Mon., 11/24 6.4-.5 Zeeman \& Hyper-fine

# Thanksgiving Break Wed 11/26-Fri 11/28 

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Daily: Kyle Jacob Spencer Gigja Anton Jessica Sean Antwain Jonathan Casey Jeremy Mark Connor Brad

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## Announcements

Daily 13.M Monday 11/24 Griffiths 6.4-.5 Hyper-Fine Structure of Hydrogen \& Zeeman Effect

## 6. Time-Independent Perturbation Theory

### 6.4 The Zeeman Effect

## Could we go over the Zeeman Effect a little more in depth?" Jeremy,

The standard treatment of the Spin-Orbit coupling effect gets us thinking about the effect of a magnetic field on the electron's energy. While that involved an argument made in the electron's reference frame, in the "lab frame", we can of course subject it to a magnetic field.

As you were reminded in the S-O section, a current loop constitutes a magnetic dipole, and the energy associated with a magnetic dipole's alignment with an external magnetic field is

$$
E=-\vec{\mu} \cdot \vec{B}_{e x t}
$$

In the lab frame, we see the electron orbiting and 'spinning', so just as we can treat the two angular momenta for these individually and add for the total, we can treat the two magnetic dipole moments separately and add for the total.

$$
\vec{\mu}_{e}=\vec{\mu}_{o r b i t}+\vec{\mu}_{s p i n}
$$

Now, the electron really can be thought of as orbiting, so we make no error in relating the associated orbital angular momentum with the orbital magnetic moment:

For circular motion it's quite easy:

$$
\vec{L}=\vec{r} \times \vec{p}=\vec{r} \times m \frac{d \vec{r}}{d t}=m r^{2} \vec{\omega}=m r^{2} \frac{2 \pi}{T} \hat{\omega}
$$

$$
\begin{gathered}
\text { while } \\
\vec{\mu}_{\text {orbit }}=I \vec{A}=\frac{d q}{d t} \pi r^{2} \hat{A}=\frac{-e}{T} \pi r^{2} \hat{A}=\frac{-e}{2 m} \vec{L}
\end{gathered}
$$

So, the quantum-mechanical operator that lets us extract the orbital magnetic moment from a wavefunction is

$$
\hat{\mu}_{\text {orbit }}=\frac{-e}{2 m} \hat{L}
$$

For the spin, if we were to model the spinning electron as simply a smaller current loop, we'd get the same relation between S and $\mu_{\text {spin. }}$. That would get all the physical parameters correct, but we need to make one correction: with a half-integer spin, the electron needs to go around twice to return to its original state. So maybe it's not too surprising that we'd be off by a factor of 2 .

$$
\vec{\mu}_{s p i n}=\frac{-e}{m} \vec{S}
$$

So the corresponding operator is

$$
\hat{\mu}_{\text {spin }}=\frac{-e}{m} \hat{S}
$$

Then the term this effect adds to the Hamiltonian is

$$
\hat{H}^{Z}=-\hat{\mu}_{e} \cdot \vec{B}_{e x t}=-\left(\hat{\mu}_{\text {orbit }}+\hat{\mu}_{\text {spin }}\right) \cdot \vec{B}_{e x t}=\frac{e}{2 m}(\hat{L}+2 \hat{S}) \cdot \vec{B}_{e x t}
$$

In case you're keeping track, we've added in three 'perturbations' to the simple Hamiltonian: some relativistic tweaks to the kinetic energy and coulombic potential energy and now the interaction with an external magnetic field. That brings the Hamiltonian up to

So, we want an approximate expression for the energies that the Hydrogen atom can have.
If one of the 'perturbations' is much smaller than the other, then we can think of it as merely a perturbation to the larger perturbation. In broad strokes, the game is to start with the exact solutions to the simple Hamiltonian, $\hat{H}^{o}$, figure out a linear combination of them that is 'good' for the largest perturbation (that have expectation values that do not change over time due to the perturbation / are good approximations for eigen states of the perturbed Hamiltonian), and then approximate that the smaller perturbation will leave the system in those states, but affect their energies. That is

$$
\begin{aligned}
& \hat{H}=\hat{H}^{o}+\hat{H}^{\prime b i g g e r}+\hat{H}^{\prime \text { smaller }} \\
& E \approx E^{o}+\left\langle\psi_{\text {good.for.big }}\right| \hat{H}^{\prime b i g g e r}+\hat{H}^{\prime \text { smaller }}\left|\psi_{\text {good.for.big }}\right\rangle
\end{aligned}
$$

For example, if we started with a particle in an infinite square well,

$\mathrm{E}_{15}=0.0547141893504$
and we added in two perturbations: raising the floor on the left side and tipping the whole floor.
Here are the effects individually: (I've made them pretty large for mere "perturbations" just so we can see their affects):


