Select/Special Topics in Atomic Physics
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Lecture - 35
Stark-Zeeman Spectroscopy

Greetings, so we will begin a new unit today, this will be on spectroscopy and in a particular what is called as Stark spectroscopy, the stark effect. And also the Zeeman spectroscopy and we will deal with various aspects of this.

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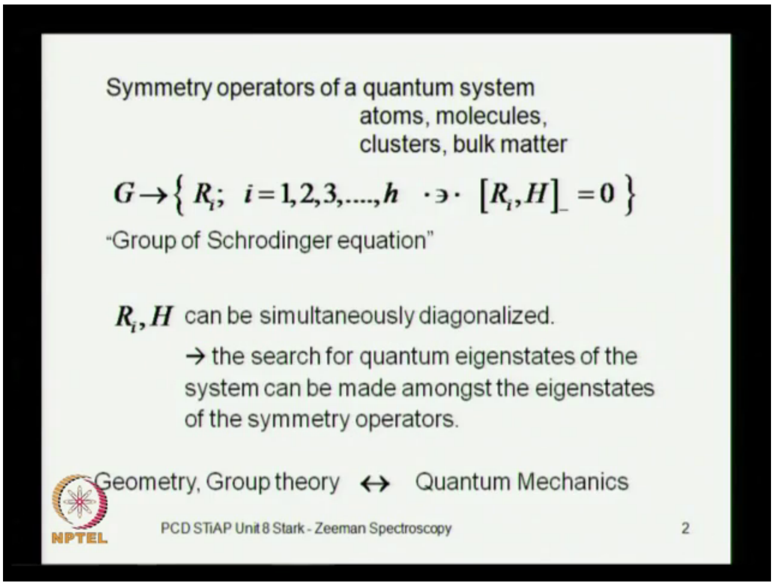

Symmetry operators of a quantum system
atoms, molecules,
clusters, bulk matter

$$G \rightarrow \left\{ R_i;\ i = 1,2,3,....,h \ \cdot\ni\cdot\ \left[R_i, H\right]_- = 0 \right\}$$

"Group of Schrodinger equation"

R_i, H can be simultaneously diagonalized.

→ the search for quantum eigenstates of the system can be made amongst the eigenstates of the symmetry operators.

Geometry, Group theory ↔ Quantum Mechanics

So, I will like to begin with the comment on symmetry of the Hamiltonian, because it plays a central role in getting the Eigen states of any contemn system. Now, quite often that problem in quantum mechanics is quite complex, especially when you are dealing with larger system, if you are dealing with molecules or clusters bulk matter and so on. The quantum mechanical problem is quite challenging, and what you can do is to exploit the symmetry of the Hamiltonian, because if you have an operation which leaves the Hamiltonian of the system variant.

Like you have an object like this, if you rotated through an arbitrary angle about X axis of symmetry, then you have a rotational symmetry about the certain access, but not about the every access. And sometimes the symmetry can be through rotation through a finite angle, all through infinitesimal angle, it could be a reflection, it could be the combination of the reflection and rotation and so on. So, if you have a symmetry operator R and there are number of symmetry operators, like R 1, R 2, R 3 and so on.

And if you stack them together, and let us say there are h number of such operations, which leave the Hamiltonian invariant, so that for every i the Hamiltonian commutes symmetry operator, it remains variant. Then these operators which have been stack together in this set, which I have called as G, is what is called a group of Schrodinger equations. And this is very advantageous, because since these two operator commute each other, they can be simultaneously diagonalize, and you can get simultaneous Eigen states of the two operators.

So, which means that if you want to find the quantum Eigen states of the system, instead of solving the quantum mechanical problem, you solve mathematical geometrical problems from group theory. And those solution will give you a basis of functions among which you can search for a Eigen states of the Hamiltonians. The problem in quantum mechanics, benefits from converting that at least partially into a problem in mathematics, in group theory or geometry. So, that is the big advantage which connects group theory and quantum mechanics. And my favorite reference for this thing Camp's book group theory and quantum mechanics, which I strongly recommend.

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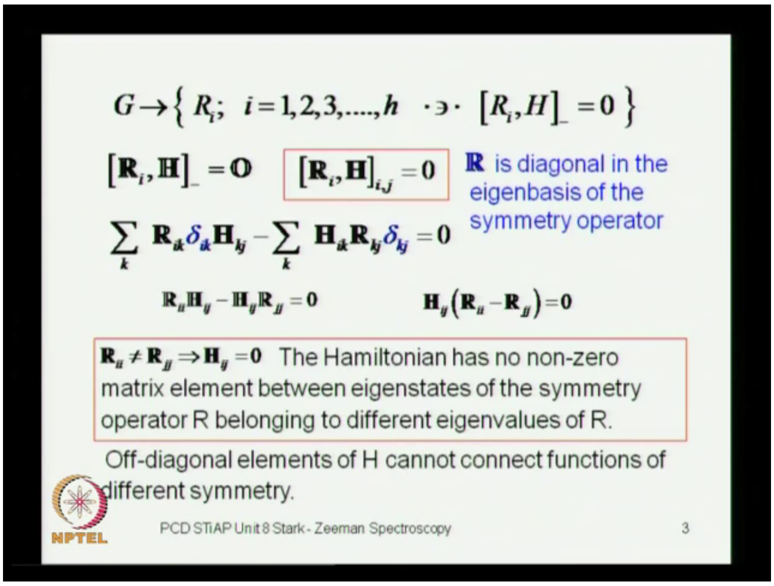

$$G \rightarrow \{ R_i;\ i = 1,2,3,\ldots,h \ \cdot\ni\cdot\ [R_i, H]_- = 0 \}$$

$$[\mathbf{R}_i, \mathbb{H}]_- = \mathbb{O} \qquad \boxed{[\mathbf{R}_i, \mathbb{H}]_{i,j} = 0}$$

$\mathbb{R}$ is diagonal in the eigenbasis of the symmetry operator

$$\sum_k \mathbf{R}_{ik}\delta_{ik}\mathbf{H}_{kj} - \sum_k \mathbf{H}_{ik}\mathbf{R}_{kj}\delta_{kj} = 0$$

$$\mathbb{R}_{ii}\mathbb{H}_{ij} - \mathbb{H}_{ij}\mathbb{R}_{jj} = 0 \qquad \mathbf{H}_{ij}(\mathbf{R}_{ii} - \mathbf{R}_{jj}) = 0$$

$\mathbf{R}_{ii} \neq \mathbf{R}_{jj} \Rightarrow \mathbf{H}_{ij} = 0$ The Hamiltonian has no non-zero matrix element between eigenstates of the symmetry operator R belonging to different eigenvalues of R.

Off-diagonal elements of H cannot connect functions of different symmetry.

And since, we are now dealing with the group of Schrodinger equation, if you have these two operations R i and H which commute, then there i j th element of this commutator would go to 0, the i j th element of the commutator, this is the i j t h element of the matrix representation. So, you can have a matrix representation in a certain basis and if you solve the geometrical problem, you get the Eigen states of the symmetry operator. And in the Eigen states of the symmetry operator, the matrix representation of the operator R will obviously, be diagonal.

So, now, you construct an Eigen basis of the symmetry operator, these are not necessarily quantum mechanical Eigen states, these are the Eigen state of the symmetry operator, in which the symmetry operator is diagonal. And if you use the fact that the i j th element is 0, then necessarily it means that, if you sum over R i k H k j minus sum over k H i k R k j, then this sum would vanish. But, R is diagonal, so R i k will implicitly include a chronicle delta, it will be non zero only 5 is equal to k, and here because of this chronicle delta, delta k j this element R k j will be non zero, only if k is equal to j.

So, the summation over k will contract and you get i i i H i j minus H i j R j j equal to 0, and now you can factor out H i j is common and you have this product, which vanishes which means that if one of the factors is not 0, the other must be 0. So, that is the comfort we get, that you do not have any off diagonal elements which connect functions of different symmetry, and this provides tremendous advantage in getting the quantum mechanics Eigen states of a system.

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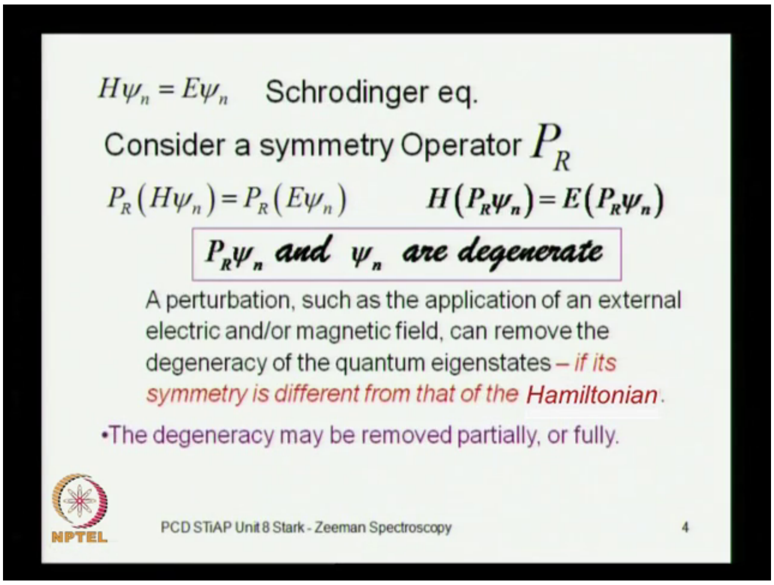

$H\psi_n = E\psi_n$ Schrodinger eq.

Consider a symmetry Operator P_R

$P_R(H\psi_n) = P_R(E\psi_n)$ $H(P_R\psi_n) = E(P_R\psi_n)$

$\boxed{P_R\psi_n \text{ and } \psi_n \text{ are degenerate}}$

A perturbation, such as the application of an external electric and/or magnetic field, can remove the degeneracy of the quantum eigenstates – *if its symmetry is different from that of the* Hamiltonian.

- The degeneracy may be removed partially, or fully.

And this is a feature that we exploit when we look at the stark effect, because this is related to a question of degeneracy, you can see how it is related to degeneracy, because if you have psi n, which is the Eigen function of the Hamiltonian. And then if you operate on the Schrodinger equation by a symmetry operator P, then P simply taken the Schrodinger equation, and I have P operating from the left on both the left side as well as the right side. And on the left side that O and H commute, so H can now be written behind P and on the right side E is the constant.

So, you find that the states psi n and the state P psi n are essentially degenerating, which is why the symmetry of the Hamiltonian, whenever you have a symmetry of the Hamiltonian you have degeneracy. And you can break the degeneracy by applying the perturbation, if the perturbation Hamiltonian has got symmetry which is different from that of the unperturbed Hamiltonian. So, in stark effect you break the symmetry of the Hamiltonian by applying can electric field, and the Zeeman effect you use the magnetic field.

So, the degeneracy can be removed by breaking the symmetry of the Hamiltonian, and you may break the symmetry either partially or fully. And then, you can look for spectroscopy transition between the states of the full Hamiltonian, which is the unperturbed Hamiltonian plus the perturbation Hamiltonian. So, you can have the transition between that, and this is what stark spectroscopy and Zeeman spectroscopy is about.

