Applications of Perturbation Theory:

The Fine Structure of Hydrogen

\[ H_0 = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{r} \]

\[ E_n^{(0)} = -\frac{me^4}{2\hbar^2} \frac{1}{n^2}, \quad n=1,2,\ldots,\infty \]

\[ \frac{1}{\mu} = \frac{1}{me} + \frac{1}{m_N} \]

\[ M = \frac{Me}{1 + \frac{me}{m_N}} \]

Fine-structure constant

\[ \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137.036} \]

\[ E_n^{(0)} = -\alpha^2 \frac{Me c^2}{2n^2} \]
These energy levels, originally found by Bohr, are not the whole story, however. We have already seen that there is an additional spin-orbit interaction, that was omitted from $H_0$. There is also a relativistic correction to the kinetic energy, which is comparable in size. Together, these two effects determine the fine structure of hydrogen. There are even higher-order effects due to quantum electrodynamics (Lamb shift)
and due to the magnetic dipole interaction of the electron and proton (hyperfine structure).

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First, the fine structure. The spin-orbit interaction is

$$H_{s.o.} = \left(\frac{9}{4m_e^2 c^2} \frac{1}{r} \frac{dV}{dr}\right) \hat{L} \cdot \hat{S},$$
where \( \gamma = 2 + \frac{\lambda}{\pi} + \ldots \approx 2.002 \),

and \( V(r) = -\frac{e^2}{r} \) (see lecture 9).

\[
\hat{H}_{s.o.} \approx \frac{e^2}{2m^2 c^2 r^3} \hat{L} \cdot \hat{S}
\]

Degenerate perturbation theory:

\[
[\hat{L}^2, \hat{H}_0] = 0, \quad [\hat{L}^2, \hat{H}_{s.o.}] = 0,
\]

so \( \hat{H}_{s.o.} \) does not couple states with different \( L \). Eigenvalues of \( \hat{H}_0 \) are independent of \( \hat{S} \) (degenerate).

Eigenstates of \( \hat{H}_{s.o.} \) are eigenstates of \( \hat{L}^2 \), with \( J = l \pm \frac{1}{2} \).

\[
\hat{L} \cdot \hat{S} \mid ls \, j m \rangle = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \mid ls \, j m \rangle
\]
\[ E^{(1)}_{s.o.} = \frac{e^2}{2m_e c^2} \langle nljm | \frac{\mathbf{L} \cdot \mathbf{S}}{r^3} | nljm \rangle \]

\[ = \frac{e^2 \hbar^2 (j(j+1) - l(l+1) - \frac{3}{4})}{4M_e c^2} \langle nl | \frac{1}{r^3} | nl \rangle \]

\[ \langle \frac{1}{r^3} \rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)\hbar^3 a_0^3} \]

Where \( a_0 = \frac{\hbar^2}{me^2} = \text{Bohr radius} \)

\[ E^{(1)}_{s.o.} = \frac{m_e c^2}{4} \left( \frac{e^2}{\hbar c} \right)^4 \frac{\ell(j+1) - l(l+1) - \frac{3}{4}}{\hbar^3 \ell(\ell+1/2)(\ell+1)} \]

\[ E^{(1)}_{s.o.} \text{ is apparently undefined for } l=0 \text{ (} j=1/2 \text{)} \]

since both numerator and denominator are zero. In fact \( E^{(1)}_{s.o.} = 0 \) for \( l=0 \), since in that case \( \ell \cdot S = 0 \)
Relativistic correction to the kinetic energy

According to Einstein, the kinetic energy of a particle of rest mass \( m_e \) is

\[
T = \sqrt{\mathbf{p}^2 c^2 + m_e^2 c^4} - m_e c^2
\]

\[
= m_e c^2 \left[ \sqrt{1 + \left( \frac{\mathbf{p}}{m_e c} \right)^2} - 1 \right]
\]

\[
= \frac{\mathbf{p}^2}{2 m_e c^2} - \frac{\mathbf{p}^4}{8 m_e^3 c^4} + \mathcal{O}(\mathbf{p}^6)
\]

The lowest-order relativistic correction is

\[
H^{(1)}_{\text{rel}} = -\frac{\mathbf{p}^4}{8 m_e^3 c^2} = -\frac{1}{2 m_e c^2} \left( \frac{\mathbf{p}^2}{2 m_e c} \right)^2
\]
\[ [H_{rel}^{(1)}, \hat{L}_z^2] = 0, \quad [H_{rel}^{(1)}, \hat{L}_z] = 0, \]

so the eigenstates of \( \hat{H}_0 \), \( \vert n l m \rangle \) are the "good" states for deg. pert. thy.

\[ E_{rel}^{(1)} = \langle n l m \vert H_{rel}^{(1)} \vert n l m \rangle \]

\[ = - \frac{1}{2mec^2} \langle \left( \frac{\vec{p}^2}{2me} \right)^2 \rangle \]

