Quantum Chemistry of Atoms and Molecules
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Lecture-41
Perturbation Theory for degenerate states

In the course of quantum chemistry of atoms and molecules some of us might be wondering are we not wandering too far away from atoms because it is been a while that we have talked about atoms as such. Well we will talk about a little bit of atoms in this module or the next but what we are doing right now is that we are learning the tricks by which we can understand how to go about handling atoms and molecules for that matter.

So we have talked about perturbation theory so far we will recap it in a moment. Today we are going to learn about perturbation theory of degenerate states.

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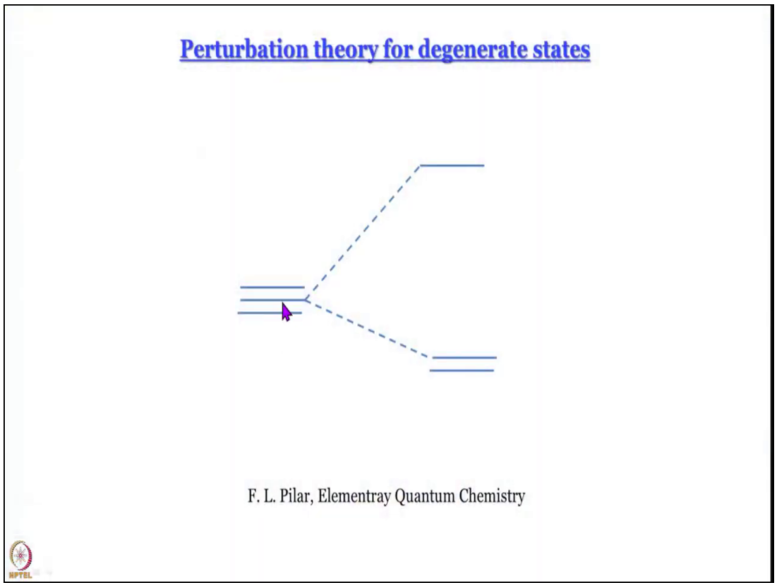

Perturbation theory for degenerate states

F. L. Pilar, Elementray Quantum Chemistry

Of course all of us know what degenerate states are these are degenerate states for example states that have the same energy perturbation more often than not changes the energies of degenerate states with respect to each other that is called lifting of degeneracy. So, you can think of such examples that you know say Zeeman's effect or stark effect application of a magnetic field or an electric field which changes the energies of orbitals that are earlier degenerate in such a way that they are no longer degenerate.

So, this is one important reason why we must acquaint ourselves with perturbation theory of degenerate states. In fact think of say metal ion complexes think of a free metal ion all that d orbital’s that degenerates. The moment you bring in this octahedral field or tetrahedral field or whatever field the d orbital’s split into 2 or more groups. So, lifting degeneracy is a very important thing that perturbations often do but it is not necessary that degeneracies will always be lifted as we will see in the 2 examples that we discuss in this context.

In one degeneracy will not be lifted at all but the energies will be affected in the other some of the degeneracies will be lifted like what we have shown here. So, in this schematic we have taken 3 energy levels and we are saying that some kind of a perturbation affects the system in such a way that in the perturbed system 2 of the energy levels have lower energy and one energy level has higher energy of course very center is same.

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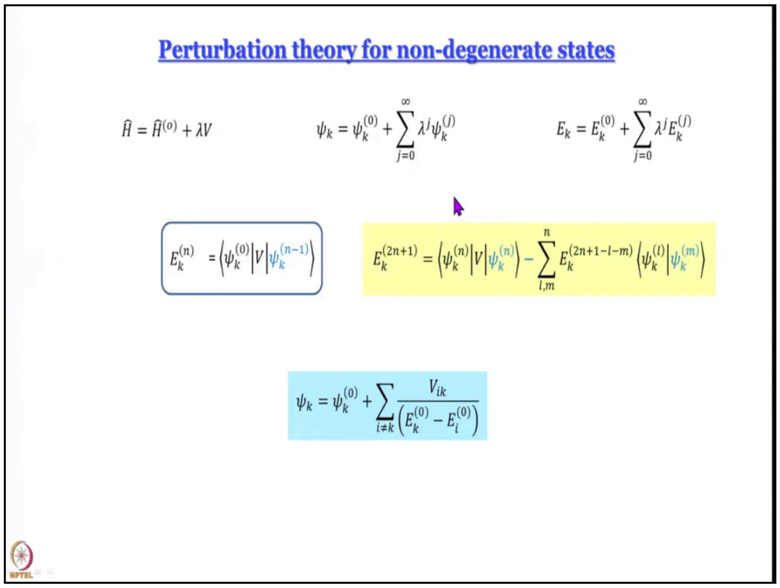

