

Phys 522

Lectures 14-16

Hydrogen spectroscopy

# Hydrogen zero-order

$$H_0 = \frac{\vec{p}^2}{2\mu} + V(R)$$

$$\mu = \frac{m_e M_p}{m_e + M_p} = m_e \frac{1}{1 + m_e/M_p}$$

$$V(R) = -\frac{1}{4\pi\epsilon_0} \frac{q^2}{R} = -\frac{e^2}{R}$$

$$e = \frac{q}{\sqrt{4\pi\epsilon_0}}$$

$$H_0 |nlm\rangle = E_n |nlm\rangle$$

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, \dots, n-1$$

s p d f

$$m = -l, \dots, l$$

$$\langle \vec{r} | nlm \rangle = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$E_n = -\frac{e^2}{2a_0 n^2}$$

$$a_0 = \frac{\hbar^2}{\mu e^2}$$

$$= -\frac{13.4 \text{ eV}}{n^2}$$

$$a_0 = \frac{\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}$$

$$= -\frac{1}{2} \mu c^2 \alpha^2 \frac{1}{n^2} \quad \alpha \equiv \frac{v}{c} \approx \frac{1}{137}$$

$$V(R) = -\frac{e^2}{a_0} \frac{a_0}{R} = -m_e c^2 \alpha^2 \frac{a_0}{R}$$

## Additional effects

① Relativistic effects — relativistic mass increase  
 spin-orbit  
 Darwin term  
 $\rightarrow v/c$

$$\frac{\Delta E_{FS}}{|E|} \sim \frac{|E_n|}{\mu c^2} \sim \alpha^2 \sim 10^{-4} \leftarrow \text{fine structure}$$

Treat in perturbation theory — gives physical  
 interp that can be generalized to more  
 complicated descriptions  
 (Dirac gives fundamental description)

$$\Delta E_{FS} \sim m_e c^2 \alpha^4$$

② Nuclear magnetic effects — orbit-nuclear spin — spin-spin (mag dipoles)

$$\Delta E_{HF} \sim \frac{m_e}{M_p} \Delta E_{FS} \quad \leftarrow \text{hyperfine structure}$$

↑  
S-O is electron magnetic moment interacting with magnetic field of nucleus

O-NS is nuclear magnetic moment interacting with magnetic field of electron

$$\frac{\Delta E_{HF}}{\Delta E_{FS}} \sim \frac{m_e}{M_p} \sim \frac{1}{2000}$$

③ Lamb Shift — interaction with vacuum em field (roughly Stark effect of vacuum field)

Splits  $2S_{1/2}$  and  $2P_{1/2}$  by  $\Delta E_{LS} \sim \frac{1}{10} \Delta E_{FS}$

Fine structure:

States:  $|n l m_L m_S m_I\rangle$  ← omit the  $s = \frac{1}{2}$  throughout  
 ↳ leave out for FS; everything 2-fold degenerate

$|n l m_L m_S\rangle$  or  $|n l J m_J\rangle$

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

↳ spectroscopic notation  
 $n l_J$   
 $2S_{1/2}$   
 $2P_{1/2}$   
 $2P_{3/2}$

Hamiltonian:

$$H = m_e c^2 + H_0 + W_{FS}$$

↑  
put  $m$  reduced mass

$$W_{FS} = \underbrace{-\frac{\vec{p}^4}{8m_e^3 c^2}}_{W_{mv}} + \underbrace{\frac{1}{2m_e^2 c^2} \frac{1}{R} \frac{dV}{dR} \vec{L} \cdot \vec{S}}_{W_{SO}} + \underbrace{\frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V}_{W_D}$$

classical relativistic effects quantum effect

$W_m:$

$$E = (c^2 p^2 + m_e^2 c^4)^{1/2}$$

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

$$\approx m_e c^2 \left(1 + \frac{p^2}{2m_e^2 c^2} - \frac{1}{8} \frac{p^4}{m_e^4 c^4} + \dots\right)$$

