Chemistry Atomic Structure and Chemical Bonding
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Lecture – 50
Time Independent Perturbation Theory for Degenerate States: First Order

Welcome back to the lectures in Chemistry and on the topic of Atomic Structure and Chemical Bonding.

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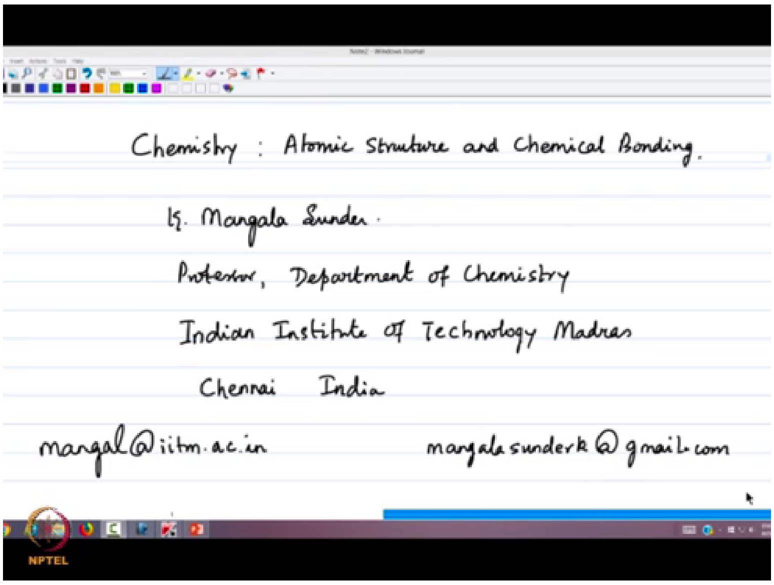

Chemistry : Atomic Structure and Chemical Bonding.

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My name is Mangala Sunder and I am in the Department of Chemistry Indian Institute of Technology, Madras. We continue to discuss perturbation theory, but in this lecture I will indicate how certain simple considerations allow us to consider perturbation theory for states which are degenerates in the absence of perturbation, and then how they change due to the perturbation and so on.

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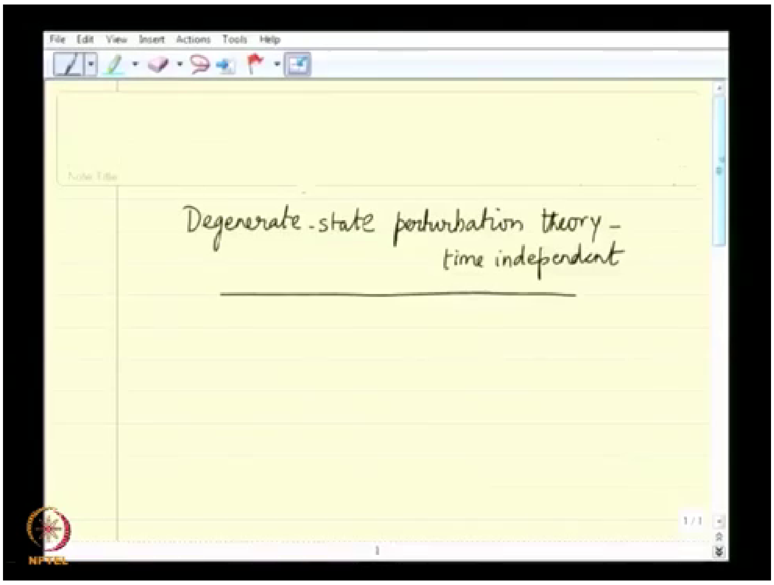

Degenerate-state perturbation theory - time independent

So, let me they give you the title of today’s lecture as degenerate state perturbation theory. It is of course, time independent Hamiltonian that we are considering.

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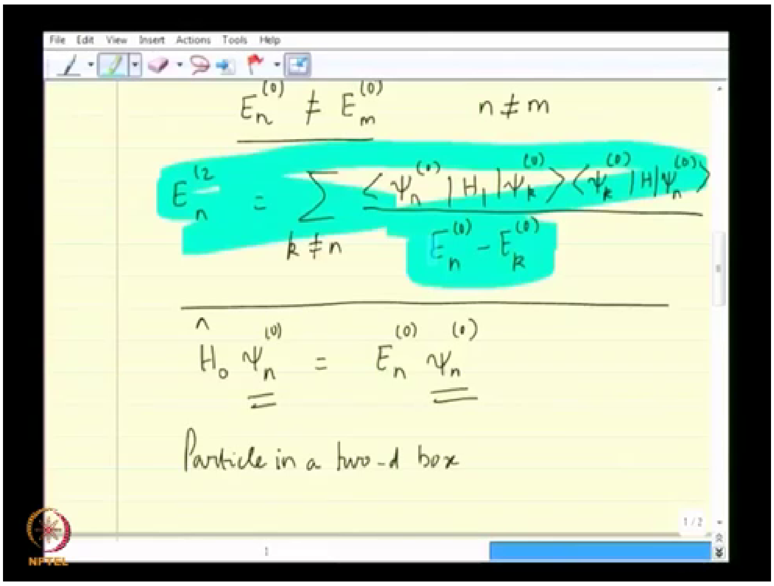

$$E_n^{(0)} \neq E_m^{(0)} \qquad n \neq m$$

$$E_n^{(2} = \sum_{k \neq n} \frac{\langle \psi_n^{(0)} | H_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | H | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

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

Particle in a two-d box

Now, what if some of the states are degenerate? That is, if we have for the 0 order Hamiltonian, solutions which are psi n 0, let me write to this E n 0 psi n 0 but then, more than 1 state is there. The standard example is the particle in a two-dimensional box you remember, the wave functions corresponding to the quantum numbers n 1 and n 2, 2 different quantum numbers. There are at least 2 wave functions which you obtain by interchanging the quantum numbers, particle in a two-d box.

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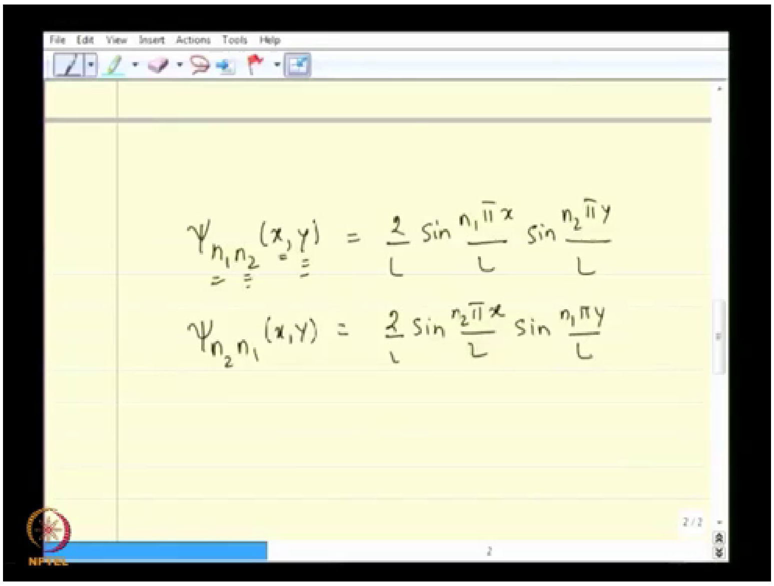

$$\psi_{n_1 n_2}(x, y) = \frac{2}{L} \sin\frac{n_1 \pi x}{L} \sin\frac{n_2 \pi y}{L}$$

$$\psi_{n_2 n_1}(x, y) = \frac{2}{L} \sin\frac{n_2 \pi x}{L} \sin\frac{n_1 \pi y}{L}$$

If you remember, psi n 1 n 2 x y the 2 coordinates of the particle in the box, if we assume the square box then things are simpler. 2 by L sin n 1 pi x by L, the coordinate x and the quantum number n 1 appear associated and sin n 2 pi y by L, the coordinate y and n 2 appear associated together. And of course, this is different from the state psi n 2 n 1 x coma y which is given by the function 2 by L sin n 2 pi x by L sin n 1 pi y by L. If we stick to the convention that the first quantum number refers to the first coordinate, second quantum number refers to the second coordinate.

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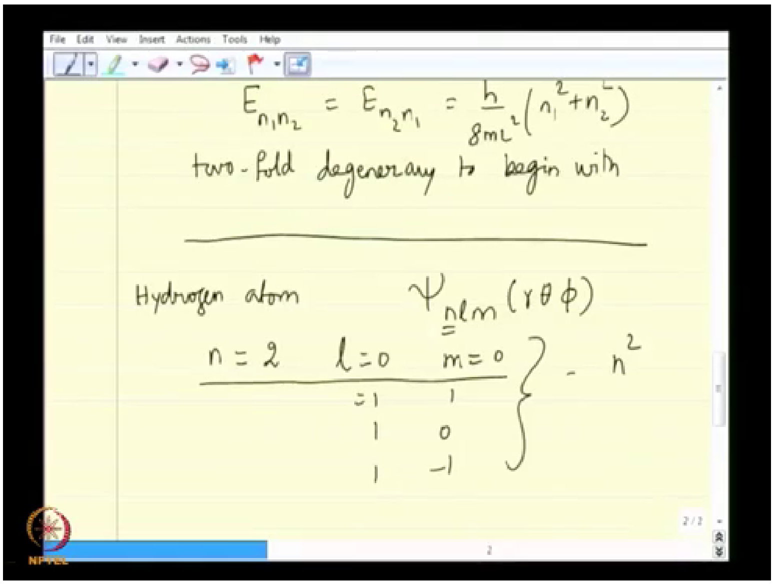

$$E_{n_1 n_2} = E_{n_2 n_1} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2)$$

two-fold degeneracy to begin with

Hydrogen atom $\quad \psi_{nlm}(r\theta\phi)$

$$\left.\begin{array}{lll} n = 2 & l = 0 & m = 0 \\ & = 1 & 1 \\ & 1 & 0 \\ & 1 & -1 \end{array}\right\} - n^2$$

But, both of the states have the same energy that E n 1 n 2 is equal to E n 2 n 1 which is given by h square by 8m L square where, L is the side or the box length or the side of the square n 1 square plus n 2 square.

