Advanced Quantum Mechanics with Applications
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Lecture – 22
Stark Effect First order in ground state

So we have learned the degenerate perturbation theory and how to calculate the energy corrections in a degenerate case. As an example let us look at this a phenomena called as Stark effect.

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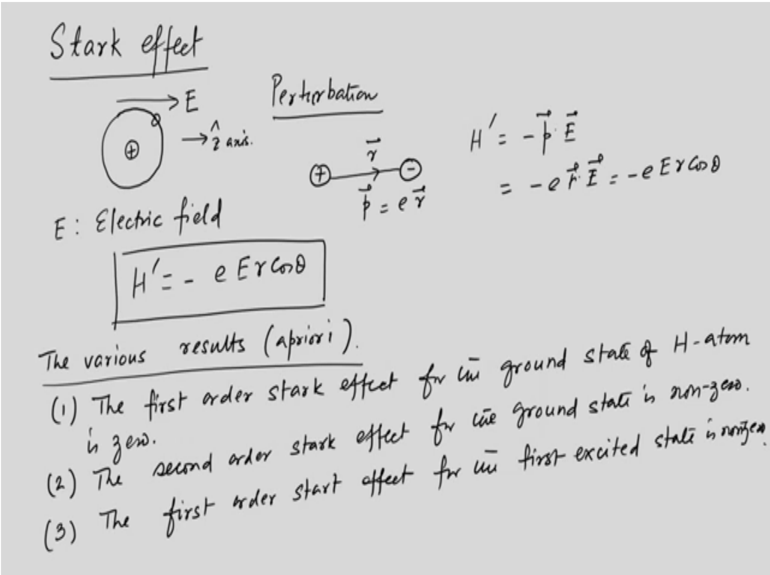

So, stark effect is application of electric field a constant electric field, for in a for a hydrogen atom. So, let us have a hydrogen atom which is the simplest atom which has a proton at the center and an electron, which is revolving round the nucleus which contains a proton and so, this is exerted upon or rather this is a in presence of an electric field we will call it E. make no mistake that this is not energy, but it is a electric field. So, will write it here so, electric field and.

So, these are there is the situation and the electric field is not strong enough. So, that it ionizes the hydrogen atom that is it knocks the electron off from its allowed orbits. So, the electron is still there bound to the nucleus and so, the electric field is not very strong and we can the effect of the electric field can be considered as a perturbation. This is what we start from and let us just look at how the perturbation term comes or what is the origin of the perturbation in this case.

So, you see the electric. So, the hydrogen atom has got an electron at the orbit and the nucleus contains the proton so, that is like a positive charge and a negative charge equal and opposite. So, that corresponds to a dipole of dipole moment given by e r where r is the vector that connects the positive to the negative charge. And we have drawn it outward because that is what usually the direction of the radial variable s. So, p equal to e r is the electric dipole moment of this charge, where e is the electronic charge.

Now, this dipole moment is in the presence of or it is feeling the presence of an electric field. So, that would give rise to a perturbation of the form which is a minus p dot E this is known from classical electrostatics. So, it is a minus p dot E which tells that this is equal to a minus e r dot E and this is nothing, but equal to minus e E r cosine theta if the direction of E is chosen to be the z axis ok.

So, we will take the perturbation term for stark effect as minus e E r cosine theta, and this is the starting point of this discussion. So, get it clear e is the electronic charge this capital E is the electric field, r is the radial variable theta is the angular variable that we are all familiar with and here of course, r denotes the radial distance.

So, now in order to start our perturbation theory, we have a priori let us say that will do particularly three cases and these are a very exhaustive for this particular problem, which means that if you do these three cases more or less everything is done about the stark effect, and the various things that we look at r and let us state the results that we are going to get so, that you know that this is what we are trying to prove.

So, 1 is that first one is that the first order stark effect for the ground state of hydrogen atom. So, hydrogen atom will simply call it as H atom is 0, which means that at the first order of perturbation theory if we are applied to the ground state of the hydrogen atom well in a brief will say what is what is the ground state and what are the first excited states and so, on.

So, the first order stark effect for the ground state is not going to give any correction, the second order stark effect for the ground state is non-zero. This is we want to show this which means that the correction comes the second order of the electric field. So, if electric field is really very small then the second order corrections can be neglected which means that there will be no stark effect, but of course, here for our discussion will consider that it still contributes the electric field still contributes to a correction even at the second order.

The first order this is slightly non trivial and not many books on quantum mechanics actually give a derivation. So, the first order stark effect for the first excited state is non zero. So, we no longer talking about the ground state we are talking about how the electric field induces a correction to the energy for the first excited state.