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

$$\frac{\Delta m}{H_0} \approx \left(\frac{v}{c}\right)^2 \approx \alpha^2 \quad \leftarrow \text{relativistic increase in mass}$$

$W_{SO}$ : Rest frame of electron

$$\vec{B}' = -\frac{1}{c^2} \vec{v} \times \vec{E}$$

$$\vec{M}'_S = g_e \mu_B \vec{S} / \hbar = g \vec{S} / m_e$$

$$\approx \frac{\hbar \vec{S}}{2m_e}$$

$$W' = -\vec{M}'_S \cdot \vec{B}'$$

$$g \vec{E} = -\frac{dV}{dR} \frac{\vec{r}}{r} = -\frac{dV}{dR} \frac{\vec{v}}{v}$$

$$\vec{B}' = +\frac{1}{c^2} \frac{\hbar \vec{p}}{m_e} \times \frac{1}{g} \frac{dV}{dR} \frac{\vec{v}}{v} = -\frac{1}{g m_e c^2} \frac{1}{r} \frac{dV}{dR} \vec{L}$$

$$W' = -\vec{M}'_S \cdot \vec{B}' = +\frac{1}{m_e^2 c^2} \frac{1}{R} \frac{dV}{dR} \vec{L} \cdot \vec{S}$$

Thomas precession: rest frame rotates backwards at half the rate predicted by this torque (purely kinematic effect), so in lab frame

$$W_{SO} = \frac{1}{2m_e^2 c^2} \frac{1}{R} \frac{dV}{dR} \vec{L} \cdot \vec{S} = \frac{e^2}{2m_e^2 c^2} \frac{1}{R^3} \vec{L} \cdot \vec{S}$$

$$\frac{W_{SO}}{H_0} \sim \frac{\frac{\hbar^2}{m_e^2 c^2} \frac{1}{R^3}}{e^2 R} \sim \frac{\hbar^2}{m_e^2 c^2} \frac{1}{R^4} \sim \frac{e^4}{\hbar^2 c^2} = \alpha^2$$

$W_D$ : Darwin term — quantum effect — Zitterbewegung interaction of electron with field over a Compton wavelength =  $\hbar/m_e c$

Slowly varying field — interacts only at quadrupole order w/ 2nd derivatives of  $V$  — diagonalizes 2nd derivative matrix, only  $\nabla^2 V$

$$W_D \sim \nabla^2 V \left( \frac{\hbar}{m_e c} \right)^2$$

$$W_D = \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V = \frac{\pi R^2 \hbar^2}{2m_e^2 c^2} \delta(\vec{R}) \leftarrow \text{only affects } S\text{-states}$$

$$-e^2 \nabla^2 \left( \frac{1}{R} \right) = +e^2 4\pi \delta(\vec{R})$$

$$W_D \sim \frac{e^2 \hbar^2}{m_e^2 c^2} \underbrace{|\psi(0)|^2}_{1/a_0^3} \sim W_{SO}$$

$$\frac{W_D}{H_0} \sim \alpha^2$$

General conclusions:

①  $W_{FS}$  is a scalar  $\Leftrightarrow$  rotationally invariant  $\Leftrightarrow$  conserves  $\vec{J} \Leftrightarrow [W_{FS}, \vec{J}] = 0$

$W_{FS}, \vec{J},$  and  $J_z$  have simultaneous eigenstates. Does this mean  $|n, l, m\rangle$  are eigenstates of  $W_{FS}$ ? No. Explain

(5)

$$\langle n'l' J' m_J' | W_{FS} | n l J m_J \rangle = 0 \text{ unless } J = J' \text{ and } m_J = m_J'$$

