331(1): Spin - Spin and Spin - Orbit Hamiltonians in ESR and NMR.

The hamiltonian developed in preceding notes and papers are augmented in the usual approach to spin - spin and spin orbit splitting, which is the most useful analytical feature of ESR and NMR. In the o(3) basis the usual hamiltonian is:

$$H = \frac{p^2}{2m} + U \quad -(1)$$

In the presence of a magnetic field this hamiltonian becomes:

$$H = \frac{1}{2m}\left(\underline{p} - e\underline{A}\right)\cdot\left(\underline{p} - e\underline{A}\right) + U \quad -(2).$$

In quantum field theory this comes from the minimal prescription:

$$p^\mu \rightarrow p^\mu - eA^\mu \quad -(3)$$

where

$$p^\mu = \left(\frac{E}{c}, \underline{p}\right) \quad -(4)$$

and

$$A^\mu = \left(\frac{\phi}{c}, \underline{A}\right) \quad -(5)$$

(L. H. Ryder, "Quantum Field Theory", Cambridge University Press, 1996)

In ECE2 theory A^μ becomes proportional to the spin curvature.

Some authors use a positive $e\underline{A}$ in eqn. (2), which can be developed as:

$$H = \frac{1}{2m}\left(p^2 - e\underline{A}\cdot\underline{p} - e\underline{p}\cdot\underline{A} + e^2A^2\right) + U \quad -(3)$$

In almost all the textbooks this term is developed non-relativistically, but in the Dirac equation $\underline{p}$ is the relativistic momentum:

$$\underline{p} = \gamma\,\underline{p}_0 \quad -(4)$$

where

$$\gamma = \left(1 - \frac{p_0^2}{m^2c^2}\right)^{-1/2} \quad -(5)$$

is the Lorentz factor.

In the non relativistic development:

$$H = \frac{1}{2m}\left(p_0^2 - e\underline{A}\cdot\underline{p}_0 - e\underline{p}_0\cdot\underline{A} + e^2A^2\right) + U \quad -(6)$$

The non relativistic quantization is:

$$\underline{p}_0\,\phi = -i\hbar\,\underline{\nabla}\phi \quad -(7)$$

where ϕ is the non relativistic wave function. From eqs (6) and (7):

$$H\phi = \frac{1}{2m}\Big(-\hbar^2\nabla^2\phi + ie\hbar\,\underline{A}\cdot\underline{\nabla}\phi + ie\hbar\,\underline{\nabla}\cdot(\underline{A}\phi) + e^2A^2\phi\Big) + U\phi \quad -(8)$$

3) in which:

$$\underline{\nabla} \cdot (\underline{A}\phi) = \phi \underline{\nabla} \cdot \underline{A} + \underline{A} \cdot \underline{\nabla}\phi \quad -(9)$$

Therefore:

$$H\phi = \frac{1}{2m}\left(-\hbar^2\nabla^2\phi + 2ie\hbar \underline{A} \cdot \underline{\nabla}\phi + ie\hbar \underline{\nabla} \cdot \underline{A}\phi + e^2A^2\phi\right) + U\phi \quad -(10)$$

There are expectation value such as:

$$H_1 = \frac{ie\hbar}{m} \langle \underline{A} \cdot \underline{\nabla}\phi \rangle \quad -(11)$$

which corresponds to the classical:

$$H_1 = -\frac{e}{m} \underline{A} \cdot \underline{p}_0 \quad -(12)$$

The usual development uses the vector potential for a static magnetic field:

$$\underline{A} = \frac{1}{2} \underline{B} \times \underline{r} \quad -(13)$$

So

$$H_1 = -\frac{e}{2m} \underline{B} \times \underline{r} \cdot \underline{p}_0 \quad -(14)$$

$$= -\frac{e}{2m} \underline{B} \cdot \underline{r} \times \underline{p}_0$$

$$= -\frac{e}{2m} \underline{B} \cdot \underline{L}_0$$

where:

$$\underline{L}_0 = \underline{r} \times \underline{p}_0 \quad -(15)$$

is the classical orbital angular momentum.

However, the correctly relativistic term is

$$H_1 = -\frac{e}{2m} \underline{L} \cdot \underline{B} \quad -(16)$$

where

$$\underline{L} = \gamma \underline{L}_0 \quad -(17)$$

is the <u>relativistic</u> angular momentum. So:

$$\boxed{H_1 = -\frac{e}{2m} \left(1 - \frac{p_0^2}{m^2 c^2} \right)^{-1/2} \underline{L}_0 \cdot \underline{B}} \quad -(18)$$

in which:

$$H_0 \psi = \left(\frac{p_0^2}{2m} + U \right) \psi \quad -(19)$$

The classical orbital angular momentum is quantized as:

$$\hat{L}_0^2 \psi = L(L+1)\hbar \psi \quad -(20)$$

$$L_{0Z} \psi = m\hbar \psi \quad -(21)$$

However, eqs. (18) and (19) introduce a new spectral effect which will be developed in the following note.