Chemistry Atomic Structure and Chemical Bonding
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Lecture - 49
First and Second Order Time Independent Perturbation Theory: Simple Examples

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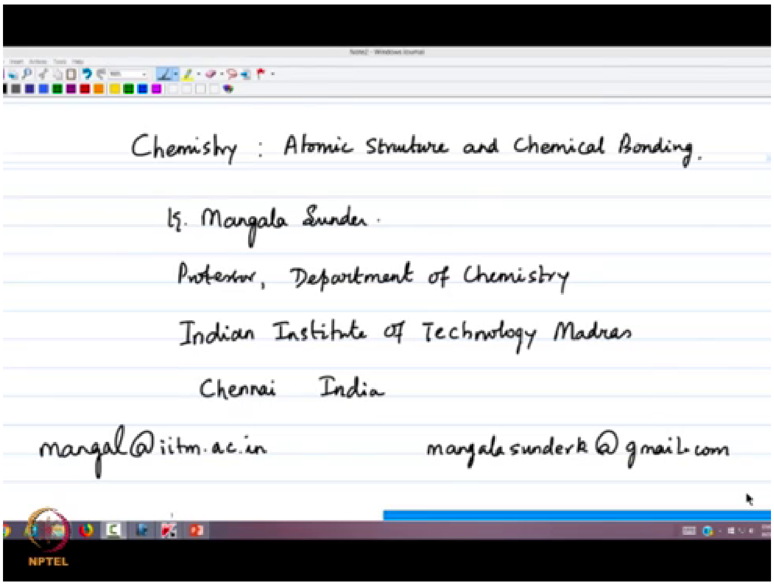

Chemistry : Atomic Structure and Chemical Bonding.

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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. In the last lecture we ended with a discussion on the model problem of a simple particle in a box and a perturbing potential that we want to apply over formulae of non degenerate perturbation theory to obtain simple results. As an application of the mechanisms I mean as an application of the formulation, we studied we started looking at this model (Refer Time: 00:59).

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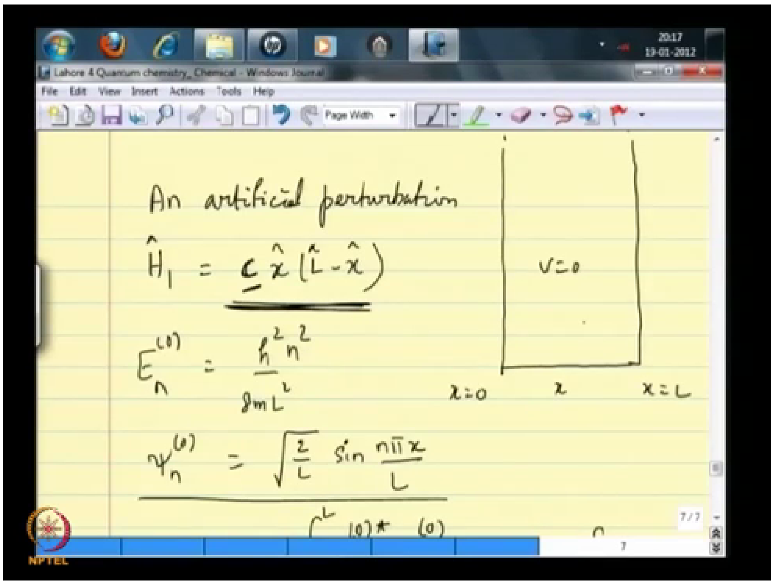

An artificial perturbation

$$\hat{H}_1 = \underline{c}\,\hat{x}(\hat{L}-\hat{x})$$

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

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

That is the box problem in which your potential H1 it is a Hamiltonian that is introduced with a small constant C, such that the potential varies as given here x times L minus x, where x is the position of the box the particle in the box at position coordinate associated with the particle wave function ok.

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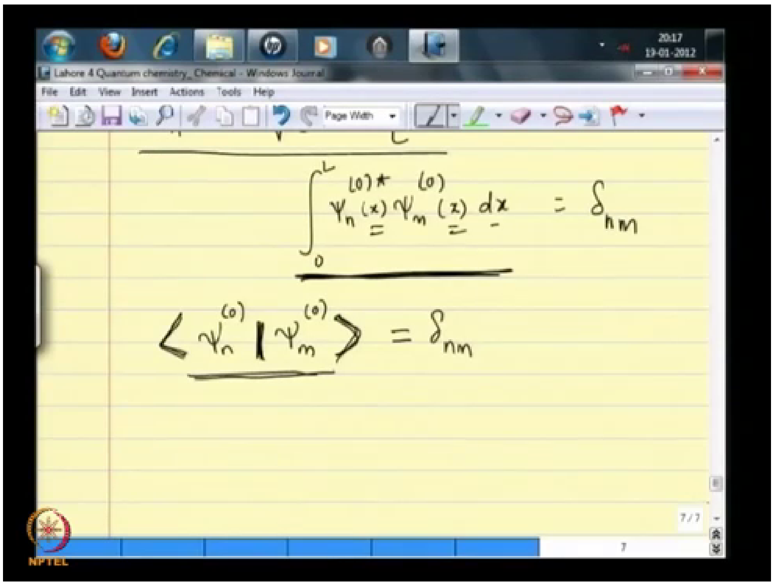

$$\int_0^L \psi_n^{(0)*}(x)\,\psi_m^{(0)}(x)\,dx = \delta_{nm}$$

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

The 0 order energies are known to us. The 0 order Eigen functions are known to us and the properties of the Eigen functions are that the Eigen functions are orthonormal.

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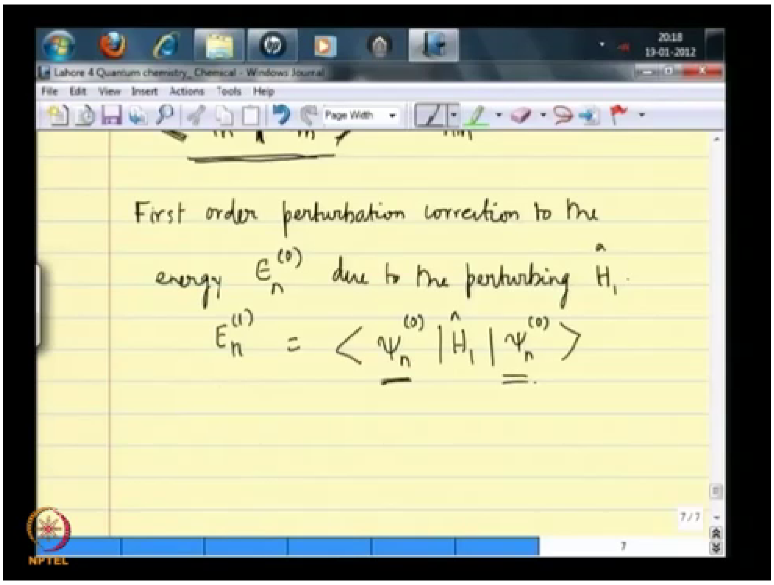

First order perturbation correction to the energy $E_n^{(0)}$ due to the perturbing $\hat{H}_1$.

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

And we want to calculate the first order perturbation correction to the energy E n 0 due to the perturbing term H 1 and we know the formal expression for the calculation of the first order correction E n 1 is given by the matrix element of the wave function matrix element of the perturbing Hamiltonian between the corresponding Eigen functions of the 0th order Hamiltonian ok.

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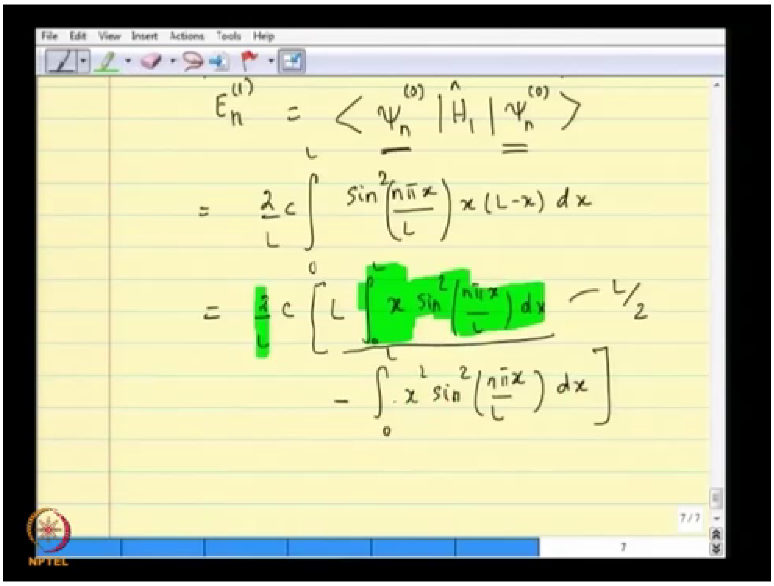

$$E_n^{(1)} = \langle \underline{\psi_n^{(0)}} | \hat{H}_1 | \underline{\underline{\psi_n^{(0)}}} \rangle$$

$$= \frac{2}{L} c \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) x (L-x)\, dx$$

$$= \frac{2}{L} c \left[L \underline{\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx} - \frac{L}{2} - \int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right) dx \right]$$

Therefore, it is a simple integral to calculate in the integral result this will turn out to be 2 by L, which is due to the root 2 by L squared the integral 0 to L and the sin 0s are since the Hamiltonian is only a multiplicative term here it is sin square n pi x by L and the constant the H 1 simply multiplies x into L minus x d x ok.

