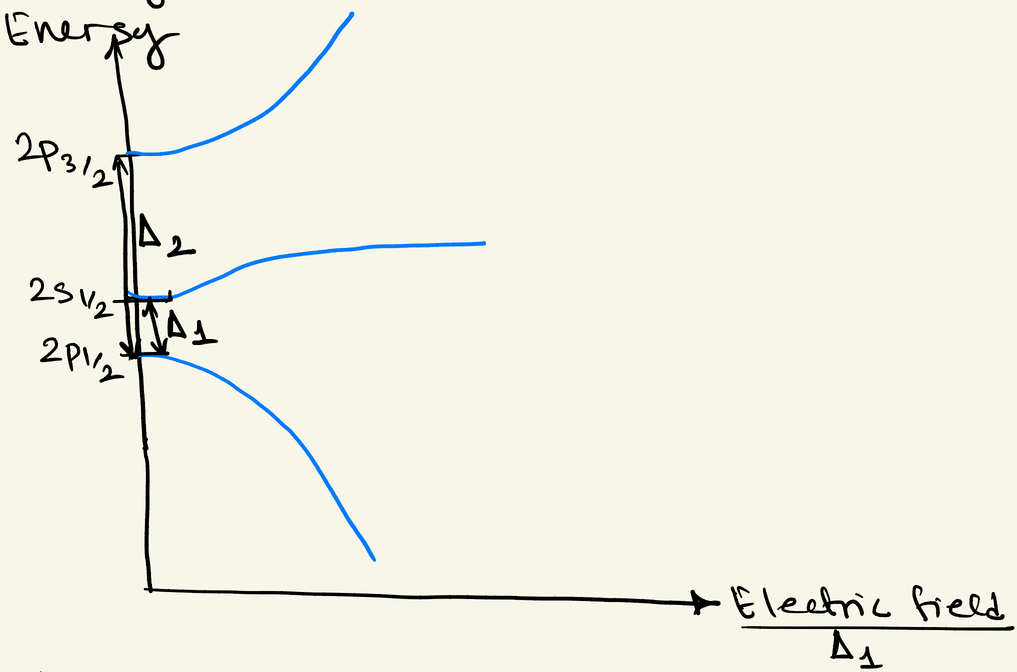
Perturbing Hydrogen atom by Electric field
(Stark effect)

Schematic sketch of the main result
(see fig 5.3 in Gottfried-Yan):



One take-away from this figure is that
when Electric field $\ll$ Δ_1 $(= E_0(2s_{1/2}) - E_0(2p_{1/2}))$,
then the energy shift due to the
electric field is quadratic in the electric
field for both $2s_{1/2}$ and $2p_{1/2}$.

In contrast, when Electric field $\gg \Delta_1$, the energy shift is approximately linear in the electric field.

Similarly, when electric field $\ll \Delta_2$ $(= E_0(2p_{3/2}) - E_0(2p_{1/2}))$, the energy shift of the $2p_{3/2}$ level is approximately quadratic in the electric field while when electric field $\gg \Delta_2$, it is approximately linear. Since $\Delta_2 \gg \Delta_1$, the shift of $2p_{3/2}$ is approximately quadratic over a bigger range of the electric field compared to that for the $2p_{1/2}$ and $2s_{1/2}$.

Let us derive the above trends using perturbation theory.

As a warm-up, let us first ignore the fine-structure effects completely, so that the Hamiltonian is:

$$H = \underbrace{\frac{p^2}{2m} - \frac{e^2}{r}}_{\text{Unperturbed Hamiltonian}} + \underbrace{e \mathcal{E} z}_{\text{perturbation}}$$

where $\mathcal{E}$ denotes the strength of the electric field and we have assumed that it points along the z-direction.

The first thing to notice is that $[\hat{\sigma}_z, H] = 0$ and therefore the spin-degeneracy can not be lifted by the electric field $\Rightarrow$ The energy shift for $\sigma_z = 1/2$ level will be identical to that for the $\sigma_z = -\frac{1}{2}$ level. Therefore, in the following, the internal spin will play no role.

