Basic Quantum Mechanics

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Module No. # 10

Time Independent Perturbation Theory

Lecture No. # 1

Time Independent Perturbation Theory

In my last lecture, we had developed the first few equations describing the first order perturbation theory. In perturbation theory, the Hamiltonian consists of two parts; H naught and H prime. For H naught, we have, we are already aware of the solutions. And, the objective is to find the effect on the energy Eigen values by introducing the additional term H prime in the Hamiltonian.

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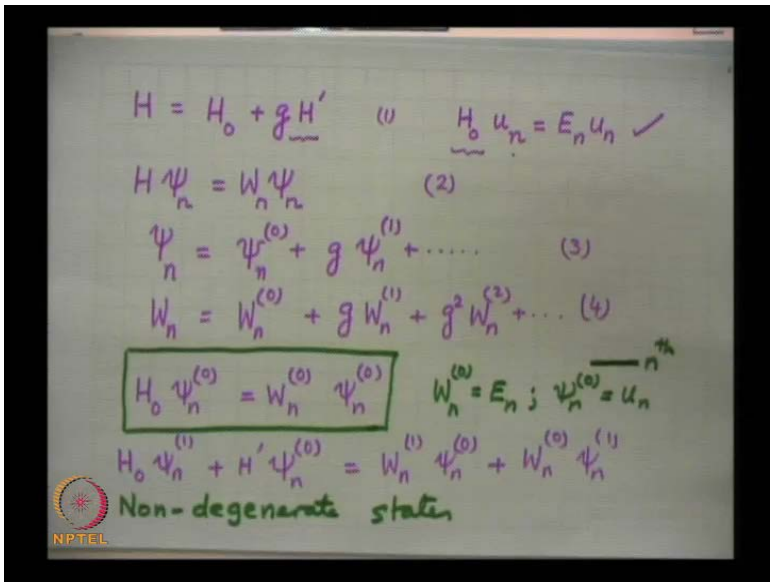

So, our Hamiltonian consists of consists of two parts; H naught, this is known as the unperturbed Hamiltonian and then plus H prime, which may be due to the presence of electric field or magnetic field or due to spin orbit interaction or relativity correction or anything that we can think of.

The effect of this term on the Eigen values of H naught are supposed to be small. We will illustrate that by means of an example. So, for H naught, we know the solution of the Eigen value equation; H naught u n is equal to E n u n.

For example, H naught may correspond to the linear harmonic oscillator problem or to a hydrogen like atom problem or something like that. So, for H naught we know this. So, we know this. Now, then on top of that we introduce the term H prime.

Our objective is to solve this equation; H psi is equal to W psi. We introduce a parameter g, which is a parameter between 0 and 1. And, make a, we made a parametric expansion of psi. So, we said. So, our objective is to find the perturbation to the n th state. So, we expand this. Make a parametric expansion of psi n. So, we write psi n 0 plus g psi n 1 plus g square psi n 2 and so on.

Similarly, W n is equal to W n 0 plus g times W n 1 plus g square times W n 2 and so on. We had substituted, say let us suppose this is equation 1, equation 2, equation 3 and equation 4. So, what we did was we substituted for psi n and W n in this equation. We used this and compared the equal powers of g on both sides. And, we ended up with these set of equations.

The first equation was H naught psi n 0 is equal to W n 0 psi n 0. This was the first equation. And then, the second equation was H naught psi n 1, this is the first order equation, plus H prime psi n 0 is equal to W n 1 psi n 0 plus W n 0 psi n 1. Now, if you look at this equation if you look at this equation, then you find that H naught psi n naught is an Eigen function of the operator H naught. So, psi n naught and the u n are the same.

Let us first consider non-degenerate states. So that, the n th state is non-degenerate state. That is, only one wave function. So, so. So, then we will have, if we consider the perturbation to the n th state, then W n naught will be equal to E n, e s of n and psi n naught will be equal to u n because this is, there is only one wave function associated with the n th state. So, we apply our analysis to non-degenerate states non-degenerate states, in which there is only one wave function. We will modify this analysis to take care of degeneracy after about dealing the course of this lecture.

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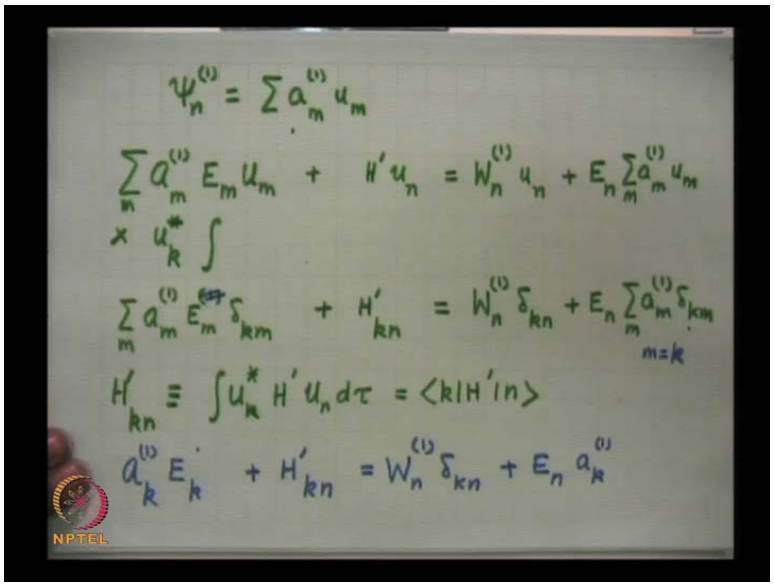

So, we have this equation that W n 0 is equal to E n and psi n 0 is equal to E n u n. Then, we write rewrite this that W n 0 is equal to E n, psi n 0… Then we assume, since u s of n form a complete set of function, so then we had psi n 1. We assumed to be equal to a m 1 u m. We multiply, we substitute it here and then H naught operating on u m will be e s of m u m. So, we substitute this in this equation. So, we get summation a m 1 e s of m u m, plus H prime u n because psi n 0 is u n. Then, W n 1 u n plus W n 0 is E n and psi n 1 is a m 1 u m. Then, we multiplied this equation by, on the left by u k star and integrated.

