$$H_{211} = -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}^* \quad -(80)$$

and a term due to the conjugate product of the electromagnetic field:

$$H_{212} = i\frac{e^2}{2m} \underline{\sigma} \cdot \underline{A} \times \underline{A}^* \quad -(81)$$

which defines the B(3) field introduced in previous chapters:

$$\underline{B}^{(3)*} = -ig \underline{A} \times \underline{A}^* = -ig \underline{A}^{(1)} \times \underline{A}^{(2)} \quad -(82)$$

Eq. (81) is the hamiltonian that defines radiatively induced fermion resonance (RFR),

extensively discussed elsewhere {1 - 10} but derived here in a rigorous way from the fermion

equation or chiral representation of the Dirac equation.

Spin orbit coupling and the Thomas factor can be derived from the H_{22}

hamiltonian defined as follows:

$$H_{22}\psi = \frac{e}{4m^2c^2}\left(\underline{\sigma} \cdot \left(\underline{p} - e\underline{A}\right)\phi \,\underline{\sigma} \cdot \left(\underline{p} - e\underline{A}\right)\right)\psi \quad -(83)$$

This hamiltonian has its origins in the following equation:

$$E\psi = \left(mc^2 + e\phi + c^2\left(\underline{p} - e\underline{A}\right)\left(E - e\phi + mc^2\right)^{-1} \cdot \left(\underline{p} - e\underline{A}\right)\right)\psi \quad -(84)$$

in the approximation:

$$E = \gamma mc^2 \sim mc^2. \quad -(85)$$

In this approximation. Eq. (84) becomes:

$$E\psi = \left(mc^2 + e\phi + \frac{1}{2m} \left(\underline{p} - e\underline{A} \right) \left(1 - \frac{e\phi}{2mc^2} \right)^{-1} \cdot \left(\underline{p} - e\underline{A} \right) \right) \psi \quad -(86)$$

and in the approximation:

$$e\phi << 2mc^2 \quad -(87)$$

the H_{22} hamiltonian is recovered as the last term on the right hand side.

In the derivation of the spin orbit coupling term several assumptions are made, but not always made clear in textbooks. The vector potential $\underline{A}$ is not considered in the derivation of spin orbit interaction, so that only electric field effects are considered. Therefore the relevant hamiltonian reduces to:

$$H_{22}\psi = \frac{e}{4m^2c^2} \, \underline{\sigma} \cdot \underline{p} \, \phi \, \underline{\sigma} \cdot \underline{p} \, \psi. \quad -(88)$$

It is assumed that the first $\underline{p}$ is the operator:

$$\underline{p} = -i\hbar\underline{\nabla} \quad -(89)$$

but that the second $\underline{p}$ is a function. This point is rarely if ever made clear in the textbooks. This assumption can be justified only on the grounds that it seems to succeed in describing the experimental data. When this assumption is made Eq. (88) reduces to:

$$H_{22}\psi = \frac{-ie\hbar}{4m^2c^2} \, \underline{\sigma} \cdot \underline{\nabla} \, \phi \, \underline{\sigma} \cdot \underline{p} \, \psi \quad -(90)$$

The $\underline{\nabla}$ operator acts on $\phi\,\underline{\sigma}\cdot\underline{p}\,\psi$, so by the Leibnitz Theorem :

$$\underline{\nabla}\left(\phi\,\underline{\sigma}\cdot\underline{p}\,\psi\right) = \underline{\nabla}\left(\underline{\sigma}\cdot\underline{p}\right)\phi\psi + \underline{\sigma}\cdot\underline{p}\,\underline{\nabla}\left(\phi\psi\right) - (91)$$

and the spin orbit interaction term emerges from:

$$H_{22}\psi = -\frac{ie\hbar}{4m^2c^2}\left(\underline{\sigma}\cdot\underline{\nabla}\left(\phi\psi\right)\underline{\sigma}\cdot\underline{p}\right). - (92)$$

In this equation the Leibnitz Theorem asserts that:

$$\underline{\nabla}\left(\phi\psi\right) = \left(\underline{\nabla}\phi\right)\psi + \phi\left(\underline{\nabla}\psi\right) - (93)$$

so the spin orbit interaction term is:

$$H_{22}\psi = -\frac{ie\hbar}{4m^2c^2}\left(\underline{\sigma}\cdot\underline{\nabla}\phi\,\underline{\sigma}\cdot\underline{p}\right)\psi - (94)$$
$$+ \cdots$$

It is seen Eq. (94) is only one out of many possible effects that emerge from the fermion equation and which should be systematically investigated experimentally.

In the development of the spin orbit term the obsolete standard physics is used as follows:

$$\underline{E} = -\underline{\nabla}\phi \quad - (95)$$

so the spin orbit hamiltonian becomes:

$$H_{22}\psi = -\frac{ie\hbar}{4m^2c^2}\,\underline{\sigma}\cdot\underline{E}\,\underline{\sigma}\cdot\underline{p}\,\psi. - (96)$$

Now use the Pauli algebra:

$$\underline{\sigma}\cdot\underline{E}\,\underline{\sigma}\cdot\underline{p} = \underline{E}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{E}\times\underline{p}$$
$$- (97)$$

so the real part of the hamiltonian from these equations becomes:

$$H_{22}\psi = \frac{e\hbar}{4m^2c^2}\ \underline{\sigma}\cdot\underline{E}\times\underline{p}\ \psi\ -(98)$$

in which p is regarded as a function, and not an operator. If this second p is regarded as an operator, then new effects appear.

