ELEMENTS OF MODERN PHYSICS

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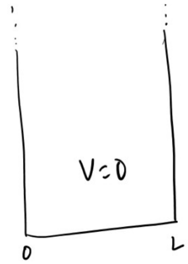
Lec 10: Degenerate Perturbation Theory, Stark Effect

So we shall continue with this discussion on perturbation theory that we have been doing. And in particular, we are talking about the time independent perturbation theory and a non-degenerate case. And just to remind you that the perturbation is small compared to the unperturbed Hamiltonian. And hence, we are allowed to use perturbation. the eigen states of the unperturbed Hamiltonian in order to find corrections to the energy and to the wave function. And we shall continue with that discussion. And then we'll talk about the degenerate perturbation theory. If you remember, the wave function correction involved an energy denominator and these energy denominator came as some En0 minus Ek0. Now that would blow up or will diverge as EN0 equal to EK0. So you need an alternate formalism for this degenerate case. And we'll do applications of the degenerate perturbation theory. And in particular, we'll talk about stark effect, which is a hydrogen atom present in presence of an, I mean, hydrogen atom in presence of an electric field, a weak electric field, which does not cause ionization, but it causes change in or rather the split in degeneracy and so on, okay. So let us start with an example so that you get a handle of how these perturbation theory problems are handled. So we are talking about a particle in a box. So this is the same problem that we have done. So you have V equal to zero here. And V is infinity at the walls, which means that the particle is actually trapped inside.

And the question is that suppose you have a perturbation of the form, which is epsilon V naught sine pi x by L. There's no need for, you know, both epsilon and V naught, but just V naught is the scale of the It has a scale of energy and epsilon is much smaller than 1. That tells you that this is a perturbation term and you want what is the correction in energy to the n equal to 2 state which means the first excited state, okay? That's the question. And the answer is simple because what you have to do is that you have to calculate the energy correction. So that's the answer which can be obtained by this unperturbed energy for the N equal to two state. And you have the H prime and then this and this can be written as two. So we'll use this. n equal to 2 state as root over 2 by L sin

2 pi x over L. So, 2 epsilon v0 and divided by L and then we have sine square 2 pi x over L and you have a sine pi x over L and integrated over dx and this is from 0 to L. So, we have to integrate this thing from 0 to L. If you look, if you do this integral by, you know, converting the sine square into cosine and so on, I leave that integral to be done by you.

Example.



$H' = \epsilon V_0 \frac{\sin \pi x}{L}$ $\epsilon << 1$.

What is the correction in energy to $n=2$ state?

$\psi_2^0 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}$

Ans. $E_n^{(1)} = \langle \psi_2^0 | H' | \psi_2^0 \rangle = \frac{2 \epsilon V_0}{L} \int_0^L \sin^2 \frac{2\pi x}{L} \sin \frac{\pi x}{L} \, dx$

$= \frac{32 \epsilon V_0}{15\pi}$.

$E_0 = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$

$E_0 = \frac{4 \hbar^2 \pi^2}{2mL^2}$.

$E = E_0 + E_n^{(1)} = \frac{4\pi^2\hbar^2}{2mL^2} + \underbrace{\frac{32 \epsilon V_0}{15\pi}}_{H'}$ Ans.

And then what you get is that you get a 32 epsilon V0 and divided by 15 pi. So that's the energy correction to the second excited state. So the second excited state, which has the unperturbed energy equal to, you know, 4 h cross square by 2 m L square. So, it is basically the unperturbed energies are given by n square pi square h cross square. So, I missed a pi square here and so 2 m L square. So, n equal to 2. So, that gives you a 4. So, 4 pi square h cross square divided by 2 L square. So, the total energy will become equal to E 0 plus these the correction that we have found out which is en1 so this is like 4 pi square h cross square divided by 2 m L square plus 32 epsilon v0 divided by 15 pi that's the answer for this and this term is purely coming because of the perturbation okay there's a contribution to h prime So let us go into the degenerate perturbation theory, which has to be, as I said, that it has to be dealt with care. And so what we have is that there are several energy states that correspond to several states, wave functions, they correspond to the same energy. So this is called as a degenerate, I'm sorry, degenerate perturbation theory. okay So the earlier formalism that you saw was really appropriate for non-degenerate case when all the levels are non-degenerate.

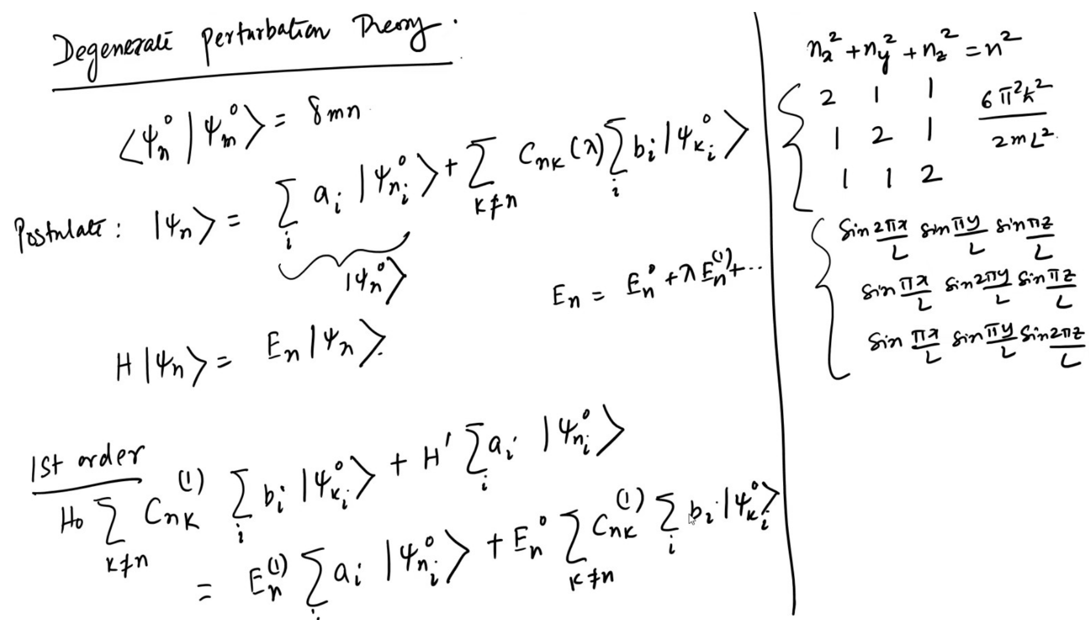
But of course, we know that as you go, you know, in two dimensions and higher than that, that is larger than one dimension, degeneracy is bound to come. And we have shown that for, say, a particle in a box. And so, for a particle in a box, let us just, you know, sort of once again remind you how the degeneracy comes, as this is what the energy would be, you know, proportional to this n squared. So we can have this as 2, 1, 1; 1, 2, 1; or 1, 1, 2. All these three will be degenerate because each one of them will give rise to 6, n squared equal to 6, and so on. I mean, in the sense that all of them will have the same energy, which is n squared, which is 4 plus 1 plus 1, that's 6. So it's like 6 pi squared h cross squared over 2 m L squared. But they would correspond to different eigenstates of the problem because this would be like sine 2 pi x over L.

sine pi y over L, sine pi z over L. And the other one, the second one, would be sine pi x over L, sine 2 pi y over L, and sine pi z over L. And the third one, the last one, would be sine pi x over L, sine pi y over L, and sine 2 pi z over L, okay? And these are distinct eigenfunctions, but they correspond to the same energy. And this is what is meant by the degenerate case. And we have to develop a perturbation theory for this degenerate case, okay? So, we still have these states, okay, which we call, you know, psi n0 and psi m0. These are all orthonormal. And if you use some other indices, such as what we are going to use here, so we make a postulate that for the total wave function, we have a psi n and there is a sum over i, a i, psi n i 0 plus sum over k, which is not equal to n, and we have a Cnk lambda, and then sum over i b i and psi k i 0, okay? And that's your answer for the wave function.