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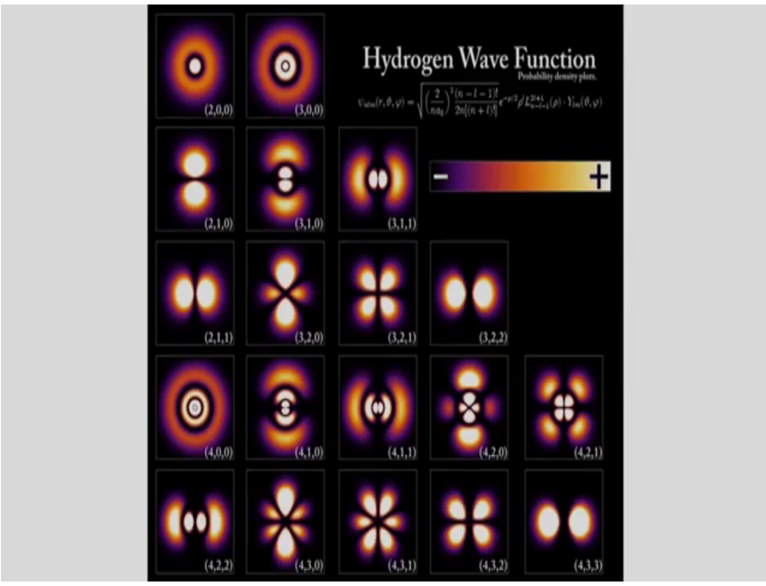

So, these are the results that we are going to show eventually but before that let us do a. So, let us do these corrections or rather little discussion on the hydrogen atom wave function.

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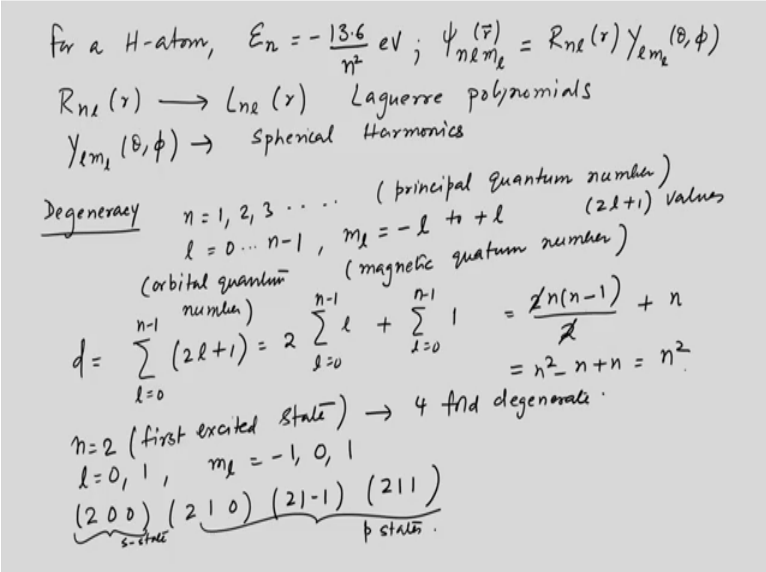

So, for hydrogen atom the energy is given by this E is energy. So, let me write it a little differently. So, that you are not confused with the electric field. So, we will write it at a curly E. So, this is equal to minus 13.6 divided by n square in electron volt. So, a electron volt is actually a large amount of energy it corresponds to a temperature if you apply the Equipartition theorem one electron volt is a nearly equal to 12000 Kelvin which is a very large energy. So, even if it looks like that its not we are only talking about electron volt and not you know giga electron volt or tera electron volt, it still is a large energy in some sense.

Now, first let us understand what is the degeneracy and how are the wave functions written. So, the wave functions are written as psi n l m, just to have correlation with this l will write the m l as a magnetic quantum number which corresponds to l, as there could be a j or a s. So, it could be a s m s or a j m j which we have seen earlier. So, just to distinguish that it is we will write it as n psi n l m l which are. So, this is a function of the vector r, which depends on a radial variable which is R nl of r and a Y lm of theta phi.

If you are not familiar with this please look at any Quantum Mechanics book that solves hydrogen atom, every book on quantum mechanics will solve hydrogen atom and these are the wave functions for these quantum numbers n l and m l. So, these are good quantum numbers for the problem and R nl is a radial variable which are related to the

Laguerre polynomials and Y lm. So, R nl r are related to this L nl r which are called as the Laguerre polynomials.

And so, will call L ml here and Y lml it is a function of the angular variables and these are called as the spherical harmonics. In fact, to familiarize yourself you should look at the properties of all these things and there in some sense there orthogonality relations because these are needed for the ortho normalization condition of the wave function.

So, the degeneracy is calculated see n can take any values between 1 to infinity, but in principle n takes values which are relevant for us is 1 2 3 etcetera anything larger than 3 or 4 will have really not any I mean it is not are relevant to the context of the discussion. So, we will talk about ns which are just integers which are 1 2 3 4 and so, on and this l takes values. So, n takes values 1 2 3 l takes values from 0 to n minus 1.

