Lecture 16: Application of TEDPT: Fine structure in Hydrogen

Relativistic effects:
Recall characteristic units in Hydrogen:

Given $m_e, e, \hbar$

⇒ Length: Bohr radius $a_0 = \frac{\hbar^2}{m_e e^2} \sim 0.5 \text{ Å}$

Energy: Hartree $E_c = \frac{e^2}{a_0} = \frac{m_e e^4}{\hbar^2} \sim 27.2 \text{ eV}$

⇒ Time: $t_c = \frac{\hbar}{E_c} = \frac{\hbar a_0}{e^2}$

⇒ Velocity: $v_{ch} = \frac{a_0}{t_c} = \frac{e^2}{\hbar}$

Relativity ⇒ New constant $\alpha$

⇒ Dimensionless unit $\alpha = \frac{v_{ch}}{c} = \frac{e^2}{\hbar c} \approx \frac{1}{137}$

Fine Structure constant

⇒ Relativistic effects small perturbation to energy levels given in non-relativistic Schrödinger equation

Exact solution ⇒ Dirac Equation
Relativistic perturbations

- Spin-orbit coupling

In the rest frame of the electron, one sees a magnetic field due to the motion of the charged proton.

\[ \mathbf{B}_{\text{frame}} = -\frac{1}{c} \mathbf{v} \times \mathbf{E} \]

\[ \Rightarrow \mathbf{B}_{\text{frame}} = -\frac{1}{c} \mathbf{v} \times \left( \frac{e}{r^3} \mathbf{r} \right) \]

\[ = \frac{e}{mc} \frac{(\mathbf{p} \times \mathbf{r})}{r^3} \]

\[ = \frac{e}{mc} \mathbf{L} \frac{1}{r^3} = \frac{e \hbar}{mc} \mathbf{\hat{r}} \frac{1}{r^3} \]

\[ = 2\mu_B \frac{\mathbf{\hat{L}}}{r^3} \quad \text{where} \quad \mu_B = \frac{e \hbar}{2mc} = \text{Bohr magneton} \]

\[ \mathbf{\hat{L}} = \frac{\mathbf{L}}{\hbar} \]

magnetic field of current loop at position of electron (magnetic moment \( \mathbf{\hat{L}} = \mu_B \mathbf{\hat{L}} \))

\[ \Rightarrow \text{We would say} \]

\[ \mathbf{H}_{60} = -\mathbf{\hat{L}} \cdot \mathbf{B}_{\text{frame}} = -2\mu_e \cdot \mu_{\text{current}} \]

\[ \Rightarrow \mu_e = g_s \mu_B \frac{\mathbf{\hat{L}}}{r^3} \]

\[ g_s = 2 \]
Perturbation to hydrogen from spin-orbit

\[ \hat{H}_{so} = \frac{4 \mu_b^2 \hat{L} \cdot \hat{S}}{r^3} \]

In dimensionless units (take out fine structure)

\[ \hat{H}_{so} = \frac{-\alpha^2 \hat{L} \cdot \hat{S}}{\bar{r}^3} \]

- Since ground state is \( l=0 \) ⇒ no shift
- First excited state: 4-fold degenerate with spin
  \[ 12s, 12p, 1, 0, -1 \]

With spin: State space is tensor product of orbital and spin degrees of freedom

\[ |n, l, m_l, m_s \rangle \Rightarrow 8 \text{ fold degenerate} \]

Degenerate perturbation theory ⇒ diagonalize \( \hat{H}_{so} \) in 8-dim subspace

However, in this case we note:
Recall \( \frac{\hat{J}}{\hbar} = \hat{L} + \hat{S} \) = Total electron angular momentum

\[ \Rightarrow \frac{\hat{J}^2}{\hbar^2} = \frac{\hat{L}^2}{\hbar^2} + \frac{\hat{S}^2}{\hbar^2} + 2 \hat{L} \cdot \hat{S} \] (Next page)
\[
\hat{H}_{50} = 4 \mu_B^2 \left( \hat{l} \cdot \hat{\mathbf{\alpha}} \right) \frac{1}{\ell^3}
\]

This is off by a factor of 2.