$\mathrm{E}_{15 \text { slope }}=\mathrm{E}_{15}+\mathrm{E}^{\prime}{ }_{15 \text { slope }}$
$\mathrm{E}^{\prime}{ }_{15 \text { slope }}=0.05379$
$\mathrm{E}_{15 \text { step }}=\mathrm{E}_{15}+\mathrm{E}_{15 \text { step }}$
(0.10850603833)
$E_{15 \text { step }}=0.04027$
(0.0949869666563)

Now, the slope were the dominant perturbation, we'd get wavefunctions and energies that were just minor tweaks off of those; if the step where the dominant perturbation, we'd get wavefunctions and energies that were just minor tweaks off of those:

$\mathrm{E}=\mathrm{E}_{15}+\mathrm{E}^{\prime}{ }_{15 \text { slope }}+0.067 * \mathrm{E}^{\prime}{ }_{15 \text { step }}$ (0.111192092033)
here $\mathrm{v}(\mathrm{j})=0.1^{*} \mathrm{vstep}(\mathrm{j})+\operatorname{vslope}(\mathrm{j})$

$\mathrm{E}=\mathrm{E}_{15}+\mathrm{E}^{\prime}{ }_{15 \text { step }}+0.078^{*} \mathrm{E}^{\prime}{ }_{15 \text { step }}$
(0.0991631736795)

$$
\mathrm{v}(\mathrm{j})=\operatorname{vstep}(\mathrm{j})+0.1 * \operatorname{vslope}(\mathrm{j})
$$

However, if the two effects are of equal strength, then there's no approximating one as a minor tweak on top of the other:

$\mathrm{E}=\mathrm{E}_{15}+0.93^{*}\left(\mathrm{E}^{\prime}{ }_{15 \text { slope }}+\mathrm{E}^{\prime}{ }_{15 \text { step }}\right)$
(0.1417546232)

Similarly, if the two relativistic correction and the Zeeman effect are of equal strength, we'll have to treat them on equal footing.

### 6.4.2 Strong-Field Zeeman Effect

I'm going to look at the strong and weak field cases in the opposite order from what Griffiths does since the Strong-Field case is simpler.

I dont really understand how to come up with all the different states. (that might be something I've forgotten) Casey P

## "Still confused about how to decide which quantum numbers are the "good" ones."

## Spencer

I am confused about this too. Jessica
I would like clarification on this too. Gigja
Now, if the Zeeman Effect is the stronger of the two, then we want to use 'good' eigenvectors according to $i t$, essentially allowing that $J$ needn't be conserved since the system isn't isolated. Instead, the states for whom $L$ and $S$ are of fixed alignment with the field / the z-axis are the 'good states' whose energies evolve smoothly as we turn on the magnetic field: $\left|n, l, m_{l}, s, m_{s}\right\rangle$ are the states we'd use. That's fine, those are essentially the states we'd come up with for the Hydrogen atom in the first place, it was through the Clebsch-Gordan table that we were able to construct states with set $j$ values (treating $l$ and $s$ as independent angular momentum freedoms).

So

$$
\begin{aligned}
& E^{Z} \approx\left\langle n, l, m_{l}, s, m_{s}\right| \frac{e}{2 m}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) B_{e x t}\left|n, l, m_{l}, s, m_{s}\right\rangle=\frac{e}{2 m}\left(m_{l} \hbar+2 m_{s} \hbar\right) B_{e x t} \\
& E^{Z}=\frac{e \hbar B_{\text {ext }}}{2 m}\left(m_{l}+2 m_{s}\right)
\end{aligned}
$$

That said, we should really go back and rethink the spin-orbit correction in terms of this basis set.

## "Can we go over how griffith's gets 6.81" Jessica

$$
\begin{aligned}
& E^{(1) s o} \approx\left\langle n, l, m_{l}, s, m_{s}\right| \hat{H}^{\prime s o}\left|n, l, m_{l}, s, m_{s}\right\rangle=\left\langle n, l, m_{l}, s, m_{s}\right| \frac{e^{2}}{8 \pi \varepsilon_{o}} \frac{\hat{S} \cdot \hat{L}}{(m c)^{2} r^{3}}\left|n, l, m_{l}, s, m_{s}\right\rangle \\
& =\frac{e^{2}}{8 \pi \varepsilon_{o}(m c)^{2}}\left\langle n, l, m_{l}, s, m_{s}\right| \frac{\hat{S}_{x} \hat{L}_{x}+\hat{S}_{y} \hat{L}_{y}+\hat{S}_{z} \hat{L}_{z}}{r^{3}}\left|n, l, m_{l}, s, m_{s}\right\rangle
\end{aligned}
$$

