PH 451/551 QM

Lecture #19

Fine structure of (H)-atom

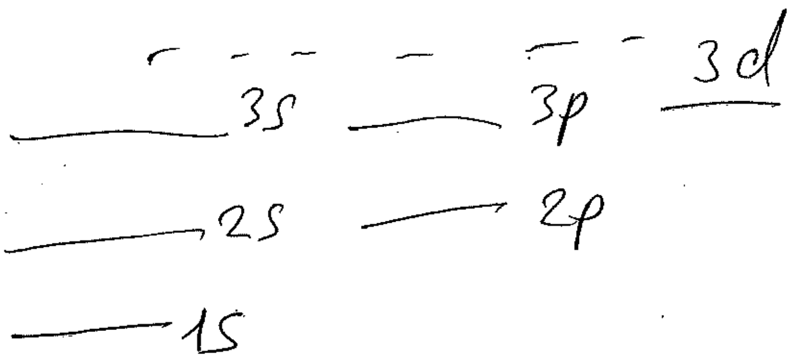
Recall: $H_0 = \frac{p^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0 r} \Rightarrow H_0|nlm\rangle = E_n^{(0)}|nlm\rangle$

$\mu = \frac{m_p m_e}{m_p + m_e} \approx m_e$

$E_n^{(0)} = -\frac{E_I}{n^2}$, $\quad E_I = \frac{1}{2}\alpha^2 \underbrace{mc^2}_{511\ keV}$, $\quad E_I = 13.6\ eV$

E_I: ionization energy a.k.a. Rydberg energy

$|nlm\rangle \doteq R_{nl}(r) Y_{lm}(\theta,\varphi)$



$n = 1, 2, 3, \ldots$; $l = 0, \ldots, n-1$, $-l \le m \le l$

n: principal quantum number; l: orb. ang. mom. quantum number; m: magnetic quantum number

$|nlm\rangle$ is the eigenbasis of $\{H_0, \vec{L}^2, L_z\}$

$\vec{L}^2|nlm\rangle = \hbar^2 l(l+1)|nlm\rangle$

$L_z|nlm\rangle = \hbar m|nlm\rangle$

Also: degeneracy of $E_n^{(0)}$ is n^2 (or $2n^2$ with e^- spin)

But: this picture doesn't account for relativistic nature of e^- in the (H) atom!

$\frac{v}{c} = \frac{e^2}{\hbar c \cdot 4\pi\varepsilon_0} \equiv \alpha = \frac{1}{137}$

α: fine structure const

How to account for relativistic effects? (2)

Solve relativistic Dirac equation instead of non-relativistic Schrödinger

$\Downarrow$

get exact solution, with $E_{n,j}$ ← energy depends on j!

$\vec{J} = \vec{L} + \vec{S}$

add relativistic correction to H_0 & use perturbation theory!

↓ we will do that!

$\Downarrow$

$$\underbrace{H'_{fine}}_{\text{perturbation}} = H'_{rel} + \underbrace{H'_{SO}}_{\text{spin-orbit}} + \underbrace{H'_D}_{\text{Darwin}}$$

1) $H'_{rel} = -\dfrac{p^4}{8\underbrace{m^3}_{m_e}c^2}$ ← due to mass dependence on velocity at relativistic speeds

relativistic energy $E = \sqrt{m^2c^4 + p^2c^2} = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} \simeq$

$$\simeq mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \ldots\right) \simeq \underbrace{mc^2}_{\text{rest-mass energy}} + \underbrace{\frac{p^2}{2m}}_{\text{kinetic energy}} -$$

$\sqrt{1+x^2} \simeq 1 + \frac{x^2}{2} - \frac{x^4}{8} + \ldots$

$$\underbrace{-\frac{p^4}{8m^3c^2}}_{H'_{rel}} + \ldots$$

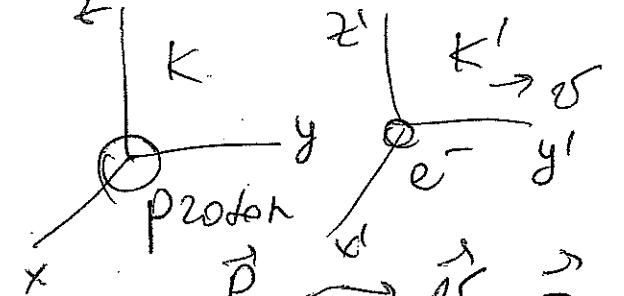
⇒ how large do we expect this perturbation to be?

$\Downarrow$

10^{-5} of unperturbed energies! ⇒ $\dfrac{p^4}{8m^3c^2} = \dfrac{p^2}{4m^2c^2} \simeq \underbrace{\dfrac{v^2}{4c^2}}_{\sim 10^{-5}} \sim \dfrac{\alpha^2}{4}$

2) Spin-orbit coupling:

$$H'_{SO} = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2 r^3}\,\vec{L}\cdot\vec{S}$$ ← will not contribute to s-states ($l=0$)



1) e^- moves in the electric field generated by proton ⇒ this generates magnetic field

$$\frac{\vec{p}}{m} \rightarrow \frac{\vec{v}}{c^2}\times\vec{E} \Rightarrow \vec{B} = \frac{e}{4\pi\varepsilon_0 m c^2 r^3}\vec{L}$$

