| 12 | Wed.,11/19 <br> Fri., $11 / 21$ | 6.2 Time-independent Perturbation, degenerate <br> 6.3 Fine Structure of Hydrogen | Daily 12.W <br> Daily 12.F |
| :---: | :--- | :--- | :--- | :--- | :--- |
| 13 | Mon., $11 / 24$ <br>  <br> Tues. $11 / 25$ | 6.4-.5 Zeeman \& Hyper-fine | Daily 13.M <br> Weekly 13 |

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

## Equipment

- Griffith's text


## Check dailies

## Announcements

Daily 12.F Friday 11/21 Griffiths 6.3 Fine Structure of Hydrogen

1. Math: 6.11 a

## 6. Time-Independent Perturbation Theory

### 6.3 The Fine Structure of Hydrogen

Today, we'll apply Perturbation Theory to refine our understanding of the Hydrogen atom / to explain subtler features in its spectrum. Of course, what we can quantitatively explain for Hydrogen, is then qualitatively understood for other atoms.

Griffiths lists some corrections and their orders of magnitude in Table 6.1 he expresses it as powers of the fine structure constant, $\alpha \equiv \frac{e^{2}}{4 \pi \varepsilon_{o} \hbar c} \approx \frac{1}{137.036}$

With Bohr energies (from just considering non-relativistic kinetic and Coulombic potential) on order of

$$
E^{o}=E_{B o h r} \sim \alpha^{2} m c^{2}
$$

The combined correction for $1^{\text {st }}$-order relativistic correction as well as the spin-orbit coupling is responsible for the "fine structure" in Hydrogen's spectrum, with energies on order of

$$
E_{\text {fine }} \sim \alpha^{4} m c^{2}
$$

Griffiths notes two more levels of correction, one that's best explained by QED (Quantum Electro Dynamics) - Lamb Shift, and one that comes from coupling between the nuclear and electronic spin - Hyper-fine Splitting.

We'll just focus on that most significant correction: the relativistic + spin-orbit coupling: the Fine Structure correction.

Griffiths' presentation of these two would make it seem merely coincidental that they are of the same order as each other. That's not the case. They both represent a $1^{\text {st }}$-order relativistic correction to the kinetic and the potential energy terms. Now, if we really wanted to get relativistic Quantum Mechanics correct, we'd be using the Dirac equation rather than making some corrections to the Schordinger equation, so perhaps it's not too surprising that we won't even get the $1^{\text {st }}$ order correction completely correct - a 'fudge factor' of order 2 will arise.

Before we delve into the, we can look to classical mechanics to see that these corrections might be called for (we always build the Schrodinger equation out of analogy with the classical equations, so this seems reasonable). Classically, we know relativistic corrections become significant as speeds approach the speed of light; factors of v/c appear in relativistically correct expressions that don't in the familiar slow-speed approximate equations. So what would be v/c for an electron in a classical orbit with the average radii and angular momenta we've determined?

$$
\begin{aligned}
& \text { Classically } \mathrm{L}=\mathrm{mvr} \text { so } \mathrm{v}=\mathrm{L} /(\mathrm{mr}) \text {, so } \\
& \frac{v}{c}=\frac{L /(m r)}{c}=\frac{\sqrt{l(l+1) \hbar}}{m c a}=\sqrt{l(l+1)} \frac{\left(1.05 \times 10^{-34} \mathrm{Js}\right)}{\left(9.11 \times 10^{-31} \mathrm{~kg}\right)\left(3 \times 10^{8} \mathrm{~m} / \mathrm{s}\right)\left(5.29 \times 10^{-11} \mathrm{~m}\right)}=7.26 \times 10^{-3}
\end{aligned}
$$

So, almost $1 \%$ of the speed of light. So, relativistic corrections will be small, but if we're good, noticeable.

### 6.3.1 The Relativistic Kinetic Correction

The Schrodinger Equation is constructed out of analogy with the classical energy expression. However, that's known to only be an approximation for slow (compared with $c$ ) speeds. At high speeds, a more accurate expression is necessary.

As you learned in Phys 231, one way of talking about it is that a particle has two forms of energy: kinetic and rest. So these two add up to the particle's total energy (potential is not included in a 'particle's energy' since it's a property of a system of particles, not the exclusive property of a single particle.)