The unperturbed levels for $n=1$ and $n=2$ principal quantum numbers are:

$$|n=2 \;\; l=0 \;\; m_l=0\rangle \otimes |\sigma_z=\pm\tfrac{1}{2}\rangle \qquad |n=2 \;\; l=1 \;\; m_l=0\rangle \otimes |\sigma_z=\pm\tfrac{1}{2}\rangle \qquad |n=2 \;\; l=1 \;\; m_l=1\rangle \otimes |\sigma_z=\pm\tfrac{1}{2}\rangle \qquad |n=2 \;\; l=1 \;\; m_l=-1\rangle \otimes |\sigma_z=\pm\tfrac{1}{2}\rangle$$

$$|n=1 \;\; l=0 \;\; m=0\rangle \otimes |\sigma_z=\pm\tfrac{1}{2}\rangle$$

Where m_l denotes $\hat{L}_z$ eigenvalue and σ_z denotes $\hat{\sigma}_z$ eigenvalue. The double lines $=$ denote the degeneracy associated with σ_z. Ofcourse, the unperturbed eigenvalues depend only on 'n' (recall that we are neglecting the fine-structure currently), and therefore, all eight levels with $n=2$ are degenerate.

Relevant selection rules:

Since the perturbation $= e\mathcal{E}\hat{z}$, we will need to calculate matrix elements of the form

$$\mathcal{M} = \langle n, l, l_z, \sigma_z | \hat{z} | n', l', l'_z, \sigma'_z \rangle .$$

Symmetries / conservation laws impose several constraints on this matrix element:

(i) Since $\hat{z}$ acts only in the real space and not on the internal spin (i.e. $\hat{z} = \hat{z} \otimes \mathbb{1}_s$), $\mathcal{M} = 0$ unless $\sigma_z = \sigma'_z$.

(ii) Under parity transformation, $\hat{z} \to -\hat{z}$, i.e. $P^\dagger \hat{z} P = -\hat{z}$ where $\hat{P}$ is the unitary operator that implements the parity symmetry. Further, as discussed previously, $\hat{P} |n, l, l_z, \sigma_z\rangle = (-)^l |n, l, l_z, \sigma_z\rangle$

$\Rightarrow \mathcal{M} = 0$ unless $|l - l'| = 1 \mod 2$, i.e. l and l' must have different parity for $\mathcal{M}$ to be non-zero.

for example, an s-orbital (i.e. $l=0$) can mix with a p-orbital ($l=1$) but not with a d-orbital ($l=2$).

(iii) $\hat{z}$ is the $l=0$ component of the vector operator $\vec{r}$ (recall a vector operator $\vec{V}=(V_x, V_y, V_z)$ satisfies $[V_i, J_j] = i\varepsilon_{ijk}\hat{V}_k$, and one can define $\hat{V}_0 = \hat{V}_z$, $\hat{V}_{\pm 1} = \mp\frac{(V_x \pm iV_y)}{\sqrt{2}}$, which satisfy $[\hat{J}_z, \hat{V}_m] = m\hat{V}_m$). Based on our discussion of tensor operators and Wigner-Eckart theorem, $\hat{z}|n, l, l_z, \sigma_z\rangle$ transforms in the same way as $|l=1, l_z=0\rangle \otimes |n, l, l_z, \sigma_z\rangle$. Therefore, using angular momentum addition rules, the state $\hat{z}|n, l, l_z, \sigma_z\rangle$ can only have orbital angular momentum

$l' = l+1$, l or $l-1$. Further, $l'_z = l_z$.

Thus, the above matrix element $\mathcal{M} = 0$ unless, $l' = l+1$, l or $l-1$ and $l'_z = 0$.

Let's start with the effect of electric field on the states $|n=1, l=0, l_z=0, \sigma_z\rangle$. Based on the selection rules just discussed, this state can only mix with $|n', l'=1, l'_z=0, \sigma_z\rangle$. Since $l' < n'$ (there is no 1p orbital), the state closest in energy that can mix with $|n=1, l=0, l_z=0, \sigma_z\rangle$ is $|n'=2, l'=1, l'_z=0, \sigma_z\rangle$.