Reason: The electron rest frame is not an inertial frame. In the rotating frame, the effect is like a fictitious magnetic field (recall Larmor's theorem). This is a purely kinematic effect, not due to EM. The appropriate fictitious field leads to Thomas Precession (see, e.g., J.D. Jackson, Electrodynamics).

With Thomas precession

\[
\hat{H}_{50} = -\frac{1}{2} \mu_{\text{electroq}} \cdot \hat{\mathbf{B}}_{\text{frame}}
\]

\[
\hat{H}_{50} = + 2 \frac{\mu_B^2}{\ell^3} \left( \hat{l} \cdot \hat{\mathbf{\alpha}} \right)
\]

so orbital coupling also known as L-S coupling.

Estimate size of effect

\[
\frac{\mu_B^2}{\ell^3} = \Delta E_{50}
\]

\[
\mu_B \approx \frac{e\hbar}{mc} = \left( \frac{e^2}{\hbar c} \right) \left( \frac{e^2}{mc^2} \right) = \alpha (e a_0)
\]

\[
\Delta E_{50} \sim \alpha^2 \frac{e^2}{a_0} = \alpha^2 (\text{Hartee})
\]
Thus, \( \hat{A} \cdot \vec{S} = \frac{1}{2} \left( \vec{A}^{2} - \vec{l}^{2} - \vec{s}^{2} \right) \)

\[ \Rightarrow \hat{A}_{so} \text{ is diagonalized in the coupled basis of angular momentum } | l \pm m \rangle \]

\[ | l \pm m \rangle = | l \rangle \otimes | l \pm m \rangle \]

\( \text{radial} \ \ \ \text{angular & spin} \)

\[ \Rightarrow \text{In this basis,} \]

\[ \hat{A}_{so} = \frac{\alpha^2}{2F^3} \left[ \frac{1}{2} (l(l+1) - l(l+1) - s(s+1)) \right] \]

For electron \( s = \frac{1}{2} \Rightarrow s(s+1) = \frac{3}{4} \)

Also, we know from the "triangle inequality"

\[ |l - s| < j < l + s \]

\[ \Rightarrow j = l - \frac{1}{2} \text{ or } j = l + \frac{1}{2} \]

\[ \hat{A}_{so} = \frac{\alpha^2}{4F^3} \begin{cases} 
  l & j = l + \frac{1}{2} \\
 -(l+1) & j = l - \frac{1}{2}
\end{cases} \]

(Next Page)
Thus the eigenvalues of $\hat{H}$ so within a manifold defined by principle $q$-number $n$

$$\Delta E_{n, l, j}^{s.o.} = \pm \frac{\alpha^2}{4} \frac{l}{l+1} \left\{ \begin{array}{ll}
\frac{l}{l+1} - (l+1) & \text{if } j = l + \frac{1}{2} \\
\frac{l}{l+1} - (l-1) & \text{if } j = l - \frac{1}{2}
\end{array} \right.$$ 

Assume: $\langle n l \mid \frac{1}{r^3} \mid n l \rangle = \frac{1}{r^3 l(l+1)(l+\frac{1}{2})}$

$$\Rightarrow \Delta E_{n, l, j}^{s.o.} = \frac{\alpha^2}{4} \frac{l}{l+1} \left\{ \begin{array}{ll}
\frac{l}{l+1} - (l+1) & \text{if } j = l + \frac{1}{2} \\
\frac{l}{l+1} - (l-1) & \text{if } j = l - \frac{1}{2}
\end{array} \right.$$ 

* For $l=0$ we have $\frac{0}{0}$ → indetermined. Work with Dirac eq.

E.g. $n=2$

- $2s, 2p$ with $s.o.$
- $2s, 2p$ no $s.o.$ with $s.o.$

Spectroscopic notation: $|nl_j\rangle$

Spin orbit coupling partially breaks degeneracy, There is still axial symmetry $\Rightarrow 2j + 1$ states for every $|nl_j\rangle$. 
Other relativistic effects

In the non-relativistic case, in the center of mass frame, the kinetic energy
\[ \frac{1}{T} = \frac{\hat{P}^2}{2\mu} = \frac{\hat{P}_p^2}{2\mu} \left( \frac{1}{m_e} + \frac{1}{M_p} \right) \]
where \( \hat{P} = \) relative coordinate. In C.O.M. frame \( \hat{P}_e = -\hat{P}_p = \hat{P}_{rel} = \hat{P} \)

