Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-42
Application of Perturbation Theory for degenerate States

In this module we are going to learn about 2 applications of perturbation theory of degenerate states in atomic systems well atomic and molecular systems.

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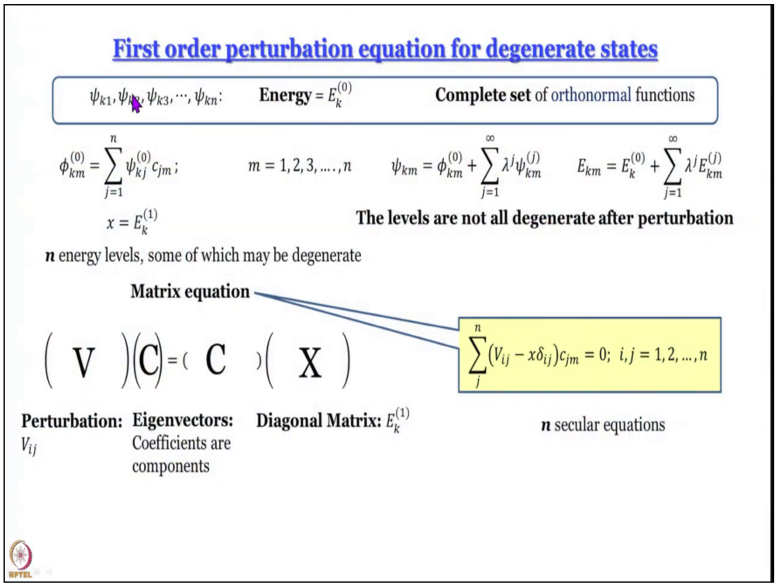

First order perturbation equation for degenerate states

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

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

$x = E_k^{(1)}$

The levels are not all degenerate after perturbation

n energy levels, some of which may be degenerate

Matrix equation

$$\big(\; V \;\big)\big(C\big) = \big(\; C \;\big)\big(\; X \;\big)$$

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

Perturbation: V_{ij}

Eigenvectors: Coefficients are components

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

n secular equations

But before that let us just remember where we had stopped in the last module we developed this first order perturbation theory for degenerate states. We understood that for degenerate states where you have n number of wave functions associated with the same unperturbed energy where the Psi denote complete set of orthonormal functions you cannot write the perturbed energies as of wave functions as psi 0th plus something.

First of all you need a linear combination because you do not know which of these functions is going to contribute in which part of wave function. They are all identical indistinguishable so well functional forms may be different but indistinguishable in the sense that energy is same. So, there is no way in which we can say that one particular wave function will contribute and the others will not cannot do that.

So this is what it is we write the wave function we start with a linear combination of a function then go to the usual definition of our corrected wave function usual definition of uncorrected energy of corrective energy. And then we arrive at this matrix equation in which we see perturbation V I J operates on this eigen vectors to give the E k first order energies as the diagonal elements of this matrix X this is something I think I forgot to say earlier this X is the matrix of first order corrections to energies.

And here the beauty is you can see from this expression here that all the off diagonal elements are going to be 0 delta ij remember. So, we are going to have this diagonal matrix where the diagonal elements are only going to be non 0 and they are going to give you the values of first order corrections to energies, we start from here.

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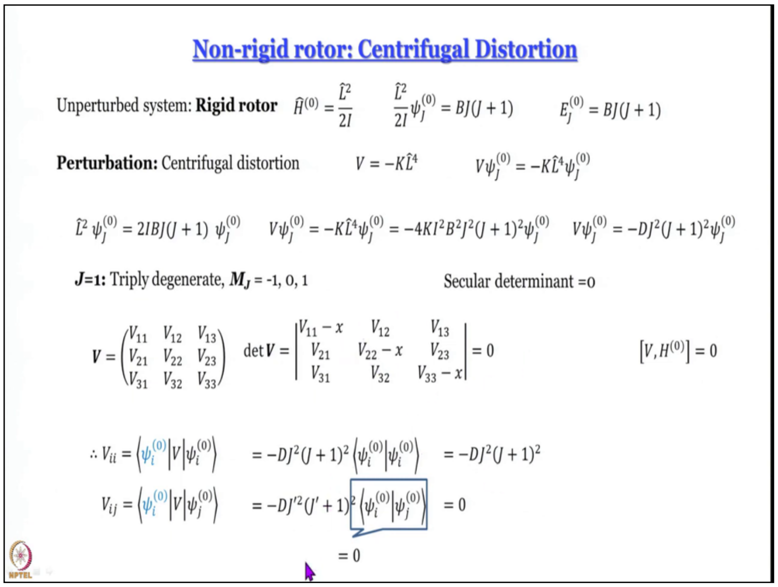

