251(4): Calculation of E_2 and E_3 Expectation Values.

The E_3 expectation value is calculated from the hamiltonian:

$$H_3 \phi = \frac{e}{2m} \underline{\sigma} \cdot \underline{B}_1 \, \underline{\sigma} \cdot \underline{L} \, \phi \quad -(1)$$

where:

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

Therefore:

$$H_3 \phi = \frac{e}{\hbar m} \underline{\sigma} \cdot \underline{B}_1 \, \underline{S} \cdot \underline{L} \, \phi \quad -(3)$$

$$= \frac{e\hbar}{2m} \left(j(j+1) - l(l+1) - s(s+1) \right) \underline{\sigma} \cdot \underline{B}_1 \, \phi$$

so the expectation value is:

$$E_3 = \frac{e\hbar}{2m} \left(j(j+1) - l(l+1) - s(s+1) \right) \int \phi^* \underline{\sigma} \cdot \underline{B}_1 \phi \, d\tau \quad -(4)$$

where:

$$\underline{\sigma} \cdot \underline{B}_1 = \underline{\sigma} \cdot \underline{B} - \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \, \underline{r} \cdot \underline{B} \quad -(5)$$

The integral $\int \phi^* \underline{\sigma} \cdot \underline{B}_1 \phi \, d\tau$ has already been evaluated in previous notes and in general is different for each wave function, so the E_3 energy levels contain a lot of very interesting information.

2) The E_2 expectation values are worked out with:

$$H_2 \phi = -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}_1 \, r \frac{d\phi}{dr} \quad -(6)$$

In general this must be worked out with computational quantum chemistry code packages. However, the hydrogenic wave functions are analytical and eq. (6) can be worked out with computer algebra. The following initial hand calculation illustrates the procedure.

If $\underline{B}$ is aligned in the Z axis then:

$$\underline{\sigma} \cdot \underline{B}_1 = \underline{\sigma} \cdot \underline{B} - \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \, \underline{r} \cdot \underline{B} \quad -(7)$$

$$= \sigma_Z B_Z (1 - \cos^2\theta)$$

$$= \sigma_Z B_Z \sin^2\theta$$

in spherical polar coordinates.

Therefore:

$$E_2 = -\frac{e\hbar \sigma_Z B_Z}{2m} \int \phi^* r \sin^2\theta \frac{d\phi}{dr} d\tau \quad -(8)$$

For a simple H wave function of the type:

$$\phi = Nx \exp(-\alpha r) \quad -(9)$$

$$= N r \sin\theta \cos\phi \exp(-\alpha r)$$

) then:

$$\frac{d\phi}{dr} = N\sin\theta\cos\phi\, e^{-\alpha r} - Nr\alpha\sin\theta\cos\phi\, e^{-\alpha r}$$

$$= N\sin\theta\cos\phi\, e^{-\alpha r}(1-\alpha r) \quad -(10)$$

Therefore:

$$E_2 = -\frac{e\hbar N^2}{2m}\int x\sin^3\theta\cos\phi(1-\alpha r)e^{-2\alpha r}\,d\tau\,\sigma_Z B_Z$$

$$= -\frac{e\hbar N^2}{2m}\int r\sin^4\theta\cos^2\phi(1-\alpha r)e^{-2\alpha r}\,d\tau\,\sigma_Z B_Z$$

$$-(11)$$

where:

$$d\tau = r^2\,dr\sin\theta\,d\theta\,d\phi, \quad -(12)$$

and:

$$N^2 = \frac{\alpha^5}{\pi}. \quad -(13)$$

Therefore:

$$E_2 = -\frac{e\hbar}{2m}\frac{\alpha^5}{\pi}\int_0^\infty r(1-\alpha r)e^{-2\alpha r}\,dr\int_0^\pi \sin^4\theta\,d\theta\int_0^{2\pi}\cos^2\phi\,d\phi\,\sigma_Z B_Z$$

$$= -\frac{e\hbar}{2m}\alpha^5\int_0^\infty r(1-\alpha r)e^{-2\alpha r}\,dr\int_0^\pi \sin^4\theta\,d\theta\;\sigma_Z B_Z$$

$$-(14)$$

Here:

$$\int \sin^4\theta\,d\theta = \frac{3\theta}{8} - \frac{\sin 2\theta}{4} + \frac{\sin 4\theta}{32}$$

$$-(15)$$

so:

$$\int_0^\pi \sin^4\theta\,d\theta = \frac{3}{8}\pi \quad -(16)$$

4) So:

$$E_2 = -\frac{3e\hbar\pi}{16}\alpha^5\sigma_2 B_2\int_0^\infty r(1-\alpha r)e^{-2\alpha r}dr \quad -(17)$$

$$= -\frac{3e\hbar\pi\alpha^5\sigma_2 B_2}{16}\left(\int_0^\infty re^{-2\alpha r}dr - \int_0^\infty \alpha r^2 e^{-2\alpha r}dr\right)$$

Now use the result:

$$\int_0^\infty r^n e^{-ar}dr = \frac{n!}{a^{n+1}} \quad -(18)$$

Therefore:

$$\int_0^\infty re^{-2\alpha r}dr = \frac{1}{(2\alpha)^2} = \frac{1}{4\alpha^2} \quad -(19)$$

and

$$\int_0^\infty r^2 e^{-2\alpha r}dr = \frac{2!}{(2\alpha)^3} = \frac{1}{4\alpha^3} \quad -(20)$$

Therefore for this orbital:

$$\boxed{E_2 = 0} \quad -(21)$$

In general, E_2 can be worked out for H orbitals with computer algebra, and computational quantum chemistry packages.

It is convenient to end this note with further details of a previous calculation of the

5) integral:

$$I = \frac{\alpha^5}{\pi}\int_0^\infty r^4 e^{-2\alpha r}\,dr \int_0^\pi \sin^3\theta\cos^2\theta\,d\theta \int_0^{2\pi}\cos^2\phi\,d\phi$$

$$= \frac{\alpha^5}{\pi}\frac{4!\,\pi}{(2\alpha)^5}\int_0^\pi \sin^3\theta\cos^2\theta\,d\theta$$

$$= \frac{3}{4}\int_0^\pi \sin^3\theta\cos^2\theta\,d\theta$$

$$= \frac{3}{4}\int_0^\pi \left(1-\cos^2\theta\right)\sin\theta\cos^2\theta\,d\theta$$

$$= \frac{3}{4}\left(\int_0^\pi \cos^2\theta\sin\theta\,d\theta - \int_0^\pi \cos^4\theta\sin\theta\,d\theta\right)$$

$$= \frac{3}{4}\left(\frac{1}{3}\left(1+(-1)^2\right) - \frac{1}{5}\left(1+(-1)^4\right)\right)$$

$$= \frac{3}{4}\cdot\frac{4}{15} = \frac{1}{3} \qquad -(22)$$

This is the result given in eq. (16) of note 251(3).

Obviously, the hand calculations become very complicated very quickly which is why computer algebra is needed. These calculations give many types of useful spectra.