So, this is a simple enough integral, I do not want to do that I will leave it to you to arrive at the result. The correction is maybe one step I will just write down 2 by L C which is just to expand this, L integral x sin square n pi x by L d x minus integral 0 to L it is x square sin square n pi x by L d x ok. You know that this is nothing, but the average value of the position, this is the average value of the position operator that you have calculated this to be you know that the answer is L by 2 including the 2 by L integral here including that and you know that this is the average value of the x square ok.

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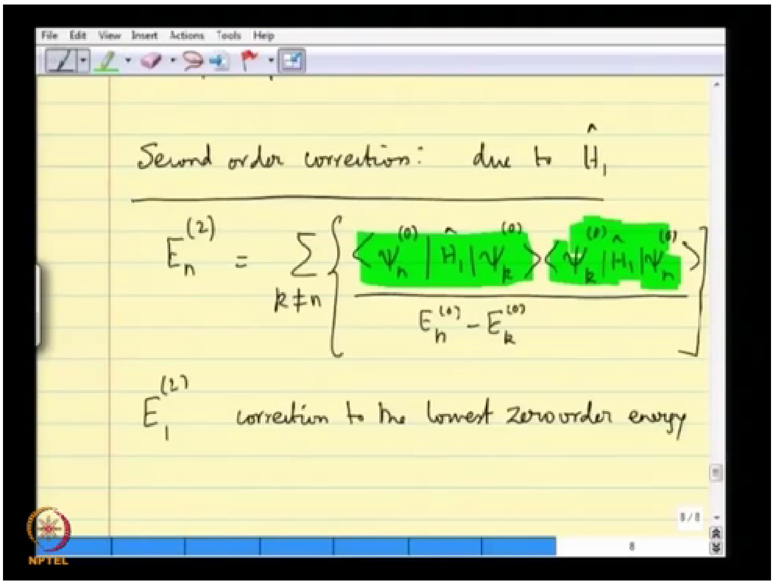

Second order correction: due to $\hat{H}_1$

$$E_n^{(2)} = \sum_{k\neq n} \left\{ \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \right]$$

$E_1^{(2)}$ correction to the lowest zero order energy

So, I would leave it to you to evaluate it. Now what about the second order correction that we want to look? At due to the same wave H 1 we know that this Hamiltonian is such that we can actually do corrections to various orders.

The integral evaluation is a fairly simple integral evaluation involving trigonometric functions and algebraic I mean polynomials therefore, it should not be a major problem for you to do that. The second order correction if you recall psi n 2 if you sorry. If you recall this expression sorry not psi n 2 the E n 2 the energy correction to second order the formula all of you know is I do not know it keeps coming ok. The formula is sum over k not equal to this n and psi n 0 H 1 psi k 0 psi k 0 H 1 psi n 0 ok. The sum is for both the numerator and the denominator namely E n 0 minus E k 0 ok. Now let us just do as a simple matter E 1 2 that is correction to the lowest 0 order energy ok.

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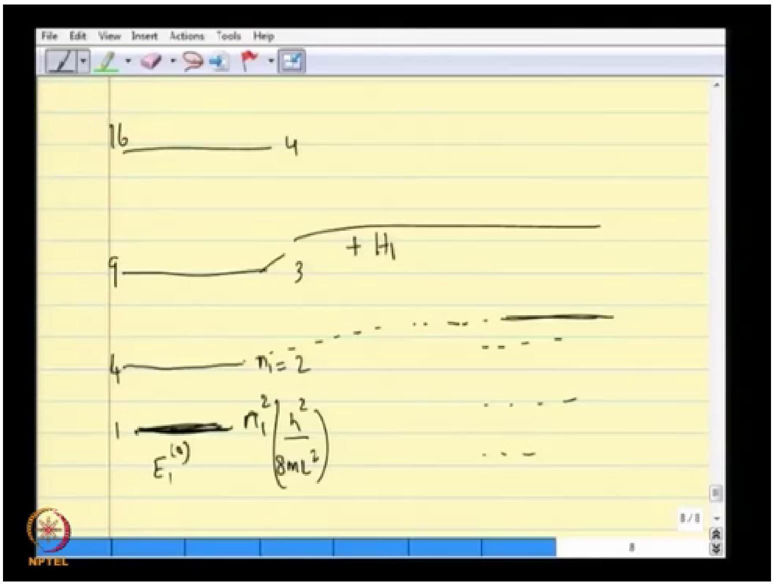

So, the picture to have in mind is the particle in a box has these energies n 1 square. So, this is 1 times that unit h bar h square h square by 8 mL square this is the unit of energy. The second one is quantum number n 1 is equal to 2 this is 4 times that energy. The third one is 9 times the energy, the fourth one is 16 times the energy and so on. So, the quantum number is 3 quantum number is 4. Now, this is in the absence of the perturbation now with the perturbation, how do these energy levels change due to the introduction. So, whether they go up or down we do not know they go up or I mean this energy goes to some other energy values this energy may go to some other energy.

So, also the idea is that the exact solution that you want to find out you are trying to find that by way of adding corrections to first order second order and so on. That is a picture that you have to have and the question that I have just now asked is what is the correction to the lowest energy E 1 0 is interesting from second order formulae, it is a general result that we have to remember.

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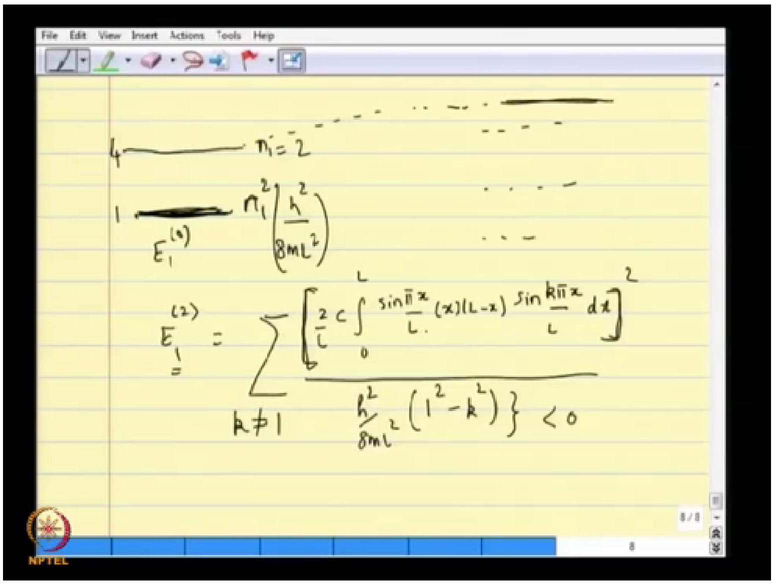

4 ——— $n_1 = 2$

1 ——— $n_1^2 \left(\frac{h^2}{8mL^2}\right)$

$E_1^{(0)}$

$$E_1^{(2)} = \sum_{k\neq 1} \frac{\left[\frac{2}{L} C \int_0^L \sin\frac{\pi x}{L} (x)(L-x) \sin\frac{k\pi x}{L}\, dx\right]^2}{\frac{h^2}{8mL^2}\left(1^2-k^2\right)\}} < 0$$

Therefore, let us write the correction E 1 2 second order correction as sum over k not equal to 1. Since we know all the formulae we can write the integrals 2 by L integral 0 to L remember there was a psi n 0. So, this is sin pi x by L the first wave function times C x into L minus x ok.

Then the other one is sin k. So, it is sin k pi x by L d x and if you recall the other integral is simply the complex conjugate of this and since this whole thing is real it is very easy for us to write this as square divided by the lowest energy is h square by 8 mL square and the next energy is k square all levels k is equal to 2, 3, 4 etcetera and we are summing over that. So, it is 1 square minus k square which is the difference in the energy. The form is particularly important because what you see on the numerator is an absolute square is a square it is never negative. This is real otherwise we have taken the number multiplied by its complex conjugate and look at this wave function the complex number here complex number here and it is complex conjugate.

Therefore the product is always positive 0 or positive if the integral is 0 its 0 otherwise its positive and then what you also have is that the denominator for every term of k is negative this term is less than 0 because k is greater than one therefore, you are summing only negative terms, the numerator is positive always and the denominator is always negative therefore, the second order correction to the lowest energy is always negative this is for non degenerate states problem that we have looked at the result can be more general.

