Quantum Chemistry of Atoms and Molecules

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Lecture-39
Higher order perturbations

We have started talking about approximation methods in general and perturbation theory in particular. So, far we have generated we have adopted a very easy convention very easy to understand simple convention with the one that is available in Macquarie's quantum chemistry book to talk about perturbation theory. And in the last module we said that we are going to talk about more applications and we are going to see how higher order perturbations are going to make results better and so on and so forth.

Before we go there we should at least learn how what the expressions are for higher order perturbation in the first place. And also I had told you very sketchily that the wave functions perturbed wave functions are written as linear sums of the unperturbed wave functions. There is another issue that deserves a little more attention at this time. So, what we will do today is that now that we are familiar with the language of quantum chemistry.

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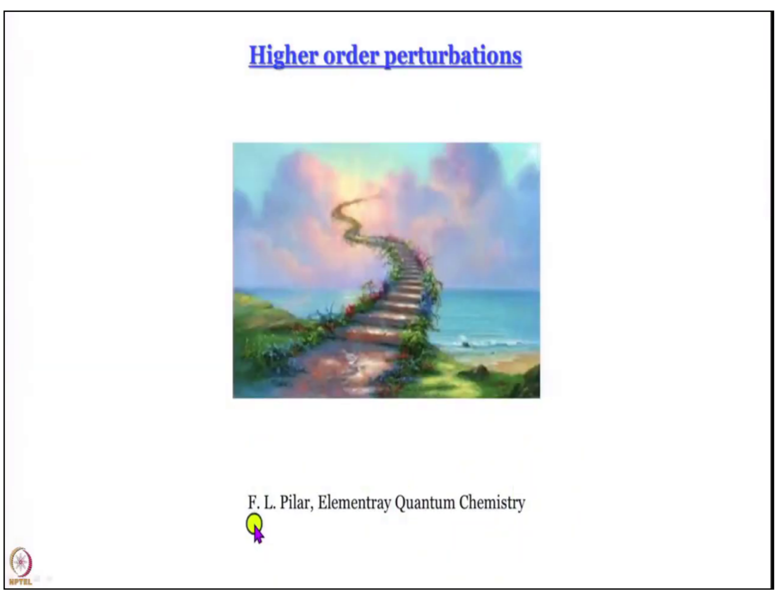

We are trying we will try to see whether we understand the way this treatment is there in a little more difficult but definitely much more detailed book by F. L. Pillar elementary quantum chemistry. And we will see what happens when we go higher up the ladder and try to do higher order perturbations this graphic is from the cover of an album stairway to heaven I leave it to you to find out which band had published this album.

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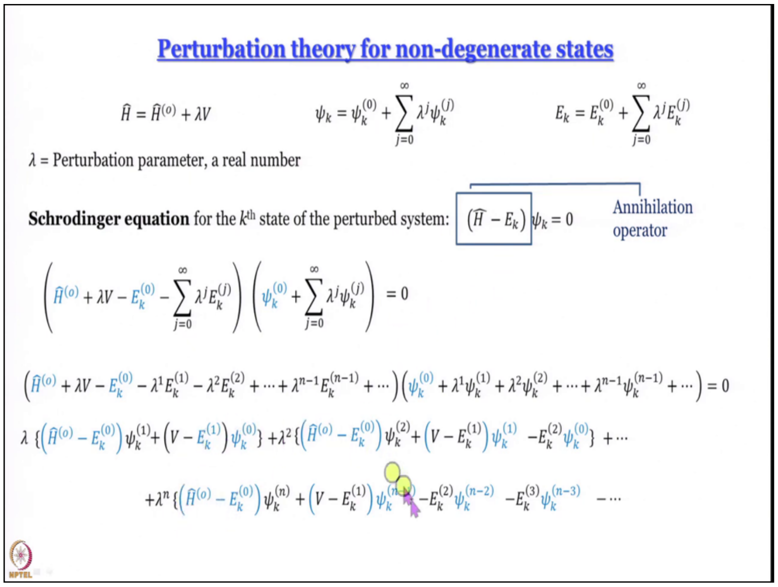

So we are discussing perturbation theory for non degenerate states which means that very quickly in one of the next modules will also have to talk about degenerate states because the treatment will be little different essentially we will get similar results. But degeneracy has to be factored later on. For now we do not worry about that we consider every state has a unique energy we do not have any two states with the same energy.