Perturbation theory for non-degenerate states

$$\hat{H} = \hat{H}^{(o)} + \lambda V \qquad \psi_k = \psi_k^{(0)} + \sum_{j=0}^{\infty} \lambda^j \psi_k^{(j)} \qquad E_k = E_k^{(0)} + \sum_{j=0}^{\infty} \lambda^j E_k^{(j)}$$

$$\boxed{E_k^{(n)} = \left\langle \psi_k^{(0)} \middle| V \middle| \psi_k^{(n-1)} \right\rangle}$$

$$E_k^{(2n+1)} = \left\langle \psi_k^{(n)} \middle| V \middle| \psi_k^{(n)} \right\rangle - \sum_{l,m}^{n} E_k^{(2n+1-l-m)} \left\langle \psi_k^{(l)} \middle| \psi_k^{(m)} \right\rangle$$

$$\psi_k = \psi_k^{(0)} + \sum_{i \neq k} \frac{V_{ik}}{\left(E_k^{(0)} - E_i^{(0)}\right)}$$

Before we go there let us remind ourselves briefly about what the salient points that we have learnt in our discussion of perturbation theory of non degenerate states. So, first of all we have learnt that you have to write the Hamiltonian as the unperturbed Hamiltonian plus a perturbation term we have written it in some other form earlier. Now the form that we are hand dealing with sorry about that the form that we are dealing with now is this Hamiltonian of the perturbed system is unperturbed Hamiltonian plus lambda into V where V is the perturbation potential and lambda is a parameter that we can regulate to increase or decrease the amount of perturbation that is there.

And lambda finds its place in the expression for corrected wave function and corrected energy here we have lambda k is equal to lambda k 0th plus sum over j equal to 0 to infinity lambda to the power j multiplied by psi k jth similar expression for energy we have learnt this. We obtained this very important relationship very important expression for the expression for the energy which is nth order correction to the energy.

We learnt this rather important expression for nth order correction to energy E k nth and that is equal to integral psi k 0th star V psi k n – 1th integrated over all space. Here if you put n equal to say one then the second wave function also becomes psi k 0th. Remember what k is k denotes the energy level or the quantum number that decides the energy level. So, for hydrogen atom k is going to be n for harmonic oscillator k is going to be V.

So, this is the expression we did not derive the expression but we at least showed it to you and we told you that it is possible to come up with this 2n + 1th correction term for energy in this manner and we found an expression for this correction to wave function as well in this manner V i k is this interaction integral you can say of involving ith and kth terms.

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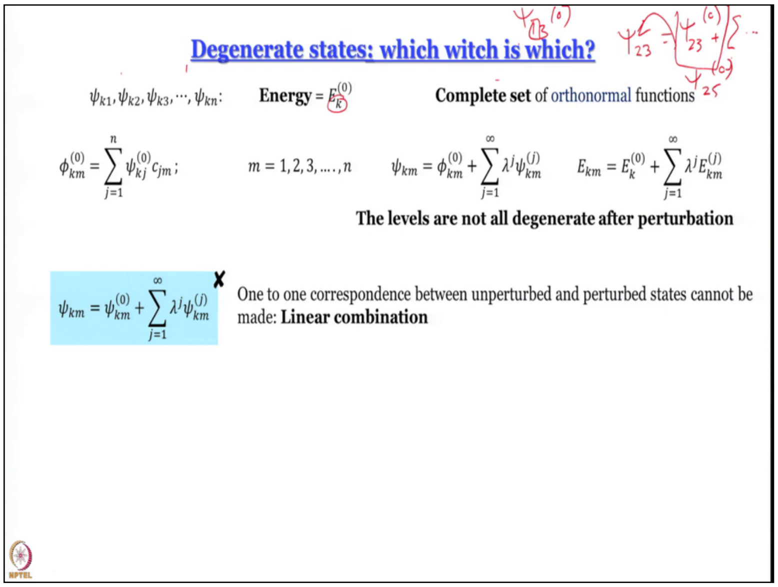

Degenerate states: which witch is which?