So, if n is equal to 1 l can only take a value 0 if n equal to 2 l can take values which are 0 and 1 and similarly m l takes values from minus l to plus l. So, thus if n is fixed n is called as a principal quantum number this l is called as the orbital quantum number and this is called as a magnetic quantum number m l ok. So, n is independent, l depends on n and m l depends on l.

So, which means that ml actually depends upon both l and n and so, the degeneracy is computed let us call it d which is equal to sum over l from 0 to n minus 1, and because m l can take values which are 2 l plus 1 number of values. So, I will write this equal to 2 l plus 1. So, this is equal to 2 l equal to 0 to n minus 1 l plus l equal to 0 to n minus 1 and this is 1. And now this is like summing n natural numbers which gives me 2 into n into n plus n minus 1 sorry n minus 1 by 2 so, that is the sum of natural numbers from 0 to n minus 1 which are n.

And then of course, I am summing 1 n times which gives me another n. So, this 2 cancels and I should get n square minus n plus n which is equal to n square. So, it is n square fold degenerate. So, let us talk about say n equal to 2 which is called as a first excited state and n equal to 2 is 4 fold degenerate. So, the values will be l equal to 0 and 1, m l will be equal to minus 1 0 and plus 1. So we will have four states because it is n square fold degenerate. So, n equal to 2 will have four states they are 2 0 0 that is so, these are n l m l and then 2 1 0 and then there is a 2 1 minus 1 and then there is a 2 1 1. So, these are the four states so, this is called as a s state, and these are called as the p states ok. So, this is the triplet and there is a singlet which is the s state.

And similarly for n equal to 3 it is a 9 fold degenerate where we have a values n equal to three would correspond to 0 1 and 2 in which case m l will take values which are minus 5, minus 4, minus 3, minus 2 sorry. So, it is from minus 2 to plus 2 so, minus 2 minus 1 0 1 and 2 and all combinations. So, they will be 9 fold degenerate anyway.

So, this is what is important for stark effect let us look at the hydrogen atom wave functions. So, you see the s state which is 2 0 0 is here it is a. So, this it is called s because it has a spherical symmetry. So, all s states have a spherical symmetry. So, you see that the wave function the cloud of the wave function or the form of the wave function has spherical symmetry so, is the 3 0 0.

Now, you see the 2 1 0 that is 1 of the p states has a dumble shape. So, there is a there are 2 sort of parts of the dumble or the balls of the dumble that are there and similarly for the 3 1 0 and 3 1 1. The 2 1 1 is also a dumble, but it is a sidewise dumble and similarly there will be a 2 1 minus 1 which is also it could be there somewhere, but if it is not there it does not matter I mean that is the same, but it just comes with a different phase factor, which is what we are going to show you in a while.

So, let us look at with if we want to do this perturbation theory now for the stark effect.

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Return to stark effect

(1) First order stark effect for ground state.

$n=1,\ l=0,\ m_l=0 \qquad \psi_{100}(\vec{r}) = R_{10}(r)\,Y_{00}(\theta,\phi)$

$R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

a_0: Bohr radius.

$$E^{(1)}_{n=1} = \langle \psi^{(0)}_{nlm_l} | H' | \psi^{(0)}_{nlm_l} \rangle = \langle \psi^{(0)}_{100} | -eEr\cos\theta | \psi^{(0)}_{100} \rangle$$

$$= -eE \int_0^\infty R_{10}^2(r)\, r^3\, dr \int_0^\pi \cos\theta \underbrace{\sin\theta\, d\theta}_{} \int_0^{2\pi} d\phi$$

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

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

$E^{(1)}_1 = 0 \Rightarrow$ no first order correction in energy due to stark effect for electron in the ground state.

So, let us return to stark effect ok. So, let us look at the first 1 so, that is the first order stark effect, which is what we have promised first order stark effect for ground state and so, we are talking about n equal to 1 which is a ground state. So, it is l equal to 0. So, it is a spherically symmetric state so, its m l is also equal to 0. So, let us write that as well. So, if l equal to 0 m l cannot be anything other than 0 so, we have a state which is psi 1 0 0 as function of r it is like R 1 0 r and Y 0 0 theta phi; Y 0 0 theta phi is actually a constant and we will tell you what. So, it is simply just a number which is something like 1 by root over 4 pi etcetera.

And so, R 1 0 actually has a form which is 2 1 by a naught whole to the power 3 by 2 exponential r by a naught where a naught is called as the Bohr radius which has a certain value which is of the order of you know angstrom. So, what is the first order correction due to this perturbation? So, we will talk about E n that is equal to 1 and of course, we are talking about n equal to 1.

So, we could put n equal to 1 as well because you are talking about the ground state and this correction is given by psi n 0 which is the unperturbed the grounds unperturbed ground state. So, we will write it like this and then the H prime and then again n l m l 0 and as we have just seen that this is nothing, but psi o1 0 0 0 and a minus e E r cosine theta and a psi 1 0 0 0 0 this 0 in the superscript denotes the unperturbed wave function alright.