Perturbatively, the energy shift is then given by :

$$\Delta E\,(n=1,\, l=0,\, l_z=0,\, \sigma_z)$$

$$= e\,\mathcal{E}\, \cancelto{0}{\langle n=1, l=0, l_z=0, \sigma_z |\, \hat{z}\, | n=1, l=0, l_z=0, \sigma_z \rangle}$$

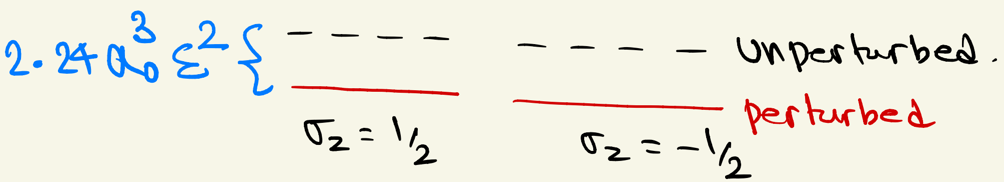
$$+ (e\mathcal{E})^2 \sum_{n'>0} \frac{\left| \langle n=1, l=0, l_z=0, \sigma_z |\, \hat{z}\, | n', l=1, l_z=0, \sigma_z \rangle \right|^2}{(E_{n=0} - E_{n'})}$$

This is an infinite series which can be summed numerically (approximately) or even exactly using the exact form of the hydrogen's wfns. However, as far as qualitative features are concerned, the main outcome is that $\Delta E = -c\, e^2 \mathcal{E}^2$ where $c \approx \dfrac{a_0^2}{e^2/a_0}$ where a_0 is the radius of the Hydrogen atom.

$$\Rightarrow \quad \Delta E \approx -\, \mathcal{E}^2 a_0^3 .$$

Due to the quadratic dependence on the electric field $\mathcal{E}$, this is called 'quadratic Stark effect' (named after its discoverer). The exact prefactor can be found and $\Delta E \simeq 2.24\, \mathcal{E}^2 a_0^3$.

Note that the energy shift does not depend on σ_z (z-component of the intrinsic spin), and therefore the levels look like:



Polarizability:

Polarizability α is defined as

$$\vec{\mu} = \alpha \vec{\mathcal{E}} \quad \text{where} \quad \vec{\mu}$$

is the induced dipole moment due to the applied field $\vec{\mathcal{E}}$.

Energy stored in the dipole moment $= \int_0^{\mathcal{E}} \mu(\mathcal{E})\, d\mathcal{E} = \frac{\alpha \mathcal{E}^2}{2}$

Equating this to ΔE calculated above, $\Rightarrow \alpha \sim a_0^3$.

Next, we consider the energy shift of the $n=2$ levels due to the electric field. Recall that unperturbed levels are:

$$\overline{\overline{\quad\quad}}\ |n=2\ l=0\ m_l=0\rangle \otimes |\sigma_z = \pm\tfrac{1}{2}\rangle \quad \overline{\overline{\quad\quad}}\ |n=2\ l=1\ m_l=0\rangle \otimes |\sigma_z = \pm\tfrac{1}{2}\rangle \quad \overline{\overline{\quad\quad}}\ |n=2\ l=1\ m_l=1\rangle \otimes |\sigma_z = \pm\tfrac{1}{2}\rangle \quad \overline{\overline{\quad\quad}}\ |n=2\ l=1\ m_l=-1\rangle \otimes |\sigma_z = \pm\tfrac{1}{2}\rangle$$

$$\overline{\overline{\quad\quad}}\ |n=1\ l=0\ m=0\rangle \otimes |\sigma_z = \pm\tfrac{1}{2}\rangle$$

Recall that the effective Hamiltonian for a given set of degenerate states is

$$\langle \alpha | H_{eff} | \beta \rangle = e\mathcal{E} \langle \alpha | \hat{z} | \beta \rangle + e^2 \mathcal{E}^2 \sum_{\mu \notin D} \frac{\langle \alpha | \hat{z} | \mu \rangle \langle \mu | \hat{z} | \beta \rangle}{\bar{E}_D - E_\mu} + \ldots$$