Note carefully that in the derivation of the Zeeman effect, ESR, NMR and the g factor of the electron, both p's are regarded as operators, but in the derivation of spin orbit interaction, only the first p is regarded as an operator, the second p is regarded as a function.

Finally in the standard derivation of spin orbit interaction, the Coulomb potential of electrostatics is chosen for the scalar potential:

$$\phi = -\frac{e}{4\pi r\epsilon_0}\qquad-(99)$$

so the electric field strength is:

$$\underline{E} = -\underline{\nabla}\phi = -\frac{e}{4\pi\epsilon_0 r^3}\ \underline{r}\ \cdot\qquad-(100)$$

The relevant spin orbit hamiltonian becomes:

$$H_{22}\psi = -\frac{e^2\hbar}{8\pi c^2\epsilon_0 m^2 r^3}\ \underline{\sigma}\cdot\underline{r}\times\underline{p}\ \psi\ -(101)$$

in which the orbital angular momentum is:

$$\underline{L} = \underline{r}\times\underline{p}\ \cdot\ -(102)$$

Therefore the spin orbit hamiltonian is:

$$H_{22}\psi = -\frac{e^2\hbar}{8\pi c^2\epsilon_0 m^2 r^3}\ \underline{\sigma}\cdot\underline{L}\ \psi\ -(103)$$

In the description of atomic and molecular spectra, the spin angular momentum

operator is defined as:

$$S = \frac{1}{2}\hbar\,\sigma \qquad - (104)$$

and the orbital angular momentum also becomes an operator. So:

$$H_{22}\psi = -\xi\, S \cdot L\, \psi = -\frac{e^2}{8\pi c^2 \epsilon_0 m^2 r^3}\, S \cdot L\, \psi \qquad - (105)$$

and the Thomas factor of two is contained in Eq. (105) as part of the denominator. The

derivation of the Thomas factor is one of the strengths of the fermion equation, which as we

have argued does not suffer from the negative energy problem of the Dirac equation.

Consider again the H_{22} hamiltonian:

$$H_{22}\psi = \frac{e}{4m^2 c^2}\, \sigma \cdot \left(p - eA\right)\psi\, \sigma \cdot \left(p - eA\right)\psi \qquad - (106)$$

and assume that:

$$A = 0 \qquad - (107)$$

so:

$$H_{22}\psi = \frac{e}{4m^2 c^2}\, \sigma \cdot p\, \psi\, \sigma \cdot p\, \psi \qquad - (108)$$

In the derivation of spin orbit coupling and the Thomas factor the first p is regarded as an

operator and the second p as a function. In the derivation of the Darwin term both p's are

regarded as operators, defined by:

$$-i\hbar \underline{\nabla} \psi = \underline{p} \psi \quad -(109)$$

with expectation value:

$$\langle \underline{p} \rangle = \int \psi^* \underline{p} \psi \, d\tau. \quad -(110)$$

Therefore the Darwin term is obtained from:

$$H_{22} \psi = \frac{e}{4m^2c^2} \left(\underline{\sigma} \cdot \left(-i\hbar\underline{\nabla} \right) \psi \, \underline{\sigma} \cdot \left(-i\hbar\underline{\nabla} \right) \right) \psi \quad -(111)$$

and is a quantum mechanical phenomenon with no classical counterpart.

From Eq. (111):

$$H_{22} \psi = -\frac{e\hbar^2}{4m^2c^2} \left(\underline{\sigma} \cdot \underline{\nabla} \psi \, \underline{\sigma} \cdot \underline{\nabla} \right) \psi \quad -(112)$$

and the fist del operator $\underline{\nabla}$ operates on all that follows it, so:

$$H_{22} \psi = -\frac{e\hbar^2}{4m^2c^2} \underline{\sigma} \cdot \underline{\nabla} \left(\psi \, \underline{\sigma} \cdot \underline{\nabla} \psi \right). \quad -(113)$$

The Leibnitz Theorem is used as follows:

$$\underline{\nabla} \left(\psi \, \underline{\sigma} \cdot \underline{\nabla} \psi \right) = \left(\underline{\nabla} \psi \right)\left(\underline{\sigma} \cdot \underline{\nabla} \psi \right) + \psi \, \underline{\nabla} \left(\underline{\sigma} \cdot \underline{\nabla} \psi \right). \quad -(114)$$

Therefore:

$$H_{22}\psi = \frac{-e\hbar^2}{4m^2c^2}\left(\underline{\sigma} \cdot \underline{\nabla}\phi \, \underline{\sigma} \cdot \underline{\nabla}\psi + \underline{\sigma} \cdot \phi \underline{\nabla}\left(\underline{\sigma} \cdot \underline{\nabla}\psi\right)\right) \quad - (115)$$

Usually the Darwin term is considered to be:

$$H_{Darwin}\psi = \frac{-e\hbar^2}{4m^2c^2}\underline{\sigma} \cdot \underline{\nabla}\phi\,\underline{\sigma} \cdot \underline{\nabla}\psi \quad -(116)$$

and the second term in Eq. (115) can be developed as:

$$\underline{\sigma} \cdot \underline{\nabla}\left(\underline{\sigma} \cdot \underline{\nabla}\psi\right) = \left(\underline{\sigma} \cdot \underline{\nabla}\right)\left(\underline{\sigma} \cdot \underline{\nabla}\right)\psi \quad -(117)$$

so:

$$H_{22}\psi = \frac{-e\hbar^2}{4m^2c^2}\left(\underline{\nabla}\phi \cdot \underline{\nabla}\psi + \phi \nabla^2\psi\right). \quad -(118)$$