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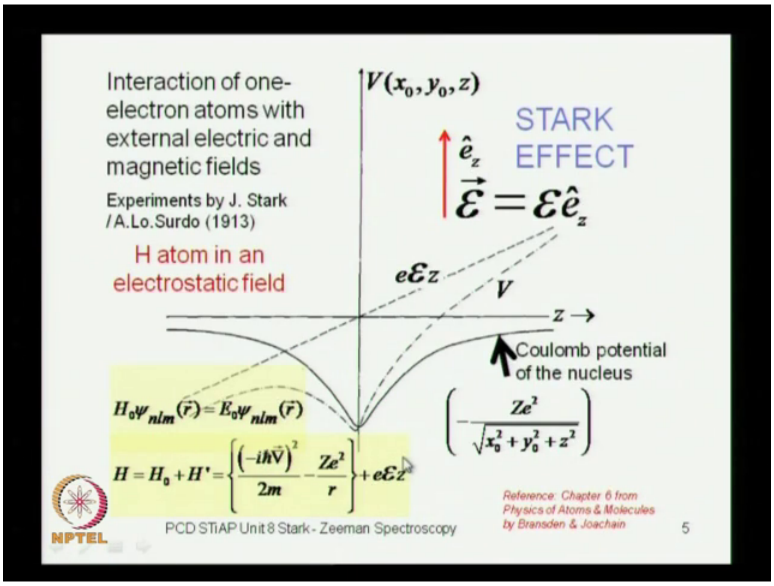

Interaction of one-electron atoms with external electric and magnetic fields

Experiments by J. Stark / A.Lo.Surdo (1913)

H atom in an electrostatic field

STARK EFFECT

$$\vec{\mathcal{E}} = \mathcal{E}\hat{e}_z$$

Coulomb potential of the nucleus

$$\left(-\frac{Ze^2}{\sqrt{x_0^2 + y_0^2 + z^2}}\right)$$

$$H_0 \psi_{nlm}(\vec{r}) = E_0 \psi_{nlm}(\vec{r})$$

$$H = H_0 + H' = \left\{\frac{(-i\hbar\vec{\nabla})^2}{2m} - \frac{Ze^2}{r}\right\} + e\mathcal{E}z$$

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Reference: Chapter 6 from Physics of Atoms & Molecules by Bransden & Joachain

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So, the first experiment were done by stark in the early part of the 20th century, and he examined the spectrum in atomic spectra in electric fields. So, let us consider the hydrogen autumn placed in an electric field, now let us say that the electric field is applied long the Z axis. And if you now plot the potential seen by the electron it is the coulomb potential which goes like this, it is minus 1 over r, but I am plotting get as a function of Z for a given value of a x 0 and y 0, for a given value of X equal to x 0 and Y equal to y 0. So, which are finite it does not go to the minus infinity, it goes to it cuts the vertical axis the potential axis over here, because that Z equal to 0 the denominator is not 0.

So, this is the coulomb potential that you have, this is plotted as a function of the Z axis and in addition to the coulomb potential, which is generated by the proton nucleus, you have the applied electric field which is the linear field. So, this will have a linear interaction, which is charged time electric field and then, you have got this e E z this is the interaction Hamiltonian of the charge in the presence of the electric field. So, now, you have the unperturbed Hamiltonian for which the Schrodinger equation solutions are well known to all of us, these hydrogen atom solutions.

And then the problem you are dealing with is that of the four Hamiltonian, which include the unperturbed Hamiltonian plus this which is the perturbation. So, we are going to use perturbation theory, which you have done in your earlier course in quantum mechanics, but I will review some of the more important parts of that for the sake of completeness.

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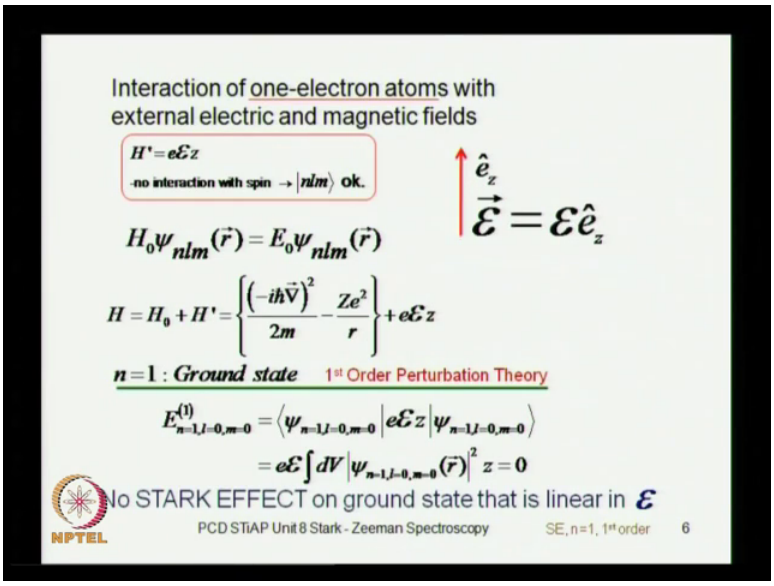

Interaction of one-electron atoms with external electric and magnetic fields

$H' = e\mathcal{E}z$

-no interaction with spin → $|nlm\rangle$ ok.

$\hat{e}_z$

$\vec{\mathcal{E}} = \mathcal{E}\hat{e}_z$

$$H_0\psi_{nlm}(\vec{r}) = E_0\psi_{nlm}(\vec{r})$$

$$H = H_0 + H' = \left\{\frac{(-i\hbar\vec{\nabla})^2}{2m} - \frac{Ze^2}{r}\right\} + e\mathcal{E}z$$

$n=1$: *Ground state* 1st Order Perturbation Theory

$$E^{(1)}_{n=1,l=0,m=0} = \langle \psi_{n=1,l=0,m=0} | e\mathcal{E}z | \psi_{n=1,l=0,m=0} \rangle$$

$$= e\mathcal{E}\int dV \left|\psi_{n=1,l=0,m=0}(\vec{r})\right|^2 z = 0$$

No STARK EFFECT on ground state that is linear in $\mathcal{E}$

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So, we will deal with the spin later, so we will deal with the non relativistic Schrodinger equation and it is solution, were the Eigen states are given by the quantum numbers n l m, which are good quantum numbers in this situation. And the perturbation is e E z, this script E is the electric field, this little e is electric field, and later considered the ground state of the hydrogen autumn. And use the result of the first order perturbation theory, from which we know that the first order perturbation correction will simply be the matrix elements of the perturbation Hamiltonian in the ground state.

So, all you have to do is to get this first order correction, and what will this turn out to be this is the 1 as state of the hydrogen atom, this is got a symmetry of X axis. So, this is got a parity, which is odd this state ((Refer Time: 11:24)), this state as well as this state both have got even parity, so this integral will essentially vanish. Because, the contributions of the plus Z will cancel the contribution from the minus Z, when you take the integral over the whole space.

So, this integral vanishes and essentially what we find is that there is no stark effect at all, it does not change the ground state energy of the hydrogen atom. If you keep it in a electric field, it is energies not going to change because the matrix element in the first order at least does not contribute anything, now so far so good what about second order perturbation effect.

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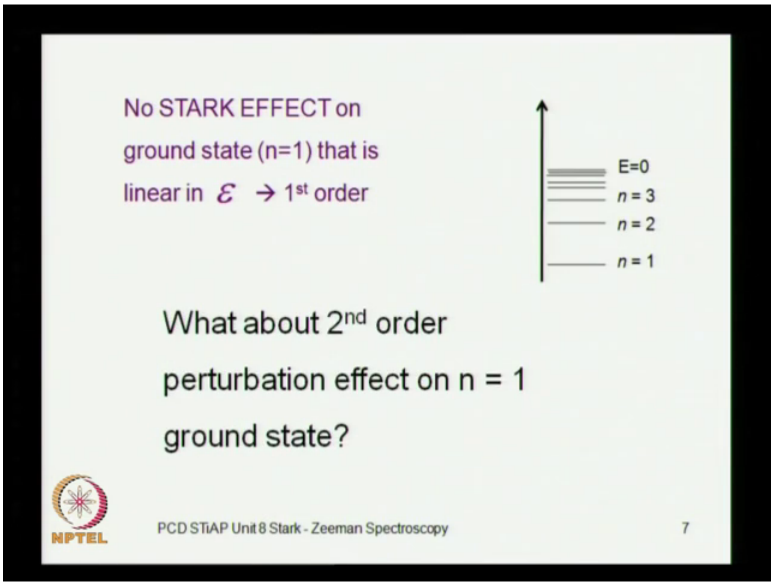

No STARK EFFECT on ground state (n=1) that is linear in $\mathcal{E}$ → 1st order

What about 2nd order perturbation effect on n = 1 ground state?

In the first order we do not have any correction, what about second corrections and there may be some, so let us not assume that they also vanish and in fact, they do not. So, let us look for the second order correction.

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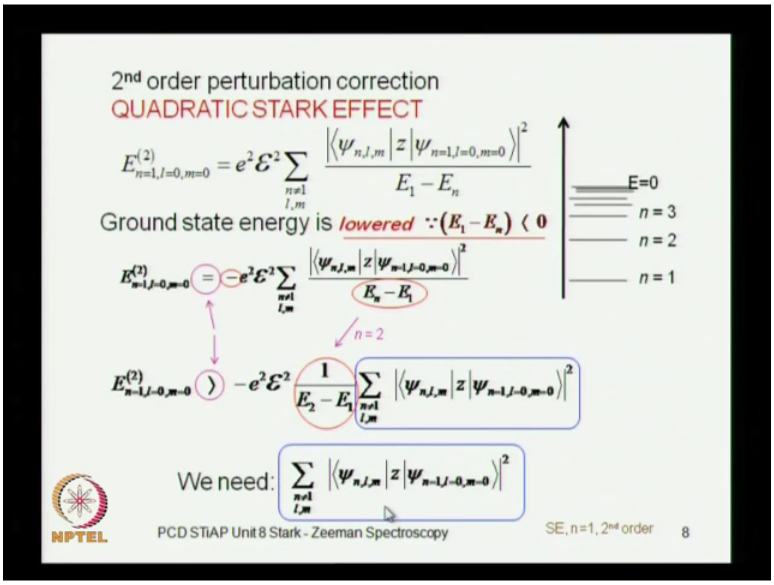

2nd order perturbation correction

QUADRATIC STARK EFFECT

$$E^{(2)}_{n=1,l=0,m=0} = e^2\mathcal{E}^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\langle \psi_{n,l,m} | z | \psi_{n=1,l=0,m=0} \rangle\right|^2}{E_1 - E_n}$$

Ground state energy is *lowered* $\because (E_1 - E_n) < 0$

$$E^{(2)}_{n=1,l=0,m=0} = -e^2\mathcal{E}^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\langle \psi_{n,l,m} | z | \psi_{n=1,l=0,m=0} \rangle\right|^2}{E_n - E_1}$$

$n=2$

$$E^{(2)}_{n=1,l=0,m=0} > -e^2\mathcal{E}^2 \frac{1}{E_2 - E_1} \sum_{\substack{n\neq 1\\ l,m}} \left|\langle \psi_{n,l,m} | z | \psi_{n=1,l=0,m=0} \rangle\right|^2$$

We need: $\sum_{\substack{n\neq 1\\ l,m}} \left|\langle \psi_{n,l,m} | z | \psi_{n=1,l=0,m=0} \rangle\right|^2$

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SE, n=1, 2nd order 8

And the second order correction is given by this term, according to the perturbation theory, this I am sure you would have done your earlier course in quantum mechanics, so I will use that result straightaway. And this is the result of the second order correction and you can already see that it will not be 0, it will not be 0 you need to sum over all values of n. So, this is your hydrogen atom bounce straight spectrum, everything converging to the Reebok surrey limit at E equal to 0.

And then, this E 1 minus E n for n not equal to 1, will be non zero and then you have got non zero terms l square, so this will give you non zero correction; now, this is the correction that we need to estimate. So, let us see how to do that first thing to recognize is that, the ground state will certainly be lower, because here these are squares, so they will be necessarily positive here, in the numerator also you have got to square. So, the sign of the entire sum will be determined by this sign and E 1 is the lowest state, so E 1 minus E n will be negative, and this will have a negative sign.

So, the energy of the ground state will be lower by second order correction, so that is the first thing we know at least a qualitative level, so let us extract this minus sign that is all we have done in this step. So, the denominator is written as E n minus E 1 in this state of E 1 minus E n and this is of course, different for different values of n, the denominator is different. But, notice that this E n minus E 1 denominator, this difference will become larger and larger as you go to higher value of n.