So,

$$
E=T+E_{\text {rest }} \text { or, } T=E-E_{\text {rest }}
$$

Rest energy is the famous $E_{\text {rest }}=m c^{2}$
There are two equivalent ways of expressing particle energy; Griffiths goes to some pains to show their equivalency, but you've met them both before, so I'll just remind you:

$$
E=\sqrt{(p c)^{2}+\left(m c^{2}\right)^{2}}
$$

So then,

$$
T=\sqrt{(p c)^{2}+\left(m c^{2}\right)^{2}}-m c^{2}
$$

We arrive at the classical approximation by doing a power series expansion for small v/c, and keeping jus the first term. Now, we're looking for the next order correction.

$$
T=m c^{2}\left(\sqrt{\left(\frac{p}{m c}\right)^{2}+1}-1\right)=m c^{2}\left(0+\frac{1}{2}\left(\frac{p}{m c}\right)^{2}-\frac{1}{8}\left(\frac{p}{m c}\right)^{4}+\ldots\right)=\left(\frac{1}{2} \frac{p^{2}}{2 m}-\frac{1}{8} \frac{p^{4}}{m^{3} c^{2}}+\ldots\right)
$$

So, the perturbation would be

$$
\hat{H}^{\prime r}=-\frac{p^{4}}{8 m^{3} c^{2}}
$$

Then non-degenerate $1^{\text {stt }}$-order Perturbation Theory would give us

$$
E_{n}^{(1)^{r}}=\left\langle\psi_{n}^{o}\right| \hat{H}^{\prime}\left|\psi_{n}^{o}\right\rangle=\left\langle\psi_{n}^{o}\right|-\frac{p^{4}}{8 m^{3} c^{2}}\left|\psi_{n}^{o}\right\rangle=-\frac{\left\langle\psi_{n}^{o}\right| p^{4}\left|\psi_{n}^{o}\right\rangle}{8 m^{3} c^{2}}
$$

Now, you may well object 'but the Hydrogen atom isn't non-degenerate, thanks to $l$ and $m_{l}$ there are plenty of states with the same energies. So are the 'unperturbed' states the 'good' states that evolve in a smooth way when we 'turn on' this 'perturbation'? Well, applying Griffiths' theorem from last time, we can dream up a hermitian operator that commutes with this perturbation: $\mathrm{p}^{2}$, and of course the wavefunctions are eigenfunctions of that, so it looks promising.

From here, Griffiths argues that, as we'd defined in the WKB section, we can replace $\mathrm{p}^{2}$ via

$$
E_{n}^{o} \psi_{n}^{o}=\frac{\hat{p}^{2}}{2 m} \psi_{n}^{o}+V(r) \psi_{n}^{o} \Rightarrow \hat{p}^{2} \psi_{n}^{o}=2 m\left(E_{n}^{o}-V(r)\right) \psi_{n}^{o}
$$

But we have $p^{4} \psi_{n}^{o}$, what is that equivalent to?
It's tempting to say

$$
\hat{p}^{4} \psi_{n}^{o}=\left(2 m\left(E_{n}^{o}-V(r)\right)\right)^{2} \psi_{n}^{o}
$$

But if we're careful, what we have is

$$
\hat{p}^{4} \psi_{n}^{o}=\hat{p}^{2} 2 m\left(E_{n}^{o}-V(r)\right) \psi_{n}^{o}
$$

(My argument here follows a different path than the one Griffiths suggests, but it'll end at the same conclusion.) So now $\hat{p}^{2}$ is operating on $2 m\left(E_{n}^{o}-V(r)\right) \psi_{n}^{o}$ not on $\psi_{n}^{o}$ alone, and if we recall that $\hat{p}^{2}=-\hbar \nabla^{2}$, it does seem unlikely that it would commute with $V(r)$; in fact, as you will see (or have seen) in another of Griffiths' texts, $\hat{p}^{2}=-\hbar \nabla^{2} \frac{-e^{2}}{4 \pi \varepsilon_{o} r}=-\hbar \frac{e^{2}}{\varepsilon_{o}} \delta^{3}(r)$, that is, it's 0 everywhere but at the origin. So, we have

