268(5): Check a & Evaluation of Spin-Orbit Splitting from the Precessing Ellipse

The precessing ellipse of relevance is:

$$\frac{1}{r} = \frac{1}{r_B}\left(1 + \epsilon \cos(x\phi)\right) \quad - (1)$$

where the Bohr radius is:

$$r_B = \frac{4\pi \epsilon_0 \hbar^2 n^2}{m e^2} \quad - (2)$$

In the hydrogen atom n is the principal quantum number. From the direct equation the Hamiltonian from eq. (1) is:

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

$$- (3)$$

where

$$k = \frac{e^2}{4\pi\epsilon_0} \quad - (4)$$

and

$$L^2 = mk\,d = mk\,r_B \quad - (5)$$

So:

$$H\phi = \left(-\frac{\hbar^2}{2m}\nabla^2 - x^2\frac{k}{r} + \frac{1}{2}(x^2-1)\frac{k\,r_B}{r^2}\right)\psi. \quad - (6)$$

The relativistic Hamiltonian for the fermion

2) equation is:

$$H\phi = (E - mc^2)\phi = \left(-\frac{k}{r} + \frac{1}{2m}\underline{\sigma}\cdot\underline{p}\left(1 - \frac{k}{2mc^2 r}\right)\underline{\sigma}\cdot\underline{p}\right)\psi$$
$$\tag{7}$$

$$= \left(-\frac{k}{r} - \frac{\hbar^2}{2m}\nabla^2 - \frac{k}{4m^2c^2}\underline{\sigma}\cdot\underline{p}\,\frac{1}{r}\,\underline{\sigma}\cdot\underline{p}\right)\phi$$

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

where the spin-orbit interaction energy is:

$$E_{so} = -\frac{k}{4m^2c^2}\,\underline{\sigma}\cdot\underline{p}\,\frac{1}{r}\,\underline{\sigma}\cdot\underline{p} \tag{8}$$

From eqns. (6) to (8) it follows that:

$$-\frac{k}{r} + E_{so} = -x^2\frac{k}{r} + \frac{1}{2}(x^2-1)\frac{k\,r_B}{r^2}$$
$$\tag{9}$$

So:

$$E_{so} = (1-x^2)\frac{k}{r} - \frac{1}{2}(1-x^2)\frac{k\,r_B}{r^2}$$

$$= (1-x^2)\frac{k}{r}\left(1 - \frac{1}{2}\frac{r_B}{r}\right) \tag{10}$$

where

$$k = \frac{e^2}{4\pi\epsilon_0} \tag{11}$$

3)

From eqs. (8) and (10) :

$$-\frac{1}{4m^2 c^2} \underline{\sigma} \cdot \underline{p} \frac{1}{r} \underline{\sigma} \cdot \underline{p} = \frac{(1-x^2)}{r}\left(1 - \frac{1}{2}\frac{r_B}{r}\right) - (12)$$

$$- (13)$$

Therefore:

$$\underline{\sigma} \cdot \underline{p} \frac{1}{r} \underline{\sigma} \cdot \underline{p} \, \phi = \frac{4m^2 c^2}{r}(x^2 - 1)\left(1 - \frac{1}{2}\frac{r_B}{r}\right)\phi$$

and

$$\left\langle \underline{\sigma} \cdot \underline{p} \frac{1}{r} \underline{\sigma} \cdot \underline{p} \right\rangle = 4m^2 c^2 (x^2 - 1)\left\langle \frac{1}{r} \right\rangle$$
$$- 2m^2 c^2 (x^2 - 1) r_B \left\langle \frac{1}{r^2} \right\rangle$$

$$- (14)$$

Eq. (14) is an equation expressing the well known expectation value on the left hand side of eq. (14) to expectation values from the precessing ellipse (1). If there were no spin-orbit coupling the theory would give a static ellipse:

$$x = 1 \quad - (15)$$

This is consistent with the structure of eq. (14)

4) Because when eqv. (15) holds there is no spin-orbit coupling.

In order for the theory to be entirely self-consistent the expectation values on the right hand side of eqv (14) must be evaluated as follows:

$$\left\langle \frac{1}{r} \right\rangle = \int \psi^* \frac{1}{r_B} \left(1 + \epsilon \cos(x\phi) \right) \psi \, d\tau$$

$$= \frac{1}{r_B} \int \psi^* \psi \, d\tau + \frac{\epsilon}{r_B} \int \psi^* \cos(x\phi) \psi \, d\tau \qquad -(16)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{r_B} \left(1 + \epsilon \int \psi^* \cos(x\phi) \psi \, d\tau \right) \qquad -(17)$$

and

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{r_B^2} \int \psi^* \left(1 + \epsilon \cos(x\phi) \right)^2 \psi \, d\tau \qquad -(18)$$

$$= \frac{1}{r_B^2} \left(1 + 2\epsilon \int \psi^* \cos(x\phi) \psi \, d\tau + \epsilon^2 \int \psi^* \cos^2(x\phi) \psi \, d\tau \right)$$

for the Hydrogenic wavefunctions

If there were no spin-orbit coupling and other effects from the left hand side of eqv. (14)

) then $\cos(x\phi)$ is replaced by $\cos\phi$ in eq. (18). In this case however, both sides of eq. (14) vanish, and the precessing ellipse reduces to an ellipse. The Hamiltonian reduces to that of the Schroedinger equation:

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{k}{r}\right)\psi \quad -(19)$$

if $x = 1$.

