Quantum Chemistry of Atoms and Molecules
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Lecture-40
Perturbation Theory for Non-Degenerate States

This is where we had stopped our discussion. Now we will go ahead and finish it in this somewhat shorter module.

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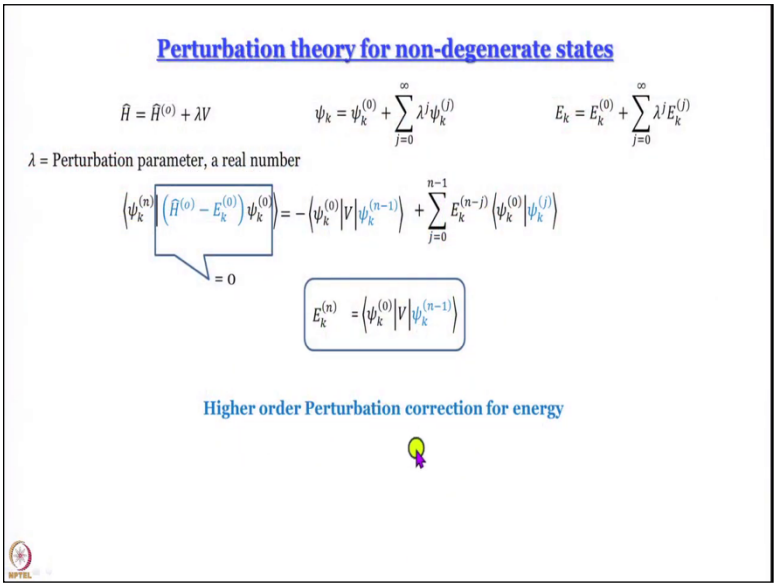

We have obtained an expression for the higher order perturbation correction for energy. And in this expression we have integral Psi k0 V Psi k n -1. Let us not bother about V for the moment; V is going to be dependent on what kind of system we look at. For an harmonic oscillator we will have one form for say interaction well that is time dependent but for non rigid rotor it will be of something else. So, depending on the system will get different kinds of V for multi electron atoms it will be electron-electron repulsion and so on and so forth.

So the problem with this expression is that what it means is that you go in steps. It is great that you have one unperturbed wave function in the integral but the other one is the n – 1th wave function. So, in order to find out a particular correction term you must have first worked out the n - 1thth correct correction term to wave function in order to find out the nth correction to the

energy. So, that is not too happy a situation and we want to see whether we can derive an expression which can do better than this.

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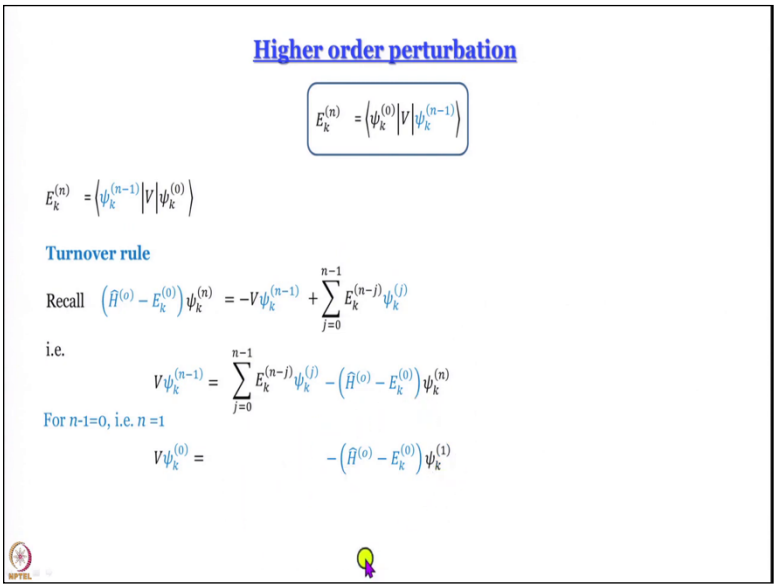

So that is our quest for now and then we will talk about what is the expression for the perturbed wave function. So, this is our higher order perturbation expression that we have derived. Now what we will do is we are going to use our old friend turnover rule and we are going to interchange the wave functions in Bra and ket vectors. We can do that because V is a real quantity, remember turnover rule.