$$
\begin{aligned}
& \hat{p}^{4} \psi_{n}^{o}=\hat{p}^{2}\left(2 m\left(E_{n}^{o}-V(r)\right) \psi_{n}^{o}\right)=\hat{p}^{2}\left(2 m\left(E_{n}^{o}-V(r)\right)\right) \psi_{n}^{o}+2 m\left(E_{n}^{o}-V(r)\right) \hat{p}^{2} \psi_{n}^{o} \\
& =\hbar \frac{2 m e^{2}}{\varepsilon_{o}} \delta^{3}(r) \psi_{n}^{o}+\left(2 m\left(E_{n}^{o}-V(r)\right)\right)^{2} \psi_{n}^{o}
\end{aligned}
$$

So,

$$
E_{n}^{(1) r}=-\frac{\left\langle\psi_{n}^{o}\right| \hbar \frac{2 m e^{2}}{\varepsilon_{o}} \delta^{3}(r)\left|\psi_{n}^{o}\right\rangle+\left\langle\psi_{n}^{o}\right|\left(2 m\left(E_{n}^{o}-V\right)\right)^{2}\left|\psi_{n}^{o}\right\rangle}{8 m^{3} c^{2}}=-\frac{\hbar e^{2}\left\langle\psi_{n}^{o}\right| \delta^{3}(r)\left|\psi_{n}^{o}\right\rangle}{4 m^{2} c^{2} \varepsilon_{o}}-\frac{\left\langle\psi_{n}^{o}\right|\left(E_{n}^{o}-V\right)^{2}\left|\psi_{n}^{o}\right\rangle}{2 m c^{2}}
$$

Now, the inner product of the delta function at $\mathrm{r}=0$ vanishes for all but the $l=0$ states. Without doing the math, you can understand why this might be by looking at table 4.7 of some of the radial functions $\mathrm{R}(\mathrm{r})$ for Hydrogen; only the $l=0$ ones have terms that don' $t$ go proportional to at least $r$. So these don't die off at $r=0$ like the others do.

So, the following works exactly for $l$ not equal to 0 states. Problem 6.15 finishes off the argument for handling the $l=0$ states exactly (or, as 'exactly' as we're doing with this first-order correction.)

$$
\begin{aligned}
& E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left\langle\psi_{n}^{o}\right|\left(E_{n}^{o}\right)^{2}-2 E_{n}^{o} V+(V)^{2}\left|\psi_{n}^{o}\right\rangle \\
& E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left(\left(E_{n}^{o}\right)^{2}-2 E_{n}^{o}\left\langle\psi_{n}^{o}\right| V\left|\psi_{n}^{o}\right\rangle+\left\langle\psi_{n}^{o}\right|(V)^{2}\left|\psi_{n}^{o}\right\rangle\right)
\end{aligned}
$$

Then being explicit about our potential,

$$
\begin{aligned}
& E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left(\left(E_{n}^{o}\right)^{2}-2 E_{n}^{o}\left\langle\psi_{n}^{o}\right| \frac{-e^{2}}{4 \pi \varepsilon_{o} r}\left|\psi_{n}^{o}\right\rangle+\left\langle\left.\psi_{n}^{o}\left(\frac{-e^{2}}{4 \pi \varepsilon_{o} r}\right)^{2} \right\rvert\, \psi_{n}^{o}\right\rangle\right) \\
& E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left(\left(E_{n}^{o}\right)^{2}+\frac{e^{2} E_{n}^{o}}{2 \pi \varepsilon_{o}}\left\langle\psi_{n}^{o}\right| \frac{1}{r}\left|\psi_{n}^{o}\right\rangle+\left(\frac{e^{2}}{4 \pi \varepsilon_{o}}\right)^{2}\left\langle\left.\psi_{n}^{o}\left(\frac{1}{r^{2}}\right)^{2} \right\rvert\, \psi_{n}^{o}\right\rangle\right)
\end{aligned}
$$