5.3 NEW ELECTRON SPIN ORBIT EFFECTS FROM THE FERMION EQUATION

On the classical standard level consider the kinetic energy of an electron of mass

m and linear momentum $\underline{p}$:

$$H = \frac{p^2}{2m} \quad - (119)$$

and use the minimal prescription (56) to describe the interaction of an electron with a

vector potential $\overline{A}$. The interaction hamiltonian is defined by:

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

$$= \frac{p^2}{2m} - \frac{e}{2m}\left(\underline{p} \cdot \underline{A} + \underline{A} \cdot \underline{p}\right) + \frac{e^2A^2}{2m}. \quad -(120)$$

As discussed in earlier chapters the vector potential can be defined by:

$$\underline{A} = \frac{1}{2} \cdot \underline{B} \times \underline{r} \, . \qquad - (121)$$

Now consider the following tem of the hamiltonian:

$$H_1 = - \frac{e}{2m} \left(\underline{p} \cdot \underline{A} + \underline{A} \cdot \underline{p} \right) = \frac{-e}{4m} \left(\underline{p} \cdot \underline{B} \times \underline{r} + \underline{B} \times \underline{r} \cdot \underline{p} \right)$$
$$- (122)$$

where the orbital angular momentum can be defined as follows:

$$\underline{p} \cdot \left(\underline{B} \times \underline{r} \right) = \underline{B} \cdot \underline{r} \times \underline{p} = \underline{B} \cdot \underline{L} \, . \quad - (123)$$

This analysis gives the well known hamiltonian for the interaction of a magnetic dipøel

moment with the magnetic flux density:

$$H_1 = - \frac{e}{2m} \underline{L} \cdot \underline{B} = - \underline{m}_D \cdot \underline{B} \, . \qquad - (124)$$

The classical hamiltonian responsible for Eq. (124) is:

$$H_1 = - \frac{e}{2m} \left(\underline{p} \cdot \underline{A} + \underline{A} \cdot \underline{p} \right) - (125)$$

which can be written in the SU(2) basis as:

$$H_1 = - \frac{e}{2m} \left(\underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} + \underline{\sigma} \cdot \underline{A} \, \underline{\sigma} \cdot \underline{p} \right) . - (126)$$

Using Pauli algebra:

$$\underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} = \underline{p} \cdot \underline{A} + i \underline{\sigma} \cdot \underline{p} \times \underline{A}$$
$$- (127)$$

$$\underline{\sigma} \cdot \underline{A} \ \underline{\sigma} \cdot \underline{p} = \underline{A} \cdot \underline{p} + i\underline{\sigma} \cdot \underline{A} \times \underline{p} \quad -(128)$$

and the same result is obtained because:

$$i\underline{\sigma} \cdot (\underline{p} \times \underline{A} + \underline{A} \times \underline{p}) = 0. \quad -(129)$$

However, as discussed for example by H. Merzbacher in "Quantum Mechanics" (Wiley, 1970):

$$\underline{\sigma} \cdot \underline{p} = \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \left(\underline{r} \cdot \underline{p} + i\underline{\sigma} \cdot \underline{L}\right) - (130)$$

$$\underline{\sigma} \cdot \underline{A} = \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \left(\underline{r} \cdot \underline{A} + i\underline{\sigma} \cdot \underline{r} \times \underline{A}\right). \quad -(131)$$

in which:

$$\frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \ \underline{\sigma} \cdot \underline{r} = 1. \quad -(132)$$

Therefore:

$$\underline{\sigma} \cdot \underline{p} \ \underline{\sigma} \cdot \underline{A} = \frac{1}{r^2} \left(\underline{r} \cdot \underline{p} \ \underline{r} \cdot \underline{A} + i\underline{\sigma} \cdot \underline{L} \ \underline{r} \cdot \underline{A} \right.$$
$$\left. + i\underline{r} \cdot \underline{p} \ \underline{\sigma} \cdot \underline{r} \times \underline{A} - \underline{\sigma} \cdot \underline{L} \ \underline{\sigma} \cdot \underline{r} \times \underline{A}\right). \quad -(133)$$

From comparison of the real and imaginary parts of Eqs (127) and (133):

$$\underline{p} \cdot \underline{A} = \frac{1}{r^2} \left(\underline{r} \cdot \underline{p} \ \underline{r} \cdot \underline{A} - \underline{\sigma} \cdot \underline{L} \ \underline{\sigma} \cdot \underline{r} \times \underline{A}\right) \quad -(134)$$

in which:

$$\underline{\sigma} \cdot \underline{p} \times \underline{A} = \underline{\sigma} \cdot \underline{L} \ \underline{r} \cdot \underline{A} + \underline{r} \cdot \underline{p} \ \underline{\sigma} \cdot \underline{r} \times \underline{A} \quad -(135)$$

$$\underline{r} \cdot \underline{A} = \frac{1}{2}\underline{r} \cdot \underline{B} \times \underline{r} = \frac{1}{2}\underline{B} \cdot \underline{r} \times \underline{r} = 0. \quad -(136)$$

