Chemistry Atomic Structure And Chemical Bonding
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Lecture – 48
First and Second Order Time Independent Perturbation Theory for Non - Degenerate States

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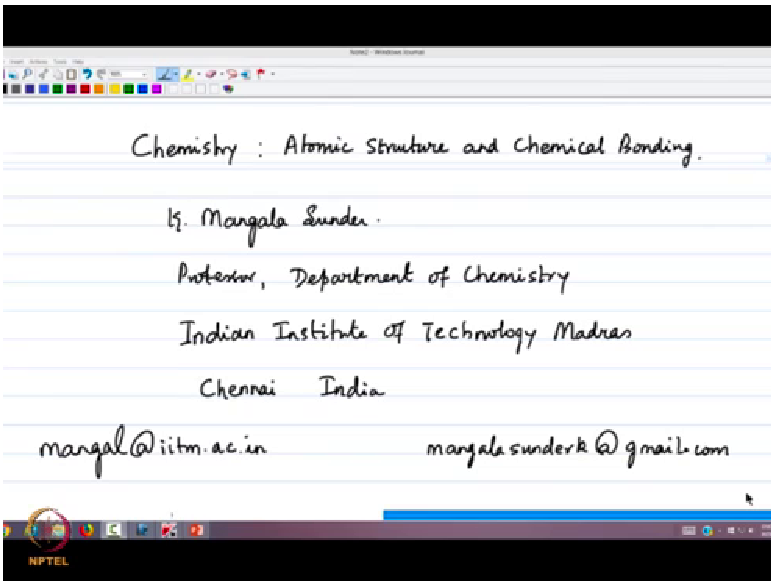

Chemistry : Atomic Structure and Chemical Bonding.

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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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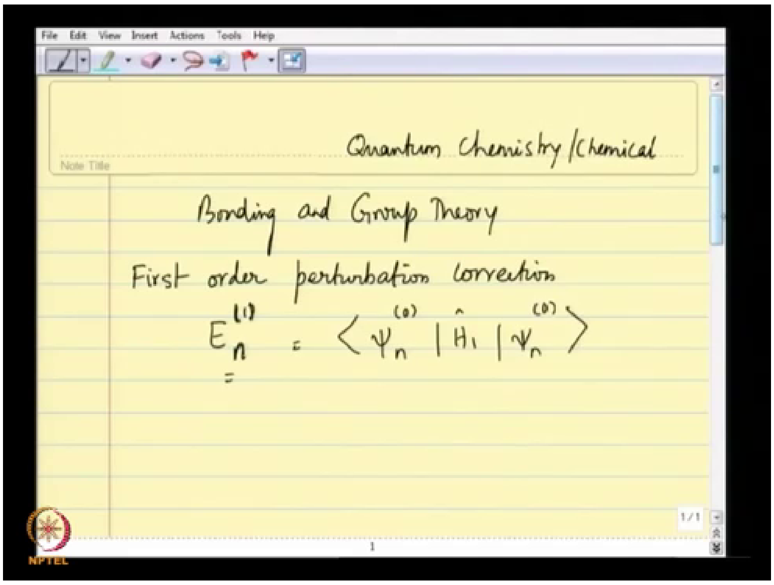

Quantum Chemistry / Chemical Bonding and Group Theory

First order perturbation correction

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

=

So, we looked at the First Order perturbation correction as the first order. So, let me write E n 1 correction to the nth energy in the absence of perturbation to order lambda, as the average value of the perturbing Hamiltonian in the eigenstates of the nth energy state namely psi n 0 H 1 psi n 0 ok.

And then, we moved on to calculate the first order correction to the wave function namely psi n 1.

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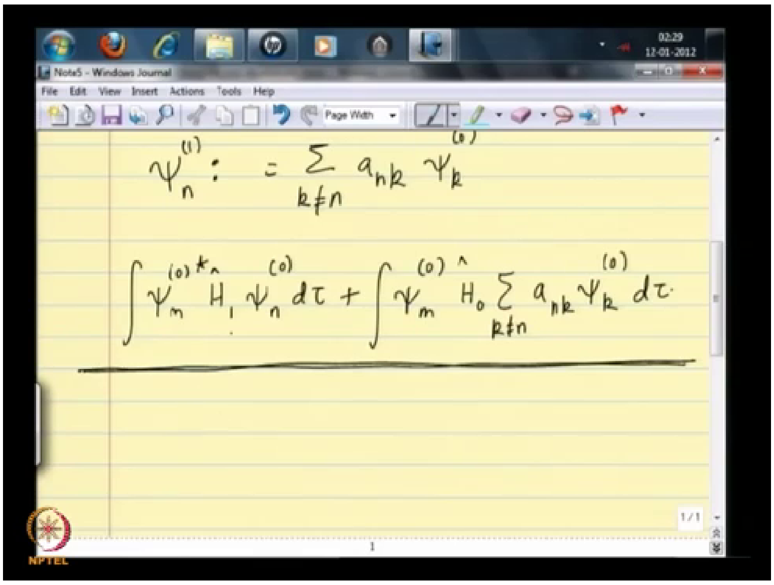

$$\psi_n^{(1)} : = \sum_{k \neq n} a_{nk} \psi_k^{(0)}$$

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

And let me now bring the last screen that you had in the last lecture. So, that we continue from that screen onwards ok.

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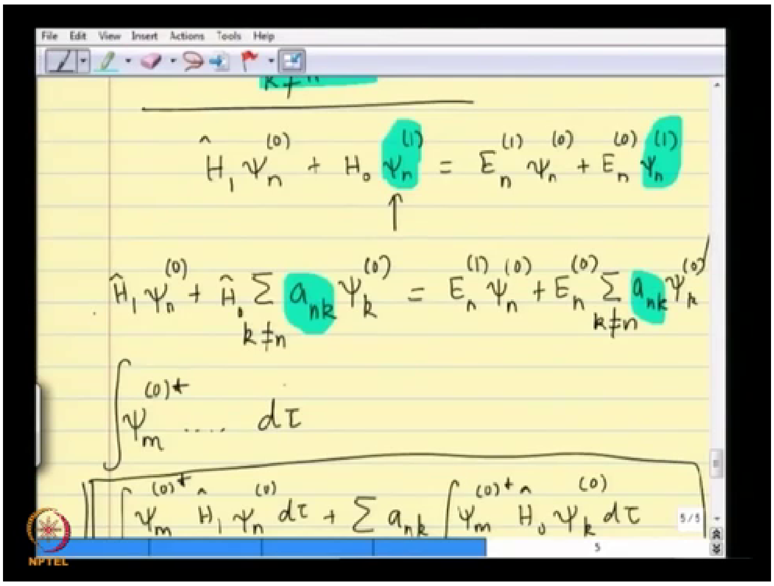

$$\hat{H}_1 \psi_n^{(0)} + H_0 \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

$$\uparrow$$

$$\hat{H}_1 \psi_n^{(0)} + \hat{H}_0 \sum_{k \neq n} a_{nk} \psi_k^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \sum_{k \neq n} a_{nk} \psi_k^{(0)}$$

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

$$\int \psi_m^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau + \sum a_{nk} \int \psi_m^{(0)*} \hat{H}_0 \psi_k^{(0)} d\tau$$

Now, if you recall this particular screen to obtain the first order correction to the wave function which is marked in green here by psi n 1 ok. What we did was to propose an expansion for the wave function psi n 1, in terms of all the basis states of the Perturbation Free Hamiltonian, the eigenstates of the Perturbation Free Hamiltonian.

But then, we made a case by saying that except the eigenstate corresponding to that nth order, nth 0 order Hamiltonian that is psi n 0, we will include all other terms.

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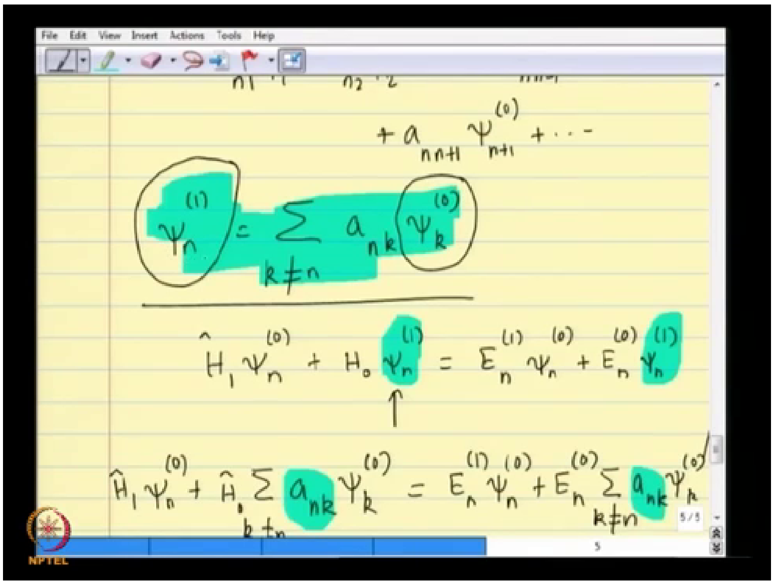

$$+ a_{nn+1}\psi_{n+1}^{(0)} + \cdots$$

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

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

$$\hat{H}_1\psi_n^{(0)} + \hat{H}_0 \sum_{k \neq n} a_{nk}\psi_k^{(0)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)} \sum_{k \neq n} a_{nk}\psi_k^{(0)}$$

So, if you recall at the series for the first order correction to the wave function that you see here on this one, psi n 1 was written in terms of a linear combination of all wave functions which are eigenfunctions of the perturbation free Hamiltonian with linear combination coefficients a and k; where, k is such that it takes all the values other than the values corresponding to the nth eigenfunction ok.