$\psi_{13}^{(0)}$ $\psi_{23} = \psi_{23}^{(0)} + \sum \ldots$ $\psi_{25}^{(0)}$

$\psi_{k1}, \psi_{k2}, \psi_{k3}, \cdots, \psi_{kn}$: **Energy** = $E_{\boxed{k}}^{(0)}$ **Complete set** of orthonormal functions

$$\phi_{km}^{(0)} = \sum_{j=1}^{n} \psi_{kj}^{(0)} c_{jm}; \quad m = 1, 2, 3, \ldots, n \quad \psi_{km} = \phi_{km}^{(0)} + \sum_{j=1}^{\infty} \lambda^j \psi_{km}^{(j)} \quad E_{km} = E_k^{(0)} + \sum_{j=1}^{\infty} \lambda^j E_{km}^{(j)}$$

The levels are not all degenerate after perturbation

$$\psi_{km} = \psi_{km}^{(0)} + \sum_{j=1}^{\infty} \lambda^j \psi_{km}^{(j)}$$ ✗

One to one correspondence between unperturbed and perturbed states cannot be made: **Linear combination**

Now when we go over to the degenerate states then we encounter an interesting situation here for the kth level that is for the level associated with energy say E k 0th we do not have one wave function. We have say n number of wave functions we designate them psi k 1 psi k 2 psi k 3 psi k n and so on and so forth. So, please do not get confused here in fact we are going to drop this k little later k here denotes the energy level.

The second number denotes the index of the wave function right. So, you can think like this think of hydrogen atom in case of hydrogen atom let us say we are talking about n equal to 2 in n equal to 2 you have several l levels do not you. So, I can have n equal to 2 and that means that the energy level we are talking about is E 2 0ths and we have associated with n equal to well I will make it simple sorry n equal to 1 let us say and we have to write too many terms if its n equal to 2.

So I change it to n equal to 1 say let us say n equal to 1 to change that as well so for that we know that l is equal to – 1, 0, +1 right. So, how many energy states do I have how many wave functions do I have yeah how many wave functions you have that is better corresponding to this energy E 1 0th I have 3 so I am calling them after this fashion psi 1 1 psi 1 0 psi 1 - 1 if i write like this that means I am writing in terms of n l so this is the psi n l form.

Or I could do something like this I could simply not write l but just write a sequence and simply say psi 1 1 psi 1 2 psi 1 3 so 1 2 3 are well like roll numbers indexes for the wave functions here. So, what I am saying here is that this - 1 this is given the index 1, 0 let us say is given the index 2, 1, n equal to 1 is given the index 3 and so on and so forth. So, that is how we are writing so please do not get confused here.

So all these n number of wave functions that I have written here actually have the same energy E k 0th and of course you can have wave functions that are not orthonormal to each other but we can always take proper linear combinations and arrive at the orthonormal functions. And we have discussed many times why we like to handle orthonormal functions. Because they are the coordinates they are the functions that define the function space completely.

So we have to take complete set of orthonormal functions let us say this psi k 1 to psi k n constitutes the complete set of orthonormal functions all with energy E k 0th this is my unperturbed system. And this is the deviation from the case of non degenerate states remember let me it is this because something is going to come up there and it is going to look very ugly. So, complete set of orthonormal functions and the problem now is that I am not allowed to write the expression I wrote earlier psi k m cannot be written as psi k m 0th plus sum over j equal to infinity lambda to the power j psi k m jth.

Why not because these are all indistinguishable from each other I do not see a wave functions right i cannot see a wave function how do I know which wave function I am handling from energy because energy energy is an experimentally measurable quantity. The problem is all these n number of wave functions have the same energy so we are back to that which, which is which kind of situation.

Remember we had encountered this when we were talking about multi electron atoms when we have 2 electrons and we say that we do not know whether one electron number one is in one s orbital electron number 2 is in 2 s orbital or the other way round right. When we talked about helium ground state excited state we encountered such a situation. Here in a little different context we have the same thing.

These wave functions are actually indistinguishable from each other because they are the same energy. So, if I write like this then i am saying that this let us take some wave function here let us say i am talking about hopefully here nothing will come so i will write here I want to know what is say psi 2 3 if I write psi 2 3 equal to psi 2 3 0th plus sum over all these things then what I am implying is that out of all these wave functions only psi 2 3 0th.

