

Advanced Quantum Mechanics with Applications
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Lecture – 23
Stark Effect Second order in ground state

So let us now look at the second order stark effect on the ground state of the hydrogen atom, which means that we are interested in calculating the energy correction to the second order or the quadratic in the electric field E to the ground state.

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Second order Stark effect on the ground state of H. atom.

Second order energy correction $E_n^{(2)} = \langle \psi_n^0 | H' | \psi_n^{(1)} \rangle$

Proof: The determining equation is,

$$(H_0 - E_n^{(0)}) |\psi_n^{(l)}\rangle = (E_n^{(l)} - H') |\psi_n^{(l-1)}\rangle + \sum_{j=2}^l E_n^{(j)} |\psi_n^{l-j}\rangle \quad (1)$$

For $l=2$

$$(H_0 - E_n^{(0)}) |\psi_n^{(2)}\rangle = (E_n^{(2)} - H') |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^0\rangle \quad (2)$$

for $l=1$

$$(H_0 - E_n^{(0)}) |\psi_n^{(1)}\rangle = (E_n^{(1)} - H') |\psi_n^0\rangle \quad (3)$$

So, we shall use this second order. So, we will use a formula for the second order energy correction, which is given by a $E_n^{(2)}$; 2 stands for the second order in the subscript rather the superscript, which is equal to a ψ_n^0 which is the unperturbed wave function, and the perturbation term which we have seen earlier and then the first order correction in the wave function.

Now how to arrive at that formula let me give a proof of this formula. So, this is the second order energy correction. So, let us box this and let us give a proof for that let us. So, we are interested to you know knowing how to arrive at that formula. So, the determining equation is $H_0 - E_n^{(0)}$ this is acting on $\psi_n^{(1)}$; 1 is the particular order that we are interested in this is equal to a $E_n^{(1)}$ which is the first order energy correction

minus $H' \psi_{n-1}$ and a plus $E_{n-1} \psi_{n-1}$ equal to $E_n \psi_n$ and then you have ψ_{n-1} .

So, this is the closed form for the perturbation series that we had written down. So, this is the first order term and then of course, there are higher order terms. So, we can actually also calculate the third order energy correction, and this is particularly important for problems where the first order does not give any finite energy correction, which we have seen for this particular case that the first order energy correction for the ground state is 0.

So, the Stark effect does not give either any splitting or the shift in energy level or the first order in the ground state. So, it is important to see the situation in the second order. Now we can put l equal to 2, and then our $H_0 - E_n^{(0)}$ that becomes a ψ_{n-2} , and then have a $E_{n-1} - H'$ and a $\psi_{n-1} + E_{n-2}$ that is the second order correction and this is on 0, and for l equal to 1 we have $H_0 - E_n^{(0)}$ acting on ψ_{n-1} , equal to $E_{n-1} - H'$ ψ_n . So, this is all by putting l equal to 2 and l equal to 1 on the expression that we have written here, on this expression that we have written here ok.

So, this is the closed form of the equations or rather this is a closed form for determining the different orders of correction in the energy all right. So, in order to get $E_n^{(2)}$ let us just put this and.

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Take inner product with $\langle \psi_n^{(0)} |$ in Eq. (2).

$$\langle \psi_n^{(0)} | (H_0 - E_n^{(0)}) | \psi_n^{(2)} \rangle = \langle \psi_n^{(0)} | (E_n^{(1)} - H') | \psi_n^{(0)} \rangle + E_n^{(2)}.$$

Taking conjugate the LHS becomes zero.

$$E_n^{(2)} = \langle \psi_n^{(0)} | (E_n^{(1)} - H') | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | H_0 - E_n^{(0)} | \psi_n^{(1)} \rangle$$

$$E_n^{(2)} = \langle \psi_n^{(0)} | H' | \psi_n^{(1)} \rangle.$$

We want $\psi_n^{(1)}$!!

$H = H_0 + H'$

So, let us take an inner product with ψ_n^0 for this. So, let us call this as equation 1 and equation 2 and this call it as equation 3. So, take inner product or we can say overlap inner product with ψ_n^0 in equation 2. So, this is a $\psi_n^0 H_0$ minus E_n^0 .

