+ \cdots$

$$\hat{H}_0 \psi_n^{(1)} + \hat{H}_1 \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

$\int \psi_n^{(0)*} \cdots d\tau$ multiply, integrate

$$\Rightarrow \int \psi_n^{(0)*} \hat{H}_0 \psi_n^{(1)} d\tau + \int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau$$

$$= \int E_n^{(1)} \psi_n^{(0)*} \psi_n^{(0)} d\tau + \int E_n^{(0)} \psi_n^{(0)*} \psi_n^{(1)} d\tau.$$

Now, we will write the equation and the make use of the properties of the orthogonality and the normalization of the wave functions. So, the first equation that we had in green that we wanted to solve is H naught on psi n 1 plus H1 on psi n 0 is equal to E n 1 psi n 0 plus E n 0 on psi n 1 ok. Is that what we have? E n 1 on psi n 0 and E n 0 on psi n 1 that is correct and this is H naught psi n 1 H naught psi n 0 ok. So, let us now do the standard trick that we do in quantum mechanics when we have operators and wave functions we want to take matrix elements out of it or we want to get numbers out of it.

So, let us multiply both sides by psi n 0 star and integrate with respect to all the coordinates which are present in the system and psi n the wave functions are expressed in terms of these coordinates. So, if we do that we have the equation namely integral psi n 0 star H naught psi n 1 d tau plus integral psi n 0 star H1 psi n 0 d tau that is equal to integral E n 1 psi n 0 star psi n 0 d tau plus integral E n 0 which is a constant times psi n 0 star psi n 1 d tau.

So, what we have done is multiply, integrate by what function? By the same wave function psi n 0, the same psi n that is there in this equation the equation that we wanted to solve. We can do either multiply this with psi n 0 or with any other psi which is not corresponding to this n psi m 0 I mean you know that these wave functions are all non degenerate they do not have the same energies. Therefore, if you want to solve this equation and you say multiply by psi n 0 you may ask the question why psi n 0, why not by some other psi n 0 some other psi n 0; yes, we will do both the first one is to use the same wave function and get the first order correction to the energy in the next step. And then you multiply by wave function which is not the same as the n, you will get the first order correction to the wave function. And that we will do if we have time today ok. So, now you can compare this.

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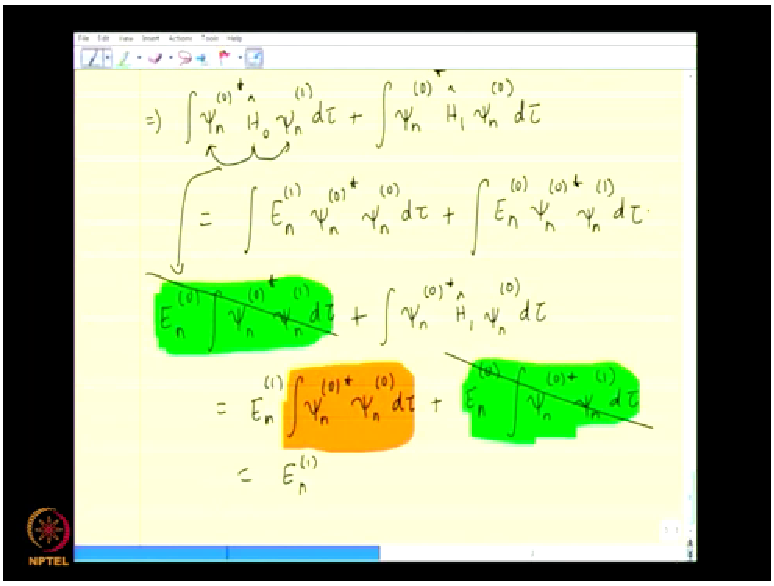

$$\Rightarrow \int \psi_n^{(0)*} \hat{H}_0 \psi_n^{(1)} d\tau + \int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau$$

$$= \int E_n^{(1)} \psi_n^{(0)*} \psi_n^{(0)} d\tau + \int E_n^{(0)} \psi_n^{(0)*} \psi_n^{(1)} d\tau$$

