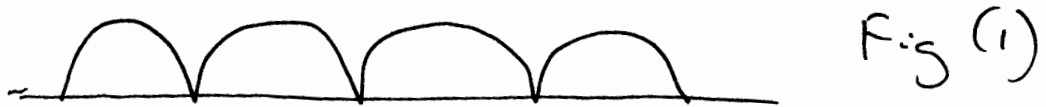


84(5) : Free and Helicity Structure in RFR.

It has been shown in note 84(4) that the main chemical shift in RFR is :

$$\omega_{res} = \frac{e^2 A^{(0)2}}{2m} \left( 1 + \frac{A_x^2 + A_y^2}{A^{(0)2}} \right)^{1/2} \quad - (1)$$

This may be generated by a wave-form of the type :



or alternatively by calculating the root mean square power density :

$$\begin{aligned} & \langle \mathbf{I} \mathbf{I}^* \rangle^{1/2} \\ & = \left( \left( A^{(0)2} + \sqrt{2} A^{(0)} (A_x - iA_y) \cos \phi \right) \left( A^{(0)2} + \sqrt{2} A^{(0)} (A_x + iA_y) \cos \phi \right) \right)^{1/2} \end{aligned} \quad - (2)$$

$$= A^{(0)} \left( A^{(0)2} + A_x^2 + A_y^2 \right)^{1/2} \quad - (3)$$

if it is assumed that :

$$\underline{A}_N = A_x \underline{i} + A_y \underline{j} \quad - (4)$$

The root mean square power density has been calculated using the same method as the power density itself :

$$\mathbf{I} \mathcal{L} \langle \mathbf{A} \mathbf{A}^* \rangle \quad - (5)$$

where :

$$\underline{A} = \underline{A}^{(1)} = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} - i\underline{j}) e^{i\phi} \quad - (6)$$

$$\underline{A}^* = \underline{A}^{(2)} = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} + i\underline{j}) e^{-i\phi} \quad - (7)$$

2)

So :

$$\langle AA^* \rangle = \frac{A^{(0)2}}{\sqrt{2}} (\underline{i} - \underline{ij}) \cdot (\underline{i} + \underline{ij}) = A^{(0)2} \quad \text{--- (8)}$$

It is seen from a comparison of eqns. (3) and (8) that the effect of the chemical shielding due to the nuclear potential (4) is :

$$A^{(0)2} \rightarrow A^{(0)} (A^{(0)2} + A_x^2 + A_y^2)^{1/2} \quad \text{--- (9)}$$

Where :

$$A_N = |A_N| = (A_x^2 + A_y^2)^{1/2} \quad \text{--- (10)}$$

It is important to note that the magnitude of  $A_N$  is responsible for the chemical shift, so the latter is non-zero after averaging.

### Fine and Hyperfine Structure in RFR

In addition to the chemical shift there is :

- 1) electron-electron spin spin interaction, fine structure,
- 2) electron-nuclear spin spin interaction, hyperfine structure,
- 3) nuclear-nuclear spin spin interaction, fine NMR structure.

The theory of this spectral structure in RFR follows the theory in ESR or NMR. In the latter theory, following the usual notation (e.g. in Atkins),

3) perturbation theory is used. This can be adapted for RFR straightforwardly. ESR and NMR are produced by a magnet and magnetic flux density  $\underline{B}$ . In perturbation theory, the unperturbed eigenstates of  $H^{(0)}$  are  $|n\rangle$ , the ground state is  $|0\rangle$ . The first order correction is:

$$E^{(1)} = -g_e \gamma_e \hbar B m_s \quad (11)$$

and the energy correction to second order is:

$$E^{(2)} = \sum_n' \left( \frac{\langle 0 | H^{(1)} | n \rangle \langle n | H^{(1)} | 0 \rangle}{E_0 - E_n} \right) \quad (12)$$

where:

$$H^{(1)} = -g_e \gamma_e \underline{s} \cdot \underline{B} + \lambda \underline{I} \cdot \underline{s} - \gamma_e \underline{I} \cdot \underline{B} \quad (13)$$

$\underline{I}$  the nuclear spin, the magnetic field dependent terms are:

$$\begin{aligned} & \langle 0 | -g_e \gamma_e \underline{s} \cdot \underline{B} | n \rangle \langle n | \lambda \underline{I} \cdot \underline{s} | 0 \rangle \\ & + \langle 0 | \lambda \underline{I} \cdot \underline{s} | n \rangle \langle n | -g_e \gamma_e \underline{s} \cdot \underline{B} | 0 \rangle \end{aligned} \quad (14)$$

This analysis gives a spin Hamiltonian of the type:

$$H^{spin} = -g_{zz} \gamma_e \hbar S_z \quad (15)$$

$$= -g_e \gamma_e \hbar S_z + 2\gamma_e \hbar \lambda \sum_n' \frac{l_{z,on} l_{z,no}}{\Delta E_n} S_z \quad (16)$$

$\underline{I}$  spin-orbit coupling for example:

4)

$$H^{(spin)} = \frac{g\mu_B}{\hbar} B S_z + A(\theta) I_z S_z + C I_z S_z$$

and:

$$m_I = I, I-1, \dots, -I$$

so there are  $2I + 1$  lines spaced by  $\frac{C + A(\theta)}{2}$ .

$I_z$  a liquid:  $\langle A(\theta) \rangle = 0$ .

It is seen that the spacing does not depend on the magnet. field strength, but if the lines are not well separated, as in ESR or NMR, the fine and hyperfine structure will overlap. In RFR this problem is solved by increasing the spacing between the main chemically shifted lines.