Are you remember ψ_n^0 is the unperturbed energy, and this is ψ_n^2 and this is equal to a ψ_n^0 plus E_n^1 minus H' and a ψ_n^1 plus a E_n^2 . Now, if I take a complex conjugate of this, this will become equal to 0; the left hand side is equal to 0 because in which case the H_0 will act on ψ_n^0 giving us E_n^0 which will cancel with the other term inside the bracket.

So, taking, so, the LHS becomes 0 that is left hand side becomes 0 and we are left with E_n^2 which is nothing, but a $\psi_n^1 E_n^1$ minus H' , ψ_n^0 and. So, basically this is the conjugate of this because E_n is real one can simply write the E_n^2 is equal to $\psi_n^0 H'$. So, let me skip one step and tell you to evaluate this and show this that this is equal to a $\psi_n^0 H'$ and ψ_n^1 ok.

And this is what it is we will use this in fact, what you should notice is that this is nothing but this is equal to H_0 minus E_n^0 and a ψ_n^1 , because of the reason that your total H is equal to H_0 plus H' . So, I leave it to you to do one just one step in order to arrive at that. So, our second order energy correction is obtained by the taking the overlap of H' between the ground the unperturbed state, and the first order correction in the wave function all right.

Now, the problem with this is that one does not know what is the first order correction in the wave function unless one actually evaluates or does a full first order perturbation theory. We have tried doing the first order perturbation theory, but that gave us a zero correction in energy. So, we could not proceed any farther the energy correction is 0 does not mean the wave function would not undergo any a modification or renormalization because of the perturbation term.

So, we want of course, the to know what is the ψ_n^1 . So, this is something that we are now looking for and.

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Use the first order equation,

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

We have shown that $E_n^{(1)} = 0$ for Stark effect.

$$(H_0 - E_n^{(0)}) |\psi_n^{(1)}\rangle = -H' |\psi_n^{(0)}\rangle \quad H' = -eEr \cos\theta \quad (1)$$

$$|\psi_n^{(0)}\rangle = |\psi_{nlm}^{(0)}\rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (= R_{10}(r) Y_{00}(\theta, \phi))$$

$$H_0 = \underbrace{-\frac{\hbar^2}{2m} \nabla^2}_{KE} - \underbrace{\frac{e^2}{r}}_{\text{Coulomb}} = -\frac{\hbar^2}{2m} (\nabla_r^2 + \nabla_{\theta, \phi}^2)$$

Postulate: $|\psi_n^{(1)}\rangle = \cos\theta e^{-r/a_0} \sum_{\alpha} C_{\alpha} r^{\alpha} = f(r) \cos\theta$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \dots$$

So, if we use the first order equation then we have. So, this is equal to H_0 minus $E_n^{(0)}$ remember we have just written down the first order equation, this is $\psi_n^{(1)}$ which is equal to $E_n^{(1)}$ minus H' $\psi_n^{(0)}$ and ok. So, this is the 1 that we have written down here as equation 3. So, this is the first order equation.

And so, we have shown that that $E_n^{(1)}$ equal to 0 for Stark effect. So, that tells that my H_0 minus $E_n^{(0)}$ acting on the first order correction to the wave function is equal to minus H' $\psi_n^{(0)}$ and of course, just to remind you that H' is equal to minus eEr cosine theta where a small e is the electronic charge and capital E is the electric field r is the radial variable and theta is the angular variable. So, this is the situation so, far.

So, we are getting that H_0 minus $E_n^{(0)}$ that has to be operated on the first order correction in wave function and that is equal to minus H' $\psi_n^{(0)}$ which is coming from the first order equation. Now of course, we know even if we do not know $\psi_n^{(1)}$ we know $\psi_n^{(0)}$. So, $\psi_n^{(0)}$ I have written it more specifically now in terms of the relevant quantum numbers, which are principal and the azimuthal and magnetic quantum number nl sorry its $n l m 0$ and that is equal to nothing, but 1 by root over πa_0^3 and its exponential r by a_0 which is nothing, but equal to $R_{10}(r)$ and a $Y_{00}(\theta, \phi)$ that is the ground state ok.

