Lecture 14

Rest of Chapter 6: apply perturbation theory to hydrogen

Thought you knew hydrogen:

$$H = \frac{p^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

(note μ = reduced mass)

Quantum numbers n, l, m

$$E_{nlm} = \frac{E_1}{n^2} \qquad E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

But some things left out.
→ small, so correct with perturbation theory

Start with special relativity

Really, $H = T + U$

T = Kinetic energy

said $T = \frac{p^2}{2m}$, but this is true only in limit $v \ll c$

Typical atomic velocity $\frac{p}{m} = \frac{\hbar}{ma} = 2.2 \times 10^6$ m/s
$\approx 10^{-2} c$

So $\frac{v}{c}$ is small, but not infinitesimal.

Correct using relativistic formula for T:

$$T = E - mc^2 = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

Square root is tough, takes Dirac equation to handle

But since $v \ll c$, we can just Taylor expand:

$$\sqrt{m^2c^4+p^2c^2} = mc^2\left(1+\frac{p^2}{m^2c^2}\right)^{1/2} = mc^2\left(1+\frac{p^2}{2m^2c^2}-\frac{1}{8}\frac{p^4}{m^4c^4}+\dots\right)$$

So $$T = \frac{p^2}{2m} \underbrace{- \frac{1}{8}\frac{p^4}{m^3c^2}}_{\text{Treat as perturbation}}$$

Especially easy: p^4 is spherically symmetric

$\Rightarrow$ commutes with L^2 and L_z

So l and m remain good quantum numbers

Can just use 1st order PT, don't need to worry about degeneracies

All off diagonal W_{ij}'s $= 0$ between degenerate states

So need to find

$\langle \psi_{nlm} | p^4 | \psi_{nlm} \rangle$ just an integral

Note $p^4 \to \nabla^4$, kind of a pain

use a trick instead: $p^4 = p^2 \cdot p^2$

p^2 is Hermitean

So $\langle \psi_{nlm} | p^4 | \psi_{nlm} \rangle = \langle p^2 \psi_{nlm} | p^2 \psi_{nlm} \rangle$

But we know

$$p^2 \psi_n = 2m(H-V)\psi_n$$

So $\langle p^2\psi_n | p^2\psi_n\rangle = \langle \psi_n | [2m(H-V)]^2 | \psi_n\rangle$

$$= 4m^2 \langle \psi_n | (H^2 - HV - VH + V^2) | \psi_n\rangle$$

$$= 4m^2 \left(E_n^2 - 2E_n \langle \psi_n | V | \psi_n\rangle + \langle \psi_n | V^2 | \psi_n\rangle \right)$$

$$= 4m^2 \left[E_n^2 + 2E_n \frac{e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \left\langle \frac{1}{r^2} \right\rangle \right]$$

Just need to know $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$

Still kind of painful, want for <u>all</u> $n\ell m$'s

Use more tricks ... boy are we lazy!

Virial theorem gives $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}$

a = Bohr radius $= \frac{4\pi\varepsilon_0 \hbar^2}{m e^2}$

Kalin will show in a bit

You'll get $\left\langle \frac{1}{r^2} \right\rangle$ in next HW:

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(\ell+\frac{1}{2}) n^3 a^2}$$

So we have $E^{(1)}_{n\ell m} = -\frac{1}{8}\frac{1}{m^3c^2}\langle p^4\rangle$

$$= -\frac{1}{8}\frac{1}{m^3c^2}\cdot 4m^2\left[\frac{E_1^2}{n^4} + 2\frac{E_1}{n^2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{n^2a} + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{\ell+\frac{1}{2}}\frac{1}{n^3a^2}\right]$$

Use $E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$

so $\frac{e^2}{4\pi\varepsilon_0} = -2E_1\frac{\hbar^2}{m}\frac{4\pi\varepsilon_0}{e^2} = -2E_1 a$

$$E^{(1)} = -\frac{1}{2mc^2}\left[\frac{E_1^2}{n^4} - 4\frac{E_1^2}{n^4} + E_1^2\frac{4}{n^3(\ell+\frac{1}{2})}\right]$$

$$= -\frac{E_1^2}{2mc^2n^4}\left[-3 + \frac{4n}{\ell+1/2}\right]$$

$$\boxed{E^{(1)} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{\ell+1/2} - 3\right]}$$

That's the 1st order relativistic correction.

See that $\frac{E^{(1)}}{E_n} \sim \frac{E_n}{mc^2} \sim \frac{13.6\text{eV}}{511\text{ keV}} = 2\times10^{-5}$

Small but easily measurable

→ Note, this breaks degeneracy in ℓ!

Next time, see another effect with similar magnitude: spin-orbit coupling.

Collectively, these are called "fine structure"