

Stark Effect

Stark Effect: deals with the splitting of the energy levels of an atom in an electric field.

Now let us apply the technique of time-independent perturbation theory to an atomic physics problem. This problem is, what happens when we apply a small electric field to a hydrogen atom. Classically, we know that applying an electric field causes the average position of the electron and proton to not coincide creating an electric dipole, $\vec{P} \propto \vec{E}$, which acts with the field to lower the energy of the atom, $Energy \propto -E^2$.

Note: For H-atom, the electrostatic potential energy is calculated as follows:

$$e\phi(\vec{r}) - e\phi(\vec{R} + \vec{r}) = e\phi(\vec{r}) - e\left[\phi(\vec{R}) - \vec{r} \cdot \nabla\phi(\vec{R})\right]$$

$$= -e\vec{r} \cdot \nabla\phi(\vec{R}) = -e\vec{r} \cdot \vec{E} = -\vec{P} \cdot \vec{E} = -eEr \cos\theta$$

Quantum mechanically, our unperturbed system is the hydrogen atom model we have already solved. The perturbation is an electric field pointing in a specific direction; however, as we can define the co-ordinates of the atom to point in any direction we chose the electric field to be along the z axis without loss of generality. Thus, the perturbation term is given by

$$\hat{H}_p = -eEr \cos\theta = -eE \sum$$

Let us consider the effect of this perturbation on the ground state of the hydrogen atom given by the wavefunction:

$$\psi_{1s}(r, \theta, \varphi) \equiv |n, \ell, m_\ell\rangle \equiv \psi_{1,0,0} = |1, 0, 0\rangle = R_{10} Y_{00}(\theta, \varphi) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \frac{1}{\sqrt{4\pi}}$$

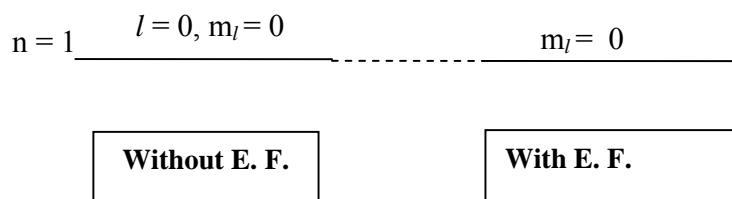
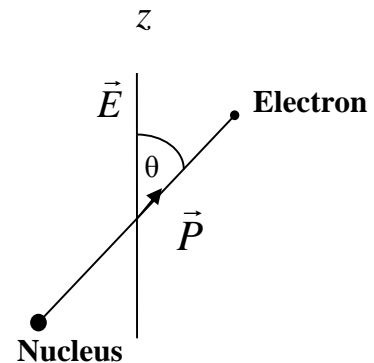
The first order correction to the energy of this state is given by

$$\epsilon_1 = E_{1,0,0}^{(1)} = \int \psi_{1,0,0}^* \hat{H}_p \psi_{1,0,0} d\tau = e |E| \langle 1, 0, 0 | \sum | 1, 0, 0 \rangle$$

$$= e |E| \int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi_{1s}|^2 r^3 \cos\theta \sin\theta dr d\theta d\varphi$$

$$= 0$$

This matrix element is zero. We can show this to be true because for every point included in the integral there is a twin point which is the opposite direction from the origin, i.e. the points given by \vec{r} and $-\vec{r}$. The wavefunction $\psi_{1,0,0}$ is even parity, i.e. it is the same at these two positions, however, the perturbation term has the same magnitude but different sign. This means that the two contributions to the integral add to give zero and the whole integral is zero. i.e. the energy of the ground state is not perturbed.



The second order correction to the energy of this state is given by

$$E_{1,0,0}^{(2)} = \sum_{k \neq j} \frac{\left| \int \psi_k^* \hat{H}_p \psi_{1,0,0} dV \right|^2}{(E_{1,0,0} - E_k)}$$

It turns out that most of the matrix elements in the sum are zero, however, the matrix elements involving $\psi_{n,1,0}$ are non-zero. Even without knowing that the value of the sum, we can show that the energy is proportional to the magnitude of the electric field squared, and the contribution to the energy is negative, as expected from classical physics.