So, this please learn it by heart that this is a ground state this is a form of the ground state, which has no theta or phi dependence it only depends on r and we have shown in

the previous discussion that it looks like a spherically symmetric the orbital looks like for the spherically symmetric; and the Y_{00} is simply just a number and H_0 is of course, nothing, but $\frac{\hbar^2}{2m}$ and $\Delta^2 - \frac{e^2}{r}$. So, this is the coulomb term. So, this is the kinetic energy and this is the coulomb interaction due to the electron and the proton it is in the inside the nucleus.

Now, it is important to see that since the ψ_{n0} does not have any theta or phi dependence, we are not going to get a theta or phi dependence in ψ_{n1} excepting for a theta dependence coming from the perturbation term. See the perturbation term is $-eEr \cos\theta$ that is operating on a term which is only a function of r . So, on the left hand side we should get only a function of a $\cos\theta$ and they will be of course, terms which are a which depends on r , and no other theta or phi dependence is possible because of this.

So, let us postulate it is like an ansatz here that, ψ_{n1} is equal to a $\cos\theta$ exponential minus r by a_0 and $e^{-\alpha r}$ to the power α . So, that is the ansatz for this and which is equal to $f(r) \cos\theta$. Where $f(r)$ is at this moment and a unknown function of r we will determine that. So, of course, H_0 contains this Δ^2 . So, this is equal to $-\frac{\hbar^2}{2m} \Delta^2 + \frac{e^2}{r}$, which has a form this called as a Laplacian and let us just write down the full form for. So, Δ^2 operator is $\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta})$.

And of course, there is also another term, which is Δ^2 the full term is there will be a $\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2}$ and things like that, which are not important as we are not getting any phi dependence from anywhere in ψ_{n1} ok. So, we have this r and theta dependence, which is which has to be computed now.

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$$\nabla_r^2 f(r) \cos\theta = \cos\theta \left[\frac{2f'(r)}{r} + f''(r) \right] \quad (2)$$

$$\nabla_\theta^2 f(r) \cos\theta = -2 \frac{f \cos\theta}{r^2} \quad (3)$$

Putting (2) & (3) in (1).

$$\frac{-\hbar^2}{2m} \cos\theta \left[\frac{2f'(r)}{r} + f''(r) - \frac{2f(r)}{r^2} \right] - \frac{e^2}{r} f(r) \cos\theta = -E_n^{(0)} f(r) \cos\theta \quad (4)$$

Dividing by $-\frac{\hbar^2}{2m} \cos\theta$, reorganizing, $\sqrt{\pi a_0^3}$.

$$f''(r) + \frac{2f'(r)}{r} - \frac{2f(r)}{r^2} + \frac{2m}{\hbar^2} \frac{e^2}{r} f(r) + \frac{2m}{\hbar^2} E_n^{(0)} f(r) = \frac{2m}{\hbar^2} \frac{eEr \bar{e}^{-r/a_0}}{\sqrt{\pi a_0^3}} \quad (5)$$

$$E_n^{(0)} = -\frac{e^2}{2a_0} = -\frac{13.6}{n^2} \text{ eV}, a_0 = \frac{\hbar^2}{me^2}$$

So, now, let us calculate del square the r part of it and f r cosine theta. Little tedious, but nothing difficult about it. So, this is cos theta 2 f prime of r by r plus f double prime r do this very carefully, I am only giving you the result.

And the theta square of f of r cosine theta. So, we are operating the H 0 on the psi n 1. So, this is equal to minus 2 f cosine theta over r square. So, these are the 2 derivatives that are required for this, and now if you put these things these 2 things in that equation. So, let us call this as let us call this one as a equation 1 this one let us call it as a equation 1 and let us call these two as a equation 2 and 3 if you put putting 2 and 3 in 1 in order to compute psi n 1.