But there is more:  $W - E \Rightarrow$

$$\begin{aligned} \langle n'l' J' m_J' | W_{FS} | n l J m_J \rangle &= \underbrace{\langle J m_J 0 | J' m_J' \rangle}_{\delta_{JJ'} \delta_{m_J m_J'}} \langle n'l' J' || W_{FS} || n l J \rangle \\ &= \delta_{JJ'} \delta_{m_J' m_J} \langle n'l' J' || W_{FS} || n l J \rangle \end{aligned}$$

Can see this directly from commutators:

$$0 = \langle n'l' J' m_J' | [W_{FS}, \vec{J}^2] | n l J m_J \rangle = \hbar^2 [J(J+1) - J'(J'+1)] \langle n'l' J' m_J' | W_{FS} | n l J m_J \rangle$$

$$0 = [W_{FS}, J_z] = \hbar (m_J - m_J')$$

$\Rightarrow$  matrix element vanishes unless  $J = J'$  and  $m_J = m_J'$ .

$$\begin{aligned} 0 = \langle n'l' J, m_J+1 | [W_{FS}, J_+] | n l J, m_J \rangle &= \hbar C_+(J, m_J) \langle n'l' J, m_J+1 | W_{FS} | n l J, m_J+1 \rangle \\ &\quad - \hbar C_-(J, m_J+1) \langle n'l' J, m_J | W_{FS} | n l J, m_J \rangle \\ &= C_+(J, m_J) \end{aligned}$$

Same conclusion for 3 pieces of  $W$ .

We are interested in doing degenerate perturbation theory in each degenerate subspace (each  $n$ ). Still need to investigate  $l$  degeneracy.  $n'=n$

②  $W_{mv}$  and  $W_D$  are scalars wrt  $\vec{L}$  and  $\vec{S} \Leftrightarrow$   
invariant under spatial and spin rotations  
Separately  $\Leftrightarrow$  conserve  $\vec{L}$  and  $\vec{S} \Leftrightarrow$

$$[W_{mv}, \vec{L}] = 0 = [W_D, \vec{L}]$$

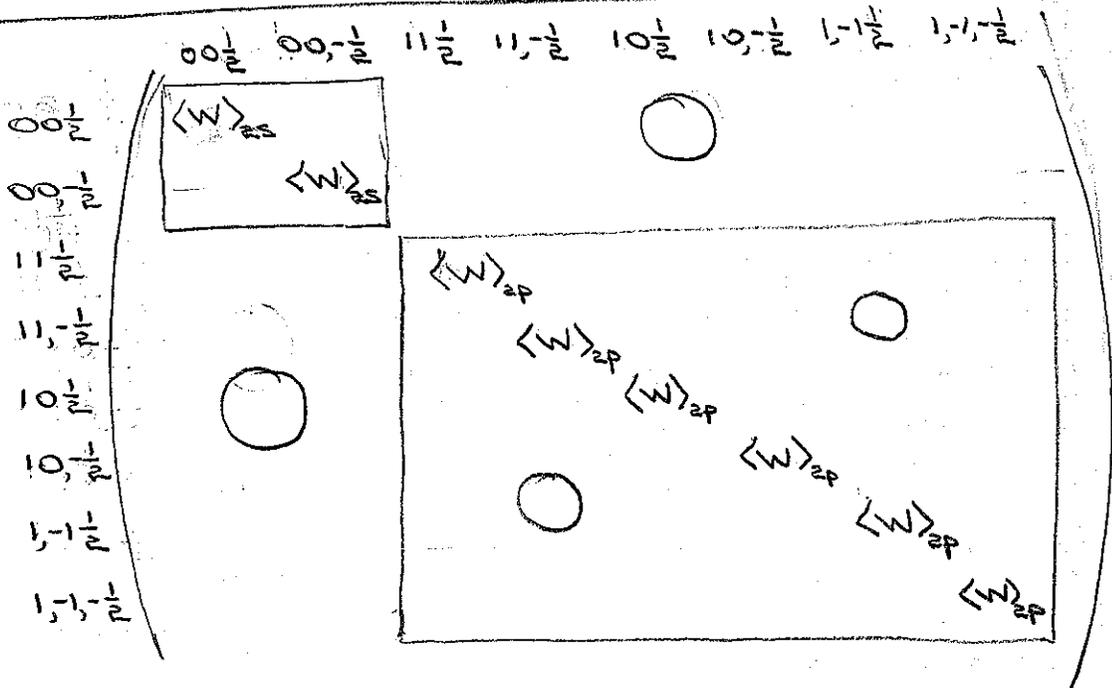
$$[W_{mv}, \vec{S}] = 0 = [W_D, \vec{S}]$$