For that now what we are doing is we are writing this perturbation to the Hamiltonian a little differently. Earlier the convention we had used is Hamiltonian is equal to 0th order Hamiltonian first plus first order plus second order so on and so forth that gives us many terms. Now we will write it in a more compact form. We will just write the Hamiltonian to be unperturbed Hamiltonian plus lambda into V.

Where lambda is a perturbation parameter I mean I could have written just V which is perturbation and I could have said that whatever is the perturbation first order second order third or the order everything is there in V. But lambda acts as a dial as Pillar has said it very nicely regulator I mean you have regulators in fan you want higher fan speed you just turn the regulator a little bit.

So, this is like a regulator of perturbation. If you want to go higher up in perturbation just have to increase the value of lambda. The expressions for wave function and energy are more or less the same wave function as Psi k the kth state wave function is equal to the unperturbed wave function for that state plus a sum of lambda to the power j, jth order corrected correction term for the wave function of kth level.

Lambda to the power j Psi k jth that is how we write it, so the coefficient becomes lambda to the power j. So, this lambda gives us a module to handle the entire problem using sort of one parameter that is the good thing about it. And we will see how we can get nice systematic results by taking this approach. Expression for energy is very similar to the similar informed the expression of the wave function E k is equal to unperturbed energy for the k state plus sum over lambda to the power j E k jth.

So this is the formulation. Now what we will do is we are going to write Schrodinger equation for the kth state of the perturbed system and we can write it in this form. Well H Psi equal to E Psi of course, so I can bring everything to the left hand side have 0 on the hand side and then on the left hand side I get this operator H hat minus E k operating on Psi k. So, we have encountered this operator earlier what I did not tell you explicitly is that when this happens when an operator operates on a function to produce 0 that means it has made the function vanish or annihilate.

So this kind of an operator is called an annihilation operator. Annihilation operators are used in quantum mechanics quite frequently to simplify complex problems. So, this is the annihilation operator and we are going to refer to this form of annihilation operator many times in our discussion in this module and may be the next. So, what we do now is that we expand this instead of H hat we write the expression H hat 0th plus lambda V instead of E k we write E k 0th plus this sum of perturbation terms.

Instead of Psi k we write this expression here, let me do that this is what the Hamiltonian becomes 0th order Hamiltonian plus lambda V minus this is the expression for E k 0th order energy for remember the kth state minus the sum of the perturbation terms. So, this is the Hamiltonian minus the energy that annihilation operator. What is the wave function and perturbed wave function plus the sum of the perturbation terms that of course will be equal to 0.

Now you see I have written these something in blue the unperturbed terms are written in blue because that helps us see something that will happen naturally later on. So, I expand this now instead of this summation I want to write well Pillar has not written it in so much of detail but I thought I just write it once so that in case you are scared with some summation signs this might be a little easier. So, I just expanded this lambda to the power one first order correction to energy minus lambda square second order correction to energy so on and so forth.

Lambda to the power n minus one n minus one net correction to the energy and so on and so forth. There is a reason why I have written n minus one and you might wonder what happened to this j equal to 0 term the j equal to 0 time is subsumed here, you can think V it is not really there is no point in writing it separately. Similarly we expand the wave function as well. Now we are going to make this operator operate on the wave function and what we will do is we will collect the terms in different powers of lambda.

While doing that let us look at the blue terms what happens when I write H hat 0 minus 0th order energy operating on 0th order wave function, what do I get is Schrodinger equation so remember H hat 08 minus E k 0H is actually annihilation operator for the unperturbed 0th order wave function. So, that term is going to vanish, will get something like this I have not written it. So, first let me collect all the terms the coefficient in lambda.

And while doing that again I will get a summation in the coefficient of lambda lambda to the power 2 lambda to the power 3 so on and so forth. I will start writing in the highest order perturbation wave function and go down. So, lambda is multiplied by what? The first thing I write is where is lambda? In the right hand side I cannot take the second order correction because lambda square is there.

The highest order correction that is required is first Psi k first is multiplied by lambda and that has to be multiplied has to be operated upon by H hat 0 minus E X hat so this is the first term that I get in the coefficient for lambda. Once again as usual please feel free to stop the video get your pen and paper work this out yourself that is the only way you will understand properly do not try to see these modules at a stretch here up to this write it out then restart.