And why do we do it all of a sudden; why do we bring Psi k; why do we bring the unperturbed wave function from the bra vector to the k vector because if you remember we had said that we have worked out this very, very important relationship in which I have something like this, I have an expression for this V operating on Psi k n – 1th. Now put n equal to one you get 0 so that is how things can simplify a little bit.

So first thing that we will do is we are going to make this V Psi k n - 1th the subject of formula bring it to the other side then on the right hand side you will be left with the summation and you have to bring this H 0th minus E k 0th operating on Psi k nth this kind of this term to the right hand side it will get a minus sign this is what you have. Now what do I do see I what am I

looking for? I am looking for V Psi k 0th my purpose is to just simplify this ket vector in the integral.

So I want an expression for V Psi k 0th. So, I put n - 1 equal to 0 because here I have n – 1. So, I put n equal to 1 essentially so when I put n equal to 1 the good thing is that we do not have to worry about the summation anymore is not it. Summation is from j equal to 0 to n - 1, n - 1 equal to 0, so I mean we are basically summing 0 term let us not worry about that. We are left with only this term and here also instead of n we are going to write 1.

So I get minus unperturbed Hamiltonian minus unperturbed of energy of k this operator operating on the first order correction to the wave function. Now please remember this 0th order Hamiltonian minus 0th order energy is not the annihilation operator for the first order correction term to Psi k it is not the annihilation operator for Psi k first it is the annihilation operator for Psi k0. Please do not get confused here these exponents have to match in order for this operator to be an annihilation operator for the wave function here they do not match.

So anyway so we have found this expression, so next step obviously is to take this expression and plug it back into the integral.

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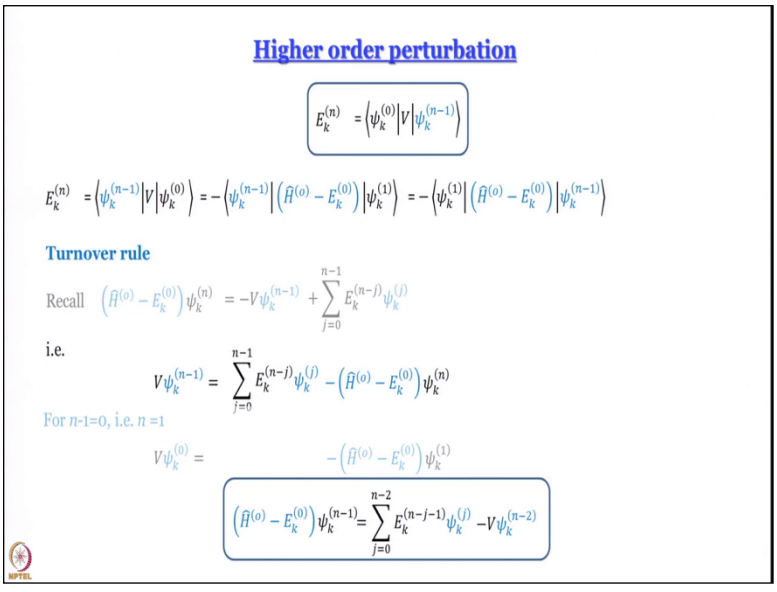

So, then this is what we get the ket vector remains the same sorry bra vector remains the same minus sign comes out in the ket vector we have H hat 0th minus E k 0th operating on Psi k first. What do I do next well I apply our old friend turnover rule once again. Why do I apply turnover rule once again because now I have brought this Psi k n – 1th here and again if you recall this expression here we have this perhaps I should have just taken this that is a more straight forward thing we have this expression we know what happens when this H hat 0th minus E k 0 operates on Psi k nth.

So all I have to do is replace n by n - 1 and I can simplify the ket vector once again. So, in two steps I am simplifying the ket vector. So, we do that we put instead of n I put n - 1 here so what do I get H 0th minus E k 0 operating on Psi k n – 1th you can just look at this expression here here relationship here is equal to sum of j equal to 0 to n - 2 here it was n - 1th here it has become n - 2 E k n - j – 1th here it was n - j instead of n everywhere I am writing n - 1th so n - j – 1th operating on Psi kj that remains same minus V operating on Psi k instead of n – 1th I write n - 2th.

Please work this out yourself please write it out then only you will understand its actually very simple nothing complicated its just like long algebraic expression nothing else. So, what have I got I have got an expression I know what to put now in the ket vector.