So, we know that these wave functions, which are Eigen functions of the operator H naught because we have H naught u n equal to E n u n; because this is a hermitian operator. So, we can, we have u k star u n d tau, which symbolically we write as k n. This is equal to the kronecker delta symbol. So, we multiply this and integrate. So, this, the first term becomes summation a m 1 E m 1 delta k m or m k, plus H prime k n; where H prime k n is defined as the u k star H prime u n d tau or and the integration is, of course over the entire space. Or, we can write it as k H prime n, plus using the kronecker delta symbols we get W n 1 delta k n plus E n summation a m 1 delta k m. So, in this series, only the m; the summation is over m, all this m is the dummy variable. The summation is over m; only the m equal to k terms survives.

And therefore, we will have, this term will be a k 1 E k 1 sorry E k just E k, this is just E k plus H prime k n is equal to W n 1 delta k n plus E n a k 1. Please remember, the sum

is over m and k is fixed, k is u k star, when u 2 star or u 3 star. So, m equal, only the m equal to k term will survive. So, this is a very important equation. And, we will be using this for the rest of our talk. So, we will, we will block this and we will try to remember this.

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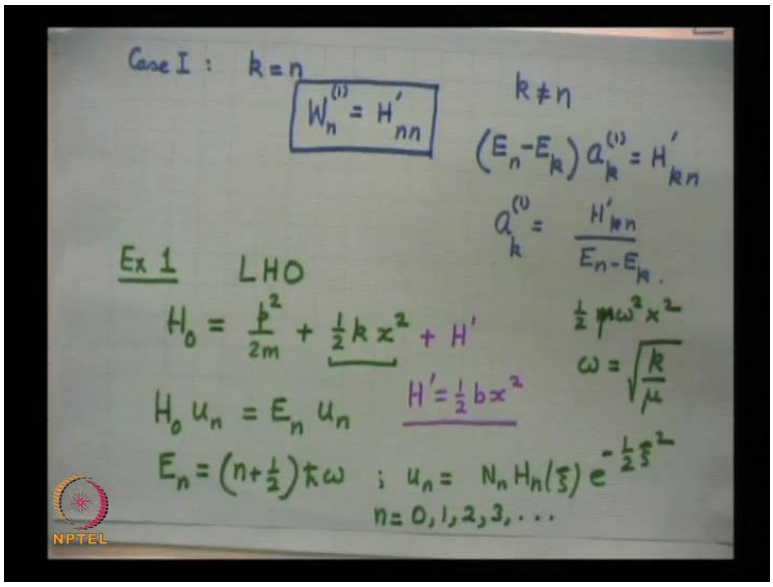

First case, you consider that k is equal to n. If k is equal to n, then this becomes 1; this delta k n becomes 1. And, this becomes, E k becomes E n. So, this term cancels out with this. And, we are left with W n 1 is equal to H prime n n.

And, when k is not equal to n, when k is not equal to n then this is 0 and then we will have, then we will have if I take this to that side, so we will have E n minus E k into a k 1 is equal to H prime k n. So, this equation can be derived, can be used to to obtain the expression for a k 1 with coefficients in the expansion. What is a k 1? It is the coefficient of expansion of psi n 1. So, a k 1 will be equal to H prime k n divided by E n minus E k. ok.

So, we obtain the first order perturbation and that is equal to H prime n n. Now, let me give a simple example. Let me consider a simple example. The example is that example one; let us consider the linear harmonic oscillator problem. And, let H naught is equal to p square by 2 m p square by 2 m plus half k x square. So, this is the potential energy; this is the linear harmonic oscillator term; the potential energy corresponding to the linear harmonic oscillator. And, one can write this as half m omega square x square. So, the

frequency is omega is equal to under root of k, the let me use this symbol mu for the mass. So, half k omega k by mu.

Now, we know the Eigen values and Eigen functions of the operator H naught, so H naught u n is equal to e s of n u n, where e s of n E n is equal to n plus half h cross omega. And, u n are the harmonic oscillator wave functions. I do not need to write down u n is equal to, say n s of n H n of psi e to the power of minus half psi square, which I am sure all of you know. And, n takes the value 0, 1, 2. These are the discrete states of the of the linear harmonic oscillator problem.

Now, we now assume that you have an additional term, which is H prime and we write H prime is equal to half b x square. And, we will treat this as a perturbation. Of course, you can immediately say that you can obtain the exact solution for the problem because k has to be replaced by k plus b.

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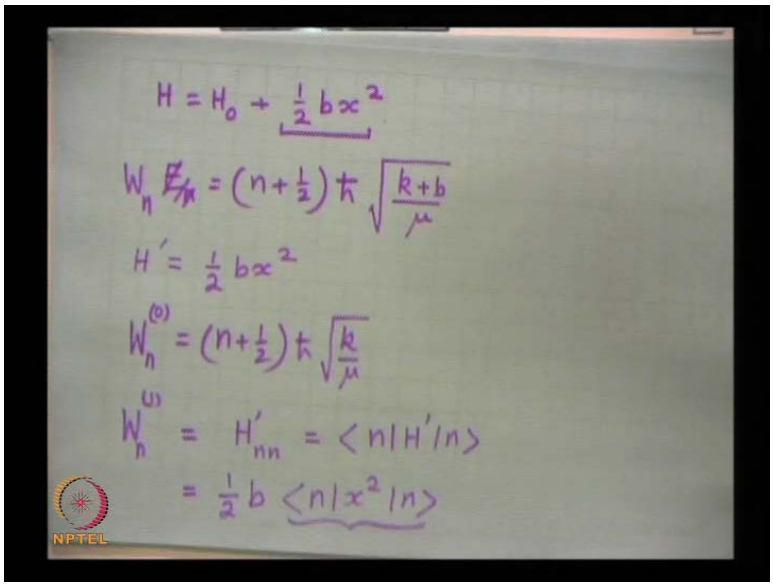

So, therefore we know that, that the exact solutions, so we know that when H, H is equal to H naught plus half b x square, we know that initially the energy Eigen values were E n is equal to n plus half h cross omega and omega was k by mu. Now, it will be k plus b by mu. So, this is my W n rigorously.

