

Lecture 11: A atom fine structure

Relativistic corrections  $\mathcal{O}(\alpha^4)$

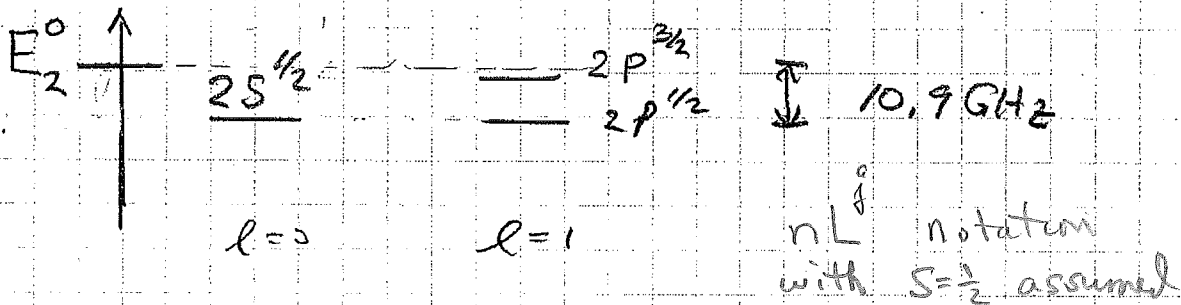
$$\vec{J} = \vec{L} + \vec{S}$$

spin-orbit coupling  $\vec{L} \cdot \vec{S}$

$$[H, \vec{J}^2] = 0$$

$$E_{n,j}$$

$$|l-s| \leq j \leq l+s, \quad \underline{\underline{s = \frac{1}{2}}}$$



$$\Delta E(2S-1S) = 10.2 \text{ eV}$$

$$\Delta E(10.9 \text{ GHz}) = 10^{10} (2\pi) 6.58 \times 10^{-16} \text{ eV}\cdot\text{s} = \underline{\underline{4.1 \times 10^{-5} \text{ eV}}}$$

$$\alpha^{-2} \approx 20,000 \quad (18768)$$

Exact Solutions from Dirac equation:

Gordon, 1928

$$E_{n,j} = mc^2 \left[ 1 + \left( \frac{Z\alpha}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - (Z\alpha)^2}} \right)^2 \right]^{-1/2}$$

Expect relativistic corrections to be small

$$\langle K \rangle = \langle T \rangle - \langle V \rangle; \quad \langle V \rangle = -e^2 \langle \frac{1}{r} \rangle = -\frac{e^2}{a_0 n^2} = 2 E_N$$

$$\langle K \rangle = \frac{1}{2} mc^2 \alpha^2 \frac{1}{n^2} \ll mc^2$$

$$\langle K \rangle_0 = \frac{1}{2} m(c\alpha)^2 = \frac{1}{2} m \langle v^2 \rangle, \quad \boxed{\sqrt{\langle v^2 \rangle} = c\alpha}$$

A few words on Dirac equation:

Dirac sought relativistic equation (1928)

linear in time:  $E = \pm \sqrt{(mc^2)^2 + (pc)^2}$

$$\hat{H} = \vec{\alpha} \cdot \vec{p} c + \beta mc^2 + V$$

$\alpha_i, \beta$  must be  $4 \times 4$  matrices

Dirac "4-spinor" wave function ( $T \equiv$  transpose)

$$\psi_D = (\psi_1, \psi_2, \psi_3, \psi_4)^T$$

spin  $\frac{1}{2}$   $e^-, e^+$   $e^+e^- \rightarrow \gamma + "E=mc^2"$

spin, antiparticle follow from adding special relativity to Q.M.

\* Dirac tried to preserve wave function as conserved probability density. Instead, fermion number is conserved, but necessarily have particles, anti-particle creation, annihilation.