And so we have used another index, as you see here, in addition to the n and m or n and k here, we have used the i index, and that index would correspond to different eigenvalues, okay. So there are these eigenvalues which may be degenerate, and these would represent this eigenvalue index. And so what we have done is that we have gone from a psi n zero, which was written earlier, to this sum over i, a i, psi n i 0. These are still the eigenfunctions, degenerate eigenfunctions corresponding to eigenvalue, say, lambda i. And that's why there is a sum over i and a i. a i is just an amplitude of the wave function which needs to be determined. And the Cnk lambda, these are powers. This can be expanded in powers of lambda, and you keep a certain, you evaluate this Schrodinger equation till a certain power of lambda, and this power of lambda would eventually talk about or rather give us the order of perturbation theory that you are dealing with. So ai's and bi's, as I said, are the coefficients that we need to determine. And of course, we see in

K alpha as well. So once again, what we do is that we put it into the equation, which is H psi n.

equal to En psi n and use this as the expansion and E n is also you know expanded in terms of lambda. Still first order, we get a term which is H0 and a k not equal to n and you have a Cnk1. So what I mean by first order is that is first order in lambda just the way we have done it for the non-degenerate perturbation case. Then there's a sum over I bi psi ki 0 plus H prime sum over AI psi n i 0 and this is equal to En 1 which is what you want that is the first order correction to energy and so basically the En is equal to En0 plus lambda En1 and so on. So, we are equating till the first order of lambda and En1 sum over i, ai, psi, ni, 0, En0, k not equal to n, and Cnk1, and sum over i, bi, psi, k0, i. It may look complicated, but the final result that we are going to get is not difficult and it is easy to actually reproduce or rather get the first order correction, very similar to what we have done it for the unperturbed case. So just bear with me for some time because these are essential steps and they cannot be avoided, especially for these degenerate perturbation theory.



So what we need to do is that we need to actually calculate this E n 1. And to get the E n 1, we follow the standard procedure of taking an overlap with this psi n with another index. I mean, in the sense that psi n 0 j. So let me write that. Okay, so what I mean by this is that you take this term, okay, so the conjugate of that and recognize that your En1, then En1 is extracted and because k is not equal to n and all that, we get some of the terms going to 0 as it happened earlier. So, this is like a psi n j 0 h prime psi n i 0 and so on. And this can be called as the matrix element h prime j i, okay? So, between the eigenstates of the unperturbed Hamiltonian and this is the energy correction and that is exactly what you need. Okay, so this is the energy correction. Now, instead of just a number, this was exactly like what we have done it in the example. You saw that we have used this. Now, because of the degenerate case, we have a sum over I and there is also an associated amplitude that need to be determined. Okay. So, this can be written as, so this a j En 1. So, there is a j which I forgot here. So, there is a j En 1. This is equal to sum over i. Now, this sum over i now has to be specified that this is, I told you that this actually is the eigenvalue of

So, it will go from 1 to D where D is the degeneracy. Suppose this n equal to 2 state is 4-fold degenerate in the hydrogen atom without leaving out the spin degeneracy. If you include that, it becomes 8-fold degenerate. So, d is that number. Like, in this example that we have talked about, the n equal to 6, or rather n squared equal to, you know, 6, is actually a 3-fold degenerate state, okay? So, because 0 is not allowed, so they can either take values, so this is the first excited state, okay? So this is I equal to 1 to d and we have a I and H prime j i. So that's a matrix element has to be considered. And the sum over I runs from 1 to d and d denotes that, as I said, it's a degree of degeneracy.

Taking an overlap with $\psi^0_{n_j} \rightarrow \langle \psi^0_{n_j}|$.

$$E_n^{(1)} a_j = \sum_i a_i \underbrace{\langle \psi^0_{n_j} | H' | \psi^0_{n_i} \rangle}_{H'_{ji}}$$

$$a_j E_n^{(1)} = \sum_{i=1}^{d} a_i H'_{ji}$$

d: degree of degeneracy.

So, that is what is important and the problem becomes slightly more complicated as compared to the non-degenerate counterpart, but then nevertheless it is a finite dimensional problem and we should be able to solve it and we will just see it for a given case. So, let us do a twofold degenerate case. this is the simplest, I mean, one-fold is the non-degenerate and two-fold is the degenerate, the first, you know, the simplest of the cases, so two-fold degenerate case. And what we have is that we have this H0 minus En0 psi n1.

It is equal to E n1 minus H prime and psi n0. And then, of course, this is the equation that we have. That is the starting point, and let us call this equation 1, and the psi n0 is at the first order. So, we are really developing this two-fold degenerate case at the first order. In fact, anything beyond first order is a little more complicated. We will see some examples but may not solve them completely. So, this is the equation that we start with. This is the first-order equation. If you go back to where we started discussing non-degenerate perturbation theory, you still have this equation written down there. So now, the psi n0 comprises two orthogonal eigenfunctions. Let us call them u1 and u2, and let me write them as a1 u1 plus a2 u2, where a1 and a2 are, in general, complex coefficients. So, these u1 and u2 are the degenerate states. That means they are themselves distinct. They are not equal to each other, nor are they linearly dependent. They are linearly independent and orthonormal. And they form this basis for, or rather, these two are the degenerate states. They correspond to the same energy, okay. And so this is like the answers that you do. And because you know that you're dealing with a two-fold degenerate case, say, for example, a two-dimensional oscillator, okay.

So, a two-dimensional oscillator will have a nx plus ny plus half plus half, corresponding to each of nx and ny, H cross omega. That's the nx, ny energy. Now, if you talk about, you know, 3H cross omega energy, so energy equal to nx, ny equal to, so this is 1. Let's talk about 2H cross omega, so that's the first excited state, 2H cross omega. This is just an example. Then, nx can be 0 and ny can be 1, or nx can be 1 and ny will be 0, and these two will give rise to a two-fold degenerate state, which is very similar to the one we are talking about. And so this, of course, is equal to 1. So, 1, these two put together will make it 1. And nevertheless, u1 and u2 are orthogonal because the corresponding wave functions are orthogonal to each other. These are these Hermite polynomials multiplied by the Gaussian function, and they are orthogonal. So, similar to that. Okay, so we have to put it there in this equation on the right-hand side. And let us call this equation 2. And so, putting 2 in 1, what we get is the following: We get H0 minus En0 psi n1. So, my sincere advice to all of you would be to do it by hand.

I am pretty sure that I'm not making a mistake, but even if I do, with either some sign or some index, that should not percolate into you. So, you should do it all by yourself and convince yourself that these are the correct steps to follow. And specifically, I'm doing it while I'm speaking for the reason that you understand. If I show you some slides, then the idea would never get across because these are mathematical steps that you need to do to arrive at the results, which are very important for us. The end results are important, but for you, it's also important how you arrive at those results. So H0 minus En0 psi n1, that's the left hand side, which remains unchanged. And then you have a En1 minus H prime. And then we put this a1 u1 plus a2 u2.and understanding is u1 and u2 is equal to 0. So, that is an overlap or the inner product equal to 0. So, this is equation 3. Now, what we can do is take an overlap. When I say overlap, what I mean is that you operate it by the conjugate of some wave function. In this case, it's the conjugate of u1. That's the bra of u1. So, if you do that—so operate it with this on both sides—this will be H0 minus En0 and a psi n1. And so En1, you don't need to worry about because it's just a number.