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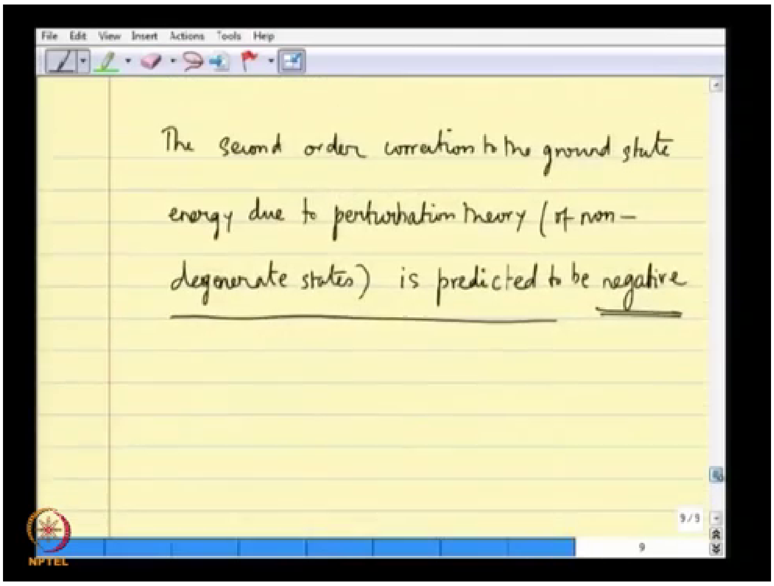

The second order correction to the ground state energy due to perturbation theory (of non-degenerate states) is predicted to be negative

The second order correction to the ground state energy, due to perturbation theory we are looking at specifically here of non degenerate states.

But let me not worry about that; the second order correction to the ground state energy due to perturbation theory is predicted to be negative it is a general result. So, this correction term that you have for the second order of second order to the ground state energy, again this integral is something that you can calculate and you see that it involves sin pi x and sin k pi x where k is not equal to 1, and it has the perturbing term x into l minus x the coordinates therefore, this is the off diagonal matrix element of the perturbation in the Eigen functions of the 0th order Hamiltonian sin pi x and sin k x.

So, everything that we said earlier is to be is illustrated here ok.

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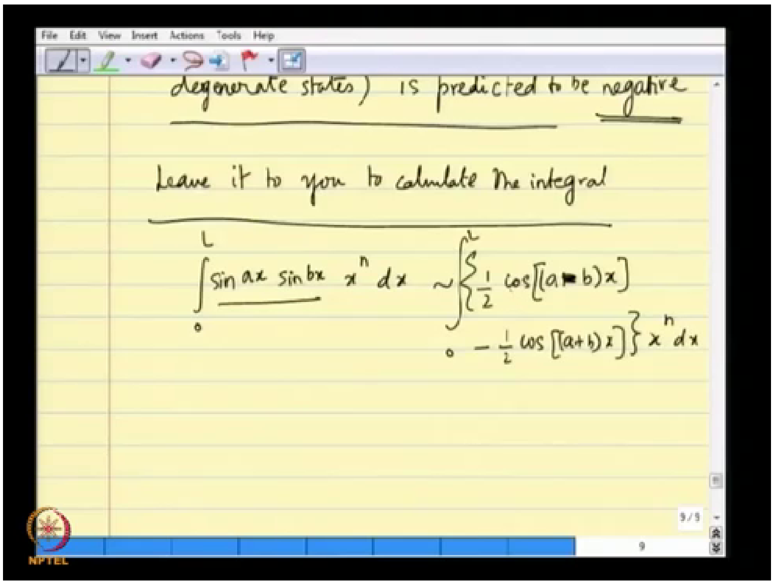

degenerate states) is predicted to be negative

Leave it to you to calculate the integral

$$\int_0^L \underline{\sin ax \sin bx} \; x^n \, dx \sim \int_0^L \left\{ \frac{1}{2} \cos[(a-b)x] - \frac{1}{2} \cos[(a+b)x] \right\} x^n \, dx$$

Now again I will leave it to you to calculate the integral, it is a very simple form. Essentially if you recall an integral of this nature sin a x sin b x x raise to n 0 to L d x should be I mean 1 simple way is to write this as the you know it is a sin sin. So, you can write this in the double angle formula namely 1 by 2 cos a minus b x minus 1 by 2 cos a plus b x multiplied by x raise to n integra L 0 to L d x and then you know cos x raise to n can be done using partial integration.

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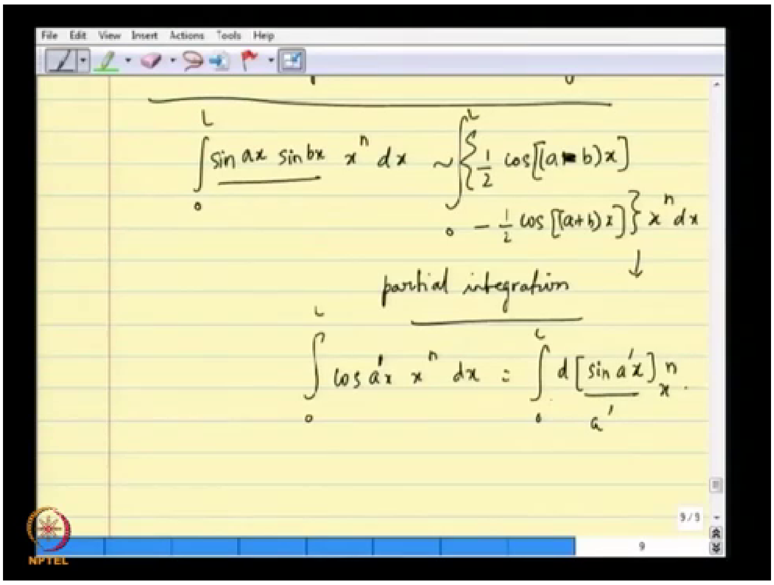

$$\int_0^L \underline{\sin ax \sin bx} \; x^n \, dx \sim \int_0^L \left\{ \frac{1}{2} \cos[(a-b)x] - \frac{1}{2} \cos[(a+b)x] \right\} x^n \, dx$$

$$\downarrow$$

partial integration

$$\int_0^L \cos a'x \; x^n \, dx = \int_0^L d\left[\frac{\sin a'x}{a'}\right] x^n$$

But if you find your own way of doing things easier way of doing things its perfectly fine, but if you what sort of lost on how we do this, this is how one normally does this use partial integration namely cos a x x raise to n integral d x for example, 0 to L.

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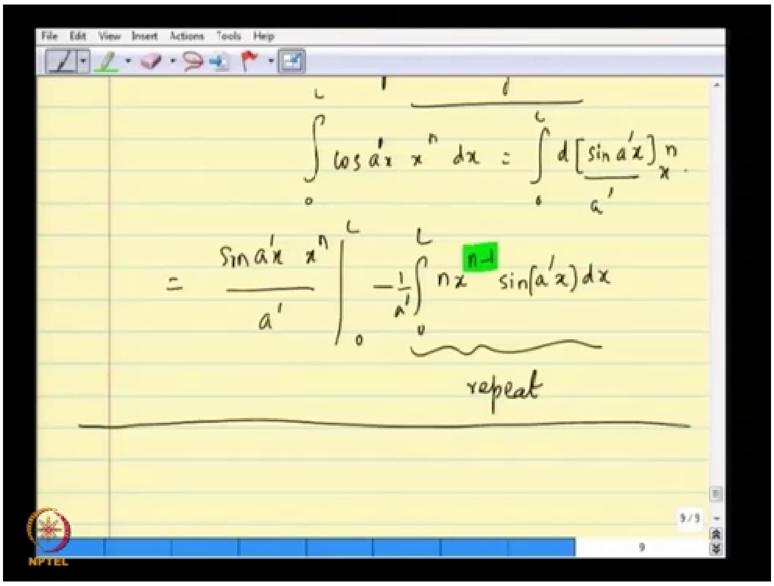

$$\int_0^L \cos a'x \, x^n \, dx = \int_0^L d\left[\frac{\sin a'x}{a'}\right] x^n .$$

$$= \left.\frac{\sin a'x \; x^n}{a'}\right|_0^L - \frac{1}{a'}\underbrace{\int_0^L n x^{\boxed{n-1}} \sin(a'x)\, dx}_{\text{repeat}}$$

Here we have a prime let us put in is to be written as integral 0 to L d of sin a prime x by a prime x raise to n and then you can use this u v formula namely sin a prime x x raise to n by a prime that is equal to between the limits 0 and L minus integral 0 to L 1 by a prime n x raise to n minus 1 sin a prime x d x. And you can repeat this process until you get rid of the powers n minus 1 x raise to n minus 1 to sorry until you get rid of this n minus 1 powers to 0 successively ok. So, that is just a algebraic step in case you wanted to know quickly how to do that so, I will leave that point.

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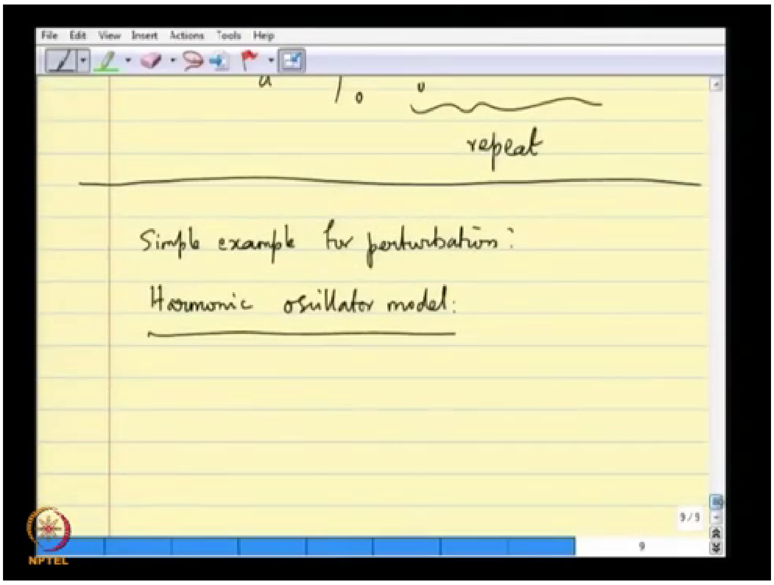

repeat

Simple example for perturbation:

Harmonic oscillator model:

The next simple example for perturbation, we shall look at the harmonic Oscillator model and we know the solutions of the harmonic oscillator. If you do not please go back and look at the solutions, I will write the results because we need the 0 order.