So, this has to be evaluated and this is quite easy to evaluate, you can in fact without evaluating. So, this is let us just I will write down the functions or rather the integral the integral is R 1 0 r square and r and this is equal. So, r is coming from this r is coming from there and we now have a volume integral which gives me a R square dr. So, that gives me a r cube dr and from 0 to infinity. So, that is the radial integral, we do not really need to evaluate it for the given reason that now what is the angular or the theta integral. So, the in the volume so, let us just write down the volume just for your reference once and for all its r squared dr sin theta d theta and d phi ok.

So, we have a sin theta d theta coming from the volume integral, but there is also a cosine theta and all these minus e E all those things will be there we are simply you know and also all these other things which are coming along with R 1 0 would have to be written down, but we are not at this moment writing it down. The theta integral remember it is from 0 to pi and there is also a d phi since the integrand does not depend upon phi we can simply write a d phi from 0 to pi.

Now, you see this thing can be written as cos theta d theta can be written as a d of or rather sin theta d theta let us just reverse the order in this particular case. So, that. So, it is a cos theta and then it is a sin theta d theta. So, sin theta d theta can be written as d of cosine theta, and now along with this integral goes from minus 1 to plus 1 instead of 0 2 pi. So, now my variable is not theta, but the variable is cosine theta which can be taken as x.

So, x dx is the integral which from minus 1 to plus 1 will give me 0. So, I really do not need to evaluate all this radial integral or the phi integral which is called azimuthal integral the theta integral gives me 0. So, that is the E 1 which is for the ground state the first order correction is equal to 0 so no correction in energy due to stark effect; no first order correction stark effect for electron in the ground state.

And if you are interested in knowing the physical reason for that let us go back to this picture. So, this is that of course, 2 0 0, but the 1 0 0 will also look something similar to this, it has a spherical symmetry. So, the electric field which is acting on the z direction will not because of this symmetric structure will not give any correction, will not be able to yield any correction to the energy.

So, this is the first one let us do the second one, which is a little elaborate, but it is quite instructive.

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(2) Second

So, 2 is second order or will do the 3 first that is the first order stark effect to the first excited state, which is slightly smaller and then of course, we will do it or let us just do it the second order stark effect. So, let us just do this one as well the first to begin with or better option is to do the first order, and then we will come back to this. So, we will do the ok. So, let us just do this the third one and we will come back to the second one.

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(3) First order Stark effect for the first excited state.

$n=2$ $\quad l=0 \quad m_l=0 \rightarrow 1$ state
$\quad\quad\quad l=1 \quad m_l=-1,0,+1 \rightarrow 3$ states $\Big\}$ 4 fold degenerate

$$|\psi_{nlm_l}\rangle: \quad u_1 \xrightarrow[l=0]{s} R_{20}Y_{00} = f(r)$$
$$u_2 \xrightarrow[l=1,\, m_l=0]{p} R_{21}Y_{10} = c_1\, g(r)\cos\theta$$
$$u_3 \xrightarrow[l=1,\, m_l=1]{p} R_{21}Y_{11} = c_2\, g(r)\sin\theta\, e^{i\phi}$$
$$u_3 \xrightarrow[l=1,\, m_l=-1]{p} R_{21}Y_{1-1} = c_3\, g(r)\sin\theta\, e^{-i\phi}$$

4 fold degenerate

have energy $\mathcal{E}_n = -\frac{13.6}{4}\,eV = -3.4\,eV$

$c_1, c_2, c_3 \quad f(r), g(r)$ can be looked upon from any book.

So, the first order stark effect for the first excited state all right. So, we have n equal to 2 that is the first excited state. So, n equal to 2 will have l equal to 0 and l equal to 1; l equal to 0 will have ml equal to 0 and l equal to 1 we will have m l equal to 1 or rather minus 1 0 and plus 1. So, these are the values that one would take.

So, this becomes a degenerate state, because n equal to 2 will have a fourfold degeneracy. So, now so, n equal to 2 has so, this is one state and these are three states and this whole thing is four fold degenerate. So, it is a fourfold degenerate state and let us write down this psi n l m. So, let us write down the psi n l m l for these things and let us just you know abbreviate them as u 1 which is equal to l equal to 0 and is called as the s state which is R 2 0 Y 0 0 and because Y 0 0 is a constant you can look at the table containing this the I mean the spherical harmonics and you will see that this is equal to constant. So, this is only a function of the radial variable r. We are not writing the exact form because you will see that the exact form is only required for one particular case where you can just look at and compute an integral for most of the cases it is not required.