As for the expectation values of $1 / \mathrm{r}$ and $1 / \mathrm{r}^{2}$,

1. Starting Weekly HW: 6.12
a. In the context of the derivation in which this result is used, you can approximate

$$
\langle E\rangle \approx\left\langle E^{o}\right\rangle
$$

In problem 6.12, you'll show that

$$
\left\langle\psi_{n}^{o}\right| \frac{1}{r}\left|\psi_{n}^{o}\right\rangle=\frac{1}{n^{2} a}
$$

It takes both problems 6.32 and 6.33 to find an expression for the average of $1 / \mathrm{r} 2$ though, so we'll simply quote that:

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

Putting them together gives

$$
E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left(\left(E_{n}^{o}\right)^{2}+\frac{e^{2} E_{n}^{o}}{2 \pi \varepsilon_{o}} \frac{1}{n^{2} a}+\left(\frac{e^{2}}{4 \pi \varepsilon_{o}}\right)^{2} \frac{1}{\left(l+\frac{1}{2}\right) n^{3} a^{2}}\right)
$$

Now, you may recall from when I first introduced Hydrogen's radial equation and made sense of $a$, I pointed out that

$$
E_{n}^{o}=-\frac{1}{2} \frac{e^{2}}{4 \pi \varepsilon_{o} a} \frac{1}{n^{2}}
$$

You'll see more of that in problem 6.12, but for now it's a convenient way to rephrase our expression for the $1^{\text {st }}$-order relativistic correction to the energy:

$$
\begin{aligned}
& E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left(\left(E_{n}^{o}\right)^{2}+4 E_{n}^{o} \frac{e^{2}}{8 \pi \varepsilon_{o} a} \frac{1}{n^{2}}+\left(\frac{e^{2}}{8 \pi \varepsilon_{o} a} \frac{1}{n^{2}}\right)^{2} \frac{4 n}{\left(l+\frac{1}{2}\right)}\right) \\
& E_{n}^{(1) r}=-\frac{1}{2 m c^{2}}\left(\left(E_{n}^{o}\right)^{2}+4 E_{n}^{o}\left(-E_{n}^{o}\right)+\left(E_{n}^{o}\right)^{2} \frac{4 n}{\left(l+\frac{1}{2}\right)}\right) \\
& E_{n}^{(1) r}=-\frac{\left(E_{n}^{o}\right)^{2}}{2 m c^{2}}\left(1-4+\frac{4 n}{\left(l+\frac{1}{2}\right)}\right) \\
& E_{n}^{(1) r}=-\frac{\left(E_{n}^{o}\right)^{2}}{2 m c^{2}}\left(\frac{4 n}{\left(l+\frac{1}{2}\right)}-3\right)
\end{aligned}
$$

Could we talk about why Griffiths using nondegenerate perturbation theory is "legitimate"?

### 6.3.2 The Relativistic Potential Correction: Spin-Orbit Coupling

Now, the right way to do this is to use the relativistically correct formulation of quantum mechanics, Dirac's equation. We're definitely not going there, but I'll quote the correct result:

$$
\hat{H}^{\prime s o}=\frac{\hat{S} \cdot \hat{L}}{2(m c)^{2}} \frac{1}{r} \frac{d}{d r} V(r)
$$

For the coulomb potential between the electron and proton, that becomes

$$
\hat{H}^{\prime s o}=\frac{e^{2}}{8 \pi \varepsilon_{o}} \frac{\hat{S} \cdot \hat{L}}{(m c)^{2} r^{3}}
$$

Now, it's still conceptually enlightening to consider the classical analog and where that would lead.

## Classically

## Rest-frame / Electric-field argument

In the rest frame, from the perspective of the proton, the classical analog would be that we have a spinning \& orbiting electron which is responsible for the electric field. However, the electric potential energy due to a moving charge isn't simply

$$
V=-\frac{1}{4 \pi x_{o}} \frac{e^{2}}{r} \text { rather, it's } V=-\frac{1}{4 \pi x_{o}} \frac{e^{2}}{r-\vec{r} \cdot \vec{v} / c} \text { (Griffiths' other text, 10.53) }
$$

On top of that, if we picture the spinning electron as a current loop, then if the circulation of that current loop is aligned with the circulation of its orbit, i.e., if $\hat{S} \cdot \hat{L}>0$, then it's actually moving faster when on the outer stretch of the loop since the orbital and spin speeds add. So the term that's subtracted off in the potential Alternatively, if they're anti-aligned, $\hat{S} \cdot \hat{L}<0$ then it's moving slower out there. So you get a qualitative hint that the potential energy will be different in these two cases. Of course, since we're trying to be relativistically correct, we'd need to add the two contributions to the velocities relativistically correctly, and we'll have different effects for the 'leading' edge of the current loop and 'trailing' edge of the current loop depending on how the spin and orbit are aligned.