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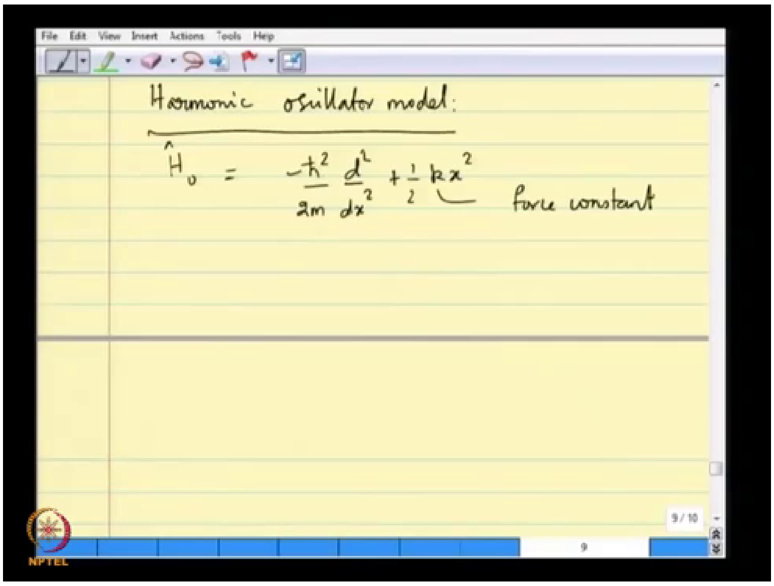

Harmonic oscillator model:

$\hat{H}_0 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}\underbrace{k}x^2$ force constant

Hamiltonian which is minus h bar square by 2 m the mass of the oscillator d square by d x square plus half k x square the force constant of the oscillator and in terms of the frequency of the oscillator.

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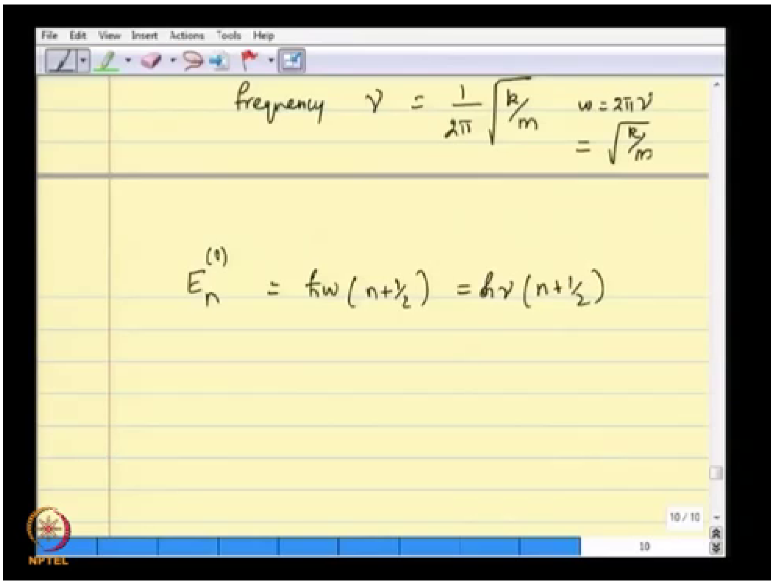

frequency $\nu = \frac{1}{2\pi}\sqrt{k/m}$ $\omega = 2\pi\nu$

$= \sqrt{k/m}$

$$E_n^{(0)} = \hbar\omega(n+\tfrac{1}{2}) = h\nu(n+\tfrac{1}{2})$$

Nu its 1 by 2 pi square root of k by m or omega which is 2 pi nu the angular frequency is equal to k by m ok, you know the recall these results and the 0 order energy E n 0 is h bar omega times n plus half where n is the quantum number is equal to h nu n plus half depending on what unit of energy frequency that you use n goes from 0, 1, 2, 3 etcetera.

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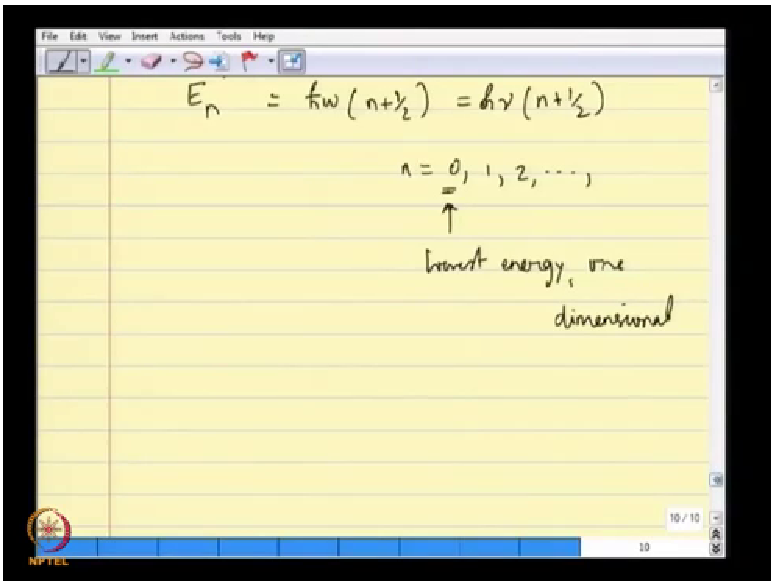

$$E_n = \hbar\omega(n+\tfrac{1}{2}) = h\nu(n+\tfrac{1}{2})$$

$$n = \underline{\underline{0}}, 1, 2, \cdots,$$

↑

lowest energy, one dimensional

And therefore, you see here the index takes 0 as the starting value this is the lowest energy. Also one dimensional therefore, the harmonic oscillator energies are one dimensional the harmonic the oscillator energies are non degenerate ok.

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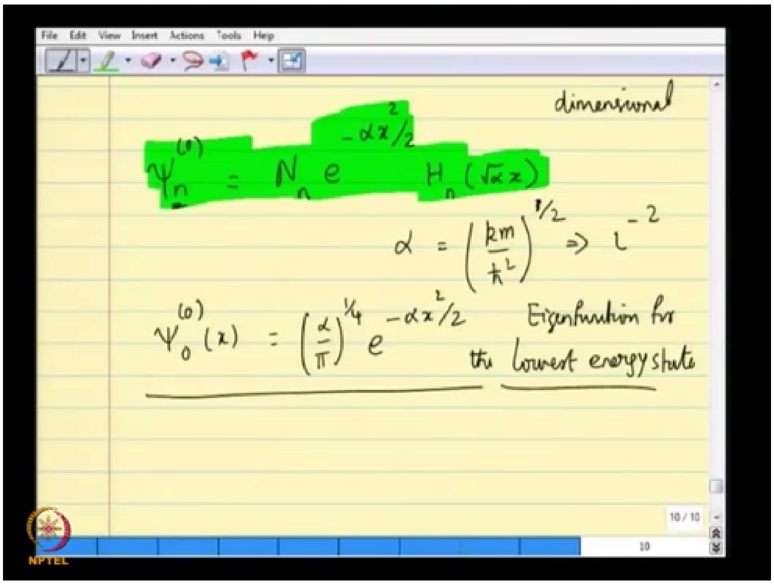


dimensional

$$\psi_n^{(0)} = N_n e^{-\alpha x^2/2} H_n(\sqrt{\alpha}\, x)$$

$$\alpha = \left(\frac{km}{\hbar^2}\right)^{1/2} \Rightarrow L^{-2}$$

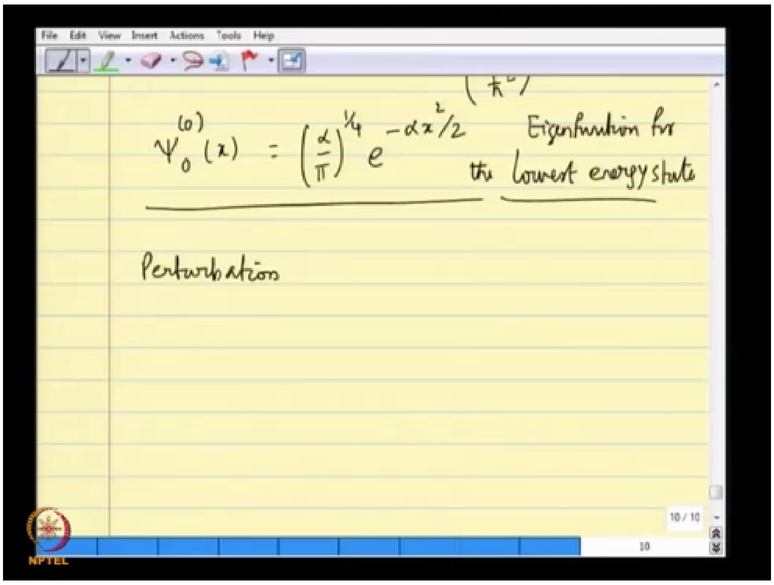
$$\psi_0^{(0)}(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

Eigenfunction for the lowest energy state

And the wave functions somewhat more complicated than the (Refer Time: 18:39) the particle in a box, the wave functions are given by a general formula with a normalization constant N which is a function of which is dependent on n times an exponential minus a constant alpha x square by 2 I will just write down and the hermite polynomials of the argument root alpha x where the constant alpha is a function of the harmonic oscillator parameters namely the mass and the force constant and alpha is given by k m by h bar square and the Planck's constant divided by 2 pi 1 by 2 ok.