So, this comes out as minus H square over 2 m cosine theta and the 2 f prime of r by r plus f double prime r minus 2 f of r by r square minus e square over r f of r cosine theta. So, this minus E n 0 f of r, which simply gets multiplied because E n 0 is just a scalar number. So, this and this is equal to minus eE r cosine theta and now we can simply write down the ground state wave function which is this. So, this is the equation that you get call it equation 4, I am just doing a bit of simplification that dividing by minus H square by 2 m cosine theta we get a f double prime, and basically then reorganizing.

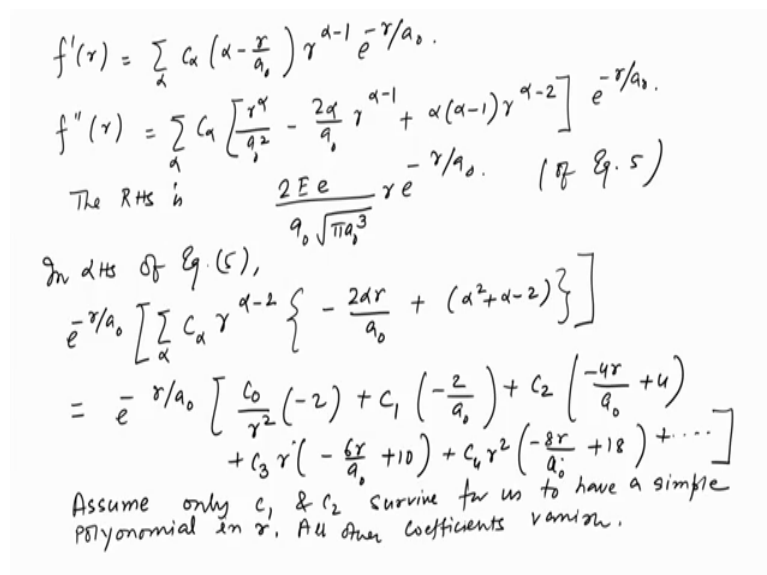
So, this plus a 2 f prime of r, remember our main unknown is f of r and that has to be settled. We have already decided that psi n 1 cannot have any other theta dependence other than just the cos theta factor because the right hand side does not allow a any other

theta dependence. So, $f''(r) = -\frac{2E}{\hbar^2} f(r)$ where $E = -13.6 \text{ eV}/n^2$. Now, I am writing everything together and in an organized manner.

So, this is $f''(r) = -\frac{2E}{\hbar^2} f(r)$ exponential minus r/a_0 divided by πa_0^3 . This is just the simplified version of equation 4 if you wish call it as equation 5; and just to remind you that $E = 0$ is nothing, but minus $e^2/2a_0$ and which has a value of course, minus 13.6 divided by n^2 electron volt for the ground state n is equal to 1. So, its minus 13.6 electron volt and also remember that the a_0 is the Bohr radius which has a form its equal to $m e^2 / \hbar^2$ let me put this in a ok.

So, this is our and of course, the e is the electric field that we have.

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$$f'(r) = \sum_{\alpha} c_{\alpha} \left(\alpha - \frac{r}{a_0}\right) r^{\alpha-1} e^{-r/a_0}$$

$$f''(r) = \sum_{\alpha} c_{\alpha} \left[\frac{r^{\alpha}}{a_0^2} - \frac{2r^{\alpha-1}}{a_0} + \alpha(\alpha-1)r^{\alpha-2} \right] e^{-r/a_0}$$

The RHS is $\frac{2Ee}{a_0 \sqrt{\pi a_0^3}} r e^{-r/a_0}$ (of Eq. 5)

In LHS of Eq. (5),

$$e^{-r/a_0} \left[\sum_{\alpha} c_{\alpha} r^{\alpha-2} \left\{ -\frac{2r}{a_0} + (\alpha^2 + \alpha - 2) \right\} \right]$$

$$= e^{-r/a_0} \left[\frac{c_0}{r^2}(-2) + c_1 \left(-\frac{2}{a_0}\right) + c_2 \left(\frac{-4r}{a_0} + 4\right) + c_3 r \left(-\frac{6r}{a_0} + 10\right) + c_4 r^2 \left(\frac{-8r}{a_0} + 18\right) + \dots \right]$$

Assume only c_1 & c_2 survive for us to have a simple polynomial in r . All other coefficients vanish.

