Physics 531 - Lecture 5 - Fine Structure

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

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

$\Rightarrow$ Length: $a_0 = \frac{\hbar^2}{m_e e^2} \cong 0.5\,\text{Å}$ (Bohr radius)

Energy: $E_0 = \frac{e^2}{a_0} = \frac{me^4}{\hbar} \cong 27.2\,eV$ (Hartree)

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

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

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

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

α = Fine structure const, characteristic coupling in quantum electrodynamics

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

Exact solution $\Rightarrow \begin{cases} \text{Q.E.D. (Dirac Spinors)} \\ \text{(Electron and Positron)} \end{cases}$

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

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

Expand in powers $\frac{v_e}{c}$ $\Rightarrow$ 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:

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

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

Physical meaning of different terms

- Relativistic correction to kinetic energy:

Excluding potential energy, the energy of the electron

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

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

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

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

$$= \alpha^2 E_0$$

In a.u. $e = \hbar = m_e = 1$, $c = \frac{1}{\alpha} = 137$) Note 1 Hartree $= \alpha^2 m_e c^2$

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

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

This field interacts with the intrinsic magnetic moment of the electron

$$\hat{H}_{int} = -\hat{\vec{\mu}}_e \cdot \vec{B}_{e\text{-frame}} \qquad \hat{\vec{\mu}}_e = \underset{\text{g-factor}}{\underset{\uparrow}{-2}} \Big(\underset{\text{Bohr magneton}}{\underset{\uparrow}{\mu_B}} \Big) \frac{\hat{\vec{S}}}{\hbar}$$

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

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

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

$$\Rightarrow \vec{B}_{e\text{-frame}} = \frac{1}{m_e c}\, \frac{1}{r}\frac{d\Phi}{dr}\, \vec{p} \times \vec{x} = -\frac{1}{m_e c}\, \frac{1}{r}\frac{d\Phi}{dr}\, \underset{\text{orbital ang. mom.}}{\underset{\uparrow}{\vec{L}}}$$

this is the field of a current loop around electron.

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

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.

• <u>Darwin term</u>

The interaction between the ~~[illegible]~~ Dirac spinor and electromagnetic field is <u>local</u>. 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".

$$\hat{H}_{Darwin} = \frac{\hbar^2}{8m_e^2c^2}\nabla^2 V = \frac{-\hbar^2 e^2}{8m_e^2c^2}\underbrace{\nabla^2\left(\frac{1}{r}\right)}_{\left(-4\pi\delta^{(3)}(\vec{x})\right)}$$

Poisson Eq. for point charge

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

Thus, the perturbation Hamiltonian

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

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

<u>Fine structure of $n=2$ of Hydrogen</u>

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 symmetry

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

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

$\Rightarrow$ $\hat{H}_{S.O}$ commutes with $\hat{L}^2$

$\Rightarrow$ <u>l remains a good quantum #</u>

(no off diagonal elements between different l)

Order basis $\left\{ |2s\rangle \otimes \begin{Bmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{Bmatrix},\ |2p, m\rangle \otimes \begin{Bmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{Bmatrix} \right\}$

$$\Rightarrow \hat{H}_{int} \doteq \begin{array}{c} \begin{array}{cc} 2s & 2p \end{array} \\ \begin{bmatrix} \boxed{2\times 2} & 0 \\ 0 & \boxed{6\times 6} \end{bmatrix} \end{array} \quad \text{Blocks}$$

<u>2s - subspace:</u> <u>($l=0$)</u>

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

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

2×2 matrices proportional to the identity

$$\hat{H}_{kin} \doteq -\underline{\langle n=2\ l=0\ m=0|\ \hat{p}^4\ |n=2\ l=0\ m=0\rangle} \left(\frac{\alpha^2}{8}\right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$= -\frac{\alpha^2}{8} \|\ \hat{p}^2\ |n=2\ l=0\ m=0\rangle \|^2 \quad \text{(norm squared)}$$

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

$$\Rightarrow \|\hat{p}^2 |nlm\rangle\| = 4\left(E_n^2 - 2E_n \langle \hat{V}\rangle_{nl} + \langle \hat{V}^2\rangle_{nl}\right)$$

$$= 4\left(+\frac{1}{4n^4} - 2\left(\frac{-1}{2n^2}\right)\left\langle\frac{-1}{r}\right\rangle_{nl} + \left\langle\frac{1}{r^2}\right\rangle_{nl}\right)$$

