ESR SATURATION AND DOUBLE RESONANCE IN LIQUIDS

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XVIII.1. INTRODUCTION TO SATURATION: A SIMPLE LINE[1,2]

The well-known result from the steady-state (s.s.) solution of the Bloch Equations is that the absorption is given by the y-component of magnetization $\tilde{M}_y$ in the rotating frame:

$$\tilde{M}_y = \frac{\gamma H_1 T_2}{1 + (T_2 \Delta\omega)^2 + \gamma^2 H_1^2 T_1 T_2} M_o \tag{1}$$

with M_o the equilibrium magnetization. When we switch to a quantum mechanical description, we can calculate:

$$M_\pm = M_x \pm iM_y = (\tilde{M}_x \pm i\tilde{M}_y)e^{\pm i\omega t} \tag{2}$$

statistically from its associated quantum mechanical operator

$$\mathcal{M}_\pm = \mathfrak{N}\hbar\gamma_e S_\pm \tag{3}$$

where $\mathfrak{N}$ is the concentration of electron spins, by taking a trace of the spin density matrix $\sigma(t)$ with the spin operator $S_\pm$:

$$M_\pm(t) = \mathfrak{N}\hbar\gamma_e \mathrm{Tr}[\sigma(t)S_\pm] \tag{4}$$

The trace is invariant to a choice of zero-order basis states. The equation of motion for $\sigma(t)$ is taken to be the relaxation matrix form given by Eq. VIII-20, and we shall neglect effects of higher order than $R^{(2)}$.

L. T. Muus et al. (eds.), *Electron Spin Relaxation in Liquids*

We have from Eq. VIII-20a, that when $\mathcal{H}_1(t) = 0$, so R = 0,

$$\sigma_{\alpha\alpha'}(t) = e^{-i\omega_{\alpha\alpha'}t}\sigma_{\alpha\alpha'}(0) \quad . \tag{5}$$

Thus if $\sigma_{\alpha\alpha'}(0) \neq 0$, then $\sigma_{\alpha\alpha'}(t)$ will be oscillatory. Now suppose we have only a simple line with $\omega_o = \omega_{ab}$ where a and b are the $M_s = +\frac{1}{2}$ and $-\frac{1}{2}$ levels, and there are no other spin levels. Then

$$\langle b|S_-|a\rangle = \langle a|S_+|b\rangle = 1 \tag{6}$$

and

$$\mathrm{Tr}[\sigma(t)S_+] = \sigma(t)_{ba}S_{+ab} = \sigma(t)_{ba} \tag{7}$$

with

$$\sigma_{ba}(t) = \exp[(-i\omega_{ba} + R_{ba,ba})t]\sigma_{ba}(0). \tag{8}$$

Since ReR is negative, $\sigma_{ba} \to 0$ for $t \gg |\mathrm{Re}R|^{-1}$. Thus, there will be no steady state absorption unless we include effects of the rf field. So we add to the Hamiltonian:

$$\hbar\mathcal{E}(t) = \tfrac{1}{2}\hbar\gamma_e B_1[S_+e^{-i\omega t} + S_-e^{+i\omega t}] \tag{9}$$

which is the interaction of the spin with a rotating field $\vec{B}_1 = B_1(\cos\omega t\hat{i} + \sin\omega t\hat{j})$. Then for our simple line the $\langle b|-|a\rangle$ matrix element of eq. VIII-20 is :

$$\dot{\sigma}_{ba} = (i\omega_o + R_{ba,ba})\sigma_{ba} - id(\sigma_{bb}-\sigma_{aa})e^{i\omega t} \tag{10}$$

where

$$d = \tfrac{1}{2}\gamma_e B_1 \tag{11}$$

Now the power absorbed from the rotating field is just:

$$P = \omega H_1 \breve{M}_y = \frac{-\omega H_1 i}{2}[M_+e^{-i\omega t} - M_-e^{i\omega t}] \tag{12}$$

where from eq. 4 $M_\pm \propto \mathrm{Tr}_\sigma[\sigma(t)S_\pm]$ and S_{+ab} requires $\sigma(t)_{ba}$ in the trace. Thus only the component of $\sigma(t)_{ba}$ oscillating as $e^{i\omega t}$ will give a net time-averaged power absorption. So, let

