

## Physics 531 - Lecture 3 - Fine Structure

Our description of the spectrum of Hydrogen used the non relativistic Schrödinger equation. How good an approximation is this?

Recall characteristic units: Given  $m_e, e, \hbar$

$$\Rightarrow \text{Length: } a_0 = \frac{\hbar^2}{m_e e^2} \approx 0.5 \text{ \AA} \quad (\text{Bohr radius})$$

$$\text{Energy: } E_0 = \frac{e^2}{a_0} = \frac{m_e c^4}{\hbar^2} \approx 27.2 \text{ eV} \quad (\text{Hartree})$$

$$\Rightarrow \text{time: } t_0 = \frac{\hbar}{E_0} = \frac{\hbar a_0}{e^2}$$

$$\text{velocity: } v_0 = \frac{a_0}{t_0} = \frac{e^2}{\hbar}$$

Relativity  $\Rightarrow$  New constant,  $c = \text{speed of light}$

$$\Rightarrow \text{Dimensionless unit } \boxed{\alpha = \frac{v_0}{c} = \frac{e^2}{\hbar c} = \frac{1}{137}} \quad \textcircled{*}$$

$\alpha \equiv$  Fine structure const, characteristic coupling in quantum electrodynamics

Since  $v_0 = \frac{1}{137} c \Rightarrow$  Relativistic effect very small perturbation

Exact solution  $\Rightarrow$   $\left\{ \begin{array}{l} \text{Q.E.D. (Dirac \& Spinors)} \\ \text{(Electron and Positron)} \end{array} \right.$

$$\text{Dirac } \hat{H}_{\text{Dirac}} = c \vec{\alpha} \cdot (\vec{p} + e \vec{A}) - e \Phi(\vec{x}) + \beta m c^2$$

$$\text{where } \vec{\alpha} = \begin{bmatrix} 0 & \hat{\sigma} \\ \hat{\sigma} & 0 \end{bmatrix} \quad \beta = \begin{bmatrix} \hat{1} & 0 \\ 0 & -\hat{1} \end{bmatrix}$$

Expand in powers  $\frac{v_0}{c} \Rightarrow$  Nonrelativistic limit

For hydrogen, with nucleus fixed in lab frame  
 $\Rightarrow$  electrostatic potential energy  $V(\vec{r}) = -e\Phi(\vec{r})$

Look only at the 2-component electron spinor.

$$\Rightarrow \hat{H}_{\text{Dirac}} = \underbrace{m_e c^2}_{\text{rest mass}} + \underbrace{\frac{\vec{p}^2}{2m_e}}_{\text{Non-relativistic electron in coulomb potential}} + V(\vec{r})$$

$$\underbrace{-\frac{\vec{p}^4}{8m_e^3 c^2} + \frac{1}{2m_e^2 c^2} \left( \frac{1}{r} \frac{dV}{dr} \right) \vec{L} \cdot \vec{S} + \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V}_{\text{Relativistic corrections of order } \frac{v_0^2}{c^2} = \alpha^2}$$

Physical meaning of different terms

• Relativistic correction to kinetic energy:

Excluding potential energy, the energy of the electron

$$E = \sqrt{p^2 c^2 + m_e^2 c^4} = m_e c^2 \left( 1 + \left( \frac{p}{m_e c} \right)^2 \right)^{1/2}$$

$$= m_e c^2 \left( 1 + \frac{1}{2} \left( \frac{p}{m_e c} \right)^2 - \frac{1}{8} \left( \frac{p}{m_e c} \right)^4 + \mathcal{O} \left[ \left( \frac{p}{m_e c} \right)^6 \right] \right)$$

$$\Rightarrow E = m_e c^2 + \frac{p^2}{2m_e} - \frac{1}{8} \frac{p^4}{m_e^3 c^2}$$

$$\text{In a.u. } p_0 = \frac{\hbar}{a_0} = \frac{m_e c^2}{\hbar} \Rightarrow \frac{p_0^4}{m_e^3 c^2} = \left( \frac{c^2}{\hbar c} \right)^2 \frac{m_e^4}{\hbar^2} = \alpha^2 E_0$$