So, this is u 2 which is equal to a p state which is equal to l equal to 1 and m l equal to 0. So, that is equal to R 2 1 Y 1 0 which is equal to a c 1 and g of r again c 1 is a constant and g of r is a radial function as a function of r the radial variable and it also has a cosine theta as long as you have m l equal to 0 there is no exponential i phi or exponential minus i phi. So, it is a purely a function of theta; u 3 which is again l equal to 1 and m l equal to 1. So, which is also a p state which is R 2 1 Y 11 now this is going to give me sin theta and exponential i phi and similarly a u 4 which is again a p state which is equal to l equal to 1, m l equal to minus 1 which is R 2 1 Y 1 minus 1 which is again another constant and the radial variable remains same because it is only changing that azimuthal or the magnetic quantum number. So, this is going to be again sin theta and you will have a exponential minus i phi.

So, what we are trying to say is that, all these things have an energy which is equal to E n equal to minus 13.6 divided by 4 electron volt which is minus 3.4 electron volt. So, that is the so, they are all. So, these are degenerate and it is a fourfold degenerate problem. And when you have a degenerate problem and you want to do a perturbation theory the degenerate perturbation theory has to be applied and please look at c 1 c 2 c 3 f of r g of r can be looked upon from any book this intentionally done. So, that you open the book and make sure that you know what these constants as well as the radial variables correspond to. In any case we will need the radial variables for one particular integral which you will see.

So, how does the problem is formulated from now on? So, this is the first order correction demands that that we have this secular equation this and minus H that equal to 0.

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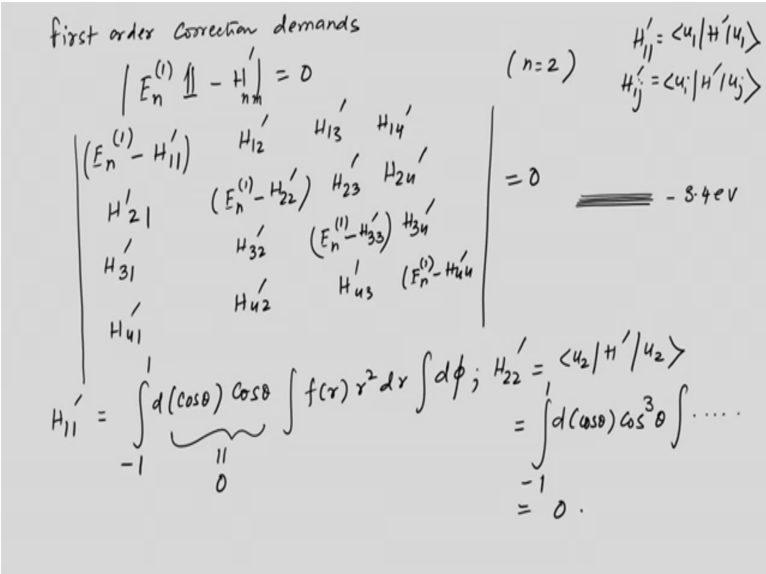

So, basically the determinant is equal to 0 or we can write n m if you want and. So, n here is equal to 2 of course, and these are the matrix element. So, we will continue writing it as E n 1 is the first order correction and corresponding to n equal to 2. So, make sure that its n equal to 2. So, then we can write this as a 4 by 4 problem as a E n 1 minus H prime 11 H prime 11 I just give you one example so, this is equal to u 1 H prime u 1 ok.

So, your u 1 is given, you have to calculate the matrix elements of the perturbation term u 1 within this u 1 of H prime within this u 1 states and H 1 2 prime H 1 3 prime H 1 4 prime and so, on. So, H ij prime is nothing, but equal to u i H prime u j where u i and u j are one of those u u 1 to u 4 all right. So, this is equal to H prime 2 1 of course, a for a Hermitian Hamiltonian H 1 2 prime and H 2 1 prime are same, we are just writing it notationally differently H 2 2 prime just putting it in bracket H 2 3 prime, H 2 4 prime H 3 1 prime again H 1 3 prime and H 31 prime are same.

H 3 2 prime E n 1 minus H 33 prime and H 34 prime and H 41 prime again that is equal to H 14 prime and its H of 42 prime and its H 43 prime and this is equal to E n 1 minus H 44 prime and the determinant of that equal to 0 will give me four values of E n 1 by solving the rather solving this equation which is the determinant equal to 0 will give non trivial solutions for four different E n ones which could be 0 which means that there is still no removal of degeneracy.

So, there are at this moment we have four degenerate energy levels, all having value minus 3.4 electron volt, they are being applied upon by an electric field uniform electric field applied in the z direction and we are trying to calculate that how the levels respond to it, how the levels react to it whether there are shifts whether there are splits of these and that is the basic goal of perturbation theory.

Now, the rest of the work is simple excepting that try to understand before you actually do all these calculate all these matrix elements which are 16 in number, you would actually see that if we try to calculate H 11 prime we are going to get d of cosine theta and a cosine theta and a minus 1 and a minus 1 and so, on and then there will be of f of r r squared dr and then there will be a d phi, but this is going to give me 0.