As just discussed, for $n=1$ levels, the only non-zero matrix elements were with states outside the degenerate subspace. Based on the selection rules discussed above, the same holds true for $|n=2, l=1, m_l = \pm 1, \sigma_z\rangle$, since there are no states with identical σ_z and m_l while having a different parity of l within the degenerate manifold. Therefore, the states $|n=2, l=1, m_l = \pm 1, \sigma_z\rangle$ will also experience a quadratic Stark effect after mixing with states of higher energy (e.g. $|n=3, l=2, m_l=\pm 1, \sigma_z\rangle$).

Therefore, $\Delta E(n=2, l=1, m_l=\pm 1, \sigma_z)$
$\approx -a_0^3 \mathcal{E}^2$.

In contrast, the states $|n=2, l=0, m_l=0, \sigma_z\rangle$ and $|n=2, l=1, m_l=0, \sigma_z\rangle$ will mix.

These states lie within the degenerate manifold and therefore the corresponding effective Hamiltonian is:

$$H_{eff} = \begin{bmatrix} 0 & e\mathcal{E}\langle n=2, l=0, m_l=0|\hat{z}|n=2, l=1, m_l=0\rangle \\ e\mathcal{E}\langle n=2, l=1, m_l=0|\hat{z}|n=2, l=0, m_l=0\rangle & 0 \end{bmatrix}$$

$$+ \; O(\mathcal{E}^2).$$

Denoting the non-zero matrix element $|\langle n=2, l=1, m_l=0|\hat{z}|n=2, l=0, m_l=0\rangle|$ as c (it turns out $c=3$), the energy shift is

$\Delta E = \pm c e \mathcal{E}$, i.e. the perturbed energy eigenvalues are

$E_1 = E^0_{n=2} - c e \mathcal{E}$ and

$E_2 = E^0_{n=2} + c e \mathcal{E}$, where $E^0_n = \frac{-13.6 eV}{n^2}$

are the unperturbed levels (again recall that we are neglecting the fine-structure in this section). The corresponding perturbed eigenvectors are

$$\frac{1}{\sqrt{2}}\left[|n=2, l=0, m_l=0, \sigma_z\rangle + |n=2, l=1, m_l=0, \sigma_z\rangle\right]$$

and

$$\frac{1}{\sqrt{2}}\left[|n=2, l=0, m_l=0, \sigma_z\rangle - |n=2, l=1, m_l=0, \sigma_z\rangle\right]$$

respectively.

Stark effect with fine structure

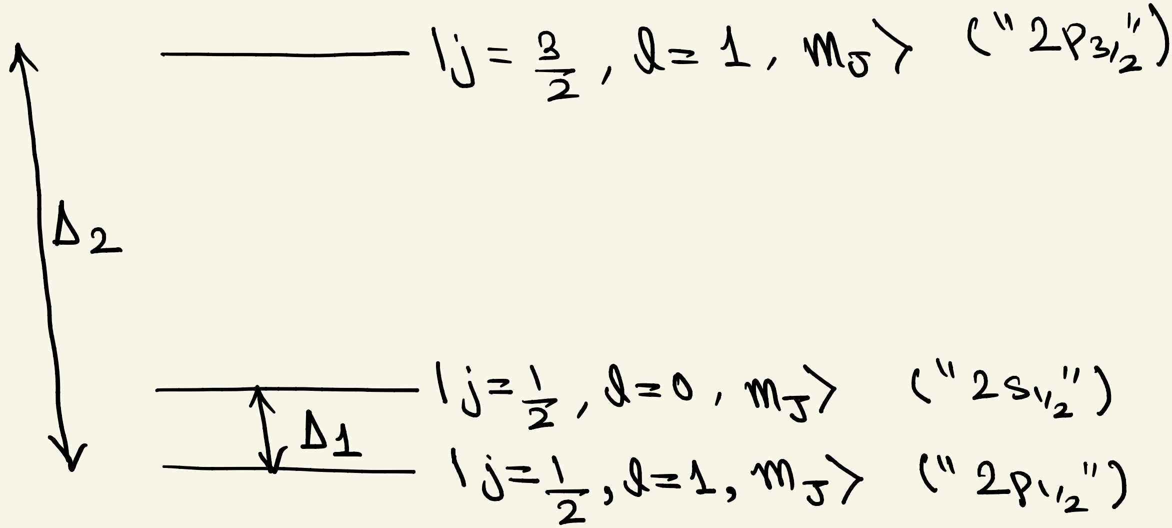
Above we neglected the fine-structure ($\sim \alpha^4$). Now let's consider the electric field perturbation while taking them into account. That is, we consider,