This was substituted in the equation for the psi n 1 and the then, what we did was to multiply that equation by the psi m 0 star and integrated both the left hand side and right hand side over all the coordinates to obtain this final equation.

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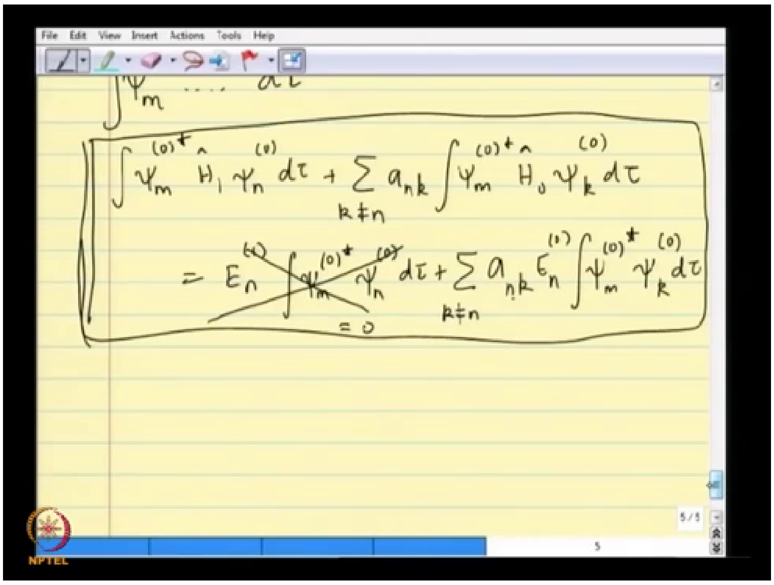

$$\int \psi_m \ldots\ldots d\tau$$

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

This is the one that I left you with in the last lecture, namely psi m 0 star H 1 psi n 0 d tau plus sum over k not equal to n; a term containing the coefficients a and k which we now have to calculate and on the right hand side the corresponding terms. So, let us now complete this task of calculating the coefficients a and k. So, for that purpose so let me do, we start with a new screen ok. This is our 3rd lecture. So, we wanted to calculate psi n 1 and we had used this a and k; k not equal to n psi k 0.

Then, we have this equation namely the integral psi m 0 star H 1 psi n 0 d tau plus the integral psi m 0 H naught and we had the summation over k not equal to n a n k psi k 0 d tau ok. This was the left hand side. Just let us check that that is what we have. Psi m 0 star H 1 psi m 0 d tau plus sum over k not equal to n a n k psi m 0 star H naught psi k 0; yes, that is what we have. That is on the left hand side.

Now, it is easy to look at this before we simplify this on the right hand side also. Let us do this right away here ok. We do know something about this integral, the second term ok. Let me go to the full screen and.

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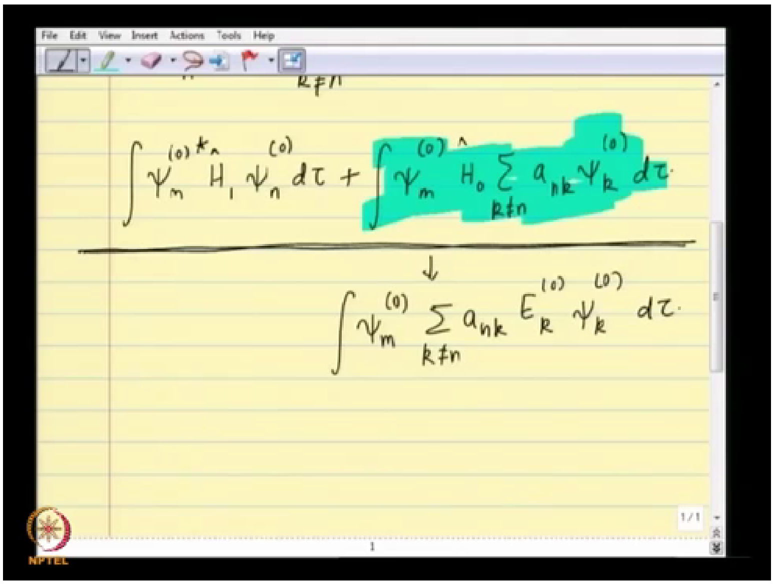

$$k \neq n$$

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

$$\downarrow$$

$$\int \psi_m^{(0)} \sum_{k \neq n} a_{nk} E_k^{(0)} \psi_k^{(0)} d\tau$$

We do know this particular term namely this one, see that the operator H naught acts on psi k 0 on the right hand side or psi m 0 on the left hand side. It does not matter which we worry about, which one that we have to worry about. But this would give you the quantity psi m 0 sum over k not equal to n a n k, H naught acting on psi k 0 will give you E k 0 psi k 0 d tau ok.

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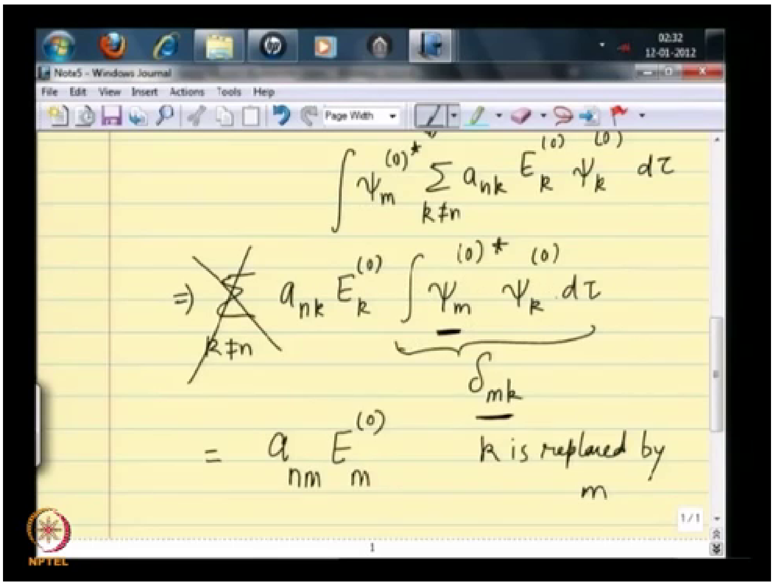

$$\int \psi_m^{(0)*} \sum_{k \neq n} a_{nk} E_k^{(0)} \psi_k^{(0)} d\tau$$

$$\Rightarrow \cancel{\sum_{k \neq n}} a_{nk} E_k^{(0)} \underbrace{\int \psi_m^{(0)*} \psi_k^{(0)} d\tau}_{\delta_{mk}}$$

$$= a_{nm} E_m^{(0)}$$

k is replaced by m

Which if I put in only those which are needed inside the integral and leave everything else out it is k not equal to n a n k E k 0 integral psi m 0 star star psi k 0 d tau. Please note that when m was chosen in getting the wave function psi n 1, m was chosen to be not equal to n ok. If you again go back to yesterday's lecture the previous lecture, the m was chosen such that this m is not equal to this n. Why? Because when we choose this m equal to n, we ended up with the first order correction to the energy already.

Therefore, now we are looking at using the projections of this equation on all wave functions other than the wave function corresponding to this m. Therefore, if you go back to this m is not equal to n; therefore, it is possible that k and m can be equal because k is also not equal to n. Therefore, there is at least 1 value of m and there is only 1 value of m for which m and k are equal. Therefore, this summation will go away and this integral will turn out to be delta m k and since here we are summing over k and this delta m k restricts the value of k to m.

What you will get is a n m E m 0; where, k is replaced by m. Only 1 term; all other terms in this integral will be 0 because the wave functions are orthogonal. So, the left hand side is simplified to now 2 sets, namely a term psi m 0 star H 1 psi n 0 and an energy contribution a m. This particular term allowed ok. So, the left hand side, therefore, becomes the following.

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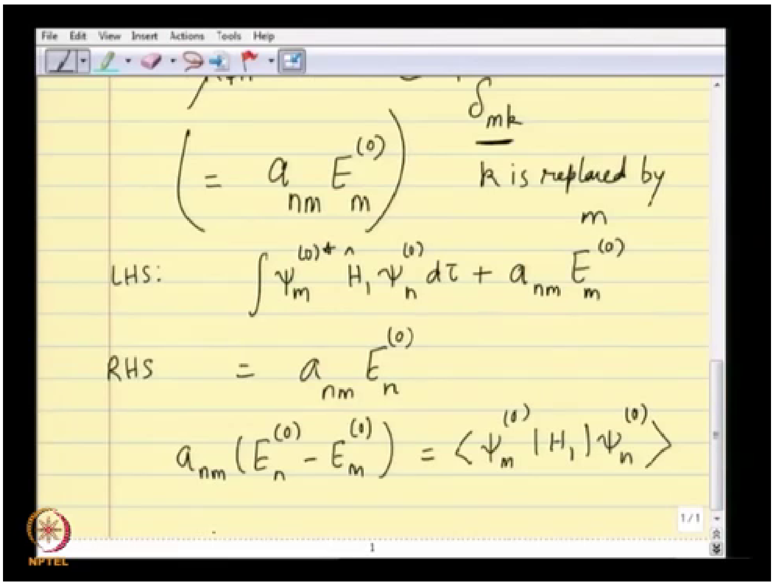

$$\left(= a_{nm} E_m^{(0)} \right)$$

δ_{mk}

k is replaced by m

$$\text{LHS:} \quad \int \psi_m^{(0)*} \hat{H}_1 \psi_n^{(0)} d\tau + a_{nm} E_m^{(0)}$$

$$\text{RHS} \quad = a_{nm} E_n^{(0)}$$

$$a_{nm} \left(E_n^{(0)} - E_m^{(0)} \right) = \langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle$$

Integral psi m 0 star H 1 psi n 0 d tau plus a n m E 0 m. What about the right hand side?