Let us now consider the effect on the degenerate $n = 2$ states. Clearly, we are going to need degenerate perturbation theory, and the first thing we need to do is decide on the correct basis wavefunctions. The conventional wavefunctions are written: For simplicity we will use the state $|\ell, m_\ell\rangle$

$$\begin{aligned} |1\rangle &= |0,0\rangle = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \\ |2\rangle &= |1,0\rangle = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0} \cos\theta \\ |3\rangle &= |1,-1\rangle = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0} \sin\theta e^{-i\varphi} \\ |4\rangle &= |1,1\rangle = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0} \sin\theta e^{i\varphi} \end{aligned}$$

We have the matrix:

$$\begin{array}{cccc} & |0,0\rangle & |1,0\rangle & |1,-1\rangle & |1,1\rangle \\ \begin{array}{l} \langle 0,0| \\ \langle 1,0| \\ \langle 1,-1| \\ \langle 1,1| \end{array} & \left| \begin{array}{cccc} H_{11} - \epsilon_1 & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - \epsilon_1 & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - \epsilon_1 & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - \epsilon_1 \end{array} \right| & = & 0 \end{array}$$

with $H_{ij} = \langle i | \hat{H}_p | j \rangle$.

Note that: to calculate the integral:

$$H_{ik} = \langle i | \hat{H}_p | k \rangle = e |E| \langle r, \theta, \varphi | r \cos\theta | r, \theta, \varphi \rangle = e |E| I_r I_\theta I_\varphi$$

we have to take into account the following procedure:

1- Using the standard integral:

$$\begin{aligned} I_\varphi &= \int_0^\varphi e^{-im\varphi} e^{ik\varphi} d\varphi = 2\pi\delta_{mk} = 2\pi \times \begin{cases} 0 & \text{if } m \neq k \\ 1 & \text{if } m = k \end{cases} \\ \Rightarrow \langle 10 | \mathcal{X} | 1\pm 1 \rangle &= 0, \quad \langle 1\pm 1 | \mathcal{X} | 10 \rangle = 0 \end{aligned}$$

It turns out

$$H_{13} = H_{31} = H_{14} = H_{41} = H_{23} = H_{32} = H_{24} = H_{42} = H_{34} = H_{43} = 0$$

2- With $m = m'$ and $l = l'$, one finds

$$I_{\theta} = \int_0^{\pi} P_{lm}(\cos\theta) \cos\theta P_{lm}(\cos\theta) \sin\theta d\theta = \int_{-1}^1 |P_{lm}(x)|^2 x dx = 0, \quad x = \cos\theta$$

The term $|P_{lm}|^2$ is even function of x , and hence the integrand is odd, which implies that

$$\langle 1\pm 1 | \hat{H}_p | 1\pm 1 \rangle = 0.$$

It turns out

$$H_{11} = H_{22} = H_{33} = H_{44} = 0$$

3- In conclusion, the only matrix elements which are non zero are: $\langle 0,0 | \hat{H}_p | 1,0 \rangle$ and $\langle 1,0 | \hat{H}_p | 0,0 \rangle$

$$\begin{aligned} \Delta = H_{12} = H_{21} &= \langle 1,0 | \hat{H}_p | 0,0 \rangle = e |E| \langle 1,0 | r \cos\theta | 0,0 \rangle \\ &= \frac{e |E| Z^3}{16\pi a_o^3} \underbrace{\int_0^{\infty} dr r^3 \left(\frac{Zr}{a_o}\right) \left(1 - \frac{Zr}{2a_o}\right) e^{-Zr/a_o}}_{\frac{36a_o^4}{Z^4}} \underbrace{\int_0^{\pi} \sin\theta \cos^2\theta d\theta}_{2/3} \underbrace{\int_0^{2\pi} d\varphi}_{2\pi} = -3a_o e |E| / Z \end{aligned}$$