Relativistically, the energy of the electron (excluding E&M potential energy) is \( \sqrt{P_e^2c^2 + (m_ec^2)^2} \). The proton is very massive so we neglect its relativistic motion.

\[ \Rightarrow \text{To lowest order in } \frac{\sqrt{c^2h}}{c} \]
\[ \sqrt{P_e^2c^2 + (m_ec^2)^2} + \frac{P^2_{Proton}}{2M_p} = m_ec^2 + \frac{P_e^2}{2m_e} - \frac{(P_e^2)^2}{8m_e^2c^2} \]
\[ + \frac{P^2_{Proton}}{2M_p} \]
\[ = m_ec^2 + \frac{P^2_{rel}}{2\mu} - \frac{1}{8} \left( \frac{P^2_{rel}}{m_e^2c^2} \right) \]
\[ \Rightarrow \hat{H}_{kin} = -\frac{1}{8} \left( \frac{P^2_{rel}}{m^3_e c^2} \right) \]

Another perturbation
\[ \hat{H}_{\text{kin}} = -\frac{1}{8} \left( \frac{P_{\text{rel}}^2}{m^3 c^2} \right) \left( \frac{1}{n} \right)^3 \approx 1 \]

\[ \Rightarrow \quad \Delta E_{\text{nlj}}^{\text{kin}} = -\frac{\langle n \ell l | \hat{p}^4 | n \ell l \rangle}{8 m^3 c^2} \]

\[ = -\frac{\| \hat{p}^2 | n \ell l \rangle \|^2}{8 m^3 c^2} \]

Aside:

\[ \langle \hat{p}^2 | n \ell l \rangle = 2m \left( E_n - \hat{V} \right) | n \ell l \rangle \]

\[ \Rightarrow \quad \langle n \ell l | \hat{p}^4 | n \ell l \rangle = 4m^2 \left( E_n^2 - 2E_n \langle \hat{V} \rangle_{n \ell l} + \langle \hat{V}^2 \rangle_{n \ell l} \right) \]

\[ \therefore \quad \Delta E_{\text{nlj}}^{\text{kin}} = -\frac{1}{2mc^2} \left( E_n^2 - 2E_n \langle \hat{V} \rangle_{n \ell l} + \langle \hat{V}^2 \rangle_{n \ell l} \right) \]

with \[ E_n = -\frac{1}{2n^2} \frac{e^2}{a_o} = -\frac{1}{2n^2} \alpha^2 mc^2 \]

\[ \Delta E_{\text{nlj}}^{\text{kin}} \left( \frac{e^2}{a_o} \right) = -\frac{m \alpha^2}{2} \left( \frac{1}{4n^4} - \frac{1}{n^2} \right) \langle \frac{1}{r^4} \rangle_{n \ell l} \]

Having used \[ \hat{V} = \frac{e^2}{r} = -\frac{e^2}{a_o} \frac{1}{r} \]

Aside:

\[ \langle \frac{1}{r^4} \rangle = \frac{1}{n^2} \quad \langle \frac{1}{r^2} \rangle = \frac{1}{n^2} \frac{1}{h^3(\ell + \frac{1}{2})} \]

\[ \therefore \quad \Delta E_{\text{nlj}}^{\text{kin}} = -\frac{m \alpha^2}{2} \left( \frac{1}{n^2 h^3(\ell + \frac{1}{2})} - \frac{3}{4} \frac{1}{n^4} \right) \]
Now let us add together these two contributions to get the total "fine structure": \( \Delta E_{\text{tot}} \) for \( l \neq 0 \)

\[
\Delta E_{\text{tot}}^{(+)} = \frac{\alpha^2}{2} \left( \frac{1}{2n^3(l+1)(l+\frac{1}{2})} - \frac{1}{n^3(l+\frac{1}{2})} + \frac{3}{4n^4} \right)
\]

\[
= \frac{\alpha^2}{2} \left( -\frac{1}{n^3(l+1)} + \frac{3}{4n^4} \right)
\]

