Fine structure of hydrogenic atoms

- So far we dealt with non-relativistic Hamiltonian $H = \frac{\vec{p}^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}$ ← only Coulomb interaction is taken into account

For a full description

$\Downarrow$

need relativistic Schrödinger equation
(or Klein-Gordon equation)
or (for spin-$\frac{1}{2}$ charged particle) Dirac equation.
See Appendix 7 in B & J.

In this case, get $E_{n,j} = \frac{m_e c^2}{\sqrt{1 + \alpha^2 (n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - \alpha^2})}}$

instead of $E_n = -\frac{E_I}{n^2}$ $\Rightarrow$ get j-dependence

j ← quantum number of $\vec{J} = \vec{L} + \vec{S}$

α ← fine structure const

$$= \underbrace{m_e c^2}_{\text{rest}} - \underbrace{\frac{E_I}{n^2}}_{\text{Coulomb } (E_n)} - \underbrace{\frac{m_e c^2 \alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)}_{\text{fine interaction}} + \ldots$$

$\uparrow$ expand in powers of α

fine interaction $= E_n \cdot \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)$ $\Rightarrow$ introduces j-dependence

Our approach: use non-relativistic Schrödinger equation and introduce corrections to the Hamiltonian (perturbation)

Validity: (H)-atom is a weakly relativistic system

$\Downarrow$

Dirac equation can be simplified by expansion of the Hamiltonian in powers of $\frac{v}{c}$

Check: $\frac{v}{c} = \,?$ $\Rightarrow$ estimate using semi-classical Bohr model $\Rightarrow$ $mvr = n\hbar$

$\uparrow$ quantization condition

$r \sim a_0, \ n = 1 \Rightarrow v \sim \frac{\hbar}{ma_0} \sim \frac{e^2}{(4\pi\varepsilon_0)\hbar}$

$a_0 = \frac{4\pi\varepsilon_0 \hbar}{me^2}$

Then, $\frac{v}{c} = \frac{e^2}{(4\pi\varepsilon_0)\hbar c} = \alpha = \frac{1}{137} \ll 1$

α: fine-structure constant

if $Z \neq 1 \Rightarrow a_0 \to \frac{a_0}{Z}$

$\Downarrow$

$\frac{v}{c} = Z\alpha \ll 1$ if Z is not too large

So, the Hamiltonian is:

$$H = \underbrace{\frac{\vec{p}^{\,2}}{2m} - \overbrace{\frac{Ze^2}{4\pi\varepsilon_0 r}}^{V(r)}}_{H_0} + \underbrace{H'_{(\text{fine})} + H'_{(\text{hyperfine})}}_{\text{perturbation}}$$

Start from $H'_{(\text{fine})} = H_1' + H_2' + H_3' \Rightarrow$

$$H_1' = -\frac{p^4}{8m^3c^2} \quad ; \quad H_2' = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S}$$

relativistic correction to the kinetic energy

spin-orbit coupling

$$H_3' = \underbrace{\frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(\vec{r})}_{\parallel} \leftarrow \text{Darwin term}$$

(non-locality of interaction between nucleus and Coulomb field)

$$\frac{\hbar^2}{8mc^2}\Delta\underbrace{\left(-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)}_{V} \leftarrow \text{a more general form}$$

Where do $H'_{1,2,3}$ come from? $\Rightarrow$

H_1': $E = c\sqrt{\vec{p}^2 + m^2c^2} = mc^2\left(1 + \frac{\vec{p}^2}{2m^2c^2} - \frac{\vec{p}^4}{8m^4c^4} + \dots\right) =$

energy of a classical relativ. particle

$\frac{v}{c} \ll 1$

$\sqrt{1+x} = 1 + \frac{x}{2} - \frac{x^2}{8} + \dots$

$$= \underbrace{mc^2}_{\text{rest mass energy}} + \underbrace{\frac{\vec{p}^2}{2m}}_{\text{non-rel. kin. energy}} - \frac{\vec{p}^4}{8m^3c^2} \leftarrow$$

1^{st}-order correction due to relativistic variation of the mass with velocity

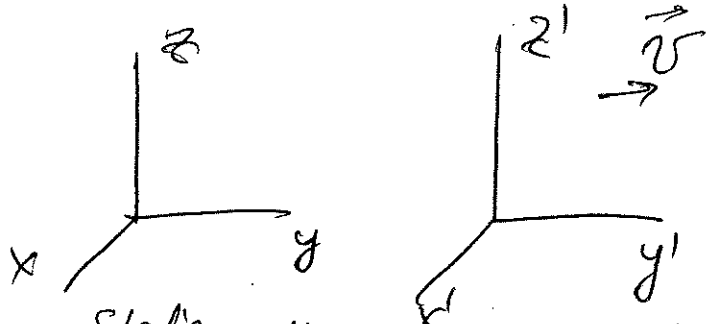
Size of the correction:

$$\frac{\frac{\vec{p}^4}{8m^3c^2}}{\frac{\vec{p}^2}{2m}} = \frac{\vec{p}^2}{4m^2c^2} \underset{\uparrow}{=} \frac{1}{4}\left(\frac{v}{c}\right)^2 \sim$$

$p = mv$

$$\sim \frac{1}{4}\alpha^2 \sim 1.3 \cdot 10^{-5}$$ ← very small!

