Lecture 14

Start applying PT to H atom

$$H^{(0)} = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Eigenstates $\psi^{(0)}_{n\ell m}$

Energies $E_n^{(0)} = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2}$

$$\equiv \frac{E_1}{n^2}$$

also write $E_1 = -\frac{\hbar^2}{2ma^2}$ for $a = \frac{\hbar^2}{m}\frac{4\pi\varepsilon_0}{e^2}$

Bohr radius $= 0.53$ Å

First perturbation: special relativity

Electron has $v \sim \sqrt{\frac{2|E_n|}{m}} \approx \frac{\hbar}{ma} \approx 10^{-2} c$ for $n=1$

So v/c small, but not negligible

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

$$= mc^2\left[\left(1 + \frac{p^2}{m^2c^2}\right)^{1/2} - 1\right]$$

Taylor expand $(1+\varepsilon)^{1/2} \approx 1 + \frac{\varepsilon}{2} - \frac{\varepsilon^2}{8}$

So $T \approx mc^2\left[1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} - 1\right]$

$$= \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{Perturbation } H'}$$

Of course, eigenstates $\psi^{(0)}_{n\ell m}$ are degenerate

E_n independent of ℓ, m

$\Rightarrow$ degenerate PT need

But... H' is spherically symmetric

So $[H', L^2] = [H', L_z] = 0$

From last time, know $\langle \psi^{(0)}_{n\ell m} | H' | \psi_{n\ell' m'} \rangle = 0$

unless $\ell' = \ell$, $m' = m$

So H' is already diagonal in $n\ell m$ basis.

Can just use 1^{st} order PT

$$E^{(1)}_{n\ell m} = \langle \psi^{(0)}_{n\ell m} | H' | \psi_{n\ell m} \rangle = -\frac{1}{8m^3c^2} \langle p^4 \rangle$$

Need to evaluate, But $p^4 = \hbar^4 \nabla^4$ ... painful

Use trick instead: $p^4 = p^2 \times p^2$

and $p^2 = 2m \times \frac{p^2}{2m} = 2m\left(H^{(0)} - V\right)$

So $\langle p^4 \rangle = \langle \psi_{n\ell m} | \left(2m\left(H^{(0)} - V\right)\right)^2 | \psi_{n\ell m} \rangle$

$$= 4m^2 \langle \psi | \left(H^{(0)}\right)^2 - H^{(0)} V - V H^{(0)} + V^2 | \psi \rangle$$

Let $H^{(0)}$ act:

$$\langle p^4\rangle = 4m^2\left(E_n^2 - 2E_n\langle\psi_{nlm}|V|\psi_{nlm}\rangle + \langle\psi|V^2|\psi\rangle\right)$$

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

Reduced to simple integrals

$$\int |\psi_{nlm}|^2 \frac{1}{r}\, d^3r$$

and $\frac{1}{r^2}$

Still hard though, if we want for all ψ_{nlm}'s

Use more tricks!

Get $\langle\frac{1}{r}\rangle$ from Virial Theorem — Jeff will prove for us

So $\langle V\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r}\right\rangle = 2E_n = -\frac{\hbar^2}{ma^2}\frac{1}{n^2}$

$$\left\langle\frac{1}{r}\right\rangle = \left(\frac{4\pi\varepsilon_0}{e^2}\right)\frac{\hbar^2}{ma^2}\frac{1}{n^2}$$

Clean up by expressing $\boxed{\frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar^2}{ma}}$ (handy)

$$\Rightarrow \boxed{\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2 a}}$$

Didn't have to do any integrals at all!

Can use tricks to get $\langle\frac{1}{r^2}\rangle$ too ... let you do in HW

(in fact can get any $\langle r^n\rangle$)

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

Plug in $\langle p^4 \rangle$

$$\langle p^4 \rangle = 4m^2 \left(E_n^2 + 2E_n \frac{e^2}{4\pi\varepsilon_0} \frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{(l+\frac{1}{2})n^3 a^2} \right)$$

Again eliminate $\frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar^2}{ma}$

$$\langle p^4 \rangle = 4m^2 \left(E_n^2 + 2E_n \frac{\hbar^2}{ma^2} \frac{1}{n^2} + \frac{\hbar^4}{m^2 a^2} \frac{1}{(l+\frac{1}{2})n^3 a^2} \right)$$

But note $E_1 = -\frac{\hbar^2}{2ma^2}$

So $\langle p^4 \rangle = 4m^2 \left(E_n^2 - 4E_n \frac{E_1}{n^2} + \frac{4E_1^2}{(l+\frac{1}{2})n^3} \right)$

and $E_n = \frac{E_1}{n^2}$

$$\langle p^4 \rangle = 4m^2 E_n^2 \left(1 - 4 + \frac{4n}{l+\frac{1}{2}} \right)$$

Finally, $E_n^{(1)} = -\frac{1}{8m^3c^2} \langle p^4 \rangle = \boxed{-\frac{1}{2} \frac{E_n^2}{mc^2} \left(\frac{4n}{l+\frac{1}{2}} - 3 \right)}$

A few things to note

1) $\frac{\Delta E_n}{E_n} \approx \frac{E_n}{mc^2}$, makes sense for a relativistic correction

Order of magnitude is $\sim \frac{13\,eV}{511\,keV} \sim 2\times10^{-5}$

Define $\frac{-E_1}{mc^2} = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right)^2 = \frac{1}{2}\alpha^2$

α = fine structure constant $\approx \frac{1}{137}$
dimensionless

Provides dimensionless measure of strength of EM force

In terms of α: $E_n^{(1)} = E_n \; \frac{\alpha^2}{n} \left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n} \right)$

2) Perturbation breaks degeneracy in l

2s state has $\Delta E = E_2 \; \frac{\alpha^2}{2} \left(2 - \frac{3}{8} \right) = \frac{13}{32} \; E_2 \alpha^2$

2p state has $\frac{7}{48} \; E_2 \alpha^2$

differ by $0.14 \; E_2 \alpha^2$

Frequency shift of $\sim \underline{6 \times 10^9 \text{ Hz}}$

Easy to understand...
s-state electron spends more time near nucleus where it moves faster