So, we have at least a two-fold degeneracy to begin with. It can be more than two-fold depending on the total energy, but the point is that it is more than 1. In the case of hydrogen atom also you had a similar problem solved namely, the quantum number n l, quantum numbers n l m corresponding to the coordinates, the radial and the angular. If n were 2. One may recall that l would have been 0 or 1 and for l equal to 0, m is equal to 0 is 1 eigenfunction 2 0 0. And then you have 1 1 1 0 minus 1. So, the degeneracy for the hydrogen atom with the principal quantum number n, is n square 4 of them and you probably recall that when it was 3, it is 9, s p d and s p d f and so on. So, the point is there are states which are degenerate all of which have the same energy minus h c Rydberg constant divided by n square. So, you have more than one state which are degenerate.

Now, perturbation theory needs to be slightly adjusted in order to account for the degeneracy, because, a blind substitution of such degeneracies cannot be put in this expression. They cannot be made in this expression sorry; E n 2, a blind substitution cannot be made here in this part. It is going to get you into trouble. So, we need to do a modification and it is a very very simple modification in principle, but which has its consequences.

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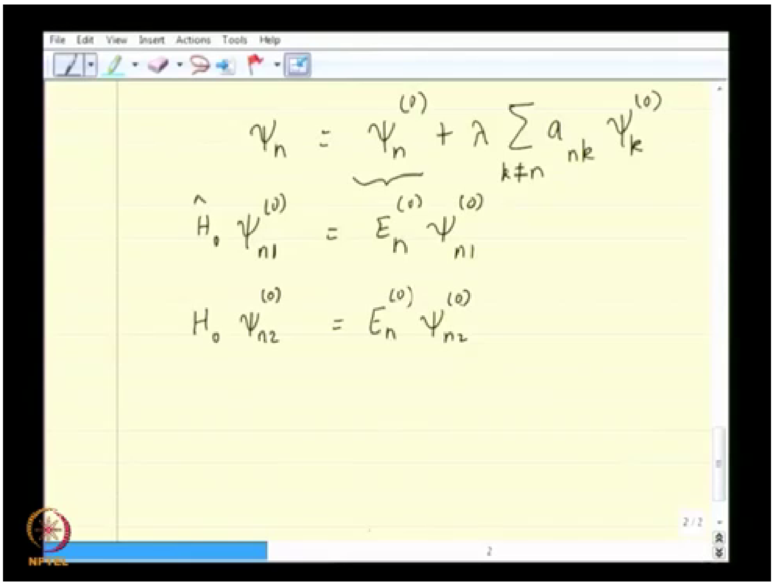

$$\psi_n = \underbrace{\psi_n^{(0)}} + \lambda \sum_{k \neq n} a_{nk} \psi_k^{(0)}$$

$$\hat{H}_0 \psi_{n1}^{(0)} = E_n^{(0)} \psi_{n1}^{(0)}$$

$$H_0 \psi_{n2}^{(0)} = E_n^{(0)} \psi_{n2}^{(0)}$$

So, the simple modification that needs to be d1 is, in the proposal for our wave function psi n, which we wrote as psi n 0 plus a lambda correction to first order ok. If you recall the correction to the first order was k not equal to n as I said, a n k psi k 0. Now here, if the state n corresponds to degeneracies then, please remember that any linear combination of degenerate wave functions is also an eigenfunction of the 0 order Hamiltonian.

So, let me write that in statement. So, we have H 0. So, let me use the notation that I am using sorry. So, we will start with the 2 wave functions psi notation we have to worry about ok, n 1 0 as E n 0 psi n 1 or n a, whatever it is. The fact is that there are 2 wave functions that we will assume correspond to the degenerate states, that there are 2 states which are degenerate n 1 and n 2, both of which have the same energy E n 0 psi n 2 0 ok. My written text may have a slightly different notation, but you can make the correspondence straight away by following this argument ok.

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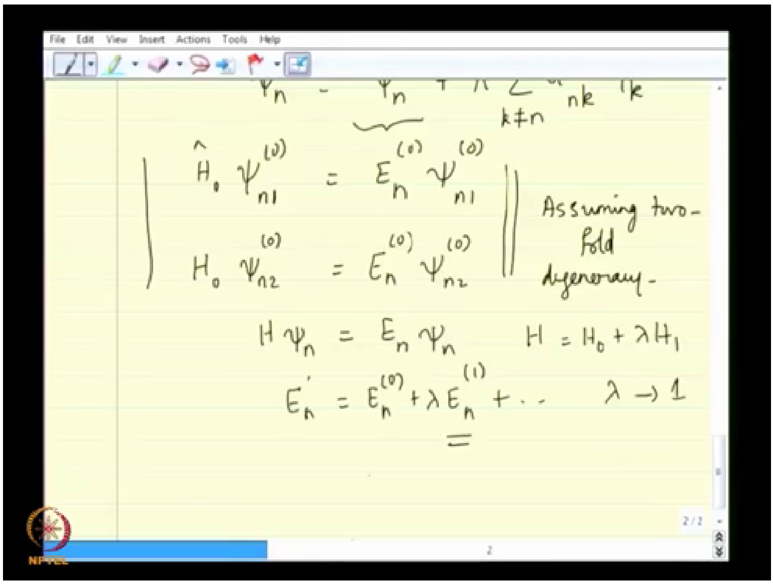

$$\psi_n = \underbrace{\psi_n} + \lambda \sum_{k \neq n} {}_{nk}\, {}_{k}$$

$$\hat{H}_0 \psi_{n1}^{(0)} = E_n^{(0)} \psi_{n1}^{(0)}$$

$$H_0 \psi_{n2}^{(0)} = E_n^{(0)} \psi_{n2}^{(0)}$$

Assuming two-fold degeneracy.

$$H \psi_n = E_n \psi_n \qquad H = H_0 + \lambda H_1$$

$$E_n' = E_n^{(0)} + \lambda E_n^{(1)} + \ldots \qquad \lambda \to 1$$

Now, given this assuming two-fold degeneracy how do we proceed? If you know, that answer, it can be generalized to n fold degeneracy or n square fold degeneracy as you see in the case of hydrogen atom and so on. The point is, this is the simplest problem in which 2 states which are degenerate, now perturbed by the Hamiltonian H psi n is equal to E n psi n, where the H is h naught plus lambda H 1 with lambda taken to one at the end of the calculation ok. So, this is the question that we pose, and we want to find out what are the corrections, E n; namely lambda E n 1 and so on, but we will only worry about E n 1 for the moment for states, which are degenerate.

I hope the problem is clear.

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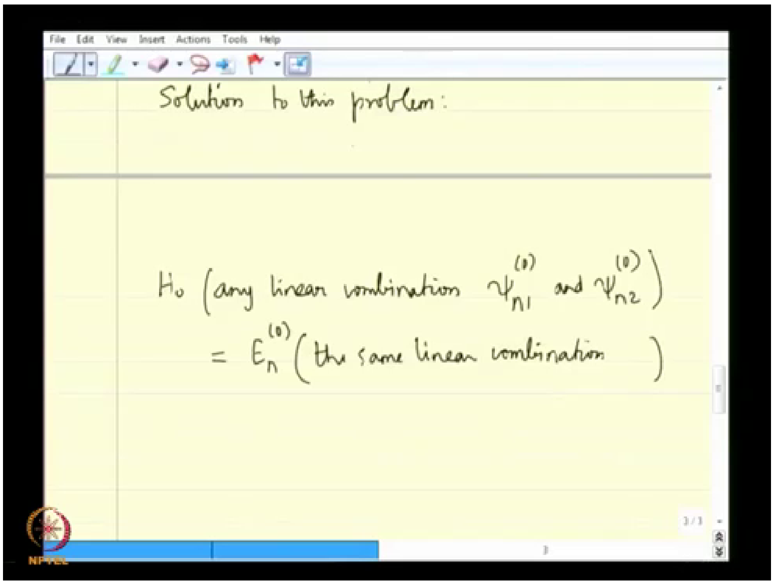

Solution to this problem:

$$H_0 \left(\text{any linear combination } \psi_{n1}^{(0)} \text{ and } \psi_{n2}^{(0)}\right)$$
$$= E_n^{(0)} \left(\text{the same linear combination}\right)$$

Now, in order to understand the solution to this problem 1 must note that H naught acting on any linear combination of the 2 states. The 0 order states psi n 1 0 and psi n 2 0 is equal to E n 0 times the same linear combination. It is see, easy to see that ok.

