Perturbations of Hydrogen

Reference: Griffiths 7.3-7.5

One of the most natural places to apply perturbation theory is to Hydrogen. You might, at this point, be feeling tired of hydrogen, but there is always more to the story. The spectrum of hydrogen proves to be a wonderful test "lab" for quantum theory.

> "The spectrum of hydrogen has proved to be the Rosetta Stone of modern physics. Once this pattern of lines had been deciphered much else could also be understood."
>
> – Schawlow & Hänsch
> Nobel Laureates.

We've learned to predict the Bohr energies from the Schrödinger equation: $E_n = -\frac{13.6\,\text{eV}}{n^2}$, but there's much more to the story...

if you "zoom in" on the spectrum, you find a surprisingly rich structure

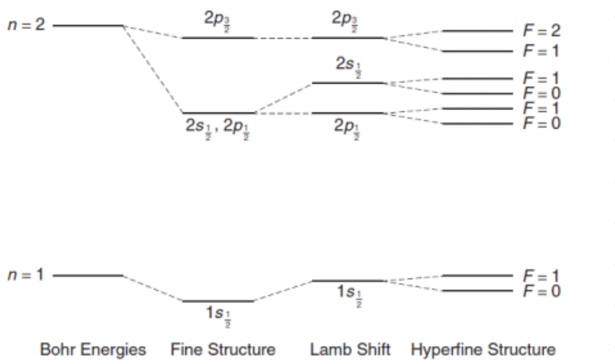

FIGURE 12.2 Corrections to the $n = 1$ and $n = 2$ Bohr energy levels ordered by magnitude (large to small, left to right). The shifts are not drawn to scale and are increasingly magnified from left to right.

Spectroscopic notation:

$n L_J$

$\vec{J} = \vec{L} + \vec{S}_{\text{electron}}$

$\vec{F} = \vec{J} + \vec{S}_{\text{proton}}$

$\ell = 0 \Rightarrow$ "s" ; $\ell = 1 \Rightarrow$ "p" ; $\ell = 2 \Rightarrow$ "d"

So, e.g. the state $2p_{3/2}$ has $n=2, \ell=1, j=\frac{3}{2}$

Perturbations of Hydrogen

There are several kinds of perturbations:

1. "Fine structure" due to internal factors from within a hydrogen atom. We'll discuss a few of these.
2. "Hyperfine structure" due to smaller internal factors. Specifically due to the interaction of the spin of the proton w/ the spin of the electron
3. Lamb Shift - A field theory effect. We won't discuss it, but you should be aware of its existence.
4. External perturbations due to an applied field
   a.) Stark Effect (from an $\vec{E}$ field)
   b.) Zeeman Effect (from a $\vec{B}$ field).

Relativistic Correction - First, let's discuss a relativistic correction this is part of the "fine structure", but it is not the only piece.

The idea is: the electron may be traveling at high enough speeds (whatever that means in QM) for relativity to be important. This should be a small correction as we can estimate as follows:

$$E = \frac{mc^2}{\sqrt{1-v^2/c^2}} \quad \text{Total energy} \quad \gamma \equiv (1-v^2/c^2)^{-1/2}$$

$$K = E - mc^2 = \gamma mc^2 - mc^2 = mc^2(\gamma - 1)$$

$$1 + \frac{K}{mc^2} = \gamma \quad \text{if we estimate } K \sim 10\,\text{eV}$$
$$mc^2 \sim 500000\,\text{eV}$$

$$1 + \frac{1}{50000} = \frac{1}{\sqrt{1-\left(\frac{v}{c}\right)^2}} \approx 1 + \frac{v^2}{2c^2} \Rightarrow \frac{v^2}{c^2} = \frac{2}{50000} \Rightarrow \frac{v}{c} \approx 0.006$$

binomial expansion.

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How could we calculate the effect of relativity on the hydrogen spectrum?

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{ke^2}{\hat{r}}$$

Kinetic term. We should use relativity here!

$$K = mc^2(\gamma - 1)$$ plan: express this in terms of $\hat{p}$!

$$E = K + mc^2 = \sqrt{p^2c^2 + m^2c^4}$$

$$K = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

$$= mc^2\Big[\underbrace{\sqrt{1 + \left(\tfrac{pc}{mc^2}\right)^2} - 1}\Big]$$

expand this, assuming $\frac{pc}{mc^2} << 1$

Binomial expansion: $(1+\varepsilon)^n \approx 1 + n\varepsilon + \frac{n(n-1)}{2}\varepsilon^2 + \ldots$

$n = \frac{1}{2}$, $\varepsilon = (pc/mc^2)^2$

$$K \approx mc^2\left[\cancel{1} + \frac{1}{2}\left(\frac{pc}{mc^2}\right)^2 + \frac{1}{2}\cdot\left(\frac{1}{2}\right)\left(\frac{-1}{2}\right)\left(\frac{pc}{mc^2}\right)^4 + \ldots - \cancel{1}\right]$$

$$\approx mc^2\left[\frac{p^2}{2mc^2} - \frac{1}{8}\frac{p^4}{m^4c^4} + \ldots\right]$$

$$\approx \underbrace{\frac{p^2}{2m}}_{\text{non relativistic}} - \underbrace{\frac{1}{8}\frac{p^4}{m^3c^2}}_{\text{relativistic correction.}} + \ldots$$

So lets add this into our Hamiltonian for Hydrogen.

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$$\hat{H} = \overbrace{\frac{\hat{p}^2}{2m} - \underbrace{\frac{1}{8}\frac{\hat{p}^4}{m^3c^2}}_{\hat{H}^1} - \frac{ke^2}{\hat{r}}}^{\hat{H}^0}$$

now treat this as a perturbation.

$$E_n^1 = \langle \psi_{n\ell m}^0 | \hat{H}^1 | \psi_{n\ell m}^0 \rangle$$

We could try to calculate $\langle p^4 \rangle$ using the wave functions $\psi_{n\ell m}$, but $p \to -i\hbar\nabla$ and this gets very messy. Instead, proceed as follows:

$$\frac{\hat{p}^2}{2m} = \hat{H}^0 + \frac{ke^2}{\hat{r}} \quad \text{and} \quad \left(\frac{\hat{p}^2}{2m}\right)^2 = \left(\hat{H}^0 + \frac{ke^2}{\hat{r}}\right)\left(\hat{H}^0 + \frac{ke^2}{\hat{r}}\right)$$

$$\frac{\hat{p}^4}{4m^2} = (\hat{H}^0)^2 + ke^2\left[\left(\frac{1}{\hat{r}}\right)\hat{H}^0 + \hat{H}^0\left(\frac{1}{\hat{r}}\right)\right] + \frac{k^2e^4}{\hat{r}^2}$$