It will take a little bit of time but then you will understand properly but is there anything else in lambda I have taken this and I have written this 0th order Hamiltonian minus 0th order energy is there anything else that I should write? Yes we have this 0th order wave function also Psi k 0th when that is operated by this say lambda V lambda V operating on Psi k 0th that will also yield a lambda. Remember lambda is a real number constant so it will go out when the operators operate so lambda V operating on Psi k 0th and there is something else minus E k first order that also is multiplied by lambda, lambda to the power 1 that also operates on Psi k 0th so this is what we get.

The coefficient of lambda is unperturbed Hamiltonian minus unperturbed energy operating on first order correction to wave function plus V minus first order correction to energy operating on 0th order wave function very nice systematic expression and as you see it is going to get more and more systematic as we go ahead. What is the second one next I want to collect all the coefficients for lambda square.

So I write lambda square what will I get in lambda square where do I have lambda square here as usual we are going to write the highest order highest order correction in wave function first. So, here I have a lambda square so lambda square goes out this Psi k second to get lambda square out of the bracket has to be operated upon by the unperturbed wave function minus the unperturbed energy. So, exactly same operator as the first term in the coefficient of lambda is observed in the first term of the coefficient of lambda square same operator but different wave function.

The wave function for the coefficient of lambda was first order correction to the wave function Psi k first the wave function for the first term in coefficient of lambda lambda square is second order correction to Psi. What else do I have do I have anything in first order correction to the wave function. So, here I have lambda Psi k first if that is operated upon by again lambda V then lambda square will come out.

And if it is operated upon by this lambda into E k first then once again lambda square will come out. So, the second term is V minus E k first operating upon Psi X Psi k first. Once again you see the operator is the same in the second term as it was in the second term for the coefficient of lambda. What is the third term is there anything else necessarily now we have to look for the 0th order wave function where we get lambda square.

See Psi k 0th where will I get lambda square when E k second operates on Psi k 0 then I am going to get it. There is no other term in the operator that will give me lambda square upon operating on the unperturbed 0th order wave function. So, this is what we get and that is the complete expression for the coefficient of lambda square. So, you see what is emerging as a trend is that the first term has the same operator.

And it operates on the nth order wave function any other correction to a function where n is the exponent to which lambda is raised. The second term is V minus E x first operating on well here it is Psi X 0 here it is Psi X first so well one is two minus one and 0 is 1 minus 1, so again this is exponent minus one and then you have this summation. So, it is not very difficult to understand I hope that when we talk about the coefficient of lambda to the power n then the expression is going to be again the first term will be the same operator H hat 0th minus E k 0 operating on this time Psi k nth.

Remember this nth means is the same exponent as lambda same exponent as to which the lambda is raised in that term. What will the second term be the same operator V minus E k first operating on the next wave function in series next correction term in series V minus E k first operating on Psi k n minus 1H. What will the third term be, now it will be minus E k second Psi k n minus 2th and so on and so forth. This is the general expression for the coefficient of lambda to the power n.

So what we will do is we will clean up this projection a little bit we will take this expression and we are going to substitute up here. Well let us not forget the; to complete it equate it to 0 and this is what it is. So, we have written this expression we have expanded we have got rid of the unperturbed Schrodinger equation and we have got this equation left hand of which is written in terms of different powers of lambda.

Lambda to the power 1 lambda to the power 2 so on and so forth lambda to the power n so on and so forth if there is more than n. Now we have encountered this earlier also see remember something we are doing exactly the same thing that we have done earlier. It is just that we are expanding the scope that is why the expressions are little more complicated that is all. So, now if this is the case then the condition for this lambda to be non-0 is that the coefficient of each power of lambda must individually be equal to 0. So if I take the general coefficient then this whole thing has to be equal to 0.

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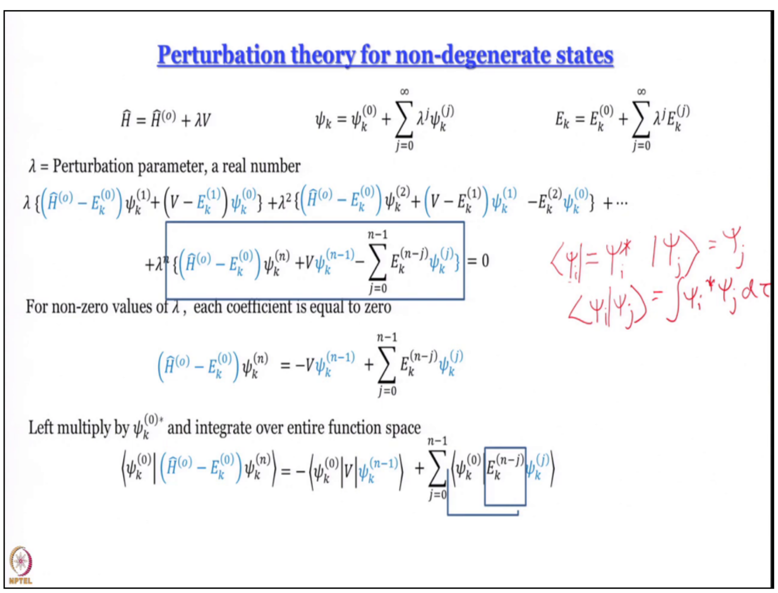