$$\text{In a.u. } e = \hbar = m_e = 1 \quad \left. \vphantom{\text{In a.u.}} \right) \text{ Note 1 Hartree} = \alpha^2 m_e c^2$$

$$c = \frac{1}{\alpha} = 137$$

• Spin-orbit coupling

Whereas the field of the proton in its rest frame is electrostatic, in the frame of the electron there is also a magnetic field. For  $\frac{v}{c} \ll 1$

$$\vec{B}_{e\text{-frame}} = -\frac{1}{c} \vec{v} \times \vec{E} \quad |\vec{B}| \ll |\vec{E}|$$

This field interacts with the intrinsic magnetic moment of the electron

$$\hat{H}_{int} = -\hat{\mu}_e \cdot \vec{B}_{e\text{-frame}}$$

$$\hat{\mu}_e = -2 \left( \frac{\mu_B}{\hbar} \right) \hat{S}$$

g-factor    Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e c}$$

Now  $\vec{v} = \frac{\vec{p}}{m_e}$

$$\vec{E} = \frac{e}{r^2} \vec{e}_r = -\frac{d\phi}{dr} \vec{e}_r = -\frac{1}{r} \frac{d\phi}{dr} \vec{x}$$

$$\Rightarrow \vec{B}_{e\text{-frame}} = \frac{1}{m_e c} \frac{1}{r} \frac{d\phi}{dr} \vec{p} \times \vec{x} = -\frac{1}{m_e c} \frac{1}{r} \frac{d\phi}{dr} \vec{L}$$

This is the field of a current loop around electron. orbital ang. mom.

$$\hat{H}_{int} = \frac{-e}{m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} \vec{L} \cdot \vec{S} = \frac{1}{m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S}$$

where  $V = -e\phi = \frac{-e^2}{r}$  (Coulomb potential)

$\Rightarrow$  Coupling of electron spin and orbital moment

\* Correction: We used a non-inertial frame.

Electron in rotating frame

$\Rightarrow$  Lorentz transformation (kinematic)

$\Rightarrow$  Thomas Precession

$$\Rightarrow \hat{H}_{so} = \frac{1}{2m_e^2 c^2} \left( \frac{1}{r} \frac{dV}{dr} \right) \vec{L} \cdot \vec{S} = \frac{\alpha^2}{2} \left( \frac{1}{r} \frac{dV}{dr} \right) \vec{L} \cdot \vec{S}$$

in a.u.

## • Darwin term

The interaction between the ~~disturbance~~ Dirac spinor and electromagnetic field is local. However, by ignoring the positron component we end up with a slightly non-local effect, extending over a range on the order of the Compton wavelength. This is the origin of the final correction term, known as the "Darwin term".

$$\hat{H}_{\text{Darwin}} = \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V = \frac{-\hbar^2 e^2}{8m_e^2 c^2} \nabla^2 \left( \frac{1}{r} \right)$$

(Poisson Eq. for point charge)  
 $(-4\pi S^{(3)}(\vec{x}))$

$$\Rightarrow \hat{H}_{\text{Darwin}} = \frac{\pi e^2 \hbar^2}{2m_e^2 c^2} \delta(\vec{x}) = \frac{\pi}{2} \alpha^2 \delta(\vec{x}) \text{ (in a.u.)}$$

Thus, the perturbation Hamiltonian

$$\hat{H}_{\text{int}} = \hat{H}_{\text{kin}} + \hat{H}_{\text{so}} + \hat{H}_{\text{Darwin}}$$

$$\hat{H}_{\text{int}} = -\frac{\alpha^2}{8} p^4 + \frac{\alpha^2}{2} \left( \frac{1}{r} \frac{dV}{dr} \right) \vec{L} \cdot \vec{S} + \alpha^2 \frac{\pi}{2} \delta(\vec{x})$$

## Fine structure of $n=2$ of Hydrogen

In the absence of the relativistic corrections, the hydrogenic eigenstates are independent of  $l$ .

