

# PHYS 487: Lecture # 9

Cliff Sun

February 17, 2026

## Lecture Span

- Hydrogen Fine structure

## Hydrogen Fine Structure

The Hamiltonian of hydrogen is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (1)$$

Here, we define the fine structure. Relativistic correction and the spin orbit coupling (magnetic field generated from electron orbiting nucleus interacts with nucleus). Next, we will define the Lamb shift. There, we take the electric field  $E$  and turn it into an operator  $\hat{E} \propto (a + a^\dagger)$ . (from QED) Finally, we will look into the hyper-fine structure. This arises from the direct magnetic moment coupling.

## Relativistic correction

The kinetic energy is

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \quad (2)$$

Relativistically,

$$T = \frac{mc^2}{\sqrt{1 - (v/c)^2}} - mc^2 \quad (3)$$

Then, assume circular orbit. Then, this balancing force must be true:

$$\frac{m_e v_n^2}{r_n} = \frac{1}{4\pi\epsilon_0} \frac{a^2}{r^2} \quad (4)$$

Note that  $v_n$  is the velocity in the n-th orbit, and  $r_n$  similar. Quantization:  $m_e v_n r_n = n\hbar$ . This is the angular momentum. Then,

$$v_n = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar} \frac{1}{n} \quad (5)$$

$$r_n = a n^2 = 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2} n^2 \quad (6)$$

For  $a = 1$ , then  $v_1 \sim 2 \times 10^6$  m/s, no relativistic correction yet. Kinetic energy is  $\sim 10$  eV. And  $mc^2 \sim 0.5$  MeV. The relativistic momentum is:

$$p = \frac{mv}{\sqrt{1 - (v/c)^2}} \quad (7)$$

Now, we know:

$$p^2 c^2 + m^2 c^2 = \frac{m^2 v^2 c^2 + m^2 c^4 [1 - (v/c)^2]}{1 - (v/c)^2} = (T + mc^2)^2 \quad (8)$$

Therefore,

$$T = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad (9)$$

This is kinetic energy as a function of momentum. Then,

$$T = mc^2 \left[ \sqrt{1 - \left(\frac{p}{mc}\right)^2} - 1 \right] = mc^2 \left[ 1 + \frac{1}{2} \left(\frac{p}{mc}\right)^2 - \frac{1}{8} \left(\frac{p}{mc}\right)^4 + \dots - 1 \right] \quad (10)$$

$$= \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3 c^2}}_{=H'_r} + \dots \quad (11)$$

Now, we begin perturbation theory. Now, we know that

$$E_n^{(1)} = \langle \psi_n | H' | \psi_n \rangle \quad (12)$$

Then, we calculate

$$E_r^{(1)} = \langle H' \rangle = -\frac{1}{8m^3 c^2} \langle \psi | p^4 | \psi \rangle$$

To calculate this, we turn towards the SWE for unperturbed states. That is,

$$p^2 |\psi\rangle = 2m(E - V) |\psi\rangle \quad (13)$$

We can take the Hermitian conjugate of everything and multiple this function from the left, then we get

$$\begin{aligned} E_r^{(1)} &= -\frac{1}{2mc^2} \langle (E - V)^2 \rangle \\ &= -\frac{1}{2mc^2} [E^2 - 2E\langle V \rangle + \langle V^2 \rangle] \quad \text{now, let } V \text{ be coulomb potential} \\ &= -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right] \\ \left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2 a} \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{(e + 1/2) n^3 a^2} \\ E_r^{(1)} &= -\frac{(E_n)^2}{2mc^2} \left[ \frac{4n}{l + 1/2} - 3 \right] \end{aligned}$$

With  $|\psi_{nlm}\rangle$ . Here, we consider a correction on the order of

$$E_n \times \frac{E_n}{2mc^2} \quad (14)$$

Consider  $E_n/2mc^2$ ,  $E_n$  is on the order of 10s of eV and the denominator is on the order of 1 MeV. Therefore, the correction is on the order of  $E_n \times \mathcal{O}(10^{-5})$ . Here, there are degeneracies lifted with respect to  $l$ . But the degeneracy with respect to the  $z$  project has not been lifted yet.