Expand exact solution:

$$E_{n,l} \approx mc^2 \left\{ 1 - \frac{1}{2} \frac{(Z\alpha)^2}{n^2} \left[ 1 + \frac{(Z\alpha)^2}{n} \left( \frac{1}{j+1/2} - \frac{3}{4n} \right) \right] \right\}$$

$$\hat{H} \approx mc^2 + \underbrace{\frac{p^2}{2m}}_{\hat{H}_k} - \underbrace{\frac{p^4}{8m^3c^2}}_{\hat{H}_k} + \underbrace{\frac{e}{2mc} \vec{S} \cdot \vec{B}}_{\hat{H}_{s.o.}} + \underbrace{\frac{\hbar^2}{8mc^2} \nabla^2 V}_{\hat{H}_D}$$

kinetic
spin-orbit
Darwin

note  $\vec{B}$  is external magnetic field due to proton current in electron rest frame.

In external magnetic field, additional piece of Hamiltonian

$$\hat{H}_{ext} = -\vec{\mu} \cdot \vec{B} = \frac{e}{2mc} (\vec{L} + \underbrace{2\vec{S}}_{\uparrow g=2}) \cdot \vec{B}$$

Kinetic energy correction

$$K = \sqrt{pc)^2 + (mc^2)^2} - mc^2$$

$$\approx mc^2 \left[ 1 + \frac{1}{2} \left( \frac{pc}{mc^2} \right)^2 - \frac{1}{8} \left( \frac{pc}{mc^2} \right)^4 \right] - mc^2$$

$$= \frac{1}{2} \frac{p^2}{m} - \frac{1}{8} \frac{p^4}{m^3 c^2}$$

$[\hat{H}_K, \hat{L}^2] = 0$ ,  $[\hat{H}_K, \hat{L}_z] = 0$  so does not mix states of different  $l, m$ :

$$E_{n,l}^{(1)} = - \langle n, l, m | \frac{1}{8} \frac{\hat{p}^4}{m^3 c^2} | n, l, m \rangle$$

trick to evaluate  $\hat{p}^4$ .

$$\left( \frac{\hat{p}^2}{2m} \right)^2 = \left( H_0 + \frac{e^2}{r} \right)^2$$

$$E_{n,l}^{(1)} = - \frac{1}{2mc^2} \langle n, l, m | \left( \frac{\hat{p}^2}{2m} \right)^2 | n, l, m \rangle$$

$$= - \frac{1}{2mc^2} \langle n, l, m | (E_n^0 + \frac{e^2}{r}) (E_n^0 + \frac{e^2}{r}) | n, l, m \rangle$$

$$= - \frac{1}{2mc^2} \left[ (E_n^0)^2 + 2 E_n^0 \langle \frac{1}{r} \rangle + \left( \frac{e^2}{r} \right)^2 \langle \frac{1}{r^2} \rangle \right]$$

$$\langle \frac{1}{r} \rangle = \frac{1}{n^3 a_0} = \frac{\alpha mc}{\hbar^2 n^2}$$

$$\langle \frac{1}{r^2} \rangle = \frac{1}{a_0^2} \frac{1}{n^3} \left( \frac{1}{e + \frac{1}{2}} \right) = \frac{(\alpha mc)^2}{n^3 \hbar^3 (e + \frac{1}{2})}$$

giving

$$E_{n,l}^{K(1)} = -\frac{\alpha^4 mc^2}{2} \left[ \frac{3}{4n^4} + \frac{1}{n^3} \left( \frac{1}{l+1/2} \right) \right]$$

note dependence on  $l$

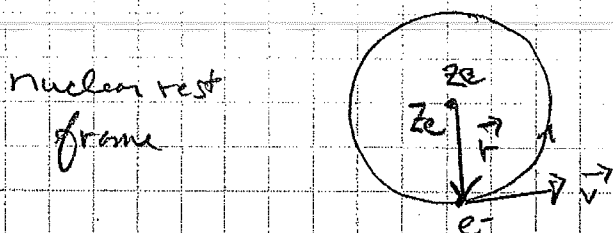
$$\frac{E_{n,l}^K}{E_n} \propto \alpha^2$$

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta E}{E} \propto \alpha^2 \approx 10^{-4}$$

Spin Orbit:

Electron orbital motion  $(l, m)$  generates magnetic field in electron rest frame.