Now, again if we look at to the right hand side of the result that we had written down, there is again only one term which is a n k k not equal to n, E n 0 psi m 0 star psi k 0 star.

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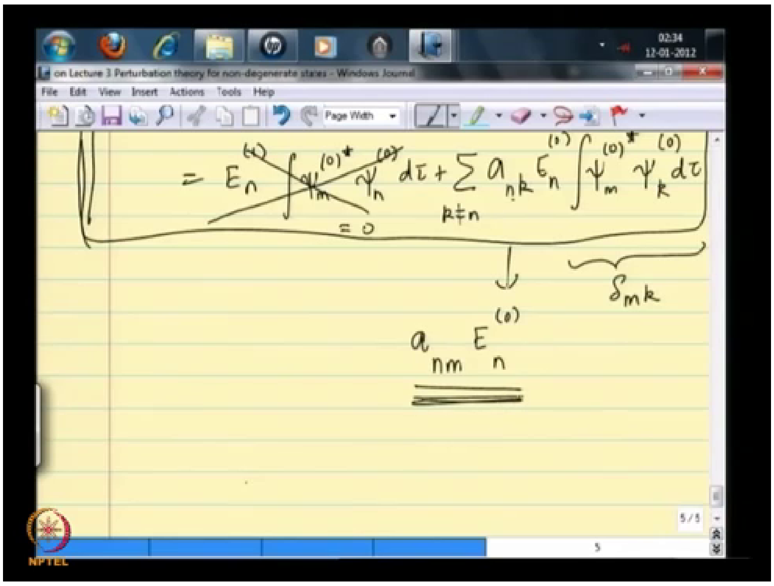

$$= E_n^{(1)} \underbrace{\cancel{\int \psi_m^{(0)*} \psi_n^{(0)} d\tau}}_{=0} + \sum_{k \neq n} a_{nk} E_n^{(0)} \underbrace{\int \psi_m^{(0)*} \psi_k^{(0)} d\tau}_{\delta_{mk}}$$

$$\downarrow$$

$$a_{nm} E_n^{(0)}$$

Therefore, right away you can see this reducing to because of this integral being delta m k and therefore, this summation in which k takes all possible values other than n. This summation is reduced to only 1 term, namely k is equal to m. So, the answer would be a n m E n 0 and only for that this integral is 1; otherwise d 0 and there is no other term.

So, what you have on the right hand side is a n m E n 0 which we will now put in our equation here; namely, right hand side is a n m E n 0 ok. So, out of all the coefficients, this way of projecting the operator or projecting the functions to the particular wave functions or the basis functions of the Hamiltonian gives you 1 coefficient, but we can now vary m. We can take the first wave function, the second wave function third wave function and therefore, we can get all the coefficients a and m 1 step at your time.

Now, the summary is that the coefficient a n m times if I bring this to the right hand side, the equation is that a and m E n 0 minus E m 0 is equal to the integral psi m 0 which we can now write using the Dirac notation ok. You will write using the Dirac notation, namely integral psi m 0 H 1 psi n 0. So, we have obtained the value for the coefficient.

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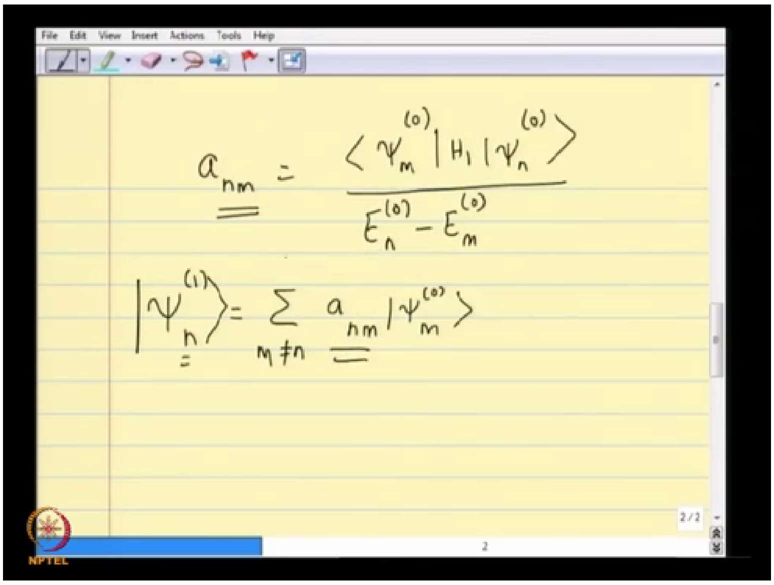

$$\underline{\underline{a_{nm}}} = \frac{\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$|\psi_{\underline{n}}^{(1)}\rangle = \sum_{m \neq n} \underline{\underline{a_{nm}}} |\psi_m^{(0)}\rangle$$

And of course, the next step is to write explicitly a and m is equal to the integral psi m 0 H 1 psi n 0 divided by E n 0 minus E m 0 ok.

So, we have a coefficient and therefore, immediately the wave function psi n 1; please remember that the expression we used was k not equal to n a n k we used the ket notation. We can start using now from this point onwards psi k 0; but we have the coefficient a and m, I mean the indices n and m; n is of course, very specific the running index is k. So, the running index here is m.

So, it does not matter. I would rather write instead of k, suppose I write m here m not equal to n; all I need to do is to make the corresponding changes here. The k is now in terms of m and this is also in terms of m. So, now we have an explicit form for this coefficient just in the previous line.

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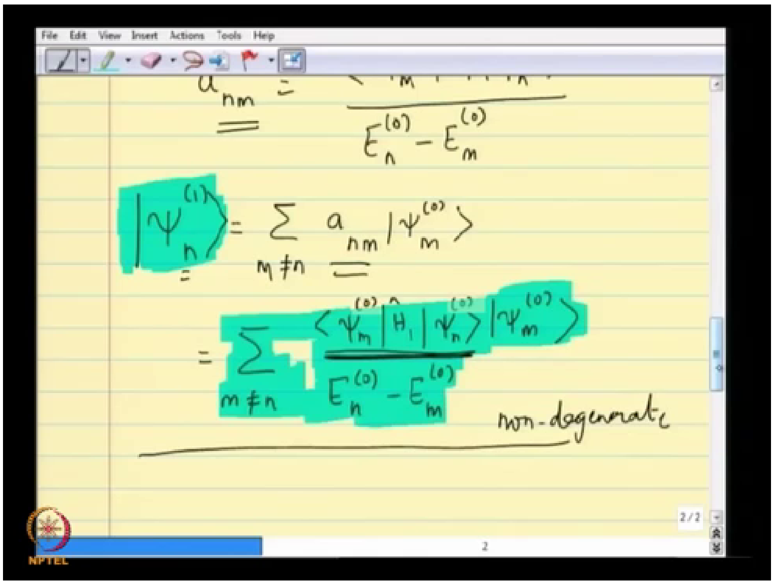

$$\underline{\underline{a_{nm}}} = \frac{}{E_n^{(0)} - E_m^{(0)}}$$

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} \underline{\underline{a_{nm}}}\, |\psi_m^{(0)}\rangle$$

$$= \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$

non-degenerate

So, if you substitute that, what we get out is what we get is the summation namely m not equal to n psi m H 1 psi n times the ket vector psi 0. Please remember this is a number is a complex number and it is also its an energy because the wave functions when integrated out will give you a number and this is the Hamiltonian operators the energy operator. So, what you have is energy and divided by this energy term E n 0 minus E m 0.

So, this is the wave function form or the first order correction which we shall highlight. Namely, psi n 1; the first order correction to the wave function is given by a sum of all matrix elements of the Perturbing Hamiltonian H 1 between that particular state n and all other states m which are not equal to m. This does not include the diagonal matrix element m equal to n. Please remember its m is not equal to n. Therefore, we have no problem with the denominator; we have assumed that the energy states are non degenerate. What does that mean? No 2 energies are equal and therefore, when the levels are different the energies are different. Therefore, the denominator never goes to 0.

Therefore, it is a well defined quantity for the first order correction to the wave function. This is what we need to use in order to obtain the second order corrections to the energy using the same method.

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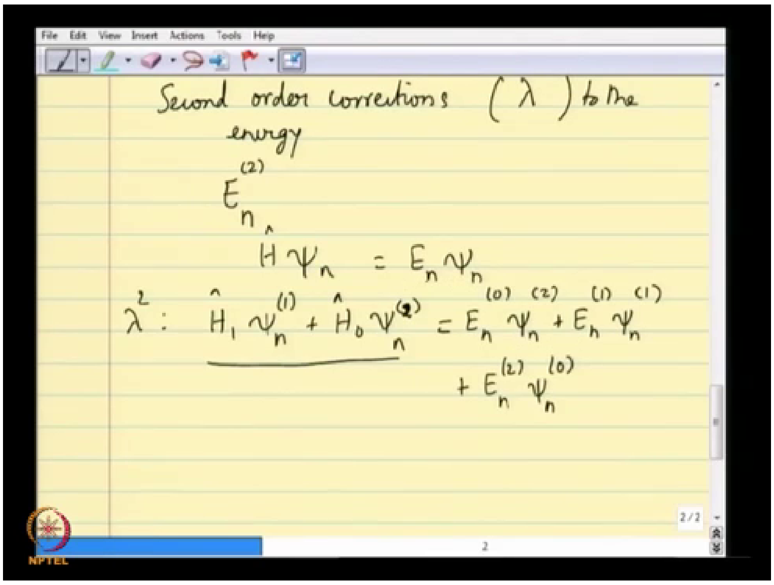

Second order corrections (λ) to the energy

$E_n^{(2)}$

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

$$\lambda^2 : \underline{\hat{H}_1\psi_n^{(1)} + \hat{H}_0\psi_n^{(2)}} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$$

Second order corrections, in the second order here essentially means that terms associated with lambda square where lambda is our perturbation parameter to the energy and that is denoted by E n 2 ok. Now, just to do that ok, we have had about almost like 15-20 minutes. So, let us take a short break here for about a few seconds and let me write down the expression for E and 2 from the original equation that we are doing all these basic tricks and then, we will continue to derive the expression for second order.