So, this has the dimensions of L inverse 2 and this is the harmonic oscillator Eigen functions this is these are the harmonic oscillator Eigen functions ok. The general formula and the hermite polynomials expressions for the hermite polynomials are given in all the textbooks the lowest order the lowest energy solution we will write down which is psi 0 0 of x the normalization constant turns out to be alpha by pi to 1 by 4. The ermite polynomial when n is 0 for all argument is 1 therefore; all that you have is e to the minus alpha x square by 2 ok. This is the lowest eigen energy Eigen function or Eigen function for the lowest energy state ok.

(Refer Slide Time: 20:41)



$$\psi_0^{(0)}(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$ Eigenfunction for the lowest energy state

Perturbation

And suppose we have a Perturbation, which is not a harmonic force, but may be the second order. So, the perturbation is like a cubic term the you remember the harmonic oscillator Hamiltonian has half k x square the harmonic term higher power is x cube x 4 etcetera may contribute to the oscillator if the amplitudes are larger than what is known as the harmonic or small amplitude limits, then the energy levels change due to this unharmonicity or non hormonicity. So, if we assume two simplest order a perturbation to act H 1 of x as some constant C times x cube, C obviously, has the dimensions of energy divided by volume ok.

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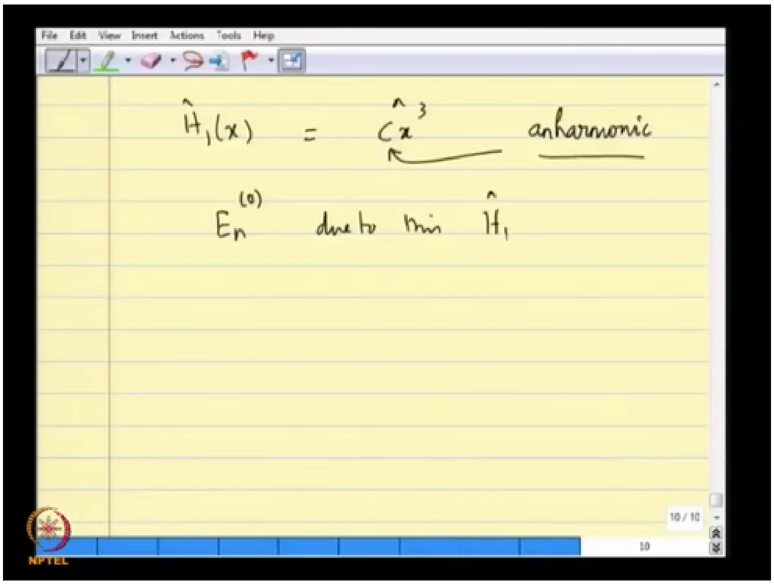

$$\hat{H}_1(x) = C\hat{x}^3$$ anharmonic

$E_n^{(0)}$ due to this $\hat{H}_1$

Because you see x cube is length cubes appropriate units it is the small quantity which is responsible for the oscillator being slightly unharmonic ok. Then one can calculate the corrections to the harmonic oscillator energy E n 0 due to this perturbation H 1. In a very simple way and here there is a very nice simple result that will follow which I will illustrate later on using a different method called the operator or the Dirac representation for the harmonic oscillators in another lecture we would introduce that, but here we will do the integrals.

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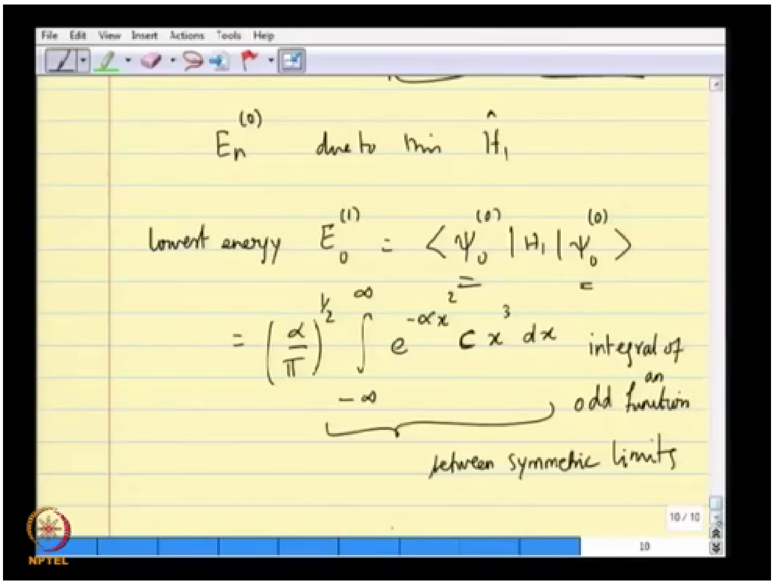

$E_n^{(0)}$ due to this $\hat{H}_1$

lowest energy $E_0^{(1)} = \langle \psi_0^{(0)} | H_1 | \psi_0^{(0)} \rangle$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \underbrace{\int_{-\infty}^{\infty} e^{-\alpha x^2} C x^3 \, dx}_{\text{between symmetric limits}}$$

integral of an odd function

The correction to say let us take the lowest energy E 0 0 and let us do the first order correction to that it is given by psi 0 0 H 1 psi 0 0 Eigen functions of the 0 order Hamiltonian H 1 and in this case the integral is you remember its alpha by pi to the 1 by 4, but we have the square.

So, it is alpha by pi into 1 by 2 and the integral the harmonic oscillator coordinates are all the way from I mean all along the real axis minus infinity to plus infinity I mean it is a it is a model and we realize that as the amplitudes are very large the harmonic oscillator is no longer oscillator, but the wave functions are such that that this limit is a theoretical limit e to the minus alpha x square because it is a psi square and the H 1 is the coefficient C which is the magnitude of the unharmonicity times x cube d x ok. This is again by symmetry one can say immediately that this is an odd function, the integral of an odd function between symmetric limits minus infinity to plus infinity therefore, the answer is that this integral is 0. There is no first order correction simple result.

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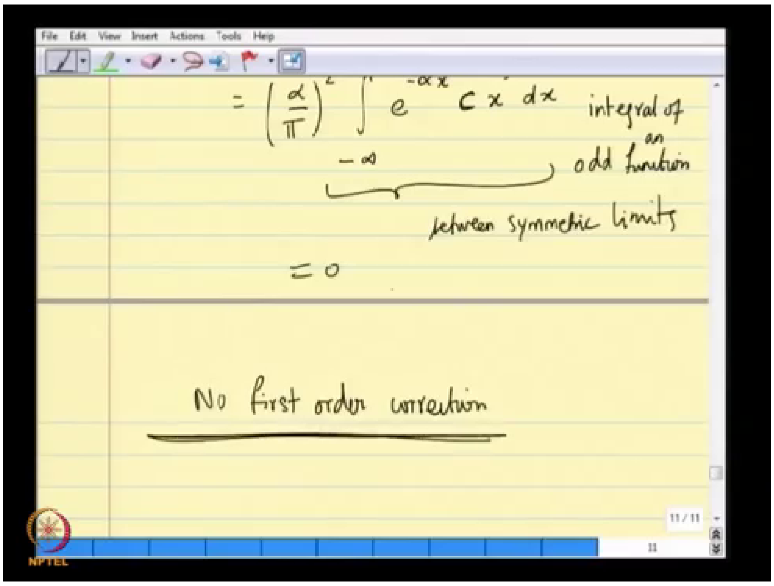

$$= \left(\frac{\alpha}{\pi}\right)^{2} \underbrace{\int_{-\infty} e^{-\alpha x} c\,x\,dx}_{\text{between symmetric limits}} \quad \text{integral of an odd function}$$

$$= 0$$

No first order correction

Therefore it is not possible for us to say that we will correct this energy we have to calculate, the first correction to the energy is not first order, but it is second order.