$$\sigma_{ba} = Ze^{i\omega t} \tag{13}$$

and assume Z is time independent to achieve the steady state solution, which is:

$$(\Delta\omega + iR_{ba,ba})Z = d(\sigma_{bb} - \sigma_{aa}) \tag{14}$$

where $(\sigma_{bb} - \sigma_{aa})$ is the population difference in the two states. Now note that σ is Hermitian, so $\sigma_{ab} = \sigma^*_{ba}$ and

$$\sigma^*_{ab} = Z^* e^{-i\omega t} \quad . \tag{15}$$

Thus

$$P \propto \mathrm{Im}Z \equiv Z'' \quad . \tag{16}$$

We may begin to suspect that Z plays the role of $\breve{M}_+$ (while Z^* is $\breve{M}_-$). Also

$$R_{ba,\,ba} = -(1/T_2)_{ba} = -(1/T_2)_{ab} \quad .$$

We are now writing the equation of motion (eq. VIII-20) as

$$\dot{\sigma} = -i[\mathcal{H}_o + \varepsilon(t), \sigma] + R\sigma \quad . \tag{17}$$

We now need the diagonal spin-density-matrix elements σ_{bb} and σ_{aa}, which in steady state are not oscillating in time. We get from eq. 17:

$$R_{aa,\,aa}\sigma_{aa} + R_{aa,\,bb}\sigma_{bb} = di(Z - Z^*) = -2d\,\mathrm{Im}Z \tag{18a}$$

$$R_{bb,\,aa}\sigma_{aa} + R_{bb,\,bb}\sigma_{bb} = 2d\,\mathrm{Im}Z \quad . \tag{18b}$$

Note that

$$R_{aa,\,bb} = R_{bb,\,aa} = 2J_{ab,\,ab} = W_{ab} = W_{ba} \tag{19a}$$

while

$$R_{aa,\,aa} = -\sum_{\gamma \neq a} W_{a\gamma} \quad . \tag{19b}$$

where W_{ab} is the transition-probability from state b to state a, which leads to spin relaxation (cf. Eq. VIII.48).

For simplicity let γ = b only, (i.e., our simple line). Then we have

$$W_{ab}(\chi_a - \chi_b) = 2dZ'' \tag{20}$$

where we have made the ad hoc replacements:

$$\sigma_{aa} \rightarrow \chi_a = \sigma_{aa} - \sigma_{oaa} \tag{21a}$$

$$\sigma_{bb} \rightarrow \chi_b = \sigma_{bb} - \sigma_{obb} \tag{21b}$$

so that the effects of the W_{ab}, etc. is to lead to thermal equilibrium in the absence of $\varepsilon(t)$. σ_o is the equilibrium value of σ. Now eq. 14 is rewritten as:

$$(\Delta\omega - iT_2^{-1})Z + d(\chi_a - \chi_b) = q\omega_o d \tag{22}$$

where the high temperature approximation:[1,2]

$$\sigma_{oaa} - \sigma_{obb} \cong \frac{e^{-E_a/kT} - e^{-E_b/kT}}{\sum_\alpha e^{-E_\alpha/kT}} \cong \frac{-\hbar\omega_{ab}}{kTA} \equiv -q\omega_o \tag{23}$$

has been used. Here A is the number of spin states (2 in our example). We now need to solve the coupled equations:

$$\begin{pmatrix} \Delta\omega & T_2^{-1} & d \\ -T_2^{-1} & \Delta\omega & 0 \\ 0 & -2d & W_{ab} \end{pmatrix} \begin{pmatrix} Z' \\ Z'' \\ (\chi_a - \chi_b) \end{pmatrix} = \begin{pmatrix} q\omega_o d \\ 0 \\ 0 \end{pmatrix} \tag{24}$$

This gives:

$$Z' = \Delta\omega T_2 Z'' \tag{24a}$$

$$Z'' = \frac{qd\omega_o T_2}{1 + \Delta\omega^2 T_2^2 + 4d^2 T_2 T_1} \tag{24b}$$

where $T_1 \equiv (2W_e)^{-1}$ and

$$(\chi_a - \chi_b) = q\omega_o 4d^2 \frac{T_2 T_1}{1 + \Delta\omega^2 T_2^2 + 4d^2 T_2 T_1} \quad . \tag{24c}$$