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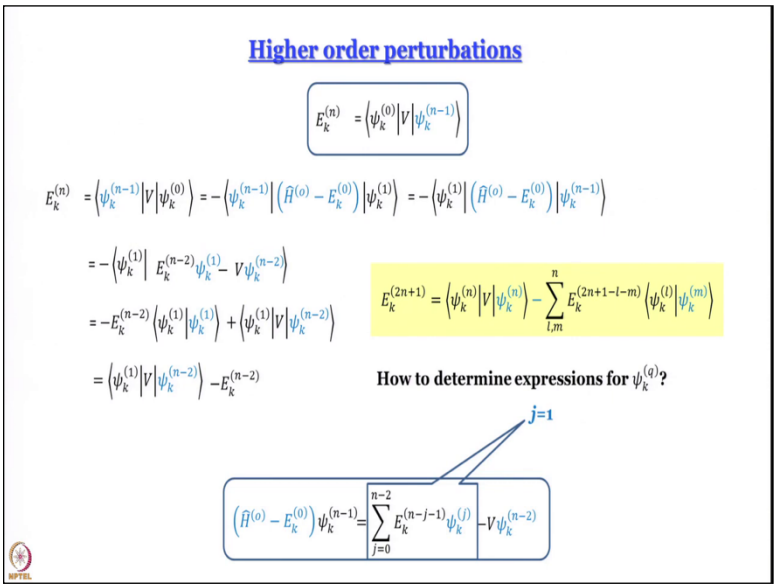

So, now I am going to take this and I am going to put put it into the ket vector. But then I will use some other trick. Now since I am going to integrate I know that while integrating since this is Psi k 1th this wave function would better be Psi k 1th all other wave functions are going to vanish anyway. I can write this sum there is no problem and you should write it while practicing. Just write this entire summary write two three terms and then write the general term.

So when you integrate your left multiply by left multiplying by the complex conjugate of Psi k 1th and then integrating over all space. So, except for Psi k 1th everything else will vanish. So, the only term that will survive is j equal to one first order perturbation. So, when I do that I put j equal to one what do I get the only energy term that survives is E kth V c k nth, nth order correction to your energy. So, well n – 2th because this min sorry I made a little mistake this is -1 here so n - 2th so I get n – 2th correction to energy multiplied by Psi k 1th as a first term second term remains minus V Psi k n - 2th.

Now I will expand I have two integrals right in the ket vector I have two terms so I might as well write it out as a sum of two integrals the first integral is going to be I can bring now since there is no more summation I can bring this E k n – 2th out of the integral sign and integral will be Psi k 1th Psi k 1th and well what is Psi k 1 and Psi k 1th plus Psi k 1th integral Psi k 1th V Psi k n - 2th. So, then this is what I get this integral the first in the first term well here I have just interchanged the two terms.

I have changed the sequence because I do not want to write a minus sign first but not difficult to see I hope that the coefficient of E k n – 2th is actually one because these are orthonormal. So, I have written 1 there and I have kept this integral and this is the expression. So, what I have got here is that if you have the n – 2th correction to the energy then you can find out the nth correction to energy.

In fact it can be shown it is not really worked out in Pillars book but the reference has been given where you can actually find out even the 2n + 1th correction term to energy by using the wave functions of this l and m. So, that is the expression we know how to get the terms for higher

order perturbations, how to get the correction in terms of energy. Now the question is this we are using this Psi k lth Psi k mth how do I find those.

What is the expression for Psi k qth? There are two ways of doing it one is by using a variational method we skip that for the time being because we are not performed a discussion of variation theorem yet variation method yet we will do that.

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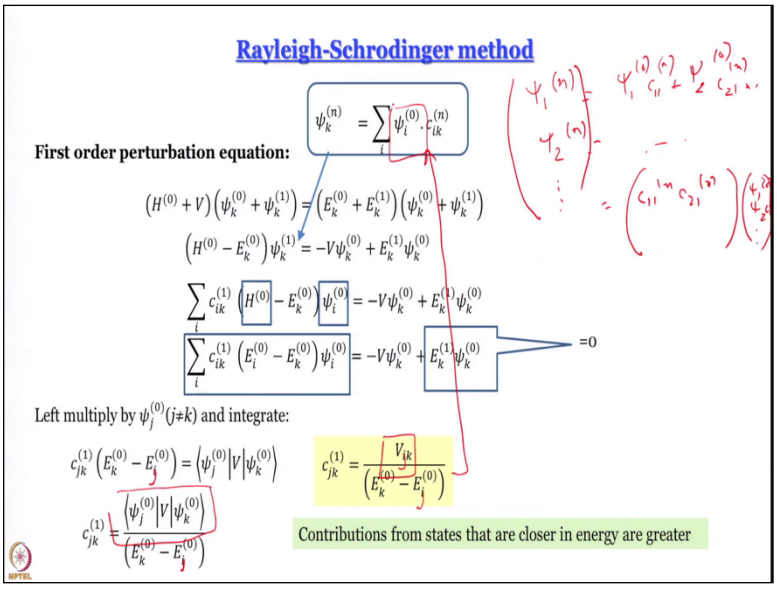