So, let us take the least value that is possible and that is for n equal to 2 and that means, you get a certain bound, which guarantees that this second order correction will be greater than this difference in which you have extracted 1 over E 2 minus E 1 outside the summation sign. So, this is the certain bound that you get and now what we want to determine, to get this bound is this summation over all values of n, n going from n not equal to 1. So, it will go from 2 all the wave up to infinity and then of course, you need to sum over corresponding value l and m as well, so this is the quantity that you want to determine.

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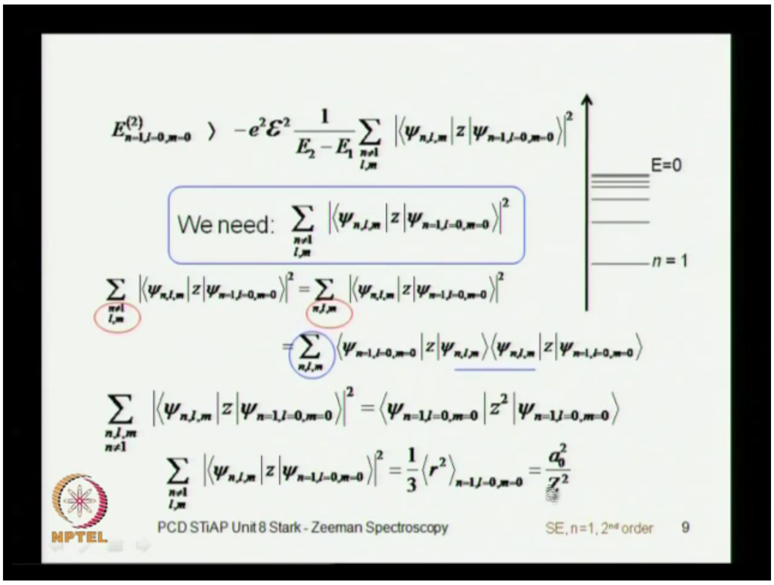

$$E^{(2)}_{n=1,l=0,m=0} > -e^2\mathcal{E}^2\frac{1}{E_2-E_1}\sum_{\substack{n\neq1\\l,m}}\left|\langle\psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2$$

We need: $\sum_{\substack{n\neq1\\l,m}}\left|\langle\psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2$

$$\sum_{\substack{n\neq1\\l,m}}\left|\langle\psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2=\sum_{n,l,m}\left|\langle\psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2$$

$$=\sum_{n,l,m}\langle\psi_{n=1,l=0,m=0}|z|\underline{\psi_{n,l,m}\rangle\langle\psi_{n,l,m}}|z|\psi_{n=1,l=0,m=0}\rangle$$

$$\sum_{\substack{n,l,m\\n\neq1}}\left|\langle\psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2=\langle\psi_{n=1,l=0,m=0}|z^2|\psi_{n=1,l=0,m=0}\rangle$$

$$\sum_{\substack{n\neq1\\l,m}}\left|\langle\psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2=\frac{1}{3}\langle r^2\rangle_{n=1,l=0,m=0}=\frac{a_0^2}{Z^2}$$

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SE, n=1, 2nd order

Let us see how we do that, so to get this summation that we do not want to include n equal to 1, but how does it matter, we can also include n equal to 1. Because, we have already found, but if we did not include n equal to 1 it contributes 0, so you can always add a 0 to an entire sum. So, we can extent this summation, which was from n not equal to 1 to infinity to include n equal to 1 to infinity. So, we need not restrict n not equal to 1 anymore, because what it is adding to the total sum is only a 0.

So, this is the summation that we want to get and this is the modular square, so this is the product of the matrix element of Z times, the complex conjugative of this and you recognize of the advantage of extending this some to include n equal to 1. Because, that is what makes this is what the salvation between a unit operator that is the resolution of the unity, and that is possible because we have included the n equal to 1 state. So, we recognize resolution of unity and we find in that what we are looking at is essentially the matrix element, not the product of the matrix element of Z, but actually the matrix elements of Z square.

So, there is a Z to the power of 1 here ((Refer Time: 16:50)) and Z to the power of 1 here, so that gives you Z square, so the sum over all state of this modules square of matrix elements of Z is equal to the matrix elements of the Z square itself. And that is not very difficult to determine, because so far the hydrogen atom in the unperturbed state is concerned it is completely symmetrical, it does not recognize any difference between Z and Y and Z. So, there will be an exactly identical expression for X square and Y square as well, so this will be 1 3rd of R square.

And the average value of the R square, the expectation value of the T square can be very easily determined for any Eigen state of the hydrogen atom, which is for n equal to 1, it is a 0 square by Z square, so now we have this result a 0 square by Z square.

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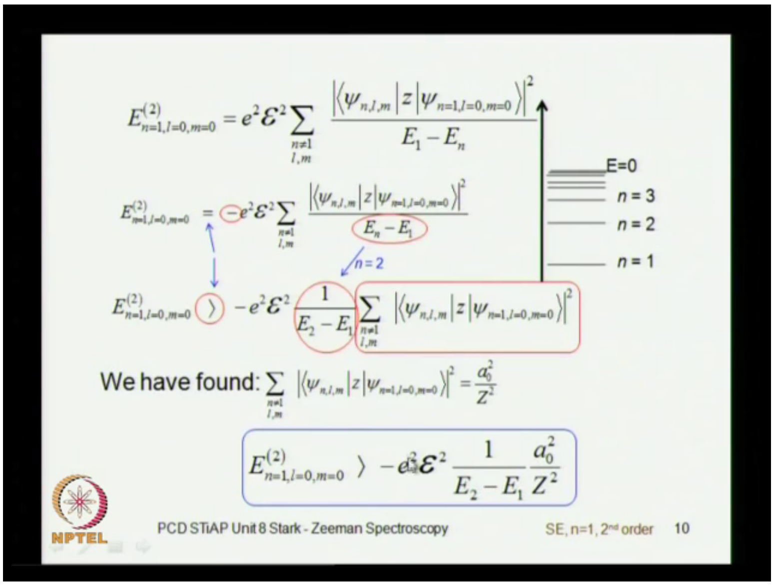

$$E^{(2)}_{n=1,l=0,m=0} = e^2\mathcal{E}^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\langle \psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2}{E_1 - E_n}$$

$$E^{(2)}_{n=1,l=0,m=0} = -e^2\mathcal{E}^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\langle \psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2}{E_n - E_1}$$

$n=2$

$$E^{(2)}_{n=1,l=0,m=0} \rangle -e^2\mathcal{E}^2 \frac{1}{E_2 - E_1} \sum_{\substack{n\neq 1\\ l,m}} \left|\langle \psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2$$

We have found: $\sum_{\substack{n\neq 1\\ l,m}} \left|\langle \psi_{n,l,m}|z|\psi_{n=1,l=0,m=0}\rangle\right|^2 = \frac{a_0^2}{Z^2}$

$$\boxed{E^{(2)}_{n=1,l=0,m=0} \rangle -e^2\mathcal{E}^2 \frac{1}{E_2 - E_1} \frac{a_0^2}{Z^2}}$$

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SE, n=1, 2nd order 10

And we have found the quantity that we needed, this is the a 0 square over Z square that we have found and using this is a 0 square over Z square. We find this bound which is the second order correction to the ground state of hydrogen atom, due to the stack effect will be certainly greater than this quantity over here, which is 1 over E 2 minus E 1 and what E 2 minus E 1 is, so you can find that out. So, you all do is to plug in the numbers and you can get this ((Refer Time: 18:19)).

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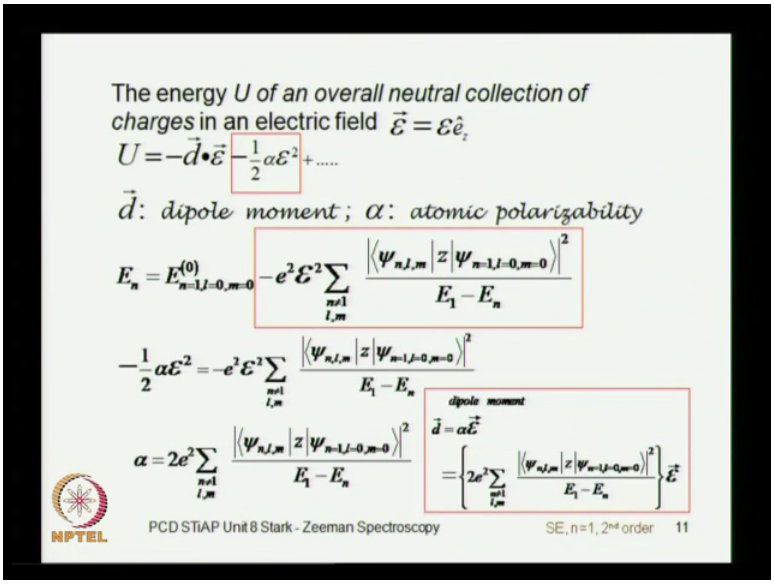

The energy *U of an overall neutral collection of charges* in an electric field $\vec{\varepsilon} = \varepsilon \hat{e}_z$

$$U = -\vec{d} \bullet \vec{\varepsilon} \boxed{-\frac{1}{2}\alpha\varepsilon^2} + \ldots\ldots$$

$\vec{d}$: *dipole moment*; α: *atomic polarizability*

$$E_n = E^{(0)}_{n=1,l=0,m=0} \boxed{-e^2\mathcal{E}^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\left\langle \psi_{n,l,m} \middle| z \middle| \psi_{n=1,l=0,m=0} \right\rangle\right|^2}{E_1 - E_n}}$$

$$-\frac{1}{2}\alpha\mathcal{E}^2 = -e^2\mathcal{E}^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\left\langle \psi_{n,l,m} \middle| z \middle| \psi_{n=1,l=0,m=0} \right\rangle\right|^2}{E_1 - E_n}$$

$$\alpha = 2e^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\left\langle \psi_{n,l,m} \middle| z \middle| \psi_{n=1,l=0,m=0} \right\rangle\right|^2}{E_1 - E_n}$$

dipole moment

$$\boxed{\begin{aligned}\vec{d} &= \alpha\vec{\mathcal{E}}\\ &= \left\{2e^2 \sum_{\substack{n\neq 1\\ l,m}} \frac{\left|\left\langle \psi_{n,l,m} \middle| z \middle| \psi_{n=1,l=0,m=0} \right\rangle\right|^2}{E_1 - E_n}\right\}\vec{\mathcal{E}}\end{aligned}}$$

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SE, n=1, 2nd order 11

Now, there are some other consequences of this, because if you look at the energy of a certain charge distribution, whatever it is. And if the overall charge distribution is neutral, then it will have depending on the centre about, which you find the multi poles the energy of this charge distribution will be given by the minus T dot E term. And then, there will be a quadratic term and there will be this complete multi pole expansion that you can look at, and that there will be other powers of E.

So, you look at you have got the dipole moment d over here, alpha is the academic polarizability and this is the classical example, this is straight out of classical electric dynamic. And then you compared it with the result that you just found in quantum mechanics, so this is exact this is n not equal to 1 and this is exact. So, here you have the unperturbed energy, that energy of the in n x state will be given by, the sum of unperturbed energy plus the energy correction in the second order, the first order correction vanishes.

And in the second order correction you have got the quadratic term in the amplitude of the electric contentcity, and now you can compare the quadratic term, because the comparison of these two quadratic term gives you the automatic polarizability. You can equate this to terms and you find the atomic polarizability is given by the summation term that we just discussed. So, from this you can also get the dipole moment, because it is proportional to the electric contentcity through the atomic polarizability.