Non-rigid rotor: Centrifugal Distortion

Unperturbed system: **Rigid rotor** $\hat{H}^{(0)} = \frac{\hat{L}^2}{2I}$ $\frac{\hat{L}^2}{2I}\psi_J^{(0)} = BJ(J+1)$ $E_J^{(0)} = BJ(J+1)$

Perturbation: Centrifugal distortion $V = -K\hat{L}^4$ $V\psi_J^{(0)} = -K\hat{L}^4\psi_J^{(0)}$

$\hat{L}^2\,\psi_J^{(0)} = 2IBJ(J+1)\,\psi_J^{(0)}$ $V\psi_J^{(0)} = -K\hat{L}^4\psi_J^{(0)} = -4KI^2B^2J^2(J+1)^2\psi_J^{(0)}$ $V\psi_J^{(0)} = -DJ^2(J+1)^2\psi_J^{(0)}$

***J*=1:** Triply degenerate, $\boldsymbol{M_J}$ = -1, 0, 1

Secular determinant =0

$$\boldsymbol{V} = \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix} \quad \det \boldsymbol{V} = \begin{vmatrix} V_{11}-x & V_{12} & V_{13} \\ V_{21} & V_{22}-x & V_{23} \\ V_{31} & V_{32} & V_{33}-x \end{vmatrix} = 0$$

$$[V, H^{(0)}] = 0$$

$$\therefore V_{ii} = \langle \psi_i^{(0)} | V | \psi_i^{(0)} \rangle = -DJ^2(J+1)^2 \langle \psi_i^{(0)} | \psi_i^{(0)} \rangle = -DJ^2(J+1)^2$$

$$V_{ij} = \langle \psi_i^{(0)} | V | \psi_j^{(0)} \rangle = -DJ'^2(J'+1)^2 \boxed{\langle \psi_i^{(0)} | \psi_j^{(0)} \rangle} = 0$$

$$= 0$$

The first system that we discuss is that of a non rigid rotor and there the perturbation that we have to consider is centrifugal distortion. We have already studied at length this unperturbed system of rigid rotors and the assumption there was that the molecule is like a rod it does not change bond length in the course of rotation or the bond length is equal to the equilibrium bond length. In a non rigid rotor what happens is the bond is flexible it is not like a rod.

So what happens if you take a spring tie some weight at the end and rotate it the spring is going to get elongated right so we are still working within right now we have not said whether bono primer approximation is valid or not. We are sort of working within it we are not considering vibration and rotation simultaneously as such but we are considering the effect of vibration that the average value of r 0 square which is the all important term in the rigid rotor Hamiltonian that average value of r 0 square is going to increase.

So we start with the unperturbed system rigid rotor for that the Hamiltonian as we know is l square by 2i when l square by 2i operates on psi J 0th we get b J into J +1 I was thinking that I am making some mistakes somewhere and I have actually written it a little later also sorry about that. Of course I think you can see that this equation is not complete you must write the wave function also 0th order psi J this is what we have learnt.

And E J 0th will be equal to then b into J into J +1 just this nothing. So, perturbation is centrifugal distortion as we said somehow it came and vanished is not it. From classical mechanics we know that the centrifugal distortion is associated with the potential that is proportional to the fourth order of angular momentum. So, we construct the operator V equal to k - k l to the power 4. Now please remember here we are going to use it what l to the power 4 means?