Now, $E_n^1 = \langle \psi_{n\ell m}^0 | -\frac{1}{8}\frac{\hat{p}^4}{m^3c^2} | \psi_{n\ell m}^0 \rangle$

$$= \frac{-1}{2mc^2} \cdot \langle \psi_{n\ell m}^0 | \frac{\hat{p}^4}{4m^2} | \psi_{n\ell m}^0 \rangle$$

sub in above expression

$$E_n^1 = \frac{-1}{2mc^2}\Big[\langle \psi_{n\ell m}^0 | \hat{H}^0 \overset{\text{act}}{\hat{H}^0} | \psi_{n\ell m}^0 \rangle + ke^2 \langle \psi_{n\ell m}^0 | \left(\frac{1}{\hat{r}}\right)\overset{\text{act}}{\hat{H}^0} | \psi_{n\ell m}^0 \rangle$$

$$+ ke^2 \langle \psi_{n\ell m}^0 | \overset{\text{act}}{\hat{H}^0}\left(\frac{1}{\hat{r}}\right) | \psi_{n\ell m}^0 \rangle + k^2e^4 \langle \psi_{n\ell m}^0 | \frac{1}{\hat{r}^2} | \psi_{n\ell m}^0 \rangle \Big]$$

But $\hat{H}^0 | \psi_{n\ell m}^0 \rangle = E_n^0 | \psi_{n\ell m}^0 \rangle$

$\langle \psi_{n\ell m}^0 | \hat{H}^0 = \langle \psi_{n\ell m}^0 | E_n^0$

$$= \frac{-1}{2mc^2}\left[(E_n^0)^2 + E_n^0\left(ke^2\left\langle \frac{1}{r}\right\rangle + ke^2\left\langle \frac{1}{r}\right\rangle\right) + k^2e^4\left\langle \frac{1}{r^2}\right\rangle \right]$$

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$$E_n^1 = -\frac{1}{2mc^2}\left[(E_n^0)^2 + 2ke^2 E_n^0 \left\langle \frac{1}{r} \right\rangle + k^2c^4 \left\langle \frac{1}{r^2} \right\rangle \right]$$

To complete the calculation, we need

$\left\langle \frac{1}{r^n} \right\rangle$ in the state $\psi^0_{n\ell m}$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{\psi^*_{n\ell m}(r,\theta,\phi)\,\psi_{n\ell m}(r,\theta,\phi)}{r^n}\, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

It only affects the radial part: $\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$
and the spherical Harmonics are normalized.

$$\left\langle \frac{1}{r^n} \right\rangle = \int_0^{\infty} [R_{n\ell}(r)]^2 \cdot r^{2-n}\, dr$$

<u>Example:</u>

Ground state: $R_{10}(r) = \frac{2}{\sqrt{a^3}} e^{-r/a}$ $\quad$ a = Bohr radius

$$E_0^1 = \int_0^{\infty} \frac{4}{a^3} e^{-2r/a} r^{2-n}\, dr \qquad \text{Let } u = \frac{2r}{a} \quad du = \frac{2}{a}dr$$

$$= \frac{4}{a^3}\int_0^{\infty} e^{-u} \left(\frac{au}{2}\right)^{2-n} \left(\frac{a}{2}\right) du$$

$$= \frac{2^2}{a^3}\, \frac{a^{3-n}}{2^{3-n}} \underbrace{\int_0^{\infty} e^{-u} u^{2-n}\, du}_{=(2-n)!}$$

as long as $n < 3$

$$\left\langle \frac{1}{r^n} \right\rangle = 2^{n-1} a^{-n} (2-n)!$$

Correction to ground state energy:

$$E_1' = -\frac{1}{2mc^2}\left[(E_1^0)^2 + 2ke^2E_1^0 \left\langle \frac{1}{r}\right\rangle_{n=1} + k^2e^4\left\langle\frac{1}{r^2}\right\rangle_{n=2}\right]$$

$$= -\frac{1}{2mc^2}\left[(E_1^0)^2 + 2ke^2E_1^0 \cdot \frac{1}{a} + k^2e^4\frac{2}{a^2}\right]$$

To simplify it, remember $E_1^0 = \frac{-ke^2}{2a}$ so $ke^2 = -2aE_1^0$

$$E_1' = -\frac{1}{2mc^2}\left[(E_1^0)^2 - 4(E_1^0)^2 + 8(E_1^0)^2\right] = -\frac{5(E_1^0)^2}{2mc^2}$$

$$\therefore \quad E_1 \cong E_1^0 + E_1' = \underset{-13.6\,eV}{E_1^0}\left[1 - \underbrace{\frac{5}{2}\left(\frac{E_1^0}{mc^2}\right)}\right]$$

relativistic correction.
≈ 1 part in 15000.

This was an example for $n=1$. The amazing thing is that you can calculate E_n^1 exactly for any value of n or ℓ! See Griffiths problems 7.15 & 7.42.

$$\boxed{E_{n\ell}^1 = \frac{-(E_n^0)^2}{2mc^2}\left[\frac{4n}{\ell+\frac{1}{2}} - 3\right]}$$

Relativistic correction to Hydrogen energy levels.

Note that this perturbation breaks the degeneracy in ℓ. The correction to the 2s state ($\ell=0$) is different than the 2p ($\ell=1$) state.

$E_{2,\ell=0} \neq E_{2,\ell=1}$ they are only approximately the same!

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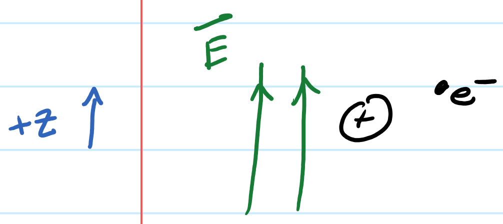
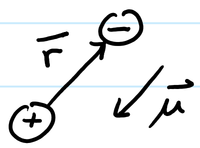
Stark Effect

Let's put perturbation theory to work in a real-world example:
Suppose you put a Hydrogen atom in an electric field. Treat the field as a weak perturbation. What is the change in the ground state energy?

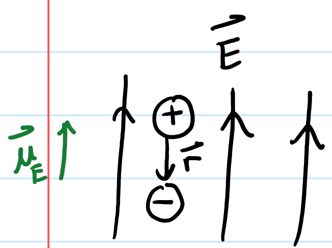


$$E_1 = -13.6\,\text{eV} + \Delta E$$

First, we need the Hamiltonian. Classically, the $e^- p^+$ pair looks like an electric dipole. The electric dipole moment is defined as $\vec{\mu}_E = -e\vec{r}$ where $\vec{r}$ points from the positive charge to the negative.

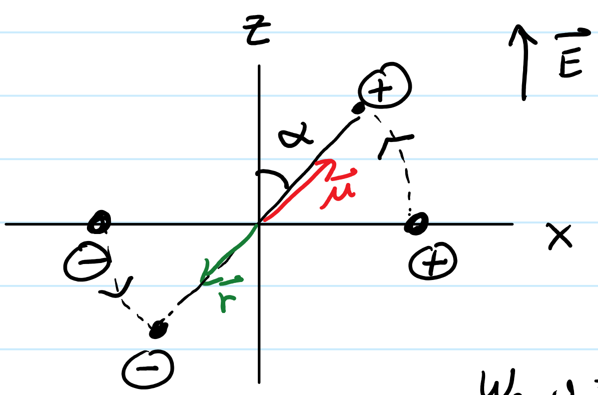


If you put the dipole in an Electric field, it tends to align with the field.