So this will be En1, and this u1, and then u1, u1 overlap will give you 1. And u1, u2 overlap will give you 0. But nevertheless, you have a u1 H prime with an a1 here, H prime u1. And there is another term which is, so that's a minus term. With A1, this is equal to 0. And then you also have a term which is, minus u1 h prime with an a2 coefficient h prime. I hope these are—they do not look like—so this, let me write it again. So, this is actually a1, a1, a2, and then you have a u1 h prime u2, okay. All right. So now calling these ones as H prime 1 1, 1 1 because that's a matrix element between these states, the unperturbed states, unperturbed degenerate states. This is H prime 1 2, okay. And we'll do the same thing for H. For u2, but look at this: H0 acting on psi—I mean, H0 will act on this u1 and give me En0, which is its eigenstate. So let me write it here. This is just an example. So let me put a red line.

So as to, you know, this is just an example that we have given. So this is separate. And so with this, you also have H0 and u1 that's equal to, you know, En0 u1 and so on. And H0 u2 is same as En0 u2. So, that tells you that this term is equal to 0 because H0 acting on this bra u1 will give me En0, and the En0 will cancel with this. So, what we have is 0 equal to En1 A1, and let me also put A11. Because we are talking about the first order, so A11 and minus H11 prime, A 1 1 and minus H 1 2 prime A 2 1. So, this is the thing that we get, and if we do a simplification of that, this 1 along with A 1 and A 2, we have not written that earlier, but then it just sort of gives you a handle to remember that you are doing a first-order perturbation theory. So, what you can do is that you can also leave that if you want, and it is not very essential to have it, but you can carry on with this if you wish. So, a 1 1.

This is E n 1 minus H11 prime, this minus a21 H12 prime, this is equal to 0, and let us call that as equation 4. So, this is what we get by just to remind you of the steps that we have written down the Schrödinger equation at the first order, that is first order in lambda, which is the smallness parameter. And then because of this degenerate case, this is the ansatz made for the degenerate case, that is, you have the two degenerate eigenstates u1 and u2, which are mutually orthogonal, and they both give rise to energy E and 0. So, we write that ansatz there, expand it, And use shorthand notations for all these matrix elements of H prime between u1, u1 and u1, u2 as H1, 1 prime and H1, 2 prime respectively. And then simplify this to arrive at 4, which gives you one equation which is useful for us and that contains these amplitudes, and because we are talking about first order, so everywhere this e n 1 etc. The 1 in the bracket denotes that we are talking about the first-order perturbation theory. Now, the same thing we can do it on equation number 3 and take an overlap with u 2. So, this is taking overlap with u1, that is this okay, and then we go to this and then say that taking overlap with u2.

Two-fold degenerate case.

1st order: $(H_0 - E_n^0)|\psi_n^{(1)}\rangle = (E_n^{(1)} - H')|\psi_n^0\rangle$ (1).

Ansatz: $|\psi_n^0\rangle = a_1|u_1\rangle + a_2|u_2\rangle$ (2).

$|u_1\rangle, |u_2\rangle$ are degenerate state — same energy. $\langle u_1|u_2\rangle = 0$.

$E_{n_x,n_y} = (n_x + n_y + \frac{1}{2} + \frac{1}{2})\hbar\omega$

$E_{n_x,n_y} = 2\hbar\omega$: $n_x = 0, n_y = 1$; $n_x = 1, n_y = 0$

$H_0|u_1\rangle = E_n^0|u_1\rangle$

$H_0|u_2\rangle = E_n^0|u_2\rangle$

Putting (2) in (1).

$$(H_0 - E_n^0)|\psi_n^{(1)}\rangle = (E_n^{(1)} - H')(a_1|u_1\rangle + a_2|u_2\rangle) \quad (3).$$

$$\underbrace{\langle u_1|(H_0 - E_n^0)|\psi_n^{(1)}\rangle}_{=0} = a_1 E_n^{(1)} - a_1\underbrace{\langle u_1|H'|u_1\rangle}_{H'_{11}} - a_2\underbrace{\langle u_1|H'|u_2\rangle}_{H'_{12}}$$

$$0 = E_n^{(1)} a_1^{(1)} - H'_{11} a_1^{(1)} - H'_{12} a_2^{(1)}.$$

$$\therefore a_1^{(1)}(E_n^{(1)} - H'_{11}) - a_2^{(1)} H'_{12} = 0. \quad (4)$$

And once you do that, you get another equation which is of the form a11 H21 prime plus a21 En1 minus H22 prime to be equal to 0, and let us call that as equation 5. Now, you see, instead of one equation for the energy correction, you have to solve a system of two equations. And these two equations can be solved—or rather, they have a unique solution—if the determinant corresponding to the coefficients of a11 and a21, that is a2 superscript 1 and a1 superscript 1 (the one inside the bracket), these coefficients vanish, or the determinant of the coefficients vanishes. And so we write it for a unique solution.

We should have this condition: that is, En1 minus H11 prime, H12 prime, minus H21 prime, and En2—sorry, En1, that is the same En1—minus H22 prime.

So, this should be equal to 0. I mean, this means that the determinant is equal to 0. So, this is actually the determinant. And the determinant is usually written between two vertical lines. So, we will just do that. So, this is equal to zero. And this has two solutions, which are the solutions for En1. So, we'll write En1. So, this one means that there are two solutions—the one in the subscript of n. That means there are two solutions, and we are talking about En1 and En2. But the superscript—so, inside the bracket—that tells you that we are talking about the first-order perturbation theory. Make all these, you know, nomenclature clear in your mind. And then we have H11 prime plus H22 prime by solving the determinant equal to 0. And plus the square root of H22 prime minus H11 prime squared plus 4 H21 prime squared. So, this is 1. Let's call it equation number six because we already have five. And the other one is H11 prime plus H22 prime and comes with a negative in front of this square root. So, it's H22 prime H11 prime squared plus 4 H21 prime squared, and the bracket closes.

Taking overlap with $\langle u_2|$

$$-a_1^{(1)} H_{21}' + a_2^{(1)} \left(E_n^{(1)} - H_{22}' \right) = 0. \quad (5)$$

For a unique solution: determinant

$$\begin{vmatrix} E_n^{(1)} - H_{11}' & H_{12}' \\ -H_{21}' & E_n^{(1)} - H_{22}' \end{vmatrix} = 0.$$

$$E_{n_1}^{(1)} = \frac{1}{2}\left[\left(H_{11}' + H_{22}' \right) + \sqrt{ \left(H_{22}' - H_{11}' \right)^2 + 4 |H_{21}'|^2 } \right] \quad (6).$$

$$E_{n_2}^{(1)} = \frac{1}{2}\left[\left(H_{11}' + H_{22}' \right) - \sqrt{ \left(H_{22}' - H_{11}' \right)^2 + 4 |H_{21}'|^2 } \right].$$

So, that tells you that these are the two energy corrections. We did not have a single algebraic equation to solve in order to get En1, but it came as a matrix equation. And for a unique solution, the determinant of the coefficient matrix will have to vanish. And that gave us these two corrections to the energy. So, suppose you have these energy levels which were earlier degenerate. Now, because of this plus-minus sign, it sort of splits like this and like this. So, this is unperturbed EN0, and these are the energy corrections. Let us call this as En1 and let us call this as En2. So, the degenerate energy level now, because of this perturbation, splits, and the splitting is apparent because of this plus and minus sign. I mean, if for some reason inside this square root these terms vanish, then, of course, there is no splitting of degeneracy. But mostly, what our experience says is that there is a split in degeneracy unless some other selection rules prohibit that there should be no split in degeneracy. We'll talk about that. Now, in order to calculate the change in the wave function, we can calculate these amplitudes, which are a21 divided by a11. This is equal to 2H2 prime. So, this is like putting 6 in 4 and so on.