$$\cancel{E_n^{(0)} \int \psi_n^{(0)*} \psi_n^{(1)} d\tau} + \int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau$$

$$= E_n^{(1)} \int \psi_n^{(0)*} \psi_n^{(0)} d\tau + \cancel{E_n^{(0)} \int \psi_n^{(0)*} \psi_n^{(1)} d\tau}$$

$$= E_n^{(1)}$$

You know the H naught can act on the right to give you the whatever the energy is, but we do not know the function on the right, but H naught can also act on the wave function to the left because the Hamiltonian is hermitical. Therefore, the H naught acting on psi n 0 star will give you the corresponding energy E n 0 which is real and therefore, this will give you the solution E n 0 times integral psi n 0 star psi n 1 d tau ok plus you have psi n 0 star we will write this as is H1 psi n 0 d tau is equal to integral we can take the energies out, energies are constants they are independent of the coordinates. Therefore, you have E n 1 and the integral is psi n 0 star psi n 0 d tau plus E n 0 integral psi n 0 star psi n 1 d tau ok.

Immediately you recognize everything that you need to namely this is equal to 1 because of the normalization of the wave functions ok. And I think we had the green earlier this quantity on the left hand side is exactly the same on the right hand side as well. Therefore, you can cancel these two things and you can see that there is 1 equation namely for the first order correction to the energy E n 1, look at it carefully.

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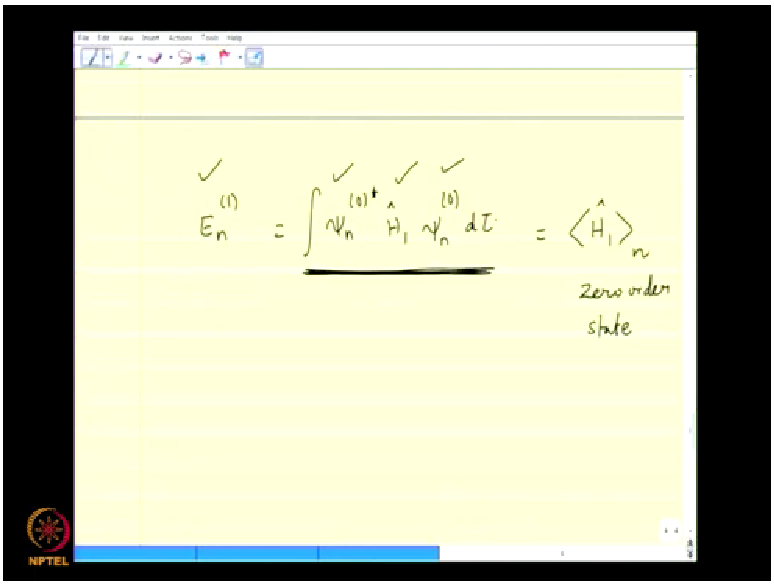

$$\overset{\checkmark}{E_n^{(1)}} = \underline{\int \overset{\checkmark}{\psi_n^{(0)*}}\, \overset{\checkmark}{\hat{H}_1}\, \overset{\checkmark}{\psi_n^{(0)}}\, d\tau} = \langle \hat{H}_1 \rangle_n$$

Zero order state

The first order correction E n 1 therefore, is whatever is left on the side which is this 1 psi n 0 star H1 psi n 0 d tau integral psi n 0 star H1 psi n 0 d tau ok. We know H1 we know psi n 0 we know psi n 0 star and therefore, now we can calculate E n 1 on the basis of quantities that we already use to define our problem and the first order correction is the average value. Yes, remember these wave functions are normalized and therefore, what you have here is the average value of the perturbing Hamiltonian in the nth zero-order state. The other terminology for this is that if you write the Hamiltonian in the form of a matrix using all these wave functions as columns and rows then this is called the diagonal matrix element of the perturbing Hamiltonian in the Eigen basis set of the zero-order Hamiltonian. If that is long let us write it down.