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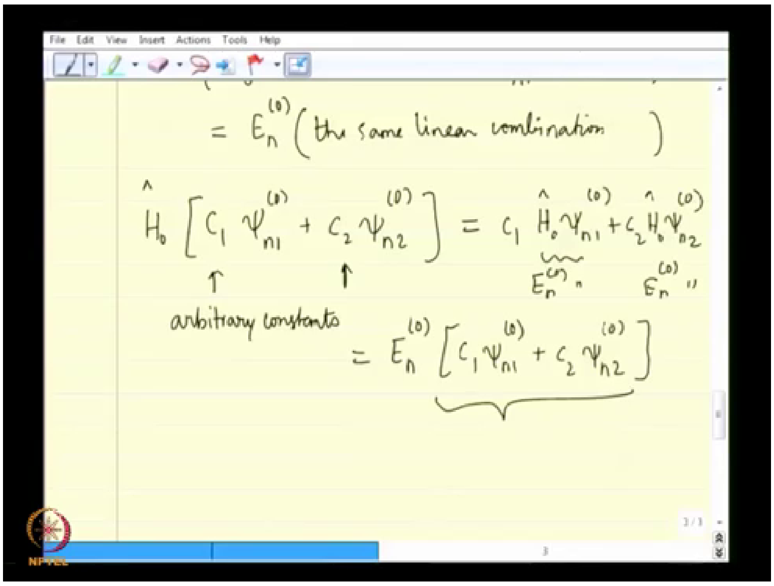

$$= E_n^{(0)} \left(\text{the same linear combination}\right)$$

$$\hat{H}_0 \left[\underset{\uparrow}{c_1} \psi_{n1}^{(0)} + \underset{\uparrow}{c_2} \psi_{n2}^{(0)} \right] = c_1 \underbrace{\hat{H}_0 \psi_{n1}^{(0)}}_{E_n^{(0)}\,''} + c_2 \underbrace{\hat{H}_0 \psi_{n2}^{(0)}}_{E_n^{(0)}\,''}$$

arbitrary constants

$$= E_n^{(0)} \underbrace{\left[c_1 \psi_{n1}^{(0)} + c_2 \psi_{n2}^{(0)} \right]}$$

So, let me write H naught C 1 psi n 1 0 plus C 2 psi n 2 0. C’s are arbitrary constants is equal to just making use of the previous statement that these are states with the energy E n, you will see that it is C 1 H naught acting on psi n 1 0 plus C 2 H naught acting on psi n 2 0 both of which give you the same answers; namely, this gives you E n 0 times the wave function. This also gives you E n 0 times the wave function. Therefore, if you take that out as a common factor, you see immediately that the linear combination is also an eigenfunction of the 0 order Hamiltonian, psi n 2.

This is the only fact that we need to make use of, in redefining our corrected wave function, this psi n the first order or second order or whatever that we need to. We need to make use of this fact that there are 2 undefined arbitrary linear constants that we will introduce. And the which will have to be carried through in the algebra for solving the equation H psi n is equal to E n psi n. What is the nature of these degenerate states? They are orthogonal and if they are I mean, they are normalized and if they are not orthogonal they can be orthogonalized. The 2 examples I gave you, the particle in a two-d box and the hydrogen atom in which you have been n is equal to 2, you have 4 wave functions, they are naturally orthogonal.

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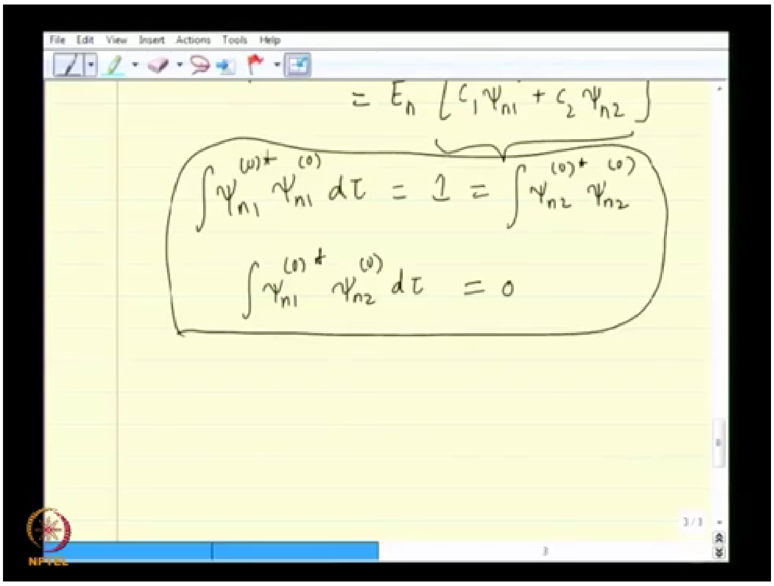

$$= E_n \underbrace{\left[c_1 \psi_{n1} + c_2 \psi_{n2} \right]}$$

$$\int \psi_{n1}^{(0)*} \psi_{n1}^{(0)} d\tau = 1 = \int \psi_{n2}^{(0)*} \psi_{n2}^{(0)}$$

$$\int \psi_{n1}^{(0)*} \psi_{n2}^{(0)} d\tau = 0$$

Therefore, the integrals that the wave functions satisfy these property namely psi n 1 0 star psi n 1 0 d tau, is 1 and also for psi n 2 0 star psi n 2 0, they are both normalized. And the case that we have been dealing with so far they are also orthogonal namely, psi n 1 0 star psi n 2 0 d tau is 0. If it is not, it is possible to orthogonalize them and then take that particular orthogonal wave functions as our starting point. Then any linear combination of those 2 will also be an eigenfunction, you have realized that.

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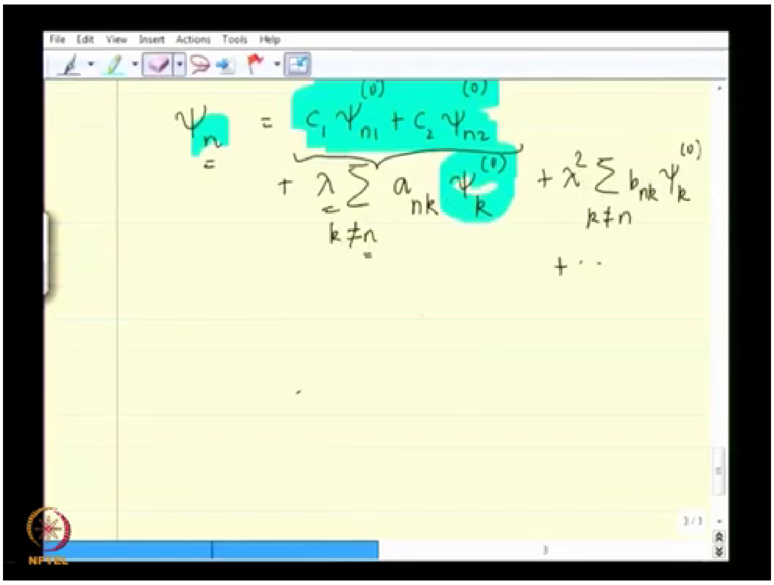

$$\psi_n = \underbrace{c_1 \psi_{n1}^{(0)} + c_2 \psi_{n2}^{(0)}} + \lambda \sum_{k \neq n} a_{nk} \psi_k^{(0)} + \lambda^2 \sum_{k \neq n} b_{nk} \psi_k^{(0)} + \cdots$$

Now, assuming that this is valid, all that we need to do in order to do perturbation theory is to propose our wave function which we do not know, as, the arbitrary 0 order state C 1 psi n 1 0 plus C 2 psi n 2 0 and nothing else changes, lambda sum over k not equal to n this n. That n corresponds to the energy and the quantum number n associated with the degeneracy. And then, all the rest of it is the same namely your coefficient a n k psi k 0. So, the only change that we make is in the definition of the wave function and if you want to compare this with the non-degenerate case, let me just move up. Compare this with the non-degenerate state, in the non-degenerate case you just had then non-degenerate 0 order wave function. In the degenerate case, now you have the arbitrary linear combinations C 1 and C 2.

Now, what are C 1 and C 2? We will determine that as we go along and as we do the corrections to the first order mean to the first order in perturbation, we will also find out C 1 and C 2. Therefore, the process of dealing with degenerate states is to correct for the degeneracy by taking the linear combination of all states which are degenerate as your 0order correction and then proceeding with the first and second order. What about degeneracies in here? Suppose there are many different states k is equal to say, some other k 1 k 2 some other sets, does not matter. They will all be included here, but the only thing is that n1 of those states will have the same energy as the nth state, psi.

Therefore, all states which have the same energy E n 0 are put together in this, they are lumped in the quantity before doing the corrections to lambda. And of course, you can also do a lambda square correction if you wish by, putting in k naught equal to n another quantity Now, it is instead of a it is some other coefficients that b n k psi k 0 and so on.

Anyway, we will not worry about the corrections to second order and so on, but this is the wave function that we need to make use of ok. It is an extremely important step that and that is the only step that we need, the rest of it is algebra. So, if you need to pass here, take a short break if you wish. And then come back and we will start doing the algebra in a sequence and arrive at what is now, n as a, a 2 by 2 matrix solution to the wave functions and see how the degeneracy is removed by the presence of the perturbation ok.