So l square psi is equal to say something what do I write let me write a psi. So, now if l square operates on this function this is a function right in l square operation l square psi what do I get? l square operating on a Psi a will come out and l square operating on psi will give me we had said a earlier, so I get a square psi right. Of course you have done this in your tutorials and all left hand side will be l to the power 4 operating on psi.

So this is the meaning of l to the power 4, l square has to operate twice that is all but of course you know it in case there is a confusion in anybody's mind I thought I just say it once. So, this is your centrifugal distortion. So, centrifugal distortion when it operates on the wave function and remember we still work with the uncorrected 0th order wave function there is no need to incorporate the correction term as we have learned a few modules ago.

We get - k l to the power 4 operating on psi J 0th, now remembering that l square by 2i operating on psi J 0th gives me b J into J +1 I can rewrite that and I can get l square operation the uncorrected wave function to give me 2i multiplied by b multiplied by J into J +1 multiplied by psi J 0th. Now what do I have to do to get this eigen value of l to the power 4 I have to make another l square operate here.

So when I do that what do I get 2i b these are all constants they come out J into J +1 constant come out so I am left with all these constants multiplied by l square operating on psi J 0th and I know that is going to give me well it is going to give me 2i b J into J + 1 multiplied by psi J 0th simple right. So, we have to make this operation and we get V operating on psi J 0th is equal to - k l to the power 4 operating on Psi 0 gives us - 4 k I square b square J square into J +1 whole square psi J 0 please do not square psi the wave function you need to understand how the operation is done I am sure you are clear with that.

So this is what I get this is the eigen value of this V operator ok. So, V operating on psi J 0th gives me in short will write - d into J square into J +1 whole square psi J 0 where d is equal to 4 k I square b square. Now see let us work with this wave function with with this level J equal to one which is strictly degenerate you can work with any level. In fact I will encourage you to work with J equal to 2 or something and see for yourself what happens.

I mean if you work with J equal to 0 that will be cheating because there is no question of degeneracy there. So, let us work with this J equal to one which is triply degenerate m J for that the magnetic quantum number equal is equal to -1, 0, +1. So, the V matrix as we have discussed earlier is going to be something like this the matrix elements will be written V 11 V 12 V 13 and so on and so forth. Our job is to find the matrix elements.

Well now if you remember the linear equations that we had written earlier in order to get solutions there the secular determinant has to be 0 right this is something that is very well known from us rule. We are going to use it and we will discuss a little more about that when we talk about variation theorem. So, secular determinant has to be equal to 0 that means the determinant corresponding to this matrix should be equal to 0.

So that V will be equal to 0 something like that right – X. Now see we will try to simplify these expressions for V 1 one V 12 and so on and so forth to do that we will remember that the psi J 0^{th} is really an eigen function of the operator V and it has an eigen value - d into J square into J +1 whole square. So, with that let us begin we will also remember that this V and H 0th actually commute right its apparent here, there is common set of wave functions.

So what is V ii? V i i will be integral psi i 0th V psi i 0th over all space do we have V ii here yeah V 12 V 22 V33 what is the value I can write like this V operating on psi i 0th I know is - d into J square into J +1 whole square all that is your all that is constant. So, will come outside the integral inside the integral you have integral psi i 0th multiplied by psi i 0th well if it is complex then psi i0 star multiplied by psi i 0th integrated over all space what is that?

We know what that is is not it we know that this is equal to 1, great so already we have simplified and we found the expressions for V i i so the expression will be - d into J square into J +1 whole square so you take this and V ij what is V ij? So, basically we are going to replace this expression here but before that let us think a little bit about V ij. V ij has 2 different wave functions integral psi i 0th whole square psi i 0th star multiplied by V operating on psi j 0th integrated over all space.

That will give me similarly d I have written j dash just to signify that this i and j are different - d dash square multiplied by j dash +1 whole square multiplied by integral psi i 0 star psi j 0th overall space and we know very well that these wave functions are orthonormal. So, this is going to be equal to 0. So, what we are saying is that V ij is equal to 0 now when I say I and J um what do I mean it is very clear what I mean by V ii when I; what do I mean when I say i and j well not so difficult.