## Spin-orbit coupling

Such an effect can lift the degeneracy of the  $z$  projection. From the point of view of the electron, the nucleus is orbiting around it with some distance  $r$ . Now, the nucleus generates a magnetic moment which interacts with that of the electron. We know that we will always have an interaction with the magnetic moment and the magnetic field:

$$\hat{H} = -\mu \cdot B \quad (15)$$

Where  $\mu$  is the magnetic moment of the electron. And  $B$  is the field from the orbiting proton (from the perspective of the electron). From Biot-savart,

$$B = \frac{\mu_0 I}{2r} \quad (16)$$

Where,  $I = e/T$  (pretty primitive, but a surprisingly good estimate) and  $T$  is the period in time. We know the orbital angular momentum of the electron as

$$L = rmv = \frac{2\pi mr^2}{T} \quad (17)$$

With  $v = 2\pi r/T$ . Therefore,

$$B = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} L \quad (18)$$

So then, we now try to find  $\mu$ . Toy model: consider a ring charge that rotates. Then

$$\mu = \frac{q}{T} \times \pi r^2 \quad (19)$$

So then, the angular momentum is

$$S = \frac{2\pi}{T} \times mr^2 \quad (20)$$

Then

$$\frac{\mu}{S} = \frac{q}{2m} \quad (21)$$

Then, we get that

$$\mu = \frac{q}{2m} \vec{S} \quad (22)$$

If you do this relativistically, then you get

$$\mu_e = -\frac{e}{m} S \quad (23)$$

The above equation is the correct result. The correction of the classical picture is related to the g-factor = 2.002... Then, our Hamiltonian is

$$H = \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} \quad (24)$$

This is the spin orbit coupling. But we are in an accelerating frame, so we correct this. (this is a grad E&M problem...) Now, we add the factor from the "Thomas precession" = 2. Therefore,

$$H = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = H'_{SO} \quad (25)$$

This is the perturbation to the spin orbit coupling Hamiltonian. Consequences: we have that

$$[H^{(0)}, L] = 0 \quad (26)$$

and

$$[H^{(0)}, S] = 0 \quad (27)$$

due to spherical symmetry. But:

$$[L \cdot S, L] = i\hbar(L \times S) \quad (28)$$

Similarly,

$$[L \cdot S, S] = i\hbar(S \times L) \quad (29)$$

So now, some symmetries are probably broken, and therefore degeneracies are probably being lifted right now. Now, we are looking for  $\hat{A}$  such that

$$[H^{(0)}, A] = 0 = [H', A] \quad (30)$$

Turns out

$$[H'_{SO}, L^2] = 0 = [H'_{SO}, S^2] = [H'_{SO}, J] \quad (31)$$

Where,  $J = L + S$  with eigenstates  $|j, m_j\rangle$ . So, we want  $\langle H'_{SO} \rangle$  and need  $\langle L \cdot S \rangle$  in terms of the good eigenstates (diagonalize  $L \cdot S$ ). So then

$$J^2 = (L + S) \cdot (L + S) = L^2 + S^2 + 2L \cdot S \quad (32)$$

So then

$$L \cdot S = \frac{1}{2} (J^2 - L^2 - S^2) \quad (33)$$

These are all conserved quantum numbers! So then, the eigenvalues are:

$$\frac{\hbar^2}{2} \{j(j+1) - l(l+1) - s(s+1)\} \quad (34)$$

Note that  $s = 1/2$ . Moreover,  $\langle 1/r^2 \rangle$ . Therefore, we are able to write down the spin orbit correction. So then,

$$E_{SO}^{(1)} = \langle H'_{SO} \rangle = \frac{(E_n)^2}{mc^2} \left\{ \frac{n(j(j+1) - l(l+1) - 3/4)}{l(l+1/2)(l+1)} \right\} \quad (35)$$

But if spin is conserved, then  $j = l \pm 1/2$  and combine the relativistic correction:

$$E_{nj} = -\frac{13.6\text{eV}}{n^2} \left( 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+1/2} - \frac{3}{4} \right) \right) \quad (36)$$

Now, all the degeneracies have been broken. Here,

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \sim \frac{1}{137} \quad (37)$$

This is the fine structure constant.