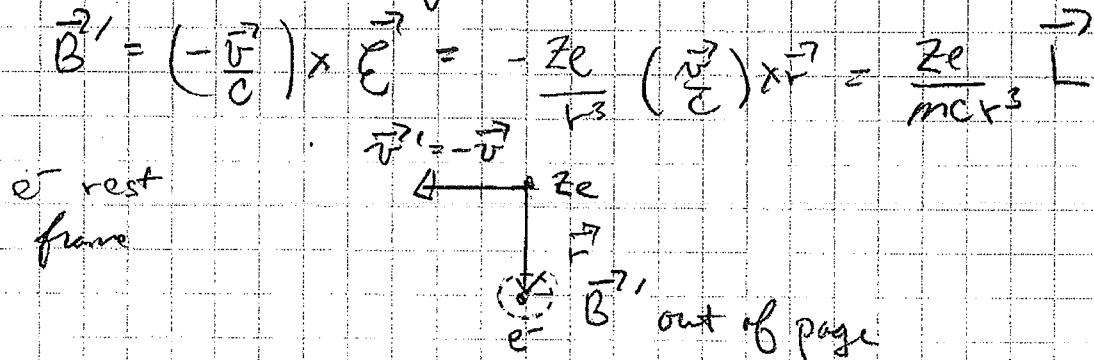
Classically:



$$\vec{L} = m \vec{r} \times \vec{v} \quad \text{out of page}$$

$$\vec{E} = \frac{Ze \vec{r}}{r^3}$$

In electron's rest frame:



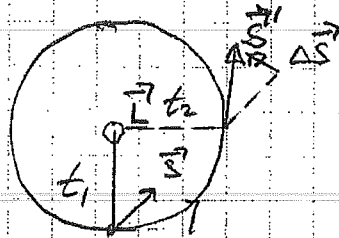
Electron spin experiences a torque in the electron rest frame

$$\left(\frac{d\vec{S}}{dt}\right)_{e\text{-rest}} = \vec{\mu} \times \vec{B}' = \left(\frac{-g e \hbar}{2 m c}\right) \vec{S} \times \left(\frac{Z e}{m c r^3}\right) \vec{L}$$

$$= \frac{-Z e^2 g \hbar}{2 m^2 c^2 r^3} (\vec{S} \times \vec{L})$$

where  $g$  is the electron gyromagnetic ratio:  $g = 2$  from Dirac equation.

projection of  $\vec{S}$  onto orbital plane will precess counter clockwise,



The energy due to this interaction is

$$\hat{H} = -\vec{\mu} \cdot \vec{B} = \frac{g e \hbar}{2 m c} \vec{S} \cdot \vec{B}$$

using  $g = 2$ , this is 2 times bigger than  $\hat{H}_{so}$  from the Dirac equation! The error, first pointed out by Thomas, is a special relativistic effect due to the transformation of the electron rotating frame.

Thomas precession ( $\vec{\omega}_T$ ) (1927)

$$\left(\frac{d\vec{S}}{dt}\right)_{\text{accelerated}} = \left(\frac{d\vec{S}}{dt}\right)_{\text{rest}} + \vec{\omega}_T \times \vec{S}$$

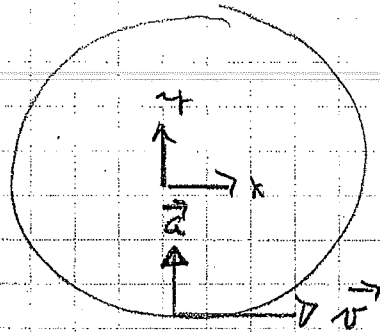
special relativistic  
effect of transformation

Refer to Taylor and Wheeler, Spacetime physics.