Rotating the dipole from this minimum energy configuration requires <u>work</u>.

Call $V=0$ when dipole is $\perp$ to the field.



If the dipole rotates to angle α the field did work

$$W_{field} = |\vec{F}|\cdot d_{\parallel} = \underbrace{|q\vec{E}|\cdot\frac{|\vec{r}|}{2}\cos\alpha}_{\text{Work on } \oplus \text{ charge}} + \underbrace{|-q\vec{E}|\frac{|\vec{r}|}{2}\cos\alpha}_{\text{Work on } \ominus \text{ charge}}$$

$$V = -W_{field} = -e|\vec{E}||\vec{r}|\cos\alpha$$

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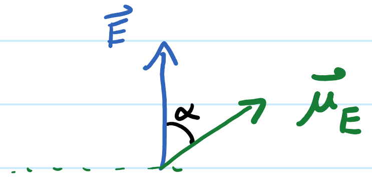
Angle between dipole $\vec{\mu}$ and $\vec{E}$

$$V = -W_{field} = -e|\vec{E}||\vec{r}|\cos\alpha$$

Now,



$$\vec{\mu}_E\cdot\vec{E} = |\vec{\mu}_E||\vec{E}|\cdot\cos\alpha$$
$$= e|\vec{r}||\vec{E}|\cos\alpha$$

By comparing these, $V = -\vec{\mu}_E\cdot\vec{E}$ with $\vec{\mu}_E = -e\vec{r}$

[This should remind you of magnetic dipoles & spins. There, $V = -\vec{\mu}_B\cdot\vec{B}$].

So, for the hydrogen atom, $\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{k_e e^2}{r}}_{\hat{H}^0} \underbrace{-\vec{\mu}_E\cdot\vec{E}}_{\hat{H}^1}$

$$= -(-e\vec{r})\cdot\vec{E}$$
$$\hat{H}^1 = e\vec{r}\cdot\vec{E}$$
$$= e|\vec{E}|\cdot z = e|\vec{E}|r\cos\theta$$

Careful w/notation : $\vec{E}$ (field)
E (energy) !

↑ angle between z-axis and $\vec{r}$.

Now, calculate the correction to the energy

$$E_1^1 = \langle \psi_{100} | e|\vec{E}|r\cos\theta | \psi_{100}\rangle$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{100}^*(r,\theta,\phi)\cdot[e|\vec{E}|\cdot r\cdot\cos\theta]\cdot\psi_{100}(r,\theta,\phi)\cdot r^2\sin\theta\, dr\, d\theta\, d\phi$$

Recall, $\psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$ $\quad a = 0.5\times10^{-10}\,m$ (Bohr radius).

$$E_1^1 = \frac{e|\vec{E}|}{(\pi a^3)}\cdot\int_0^{2\pi}d\phi \underbrace{\int_0^{\pi}\cos\theta\sin\theta\, d\theta}_{\text{Look at this integral}} \int_0^{\infty} r^3 e^{-r/a}\, dr$$

The θ integral is $\displaystyle\int_0^\pi \sin\theta\cos\theta\, d\theta = \frac{1}{2}\int_0^\pi \sin(2\theta)\, d\theta$

$$= -\frac{1}{4}\cos(2\theta)\Big|_0^\pi = 0$$

This is a little disappointing, but also interesting. It shows that to first order in perturbation theory, there is no correction to the ground state energy.

Physically, this means that the ground state does not have a permanent electric dipole moment. But, we expect the field to have some effect. How about at 2nd order?

$$E_1^2 = \sum_{m\neq 1} \frac{|\langle \psi_m^0 | \hat{H}' | \psi_1^0 \rangle|^2}{E_1^0 - E_m^0}$$

$E_1^0 = -13.6\,\mathrm{eV}$

$E_m^0 = -13.6\,\mathrm{eV}/m^2$

sum all states other than ground state.

$$E_1^2 = \sum_{\substack{n\ell m \\ n\neq 1}} \frac{|\langle \psi_{n\ell m} | e|E| r\cos\theta | \psi_{100} \rangle|^2}{-13.6\,\mathrm{eV} + \frac{13.6\,\mathrm{eV}}{n^2}}$$

$$E_1^2 = \frac{e^2|E|^2}{13.6\,\mathrm{eV}} \cdot \underbrace{\sum_{\substack{n\ell m \\ n\neq 1}} \left(\frac{n^2}{1-n^2}\right) |\langle \psi_{n\ell m} | r\cos\theta | \psi_{100} \rangle|^2}$$

Doing this infinite sum is possible, but not for the faint of Heart. The result is...

[see e.g. Shankar Principles of QM, 2nd Ed. §17.2]

$$E_1^{(2)} \approx -\frac{9}{4} \cdot \frac{|E|^2 a^3}{ke} \approx -1.95\times 10^{-18}\,\mathrm{eV}\left(\frac{|E|}{\mathrm{V/cm}}\right)^2$$

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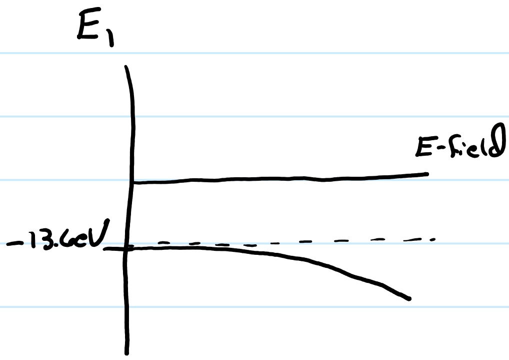
That's a <u>very</u> small shift!

$$E_1 = -13.6\,\text{eV} - 1.95\times 10^{-18}\,\text{eV}\left(\frac{|\vec{E}|}{\text{V/cm}}\right)^2$$



I'd need a field of $|\vec{E}| = 10^9$ V/cm to get a shift of about 2eV in the ground state.