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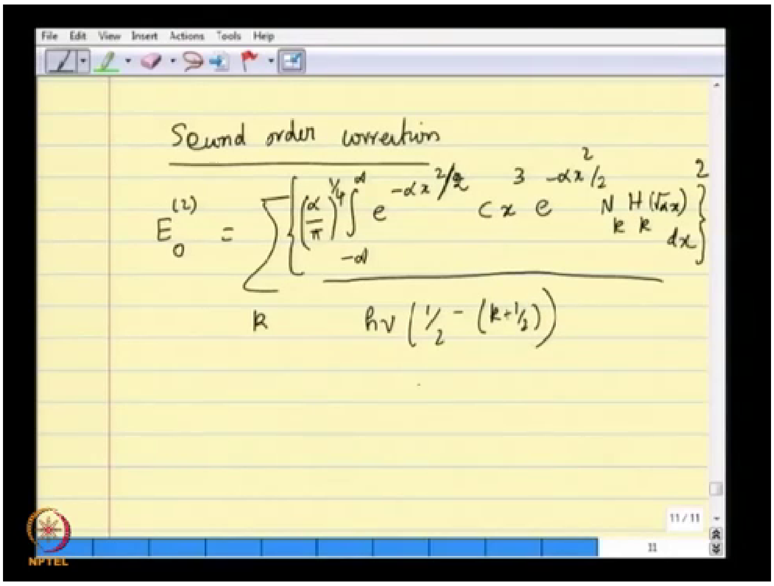

Second order correction

$$E_0^{(2)} = \sum_k \frac{\left\{\left(\frac{\alpha}{\pi}\right)^{1/4} \int_{-\infty}^{\infty} e^{-\alpha x^2/2}\, c\,x^3\, e^{-\alpha x^2/2} N_k H_k(\sqrt{\alpha}x)\, dx\right\}^2}{h\nu\left(\frac{1}{2} - \left(k+\frac{1}{2}\right)\right)}$$

And again the result for second order is somewhat simpler than what we would write down, but let us first write down the corrections namely E the lowest energy level 0 and the second order correction 2 is given by sum over k.

The integral alpha by pi to the 1 by 2 e to the minus alpha x square by 2 sorry alpha x square by 2 not even 1 by 2 I think we should be careful here, I will just write only the 1 by 4 corresponding to this part of the left side of the wave function, which is the ground state then you have C x cube and the other wave function is KTh order which is E to the minus alpha x square by 2 N k the normalization constant and H k of root alpha x between the limits minus infinity to plus infinity d x this whole thing square ok. Divided by the 0 order energy is half h nu and any other energy state is k plus half h nu.

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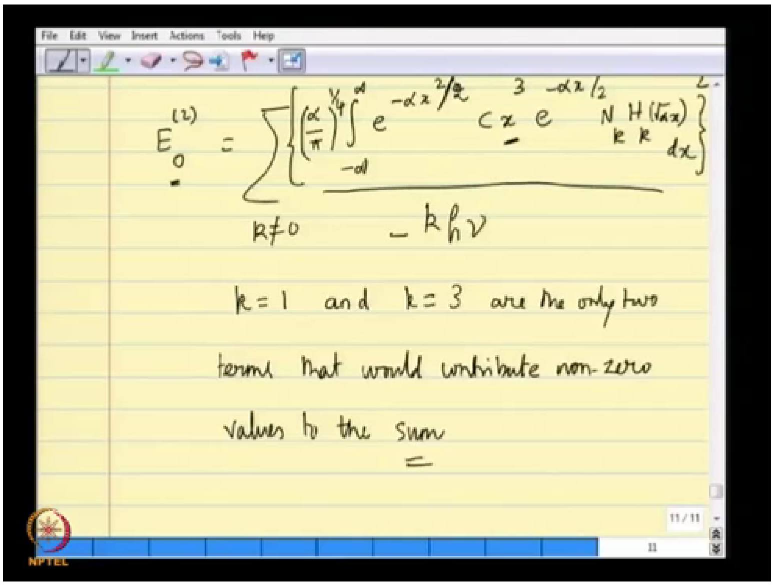

$$E_0^{(2)} = \sum_{k \neq 0} \frac{\left\{\left(\frac{\alpha}{\pi}\right)^{1/4} \int_{-\infty}^{\infty} e^{-\alpha x^2/2}\, C x^3\, e^{-\alpha x^2/2} N_k H_k(\sqrt{\alpha} x)\, dx\right\}^2}{-k h\nu}$$

k = 1 and k = 3 are the only two terms that would contribute non-zero values to the sum

So, we can rewrite this as minus k h nu ok. Now the integral appears like k is not equal to 0 some you will find out in another lecture that is the way we have written it appears that we may have to calculate all the hermite polynomials for different values of k and calculate this integral and so on.

But in a later lecture you will find out that this expression is not as hard as it looks like, that you only need to worry about k is equal to 1 and k is equal to 3 we started with 0 or the only two terms that would contribute non zero values to the sum ok, it is x cube; its x cube we have taken the harmonic correction the unharmonic correction to be x cube and

I am already guessing the result from some other way of studying the harmonic oscillator problem.

Namely using the operator method we will find out that you have the 0 order wave function and the kth wave function, kth Eigen value Eigen vector and you will see for x cube that only these are the two terms. In fact, I have state the result, but we will verify it later that.

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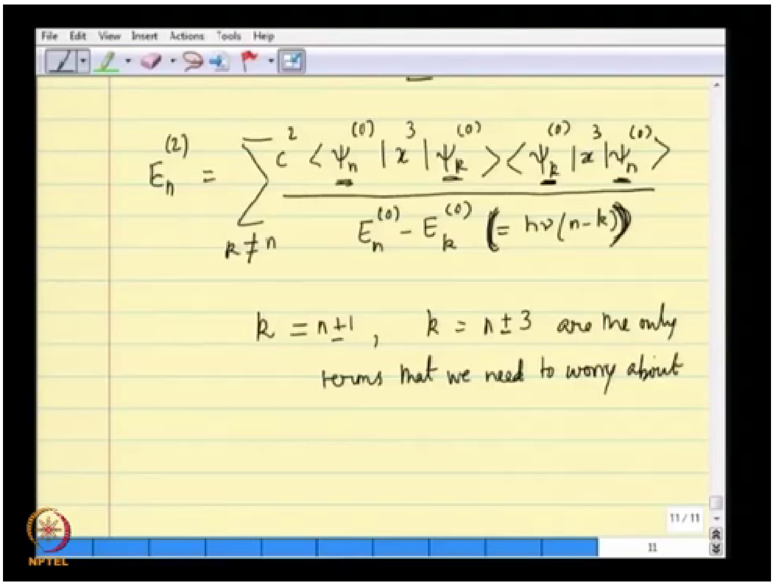

$$E_n^{(2)} = \sum_{k \neq n} \frac{c^2 \langle \psi_n^{(0)} | x^3 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | x^3 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)} \; (= h\nu(n-k))}$$

$k = n \pm 1$, $k = n \pm 3$ are the only terms that we need to worry about

If we are looking for second order correction E n 2 to the harmonic oscillator, and if we do the symbolic writing using the Dirac notation k not equal to n psi n 0 x cube times C square psi k 0, psi k 0 x cube psi n 0 divided by E n 0 minus E k 0 which is essentially equal to h nu into n minus k ok. If we have to calculate this integral for harmonic oscillator Eigen function 0 order these Eigen functions ok.

The general result that will follow is that k is either equal to n plus 1 or minus 1and k is equal to n plus or minus 3 are the only terms that we need to worry about. If instead of cubic we have additional corrections like the quartic and so, on. This result can in principle be generalized to adding only specific terms, but anyway that is the other simple example.

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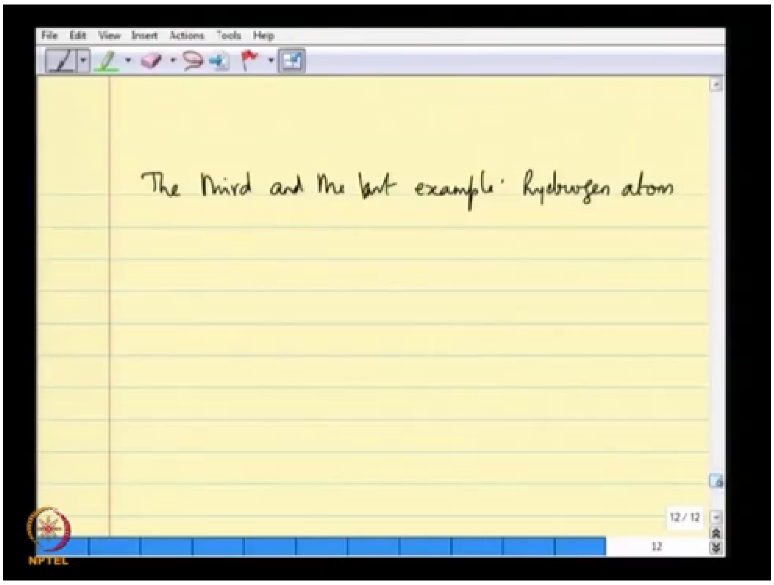

The third and the last example: Hydrogen atom

The third and the last example for today's lecture again I will leave it to you to calculate these integrals and if you need help on this please look into the assignment section of the website and you can download all these things as P D F files for your own personal use therefore, please supplement this lecture along with I mean with the lecture notes that is provided on the website ok.

The third and last example is Hydrogen atom these are the 3 models that you are supposed to have been familiar in the study through the study of the first level quantum cores. So, in the case of hydrogen atom, all of you know that the 0 order Hamiltonian is given.

