251(2): Expectation Value of Energy

In the previous note the hamiltonian was derived in the format:

$$\hat{H}\phi = -\frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B_1}\left(\phi + r\frac{\partial\phi}{\partial r}\right) + \frac{e}{2m}\underline{\sigma}\cdot\underline{B_1}\,\underline{\sigma}\cdot\underline{L}\,\phi \quad -(1)$$

where:

$$\underline{B_1} = \underline{B} - \underline{e}_r(\underline{e}_r\cdot\underline{B}) \quad -(2)$$

and

$$\underline{e}_r = \frac{\underline{r}}{r} \quad -(3)$$

Therefore there are three types of hamiltonian:

$$\hat{H}_1\phi = -\frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B_1}\,\phi \quad -(4)$$

$$\hat{H}_2\phi = -\frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B_1}\,r\frac{\partial\phi}{\partial r} \quad -(5)$$

$$\hat{H}_3\phi = \frac{e}{2m}\underline{\sigma}\cdot\underline{B_1}\,\underline{\sigma}\cdot\underline{L}\,\phi \quad -(6)$$

The energy expectation values are:

$$E_1 = -\frac{e\hbar}{2m}\int\phi^*\,\underline{\sigma}\cdot\underline{B_1}\,\phi\,d\tau \quad -(7)$$

$$E_2 = -\frac{e\hbar}{2m}\int\phi^*\,\underline{\sigma}\cdot\underline{B_1}\,r\frac{\partial\phi}{\partial r}\,d\tau \quad -(8)$$

$$E_3 = \frac{e}{2m}\int\phi^*\,\underline{\sigma}\cdot\underline{B_1}\,\underline{\sigma}\cdot\underline{L}\,\phi\,d\tau \quad -(9)$$

2) so there are three different types of resonance spectra. In note 251(1) the evaluation was initiated of type (9) with hydrogenic wave functions.

The eigenfunctions of type (7) contain the conventional ESR hamiltonian:

$$\hat{H}_{ESR} \phi = - \frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B} \phi \quad - (10)$$

The next note will evaluate some of these eigenvalues by hand for the simplest hydrogenic wave functions. In general, all three hamiltonians will be affected by the chemical shift.

Therefore a remarkable amount of new information has emerged from the well known:

$$\hat{H} \phi = - \frac{e}{2m} \left(\underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} + \underline{\sigma} \cdot \underline{A} \, \underline{\sigma} \cdot \underline{p} \right) \phi \quad - (11)$$