Let us write that. So equation 6 in equation 4. So 2H21 prime divided by H11 prime minus H22 prime plus root over of that. And we have H22 prime minus H11 prime square plus 4H21 prime square and so on. So this is equation 8. So that's the first order correction to the amplitudes which will eventually give this the change in the wave function. But this appears in the ratio of these two coefficients at the first order level. But do not forget that there is another equation. Coming from the normalization condition, which makes it the other equation. So, which means that the A11 mod square plus, now this mod square doesn't have any meaning because this real, if all these H primes or the matrix elements of H prime are real, but we still write it notionally as mod square. And this is a to 1 mod square is equal to 1. So these two equations will allow you to solve this problem. And putting 7 in 5, we have so this is 6 in 4 and 7 in 5. So, we have these you know a 1 2 divided by a 2 2 that is for the other eigenvalue.

Putting (6) in (4)

$$\frac{a_2^{(1)}}{a_1^{(1)}} = \frac{2H_{21}'}{(H_{11}' - H_{22}') + \sqrt{(H_{22}' - H_{11}')^2 + 4|H_{21}'|^2}} \quad (8)$$

$$|a_1^{(1)}|^2 + |a_2^{(1)}|^2 = 1. \quad (9)$$

Putting (7) in (5).

$$\frac{a_1^{(2)}}{a_2^{(2)}} = -\frac{2H_{21}'}{(H_{11}' - H_{22}') + \sqrt{(H_{22}' - H_{11}')^2 + 4|H_{21}'|^2}} \quad (10)$$

$$|a_1^{(2)}|^2 + |a_2^{(2)}|^2 = 1. \quad (11)$$

So, And this is with a negative sign and 2 H21 prime. And we have this H11 prime minus H22 prime plus root over of H2. 2 2 prime minus H 1 1 prime square plus 4 H 2 1 prime square and so on. And then again you have this A 1 2 mod square plus A 2 2 mod square should be equal to 1 and these are equations 10 and 11. and put together all these energy corrections En1 and En2 which are written here. So, equation 6 and 7 are the energy corrections and equations 8, 9, 10, 11 are the corrections to the wave function and put together they give you the entire problem, the solution to this twofold degenerate problem. It's simple, but nevertheless, you have to solve a matrix equation, a system of equations rather. And what's the dimension of that system of equations that you have to solve? That simply depends upon what is the degeneracy of your system or, you know, what kind of, what's the level of degeneracy and so on. So now, since we have done a simple problem, let me show you another one, which is slightly more complicated and directly related to the next problem that we are going to do. That is stark effect. That's a fourfold degeneracy. So, four-fold degenerate state, we will not do a derivation of that, but we will write down the final results.

So, it is a four-fold degenerate state, how to deal with that. So, let us say that we have now all these u1, u2, u3 and u4, all of which correspond to the same energy. Let's call that energy to be equal to some En0. And so your psi En0 is actually the, you know, so psi En0 is a1 u1 plus a2 u2 plus a3 u3 and plus an a4 u4. And it's almost obvious that you have this four-fold degenerate problem. So, we'll have four different energy corrections to each one of them. It may lift the degeneracy completely or it may lift the degeneracy partially or it may not lift the degeneracy at all. Say we are talking about n equal to 2 of hydrogen atom. This is an example. And without including the spin degeneracy, this is four-fold degenerate. And we are really talking about that. So, all these n equal to two states of the hydrogen atom would have a structure like this. They all correspond to the same energy. So, we have this set of four equations which we have to solve. So, they are written following what we have done is H12 prime, a2 plus H13 prime, a3 plus H14 prime, a4 equal to En1, a1.

And we have H21 prime a1 plus H22 prime a2 plus H23 prime a3 plus H24 prime a4 is equal to En1 a2. H31 prime a1 plus H32 prime a2 plus H33 prime a3 plus H34 prime a4 is equal to En1 a3 and Finally, we have H41 prime a1 plus H42 prime a2 plus H43 prime a3 plus H44 prime a4 equal to En1 a4. So, this is just a 4 by 4 equation which needs to be solved.

4-fold degenerate state

$|u_1\rangle, |u_2\rangle, |u_3\rangle, |u_4\rangle \rightarrow E_n^0$

Example

$n=2 \rightarrow$ 4 fold degenerate

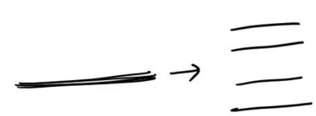
$$|\psi_n^0\rangle = a_1|u_1\rangle + a_2|u_2\rangle + a_3|u_3\rangle + a_4|u_4\rangle$$

$$H'_{11}a_1 + H'_{12}a_2 + H'_{13}a_3 + H'_{14}a_4 = E_n^{(1)}a_1$$
$$H'_{21}a_1 + H'_{22}a_2 + H'_{23}a_3 + H'_{24}a_4 = E_n^{(1)}a_2$$
$$H'_{31}a_1 + H'_{32}a_2 + H'_{33}a_3 + H'_{34}a_4 = E_n^{(1)}a_3$$
$$H'_{41}a_1 + H'_{42}a_2 + H'_{43}a_3 + H'_{44}a_4 = E_n^{(1)}a_4$$

The unique solution is determined by the fact that the solution is obtained—let us write it here—when the determinant of this vanishes. So, it is En1 minus H11 prime, H12 prime, H13 prime, H14 prime, and then it is H21 prime, En1 minus H22 prime, H23 prime, H24 prime, and H31 prime, H32 prime, En1 minus H33 prime, and H34 prime, H41 prime, H42 prime, H43 prime, and En1 minus H44 prime. This has to be equal to 0. And I hope you understand that H ij or this H prime i j is nothing but u i H prime u j. That is the matrix elements of the perturbation term taken between the different degenerate eigenstates of the system. So, this has to vanish in order to give us these four energy corrections. This will give us En1 1, En2 1, En3 1, and En4 1. So, this is the correction to different eigenvalues. So, this is the different eigenvalue index, and this tells about the order of perturbation theory. Once we get this, then the levels that are fourfold degenerate, which are like this.

$$\begin{vmatrix} E_n^{(1)} - H'_{11} & H'_{12} & H'_{13} & H'_{14} \\ H'_{21} & E_n^{(1)} - H'_{22} & H'_{23} & H'_{24} \\ H'_{31} & H'_{32} & E_n^{(1)} - H'_{33} & H'_{34} \\ H'_{41} & H'_{42} & H'_{43} & E_n^{(1)} - H'_{44} \end{vmatrix} = 0$$