I just want to tell you how to use the perturbation theory and consider this term as a perturbation and carry out a perturbation analysis. So, you have, so I know the exact

results. Let me see what the perturbation theory gives us. So, we have H prime is now, half b x square and the perturbation, that is W n. Of course, W n 0 is equal to n plus half h cross omega; that is under root of k by mu. This is W n 0. And, W n 1, according to our perturbation theory is equal to as, we had derived earlier, this is equal to H prime n n. So, this is equal to H prime n n or this is equal to bracket n H prime ket n. And therefore, if I substitute the value of H prime, so it will be half b n x square n. So, if I am able to calculate this matrix element, then my problem is solved. So, let me use operator algebra to calculate this matrix element.

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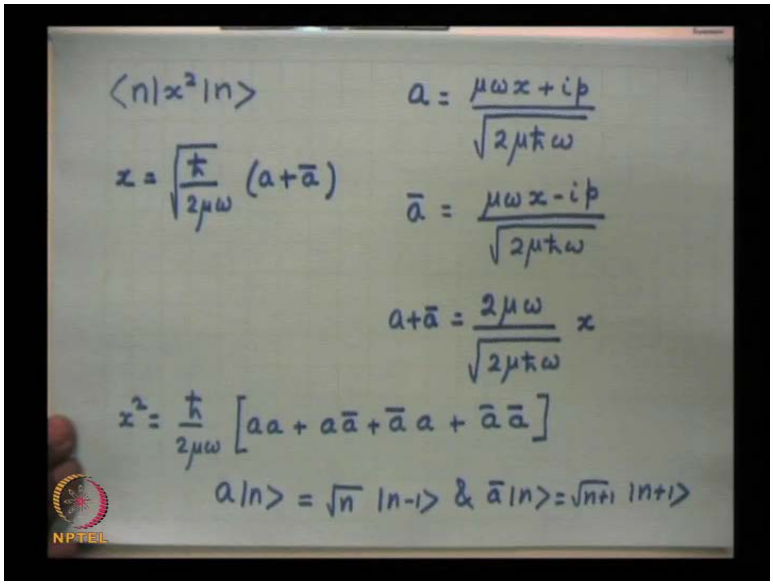

So, our objective our objective is to calculate n x square ket n. If you remember, we had introduced two operators in the linear harmonic oscillator problem; a is equal to mu omega x plus i p divided by under root of 2 mu h cross omega. And then, if you recall a bar was equal to x and x is a real operator. So, x bar is x minus i p divided by under root of 2 mu h cross omega.

So, a plus a bar a plus a bar is equal to 2 mu omega divided by under root of 2 mu h cross omega x. This implies that, x is equal to h cross by 2 mu omega a plus a bar. What is x square? x square is x times x. So, therefore, x square is equal to h cross by 2 mu omega, a plus a bar times a plus a bar. So, that is a a plus a a bar plus a bar a plus a bar a bar. Now, as you know that a ket n, this you must remember this equal to square root of n ket n minus 1 and a bar ket n is equal to square root of n plus 1 ket n plus 1.

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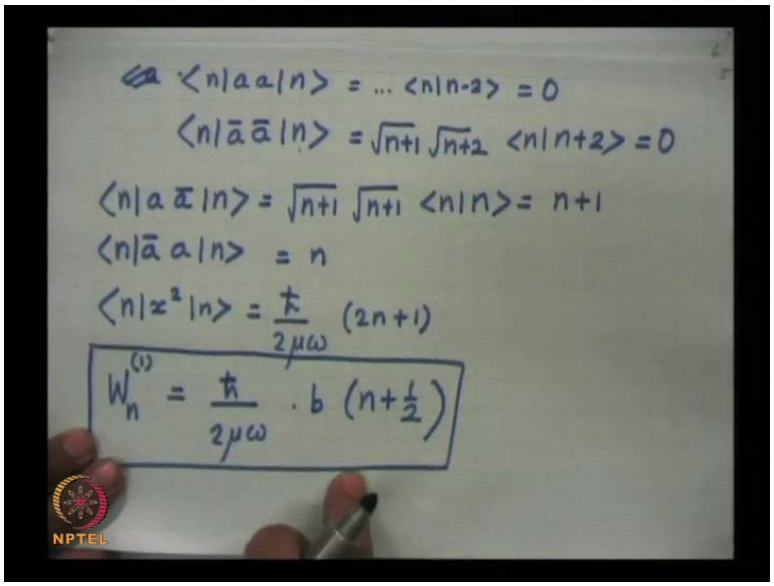

So, therefore, so therefore, you will have a, sorry, so, therefore, you will have n a a n. So, this will be a ket n is proportional to n minus 1 and then a ket n minus 1 will be proportional to n minus 2. So, this will be something multiplied by n n minus 2, which is 0. Similarly, n a bar a bar. So, this is n plus 1, square root of n plus 1. So, this will be square root of n plus 1 and then a bar n. n plus 1 is square root of n plus 2, n n plus 2. So, this is also 0 because these two numbers are differ by two. The only non-vanishing matrix elements will be n a a bar n. So, this is very easy to calculate. This will be square root of n plus 1 n plus 1 ket n plus 1 a ket n plus 1 square root of n plus 1 ket n. So, this will be n n. So, this is n plus 1.

And then, you will have n a bar a a ket bar n to the square root of n. And then, square root of n. So, this will be n. So, if I sum them up, 2 n plus 1. So, therefore, n x square n will be equal to h cross by 2 omega 2 mu omega 2 n plus 1.

And therefore, my, therefore if you recollect that the matrix element, the perturbation was equal to n x square n. So, this will be, the perturbation will be, first order perturbation will be half b h cross half b. And therefore, this will be h cross by 2 mu omega into b half times n n plus half. So, this is the first order perturbation. As I told you that for this, we have the exact solutions. Also, I think I have wrote it down somewhere here. Yes, these are the these are the exact solutions. So, I can write it down as n plus

half h cross. If I take k outside under root of k by mu, then this will be 1 plus b by k raised to the power of half.