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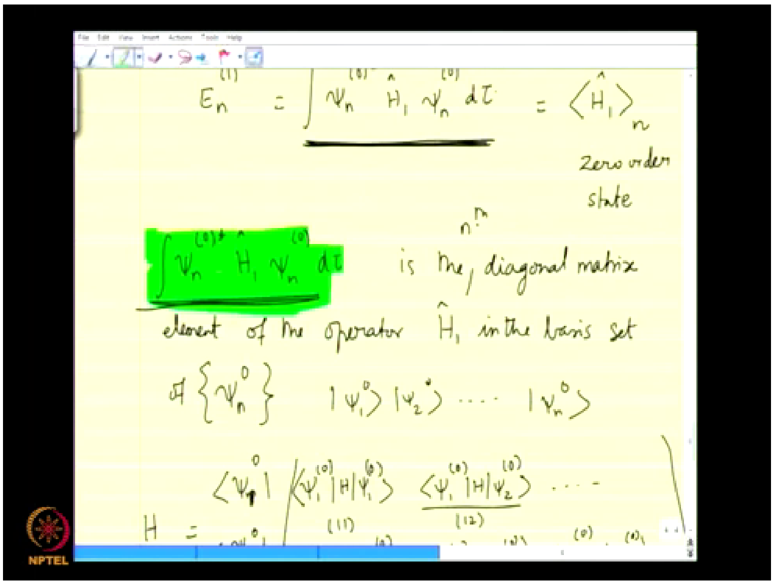

$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau = \langle \hat{H}_1 \rangle_n$

zero order state

$\int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau$ is the n^{th} diagonal matrix element of the operator $\hat{H}_1$ in the basis set of $\{\psi_n^0\}$ $|\psi_1^0\rangle |\psi_2^0\rangle \cdots |\psi_n^0\rangle$

$H = \langle\psi_1^0| \; \langle\psi_1^{(0)}|H|\psi_1^{(0)}\rangle_{(11)} \; \langle\psi_1^{(0)}|H|\psi_2^{(0)}\rangle_{(12)} \cdots$

The integral psi n 0 star H1 psi n 0 d tau is the diagonal matrix element of the operator H1 is the nth diagonal matrix of the operator H1 in the basis set of psi n 0.

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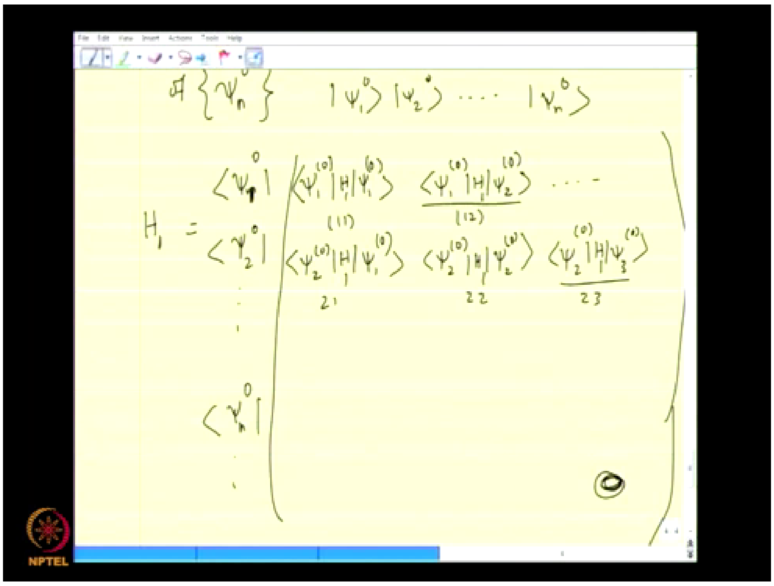

of $\{\psi_n^0\}$ $|\psi_1^0\rangle |\psi_2^0\rangle \cdots |\psi_n^0\rangle$

$$H_1 = \begin{array}{c} \langle\psi_1^0| \\ \langle\psi_2^0| \\ \vdots \\ \langle\psi_n^0| \\ \vdots \end{array} \begin{pmatrix} \underbrace{\langle\psi_1^{(0)}|H|\psi_1^{(0)}\rangle}_{(11)} & \underbrace{\langle\psi_1^{(0)}|H|\psi_2^{(0)}\rangle}_{(12)} & \cdots \\ \underbrace{\langle\psi_2^{(0)}|H|\psi_1^{(0)}\rangle}_{21} & \underbrace{\langle\psi_2^{(0)}|H|\psi_2^{(0)}\rangle}_{22} & \underbrace{\langle\psi_2^{(0)}|H|\psi_3^{(0)}\rangle}_{23} \\ & & \\ & & \end{pmatrix}$$