The 0th order wave function psi contributes to the perturbed wave function psi 2 3 how do you know who has said that you cannot have any contribution from say psi 25 0th, can I have a contribution from psi 1 ok what is this 1 2 3, I wrote so can I have a contribution from psi 1 3 0th actually I cannot because the moment I change the first index the first index remember stands for k the index of energy, energy will change it will no longer remain degenerate.

But if I am talking about psi 2 3 there is no way in which I can say confidently that psi 2 3 will a contribution only from psi 2 3 0th and not from say psi to ten 0thth or psi to one 0th or any other wave function which has the energy E 2 0th. So, what do we do in such a situation well we do what we did earlier we take a linear combination. What are the coefficient coefficients of linear combination how do I find them we will worry about those later but to start with the way to go is take a linear combination.

So that we do not rule out a priory the possibility that other index wave functions unperturbed wave functions with other indexes also contribute to this perturbed function. So, we take a linear combination like this psi k m 0th is equal to sum over j equal to 1 to n psi k j 0th c j m, c j m is the coefficient. So, what kind of coefficient it is the contribution of the jth wave function in the among the wave functions that have energy k0th in the mth wave function of the newly created set and m of course has to be equal to 1 2 3 4 until n.

So just take a linear combination right now let us not bother about the form of the coefficient and how do we know it and we will talk about it later. But if I write this then I am safe psi k m the perturbed wave function is equal to phi k m 0th plus this correction term. See what I have done is in the correction term I have written it in terms of psi it does not matter its you do not have to write phi there because after all phi is generated by taking linear combination of psi.

And this is how we write the expression for energy also. Now so what do I get I get n number of perturbations n number of expressions for this correction to energy so I get n number of wave functions which may or may not have the same energy right. When will they have the same energy when the all the energy levels or some of the energy levels are increased or decreased by an equal amount of energy as a result of the perturbation.

When will they not have degeneracy? When different levels are affected to different extents, so we will have a look at both kinds of systems but before that let us work out this nice expression.

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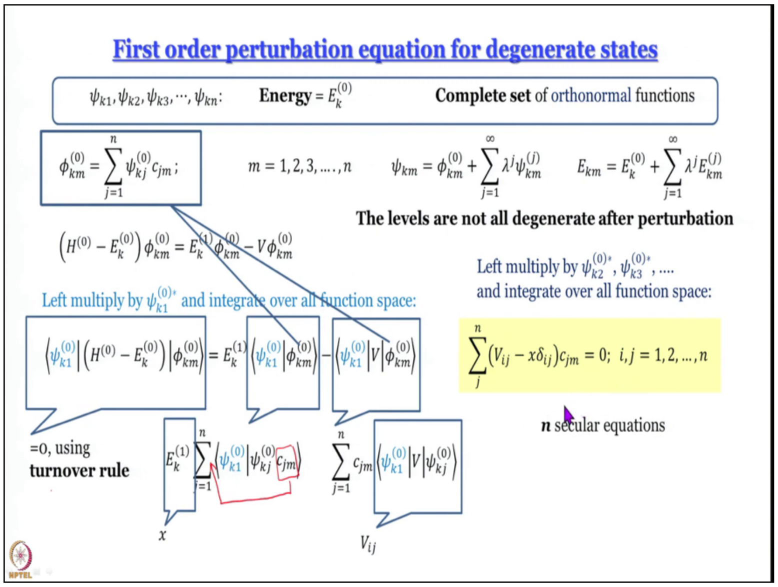

First order perturbation equation for degenerate states

$\psi_{k1}, \psi_{k2}, \psi_{k3}, \cdots, \psi_{kn}$: **Energy** = $E_k^{(0)}$ **Complete set** of orthonormal functions

$$\phi_{km}^{(0)} = \sum_{j=1}^{n} \psi_{kj}^{(0)} c_{jm}; \quad m = 1, 2, 3, \ldots, n \quad \psi_{km} = \phi_{km}^{(0)} + \sum_{j=1}^{\infty} \lambda^j \psi_{km}^{(j)} \quad E_{km} = E_k^{(0)} + \sum_{j=1}^{\infty} \lambda^j E_{km}^{(j)}$$