So, because there is no theta here the theta term will going to give me 0 what happens to H 2 2 prime? H 2 2 prime that is this is equal to u 2 H prime u 2. Now this is equal to d cosine theta see u 2 has got a cosine theta. So, there are 2 of these u 2 so, I will get a cosine cube theta 2 cosine theta coming from the u 2 and one cosine theta coming from h prime. So, this is from minus 1 to plus 1 and the rest of the integrals which would remain.

Now this is again it is a dx and x cube which the integral between minus 1 to plus 1 will again give me 0. So, this is again 0 as well. So, H 11 prime H 2 2 prime which are equal to 0 you see that fortunately and strangely the H 13 prime is also equal to 0 for a different reasons.

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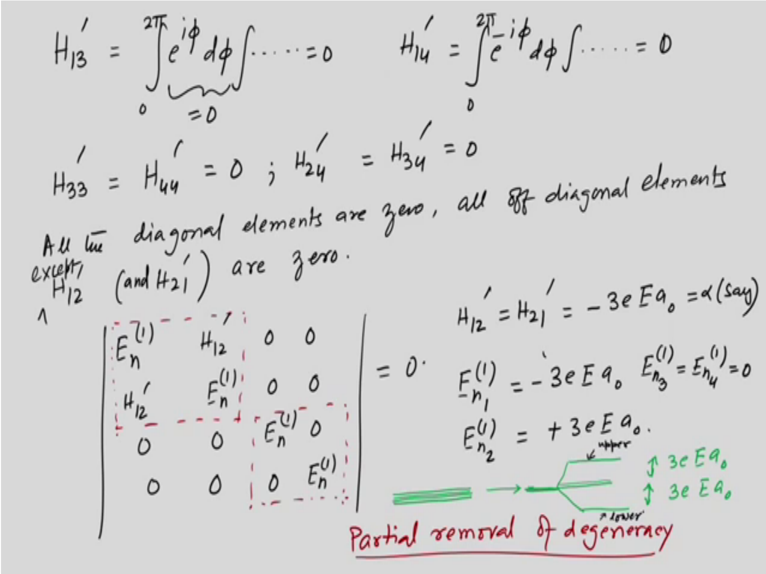

That has exponential i phi d phi from now the phi integral is from 0 to 2 pi and of course, the rest of the integrals are there f of r and things like that which we are not interested in writing at this moment this is equal to 0 as well, and similarly the H 14 prime that is equal to 0 as well and 0 to 2 pi exponential minus i phi d phi and all these integrals all right.

So, what it means is that the all these integrals I am sorry we have missed a calculation of this H 33 prime and H 44 prime, which would also be equal to 0 for the same reason as we have you know enumerated for the H 11 prime and H 22 prime these will be 0 because it is a integral over theta will give us 0 so, this is equal to 0 as well.

So, that tells us the very large number of matrix elements are equal to 0,all the diagonal elements are equal to 0 and all I mean some of the off diagonals elements are equal to 0 and also you can see that h 2 4 prime and H 34 prime those are also equal to 0. So, which means that you see none of the off diagonal elements survive see if H 24 prime equal to 0 then H 4 2 prime is equal to also equal to 0 see there is a H 4 2 prime.

And similarly if H 34 prime equal to 0, which means that H 43 prime is also equal to 0 similarly this means that H 13 prime equal to 0 which means that this is equal to 0 as well H 31 prime and so, this is equal to 0. So, let us just list out how many elements are identically equal to 0 because of the theta and the phi integrals. So, all the diagonal elements are 0 all of diagonal elements except H 12 prime or H 21 prime which is not zero. So, this is except ornate or and which means and. So, these 2 are not equal to 0 the rest of them are all equal to 0.

So, that is a tremendous simplification that we have you know achieved in this particular case. So, we will have this thing written as E n 1 H 12 prime which is non zero and a 0 0 this is H 2 1 prime, but which is equal to H 12 prime. So, we will simply write it as H 1 2 prime 0 0 then it is 0 0 E n 1 E n 1 0 and then 0 0 0 E and 1.

Now, the this is equal to 0 now you see that determinant of this kind can actually be broken down into because of this of these off diagonal elements becoming 0 you have 2 blocks which are completely decoupled from each other. So, you can simply work with these 2 blocks, and very easy to see that there is no energy correction from coming from the lower block the lower right block, which means that the E n 1 is identically equal to 0 only thing that is a non zero is coming from the E n 1 and for that we have to calculate H 1 2 prime. This is one exercise that I leave it to you, but I will give you the answer. So, it is a H 12 prime which is same as H 2 1 prime which is equal to a minus 3 e E a 0 let us call it as alpha say ok.