So, if you remember the matrix representation for the Hamiltonian or any operator a is, if you have a set of wave functions psi n psi 1 0 psi 2 0 psi n 0 and so on. And you have psi 1 0 psi 2 0 psi n 0 please note that the matrix elements are written by psi 1 0. Now I will use the bracket notation H psi 1 0 and if I use the bracket notation I must keep this as the bra states and these as the ket states is as the ket states. This is the first diagonal matrix element the next matrix element is psi 1 0 H psi 2 0.

This is the 1 2 element; this is the 1 1 element and so on. And what about this one? This is psi 2 0 H psi 1 0 this is psi 2 0 H psi 2 0 and any one of these is nothing but the integral psi 1 0 star d tau H psi 2 0 d tau sorry psi 1 0 star tau H psi 2 0 tau d tau the integral it is the same thing that is written in the form of the ket the bracket notation and you can see that the third element is psi 2 0 H psi 3 0 and so on.

So, this is the 2 3, this is the 2 2, this is the 2 1, following the matrix notation and therefore, what you see here is this integral psi n 0 star H1 psi n, this one is the nth diagonal element then we write H1 and the write H1 H1 H 1. So, this is the nth matrix element diagonal matrix elements somewhere here ok. Therefore, the first order correction to the first state the first energy is the first diagonal matrix element, the Eigen function corresponding to the zero-order state and the Hamiltonian H1 the second is that of the second the third is that of the third.

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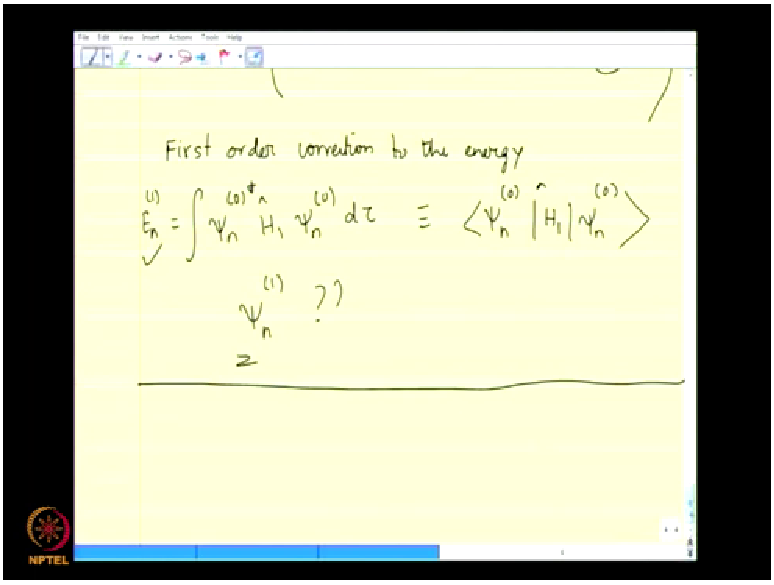

First order correction to the energy

$$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau \equiv \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

$\psi_n^{(1)}$??

So, this is the simple result known as the first order correction to the energy. Two ways of writing it you have written this in the form of psi n 0 star H1 psi n 1 psi n 0 d tau. And this is what is called as E n 1 and the other way of writing this equivalent is that psi n 0 H1 psi n 0 ok. So, we know now we would like to find out what is the first order correction to the wave function psi n 1. What about that? Now again go back to this equation which was one that we solved, the one in the green H naught psi n 1 contains the psi n 1 obviously. And on the right hand side the corresponding quantity also contains psi n 1. So, we would like to find out what is psi n 1, I mean how do we obtain the corrections to psi n 1 through this process.