Therefore we obtain the important identities:

$$\underline{p} \cdot \underline{A} = -\frac{1}{r^2}\underline{\sigma} \cdot \underline{L}\, \underline{\sigma} \cdot \underline{r} \times \underline{A}, \quad -(137)$$

$$\underline{\sigma} \cdot \underline{p} \times \underline{A} = \underline{r} \cdot \underline{p}\, \underline{\sigma} \cdot \underline{r} \times \underline{A}. \quad -(138)$$

The hamiltonian (125) can therefore be written as:

$$H_1 = -\frac{e}{m}\underline{p} \cdot \underline{A} = \frac{e}{mr^2}\underline{\sigma} \cdot \underline{L}\, \underline{\sigma} \cdot \underline{r} \times \underline{A} = -\underline{m}_B \cdot \underline{B}. \quad -(139)$$

Finally use eqs. (121) and (139) to find:

$$H_1 = \frac{e}{2m}\underline{\sigma} \cdot \underline{L}\left(\underline{\sigma} \cdot \underline{B} - \frac{\underline{\sigma} \cdot \underline{r}}{r^2}\underline{B} \cdot \underline{r}\right) \quad -(140)$$

$$= -\underline{m}_D \cdot \underline{B}$$

It can be seen that the well known hamiltonian responsible for the Zeeman effect has been developed into a hamiltonian that gives electron spin resonance of a new type, a resonance that arises from the interaction of the Pauli matrix with the magnetic field as in Eq. (140). If the magnetic field is aligned in the Z axis then:

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad -(141)$$

and the electron spin orbit (ESOR) resonance frequency is:

$$\omega = \frac{eB}{m\hbar}\underline{\sigma} \cdot \underline{L} \quad -(142)$$

This compares with the usual ESR frequency:

$$\omega = \frac{eB}{m} \quad - (143)$$

from the hamiltonian derived already in this chapter from the fermion equation.

The ESOR hamiltonian contains a novel spin orbit coupling when quantized:

$$H_1 \psi = \frac{e}{2m} \, \underline{\sigma} \cdot \underline{B} \, \underline{\sigma} \cdot \underline{L} \, \psi . \quad - (144)$$

Defining the spin angular momentum as:

$$\underline{S} = \frac{1}{2} \hbar \underline{\sigma} \quad - (145)$$

gives {1 - 10}:

$$\underline{L} \cdot \underline{S} \, \psi = \frac{1}{2} \left(J^2 - L^2 - S^2 \right) \psi$$

$$= \frac{1}{2} \hbar^2 \left(J(J+1) - L(L+1) - S(S+1) \right) \psi \quad - (146)$$

so the energy levels of the ESOR hamiltonian operator are:

$$E = \frac{e\hbar}{2m} \left(J(J+1) - L(L+1) - S(S+1) \right) \underline{\sigma} \cdot \underline{B} \quad - (147)$$

giving the ESOR frequency:

$$\omega = \frac{e\hbar}{2m} \left(J(J+1) - L(L+1) - S(S+1) \right) \quad - (148)$$

in which the total angular momentum J is defined by the Clebsch Gordan series:

$$J = L + S, L + S - 1, \ldots, |L - S| \quad -(149)$$

Eq. (144) was first derived in UFT 249 and is different from the well known ESR spin

hamiltonian:

$$H_{ESR} = -\frac{e}{2m} \underline{L} \cdot \underline{B} + \lambda \underline{S} \cdot \underline{L} - \frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B} = -g_{spin} \frac{\underline{\sigma} \cdot \underline{B}}{2} \quad -(150)$$

It was derived using well known Pauli algebra together with the fermion equation and

potentially gives rise to many useful spectral effects.

For chemical physicists and analytical chemists therefore the most useful format

of the fermion equation is:

$$E\psi = \left(mc^2 + e\phi + \frac{1}{2m} \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \left(1 + \frac{e\phi}{2mc^2} \right) \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \right) \psi \quad -(151)$$

and a few examples have been given in this chapter of its usefulness. In ECE theory Eq. (151)

has been derived from Cartan geometry and by using the minimal prescription. The fermion

equation as argued is the chiral Dirac equation without the problem of negative energy, which

to chemists was never of much interest. In chemistry the subject is approached as follows.

Consider one term of the complete equation (151):

$$H_1 \psi = -\frac{e}{2m} \left(\underline{\sigma} \cdot \underline{A} \, \underline{\sigma} \cdot \underline{p} + \underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} \right) \psi. \quad -(152)$$

By regarding $\underline{\sigma}$ as a function rather than an operator this term can be developed using

Pauli algebra as follows:

$$H_1 \psi = -\frac{e}{2m}\left(\underline{A}\cdot\underline{p} + \underline{p}\cdot\underline{A} + i\underline{\sigma}\cdot(\underline{A}\times\underline{p} + \underline{p}\times\underline{A})\right) - (153)$$

For a uniform magnetic field:

$$\underline{A} = \tfrac{1}{2}\,\underline{B}\times\underline{r} \qquad - (154)$$

so:

$$H_1\psi = -\frac{e}{4m}\left(\underline{B}\times\underline{r}\cdot\underline{p} + \underline{p}\cdot\underline{B}\times\underline{r} \qquad - (155)\right.$$
$$\left. + i\,\underline{\sigma}\cdot\left((\underline{B}\times\underline{r})\times\underline{p} + \underline{p}\times(\underline{B}\times\underline{r})\right)\right)\psi .$$