Also I mean that we are talking about 2 different degenerate wave functions that is equal to 0. So, now the secular determinant I just show you that once again so remember all these diagonal terms will become this - d into j square into j +1 whole square - x all of of diagonal terms as we see here is going to become 0.

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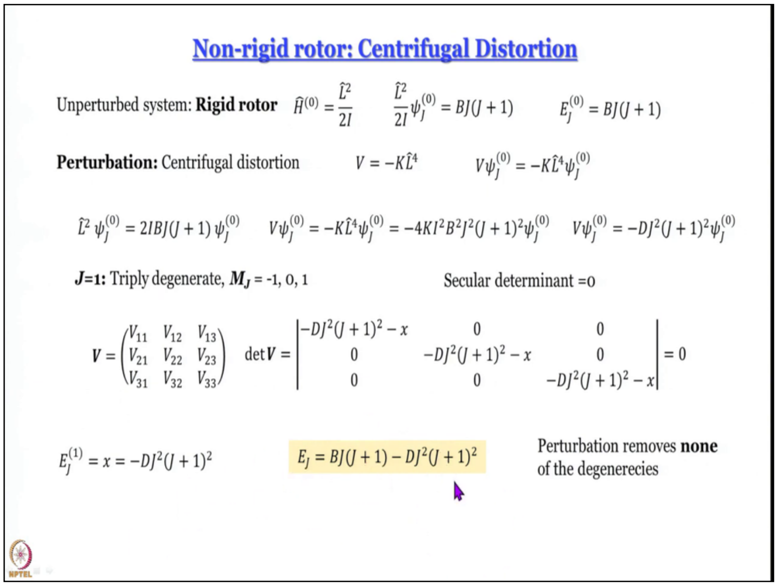

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$E_J^{(1)} = x = -DJ^2(J+1)^2$

$E_J = BJ(J+1) - DJ^2(J+1)^2$

Perturbation removes **none** of the degenerecies

So, this is the secular determinant that is equal to 0 very simple right take the determinant this multiplied by this multiplied by this equal to 0 um the expression that you get for x which is the first order correction to energy is - d j square into j +1 whole square it has 3 roots but the 3 roots are identical is not it because what we have essentially is - d into J square into J +1 whole square – x whole square whole cube equal to 0.

So the roots are identical roots are the same and we have the same amount of correction to energy for centrifugal distortion no matter what l value we have chosen, well no matter what m value we have chosen rather. So, this is the expression that we get E J now instead of b J into J +1 becomes – d becomes b J into J +1 - d J square into J +1 whole square. So, this is a case where perturbation removes none of the degeneracies whatever degeneracy was there will remain right.

We have started we have demonstrated this with this J equal to 1 state which is strictly degenerate. So, what we see is that energies will go up but a term in m is not coming in, so all the 3 m sub levels have gone up by the total energy by the same amount. The total energy has gone up by the same amount for all the 3 sub levels. This is an example of perturbation theoretical treatment of degenerate systems where degeneracy is not lifted at all but do not think there is no effect.

The energy is changing energy of E J level is decreased by d J square into J +1 whole square so much for our non rigid router. But now we want to discuss something in which actually degeneracy is lifted.

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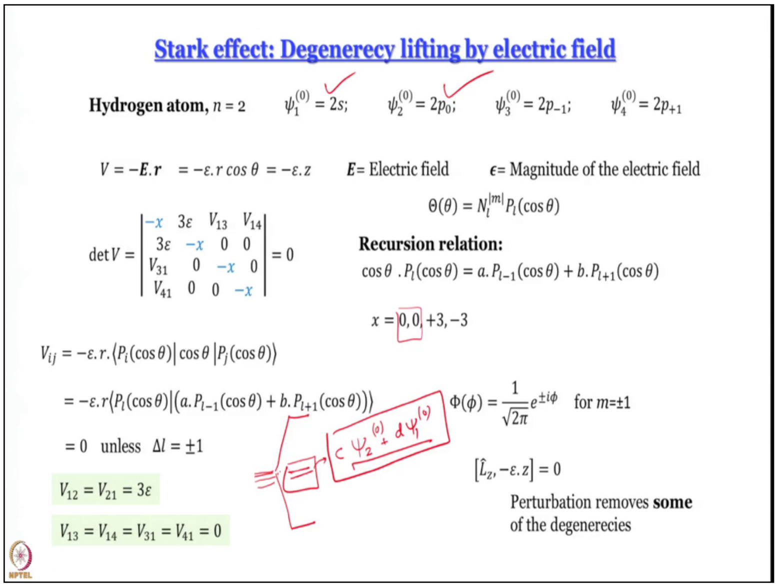