$H'_{ij} = \langle u_i | H' | u_j \rangle$



$E_{n_1}^{(1)}, E_{n_2}^{(1)}, E_{n_3}^{(1)}, E_{n_4}^{(1)}$

(1) → order of perturbation theory

n_1 → Diff e-value index

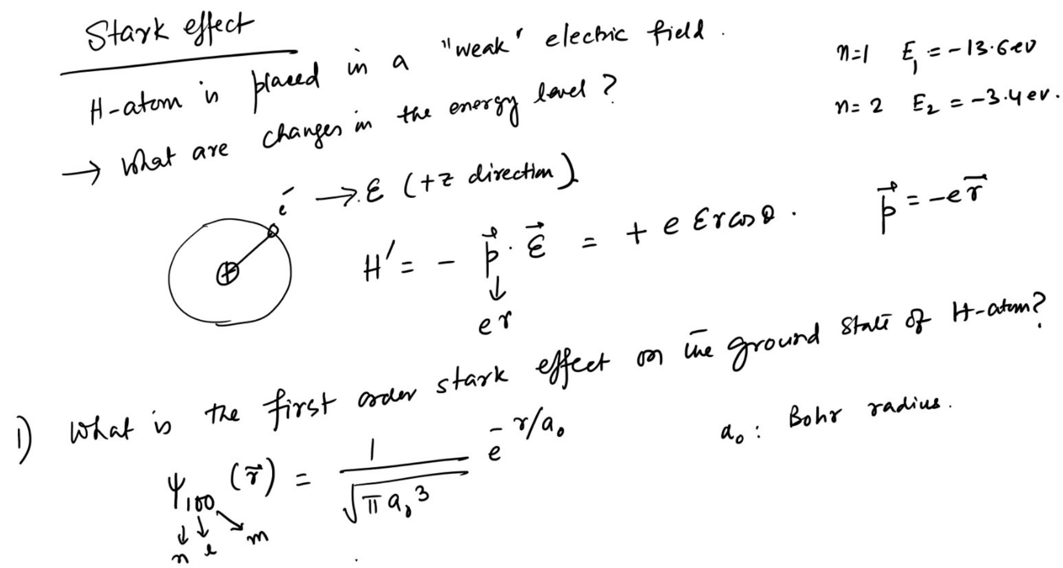
So, we are writing this as fourfold degenerate. Then you can have a split in degeneracy as if like two will be shifted up and two will be shifted down, depending on these matrix elements and the solution of this. So, let us apply to a problem which we are, you know, one usually does in this context, that is called the Stark effect. And what is the Stark effect? The Stark effect is that the hydrogen atom, the simplest atom—we have told this several times—has one electron and one proton. It is placed in a weak—and this word weak is important because we are going to apply perturbation theory—and it certainly does not cause any ionization of the hydrogen atom. So, the electron is never, you know, knocked out, and it remains very close to the ground state. That is the weak electric field, and we want to find what the changes in the energy level are. And we have discussed earlier that these can be the hydrogen atom energy levels, which can be photographed in a spectrometer or spectrograph. Then if you see that this n equal to 2 line, which corresponds to, say, or n equal to 1 line, which corresponds to minus 13.6 electron volt. So, n equal to 1 has an energy which is equal to minus 13.6 electron volt—let us call it E1. N equal to 2 has an energy which is minus 3.4 electron volt, which is this 13.6 divided by 4.

How these different energy levels respond to the perturbation due to that electric field being applied is a weak electric field. Then the question is: how does the hydrogen atom, or what degree of freedom, couple with the electric field? That is the main question. And just to give a sort of physical answer, you have—and this you must have done in classical electrodynamics—that there is an electron here and a proton there inside. So, this is like a dipole because equal and opposite charges are there at a distance, with the distance being nothing but the atomic radius, which is something similar to the Bohr radius. So, an electric field is, say, applied in this direction, and so this is the electric field. We will write it as this curly E because we do not want any interference with the energy, which we write as the normal capital E. So, you know, there is no confusion that arises because of these notations. And this is, say, in the plus z direction. This is just, you know, a sort of notation that one uses for convenience. It really does not matter which direction it is, but it is only in the z direction that you do not have any azimuthal dependence—that there is no phi dependence. So, what happens is that because of this electric field, the dipole actually gets elongated. And so the dipole moment, which is nothing but the charge multiplied by the distance between the two charges—the magnitude of the charge and the distance between the two charges—

This interacts with the electric field as a dot product. So, the potential energy that you get is minus P dot E. And this is precisely what our perturbation term is: it's minus P dot E. And so this is, you know, and P is nothing but this is nothing but e r, okay. And r is a radial variable. And because there is a dot product, this is equal to minus r e E r cosine theta. So, there is an angle between the P and the direction of E, and that is why it is minus e E r cos theta. And usually, because of this minus sign and the fact that the electric charge is also negative, we put a positive sign here. So, P is equal to minus e, you know, r. Okay, so that is the understanding, and that minus sign gets cancelled. And we have this potential energy, which is the perturbation term for us, and we have to calculate what happens because of this perturbation, which is a product of the electronic charge e, small e, and the electric field, curly E. And then we have this radial variable r multiplied by the cosine of this angle. And so the first question is the simplest one: what is the first-order Stark effect?

on the ground state of the hydrogen atom. So, that's the question, and it's a valid question. What it means is the following: the electron is assumed to be in the ground state of the hydrogen atom. Now, you have applied an electric field, and you want this energy, minus 13.6 electron volts, to shift up or down. And so, I mean, down is not possible because you have a positive perturbation. So, it's going to shift up. Whether it really does, and if it does, then by what amount, okay? I told you earlier that there is no real necessity that it will get shifted, and it may not. In fact, it will depend upon a lot of symmetry arguments. If it doesn't, then there is some argument that is always there. And in this particular case, a priori, I can tell you that there is no shift in the energy of the hydrogen atom in the ground state. And that's a non-degenerate problem. But nevertheless, what we can show easily by writing—so, what's the ground state of the hydrogen atom? It's called the 1 0 0 state, where this is the n index, the first one, and then there is the l index, and then there is the m index. So, n equal to 1 means l can only take the value 0, and if l is equal to 0, m equal to 0, that is the ground state, which has this energy, which is minus 13.6 electron volts, and this is nothing but root over pi a naught cube.

e to the power minus r over a naught, where a naught is called as a Bohr radius, having a value which is very close to like 0.5 Angstrom and so on. In fact, you can use this and take a mod square of this which gives you the probability density and you can ask this question that at what distance this probability density goes to 0 or rather it has you know it has a minimum value or where this I mean till what distance the hydrogenic wave function in its ground state is most likely to persist and that answer is given by, so you calculate P of r, that is the probability by taking the mod square of this psi 100, take a dp dr, put that equal to 0 and you will calculate r in terms of a0, r comes out as a0. Anyway, that is not the point that we are trying to make here. We are asking this question that what is this thing that is going to give you. So, it is minus 13.6 electron volt is unperturbed energy and we want to calculate what is En1. And because n is equal to 1, we call it E11. And this n is the index for the quantum number or the principal quantum number that identifies which state it is in. And the superscript just talks about the order of correction in energy.



And now the matter is simple because you have to just take a psi 100 star r and then you have this perturbation term, which is minus e E r cosine theta and psi 100. Now, you have to be careful in writing this integration or rather the dr. In 1D, we can simply write as dx, but this problem has spherical symmetry. So, you have to write a dv. So, it has to be integrated over all volume. And that tells us that if you write a dV, then a dV is written as r squared dr sine theta d theta and d phi, okay? And this r goes from 0 to infinity, okay? It goes all the way from 0 to infinity, theta goes from 0 to pi and phi goes from 0 to 2 pi. So, there without really doing everything because there is an r integral psi 1 0 0 does not depend upon theta or phi. The phi integral is trivial here because there is no phi term there. So, we can take this 2 pi out. And so the only you know you have to look at before you do the r integral let us look at the theta integral and the theta integral is cos theta d theta and you have a sin theta because there is a sin theta here so sin theta cos theta sin theta d theta. And this is from 0 to pi.

Now you see that what you can do is that either you show that this is equal to 0 or you can write the sine theta d theta as d of cos theta and then this limit goes from minus 1 to plus 1 and you can still show that it is equal to 0. So we have a cos theta d of cos theta and then this integral really goes from minus 1 to plus 1. It is again equal to 0. So, that gives us a lesson that the first order energy correction to the ground state of hydrogen atom is 0 due to a weak electric field. So, it says first order stark effect on the ground state vanishes. This is an important result and you may be asked a question say a multiple choice question that what is the value in this and just keep this result in mind and the result comes because of this theta integral the all the other integrals are non-zero okay. So, there is no shift in energy because of this electric field to the ground state. So, to see what really exists. So, we have two options. We can look at the second order correction to energy in the ground state which is going to be a more difficult problem. I will not do that problem, but I'll simply state the result.

$$E_n^{(1)} = E_1^{(1)} = \int \psi_{100}^*(\vec{r})\left[-e\mathcal{E}r\cos\theta\right]\psi_{100}(\vec{r})\,dv.$$

$$\int_0^{\pi} \cos\theta\sin\theta\,d\theta = 0.$$

$$\int_{-1}^{1} \cos\theta\,d(\cos\theta) = 0.$$

$dv \rightarrow r^2 dr \sin\theta\, d\theta\, d\phi$

$r: 0 \rightarrow \infty$

$\theta: 0 \rightarrow \pi$

$\phi: 0 \rightarrow 2\pi.$

1st order stark effect on the ground state of H-atom Vanishes!!