By regarding p as a function:

$$\underline{B}\times\underline{r}\cdot\underline{p} = \underline{B}\cdot\underline{r}\times\underline{p} = \underline{B}\cdot\underline{L} \quad - (156)$$

so the hamiltonian becomes:

$$H_1\psi = -\frac{e}{2m}\underline{L}\cdot\underline{B}\,\psi + \left(i\,\underline{\sigma}\cdot\underline{A}\times\underline{p} + i\,\underline{\sigma}\cdot\underline{p}\times\underline{A}\right)\psi - (157)$$

At this stage p is regarded as an operator so the second term on the right hand side of eq. (157) does not vanish. The use of p and $\underline{\sigma}$ as functions or operators is arbitrary, and justified only by the final comparison with experimental data. From Eqs. (157) and (154) the hamiltonian can be written in the format used in chemistry

$$H_1\psi = \left(-\frac{e}{2m}\underline{L}\cdot\underline{B} - \frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B}\right)\psi \qquad - (158)$$
$$= -\frac{e}{2m}\left(\underline{L} + 2\underline{S}\right)\psi$$

The total angular momentum is conserved so Eq. (158) can be written as:

$$H_1 \psi = -\frac{e}{2m} g_L \underline{J} \cdot \underline{B} \psi \qquad -(159)$$

where:

$$J = L + S, \quad \ldots, \quad |L - S| \qquad -(160)$$

from the Clebsch Godan series.

The conventional spin orbit term emerges as described earlier in this chapter from another term of the hamiltonian:

$$H_{so} \psi = \frac{e}{4mc^3} \underline{\sigma} \cdot \left(\underline{p} - e\underline{A}\right) \phi \; \underline{\sigma} \cdot \left(\underline{p} - e\underline{A}\right) \psi \qquad -(161)$$

in which the first p is described as an operator but in which the second p is a function, giving the spin orbit term:

$$H_{so} \psi = -\frac{ie\hbar}{4m^2 c^3} \underline{\sigma} \cdot \underline{\nabla} \phi \; \underline{\sigma} \cdot \underline{p} \psi \qquad -(162)$$

So the complete ESR hamiltonian is:

$$H \psi = \left(-\frac{e}{2m} \underline{L} \cdot \underline{B} - \frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B} - \xi \underline{S} \cdot \underline{L} \right) \psi \qquad -(163)$$

in which the spin orbit coupling constant is:

$$\xi = \frac{e}{4\pi c^2 \epsilon_0 m^2 r^3} \qquad -(164)$$

Finally both S and L are operators, so:

$$\underline{S} \cdot \underline{L} \,\psi = \frac{\hbar^2}{2}\left(J(J+1) - L(L+1) - S(S+1)\right)\psi \quad -(165)$$

The above is the very well known conventional description of ESR in the language used by chemists, and is a description based in ECE theory on geometry. In ECE theory it can be developed in many ways because it is generally covariant while the obsolete standard description is Lorentz covariant.

However, several new spectroscopies can be developed using a well known Pauli algebra but one which seems never to have been applied to fermion resonance spectroscopies:

$$\underline{\sigma} \cdot \underline{p} = \frac{1}{r^2}\, \underline{\sigma} \cdot \underline{r}\left(\underline{r} \cdot \underline{p} + i\underline{\sigma} \cdot \underline{L}\right) \quad -(166)$$

$$\underline{\sigma} \cdot \underline{A} = \frac{1}{r^2}\, \underline{\sigma} \cdot \underline{r}\left(\underline{r} \cdot \underline{A} + i\underline{\sigma} \cdot \underline{r} \times \underline{A}\right). \quad -(167)$$

For a uniform magnetic field:

$$\underline{r} \cdot \underline{A} = 0 \quad -(168)$$

so:

$$\underline{p} \cdot \underline{A} = \frac{1}{r^2}\, \underline{\sigma} \cdot \underline{L}\; \underline{\sigma} \cdot \underline{A} \times \underline{r} \quad -(169)$$

and

$$\underline{\sigma} \cdot \underline{p} \times \underline{A} = \frac{1}{r^2}\, \underline{r} \cdot \underline{p}\; \underline{\sigma} \cdot \underline{r} \times \underline{A} \quad -(170)$$

as in note 250(7) accompanying UFT 250 on www.aias.us. Using these results it is found that:

$$H_1 \psi = -\frac{e}{2m} \left(\underline{p} \cdot \underline{A} + \underline{A} \cdot \underline{p} \right) \psi$$

$$= -\frac{e}{mr^2} \, \underline{\sigma} \cdot \underline{A} \times \underline{r} \, \underline{\sigma} \cdot \underline{L} \, \psi. \quad -(171)$$

Using Eq. (171) for a uniform magnetic field gives:

$$\underline{A} \times \underline{r} = \frac{1}{2} \left(\underline{B} \times \underline{r} \right) \times \underline{r} = \frac{1}{2} \left(\frac{\underline{r} \left(\underline{r} \cdot \underline{B} \right) - r^2 \underline{B}}{-(172)} \right)$$

giving a novel spin orbit hamiltonian in the useful form:

$$H_1 \psi = \frac{e}{\hbar m} \, \underline{\sigma} \cdot \left(\underline{B} - \frac{\underline{r}}{r^2} \left(\underline{r} \cdot \underline{B} \right) \right) \underline{S} \cdot \underline{L} \, \psi. \quad -(173)$$

Its expectation value is:

$$\langle H_1 \rangle = \frac{e}{\hbar m} \int \psi^* H_1 \psi \, d\tau \quad -(174)$$

with the normalization:

$$\int \psi^* \psi \, d\tau = 1. \quad -(175)$$

Using the result:

$$\underline{S} \cdot \underline{L} \, \psi = \frac{\hbar^2}{2} \left(J(J+1) - L(L+1) - S(S+1) \right) \psi \quad -(176)$$

the energy eigenvalues of the hamiltonian are:

$$E = \frac{e\hbar}{2m}\left(J(J+1)-L(L+1)-S(S+1)\right)\left(\underline{\sigma}\cdot\underline{B} - \int \phi^* \frac{\underline{\sigma}\cdot\underline{r}}{r^2} \underline{r}\cdot\underline{B}\,\phi\,d\tau\right) \quad -\left(177\right)$$

as in note 250(9) accompanying UFT 250 on www.aias.us.