These results are very similar to steady state solutions of the Bloch Eqs. and we can get correspondence if:

$$2M_o = q\omega_o = \frac{\hbar\omega_o}{AkT} = \sigma_{oaa} - \sigma_{obb} \tag{25a}$$

$$T_2 = (T_2)_{ab}, \quad T_1 = (T_1)_{ab} \tag{25b}$$

$$\gamma\vec{H} = -\omega_o\vec{k} + 2|d|\{\hat{i}\cos\omega t + \hat{j}\sin\omega t\} \tag{25c}$$

$$Z' = \breve{M}_x, \quad Z'' = \breve{M}_y, \quad Z = \breve{M}_+ \tag{25d}$$

$$\chi_a - \chi_b = 2(M_o - M_Z) \tag{25e}$$

The above treatment, is based on the high field approximation $|B_o| >> |B_1|$, as well as the fast motional condition $|\mathcal{H}_1|\tau_c << 1$.

It also requires that $|\gamma B_1|\tau_c << 1$ in order that the R matrix is not significantly affected by the presence of the rf field. This can be seen as follows. When we have a time-dependent Hamiltonian,

$$E(t) = \mathcal{H}_o + \epsilon(t)$$

we must define a new interaction representation:

$$\sigma^{\ddagger} = U(t)\sigma(t)U^{-1}(t) \tag{26a}$$

$$\mathcal{H}_1^{\ddagger}(t) = U(t)\mathcal{H}_1(t)U^{-1}(t) \tag{26b}$$

where the unitary operator $U(t) \equiv U(t,0)$ is a solution of the differential equation:

$$\frac{d}{dt}U(t,0) = iU(t,0)E(t) \tag{27}$$

with $U(t_o,t_o) = 1$ and $U(t-\tau,0) = U(t,0)U(t-\tau,t)$. Its solution is the time-ordered exponential:

$$U(t,0) = \exp_o\left(\int_o^t iE(t')dt'\right) . \tag{28}$$

Since U is unitary, the differential equation for U^{-1} is obtained by taking Hermitian conjugates of Eq. 27. Thus:

$$\dot{U}^{-1} = -iE(t)U^{-1} \tag{29}$$

Then we have in the interaction representation:

$$\dot{\sigma}^{\ddagger} = -i\mathcal{H}_1^{\ddagger\times}\sigma^{\ddagger} \tag{30}$$

as before (cf. Eq. VIII-5). Thus, to second order (assuming $K_1 = 0$, cf. eq. VIII-13a) the cumulant average is, in the long time limit:

$$\begin{aligned}\dot{\sigma}^{\ddagger} &\cong \int_o^{\infty} d\tau \langle \mathcal{H}_1^{\ddagger}(t)^{\times}\mathcal{H}_1^{\ddagger}(t-\tau)^{\times}\rangle_c\sigma^{\ddagger}(t) \\ &= -U(t)\int_o^{\infty}\{\langle \mathcal{H}_1(t)^{\times}[U(t-\tau,t)\mathcal{H}_1(t-\tau)U^{-1}(t-\tau,t)^{\times}\rangle_c\sigma\} \\ &\qquad \times d\tau U^{-1}(t)\end{aligned} \tag{31}$$

Then

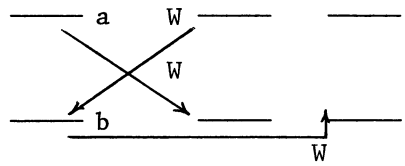
$$\dot{\sigma} = -i[E(t),\sigma] - \int_o^{\infty} d\tau \langle \mathcal{H}_1(t)^{\times}[U(t-\tau,t)\mathcal{H}_1(t-\tau)U^{-1}(t-\tau,t)]^{\times}\rangle_c\sigma(t) \tag{32}$$

Now the integral in eq. 32 is non-negligible only for $\tau \leq \tau_c$, but since $|\varepsilon|\tau_c << 1$ we can in this interval write

$$U(t-\tau) = e^{-i\mathcal{H}_o\tau} + 0|\varepsilon(t)|\tau_c \cong e^{-i\mathcal{H}_o\tau} \tag{33}$$

which when substituted into eq. 32 gives the desired result. A similar analysis applies for the higher order cumulants in the long time limit yielding R to all orders.

