Lecture 14

Hydrogen Fine Structure

\[ H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \left( \frac{\hbar^2}{2m} \frac{e^2}{r^2} - \frac{e^2}{4\pi\epsilon_0 \frac{1}{r}} \right) \]

\[ \Delta E_0 = -\frac{\hbar^2}{2m} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{(N+1)^2} \quad N = 1, 2, 3, \ldots \]

\[ \Delta E_{\text{rel}} = -\frac{1}{8} \frac{\hbar^2}{m^3 c^2} \]

used Feynman Hellman theorem

\[ \langle \psi | \frac{\partial H}{\partial \alpha} | \psi \rangle = \frac{\partial \Delta E}{\partial \alpha} \quad \text{eigenstate of } H \]

\[ \Delta E = \frac{m}{8\hbar^4 c^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{N^3} \left( 3 - \frac{4}{8+\frac{1}{N}} \right) \]

used

\[ \langle \psi | \frac{\gamma}{\gamma} | \psi \rangle = \frac{m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{N^2} \]

\[ \langle \psi | \frac{1}{r} | \psi \rangle = \frac{2m^2}{\hbar^2} \frac{1}{2\ell+1} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{N^3} \]

The next correction is due to the magnetic moment of the electron interacting with the electric field of the proton.
While this is a direct consequence of the Dirac equation, we use a classical analysis to understand the physics.

1. Assume a circular orbit.
2. Consider the rest frame of the electron.

In that frame, the proton orbits the electron. The magnetic field at the center of the circle can be calculated using the Biot-Savart law:

\[
\mathbf{B} = \frac{\mu_0 I}{4\pi} \int \frac{\mathbf{dl} \times \mathbf{r}}{r^3}
\]

\[
= \frac{\mu_0 I}{4\pi} \frac{2\pi r \cdot r}{r^3}
\]

\[
= \frac{\mu_0 I}{2r} \hat{z}
\]

The current of the proton is

\[
I = \frac{q}{T}
\]

\(T\) = period of orbit.
we can calculate $T$ by considering the orbiting electron

\[ L = \mathbf{r} \times \mathbf{p} = \dot{r} \mathbf{m} \mathbf{v} = \mathbf{r} \mathbf{m} \frac{2\pi r}{T} = 2\pi \mathbf{m} \frac{r^2}{T} \]

\[ \frac{1}{T} = \frac{L}{2\pi \mathbf{m} r^2} \]

where $L$ is the orbital angular momentum of the electron

using these

\[ B = \frac{u_0}{2\pi} \cdot \frac{9}{r} = \frac{u_0}{2\pi} \cdot \frac{9}{2\pi r^2} \]

we get \( u_0 e_0 = \frac{l}{c^2} \)

\[ u_0 = \frac{l}{e_0 c^2} \]

\[ B = \frac{1}{mc^2} \left( \frac{q}{4\pi e_0} \right) \cdot \frac{l}{r^3} \]

using \( q = -e \)

\[ \mathbf{B} = \frac{1}{mc^2} \left( \frac{e}{4\pi e_0} \right) \frac{L}{r^3} \]

this field interacts with the magnetic moment of the electron
\[ \Delta \mathbf{E} = -\mathbf{u} \cdot \mathbf{B} \]

For a current loop

\[ \mathbf{u} = I \mathbf{A} = \frac{q}{r} \pi r^2 = q \pi r \frac{L}{r} \]

\[ = q \frac{1}{2} \mathbf{2} \frac{\pi r}{r} = q \frac{L}{2m} m v r \]

\[ \mathbf{u} = q \frac{L}{2m} \]

For systems that are not point charges this gets modified by

\[ \mathbf{u} = q \frac{\mathbf{L}}{2m} \]

where \( q \) is called the Landé \( g \) factor.

For a spin \( \frac{1}{2} \) electron the magnetic moment due to the electron's spin has a \( g \) factor of 2

\[ \mathbf{u}_{\text{elect}} = \frac{q}{m} \mathbf{S} \]
This can be measured experimentally—it is predicted correctly by the Dirac equation—which was one of the reasons for accepting the Dirac equation.

