Note 253(7): Relativistic Corrections to Magnetic Effects from the Fermion Equation

Start with the Einstein energy equation and minimal prescription:

$$(E-e\phi)^2 = c^2(\underline{p}-e\underline{A})^2 + m^2c^4 \quad -(1)$$

So

$$(E-e\phi)^2 - m^2c^4 = c^2(\underline{p}-e\underline{A})^2 \quad -(2)$$

$$= (E-e\phi-mc^2)(E-e\phi+mc^2).$$

It follows that:

$$E = e\phi + mc^2 + \frac{c^2(\underline{p}-e\underline{A})^2}{E-e\phi+mc^2} \quad -(3)$$

in which

$$E = \gamma mc^2 \quad -(4)$$

Eq (3) can be written as:

$$E = e\phi + mc^2 + \frac{1}{2m}\frac{(\underline{p}-e\underline{A})^2}{\frac{E+mc^2}{2mc^2} - \frac{e\phi}{2mc^2}} \quad -(5)$$

$$= e\phi + mc^2 + \frac{1}{2m}\frac{(\underline{p}-e\underline{A})^2}{\frac{\gamma+1}{2} - \frac{e\phi}{2mc^2}}$$

$$= e\phi + mc^2 + \frac{1}{2m}\left(\frac{2}{\gamma+1}\right)\frac{(\underline{p}-e\underline{A})^2}{1-\frac{2}{\gamma+1}\frac{e\phi}{2mc^2}}$$

2) Now consider the Hamiltonian:

$$\hat{H}\phi = \frac{1}{2m}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\left(\frac{\gamma+1}{2}-\frac{e\phi}{2mc^2}\right)^{-1}\underline{\sigma}\cdot(\underline{p}-e\underline{A})\phi \qquad -(6)$$

$$= \frac{1}{2m}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\left(\frac{2}{\gamma+1}\left(1-\frac{e\phi}{(\gamma+1)mc^2}\right)^{-1}\right)\underline{\sigma}\cdot(\underline{p}-e\underline{A})\phi$$

This can be approximated by:

$$H\phi = \frac{1}{2m}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\frac{2}{\gamma+1}\left(1+\frac{e\phi}{(\gamma+1)mc^2}\right)\underline{\sigma}\cdot(\underline{p}-e\underline{A})\phi \qquad -(7)$$

In this equation:

$$\gamma+\underline{1} = \left(1-\frac{v^2}{c^2}\right)^{-1/2}+\underline{1} \doteq \underline{1}+\underline{1}+\frac{1}{2}\frac{v^2}{c^2}$$

$$= 2+\frac{1}{2}\frac{v^2}{c^2} \qquad -(8)$$

So:

$$\frac{2}{\gamma+1} = \frac{2}{2+\frac{1}{2}\frac{v^2}{c^2}} = \left(1+\frac{1}{4}\frac{v^2}{c^2}\right)^{-1}$$

$$\sim 1-\frac{v^2}{4c^2} \qquad -(9)$$

Therefore the Hamiltonian (7) can be approximated using eq. (9) as:

$$H'\phi = \frac{1}{2m}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\left(\left(1-\frac{1}{4}\frac{v^2}{c^2}\right)\left(1+\frac{1}{2}\left(1-\frac{1}{4}\frac{v^2}{c^2}\right)\right)\frac{e\phi}{mc^2}\right)\cdot\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\phi \qquad -(10)$$

$$H\phi = \frac{1}{2m}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\left(1-\frac{1}{4}\frac{v^2}{c^2}\right)\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\phi + \frac{1}{2m}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\left(1-\frac{1}{4}\frac{v^2}{c^2}\right)^2\frac{e\phi}{2mc^2}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\phi \qquad -(11)$$

This gives relativistic corrections to all the terms usually obtained with the assumption

$$E \sim mc^2. \qquad -(12)$$

Now note that:

$$v^2 = (\underline{p}-e\underline{A})\cdot(\underline{p}-e\underline{A})/m^2. \qquad -(13)$$

In the Pauli basis:

$$v^2 = \underline{\sigma}\cdot\underline{v}\;\underline{\sigma}\cdot\underline{v} = \frac{1}{m^2}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\underline{\sigma}\cdot(\underline{p}-e\underline{A}) \qquad -(14)$$

Therefore the first term in eq. (11) is given by the usual term plus a relativistic correction:

4)

$$H_1\phi = \frac{1}{2m}\underline{\sigma}\cdot(\underline{p}-e\underline{A})\left(1-\frac{1}{4m^2c^2}\underline{\sigma}\cdot(\underline{p}-e\underline{A})\underline{\sigma}\cdot(\underline{p}-e\underline{A})\right) \quad -(15)$$

$$\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\phi$$

The first term in this equation was developed in note 248(6) and is the usual term. It is:

$$H_{11}\phi = \frac{1}{2m}\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\phi. \quad -(16)$$