The next most complicated case, is a simple line, coupled by relaxation to other spin eigenstates:



Then we have:

$$\sum_{\alpha\neq a} W_{a\alpha}(\chi_a - \chi_\alpha) = 2d\,\mathrm{Im}Z \tag{34a}$$

$$\sum_{\alpha\neq b} W_{b\alpha}(\chi_b - \chi_\alpha) = -2d\,\mathrm{Im}Z \quad . \tag{34b}$$

And, for $\alpha \neq a, b$ we get A-2 equations:

$$\sum_{\alpha} W_{\alpha\beta}(\chi_\alpha - \chi_\beta) = 0 \qquad \beta \neq \alpha \quad . \tag{34c}$$

In eq. 34c we have assumed all transitions other than $a \rightarrow b$ are too far off-resonance to have any appreciable off-diagonal density matrix elements; i.e. they are not excited by the rf field. The conservation of probability is:

$$\mathrm{Tr}\sigma = \mathrm{Tr}\sigma_o = 1, \text{ or } \mathrm{Tr}\chi = 0 \quad . \tag{35}$$

This is needed, because the above set of A equations are not all linearly independent. We can write these A equations in matrix notation as:

$$\bar{W}\,\bar{\chi} = \bar{U} \quad . \tag{36}$$

When the rank of $\bar{W}$ is A-1, then replacement of any one equation by eq. 35 yields the matrix $\bar{W}^i$, which is now non-singular, and we have:

$$\bar{\chi} = (\bar{W}^i)^{-1}\bar{U}^i \quad . \tag{36a}$$

Proper solutions of this $\bar{W}$ inversion are crucial in all saturation and double resonance analyses. It is possible to obtain solutions in the form:[1,5]

$$(\chi_a - \chi_b) = \Omega_{ba,ba} V_{ba} [q\omega_o - (\chi_a - \chi_b)] \tag{37}$$

and from eq. 34

$$dZ'' = V_{ba} [q\omega_o - (\chi_a - \chi_b)] \tag{38}$$

where

$$V_{ba} = 2d^2 T_2 / (1 + T_2^2 \Delta\omega^2) \tag{39}$$

and

$$\Omega_{ba,ba} = 2C_{ba,ba}/C \tag{40}$$

where C is any cofactor of $\bar{W}$, (they are all equal, as may be shown from the properties of $\bar{W}^{-1}$); and $C_{ba,ba}$ is the double cofactor of $\bar{W}$ obtained as the (signed) determinant resulting when the a^{th} and b^{th} rows and columns are deleted from $\bar{W}$. More generally we write

$$\Omega_{\alpha\beta,\gamma\delta} = 2C_{\alpha\beta,\gamma\delta}/C \tag{40a}$$

where $C_{\alpha\beta,\gamma\delta}$ is the double cofactor of $\bar{W}$ obtained by deleting the α^{th} and β^{th} rows and the γ^{th} and δ^{th} columns of $\bar{W}$ and giving it the correct sign.

The net result is to obtain our earlier results of eq. 24 but now

$$T_1 \rightarrow \tfrac{1}{4}\Omega_{ba,ba} \equiv \tfrac{1}{4}\Omega_{ba} \tag{41}$$

where Ω_{ba} is the saturation parameter for the $b \leftrightarrow a$ transition. It is not a simple T_1, nor decay time. In fact there are as many as (A-1) different, non-zero decay constants in the transient solution (which come from diagonalizing the $\bar{W}$ matrix).

This Ω_{ba} may be regarded as a steady-state self-impedance representing the response of the $b \leftrightarrow a$ transition to the application

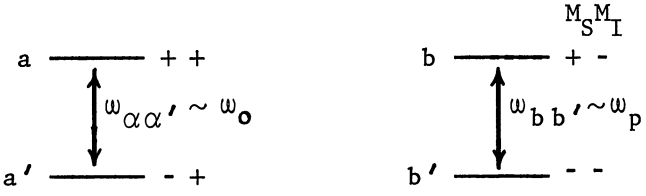
of an rf field. I.e., we rewrite eqs. 37 and 38 as:

$$(\chi_a - \chi_b) = \Omega_{ba} \cdot (dZ'') \tag{42}$$

and make the electrical circuit analogy by letting $(\chi_a - \chi_b) = E$, $\Omega_{ba} = R$, and $dZ'' = I$. Thus we see that inducing a resonant transition is formally equivalent to inducing a current flow, which causes a voltage drop $(\chi_a - \chi_b)$ proportional to the resistance Ω_{ba}.