Stark effect in excited states ($n=2$)

Let's see what the effect of the $\vec{E}$-field has on the 2^{nd} order energy levels. There are 4 states: $|n\ell m\rangle$

$$|200\rangle, |211\rangle, |210\rangle, |21{-1}\rangle$$

These states are <u>degenerate</u> so we need degenerate perturbation theory. Degenerate PT tells us that we need to diagonalize the matrix:

$\langle n\ell m|\hat{H}'|n'\ell' m'\rangle$. In other words, we need the "good" combinations of these 4 eigenstates. To do that, we need the eigenvalues & eigenvectors of this matrix:

$$\begin{pmatrix}
\langle 200|\hat{H}'|200\rangle & \langle 200|\hat{H}'|211\rangle & \langle 200|\hat{H}'|210\rangle & \langle 200|\hat{H}'|21{-1}\rangle \\
\langle 211|\hat{H}'|200\rangle & \langle 211|\hat{H}'|211\rangle & \langle 211|\hat{H}'|210\rangle & \langle 211|\hat{H}'|21{-1}\rangle \\
\langle 210|\hat{H}'|200\rangle & \langle 210|\hat{H}'|211\rangle & \langle 210|\hat{H}'|210\rangle & \langle 211|\hat{H}'|21{-1}\rangle \\
\langle 21{-1}|\hat{H}'|200\rangle & \langle 21{-1}|\hat{H}'|211\rangle & \langle 21{-1}|\hat{H}'|210\rangle & \langle 21{-1}|\hat{H}'|21{-1}\rangle
\end{pmatrix}$$

Recall, $\hat{H}' = e|\vec{E}|r\cos\theta$ is independent of ϕ. So the integrals we need are:

$$\langle 2\ell m|\hat{H}'|2\ell' m'\rangle = e|\vec{E}|\int_0^\infty\int_0^\pi\int_0^{2\pi} \psi_{2\ell m}^*(\vec{r})\, r\cos\theta\, \psi_{2\ell' m'}(r)\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

The perturbation doesn't affect the ϕ integral at all. Remember that

$\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\cdot Y_\ell^m(\theta,\phi) = R_{n\ell}(r)\, P_\ell^m(\cos\theta)\, e^{im\phi}$ so the ϕ integral is:

$$\int_0^{2\pi} e^{i(m'-m)\phi}\, d\phi = \frac{1}{i(m-m')}\left[e^{i(m-m')\phi}\right]_0^{2\pi}$$

$$= \frac{-i}{(m-m')}\left[e^{2\pi i(m-m')} - 1\right]$$

if $m \neq m'$, we have $m-m'$ = integer ($e^{2\pi i(m-m')} = 1$, and so the integral is zero if $m \neq m'$!

This kills most of the matrix elements.

$$\begin{pmatrix} \boxed{\langle 200|\hat{H}'|200\rangle} & \cancel{\langle 200|\hat{H}'|211\rangle} & \boxed{\langle 200|\hat{H}'|210\rangle} & \cancel{\langle 200|\hat{H}'|21{-1}\rangle} \\ \cancel{\langle 211|\hat{H}'|200\rangle} & \boxed{\langle 211|\hat{H}'|211\rangle} & \cancel{\langle 211|\hat{H}'|210\rangle} & \cancel{\langle 211|\hat{H}'|21{-1}\rangle} \\ \boxed{\langle 210|\hat{H}'|200\rangle} & \cancel{\langle 210|\hat{H}'|211\rangle} & \boxed{\langle 210|\hat{H}'|210\rangle} & \cancel{\langle 211|\hat{H}'|21{-1}\rangle} \\ \cancel{\langle 21{-1}|\hat{H}'|200\rangle} & \cancel{\langle 21{-1}|\hat{H}'|211\rangle} & \cancel{\langle 21{-1}|\hat{H}'|210\rangle} & \boxed{\langle 21{-1}|\hat{H}'|21{-1}\rangle} \end{pmatrix}$$

We need to calculate the diagonal elements and <u>one</u> off diagonal one.

$$\langle 2\ell m|\hat{H}'|2\ell' m\rangle = e|\vec{E}|\cdot \underbrace{2\pi}_{\text{from } \phi \text{ integral}} \cdot \int_0^\infty\int_0^\pi R_{2\ell}^*(r) R_{2\ell'}(r)\, Y_{\ell m}^*(\theta,0)\, Y_{\ell' m}(\theta,0) \times r^3 \cdot \sin\theta\cos\theta\, d\theta\, dr$$

Let's focus on the angular integral $\int_0^\pi Y_{\ell m}^*(\theta\ 0)\, Y_{\ell' m}(\theta,0)\sin\theta\cos\theta\, d\theta$

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$$\int_0^\pi Y^*_{\ell m}(\theta\, 0) Y_{\ell' m}(\theta, 0) \sin\theta \cos\theta\, d\theta$$

Diagonal terms:

$\ell = \ell' = 0$, $m = 0$

$$\int_0^\pi \left(\frac{1}{\sqrt{4\pi}}\right)\left(\frac{1}{\sqrt{4\pi}}\right) \cdot \sin\theta \cos\theta\, d\theta = 0$$

This vanishes for the same reason that the ground state vanished.

$\ell = \ell' = 1$, $m = 1$

$$\int_0^\pi \left(-\sqrt{\frac{3}{8\pi}} \sin\theta\right)\left(-\sqrt{\frac{3}{8\pi}} \sin\theta\right) \sin\theta \cos\theta\, d\theta$$

$$\frac{3}{8\pi} \int_0^\pi \sin^3\theta \cos\theta\, d\theta = \frac{3}{32\pi} \sin^4\theta \Big|_0^\pi = 0$$

$\ell = \ell' = 1$, $m = -1$ $\quad = \quad 0 \quad$ (same as $m = +1$)

$\ell = \ell' = 1$, $m = 0$

$$= \int_0^\pi \left(\sqrt{\frac{3}{4\pi}} \cos\theta\right)\left(\sqrt{\frac{3}{4\pi}} \cos\theta\right) \sin\theta \cos\theta\, d\theta =$$

$$= \frac{3}{4\pi} \int_0^\pi \cos^3\theta \sin\theta\, d\theta \qquad u = \cos\theta, \quad du = -\sin\theta\, d\theta$$

$$= \frac{3}{4\pi} \int_{-1}^{1} u^3\, du = 0$$

All diagonal terms are zero! Now, the off-diagonal term:

$\ell = 0$, $\ell' = 1$, $m = 0$

$$= \int_0^\pi \left(\sqrt{\frac{1}{4\pi}}\right)\left(\sqrt{\frac{3}{4\pi}} \cos\theta\right) \cos\theta \sin\theta\, d\theta$$

$$= \frac{\sqrt{3}}{4\pi} \int_{-1}^{1} u^2\, du = \frac{\sqrt{3}}{4\pi} \cdot \frac{2}{3} = \frac{1}{2\pi\sqrt{3}}$$

$$\langle 210 | \hat{H}' | 200 \rangle = e|\vec{E}| \cdot 2\pi \cdot \int_0^\infty \cdot R_{21}(r) R_{20}(r)^* r^3 dr \cdot \frac{1}{2\pi\sqrt{3}}$$

$$= \frac{e|\vec{E}|}{\sqrt{3}} \int_0^\infty \left[\frac{1}{2\sqrt{6a^3}} \left(\frac{r}{a}\right) e^{-r/2a}\right]\left[\frac{1}{\sqrt{2a^3}}\left(1 - \frac{r}{2a}\right) e^{-r/2a}\right] r^3 dr$$

$$= \frac{e|\vec{E}|}{12} \int_0^\infty \left(\frac{r}{a} - \frac{r^2}{2a^2}\right) e^{-r/a} \cdot \frac{r^3}{a^3}\, dr$$

