268(6): Schroedinger Angular Momentum in the Theory of Spin-Orbit Splitting from x Theory.

The basic hamiltonian from x theory is:

$$H\phi = \left(-\frac{\hbar^2}{2m}\nabla^2 - x^2\frac{k}{r} + \frac{(x^2-1)L^2}{2mr^2} \right)\phi. \quad -(1)$$

Now use:

$$L^2\phi = \ell(\ell+1)\hbar^2\phi \quad -(2)$$

so

$$\langle L^2 \rangle = \ell(\ell+1)\hbar^2 \quad -(3)$$

This replaces the Bohr quantization of the previous note:

$$\langle L^2 \rangle_{Bohr} = n^2\hbar^2. \quad -(4)$$

This replacement ensures that the ellipticity is non-zero in general, and is needed for a self consistent theory.

The hamiltonian from the fermion equation is:

$$(E - mc^2)\phi = \left(-\frac{\hbar^2\nabla^2}{2m} - \frac{k}{r} + E_{so} \right)\phi \quad -(5)$$

where E_{so} is the spin orbit energy. Comparing eqs. (1) and (5):

$$-x^2\frac{k}{r} + \frac{(x^2-1)\ell(\ell+1)\hbar^2}{2mr^2} = -\frac{k}{r} + E_{so} \quad -(6)$$

so:

2)

$$\boxed{E_{SO} = (x^2 - 1) V_{eff}} \quad -(7)$$

where the effective potential energy is:

$$V_{eff} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2} \quad -(8)$$

This is a balance of the Coulombic attraction and the centrifugal repulsion for $l > 0$. For $l = 0$, the s orbitals are purely attractive. Eq. (8) is the same as that obtained from the Schroedinger equation.

Self consistently, for:

$$x = 1 \quad -(9)$$

there is no spin orbit coupling and no fine structure:

$$E_{SO} = 0. \quad -(10)$$

The spin orbit energy is defined from the fermion equation by:

$$E_{SO}\phi = -\frac{e^2}{16\pi\epsilon_0 m^2 c^2} \underline{\sigma} \cdot \underline{p} \frac{1}{r} \underline{\sigma} \cdot \underline{p} \phi$$

$$= \frac{ie^2\hbar}{16\pi\epsilon_0 m^2 c^2} \underline{\sigma} \cdot \underline{\nabla} \left(\frac{1}{r} \underline{\sigma} \cdot \underline{p} \phi \right)$$

$$= -\frac{ie^2\hbar}{16\pi\epsilon_0 m^2c^2r^3}\,\underline{\sigma}\cdot\underline{r}\,\underline{\sigma}\cdot\underline{p}\,\phi + \dots \qquad -(11)$$

By Pauli algebra:

$$\underline{\sigma}\cdot\underline{r}\,\underline{\sigma}\cdot\underline{p} = \underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{r}\times\underline{p}$$

$$= \underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{L} \qquad -(12)$$

Therefore the real part of eq. (11) is

$$E_{so}\,\phi = \frac{e^2\hbar}{16\pi\epsilon_0 m^2c^2r^3}\,\underline{\sigma}\cdot\underline{L}\,\phi \qquad -(13)$$

$$= \frac{e^2}{8\pi\epsilon_0 m^2c^2r^3}\,\underline{S}\cdot\underline{L}\,\phi$$

where the spin angular momentum is defined by:

$$\underline{S} = \frac{1}{2}\hbar\,\underline{\sigma} \qquad -(14)$$

So:

$$\langle E_{so}\rangle = \frac{e^2}{8\pi\epsilon_0 m^2c^2}\left\langle \frac{\underline{S}\cdot\underline{L}}{r^3}\right\rangle \qquad -(15)$$

and gives the fine structure of atomic hydrogen.
A representation of angular momentum coupling theory is chosen so that:

$$\langle \underline{S} \cdot \underline{L} \rangle = \hbar^2 \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \quad -(16)$$

where:

$$j = \ell + s,\ \ell + s - 1,\ \ldots,\ |\ell - s|, \quad -(17)$$

the Clebsch Gordan series.