So, now, from the ansatz my f' ; or f' prime of r equal to sum over α c_{α} $(\alpha - r/a_0) r^{\alpha-1} e^{-r/a_0}$ that is my the first derivative of f with respect to r and f'' are equal to sum over α $c_{\alpha} r^{\alpha} / a_0^2 - 2r^{\alpha-1}/a_0 + \alpha(\alpha-1)r^{\alpha-2}$ exponential minus r/a_0 .

So, of course, the right hand side is a simple its $2Ee / (a_0 \pi a_0^3)$ into $r e^{-r/a_0}$. So, we put in LHS of equation 5. So, this is RHS of equation 5. It is we put all these f' and f'' and this can be written as

exponential minus r by a 0 and there is a summation over α C α r to the power minus 1 mean r to the power α minus 2 , and there is a minus 2 α r by a 0 plus α square plus α minus 2 ; you should check all these factors is this, which can be simplified as a exponential minus r by a 0 which is C 0 by r square minus 2 plus C 1 minus 2 by a naught this expanding all these things which is because α is α goes from 0 to ∞ . So, this is what answers is there.

So, this α is it goes from you know 0 to some value. So, these are is expanded with the power series of r and. So, this is equal to a 4 r by 0 plus 4 plus C 3 r minus 6 r by a 0 plus 10 plus C 4 r square minus 8 r by a 0 plus 18 and so, on. So, these are. So, of course, we want a simple polynomial in r because we have seen that the ψ_0 is a simple polynomial which has got r dependence only in the exponent, which is exponential minus r by a zero.

So, we do not want a very complicated polynomial because it is being generated from the ground state according to this equation which is we have called it equation number 1. So, if we have this, then let us expect or rather assume that only C_1 and C_2 survive for us to have a simple polynomial in r all other coefficients vanish all right.

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$$\begin{aligned}
 & -\frac{2C_1}{a_0} + 4C_2 = 0 \\
 & \frac{C_1}{a_0} = 2C_2 \Rightarrow C_1 = 2a_0 C_2 \\
 & \text{Equating coefficients in both sides,} \\
 & C_2 = -\frac{E}{2e\sqrt{\pi a_0^3}} \\
 & f(r) = e^{-r/a_0} (C_1 r + C_2 r^2) \\
 & \text{Putting } C_1 \text{ and } C_2, \\
 & \boxed{f(r) = \frac{E e^{-r/a_0}}{e\sqrt{\pi a_0^3}} \left(a_0 r + \frac{1}{2} r^2 \right)}
 \end{aligned}$$

So, then in which case we can simply write it as a minus 2 C_1 by a 0 that is the second term that you have just seen plus a 4 C_2 this is equal to 0 . So, which means that C_1 by a 0 equal to C_2 C_2 which tells you that C_1 equal to 2 a 0 C_2 .

So, if we equate the coefficients in both sides C 2 equal to minus E divided by 2 e by a 0 cube. So, f of r equal to exponential minus r by a 0 and C 1 plus C 2 r square now putting C 1 and C 2 just what we have found, f of r becomes E exponential r by a 0; this e is a electric field not energy its e pi a 0 cube and there is a 0 r plus a half r square. So, that is the polynomial in r that we have postulated made an ansatz off and this is the form of that polynomial finally, we get of course, we have ignored terms which are coefficients having coefficients of C 3 and C 4 and so, on.

But in any case we wanted a simple polynomial or consisting of a just a few terms there and this is such a polynomial all right. So, our purpose is almost.