To estimate \( \langle \left( \frac{\vec{p}^2}{2me} \right)^2 \rangle \), note that

\[ \langle \frac{\vec{p}^2}{2me} \rangle = \frac{m_e e^4}{2\hbar^2} \frac{1}{n^2}. \]

Thus, one would expect

\[ \langle \left( \frac{\vec{p}^2}{2me} \right)^2 \rangle \sim \left( \frac{m_e e^4}{2\hbar^2 n^2} \right)^2 = \left( E_n^{(0)} \right)^2 \]
In fact,

\[
\langle \left( \frac{\vec{p}}{2mc} \right)^2 \rangle = \left[ \frac{4n}{\ell + \frac{3}{2}} \right] \left( E_n^{(0)} \right)^2
\]

(same dependence on \( mc^2, e, \) and \( \ell \); different dep. on \( n + \ell \).

Finally,

\[
E_{\text{rel}}^{(1)} = -\frac{Mec^2}{8} \left( \frac{e^2}{\hbar c} \right)^4 \frac{1}{n^4} \left[ \frac{4n}{\ell + \frac{3}{2}} \right]
\]

As promised, both \( E_{\text{s.o.}}^{(1)} \) and \( E_{\text{rel}}^{(1)} \) are \( O(mec^2 \alpha^4) \). Combining them gives

\[
E_{\text{f.s.}}^{(1)} = \frac{(E_n^{(0)})^2}{2Mec^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right)
\]
The energy levels of hydrogen, including the fine structure, are

\[ E_n^j = -\frac{\mu e^4}{2\hbar^2 n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right] \]

The energy shift due to fine structure is always negative.

The good quantum numbers are \( n, l, s, j, \) and \( m_j \) (not \( m_s \) or \( m_l \)). For a given \( n \), the degeneracy for \( l = 0, 1, \ldots, n-1 \) is lifted.
Energy levels of hydrogen, including the fine structure (not to scale).
Hyperfine Splitting

The proton also has a magnetic dipole moment

\[ \vec{\mu}_p = \frac{g_p e}{2m_p} \vec{S}_p, \quad (\vec{\mu}_e = -\frac{e}{m_e} \vec{S}_e) \]

with \( g_p = 5.59 \).

According to classical electrodynamics, a dipole \( \vec{\mu} \) sets up a magnetic field

\[ \vec{B} = \frac{3(\vec{\mu} \cdot \hat{r})\hat{r} - \vec{\mu}}{r^3} + \frac{8\pi}{3} \vec{\mu} \delta(\hat{r}). \]

The hyperfine Hamiltonian, describing
The magnetic dipole-dipole interaction of the electron and proton, is thus

\[ H_{\text{h.f.}}^{(1)} = \frac{g_p e^2}{2m_p m_e} \frac{3 (\vec{S}_p \cdot \vec{r})(\vec{S}_e \cdot \vec{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} \]

\[ + \frac{4\pi g_p e^2}{3m_p m_e} \vec{S}_p \cdot \vec{S}_e \mathcal{S}(\vec{r}) \]

\[ E_{\text{h.f.}}^{(1)} = \frac{g_p e^2}{2m_p m_e} \left\langle \frac{3 (\vec{S}_p \cdot \vec{r})(\vec{S}_e \cdot \vec{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} \right\rangle \]

\[ + \frac{4\pi g_p e^2}{3m_p m_e} \left\langle \vec{S}_p \cdot \vec{S}_e \right\rangle \left| \psi(0) \right|^2. \]

In the ground state (or any other state with \( l=0 \)), the wave function is spherically symmetric, so the first expectation value vanishes.
On the other hand

\[ |\chi_{100}(0)|^2 = \frac{1}{11} a_0^3 \]

so

\[ E_{\text{h.f.}}^{(1)} = \frac{4 g_p e^2}{3 m_p m_e a_0^3} \langle \vec{s}_p \cdot \vec{s}_e \rangle \]

in the ground state.

Recall

\[ \vec{s}_p \cdot \vec{s}_e = \begin{cases} \hbar^2/4 & \text{(triplet)} \\ -3\hbar^2/4 & \text{(singlet)} \end{cases} \]

\[ \Delta E_{\text{h.f.}} = \frac{4 g_p e^2 \hbar^2}{3 m_p m_e a_0^3} = 5.88 \times 10^{-6} \text{ eV} \]

\[ = \frac{4 g_p m_e}{3 m_p} \left( \frac{mc^2}{\hbar c} \right) \left( \frac{e^2}{\hbar c} \right)^4 \]
Hyperfine splitting:

\[ E^{(0)}_1 \rightarrow \text{triplet} \uparrow \Delta E \downarrow \text{singlet} \]

\[ \nu = \frac{\Delta E}{h} = 1420 \text{ MHz} \]

\[ \lambda = \frac{c}{\nu} = 21 \text{ cm} \]

This characteristic microwave radiation from hydrogen permeates the universe.