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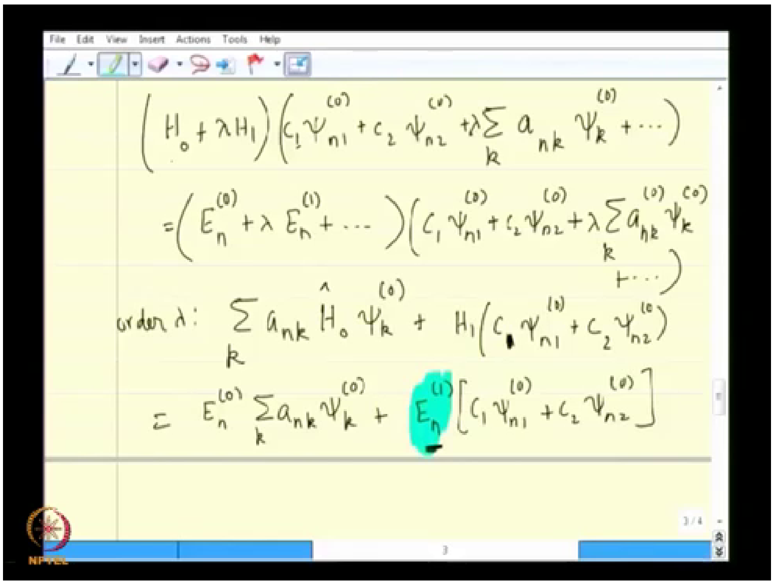

$$\left(H_0 + \lambda H_1\right)\left(c_1\psi_{n1}^{(0)} + c_2\psi_{n2}^{(0)} + \lambda\sum_k a_{nk}\psi_k^{(0)} + \cdots\right)$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \cdots\right)\left(c_1\psi_{n1}^{(0)} + c_2\psi_{n2}^{(0)} + \lambda\sum_k a_{nk}^{(0)}\psi_k^{(0)} + \cdots\right)$$

order λ: $\sum_k a_{nk}\hat{H}_0\psi_k^{(0)} + H_1\left(c_1\psi_{n1}^{(0)} + c_2\psi_{n2}^{(0)}\right)$

$$= E_n^{(0)}\sum_k a_{nk}\psi_k^{(0)} + E_n^{(1)}\left[c_1\psi_{n1}^{(0)} + c_2\psi_{n2}^{(0)}\right]$$

So, we shall substitute our proposal for the wave function in the solution namely, H naught plus lambda H 1 in the wave function namely C 1 psi n 1 0 plus C 2 psi n 2 0 plus sum over k to order lambda a n k psi k 0 plus as, E n 0 plus e lambda times E n 1 plus etcetera on the same wave function C 1 psi n 1 0 plus C 2 psi n 2 0 plus lambda times sum over k a n k 0 psi k 0 plus so on.

So, if you collect to the coefficients 2 lambda to the power 0 lambda lambda square etcetera. You remember the way you did that in the perturbation theory 2 lectures ago, the first term will be the statement that we made already namely h naught acting on this linear combination gives you E n 0 on the linear combination. Of course, we already know that. Therefore, to order lambda if we collect to the coefficients, then what you have is sum over k a n k H naught acting on psi k z 0 ok. That is plus to order lambda H 1, acting on some sorry acting on these 2 terms namely, let us not use the summation index. I will write them explicitly, H 1 C 1 psi n 1 0 plus C 2 C 1 C 2 psi n 2 0. That is the right hand side sorry that the that is the left hand side and on the right hand side what you have is, the corresponding term for the lambda namely, E n 0 sum over k a n k psi k 0 plus E n 1 C 1 psi n 1 0 plus C 2 psi n 2 0. I have just collected the coefficients corresponding to the power lambda on both sides.

Again, the same treatment that we have namely we want to find out to the E n 1, our objective is to determine the E n 1 the first order correction ok. Therefore, we want to identify, we want to manipulate this equation and the usual method of multiplying this with your wave function, 0 order wave function on the left-hand side and then doing the integration.

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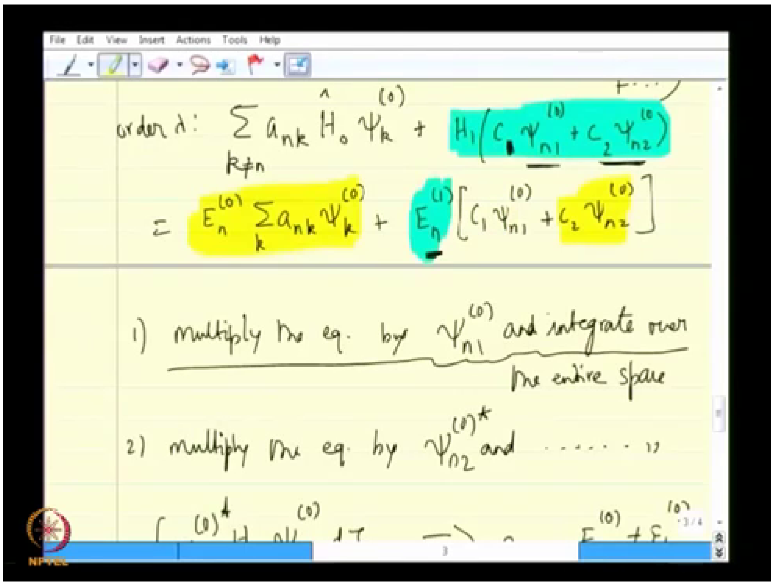

order λ: $\sum_{k\neq n} a_{nk} \hat{H}_0 \psi_k^{(0)} + H_1\left(c_1 \underline{\psi_{n1}^{(0)}} + c_2 \underline{\psi_{n2}^{(0)}}\right)$

$= E_n^{(0)} \sum_k a_{nk} \psi_k^{(0)} + E_n^{(1)} \left[c_1 \psi_{n1}^{(0)} + c_2 \psi_{n2}^{(0)}\right]$

1) multiply the eq. by $\psi_{n1}^{(0)}$ and integrate over the entire space

2) multiply the eq. by $\psi_{n2}^{(0)*}$ and . . . . . . "

Except that, now we have 2 wave functions, which are in the 0th order same eigenvalue, namely psi n 0 and psi n 2 0. So, let us do 2 steps. 1, multiply the equation by psi n 1 0 and integrate over all coordinates, over the entire space. The second step would be, multiply the equation by the other quantities, psi n 2 0 and integrate over the entire space. So, we do it in 2 steps and it is easy to see what will happen ok. I am going to tell you without writing things down, I am going to tell you here.

Please remember h naught on psi k 0 gives you E k 0 times psi k 0, but this wave function is k naught equal to n. Therefore, if I multiply on the left-hand side by the n 1 or n 2, both of which correspond to a different energy 0 order energy and I integrate, this term will vanish. Orthogonality of the 2 wave functions corresponding to different energies will wipe the term off.

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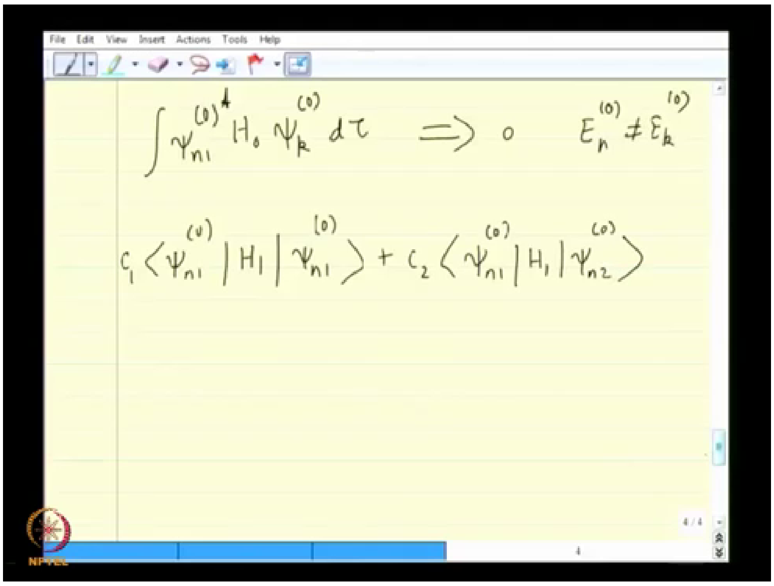

$$\int \psi_{n1}^{(0)*} H_0 \psi_k^{(0)} d\tau \Rightarrow 0 \qquad E_n^{(0)} \neq E_k^{(0)}$$

$$c_1 \langle \psi_{n1}^{(0)} | H_1 | \psi_{n1}^{(0)} \rangle + c_2 \langle \psi_{n1}^{(0)} | H_1 | \psi_{n2}^{(0)} \rangle$$

Therefore, the term the integral psi n 1 0 star well, I should put a 0 star here if you wish and the term is H naught psi k 0 d tau goes to 0 ok, because E n 0 is not equal to E k 0. All the other states which are not connected to that ok. The second term in this expression, the second term is this. The perturbing Hamiltonian H 1 on psi n 1 0 may give you psi n 1 0 or something else.

