# Fine Structure 

Lecture 33
Physics 342
Quantum Mechanics I

Friday, April 25th, 2008

We can use our perturbation theory to calculate corrections to the Hydrogen atom. Specifically, there are relativistic and electromagnetic effects we have missed in our treatment of the pure Coulombic, classical approach. These are relatively easy to put back in perturbatively. Fine structure consists of two separate physical effects: one relativistic correction, one associated with spin-orbit coupling.

### 33.1 Relativistic Hamiltonian

In classical mechanics, a free particle is described by the action:

$$
\begin{equation*}
S_{c}=\int \frac{1}{2} m\left(\dot{x}^{2}+\dot{y}^{2}+\dot{z}^{2}\right) d t \tag{33.1}
\end{equation*}
$$

leading to the usual Lagrangian $L=\frac{1}{2} m v^{2}$. But this free particle action can be written suggestively by noting that the distance travelled along the dynamical trajectory (a curve $\mathbf{x}(t)$ parametrized by $t$ ) is

$$
\begin{equation*}
d \ell^{2}=d x^{2}+d y^{2}+d z^{2}=\left(\dot{x}^{2}+\dot{y}^{2}+\dot{z}^{2}\right) d t^{2} \tag{33.2}
\end{equation*}
$$

so that the classical action is basically the length (squared) along the curve. When we extremize $S_{c}$ in the force free case, then, we expect to get "lengthexteremized" trajectories, or "straight lines" in this setting.

The same is true for relativistic mechanics - we start with a "length" given by the relativistic line element:

$$
\begin{equation*}
d s^{2}=-c^{2} d t^{2}+d x^{2}+d y^{2}+d z^{2}, \tag{33.3}
\end{equation*}
$$

and then the length along a curve parametrized by $\lambda$ (some parameter, not necessarily time) is

$$
\begin{equation*}
d s=\sqrt{-c^{2} \dot{t}^{2}+\dot{x}^{2}+\dot{y}^{2}+\dot{z}^{2}} d \lambda \tag{33.4}
\end{equation*}
$$

If we want the same basic free-particle action, one proportional to length-along-the-curve, then we would naturally take:

$$
\begin{equation*}
S_{r}=\alpha \int \sqrt{-c^{2} \dot{t}^{2}+\dot{x}^{2}+\dot{y}^{2}+\dot{z}^{2}} d \lambda \tag{33.5}
\end{equation*}
$$

This action is manifestly reparametrization invariant - meaning that we can change $\lambda$ without changing the fundamental interpretation of extremal length for the solutions to the equations of motion. To see this, note that if we had another parameter $\gamma(\lambda)$, then the change-of-variables in the action would be governed by:

$$
\begin{equation*}
\dot{x}=\frac{d x}{d \lambda}=\frac{d x}{d \gamma} \frac{d \gamma}{d \lambda}, \tag{33.6}
\end{equation*}
$$

for example, so that

$$
\begin{align*}
S_{r} & =\alpha \int \sqrt{-c^{2}\left(\frac{d t}{d \gamma}\right)^{2}+\left(\frac{d x}{d \gamma}\right)^{2}+\left(\frac{d y}{d \gamma}\right)^{2}+\left(\frac{d z}{d \gamma}\right)^{2}} \frac{d \gamma}{d \lambda} \frac{d \lambda}{d \gamma} d \gamma  \tag{33.7}\\
& =\alpha \int \sqrt{-c^{2} \dot{t}^{2}+\dot{x}^{2}+\dot{y}^{2}+\dot{z}^{2}} d \gamma,
\end{align*}
$$

where now dots refer to derivatives w.r.t. $\gamma$.
We can, in particular, and in order to compare with classical mechanics, take $\gamma=t$, the coordinate time. This means that we will be using the relativistic action, but in the context of the laboratory frame (with the clock on its wall as our parameter for motion). With this parametrization, the action becomes:

$$
\begin{equation*}
S_{r}=\alpha \int \sqrt{-c^{2}+v^{2}} d t=\alpha i c \int \sqrt{1-\frac{v^{2}}{c^{2}}} d t \tag{33.8}
\end{equation*}
$$