In spherical polar coordinates:
$$X = r\sin\theta\cos\phi \qquad -\left(178\right)$$
$$Y = r\sin\theta\sin\phi$$
$$Z = r\cos\theta$$

and integration of a function over all space means:
$$\int\int f\,d\tau = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{0}^{\infty} f\,r^2\sin\theta\,dr\,d\theta\,d\phi. \quad -\left(179\right)$$

If the magnetic field is aligned in the Z axis then in Cartesian coordinates:
$$\frac{\underline{\sigma}\cdot\underline{r}}{r^2}\,\underline{r}\cdot\underline{B} = \sigma_z B_z\left(\frac{Z^2}{X^2+Y^2+Z^2}\right) -\left(180\right)$$

and if it is assumed on average that:
$$\left\langle\frac{Z^2}{X^2+Y^2+Z^2}\right\rangle = \frac{1}{3} \quad -\left(181\right)$$

the Eq. (177) reduces to:
$$E = \frac{1}{3}\frac{e\hbar}{m}\sigma_z B_z\left(J(J+1)-L(L+1)-S(S+1)\right) \quad -\left(182\right)$$

and electron spin orbit resonance occurs at:
$$\omega = \frac{2}{3}\frac{e}{m}B_z\left(J(J+1)-L(L+1)-S(S+1)\right). \quad -\left(183\right)$$

In spherical coordinates:

$$\frac{Z^2}{x^2 + y^2 + Z^2} = \cos^2\theta \quad -(184)$$

so:

$$\int \phi^* \frac{\sigma \cdot r}{r^2} \, r \cdot \underline{B} \phi \, d\tau = B_Z \sigma_Z \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \phi^* \cos^2\theta \phi \, r^2 \sin\theta \, dr \, d\theta \, d\phi \quad -(185)$$

It is seen that this part of the hamiltonian is r dependent and must be evaluated for each wave function ϕ . The only analytical wave functions are those of atomic H, so computational methods can be used to evaluate the energy levels of Eq. (185) for the H atom. The results are given in UFT 250 on www.aias.us and summarized later in this chapter.

Consider now the hamiltonian:

$$H = -\frac{e}{2m} \left(\underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} + \underline{\sigma} \cdot \underline{A} \, \underline{\sigma} \cdot \underline{p} \right) \quad -(186)$$

in its quantized form:

$$H\phi = -\frac{e}{2m} \frac{\hbar}{i} \left(\underline{\sigma} \cdot \underline{\nabla} \, \underline{\sigma} \cdot \underline{A} + \underline{\sigma} \cdot \underline{A} \, \underline{\sigma} \cdot \underline{\nabla} \right) \phi \quad -(187)$$

Note that:

$$\underline{r} \cdot \underline{p} = \frac{\hbar}{i} r \, \underline{e}_r \cdot \underline{\nabla} = \frac{\hbar}{i} r \frac{\partial}{\partial r} \quad -(188)$$

where the radial unit vector is defined as:

$$\underline{e}_r = \frac{\underline{r}}{r} \quad -(189)$$

From Pauli algebra:

$$\underline{\sigma} \cdot \underline{A} = \frac{\underline{\sigma} \cdot \underline{r}}{r^2} \left(\underline{r} \cdot \underline{A} + i \underline{\sigma} \cdot \underline{r} \times \underline{A} \right) - (190)$$

and for a uniform magnetic field

$$\underline{A} = \frac{1}{2} \underline{B} \times \underline{r} - (191)$$

in which:

$$\underline{r} \cdot \underline{A} = 0 \qquad - (192)$$

it follows that:

$$\underline{\sigma} \cdot \underline{A} = i \frac{\underline{\sigma} \cdot \underline{r}}{r^2} \underline{\sigma} \cdot \underline{r} \times \underline{A} - (193)$$

As in note 251(1) accompanying UFT 251 on www.aias.us it follows that:

$$\left(\underline{\sigma} \cdot \underline{p} \; \underline{\sigma} \cdot \underline{A} \right) \phi = \frac{\hbar}{r} \left(\underline{\sigma} \cdot \underline{r} \times \underline{A} \frac{\partial \phi}{\partial r} + \frac{\partial}{\partial r} \left(\underline{\sigma} \cdot \underline{r} \times \underline{A} \right) \phi \right)$$

$$- \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \times \underline{A} \; \underline{\sigma} \cdot \underline{L} \; \phi \quad - (194)$$