Thus, the matrix representation of the perturbation for this set of degenerate states is

$$\begin{pmatrix} -\epsilon_1 & \Delta & 0 & 0 \\ \Delta & -\epsilon_1 & 0 & 0 \\ 0 & 0 & -\epsilon_1 & 0 \\ 0 & 0 & 0 & -\epsilon_1 \end{pmatrix}$$

In this case the first order corrections to the energy of the states are

$$-3ea_o |E| / Z, \quad 3ea_o |E| / Z, \quad 0, \quad 0$$

The shifts in energy calculated above are observed in experiments and are called the linear Stark shifts. The set of unperturbed states we require are

$$\psi_- = \frac{1}{\sqrt{2}}(\psi_{2,0,0} + \psi_{2,1,0}), \quad \psi_+ = \frac{1}{\sqrt{2}}(\psi_{2,0,0} - \psi_{2,1,0}), \quad \psi_{2,1,1} \text{ and } \psi_{2,1,-1}$$

H.W. Are the functions $\psi_{\pm} = \frac{1}{\sqrt{2}}(\psi_{2,0,0} \pm \psi_{2,1,0})$ eigen function of the operator \hat{L}^2 ? \hat{L}_z ?

Thus

- 1- Stark linear phenomenon depends mainly on the splitting of different levels as a result of the impact of the external electric field. This splitting resulted from the special character of the Coulombic potential, and therefore, it applies only to the hydrogen atom.
- 2- Levels split will not become an eigenfunction of the operator \hat{L}^2 (or the parity operator), but still functions of \hat{L}_z . This means that the simple perturbation has changed the form of Hamiltonian so that it is non-commute with \hat{L}^2 . This is a result of that the electric field takes certain direction (in the direction z-axis presumably) and thus the system will not be the symmetric with any optional rotation, but will remain the same as rotation around the z-axis only and therefore \hat{L}_z will remain commute with total Hamiltonian.
- 3- The H-atom in its first excited state behaves as though it has a permanent electric dipole moment $3a_0e/Z$ that can be oriented in three different ways as in the following figure. It then follows that the three energy states correspond to parallel, antiparallel, and transverse orientations of this dipole with respect to the electric field.
- 4- As shown in the figure, the states with $m_l = \pm 1$ remain degenerate and so, degeneracy is partially lifted.

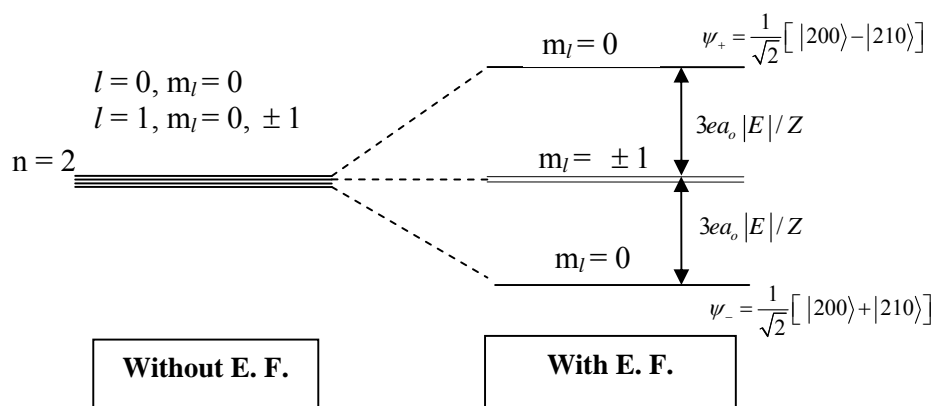


Figure: Stark effect (splitting of the n = 2 level) in H-atom. E is the field strength of the applied electric field.

In Summary: Due to Stark effect the total Hamiltonian is no longer invariant under rotation except around the field direction, i.e. z-axis. ℓ is not a good quantum number. In the field, eigenfunctions of the atom are generally combinations (mixing) of the field free functions. The dipole matrix elements connected different states appears as combinations of matrix elements of field free states, same for life time.

Amount of mixing depends on:

- 1- The strength of the field perturbation. High electric field will produce ionization.
- 2- The energy separation of the field free states.