Including spin the 2s shell has 2 states  
 2p shell has  $2 \times 3 = 6$  states

$$\Rightarrow 8 \text{ degenerate sublevels} = 2 \times (n=2)^2$$

The relativistic perturbation (partially) breaks the degeneracy. The substructure is called "fine structure".

In the degenerate manifold we must diagonalize  $\hat{H}_{int}$

Note:  $\hat{H}_{kin}$  and  $\hat{H}_{Darwin}$  are rotationally symmetric

$\Rightarrow$  they commute with  $\hat{L}^2$

Also  $\hat{L}^2$  commutes with all components of  $\vec{L}$  and  $\vec{S}$

$\rightarrow \hat{H}_{s.o.}$  commutes with  $\hat{L}^2$

$\Rightarrow$   $l$  remains a good quantum #

(no off diagonal elements between different  $l$ )

Order basis  $\{ |2s, \uparrow\rangle \oplus \begin{Bmatrix} |1\uparrow\rangle \\ |1\downarrow\rangle \end{Bmatrix}, |2p, m\rangle \oplus \begin{Bmatrix} |1\uparrow\rangle \\ |1\downarrow\rangle \end{Bmatrix} \}$

$$\Rightarrow \hat{H}_{int} = \begin{bmatrix} \begin{matrix} 2s & 2p \\ 2 \times 2 & 0 \end{matrix} & \\ 0 & \begin{matrix} 6 \times 6 \end{matrix} \end{bmatrix} \quad \text{Blocks}$$

2s-subspace: ( $l=0$ )

In this subspace  $\hat{H}_{s.o.} = 0$  since  $l=0$

$\hat{H}_{kin}$  and  $\hat{H}_{Darwin}$  independent of spin  $\Rightarrow$  both

$2 \times 2$  matrices proportional to the identity

$$\begin{aligned} \hat{H}_{kin} &\doteq - \frac{\langle n=2, l=0, m=0 | \hat{p}^4 | n=2, l=0, m=0 \rangle}{\langle n=2, l=0, m=0 | n=2, l=0, m=0 \rangle} \left( \frac{\hbar^2}{8} \right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \\ &= - \frac{\hbar^2}{8} \| \hat{p}^2 | n=2, l=0, m=0 \rangle \|^2 \quad (\text{norm squared}) \end{aligned}$$

Aside:  $\hat{p}^2 |nlm\rangle = 2(E_n - \hat{V}) |nlm\rangle$

$$\begin{aligned} \Rightarrow \| \hat{p}^2 |nlm\rangle \|^2 &= 4 (E_n^2 - 2E_n \langle \hat{V} \rangle_{nl} + \langle \hat{V}^2 \rangle_{nl}) \\ &= 4 \left( +\frac{1}{4n^4} - 2 \left( \frac{-1}{2m^2} \right) \langle \frac{-1}{r} \rangle_{nl} + \langle \frac{1}{r^2} \rangle_{nl} \right) \end{aligned}$$

From Problem Set:

$$\langle \frac{1}{r} \rangle = \frac{1}{n^2}$$

$$\langle \frac{1}{r^2} \rangle = \frac{1}{n^3(l+\frac{1}{2})}$$

$$\Rightarrow \hat{H}_{kin} = -\frac{\alpha^2}{2} \left( \frac{-3}{4n^4} + \frac{1}{n^3(l+\frac{1}{2})} \right) \Big|_{n=2, l=0} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\bullet \hat{H}_{kin} = \frac{-13}{128} \alpha^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ in } \underline{2s \text{ subshell}}$$

For Darwin term

$$\langle n=2, l=0, m=0 | \hat{H}_{\text{Darwin}} | n=2, l=0, m=0 \rangle$$

$$= \alpha^2 \frac{\pi}{2} |\psi_{200}(0)|^2 = \alpha^2 \frac{\pi}{2} \frac{1}{4\pi} \underbrace{|R_{20}(0)|^2}_{\frac{1}{2}}$$

$$\Rightarrow \hat{H}_{\text{Darwin}} = \frac{\alpha^2}{16} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ in } 2s \text{ subshell}$$