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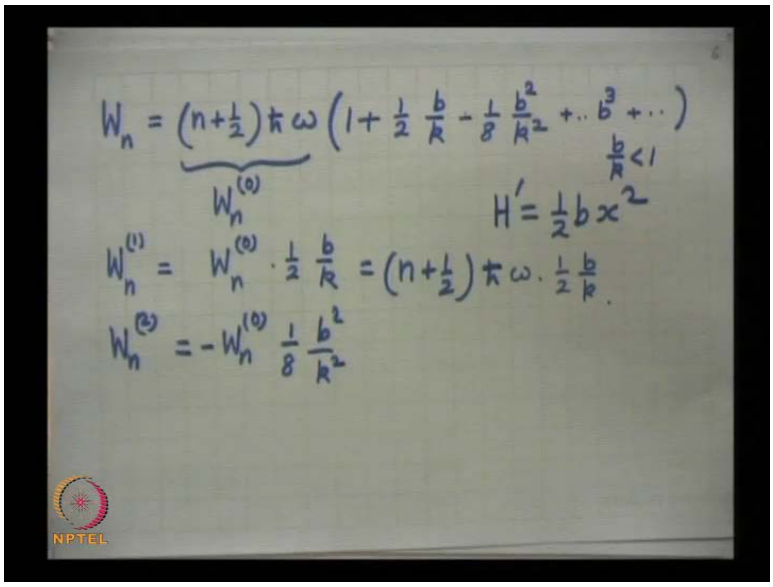

So, let me write this down. Let me write this down. So, I have, excuse me. So, I have W of n. These are the rigorously correct. So, n plus half h cross and this is omega. And, if I make a binomial expansion and that is possible when d by k modulus is less than 1. So, I will get 1 plus half b by k plus minus 1 by 8 b square by k square plus terms proportional to b cube, then b 4 etcetera.

And, this is W n zero. So, I have W n 1 from this. We say that the first term is equal to W n 0 times half b by k. And, the second order perturbation can also be found out from there. Here, second order perturbation will be… it will be proportional to b square. So, W n 0 which is n plus half h cross omega with a minus sign 1 by 8 b square by k square. Notice that, my perturbation was H prime is equal to half b x square. The first term is proportional to b; the second term is proportional to b square. So, our parametric expansion in powers of g is therefore justified. But, one must remember that this is a series which is, alright, only a b by k is less than 1. And, in fact we cannot make this expansion in b by k is greater than 1.

So, therefore there are domains of validity of perturbation theory. It is valid for small values of b or small values of b by k; nevertheless, this is my first order perturbation. So, this is n plus half h cross omega times half b by k. And, I leave it as an exercise for you

to show that this term and this term is the same. So, this is the way that we use the perturbation theory. And, that is for any problem.

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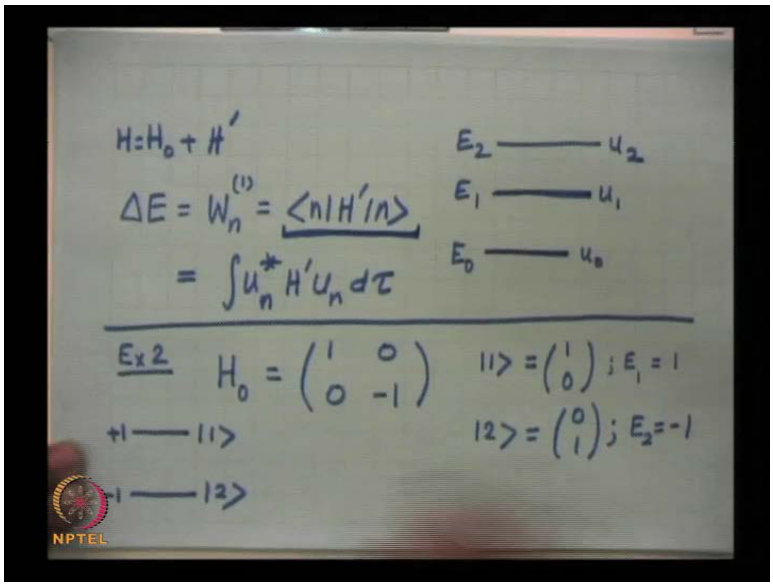

Let us suppose H naught. This is u 0, this is u 1, this is u 2; the energy Eigen values are E 0, E 1 and E 2 and my Hamiltonian is H naught. If now, there is an additional term because of the presence of magnetic field or electric field as we will consider later, then each energy level gets shifted. And, I am assuming that this energy state is non-degenerate, so that corresponding to a particular value of energy there is only one state. And, the perturbation delta E is equal to W n 1. This is equal to n H prime n. And, this is also written as u n star H prime u n d tau.

The, it is always more convenient to write it in terms of the bracket notation; because you will, if you ask me that is it a integration, one dimensional integration or two dimensional integration, the answer is in depend on the problem. If it is the hydrogen atom problem, it is of course a three dimensional integration; d x, d y, d z or r square d r sin theta d theta d phi. If it is a harmonic oscillator problem, then it is only integration over x and so on. If it is a two dimensional oscillator problem, it is d x, d y. So, it is more convenient to write it in this particular form.

Let me consider a simpler example. Example two: an example for matrix algebra. So, we assume H naught. This is an example from matrix algebra, so I have 1, 0, 0, minus 1. So, it is two Eigen states; ket 1, we denote by ket 1, 0 and the Eigen value is E 1 is equal to

1. This is a diagonal matrix. This is a Pauli spin matrix, if you recollect. And, the other Eigen state is 2; which is 0, 1. And, E 2 is equal to minus 1. So, I have two states. So, plus 1 and minus 1, plus 1 and minus 1; I denote this by ket 1 and denote this by ket 2.