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$$\langle 210|\hat{H}'|200\rangle = \frac{e|\vec{E}|}{12}\int_0^\infty \left(\frac{r}{a}-\frac{r^2}{2a^2}\right)e^{-r/a}\cdot\frac{r^3}{a^3}\,dr$$

Let $u=\frac{r}{a}$ $\quad du=\frac{1}{a}dr$

$$= \frac{e|\vec{E}|a}{12}\int_0^\infty \left(u-\frac{u^2}{2}\right)u^3e^{-u}\,du$$

$$= \frac{e|\vec{E}|a}{12}\int_0^\infty \left(u^4-\frac{u^5}{2}\right)e^{-u}\,du = \frac{e|\vec{E}|a}{12}\left[4!-\frac{5!}{2}\right]$$

$$= \underline{\underline{-3|\vec{E}|ea}}$$

So, our matrix is:

$$-3|\vec{E}|ea\;\begin{array}{cccc} |200\rangle & |211\rangle & |210\rangle & |21{-1}\rangle \\ \end{array}$$
$$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The eigenvalues are $\pm 3|\vec{E}|ea$

eigenvectors: Lower E $\rightarrow \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right)$

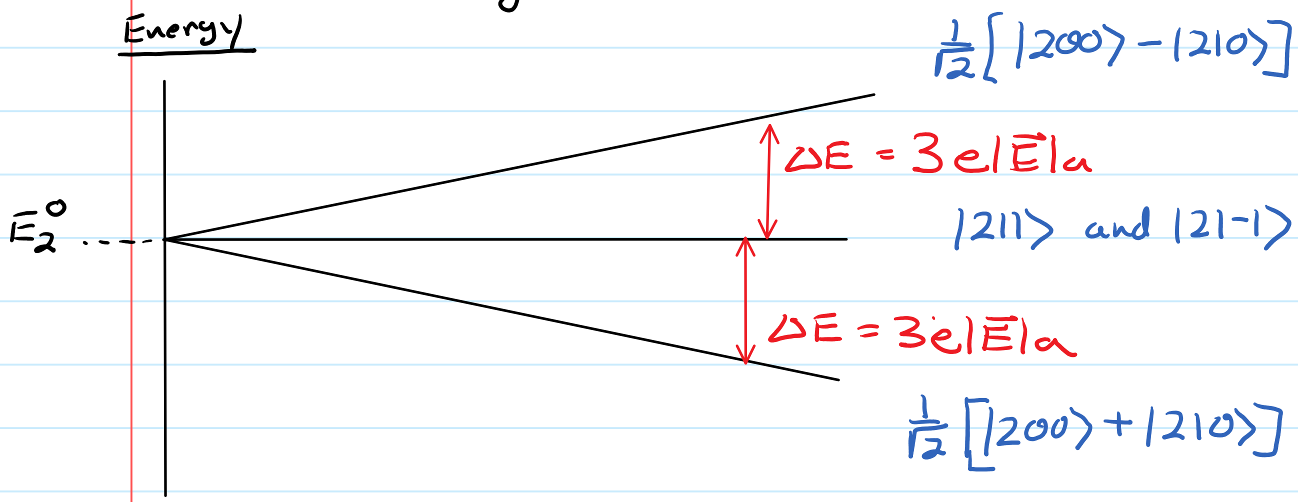
Higher E $\rightarrow \frac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right)$

Energy unchanged $\rightarrow \left\{ \begin{array}{l} |211\rangle \\ |21{-1}\rangle \end{array}\right.$

The "good" states.

Perturbations of Hydrogen

And so we've figured out the modification to the energy levels:



Note that, unlike the ground state, we see an effect from first order perturbation theory. The (4x) degenerate state splits into 3!

$E_+ = E_2^0 + \Delta E$ (1 state)

E_2^0 (2 states)

$E_- = E_2^0 - \Delta E$ (1 state)

Numerically: $\Delta E = 3e\,|\vec{E}|\cdot a$

$$= 3eV\left(\frac{|\vec{E}|}{V}\right)\cdot cm\cdot\left(\frac{a}{cm}\right)$$

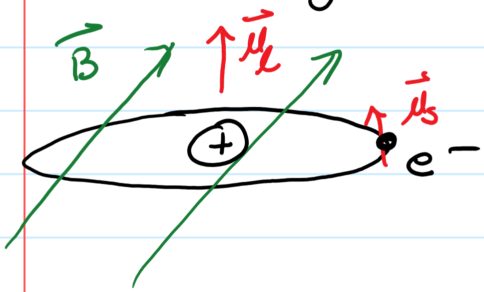
$$= 3eV\left(\frac{|\vec{E}|}{V/cm}\right)\cdot\left[0.5\times 10^{-8}\right]$$

$$\boxed{\Delta E = 1.5\times 10^{-8}\left(\frac{|\vec{E}|}{V/cm}\right)\,eV}$$

Perturbations of Hydrogen

Zeeman Effect

Now, instead of an electric field, what if we put a Hydrogen atom in a magnetic field?



Remember, the system has a magnetic moment for two reasons:

1. The electron may have some orbital angular momentum
2. The electron has spin and has an intrinsic magnetic moment.

As in our earlier discussion of the Stern-Gerlach experiment, the potential energy is $\hat{H}_Z = -\vec{\mu}\cdot\vec{B}$ so the system tends toward the lowest energy configuration, when $\vec{\mu}$ is parallel to $\vec{B}$.

$\hat{H}_Z$ called the "Zeeman" Hamiltonian after Pieter Zeeman who was an experimentalist who discovered the effect. He won the Nobel Prize in 1902 along with Hendrik Lorentz (theorist) for work on the subject.

$\vec{\mu} = \vec{\mu}_\ell + \vec{\mu}_S$ including both spin and orbital effects.

"g-factor" ≈ 2. The magnetic moment is about twice the expected classical value.

$$= \underbrace{\left(\frac{-e}{2m_e}\right)}\vec{L} + \left(\frac{-ge}{2m_e}\right)\vec{S}$$

we derived this in the Stern-Gerlach lecture by considering an electron orbiting a proton as a current loop.