For now what we do is we briefly discuss what is called the Rayleigh Schrodinger method. And Rayleigh Schrodinger method starts from this expression which we had introduced in one of the earlier modules Psi k nth is equal to sum over i Psi i 0th c i k nth well this is just a coefficient what is the meaning of c i k the contribution of the ith unperturbed wave function in the kth perturbed wave function. So, you can understand we can write this as matrix equation I am writing it only for one state.

If I write it for many states Psi k nth Psi 1 nth Psi 2 nth Psi 3 nth Psi 4 nth Psi k n and so on and so forth. Then I am going to get a system of linear equations on the right hand side I will get a summation and that can be easily written as a matrix equation. So, this c i k nth this is essentially a matrix element I hope I have been able to make myself clear here what I am saying is I can write like this Psi 1 nth is equal to Psi 1 0 c 11 nth + Psi 2 0 c 21 so on and so forth.

I can write something similar for Psi two nth and I can go on, so what do I get on the right hand side I can write this as a matrix left hand side on the hand side I can write it like this c 11 nth c 21 nth so on and so forth. So, I can write f square matrix and here I am going to have Psi 1 0th Psi 2 0th and so on and so forth. I can write it as a matrix equation. So, this coefficients are essentially matrix elements this is something that is used ubiquitously in quantum mechanics.

So please do not get confused if I all of a sudden say that this is a matrix element and i and k essentially tell us what the position of the matrix element is 11 22 13 35 so on and so forth. So, what I will do is I will use this kind of an expression and plug it into the first order perturbation equation here I have not written from the beginning I have just used it in a more compare written it in a more compact form H 0 plus V operates on Psi k 0th plus Psi k 1th to give us the energy of the of the corrected energy plus the wave multiplied by the wave function eigen value equation.

And from there I can rearrange and while rearranging I have neglected certain terms because this H 0 Psi k 0th will be equal to E k 0 Psi k 0th so they are going to cancel each other so this is what we are left with I think we have done this earlier also. So, on the left hand side I have the well annihilation operator but not for Psi k 1th for Psi k 0th it is not going to annihilate Psi k 1th. So, this H 0th minus E k 0th sorry for missing the hat here operating on Psi k 1th gives me minus V Psi k 0th plus E k 1th Psi k 0.

So now I am going to plug in the expression for Psi k nth here putting n equal to 1. So, I get sum over c i k 1th multiplied by H 0th minus E k 0th operating on Psi i 0th is equal to minus V Psi k 0th plus E k 1th Psi k 0 ok I just taken this and plugged it in here. Now what will happen I know what happens when H 0th the unperturbed Hamiltonian operates on the ith unperturbed wave function Psi i 0th. What do I get eigen value equation I should get E i 0th multiplied by Psi i 0^{th}.

So this is the expression I get I get c i k 1th multiplied by E i 0th minus E k 0th Psi i 0th is equal to right hand side is getting nicer I have replaced an operator by a value and that to; of the value of an unperturbed energy this is great it is turning out to be very nice, what do I do next? By now you should have been used to it I am going to left multiply by a wave function in this case again I am going to left multiply by an unperturbed wave function.

A particular unperturbed wave function j is not a general index here Psi jth Psi j 0th where j is not equal to k also why because then when I integrate then this term is going to vanish. So, we left multiply by Psi j 0 where j is not equal to k and we integrate over all space. So, this is going to give me an integral in which only one term is going to survive. In this entire summation which term will survive the term in which i is equal to j is not it.