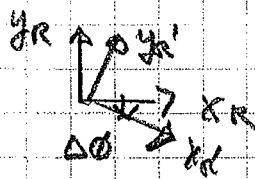
Essentially, the product of "boosts" in different directions is equal to a boost + rotation (general Lorentz transformation)

Consider rotating frame with acceleration  $\vec{a}$ .

x-y denotes fixed inertial frame



rotating frame will precess clockwise by an amount  $\Delta\phi$  per rotation



$$\Delta\phi = \pi \left(\frac{v}{c}\right)^2$$

$$|\vec{\omega}_T| = \Delta\phi \left(\frac{v}{2\pi r}\right) = \frac{v^2}{c^2} \left(\frac{v}{2r}\right) = \frac{1}{2} \frac{v}{c^2} a$$

$a = \frac{v^2}{r}$  for uniform circular motion

$$\vec{\omega}_T = -\frac{1}{2c^2} \vec{v} \times \vec{a}$$

Lorentz group has 6 generators: 3 boosts, 3 rotations

Acceleration of  $e^-$  in atom is due to nuclear field.

$$\vec{a} = \frac{-e}{m} \vec{E} = -\frac{Ze^2}{mr^3} \vec{r}$$

$$\vec{\omega}_T = \left(\frac{-1}{2c^2}\right) \vec{v} \wedge \left(-\frac{Ze^2 \vec{r}}{mr^3}\right) = \frac{-e}{2mc} \vec{B}'$$

Correct formula for torque  $\omega$

$$\begin{aligned} \left(\frac{d\vec{S}}{dt}\right)_{\text{nuclear}} &= \frac{-Ze^2}{2m^2c^2r^3} \left( g\vec{S} \times \vec{L} + \underbrace{\vec{L} \times \vec{S}}_{\text{Thomas term}} \right) \\ &= \frac{-Ze^2}{2m^2c^2r^3} (g-1) \vec{S} \times \vec{L} \end{aligned}$$

Since  $g=2$ , we find  $\frac{1}{2}$  of our previous result:

$$\hat{H}_{so} = \frac{Ze^2}{2m^2c^2r^3} (\vec{L} \cdot \vec{S}) = \frac{e}{2mc} \vec{S} \cdot \vec{B}'$$

In agreement with Dirac.

The constants can be arranged as

$$\hat{H}_{so} = \frac{1}{4} (Z\alpha)^4 mc^2 \left(\frac{a_0}{Zr}\right)^3 \frac{2 \vec{L} \cdot \vec{S}}{\hbar^2}$$

showing  $O(\alpha^4)$  dependence



## $\vec{L} \cdot \vec{S}$ coupling

Hamiltonian will be diagonal in state of total  $\vec{J}^2, \vec{J}_z$  where  $\vec{J} = \vec{L} + \vec{S}$

$$|l, m_l\rangle \otimes |\frac{1}{2}, m_s\rangle \xleftrightarrow{\text{mix}} |j, m_j\rangle$$

$$(2l+1)(2\frac{1}{2}+1) = 2(2l+1) \text{ states}$$

Formally, this is just as with 2-spin system.

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

Components of  $\vec{L}, \vec{S}$  commute:  $[\hat{L}_i, \hat{S}_j] = 0$

Since  $\vec{L} \cdot \vec{S}$  is rotationally invariant, we expect

$$[\vec{J}^2, \vec{L} \cdot \vec{S}] = 0$$

$$[\vec{J}_z, \vec{L} \cdot \vec{S}] = 0$$

so eigenvalues  $j, m_j$  are good quantum numbers

$$\text{also } [\vec{L}^2, \vec{L} \cdot \vec{S}] = 0$$

$$[\vec{S}^2, \vec{L} \cdot \vec{S}] = 0$$

However,

$$\begin{aligned}
 [\hat{L}_z, \vec{S}] &= [\hat{L}_z, \hat{L}_x] \hat{S}_x + [\hat{L}_z, \hat{L}_y] \hat{S}_y \\
 &= i\hbar(\hat{L}_y \hat{S}_x - \hat{L}_x \hat{S}_y) \neq 0
 \end{aligned}$$

similarly,

$$[\hat{S}_z, \vec{L}] = i\hbar(\hat{L}_x \hat{S}_y - \hat{L}_y \hat{S}_x) \neq 0$$