So, the Hamiltonian becomes:

$$\hat{H}_Z = -\vec{\mu}\cdot\vec{B} = \frac{e}{2m_e}\left[\hat{\vec{L}} + 2\hat{\vec{S}}\right]\cdot\vec{B} = \frac{e}{2m_e}\left[\hat{\vec{L}}\cdot\vec{B} + 2\hat{\vec{S}}\cdot\vec{B}\right]$$

We can, without loss of generality choose the Z-axis to point along the direction of $\vec{B}$. Then, the full Hamiltonian for Hydrogen is:

$$\vec{B} = B_0\hat{k}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{ke^2}{r} + \frac{eB_0}{2m_e}\left[\hat{L}_z + 2\hat{S}_z\right]$$

Now, the states $\psi_{n\ell m}(\vec{r})|\uparrow\rangle$ and $\psi_{n\ell m}(\vec{r})|\downarrow\rangle$ are eigenstates of $\hat{H}$ if $\vec{B}=0$. But, its easy to see that they are also eigenstates of $\hat{H}$ if $\vec{B}\neq 0$.

$$\hat{H} = \hat{H}(\vec{B}=0) + \frac{eB_0}{2m_e}\left[\hat{L}_z + 2\hat{S}_z\right]$$

$$\hat{H}\left[\psi_{n\ell m}(\vec{r})|\uparrow\rangle\right] = -\frac{E_1}{n^2}\psi_{n\ell m}(\vec{r})|\uparrow\rangle + \frac{eB_0}{2m_e}\left[\hat{L}_z\psi_{n\ell m}(\vec{r})|\uparrow\rangle + 2\psi_{n\ell m}(\vec{r})\hat{S}_z|\uparrow\rangle\right]$$

$$= \frac{-E_1}{n^2} + \frac{eB_0}{2m_e}\left[m\hbar + 2\cdot\frac{\hbar}{2}\right]\psi_{n\ell m}(\vec{r})|\uparrow\rangle$$

$$= \left\{\frac{-E_1}{n^2} + \frac{eB_0\hbar}{2m_e}\left[m+1\right]\right\}\psi_{n\ell m}(\vec{r})|\uparrow\rangle$$

And, we would have a similar expression for $\psi_{n\ell m}(\vec{r})|\downarrow\rangle$ with $m+1 \rightarrow m-1$

<u>Therefore:</u> $$E_{nm} = -\frac{E_1}{n^2} + \frac{eB_0\hbar}{2m_e}\left[m \pm 1\right]$$

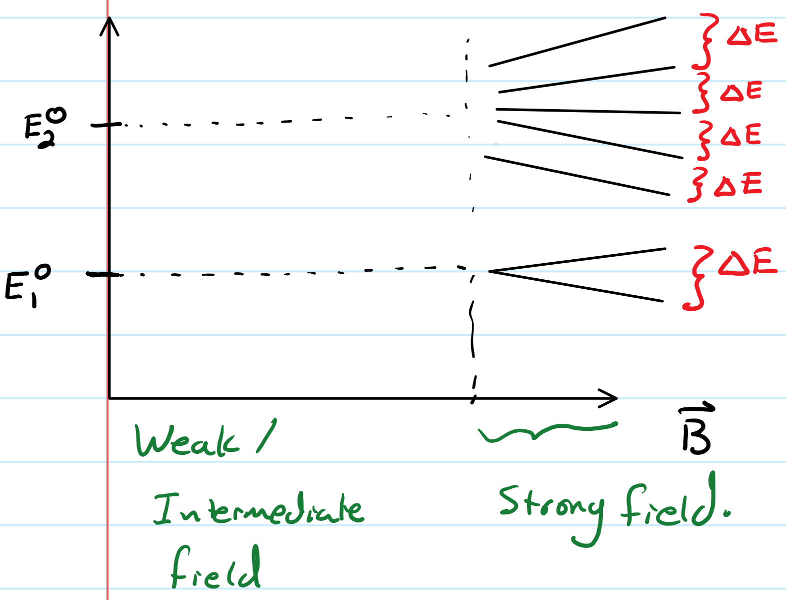
Notice, the magnetic field breaks the degeneracy in m.
<u>HW</u> <u>exercise:</u> How big is this splitting? Write it as

$$E_{nm} = -\frac{13.6\,eV}{n^2} + (\#\,eV)\left(\frac{B_0}{T}\right)(m \pm 1)$$

Tesla.

How do the states split?
Ground state splits into 2 $(m=0)$

First excited state splits into 5 $(m = 0, +1, -1)$



There is, of course more to the story ... to get everything exactly right you also need to include the fine structure corrections to $\hat{H}$

$$\hat{H} = \hat{H}_{B=0} + \hat{H}_{fs} + \hat{H}_Z$$

People typically discuss 3 regions:

① Weak Zeeman effect (when $\hat{H}_Z \ll \hat{H}_{fs}$)
then we have the fine structure + a small perturbation due to $\vec{B}$-field

② Strong Zeeman Effect (when $\hat{H}_Z \gg \hat{H}_{fs}$)
Here, you take what we did & add the fine structure as a perturbation. [This is what we calculated with $\hat{H}_{fs} = 0$]

③ Intermediate Zeeman Effect (when $\hat{H}_Z \sim \hat{H}_{fs}$)
Both effects are comparable. The full effect looks like this:

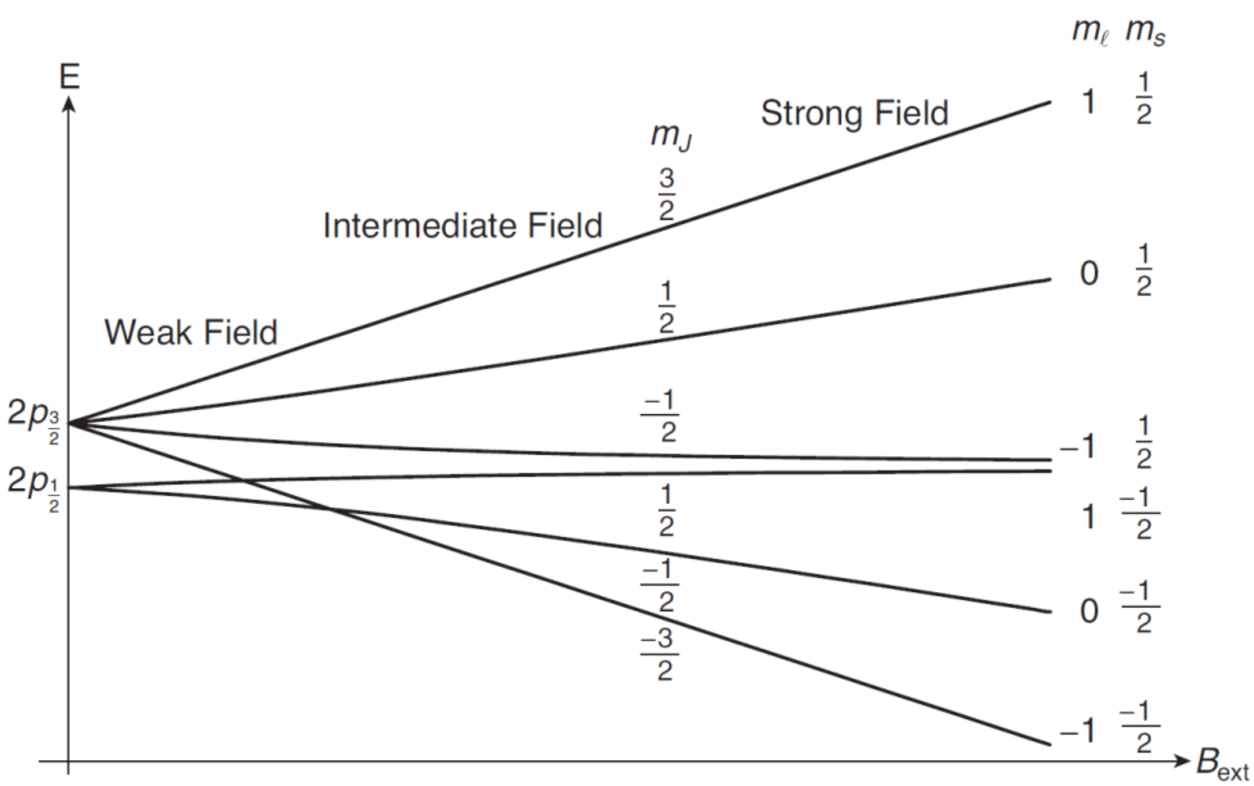
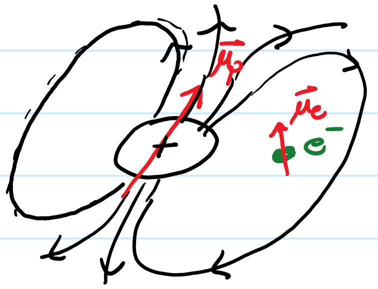