But a more doable problem, which is more relatable to what we have just discussed about degenerate perturbation theory, is the first-order Stark effect on the first excited state. Alright, so now this is important because the first excited state which is n equal to 2 is really 2-fold degenerate, 4-fold sorry, 4-fold degenerate because it is n-square-fold degenerate. So, we have a real degenerate problem, degenerate perturbation theory problem And that will tell us whether we'll have a shift in energy or not, whether there is a complete removal of degeneracy or just a partial removal of degeneracy. Okay, so there are four states. And what are those four states? Because if n is equal to 2, l can take values 0 and 1. m l can correspondingly take values which are you know if l is 0, m l is 0. If L is 1, m l is 1 or 0 or minus 1. So, we have how many states that we have now? So, we have 2, n equal to 2, L equal to 0, m l equal to 0 and This is called as a psi 2 0 0 state in our notation that we use psi n lm and if n equal to 2.

then l equal to 1, so we have l equal to 1, we have m l which is which can be equal to 1 and let us call that as psi 2 1 1, we will use them in some order while doing the calculation and then we have 2 and then 1 and 0, so this we call psi 2 1 0. And then again, we have the other one as 2, 1 and minus 1 and we call it a psi 2, 1, minus 1 r. And this fellow is called as the s state. s corresponds to this notation when l is equal to 0. This angular momentum, this quantum number is equal to 0, the azimuthal quantum number. And these are called as the P states. The P states are three of them, and each one has an energy equal to E2, which is minus 3.4 electron volts, coming from minus 13.6 divided by 4. So, each one of them has this energy. So, we will call this—now let me change this order a little to maintain consistency with the notation I am using. Let us call u1 r equal to psi_200. That is the notation that we have used earlier, this u1, u2, etc. And explicitly writing what these are, this you can look at any book and get these explicit forms. We have shown them by plots and sometimes have even written them down. But there is no need to remember them because if there is a

excepting maybe the ground state you should remember, which is what we have just shown here, which is this one by root, this root over pi a0 cube exponential minus r by a0. The others will most likely will be supplied. So, this 2 r by a0 exponential r by 2 a 0 and so on and u 2 r this is equal to psi. Now, this I do not use the this ordering that we have done. So, we write it 2 1 0. So, this is equal to 1 by 4 root over 2 pi r over a naught cosine theta exponential r over 2 a naught. You see the l equal to 0 does not have any theta or phi dependence whereas, if l is not equal to 0 then it has a theta dependence. In addition, if m is not equal to 0, it also has a phi dependence. u3 r, this is equal to psi 211 and this is equal to 1 by 8 root pi 1 over a0 whole to the power 3 by 2. sine theta e to the power i phi e to the power minus r by 2 a0. Finally, we have u4, which is the last one: 2, 1, minus 1 r. So, there is a 1 over 8 root(pi) times (1 over a0)^(3/2) sine theta, and now we have an exponential minus i phi—that's why they're bunched together—times r over 2a0. All right.

First order stark effect on the 1st excited state (n=2)

$n = 2, \quad l = 0, 1, \quad m_l = 0, 1, 0, -1.$ $n = 2 \rightarrow$ 4 fold degenerate

$(2,0,0) \rightarrow \psi_{200}(\vec{r}) \longrightarrow$ s-state

$(2,1,1) \rightarrow \psi_{211}(\vec{r})$

$(2,1,0) \rightarrow \psi_{210}(\vec{r})$ } p-states.

$(2,1,-1) \rightarrow \psi_{21-1}(\vec{r})$

$E_2 = -3.4eV = -\frac{13.6}{4}$ eV.

$$u_1(\vec{r}) = \psi_{200}(\vec{r}) = \frac{1}{4\sqrt{2\pi}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$u_2(\vec{r}) = \psi_{210}(\vec{r}) = \frac{1}{4\sqrt{2\pi}} \frac{r}{a_0} \cos\theta \, e^{-r/2a_0}$$

$$u_3(\vec{r}) = \psi_{211}(\vec{r}) = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \sin\theta \, e^{i\phi} e^{-r/2a_0}$$

$$u_4(\vec{r}) = \psi_{21-1}(\vec{r}) = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \sin\theta \, e^{-i\phi} e^{-r/2a_0}$$

So these are the four eigenstates. And then the solution is clear because we have laid down the basis for this problem. And you have to calculate, you know, how many of these matrix elements really there are four into four, 16 matrix elements, which are all these H prime ideas. And before you actually go ahead and calculate all of them, you'd be able to appreciate that some of them, you know, simply goes to zero without doing a calculation and we'll see that. So the first order energy correction is obtained as is obtained from this equation, which is H i j prime minus E n 1. And of course, we should write because H i j prime is okay, it is not that required, but you can just say that determinant of this is equal to 0. Okay, so I just put this identity matrix because it is there everywhere along the diagonal part. So, just to make sure that that information is carried. So, this is the you have to do it for the 4 fold degenerate problem and exactly what has been shown. So, you have to solve a 4 by 4 determinant putting that equal to 0, but you may be lucky enough not to have a 4 by 4 problem to be solved in its entirety.

What could happen is that some of the elements would be 0 in such a fashion that you have a block of 2 by 2. If that happens, then of course, that is the best thing that you are looking for. So, if you look for this H11 prime, that is the matrix elements of the perturbation term between these u1 terms. Now, you see that u1 term does not have any theta. So, the only theta will come from the sin theta d theta from 0 to pi which is equal to 0. So, H11 prime is will be 0 because you have cosine theta d of cosine theta, which is minus 1 to plus 1, which is the same as the sine theta d theta, you know, from 0 to pi, this is equal to 0 and so on. So, only theta, I mean, theta integral gives 0. So what about H22 prime? That is the one that you have. Now you see H22 prime will have a cosine theta there and I mean this I have written it in the sense that so there is a sine theta cos theta. So there is a kind of sine theta coming from this integral and then there is a cos theta which I forgot to write. So this is there. And H22 prime will have a minus 1 to plus 1 and a cos cube of theta d of cos theta. So, just take cos theta as some x variable. So, it is x cube dx from minus 1 to plus 1 that will again be 0. And similarly, the H33 prime, again, because of all these, you know, the theta integral, I'm not saying they are equal, but they both are zero. That's what I'm trying to show.

First order energy correction:

$$\left| H'_{ij} - E_n^{(1)} \mathbb{1} \right| = 0 \quad \rightarrow \text{4-fold degenerate}$$

$$H'_{11} = \int_{-1}^{1} \cos\theta \, d(\cos\theta) = \int_{0}^{\pi} \sin\theta \cos\theta \, d\theta = 0 \quad \longrightarrow \theta \text{ integral.}$$

$$H'_{22} = \int_{-1}^{1} \cos^3\theta \, d(\cos\theta) = 0$$

$$H'_{33} = \int_{0}^{\pi} \sin^2\theta \cos\theta \, d\theta = 0 \Rightarrow H'_{44} = 0$$

All the diagonal terms are zero!!