So good quantum numbers are

$$j, m_j, l, s \quad \text{where } s = \frac{1}{2}$$

$H_{so}$  mixes states of same  $l, s$  to get  $j = l \pm \frac{1}{2}$   
 such that  $m_j = m_l \pm \frac{1}{2}$

$$|j, m_j = \frac{1}{2}\rangle = C_+ |l, m_l\rangle |\frac{1}{2}, \frac{1}{2}\rangle + C_- |l, m_l + 1\rangle |\frac{1}{2}, -\frac{1}{2}\rangle$$

$$|j, m_j = -\frac{1}{2}\rangle = C'_+ |l, m_l - 1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + C'_- |l, m_l\rangle |\frac{1}{2}, -\frac{1}{2}\rangle$$

$$\uparrow \\
 m_j = m_l \pm \frac{1}{2}$$

Constants  $C$  are called Clebsch-Gordan (C-G) coefficients and are worked out using

$SU(2)$  group theory and looked upon a Clebsch-Gordan table

posted on web page

Example 2p states of Hydrogen

for  $n=2$ ,  $l=0,1$   $H_{so}$  will be diagonal  
in states  $|j, m_j\rangle$ .

Irrep (irreducible representation) decomposition:

$$\underset{\sim}{3} \otimes \underset{\sim}{2} = \underset{\sim}{4} \oplus \underset{\sim}{2}$$

multiplicities

$$\underset{\sim}{1} \otimes \underset{\sim}{\frac{1}{2}} = \underset{\sim}{\frac{3}{2}} + \underset{\sim}{\frac{1}{2}}$$

eigenvalues

following the rule  $j = l \pm \frac{1}{2}$   
 $= \begin{cases} 3/2 \\ 1/2 \end{cases}$

These multiplets are labeled as  $2p^{3/2}$ ,  $2p^{1/2}$   
 4-plet, 2-plet  
 indicating  $n, l, j$  ( $s = \frac{1}{2}$  is assumed)

$m_j$  follow the rule  $m_j = -j, -j+1, \dots, j$

$\frac{2\vec{L} \cdot \vec{S}}{\hbar^2}$  energy can be easily found from

$$\frac{2\vec{L} \cdot \vec{S}}{\hbar^2} = \frac{1}{\hbar^2} \begin{pmatrix} L^2 & L^2 & L^2 \\ J^2 & -L^2 & -S^2 \end{pmatrix}$$

$$\begin{aligned} \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} |2p^j\rangle &= \left[ j(j+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1) \right] |2p^j\rangle \\ &= \left[ j(j+1) - \frac{11}{4} \right] |2p^j\rangle = \lambda_j |2p^j\rangle \end{aligned}$$

we find  $\lambda_{3/2} = 1$   
 $\lambda_{1/2} = -2$

To find eigenstates, we can look up C-G coefficients in table or explicitly diagonalize  $\vec{L} \cdot \vec{S}$ .