We have to actually know, H 1 we have to know, the wave functions in order to therefore, this is not a simple statement. So, what you have is when you multiply on the left-hand side by psi n 0 psi n 1 0, you get 2 terms namely, integral psi. Well, let me write this in the bracket rotation ok. psi n 1 0 H 1 there is a coefficient C 1 and psi n 1 0 plus C 2 the coefficient psi n 1 0 H 1 psi n 2 0. That will be the quantity on the left-hand side when you do this multiply the equation by psi n 0 and integrate over the entire space. Please see that this is the green term which when you multiply on the left with that, this is what you get.

What do you get on the right-hand side? Again, it is very clear that the first term on the right-hand side namely this 1 E n 0 a n k psi k 0, when it is multiplied with psi n 1 0 star and integrated, I mean you are taking the scalar product of 2 wave functions corresponding to 2 different eigenvalues, therefore that is 0. The second if you look at this term, we have already said that psi n 1 and psi n 2 are orthogonal to each other. And therefore, this will also go away when you do the integration multiply and integrate. So, what is left over is only 1 term and this will give you a normalized psi n 0 star psi n psi n 1 0 star psi n 1 0 d tau, it will be 1.

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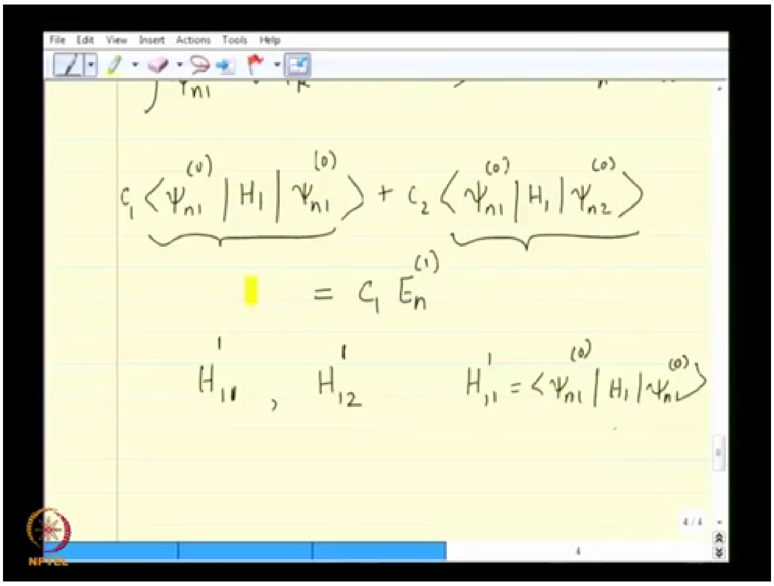

$$c_1 \underbrace{\langle \psi_{n1}^{(0)} | H_1 | \psi_{n1}^{(0)} \rangle} + c_2 \underbrace{\langle \psi_{n1}^{(0)} | H_1 | \psi_{n2}^{(0)} \rangle}$$

$$= c_1 E_n^{(1)}$$

$$H'_{11} , \quad H'_{12} \qquad H'_{11} = \langle \psi_{n1}^{(0)} | H_1 | \psi_{n1}^{(0)} \rangle$$

So, the answer on the right-hand side will be simply C 1 E n 0. E n 1, I am sorry E n 1 E n 1 ok. Now, one of the things that we normally do is to write this by a notation as a matrix element of H 1 between the 2 wave functions and I will call this H 1 11 and H 1 12 for the nth state ok. So, H 1 11 is psi n 1 0 H 1 psi n 1 0 and likewise H 1 12 is psi n 1 0 H 1 psi n 2 0 ok.

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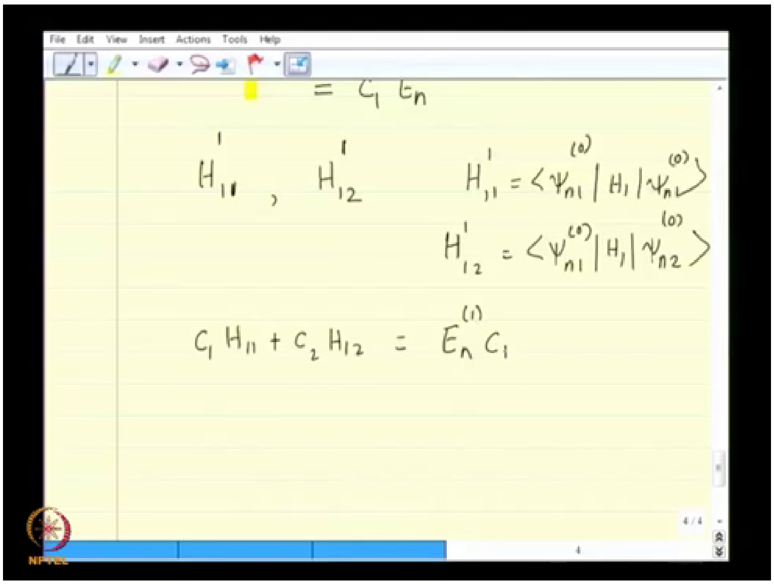

$$= C_1 E_n$$

$$H'_{11}, \quad H'_{12}$$

$$H'_{11} = \langle \psi^{(0)}_{n1} | H_1 | \psi^{(0)}_{n1} \rangle$$

$$H'_{12} = \langle \psi^{(0)}_{n1} | H_1 | \psi^{(0)}_{n2} \rangle$$

$$C_1 H_{11} + C_2 H_{12} = E_n^{(1)} C_1$$

So, the equation that we have is C 1 H 1 1 plus C 2 H 1 2 is equal to E n 1 C 1 ok. This is for doing this first step, multiply the lambda term, coefficient term with psi n 1.

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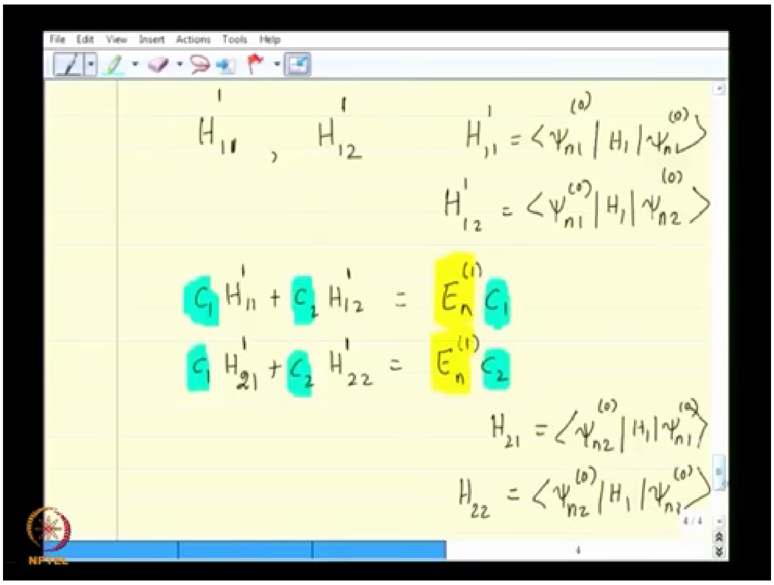

$$H'_{11}, \quad H'_{12}$$

$$H'_{11} = \langle \psi^{(0)}_{n1} | H_1 | \psi^{(0)}_{n1} \rangle$$

$$H'_{12} = \langle \psi^{(0)}_{n1} | H_1 | \psi^{(0)}_{n2} \rangle$$

$$C_1 H'_{11} + C_2 H'_{12} = E_n^{(1)} C_1$$

$$C_1 H'_{21} + C_2 H'_{22} = E_n^{(1)} C_2$$

$$H_{21} = \langle \psi^{(0)}_{n2} | H_1 | \psi^{(0)}_{n1} \rangle$$

$$H_{22} = \langle \psi^{(0)}_{n2} | H_1 | \psi^{(0)}_{n2} \rangle$$

Now, without repeating it I would leave it to you to verify, that when you do this with the psi n 2 star 0 star this, that the equation that you will get, verify it yourself is C 1 H 21 plus C 2 H 22 is equal to E n 1 C 2 where H 21 is psi n 2 0 H 1 psi n 1 0 and H 22 is psi n 2 0 H 1 psi n 2 0.

So, we have a pair of equations that we need to solve in order to obtain the first order correction E n 1, E n 1 and this looks very familiar to you now, because these are arbitrary coefficients, the linear combination coefficients that you have here C 1 C 1 C 2 C 2 C 1 C 2. So, you can see immediately that if you bring it to the left-hand side you have a pair of homogeneous linear equations in C 1 and C 2 H 11 what did I do sorry, we used a superscript 1. So, will use the superscript 1 superscript this is for the perturbing Hamiltonian. So that is important.