For this action, our relativistic Lagrangian becomes (just the integrand of the above)

$$
\begin{equation*}
L_{r}=\alpha i c \sqrt{1-\frac{v^{2}}{c^{2}}} . \tag{33.9}
\end{equation*}
$$

We can set the overall constant $\alpha$ by taking the slow-motion limit and demanding that the relativistic Lagrangian reduce to the classical one:

$$
\begin{equation*}
L_{r} \sim \alpha i c\left(1-\frac{1}{2} \frac{v^{2}}{c^{2}}\right)=\alpha i c-\frac{1}{2} i \alpha \frac{v^{2}}{c} . \tag{33.10}
\end{equation*}
$$

Additive constants don't change the Euler-Lagrange equations, so the constant factor $\alpha i c$ is irrelevant to the predictions of this low-velocity limit. From the above, we see that we must have

$$
\begin{equation*}
-\frac{i \alpha}{c}=m \longrightarrow \alpha=i m c \tag{33.11}
\end{equation*}
$$

Our final form for the relativistic Lagrangian is

$$
\begin{equation*}
L_{r}=-m c^{2} \sqrt{1-\frac{v^{2}}{c^{2}}} \tag{33.12}
\end{equation*}
$$

The point of all of this is to find out what the free-particle Hamiltonian is, that way we would know how to correct the Schrödinger equation. From the above Lagrangian, we find the Hamiltonian in the usual way, first by identifying the relativistic momenta:

$$
\begin{equation*}
\mathbf{p}=\frac{\partial L}{\partial \mathbf{v}}=\frac{m \mathbf{v}}{\sqrt{1-\frac{v^{2}}{c^{2}}}} \tag{33.13}
\end{equation*}
$$

and then, forming the Hamiltonian via Legendre transform:

$$
\begin{align*}
H & =\mathbf{v} \cdot \mathbf{p}-L=\frac{m v^{2}}{\sqrt{1-\frac{v^{2}}{c^{2}}}}+\frac{m c^{2}\left(1-\frac{v^{2}}{c^{2}}\right)}{\sqrt{1-\frac{v^{2}}{c^{2}}}}  \tag{33.14}\\
& =\frac{m c^{2}}{\sqrt{1-\frac{v^{2}}{c^{2}}}}
\end{align*}
$$

If we "finish the job" and write the Hamiltonian entirely in terms of the (relativistic) momentum by inverting (33.13)

$$
\begin{equation*}
v^{2}=\frac{p^{2} c^{2}}{p^{2}+m^{2} c^{2}} \longrightarrow H=m c^{2} \sqrt{\frac{p^{2}}{m^{2} c^{2}}+1} \text {. } \tag{33.15}
\end{equation*}
$$

We see that this total energy is made up of a contribution from the motion of the particles and the rest energy of the particles (note that $H=m c^{2}$ at $p=0)$. To make the kinetic energy portion by itself we subtract off the rest energy:

$$
\begin{equation*}
T=H-m c^{2}=m c^{2} \sqrt{\frac{p^{2}}{m^{2} c^{2}}+1}-m c^{2} \tag{33.16}
\end{equation*}
$$

What we have been doing so far, with the Schrödinger equation, is taking $\frac{p^{2}}{2 m}$ as the kinetic energy (with the classical $\mathbf{p}=m \mathbf{v}$ ), and using the replacement: $\mathbf{p} \rightarrow \frac{\hbar}{i} \nabla$ to generate the quantum system. Now we see that there are . . . relativistic difficulties. Our first move is to replace (in our minds) the classical $\mathbf{p}$ with the relativistic form. That doesn't change anything in theory. The more important shift is to expand this relativistic kinetic energy (it is difficult to modify it directly with the square root in place) and generate corrective terms based on the low- $p$ expansion:

$$
\begin{align*}
T & \sim m c^{2}\left(1+\frac{1}{2} \frac{p^{2}}{m^{2} c^{2}}-\frac{1}{8}\left(\frac{p^{2}}{m^{2} c^{2}}\right)^{2}+\ldots\right)-m c^{2}  \tag{33.17}\\
& =\frac{p^{2}}{2 m}-\frac{p^{4}}{8 m^{3} c^{2}} .
\end{align*}
$$