Putting these together give

\[ \Delta H = - \vec{u}_c \cdot \vec{B} \]

\[ = - \left( \frac{e}{m} \right) \vec{a} \cdot \left( - \frac{e}{4\pi \varepsilon_0} \right) \cdot \frac{E}{mc^2} \cdot \frac{l}{r^3} \]

\[ = \frac{e}{m^2c^2} \left( \frac{e}{4\pi \varepsilon_0} \right) \frac{\vec{S} \cdot \vec{E}}{r^3} \]

It turns out that there is another error with this derivation because it was derived in an accelerated coordinate system—the correct answer is \( \frac{1}{2} \) of the above.

\[ \Delta H = \frac{1}{2m^2c^2} \left( \frac{e^2}{4\pi \varepsilon_0} \right) \frac{\vec{S} \cdot \vec{E}}{r^3} \]

*NOTE* \( \Delta H = 0 \) for \( l^2 = 0 \)
This is called the spin orbit correction. While it is rotationally invariant, it does not commute with $S_x$ or $L_z$.

\[
[S_3, S_1 L_1] = \\
[S_3, S_2] L_2 + [S_3 S_1, L_1] \\
-i \hbar S_1 L_2 + i \hbar S_2 L_1 \\
-i \hbar (S \times L)_z \neq 0
\]

This means that states with different values of $m$ and spin components will have different energies.

This requires using degeneracy perturbation. The problem is to diagonalize

\[
H_0 + A H_1
\]

on a subspace with a given value of $n, \ell$. 

recall that this involves finding a linear combination of eigenstates of $H_0$ with the same energy that diagonalize $H_0 + \Delta H$ on the subspace spanned by the degenerate eigenstates.

If we note that

$$\vec{J} = \vec{L} + \vec{S}$$
$$J^2 = L^2 + S^2 + 2 \vec{L} \cdot \vec{S}$$
$$\vec{L} \cdot \vec{S} = \frac{1}{2} (J^2 - L^2 - S^2)$$

the full Hamiltonian commutes with $J^2, L_z, S_z, J_\pm$, states

$$| n J J_2 L^2 S^2 > = \sum_{L_2 S_2 J_z} C^{L_2 S_2 J_z}_{L_2 S_2 J_z} | L_2 S_2 J_z > | S^2 S_2 > | L^2 L_2 > | n J >$$

where the $C^{L_2 S_2 J_z}_{L_2 S_2 J_z}$ are Clebsch-Gordan coefficients. The states on the right all have the same unperturbed energy, $E_{nl}$.
These linear combinations diagonalize $\Delta H$.

This means that the first order corrections due to the spin-orbit interaction are

\[ \langle n_1 j_1 \ell_1 s_1 | \Delta H | n_2 j_2 \ell_2 s_2 \rangle = \]

\[ \frac{1}{2m^2c^2} \left( \frac{e^2}{4\pi\epsilon} \right) \frac{\hbar^2 (\ell_1 + \ell_2) - \ell(\ell_1 + \ell_2)}{2} \langle n_1 \ell_1 \frac{1}{r_3} \ell_1 n_1 \ell_1 \rangle \]

We see that for a fixed value of $\ell$ and any $j_2$, the energies can have different values depending on $j_1$.

To actually calculate this quantity, we need to evaluate

\[ \langle n_1 j_1 \ell_1 s_1 | \frac{1}{r_3} \ell_1 n_1 j_2 \ell_2 \rangle = \langle n_1 \frac{1}{r_3} \ell_1 n_1 \ell_1 \rangle \]

This requires computing

\[ \int_0^\infty R_n(r) \frac{r^3}{n_3} R_n(r) \]

\[ \int_0^\infty U_n(r) \frac{dr}{n_3} U_n(r) \]
To compute this we use a modified version of the Feynman
Hellman theorem. Consider

\[- \frac{k^2}{2m} \frac{\partial^2}{\partial r^2} u + \left( \frac{k^2}{2m} \frac{\partial (\rho H)}{\rho r^2} - \frac{e^2}{4\pi \epsilon} \frac{1}{r} \right) u - EU = 0\]

Next differentiate the above equation
with respect to \( r \)

\[- \frac{k^2}{2m} \frac{\partial^3}{\partial r^3} u + \left( \frac{k^2}{2m} \frac{\partial (\rho H)}{\rho r^2} - \frac{e^2}{4\pi \epsilon} \frac{1}{r} \right) \frac{\partial u}{\partial r} - EU' = 0\]

\[- \frac{2k^2}{2m} \frac{\partial (\rho H)}{\rho r^3} + \frac{e^2}{4\pi \epsilon} \frac{1}{r^2} \frac{\partial u}{\partial r} = 0\]