FIGURE 12.10 Perturbation of the hydrogen $2p$ states caused by the Zeeman effect and the fine structure as a function of the applied magnetic field.

Perturbations of Hydrogen

Hyperfine Interaction

There's one more perturbation I want to discuss. The proton itself has spin, and it has a magnetic moment too. The proton sets up a $\vec{B}$-field and the electron (which also has a magnetic moment) responds to this.



The potential energy is

$$V = -\vec{\mu}_e \cdot \vec{B}_p$$

Now, the $\vec{B}$-field from a dipole can be found classically

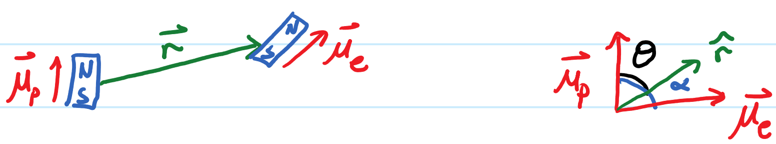
$$\vec{B}_p = \frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}_p \cdot \hat{r})\hat{r} - \vec{\mu}_p\right] + \frac{2\mu_0}{3}\vec{\mu}_p \delta^3(\vec{r})$$

proton's magnetic moment.

μ_0 = permeability of free-space $= 4\pi \times 10^{-7} \frac{T \cdot m}{A}$

$$V = \frac{-\mu_0}{4\pi r^3}\left[3(\vec{\mu}_p \cdot \hat{r})(\vec{\mu}_e \cdot \hat{r}) - \vec{\mu}_p \cdot \vec{\mu}_E\right] - \frac{2\mu_0}{3}\vec{\mu}_p \cdot \vec{\mu}_E \delta^{(3)}(\vec{r})$$

Think of the proton & electron as tiny magnets



We can choose $\vec{\mu}_p$ along z axis without loss of generality. Then

$$(\vec{\mu}_p \cdot \hat{r})(\vec{\mu}_e \cdot \hat{r}) = |\vec{\mu}_p| \cos\theta \cdot |\vec{\mu}_e| \cos(\alpha - \theta)$$

$$V = \frac{-\mu_0}{4\pi r^3}\left[3|\vec{\mu}_p||\vec{\mu}_e| \cos\theta \cos(\alpha-\theta) - |\vec{\mu}_p||\vec{\mu}_e| \cos\alpha\right] - \frac{2\mu_0}{3}|\vec{\mu}_p||\vec{\mu}_e| \cos\alpha \, \delta^3(\vec{r})$$

$$= -\mu_0 |\vec{\mu}_p||\vec{\mu}_e| \left\{ \frac{1}{4\pi r^3}\left(3\cos\theta\cos(\alpha-\theta) - \cos\alpha\right) + \frac{2}{3}\cos\alpha\, \delta^{(3)}(\vec{r}) \right\}$$

$$= -\mu_0 |\vec{\mu}_p||\vec{\mu}_e| \left\{ \frac{1}{4\pi r^3}\left(3\cos^2\theta\cos\alpha + 3\cos\theta\sin\alpha\sin\theta - \cos\alpha\right) + \frac{2}{3}\cos\alpha\, \delta^{(3)}(\vec{r}) \right\}$$

[using trig identity $\cos(A-B) = \cos A \cos B + \sin A \sin B$]

Now, suppose you want to find the effect of this perturbation on the hydrogen ground state. We'd need to integrate $\langle \psi_{100} | \hat{H}' | \psi_{100} \rangle$

Look at the angular integral of the first term

$$\int_0^{2\pi}\int_0^{\pi}\left[3\cos^2\theta\cos\alpha + 3\cos\theta\sin\theta\sin\alpha - \cos\alpha\right]\sin\theta\, d\theta\, d\phi$$

$$= \int_0^{2\pi} d\phi \left[\cos\alpha \underbrace{\int_0^{\pi}(3\cos^2\theta - 1)\sin\theta\, d\theta}_{=0} + \sin\alpha \underbrace{\int_0^{\pi} 3\cos\theta\sin^2\theta\, d\theta}_{0}\right]$$

$u = \cos\theta$

$du = -\sin\theta\, d\theta$

$$\int_{-1}^{1}(3u^2-1)\,du \qquad = \tfrac{1}{3}\sin^3\theta\Big|_0^{\pi} = 0$$

$$= u^3 - u\Big|_{-1}^{1}$$

$$= (1^3 - 1) - (-1)^3 - (-1)$$

$$= 0$$

So these integrals vanish for the ground state. Then,

$$\hat{H}' = \frac{-2\mu_0}{3}|\vec{\mu}_p||\vec{\mu}_e|\cos\alpha\, \delta^{(3)}(\vec{r}) = -\frac{2\mu_0}{3}\vec{\mu}_p\cdot\vec{\mu}_e\, \delta^{(3)}(\vec{r})$$

Hyperfine perturbation of Ground state.

Now, $\vec{\mu}_p = \dfrac{g_p e}{2m_p}\hat{\vec{S}}_p \qquad \vec{\mu}_e = -\dfrac{g_e \cdot e}{2m_e}\hat{\vec{S}}_e$

g = "g-factor" ; $g_e \cong 2$, $g_p \cong 5.59$

$$\hat{H}' = \underbrace{\frac{\mu_0 g_p e^2}{3 m_p m_e}}_{\text{constant}} \underbrace{(\hat{\vec{S}}_e \cdot \hat{\vec{S}}_p)}_{\text{spin part}} \underbrace{\delta^{(3)}(\vec{r})}_{\text{spatial part.}}$$

$= -c$

Now, we want to know the effect of $\hat{H}'$ on the ground state energy. Including the spin part,

$$|\psi_a\rangle = \underbrace{|100\rangle}_{\text{spatial part}} \underbrace{|\chi_a\rangle}_{\text{spin part}}$$

$|\chi_a\rangle = |\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$
4x degenerate!