$\Rightarrow$  Under the effect of lowest order <sup>relativistic</sup> corrections ~~to~~ from the Dirac equation, the 2s subshell is shifted lower by

$$\Delta E_{2s} = -\frac{5}{128} \alpha^2 \text{ Hartrees}$$

$$= 56.6 \text{ } \mu\text{eV}$$

$$\text{Note } 1 \text{ eV} = h\nu \Rightarrow \nu = 2.4 \times 10^{14} \text{ Hz}$$

$$\text{or } 1 \text{ GHz} = 4.1 \text{ } \mu\text{eV}$$

$$\Rightarrow \Delta E_{2s} = 138 \text{ GHz}$$



⇒ Diagonal matrix elements of spin-orbit Hamiltonian

$$\frac{\alpha^2}{2} \langle n\ell | \frac{1}{r} \frac{dV}{dr} | n\ell \rangle \langle \ell s m_\ell | \vec{L} \cdot \vec{S} | \ell s m_\ell \rangle$$

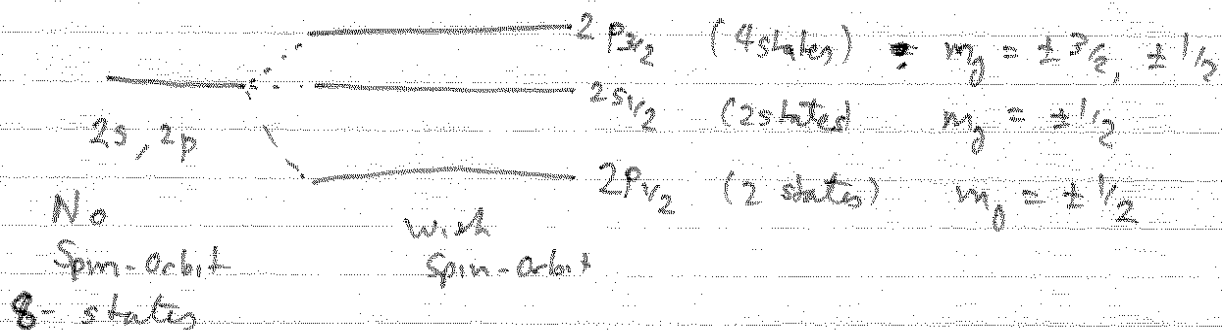
with  $V(r) = -\frac{1}{r}$  in a.u.  $\frac{1}{r} \frac{dV}{dr} = \frac{1}{r^3}$

From Problem set  $\langle n\ell | \frac{1}{r^3} | n\ell \rangle = \frac{1}{n^3 \ell(\ell+1)(\ell+\frac{1}{2})}$

and  $\langle \ell s m_\ell | \vec{L} \cdot \vec{S} | \ell s m_\ell \rangle = \frac{1}{2} \begin{cases} \ell & \text{when } j = \ell + \frac{1}{2} \\ -(\ell+1) & \text{when } j = \ell - \frac{1}{2} \end{cases}$

⇒  $\langle n\ell s m_\ell | \hat{H}_{s.o.} | n\ell s m_\ell \rangle = \frac{\alpha^2}{4n^3 \ell(\ell+1)(\ell+\frac{1}{2})} \begin{cases} \ell & j = \ell + \frac{1}{2} \\ -(\ell+1) & j = \ell - \frac{1}{2} \end{cases}$

Spectroscopic notation:  $n\ell_j$  ← new quantum #



$$\langle 2p_{3/2} | \hat{H}_{s.o.} | 2p_{3/2} \rangle = \frac{\alpha^2}{96}$$

$$\langle 2p_{1/2} | \hat{H}_{s.o.} | 2p_{1/2} \rangle = -\frac{\alpha^2}{48}$$

$$\langle 2s_{1/2} | \hat{H}_{s.o.} | 2s_{1/2} \rangle = 0 \quad \text{since } \ell = 0$$