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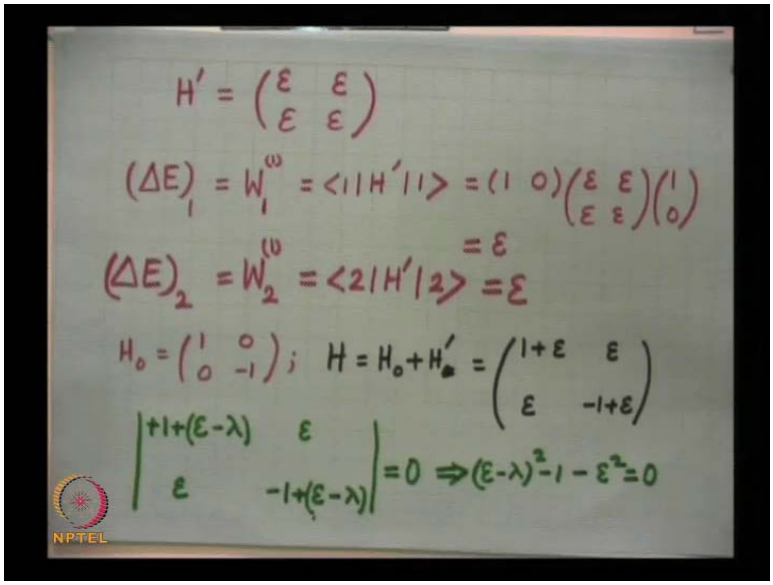

Now, let us suppose there is a perturbation. There is a perturbation that I apply. And, let that perturbation be denoted by H prime. And, that is equal to a very simple matrix epsilon, epsilon, epsilon, and epsilon. So, what is the, what is the perturbation to this. So, I can calculate delta E 1 which is equal to, say perturbation, the first order perturbation to the first state. The superscript 1 represents this is the first order perturbation. The subscript means that it is the first state. So, this will be bracket 1 H prime ket 1. And, so if I do this, 1, 0; epsilon, epsilon, epsilon; 1, 0; so, if you multiply this out, you will get epsilon. So, the first order perturbation is therefore, this is plus epsilon.

So, the energy levels shifts the, Eigen values shifts by epsilon. Similarly, I can write down delta E 2 which is the perturbation to the second state. First order perturbation to the second state. So, this is 2 H prime 2. And, I leave it as an exercise for you to show that, that is also equal to epsilon. So, this states shifts by E; this states also shifts by epsilon. This is the perturbation.

Once again, you can say, can we not solve this problem exactly? the answer is yes. So, I have H naught is equal to, H naught if you recollect is 1, 0, 0, minus 1; so, my complete matrix. So, the complete matrix is H which is equal to H naught plus H prime sorry sorry

H naught plus H prime. So, this will be equal to 1 plus epsilon, epsilon, epsilon, minus 1 plus epsilon.

So, this is my total matrix and the determination of Eigen value is very straight forward. I write down the determinant. So, this will be minus 1 plus epsilon minus lambda, epsilon, epsilon, sorry, plus 1, here it is plus 1 and here it is minus 1 plus epsilon minus lambda. So, this gives me this times this. This is epsilon minus lambda. If I put it in bracket, plus 1 this is epsilon minus lambda minus 1. So, this becomes epsilon minus lambda whole square minus 1 minus epsilon square is equal to 0. The solution of this equation will give me the Eigen values of the problem.

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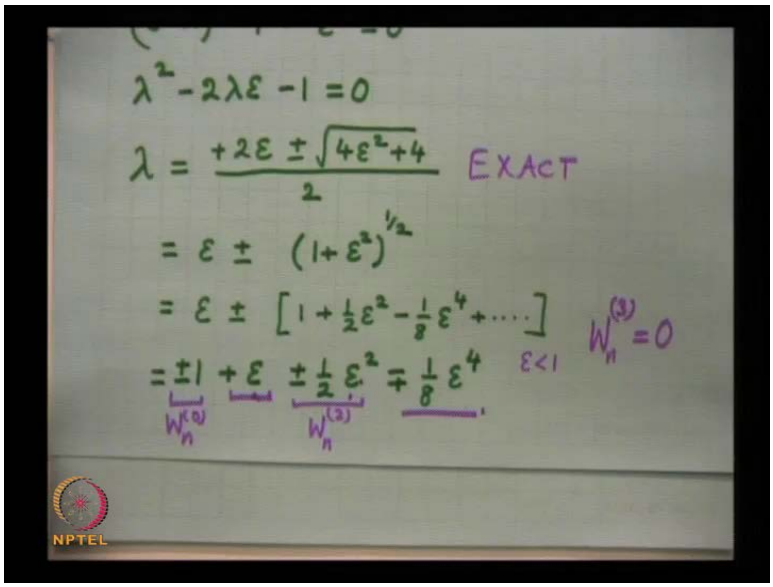

So, let me write it down once again. So, I have, in order to find the values of lambda, epsilon minus lambda whole square minus 1 minus epsilon square is equal to 0. So... So, the first term is epsilon square. That cancels out with this. So, you have lambda square minus 2 lambda epsilon minus 1 is equal to 0. So, if the roots of this equation if lambda is minus b; that is, plus 2 epsilon plus minus 4 epsilon square minus 4 a c, that is plus 4 divided by 2.

So, this will be epsilon plus minus 1 plus epsilon square raised to the power of half. So, assuming epsilon to be less than 1, we can make a binomial expansion. So, you get epsilon plus minus 1 plus half epsilon square minus 1 by 8 epsilon to the power of 4 plus epsilon to the power of 6.

So, I get, I get, please see this. The Eigen values as plus minus 1 plus epsilon plus minus half epsilon square minus plus minus plus 1 by 8 epsilon to the power of 4. So, please see this. That, this is W n 0, the unperturbed Eigen value in the presence of epsilon going to 0, for epsilon going to 0.