So:

$$\langle E_{SO} \rangle = \frac{e^2 \hbar^2}{8\pi\epsilon_0 m^2 c^2} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \left\langle \frac{1}{r^3} \right\rangle \quad -(18)$$

$$= (1 - x^2) \left(\frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle - \frac{\ell(\ell+1)\hbar^2}{2m} \left\langle \frac{1}{r^2} \right\rangle \right).$$

It is seen that the transition from the non relativistic to the relativistic theory is governed by the precession factor x of the ellipse:

$$r = \frac{\alpha}{1 + \epsilon \cos(x\theta)} \quad -(19)$$

The expectation values in eq. (18) are:

$$\left\langle \frac{1}{r} \right\rangle, \left\langle \frac{1}{r^2} \right\rangle, \text{ and } \left\langle \frac{1}{r^3} \right\rangle.$$

They are evaluated from:

$$\frac{1}{r} = \frac{1}{\alpha} \left(1 + \epsilon \cos(x\theta) \right) \quad -(20)$$

with hydrogenic wavefunctions. So:

$$\int \psi^* \frac{1}{r^n} \psi \, d\tau = \int \psi^* \frac{1}{\alpha^n} \left(1 + \epsilon \cos(x\theta)\right)^n \psi \, d\tau \quad -(21)$$

where

$$n = 1, 2, 3.$$

The half right latitude and the ellipticity can be worked out as follows.

$$\alpha = \frac{L^2}{mk} = \frac{4\pi\epsilon_0 l(l+1)\hbar^2}{me^2} \quad -(22)$$

$$\boxed{\alpha = l(l+1) r_{B0}} \quad -(23)$$

where r_{B0} is the Bohr radius for $n=1$:

$$r_{B0} = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \quad -(24)$$

The ellipticity is given by:

$$\epsilon^2 = 1 + \frac{2EL^2}{mk^2} \quad -(25)$$

$$= 1 - \frac{me^4 l(l+1)\hbar^2}{16\pi^2\epsilon_0^2\hbar^2 n^2} \cdot \frac{16\pi^2\epsilon_0^2}{me^2}$$

$$= 1 - \frac{l(l+1)}{n^2} \quad -(26)$$

6) So
$$\boxed{\epsilon^2 = 1 - \frac{l(l+1)}{n^2}} \quad -(27)$$

where:
$$l = 0, 1, 2, \ldots, n-1 \quad -(28)$$

For example, in the 2p orbital:
$$n = 2, \; l = 1 \quad -(29)$$

so
$$\epsilon^2 = \frac{1}{2}, \; \epsilon = \frac{1}{\sqrt{2}} = 0.7071 \quad -(30)$$

In the 2p orbital:
$$j = 3/2 \text{ or } 1/2 \quad -(31)$$

and
$$d = 2r_{Bo} = 1.05835 \times 10^{-10} \text{ m.}$$

So in evaluating x from eq. (18) for the 2p orbital use:
$$\left. \begin{array}{l} d = 1.05835 \times 10^{-10} \text{ m}, \; \epsilon = 0.7071, \\ n = 2, \; l = 1, \; j = 3/2, \text{ or } j = 1/2. \end{array} \right] -(32)$$

If $j = 3/2$, $l = 1$, $s = 1/2$, then:
$$\langle E_{so} \rangle_{3/2} = \frac{e^2 \hbar^2}{8\pi \epsilon_0 m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \quad -(33)$$

) If $j = 1/2$, $l = 1$, $s = 1/2$ then:

7)
$$\langle E_{so} \rangle_{1/2} = -\frac{e^2\hbar^2}{4\pi\epsilon_0 m^2 c^2}\left\langle \frac{1}{r^3} \right\rangle \quad -(34)$$

These results are sketched in the following figure:

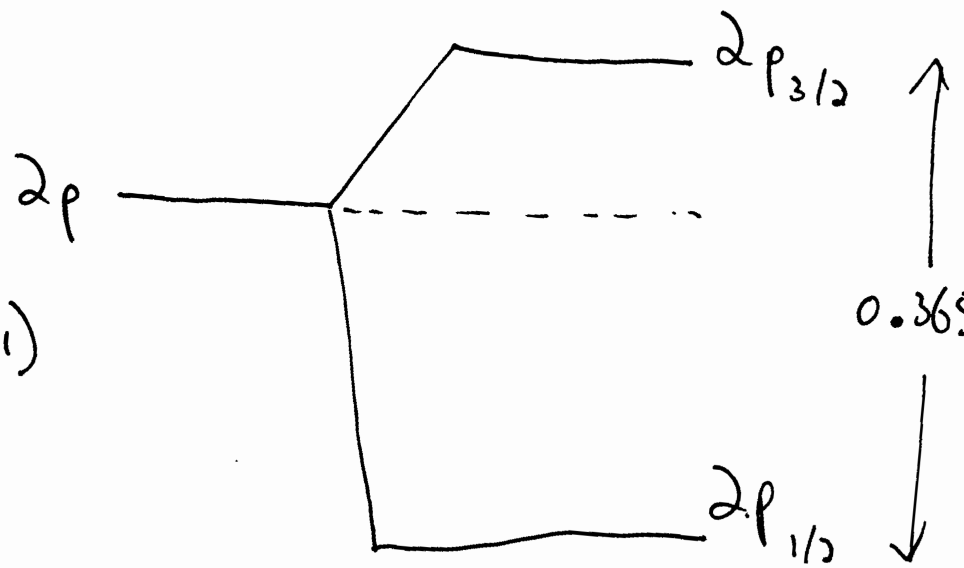

Fig. (1)

The splitting in joules is:

$$\langle E_{so} \rangle_{3/2} - \langle E_{so} \rangle_{1/2}$$

$$= \frac{3}{8\pi}\frac{e^2\hbar^2}{\epsilon_0 m^2 c^2}\left\langle \frac{1}{r^3} \right\rangle \quad -(35)$$

$$= 0.365 \text{ cm}^{-1}$$

To convert wavenumbers to joules use:

$$E = \hbar\omega = 2\pi f\hbar = 2\pi\bar{\nu}c\hbar \quad -(36)$$

Here c must be in cm per second:

$$c = 2.998\times10^{10} \text{ cm s}^{-1} \quad -(37)$$

5) So:

$$1\,J = 5.03445 \times 10^{22}\ cm^{-1} \quad -(38)$$

It follows that:

$$\frac{3}{8}\frac{e^2\hbar^2}{\epsilon_0 m^2 c^2}\left\langle \frac{1}{r^3}\right\rangle = 7.25 \times 10^{-24}\ J \quad -(39)$$

Therefore it is possible to obtain an experimental value for $\langle 1/r^3 \rangle$: $\quad -(40)$

$$\left\langle \frac{1}{r^3}\right\rangle_{2p} = \frac{8}{3}\times 7.25 \times 10^{-24}\cdot\left(\frac{\epsilon_0 m^2 c^2}{e^2\hbar^2}\right) m^{-3}$$

where

$$\epsilon_0 = 8.854188\times 10^{-12}\ J^{-1} C^2 m^{-1}$$
$$m = 9.10953\times 10^{-31}\ kg$$
$$c = 2.997925\times 10^{8}\ m\,s^{-1}$$
$$e = -1.60219\times 10^{-19}\ C$$
$$\hbar = 1.05459\times 10^{-34}\ Js$$

First check that the units are correct:

$$\left\langle \frac{1}{r^3}\right\rangle_{2p} = \frac{J\,J^{-1} C^2 m^{-1}\,kg\,m^2 m^2 s^{-2}}{J^2 s^2}$$

$$= \frac{kg\,m^2\,m\,s^{-4}}{kg^2\,m^4 s^{-4}} = m^{-3}$$

So

$$\boxed{\left\langle \frac{1}{r^3}\right\rangle_{2p} = 4.4719\times 10^{52}\ m^{-3}}$$

(41)

9) For this splitting it follows that:

$$(1-x^2)\left(\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle-\frac{\hbar^2}{m}\left\langle\frac{1}{r^2}\right\rangle\right)$$

$$= 7.25\times10^{-24} \text{ Joules} \quad -(42)$$

i.e.

$$(1-x^2)\left(2.3071\times10^{-48}\left\langle\frac{1}{r}\right\rangle-1.221\times10^{-38}\left\langle\frac{1}{r^2}\right\rangle\right)$$

$$= 7.25\times10^{-24} \quad -(43)$$

$$-(44)$$

Here:

$$\left\langle\frac{1}{r}\right\rangle=\int\psi_{2p}^{*}\,\frac{1}{\alpha}\left(1+\epsilon\cos(x\phi)\right)\psi_{2p}\,d\tau \quad -(45)$$

and

$$\left\langle\frac{1}{r^2}\right\rangle=\int\psi_{2p}^{*}\,\frac{1}{\alpha^2}\left(1+\epsilon\cos(x\phi)\right)^2\psi_{2p}\,d\tau \quad -(46)$$

with

$$\alpha = 1.05835\times10^{-10}\text{ m} \quad -(47)$$

$$\epsilon = 0.7071 \quad -(48)$$

The 2p hydrogenic wave function is used in eq. (45) and (46). So x can be found for $(n=2, l=1, j=3/2)-(n=2, l=1, j=1/2)$ with $s = 1/2$.