- I- For perfectly degenerate states, the slightest electric field would produce a complete mixing.

- II- In Hydrogen atoms, all substates (of given Q. N. n) are almost degenerate. They are separated only by fine structure and Lamb-shifts factors, but both factors decreases when n increases.
- III- Vanishingly small fields are able to produce considerable mixing in Hydrogen Rydberg states (with high value of n).
- IV- In atoms with several electrons, the absence of degeneracy strongly reduced the mixing.

Quenching of the 2s-state

Since ℓ is not a good quantum number in the presence of an external electric field, it is clear that the selection rules concerning ℓ must be modified. In particular, because the operator $\hat{H}_p = eE \sum x_i$ has a non-vanishing matrix element between the 2s and 2P₀ states, these two states are ‘mixed’ by the perturbation \hat{H}_p with the result that the metastable 2s state is ‘contaminated’ by the unstable 2p state. Thus a radiative transition from the 2s state to the 1s state can be induced by an external electric field, so that the lifetime of the 2s state shortened by comparison with its value in the absence of an electric field.

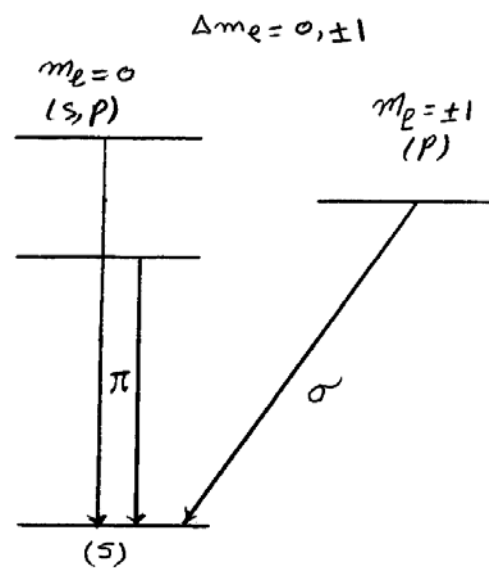


Figure Splitting of the n = 2 level of atomic hydrogen due to the linear Stark effect. The various possible transitions are shown; those with $\Delta m_\ell = 0$ corresponding π lines and those with $\Delta m_\ell = \pm 1$ to σ lines.

The $\Delta m_\ell = 0$ transitions are said to correspond to π components, and the $\Delta m_\ell = \pm 1$ to σ components.

Let us assume that as a result of some excitation process the atom at the initial time $t = 0$ is in the state ψ_{s0} . For $t > 0$ the time-dependent wave function of the atom in an electric field $\mathcal{E}(t)$ can be written in the form of a linear combination of the wave functions of the stationary states $n_1 = 1, n_2 = 0, m = 0$ and $n_1 = 0, n_2 = 1, m = 0$

$$\Psi(t) = A\psi_{100} e^{-i(E_0+\Delta)t/\hbar} + B\psi_{010} e^{-i(E_0-\Delta)t/\hbar}, \quad (7.42)$$

where, in accordance with (7.36), $\Delta = 3ea_0 \mathcal{E}$.

The coefficients A and B are found from the initial condition: when $t = 0$, $\Psi(0) = \psi_{s0}$. Substituting (7.41) in (7.42), we have

$$\begin{aligned} \Psi(t) &= \frac{1}{\sqrt{2}} \psi_{100} e^{-i(E_0+\Delta)t/\hbar} + \frac{1}{\sqrt{2}} \psi_{010} e^{-i(E_0-\Delta)t/\hbar} \\ &= \left[\psi_{s0} \cos \frac{\Delta}{\hbar} t + \psi_{p0} i \sin \frac{\Delta}{\hbar} t \right] e^{-iE_0 t/\hbar}. \end{aligned} \quad (7.43)$$

It follows from (7.43) that the orbital angular momentum of an electron is not conserved in an electric field. The atom oscillates between the states ψ_{s0} and ψ_{p0} with a period $T = \pi\hbar/\Delta$. Let us estimate the magnitude of this period. When $\mathcal{E} \sim 300 \text{ V cm}^{-1}$, $\Delta/\hbar \sim 7.5 \times 10^8$. Consequently, even in such a weak field the period of oscillation between the states $2s_0$ and $2p_0$ is of the same order as the time τ necessary for the radiative transition $2p \rightarrow 1s$.