The first order perturbation is the same for both states. And, this is what I have obtained here also. This was 1 plus epsilon; this was 1 minus epsilon. This is the first order perturbation. This is the first order perturbation. The second order perturbation, this is W n 2. So, this is half epsilon square and minus half epsilon square. Half epsilon square for the plus 1 corresponding to the half Eigen values minus...And, then W n 3; the third order perturbation is 0. And, this is the fourth order perturbation. So, this is the exact result. And we see that the first term is first order perturbation, second order perturbation, the third order perturbation is 0, and this is the fourth order perturbation.

Once again, this binomial expansion is only valid when epsilon is less than 1. So, therefore the perturbation theory will not be valid when epsilon is greater than 1. So, therefore, the perturbation theory is usually valid, we say for small perturbation. In fact, it will be a divergence series if epsilon is greater than 1. So, therefore, it does not work often when the parameter becomes large. So, I am giving you one example from the harmonic oscillator problem and another example from the theory of matrices.

Now, we go back to our first slide and we try to, where did I put? Yes. We go back to our this slide. We said that n is equal to k. n is equal to k, then we had W n 1 is equal to H prime n n.

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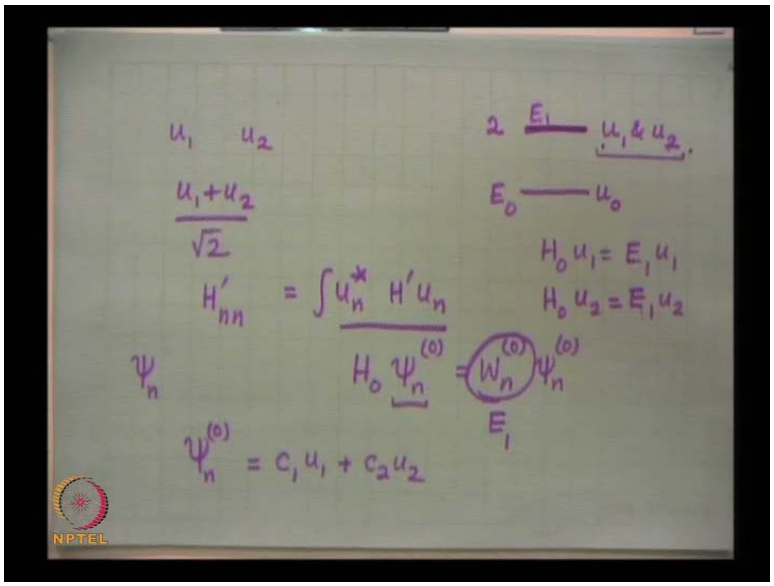

But, let us suppose I have the state is, the ground state is represented by u 0. And, the first excited state is let us suppose 2, 4 degenerate; that means there are two Eigen kets corresponding to that; a u 1, u 2, two Eigen functions corresponding to that.

We know that, if this is the degenerate state, a 2, 4 degenerate states, then you can have any linear combination of that to be also an Eigen Eigen function. That is, that is if u 1 is an Eigen function and u 2 is an Eigen function corresponding to and degenerate state, then u 1 plus u 2 by root 2 is also an Eigen function. And, so therefore, the question arises. If I want to calculate H prime n n, then it is u n star H prime u n. Then for this, for to calculate this, should I use u 1, should I use u 2 or some linear combination of that.

So, therefore psi n 0, we said, we had said that H naught psi n 0 was equal to W n 0 psi n 0. Now, I can consider the perturbation to the second state; so, W n 0. I know this is equal to, say E 1. This is equal to 0 and the energies are the energy is E 1. So, E 1 and u 2 are equal. So, you have H 0 u 1 is equal to E 1 u 1. And, H 0 u 2 is also equal to E 1 u 2. This is the same Eigen values. That is the concept of degeneracy. This is two linearly independent wave functions, which corresponds to the same energy Eigen values.

Then the question arises, will psi n naught be u 1 or u 2 or some linear combination of that. So, we do not know. And, so therefore, let us consider 2, 4 degeneracy and we assume that this is equal to c 1 u 1 plus c 2 u 2. We take any two sets, any two functions, which are orthonormal to each other. Which are orthonormal to each other. And, we

write psi n 0 as a linear combination of that. And, our objective is to determine the values of c 1 and c 2.

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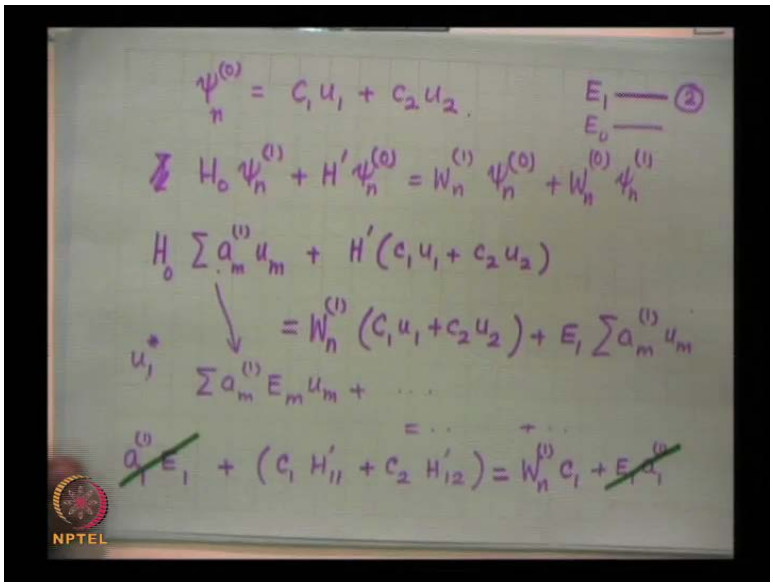

So, we once again assume that psi n 0 is equal to c 1 u 1 plus c 2 u 2. Then, we will have that, so therefore you will have the equation, a summit. We will write this equation, let me let me go from one step behind. And, let me just go back to that slide. Yes, we start with this equation. We start with this equation.