### 33.2 Hydrogen Correction

We see that our perturbation is, effectively, $-\epsilon p^{4}$ with $\epsilon=\frac{1}{8 m^{3} c^{4}}$. If we want to calculate the perturbed energies of the Hydrogen atom, then, we must be able to evaluate:

$$
\begin{equation*}
\Delta E \equiv E_{1}^{\prime}-E_{1}=-\epsilon\left\langle\psi_{n}\right| p^{4}\left|\psi_{n}\right\rangle \tag{33.18}
\end{equation*}
$$

For most states of Hydrogen, $p^{4}$ is a Hermitian operator, and we can factor the operator into a $p^{2}$ portion acting on $\left|\psi_{n}\right\rangle$ and another acting on $\left\langle\psi_{n}\right|$ :

$$
\begin{equation*}
\Delta E=-\epsilon\left\langle p^{2} \psi_{n}\right| p^{2}\left|\psi_{n}\right\rangle . \tag{33.19}
\end{equation*}
$$

Now in general, finding the expectation value of $p^{4}$ would require taking a bunch of derivatives and integrating. We are going to try to avoid that, by noting that the unperturbed Hamiltonian for Hydrogen is

$$
\begin{equation*}
H=\frac{p^{2}}{2 m}+V(r) \tag{33.20}
\end{equation*}
$$

so that the operator $p^{2}$ acts according to

$$
\begin{equation*}
p^{2}\left|\psi_{n}\right\rangle=2 m\left(E_{n}-V(r)\right)\left|\psi_{n}\right\rangle, \tag{33.21}
\end{equation*}
$$

and we can write

$$
\begin{equation*}
\Delta E=-\epsilon\left\langle\left(4 m^{2}\left(E_{n}-V(r)\right)^{2}\right)\right\rangle=-\frac{1}{2 m c^{4}}\left(\left\langle E_{n}\right\rangle^{2}-2\left\langle E_{n} V(r)\right\rangle+\left\langle V(r)^{2}\right\rangle\right), \tag{33.22}
\end{equation*}
$$

where all the expectation values are w.r.t. the state $\left|\psi_{n}\right\rangle$ - i.e. for the above, $\left\langle E_{n}\right\rangle=\left\langle\psi_{n}\right| E_{n}\left|\psi_{n}\right\rangle$. The energy $E_{n}$ is just a number, so comes out of all expectation values. For Hydrogen, the potential is

$$
\begin{equation*}
V(r)=-\frac{e^{2}}{4 \pi \epsilon_{0} r} \tag{33.23}
\end{equation*}
$$

and we see that in order to evaluate the expectation values $\langle V(r)\rangle$ and its square, we will need to know the expectation values: $\left\langle\frac{1}{r}\right\rangle$ and $\left\langle\frac{1}{r^{2}}\right\rangle$.
The full target expression is

$$
\begin{equation*}
\Delta E=\frac{1}{2 m c^{4}}\left(E_{n}^{2}+2 E_{n} \frac{e^{2}}{4 \pi \epsilon_{0}}\left\langle\frac{1}{r}\right\rangle+\left(\frac{e^{2}}{4 \pi \epsilon_{0}}\right)^{2}\left\langle\frac{1}{r^{2}}\right\rangle\right) . \tag{33.24}
\end{equation*}
$$

### 33.2.1 Feynman-Hellmann Formula

The Feynman-Hellmann theorem concerns the change in energy of a quantum mechanical system given a change in some parameter in the Hamiltonian. For a Hamiltonian dependent on a parameter $\lambda: H(\lambda)$, we have

$$
\begin{equation*}
H(\lambda)\left|\psi_{n}\right\rangle=E_{n}\left|\psi_{n}\right\rangle \tag{33.25}
\end{equation*}
$$

and both the energy and potentially the state $\left|\psi_{n}\right\rangle$ inherit dependence on $\lambda$ through the eigenvalue equation.