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$$\begin{aligned}
 |\psi_n^{(1)}\rangle &= f(r) \cos\theta \\
 &= \frac{-E e^{-r/a_0}}{e \sqrt{\pi a_0^3}} \left(a_0 r + \frac{1}{2} r^2 \right) \cos\theta \\
 E_n^{(2)} &= \langle \psi_n^{(0)} | H' | \psi_n^{(1)} \rangle \\
 &= \int d^3r \left(\frac{1}{\sqrt{\pi a_0^3}} \right) e^{-r/a_0} \left(\phi E r \cos\theta \right) \left(\frac{-E e^{-r/a_0}}{\left(a_0 r + \frac{1}{2} r^2 \right) a_0} \right) \\
 \int d^3r &\rightarrow \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\
 \theta \text{ integration} & \int_{-1}^1 d(\cos\theta) \cos^2\theta = \left. \frac{x^3}{3} \right|_{-1}^1 = \frac{2}{3}
 \end{aligned}$$

Solved because we got psi n 1 it was f of r and cosine theta, which now becomes minus E exponential r over a 0 e pi a 0 cube a 0 r plus half r square. So, that is all about the r dependence and then there is of course, a cos theta. So, this is not an exact first order wave function, but this is what we get from all a physical arguments and is good enough for our purpose ok.

So, the second order energy correction is now given by a psi n 0 according to our formula that we have proved it is this. So, I can simply write it as a d cube r, and a 1 over pi a 0 cube because there is a pi a 0 cube root over a pi a 0 cube in both. So, I can simply write that and there is a exponential this also a 1 over e etcetera that is there. So, there is a 1 over e let me write that there, and there is a exponential r by a 0 and there is a eE r

cosine theta which of course, this e cancels with this e and we have a minus E exponential minus r by a 0 and that is it.

And then we have of course, the d cube r will give me r square d r and then there will be d of cos theta and so, on. So, this is simply equal to sorry we have forgotten writing down the. So, this and then of course, I have the a 0 r plus half r square cosine theta. So,. So, the d cube r that integral will of course, have a 0 to infinity, r square dr that is the that has to be there and its a 0 to pi a sin theta d theta and a 0 to 2 pi d phi.

Now, of course, the let us look at each of the integrals separately, the theta integral or theta integration we have here a minus 1 to plus 1 and a d of cosine theta and there is a cosine theta coming from here. So, there are 2 cosine theta one coming from here and one coming from here. So, there are 2 cosine thetas. So, let us write a cosine squared theta now this is of course, not equal to 0 it is a cos cube theta. So, it is like xs squared dx from minus 1 to plus 1 which is not equal to 0 and this is equal to x cube by 3 from minus 1 to plus 1 assuming that x equal to cos theta.

So, this is equal to two third. So, that is the theta integration and of course, there is no phi will give a 2 pi and now the r integration.

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The image shows handwritten mathematical derivations. At the top, it is titled "gamma-integration" and shows the formula: $\int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}$. Below this, two integrals are shown: $\int_0^{\infty} r^4 e^{-2r/a_0} dr$ and $\int_0^{\infty} r^5 e^{-2r/a_0} dr$. The first integral is evaluated as $\frac{4!}{(a_0/2)^5}$ and the second as $\frac{5!}{(a_0/2)^6}$. Then, the induced dipole moment is calculated: $E_n^{(2)} = -\frac{q}{4} E^2 a_0^3 = -(\text{const}) \cdot E^2$. This is equated to $-\frac{1}{2} \alpha_{ind} E^2$, leading to $\alpha_{ind} = \frac{q}{2} a_0^3$. A definition of polarisability is given: $\alpha : \text{polarisability} = \frac{\text{induced electric dipole moment}}{E}$. Finally, the permanent dipole moment is noted as $E_n^{(1)} = (\text{permanent dipole moment}) E = \alpha E$ with $\alpha = 0$.

Now, for r integration you should use the formula and also remember it, that formula is the gamma function which is r to the power n exponential of minus alpha rdr that is equal

to n factorial divided by α to the power $n + 1$, α is a constant which comes in the argument of the exponent.