The levels are not all degenerate after perturbation

$$\left(H^{(0)} - E_k^{(0)}\right) \phi_{km}^{(0)} = E_k^{(1)} \phi_{km}^{(0)} - V \phi_{km}^{(0)}$$

Left multiply by $\psi_{k1}^{(0)*}$ and integrate over all function space:

$$\left\langle \psi_{k1}^{(0)} \middle| \left(H^{(0)} - E_k^{(0)}\right) \middle| \phi_{km}^{(0)} \right\rangle = E_k^{(1)} \left\langle \psi_{k1}^{(0)} \middle| \phi_{km}^{(0)} \right\rangle - \left\langle \psi_{k1}^{(0)} \middle| V \middle| \phi_{km}^{(0)} \right\rangle$$

=0, using **turnover rule**

$$\underbrace{E_k^{(1)}}_{x} \sum_{j=1}^{n} \left\langle \psi_{k1}^{(0)} \middle| \psi_{kj}^{(0)} c_{jm} \right\rangle \qquad \sum_{j=1}^{n} c_{jm} \underbrace{\left\langle \psi_{k1}^{(0)} \middle| V \middle| \psi_{kj}^{(0)} \right\rangle}_{V_{ij}}$$

Left multiply by $\psi_{k2}^{(0)*}, \psi_{k3}^{(0)*}, \ldots$ and integrate over all function space:

$$\sum_{j}^{n} (V_{ij} - x\delta_{ij}) c_{jm} = 0; \quad i, j = 1, 2, \ldots, n$$

n **secular equations**

This is what we have now what i will do is will write the first order perturbation equation for degenerate states. You know how to write first order perturbation equations. We have done it earlier so I am skipping a few steps but i hope it will not be a problem for anyone so this is what it is H 0th - E k 0th operating on phi k m 0th equal to E k first order multiplied by phi k m 0th - V operating on phi k m 0th remember I have jumped steps.

So I strongly recommend that you please work this out yourself because otherwise when I say things in the flow of the lecture you feel is as if you have understood everything. But then if you sit down with a pen and paper and try to work it out yourself then if you do not have a question about how I have done things that means you have not perhaps understood everything. You should be surprised you should be puzzled you should get confused should have questions then only you will understand this.

So please work this out yourself even though I have skipped it you should not and you should work it out after the fashion that we use for the non degenerate case. So, this is the first order perturbation equation let us see what we get from here. So, as usual like what we did earlier we are going to left multiply by psi k 1 0th well complex conjugate of that and integrate over all function space what do I get? I write psi k 0th well complex conjugates of that on the left hand side integrate that will be the left hand side.

Right hand side when I integrate I get 2 terms in one this E k first is going to come out because it is a constant. Second one will involve a triple product second integral of phi k one 0thth V and phi k m 0th. So, this is what we get not very difficult to understand. Now what do we do now well first of all you might remember that this H 0th - E k 0th is the annihilation operator not for the phi 0th terms but for the psi 0th terms right.

And I can easily get psi 0th and phi 0th to interchange using a tool that is by now familiar to us the turnover rule. So, when h 0thth minus E k 0th operates on psi k one 0th I get 0th then we do not even have to bother about the other wave function. So, left hand side is taken care of that is equal to 0th what am I trying to do I am trying to find an expression for the first order correction to energy right. Now the next step obviously is to take this expression of the phi's phi 0th and plug it into this integrals.

Plug in this linear combinations into this integrals and this is what you get. Well actually what I should also do is this, this coefficient is a constant. So, it has no business being in the bracket so we will bring it outside the bracket but will not bring it outside the summation all right please do not forget there is this cjm j is there so if you bring out bring it out of the summation then it has no meaning. So, will not do that; we will bring it outside the integral but inside the summation.

Next this one is going to become again phi k m 0th is replaced by sum over j equal to n sum over j equal to one to n phi k j 0th c j m, c j m is a coefficient so I bring it outside the integral but not outside the summation sign all right. So, when we do that we get this well we have to remember something, we have to remember that this size are actually your I should have written 0th everywhere this for I mean please note that.

But when we remember that these are actually orthonormal functions and when we plug them in then what will we get? We will get something like this right. We will get this well let us see what we will get? But before that will repeat the operation for 2 3 4; and so on and so forth. So, when we integrate over all function space this is what we get? We get n number of what are called secular equations.