Now, here I have to use the fundamental processes I mean the principle of quantum mechanics that if you define your basis set for your problem we have defined the basis set for our problem as the a wave function psi n 0's. If you define a basis set then any arbitrary wave function that we want to find out can be expressed as a linear combination of the elements of the basis set. Therefore, if you want to know psi n 1 it is possible for us to write psi n 1 in the form of a linear combination of all the basis functions psi 1 0, psi 2 0, psi 30 etcetera. Therefore, in principle we may want to do the following.

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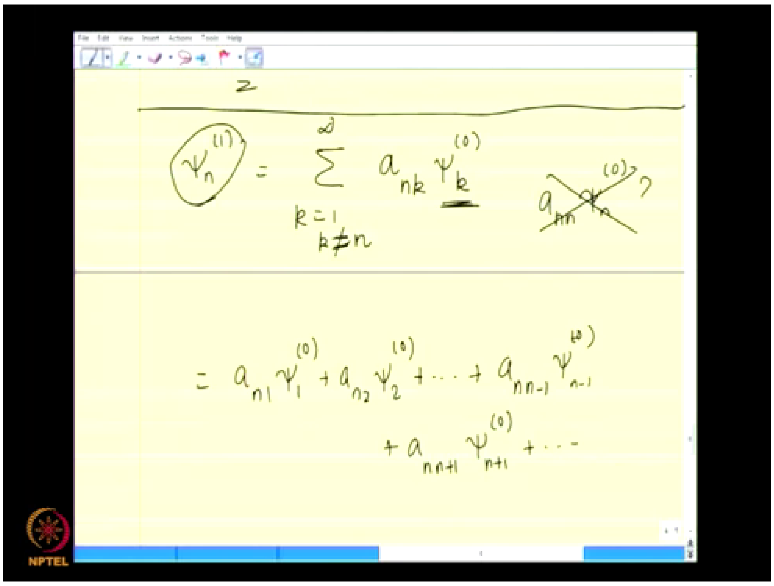

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$$\boxed{\psi_n^{(1)}} = \sum_{\substack{k=1 \\ k \neq n}}^{\infty} a_{nk} \psi_{\underline{k}}^{(0)} \qquad \cancel{a_{nn} \psi_n^{(0)}} ?$$

$$= a_{n1}\psi_1^{(0)} + a_{n2}\psi_2^{(0)} + \dots + a_{nn-1}\psi_{n-1}^{(0)} + a_{nn+1}\psi_{n+1}^{(0)} + \dots$$

We may want to write psi n 1. As a linear combination including the psi n 0 like what I would do is let me sorry rewrite this in a slightly different way they sum over n equal to 1 not 1 n let me see, m equal to 1 to infinity a m n. Let me see if I have what rotation I have used in the notes is that I have used n k.

So, not m I have not used m in my print notes so, I have used a symbol k. So, it is a n k psi k 0, so k 0. Now, only one thing that needs to be taken care of is that this is fine, but why include in psi n 1 the quantity a m n psi n 0; why include that? We do not need to because if you remember the correction to the first order wave function. If you look at let us go up a little bit. We have written the wave function psi n 1 which is now writing we are writing the correction to this term we are writing the correction to this term ok. As a linear combination of all wave functions including psi n 0, but please remember psi n 0 is already there in this expansion as the leading term.

Therefore it is only appropriate for us to write this by saying by excluding the term k not equal to n that is we will not include that. Which is a way of saying a n 1 psi 1 0 plus a n two psi 2 0 But when it comes to the last the term it is n minus 1 psi n minus 1 0 and the next term that we have is a n n plus 1 psi n plus 1 0 and so on. Therefore, we will exclude in this summation the basis function corresponding to the zero-order basis function of this namely k not equal to n.