An electric field applied to the atom in the state $2s$ can induce a radiative transition to the state $1s$. The probability of this transition for $E \sim 300 \text{ V cm}^{-1}$ is approximately equal to the probability of the allowed transition $2p \rightarrow 1s$.

In a strong electric field, when $T \ll \tau$, during the whole time of decay the states $2s_0$ and $2p_0$ are populated roughly equally (independent of which state the atom was in at the initial moment $t = 0$). Therefore, the probabilities of radiative transitions $2s \rightarrow 1s$, $2p \rightarrow 1s$ in the presence of a strong electric field are the same. It is obvious that an electric field also violates the restrictions on other $n_s \rightarrow n_s$ transitions.

H.W. Do the linear Stark effect for the $n=3$ level and show all the transition lines in the case of $n=3$ to $n=2$.

Discussion of Stark Effect in Ground State Hydrogen

First, let's look at the size of this perturbation to the potential energy. Taking the radius of the ground state atom to be the Bohr radius, the Coulomb potential energy is

$$-\frac{ke^2}{r} = -\frac{(9 \times 10^9 \text{ Nm}^2 / \text{C}^2)(1.6 \times 10^{-19} \text{ C})^2}{(0.53 \times 10^{-10} \text{ m})} = -4.35 \times 10^{-18} \text{ J} = \underline{\underline{-27.2 \text{ eV}}}$$

(Do you remember that you showed that the potential energy is twice the total energy for a $1/r^2$ force? This is the "virial theorem".) Let's pick a realistic electric field size of 10000 V/m. This could be produced easily in the lab by applying a voltage difference of 100 V across a set of parallel plates separated by 1 cm. With this value for the field, the maximum potential energy of the electron would be

$$e\epsilon r = (1.6 \times 10^{-19} \text{ C})(10000 \text{ V / m})(0.53 \times 10^{-10} \text{ m}) = 8.48 \times 10^{-26} \text{ J} \approx \underline{\underline{5 \times 10^{-7} \text{ eV}}}$$

This is approximately 50 million times smaller than the Coulomb potential energy! This is indeed a small perturbation, perhaps so small that the perturbation is negligible? We will see.

A quick calculation shows that if the potential energy due to the field is to be comparable to the Coulomb potential energy, then the field has to be on the order of 500 *billion* Volts per meter ($5 \times 10^{11} \text{ V/m}$)! Thus, we can say with some confidence that any electric field we can apply to the atom can be treated as a perturbation.

You will show in Problem [6.3] that the first order correction to the ground state energy is zero. This tells us that the perturbation to the energy is going to be small. You will show in Problem [6.4] that the second order correction is

$$\epsilon_2 = -1.68 \frac{a_o^3 \epsilon^2}{k}$$

Note that the electric field lowers the energy of the electron since ϵ_2 is negative and the unperturbed energy is also negative (-13.6 eV). Also note that the second order correction to the energy depends on the square of the field as we expect (since the Hamiltonian perturbation depends linearly on the field size).

Taking our field value of 10000 V/m from above, the energy is lowered by

$$|\epsilon_2| = 1.68 \frac{(0.53 \times 10^{-10} \text{ m})^3 (10000 \text{ V / m})^2}{9 \times 10^9 \text{ Nm}^2 / \text{C}^2} = 2.8 \times 10^{-33} \text{ J} \approx \underline{\underline{1.7 \times 10^{-14} \text{ eV}}}$$