$$\langle n l' m'_l m'_s | W_{mv} | n l m_l m_s \rangle = \delta_{m'_l m_l} \delta_{m'_s m_s} \langle n l' m'_l | W_{mv} | n l m_l \rangle$$

$$\delta_{m'_l m'_s} \delta_{l' l} \langle n l' || W_{mv} || n l \rangle$$

$$\langle n l' m'_l m'_s | W_{mv} | n l m_l m_s \rangle = \delta_{l' l} \delta_{m'_l m_l} \delta_{m'_s m_s} \langle n l' || W_{mv} || n l \rangle$$

$n = P:$



How does this look in the  $|n l J M_J\rangle$  basis?

$$\langle n l' J' m'_J | W_{mv} | n l J m_J \rangle = \delta_{l' l} \delta_{J' J} \delta_{m'_J m_J} \langle W_{mv} \rangle_{nl}$$

How evaluate reduced matrix element?

$$\langle W_{mv} \rangle_{nl} = \langle n l || W_{mv} || n l \rangle = \langle n l 0 | W_{mv} | n l 0 \rangle$$

$$\frac{\vec{p}^2}{2m_e} = H_0 - V(R) \Rightarrow \vec{p}^4 = 4m_e^2 (H_0 - V(R))^2$$

$$W_{mv} = -\frac{\vec{p}^4}{8m_e^3 c^2} = -\frac{1}{2m_e c^2} (H_0 - V(R))^2$$

$$\langle W_{mv} \rangle_{nl} = -\frac{1}{2m_e c^2} \langle n l 0 | (H_0^2 - V(R)H_0 - H_0 V(R) + V^2(R)) | n l 0 \rangle$$

$$= -\frac{1}{2m_e c^2} \left( E_n^2 - 2E_n \langle n l 0 | V(R) | n l 0 \rangle + \langle n l 0 | V^2(R) | n l 0 \rangle \right)$$

$$\langle W_{mv} \rangle_{nl} = -\frac{1}{2} m_e c^2 \alpha^4 \left( \frac{1}{4n^2} - \frac{1}{n^2} \left\langle \frac{R_0}{R} \right\rangle_{nl} + \left\langle \left( \frac{R_0}{R} \right)^2 \right\rangle_{nl} \right)$$

$$E_n = -\frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2}$$

$$V(R) = -m_e c^2 \alpha \frac{R_0}{R}$$

$$\langle W_{mv} \rangle_{nl} = -\frac{1}{2} m_e c^2 \alpha^4 \left( \frac{1}{4n^2} - \frac{1}{n^2} \left\langle \frac{R_0}{R} \right\rangle_{nl} + \left\langle \left( \frac{R_0}{R} \right)^2 \right\rangle_{nl} \right)$$

$$\left\langle \left( \frac{R_0}{R} \right)^k \right\rangle_{nl} = \int r^2 dr d\Omega \left( \frac{R_0}{r} \right)^k |\Psi_{nl0}(\vec{r})|^2$$

$$= \int_0^\infty dr r^2 R_{nl}^2(r) \left( \frac{R_0}{r} \right)^k$$

Smaller as  $n \uparrow$   
Why?