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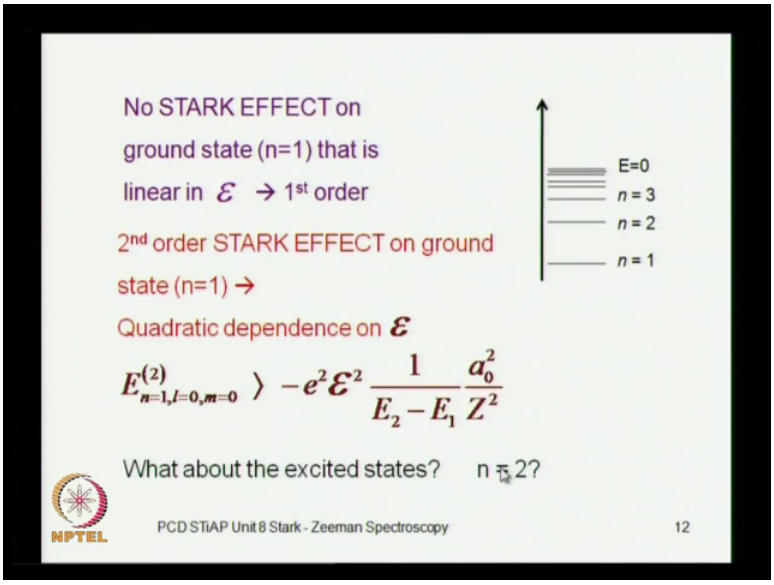

No STARK EFFECT on ground state (n=1) that is linear in $\mathcal{E}$ → 1st order

2nd order STARK EFFECT on ground state (n=1) →

Quadratic dependence on $\mathcal{E}$

$$E^{(2)}_{n=1,l=0,m=0} \rangle -e^2\mathcal{E}^2 \frac{1}{E_2-E_1}\frac{a_0^2}{Z^2}$$

What about the excited states? n = 2?

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So, now we have found that there is no stack effect in the first order ground state, we found that the second order stack effect on the ground state. It had quadratic dependence on the electric intensity, and now we ask what happens to the excited states.

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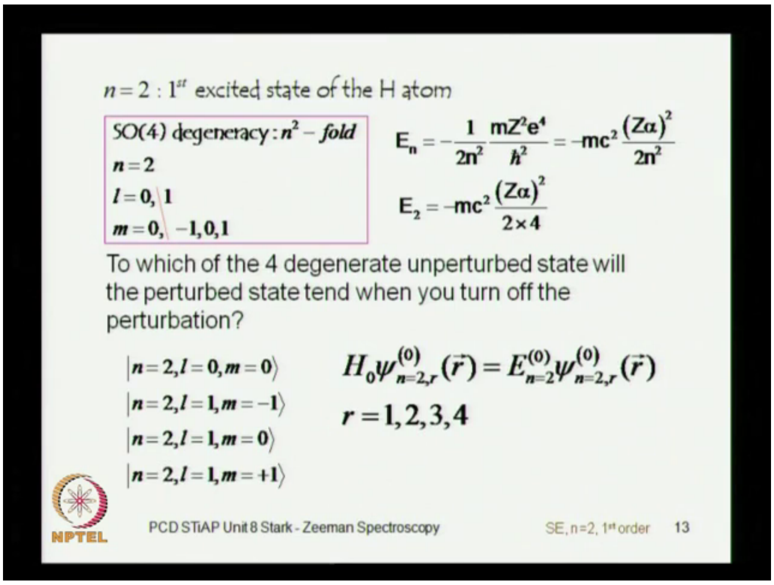

$n=2$: 1^{st} excited state of the H atom

SO(4) degeneracy : n^2 – fold
$n=2$
$l=0,\ 1$
$m=0,\ -1,0,1$

$$E_n = -\frac{1}{2n^2}\frac{mZ^2e^4}{\hbar^2} = -mc^2\frac{(Z\alpha)^2}{2n^2}$$

$$E_2 = -mc^2\frac{(Z\alpha)^2}{2\times 4}$$

To which of the 4 degenerate unperturbed state will the perturbed state tend when you turn off the perturbation?

$|n=2,l=0,m=0\rangle$
$|n=2,l=1,m=-1\rangle$
$|n=2,l=1,m=0\rangle$
$|n=2,l=1,m=+1\rangle$

$$H_0\psi^{(0)}_{n=2,r}(\vec{r}) = E^{(0)}_{n=2}\psi^{(0)}_{n=2,r}(\vec{r})$$

$$r=1,2,3,4$$

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Now, we have to be a little careful because once you go to the excited state like n equal to 2, so let us take the first excited state of the hydrogen atom, and that the energy of the excited state will be given by with this 1 over n square formula, for the hydrogen atom. But, then you also know that these states are n square for degenerate, this comes from the SO(4) symmetry for hydrogen atom. So, you do not have a unique Eigen state belonging to a given Eigen value, you have more than one Eigen function.

And in a particular n equal to 2, you have got the 2 s and the 2 P states, and the 2 P states again it is triply degenerate. So, you have the total of four degenerate states here, for n equal to 2 and these four states are written out over here, so for n equal to 2. So, you have 1 coming from l equal to 0 which is the 2 s and 3 coming from l equal to 1 which are the 2 P state with m equal to minus 1 0 and plus 1. So, these are the four state and all of those four states, from r going from 1, 2, 3, 4 they all belong to the same Eigen value, which is the unperturbed Eigen state corresponding to n equal to 2.

So, there are all degenerate, so now you can ask the question that, if you applied in the electric field which was to remove this degeneracy. And now, you switch off the electric field to which of this states, to which of this four states will the perturbed wave function collapsed in two, you cannot get the unique answer, because there are four alternatives over there.

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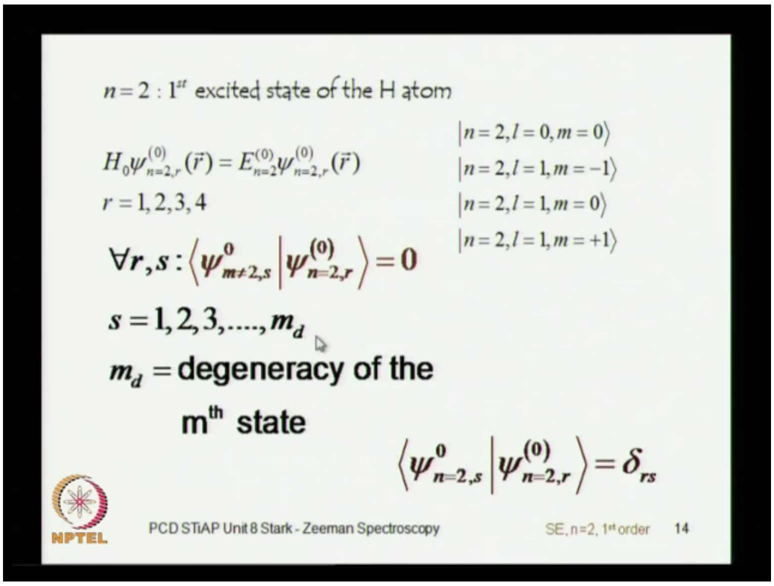

$n = 2$: 1st excited state of the H atom

$H_0\psi^{(0)}_{n=2,r}(\vec{r}) = E^{(0)}_{n=2}\psi^{(0)}_{n=2,r}(\vec{r})$

$r = 1, 2, 3, 4$

$|n=2, l=0, m=0\rangle$

$|n=2, l=1, m=-1\rangle$

$|n=2, l=1, m=0\rangle$

$|n=2, l=1, m=+1\rangle$

$\forall r, s : \langle \psi^{0}_{m\neq 2,s} | \psi^{(0)}_{n=2,r} \rangle = 0$

$s = 1, 2, 3, \ldots., m_d$

m_d = degeneracy of the m^th state

$\langle \psi^{0}_{n=2,s} | \psi^{(0)}_{n=2,r} \rangle = \delta_{rs}$

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So, you have to remember that all of these four states, are orthogonal to each other and there also are orthogonal to all the states for m not equal to 2. So, whenever m not equal to 2 and I have an additional quantum number over here and additional index s, because the m not equal to 2 state, it may also be degenerate and if this degeneracy is m d 4, then you will have 1, 2, 3 up to m d linearly independent functions, which belongs to the same Eigen value for m for the m th state.

And the n equal to 2 state is orthogonal to each one of them, so this is the degeneracy of the m th state and of course, these four state are orthogonal to each other within themselves. So, for r not equal to s this projection this inner product would vanish, so we need to use what is called as degenerate perturbation theory in this case.

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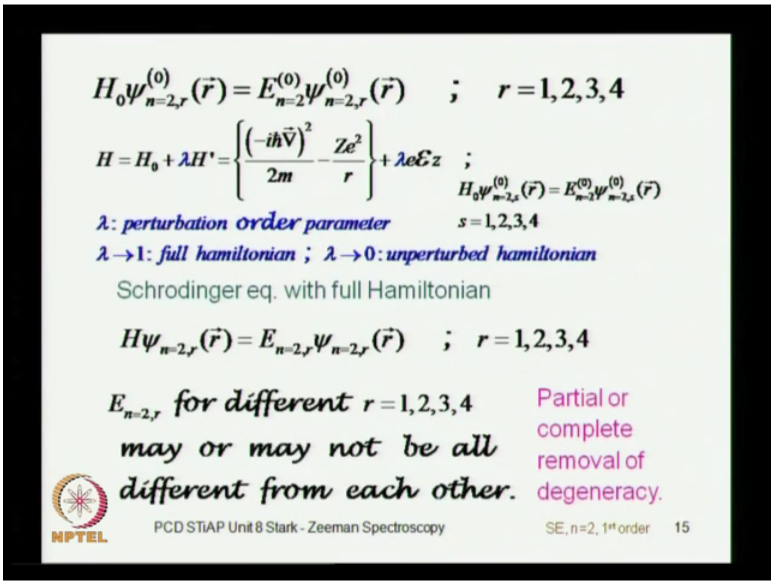

$$H_0\psi^{(0)}_{n=2,r}(\vec{r}) = E^{(0)}_{n=2}\psi^{(0)}_{n=2,r}(\vec{r}) \quad ; \quad r = 1,2,3,4$$

$$H = H_0 + \lambda H' = \left\{\frac{\left(-i\hbar\vec{\nabla}\right)^2}{2m} - \frac{Ze^2}{r}\right\} + \lambda e\mathcal{E}z \quad ;$$

$$H_0\psi^{(0)}_{n=2,s}(\vec{r}) = E^{(0)}_{n=2}\psi^{(0)}_{n=2,s}(\vec{r})$$

$$s = 1,2,3,4$$

λ: *perturbation order parameter*

$\lambda \to 1$: *full hamiltonian* ; $\lambda \to 0$: *unperturbed hamiltonian*

Schrodinger eq. with full Hamiltonian

$$H\psi_{n=2,r}(\vec{r}) = E_{n=2,r}\psi_{n=2,r}(\vec{r}) \quad ; \quad r = 1,2,3,4$$

$E_{n=2,r}$ for different $r = 1,2,3,4$ may or may not be all different from each other.

Partial or complete removal of degeneracy.

And we will consider first order correction to the n equal to 2, which is the first excited state of the hydrogen atom using degenerate perturbation, so you have got these four states which are degenerate. And the perturbation is e times script E time z, this is the charge the script E is the electric field and the perturbation order parameter is lambda, lambda equal to 1 gives you the full Hamiltonian, lambda going to 0 will give you the unperturbed Hamiltonian.

And now you can write the Schrodinger equation with full Hamiltonian, so this is H psi for n equal to 2, which includes the perturbation now, E equal to E psi and this E will be different from this E 0 and this Hamiltonian is this H 0 plus the perturbation. So, one might expect that this E, which is the Eigen value of the full Hamiltonian for different values of r may be different, but not necessarily so. Because, it depends on to what extent the degeneracy is removed by this perturbation, the degeneracy may be removed either partially or fully and that is something, that we will have to take into account. So, in this case in fact, it will turn out that the degeneracy not fully removed, but it is partially removed and that is good, because it is produces our problem considerably.