And hopefully, in the remaining time also that just try and calculate a 1 simple problem that is as an example we will take either a particle in a one dimensional box or other problems where we do not have an exact solution and there we can use the perturbation theory. So, will pause for a few seconds break right now.

So, second order correction to the energy, we need to go back to the equation H psi n is equal to E n psi n and pull out the terms corresponding to lambda square and please look back, look through your lectures a little bit back and then, they call this term namely H 1 psi n 1 plus H naught psi n 0, sorry psi n 2 psi n 2 is equal to E n 0 psi n 2 plus E n 1 psi n 1 plus E n 2 psi n 0.

This is the coefficient of lambda square on the left hand side of this equation, the H psi n component and the coefficient that the coefficient of lambda square on the right hand side is what you have here from E n psi n. So, this was derived yesterday.

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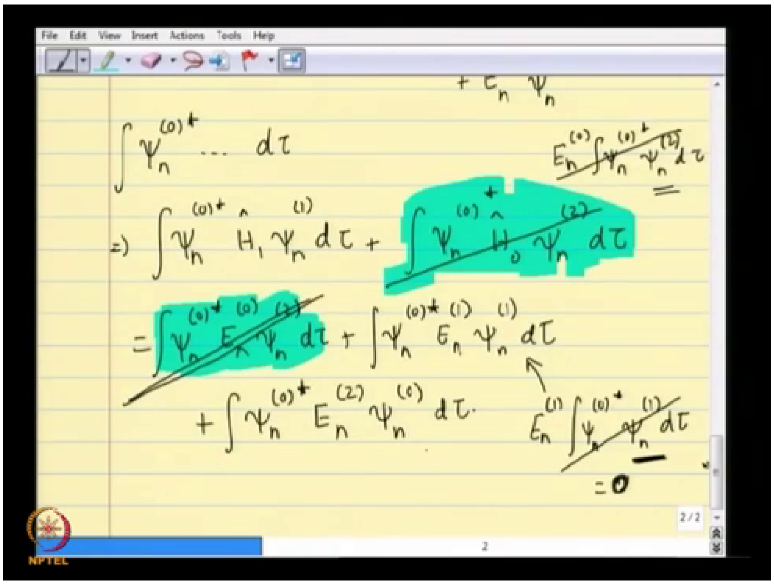

$+ E_n \psi_n$

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

$E_n^{(0)} \cancel{\int \psi_n^{(0)*} \psi_n^{(2)} d\tau}$
$=$

$\Rightarrow \int \psi_n^{(0)*} \hat{H}_1 \psi_n^{(1)} d\tau + \cancel{\int \psi_n^{(0)*} \hat{H}_0 \psi_n^{(2)} d\tau}$

$= \cancel{\int \psi_n^{(0)*} E_n^{(0)} \psi_n^{(2)} d\tau} + \int \psi_n^{(0)*} E_n^{(1)} \psi_n^{(1)} d\tau$

$+ \int \psi_n^{(0)*} E_n^{(2)} \psi_n^{(0)} d\tau.$

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

Now, what we need to do is do the same trick that we did namely multiply this by psi n 0 star and integrate both the left hand and right, left hand side and the right hand side. This n is the same as the n for which we are looking for the corrections ok, second order corrections. So, when we do that, the equation is psi n 0 star H 1 psi n 1 d tau plus the integral psi n 0 star H 0 psi n 2 d tau and on the right hand side, we do the same thing namely psi n 0 star E n 0 psi n 2 d tau plus you have psi n 0 star E n 1 psi n 1 d tau plus integral psi n 0 star E n 2 psi n 0 d tau.

So, you have on the left hand side 2 terms and on the right hand side 2 terms. We can look at this and cancel some of the terms immediately ok. Let us look at this term, you see that H naught acting on the wave function psi n 2 which we still do not know what the second order correction to the wave function is. We only know the first order correction.

Therefore, H naught can also act on the wave function on the left hand side; being a Hermitian Hamiltonian, it gives you the eigenvalue corresponding to the psi and 0 star which is also E n 0. Therefore, this term is immediately you can write it is E n 0 followed by this integral psi n 0 star psi n 2 d tau ok. No matter what the psi n 2 is; whether this integral is 0 or not, we can right away cancel this term with the corresponding term that you have here which is star namely the psi n 0 star E n 0 psi n 2 d tau.

So, they are both gone. This is gone; canceled by that. So, what is left over is the integral psi n 0 star H 1 psi n 1 and on the right hand side, we have a couple of terms ok. We have E n 1 which is the first order correction, it is a constant therefore, this term can be written as E n 1 integral psi n 0 star psi n 1 d tau ok. Now recall how we define the psi n 1? We defined psi n 1 in such that it does not contain the psi n 0. It has all the linear combinations of all the term, all the wave functions other than this term. Therefore, no matter what you do; how many terms you expand, this will be 0 ok.

Therefore, there is no correction ok. There is no correction from this term, it is all 0. So, what is left over on the right hand side is only 1 term. Now, we collect that. The right hand side is of course, E n 2 is the constant that we are looking for.

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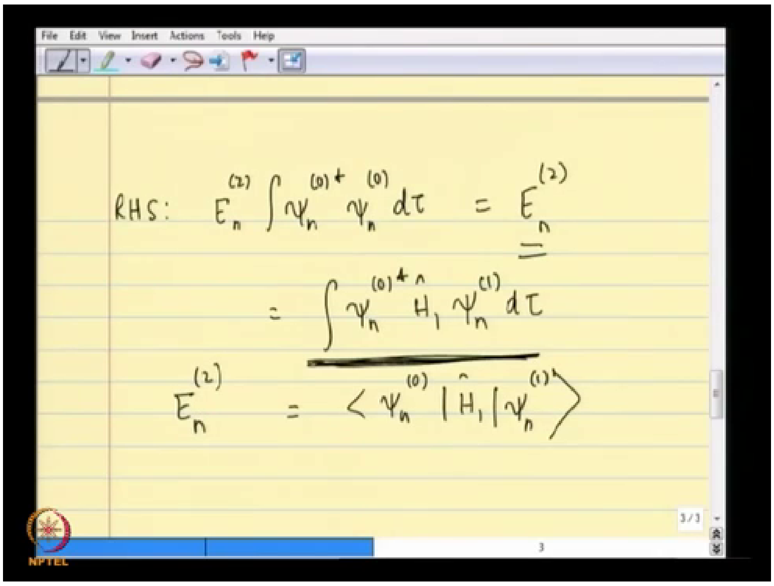

RHS: $E_n^{(2)} \int \psi_n^{(0)*} \psi_n^{(0)} d\tau = \underline{\underline{E_n^{(2)}}}$

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

$$E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(1)} \rangle$$

Therefore, if we write the right hand side first and say E n 2 times the integral psi n 0 star psi n 0 d tau, we know that this integral is equal to 1 and therefore, the right hand side has only 1 term the second order correction that we are looking for. What does the left hand side contain? It contains again only 1 term; namely, it contains this term psi n 0 star H 1 operator psi n 1 d tau ok.

Please note that the H 1 does not act on the wave function to give you in diagonal correction because H 1 is something is a perturbation. Therefore, we do not have that property that H 1 has diagonal or it has both diagonal and off diagonal contributions.

Therefore, the second order correction is given by this integral. But we know if you have to write this integral, it is in terms of Dirac ket it is psi n 0 H 1 psi n 1 E n 2 ok.

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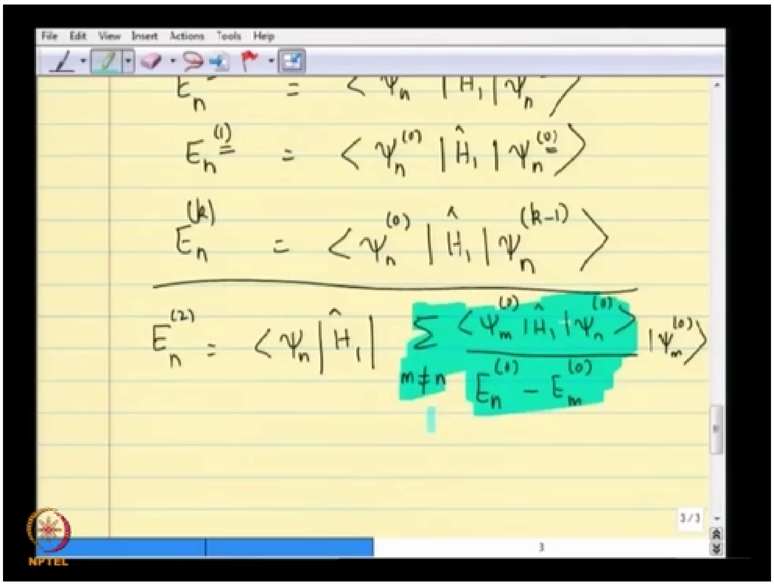

$$E_n = \langle \psi_n | H_1 | \psi_n \rangle$$

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

$$E_n^{(k)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(k-1)} \rangle$$

$$E_n^{(2)} = \langle \psi_n | \hat{H}_1 | \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} | \psi_m^{(0)} \rangle$$

Now, just by coincidence you might recall that E n 1 was given by psi n 0 H 1 psi n 0 1 and 0 2 and 1.