For the denominator, the same argument applies as did before,

$$
\left\langle\frac{1}{r^{3}}\right\rangle=\frac{1}{l\left(l+\frac{1}{2}\right)(l+1) n^{3} a^{3}}
$$

But now, the x and y components off the spin and orbital angular momentum are not defined; indeed, there's no reason for the system to prefer one orientation or another, and we have two independent a cones of possible $S$ and $L$ values, visualized by


So we don't really have to do the integrals to find the expectation values for the x and y components of the angular momenta, they're going to average out to

$$
\left\langle\hat{S}_{x}\right\rangle=\left\langle\hat{L}_{x}\right\rangle=\left\langle\hat{S}_{y}\right\rangle=\left\langle\hat{L}_{y}\right\rangle=0
$$

Which just leaves

$$
\left\langle\hat{S}_{z} \hat{L}_{z}\right\rangle=m_{s} \hbar m_{l} \hbar
$$

So, in the strong-field limit,

$$
E^{(1) s o}=\frac{e^{2}}{8 \pi \varepsilon_{o}(m c)^{2}} \frac{m_{s} m_{l} \hbar^{2}}{l\left(l+\frac{1}{2}\right)(l+1) n^{3} a^{3}}
$$

Or using $E_{o}^{o}=-\frac{1}{2} \frac{e^{2}}{4 \pi \varepsilon_{o} a} \frac{1}{n^{2}}$ to write this a little neater

$$
E^{(1) s o}=-E_{n}^{0}\left(\frac{\hbar}{m c a}\right)^{2} \frac{m_{s} m_{l}}{l\left(l+\frac{1}{2}\right)(l+1) n}
$$

For that matter, if you write out a in terms of fundamental constants and the fine-structure constant in terms of fundamental constants, you'll see that

$$
\alpha=\frac{\hbar}{m c a}
$$

So,

$$
E^{(1) s o}=-E_{n}^{0} \alpha^{2} \frac{m_{s} m_{l}}{l\left(l+\frac{1}{2}\right)(l+1) n}
$$

1. Math: 6.22: starting with 6.80 use $6.57,6.61,6.64$, and 6.81 to arrive at 6.82 .

So the full Fine-Splitting energy in this case is

$$
\begin{aligned}
E^{(1) f i n e} & =E^{(1) r}+E^{(1) s o} \\
E^{(1) f i n e} & =-\frac{\left(E_{n}^{o}\right)^{2}}{2 m c^{2}}\left(\frac{4 n}{\left(l+\frac{1}{2}\right)}-3\right)-E_{n}^{0} \alpha^{2} \frac{m_{s} m_{l}}{l\left(l+\frac{1}{2}\right)(l+1) n}
\end{aligned}
$$

Which requires only a little more combining and regrouping of constants to get Griffiths’ expression

$$
E^{(1) \text { fine }}=\frac{E_{o}^{o} \mid \alpha^{2}}{n^{3}}\left(\frac{3}{4 n}-\frac{l(l+1)-m_{s} m_{l}}{l\left(l+\frac{1}{2}\right)(l+1)}\right)
$$

### 6.4.1 Weak-Field Zeeman Effect

Now, if the external magnetic field is quite weak, our system is nearly isolated, so the total angular momentum (both magnitude, quantized by $j$ and direction, quantized by $m_{j}$ ) must remain nearly constant. Furthermore, we'd found that $S$ and $L$ commuted with the spin-orbit energy term, so $s$ and $l$ (though not $m_{s}$ and $m_{l}$ ) remain constant too.

So, the approximation we'll make is that the wavefunctions that were good for the spin-orbit are also still pretty good when we have a weak enough external magnetic field. That's tantamount to approximating that the total angular momentum is still conserved (it isn't perfectly, but we're just after approximate energies after all.)

$$
E^{z} \approx\left\langle\psi_{n, j, m j, l, s}\right| \hat{H}^{Z}\left|\psi_{n, j, m j, l, s}\right\rangle=\left\langle\psi_{n, j, m j, l, s}\right| \frac{e}{2 m}(\hat{L}+2 \hat{S}) \cdot \vec{B}_{e x t}\left|\psi_{n, j, m j, l, s}\right\rangle
$$

Defining the z direction to be that along which $B_{\text {ext }}$ points, just the z -components of the two operators survive the dot product (and using the more concise notation for the states)

$$
E^{Z} \approx\langle n, j, m j, l, s| \frac{e}{2 m}\left(\hat{L}_{z}+2 \hat{S}_{z}\right) B_{e x t}|n, j, m j, l, s\rangle
$$