Now use:

$$\underline{p} = -i\hbar\underline{\nabla} \quad -(17)$$

as in Note 248(6) to find:

$$H_{11}\phi = \frac{1}{2m}\Big(-\hbar^2\nabla^2\phi + e^2A^2\phi + ie\hbar\,\underline{\nabla}\cdot(\underline{A}\phi)$$

$$-e\hbar\,\underline{\sigma}\cdot\underline{\nabla}\times(\underline{A}\phi) + ie\hbar\,\underline{A}\cdot\underline{\nabla}\phi - e\hbar\,\underline{\sigma}\cdot\underline{A}\times\underline{\nabla}\phi\Big) \quad -(18)$$

$$= -\frac{e\hbar}{2m}\underline{\sigma}\cdot\left(\underline{\nabla}\times(\underline{A}\phi) + \underline{A}\times\underline{\nabla}\phi\right) + \cdots$$

$$= -\frac{e\hbar}{2m}\underline{\sigma}\cdot\left((\underline{\nabla}\times\underline{A})\phi + \underline{\nabla}\phi\times\underline{A} + \underline{A}\times\underline{\nabla}\phi\right) + \cdots$$

$$= -\frac{e\hbar}{2m}\underline{\sigma}\cdot(\underline{\nabla}\times\underline{A})\phi + \cdots$$

$$= -\frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B}\phi + \cdots$$

5) The second term in eq. (15) is:

$$H_{12}\phi = -\frac{1}{8m^3c^2}\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\,\underline{\sigma}\cdot(\underline{p}-e\underline{A})\phi \quad -(18)$$

and can be developed in many different ways to give rise to numerous new spectroscopic effects.

For example if the first two terms are considered such that $\underline{p}$ is a function then:

$$H_{12}\phi = -\frac{1}{8m^3c^2}(\underline{p}-e\underline{A})\cdot(\underline{p}-e\underline{A})\,\underline{\sigma}\cdot(-i\hbar\underline{\nabla}-e\underline{A})\,\underline{\sigma}\cdot(-i\hbar\underline{\nabla}-e\underline{A})\phi \quad -(19)$$

$$= \frac{e\hbar}{8m^3c^2}\,\underline{\sigma}\cdot\underline{B}\,(\underline{p}-e\underline{A})\cdot(\underline{p}-e\underline{A})\phi + \dots$$

$$= \frac{e\hbar}{8m^3c^2}\,\underline{\sigma}\cdot\underline{B}\,(p^2-2e\underline{p}\cdot\underline{A}+e^2A^2)\phi + \dots$$

Assume a uniform magnetic field:

$$\underline{A} = \frac{1}{2}\underline{B}\times\underline{r} \quad -(20)$$

and use

$$\underline{p}\cdot\underline{B}\times\underline{r} = \underline{B}\cdot\underline{r}\times\underline{p} = \underline{B}\cdot\underline{L} \quad -(21)$$

Therefore:

$$\boxed{H_{12}\phi = -\frac{e^2\hbar}{8m^3c^2}\,\underline{L}\cdot\underline{B}\,\underline{\sigma}\cdot\underline{B}\,\phi + \dots}$$

(22)

6) This is a term quadratic in the magnetic flux density involving a product of the orbital and spin angular momentum terms.

Units Check

$$B = J s C^{-1} m^{-2}, \quad \hbar = L = Js, \text{ so}$$

$$H_{12} = \frac{C^2 J^2 s^2 J^2 s^2 C^{-2} m^{-4}}{kg^3 m^2 s^{-2}} \quad \checkmark$$

$$= \frac{J^4}{kg^3 m^6 s^{-6}} = \frac{J^4}{J^3} = J$$

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

$$H_{12}\phi = -\frac{e^2 \hbar}{8 m^3 c^2} L_z \sigma_z B_z^2 \phi \quad -(23)$$

Now use:

$$\underline{S} = \frac{\hbar}{2}\underline{\sigma} \quad -(24)$$

so

$$H_{12}\phi = -\frac{e^2}{4 m^3 c^2} L_z S_z B_z^2 \phi$$

$$= -\frac{e^2 \hbar^2 B_z^2}{4 m^3 c^2} m_L m_s \phi \quad -(25)$$

where

$$m_L = -L, \ldots, L \quad -(26)$$
$$m_s = -S, \ldots, S$$

This is a second order spin orbit splitting.

7) The energy levels are:

$$E_{12} = -\frac{e^2 \hbar^2 B_Z^2}{4m^3 c^2} m_L m_S \quad -(27)$$

Here:

$$e = 1.60219 \times 10^{-19} \, C$$
$$\hbar = 6.62618 \times 10^{-34} \, Js$$
$$m = 9.10953 \times 10^{-31} \, kgm$$
$$c = 2.997925 \times 10^{8} \, ms^{-1}$$

So

$$E_{12} \doteq -4.147 \times 10^{-32} B_Z^2 \text{ joules}$$

$$\boxed{E_{12} = -4.147 \times 10^{-32} m_L m_S B_Z^2 \text{ joules}}$$

$$-(28)$$

The first order energy is:

$$E_0 = -\frac{e\hbar}{2m} m_S B_Z \text{ joules}$$

$$= -5.82 \times 10^{-23} m_S B_Z \text{ joules}$$

Now use

$$1 \, J = 5.03445 \times 10^{22} \, cm^{-1}$$

$$1 \, cm^{-1} = 30 \, GHz$$

so $E_{12} = -62.63 \, m_L m_S B_Z^2 \, Hz \quad -(29)$

If resonance is induced between states of m_S

8) then the resonance frequency is:

$$f_{12} = 125.26\, m_L B_Z^2 \ \text{Hz} \quad -(30)$$

The first order resonance frequency is:

$$\omega = \frac{e}{m} B_Z \quad -(31)$$

so

$$f = \frac{\omega}{2\pi} = \frac{e}{2\pi m} B_Z \ \text{Hz} \quad -(32)$$

$$= 2.80 \times 10^{10} B_Z \ \text{Hz}.$$

So this type of relativistic effect is a small shift on top of the ESR frequency. The number of lines depends on:

$$m_L = -L, \ldots, L \quad -(33)$$

and it is proportional to B_Z^2.

It is not very much different from the magnitude of the chemical shift, so should be observable. There are many other effects of this type

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