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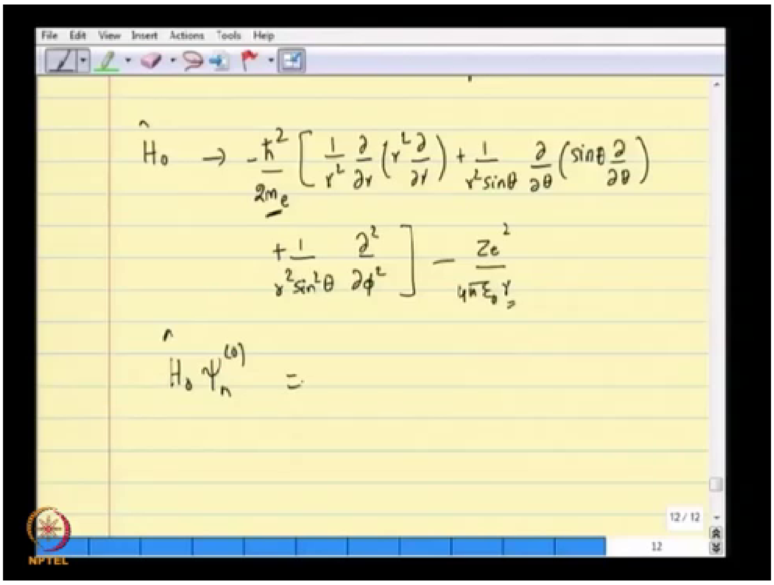

$$\hat{H}_0 \rightarrow -\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{H}_0\psi_n^{(0)} =$$

In polar coordinates by minus h bar square by 2 m e it is a long expression 1 by r square dou by dou r, r square dou by dou r plus one by r square sin theta dou by dou theta sin theta dou by dou theta plus 1 by r square sin square theta, dou square by dou phi square corresponding to the kinetic energy of the electron in a reduced mass system where we replace the mass of the reduced particle as the mass of the electron.

Because the nuclear mass is very very large minus the Z e square by 4 pi epsilon naught or the relative coordinate of the two particle system and we know that the energy is H naught psi n zeros we know the solution this is an exact problem that Schrodinger first solved and everybody else has later on followed this by other methods as well.

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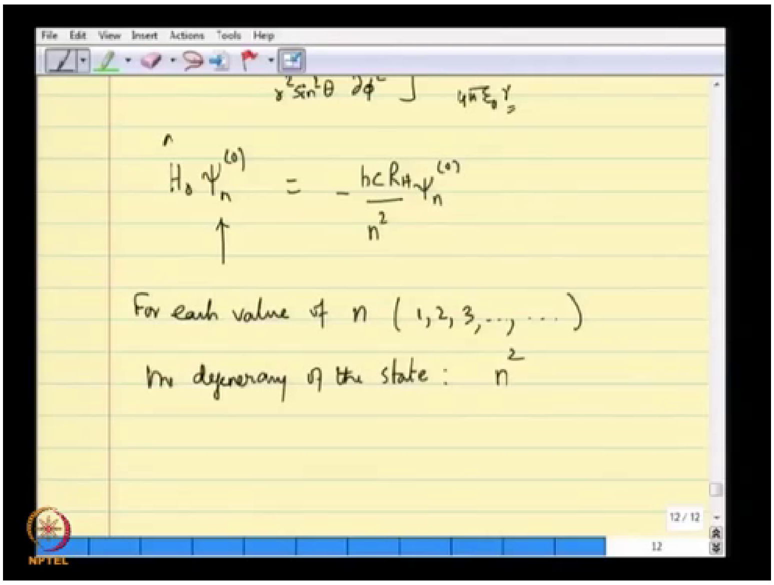

$r^2\sin^2\theta\,\partial\phi^2]$ $4\pi\varepsilon_0 r$

$$\hat{H}_0\psi_n^{(0)} = -\frac{hcR_H}{n^2}\psi_n^{(0)}$$

$\uparrow$

For each value of n $(1, 2, 3, \ldots, \ldots)$

The degeneracy of the state : n^2

The answer is h c the there it by constant by n square psi n 0 and we know that this n for each value of n going from 1, 2, 3 etcetera. The degeneracy of the state is n square. So, that when n is 1 you have only one state, which we usually label as 1 s orbital of the hydrogen atom and then n is 2 we have 4 orbitals or wave functions known as the 2 s and the 3 2 p wave functions and then n is 3 it is the 3 s the 3 3 p wave functions and the phi 3 d wave functions and so, on.

Therefore this is both a non degenerate and the degenerate system the lowest energy of the hydrogen atom 1s orbital is the only non degenerate system non degenerate energy level and if we place the hydrogen atom in a small magnetic field or in a small electric field it is possible for us to obtain the corrections to the energies. The lowest as well as higher order, but higher order energies being degenerate we have not yet dealt with the degenerate state perturbation theory, but we can correct the lowest order correction the sorry the correction to the lowest energy level.

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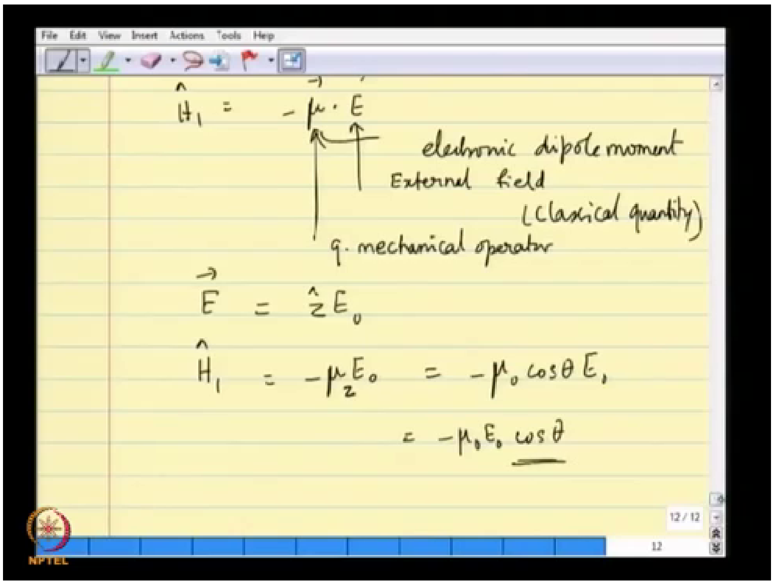

$\hat{H}_1 = -\vec{\mu}\cdot\vec{E}$

electronic dipole moment

External field

(classical quantity)

q. mechanical operator

$\vec{E} = \hat{z}E_0$

$\hat{H}_1 = -\mu_z E_0 = -\mu_0 \cos\theta E_0$

$= -\mu_0 E_0 \cos\theta$

So, if we assume the perturbation H 1 to be of a specific form let me see which I have used in my lecture notes we will. So, I have used the electric field, the electric dipole moment in the presence of an external field a this is the electronic dipole moment of the system and E is the external field. The external field is treated as a classic classical quantity and the dipole moment is the quantum mechanical operator and if the field direction is chosen as the z direction please remember that in the hydrogen atom the z axis for the sphere is arbitrary and the moment we put in a static field we can choose the direction of the field as the z axis and therefore, if we write the electronic or the electric field as z times E naught. then what we have is H 1 is minus mu E naught z.

The z component of the electronic dipole moment, which in the form of a magnitude is given by the value mu naught times cos theta please remember the z coordinate in the spherical polar system is the radius whatever is the magnitude multiplied by cos theta and therefore, you have this expression namely minus mu naught E naught the strength of the electric field times cos theta, where this theta is the same as the theta that we have written down here. Therefore, if you use the wave functions 1s wave functions and the 2s, 2p wave functions in r theta pi coordinate we have the Hamiltonian also expressed in that coordinate system its immediately obvious that we can calculate these integrals as simple integrals involving exponentials and polynomials ok.

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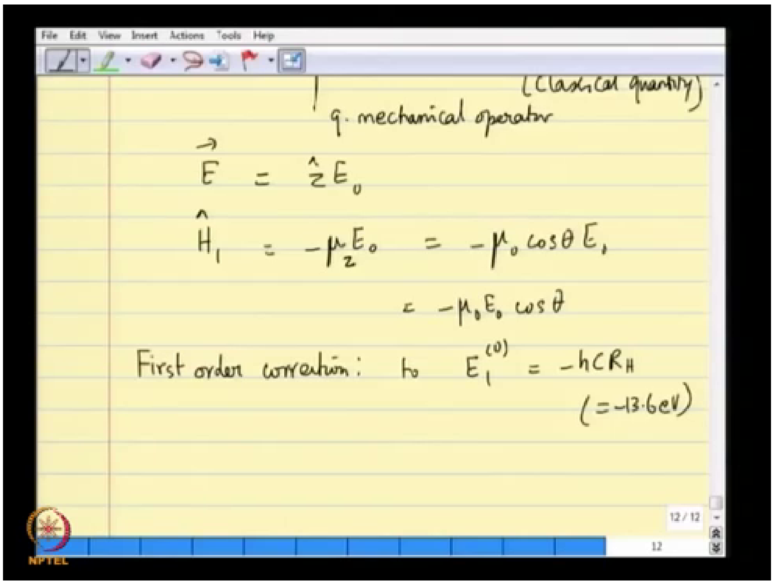

(Classical quantity)

q. mechanical operator

$$\vec{E} = \hat{z} E_0$$

$$\hat{H}_1 = -\mu_z E_0 = -\mu_0 \cos\theta E_0$$

$$= -\mu_0 E_0 \cos\theta$$

First order correction: to $E_1^{(0)} = -hcR_H$

$(= -13.6 eV)$

So, let us take the first order correction again to E 1 0 which is minus h C R H and you remember that this value is minus 13.6 electron volts ok. So, if we place this hydrogen atom in a small magnetic field the electric field with a magnitude E naught, this energy is likely to be perturb is a first order or second order we will find out very quickly I would not do the integrals, but I will give you the formula so, that the integrals can be evaluated by you the first order correction E 1 1 ok.