Let us equate that to 0 and this is what we get this is a very, very important equation and we will have to refer to it time and again in the subsequent discussion. So, what have I done I have taken the coefficient of lambda to the power n and we have equate it to 0 because lambda is non 0 so every coefficient; coefficient of every power of lambda must be equal to 0 by themselves so I have H hat 0th minus E k 0th operating on Psi k nth is equal to minus V operating on Psi k n minus 1th plus summation j equal to 0 to n minus one E k n minus jth operating on Psi k jth.

Extremely useful equation is going to come handy time and again do we have to remember it please do not there is absolutely no need to remember please try to understand. So, now when we have something like this to simplify as we have said earlier the most common technique in quantum mechanics is left multiply by a complex conjugate of an appropriate wave function integrate over the function space.

The appropriate wave function in this case is Psi k 0th we are working with the k state. So, it is natural that we are going to left multiply by complex conjugate of one of the wave functions associated with this state and the best thing to do is to take Psi k0 because that is the unperturbed wave function that is going to simplify the problem as we will see. So, left multiply by Psi k0 and integrate over all space we are going to write the rest of the discussion in bracket notation.

I hope we have not forgotten bracket notation I think we have said it several times but since we have we are recording it over some time I have also forgotten to what extent we have written what we say is this if I write say Psi this is called the bra vector Psi bra vector means in essentially Psi star this is called get vector Psi k vector essentially means Psi and we will write Psi i and Psi j then when we combine if we write this is called bracket brass ii get Psi j this essentially means integral over all space Psi i star Psi j d tau it is as simple as that.

I think we have said it several times earlier but still just in case somebody is confused. So, we left multiply and integrate over all function space this is what we get Psi k 0th remember when I write Psi k 0th in bra vector it essentially means its complex conjugate please do not get confused about that multiplied by H 0th minus E k 0th operating on Psi k nth usually we write another vertical draw another vertical line here to just make it look good.

Right hand side what I have got I have got minus Psi k 0 star V Psi k n minus 1th integrated over all space and I have got summation j equal to 0 to n minus 1th see I am multiplying by one quantity right so there is no problem there is a specific quantity Psi k 0s no problem in taking it inside and then integrating. So, I have sum of integrals each of it which is Psi k0 E k n minus jth Psi kj. Let us see how this helps simplify the situation.

To do that we realize we understand that this E k n minus j is a constant it is a value of energy right value of some correction to energy its a number. So, I can bring it out bring it out outside the integral but not outside the summation sign. The sum summing over j here we have n minus j so we cannot bring it outside the summation inside the summation but outside the integral. Good thing is then the integral becomes Psi k 0 0th Psi k jth and as we will see that simplifies to a very beautiful expression, we will see.

What about the left hand side? In the left hand side these two wave functions can change places if we use the turnover rule that we had studied in one of the earlier modules as the property of hermitian operator remember I did not tell you explicitly at that time that this is called turnover rule but here it is for you, you know what it is. So, I can just interchange Psi k0 and psi k nth, why? Because we know that H 0th minus E k 0 will operate on Psi k 0 not only that it will make it 0 remember annihilation operator.

So we use the turnover rule and we get this expression. We get integral Psi k nth 0th minus E k 0th operating on Psi k 0 integral over all space is equal to minus Psi k 0th star V Psi k n minus 1th integrated over all space plus this summation where I have taken the integral out of the in sorry I have taken this energy out of the integral sign but definitely not outside side the summation.