Going down this path should get the right answer to within a factor of 2; that factor just can't be gotten by treating spin in this hokey 'pretend it's a current loop' way, but needs spin treated correctly, which only the real relativistic quantum mechanics does.

Orbiting frame - Magnetic-field argument
Given both the classical "fraud" and the quantum mechanical flaw, we can't call what follows a "derivation", but perhaps a "motivation."

The argument is that there is energy associated with the alignments of two current loops - if they aren't aligned, the net magnetic force due to one current loop on the other acts to rotate it into alignment. At least classically, the electron, with its spin would constitute one 'current loop,' while, from its perspective, the nucleus orbiting $i t$, would constitute the other. With the electron in the center of the nucleus's orbit, it's convenient to express the energy as

$$
E=-\vec{\mu} \cdot \vec{B}
$$

where $\vec{\mu}$ is the "magnetic moment" of the spinning electron

## Relating $\vec{\mu}$ and $S$

Now, classically, the magnetic moment for a current loop turns out being the current times the enclosed area. So, for a circular loop,
$\mu=I A=\frac{d q}{d t} \pi r^{2}$ or, phrased in terms of the total charge and the period of circulation,
$\mu=I A=\frac{q}{T} \pi r^{2}$
As the magnetic moment is something of a measure of the rate with which charge orbits, and angular momentum is something of a measure of the rate with which mass orbits, it shouldn't be surprising that the two are simply related.

$$
S=m v r=m \frac{2 \pi r}{T} r=m \frac{2 \pi}{T} r^{2}
$$

So, $\frac{\mu}{S}=\frac{\frac{q}{T} \pi r^{2}}{m \frac{2 \pi}{T} r^{2}}=\frac{q}{2 m} \Rightarrow \vec{\mu}=\frac{q}{2 m} \vec{S}$
If, say, it's an electron of charge that's circulating, with $q=-e$,

$$
\vec{\mu}=\frac{-e}{2 m} \vec{S}
$$

Note:
In a footnote, Griffiths points out the most direct argument form here is to observe that a moving magnetic dipole has an electric dipole moment, and that then interacts with the proton's electric field to tweak the energy.

However, a more transparent approach is to imagine things in the electron's perspective (all be it, a non-inertial, accelerating perspective.)

## Relating $B$ and $L$

The spinning electron
Classically, we'd think of an electron in its energy level with angular momentum $L$ as truly 'orbiting' the nucleus.

$$
L=m v r=m \frac{2 \pi r}{T} r=m \frac{2 \pi}{T} r^{2}
$$



Of course, from the electron's perspective, it's the nucleus that's orbiting it at this distance and with this period. Now, the nucleus has charge $+e$, so this constitutes a current loop, with +e passing every T :

$$
I=\frac{e}{T}
$$



Sitting at the center of a current loop, it may be familiar from Phys 232 or Phys 332 that there will be a magnetic field of strength

$$
B=\frac{\mu_{o} I}{2 r}=\frac{\mu_{o} e}{2 r T}
$$

Using the expression for angular momentum to substitute out the period,

$$
\frac{L}{m 2 \pi r^{2}}=\frac{1}{T}
$$

So,

$$
B=\frac{\mu_{o} e}{2 r} \frac{L}{m 2 \pi r^{2}}=\frac{\mu_{o} e}{4 \pi} \frac{L}{m r^{3}}=\frac{e}{4 \pi \varepsilon_{o}} \frac{L}{m c^{2} r^{3}} \text { using } c^{2}=\frac{1}{\varepsilon_{o} \mu_{o}}
$$

And this points in the same direction as the angular momentum.