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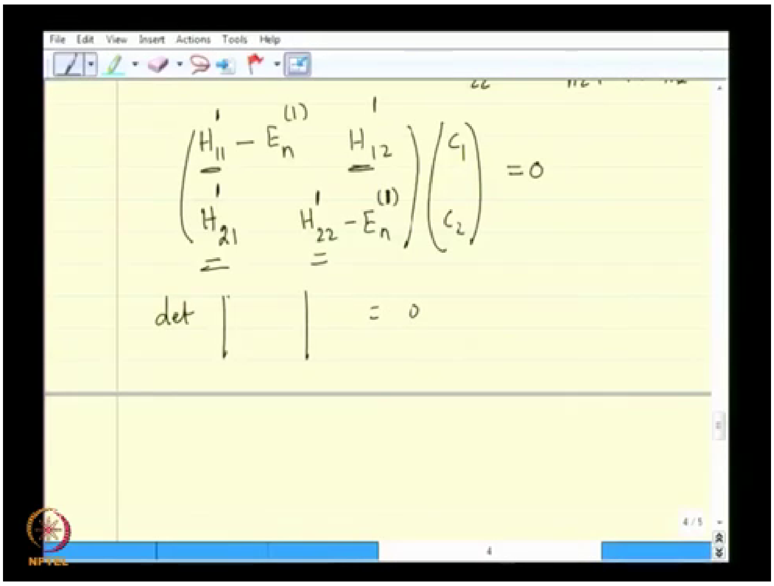

$$\begin{pmatrix} \underline{H'_{11}} - E_n^{(1)} & \underline{H'_{12}} \\ \underline{H'_{21}} & \underline{H'_{22}} - E_n^{(1)} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

$$\det \left| \quad \right| = 0$$

So, H 1 11 minus E n 1 H 1 21 H 21 1 H 22 minus E n 1 C 1 C 2 is equal to 0.

So, now you can see immediately that this is nothing, but the eigenvalue equation for the matrix of H 1 in the pair of degenerate states, psi n 1 of 0 and psi n 2 of 0 you can see that, that is what these things are. That is a Hamiltonian sorry H 1 22 that is a Hamiltonian and that Hamiltonian is what you see here is the matrix of the Hamiltonian in those 2 eigenstates which are degenerate, and the eigenvalue of that matrix happens to be the first order correction to the energy ok. So, the immediate answer is that the determinant of this is 0 namely, determinant of this matrix is 0 and the determinant if you want to write it is H 1 11 minus E n 1 times H 1 22 minus E n 1 minus H 1 21 H 21.

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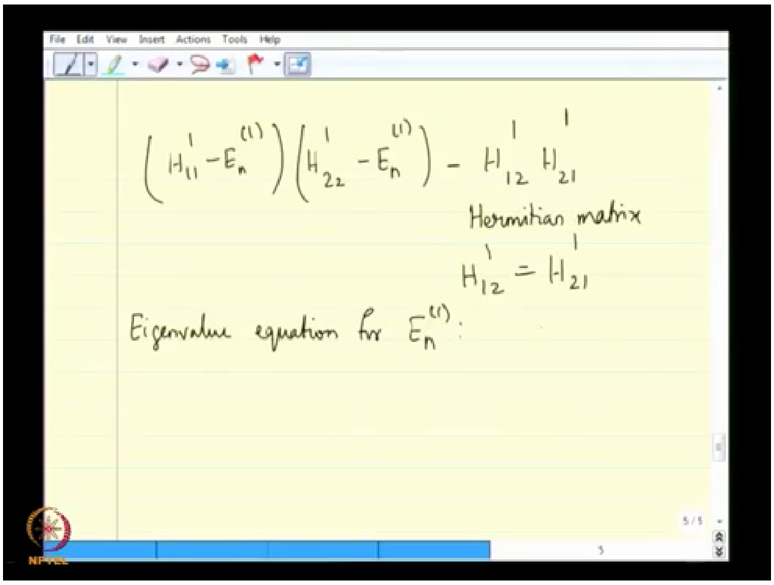

$$\left(H'_{11} - E_n^{(1)}\right)\left(H'_{22} - E_n^{(1)}\right) - H'_{12}\, H'_{21}$$

Hermitian matrix

$$H'_{12} = H'_{21}$$

Eigenvalue equation for $E_n^{(1)}$:

The Hamiltonian is the Hermitian quantity and if these wave functions are real and if the matrix element of the Hamiltonian is obviously real, then you know, that Hermitian matrix implies that H 1 21 is equal to H 21 1 ok. Therefore, you are left with the eigenvalue equation for E n 1 E n 1 ok, which is given by E n 1 square minus E n 1 times H 11 1 plus H 22 1, it is just the algebraic equation.

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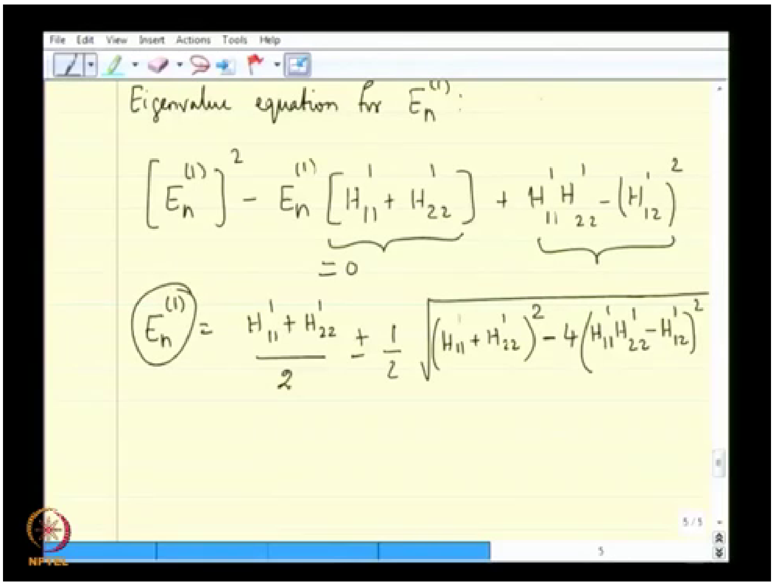

Eigenvalue equation for $E_n^{(1)}$:

$$\left[E_n^{(1)}\right]^2 - E_n^{(1)}\underbrace{\left[H'_{11} + H'_{22}\right]}_{=0} + \underbrace{H'_{11}H'_{22} - \left(H'_{12}\right)^2}$$

$$\boxed{E_n^{(1)}} = \frac{H'_{11} + H'_{22}}{2} \pm \frac{1}{2}\sqrt{\left(H'_{11} + H'_{22}\right)^2 - 4\left(H'_{11}H'_{22} - H'^{2}_{12}\right)}$$

Then you have plus H 1 11 H 1 22 minus you have this quantity namely this one, H 1 12 H 1 12 square is equal to 0. So, this is a x square plus b x plus c is equal to 0. So, you know, the x is equal to minus b plus or minus square root of that minus the a plus or minus square root of b square minus 4 a c, that discriminant formula you can write. So, if you write to this. Therefore, the solution E n 1 is minus b and this is the b, this will be H 1 11 plus H 1 22 by 2 plus or minus square root of b square by 4 a c. So, there is a 1 over 2 and this b square is H 11 plus H 1 22 whole square minus 4, this is the c, this is a is equal to 1. So, it is a whatever it is you have H 11 1 H 22 1 minus H 1 2 1 whole square square root.

This is the solution to be E n 1 and you have obviously, 2 solutions which you can simplify further.

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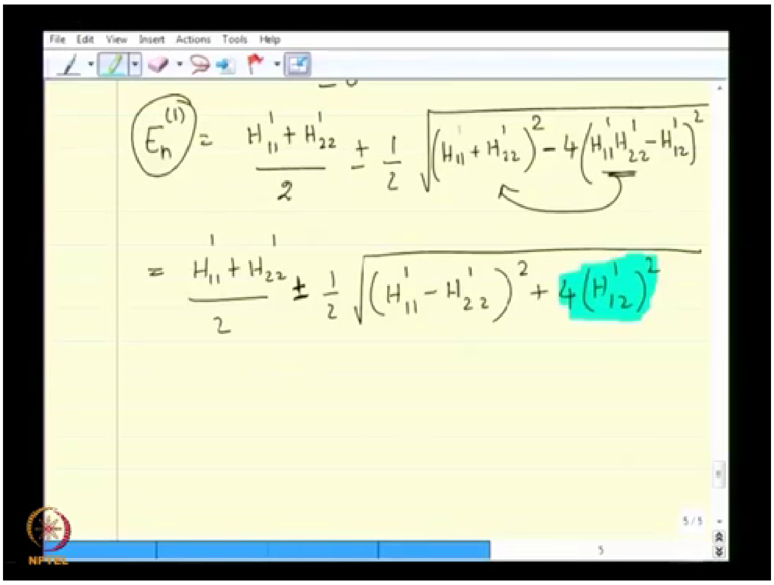

$$\boxed{E_n^{(1)}} = \frac{H^1_{11}+H^1_{22}}{2} \pm \frac{1}{2}\sqrt{\left(H^1_{11}+H^1_{22}\right)^2 - 4\left(H^1_{11}H^1_{22}-H^1_{12}\right)^2}$$

$$= \frac{H^1_{11}+H^1_{22}}{2} \pm \frac{1}{2}\sqrt{\left(H^1_{11}-H^1_{22}\right)^2 + 4\left(H^1_{12}\right)^2}$$

H 11 1 plus H 22 1 by 2 plus or minus 1 by 2 square root, you can take this in here to write to this as H 11 1 minus H 22 1 whole square plus 4 H 12 1 whole square. So, you have 2 eigenvalues given by the plus and the minus and if the perturbation was not there the 2 eigenvalues would have been, because this is 0 H 1. Once you see the correction how it appears, it appears as that inside the square root.

So, you see that if this where 0 then your original solution is in the absence of perturbation of course the energy levels do not change, but in the presence of perturbation the degenerate levels both of which have the same energy E n 0. Now get corrected by the 2 the energies namely, E n 0 plus or minus when we set lambda is equal to 1, it is E n 1 and for this there are two solutions.