Stark effect: Degenerecy lifting by electric field

Hydrogen atom, $n = 2$ $\psi_1^{(0)} = 2s;$ $\psi_2^{(0)} = 2p_0;$ $\psi_3^{(0)} = 2p_{-1};$ $\psi_4^{(0)} = 2p_{+1}$

$V = -\boldsymbol{E}.\boldsymbol{r} = -\varepsilon.r\cos\theta = -\varepsilon.z$ $\boldsymbol{E}$= Electric field ϵ= Magnitude of the electric field

$\Theta(\theta) = N_l^{|m|} P_l(\cos\theta)$

$$\det V = \begin{vmatrix} -x & 3\varepsilon & V_{13} & V_{14} \\ 3\varepsilon & -x & 0 & 0 \\ V_{31} & 0 & -x & 0 \\ V_{41} & 0 & 0 & -x \end{vmatrix} = 0$$

Recursion relation:

$\cos\theta\ .P_l(\cos\theta) = a.P_{l-1}(\cos\theta) + b.P_{l+1}(\cos\theta)$

$x = \boxed{0, 0}, +3, -3$

$V_{ij} = -\varepsilon.r.\langle P_i(\cos\theta)|\cos\theta\,|P_j(\cos\theta)\rangle$

$= -\varepsilon.r\langle P_l(\cos\theta)|(a.P_{l-1}(\cos\theta) + b.P_{l+1}(\cos\theta))\rangle$

$= 0$ unless $\Delta l = \pm 1$

$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$ for m=±1

$c\,\psi_2^{(0)} + d\,\psi_1^{(0)}$

$[\hat{L}_z, -\varepsilon.z] = 0$

$V_{12} = V_{21} = 3\varepsilon$

$V_{13} = V_{14} = V_{31} = V_{41} = 0$

Perturbation removes **some** of the degenerecies

And that example is provided by stark effect. Stark effect means lifting of degeneracy by electric field and we are going to learn stark effect, we are going to go a little quickly through this because we have actually introduced all the necessary tools I really would like you to try and do things yourself. So, let us talk about the principle quantum number 2 for hydrogen atom now. I hope the change in gear was not very quick we are talking about non rigid rotor so far.

Now we are talking about shark effect in hydrogen atom n equal to 2. For n equal to 2 what are the orbitals the first wave function is 2 s second one is 2 p 0 third one is 2 p - 1 fourth one is to be +1 and once again even though it might have become a cliche please do not forget 2 p - 1 is neither 2 p x not 2 p z not not to b y 2 V +1 is neither 2 p x not to p y but rather a linear combination of them 2 p x and 2 p y are obtained by linear combinations of this 2 p - 1 and to p + 1 as well.

2 p z is actually equal to 2 p 0 when m equal to 0 then we actually get the p z orbital we have discussed this in significant detail while talking about orbital's. So, V in this case is minus equal to r where is the electric field and we can write it as - epsilon r cos theta because it can be at an angle right so that we can write as – epsilon into z where epsilon is the magnitude of the electric field. Now this is a secular determinant that is equal to 0 here it is important to remember what V 12 V 2 13 and all that is.

Here we are designating 2s as 1, so V 11e would be the perturbation term involving 2 s orbital and 2 s orbital same with V 22 V33 with V 44 fine. What about V 12 it involves 2 s orbital and 2p 0 orbital what is V 13? It involves 2 s orbital and your 2 p - 1 orbital and so on and so forth. All right now as usual first let us write down the wave function actually I should have written the theta phi part here as well but anyway to start with theta is fine.