To see how this goes,

$$|3/2, \pm 3/2\rangle = |1, \pm 1\rangle |1/2, \pm 1/2\rangle$$

we must diagonalize two, 2x2 sub-matrices

for  $|1, 0\rangle |1/2, 1/2\rangle, |1, 1\rangle |1/2, -1/2\rangle$   $m_j = +1/2$

and for  $|1, -1\rangle |1/2, 1/2\rangle, |1, 0\rangle |1/2, -1/2\rangle$   $m_j = -1/2$

$m_j = +1/2$  case: use basis  $|1\rangle = |1, 0\rangle |1/2, 1/2\rangle$   
 $|2\rangle = |1, 1\rangle |1/2, -1/2\rangle$

$$\text{write } \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} = \frac{1}{\hbar^2} [\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+ + 2\hat{L}_z \hat{S}_z]$$

$$\langle 1 | \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} | 1 \rangle = \langle 1 | \frac{2}{\hbar^2} \hat{L}_z \hat{S}_z | 1 \rangle = 0$$

$$\langle 2 | \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} | 2 \rangle = \langle 2 | \frac{2}{\hbar^2} \hat{L}_z \hat{S}_z | 2 \rangle = -1$$

$$\langle 2 | \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} | 1 \rangle = \langle 2 | \frac{1}{\hbar^2} \hat{L}_+ \hat{S}_- | 1, 0 \rangle | 1/2, 1/2 \rangle$$

$$= \sqrt{2} \sqrt{\frac{1}{2}(1/2+1)} - \frac{1}{2}(1/2-1) = \sqrt{2}$$

giving  $\left[ \frac{2 \vec{L} \cdot \vec{S}}{\hbar^2} \right]_{1/2} = \begin{pmatrix} 0 & \sqrt{2} \\ \sqrt{2} & -1 \end{pmatrix}$

-13-

eigenvalue equation

$$\begin{pmatrix} 0 & \sqrt{2} \\ \sqrt{2} & -1 \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = \lambda \begin{pmatrix} c_+ \\ c_- \end{pmatrix}$$

$$\det \begin{vmatrix} -\lambda & \sqrt{2} \\ \sqrt{2} & -1-\lambda \end{vmatrix} = \lambda(1+\lambda) - 2 = 0$$

$$(\lambda - 1)(\lambda + 2) = 0 \quad \lambda = 1, -2$$

and eventually eigenvectors

$$\lambda = 1 \quad \left| \frac{3}{2}, \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$$

$$\lambda = -2 \quad \left| \frac{1}{2}, \frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$$

from CG table: (with Condon-Shortley phase convention)

$$\left| \frac{3}{2}, -\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

$$\left| \frac{1}{2}, -\frac{1}{2} \right\rangle = +\sqrt{\frac{1}{3}} |1, 0\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

By rotational invariance, all states with

same  $j$  have same energy  $[\hat{H}_{SO}, \hat{J}^2] = 0$

$$j = \frac{3}{2} \rightarrow \lambda = 1$$

$$j = \frac{1}{2} \rightarrow \lambda = -2$$

as on p. 12

note in each term  $m_j = m_l + m_s$

so in diagonal basis

$$|3/2, 3/2\rangle |3/2, 1/2\rangle |3/2, -1/2\rangle |3/2, -3/2\rangle |1/2, 1/2\rangle |1/2, -1/2\rangle$$

$$\left[ \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} \right] = \text{diag}(1, 1, 1, 1, -2, -2)$$

Spin-orbit energy

$$\hat{H}_{SO} = \frac{1}{4} mc^2 (Z\alpha)^4 \left( \frac{a_0}{Zr} \right)^3 \left( \frac{2\vec{L} \cdot \vec{S}}{\hbar^2} \right)$$

$$\left\langle \left( \frac{a_0}{Zr} \right)^3 \right\rangle_{n,l} = \frac{1}{n^3 l(l+1/2)(l+1)} = \frac{1}{2^3 \cdot 3} = \frac{1}{24}$$

$$n=2$$

$$l=1$$

$$j=3/2$$

$$j=1/2$$

$$E_{SO}^{(1)} = \left( \frac{1}{96} \right) mc^2 (Z\alpha)^4 \begin{cases} 1 \\ -2 \end{cases}$$

Next, Darwin term.