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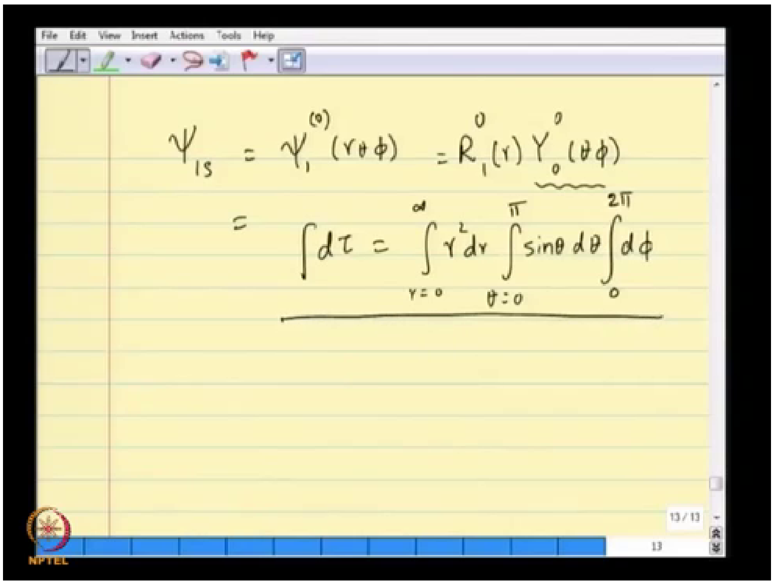

$$\psi_{1s} = \psi_1^{(0)}(r\theta\phi) = R_1^0(r)\underbrace{Y_0^0(\theta\phi)}$$

$$= \qquad \int d\tau = \int_{r=0}^{\infty} r^2 dr \int_{\theta=0}^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

So, let us write the wave functions the 1s wave function psi 1s which is the psi one 0 or theta v is given by, let us see I will write the general formula for this. So, it is easier, it is given by R1 0 the log r polynomial to first order and the spherical harmonic L m which is Y 0 0 theta v and this is a constant it is independent of theta p ok. Let me see if I have the (Refer Time: 38:56) here I am not written that, but anyway we can worry about it the integral d tau is essentially r equal to 0 to infinity r square d r integral theta is equal to 0 to infinity sorry 0 to pi sin theta d theta and integral d phi 0 to 2 pi that is the coordinate integration one has to worry about and if we have to look at the first order correction E 1 1.

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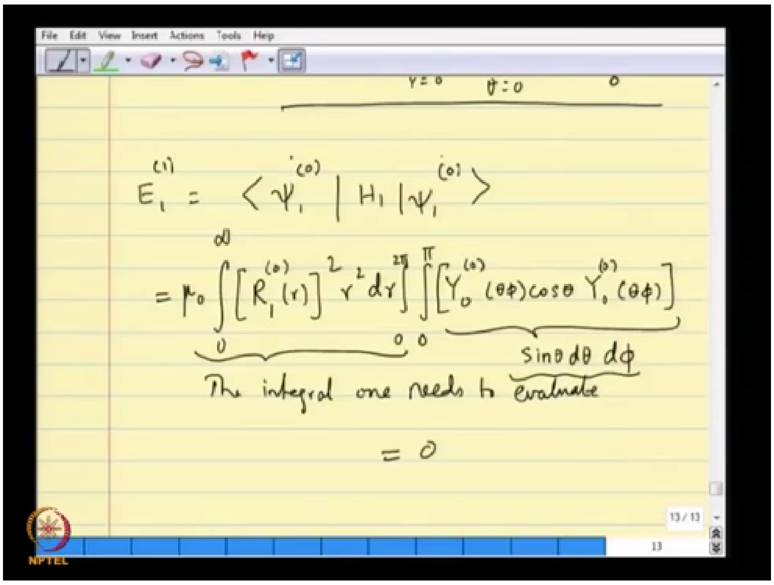

$r = 0 \quad \theta = 0 \quad 0$

$$E_1^{(1)} = \langle \psi_1^{(0)} | H_1 | \psi_1^{(0)} \rangle$$

$$= \mu_0 \underbrace{\int_0^\infty \left[R_1^{(0)}(r)\right]^2 r^2 dr}_{} \int_0^{2\pi}\int_0^{\pi} \underbrace{\left[Y_0^{(0)}(\theta\phi)\cos\theta\, Y_0^{(0)}(\theta\phi)\right]}_{\sin\theta\, d\theta\, d\phi}$$

The integral one needs to evaluate

$= 0$

Then its psi 1 0 H 1 psi 1 0 and I have written this down as R 1 0 or n l of r square due to the two wave functions that you have here and the Hamiltonian does not contain any or dependency it only contains cos theta therefore, we can write r square d r 0 to infinity ok, times a mu naught then followed by the integral 0 to pi.

We have Y L m Y 0 0 theta phi cos theta Y 0 0 theta phi this is the angular part multiplied by sin theta d theta d phi and since there is no phi dependence here we can also write this as 0 to 2 pi ok. So, just let me make sure that the pi is associated with the theta integral and this is the integral that one needs to evaluate. With all these elaborations you will be very disappointed to know that this integral is actually 0 because of the properties associated with the cos theta sin theta d theta d phi Y 0 0 is a constant its one by root 4 pi. Therefore, the essential integral and this is a radial function r square d r from 0 to infinity this is the radial function normalized. So, this gives you one if you put in the right constants.

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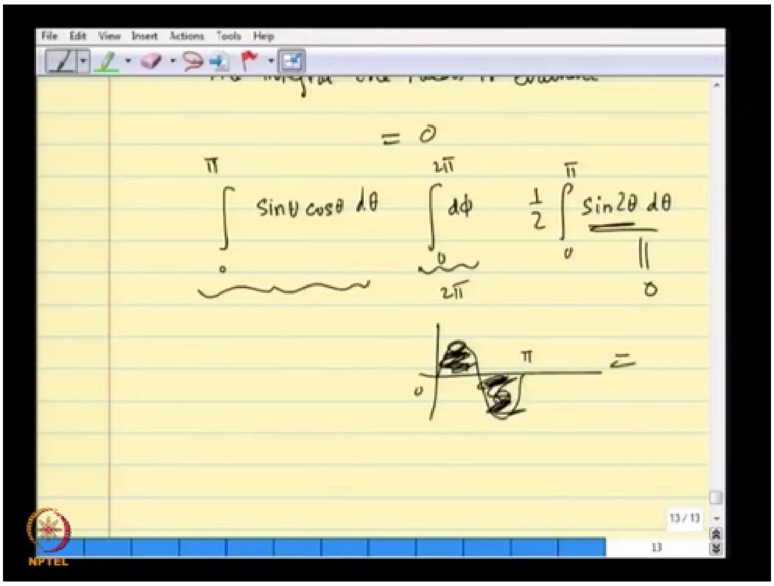

$$= 0$$

$$\underbrace{\int_0^{\pi} \sin\theta \cos\theta \, d\theta} \qquad \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \qquad \frac{1}{2}\int_0^{\pi} \underline{\sin 2\theta \, d\theta} = 0$$

So, what is left over is the only integral 0 to pi sin theta cos theta d theta and the integral d phi is of course, 0 to 2 pi will give you 2 pi that will go away with the normalization constants that you have already defined this integral sin theta cos theta d theta is 0 to pi is integral 0 to pi 1 by 2 sin 2 theta. And please remember sin 2 theta n 0 to pi actually completes one whole cycle 0 to pi therefore, the area cancels out which is what this integral is area cancel out and this whole thing goes to 0.

So, I mean doing all these things finally, one recognizes that there is some symmetry involved and the first order correction is 0. So, now, it is possible to do second order correction by using all other hydrogen atom wave functions I will not do that, but this whole exercise today's lecture is to give you an illustration of how to use the formulae that were proposed in the last two or two lectures.

We will continue this in the next lecture with what is known as the non sorry with known as the degenerate state perturbation theory and you will find out that, all we need to do is one small modification of everything that we have done in the non degenerate perturbation theory in order to solve problems in which the states the 0 order states are degenerate, and the perturbation spoils the degeneracy or I mean in a more flowery language one can say it lifts the degeneracy and makes them non degenerate.

It is possible that the perturbation lifts all of the degeneracy out or it its possible there it only lives partially the degeneracy and so on that depends on the problem that we choose. But it is a slightly more interesting problem with that the time independent perturbation theory account will be reasonably complete for our level that we are dealing with until then.

Thank you very much.