Using Eq. (191) it follows that:

$$\frac{1}{r} \underline{r} \times \underline{A} = \frac{r}{2} \left(\underline{B} - \underline{e}_r \left(\underline{B} \cdot \underline{e}_r \right) \right) - (195)$$

and that:

$$\frac{1}{r}\frac{\partial}{\partial r}\, \underline{r} \times \underline{A} = \underline{B} - \frac{1}{2r}\frac{d}{dr}\left(r^2 \underline{e}_r (\underline{e}_r \cdot \underline{B})\right)$$

$$= \underline{B} - \underline{e}_r (\underline{e}_r \cdot \underline{B}) \qquad -(196)$$

so:

$$\underline{\sigma}\cdot\underline{p}\;\underline{\sigma}\cdot\underline{A}\,\psi = \underline{\sigma}\cdot\underline{B}_1\left(\hbar\psi + \frac{1}{2}r\frac{d\psi}{dr} - \frac{1}{2}\underline{\sigma}\cdot\underline{L}\,\psi\right)$$
$$-(197)$$

in which the modified magnetic flux density is:

$$\underline{B}_1 = \underline{B} - \underline{e}_r(\underline{e}_r \cdot \underline{B}) \qquad -(198)$$

The hamiltonian (187) can therefore be developed as:

$$H\psi = -\frac{e\hbar}{2m}\,\underline{\sigma}\cdot\underline{B}_1\left(\psi + r\frac{d\psi}{dr}\right) + \frac{e}{2m}\,\underline{\sigma}\cdot\underline{B}_1\;\underline{\sigma}\cdot\underline{L}\,\psi$$
$$-(199)$$

Recall that the conventional development of the hamiltonian is well known:

$$H\psi = \frac{ie\hbar}{2m}\left(\underline{\nabla}\cdot(\underline{A}\,\psi) + \underline{A}\cdot\underline{\nabla}\psi\right) \qquad -(200)$$

$$- \frac{e\hbar}{2m}\,\underline{\sigma}\cdot\underline{\nabla}\times(\underline{A}\,\psi) + \underline{A}\times\underline{\nabla}\psi$$

$$= -\frac{e\hbar}{2m}\,\underline{\sigma}\cdot\underline{B} + \frac{ie\hbar}{2m}\left((\underline{\nabla}\cdot\underline{A})\psi + 2\underline{\nabla}\psi\cdot\underline{A}\right)$$

and misses the information given in Eq. (199).

As in note 251(2) on www.aias.us It is possible to define three novel types of

hamiltonian:

$$H_1 \psi = -\frac{e\hbar}{2m} \, \underline{\sigma} \cdot \underline{B}_1 \psi \quad - (201)$$

$$H_2 \psi = -\frac{e\hbar}{2m} \, \underline{\sigma} \cdot \underline{B}_1 \, r \frac{\partial \psi}{\partial r} \quad - (202)$$

$$H_3 \psi = \frac{e}{2m} \, \underline{\sigma} \cdot \underline{B}_1 \, \underline{\sigma} \cdot \underline{L} \, \psi \quad - (203)$$

whose energy expectation values are:

$$E_1 = -\frac{e\hbar}{2m} \int \psi^* \, \underline{\sigma} \cdot \underline{B}_1 \psi \, d\tau \quad - (204)$$

$$E_2 = -\frac{e\hbar}{2m} \int \psi^* \, \underline{\sigma} \cdot \underline{B}_1 \, r \frac{\partial \psi}{\partial r} \, d\tau \quad - (205)$$

$$E_3 = \frac{e}{2m} \int \psi^* \, \underline{\sigma} \cdot \underline{B}_1 \, \underline{\sigma} \cdot \underline{L} \, \psi \, d\tau \quad - (206)$$

with the Born normalization:

$$\int \psi^* \psi \, d\tau = 1 \quad - (207)$$

These are developed in UFT 251 for the hydrogenic wavefunctions, giving many novel results of usefulness to analytical chemisty.

The use of well known Pauli algebra in a new way is illustrated on the simplest level in UFT 252 with the kinetic energy hamiltonian itself:

$$H\psi = \frac{1}{2m} \, \underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{p} \, \psi \quad - (208)$$

in which the Pauli algebra is:

$$\underline{\sigma} \cdot \underline{p} = \frac{1}{r^2} \left(\underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{L} \right) \quad - (209)$$

Therefore:

$$\underline{\sigma} \cdot \underline{p} \; \underline{\sigma} \cdot \underline{p} = \frac{1}{r^2} \left(\underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{L} \right) \left(\underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{L} \right)$$

$$= \frac{1}{r^2} \left(\underline{r} \cdot \underline{p} \; \underline{r} \cdot \underline{p} + i \left(\underline{r} \cdot \underline{p} \; \underline{\sigma} \cdot \underline{L} + \underline{\sigma} \cdot \underline{L} \; \underline{r} \cdot \underline{p} \right) \right.$$
$$\left. - L^2 - i \underline{\sigma} \cdot \underline{L} \times \underline{L} \right) \quad - (210)$$

which can be quantized using:

$$\underline{r} \cdot \underline{p} \, \psi = \frac{\hbar}{i} r \frac{\partial \psi}{\partial r} \quad - (211)$$

$$L^2 \psi = \hbar^2 \ell(\ell+1) \psi, \quad \underline{L} \times \underline{L} \, \psi = i \hbar \psi,$$

$$\underline{S} \cdot \underline{L} \, \psi = \frac{\hbar^2}{2} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \psi.$$

Therefore there are results such as the following which are instructive in the use of operators

in quantum mechanics:

$$\underline{r} \cdot \underline{p} \left(\underline{r} \cdot \underline{p} \, \psi \right)$$

$$= \frac{\hbar}{i} r \left(\frac{\partial}{\partial r} \left(\left(\frac{\hbar}{i} r \frac{\partial}{\partial r} \right) \psi \right) \right) \quad - (211)$$

