# 268(4): Expectation Values of the Fermion and Elliptical Equations applied to Atomic H.

The expectation values from the fermion equation are:

$$\left\langle E - mc^2 \right\rangle = \left\langle \frac{p^2}{2m} \right\rangle - \left\langle \frac{e^2}{4\pi\epsilon_0 r} \right\rangle \quad -(1)$$

$$- \frac{e^2}{16\pi m^2 c^2 \epsilon_0} \int \psi^* \underline{\sigma} \cdot \underline{p} \frac{1}{r} \underline{\sigma} \cdot \underline{p} \, \psi \, d\tau$$

where:

$$\left\langle \frac{p^2}{2m} \right\rangle = - \frac{\hbar^2}{2m} \int \psi^* \nabla^2 \psi \, d\tau \quad -(2)$$

and

$$\left\langle \frac{e^2}{4\pi\epsilon_0 r} \right\rangle = \frac{e^2}{4\pi\epsilon_0} \int \psi^* \frac{1}{r} \psi \, d\tau \quad -(3)$$

In eqns (1) to (3) the orbitals are the hydrogenic orbitals. Using the Leibniz theorem the third term in eq. (1) may be expanded to give several spectral effects of basic importance. In this term:

$$\underline{p} = - i\hbar \underline{\nabla} \quad -(4)$$

and

$$\frac{1}{r} = \frac{1}{\alpha} \left( 1 + \epsilon \cos\theta \right). \quad -(5)$$

The Leibniz Theorem means that:

$$\underline{\nabla} \left( \frac{1}{r} \underline{\sigma} \cdot \underline{p} \, \psi \right) = \underline{\nabla} \left( \frac{1}{r} \right) \left( \underline{\sigma} \cdot \underline{p} \, \psi \right) + \frac{1}{r} \underline{\nabla} \left( \underline{\sigma} \cdot \underline{p} \, \psi \right) \quad -(6)$$

2) where:

$$\underline{\nabla}\left(\underline{\sigma}\cdot\underline{p}\,\psi\right) = \left(\underline{\nabla}\left(\underline{\sigma}\cdot\underline{p}\right)\right)\psi + \left(\underline{\sigma}\cdot\underline{p}\right)\underline{\nabla}\psi \quad -(7)$$

The spin orbit term is:

$$\langle E_{so}\rangle = \frac{-i\hbar e^2}{16\pi m^2 c^2 \epsilon_0}\int \psi^* \underline{\sigma}\cdot\underline{\nabla}\left(\frac{1}{r}\right)\underline{\sigma}\cdot\underline{p}\,\psi\, d\tau \quad -(8)$$

in which:

$$\underline{\nabla}\left(\frac{1}{r}\right) = -\frac{\underline{r}}{r^3}. \quad -(9)$$

So

$$\langle E_{so}\rangle = \frac{i\hbar e^2}{16\pi m^2 c^2 \epsilon_0}\int \psi^* \frac{\underline{\sigma}\cdot\underline{r}\,\underline{\sigma}\cdot\underline{p}}{r^3}\,\psi\, d\tau. \quad -(10)$$

In this expression:

$$\underline{\sigma}\cdot\underline{r}\,\underline{\sigma}\cdot\underline{p} = \underline{r}\cdot\underline{p} + i\,\underline{\sigma}\cdot\underline{r}\times\underline{p} \quad -(11)$$

where the orbital angular momentum is:

$$\underline{L} = \underline{r}\times\underline{p}. \quad -(12)$$

So the real part of Eq. (10) is:

$$\mathrm{Re}\langle E_{so}\rangle = -\frac{\hbar e^2}{16\pi m^2 c^2 \epsilon_0}\int \psi^* \frac{\underline{\sigma}\cdot\underline{L}}{r^3}\,\psi\, d\tau \quad -(13)$$