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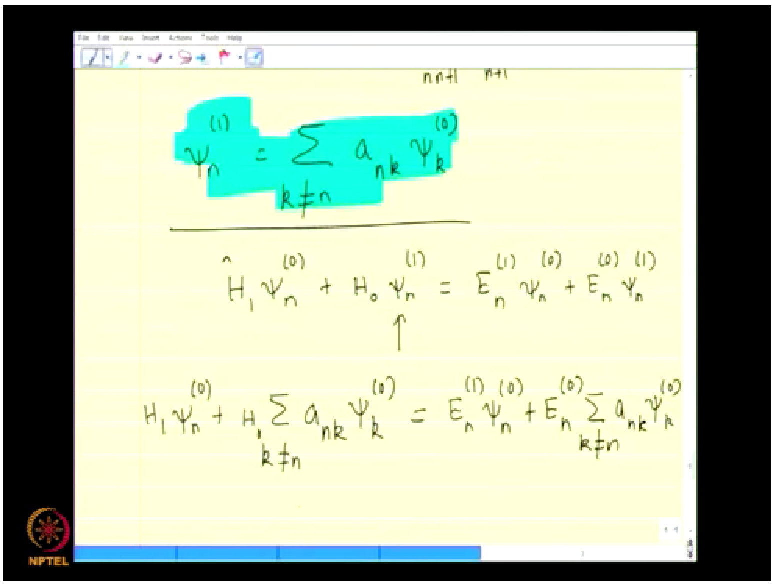

n n+1 n+1

$$\psi_n^{(1)} = \sum_{k \neq n} a_{nk} \psi_k^{(0)}$$

$$\hat{H}_1 \psi_n^{(0)} + H_0 \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

$$\uparrow$$

$$H_1 \psi_n^{(0)} + H_1 \sum_{k \neq n} a_{nk} \psi_k^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \sum_{k \neq n} a_{nk} \psi_k^{(0)}$$

So, this is the proposal that we have to make use of namely psi n 1 is equal to sum over k not equal to n a n k psi k 0 ok. If we use this and now we will go back to the equation for the psi n 1 namely E n 1 psi n 0, sorry the Hamiltonian operators no one that we need to put on the left hand side. So, we have H1 psi n 0 plus H naught psi n 1 is equal to E n 1 psi n 0 plus E n 0 psi n 1 ok. That is equation we want to solve H naught psi n 1 and H1 psi 0 E n psi n 0 psi n 1 yes.

Now substitute in here the expression that we have just know obtained this one namely, psi n 1 in terms of this we will bring that in here and the equation is H1 psi n 0 plus H naught sum over k not equal to n a n k psi k 0 is equal to E n 1 psi n 0 plus E n 0 sum over k not equal to n a n k psi k 0.

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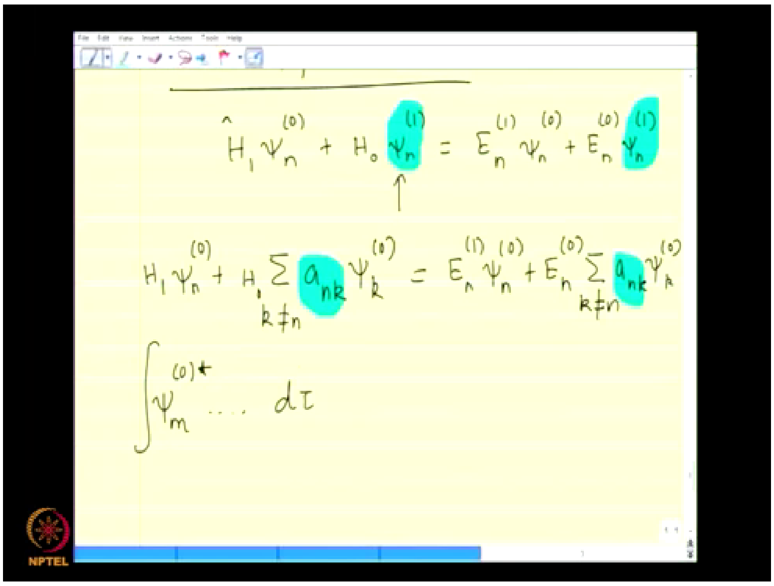

$$\hat{H}_1 \psi_n^{(0)} + H_0 \underset{\uparrow}{\psi_n^{(1)}} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

$$H_1 \psi_n^{(0)} + H_0 \sum_{k \neq n} a_{nk} \psi_k^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \sum_{k \neq n} a_{nk} \psi_k^{(0)}$$

$$\int \psi_m^{(0)*} \cdots \, d\tau$$

Therefore, the task of finding psi n 1 is now the same as the task of finding the coefficient a n k all of them because we know psi k 0 anyway what the entire basis set. So, we have only transformed the task of getting the wave function in terms of getting the linear combination coefficients. And this know having substituted this, now we will multiply this equation by this a wave function which is not equal to the n. Let us use psi m 0 star, multiply it on the multiply this equation with psi m 0 star and integrated detail.