Tabulate (C-T B<sub>xii</sub>):

$$\left\langle \frac{R_0}{R} \right\rangle_{1s} = 1, \quad \left\langle \frac{R_0}{R} \right\rangle_{2s} = \frac{1}{2}, \quad \left\langle \frac{R_0}{R} \right\rangle_{2p} = \frac{1}{4}$$

$$\left\langle \left( \frac{R_0}{R} \right)^2 \right\rangle_{1s} = 2, \quad \left\langle \left( \frac{R_0}{R} \right)^2 \right\rangle_{2s} = \frac{1}{2}, \quad \left\langle \left( \frac{R_0}{R} \right)^2 \right\rangle_{2p} = \frac{1}{12}$$

$$\left\langle \left( \frac{R_0}{R} \right)^3 \right\rangle_{2p} = \frac{1}{24}$$

$$\langle W_{mv} \rangle_{1s} = -\frac{101}{810} m_e c^2 \alpha^4$$

$$\langle W_{mv} \rangle_{2s} = -\frac{13}{128} m_e c^2 \alpha^4$$

$$\langle W_{mv} \rangle_{2p} = -\frac{7}{384} m_e c^2 \alpha^4$$

We can get  $\langle R_0/R \rangle_{nl}$  from the virial theorem

$$-\langle 2^2/R \rangle = \langle V(R) \rangle = 2E_n = -\frac{e^4}{2a_0 n^2}$$

$$\Rightarrow \langle 1/R \rangle = 1/a_0 n^2$$

$$\langle R_0/R \rangle_{nl} = 1/n^2$$

$$\textcircled{b} \langle W_D \rangle_{nl} = \langle nl || W_D || nl \rangle = \delta_{l0} \langle n00 | W_D | n00 \rangle$$

$$\begin{aligned} \langle n00 | W_D | n00 \rangle &= \frac{\pi e^2 \hbar^2}{2 m_e^2 c^2} \underbrace{|\psi_{n00}(0)|^2}_{R_{n0}^2 Y_0^2} \sim 1/n^6 \\ &= \frac{1}{4\pi} R_{n0}^2 \underbrace{Y_0^2}_{1/4\pi} \\ &= \frac{1}{4\pi^2} R_{n0}^2 \\ &= \frac{1}{8} \frac{e^2 \hbar^2}{m_e^2 c^2 a_0^3} R_{n0}^2 \\ &= m_e c^2 \alpha^4 \end{aligned}$$

$$\langle W_D \rangle_{nl} = \delta_{l0} \frac{1}{8} m_e c^2 \alpha^4 a_0^3 R_{n0}^2$$

Smaller as  
n ↑  
why?

n=1: 4  
n=2: 8/2

$$\langle W_D \rangle_{1s} = \frac{1}{2} m_e c^2 \alpha^4$$

$$\langle W_D \rangle_{2s} = \frac{1}{16} m_e c^2 \alpha^4$$

$$\langle W_D \rangle_{2p} = 0$$



Need  $\langle W_{SO} \rangle_{nlJ} = \langle nlJm_J | W_{SO} | nlJm_J \rangle$

$$= \frac{1}{2} \frac{e^2 \hbar^2}{m_e^2 c^2} \frac{1}{a_0^3} \langle nlJm_J | \left(\frac{R_0}{R}\right)^3 \frac{\vec{L} \cdot \vec{S}}{\hbar^2} | nlJm_J \rangle$$

$$= \frac{1}{2} m_e c^2 \alpha^4 \langle nlJm_J | \left(\frac{R_0}{R}\right)^3 \frac{\vec{L} \cdot \vec{S}}{\hbar^2} | nlJm_J \rangle$$

$$\vec{J} = \vec{L} + \vec{S} \Rightarrow \vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$

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

Same trick we used for the Lande g-factor

$$\frac{1}{2} [J(J+1) - l(l+1) - \frac{3}{4}] \langle nlJm_J | \left(\frac{R_0}{R}\right)^3 | nlJm_J \rangle$$

$$\langle \left(\frac{R_0}{R}\right)^3 \rangle_{nl}$$

$$\langle W_{SO} \rangle_{nlJ} = \frac{1}{4} m_e c^2 \alpha^4 [J(J+1) - l(l+1) - \frac{3}{4}] \langle \left(\frac{R_0}{R}\right)^3 \rangle_{nl}$$