From Problem Set:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2} \qquad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{n^3(\ell+\frac{1}{2})}$$

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

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

For Darwin term

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

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

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

$\Rightarrow$ Under the effect of lowest order relativistic corrections ~~[illegible]~~ from the Dirac equation, the 2s subshell is shifted lower by

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

$$= 56.6\ \mu eV$$

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

or 1 GHz $= 4.1\ \mu eV$

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

2p sub shell

Again, the kinetic and Darwin terms produce the same shift for all states in this manifold

$$\langle \hat{H}_{kin} \rangle_{n=2,\,l=1} = -\frac{7}{384}\alpha^2$$

$$\langle \hat{H}_{Darwin} \rangle_{n=2,\,l=1} = \frac{\alpha^2}{2}|R_{21}(0)|^2 = 0 \quad \left(\begin{array}{l}\text{only s-states}\\ \text{have non-zero}\end{array}\right)$$

The spin-orbit Hamiltonian is <u>not</u> diagonal in this subspace since $\hat{L}_z$ and $\hat{S}_z$ do not commute with $\vec{L}\cdot\vec{S}$

~~Also~~ The basis $|2p\rangle|m_l\rangle|m_s\rangle$ where $|m_l\rangle = |+1\rangle\,|0\rangle\,|-1\rangle$
is the <u>uncoupled representation</u> $|m_s\rangle = |\uparrow\rangle\;|\downarrow\rangle$

$\vec{L}\cdot\vec{S}$ is a scalar under the total ~~ex~~ angular momentum $\vec{J} = \vec{L}+\vec{S}$

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

Thus, spin-orbit is diagonalized in the <u>coupled representation</u>

New quantum numbers $j,\ \underset{1}{\overset{\shortparallel}{l}},\ \underset{\frac{1}{2}}{\overset{\shortparallel}{s}},\ m_j$

Possible values of j: $j = l+s$ ~~or~~ $\to |l-s|$
in integer units

$$\Rightarrow \begin{cases} j = \frac{3}{2} & m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \\ \text{or} \quad j = \frac{1}{2} & m_j = -\frac{1}{2}, \frac{1}{2} \end{cases}$$

$$\langle j\,l\,s\,m_j|\vec{L}\cdot\vec{S}|j\,l\,s\,m_j\rangle = \frac{1}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$\Rightarrow$ Diagonal matrix elements of spin-orbit Hamiltonian

$$\frac{\alpha^2}{2} \langle n l | \frac{1}{r}\frac{dV}{dr} | n l \rangle \; \langle j l s m_j | \vec{L}\cdot\vec{S} | j l s m_j \rangle$$

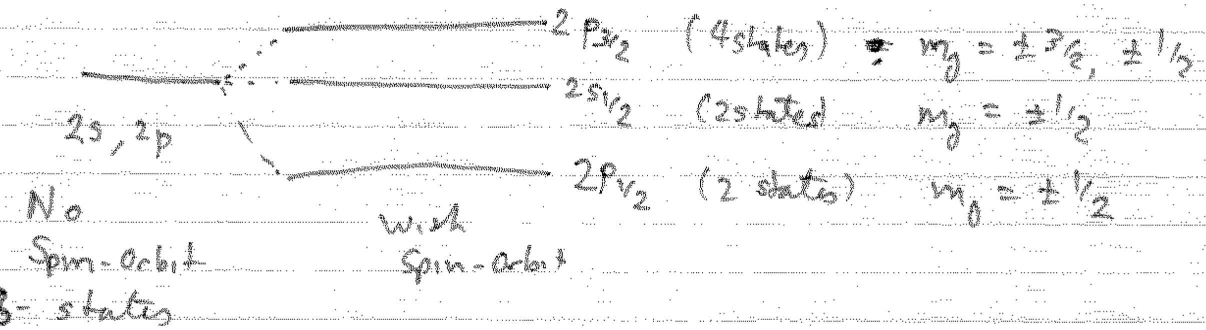
with $V(r) = -\frac{1}{r}$ in a.u. $\quad \frac{1}{r}\frac{dV}{dr} = \frac{1}{r^3}$

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

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

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

Spectroscopic notation: $n l_j$ ← new quantum #



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

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

$$\langle 2s_{1/2} | \hat{H}_{so} | 2s_{1/2} \rangle = 0 \quad \text{since } l = 0$$

