268(7): Order of Magnitude Estimate of x and Eckardt Quantization Scheme.

In note 268(6) it was shown that:

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

In this equation:

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

where

$$\alpha = l(l+1)\, r_{B0} \quad -(3)$$

$$\epsilon = 1 - \frac{l(l+1)}{n^2} \quad -(4)$$

$$r_{B0} = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} \quad -(5)$$

Note that

$$\frac{\hbar^2}{m\, r_{B0}} = \frac{e^2}{4\pi\epsilon_0} \quad -(6)$$

So eq. (1) is:

$$\langle E_{so} \rangle = \frac{(x^2-1)\, k}{l(l+1)\, r_{B0}}\left(-\langle 1 + \epsilon\cos(x\phi) \rangle + \langle (1+\epsilon\cos(x\phi))^2 \rangle \right) \quad -(7)$$

where

$$\frac{k}{r_B} = 4.36 \times 10^{-18} \text{ Joules} \quad -(8)$$

2) with

$$k = \frac{e^2}{4\pi\epsilon_0} \quad -(9)$$

So: $\quad -(10)$

$$\boxed{\langle E_{so}\rangle = 4.36\times10^{-18}\frac{(x^2-1)}{\ell(\ell+1)}\left(\langle(1+\epsilon\cos(x\phi))^2\rangle - \langle 1+\epsilon\cos(x\phi)\rangle\right)}$$

3) Application to 2p Fine Structure of H

In this case:

$$n = 2,\ \ell = 1,\ \epsilon = 0.7071 \quad -(11)$$

and

$$\langle E_{so}\rangle = 7.25\times10^{-24}\ \text{Joules} = 0.365\ \text{cm}^{-1} \quad -(12)$$

so

$$\boxed{x^2 - 1 \sim 10^{-6}} \quad -(13)$$

This is very similar to the result found for planetary precession, suggesting that the factor x has a universal significance.

The expectation values in eq. (10) have already been worked out by Horst Eckardt so

3) x can be found accurately. It can be found for any type of spectroscopic fine structure in atoms and molecules.

2) Application to Eckardt Quantization

In this case x is a quantum number. Assume in the first instance that it is the principal quantum number:

$$x = n. \quad -(14)$$

For the 2p fine structure:

$$x = 2, \; l = 1, \; \epsilon = 0.7071 \quad -(15)$$

In order to obtain the experimental result (12), it is therefore necessary that:

$$7.25 \times 10^{-24} = 4.36 \times 10^{-18} \times \frac{3}{2} \left(\langle A^2 \rangle - \langle A \rangle \right) \quad -(16)$$

i.e.
$$\langle A^2 \rangle - \langle A \rangle = 1.109 \times 10^{-6} \quad -(17)$$

We denote this quantity as the Eckardt function.

It is a geometrical function made up of expectation values of θ and ϕ of the spherical coordinate system. In this case of a 2p orbital the basis functions are $\langle 1+0.7071\cos 2\theta \rangle$, $\langle 1+0.7071\cos 2\phi \rangle$, $\langle (1+0.7071\cos 2\theta)^2 \rangle$ and $\langle (1+0.7071\cos 2\phi)^2 \rangle$ and combinations of these basis functions give the experimentally observed splitting, eq. (17).

This is somewhat similar to linear combination of atomic orbitals, a well known method in computational quantum chemistry. It is known that the Eckardt ellipse:

$$r = \frac{\alpha}{1+\epsilon\cos n\theta}, \quad - (18)$$

where

$$n = 1, 2, 3, 4 \ldots \quad - (19)$$

gives waves superimposed on the static ellipse. These are essentially de Broglie waves. These occur in Bohr quantization and also in Schroedinger and Dirac quantization. All these theories are related in this note.