$$
\vec{B}=\frac{e}{4 \pi \varepsilon_{o}} \frac{\vec{L}}{m c^{2} r^{3}}
$$

Putting $\mu$ and $B$ together for Energy
So putting these two expressions together,

$$
E=-\vec{\mu} \cdot \vec{B}
$$

Could be rephrased as

$$
E=-\left(\frac{-e}{2 m} \vec{S}\right) \cdot\left(\frac{e}{4 \pi \varepsilon_{o}} \frac{\vec{L}}{m c^{2} r^{3}}\right)=\frac{e^{2}}{8 \pi \varepsilon_{o}} \frac{\vec{S} \cdot \vec{L}}{(m c)^{2} r^{3}}
$$

Now, if we leave off there and translate to quantum mechanical operators, we'll luck out and two wrongs will actually make a right. One wrong is that we need to translate from the orbiting frame to the rest frame to see how the situation would look to us . Jackson section 11.8 does that; at the end of the day, it corrects this by a factor of 2 .

The other wrong is that we were modeling the spinning electron rather hokey-ly as a current loop; that's not really what spin is. Working things out with the Dirac equation gets another factor of 2 , which conveniently cancels this one.

## Quantum Mechanically

The game is to take inspiration from the classical expression to generate the Quantum Mechanical Hamiltonian.

It turns out that, there are two things wrong with this 'derivation', and they pretty well cancel each other. One is classically wrong: that we're analyzing things in the non-inertial reference frame of an orbiting electron; the other is quantum mehcnaically wrong:, electron "spin" isn't exactly, well, spin in a classical sense. For one thing, with a spin of $1 / 2$, it takes two rotations to return to the original orientation, so it may not be too surprising that the correct relation between the spin and magnetic moment operators differs from the classical relation by a factor of 2 :

$$
\begin{aligned}
& \hat{\mu}_{e} \approx \frac{-e}{m} \hat{S} \\
& \hat{H}^{\prime s o} \approx \frac{e^{2}}{8 \pi \varepsilon_{o}} \frac{\hat{S} \cdot \hat{L}}{(m c)^{2} r^{3}}
\end{aligned}
$$

## "Can we go over the derivation to 6.65?" Jessica

Now recall from chapter 3 that

$$
\frac{d\langle\hat{Q}\rangle}{d t}=\frac{i}{\hbar}\langle[\hat{H}, \hat{Q}]\rangle+\left\langle\frac{\partial \hat{Q}}{\partial t}\right\rangle
$$

Now, clearly, the operators $\hat{S}$ and $\hat{L}$ have no explicit time dependence, so the last term is 0 for either; however, with a Hamiltonian of

$$
\begin{aligned}
& \hat{H}=\hat{H}^{o}+\hat{H}^{\prime s o} \\
& \frac{\hbar}{i} \frac{\partial}{\partial t}=-\frac{\hbar^{2}}{2 m} \nabla^{2}+\frac{e^{2}}{8 \pi \varepsilon_{o}} \frac{\hat{S} \cdot \hat{L}}{(m c)^{2} r^{3}}
\end{aligned}
$$

It's no longer true that the commutator is 0 .
In fact, Math: $6.16 \ldots$
However, in this problem, you also find that $\hat{S}_{z}, \hat{L}_{z}$ do not commute, but
$\hat{S}^{2}, \hat{L}^{2}, \hat{J}=\hat{L}+\hat{S}$ all do commute.
Of course, our new theorem from the previous section tells us that this means that eigenfunctions of $\hat{S}_{z}, \hat{L}_{z}$ are not "good" eigenfunctions for the new Hamiltonian (or by our old time-evolution equation, that the average z-components time evolve.), but eigenfunctions of $\hat{S}^{2}, \hat{L}^{2}, \hat{J}=\hat{L}+\hat{S}$ are "good" eigenfunctions for the new Hamiltonian (and measurements of their values remain constant.)

What that means is that states with definite $l, m_{l}$ and $s$ and $m_{s}$ time evolve / are not eigen states of the new, perturbed Hamiltonian. However, as you also show in problem 6.16, the total angular momentum does commute with the new, perturbation term in the Hamiltonian. So this does not change over time.