Suppose we perturb $\lambda$ a bit: $\lambda \longrightarrow \lambda+d \lambda$, how does the energy of a particular eigenstate respond? This is basically the same question we've been asking all along in this perturbation section, so we know the answer already:

$$
\begin{equation*}
H(\lambda+d \lambda)=H(\lambda)+\frac{\partial H}{\partial \lambda} d \lambda+O\left(d \lambda^{2}\right) \tag{33.26}
\end{equation*}
$$

and assuming that $E_{n} \longrightarrow E_{n}+\bar{E}_{n} d \lambda,\left|\psi_{n}\right\rangle \longrightarrow\left|\psi_{n}\right\rangle+d \lambda\left|\bar{\psi}_{n}\right\rangle$, we have

$$
\begin{equation*}
E_{n}+\bar{E}_{n} d \lambda=E_{n}+\left\langle\psi_{n}\right| \frac{\partial H}{\partial \lambda}\left|\psi_{n}\right\rangle d \lambda \tag{33.27}
\end{equation*}
$$

This tells us that

$$
\begin{equation*}
\bar{E}_{n}=\left\langle\psi_{n}\right| \frac{\partial H}{\partial \lambda}\left|\psi_{n}\right\rangle \tag{33.28}
\end{equation*}
$$

to first order in $d \lambda$ - but viewing $E_{n}(\lambda)$ as itself a function of the parameter $\lambda$, we can also Taylor expand: $E_{n}(\lambda+d \lambda)=E_{n}(\lambda)+\frac{\partial E_{n}}{\partial \lambda} d \lambda+$ ..., leading to the final identification:

$$
\begin{equation*}
\frac{\partial E_{n}}{\partial \lambda}=\left\langle\psi_{n}\right| \frac{\partial H}{\partial \lambda}\left|\psi_{n}\right\rangle, \tag{33.29}
\end{equation*}
$$

which is the Feynman-Hellmann formula. Note that the "other" terms in the expansion would be associated naturally with higher derivatives of $E_{n}$, evaluated about the point $\lambda$.

The utility of (33.29) should be clear - think of the radial Hamiltonian for Hydrogen:

$$
\begin{equation*}
H_{r}=-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d r^{2}}+\frac{\hbar^{2}}{2 m} \frac{\ell(\ell+1)}{r^{2}}-\frac{e^{2}}{4 \pi \epsilon_{0} r}, \tag{33.30}
\end{equation*}
$$

the "parameter" $e$ leads to

$$
\begin{equation*}
\frac{\partial H_{r}}{\partial e}=-\frac{e}{2 \pi \epsilon_{0}} \frac{1}{r}, \tag{33.31}
\end{equation*}
$$

while the derivative w.r.t. the "parameter" $\ell$ gives

$$
\begin{equation*}
\frac{\partial H_{r}}{\partial \ell}=\frac{\hbar^{2}}{2 m} \frac{1+2 \ell}{r^{2}} \tag{33.32}
\end{equation*}
$$

and we need expectation values w.r.t. both of these $r$-dependencies. We also happen to know the associated derivatives w.r.t. energy, since $E_{n}$ is just

$$
\begin{equation*}
E_{n}=-\frac{m e^{4}}{32 \pi^{2} \epsilon_{0}^{2} \hbar^{2}\left(j_{m}+\ell+1\right)^{2}} \tag{33.33}
\end{equation*}
$$