Unfortunately, the wavefunctions we're dealing with don't have constant / well-defined $\mathrm{L}_{z}$ or $\mathrm{L}_{\mathrm{s}}$ values. That is to say, we're approximating the system as isolated so the total angular momentum is conserved (both magnitude, $j$, and direction, $m_{j}$ ). We can take a step inte right direction by rewriting

$$
\left(\hat{L}_{z}+2 \hat{S}_{z}\right)=\hat{J}_{z}+\hat{S}_{z}
$$

So we have
$E^{Z} \approx \frac{e}{2 m}\left\langle n, j, m_{j}, l, s\right|\left(\hat{J}_{z}+\hat{S}_{z}\right)\left|n, j, m_{j}, l, s\right\rangle B_{e x t}=\frac{e B_{e x t}}{2 m}\left(\left\langle n, j, m_{j}, l, s\right| \hat{J}_{z}\left|n, j, m_{j}, l, s\right\rangle+\left\langle n, j, m_{j}, l, s\right| \hat{S}_{z} \mid n, j, m_{j}, l,\right.$,
$E^{Z} \approx \frac{e B_{e x t}}{2 m}\left(\left\langle n, j, m_{j}, l, s\right| m_{j} \hbar\left|n, j, m_{j}, l, s\right\rangle+\left\langle n, j, m_{j}, l, s\right| \hat{S}_{z}\left|n, j, m_{j}, l, s\right\rangle\right)$
$E^{Z} \approx \frac{e B_{e x t}}{2 m}\left(m_{j} \hbar+\left\langle n, j, m_{j}, l, s\right| \hat{S}_{z}\left|n, j, m_{j}, l, s\right\rangle\right)$
It turns out that, while $m_{s}$ isn't well defined / constant, we can still reason out what its expectation value will be, and that's generally what the inner product gets us (not what it will be every moment you measure, but what it is on average).

If the length and direction of $J$ are set, and the lengths of $L$ and $S$ are set, and $J=L+S$, then we have a cone of possible $S$ and $L$ values, visualized by


On average, whatever components S has that are perpendicular to J average out to 0 , leaving only its projection in the J direction. That is to say
$\vec{S}_{\text {ave }}=\left(\vec{S} \cdot \frac{\vec{J}}{|J|}\right) \frac{\vec{J}}{|J|}$ (where the ratios $\frac{\vec{J}}{|J|}$ are what we'd traditionally call J-hat, except we've been using the hat to denote operators).

So

$$
\left\langle\hat{S}_{z}\right\rangle=\left\langle\left(\frac{\hat{S} \cdot \hat{J}}{\hat{J}^{2}}\right) \hat{J}_{z}\right\rangle=\frac{\langle\hat{S} \cdot \hat{J}\rangle}{j(j+1) \hbar^{2}} m_{j} \hbar
$$

To rephrase $\hat{S} \cdot \hat{J}$, we can use

$$
L^{2}=(\vec{J}-\vec{S})^{2}=J^{2}+S^{2}-2 \vec{S} \cdot \vec{J} \Rightarrow \vec{S} \cdot \vec{J}=\frac{J^{2}+S^{2}-L^{2}}{2}
$$

All of which have well-defined, constant expectation values.

$$
\left\langle\hat{S}_{z}\right\rangle=\frac{\left\langle J^{2}+S^{2}-L^{2}\right\rangle}{2 j(j+1) \hbar^{2}} m_{j} \hbar=\frac{j(j+1) \hbar^{2}+s(s+1) \hbar^{2}-l(l+1) \hbar^{2}}{2 j(j+1) \hbar^{2}} m_{j} \hbar
$$

Of course, s isn't much of a variable, $\mathrm{s}=1 / 2$, so $1 / 2(1 / 2+1)=3 / 4$

$$
\left\langle\hat{S}_{z}\right\rangle=\frac{\left\langle J^{2}+S^{2}-L^{2}\right\rangle}{2 j(j+1) \hbar^{2}} m_{j} \hbar=\frac{j(j+1)-l(l+1)+\frac{3}{4}}{2 j(j+1)} m_{j} \hbar
$$

There we have it,

$$
\begin{aligned}
& E^{Z} \approx\left\langle n, j, m_{j}, l, s\right| \frac{e}{2 m}(\hat{L}+2 \hat{S}) \cdot \vec{B}_{e x t}\left|n, j, m_{j}, l, s\right\rangle \\
& E^{Z} \approx \frac{e B_{e x t}}{2 m}\left(1+\frac{j(j+1)-l(l+1)+\frac{3}{4}}{2 j(j+1)}\right) m_{j} \hbar
\end{aligned}
$$

Problem 6.21: for the eight $\mathrm{n}=2$ states, $\left|2, j, m_{j}, l, s\right\rangle$, determine the $\mathrm{E}_{\mathrm{z}}$ values and create a diagram like Figure 6.11 with slopes labeled.