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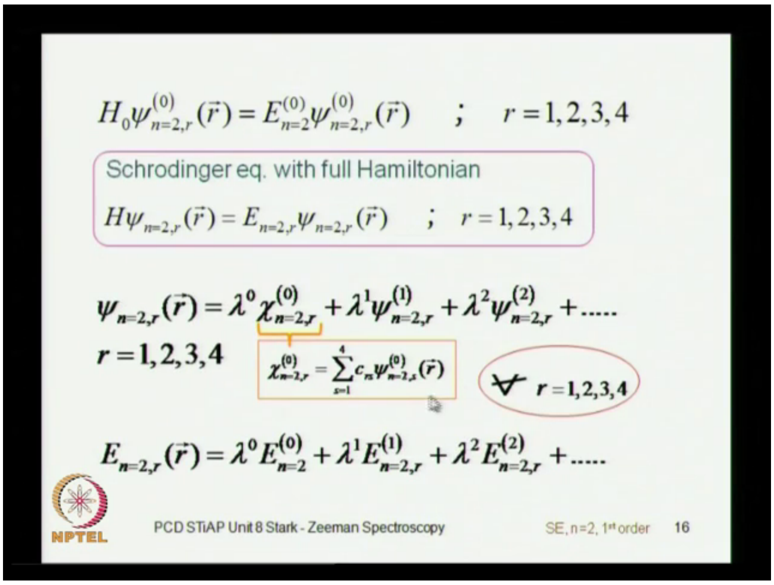

$$H_0\psi^{(0)}_{n=2,r}(\vec{r}) = E^{(0)}_{n=2}\psi^{(0)}_{n=2,r}(\vec{r}) \quad ; \quad r=1,2,3,4$$

Schrodinger eq. with full Hamiltonian

$$H\psi_{n=2,r}(\vec{r}) = E_{n=2,r}\psi_{n=2,r}(\vec{r}) \quad ; \quad r=1,2,3,4$$

$$\psi_{n=2,r}(\vec{r}) = \lambda^0\underbrace{\chi^{(0)}_{n=2,r}}_{\boxed{\chi^{(0)}_{n=2,r} = \sum_{s=1}^{4} c_n\psi^{(0)}_{n=2,s}(\vec{r})}} + \lambda^1\psi^{(1)}_{n=2,r} + \lambda^2\psi^{(2)}_{n=2,r} + \dots..$$

$r=1,2,3,4$

$\forall \; r=1,2,3,4$

$$E_{n=2,r}(\vec{r}) = \lambda^0 E^{(0)}_{n=2} + \lambda^1 E^{(1)}_{n=2,r} + \lambda^2 E^{(2)}_{n=2,r} + \dots..$$

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SE, n=2, 1st order

So, this is the Schrodinger equation with the full Hamiltonian, and we will expand and the perturbed solution, the Eigen state of the perturbed Hamiltonian as an expansion in the perturbation order parameter lambda. So, you have got the term to the lambda power 0, which will be unperturbed state, but the unperturbed state is not unique, it will be a linear superposition of all the four Eigen states. And then you will have corrections, in the first order corrections and the second order and so on, and typically lambda is small tiny parameter. So, the series can converge hopefully not that is always does.

So, this unperturbed part is a linear superposition of the four unperturbed Eigen state, we have already met them these are the four linearly independent Eigen functions, which belong to the same Eigen value of the hydrogen atom for n equal to 2. So, this is e equal to 2 and s takes four values going from 1 through 4 and then, these coefficients C we do not know yet we will have to find a mechanism to determine these coefficients, which is the part of this exercise.

And this is the expansion for the wave function and you have got the corresponding expansion also for the energy, this is the energy of including the perturbation. So, it will be the unperturbed energy plus the correction in the first order, the correction in the second order and so on. So, this is the perturbation order for expansion and you have got the similar relation for each value r going from 1 through 4.

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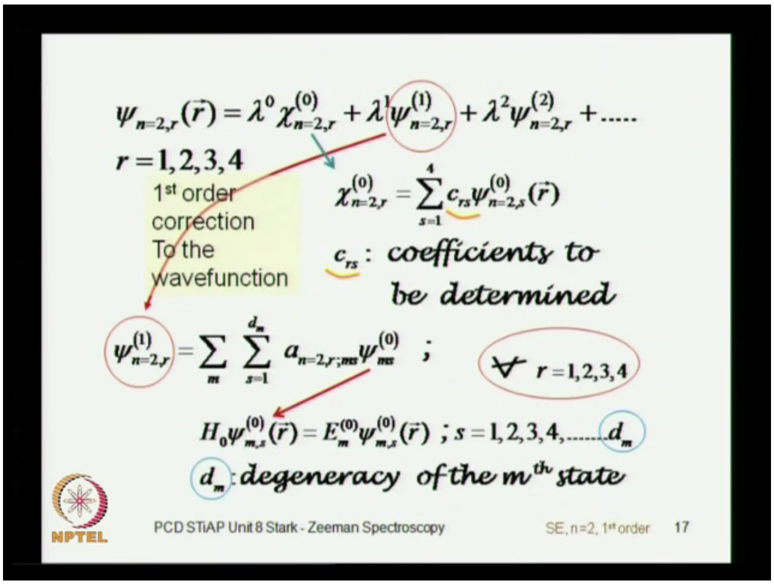

$$\psi_{n=2,r}(\vec{r}) = \lambda^0 \chi^{(0)}_{n=2,r} + \lambda^1 \psi^{(1)}_{n=2,r} + \lambda^2 \psi^{(2)}_{n=2,r} + ...$$

$r = 1,2,3,4$

1st order correction To the wavefunction

$$\chi^{(0)}_{n=2,r} = \sum_{s=1}^{4} c_{rs} \psi^{(0)}_{n=2,s}(\vec{r})$$

c_{rs} : coefficients to be determined

$$\psi^{(1)}_{n=2,r} = \sum_{m} \sum_{s=1}^{d_m} a_{n=2,r;ms} \psi^{(0)}_{ms} \;; \quad \forall \; r = 1,2,3,4$$

$$H_0 \psi^{(0)}_{m,s}(\vec{r}) = E^{(0)}_m \psi^{(0)}_{m,s}(\vec{r}) \;; s = 1,2,3,4,.......d_m$$

d_m : degeneracy of the m^{th} state

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SE, n=2, 1st order 17

So, let us look at this wave function now, and this unperturbed part is a linear superposition of the four degenerate unperturbed Eigen states. It cannot be unique, because there are four linearly independent function and these coefficients C our yet to be determined, so we now look at the first order correction. The first order wave function will again, because of the perturbation theory we expect it to be written as a superposition of all the unperturbed states, otherwise the perturbation theory will not work.

So, the perturbation theory works, because of our contention that the perturbation is expressible, in terms of superposition of unperturbed states. So, this is the superposition of overall quantum number is m of this unperturbed state, but for the each value of m, there may be d number of degenerate Eigen states. And you already know that there are n square 4, there is than n square 4 degeneracy, so you must include a summation over all of this degenerate states.

So, the coefficient will therefore, be index by r and also by m and s, and this is the coefficient coming in the expansion for the perturbation solution for the n equal to 2, so I carried that index n equal to 2 as well. So, the coefficient a here has got the number of n dices over here and all of them are important, suppose that you have followed by each index is of significance. So, this is off course the unperturbed Eigen state corresponding to the m th degenerate state, but this depends on towards extent the level E m is degenerate. And this will again go has 1 over n square n equal to m, so that is the degeneracy of the m th state.

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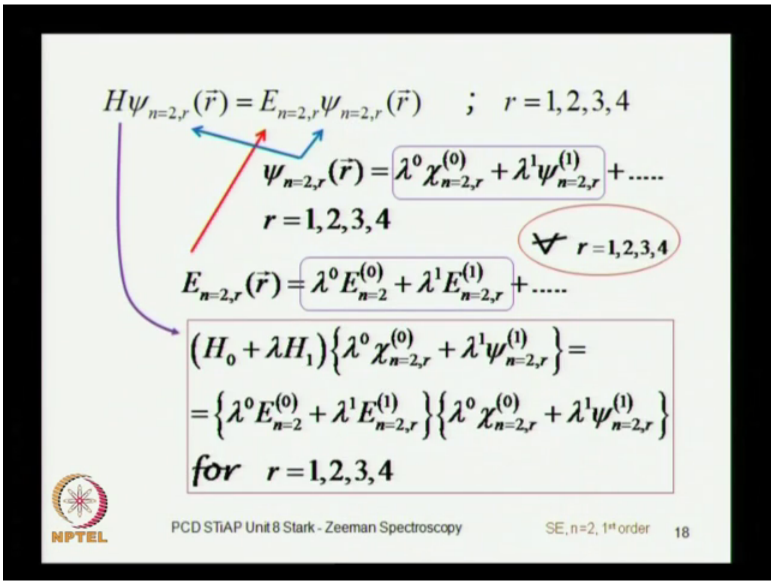

$$H\psi_{n=2,r}(\vec{r}) = E_{n=2,r}\psi_{n=2,r}(\vec{r}) \quad ; \quad r = 1,2,3,4$$

$$\psi_{n=2,r}(\vec{r}) = \boxed{\lambda^0\chi^{(0)}_{n=2,r} + \lambda^1\psi^{(1)}_{n=2,r}} + \ldots..$$

$$r = 1,2,3,4$$

$$\forall \; r = 1,2,3,4$$

$$E_{n=2,r}(\vec{r}) = \boxed{\lambda^0 E^{(0)}_{n=2} + \lambda^1 E^{(1)}_{n=2,r}} + \ldots..$$

$$\boxed{\begin{aligned}&(H_0 + \lambda H_1)\left\{\lambda^0\chi^{(0)}_{n=2,r} + \lambda^1\psi^{(1)}_{n=2,r}\right\} = \\ &= \left\{\lambda^0 E^{(0)}_{n=2} + \lambda^1 E^{(1)}_{n=2,r}\right\}\left\{\lambda^0\chi^{(0)}_{n=2,r} + \lambda^1\psi^{(1)}_{n=2,r}\right\} \\ &\text{for} \quad r = 1,2,3,4\end{aligned}}$$

And now we can put all of this together by in the full Schrodinger equation, which is the full Hamiltonian operating on the full wave function, and this wave function is a linear superposition, which is expanded in the perturbation order parameter. So, you can substitute this expansion over here, as well as on the left hand side, as well as on the right hand side. The energy is similarly a expansion over the lambda parameters, which is the perturbation order parameter and you can substitute this expansion over here, and the Hamiltonian itself H 0 plus lambda, so you have rewritten this Schrodinger equation for the full Hamiltonian. Now, using the lambda parameters, but now that all terms in corresponding powers of lambda must be equal, so you can equate the terms for lambda equal to 0 on both side of the equation to each other. Likewise you can equate the terms lambda equal to 1 on both side to each other.