So, in principle, if I need to know the correction to any nth order or any kth order whatever it is; third, fourth, fifth etcetera all I need to do is to do this quantity, calculate this quantity psi n 0 H 1 psi sorry yeah psi n k minus 1'th order wave function if you have to calculate ok. Is it true or not, I want you to check it in your calculation.

But we will just now do the complete the second order correction namely E n 2 is integral psi n. This is the ket that the bra state that we are writing and now you remember psi n 1 was given by n infinite by a series namely sum over I think if I wrote probably m not equal to n, then we had psi m 0 H 1 psi n 0 divided by E n 0 minus E m 0 times psi m 0 ok.

This whole thing that you see, this whole thing is a complex number or real number depending on the value of this matrix element, summed over. Therefore, you can immediately take that out and write this in a more compact form.

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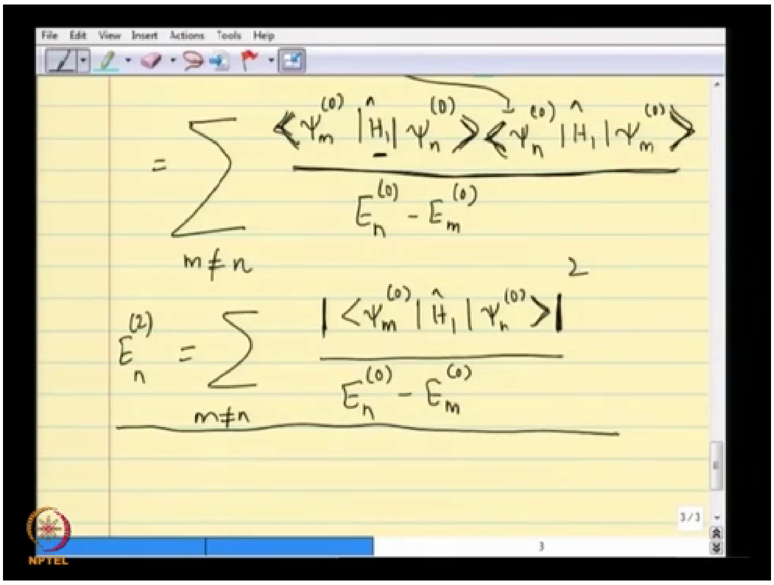

$$= \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \hat{H}_1 | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

Namely, sum over m not equal to n psi m 0 H 1 psi n 0 and then, we will write this part here namely psi n 0 sorry, I should have a 0 here psi n 0 H 1 psi m 0 divided by E n 0 minus E m 0 ok. Now the summation is for both the denominator and the numerator.

So, you have to be careful that you write this as m not equal to n; you have 2 wave function matrix a 2 Hamiltonian matrix elements perturbation H 1 matrix element psi m 0 H 1 psi n 0, psi n 0 H 1 psi m 0 and if you know the Dirac ket bras, the bracket properties, this bracket is the complex conjugate of this bracket. That is whatever is the value of this the complex conjugate the start value is what you will get here. And therefore, even more compactly, we can write this a number multiplied by its complex conjugate is nothing but the absolute square of the complex conjugate. Therefore, we can write the sum as m not equal to n. The absolute value of this matrix element H 1 psi n 0 squared divided by E n 0 minus E m 0 ok.

This is equal to E n 2 and this is a very very standard Second Order Perturbation Theory correction for non-degenerate state.

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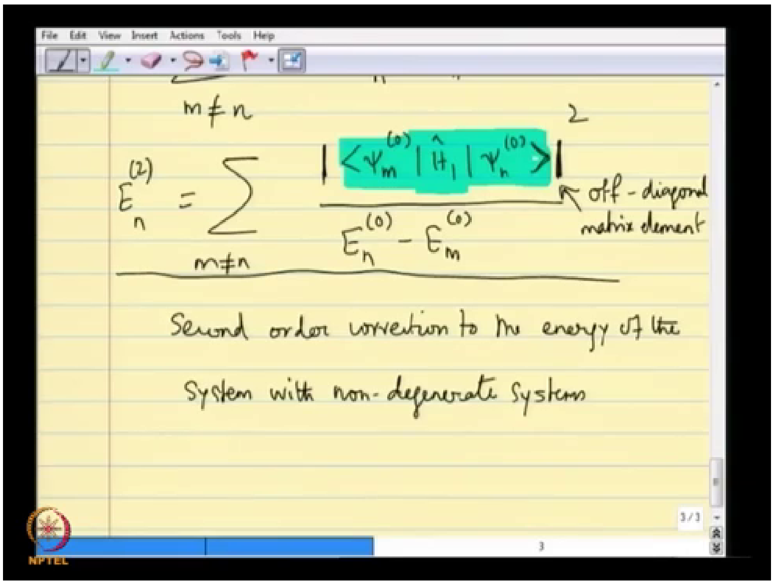

$m \neq n$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

off-diagonal matrix element

Second order correction to the energy of the System with non-degenerate System

Second order correction to the energy of the system with non-degenerate state. So, what you are looking at is that you have a matrix element if you recall the last lecture, I drew the matrix for H 1 and I showed you that there are diagonal elements and off diagonal elements if you organize the basis functions of the 0 order Hamiltonian in an order in the same order as you have it in the different rows and also in the different columns. Then, the matrix element between the bras state of a particular row, the Hamiltonian and the ket state of that particular column is what is called the matrix element of the Hamiltonian.

So, now if you look at that the term that you have here namely the psi m 0 H 1 psi n 0 is your matrix element, but please remember m is not equal to n and therefore, this is the off-diagonal matrix element ok. The off-diagonal matrix element; but unfortunately the perturbation correction does not depend only on that. The magnitude of the off-diagonal matrix elements squared divided by the energy difference between the corresponding diagonal and the off-diagonal quantity. Now, let us see that pictorially what it means.

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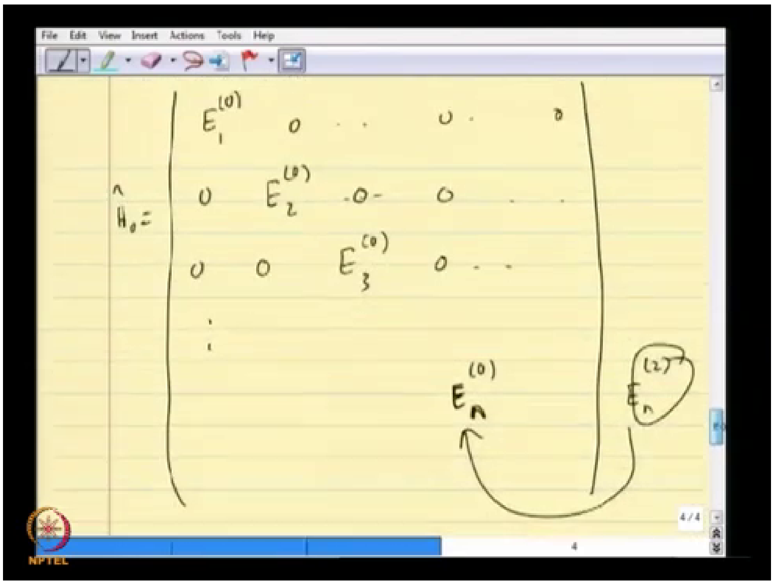

$$\hat{H}_0 = \begin{pmatrix} E_1^{(0)} & 0 & \cdots & 0 & \cdot & 0 \\ 0 & E_2^{(0)} & 0 & 0 & \cdots & \\ 0 & 0 & E_3^{(0)} & 0 & \cdots & \\ \vdots & & & & & \\ & & & E_n^{(0)} & & \end{pmatrix} \quad E_n^{(2)}$$

Let us draw the matrix for H 1 ok. First let us draw the matrix for H naught ok. We know that the basic functions are eigenfunctions of H naught. Therefore, the matrix of H naught is only diagonal it is E 1 0, everywhere else it is 0. E 2 0, everywhere else it is 0 that is how we started the perturbation theory. That is we know a 0 order problem. The solutions to the 0 order problem, E 0 and so on. What was the matrix for H 1?