XVIII.2. ELDOR[3]

Now we introduce a second ESR microwave field. Assume there are only two transitions of interest.



Now we have

$$\epsilon(t) = \tfrac{1}{2}\gamma_e B_o [S_+ \exp(-i\omega_o t) + S_- \exp(+i\omega_o t)] + \tfrac{1}{2}\gamma_e B_p [S_+ \exp(-i\omega_p t) + S_- \exp(+i\omega_p t)] \quad . \tag{43}$$

We are looking to the applied fields to generate s.s. off-diagonal density matrix elements as a result of the resonance phenomena. We assume

$$|\gamma_e B_o|, \ |\gamma_e B_p|, \ |R| \ll |\omega_{aa'} - \omega_{bb'}| \sim |a| \quad , \tag{44}$$

so the hyperfine lines always remain well separated. Then we may have $\omega_{aa'} - \omega_o = \Delta\omega_o \sim 0$, while $|\omega_{aa'} - \omega_p| \sim |a|$ and $\omega_{bb'} - \omega_p = \Delta\omega_p \sim 0$, while $|\omega_{bb'} - \omega_o| \sim |a|$. Thus, the important elements are:

$$\sigma_{a'a} = \chi_{a'a} = Z_{a'a} \exp(i\omega_o t) \equiv Z_o \exp(i\omega_o t) \tag{45a}$$

$$\sigma_{b'b} = \chi_{b'b} = Z_{b'b} \exp(i\omega_p t) \equiv Z_p \exp(i\omega_p t) \tag{45b}$$

We obtain from eq. 17:

$$[\Delta\omega_o - i/T_{2,o}] Z_o + d_o(\chi_a - \chi_{a'}) = q\omega_{aa'} d_o \cong q\omega_e d_o \tag{46a}$$

$$[\Delta\omega_p - i/T_{2,p}]Z_p + d_p(\chi_b - \chi_{b'}) = q\omega_{bb'}d_p \cong q\,\omega_e d_p \qquad (46b)$$

Also, the analogues of eqs. 34 are now:

$$\sum_{\alpha\neq a} W_{a\alpha}(\chi_a - \chi_\alpha) = 2d_o Z''_o \qquad (47a)$$

$$\sum_{\alpha\neq a} W_{a'\alpha}(\chi_{a'} - \chi_\alpha) = -2d_o Z''_o \qquad (47b)$$

$$\sum_{\alpha\neq b} W_{b\alpha}(\chi_b - \chi_a) = 2d_p Z''_o \qquad (47c)$$

$$\sum_{\alpha\neq b'} W_{b'\alpha}(\chi_{b'} - \chi_\alpha) = -2d_p Z''_o \quad . \qquad (47d)$$

These equations may be rewritten in matrix form as:

$$(\bar{K} + i\bar{R})\bar{Z} = \overline{D\chi} + \bar{Q} \qquad (48a)$$

$$(\bar{W}^j)(\bar{\chi}) = -2\bar{D}^{trj}\bar{Z}'' \qquad (48b)$$

where

$$\bar{Q} \cong q\omega_e \begin{pmatrix} d_o \\ d_p \end{pmatrix} \qquad (49a)$$

$$K = \begin{pmatrix} \Delta\omega_o & 0 \\ 0 & \Delta\omega_p \end{pmatrix} \qquad (49b)$$

$$-R = \begin{pmatrix} T_{2,o}^{-1} & 0 \\ 0 & T_{2,p}^{-1} \end{pmatrix} \qquad (49c)$$

$$-\bar{D} = \begin{pmatrix} d_o & -d_o & 0 & 0 \\ 0 & 0 & d_p & -d_p \end{pmatrix} . \qquad (49d)$$