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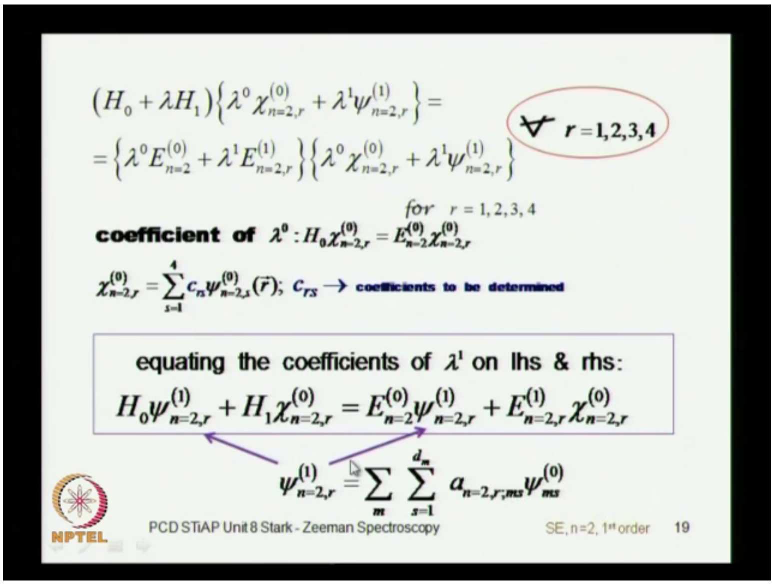

$$(H_0 + \lambda H_1)\left\{\lambda^0 \chi^{(0)}_{n=2,r} + \lambda^1 \psi^{(1)}_{n=2,r}\right\} =$$

$$= \left\{\lambda^0 E^{(0)}_{n=2} + \lambda^1 E^{(1)}_{n=2,r}\right\}\left\{\lambda^0 \chi^{(0)}_{n=2,r} + \lambda^1 \psi^{(1)}_{n=2,r}\right\}$$

$\forall\ r = 1,2,3,4$

for $r = 1, 2, 3, 4$

coefficient of $\lambda^0 : H_0 \chi^{(0)}_{n=2,r} = E^{(0)}_{n=2} \chi^{(0)}_{n=2,r}$

$\chi^{(0)}_{n=2,r} = \sum_{s=1}^{4} c_{rs} \psi^{(0)}_{n=2,s}(\vec{r})$; $c_{rs} \rightarrow$ **coefficients to be determined**

equating the coefficients of λ^1 on lhs & rhs:

$$H_0 \psi^{(1)}_{n=2,r} + H_1 \chi^{(0)}_{n=2,r} = E^{(0)}_{n=2} \psi^{(1)}_{n=2,r} + E^{(1)}_{n=2,r} \chi^{(0)}_{n=2,r}$$

$$\psi^{(1)}_{n=2,r} = \sum_{m} \sum_{s=1}^{d_m} a_{n=2,r;ms} \psi^{(0)}_{ms}$$

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SE, n=2, 1st order 19

And if you do that, then the coefficient of lambda which is equal to 0, so from that you get this unperturbed solution, but the Eigen state is actually a superposition of this degenerate state. And the superposition consist of this coefficient C r s both r and s can take the four values, you have got the similar relation for the each value of r, but the summation over four states. So, s will go from 1 through 4 and these are the coefficients to be determined.

If you now do the same equate the coefficient of the left hand side with the coefficient of the lambda power 1 on both side, left hand side and right hand side. Then you get H 0 and then you have 1 lambda to the power here on the left hand side, and then here is the term which is called lambda to the power 1. So, you got H 1 operating on this chi 0, so these are the two terms that you get on the left hand side, at the right-hand side this is the lambda to the power 0.

So, you will have this term to gather with the term corresponding to lambda for the force power which is this, so you get E 0 psi 1. And then you have the second term, which is lambda 1, but the lambda 1 and this term will give you the second power of lambda that is quadratic term, but in first order perturbation theory you will throw it. So, in the first order term, you will have only lambda 1 and this is lambda to the 0, you will get E 1 psi 0, which is what you have over here, so E 1 psi 0.

So, this is what you get on right on side, so essentially what we are doing it is first order perturbation theory of the degenerate state. Now, the first order correction we have seen is written as a superposition of all the unperturbed state, the superposition consist of the coefficients a, for all values of m which appears an index m. But, then it also must include summation over all the degenerate state, which belongs to the same Eigen value for the given value of n. So, there is a summation over s going from 1 to the degeneracy m th state, so there is an additional index m over here.

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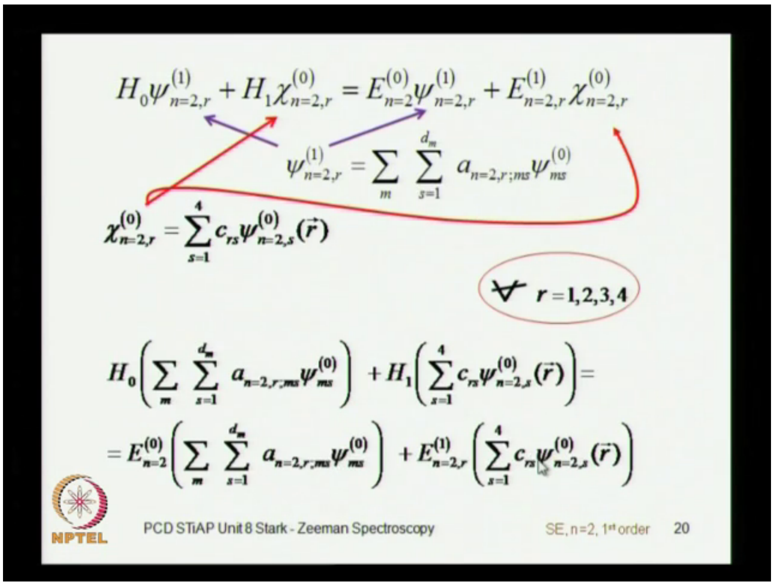

$$H_0\psi^{(1)}_{n=2,r} + H_1\chi^{(0)}_{n=2,r} = E^{(0)}_{n=2}\psi^{(1)}_{n=2,r} + E^{(1)}_{n=2,r}\chi^{(0)}_{n=2,r}$$

$$\psi^{(1)}_{n=2,r} = \sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\psi^{(0)}_{ms}$$

$$\chi^{(0)}_{n=2,r} = \sum_{s=1}^{4} c_{rs}\psi^{(0)}_{n=2,s}(\vec{r})$$

$$\forall\ r = 1,2,3,4$$

$$H_0\left(\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\psi^{(0)}_{ms}\right) + H_1\left(\sum_{s=1}^{4} c_{rs}\psi^{(0)}_{n=2,s}(\vec{r})\right) =$$

$$= E^{(0)}_{n=2}\left(\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\psi^{(0)}_{ms}\right) + E^{(1)}_{n=2,r}\left(\sum_{s=1}^{4} c_{rs}\psi^{(0)}_{n=2,s}(\vec{r})\right)$$

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SE, n=2, 1st order 20

So, this is the first order correction, which we have found and this unperturbed state is a superposition of all the degenerate, unperturbed state corresponding to n equal to 2. So, now you can write the summation, the double summation over here and this summation over here. And this whole equation can be rewritten with H 0 and this chi 1, which is the first order correction which is written in terms of the expansion, so that goes into this bracket plus H 1 operating on this chi 0.

But, this chi 0 is this expansion over four degenerate state, so this is the chi 0 on the left hand side, and the right hand side you have got E 0 psi 1. So, you have got E 0 psi 1 is this expansion over m and then, the last term is E 1 chi 0, so which is expansion over s, so this is E 1 chi 0. So, all we have done is to substitute corresponding expansions, so that is not really very difficult and all we have done is to substitute these terms.

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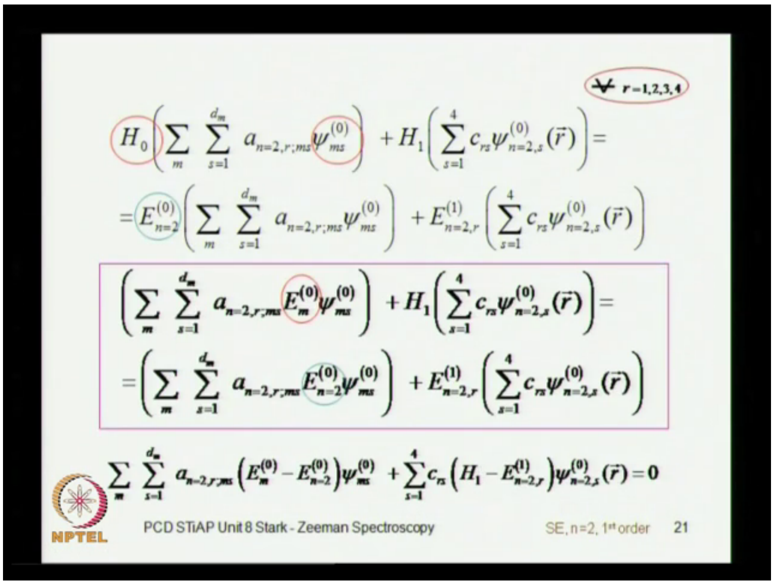

$\forall\ r=1,2,3,4$

$$H_0\left(\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\psi_{ms}^{(0)}\right)+H_1\left(\sum_{s=1}^{4}c_{rs}\psi_{n=2,s}^{(0)}(\vec{r})\right)=$$

$$=E_{n=2}^{(0)}\left(\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\psi_{ms}^{(0)}\right)+E_{n=2,r}^{(1)}\left(\sum_{s=1}^{4}c_{rs}\psi_{n=2,s}^{(0)}(\vec{r})\right)$$

$$\boxed{\begin{aligned}&\left(\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}E_{m}^{(0)}\psi_{ms}^{(0)}\right)+H_1\left(\sum_{s=1}^{4}c_{rs}\psi_{n=2,s}^{(0)}(\vec{r})\right)=\\&=\left(\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}E_{n=2}^{(0)}\psi_{ms}^{(0)}\right)+E_{n=2,r}^{(1)}\left(\sum_{s=1}^{4}c_{rs}\psi_{n=2,s}^{(0)}(\vec{r})\right)\end{aligned}}$$

$$\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\left(E_{m}^{(0)}-E_{n=2}^{(0)}\right)\psi_{ms}^{(0)}+\sum_{s=1}^{4}c_{rs}\left(H_1-E_{n=2,r}^{(1)}\right)\psi_{n=2,s}^{(0)}(\vec{r})=0$$

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And now notice that this H 0 when operates on psi 0 will give you E 0 psi 0, and you have got similar terms on the right hand side as well, but which are the Eigen value of the and perturbed Hamiltonian. But, mind you here the unperturbed Eigen value is that corresponding to n equal to 2 state, whereas in this case this m will take the entire spectrum. So, you have to be careful about it, but then you have got similar expression in the first terms and then, you have got the remaining two terms.

The second term on the left-hand side, and the second term on the right-hand side, which has been written or rewritten just as it is. So, I take all the terms to the left and set everything equal to 0 instead of having left hand side and the right hand side, have taken all the terms on the right hand side to 0 change the sign. So, on the left hand side I will get this E n 0 minus E n 0 from the combination of these two, and on the right hand side I will get these coefficients are the same.

So, it is summation over s going for 1 through 4, C r s this coefficients are essentially the same in both and then, you will have H 1 minus E 1. So, this is just the perturbation correction, but this is unperturbed Hamiltonian, which is this is the perturbation Hamiltonian which is e times E the script E time z, so this is the perturbation and Hamiltonian.

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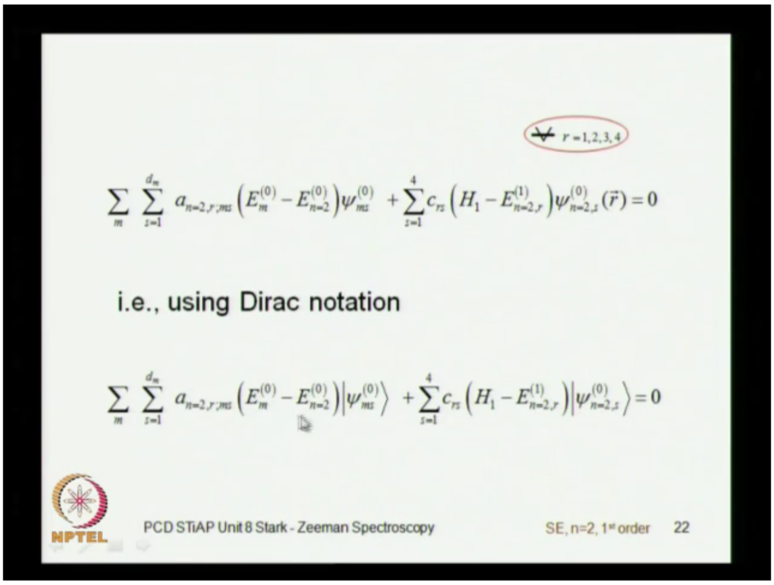

$\forall\, r = 1,2,3,4$

$$\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\left(E_m^{(0)} - E_{n=2}^{(0)}\right)\psi_{ms}^{(0)} + \sum_{s=1}^{4} c_{rs}\left(H_1 - E_{n=2,r}^{(1)}\right)\psi_{n=2,s}^{(0)}(\vec{r}) = 0$$

i.e., using Dirac notation

$$\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\left(E_m^{(0)} - E_{n=2}^{(0)}\right)\left|\psi_{ms}^{(0)}\right\rangle + \sum_{s=1}^{4} c_{rs}\left(H_1 - E_{n=2,r}^{(1)}\right)\left|\psi_{n=2,s}^{(0)}\right\rangle = 0$$

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So, it is easier to look at this using the Dirac notation, so this same expression has been rewritten here in the Dirac notation.