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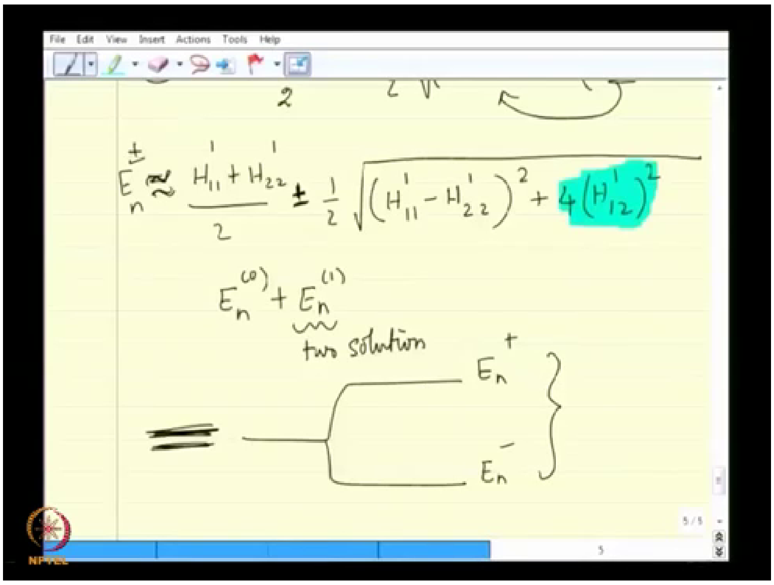

$$E_n^{\pm} \approx \frac{H'_{11}+H'_{22}}{2} \pm \frac{1}{2}\sqrt{(H'_{11}-H'_{22})^2 + 4(H'_{12})^2}$$

$$E_n^{(0)} + \underbrace{E_n^{(1)}}_{\text{two solution}}$$

E_n^{+}

E_n^{-}

And the two solutions essentially mean if the levels were degenerate then the positive quantity adds a positive correction to that. And the negative quantity adds a negative correction to that, so that the degeneracy gets a split. So, this will be the E plus, if you have to write this as E n plus or minus to first order correction, because we are only doing first order here to order lambda you can see that this is E n plus and this is E n minus. The corrections are such that the sum of the 2 energies will still give you exactly twice this. So, they are split symmetrically about the degenerate level. So, this is the wave function, this is the energy. What about the wave function?

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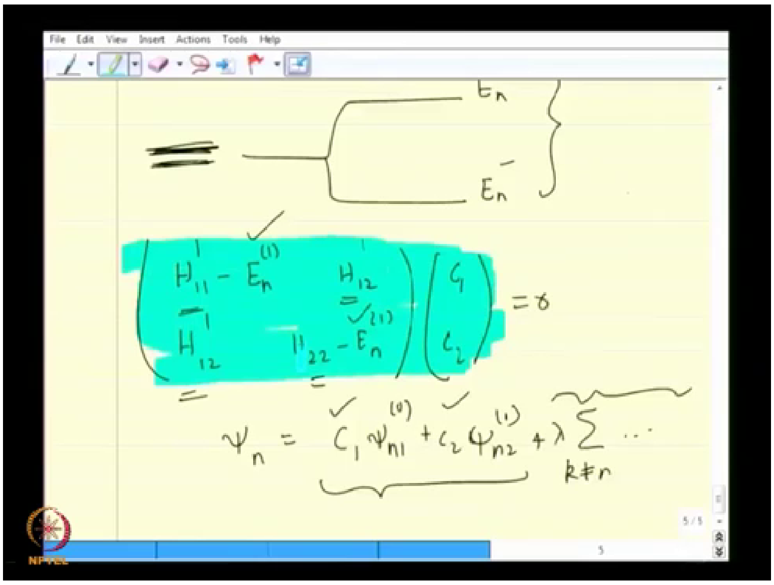

E_n^{+}

E_n^{-}

$$\begin{pmatrix} H'_{11}-E_n^{(1)} & H'_{12} \\ H'_{12} & H'_{22}-E_n^{(1)} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\psi_n = \underbrace{c_1\psi_{n1}^{(0)} + c_2\psi_{n2}^{(1)}}_{} + \lambda\sum_{k\neq n}\cdots$$

Now, we have the matrix H 1 1 1 minus E n 1 H 12 1 H 12 1 H 22 minus E n 1, this multiplied by C 1 C 2 is equal to 0, that was the solution that we were just now discussing. And therefore, if we know, these two things from that the square root factor, then there are 2 sets of equations 1 with 1 value of E n 1 for C 1 and C 2, with another value of E n 1 for C 1 and C 2. Therefore, we get 2 sets of C 1 and C 2.

Therefore, what we get is the eigenvector corresponding to this perturbing Hamiltonian expressed in the pair of degenerate states as a matrix, its eigenvalues are the 2 energies E n 1, its eigenvectors are the 2 coefficients C 1 prime, C 2 prime, C 1 double prime, C 2 double prime whatever it is 2 sets. And therefore, you also have the wave function now. psi n, with precise values for C 1 of course, this is a homogeneous equation. So, you will not know, C 1 and C 2 individually, but you will know the ratios C 1 by C 2. So, you will still get when you normalize this to C 1 psi n 1 0 plus C 2 psi n 2 0 you will get to know these 2 things and of course, you do not know, the other terms namely lambda sum over k not equal to n whatever that is, but you remember that is the first order correction to the wave function. We never needed it to determine the first order correction to the energy.

Now, first order correction to the energy fixes this these coefficients C 1 and C 2 precisely as the eigenvector coefficients eigenvector, the elements of the eigenvector for the solution of this matrix for the solution of this matrix problem ok. Therefore, that is all that one needs to do in order to correct for the effect of the degenerate states in the presence of a perturbation and this is to first order Now, what if not 2 states are degenerate, but more than 2 states are degenerate, as in the case of say hydrogen atom when you take, n is equal to 2.

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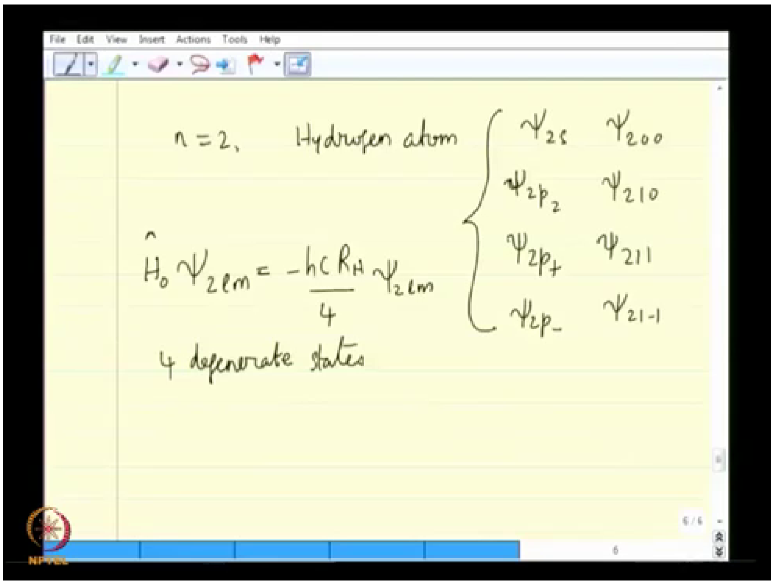

n = 2, Hydrogen atom

$$\left\{\begin{matrix} \psi_{2s} & \psi_{200} \\ \psi_{2p_z} & \psi_{210} \\ \psi_{2p_+} & \psi_{211} \\ \psi_{2p_-} & \psi_{21-1} \end{matrix}\right.$$

$$\hat{H}_0 \psi_{2lm} = -\frac{hcR_H}{4} \psi_{2lm}$$

4 degenerate states

Please remember for n is equal to 2, in case of hydrogen atom 4 wave functions are degenerate, namely psi 2 s orbital which is given by the quantum numbers 2 0 0, psi 2 p z orbital which is psi 2 1 0 and if we write psi 2 p plus which is psi 2 1 1 it is a complex function. It is not the 2 p x or 2 p y, 2 p x and 2 p y are linear combinations of these 2 orbitals psi 2 p plus and psi 2 p minus which is given by the quantum numbers psi 2 1 minus 1.

There are 4 states all of which have the same energy namely H naught, the hydrogen atom Hamiltonian on psi 2 l m it does not matter which l and l m is, that is 0 0 1 0 1 1 1 minus 1 all of these have the same energy minus sorry if you remember the Rydberg constant minus h c Rydberg constant by 4 times psi 2 l m. Therefore, you have 4 states, 4 degenerate states. So, all that you need to do is instead of taking an arbitrary linear combination of 2 degenerate states that you started with in the previous problem. Here, we have to take an arbitrary linear combination of all the 4 degenerate states as the necessary 0 order wave function.