$\bar{W}^j$ is a 4 x 4 transition probability matrix in the space of the 4 spin eigenstates with the j^{th} row replaced by ones, and $\bar{D}^{trj}$ is the transpose of $\bar{D}$ with the j^{th} row replaced by zero. $\bar{Z}$ is a vector in the 2 dimensional space of induced transitions. The formal solution is given by:

$$\bar{Z}'' = \bar{M}^{-1}(-\bar{R}^{-1})\bar{Q} \qquad (50a)$$

$$\bar{Z}' = (-\bar{R}^{-1})\overline{KZ}'' \qquad (50b)$$

$$\overline{D\chi} = -\bar{S}\,\bar{Z}'' \qquad (50c)$$

where

$$\bar{\bar{M}} = 1 + (\bar{\bar{R}}^{-1}\bar{\bar{K}})^2 + (-\bar{\bar{R}}^{-1})\bar{\bar{S}} \tag{51a}$$

and

$$\bar{\bar{S}} = 2[\bar{\bar{D}}(\bar{\bar{W}}^j)^{-1}\bar{\bar{D}}^{tr}j] \quad . \tag{51b}$$

Suppose $d_p = 0$. One recovers the single-line, simple saturation result and by comparison, we find

$$S_{o,o} = d_o^2\Omega_{aa',aa'} \equiv d_o^2\Omega_{o,o} \tag{52}$$

One finds more generally:[1]

$$S_{i,j} = d_i d_j \Omega_{i,j} \tag{53}$$

where $\Omega_{i,j}$ is a cross-impedance (cross-saturation parameter) which is determined solely by the spin relaxation processes and represents the impedance at transition i from an external disturbance (e.g., a resonant rf field) on the transition j. [It is obtained by eq. 40a with $\alpha \to \beta$ being the i^{th} transition and $\gamma \to \sigma$ the j^{th} transition.]

Thus eq. 50c is a generalization of eq. 42 for the single resonance case. In fact it gives

$$(\chi_a - \chi_{a'}) = d_o\Omega_{o,o}Z_o'' + d_p\Omega_{o,p}Z_p'' \tag{54a}$$

$$(\chi_b - \chi_{b'}) = d_p\Omega_{p,p}Z_p'' + d_o\Omega_{p,o}Z_o'' \quad . \tag{54b}$$

with an electrical circuit analogy similar to that of eq. 42. It follows from eqs. 49-53 that:

$$M = \begin{pmatrix} 1 + \Delta\omega_o^2 T_{2,o}^2 + d_o^2 T_o \Omega_o & d_o d_p \Omega_{o,p} T_{2,o} \\ d_p d_o \Omega_{p,o} T_{2,p} & 1 + \Delta\omega_p^2 T_{2,p}^2 + d_p^2 T_{2,p} \Omega_p \end{pmatrix} , \tag{55}$$

where we have let $\Omega_{o,o} = \Omega_o$ and $\Omega_{p,p} = \Omega_p$. Then from eq. 50a:

$$Z_o'' = q\omega_e T_{2,o} d_o \frac{1 - \xi_o/\Omega_{p,o}}{1 + \Delta\omega_o^2 T_{2,o}^2 + d_o^2 T_{2,o}(\Omega_o - \xi_o)} \tag{56}$$

with

$$\xi_o = d_p^2 T_{2,p} \Omega_{o,p} \Omega_{p,o} / (1 + \Delta\omega_p^2 T_{2,p}^2 + d_p^2 T_{2,p} \Omega_p) \quad . \tag{56a}$$

Now consider some special cases. Let us have $\Delta\omega_p = 0$ (represented by a superscript r) and very strong saturation of the pump mode:

$$d_p^2 T_p \Omega_p \gg 1 \quad . \tag{57}$$

Then:

$$\xi_o^r (d_p^2 \to \infty) = \Omega_{o,p}\Omega_{p,o}/\Omega_p \tag{58}$$

which is just relaxation determined. We now let $T_{2,p} = T_p$, etc. Then

$$Z_o'' = q\omega_e T_o d_o \frac{(\Omega_p - \Omega_{o,p})/\Omega_p}{1 + T_o^2 \Delta\omega_o^{\,2} + d_o^2 T_o (\Omega_o\Omega_p - \Omega_{o,p}\Omega_{p,o})/\Omega_p} \quad . \tag{59}$$