As shown in detail in UFT 252 the hamiltonian (208) can be developed as:

$$-\frac{\hbar^2}{2m} \, \underline{\sigma} \cdot \underline{\nabla} \, \underline{\sigma} \cdot \underline{\nabla} \psi .$$

$$= -\frac{\hbar^2}{2m} \nabla^2 \psi + \frac{1}{m} \left(\frac{\underline{S} \cdot \underline{L}}{r} \left(2 \frac{d\psi}{dr} + \frac{\psi}{r} \right) \right) \quad - (212)$$

where the wavefunctions are the spherical harmonics:

$$\psi = Y_\ell^m \quad - (213)$$

The analysis gives two novel classes of energy expectation values:

$$E_1 = \frac{\hbar^2}{m} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \int \psi^* \frac{1}{r} \frac{d\psi}{dr} \, d\tau \quad - (214)$$

and

$$E_2 = \frac{\hbar^2}{2m} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \int \psi^* \frac{1}{r^2} \psi \, d\tau \quad - (215)$$

which are evaluated by computer in UFT 252.

Similarly the hamiltonian quadratic in the potential:

$$H_S = \frac{e^2}{2m} \, \underline{\sigma} \cdot \underline{A} \, \underline{\sigma} \cdot \underline{A} \psi \quad - (216)$$

can be developed as in UFT 252 using Eq. (191) as:

$$H_5 \psi = \frac{e^2 B_z^2}{8m} \cdot r^2 \left(1 - \cos^2\theta\right) \psi \quad - (217)$$

again giving novel types of spectroscopy.

The hamiltonian:

$$H_7 \psi = \frac{1}{2m} \underline{\sigma} \cdot \underline{p} \left(1 + \frac{e\phi}{2mc^2}\right) \underline{\sigma} \cdot \underline{p} \, \psi \quad - (218)$$

from the fermion equation gives the spin orbit component:

$$H_8 \psi = \frac{e}{4m^2 c^2} \underline{\sigma} \cdot \underline{p} \, \phi \, \underline{\sigma} \cdot \underline{p} \, \psi \quad - (219)$$

as we have seen and Eq. (219) can also be developed using Eq. (209) to give:

$$H_8 \psi = \frac{e}{4m^2 c^2} \left(\underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{L}\right) \frac{\phi}{r^2} \left(\underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{L}\right) \quad - (220)$$

There are several terms in this equation that can be developed as in UFT 252. For example:

$$H_9 \psi = \frac{e}{4m^2 c^2} \underline{r} \cdot \underline{p} \left(\frac{\phi}{r^2} \underline{r} \cdot \underline{p} \, \psi\right) \quad - (221)$$

in which:

$$\underline{r} \cdot \underline{p} \, \psi = -i\hbar r \frac{\partial \psi}{\partial r} \quad - (222)$$

So the hamiltonian gives:

$$H_9 \psi = \frac{e^2 \hbar^2}{16 m^2 c^2 \pi \epsilon_0} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \frac{1}{r^3} \left(3\psi - r \frac{d\psi}{dr} \right) \quad - (223)$$

and two types of energy expectation values:

$$E_{91} = \frac{3 e^2 \hbar^2}{16 \pi \epsilon_0 m^2 c^2} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \int \frac{\psi \psi^*}{r^3} \, d\tau \quad - (224)$$

and

$$E_{92} = \frac{- e^2 \hbar^2}{16 \pi \epsilon_0 m^2 c^2} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \int \frac{\psi \psi^*}{r^2} \, d\tau \quad - (225)$$

which give observable new fermion resonance spectra.

The main spin orbit hamiltonian (220) can be developed into the following

four hamiltonians:

$$H_{10} \psi = \frac{e}{4 m^2 c^2} \underset{\sim}{r} \cdot \underset{\sim}{\rho} \left(\frac{\phi}{r^2} \underset{\sim}{r} \cdot \underset{\sim}{\rho} \, \psi \right) \quad - (226)$$

$$H_{11} \psi = \frac{i e}{4 m^2 c^2} \sigma \cdot L \left(\frac{\phi}{r^2} \underset{\sim}{r} \cdot \underset{\sim}{\rho} \, \psi \right) \quad - (227)$$

$$H_{12} \psi = \frac{i e}{4 m^2 c^2} \underset{\sim}{r} \cdot \underset{\sim}{\rho} \left(\frac{\phi}{r^2} \, \sigma \cdot \underline{L} \, \psi \right) \quad - (228)$$

$$H_{13} \psi = \frac{- e}{4 m^2 c^2} \sigma \cdot \underline{L} \left(\frac{\phi}{r^2} \, \sigma \cdot \underline{L} \, \psi \right) \quad - (229)$$

and these are evaluated systematically in UFT 252 giving many new results.

Finally in this section the effect of gravitation on fermion resonance spectra can be

evaluated as in UFT 253 using the gravitational minimal prescription:

$$E \rightarrow E + m \Phi \quad - (230)$$

where the gravitational potential is:

$$\vec{\Phi} = -\cdot \frac{GM}{r} \quad —(231)$$

where G is Newton's constant and where Φ is the gravitational potential. Here M is a mass that is attracted to the mass of the electron m. Vriosu effects of gravitaton are developed in UFT 253.

5.4 REFUTATION OF INDETERMINACY