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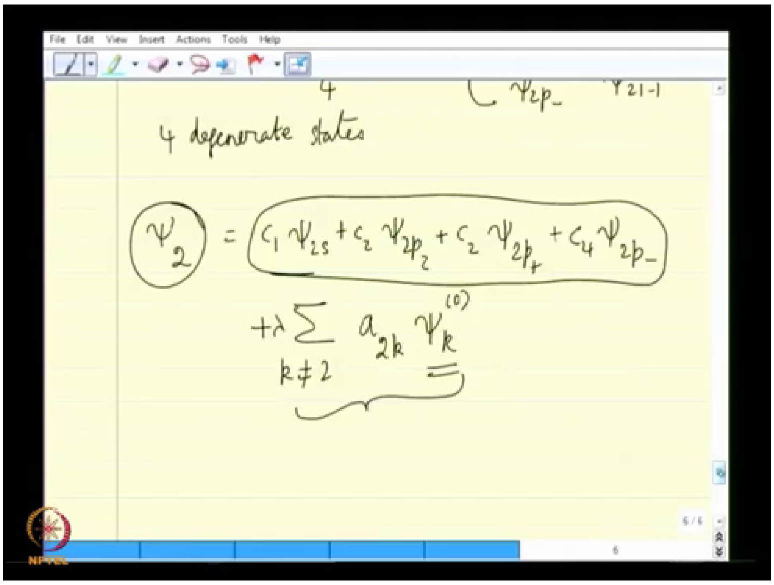

4 ψ_{2p_-} ψ_{21-1}

4 degenerate states

$$\boxed{\psi_2} = \boxed{c_1 \psi_{2s} + c_2 \psi_{2p_z} + c_2 \psi_{2p_+} + c_4 \psi_{2p_-}}$$

$$+ \lambda \underbrace{\sum_{k \neq 2} a_{2k} \psi_k^{(0)}}$$

That is, we need to write psi n as C 1 psi 2 s plus C 2 psi 2 p z plus c 3 psi 2 p plus plus c 4 psi 2 p minus plus all the other wave functions to order lambda k not equal to 2, because n is 2 here ok.

We can even put that in explicitly by saying, this is the second wave function that we are looking at psi 2 and k not equal to 2, you can now write a 2 k psi k 0 where this can be 1 s orbital. This can be 3 s orbital, 3 p orbital 3 d 3 f 4 s 4 p 4 d all the combinations in which k is not equal to 2 can be put in as a correction to order lambda and one can obtain the wave function psi 2 and for the only thing that changes is the fact that you have a linear combination of 4 orbitals, how does that change? The answer that you have to get it is also very straight forward to see now.

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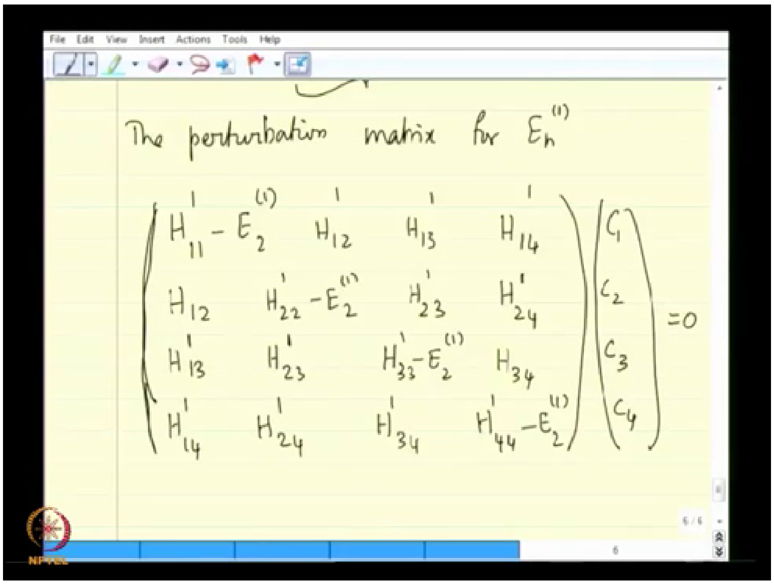
The perturbation matrix for $E_n^{(1)}$

$$\begin{pmatrix} H'_{11} - E_2^{(1)} & H'_{12} & H'_{13} & H'_{14} \\ H'_{12} & H'_{22} - E_2^{(1)} & H'_{23} & H'_{24} \\ H'_{13} & H'_{23} & H'_{33} - E_2^{(1)} & H'_{34} \\ H'_{14} & H'_{24} & H'_{34} & H'_{44} - E_2^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

That the perturbation matrix element that you have to obtain; the perturbation matrix for E n 1 will now contain. If you write these as n 1 n 2 sorry it is n is 2 now ok. We have a notation to worry about. So, if we write these the matrix will be H 1 11 minus E 2 correction to order lambda the first order H 12 1 H 13 of 1 H 14 of 1 and H 12 H 22 minus E 2 of 1 H 23 1 1. This is for perturbing Hamiltonian H 1 24 H 13 of 1 H 23 of 1 H 33 of 1 minus E 2 of 1 H 34 H 1 14 H 1 24 H 1 34 and H 1 44 minus E 2 of 1 the 4 coefficients that we do not know, C 1 C 2 C 3 C 4 and this is equal to 1.

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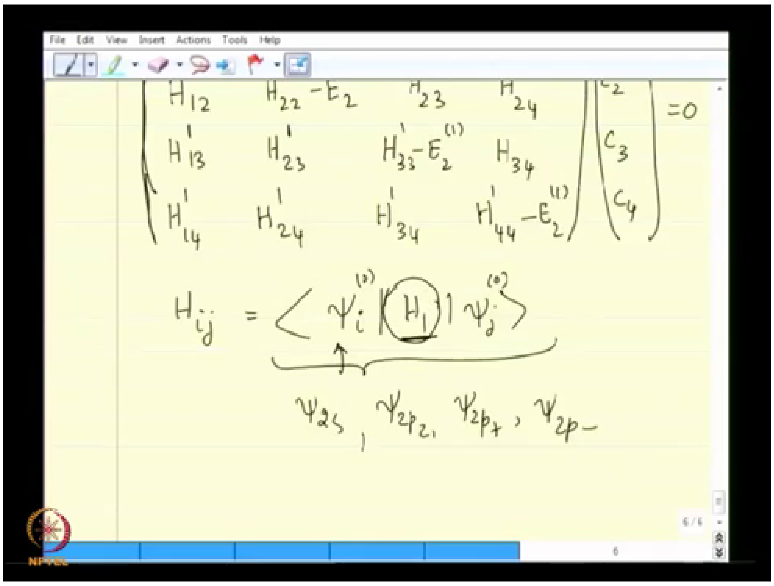
$$\begin{pmatrix} H_{12} & H_{22} - E_2 & H_{23} & H_{24} \\ H'_{13} & H'_{23} & H'_{33} - E_2^{(1)} & H_{34} \\ H'_{14} & H'_{24} & H'_{34} & H'_{44} - E_2^{(1)} \end{pmatrix} \begin{pmatrix} c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

$$H_{ij} = \underbrace{\langle \psi_i^{(0)} | \boxed{H_1} | \psi_j^{(0)} \rangle}_{\psi_{2s},\ \psi_{2p_z},\ \psi_{2p_+},\ \psi_{2p-}}$$

Now, you can remember that in this case whatever we call as H ij, is essentially psi i H 1 psi j where psi i is from any one of this psi 2 p 0 to order 0 ok; psi 2 p psi 2 s, start with 2 s, psi 2 p z, psi 2 p plus psi 2 p minus. And this is the perturbing Hamiltonian, such as the Hamiltonian the hydrogen atom placed in the magnetic field or placed in an electric field has this additional interaction due to the magnetic or the electric terms and so, that can be a perturbation. And to order lambda or to a very low order of the field, external field you see that the correction that one has to calculate depends on calculating the matrix elements of the perturbing Hamiltonian in the 0 order wave functions which are degenerate, and then substituting them in a Hamiltonian matrix which is 4 dimensional now 4 by 4, because the basis functions are 4 fold degenerate.

If you are talking about the corrections to n equal to 3 in the case of hydrogen, there are 9 basis functions, because it is n square degeneracy and the matrix that 1 has to solve is; in a very simple extension to what I have said the matrix will be a 9 by 9 matrix and there will be 9 eigenvalues and eigenvectors some of which may be 0, the others may not be 0 and so on. But one has to look at the symmetry of the problem more, to simplify that further.

But the essential point when you have degenerate energy levels and when you want to do perturbation theory time independent. For a correction term in the Hamiltonian such as H 1 is that, one has to set up the matrix elements of the Hamiltonian the perturbing Hamiltonian in the 0 order states which are degenerate and solve for the eigenvalues and eigenvectors of that, to get the first order corrections to the energy and the correct 0 order wave functions. We will not do the second order third order etcetera in this case, but the extension is rather straightforward. And if you have to do that it is only a question of hour, but the substituting these things and proceeding the same way that you did before ok.

Therefore, it is an extremely important extension to the time independent non degenerate state perturbation theory. And in this one lecture I hope to have captured the minimal essential changes that one has to make in correcting to the first order the energy levels and the splitting of the degenerate energies into 2 independent or 4 independent. In the case of hydrogen it may not be all the 4 energy levels, all the degeneracy 4 fold will not be completely removed or whatever, but it does not matter. The degeneracy will in any case be lifted, because some of the eigenvalues for E 2 1 will not be 0. And therefore there are corrections. If one has to work that out, in a problem section I will independently deal with the hydrogen atom as 1 example in the future ok.

Until then, thank you very much.