So if the equality sign bothers you, then you can say both. So we can write it separately. So, this is equal to 0 to pi, again a sine squared theta, a cos theta, that is d theta, that is equal to 0. And similarly, h 4 4 prime is equal to 0 as well, okay, for the same reason. So, all the diagonal terms are 0. So, you are maybe lucky but not so much because you want the off diagonal terms to vanish because in order for this size of the 4 by 4 matrix to come down and you are probably lucky there as well because if you see you have H13 prime which means nothing but u1 H prime u3. And which means nothing but u1 star h prime, which is nothing but this e E r cosine theta u3. And then you have r squared dr sine theta d theta and d phi. And this is again, it is equal to 0 because now because of the phi integral. So the phi integral makes it 0 because 3 has a phi which is d phi e to the power i phi and from 0 to 2 pi.

Because of this phase, phi being, you know, 2 pi symmetric, which means that exponential, I mean, phi equal to 0 and phi equal to 2 pi, they are same. So this is equal to 0. And that's the same reason that your H14 prime equal to 0 as well, because of this reason that 0 to 2 pi d phi e to the power minus i phi, that's also equal to 0. So, you can show similarly that there are other terms which are, so H24 prime, H42 prime equal to H34 prime, all of these equal to 0. And for this particular case, and you are only left with H12 prime and H21 prime are only non-zero, okay.

$$H_{13}' = \langle u_1 | H' | u_3 \rangle = \int u_1^* (e\mathcal{E} r \cos\theta) u_3 \; r^2 dr \sin\theta d\theta d\phi$$

$\rightarrow \phi$ integral $\quad \int_0^{2\pi} d\phi \, e^{i\phi} = 0.$

$H_{14}' = 0 \quad \int_0^{2\pi} d\phi \, e^{-i\phi} = 0.$

$H_{24}' = H_{42}' = H_{34}' = H_{43}' = 0.$

H_{12}' & H_{21} are only non-zero.

$$H_{12}' = \frac{e\mathcal{E}}{32\pi} \int_0^\infty \left(2 - \frac{r}{a_0}\right)\left(\frac{r}{a_0}\right) r^3 e^{-r/a_0} \underbrace{\int_{-1}^{1} \cos^2\theta \, d(\cos\theta)}_{2/3} \int_0^{2\pi} d\phi$$

$$= \frac{e\mathcal{E}}{16} \times \frac{2}{3} \left[\frac{1}{a_0} \int_0^\infty r^4 e^{-r/a_0} dr - \frac{1}{a_0^2} \int_0^\infty r^5 e^{-r/a_0} dr \right]$$

$$\Gamma(n) = \int_0^\infty r^{n-1} e^{-r} dr$$

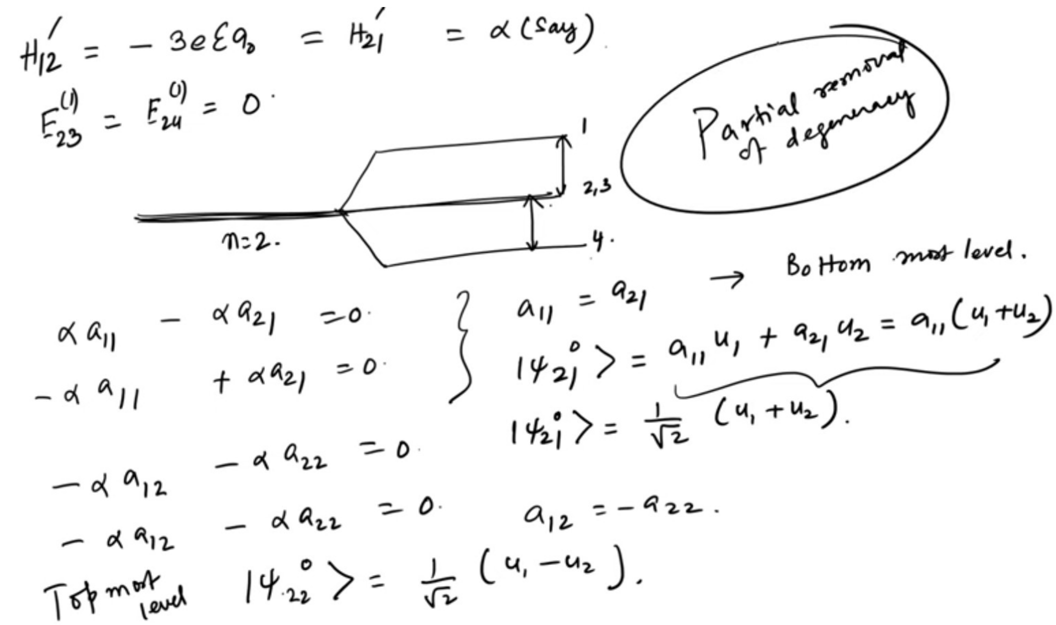
If that's the case, we have to calculate H12 prime and H21 prime. Now you see that in this equation, this equation that we have, that entirely the lower block is 0 and all the, you know, these, 1 on the right, this block, let me show it by a laser pointer. So, this block is 0, this block is 0, all these diagonal terms are 0, leaving you with only E1 here and E1 here. The only non-zero terms, diagonal terms are 0 here as well. The only non-zero terms that exist are H12 prime and H21 prime. And that is what we are trying to calculate now. Okay. So, H12 prime is equal to e E divided by 32 pi epsilon 0. So, we are taking the overlap of this perturbation term between u1 and u2.

So, 32 pi and then you have a 0 to infinity 2 minus r by a0. and r by a0 and then you have r cubed exponential minus r over a0 and then you have a minus 1 to 1 cosine squared. Now, the cosine doesn't let you go to 0 because of this even power of cosine theta and d of cosine theta. So, we write down this theta integral usually because there is a sine theta cos theta we write it in terms of cos square theta d of cos theta and so on and then d phi is simply from 0 to pi. So, this is the r integral theta integral and phi integral that you see there. From the theta integral, it is easy to see that you get a factor of 2 by 3 and a little bit of simplification can be done. So, E epsilon by 16 and it becomes 2 by 3 and the phi integral will give you a 2 pi. So, you have a 2 pi there. So, 2 pi cancels with this pi here and makes it a 16 in the denominator and now we have this 1 over a naught. and you have a 0 to infinity r to the power 4 e to the power minus r by a0 dr and a minus 1 by a0 square and 0 to infinity and you have a r to the power 5 e to the power minus r by a0 square d r and so on. So, this integral has to be solved.

And what can be done is that you can use a gamma function form. So, gamma of n, this is equal to 0 to infinity. This is called as a gamma function integral r to the power n minus 1 e to the power minus r dr, this is equal to gamma n and gamma function has some property. So, one can actually do this simplification. Now, this equation or rather this integral is given to you. So, you can write it down in terms of these. So, H12 prime becomes minus 3 e E a0. And when you calculate the H21 prime, it of course gives you the same result because it is simply the perturbation term does not alter the ket or the wave function that is coming on its right. So, this will be same. And let us call this as alpha. I mean, basically just not to carry around this factor every time. Now, what happens is that If you look at this lower block, this block does not yield anything that is it gives you the eigenvalues of this is equal to 0 and this becomes just an upper block on the left and a lower block on the right and the lower block on the right gives you two corrections to be equal to 0. which means that we have E231 is equal to E241 is equal to 0, which means that there is a partial removal of degeneracy. That means this fourfold degenerate, two of them continues to be degenerate even in the presence of this perturbation term.