So, finding the expected correction for the 'good' eigenfunctions:

$$
E^{(1) s o}=\left\langle\psi_{j l s}\right| \hat{H}^{\prime s o}\left|\psi_{j l s}\right\rangle=\left\langle\frac{e^{2}}{8 \pi \varepsilon_{o}} \frac{\hat{S} \cdot \hat{L}}{(m c)^{2} r^{3}}\right\rangle=\frac{e^{2}}{8 \pi \varepsilon_{o}(m c)^{2}}\langle\hat{S} \cdot \hat{L}\rangle\left\langle\frac{1}{r^{3}}\right\rangle
$$

Again, one must resort to problem 6.35 to get the average of $1 / \mathrm{r}^{3}$, so we simply quote that,

$$
E^{(1) s o}==\frac{e^{2}}{8 \pi \varepsilon_{o}(m c)^{2}} \frac{\langle\hat{S} \cdot \hat{L}\rangle}{l\left(l+\frac{1}{2}\right)(l+1) n^{3} a^{3}}
$$

As for $\langle\hat{S} \cdot \hat{L}\rangle$,

Since $\hat{J}=\hat{L}+\hat{S}$,
we can say that

$$
\hat{J}^{2}=(\hat{L}+\hat{S}) \cdot(\hat{L}+\hat{S})=\hat{L}^{2}+\hat{S}^{2}+\hat{L} \cdot \hat{S}+\hat{S} \cdot \hat{L}
$$

but since $L$ and $S$ commute, that's as good as

$$
\hat{J}^{2}=\hat{L}^{2}+\hat{S}^{2}+2 \hat{S} \cdot \hat{L} \Rightarrow \hat{S} \cdot \hat{L}=\frac{1}{2}\left(\hat{J}^{2}-\hat{L}^{2}-\hat{S}^{2}\right)
$$

Then $\langle\hat{S} \cdot \hat{L}\rangle=\frac{1}{2}\left(\left\langle\hat{J}^{2}\right\rangle-\left\langle\hat{L}^{2}\right\rangle-\left\langle\hat{S}^{2}\right\rangle\right)$
Also, how did Griffiths get the eigenvalues for [6.63]?" Spencer

Again, spelling out the brackets, we're using "good" eigenfunctions which are eigenfunctions of $\mathrm{J}^{2}, \mathrm{~L}^{2}$, and $\mathrm{S}^{2}$.

$$
\left\langle\psi_{j l s}\right| \hat{S} \cdot \hat{L}\left|\psi_{j l s}\right\rangle=\frac{1}{2}\left(\left\langle\psi_{j l s}\right| \hat{J}^{2}\left|\psi_{j l s}\right\rangle-\left\langle\psi_{j l s}\right| \hat{L}^{2}\left|\psi_{j l s}\right\rangle-\left\langle\psi_{j l s}\right| \hat{S}^{2}\left|\psi_{j l s}\right\rangle\right)
$$

And you may remember that for any angular momentum,

$$
\hat{J}^{2}\left|\psi_{j l s}\right\rangle=j(j+1) \hbar^{2}\left|\psi_{j l s}\right\rangle, \text { so using that (and the normality of the functions), }
$$

For a state that is an eigen state of J, L and S (which we've recently argued are "good" states for this perturbation.)

$$
\langle\hat{S} \cdot \hat{L}\rangle=\frac{1}{2}(j(j+1)-l(l+1)-s(s+1)) \hbar^{2}
$$

So,

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

This tidies up a little to read $E^{(1) s o}=\frac{\left(E_{n}\right)^{2}}{m c^{2}} \frac{n(j(j+1)-l(l+1)-3 / 4) \hbar^{2}}{l\left(l+\frac{1}{2}\right)(l+1)}$ (using that $\left.\mathrm{s}=1 / 2\right)$

Then in the homework, 6.17, you'll show that putting this together with

$$
E_{n}^{(1) r}=-\frac{\left(E_{n}^{o}\right)^{2}}{2 m c^{2}}\left(\frac{4 n}{\left(l+\frac{1}{2}\right)}-3\right)
$$

Yields the surprisingly simple

$$
E^{(1) f s}=E^{(1) s o}+E^{(1) r}=\frac{\left(E_{n}\right)^{2}}{2 m c^{2}}\left(3-\frac{4 n}{j+\frac{1}{2}}\right)
$$