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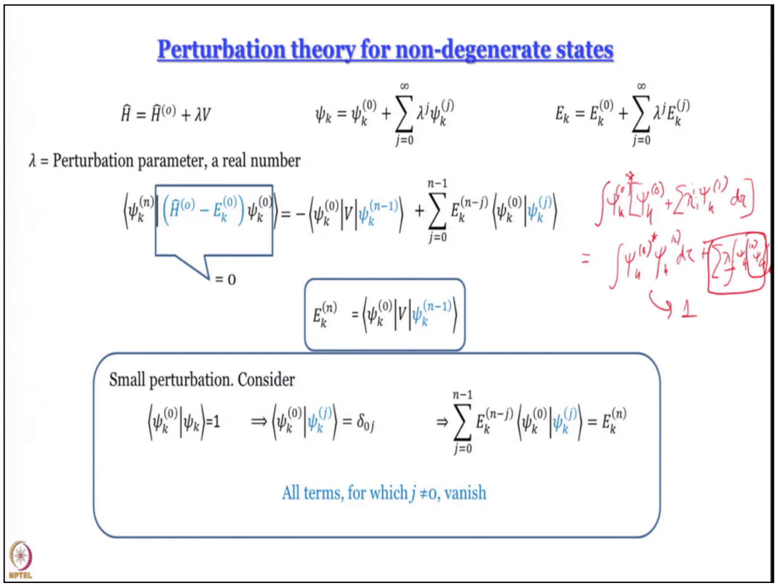

Now life is getting a little simpler. So, this is remember annihilation operator operating on the wave function that is going to become 0. So, the entire left hand side becomes 0. What about the right hand side? In the right hand side I am left with this integral Psi k 0th V Psi k n minus 1th and I am left with this summation. So, we now need to think how this summation pans out. So, we need to see whether it is possible to simplify the summation a little more. Let us see, to do that we remember that perturbation theory is valid only for small disturbances and in fact we have said this earlier in some other context. So, it is without any loss in generality we can consider that integral Psi k 0 star Psi k is equal to 1, does this make sense. Integral what I am saying is Psi k 0th for the time being I will be lazy and not write the star if it is complex we have to write the star let us not worry about it.

This multiplied by instead of Psi k what will I write I will write Psi k 0th plus well summation lambda i Psi k pi s lambda E to the power i d tau so what does it boil down to it boils down to integral of Psi k 0th I will write star what is there Psi k 0 star Psi k 0th integrated over all space plus now see I will get summation some lambda will be there I am going to power whatever integral Psi k 0th Psi k ith d tau now remember this is small yeah remember this is small.

So we might as well neglect this term and this we said to be approximate to be equal to 1 because the entire normalization constant normalization constant for the entire wave function Psi k has to hold so we consider Psi k integral Psi k 0 Psi k to be equal to 1. So, what we have also done here explicitly is that we have written integral Psi k 0th Psi k jth is equal to delta 0 j see in all these integrals only when j was equal to 0 then it survived and it was 1 whenever j was anything other than 0 it was 0.

So we write this delta function Psi k 0th Psi k j well Psi k 0 star Psi kj integrated over all Psi kj integrated over all space turns out to be delta 0 j, 1 for j equal to 0 and 0 for j non 0 all other values of j. So, how does that help our cause what are we trying to find out we are trying to evaluate this integral sorry I we are trying to evaluate the summation. In this summation we have integral Psi k 0th Psi k jth.

So what are we saying here we are saying here that that integral turns out to be Kronecker delta delta 0 jth okay. So, that is great because in that case in this summation only one term will survive the term for which j is equal to 0 everything else is vanish going to vanish. So, for term when j equal to 0 what happens this integral is 1, fine and here we put 0 you get E k nth and everything else vanishes you get E k nth. So, this integral that we have obtained here integral Psi k 0 star V Psi k n minus 1 it that integral turns out to be the expression for the nth order perturbation to the energy of the kth state.

Okay see so far we had only done first order perturbation. Now we have got an expression for the nth order perturbation energy correction to energy for nth order perturbation and look at this expression it is remarkably similar to what we had got for the first order perturbation. Not only that what we got for the first order perturbation is not surprisingly a special case of this nth order perturbation.

Just put n equal to one what will you get this becomes Psi k 0th was not that the expression for the first order perturbation term first order correction to energy integral Psi k 0 star V Psi k 0 so this here gives us the expression very nicely for the nth order perturbation of for the correction to energy because of nth order perturbation. Well we are almost done with this discussion but we would like to close the module here come back for a shorter module.

So that you get time to go up go through this and make sure that all of us have understood everything before embarking on the next part of the story.