Both the left hand side and the right hand side let me write the equation because of the time running out what we will do is we will solve the equation and obtain the first order correction to the wave function. And the second order correction to the energy in the next lecture and then also use some examples to highlight or to apply these two results namely the first order correction to the energy second order correction to the energy etcetera for some of the model systems ok.

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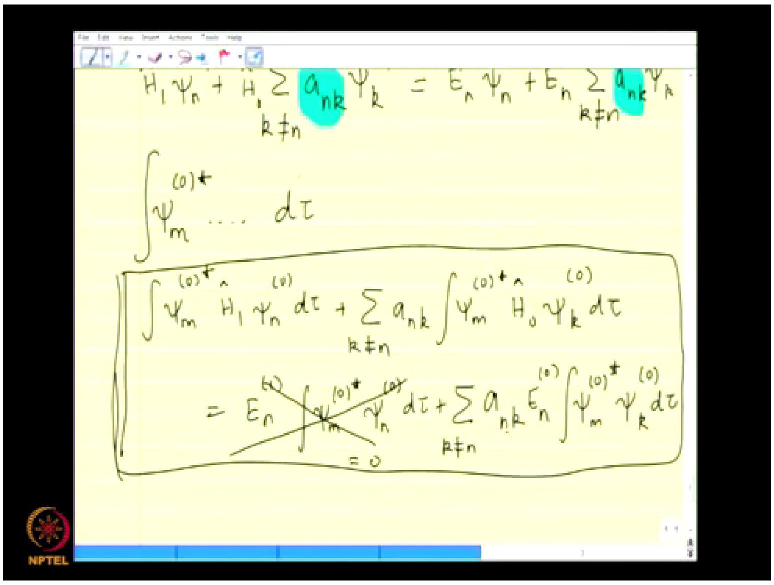

$$\hat{H}_1 \psi_n + \hat{H}_1 \sum_{k\neq n} a_{nk} \psi_k = E_n \psi_n + E_n \sum_{k\neq n} a_{nk} \psi_k$$

$$\int \psi_m^{(0)*} \ldots d\tau$$

$$\boxed{\int \psi_m^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau + \sum_{k\neq n} a_{nk} \int \psi_m^{(0)*} \hat{H}_0 \psi_k^{(0)} d\tau = E_n^{(1)} \underset{=0}{\cancel{\int \psi_m^{(0)*} \psi_n^{(0)} d\tau}} + \sum_{k\neq n} a_{nk} E_n^{(0)} \int \psi_m^{(0)*} \psi_k^{(0)} d\tau}$$

So, let me write the last step namely integral psi m 0 star H1 have to have that and also the correct H1 psi n 0 d tau plus integral psi m 0 star H naught. So, let me just write this by taking the coefficients in the summations out you will write the summation term k not equal to n, a n k and then write the integral namely psi m 0 star H naught psi k 0 d tau. And on the right hand side what we have is E n 1 sum over sorry E n 1 sorry there is no sum integral psi m 0 star psi n 0 d tau plus we have sum over k not equal to n a n k E n 0 then the integral namely psi m 0 star psi k 0 d tau ok. So, this I will let us check that I have not made any mistake here. In this psi m 0 star H1 psi n 0 d tau a n k psi m 0 star H naught psi k 0 d tau is equal to E n 1 psi m 0 star psi 0 d tau and a n k E n 0 psi m star psi k 0 d tau ok.

So, let me conclude by saying that this is 0 due to orthogonality of the wave function. We will continue from this equation and then derive an expression for the coefficients a n k. And once we know the expression for the coefficient in terms of quantities that we can calculate we know the first order correction to the wave function. And that can be used to obtain the second order correction for the energy and so on. So, this lecture will have to be read intend them with the next lecture in order to understand the first and second order corrections together, until then let me say.

Thank you, and see you later.