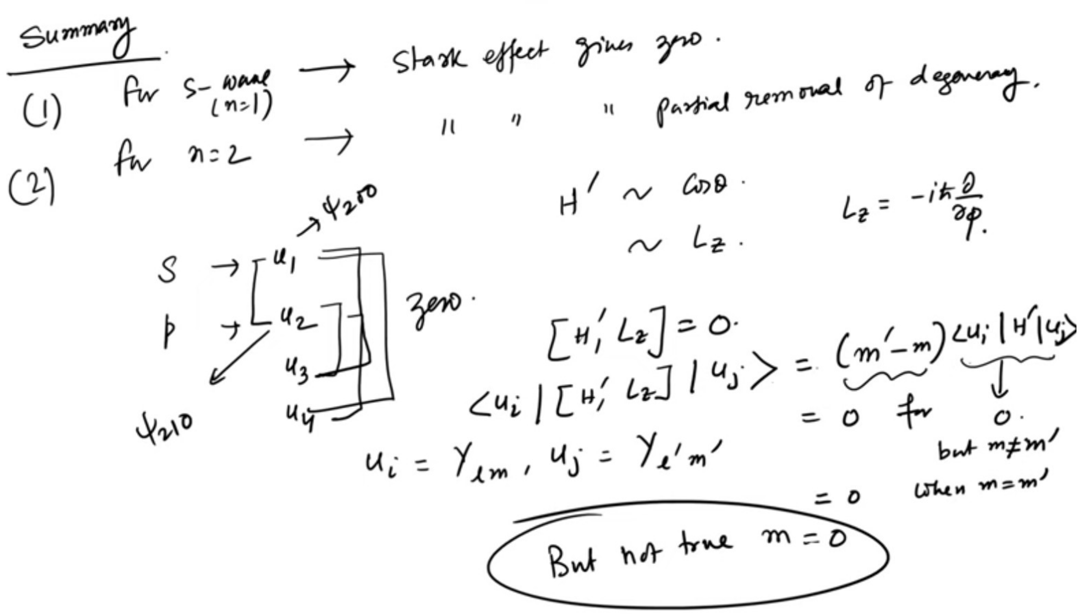
And the other two get, you know, they sort of degenerate and are removed. What you have is that, pictorially, we have a fourfold degenerate, so these four lines that you see merging together tell you that the unperturbed thing continues to be a twofold degenerate, and these two are. And this shift is calculated using, so one of them will shift upward and the other will shift downward and so on. So, this n equals 2 and these are proportional to this alpha. So, we can actually, because of this simple feature that the 4 by 4 matrix splits into 2 by 2 block matrices, one can calculate the eigenfunctions corresponding to that. And you use this alpha and write this as a11 minus alpha a21, minus alpha a, so this is equal to 0, and a11 plus alpha a21 is equal to 0. So, that tells you that a11 is equal to a21. So, the bottommost level, you see here, corresponds to 0.

So, this one that you see here corresponds to this psi 1 or rather psi 2 1 0, this is equal to a 1 1 u 1 plus a 2 1 u 2, this is equal to a 1 1 u 1 plus u 2, that is the bottommost level, that is the, let us call this as 2, 3, 1, and 4, okay? So, as if all these 4 were there, do not, you know, confuse this with u1 and u2, like they are not u1, u2, u3, u4, but the fourth one, that is the bottommost one, is a combination of u1 and u2 in this particular fashion. And so, it is easy to normalize it because there are two functions and this has to be normalized. So, your psi 2 1 0, this is equal to 1 by root 2 u1 plus u2. That is the lowest one. And for the topmost level, we have the other two equations corresponding to these, you know, the changes in the energy. And this is alpha a12 minus alpha a22. This is equal to 0 and minus alpha a12, minus alpha a22, this is equal to 0 as well. So, we have then this has a12 equal to minus a22, minus a22. So, the topmost level is the topmost level. This is equal to psi 220, this is equal to 1 by root 2 u1 minus u2. So, there is a partial removal of degeneracy.



Two levels continue to be degenerate and so on, and so let me, you know, write down the summary of these results that you have seen here, and the summary says that for the purely S wave state, Stark effect is 0, which means that there is no change in energy, so Stark effect gives 0. So, for n equal to 2, so this is for n equal to 1. So, for n equal to 2, which are combinations of S and P, this Stark effect gives partial removal of degeneracy. So it's important to understand that this degeneracy is only removed when S is coupled to P. So let me show this. So S is this u1 state. Right. And these all these are P states. So P corresponds to this u2, u3, and u4. So the matrix elements of H prime between this. Between this and between this and between this, they are all 0. So, all these are 0 and the only one that is non-zero is this one. So, that tells you that when the m l value or m value, rather the magnetic quantum number, changes by 1, then the Stark effect actually gives a removal of degeneracy, and this can be easily understood if you really think that the H prime term which is proportional to the cosine theta.

Now, the cosine theta, according to the theory of angular momentum, it looks like z. So, that tells you that, so Lz is like minus i h cross del del phi. That is the form. So, H prime is like z. So, H prime and Lz, they commute, right? And that means the u i and H prime Lz that also becomes equal to 0 between two states, right. So, let us say u i is like Y l m l, l m sorry, not m l. I mean, sometimes because of these other quantum number that is j corresponding to the quantum total angular momentum so we use m j but that's not the case here and then this is say the other one is like the Y l prime m prime okay so these thing will become equal to is m prime minus m and then u i H prime u j okay now this is equal to 0 for m when m is not equal to m prime but this is 0 okay but m not equal to m prime that is one of them.



So, it is not 0 because of that, but it is 0 because of this. And in the other case, this is equal to 0 when m equal to m prime. And that is why all these are 0, excepting the one, see 3 and 4 is 0 because m is equal to m prime. We do not have to have the other, the matrix element to be equal to 0, but not true for m equal to 0. So, that is the one that gives you contribution between u1 and u2, which corresponds to psi 2 0 0 and this corresponds to psi 2 1 0. And that is where you have a non-zero contribution coming from. Now, I will skip, as I said, the second-order Stark effect in the ground state because it's mathematically complicated, but I will just simply state the final result, and the final result tells you that, so what about second-order Stark effect? in ground state? And the answer is that, that En2 that is the second order correction in energy to the ground state is actually a minus can be written as minus alpha induced.

This is called the induced electric dipole moment and is proportional to the as expected proportional to the square of the electric field. Of course, if electric field is weak, the second order should be even smaller. And this alpha end is equal to the induced dipole moment. And this is as a value which is 9 over 2 a0 cube where a0 is the Bohr radius. So, though atomic hydrogen do not have a permanent dipole moment, the induced dipole moment of course, exists in presence of a dipole of an electric field. And as I said that I do not give a derivation of this, but it is not undoable. It is a long derivation, but it is good enough for you that if you remember that is E n2, that is the second order on the ground state. This is nothing but minus 9 over 4 a0 cubed E squared. So there is a change in the eigenvalue or rather the energy eigenvalue. because of this energy correction, and it will, you know, shift from its position, minus 13.6. So, and in the ground state, it will be En equal to En0 minus, so this En0 is minus 13.6 electron volt, and plus a 9 over 4 a0 cube e squared. So, it will shift up by this amount and because of this induced dipole moment.

What about 2nd order Stark effect in ground state?

$$E_n^{(2)} = -\frac{1}{2}\alpha_{ind}\,\mathcal{E}^2$$

$$\alpha_{ind} = \text{induced dipole moment} = \frac{9}{2}a_0^3$$

$$\boxed{E_n^{(2)} = -\frac{9}{4}a_0^3\,\mathcal{E}^2}$$

$$E_n = \underset{\downarrow \atop -13.6\,eV}{E_n^0} + \frac{9}{4}a_0^3\,\mathcal{E}^2.$$

So, we have talked about degenerate perturbation theory and discussed how the Stark effect can be analyzed, noting that the first-order Stark effect on the ground state equals zero because the s orbital is spherically symmetric. The electric field, which tries to create a dipole moment on a spherically symmetric orbital, has no effect. We observed this for the first-order Stark effect in the first excited state. There we have seen that it is only when S couples to P, S state couples to the P state, then you have a change in correction or so there is a partial removal of degeneracy. Two of the levels continue to have the same energy and the other two shift symmetrically up or down compared to the minus 3.4 electron volt. There is also a finite second-order Stark effect on the ground state of the hydrogen atom. We will stop here and continue with more applications of perturbation theory in the next class. Thank you.