So this is the theta part of the wave function as you know and now I do not remember exactly if I have we did talk about recursion relations but I do not remember if I talked about this if not just take it axiomatically that when you take a what kind of polynomials are these like where no, Legendre. So, when a Legendre polynomial is multiplied by the coordinate then you get a linear sum of the polynomial before and polynomial after I think we did it yes recursion relation we actually discussed it right.

So here our variable is cos theta so I have written cos theta multiplied by the Legendre polynomial in cos theta and here I have written l because I am talking about hydrogen atoms. Sometimes by mistake I might have written J please correct it when talking about hydrogen atoms. So it is a linear sum of the polynomial in l - 1 and polynomial in l + 2. So, now what is your V ij? V ij is equal to - epsilon r multiplied by p i cos theta cos theta p j cos theta integrated over all function space.

Here we have our good friend cos theta multiplied by p j cos theta. So, of course you can expand using this recursion relation and you get - epsilon r I hope I have not missed brackets here - epsilon ; no there is no question integral I can write p l of cos theta multiplied by a into p l - 1 of cos theta + b into p l +1 cos theta, so naturally we get 2 terms and this gives me 0 right. Let us see. So, let us take these 2 what do I get?

I get something like integral p l of cos theta will start of that if it is not real actually it is real here multiplied by p l - 1 of cos theta and this gives you something similar this one is p l cos theta second one is p l +1 in cos theta so I get 2 integrals and now see once again do not forget that these are wave functions right an orthonormal set. So, this integral p l in cos theta and multiplied by p l - 1 into cos theta integrator overall space that has to be equal to 0 yeah that must be equal to 0 because they are orthogonal to each other same here.

So finally after all this you get the answer to be 0 V ij is equal to 0 unless your delta l equal to + - 1, what will happen if delta l is equal to + - 1? Delta l means the difference between i and j, if j equal to i +1 or if j equal to i - 1 then one of these integrals is going to survive right. So, if only if delta l equal to +- 1 we are going to get V ij non 0 otherwise in all other cases you are going to get V ij equal to 0.

Now let us think V 11 that is 0 V 22 V33 V 44 very easily they are all equal to 0 you do not have to worry much yeah because of course delta l is not equal to +- 0 sorry +- 1 it is +- 0 so this V 11 V 22 V33 V 44 are gone what about V 12 for V 12 is delta l equal to 0 let us see 1 means 2s, 2 means 2p0. So, of course for this l equal to 0 for this l equal to is it 0, is it 1 is it 1 yeah yes it is 1, delta l is equal to 1 m here is 0 not l please do not get confused even if I try to confuse you.

So what we see is this one 12 is going to be non 0 because delta l equal to + - 1 similarly V 21 is also going to be non 0 because delta l equal to +- 1 right. In case I talk too much and confused you over the last 2 minutes let me just say it once. We have proven that V ij is equal to 0 unless delta l equal to + - 1 for V i i V 11 V 22 V33 V 44 since delta l equal to 0 that is not +- 1 V ij we say V ii is equal to 0 no problem.

V 12 and V 21 are non 0 because delta l equal to +- 1 here l is 0 here l is one. In fact since our time for this module is getting over I leave it to you to work out and prove that V 12 equal to V 21 is equal to 3 epsilon remember what epsilon is this is epsilon magnitude of the electric field not very difficult to work out. So, we get this kind of an expression we just go back here. What about V 23? V 23 means 2 p 0 and 2 p - 1 for both l equal to 1 so delta l is 0 again.

Same with V 24 V 43 V 42 V 32 for all these delta l equal to 0 so all these are equal to 0. So, I have already told you what V 12 and V 21 are 3 epsilon and I need to figure out what is V 13 V 14 V 31 V 41 for that well I have put the card before the hearts and I have shown you the answer first so even these are equal to 0, why? Because now we need to worry about the non; well we have to worry about the imaginary phi dependent part of the wave function also.