$\langle \psi_a | \hat{H}' | \psi_b \rangle$ factor the spatial & spin parts.

$$= \langle 100 | \hat{H}'_{space} | 100 \rangle \langle \chi_a | \hat{H}'_{spin} | \chi_b \rangle$$

$$= \left[c \cdot \int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi_{100}(\vec{r})|^2 \cdot \delta^{(3)}(\vec{r}) d^3 r \right] \langle \chi_a | \hat{H}'_{spin} | \chi_b \rangle$$

$$= c \cdot |\psi_{100}(0)|^2 \langle \chi_a | \hat{H}'_{spin} | \chi_b \rangle$$

$$= \frac{c}{\pi a^3} \langle \chi_a | \hat{H}'_{spin} | \chi_b \rangle = \frac{c}{\pi a^3} \langle \chi_a | \hat{\vec{S}}_e \cdot \hat{\vec{S}}_p | \chi_b \rangle$$

Now, the spin basis is degenerate $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$
So we need to construct this matrix & find the eigenvalues.

Luckily, we already did this in the addition of angular momentum lecture.

$$\hat{S}^2 = \underbrace{\hat{S}^2_{(1)} + \hat{S}^2_{(2)}} + \underbrace{2\hat{S}^{(1)}_z \hat{S}^{(2)}_z} + \underbrace{2\hat{S}^{(1)}_x \hat{S}^{(2)}_x + 2\hat{S}^{(1)}_y \hat{S}^{(2)}_y}$$

$$= \underbrace{\frac{3\hbar^2}{2}\begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&0 \\ 0&0&0&1 \end{pmatrix}} + \underbrace{\frac{\hbar^2}{2}\begin{pmatrix} 1&0&0&0 \\ 0&-1&0&0 \\ 0&0&-1&0 \\ 0&0&0&1 \end{pmatrix}} + \underbrace{\frac{\hbar^2}{2}\begin{pmatrix} 0&0&0&0 \\ 0&0&2&0 \\ 0&2&0&0 \\ 0&0&0&0 \end{pmatrix}}$$

Perturbations of Hydrogen

Add the blue + green pieces:

$$\hat{\vec{S}}_e \cdot \hat{\vec{S}}_p = \frac{\hbar^2}{4} \begin{array}{c} \begin{array}{cccc} |\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \end{array} \\ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \end{array}$$

So, in the space of degenerate spin states,

$$\hat{H}' \rightarrow \frac{C}{\pi a^3} \cdot \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

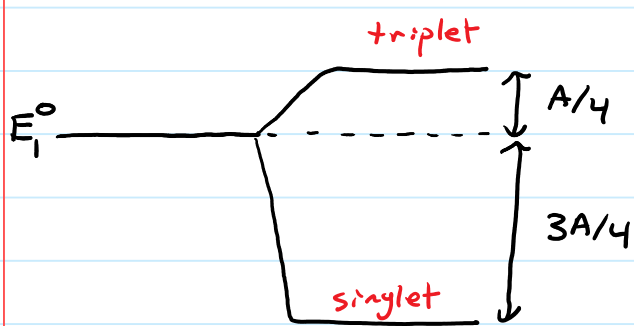
E_1' "Good" States

eigenvalues: & eigenvectors

$\frac{C\hbar^2}{4\pi a^3}$: $|\uparrow\uparrow\rangle$, $\frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right]$, $|\downarrow\downarrow\rangle$ } Triplet

$-\frac{3C\hbar^2}{4\pi a^3}$: $\frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$ Singlet.

The spin-spin interaction splits the ground state into two. The triplet spin states have a slightly higher energy than the singlet state.



Perturbations of Hydrogen

How large is the splitting?

$$\Delta E = \frac{4C\hbar^2}{4\pi a^3} = \frac{\mu_0 g_p e^2 \hbar^2}{3\pi m_p m_e a^3}$$

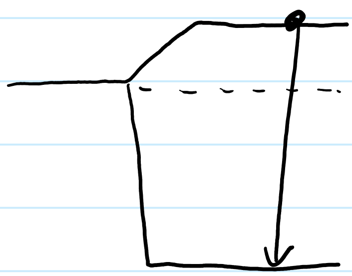
Note: $c^2 = \frac{1}{\mu_0 \varepsilon_0} \Rightarrow \mu_0 = \frac{1}{c^2 \varepsilon_0}$

$$\varepsilon_0 = 552000 \frac{e}{V\text{-cm}} \times \frac{1\,\text{cm}}{10^7\,\text{nm}} = 0.0552 \frac{e}{V\cdot\text{nm}}$$

$$\Delta E = \frac{g_p \cdot e^2 \cdot \hbar^2}{3\pi \varepsilon_0 (m_p c^2) m_e a^3} = \frac{g_p \cdot e^2 \cdot (\hbar c)^2}{3\pi \varepsilon_0 (m_p c^2)(m_e c^2) a^3}$$

$$= \frac{5.59 \cdot e^{\cancel{2}} \cdot (197.3\, \cancel{eV} \cdot \cancel{nm})^2}{3\pi \cdot \frac{0.0552\, \cancel{e}}{V \cdot \cancel{nm}} \cdot 938\times10^6\, \cancel{eV} \cdot 511000\, \cancel{eV} (0.053\, \cancel{nm})^3}$$

$$= 5.9\times10^{-6}\,\text{eV}$$



the frequency and wavelength of the emitted photon are:

$$\lambda = \frac{hc}{\Delta E} = \frac{1240\,\text{eV}\cdot\text{nm}}{5.9\times10^{-6}\,\text{eV}}$$

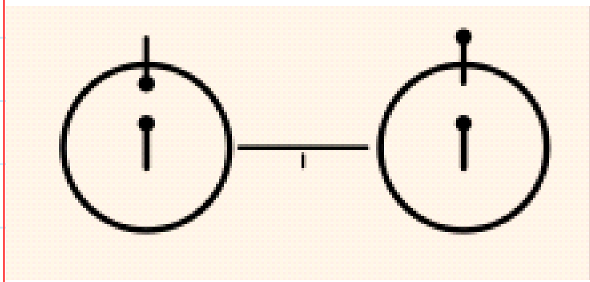
$$= 2.1\times10^8\,\text{nm} = \underline{\underline{21\,\text{cm}}}$$

$$f = \frac{c}{\lambda} = \frac{3\times10^{10}\,\text{cm/s}}{21\,\text{cm}} \approx 1420\,\text{MHz}$$

This is the famous "21 cm line" for hydrogen which is used all the time by radio astronomers. Any region of the universe containing hydrogen will emit this radiation & it can be used along with the Doppler shift to determine the velocity of parts of our galaxy. It is also this kind of transition (in Cesium, not Hydrogen) which is used for atomic clocks.

Perturbations of Hydrogen

The hyperfine splitting is considered so important that it Carl Sagan put it on the Pioneer probe in hopes that extraterrestrials encountering the probe could use it to determine both a unit of length (21cm) and of time $T = 1/f \approx 0.7ns$



Hyperfine transition as illustrated on the pioneer plaque.