1) Development of the Fundamental Hamiltonian, Note 251(1)

The fundamental hamiltonian being considered is:

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

This is developed with the Pauli algebra:

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

$$= \frac{\underline{\sigma}\cdot\underline{r}}{r^2}\,\underline{\sigma}\cdot\underline{r}\,\underline{\sigma}\cdot\underline{p}$$

$$= \frac{\underline{\sigma}\cdot\underline{r}}{r^2}\left(\underline{r}\cdot\underline{p} + i\,\underline{\sigma}\cdot\underline{r}\times\underline{p}\right)$$

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

where

$$\underline{L} = \underline{r}\times\underline{p} \quad -(3)$$

is the classical orbital angular momentum.

In order to quantize eq. (1) use:

$$\hat{\underline{p}} = -i\hbar\underline{\nabla} = \frac{\hbar}{i}\underline{\nabla} \quad -(4)$$

so:

$$\hat{H}\psi = -\frac{e}{2m}\left(\frac{\hbar}{i}\left(\underline{\sigma}\cdot\underline{\nabla}\,\underline{\sigma}\cdot\underline{A} + \underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{\nabla}\right)\psi\right) \quad -(5)$$

Note that

$$\underline{r}\cdot\underline{p} = \frac{\hbar}{i}r\,\underline{e}_r\cdot\underline{\nabla}$$

$$= \frac{\hbar}{i}r\,\underline{e}_r\cdot\underline{e}_r\frac{\partial}{\partial r} \quad -(6)$$

$$= \frac{\hbar}{i}r\frac{\partial}{\partial r}$$

d) Similarly:

$$\underline{\sigma} \cdot \underline{A} = \frac{\underline{\sigma} \cdot \underline{r}}{r^2} \left(\underline{r} \cdot \underline{A} + i \underline{\sigma} \cdot \underline{r} \times \underline{A} \right) \quad - (7)$$

For a uniform magnetic field:

$$\underline{A} = \frac{1}{2} \underline{B} \times \underline{r} \quad - (8)$$

so in this case:

$$\underline{r} \cdot \underline{A} = 0 \quad - (9)$$

and

$$\underline{\sigma} \cdot \underline{A} = i \frac{\underline{\sigma} \cdot \underline{r}}{r^2} \underline{\sigma} \cdot \underline{r} \times \underline{A} \quad - (10)$$

It follows that: $\quad - (11)$

$$\underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} = \frac{i}{r} \left(-i\hbar \frac{\partial}{\partial r} + \frac{i}{r} \underline{\sigma} \cdot \underline{L} \right) \underline{\sigma} \cdot \underline{r} \times \underline{A}$$

and:

$$\left(\underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{A} \right) \phi = \left(\frac{\hbar}{r} \underline{r} \cdot \underline{\nabla} \, \underline{\sigma} \cdot \underline{r} \times \underline{A} + \frac{1}{r^2} \underline{\sigma} \cdot \underline{L} \, \underline{\sigma} \cdot \underline{A} \times \underline{r} \right) \phi \quad - (12)$$

$$= \frac{\hbar}{r} \frac{\partial}{\partial r} \left(\underline{\sigma} \cdot \underline{r} \times \underline{A} \phi \right) - \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \times \underline{A} \, \underline{\sigma} \cdot \underline{L} \phi$$

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

$$- \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \times \underline{A} \, \underline{\sigma} \cdot \underline{L} \phi$$

using the Leibnitz theorem.

Now we:

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

So:

$$\underline{r} \times \underline{A} = \frac{1}{2}\underline{r} \times (\underline{B} \times \underline{r}) \quad -(14)$$

$$= \frac{1}{2}\left(r^2 \underline{B} - \underset{\sim}{r}(\underset{\sim}{r} \cdot \underline{B})\right)$$

It follows that:

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

$$= \frac{r}{2}\left(\underline{B} - \underline{e}_r(\underline{B} \cdot \underline{e}_r)\right) \quad -(15)$$

where

$$\underset{\sim}{r} = r\underline{e}_r \quad -(16)$$

is the definition of $\underline{r}$ in cylindrical polar coordinates.