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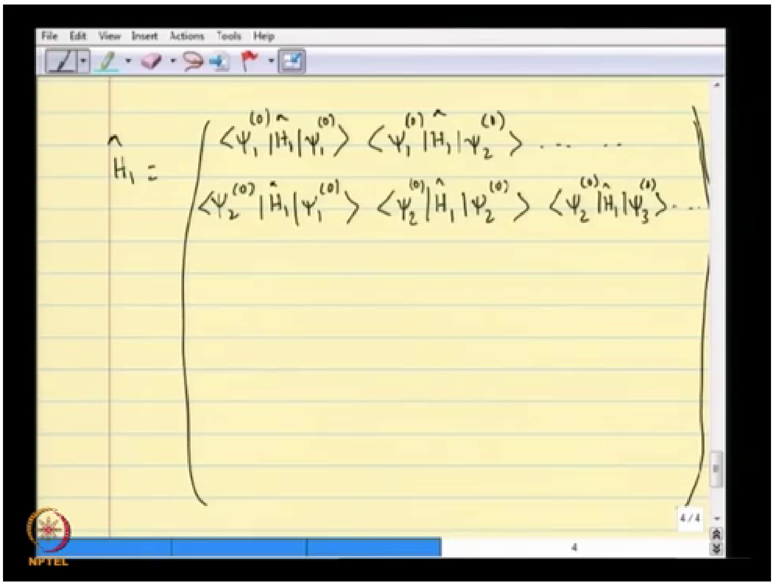

$$\hat{H}_1 = \begin{pmatrix} \langle \psi_1^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle & \langle \psi_1^{(0)} | \hat{H}_1 | \psi_2^{(0)} \rangle & \cdots & \cdots \\ \langle \psi_2^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle & \langle \psi_2^{(0)} | \hat{H}_1 | \psi_2^{(0)} \rangle & \langle \psi_2^{(0)} | \hat{H}_1 | \psi_3^{(0)} \rangle & \cdots \end{pmatrix}$$

We wrote the matrix element; psi 1 0 H 1 psi 1 0 and this first row the second element was psi 1 0 H 1 psi 2 0 and so on as many basis functions. So, if you have an infinite basis set, this matrix is an infinite dimensional matrix basis the infinite dimensional matrix and what is the second one? It is psi 2 0 H 1. Let me make sure that the hats are all there and psi 1 0 psi 2 0 H 1 psi 2 0 and of course, this one is psi 2 0 H 1 psi 3 0 and so on.

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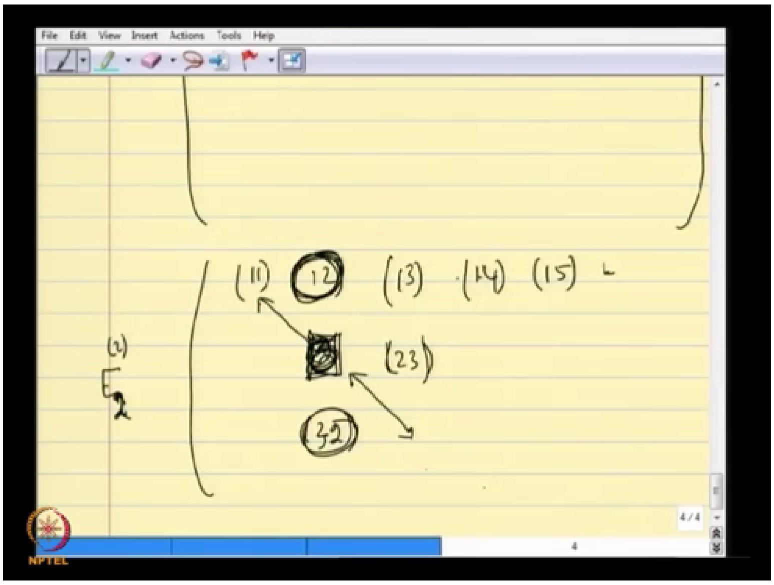

Now, so, if I have to write it even more symbolically what I have is I want to look at the correction to the nth element that is the nth diagonal element. Please remember E n 0 if it is here, E n 2 represents the second order correction to this value due to the perturbation ok. Now, what you see is that the second order correction to this value is now given by a summation of all possible values with energy denominators. The energy denominators are suppose you have E n 0, we start with and let us put the first here is the first one, the expression here.

Let us assume that some value of n; m will be 1 to start with. So, we take the matrix element of psi 1 0 H 1 psi n 0, whatever that n may be divided by E n 0 E n 0 minus E 1 0 ok. Therefore, we are taking the if you write this as 1 2 3 4 corresponding to various matrix element 5 etcetera sorry 1 1 1 2, I think that is the better way of writing it 1 3 1 4 1 5 and so on and if you do that the perturbation correction to E n 2 is given by the matrix element. Suppose this is 2; second energy level, then we have the matrix element 1 2 as the first item divided by the energy difference between 1 1 and 2 2.

If the n is 2, 2 minus 1, this 2 is the diagonal matrix element of the 0 (Refer Time: 33:46) Hamiltonian second row, second column. So, it is 2 2. This is the first row, first column 1 1. So, it involves the difference between the 2 energies and the corresponding of diagonal matrix element this one. We are looking for correction to this term ok, looking for corrections to this term E n 2. But it does not stop with that. It is also looking at the corrections to this is the next term in the summation if you look at the m; m cannot be 2, but m can be 3.

So, 2 3 will be there, here. When n is 2, m can be 1, 3, 4, 5 etcetera; if m is 3, we have 3 2 divided by 2 minus 3. So, 2 3 or 3 2; this is the 3 2 matrix element ok. So, it is also 3 2 matrix element, but the difference between the energy is 3 and 2 and what about the next one? The next one will be 4 2.

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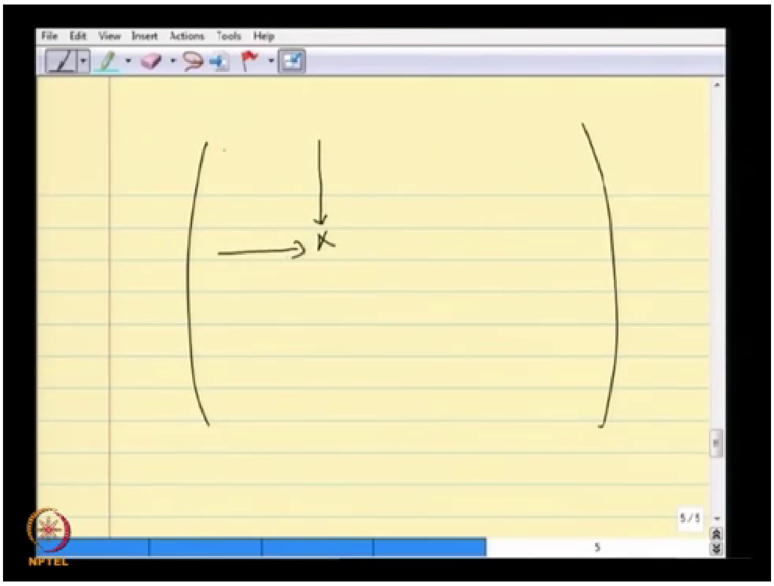

So, if you look at the perturbation, what perturbation does is any energy gets corrected by the corresponding off diagonal matrix element; off diagonal matrix element with that energy and the difference between the two.

Therefore, if you now assume that the energy levels are further and further and further way, you will see that the matrix element is of the perturbing Hamiltonian has a certain value, but the energy denominators increase. If the energy denominators increase to very large values, but the matrix element of the Hamiltonian Perturbing Hamiltonian remains more or less the same, you can see that higher order correction, the higher the corrections of terms further away are going to be less and less. So, all we can hope for is that if these energies are very far apart that we even in that summation, we do not need to calculate many terms ok.

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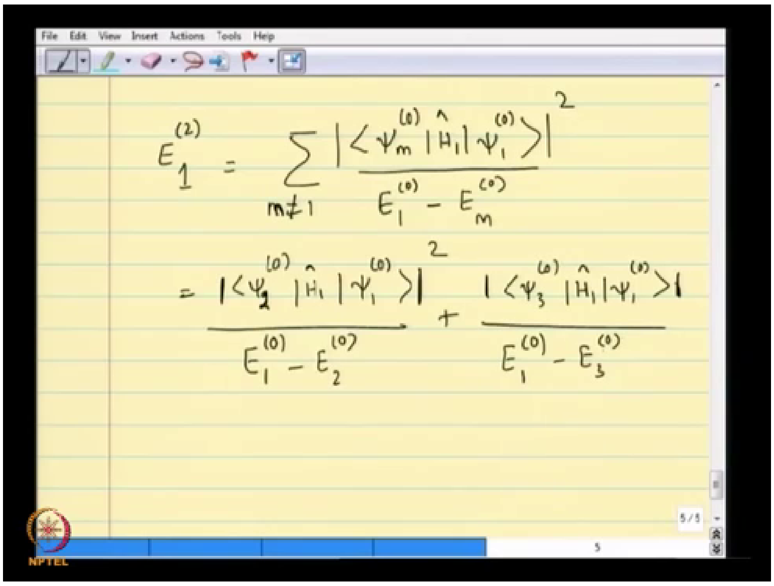

$$E_1^{(2)} = \sum_{m\neq 1} \frac{|\langle \psi_m^{(0)}|\hat{H}_1|\psi_1^{(0)}\rangle|^2}{E_1^{(0)} - E_m^{(0)}}$$

$$= \frac{|\langle \psi_2^{(0)}|\hat{H}_1|\psi_1^{(0)}\rangle|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{|\langle \psi_3^{(0)}|\hat{H}_1|\psi_1^{(0)}\rangle|}{E_1^{(0)} - E_3^{(0)}}$$

Let me just put that in perspective by writing an explicit second order correction to energy level 1. So, we will do that. The expression would be n not equal to 1 psi sorry m, m not equal to 1 psi m 0 H 1 psi 1 0 the absolute square divided by E 1 0 minus E m 0 isn’t it? We had the correction is E n, yeah 1 0. So, if we expand to this; it is like this. Psi 2 m will be the first value will be m equal to 2 psi 2 0 H 1 psi 1 0 square by E 1 0 minus E 2 0 plus the next term will be m equal to 3 which means psi 3 0 H 1 psi 1 0 divided by E 1 0 minus E 3 0 plus so on; so, 2 3 4 5 etcetera.