So, if you do that. So, how many r s are there? Of course, there is an exponential minus $2r$ by a_0 and there are terms which are $r^2 dr$, and then there are terms which are r into r^2 and r^2 . So, its r to the power a_5 . So, 1 will be r to the power 4 and the other will be r to the power 5 . So, we have terms such as r to the power 4 exponential minus $2r$ by $a_0 dr$ and we also have of course, from 0 to infinity, and we also have 0 to infinity r to the power 5 exponential $2r$ by $a_0 dr$.

Just use them this is equal to 4 factorial divided by α is equal to a_0 by 2 . So, it is a_0 by 2 a_0 by 2 to the power 5 , and this one will be again 5 factorial divided by a_0 by 2 whole to the power 6 and so, on. Once when these things are done do a little carefully and then $E_{n=2}$ becomes equal to minus 9 by 4 E^2 a naught cube, which is equal to minus; the now this thing for a given problem is a constant. So, not this one sorry we are just talking about I mean the what is constant is this one the 9 by 4 is of course, a number and a_0 cube is a constant.

So, its basically a constant multiplied by e^2 ok. So, we always wanted to get a correction which is of the order of e^2 because we are talking about the second order Stark effect, and this is called as or rather it is written as α induced E^2 which is called as the induced dipole moment. So, α induced is equal to 9 by 2 a naught cube. So, this is. So, α is called as the polarizability, which is equal to the induced electric dipole moment and this by E . So, $E_{n=1}$ its equal to the permanent dipole moment, this is the general definition dipole moment multiplied by E and this is equal to its called as a αE .

So, here of course, α equal to 0 because there is no energy correction. So, the hydrogen atom has no permanent dipole moment, but there is an induced dipole moment which is given by 9 by 2 a naught q . So, what we have learned is that, you can we got initially 0 energy correction for the ground state of the hydrogen atom due to an externally applied electric field; the electric field being homogeneous that is uniform and is a say pointing in a particular direction.

And the first order energy correction was 0 then we of course, wanted and saw that the first order energy correction in the first excited state is nonzero and we have obtained

solved degenerate perturbation theory, in which case the degree of degeneracy is 4 because we are talking about the first excited state, which is n equal to 2 and we know that the n at the each energy level electronic energy level for a hydrogen atom is n square fold degenerate.

So, n equal to 2 is a fourfold degenerate. So, we solved a 4 I mean perturbation theory, which is 4 fold degenerate and then we have calculated corrections. What we saw is that even for the ground state there is only a partial removal of degeneracy, because of the presence of the electric field. So, one state is moved up and the other state was moved down and 2 other states of those 4 degenerate states they continue to be degenerate at the same value of energy that we have obtained.

Now, here we have obtained the second order correction to the ground state. Remember its a second order correction and so, we should have gotten it a proportional to e square and this is what we have got that the second order energy correction if you write it in terms of half α e square α being the polarizability then the induced polarizability is given by 9 by 2 is a naught q . So, there are many applications of perturbation theory as, we have already stressed that once you cannot solve a Hamiltonian exactly that does not imply that the roads are all closed.

In fact, there are a ways most of the problems are actually unsolvable. So, there has to be ways in order to solve those problems, and perturbation theory is one approach where the strength of the perturbation if it is not a large that is small compared to the unperturbed Hamiltonian, then you can calculate various orders of energy correction also can calculate the wave functions corresponding to those corrections or rather corresponding to those states, for which you seek a perturbation theory..

Just requires you to solve few integrals most of these things which are related to hydrogen atom are have a spherical symmetry. So, you need to solve these volume integral, which are relevant to the spherical polar coordinates, but you could also have problems which are in Cartesian coordinate.

Suppose you say that there is a particle in a box and which is being applied perturbation, which could be you know I mean a proportional to the electric field, if there is a charged particle inside or there could be simply a geometric perturbation that is you make the well slightly asymmetric, and seek for the solution that that gives that there is some

energy correction to the first order to the unperturbed energy, because of that perturbation because of the geometric perturbation.

So, this is one of the ways of solving problems which cannot be solved exactly. In fact, as I said earlier most of the problems in quantum mechanics cannot be solved exactly because of the complexity of the situation.