$$H = \frac{p^2}{2m} - \frac{e^2}{r} + H_{fs} + e\mathcal{E}z$$

where H_{fs} denote the correction to the non-relativistic Hamiltonian due to $O(\alpha^4)$ relativistic effects. We will assume that $e\mathcal{E}a_0$ is much smaller than $\frac{e^2}{a_0}$, so that only levels with same principal q. number 'n' can mix.

Since for $n=1$, $\vec{L}=0 \Rightarrow$ the discussion is unchanged and there is no linear stark effect as discussed above.

For $n=2$, the unperturbed levels are



where $\Delta_2 \sim \alpha^2 \dfrac{e^2}{a_0}$ and $\Delta_1 \sim \alpha^3 \dfrac{e^2}{a_0}$

("Lamb shift") i.e. $\Delta_1 \ll \Delta_2$.

Since $\hat{z}\,|j, l, m_J\rangle$ transforms as

$|l=1, m_l=0\rangle \otimes |j, l, m_J\rangle$, for the

matrix element $\langle j', l', m_J' | \hat{z} | j, l, m_J\rangle$

to be non-zero, one now requires

$|j-j'| = 0$ or 1 and $m_J = m_J'$.

Since there is a unique state with $m_J = \frac{3}{2}$, or $m_J = -\frac{3}{2}$, namely the states $|j=\frac{3}{2}, l=1, m_J = \pm\frac{3}{2}\rangle$, these states do not mix with any state within the $n=2$ multiplet, and therefore the corresponding energy shift must be atleast quadratic in $\mathcal{E}$. Since we are assuming $e\mathcal{E}a_0 \ll \frac{e^2}{a_0}$ we will ignore such shifts and focus on shifts for only those states that have non-zero matrix elements with any other states in the $n=2$ multiplet.

There is no symmetry that prohibits the mixing of $2p_{1/2}$ with $2s_{1/2}$, or the mixing of $2s_{1/2}$ with $2p_{3/2}$, and therefore the effective Hamiltonian for these states is the 3x3 matrix:

$$
H_{eff} = \begin{array}{ccc}
|2p_{1/2}\rangle = & |2s_{1/2}\rangle = & |2p_{3/2}\rangle = \\
|j=\tfrac{1}{2}, l=1, m_J\rangle & |j=\tfrac{1}{2}, l=0, m_J\rangle & |j=\tfrac{3}{2}, l=1, m_J\rangle
\end{array}
$$

$$
\begin{bmatrix}
0 & c_1 \mathcal{E} e & 0 \\
c_1^* e \mathcal{E} & \Delta_1 & e \mathcal{E} c_2 \\
0 & c_2^* e \mathcal{E} & \Delta_2
\end{bmatrix}
$$

where we have denoted the non-zero matrix elements by some complex numbers. These can be calculated and one finds $c_1 = \sqrt{3}$ and $c_2 = -\sqrt{6}$, but we don't need these values for our qualitative discussion. Since the electric field does not break the time-reversal symmetry, c_1, c_2 are gaurranteed to be real numbers.

Although the above 3x3 matrix can be diagonalized exactly, it is more illuminating to consider various limits so that the problem simplifies.