So, we have H naught psi n 1 plus H prime psi n 0 is equal to W n 1 psi n 0 plus W n 0 psi n 1. Now, we are assuming this is E 0 and this is the second state, which is 2, 4 degenerate state. So, we have H naught psi n 1. So, we the wrote down that H naught summation a s of m 1 u m plus H prime c 1 u 1 plus c 2 u 2 is equal to W n 1 c 1 u 1 plus c 2 u 2 and W n 0 is E 1. So, this is E 1 summation a m 1 u m.

Now, I first multiply this by u 1 star and integrate. So, H naught, sorry, this I have to write again. I have to write again because the first term will be H. The first term will be summation a m 1 E m u m. So, first we multiply, this this term becomes this term and the remaining term remains the same. I do not want to rewrite it. I then multiply with E 1 star and integrate. So, I get a 1 1 E 1 because only the first term will survive, plus within brackets c 1 H prime 1 1 plus c 2 H prime 1 2 is equal to, sorry, is equal to W n 1. I multiply by E 1 star. So, this is just c 1. And, this will be 0. E 1 star E 2 will be 0, plus E

1 a 1 1. So, as you can see that this term cancels out with this term. And, if I take from this, on this side, we will get the equation.

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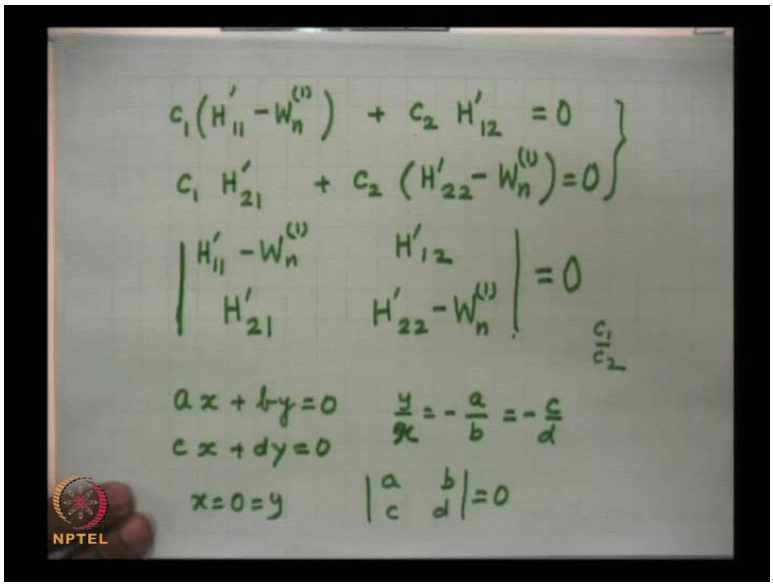

We will get the equation c 1 H prime 1 1 minus W n 1 plus c 2 H prime 1 2 is equal to 0. This is one equation. Then, what we do is I multiplied by u 2 star and integrate. So, this will become a 2 1. But, this will be E 1 because E 1 is equal to E 2. E 1 is equal to E 2. we have said that H naught u 1 is equal to E 1 u 1 and H naught u 2 is also equal to E 1 u 2.

They correspond to the same energy Eigen value. So, this term and this term will again cancel out. And, what will be remaining is c 1 H prime 2 1 plus c 2 H prime 2 2 minus W n 1.

This is a set of linear homogeneous equations. And, for non trivial solutions, the determinant must be 0. That is, H prime 1 1 minus W n 1, H prime 1 2, H prime 2 1, H prime 2 2 minus W n 1. This determinant must be equal to 0.

So, that solves my problem. That solves my problem that solves my problem. This is… I hope all of you understand that. for example, if I had an equation like this, a x plus b y is equal to 0 and c x plus d y is equal to 0, then the trivial solution is x is equal to 0 and y is equal to 0. And, that is the trivial solution. But, otherwise you will have a, b, c, d. The determinant of that will be 0 because y by a y by a will be equal to minus a by, oh sorry y

by x will be minus a by b is equal to minus minus c by d. So, a d will be equal to c b. So, these are, this is a set of linear homogeneous equations for c 1 and c 2. The trivial solution, the trivial solution corresponds to c 1 is equal to 0 and c 2 is equal to 0.

But, for non trivial solutions, you will have the determinant equal to 0. Now, this determinant, this is a, you will obtain a quadratic equation in W n 1. It will allow us to give two roots, in general two different roots. For each root, you will obtain two different values of c 1 by c 2. And, that will give me two different Eigen functions of the system.

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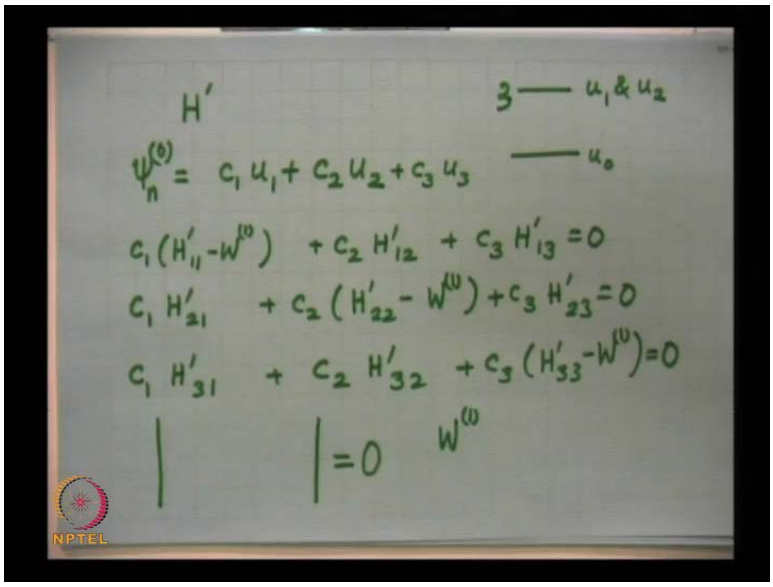

And therefore, the recipe is this. The recipe is this. That, if I have a 2, 4 degenerate state, the corresponding Eigen functions are u 1 and u 2. And, let us suppose this is u 0 and u 3, u 4 can be anything. The recipe is this. My perturbation is H prime. I assume psi n 0 is equal to c 1 u 1 plus c 2 u 2. When I obtain, these set of two equations. And, from these set of two equations, we obtain these secular determinant equal to 0. The solution of this equation will give me two values of W n 1. And, for each value of W n 1, I will get the ratio c 1 by c 2.