- $\langle W_{SO} \rangle_{1S, 1/2} = 0$
- $\langle W_{SO} \rangle_{2S, 1/2} = 0$
- $\langle W_{SO} \rangle_{2P, 1/2} = -\frac{1}{48} m_e c^2 \alpha^4$
- $\langle W_{SO} \rangle_{2P, 3/2} = \frac{1}{96} m_e c^2 \alpha^4$

$$= \begin{cases} l, & J = l + 1/2 \\ -(l+1), & J = l - 1/2 \end{cases}$$

$\frac{1}{96}$

$$m_e c^2 \alpha^4 / h = 350.87 \text{ GHz}$$

Gather results:

$$m_e = 9.1095 \times 10^{-31} \text{ kg}$$

$$c = 2.9979 \times 10^8 \text{ m/s}$$

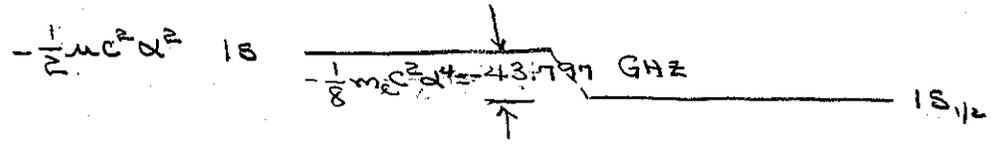
$$\alpha = 1/137.036$$

$$h = 6.6262 \times 10^{-34} \text{ J-s}$$

$$1S_{1/2}: \langle W_{FS} \rangle_{1S_{1/2}} = \langle W_{mv} \rangle_{1S} + \langle W_D \rangle_{1S} + \langle W_{SO} \rangle_{1S_{1/2}} = -\frac{1}{8} \mu c^2 \alpha^2$$

$$= -\frac{5}{8} \mu c^2 \alpha^2 \quad = \frac{1}{2} \mu c^2 \alpha^2 \quad = 0$$

n=1



$$2S_{1/2}: \langle W_{FS} \rangle_{2S_{1/2}} = \langle W_{mv} \rangle_{2S} + \langle W_D \rangle_{2S} + \langle W_{SO} \rangle_{2S_{1/2}} = -\frac{5}{128} \mu c^2 \alpha^2$$

$$= -\frac{13}{128} \mu c^2 \alpha^2 \quad = \frac{1}{16} \mu c^2 \alpha^2 = \frac{8}{128} \mu c^2 \alpha^2 \quad = 0$$

accidental

$$2P_{1/2}: \langle W_{FS} \rangle_{2P_{1/2}} = \langle W_{mv} \rangle_{2P} + \langle W_D \rangle_{2P} + \langle W_{SO} \rangle_{2P_{1/2}} = -\frac{15}{384} \mu c^2 \alpha^2 - \frac{5}{128} \mu c^2 \alpha^2$$

$$= -\frac{7}{384} \mu c^2 \alpha^2 \quad = 0 \quad = -\frac{1}{48} \mu c^2 \alpha^2 = -\frac{8}{384} \mu c^2 \alpha^2$$

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$$2P_{3/2}: \langle W_{FS} \rangle_{2P_{3/2}} = \langle W_{mv} \rangle_{2P} + \langle W_D \rangle_{2P} + \langle W_{SO} \rangle_{2P_{3/2}} = -\frac{3}{384} \mu c^2 \alpha^2 - \frac{1}{128} \mu c^2 \alpha^2$$

$$= -\frac{7}{384} \mu c^2 \alpha^2 \quad = 0 \quad = \frac{1}{96} \mu c^2 \alpha^2$$

n=2