Darwin term

(Charles Darwin's Grandson)

$$\hat{H}_D = \frac{\hbar^2}{8m^2c^2} e (\vec{\nabla} \cdot \vec{E})$$

where  $\vec{E} = -\vec{\nabla}\phi$ ,  $V = -e\phi$

$$e (\vec{\nabla} \cdot \vec{E}) = (e\vec{\nabla}) (-\vec{\nabla}\phi) = \nabla^2 V$$

now to the point,  $\vec{\nabla} \cdot \vec{E} = 4\pi\rho = Ze 4\pi \delta^3(\vec{r})$

$$\hat{H}_D = \frac{\hbar^2 \pi}{2m^2c^2} \frac{Ze^2}{a_0^3} \left( \frac{a_0^3}{Z^3} \delta^3(\vec{r}) \right)$$

with  $e^2 = \hbar c \alpha$ ,  $a_0 = \frac{\hbar}{mc\alpha}$

$$\hat{H}_D = \frac{\pi}{2} mc^2 (Z\alpha)^4 \left( \frac{a_0}{Z} \right)^3 \delta^3(\vec{r})$$

only  $l=0$  states are non-zero  
origin

$$\begin{aligned} E_D^{(1)} n_{1,0} &= \langle \hat{H}_D \rangle_{n_{1,0}} = \frac{\pi}{2} (mc^2) (Z\alpha)^4 \left( \frac{a_0}{Z} \right)^3 |\psi_{1,0}(0)|^2 \\ &= |\psi_{1,0}(0)|^2 \left( \frac{Z}{na_0} \right)^3 \frac{1}{\pi} \end{aligned}$$

giving

$$E_{D, n, 0}^{(1)} = \left( \frac{1}{2n^3} \right) mc^2 (Z\alpha)^4 \Big|_{n=2} = +\frac{1}{16} mc^2 (Z\alpha)^4$$

N=2 fine structure

$$E_{2S^{1/2}}^{(0)} = E_K + E_D = \left( \frac{-13}{128} + \frac{1}{16} \right) mc^2 (Z\alpha)^4$$

$$\underline{-5/128}$$

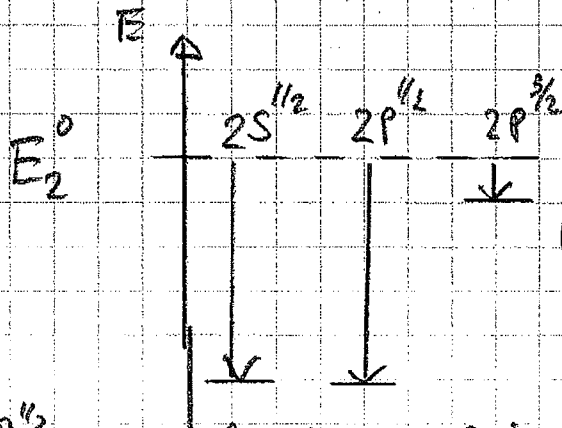
$$E_{2P^{3/2}}^{(0)} = E_K + E_{SO} = \left( \frac{-7}{384} + \frac{1}{96} \right) mc^2 (Z\alpha)^4$$

$$\underline{-1/128}$$

$$E_{2P^{1/2}}^{(0)} = E_K + E_{SO} = \left( \frac{-7}{384} - \frac{2}{96} \right) mc^2 (Z\alpha)^4$$

$$\underline{-5/128}$$

as for exact solution, E depends only on j!



$$\left\{ \begin{aligned} \Delta E_{fine} &= \frac{4}{128} mc^2 (Z\alpha)^4 \\ \Delta \nu_{fine} &= \frac{\Delta E}{h} = 10.9 \text{ GHz} \end{aligned} \right.$$

Exp.  $2S^{1/2}$ ,  $2P^{1/2}$  split by Lamb shift -  $\Delta \nu_L = 1.057 \text{ GHz}$