<u>Total energy shifts</u>

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

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

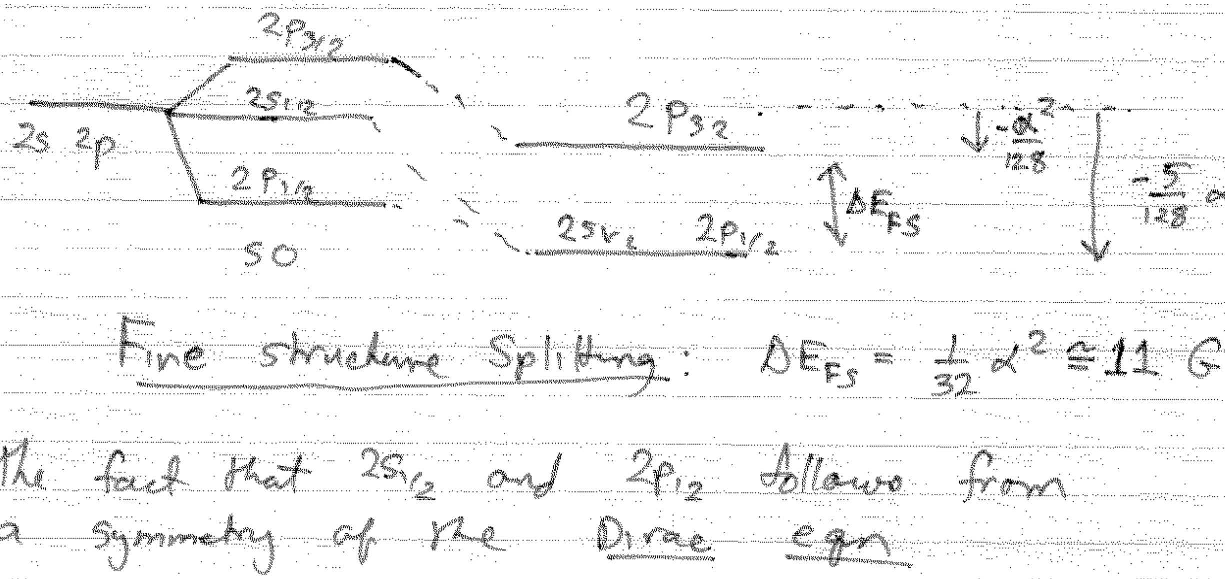
- $2p_{1/2}$ $\Delta E_{2p_{1/2}} = \langle 2p_{1/2} | \hat{H}_{kin} | 2p_{1/2} \rangle + \langle 2p_{1/2} | \hat{H}_{SO} | 2s_{1/2} \rangle$

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

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

- $2p_{3/2}$ $\Delta E_{2p_{3/2}} = \langle 2p_{3/2} | \hat{H}_{kin} | 2p_{3/2} \rangle + \langle 2p_{3/2} | \hat{H}_{SO} | 2p_{3/2} \rangle$

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



<u>Fine structure Splitting</u>: $\Delta E_{FS} = \frac{1}{32} \alpha^2 \cong 11\ GHz$

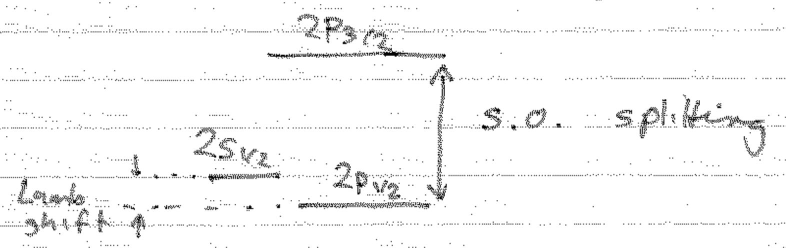
The fact that $2s_{1/2}$ and $2p_{1/2}$ follows from a symmetry of the <u>Dirac eqn</u>

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

To Lowest orders:

$$E_{nj} = m_e c^2 - m_e c^2 \alpha^2 \Bigg(\underset{\uparrow \text{ Rydberg}}{-\frac{1}{2n^2}} \underbrace{- \frac{\alpha^2}{2n^4} \left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right)}_{\text{Fine structure}} \Bigg)$$

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



$\Delta E_{lamb} \cong 1$ MHz