Multiply the first equation by \( u' \) and the second by \( u \) and calculate the difference

\[- \frac{k^2}{2m} (u'u'' - uu'') + \left( \frac{k^2}{m} \frac{\partial (\rho H)}{\rho r^3} - \frac{e^2}{4\pi \epsilon} \frac{1}{r^2} \right) u^2 = 0\]

\[- \frac{k^2}{2m} \frac{d}{dr} (u'u'' - uu'') + \left( \frac{k^2}{m} \frac{\partial (\rho H)}{\rho r^3} - \frac{e^2}{4\pi \epsilon} \frac{1}{r^2} \right) u^2 = 0\]

Integrating from \( 0 \) to \( \infty \) gives

\[- \frac{k^2}{2m} (u'(r)u''(r) - uu'(r)) \bigg|_0^\infty + \frac{k^2}{m} \frac{\partial (\rho H)}{\rho r^3} \left( + \frac{1}{r_1} \frac{1}{r_2} \right) + \frac{e^2}{4\pi \epsilon} \left( + \frac{1}{r_1} \frac{1}{r_2} \right) = 0\]
Recall \( U_{\text{ne}} = R_{\text{ne}} \quad U'_{\text{ne}} = R_{\text{ne}} + R_{\text{ne}}' \)

at \( r = \infty \) \( u, u', u'' \) all vanish

at \( r = 0 \) \( u(0) = 0 \quad u'(0) = R(0) \)

However

\( l \neq 0 \quad R_{\text{ne}} \quad (\alpha) = 0 \)

and \( l = 0 \quad \Delta H = 0 \)

\[
\langle u_1 \frac{1}{r^3} u \rangle = \frac{m}{\hbar^2 \langle \Phi \rangle} \frac{e^1}{4\pi \epsilon_0} \langle u_1 \frac{1}{r^2} u \rangle \quad l \neq 0
\]

since we already used the Feynman-Hellman theorem to compute \( \langle u_1 \frac{1}{r^3} u \rangle \)

\[
\langle u_1 \frac{1}{r^3} u \rangle = \frac{2m^3}{\hbar^4} \frac{1}{2\hbar} \left( \frac{e^1}{4\pi \epsilon_0} \right)^2 \frac{1}{h^3}
\]

\[
\langle u_1 \frac{1}{r^3} u \rangle = \frac{2m^3}{\hbar^6} \left( \frac{e^1}{4\pi \epsilon_0} \right)^3 \frac{1}{(2\hbar)^3}
\]

Using this in the expression for \( \Delta E \)
\[ \langle n \mid \Delta H \mid n \rangle = \]

\[
\frac{1}{2m^2c^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{k^2 (\delta(h\bar{\eta}) - \epsilon(\bar{\eta}h) - s(s+1))}{2} \frac{2m^3}{h^6} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^3 \frac{1}{(2\pi h)(\bar{h})(\bar{\eta})} \frac{1}{\bar{\eta}^3}
\]

\[
= \frac{m}{2\pi^4 c^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^4 \frac{\delta(h\bar{\eta}) - \epsilon(\bar{\eta}h) - s(s+1)}{\epsilon(\bar{\eta}h)(2\pi^4)} \frac{1}{\bar{\eta}^3} \quad \lambda \neq 0
\]

We note that the coefficients with dimensions are the same as the relativistic corrections—so both corrections are the same size.

Since \[ \mathcal{E} P^q \cdot \mathcal{L} = \mathcal{E} P^q \cdot \mathcal{L} = \mathcal{E} P^q \cdot \mathcal{L} \]
\( \Delta E_{\text{rel}} \) only depends on \( \eta \) so it is also diagonal in the \( n \mid \Delta H \mid n \rangle \) basis.
The next correction is the hyperfine splitting, the proton has a magnetic moment

\[ \mu_p = g_p \frac{q_p}{2m_p} \vec{S}_p = - q_p \frac{e}{2m_e} \vec{S}_p \]

The proton is not a point particle - it is composed of quarks. The measured value of \( q_p = 5.55 \)

Since \( m_p \approx 2000 \times m_e \) the magnetic moment of the proton is much smaller than the magnetic moment of an electron.