The conventional way of evaluating this is to

3) use:

$$\hat{\underline{\sigma}} \cdot \hat{\underline{L}} \phi = \hbar \left( j(j+1) - l(l+1) - s(s+1) \right) \phi \quad -(14)$$

where $j$, $l$ and $s$ are quantum numbers:

$$j = l + s,\ l + s - 1, \ldots,\ |l - s| \quad -(15)$$

For hydrogenic orbitals:

$$\int \phi^* \frac{1}{r^3} \phi \, d\tau = \left( \frac{1}{r_B} \right)^3 \left( n^3 l (l + 1/2)(l+1) \right)^{-1} \quad -(16)$$

for:

$$l > 0 \quad -(17)$$

where $n$ is the principal quantum number and where the Bohr radius is, for $n = 1$:

$$r_{B0} = \frac{4\pi \epsilon_0 \hbar^2}{m e^4} \quad -(18)$$

So:

$$\mathrm{Re} \langle E_{so} \rangle = -\frac{e^2 \hbar^2 \left( (j(j+1) - l(l+1) - s(s+1) \right)}{16\pi m^2 c^2 \epsilon_0 r_B^3} \left( n^3 l (l+1/2)(l+1) \right)^{-1} \quad -(19)$$

and can be evaluated for various $n$, $j$, $l$ and $s$, provided in Eq. (19) that $l > 0$. This gives the fine structure of the hydrogen atom.

4) In x theory:

$$\int \psi^* \frac{1}{r^3} \psi \, d\tau = \frac{1}{d^3} \int \psi^* (1 + \epsilon \cos\theta)^3 \psi \, d\tau$$

$$= \frac{1}{d^3} \int \psi^* \left(1 + 3\epsilon\cos\theta + 3\epsilon^2 \cos^2\theta + \epsilon^3 \cos^3\theta\right) \psi \, d\tau \quad -(20)$$

In eq. (20) assume that:

$$d = r_B \quad -(21)$$

From eqs. (19) and (20):

$$\int \psi^* (1 + \epsilon \cos\theta)^3 \psi \, d\tau \quad -(22)$$

$$= - \frac{e^2 \hbar^2 \left( j(j+1) - l(l+1) - s(s+1) \right)}{16 \pi m^2 c^2 \epsilon_0 n^3 l (l + 1/2)(l+1)}$$

so the ellipticity $\epsilon$ can be found for a given $n, j, l, s$. This is the ellipticity of x theory for spin orbit interaction in H.

Note carefully that the left hand side of eq. (22) is analytical but the direct

) evaluation of $\int \psi^* \frac{1}{r^3} \phi \, d\tau$ leads to a singularity and is numerically difficult.

It is also possible to evaluate $\langle E_{so} \rangle$ from Eq. (19) of Note 268(3):

$$\langle E_{so} \rangle = (x^2 - 1)\left( \frac{L^2}{2m} \left\langle \frac{1}{r^2} \right\rangle - \left\langle \frac{k}{r} \right\rangle \right) \quad -(20)$$

in which:

$$\frac{1}{r^2} = \frac{1}{\alpha^2}\left(1 + \epsilon \cos(x\theta)\right)^2 \quad -(21)$$

and

$$\frac{1}{r} = \frac{1}{\alpha}\left(1 + \epsilon \cos(x\theta)\right) \quad -(22)$$

Here:

$$\alpha = r_B \quad -(23)$$

$$= \frac{4\pi \epsilon_0 \hbar^2 n^2}{m e^2} \quad -(24)$$

$$= \frac{L^2}{mk}$$

where

$$k = \frac{e^2}{4\pi \epsilon_0} \quad -(25)$$

so

$$L^2 = m k r_B \quad -(26)$$

6)

It follows that:

$$\langle E_{so} \rangle = (x^2 - 1)\left( \frac{k r_B}{2} \left\langle \frac{1}{r^2} \right\rangle - \left\langle \frac{k}{r} \right\rangle \right)$$

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

$$= (x^2 - 1)\left( \frac{\hbar^2 n^2}{2m} \left\langle \frac{1}{r^2} \right\rangle - \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle \right) \quad -(27)$$

where:

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

$$= \int \psi^* \frac{1}{r^2} \psi \, d\tau \quad -(28)$$

and

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

$$= \int \psi^* \frac{1}{r} \psi \, d\tau \quad -(29)$$

so $x$ can be found and $\epsilon$ can be found in terms of $n$, $j$, $l$ and $s$.