So all the well known physics from the left hand side of eq. (14) is attributed to x for a given hydrogenic wave function.

The most well known example is the fine structure of atomic hydrogen. In this case the relevant term is:

$$\left\langle \underline{\sigma}\cdot\underline{p} \, \frac{1}{r} \, \underline{\sigma}\cdot\underline{p} \right\rangle = \hbar^2 \int \psi^* \frac{\underline{\sigma}\cdot\underline{L}}{r^3} \psi \, d\tau$$

$$= 2 \int \psi^* \frac{\underline{S}\cdot\underline{L}}{r^3} \psi \, d\tau \quad -(20)$$

where:

$$\underline{S} = \frac{1}{2}\hbar\underline{\sigma} \quad -(21)$$

is the spin angular momentum operator. From eqs.) and (20):

$$\int \psi^* \frac{S \cdot L}{r^3} \psi \, d\tau = \left\langle \frac{S \cdot L}{r^3} \right\rangle$$

$$= 2m^2 c^2 (x^2 - 1) \left\langle \frac{1}{r} \right\rangle - m^2 c^2 (x^2 - 1) \left\langle \frac{r_B}{r^2} \right\rangle$$

$$= 2m^2 c^2 (x^2 - 1) \left(\left\langle \frac{1}{r} \right\rangle - \frac{1}{2} \left\langle \frac{r_B}{r^2} \right\rangle \right)$$

$$- (22)$$

It is seen that spin orbit interaction is due entirely to x, _and_ $x \neq 1$.

In standard calculations:

$$S \cdot L \, \psi = \frac{1}{2} \hbar^2 \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \psi$$

$$- (23)$$

and

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

$$- (24)$$

Also:

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

$$- (25)$$

So:

$$\left\langle \frac{S \cdot L}{r^3} \right\rangle = \frac{\hbar^2}{2 r_{Bo}^3} \left[\frac{j(j+1) - \ell(\ell+1) - s(s+1)}{n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \right]$$

$$- (26)$$

7) where

$$r_{B0} = r_B(n=1) = \frac{4\pi \epsilon_0 \hbar^2}{m e^2} \quad -(27)$$

Therefore:

$$\frac{\hbar^2}{2r_B^3}\left[\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{\ell(\ell+\frac{1}{2})(\ell+1)}\right] = 2m^2c^2(x^2-1)\left\langle\frac{1}{r}\right\rangle - \frac{r_B}{2}\left\langle\frac{1}{r^3}\right\rangle \quad -(28)$$

in which:

$$j = \ell+s, \ell+s-1, \ldots, |\ell-s| \quad -(29)$$

For S orbitals there is no orbital quantum number

$$\ell = 0 \quad -(30)$$

So

$$j = \frac{1}{2}, -\frac{1}{2} \quad -(31)$$

$$s = \frac{1}{2}, -\frac{1}{2} \quad -(32)$$

In this case:

$$x = 1 \quad -(33)$$

For the 2P orbital:

$$\ell = 1 \quad -(31)$$

and

$$j = \frac{3}{2}, \frac{1}{2} \quad -(32)$$

This gives a fine structure splitting of 0.365 cm^{-1}

and $x \neq 1$.

8) Therefore each set of quantum numbers n, j, ℓ and s is described by x and ϵ. The ellipticity is defined by:

$$\epsilon^2 = 1 + \frac{2EL^2}{mk^2}$$

$$= 1 + \frac{2E n k r_B}{mk^2} \quad -(33)$$

$$= 1 + \frac{2E r_B}{k}.$$

The unsplit energy levels of H are given by:

$$E = -\frac{mk^2}{2L^2} \quad -(34)$$

in which case $\epsilon = 0 \quad -(35)$ but the spin orbit coupling splits the energy levels

For $^2P_{3/2}$:

$$E = E + \frac{1}{2} \hbar c \zeta \quad -(36)$$

$$= E(^2P_{3/2})$$

and for $^2P_{1/2}$:

$$E(^2P_{1/2}) = E - \hbar c \zeta \quad -(37)$$

where ζ is the spin orbit coupling constant.

9) Therefore E can be related to z and can be worked out completely for a given set of quantum numbers. This will be the subject of the next note.

Therefore spin orbit coupling can be worked out entirely in terms of x.