(where $j_{m}=n-\ell-1$ ).
From (33.31), we have

$$
\begin{equation*}
-\frac{4 m e^{3}}{32 \pi^{2} \epsilon_{0}^{2} \hbar^{2}\left(j_{m}+\ell+1\right)^{2}}=-\frac{e}{2 \pi \epsilon_{0}}\left\langle\frac{1}{r}\right\rangle, \tag{33.34}
\end{equation*}
$$

or, reverting to $n$ notation,

$$
\begin{equation*}
\left\langle\frac{1}{r}\right\rangle=\frac{4 m e^{2}}{16 \pi \epsilon_{0} \hbar^{2} n^{2}}, \tag{33.35}
\end{equation*}
$$

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and finally, in terms of the Bohr radius, $a=\frac{4 \pi \epsilon_{0} \hbar^{2}}{m e^{2}}$,

$$
\begin{equation*}
\left\langle\frac{1}{r}\right\rangle=\frac{1}{a n^{2}} . \tag{33.36}
\end{equation*}
$$

For the $r^{-2}$ expectation value, we will use (33.32)

$$
\begin{equation*}
\frac{2 m e^{4}}{32 \pi^{2} \epsilon_{0}^{2} \hbar^{2}\left(j_{m}+\ell+1\right)^{3}}=\frac{\hbar^{2}(1+2 \ell)}{2 m}\left\langle\frac{1}{r^{2}}\right\rangle \tag{33.37}
\end{equation*}
$$

or

$$
\begin{equation*}
\left\langle\frac{1}{r^{2}}\right\rangle=\frac{m^{2} e^{4}}{8 \pi^{2} \epsilon_{0}^{2} \hbar^{4}(1+2 \ell) n^{3}}=\frac{2}{a^{2}(1+2 \ell) n^{3}} . \tag{33.38}
\end{equation*}
$$

Putting it all together back in (33.24), we have:

$$
\begin{equation*}
\Delta E=\frac{1}{2 m c^{4}}\left(E_{n}^{2}+2 E_{n} \frac{e^{2}}{4 \pi \epsilon_{0}} \frac{1}{a n^{2}}+\left(\frac{e^{2}}{4 \pi \epsilon_{0}}\right)^{2} \frac{2}{a^{2}(1+2 \ell) n^{3}}\right) . \tag{33.39}
\end{equation*}
$$

We can clean this up a little,

$$
\begin{equation*}
\Delta E=-\frac{E_{n}^{2}}{2 m c^{2}}\left(\frac{8 n}{1+2 \ell}-3\right) . \tag{33.40}
\end{equation*}
$$

## Homework

Reading: Griffiths, pp. 266-270.

## Problem 33.1

Find the first order relativistic correction to the energies for the harmonic oscillator. Use $\epsilon H^{\prime}=-\frac{p^{4}}{8 m^{3} c^{2}}$ and note (2.69) from the book.

## Problem 33.2

Here we will look at the change in motion implied by the relativistic Lagrangian.
a. For a particle of mass $m$ that starts from rest at $t=0$, moving under the influence of gravity near the earth, the classical Lagrangian has the form:

$$
\begin{equation*}
L=\frac{1}{2} m v^{2}-m g x . \tag{33.41}
\end{equation*}
$$

Find $v(t)$ from the Euler-Lagrange equation of motion (this is a onedimensional problem). Plot $v(t)$ as a function of time - there is a violation of special relativity here, make sure this is clear on your plot.
b. The relativistic Lagrangian for a free particle of mass $m$ is:

$$
\begin{equation*}
L=-m c^{2} \sqrt{1-\frac{v^{2}}{c^{2}}} . \tag{33.42}
\end{equation*}
$$

Introduce the potential from above to write the relativistic Lagrangian for a particle of mass $m$ moving under the influence of gravity near the earth. Using the Euler-Lagrange equations of motion, again solve for $v(t)$ with $v(0)=0$. Plot your result, the velocity should now be in accord with special relativity, make sure this is demonstrated on your plot.