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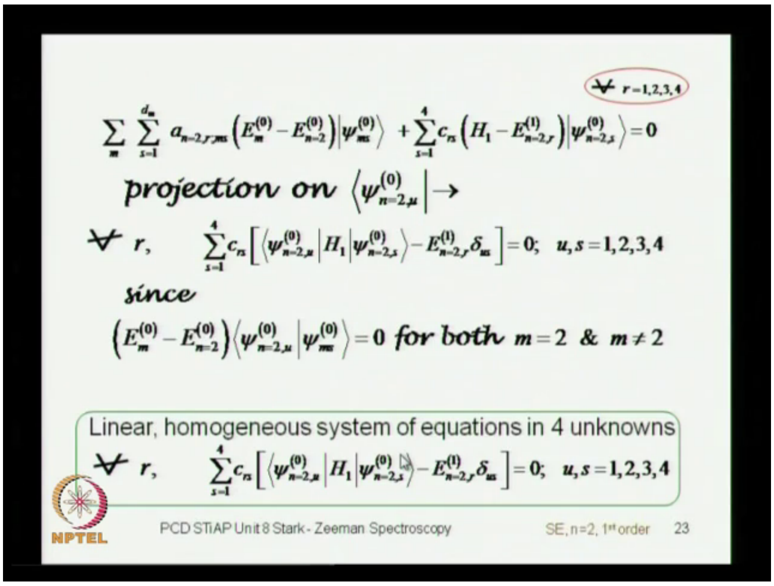

$\forall\, r = 1,2,3,4$

$$\sum_{m}\sum_{s=1}^{d_m} a_{n=2,r;ms}\left(E_m^{(0)} - E_{n=2}^{(0)}\right)\left|\psi_{ms}^{(0)}\right\rangle + \sum_{s=1}^{4} c_{rs}\left(H_1 - E_{n=2,r}^{(1)}\right)\left|\psi_{n=2,s}^{(0)}\right\rangle = 0$$

projection on $\left\langle\psi_{n=2,u}^{(0)}\right| \rightarrow$

$$\forall\, r, \quad \sum_{s=1}^{4} c_{rs}\left[\left\langle\psi_{n=2,u}^{(0)}\middle|H_1\middle|\psi_{n=2,s}^{(0)}\right\rangle - E_{n=2,r}^{(1)}\delta_{us}\right] = 0; \quad u,s = 1,2,3,4$$

since

$$\left(E_m^{(0)} - E_{n=2}^{(0)}\right)\left\langle\psi_{n=2,u}^{(0)}\middle|\psi_{ms}^{(0)}\right\rangle = 0 \text{ for both } m = 2 \ \& \ m \neq 2$$

Linear, homogeneous system of equations in 4 unknowns

$$\forall\, r, \quad \sum_{s=1}^{4} c_{rs}\left[\left\langle\psi_{n=2,u}^{(0)}\middle|H_1\middle|\psi_{n=2,s}^{(0)}\right\rangle - E_{n=2,r}^{(1)}\delta_{us}\right] = 0; \quad u,s = 1,2,3,4$$

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And having written it Dirac notation over here I take the projection, for 1 of the 4 degenerate states of n equal to 2, anyone which does not matter, so I take the projection on one of them which is labeled as u, but then I can do it for all values of u going from 1 through 4. So, I know u and s both go from 1, 2, 3 and 4 and when I take the projection, if you look at this term, in this if m is equal to 2, this difference in energy will vanish.

And if m is not equal to 2 than this projection will vanish, because E states we know orthogonal to each other. So, we do not get any contribution from this side, when you take the projection and then you have left with a system of linear homogeneous equations coming from here. So, you have got for every r a system of linear homogeneous equations, there are four unknowns for every value of r. And this is the system of equation that we know now want to solve, so is standard mathematical techniques which your familiar with, so this is how you solve linear homogeneous equation.

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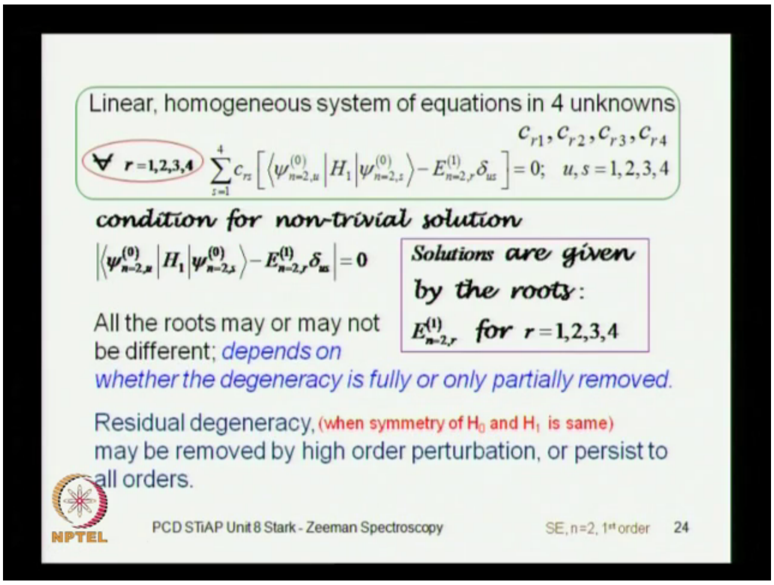

Linear, homogeneous system of equations in 4 unknowns $c_{r1}, c_{r2}, c_{r3}, c_{r4}$

$$\forall\ r=1,2,3,4 \quad \sum_{s=1}^{4} c_{rs}\left[\left\langle \psi^{(0)}_{n=2,u} \middle| H_1 \middle| \psi^{(0)}_{n=2,s} \right\rangle - E^{(1)}_{n=2,r}\delta_{us}\right] = 0; \quad u,s=1,2,3,4$$

condition for non-trivial solution

$$\left| \left\langle \psi^{(0)}_{n=2,u} \middle| H_1 \middle| \psi^{(0)}_{n=2,s} \right\rangle - E^{(1)}_{n=2,r}\delta_{us} \right| = 0$$

Solutions are given by the roots: $E^{(1)}_{n=2,r}$ *for* $r=1,2,3,4$

All the roots may or may not be different; *depends on whether the degeneracy is fully or only partially removed.*

Residual degeneracy, (when symmetry of H_0 and H_1 is same) may be removed by high order perturbation, or persist to all orders.

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You know that non-trivial solution were come for this condition, this is the condition that must be satisfied that the determinant of this matrix over vanish. So, this is the condition to get non trivial solution and the roots will give you the corrections, the energy corrections that you are looking for. So, these are the four roots that you are looking for, they may all be different from each other, if the degeneracy is only resolved, if not some of them may be the same or they may or be the same, so you have never done.

But, these are the solutions that you are looking for and the degeneracy will be resolved, if the Hamiltonian is perturbed, if the original Hamiltonian is perturbed, which has got this entry which is different from that of the original Hamiltonian. So, the residual degeneracy there may be some, it can be either removed by higher order perturbation or else it can even persist to all orders. And then, you might want to if you need to break it you may have to use different perturbation altogether, this particular perturbation will not do it.

So, that depends on what is this symmetry of the perturbation Hamiltonian compared to the symmetry of the original Hamiltonian as we have seen earlier. Because, degeneracy and symmetry goes together, the degeneracy can be broken only, if you break this symmetry of the Hamiltonian.

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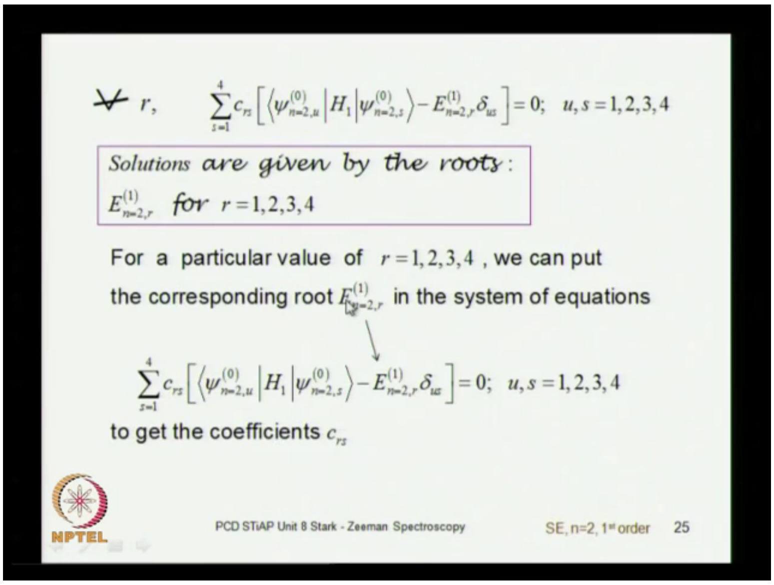

$$\forall\ r,\quad \sum_{s=1}^{4} c_{rs}\left[\left\langle \psi^{(0)}_{n=2,u}\right|H_1\left|\psi^{(0)}_{n=2,s}\right\rangle - E^{(1)}_{n=2,r}\delta_{us}\right]=0;\quad u,s=1,2,3,4$$

Solutions are given by the roots: $E^{(1)}_{n=2,r}$ for $r=1,2,3,4$

For a particular value of $r=1,2,3,4$, we can put the corresponding root $E^{(1)}_{n=2,r}$ in the system of equations

$$\sum_{s=1}^{4} c_{rs}\left[\left\langle \psi^{(0)}_{n=2,u}\right|H_1\left|\psi^{(0)}_{n=2,s}\right\rangle - E^{(1)}_{n=2,r}\delta_{us}\right]=0;\quad u,s=1,2,3,4$$

to get the coefficients c_{rs}

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So, this is the system of equation that we want to solve, and the solutions are given by the roots of this equation, so what you will do is for each value of r, you can put after you get the roots of the equations, you can put those roots and then get the coefficient c. So, now you know how to determine the coefficient C, because these where the undetermined factor which we had, but we have found a mechanism to determine this by plugging in the roots that you get. And for each route you can solve this set of equations and from the set of equations, you can get the corresponding coefficient C r s, so that is the mechanism to get the solutions.