This shift is undetectable! What kind of shift is detectable? Recall that the spin-orbit interaction produced an energy shift on the order of 10^{-4} eV . This is detectable using optical spectroscopy and measuring the transition wavelengths between shifted energy levels. The wavelength of a photon emitted in a transition is given by

$$\lambda = hc/E$$

where E is the transition energy. Differentiating both sides of this equation will tell us how a perturbation to the energy affects the wavelength:

$$d\lambda = \frac{-hc}{E^2} dE$$

For example, if the atom makes a transition from the $n=2$ state ($E_2 = -3.4 \text{ eV}$) to the ground state ($E_1 = -13.6 \text{ eV}$), the transition energy in the absence of any perturbations is 10.2 eV. If the transition energy is lowered by 10^{-4} eV , then the transition wavelength increases by

$$d\lambda = \frac{-12400 \text{ eV}\text{\AA}}{(10.2 \text{ eV})^2} (-10^{-4} \text{ eV}) \approx 0.01 \text{ \AA}$$

This is about the limit of resolution in spectroscopy so that energy shifts smaller than 10^{-4} eV are just too small to detect.

Suppose we did just want to see the perturbation due to the Stark effect. Solving (6.47) for the electric field necessary to give a second order correction of $\epsilon_2 = -10^{-4}$ eV = -1.6×10^{-23} J gives

$$\epsilon = \left[\frac{k \epsilon_2}{-1.68 a_o^3} \right]^{1/2} = \left[\frac{(9 \times 10^9 \text{ Nm}^2 / \text{C}^2)(-1.6 \times 10^{-23} \text{ J})}{-1.68(0.53 \times 10^{-10} \text{ m})^3} \right]^{1/2} \approx \underline{8 \times 10^8 \text{ V/m}}$$

This is an extremely large field! (Air experiences dielectric breakdown at about 3×10^6 V/m.) Wouldn't this extremely large field exert a tremendous force on the electron and actually ionize the atom (i.e. strip the electron from the proton)? No! This electric field would exert a force of

$$F_e = e\epsilon = (1.6 \times 10^{-19} \text{ C})(8 \times 10^8 \text{ N/C}) = \underline{1.3 \times 10^{-10} \text{ N}}$$

on the electron. The Coulomb force holding the electron to the proton is

$$F_C = \frac{ke^2}{a_o^2} = \frac{(9 \times 10^9 \text{ Nm}^2 / \text{C}^2)(1.6 \times 10^{-19} \text{ C})^2}{(0.53 \times 10^{-10} \text{ m})^2} = \underline{8.2 \times 10^{-8} \text{ N}}$$

The Coulomb force is approximately 600 times stronger than the electric force, even with this extremely large field. The atom will not ionize!

What can we say in summary about the Stark effect in ground state Hydrogen? The effect is extremely small. For it to be easily detected requires extremely large fields on the order of hundreds of millions of Volts per meter.

A final note of interest should be made between magnetic field effects and electric field effects on the Hydrogen atom. Recall that magnetic field effects are readily observable. The spin-orbit interaction produces a detectable energy splitting with an internal magnetic field produced by the orbiting electron that is approximately 1 Tesla. An external field that is comparable to this or greater can produce larger energy shifts.

Why is the atom so sensitive to magnetic fields but not so sensitive to electric fields when it comes to energy perturbations? Is it because the magnetic forces are typically much larger than the electric forces? Consider the relative sizes of the electric and magnetic forces exerted by the fields. The electric force depends only on the product of charge and the electric field. The magnetic force depends on the product of charge, magnetic field, *and* the speed of the electron. In the ground state, the average speed of the electron is $\sim 2.2 \times 10^6$ m/s. For a magnetic field of $B = 1$ T, the magnetic force is on the order of

$$F_M = evB = (1.6 \times 10^{-19} \text{ C})(2.2 \times 10^6 \text{ m/s})(1\text{T}) \approx \underline{3.5 \times 10^{-13} \text{ N}}$$

This is roughly 370 times *smaller* than the electric force required to produce an energy shift comparable to the shift produced by the magnetic field. (Compare this force to the 1.3×10^{-10} N we calculated above.) So the answer isn't the size of the forces involved. Then what does cause this difference?

