249(5) : Resonance Frequency of ESOR

This is calculated with the result:

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

For a uniform magnetic field:

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

so

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

$$= -\frac{1}{2r^2} \underline{\sigma} \cdot \underline{L} \; \underline{\sigma} \cdot \left( r^2 \underline{B} - \underline{r} (\underline{B} \cdot \underline{r}) \right)$$

$$= -\frac{1}{2} \left( \underline{\sigma} \cdot \underline{L} \; \underline{\sigma} \cdot \underline{B} - \frac{\underline{r}}{r^2} (\underline{B} \cdot \underline{r}) \right) . \quad -(3)$$

Now consider the Hamiltonian:

$$H = \frac{1}{2m} (\underline{p} - e\underline{A}) \cdot (\underline{p} - e\underline{A}) \quad -(4)$$

$$= \frac{p^2}{2m} - \frac{e}{2m} (\underline{p} \cdot \underline{A} + \underline{A} \cdot \underline{p}) + \frac{e^2}{2m} A^2$$

From eq. (3):

$$\underline{p} \cdot \underline{A} + \underline{A} \cdot \underline{p} = - \underline{\sigma} \cdot \underline{L} \; \underline{\sigma} \cdot \underline{B} + \dots \quad -(5)$$

so the resonant part of the Hamiltonian (4) is:

)

$$\boxed{H = \frac{e}{2m} \underline{\sigma} \cdot \underline{L} \, \underline{\sigma} \cdot \underline{B}} \quad - (6)$$

This is the result of the classical hamiltonian (4) without the use of the Dirac equation.

The ESOR resonance frequency from eq. (6) is

$$\boxed{\omega = \left( \frac{\underline{\sigma} \cdot \underline{L}}{\hbar} \right) \left( \frac{eB}{m} \right)} \quad - (7)$$

From the Dirac or fermion equation the ESR frequency of the unshielded electron is:

$$\omega_1 = \frac{eB}{m} \quad - (8)$$

from the hamiltonian:

$$H = \frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B} \quad - (9)$$

It is obvious that eq. (7) is a new phenomenon which is named electron spin orbit resonance (ESOR). In eq. (7), $\underline{L}$ is the angular momentum of the electron. Quantization of the hamiltonian (6) produces:

3)
$$\hat{H}\psi = \frac{e}{2m}\underline{\sigma}\cdot\underline{B}\ \hat{\underline{\sigma}}\cdot\hat{\underline{L}}\psi \quad -(10)$$

where
$$\hat{S} = \frac{1}{2}\hbar\underline{\sigma} \quad -(11)$$

So
$$\hat{H}\psi = \frac{e}{2m}g\underline{\sigma}\cdot\underline{B}\ \hat{\underline{S}}\cdot\hat{\underline{L}}\psi \quad -(12)$$

where
$$g = 2 \quad -(13)$$

is the electron g factor.

It is well known that:
$$\hat{\underline{L}}\cdot\hat{\underline{S}}\psi = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)\psi \quad -(14)$$
$$= \frac{1}{2}\hbar^2\left(J(J+1) - L(L+1) - S(S+1)\right)\psi$$

so the energy levels in eq. (10) are:
$$E = \frac{eg\underline{\sigma}\cdot\underline{B}}{2m}\left(\frac{1}{2}\hbar\left(J(J+1)-L(L+1)-S(S+1)\right)\right)$$
$$= \frac{eg\hbar}{4m}\left(J(J+1)-L(L+1)-S(S+1)\right)\underline{\sigma}\cdot\underline{B} \quad -(15)$$

so
$$\boxed{\omega = \frac{eB}{m}\left(J(J+1)-L(L+1)-S(S+1)\right)} \quad -(16)$$

) From the Clebsch Gordan series:

$$J = L + S,\ L + S - 1,\ \ldots,\ |L - S| \quad -(17)$$

For example, if:

$$L = 1,\ S = 1/2 \quad -(18)$$

$$J = \frac{3}{2} \text{ or } \frac{1}{2} \quad -(19)$$

It is clear that eq. (16) is completely different from ESR, which is usually developed as:

$$H_{ESR} = -\frac{e}{2m}\underline{L}\cdot\underline{B} + \lambda\,\underline{S}\cdot\underline{L} - \frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B} \quad -(20)$$

$$= -g_{spin}\,\underline{\sigma}\cdot\underline{B},$$

the "spin hamiltonian".

The most useful result of eq. (15) occurs in the chemical shift:

$$B \rightarrow B(1-\sigma) \quad -(21)$$

so eq. (16) can be adapted for NMR and MRI at high resolution.