↑ electric field created by proton; ↑ orb. ang. mom. of e^-

$\vec{E} = \frac{e}{4\pi\varepsilon_0 r^3}\vec{r}$ ⇐

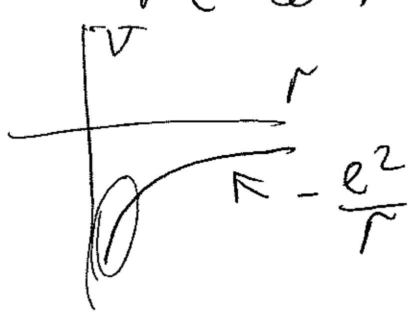
2) e^- spin interacts with this B-field ⇓

$$\vec{\mu} = -\frac{e}{m}\vec{S} \Rightarrow H'_{SO} = -\vec{\mu}\cdot\vec{B}$$

↑ magnetic moment ↑ spin

(3) Darwin term ← like Fermi's contact term, $\neq 0$ only for s-states

↑ jittering motion of e^- at $r \to 0$ (where $V(r)$ changes dramatically)



$$H'_D = \frac{\hbar^2 e^2}{8 m^2 c^2 \varepsilon_0}\delta(\vec{r})$$

↑ $\sim \vec{\nabla}^2 \underbrace{V(r)}_{-\frac{e^2}{4\pi\varepsilon r}} \Rightarrow \vec{\nabla}^2\left(\frac{1}{r}\right) = -4\pi\delta(\vec{r})$

Note: all three fine structure corrections are of the order of $\alpha^2 \sim 10^{-5}$ of unperturbed energies!

So the energy correction $\Rightarrow$

$$E^{(1)}_{rel} = \langle nlm | H'_{rel} | nlm \rangle = -\frac{1}{8m^3c^2} \cdot \langle nlm | p^4 | nlm \rangle \underset{HW!}{=} -\frac{1}{2}\alpha^4 mc^2 \cdot \left[\frac{1}{n^3(l+\frac{1}{2})} - \frac{3}{4n^4}\right]$$

$$E^{(1)}_{SO} = \langle H'_{SO} \rangle = \frac{e^2}{8\pi\varepsilon_0 \cancel{m c^2}} \cancel{\langle n l m_l m_s | \frac{\vec{L}\cdot\vec{S}}{r^3} | n l m_l m_s \rangle} =$$

will not be diagonal in this basis!

use coupled basis instead!

$$H'_{SO} = \frac{e^2}{8\pi\varepsilon_0 m^2c^2 r^3} \underbrace{\vec{L}\cdot\vec{S}}_{=\frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)}$$

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

recall hyperfine splitting!

$$= \frac{e^2}{8\pi\varepsilon_0 m^2c^2} \left\langle \frac{1}{r^3} \right\rangle_{nl} \underbrace{\langle \overset{j_1 j_2 J M}{l s j m_j} | \vec{L}\cdot\vec{S} | l s j m_j \rangle}_{=\frac{1}{2}\hbar^2 (j(j+1) - l(l+1) - s(s+1))} =$$

$$= \frac{1}{4}\alpha^4 mc^2 \frac{j(j+1) - l(l+1) - 3/4}{n^3 \, l\,(l+\frac{1}{2})(l+1)} \quad \text{for } l \neq 0$$

$$E_D^{(1)} = \frac{\hbar^2 e^2}{8 m^2 c^2 \varepsilon_0} \underbrace{\langle n l m | \delta(\vec{r}) | n l m \rangle}_{= |\psi_{nlm}(0)|^2}$$ (only for $l = 0$!)

Putting everything together:

$$E_{fine}^{(1)} = E_{rel}^{(1)} + E_{SO}^{(1)} + E_D^{(1)} =$$

$$= -\frac{1}{2} \alpha^4 m c^2 \frac{1}{n^3} \left[\frac{1}{j + 1/2} - \frac{3}{4n} \right]$$

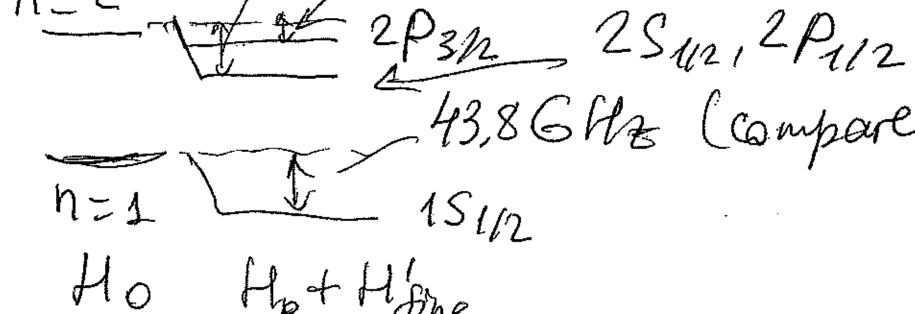
$$E_{n,j} \overset{\text{relativistic Dirac theory}}{=} \frac{mc^2}{\sqrt{1 + \alpha^2 \left(n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - \alpha^2}\right)}} \approx$$

$$\approx \underbrace{mc^2}_{\text{rest-mass energy}} \underbrace{- \frac{1}{2} \alpha^2 m c^2 \cdot \frac{1}{n^2}}_{= E_n} + \underbrace{\alpha^2 E_n \frac{1}{n} \left[\frac{1}{j + 1/2} - \frac{3}{4n} \right]}_{E_{fine}^{(1)}} + \ldots$$

Taylor-expand

$$E_n = -\frac{E_I}{n^2}$$

Note: $E_{n,j}$ now depends on n, j, but not on l!



(compare with 1.42 GHz for hyperfine!)