Remember there is one summation over j right that gives you from left to right of n of the left hand side of an equation there is another summation over i let us not forget that. So, this is what we get. Now how do I solve this? Remember to make things simple we have written this as V i j and also we have written this first order correction to energy as x. Now I hope you see that this x here is multiplied by delta i j why because we are working with a complete set of orthonormal functions.

So when i is equal to j then we are going to get one the integral will be equal to one when i is not equal to j then the integral is going to be 0th which integral this integral not this because here you have this V in between this one is going to be either + 1th or - 1 that is written as delta i j.

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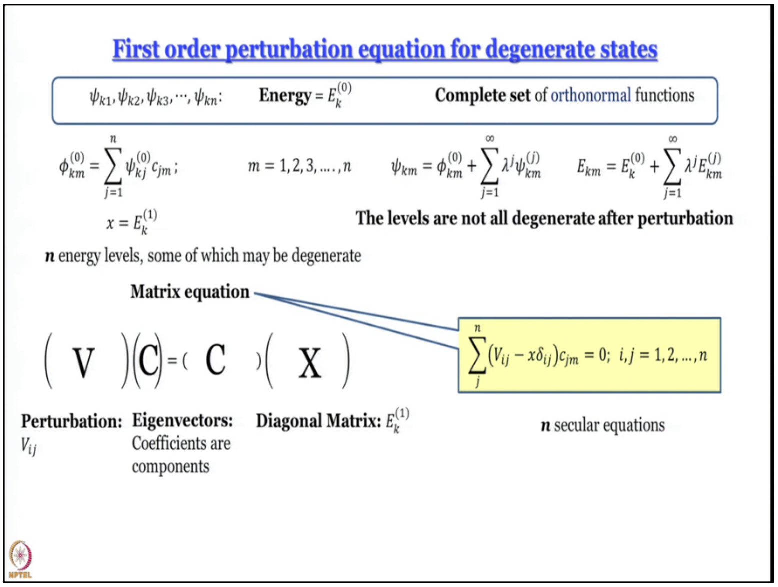

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$x = E_k^{(1)}$

The levels are not all degenerate after perturbation

n energy levels, some of which may be degenerate

Matrix equation

$$(V)(C) = (C)(X)$$

$$\sum_{j}^{n} (V_{ij} - x\delta_{ij}) c_{jm} = 0; \quad i, j = 1, 2, \ldots, n$$

Perturbation: V_{ij}

Eigenvectors: Coefficients are components

Diagonal Matrix: $E_k^{(1)}$

n secular equations

So, now this is what we have got so far x equal to first order correction of energy and we want to find a better expression for that. Great so as we said we have created this n energy level some of which may or may not be generate. Now we write this in secular equations in the form of a matrix. Whenever we have a system of secular equations always write it in the matrix form and when we do that this is what you get.

We get V matrix multiplied by c matrix is equal to c matrix multiplied by x matrix what is V? V is the matrix whose elements are the perturbation terms V i j. So, see how beautifully this problem is gets formulated it becomes a matrix equation. So, V i j essentially i and j denote the position of V i j in the matrix V capital V. So, this perturbation takes up these i j positions in the matrix c's are called the eigenvectors.

If you want to know more about vectors please go through our lectures on group theorem chemistry so eigen vectors, eigen vectors are essentially coefficients. So, the coefficients are the components and capital x turns out gives us the values of the first order correction to the kth level energy right and this is also diagonalized. So, beautiful form can be solved by many different techniques no worries really.

Now the field is set for discussion of 2 examples that we are going to do next day but before that the salient points. First of all the degenerate states are such that several eigen functions can actually have the same energy. so, you cannot express a perturbed wave function as a; an unperturbed of wave function just, like that plus the correction term you have to generate a linear combination of the unperturbed wave functions from where we are going to begin.

Because there is no saying which unperturbed wave function has contribution in which perturbed wave function it is not just f wave function and its perturbed form they are indistinguishable so many can make contributions that is point number one. Point number 2 is when you accept that you are going to get this very nice matrix equations in which this x values are going to turn out to be the x values here first order correction to energy.

So that is where we stop this module today in the next module we are going to discuss hopefully 2 examples, one is non rigid rotor the other is stark.