And it is not very difficult to see that this l z of which this capital phi is an eigen function and minus epsilon z that is just said they are going to have common eigen functions. So, by applying the logic that we have done already we can obtain we can establish that these are 0 and you can also figure out that x is equal to 00 +3 and -3 in terms of epsilon ok. So now what has happened if x what is x? X is the first order correction to energy.

So if that is equal to 0 that means there is no change in energy so what we see is that for these 4 orbital's, s, p, z, 2s, 2p0, 2p – 1, 2p +1, 2 of them do not change in energy, one is stabilized one is destabilized. Which one will be stabilized which one will be destabilized not very difficult to say that the one that is aligned with the electric field the; orbital whose angular momentum is aligned with the electric field will get stabilized.

The one for which it is not aligned with electric field that will get destabilized so that has to be +1 and – 1. So, let me just draw a schematic diagram i request you to have a look at Pillars book for a more detailed level diagram here I am just going to draw a little sketchy sketch if I call it that here we had these 4 orbital's 2s, 2p0, 2p – 1, 2p +1. Out of these 2 are stabilized and destabilized and I have told you that one has one of them is 2p +1 one of them is to be - 1 I have told you the direction of angular momentum with respect to the electric field now I would like you to it is very simple figure out whether +1 is stabilized or - 1 very easy.

Most of you would have got the answer by the time you finish the question but please do it. Sometimes it is better to ask oneself easy questions also. Now what I want to draw your attention to is that 2 orbitals do not change in energy. So, out of these 2 which is s and which is p, 2s and 2p0 they do not change energy right for them your x is equal to 0. So, here can I say that this one is 2s and that one is 2p how will I do it?

Because again energy is the same so I cannot do it. So, here I have to take linear combination. So, I have to take something like c 1 probabilities I wil call it maybe c and d and not even write one, so you can write c psi 2 0th + d psi 1 0 there is no reason for writing 2 before 1 but then it does not really matter. So, these are actually linear combinations of this 2s and the 2p0 orbital's how to find the coefficient of that, it is easy and suppose what I am saying is not even right.

Suppose there is orbital and p orbital they do not combine even then this is fine because in that case one of the coefficients will be equal to 0. So, this is general expression and now for the first time we have encountered the mixing of orbital's right when we write linear combination what we are doing essentially is that we are saying that the orbitals have mixed. So, in orbitals mixed, mix you get what are called hybrid orbitals.

You familiar with hybrid orbitals we talked about we have learnt earlier about hydro orbitals in valence bond theory. so, here what are we doing we are mixing 2s and 2p0 we are getting hybrid orbitals and in this case the 2 hybrid orbitals are the same energy right. And we have discussed a situation in which perturbation removes some of the degeneracies not all not none. Some this +1 and - 1 get very different energies well get different energies and the 2s and 2p0 these orbitals mix and the energy is not changed that leads us to the concept of hybrid orbitals.

This is the discussion of perturbation theory that I wanted to perform. So, the stage is set to go and talk about go back to our multi electron atoms if I only want to talk about perturbation theory. But there is another method that we want to learn and that is variation method that is what we will do and then we will see how variation method and perturbation method both can be used to take us back to multi electron atoms and then we will discuss a little further.

So as you see 41 lectures I think are over it is supposed to be a 60 to 70 lecture course. So, about 2 third of the course is over and we are now we are near molecules that is because the tools that we develop while learning multi electron atoms are very, very useful when you want to talk about molecular systems. We do want to talk about approximation methods that are typical of molecular systems as well like Huckel method.

But those are easy these are more fundamental more interesting and require a little more attention that is why we are spending so much of time on learning these techniques. And before ending the module let me also say this it is impossible to understand this unless you go back and work out everything by yourself. Also you should refer to books see I am typing all this on the slides it is human to error, so it is very possible that there will be error in the slides that I might not notice. So, it is important that you also read the book books also have typos but well to a lesser extent perhaps or maybe mine is a lesser extent.

So please do read the books that we have referred to and please do write it out its important to write out these things then only you will understand. So, I trust that you will be able to do that and next time we are going to talk about variation methods.