Let's have a start at that. What are the eight states? Well, the freedoms are
Since $l<n$ we have $l=1$ or 0
And for $l=1$, there's the question of whether $s$ is aligned with it or anti-aligned with it.

and then there's the question of how much $j$ is aligned with the magnetic field / z-axis.
For $\mathrm{j}=3 / 2$, there are 4 choices:


### 6.4.3 Intermediate-Field Zeeman Effect

Now we really to have to bite the bullet and deal with the fact that we have degenerate energies. We'll want to work out all the elements of the W matrix as discussed in the section on degenerate states. $W_{a b}=\left\langle\psi_{a}\right| H^{\prime}\left|\psi_{b}\right\rangle$. Thanks to the Clebsch-Gordan table, we can express the wavefunctions either in terms of $j$ and $m_{j}$ or in terms of $l, m_{l}, s, m_{s}$. So, we have

$$
|\psi\rangle_{a}=\left|j, m_{j}\right\rangle_{a}=c_{1, a}\left|l, m_{l l}\right\rangle_{1 a}\left|s, m_{s s}\right\rangle_{1 a}+c_{2}\left|l, m_{l}\right\rangle_{2 a}\left|s, m_{s s}\right\rangle_{2 a}+\ldots
$$

Then

$$
W_{a b}=\left\langle\psi_{a}\right| H^{\prime}\left|\psi_{b}\right\rangle=\left\langle\psi_{a}\right| H^{\prime \text { fine }}+H^{\prime Z}\left|\psi_{b}\right\rangle=\left\langle\psi_{a}\right| H^{\prime \text { fine }}\left|\psi_{b}\right\rangle+\left\langle\psi_{a}\right| H^{\prime Z}\left|\psi_{b}\right\rangle=W_{a b}^{\text {fine }}+W_{a b}^{Z}
$$

Let's see how one would build the W matrix Griffiths gives.
"In finding H'z and H'fs is it appropriate to use eq6.76 and eq.6.82 or is there some other way?" Kyle B,
Looking at just a couple of terms will give the idea of how it works.

$$
W_{7,8}^{Z}=\left\langle\psi_{7}\right| H^{\prime Z}\left|\psi_{8}\right\rangle
$$

Since

$$
H^{\prime z}=\frac{e B_{e x t}}{2 m} \hat{L}_{z}+2 \hat{S}_{z}
$$

We'll want to express the two states in terms of $L_{z}$ and $S_{z}$ 's (ortho-normal) eigen vectors.

$$
W_{7,8}^{Z}=\left\langle\psi_{7}\right| H^{\prime Z}\left|\psi_{8}\right\rangle
$$

Where

$$
\begin{aligned}
& H^{\prime Z}\left|\psi_{8}\right\rangle=\frac{e B_{e x t}}{2 m}\left(\hat{L}_{z}+2 \hat{S}_{z}\right)\left(-\sqrt{\frac{2}{3}}|1,-1\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle+\sqrt{\frac{1}{3}}|1,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right) \\
& =\frac{e B_{e x t}}{2 m}\left[\left(-\sqrt{\frac{2}{3}}\right)\left((-\hbar)+2\left(\frac{1}{2} \hbar\right)\right)|1,-1\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle+\left(-\sqrt{\frac{1}{3}}\right)\left((0)+2\left(-\frac{1}{2} \hbar\right)\right)|1,0\rangle\left\langle\frac{1}{2},-\frac{1}{2}\right\rangle\right] \\
& =\frac{e B_{e x t}}{2 m}\left[\left(-\sqrt{\frac{2}{3}}\right)(0)|1,-1\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle+\left(\sqrt{\frac{1}{3}}\right)(-\hbar)|1,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle\right] \\
& =-\sqrt{\frac{1}{3}} \hbar \frac{e B_{e x t}}{2 m}|1,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle
\end{aligned}
$$