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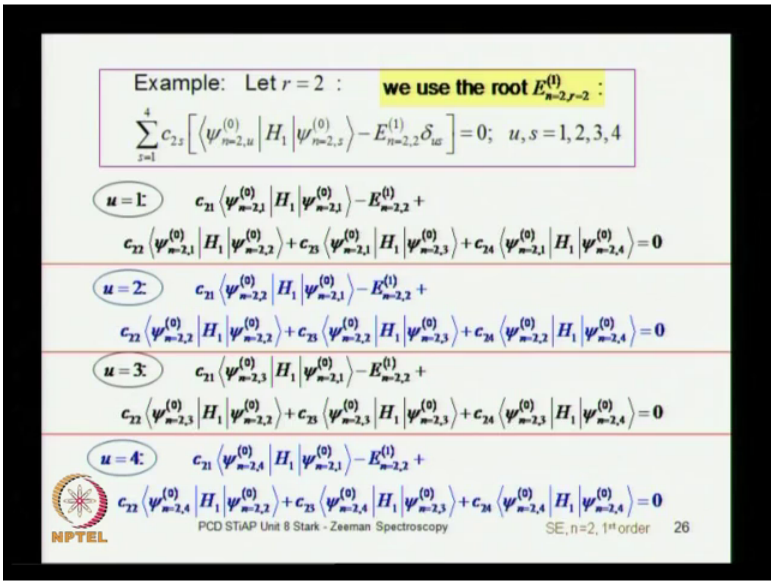

Example: Let $r = 2$: **we use the root $E^{(1)}_{n=2,r=2}$:**

$$\sum_{s=1}^{4} c_{2s}\left[\left\langle \psi^{(0)}_{n=2,u} \middle| H_1 \middle| \psi^{(0)}_{n=2,s} \right\rangle - E^{(1)}_{n=2,2}\delta_{us}\right] = 0; \quad u, s = 1, 2, 3, 4$$

$u = 1$:
$$c_{21}\left\langle \psi^{(0)}_{n=2,1} \middle| H_1 \middle| \psi^{(0)}_{n=2,1} \right\rangle - E^{(1)}_{n=2,2} +$$
$$c_{22}\left\langle \psi^{(0)}_{n=2,1} \middle| H_1 \middle| \psi^{(0)}_{n=2,2} \right\rangle + c_{23}\left\langle \psi^{(0)}_{n=2,1} \middle| H_1 \middle| \psi^{(0)}_{n=2,3} \right\rangle + c_{24}\left\langle \psi^{(0)}_{n=2,1} \middle| H_1 \middle| \psi^{(0)}_{n=2,4} \right\rangle = 0$$

$u = 2$:
$$c_{21}\left\langle \psi^{(0)}_{n=2,2} \middle| H_1 \middle| \psi^{(0)}_{n=2,1} \right\rangle - E^{(1)}_{n=2,2} +$$
$$c_{22}\left\langle \psi^{(0)}_{n=2,2} \middle| H_1 \middle| \psi^{(0)}_{n=2,2} \right\rangle + c_{23}\left\langle \psi^{(0)}_{n=2,2} \middle| H_1 \middle| \psi^{(0)}_{n=2,3} \right\rangle + c_{24}\left\langle \psi^{(0)}_{n=2,2} \middle| H_1 \middle| \psi^{(0)}_{n=2,4} \right\rangle = 0$$

$u = 3$:
$$c_{21}\left\langle \psi^{(0)}_{n=2,3} \middle| H_1 \middle| \psi^{(0)}_{n=2,1} \right\rangle - E^{(1)}_{n=2,2} +$$
$$c_{22}\left\langle \psi^{(0)}_{n=2,3} \middle| H_1 \middle| \psi^{(0)}_{n=2,2} \right\rangle + c_{23}\left\langle \psi^{(0)}_{n=2,3} \middle| H_1 \middle| \psi^{(0)}_{n=2,3} \right\rangle + c_{24}\left\langle \psi^{(0)}_{n=2,3} \middle| H_1 \middle| \psi^{(0)}_{n=2,4} \right\rangle = 0$$

$u = 4$:
$$c_{21}\left\langle \psi^{(0)}_{n=2,4} \middle| H_1 \middle| \psi^{(0)}_{n=2,1} \right\rangle - E^{(1)}_{n=2,2} +$$
$$c_{22}\left\langle \psi^{(0)}_{n=2,4} \middle| H_1 \middle| \psi^{(0)}_{n=2,2} \right\rangle + c_{23}\left\langle \psi^{(0)}_{n=2,4} \middle| H_1 \middle| \psi^{(0)}_{n=2,3} \right\rangle + c_{24}\left\langle \psi^{(0)}_{n=2,4} \middle| H_1 \middle| \psi^{(0)}_{n=2,4} \right\rangle = 0$$

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So, let us illustrate this for a particular case I will take the case of r equal to 2 just any one of those four values, and you take the roots corresponding to r equal to 2, whatever it is. And then for each value of u, u going from 1, 2, 3 and 4 you will have four sets of equations, so this is the equation for u equal to 1. So, all we have done over here is to put r equal to 2 and u equal to 1 in this and then, there are four terms coming in from here and this is the fifth the term.

But, this term has a chronicle delta, delta u s, so it will give you non zero contribution only when u is equal to s, so you will have a total of these five terms, and there is a similar set of terms for u equal to 2, a similar set of terms for u equal to 3 and a similar set of terms for u equal to 4. So, all you do is to substitute the different values of r, u and s, we are illustrating here this example for r equal to 2, and solving this equations will give you the coefficient C. And you notice that in this system of equation, you have the matrix element of H 1 which is the perturbation Hamiltonian in the unperturbed states corresponding to n equal to 2, to all those four degenerate states.

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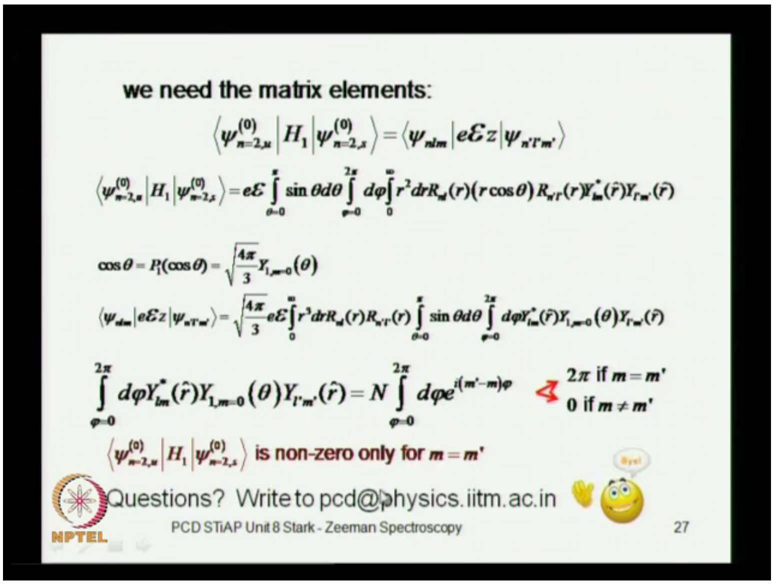

we need the matrix elements:

$$\langle \psi^{(0)}_{n=2,u} | H_1 | \psi^{(0)}_{n=2,s} \rangle = \langle \psi_{nlm} | e\mathcal{E} z | \psi_{n'l'm'} \rangle$$

$$\langle \psi^{(0)}_{n=2,u} | H_1 | \psi^{(0)}_{n=2,s} \rangle = e\mathcal{E} \int_{\theta=0}^{\pi} \sin\theta d\theta \int_{\varphi=0}^{2\pi} d\varphi \int_{0}^{\infty} r^2 dr R_{nl}(r)(r\cos\theta) R_{n'l'}(r) Y^*_{lm}(\hat{r}) Y_{l'm'}(\hat{r})$$

$$\cos\theta = P_1(\cos\theta) = \sqrt{\frac{4\pi}{3}} Y_{1,m=0}(\theta)$$

$$\langle \psi_{nlm} | e\mathcal{E} z | \psi_{n'l'm'} \rangle = \sqrt{\frac{4\pi}{3}} e\mathcal{E} \int_{0}^{\infty} r^3 dr R_{nl}(r) R_{n'l'}(r) \int_{\theta=0}^{\pi} \sin\theta d\theta \int_{\varphi=0}^{2\pi} d\varphi Y^*_{lm}(\hat{r}) Y_{1,m=0}(\theta) Y_{l'm'}(\hat{r})$$

$$\int_{\varphi=0}^{2\pi} d\varphi Y^*_{lm}(\hat{r}) Y_{1,m=0}(\theta) Y_{l'm'}(\hat{r}) = N \int_{\varphi=0}^{2\pi} d\varphi e^{i(m'-m)\varphi} \quad \begin{matrix} 2\pi \text{ if } m = m' \\ 0 \text{ if } m \neq m' \end{matrix}$$

$\langle \psi^{(0)}_{n=2,u} | H_1 | \psi^{(0)}_{n=2,s} \rangle$ is non-zero only for $m = m'$

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And you need to determine this matrix element, and now you can put in the exact explosive expression for the perturbation Hamiltonian, which is this e E z and you have to get this is the overall integral that you must determine. So, this integration is a space integration, integration overall value of r theta and phi, phi going from 0 to 2 phi theta going from 0 to phi and r going from 0 to infinity. So, you separate the radial part and the angular part carryout the integration, here you have got z, has got an angle dependent factor as well, because z is r cosine and theta.

So, z contains r as well as cosine theta, so cos theta however, is the general polynomial for l equal to 1, so you can put the spherical harmonic in this angular integration. So, you first carry out the angle integration over phi, but this is cos and theta for m equal to 0, so which means that the only the m quantum numbers, which will come are those from this Y l prime m prime and from Y l m, because this is got l equal to 1 and m equal to 0. So, essentially in the five integration you will have integration over phi of each of the i m prime minus m times phi, this is m prime and this is m, so you get m prime minus i times phi.

And ((Refer Time: 43:52)) this is non zero only in the case that m is equal to m prime, that is the only case which is of interesting, and that really offers main disadvantage in our case. It also means that the degeneracy is not fully removed, and you will see this, we will discuss from this point in the next class, I will conclude today's class by recognizing that the only terms which will give you non zero values to this matrix elements of the perturbation Hamiltonian, are those corresponding to m equal to m prime.

And you will remember that in the four degenerate states, you have the 2 s and the 2 P, so the 2 P has got m quantum numbers going from minus 1 to plus 1. So, the terms corresponding to minus 1 and plus 1 will make no contribution, only the term corresponding to m equal to 0 will contribute. So, we will continue from this point in our next class, if there is any question I will be happy today, yes.

Student: Expressing perturbation in the Eigen basis of original Hamiltonian, so how is that symmetry different between the original Hamiltonian and that perturbation Hamiltonian.

The symmetry of the perturbation is of course, different from that of the unperturbed Hamiltonian, but the premise of perturbation theory is that, whatever the perturbation does is expressible as a linear superposition of unperturbed Eigen state. So, there is no conflict in this at all, perturbation theory works essentially on this basis, that the perturbation does not throw the system outside it is Hilbert space. The unperturbed Hamiltonian has got a certain Hilbert space, so there is a certain basis, Eigen basis of the unperturbed Hamiltonian.

And even after you impose the perturbation, the solution will be expressible as a linear super position of basis function of the unperturbed Hamiltonian, that is the whole contention of the perturbation theory. That certainly does not mean, that the perturbation as to have the symmetry of the Hamiltonian as a matter of fact, if the perturbation does not have the symmetry of the Hamiltonian, it is not go to ever break the degeneracy, there is absolutely no complicity.

The contention of perturbation theory is that the perturbation results in a new wave function, which is never the less expressible as a linear superposition of the Eigen state of the unperturbed Hamiltonian. So, whatever you do to the unperturbed Hamiltonian it is not so wild that you cannot express the total wave function, as a linear superposition of the unperturbed state; that is the whole premise of perturbation theory. And that does not require the symmetry of the perturbation to be the same of the, as a symmetry of the unperturbed Hamiltonian, there is absolutely no such requirement.

Why would there be such a requirement, the question of symmetry relates to a different aspect of this issue, which is the degeneracy of the state. So, the symmetry is important in the context of degeneracy that, if the perturbation has got the symmetry, which is different from that of symmetry of original Hamiltonian; it would remove the degeneracy either partially or fully. Whether it does so fully or not depends on certain details, which is what we are examining over here, like we have already seen that you get are non zero connection between the states, only if m is equal to m prime not at the y.

So, m equal to minus 1 and plus 1 states of the 2, n equal to 2 quantum number for n equal to 2, the non relativistic hydrogen atom has got four degenerate states n square, which is the 2 i s. And the three linearly independent Eigen functions of 2 P which is for n equal to 2, l equal to 1 and m going from minus 1, 0 and plus 1. So, out of these three the m equal to minus 1 and plus 1 will not contribute anything to this matrix element, so that is where the question of symmetry comes in. And it does not put any restriction on expanding the system Eigen state of the perturbed Hamiltonian of the four Hamiltonian, as a linear superposition of the unperturbed state. In fact, that is the very premise of perturbation theory, yea any other question, so good bye for now.