So, then E n 1 is I mean one of them is minus 3 e E a 0 and E n 21 is plus 3 e E a 0. So, which means that these are four levels let us draw it with a different color. So, there are these almost the same color let us just take another color. So this four levels which were earlier degenerate, now 2 of them continue to be degenerate one of them shifts up the other shifts down by an amount which is 3 e E a 0. And clearly this is the first order result and because it is a first order in e and at the other these things are they continue to be equal to 0 let us just write that as well.

So, E n E n 3 1 equal to E n 4 1 equal to 0 so, these are unaffected by this stark effect and. So, these are so, basically 2 of them continue to. So, these 2 are there and only so, it is a partial removal of degeneracy. So, let us call write it partial removal of degeneracy it is partially removed.

Now, what are the wave functions they look like basically the corrected wave function that is not to difficult to find out. So, we need to find out these is or the coefficients.

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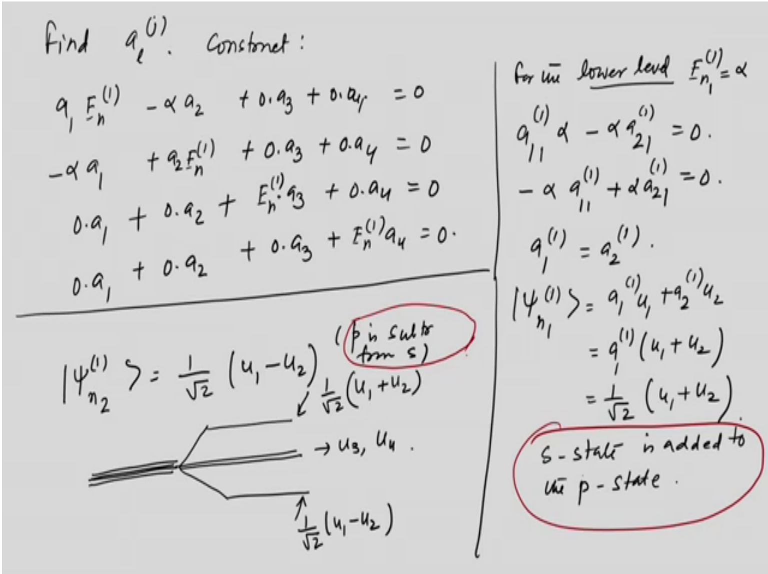

So, let us call it as a a l j. So, you construct a one E n 1 minus alpha a 2 plus 0 a 3 plus 0 a 4 because these are all 0. So, this is minus alpha a 1 plus a 2 E n 2 I mean E n 1 basically these are 2 values 0 a 3 plus 0 a 4 this is equal to 0 this is equal to 0 then it is 0 a 1, 0 a 2, 0 a 3 or its not 0 a 3, but its E n which is equal to 0. So, 0 a 4 which is equal to 0 and 0 a 1 plus 0 a 2 plus 0 a 3 plus E n 1 a 4 equal to 0.

So, these are the four things that we get from. So, for the lowest level that is this level that we are here. So, this level that we are talking about this level and so, this is the lower and this is the upper so, upper and lower. So, for the lower level so, this is let us take the lower level to be equal to E n 1 equal to alpha let us call that the lower one as 1. So, I have a a 1 1 corresponding to this one that is alpha. So, this is alpha minus alpha a 2 11 that is equal to 0, and minus alpha a 111 plus alpha a 2 1 1 equal to 0. So, just make sure that this the next one in the subscript actually talks about that we are taking the plus alpha the one of the 2 eigenvalues which we have obtained to be nonzero. So, that one corresponds to that if we take a minus alpha this will be 2.

Now, this gives that a 11 equal to a 2 1 and you can also show that. So, this gives the psi n 1 this is equal to a 1 u 1 plus a 2 1 u 2 and because they are same. So, this is equal to a 11 and u 1 plus u 2 and this is equal to 1 by root 2 u 1 plus u 2 ok. So, the just once again to remind you let me just complete the calculation for this other one. The other one you can just simply show that this psi n this is corresponding to the first one this corresponding to the second one let us just write one here and so, this is equal to so, 1 by root 2 u 1 minus u 2.

So, that is the so, these are the 2 wave functions once again let me just draw that same diagram. So, this was initially fourfold degenerate, then what happens is that it continues to be twofold degenerate this one corresponds to 1 by root 2 u 1 minus u 2 u 1 and u 2 were written earlier. So, this is one by root 2 u 1 plus u 2 and this continue to be u 3 and u 4. So, this is that partial removal of degeneracy.

So, this one the S state because u 1 is the S state; S state is added to the P state and this is s P state is subtracted. So, P is subtracted from S so, let us box this statements so, that is the. So, let us just tell you the summary of this and.