In general, if it is, let us suppose a 3, 4 degenerate state or a 4,4, let us suppose it is 3,4 degenerate, so, then I must write down c 3 u 3. And then, we will have a set of three equations. You see, c 1 H prime 1 1 minus W 1 plus c 2 H prime 1 2 plus c 3 H prime 1 3. This is equal to 0. And, similarly c 1 H prime 2 1 plus c 2 H prime 2 2 minus W 1 plus

c 3 H prime 2 3 equal to 0. And then, c 1 H prime 3 1 plus c 2 H prime 3 2 plus c 3 H prime 3 3 minus W 1 equal to 0.

This will lead to a 3 by 3 determinant for non-trivial solutions. And, for, non for therefore we will get three roots of W 1. And, for each value of this we will get c 1 by c 2 and c 1 by c 3, if all three of them are different. So, that is the recipe for the for the degenerate state perturbation theory calculations.

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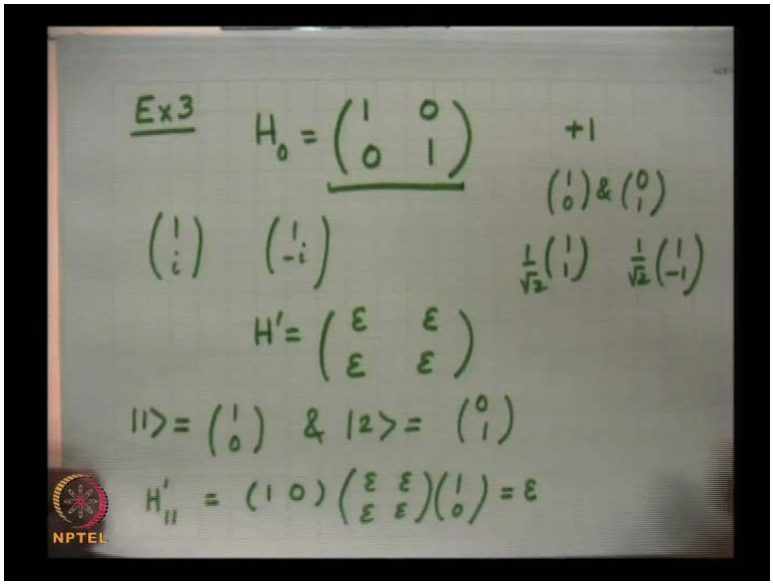

Let me take an example. And, we will take an example from… So, this is my example three from matrix algebra. So, let me consider H naught is equal to 1, 0, 0, 1. one 0 0 1. Then, we will have that; this, as you know has only one Eigen value; plus 1. What are the Eigen functions? It will be, it can be, either you can choose 1 0 or 0 1. This is a unique matrix. Or, I can choose 1 1 under root of root 2 and 1 over root 2 1 minus 1.

It does not really matter. I can choose these two as Eigen kets or these two as Eigen kets. Any linear combination of these two can also be an Eigen ket. I can choose as 1, plus i and 1 minus, i. you remember these are the Eigen functions of the Eigen kets of the Pauli matrices.

So, this is a… So, the question arises. Let us suppose that, my H prime is once again epsilon, epsilon, epsilon, and epsilon. So, let me choose this as my ket, base kets. That is, ket 1 is equal to 1, 0 and ket 2 is equal to 0, 1.

So, therefore H prime 1 1, I have to calculate all four matrix elements. H prime 1 1 will be 1, 0; epsilon, epsilon, epsilon, epsilon; 1, 0. So, this will come out to be epsilon. So, all the values; so, H prime 2 2, H prime 2 1, everything.

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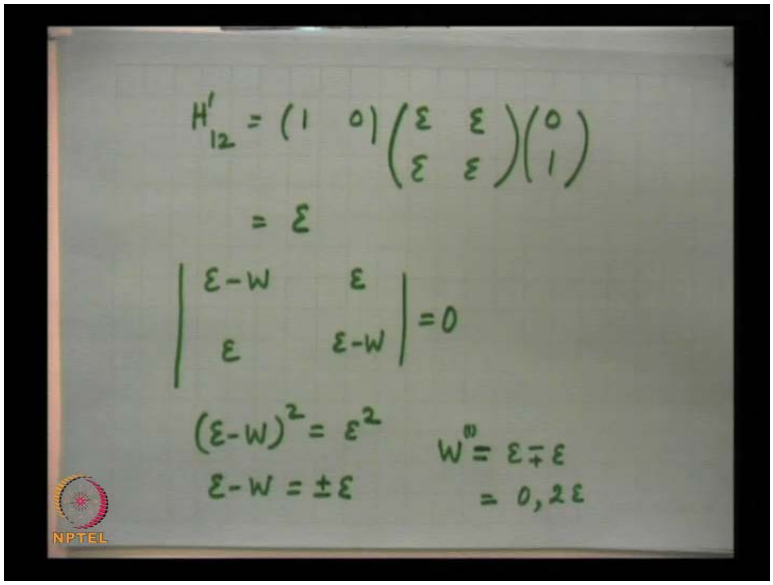

So, H prime 1 2 let us suppose, H prime 1 2 is 1, 0; epsilon, epsilon, epsilon, epsilon and this is 0, 1. So, this is again 0, 1. So, all matrix elements are epsilon. So, the determinant, the secular determinant becomes epsilon minus W, epsilon, epsilon, epsilon minus W is equal to 0.

So, you have epsilon minus W whole square is equal to epsilon square. Epsilon minus W is equal to plus minus epsilon. Or, you have W is equal to, is equal to the first order perturbation. First order perturbation will be, if I take an epsilon here. So, epsilon minus plus epsilon; so, 1 will be 0 or 2 epsilon. These are the two perturbations. So, we will continue from this point onwards in my, in our next lecture. So, we end here. Thank you.