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

\[
\Delta E_{\text{tot}}^{(-)} = \frac{\alpha^2}{2} \left( -\frac{1}{2n^3 l(l+\frac{1}{2})} - \frac{1}{n^3(l+\frac{1}{2})} + \frac{3}{4n^4} \right)
\]

\[
= \frac{\alpha^2}{2} \left( -\frac{1}{n^3 l} + \frac{3}{4n^4} \right)
\]

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

Thus, we see that the fine structure in \( \Delta E_{\text{tot}} \) (first relativistic correction) depends only on the total electron angular momentum, not on the total electron angular momentum \( j \).

\[
\Delta E_{\text{tot}} = -\frac{\alpha^2}{2n^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right)
\]

**Note:** the "exact solution" in the Dirac equation is

\[
E_{\text{tot}} = mc^2 \left[ 1 + \alpha^2 (n-j-\frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 + \Delta^2}) \right]^{-\frac{1}{2}}
\]

(includes rest mass and zeroth order)
\[ \Delta E_{n_{l=0}} = -\frac{\alpha^2}{2} \left( \frac{1}{n^3} - \frac{3}{4} \frac{1}{n^4} \right) \]

There is one additional effect that is of order $\alpha^2$ in atomic units that arises in the relativistic theory of the electron. The true relativistic theory is not a single-particle theory. Electrons and positrons can be created and annihilated when one looks at the Dirac theory as a single electron theory in the non-relativistic limit one finds that the even for a free particle the position is rapidly fluctuating. Schrödinger referred to this as "zitterbewegung" or "trembling motion". The end result is that the position of the electron is "smearred out" on the order of $\Delta r = \frac{\hbar}{mc}$ (near the Compton wavelength).

The Coulomb energy is thus smearred out

\[ V(r + \Delta \mathbf{r}) = V(r) + \Delta \mathbf{r} \cdot \nabla V + \frac{1}{2} \sum \Delta r_i \Delta r_j \frac{\nabla^2}{2 \mathbf{r}_i \cdot \mathbf{r}_j} \]

Averaging over the fluctuation

\[ \langle \Delta \mathbf{r} \rangle = 0 \quad \langle \Delta r_i \Delta r_j \rangle = \frac{1}{3} \langle \Delta \mathbf{r}^2 \rangle = \frac{\hbar^2}{3mc^2} \]

\[ \Delta V(r + \Delta \mathbf{r}) \approx V(r) + \frac{\hbar^2}{6mc^2} \nabla^2 V(r) \]

For the Coulomb potential, $V(r) = \frac{e^2}{r}$, $\nabla^2 V = \frac{e^2}{4\pi \epsilon_0 r^3}$

\[ \nabla^2 V = \frac{e^2}{4\pi \epsilon_0 r^3} \]

Perturbation $H_{pert} = \frac{\hbar^2 e^2}{8m^2c^2} 4\pi \delta(x) = \frac{\hbar^2 e^2}{8m^2c^2} 4\pi \delta(3\mathbf{x})$ (known as "Dirac form")

\[ \frac{\hbar^2 e^2}{8m^2c^2} \frac{4\pi \delta(\mathbf{x})}{\mathbf{x}} \]

This perturbation only contributes for $s$-states since $\mathbf{r}_n < \mathbf{r}_l$

\[ \Delta E_{n_{l=0}} = \frac{\alpha^2}{2} \left( \frac{1}{n^3} - \frac{3}{4} \frac{1}{n^4} \right) \]
The relativistic corrections to the $n=2$ state of $\text{H}$ are sketched below:

\[ \Delta E \propto \frac{2e^2}{2n^3} \left( 1 - \frac{3}{4n} \right) = -\frac{2e^2}{2n^3} \left( \frac{1}{\nicefrac{1}{2}} - \frac{3}{4n} \right) \]

Here we have shown in the last diagram an effect not included in the Dirac equation -- coupling to the electromagnetic vacuum. These fluctuation yield a shift of the $2s_{1/2}$ known as the "Lamb shift". It comes from QED and is of order $\alpha^3$ (in atomic units). It is odd.

Thus the true spectrum of Hydrogen (neglecting the hyperfine splitting to be discussed next lecture)

\[ \Delta E_{\text{FS}} = \frac{10.969}{\hbar} \text{ GHz} \]

\[ \Delta E_{\text{Lamb}} = \frac{1.0698}{\hbar} \text{ GHz} \]