Also:

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

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

$$= \underline{B} - \underline{e}_r(\underline{e}_r \cdot \underline{B}) \quad -(17)$$

So:

$$\underline{\sigma} \cdot \underline{p}\, \underline{\sigma} \cdot \underline{A}\, \phi = \hbar\, \underline{\sigma} \cdot \left(\underline{B} - \underline{e}_r(\underline{e}_r \cdot \underline{B})\right)\phi$$

$$+ \frac{\hbar\, \underline{\sigma}}{2} \cdot \left(\underline{B} - \underline{e}_r(\underline{B} \cdot \underline{e}_r)\right) r \frac{\partial \phi}{\partial r} \quad -(18)$$

$$\frac{1}{\;}\, \underline{\sigma} \cdot \underline{r} \times \underline{A}\, \underline{\sigma} \cdot \underline{L}\, \phi$$

4) Now use the result:

$$\frac{1}{r^2}\,\underline{\sigma}\cdot\underline{r}\times\underline{A} = \frac{1}{2}\left(\underline{B} - \underline{e}_r(\underline{e}_r\cdot\underline{B})\right) \quad -(19)$$

and denote:

$$\underline{B}_1 := \underline{B} - \underline{e}_r(\underline{e}_r\cdot\underline{B}) \quad -(20)$$

It follows that:

$$\underline{\sigma}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{A}\,\phi = \hbar\left(\underline{\sigma}\cdot\underline{B}_1\phi + \frac{1}{2}\underline{\sigma}\cdot\underline{B}_1\, r\frac{\partial\phi}{\partial r}\right.$$

$$\left. - \frac{1}{2}\,\underline{\sigma}\cdot\underline{B}_1\,\underline{\sigma}\cdot\underline{L}\,\phi\right)$$

$$= \underline{\sigma}\cdot\underline{B}_1\left(\hbar\phi + \frac{1}{2}r\frac{\partial\phi}{\partial r} - \frac{1}{2}\underline{\sigma}\cdot\underline{L}\,\phi\right) \quad -(21)$$

Similarly:

$$\underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{p}\,\phi = \underline{\sigma}\cdot\underline{B}_1\left(\frac{1}{2}r\frac{\partial\phi}{\partial r} - \frac{1}{2}\underline{\sigma}\cdot\underline{L}\,\phi\right) \quad -(22)$$

Therefore:

$$\left(\underline{\sigma}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{A} + \underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{p}\right)\phi \quad -(23)$$

$$= \underline{\sigma}\cdot\underline{B}_1\left(\hbar\left(\phi + r\frac{\partial\phi}{\partial r}\right) - \underline{\sigma}\cdot\underline{L}\,\phi\right)$$

The complete Hamiltonian is:

$$\boxed{\begin{aligned}\hat{H}\phi &= -\frac{e}{2m}\left(\underline{\sigma}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{A} + \underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{p}\right)\phi \\ &= -\frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B}_1\left(\phi + r\frac{\partial\phi}{\partial r}\right) + \frac{e}{2m}\underline{\sigma}\cdot\underline{B}_1\,\underline{\sigma}\cdot\underline{L}\,\phi \quad -(24)\end{aligned}}$$

5) It is important to note that this hamiltonian contains the ESR term:

$$\hat{H}_{ESR}\,\phi = -\frac{e\hbar}{2m}\,\underline{\sigma}\cdot\underline{B} \qquad -(25)$$

and also the electron spin orbit resonance term:

$$\hat{H}_{ESOR}\,\phi = \frac{e}{2m}\,\underline{\sigma}\cdot\underline{B}_1\,\underline{\sigma}\cdot\underline{L}\,\phi \qquad -(26)$$

and also contains several new resonance terms each of which we potentially very useful in spectroscopy. The hamiltonian is defined in terms of the magnetic field:

$$\boxed{\underline{B}_1 = \underline{B} - \underline{e}_r\,(\underline{e}_r\cdot\underline{B})} \qquad -(27)$$

where

$$\underline{e}_r = \frac{\underline{r}}{r} \qquad -(28)$$

is the radial unit vector of the cylindrical polar coordinate system.

The conventional development of the hamiltonian is well known and is given as follows. It misses most of the information given in the new hamiltonian (24). The conventional hamiltonian is developed as:

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

$$= \frac{ie\hbar}{2m}\left(\underline{\nabla}\cdot(\underline{A}\phi) + \underline{A}\cdot\underline{\nabla}\phi\right)$$

$$- \frac{e\hbar}{2m}\underline{\sigma}\cdot\left(\underline{\nabla}\times(\underline{A}\phi) + \underline{A}\times\underline{\nabla}\phi\right) \quad -(29)$$

$$= \frac{ie\hbar}{2m}\left((\underline{\nabla}\cdot\underline{A})\phi + \underline{\nabla}\phi\cdot\underline{A} + \underline{A}\cdot\underline{\nabla}\phi\right)$$

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

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

using

$$\underline{B} = \underline{\nabla}\times\underline{A} \quad -(30)$$

It is seen that the ESR term is contained in the result (29), but all the other terms of eq. (24) are missing, in the sense that the resonance terms of eq. (24) are obscured by eq. (29).

The new resonance terms of eq. (24) all give useful new spectroscopies.