Magnetic moments generate a magnetic field

\[ \vec{B} = \frac{\mu_0}{4\pi r^3} \left( 3 \vec{\mu}_p \cdot \vec{r} \right) \vec{r} - \vec{\mu}_p \] + \( \frac{2\mu_0}{3} \vec{\mu}_p \cdot \vec{j} \) \( (\vec{r}) \)

This interacts with the magnetic moment of the electron

\[ \vec{\mu}_e = \frac{e}{m_e} \vec{S}_e \]

\[ \Delta H = \] \[ \Delta H_{HF} = - \vec{\mu}_e \cdot \vec{B}_p . \]
\[ \Delta H = - \frac{\mu_0}{4\pi r^3} \left( \vec{3} \vec{u}_p \cdot \vec{r} \right) \vec{r} \cdot \vec{u}_e - \vec{u}_p \cdot \vec{u}_e \right) - \frac{2\mu}{3} \vec{u}_p \cdot \vec{u}_e \delta(r) \]

\[ = \frac{e^2 q_p}{2 m_p m_e} \left( \frac{\mu_0}{4\pi r^3} \left( 3 \vec{r} \cdot \vec{s}_e \cdot \vec{s}_p - \vec{s}_e \cdot \vec{s}_p \right) + \frac{2\mu}{3} \vec{s}_p \cdot \vec{s}_e \delta(r) \right) \]

The expectation value of this quantity gives the Hypercentre splitting.

In \( E=0 \) states the quantity \((3 \vec{r} \cdot \vec{s}_p - \vec{s}_e \cdot \vec{s}_p)\) averages to 0.

This is because multiplying by \( r^2 \)

\[ \langle 3 \vec{r} \cdot \vec{s}_e \cdot \vec{s}_p - \vec{s}_e \cdot \vec{s}_p \rangle = \]

\[ = 3 \left( s_p x s_e <x^1> + s_p y s_e <y^1> + s_p z s_e <z^1> \right) - \vec{s}_e \cdot \vec{s}_p \left( <x^2> + <y^1> + <z^1> \right) \]

Since \(<x^2> = <y^1> = <z^1>\) for spherical symmetry - we get 0

In that case only the last term contributes.
\[
\langle \Delta H \rangle = \frac{e^2 g_\rho}{2m_p m_e} \left( \frac{2\mu^*}{3} \right) S_p \cdot S_e |R_{nu}(u)|^2
\]

In this case \( S_p \), \( S_e \) are not conserved so

\[
S_p \cdot S_e = \frac{1}{2} \left( \frac{S^2 - S_p^2 - S_e^2}{1} \right) \mu
\]

\[
= \frac{\mu}{2} \left( S^2 - \frac{3}{4} - \frac{3}{4} \right) \quad (S^2 = (1)(11) = 0, 10)
\]

So the splitting depend on whether the total spin state is a triplet or singlet.

Another application of perturbation theory occurs when an atom is placed in an external magnetic field.

In this case the additional interaction is

\[
H_z = -(\mu_e + \mu_s) \cdot \vec{B}_{\text{ext}}
\]

where for a single electron atom

\[
\mu_e = -\frac{e}{m} \frac{S}{S}
\]

\[
\mu_s = \frac{e}{2m} \frac{L}{L}
\]
\[ H_2 = -\frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B_{ext}} \]

For the Zeeman effect, the strength of the magnetic field can be controlled externally — how the problem is treated depends on the relative size of \( H_2 \) compared to \( H_{LS} \).

The issue is

\[(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} \text{ is diagonal in } \left| \text{III} \right\rangle \text{ states}\]

while

\[\mathbf{L} \cdot \mathbf{S} \text{ is diagonal in } \left| \text{I} \right\rangle \text{ states}\]

and relativistic correction is diagonal in both bases.
when \( (\Delta E)_2 \gg (\Delta E)_l^s \)

\[ H_0' = H_0 + \Delta H_z \]

where the perturbation is \( (\Delta E)_l^s \)

when \( (\Delta E)_l^s \gg (\Delta E)_2 \)

\[ H_0' = H_0 + \Delta H_{l^s} \]

where the perturbation is \( (\Delta E)_2 \)

when these are comparable
then we can

\[ H_0' = H_0 \]

and treat \( \Delta H_{l^s} + \Delta H_z \) as a perturbation, you also have to make a basis choice - this will diagonalise one of these while to get the other it will be necessary to use the Clebsch-Gordan coefficient.