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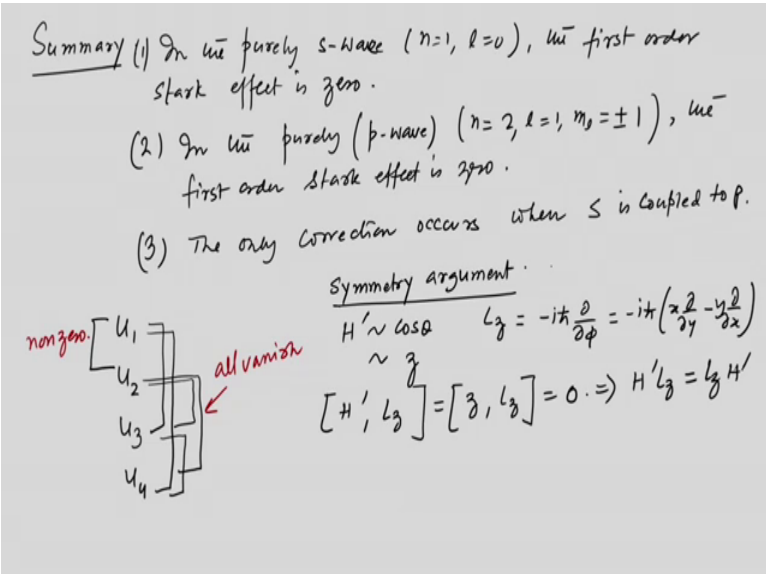

So, in the purely s wave n equal to 1 l equal to zero the first order stark effect is 0 which we have seen in the first problem so, that is one. The second one says that in the purely p wave which is n equal to 2 l equal to 1 and m l equal to plus 1 or minus 1 again the first order stark effect is zero ok.

You saw that this u 3 and u 4 are unchanged there is no energy correction to that. So, these corresponds to the purely P states. So, the only correction occurs when Ss is or S hybridizes with P or S is coupled to P. Let us give a short graphical this thing. So, u 1 u 2 u 3 u 4 you would get a nice idea. So, all these things will vanish like u 1 u 3 will vanish u 1 u 4 will vanish u 3 u 4 will vanish u 2 u 3 will vanish u 3 u 4 will vanish and so, on so, all vanish.

So, the only thing that is non-zero is this one. So, let us give a very nice a symmetry argument which is very elegant and these are very much needed for such you know for one to understand before one does the calculation. So, our so, let us call it a symmetry argument and. So, H prime it goes like cos theta we have seen the theta variation is cos theta.

Now, L z is equal to minus i h cross del del phi that is the z component of the angular momentum. Now this is like z that is why the z component of the angular momentum cos theta is like z r cos theta is z. Now because I mean the H prime and the L z would commute because this is nothing, but like minus i h cross x del del y minus y del del x. So, H prime and L z which is equal to z and L z they would commute that tells that H prime L z is equal to L z h prime.

Now, evaluate let us go to the next page.

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Evaluate $\langle u_i | (H' L_z - L_z H') | u_j \rangle$

$u_i \sim Y_{l m_l}$. $u_j = Y_{l' m_l'}$

$L_z |u_i\rangle \to m_l |u_i\rangle$ $\quad L_z |u_j\rangle = m_l' |u_j\rangle$

$$\langle u_i | L_z H' - H' L_z | u_j \rangle = 0 = (m_l' - m_l) \langle u_i | H' | u_j \rangle$$
$$= 0 \text{ if } m_l' = m_l$$
$$= 0 \text{ if } m_l' \neq m_l \text{ if } \langle u_i | H' | u_j \rangle.$$

$\boxed{\text{This is only untrue when } m_l = m_l' = 0.}$

Evaluate u 1 which is one of the 1 2 3 4. So, i is can be any of these H prime L z minus L z H prime this acting on a u j now u i the angular dependencies are like Y l m l and u j is another say its Y l prime ml prime. So, L z acting on u 1 will give m l u 1 u i or any of these u i and L z acting on u j will give a ml prime u j. So, because there are like Y lm functions that is u i is a u j is are y lm functions. So, L z acting on which are Y lms are the or the spherical harmonics are the eigen states of L z.

So, then u i L z L z H prime minus H prime L z is anyway equal to 0. So, this is equal to 0 and this is equal to m l prime minus ml u i H prime u j now you see that this is equal to 0 if m l prime equal to m l. So, which are if your m l equal to 1 and m l equal to also equal to 1 then of course, this is equal to 0 and or m l equal to and is also equal to 0 if m l not equal to m l m l prime not equal to m l because are the left hand side is anyway equal to 0. So, in which in which case this matrix element will be equal to 0 if this u i H prime u j will be equal to 0.

So this is only untrue or invalid when m l equal to m l prime equal to 0 and that is why there is a non-zero correction between the SNP states but remember those SNP states both of them correspond to l equal to m l equal to 0. So, one is l equal to 0 m l equal to 0 the other is l equal to 1 and m l equal to 0 that is the only non-zero correction that one obtains here. So, this is the so, we get a first order correction to the first excited state, next we shall look at the second that is this correction and the second order correction to the ground state of the hydrogen atom.