Because this I am going to integrate I am going to get something like integral Psi i 0th Psi i 0 Psi j 0th star Psi i 0th d tau integral. So, that will only be equal to 1 when i equal to j for all other values of i is going to be 0 and what about the right hand side? The second term on the right hand side when I left multiply by Psi j j 0th says Psi k k is a particular value j is a particular value and I am saying specifically that I have chosen it in such a way that j is not equal to k so of course integral of Psi j 0th Psi k 0th d tau is going to be 0.

So, very nice on the right hand side out of the two terms one has become 0 what about the first term this will become some integral involving a triple product involving a wave function and is operator operating on this another wave function. Left hand side simply becomes c j k 1th multiplied by E k 0th minus E i 0th is that sure is that instead of i have to write j okay that is I have done that and I have interchanged I should have written a j here I am sorry about not doing it here this is actually j.

I think I have made that mistake throughout later on please correct it this i because you understand what is happening here i here is a general index. Now all values of i have vanished except for i equal to j so here I should have written j the other part is simple I have I want to take this minus sign to the left hand side so I have just interchanged the sequence here. So, sorry about this, this E k 0th remains there but this this should be E j 0^{th}.

And this integral is 1 for E i equal to j right hand side I get integral Psi j 0 star V Psi k 0 do I know what that integral is not until I know what V is? Until now we leave it at that. So, now I get i written i everywhere should have been j sorry so c j k 1th is equal to integral Psi j 0th I just

write it by hand at least, so this is not i this is j this is not i this is j. So, c j k first is equal to this integral Psi j 0th star V Psi k 0 divided by E k 0 minus E j 0th.

So, what I will do is I will write this integral here sorry I will write this integral here as V j k not I, k V j k and this is again going to be j sorry again; perhaps for the first time we are using something that we keep doing all the time. We have an integral we do not know what the form is we just give it a name we use indices that help us identify what kind of an integral it is and we leave it at that. When an opportune moment comes that is when we try to solve it.

So I have an expression for c j k 1 so then you can just take this and substitute here I have not done it on purpose I wanted you to do it before I show you the result in the next module. But one important point I want to make is that see what is this coefficient it is the this coefficient is essentially the coefficient for some; your wave function is coefficient for some particular unperturbed wave function.

So what we are saying here is that this coefficient is going to blow up when the energies are close remember we are expanding we are trying to get the we are working with the kth state. So, when the energies are close to those of the kth state contributions of state that have whose energies are closer to the; that of kth and at the kth state they are the ones that are going to contribute the most. So if you plot the coefficient against the index of the wave function i it will be something like this.

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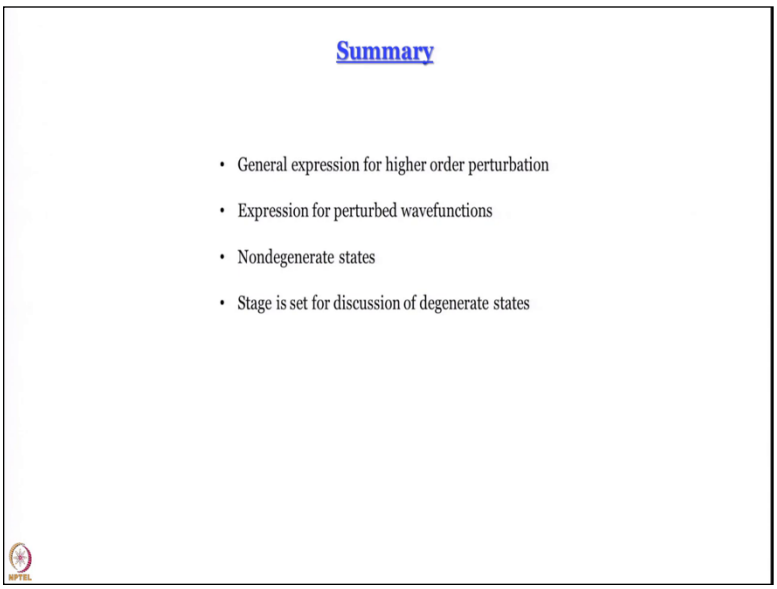

So, that is very important and to summarize we have learnt today over the last two modules a general expression for higher order perturbation correction to energy we have got this expression and we have got it in a couple of ways. We have done it for non degenerate states and we have also got you we have write it here an expression for the corrections of the wave functions. So, now the stage is set for discussion of degenerate states that is what we will do in the next module.