## Total energy shifts

$$\bullet \ 2S_{1/2}: \quad \Delta E_{2S_{1/2}} = \langle 2S_{1/2} | \hat{H}_{kin} | 2S_{1/2} \rangle + \langle 2S_{1/2} | \hat{H}_{Darwin} | 2S_{1/2} \rangle$$

$$= -\frac{5}{128} \alpha^2$$

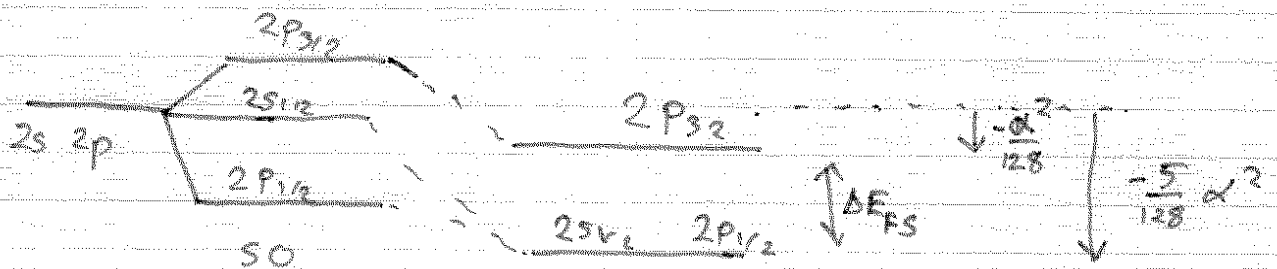
$$\bullet \ 2P_{1/2}: \quad \Delta E_{2P_{1/2}} = \langle 2P_{1/2} | \hat{H}_{kin} | 2P_{1/2} \rangle + \langle 2P_{1/2} | \hat{H}_{SO} | 2S_{1/2} \rangle$$

$$= \left( -\frac{7}{384} - \frac{1}{48} \right) \alpha^2 = -\frac{5}{128} \alpha^2$$

Degenerate with  $2S_{1/2}$  again!

$$\bullet \ 2P_{3/2}: \quad \Delta E_{2P_{3/2}} = \langle 2P_{3/2} | \hat{H}_{kin} | 2P_{3/2} \rangle + \langle 2P_{3/2} | \hat{H}_{SO} | 2P_{3/2} \rangle$$

$$= \left( -\frac{7}{384} + \frac{1}{96} \right) \alpha^2 = -\frac{1}{128} \alpha^2$$



Fine structure Splitting:  $\Delta E_{FS} = \frac{1}{32} \alpha^2 \approx 11 \text{ GHz}$

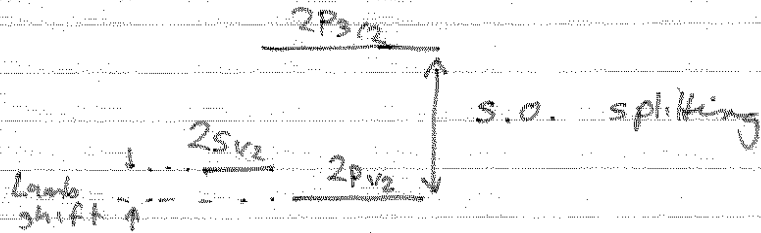
The fact that  $2S_{1/2}$  and  $2P_{1/2}$  follows from a symmetry of the Dirac eqn.

Energy eigenvalues  $E_{ng} = m_e c^2 \sqrt{1 + \alpha^2 \left( n - g - \frac{1}{2} + \sqrt{\left( g + \frac{1}{2} \right)^2 - \alpha^2} \right)^2}$

To Lowest orders:

$$E_{ng} = m_e c^2 - m_e c^2 \alpha^2 \left( \underbrace{-\frac{1}{2n^2}}_{\text{Rydberg}} - \underbrace{\frac{\alpha^2}{2n^4} \left( \frac{n}{g+1/2} - \frac{3}{4} \right)}_{\text{Fine structure}} \right)$$

The Dirac equation does not include a quantized Electromagnetic field. When one does that, the  $2S_{1/2}$  is raised in energy



$$\Delta E_{\text{Lamb}} \approx 1 \text{ MHz}$$