So,

$$
\begin{aligned}
& W_{7,8}^{Z}=\left\langle\psi_{7}\right| H^{\prime Z}\left|\psi_{8}\right\rangle=\left(\sqrt{\frac{1}{3}}\langle 1,-1|\left\langle\frac{1}{2}, \frac{1}{2}\right|+\sqrt{\frac{2}{3}}\langle 1,0|\left\langle\frac{1}{2},-\frac{1}{2}\right|\right)\left(-\sqrt{\frac{1}{3}} \hbar \frac{e B_{e x t}}{2 m}\right)|1,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle \\
& W_{7,8}^{Z}=-\sqrt{\frac{1}{3}}\langle 1,-1|\left\langle\frac{1}{2}, \frac{1}{2}\right| \sqrt{\frac{1}{3}} \hbar \frac{e B_{e x t}}{2 m}|1,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle-\sqrt{\frac{2}{3}}\langle 1,0|\left\langle\frac{1}{2},-\frac{1}{2}\right| \sqrt{\frac{1}{3}} \hbar \frac{e B_{e x t}}{2 m}|1,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle \\
& W_{7,8}^{Z}=-\frac{1}{3} \hbar \frac{e B_{\text {ext }}}{2 m}\langle\left.\underbrace{}_{0}\langle 1,-1|\left\langle\frac{1}{2}, \left.\frac{1}{2} \right\rvert\, 1,0\right\rangle \right\rvert\, \frac{1}{2},-\frac{1}{2}\rangle-\frac{\sqrt{2}}{3} \hbar \frac{e B_{e x t}}{2 m} \underbrace{\langle 1,0|\left\langle\frac{1}{2},-\frac{1}{2} \| 1,0\right\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle}_{1} \underbrace{2 m}_{1}=-\frac{\sqrt{2}}{3} \hbar \frac{e B_{e x t}}{2 m} W_{7,8}^{Z}
\end{aligned}
$$

As for

$$
W_{7,8}^{\text {fine }}=\left\langle\psi_{7}\right| H^{\prime \text { fine }}\left|\psi_{8}\right\rangle
$$

It's easiest to express the wavefunctions in terms of the $j, m_{j}$ basis set since then it's easy to express the energies:

$$
\begin{aligned}
& H^{\prime \text { fine }}\left|j, m_{j}\right\rangle=\frac{\left(E_{o}\right)^{2}}{2 m c^{2} n^{4}}\left(3-\frac{4 n}{j+\frac{1}{2}}\right)\left|j, m_{j}\right\rangle \\
& H^{\prime \text { fine }}\left|\psi_{8}\right\rangle=\frac{\left(E_{2}\right)^{2}}{2 m c^{2} 2^{4}}\left(3-\frac{4 \cdot 2}{\frac{1}{2}+\frac{1}{2}}\right)\left|\frac{1}{2},-\frac{1}{2}\right\rangle=\frac{\left(E_{o}\right)^{2}}{2 m c^{2} 16}(3-8)\left|\frac{1}{2},-\frac{1}{2}\right\rangle=-\frac{\left(E_{o}\right)^{2}}{m c^{2} 32} 5\left|\frac{1}{2},-\frac{1}{2}\right\rangle
\end{aligned}
$$

However, all this work is for nothing because

$$
W_{7,8}^{\text {fine }}=\left\langle\frac{3}{2},-\frac{1}{2}\right|-\frac{\left(E_{o}\right)^{2}}{m c^{2} 32} 5\left|\frac{1}{2},-\frac{1}{2}\right\rangle=-\frac{\left(E_{o}\right)^{2}}{m c^{2} 32} 5\left\langle\frac{3}{2},-\frac{1}{2} \| \frac{1}{2},-\frac{1}{2}\right\rangle=0
$$

So,

$$
W_{7,8}=W_{7,8}^{\text {fine }}+W_{7,8}^{Z}=0-\frac{\sqrt{2}}{3} \hbar \frac{e B_{e x t}}{2 m}
$$

That's the $-W_{7,8}^{Z}=\frac{\sqrt{2}}{3} \beta$ that Griffiths has in the 7,8 (and the 8,7 ) location of the -W matrix.

As for the energies, they'd be gotten from the 'characteristic equation'; however, since the matrix is diagonal for the first four states, it's easy to read the energies right off the diagonal.

$$
E_{3}^{\prime(1)}=W_{3,3}=W_{3,3}^{Z}+W_{3,3}^{\text {fine }}=-(\gamma-2 \beta)=-\gamma+2 \beta
$$

For the next two, this could be broken down into the a sub matrix, and you can find $i t$ 's characteristic equation yields the two energy corrections.