$\uparrow$ $\frac{v}{c} = \alpha$



H_2': Recall E&M;

In the frame K' magnetic field $\vec{B}' = -\frac{\vec{v}}{c}\times\vec{E}$

to the 1st order in $\frac{v}{c}$

$\vec{E}$: electric field created by proton

stationary system K ⇓ proton

system K' moving with velocity $\vec{v}$ ⇓ electron

Interaction between the electron's magnetic moment $\vec{M}_s = \frac{e}{mc}\vec{S}$, and $\vec{B}' \Rightarrow H_2' \sim -\vec{M}_s\cdot\vec{B}' =$

$$= \frac{e}{mc^2}\vec{S}\cdot(\vec{v}\times\underset{\uparrow}{\vec{E}}) = -\frac{e^2}{mc^2r^3(4\pi\varepsilon_0)}\vec{S}\cdot(\underbrace{\vec{v}}_{\frac{\vec{p}}{m}}\times\vec{r}) =$$

$$\vec{E} = \frac{\vec{F}}{e} = \frac{1}{e}\underbrace{\left(-\frac{dV(r)}{dr}\right)}_{\frac{Ze^2}{4\pi\varepsilon_0 r^2}}\frac{\vec{r}}{r} = -\frac{Ze^2}{4\pi\varepsilon_0 r^3}\vec{r}$$

$$= -\frac{Ze^2}{(4\pi\varepsilon_0)m^2c^2r^3}\vec{S}\underbrace{(\vec{p}\times\vec{r})}_{=-\vec{L}} = \frac{Ze^2}{4\pi\varepsilon_0 c^2r^3m^2}\vec{L}\cdot\vec{S}$$

$-\vec{L}$ ← orb ang mom

a factor of $\frac{1}{2}$ is missing since we took into account only translation of K' and not rotation

Order of magnitude: $|\vec{L}|, |\vec{S}|$

$$\frac{H_2'}{\frac{Ze^2}{4\pi\varepsilon_0 r}} \sim \frac{\frac{Ze^2}{4\pi\varepsilon_0 c^2 r^3 m^2}\cdot\hbar^2}{\frac{Ze^2}{4\pi\varepsilon_0 r}} \sim \frac{\hbar^2}{m^2c^2r^2} \simeq \frac{\hbar^2 \cancel{m^2} e^4 Z^2}{\cancel{m^2} c^2 (4\pi\varepsilon_0)^2 \hbar^4} =$$

$r \sim \frac{a_0}{Z} = \frac{(4\pi\varepsilon_0)\hbar^2}{me^2Z}$

$$= \frac{e^4 Z^2}{\hbar^2 c^2 (4\pi\varepsilon_0)^2} = \alpha^2 Z^2$$

H_3': Darwin term

$$H_3' = \frac{\hbar^2}{8m^2c^2}\Delta\left(-\frac{Ze^2}{4\pi\varepsilon_0 r}\right) = -\frac{\hbar^2 Ze^2}{8m^2c^2(4\pi\varepsilon_0)}\underbrace{\Delta\left(\frac{1}{r}\right)}_{= -4\pi\delta(\vec{r})} = \frac{\pi\hbar^2}{2m^2c^2}\cdot\frac{Ze^2}{4\pi\varepsilon_0}\delta(\vec{r})$$

Order of magnitude: $\langle\psi|H_3'|\psi\rangle \sim \frac{\pi e^2 Z\hbar^2}{2m^2c^2}\cdot$

$$\cdot\frac{1}{4\pi\varepsilon_0}\underbrace{\int|\psi|^2\delta(\vec{r})\,d\vec{r}}_{|\psi(0)|^2} = \frac{\pi Ze^2\hbar^2}{2m^2c^2}\cdot\frac{1}{4\pi\varepsilon_0}|\psi(0)|^2$$

at $\vec{r}=0$

Recall: $\psi \sim C r^l e^{-\frac{Zr}{na_0}} Y_{lm}(\theta,\varphi) \sim r^l \Rightarrow$

at small r's

$\psi(0) \neq 0$ only for s-states!

So, order of magnitude for $|\Psi(0)|^2$? 6 $\Rightarrow$

$$\int |\Psi(\vec{r})|^2 dV = 1 \Rightarrow \underset{\uparrow}{|\Psi(0)|^2} \cdot \frac{4\pi a_0^3}{3} \sim 1 \Rightarrow$$

s-states are localised around 0

H-atom ; $a_0 \to \frac{a_0}{Z}$ if $Z \neq 1$

$|\Psi(0)|^2 \sim \frac{3}{4\pi a_0^3}$

$$\langle\Psi|H_3'|\Psi\rangle \sim \frac{\pi Z e^2 \hbar^2}{2m^2c^2} \cdot \frac{1}{4\pi\varepsilon_0} \cdot \frac{3Z^3}{4\pi a_0^3} = \frac{3}{8} Z^4 m c^2 \alpha^4$$

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$

$$\frac{\langle\Psi|H_3'|\Psi\rangle}{\frac{p^2}{2m} \text{ or } \frac{Ze^2}{4\pi\varepsilon_0 r}} = \frac{\frac{3}{8} Z^4 m c^2 \alpha^4}{\frac{Z e^2}{4\pi\varepsilon_0 a_0}} = \frac{3}{8} Z^4 \cancel{m} c^2 \alpha^4 \cdot \frac{(4\pi\varepsilon_0)^2 \hbar^2}{\cancel{m} Z^2 e^4} =$$

$$= \frac{3}{8} Z^2 \alpha^2$$

but in many-electron atoms $H_2' \sim \vec{L}\cdot\vec{S}$ dominates!!

So, all three terms $\to H'_{1,2,3}$ are $\sim \alpha^2$ order as compared to unperturbed Hamiltonian

Next step $\Rightarrow$ find energy corrections due to $H'_{1,2,3}$ perturbation $\Rightarrow \Delta E_{1,2,3} = \langle\Psi|H'_{1,2,3}|\Psi\rangle$

time-independent perturbation theory

unperturbed state $|nlm\rangle$