The answer is electron spin! The magnetic field interacts with the electron spin to produce these energy shifts. Recall that we found the energy shifts by modeling the electron spinning on its axis as producing a magnetic dipole moment which interacts with the magnetic field. The electric field has no interaction with the spin of the electron. Thus, the electric field's effect on energy is much less noticeable.

Hydrogen Atom Ground State in a E-field, the Stark Effect.

We have solved the Hydrogen problem with the following Hamiltonian.

$$H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{r}$$

Now we want to find the correction to that solution if an **Electric field is applied to the atom**. We choose the axes so that the Electric field is in the z direction. The **perturbation** is then.

$$\hat{H}_p = -eEr \cos \theta = -eE z$$

It is typically a small perturbation. **For non-degenerate states**, the first order correction to the energy is zero because the expectation value of z is an odd function.

$$\begin{aligned} \epsilon_1 = E_{1,0,0}^{(1)} &= \int \psi_{1,0,0}^* \hat{H}_p \psi_{1,0,0} d\tau = e |E| \langle 1,0,0 | z | 1,0,0 \rangle \\ &= e |E| \int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi_{1s}|^2 r^3 \cos \theta \sin \theta dr d\theta d\phi \\ &= 0 \end{aligned}$$

We therefore need to calculate the **second order correction**. This involves a sum over all the other states.

$$\epsilon_2 = e^2 |E|^2 \sum_{n\ell m \neq 1,0,0} \frac{|\langle n, \ell, m | r \cos \theta | 1,0,0 \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

We need to compute all the matrix elements of z between the ground state and the other Hydrogen states.

$$\langle n, \ell, m | r \cos \theta | 1,0,0 \rangle = \int R_{n\ell}^* Y_{\ell m}^* (r \cos \theta) R_{10} Y_{00} d\tau$$

We can do the angular integral by converting the $\cos \theta$ term into a spherical harmonic.

$$Y_{00} \cos \theta = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}} Y_{10} = \frac{1}{\sqrt{3}} Y_{10}$$

Then we can just use the orthonormality of the spherical harmonics to do the angular integral, leaving us with a radial integral to do.

$$\langle n, \ell, m | r \cos \theta | 1,0,0 \rangle = \frac{1}{\sqrt{3}} \int_0^\infty r^3 dr \underbrace{R_{n\ell}^* R_{10}}_{a_0 \sqrt{\frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}}}} \underbrace{\int Y_{\ell m}^* Y_{10} d\Omega}_{\delta_{\ell,1} \delta_{m,0}}$$

The radial part of the integral can be done with some work, yielding.

$$|\langle n, \ell, m | r \cos \theta | 1,0,0 \rangle|^2 = \frac{1}{3} \frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}} a_0^2 \equiv f(n) a_0^2$$

We put this back into the sum. The Kronecker deltas eliminate the sums over ℓ and m . We write the energy denominators in terms of the Bohr radius.

$$\begin{aligned} \epsilon_2 &= e^2 |\mathbf{E}|^2 \sum_{n=2} \frac{f(n)a_o^2}{-\frac{e^2}{2a_o} + \frac{e^2}{2a_o n^2}} = -2a_o^3 |\mathbf{E}|^2 \sum_{n=2} \frac{f(n)n^2}{n^2 - 1} \\ &= -2a_o^3 |\mathbf{E}|^2 (0.74 + 0.10 + \dots) \\ &\approx -2(0.93)a_o^3 |\mathbf{E}|^2 \end{aligned}$$

The first two terms of the sum get us pretty close to the right answer. We could have just done those radial integrals.

Now we compute d , the **electric dipole moment** of the atom which is induced by the electric field.

$$d = -\frac{\partial \epsilon_2}{\partial |\mathbf{E}|} = 4(0.93)a_o^3 |\mathbf{E}| = \alpha |\mathbf{E}|$$

α is the polarizability. The dipole moment is proportional to the Electric field, indicating that it is induced. The E field induces the dipole moment, then the dipole moment interacts with the E field causing a energy shift. This indicates why the energy shift is second order.

$$\alpha = 4(0.93)a_o^3 = 3.72a_o^3$$

The exact is

$$\alpha_{exact} = 4.5a_o^3$$