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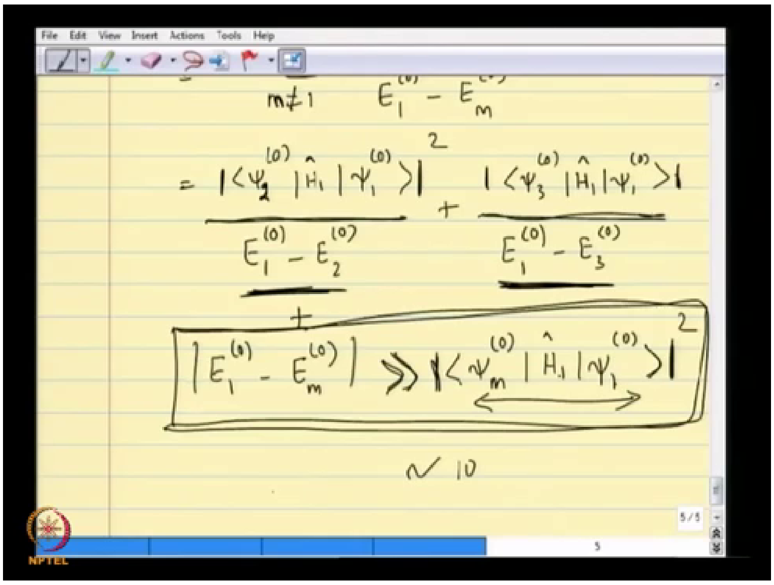

$$m \neq 1 \qquad E_1^{(0)} - E_m^{(0)}$$

$$= \frac{|\langle \psi_2^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{|\langle \psi_3^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle|}{E_1^{(0)} - E_3^{(0)}} +$$

$$\boxed{|E_1^{(0)} - E_m^{(0)}| \gg |\langle \psi_m^{(0)} | \hat{H}_1 | \psi_1^{(0)} \rangle|^2}$$

$$\sim 10$$

If these denominators energies, if the energies are further and further apart as for the 0 order Hamiltonian 1 2 3 4 etcetera, you can see that this itself assuming that the magnitude of these matrix elements on the numerator are more or less the same that, they do not very too much. Assuming, you would see that these terms will decrease in size and therefore, as we compute even second order perturbation correction, we do not have to include many many terms. It is possible that we do 2 3 4 maybe 5 terms of this and then, the corrections are not very significant provided the energies E 1 0 minus E m 0 is much larger ok.

Then, psi m 0 H 1 psi 1 0 absolute square ok. Now, this is a precise statement of the validity of Perturbation Theorem that is the difference between the 0 order energy levels connected by the perturbation, connected by the perturbation H 1 connects 1 to m. Therefore, the 0 order energy level differences for those energies connected by the perturbations are very large.

The magnitude of the Perturbing Hamiltonian itself is very small such that the ratio is much much less than 1 that is a statement to say that Perturbation Theory will work very well when this condition is satisfied. Of the order of 10, then you take the ratio that is E 1 0 minus m 0 is 10 times less, Perturbation Theory is good; 5 times, the convergence is poor and anything else, it is poorer and therefore, maybe we will have to calculate many more terms. Not only this that is only for E n 2.

But if this condition is valid, if this condition is not valid sorry if this condition is violated; we may even need to calculate E n 3, E n 4, E n 5 and so on. Therefore, we have to be very careful about the use of Perturbation Theory particularly we need to check the magnitudes of the quantities involved and this is a statement which you might want to remember as a condition for perturbation theory ok. So, let me then summarize the results that we have ok, for this lecture.

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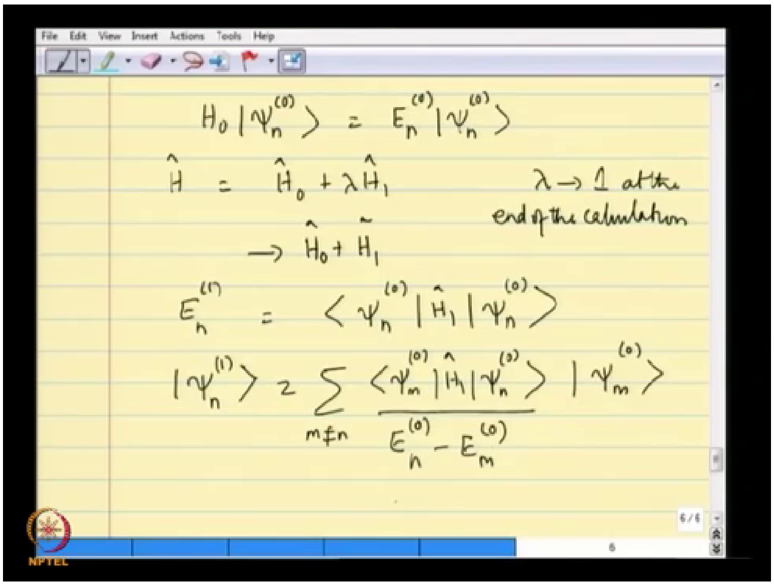

$$H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$$

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

$\lambda \to 1$ at the end of the calculation

$$\to \hat{H}_0 + \tilde{H}_1$$

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \, |\psi_m^{(0)}\rangle$$

We started with H naught psi n 0. Now, everything is written in terms of the bracket notation as E n 0 psi n 0 ok. We the Hamiltonian that we used was H naught plus lambda H 1 lambda to be set to 1 at the end of the calculation. So, that the Hamiltonian becomes essentially it goes to H naught plus H 1 and now, we have done the 2 calculations with lambda and lambda square, the first order correction E n 1 was given as the matrix element of psi n 0 H 1 psi n 0.

The first order correction to the wave function psi n 1 that we wrote was just want to make sure that I do not have (Refer Time: 41:39) sum over m not equal to n. We had psi m 0 H 1 psi n 0 times the wave function psi m 0, the ket divided by the energies E n 0 minus E m 0.

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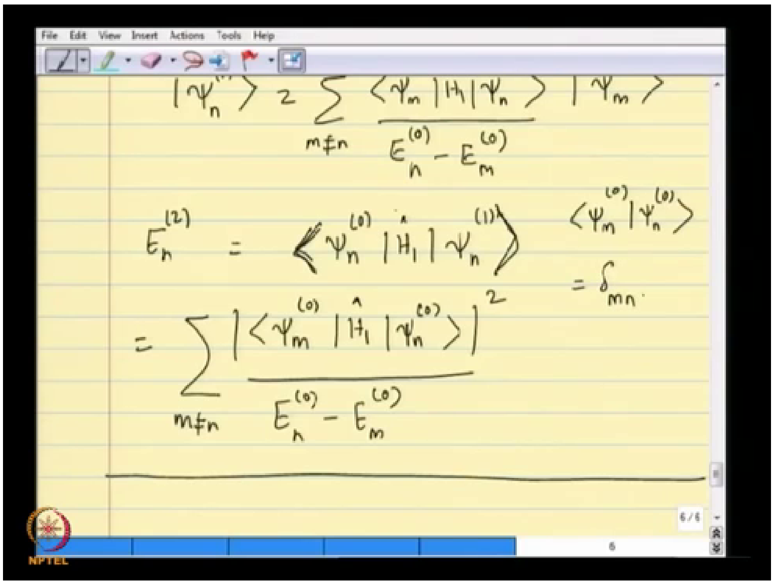

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\psi_m|H_1|\psi_n\rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m\rangle$$

$$E_n^{(2)} = \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle$$

$$= \sum_{m\neq n} \frac{|\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}.$$

And finally, the energy correction to second order E n 2 as the corrections psi n 0 H 1 psi n 1 and that was given as sum over m not equal to n psi m 0 H 1 psi n 0, the absolute square divided by E n 0 minus E m 0.

These are the 3 most important results and of course, we have used the conditions psi m 0 psi n 0 is the Dirac is the Croneker delta delta m n which is 1, if m is equal to n or 0 if m is not equal to n. So, this together is the summary of the 2 lectures that we have and what we will do is in the remaining time that we have will start looking for 1 or 2 simple examples of how to apply these formulas ok.

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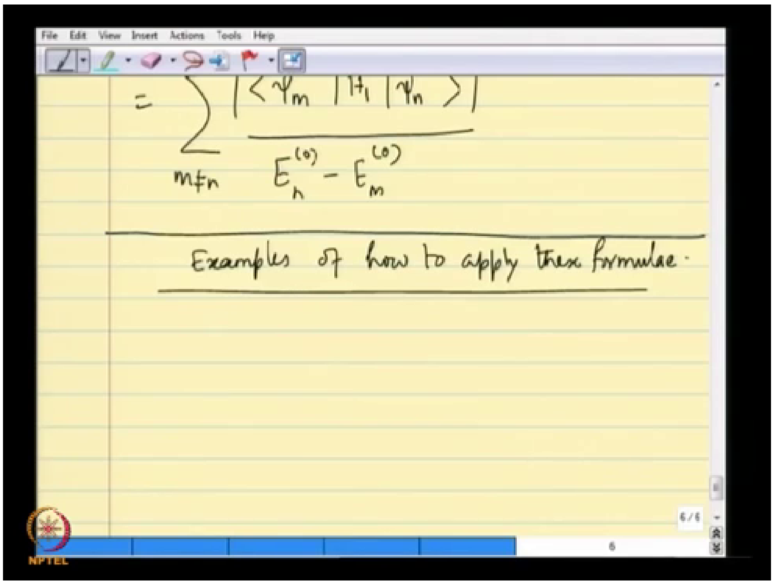

$$= \sum_{m \neq n} \frac{|\langle \psi_m | H_1 | \psi_n \rangle|}{E_n^{(0)} - E_m^{(0)}}$$

Examples of how to apply these formulae.

Now, let us take the first problem that we want to look at as a simple example will consider the particle I would not be able to complete that, but I will start this so that in the next lecture, we will continue from every left. And you will also have some time to look at and probably progress on your own to anticipate what I would like to say in that lecture. So, let us take the particle in a one dimensional box.