### 6.5 Hyperfine Splitting (of ground state)

Even without our impose an external magnetic field or transforming to a co-orbiting frame, we should see that the electron is subject to a magnetic field due to the circulation of the charge within the nucleus which is, in this simple case, the proton (thus the two $+2 / 3 \mathrm{e}$ and the one $-1 / 3 \mathrm{e}$ charged quarks within it ). Its magnetic dipole moment can similarly be related to its spin, though there's a bit of internal detail that we'll sweep under the rug with a "gyromagnetic ratio" $g_{p}=$ 5.59.

$$
\hat{\mu}_{p}=\frac{g_{p} e}{2 m} \hat{S}_{p}
$$

Without delving too deeply into Griffiths' other text, we simply quote that the magnetic field due to a magnetic dipole is

$$
\vec{B}_{p}=\frac{1}{4 \pi \varepsilon_{o} c^{2} r^{3}}\left[3\left(\vec{\mu}_{p} \cdot \hat{r}\right) \hat{r}-\vec{\mu}_{p}\right]+\frac{2}{3 \varepsilon_{o} c^{2}} \vec{\mu}_{p} \delta^{3}(\vec{r}) \quad \text { (where I've replace } \mu_{\mathrm{o}} \text { with } 1 /\left(\varepsilon_{0} \mathrm{c}^{2}\right) \text { ). }
$$

So the shape of the field is the familiar loops about a current loop.
So, the energy associated with the electron's spin interacting with the proton's spin is

$$
E^{e, p}=-\vec{\mu}_{e} \cdot \vec{B}_{p}=-\frac{1}{4 \pi \varepsilon_{o} c^{2} r^{3}}\left[3\left(\vec{\mu}_{p} \cdot \hat{r}\right)\left(\vec{\mu}_{e} \cdot \hat{r}\right)-\vec{\mu}_{e} \cdot \vec{\mu}_{p}\right]+\frac{2}{3 \varepsilon_{o} c^{2}} \vec{\mu}_{e} \cdot \vec{\mu}_{p} \delta^{3}(\vec{r})
$$

Now, it's unclear to me how the electron's orbit would interact with the proton's spin, but it does seem that, for $l$ not equal to 0 , there would be a contribution. In any event, Griffiths focuses on the ground state, so $l=0$. In that case,

$$
\hat{\mu}_{e_{1}}=\frac{-e}{m} \hat{S}
$$

So, the term in the Hamiltonian would be

$$
\hat{H}_{1}^{e, p}=\frac{g_{p} e^{2}}{2 m_{e} m_{p}}\left(\frac{1}{4 \pi \varepsilon_{o} c^{2} r^{3}}\left[3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right]+\frac{2}{3 \varepsilon_{o} c^{2}} \hat{S}_{e} \cdot \hat{S}_{p} \delta^{3}(\vec{r})\right)
$$

So,

$$
\begin{aligned}
& E_{1}^{(1) e, p}=\left\langle\Psi_{1}\right| \hat{H}_{1}^{e, p}\left|\Psi_{1}\right\rangle \\
& E_{1}^{(1) e, p}=\frac{g_{p} e^{2}}{2 m_{e} m_{p}}\left\langle\left.\Psi_{1}\left(\frac{1}{4 \pi \varepsilon_{o} c^{2} r^{3}}\left[3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right]+\frac{2}{3 \varepsilon_{o} c^{2}} \hat{S}_{e} \cdot \hat{S}_{p} \delta^{3}(\vec{r})\right) \right\rvert\, \Psi_{1}\right\rangle \\
& E_{1}^{(1) e, p}=\frac{g_{p} e^{2}}{2 m_{e} m_{p}}\left(\frac{1}{4 \pi \varepsilon_{o} c^{2}}\left\langle\Psi_{1}\right| \frac{\left.3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right]}{r^{3}}\left|\Psi_{1}\right\rangle+\frac{2}{3 \varepsilon_{o} c^{2}}\left\langle\Psi_{1}\right| \hat{S}_{e} \cdot \hat{S}_{p} \delta^{3}(\vec{r})\left|\Psi_{1}\right\rangle\right)
\end{aligned}
$$

Now, since we're focusing on the ground state, we can get explicit about these inner products.

$$
\begin{aligned}
& \left\langle\Psi_{1}\right| \frac{\left[3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right]}{r^{3}}\left|\Psi_{1}\right\rangle=\int_{0}^{2 \pi \pi} \int_{0}^{\infty} \int_{0}^{\infty} \frac{e^{-2 r / a}}{\pi a^{3} r^{3}} r^{2}\left[3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right] d r \sin \theta d \theta d \phi \\
& \frac{1}{\pi a^{3}} \int_{0}^{\infty} \frac{e^{-2 r / a}}{r} d r \int_{0}^{2 \pi \pi} \int_{0}\left[3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right] \sin \theta d \theta d \phi \\
& =\frac{1}{\pi a^{3}} \int_{0}^{\infty} \frac{e^{-2 r / a}}{r} d r\left[\int_{0}^{2 \pi \pi} 3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right) \sin \theta d \theta d \phi-\int_{0}^{2 \pi \pi} \int_{0}^{2}\left[3\left(\hat{S}_{p} \cdot \hat{r}\right)\left(\hat{S}_{e} \cdot \hat{r}\right)-\hat{S}_{e} \cdot \hat{S}_{p}\right] \sin \theta d \theta d \phi\right] \\
& =\frac{1}{\pi a^{3}} \int_{0}^{\infty} \frac{e^{-2 r / a}}{r} d r\left[4 \pi \hat{S}_{e} \cdot \hat{S}_{p}-\int_{0}^{2 \pi \pi} \int_{0}^{\infty} \hat{S}_{e} \cdot \hat{S}_{p} \sin \theta d \theta d \phi\right]=\frac{1}{\pi a^{3}} \int_{0}^{\infty} \frac{e^{-2 r / a}}{r} d r\left[4 \pi \hat{S}_{e} \cdot \hat{S}_{p}-4 \pi \hat{S}_{e} \cdot \hat{S}_{p}\right]=0
\end{aligned}
$$