First consider, $e\mathcal{E}a_0 \ll \Delta_1$. In this limit, $2s_{1/2}$ and $2p_{1/2}$ are not nearly degenerate (since $\frac{\langle\alpha|H_1|\beta\rangle}{E_\alpha - E_\beta} \ll 1$), and therefore one can simply use non-degenerate perturbation theory to conclude $\Delta E_{2P_{1/2}} \simeq \dfrac{c_1^2 e^2 \mathcal{E}^2}{\Delta_1}$

and $\Delta E_{2S_{1/2}} \simeq -\dfrac{c_1^2 e^2 \mathcal{E}^2}{\Delta_1}$ i.e. these levels experience quadratic Stark effect when $e\mathcal{E}a_0 \ll \Delta_1$, consistent with fig. 5.3 in Gottfried-Yan.

Ofcourse, the level $2P_{3/2}$ also experience quadratic Stark effect with

$\Delta E_{2P_{3/2}} \simeq \dfrac{c_2^2 e^2 \mathcal{E}^2}{\Delta_2}$ (recall $\Delta_2 \gg \Delta_1$).

Next consider the limit $e\mathcal{E}a_0 \gg \Delta_1$ but $e\mathcal{E}a_0 \ll \Delta_2$. In this limit, the levels $2S_{1/2}$ and $2P_{1/2}$ are approximately degenerate while the level $2p_{3/2}$ is not degenerate with these levels. Therefore, the effective Hamiltonian within the subspace $|2s_{1/2}\rangle$, $|2p_{1/2}\rangle$ is

$$\begin{bmatrix} \bar{E}_D & c_1 \mathcal{E} e \\ c_1 \mathcal{E} e & \bar{E}_D \end{bmatrix} \quad \text{where } \bar{E}_D \simeq \frac{\Delta_1}{2} \simeq 0.$$

The eigenvalues and eigenvectors are therefore $\bar{E}_D \pm |c_1| \mathcal{E} e$,

$|2s_{1/2}\rangle \mp |2p_{1/2}\rangle$. Therefore, in this limit, the energy shift for these two levels is linear in $\mathcal{E}$.

In contrast, the level $2p_{3/2}$ is still not degenerate with these levels (since $e\mathcal{E}a_0 \ll \Delta_2$ by assumption), and therefore $\Delta E_{2p_{3/2}} \approx \dfrac{c_2^2 e^2 \mathcal{E}^2}{\Delta_2}$

as before.

Finally, consider the limit

$-13.6\text{eV} \gg e\mathcal{E}a_0 \gg \Delta_2 \ (\gg \Delta_1)$, so that

all three levels appear nearly degenerate.

One may approximate the effective

Hamiltonian as:

$$\begin{bmatrix} \bar{E}_D & e\mathcal{E}c_1 & 0 \\ e\mathcal{E}c_1 & \bar{E}_D & e\mathcal{E}c_2 \\ 0 & e\mathcal{E}c_2 & \bar{E}_D \end{bmatrix}$$

where $\bar{E}_D = \dfrac{0 + \Delta_1 + \Delta_2}{3} = \dfrac{\Delta_1 + \Delta_2}{3}$.

Diagonalizing this Hamiltonian is easier compared to the original 3x3 matrix written above (where we didn't make the assumption $e\mathcal{E}a_0 \gg \Delta_2$).

The eigenvalues are :

$$E_1 = \bar{E}_D$$

$$E_2 = \bar{E}_D - e\mathcal{E}\sqrt{c_1^2 + c_2^2}$$

$$E_3 = \bar{E}_D + e\mathcal{E}\sqrt{c_1^2 + c_2^2}$$

while the (unnormalized) eigenvectors are :

$$|E_1\rangle = -c_2|2p_{1/2}\rangle + c_1|2p_{3/2}\rangle,$$

$$|E_2\rangle = c_1|2p_{1/2}\rangle - \sqrt{c_1^2+c_2^2}\,|2s_{1/2}\rangle + c_2|2p_{3/2}\rangle,$$

$$|E_3\rangle = c_1|2p_{1/2}\rangle + \sqrt{c_1^2+c_2^2}\,|2s_{1/2}\rangle + c_2|2p_{3/2}\rangle$$

respectively. Therefore $2p_{3/2}$ and $2p_{1/2}$ experience linear Stark effect while $2s_{1/2}$ experiences no Stark effect (again see fig. 5.3 in Gottfried-Yan).