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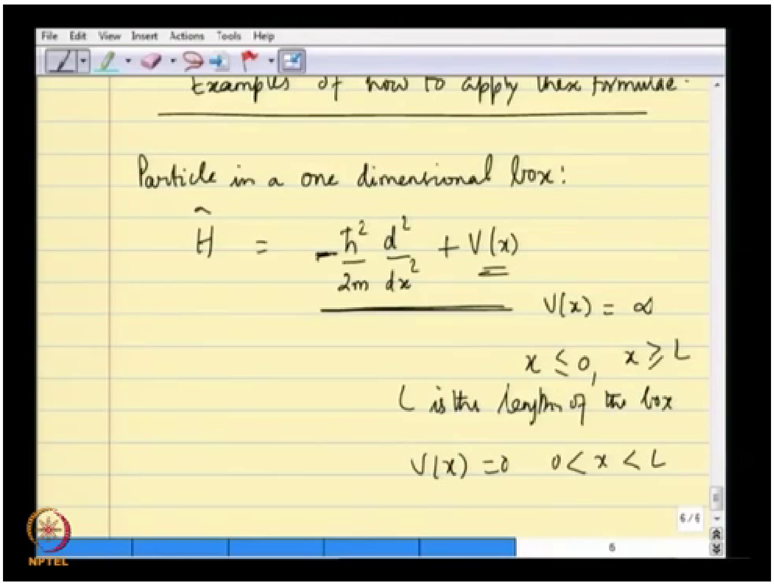

Examples of how to apply these formulae.

Particle in a one dimensional box:

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

$V(x) = \infty$

$x \leq 0, \; x \geq L$

L is the length of the box

$V(x) = 0 \quad 0 < x < L$

And we all know that the Hamiltonian 0th order is minus H bar square by 2 m d square by d x square plus your v of x, where the v of x is such that v of x is infinity infinite;

very very large for say x less than or equal to 0 x greater than or equal to l, where L is the length of the box, length of the box and v of x is 0 if x is between 0 and L less than x; x is 0 less than x less than L ok.

So, the boundaries are at 0 and L and at the boundaries and any point beyond the boundary on either side of the boundary is the potential is infinite and inside the box the potential is 0. That is a correct form; very often you use minus H bar square by 2 m d square by d x square. Please remember that can lead to confusion because remember that the wave function for the particle in a one dimensional box is not an eigenfunction of the momentum operator.

Precisely for this reason that the boundary condition has actually destroyed that, the commutativity between the free momentum operator of the particle in a box and the total energy operator which is not just p square by 2 m. But it is p square by 2 m plus v such that v is infinite and all points other than the box and v is 0, the points inside the box. These 2 statements have to go together ok.

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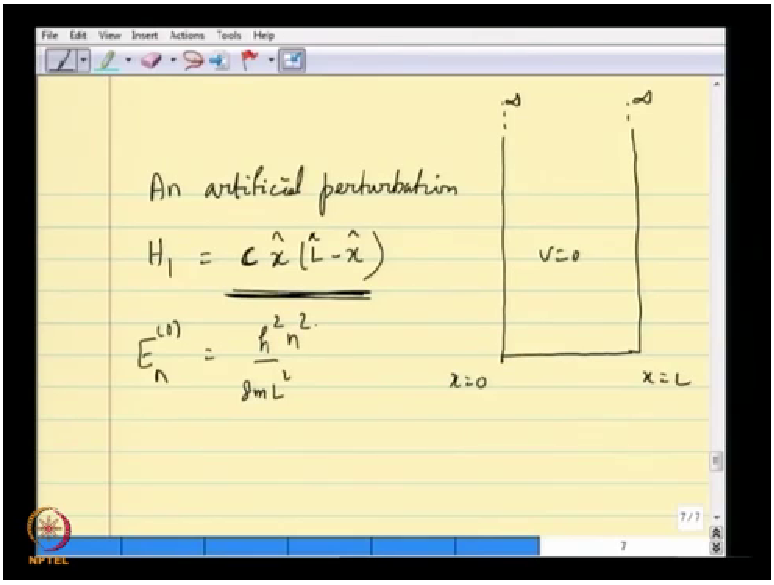

An artificial perturbation

$$H_1 = c\hat{x}(\hat{L}-\hat{x})$$

$$E_n^{(0)} = \frac{h^2 n^2}{8mL^2}$$

So, if you remember that, then we will consider an artificial perturbation to the box problem. So, sorry that is a poor drawing let me just write let us see ok. This line is there because I can draw on top of it, but this line let us just do that ok. So, this is x is equal to 0; x is equal to L. The dot dots to tell the potential is infinity; infinity and these 0 ok.

Now, we are going to consider obviously, a perturbation that exists only in the box. There is no point in adding perturbations to the walls it is already in finite potential. So, let us consider v of x the perturbation sorry the H which we have been using H 1. H 1 is a potential of this form C some constant times x into L minus x. Please remember when we write the Hamiltonian, all the quantities that we have are operators x is operator well, L is actually a number; but L is multiplied by the identity operator. So, I guess it is correct to put that L minus x ok.

Now, you see that the potential the perturbing potential is 0 at the ends, but its non-zero inside the box and how do we calculate corrections to the particle in a box energy. What are the energies? The E n 0's for the particle in the box are all given by H square by 8 m L square n square.

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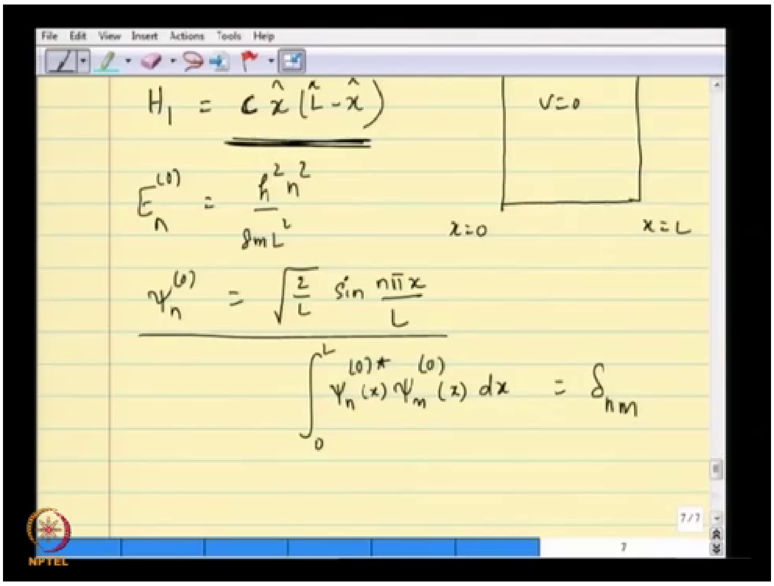

$$H_1 = c\hat{x}(\hat{L}-\hat{x})$$

$$E_n^{(0)} = \frac{h^2 n^2}{8mL^2}$$

$$\psi_n^{(0)} = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$\int_0^L \psi_n^{(0)*}(x)\,\psi_m^{(0)}(x)\,dx = \delta_{nm}$$

And the wave functions are all given by psi n 0 as square root of 2 by L sin n pi x by L ok. Let me just write that carefully; sin n pi x by L. So, this is the 0 order wave function and we also know that this integral psi n 0 star psi m 0 here it is a coefficient the degree of freedom is the particle position d x between 0 and L is delta n m.

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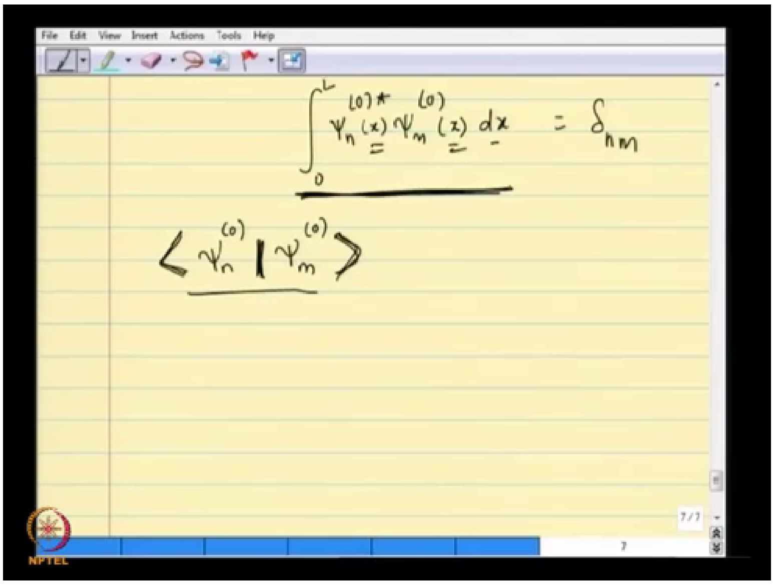

$$\underline{\int_0^L \psi_n^{(0)*}(\underline{x})\,\psi_m^{(0)}(\underline{x})\,d\underline{x}} = \delta_{nm}$$

$$\underline{\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle}$$

Now, before I close, I just like to tell you that this is the same thing as psi n 0 psi m 0, where you have seen that this x x and the integral d x have all been taken care of by this notation ok. That is the integration over all the coordinates is not represented, I mean it is understood when you do this bracket and what you have is an abstract sort of a linear algebraic notation that the way the eigen kets are orthogonal to each other. And the eigen kets in the coordinate representation or orthogonal as given by this integral.

So, we shall keep this in mind when we solve the problem of correcting the energies due to this perturbation in the next lecture. But if you wish to, please go ahead and solve some of these elementary things yourself before coming to the next lecture, before listening to the next lecture, until then.

Thank you very much.