As for doing away with the $1 / \mathrm{r}$ term, while this does indeed blow up at $r=0$, realy this integral should be done for $\mathrm{r}>0$; the delta function handles at $\mathrm{r}=0$. So the absolute 0 in the denominator would kill off this $1 / \mathrm{r}$ that approaches but never quite reaches $1 / 0$.

So, all we're left with is the delta-function term.

$$
E_{1}^{(1) e, p}=\frac{g_{p} e^{2}}{3 \varepsilon_{o} c^{2} m_{e} m_{p}}\left\langle\Psi_{1}\right| \hat{S}_{e} \cdot \hat{S}_{p} \delta^{3}(\vec{r})\left|\Psi_{1}\right\rangle
$$

Now, what is $\hat{S}_{e} \cdot \hat{S}_{p}$ ?
We can do a similar trick as when confronted with the other dot products of spins:
For the proton + electron system,

$$
\begin{aligned}
& \vec{S} \equiv \hat{S}_{e}+\hat{S}_{p} \Rightarrow S^{2}=S_{e}^{2}+S_{p}^{2}+2 \hat{S}_{e} \cdot \hat{S}_{p} \Rightarrow \hat{S}_{e} \cdot \hat{S}=\frac{1}{2}\left(S^{2}-S_{e}^{2}-S_{p}^{2}\right) \\
& E_{1}^{(1) e, p}=\frac{g_{p} e^{2}}{6 \varepsilon_{o} c^{2} m_{e} m_{p}}\left\langle\Psi_{1}\right|\left(s(s+1) \hbar^{2}-s_{e}\left(s_{e}+1\right) \hbar^{2}-s_{p}\left(s_{p}+1\right) \hbar^{2}\right) \delta^{3}(\vec{r})\left|\Psi_{1}\right\rangle
\end{aligned}
$$

And since the electron and proton are both spin $1 / 2$, that cleans up to

$$
E_{1}^{(1) e, p}=\frac{g_{p} e^{2}\left(s(s+1)-\frac{3}{2}\right) \hbar^{2}}{6 \varepsilon_{o} c^{2} m_{e} m_{p}}\left\langle\Psi_{1}\right| \delta^{3}(\vec{r})\left|\Psi_{1}\right\rangle=\frac{g_{p} e^{2}\left(s(s+1)-\frac{3}{2}\right) \hbar^{2}}{6 \varepsilon_{o} c^{2} m_{e} m_{p}}\left|\Psi_{1}(0)\right|^{2}=\frac{g_{p} e^{2}\left(s(s+1)-\frac{3}{2}\right) \hbar^{2}}{6 \varepsilon_{o} c^{2} m_{e} m_{p} \pi a^{3}}
$$

Now, this is a system of two spin- $1 / 2$ particles, so either the two spins aligned in one of the three triplet states, giving $\mathrm{s}=1$; or their anti-aligned giving $\mathrm{s}=0$.

$$
E_{1}^{(1) e, p}=\frac{g_{p} e^{2} \hbar^{2}}{3 \varepsilon_{o} c^{2} m_{e} m_{v} \pi a^{3}}\left\{\begin{array}{lr}
\frac{1}{4} & \text { triplet } \\
-\frac{3}{4} & \text { singlet }
\end{array}=\Delta E \begin{cases}\frac{1}{4} & \text { triplet } \\
-\frac{3}{4} & \text { singlet }\end{cases}\right.
$$

Homework note: this is a more accurate expression than equation 6.92 in that this can readily be modified to handle other hydrogen-like atoms as in the homework. For that, note a more accurate definition for $a$ would be $a \equiv \frac{4 \pi \varepsilon_{o} \hbar^{2}}{e^{2}}\left(\frac{1}{m_{p}}+\frac{1}{m_{e}}\right)$. This uses the 'reduced mass' and comes from allowing that both the electron and the proton are free to move. This becomes important when you start determining the energy splitting for exotic hydrogen-like "atoms."

