330(2) : New Type of Spin Orbit Fine Structure in the Spectroscopy of Atoms and Molecules.

From Note 330(1) the new term is:

$$\mathrm{Re}\, H_{SO}\,\phi = \frac{e^2\hbar}{16\pi\epsilon_0 m^2c^2r^3}\,\gamma\,\underline{\sigma}\cdot\underline{L}\,\phi \quad -(1)$$

where

$$\gamma = \left(1 - \frac{p_0^2}{m^2c^2}\right)^{-1/2} \quad -(2)$$

and

$$p_0^2 = 2m\,(H_0 - U) \quad -(3)$$

in the same notation as Note 330(1). The spin operator is defined by:

$$\underline{\hat{S}} = \frac{\hbar}{2}\,\underline{\hat{\sigma}} \quad -(4)$$

so:

$$\mathrm{Re}\, H_{SO}\,\phi = \frac{e^2}{8\pi\epsilon_0 m^2c^2}\left(1 - \frac{p_0^2}{m^2c^2}\right)^{-1/2}\frac{\underline{\hat{S}}\cdot\underline{\hat{L}}}{r^3}\,\phi \quad -(5)$$

Now use:

$$\left(1 - \frac{p_0^2}{m^2c^2}\right)^{-1/2} \sim 1 + \frac{1}{2}\frac{p_0^2}{m^2c^2} \quad -(6)$$

$$= 1 + \frac{H_0 - U}{mc^2}$$

So:

$$ReH_{so}\phi = \frac{e^2}{8\pi\epsilon_0 m^2c^2}\left(1 + \frac{H_0 - U}{mc^2}\right)\frac{\underline{\hat{S}}\cdot\underline{\hat{L}}}{r^3}\phi \quad -(7)$$

where for the H atom:

$$H_0 = \langle H_0 \rangle = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2} \quad -(8)$$

and

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

Therefore:

$$ReH_{so}\phi = \frac{e^2}{8\pi\epsilon_0 m^2c^2}\left(1 - \frac{e^4}{32\pi^2\epsilon_0^2\hbar^2c^2n^2}\right)\frac{\underline{\hat{S}}\cdot\underline{\hat{L}}}{r^3}\phi$$

$$+ \frac{e^4}{32\pi^2\epsilon_0^2m^3c^4}\frac{\underline{\hat{S}}\cdot\underline{\hat{L}}}{r^4}\phi \quad -(10)$$

and the energy levels are:

$$\langle ReH_{so}\rangle = \frac{e^2}{8\pi\epsilon_0 m^2c^2}\left(1 - \frac{e^4}{32\pi^2\epsilon_0^2\hbar^2c^2n^2}\right)\left\langle\frac{\underline{\hat{S}}\cdot\underline{\hat{L}}}{r^3}\right\rangle$$

$$+ \frac{e^4}{32\pi^2\epsilon_0^2m^3c^4}\left\langle\frac{\underline{\hat{S}}\cdot\underline{\hat{L}}}{r^4}\right\rangle \quad -(11)$$

3) where:

$$\left\langle \frac{\underline{\hat{S}} \cdot \underline{\hat{L}}}{r^3} \right\rangle = \frac{\hbar^2\left(J(J+1) - L(L+1) - S(S+1)\right)}{2a_0^3 n^3 L(L+1/2)(L+1)} \quad -(12)$$

and

$$\left\langle \frac{\underline{\hat{S}} \cdot \underline{\hat{L}}}{r^4} \right\rangle = \frac{\hbar^2}{2}\left(J(J+1) - L(L+1) - S(S+1)\right) \times \left\langle \frac{1}{r^4} \right\rangle \quad -(13)$$

where

$$\left\langle \frac{1}{r^4} \right\rangle = \int \phi^* \frac{1}{r^4} \phi \, d\tau \quad -(14)$$

Therefore the usual fine structure is shifted by the first term on the right hand side of eq. (11) and a new type of fine structure appears, given by the second term on the right hand side of eq. (11). This second term depends on the $1/r^4$ expectation value of eq. (14).

These terms are completely new and affect all atoms and molecules, and all of computational quantum chemistry