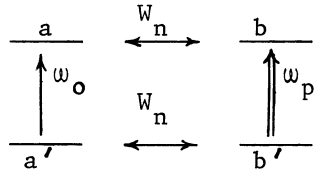
If we also introduce the generalized no-saturation condition for the observing mode:

$$d_o^2 T_o [(\Omega_o\Omega_p - \Omega_{o,p}\Omega_{p,o})/\Omega_p] \ll 1 \tag{60}$$

one has the simple result that:

$$Z_o'' = \frac{T_o q\omega_e d_o}{1+\Delta\omega_o^{\,2} T_o^2}\left[1 - \frac{\Omega_{o,p}}{\Omega_p}\right] \quad . \tag{61}$$

Since Ω_p is always positive,[1] it follows from eq. 61 that for $\Omega_{o,p} > 0$ the signal is reduced by the presence of the resonant pump field, while for $\Omega_{o,p} < 0$ the signal is amplified. The limiting (but not realistic) case for eq. 61 occurs when W_n is very strong and W_e is negligible. (Here W_e and W_n are respectively the lattice-induced electron-spin flip and nuclear-spin flip rates.) Then the case for the energy levels shown:



is easily understood. Let P_i be the population of the i^{th} state. Then saturation by ω_p causes $P_b = P_{b'}$; a strong W_n causes $P_a = P_b$ and $P_{a'} = P_{b'}$ leading to a reduction in intensity of the observed signal. This extreme will be seen to be equivalent to

$\Omega_{o,p} = \Omega_o = \Omega_p$.

There are actually 2 effects that can be seen in ELDOR.

Effect 1. The no-saturation effect discussed above is a polarization effect (not unlike an Ovehauser effect in NMR) but the two transitions involved have no level in common, and this places special requirements on the relaxation processes in order to obtain significant effects.

Effect 2. It is important only when Z_o'' is being saturated. It reflects the fact that the induced absorption mode Z_p'' acts as an induced transition which, in conjunction with lattice-induced transitions, can facilitate the rate of energy transferred from the observing radiation field to the lattice via the spin systems.

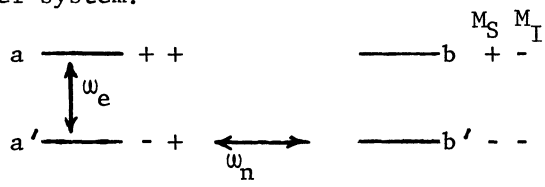
Effect 1 is the main effect in ELDOR, while the analogue to effect 2 is the dominant one in ENDOR.

XVIII.3. ENDOR[1,4,5]

We again consider our 4 level system, but now:

$$\begin{aligned}\mathcal{E}(t) = {} & \tfrac{1}{2}\gamma_e B_e [S_+ \exp(-i\omega_e t) + S_- \exp(+i\omega_e t)] \\ & + \tfrac{1}{2}\gamma_n B_n [I_+ \exp(-i\omega_n t) + I_- \exp(+i\omega_n t)] \\ & + \tfrac{1}{2}\gamma_e B_n [S_+ \exp(-i\omega_n t) + S_- \exp(i\omega_n t)] \\ & + \tfrac{1}{2}\gamma_n B_e [I_+ \exp(-i\omega_e t) + I_- \exp(i\omega_e t)] \quad . \end{aligned} \tag{62}$$

In eq. 62, the microwave field at frequency ω_e is to induce electron-spin flips, while the rf field at frequency ω_n is to induce nuclear-spin flips. Thus the last term in eq. 62 can be neglected as being too far off resonance to affect the nuclear spins. We neglect the 3rd term in eq. 62 for simplicity, even though it does have a non-trivial effect on the effective transition moment of the nuclear spins.[1] Let us assume the following four-level system:



with

$$\Delta_e \equiv \omega_e - \omega_{aa'} \approx 0 \tag{63a}$$

$$\Delta_n \equiv \omega_n - \omega_{a'b'} \approx 0 \quad . \tag{63b}$$

Then, for assumptions similar to the ELDOR case, we expect important s.s. off-diagonal density-matrix elements:

$$\chi_{a'a} = Z_{a'a} e^{i\omega_e t} \equiv Z_e e^{i\omega_e t} \tag{64a}$$

$$\chi_{b'a'} = Z_{b'a'} e^{i\omega_n t} \equiv Z_n e^{i\omega_n t} \quad . \tag{64b}$$

We obtain the series of equations:

$$[\Delta_e - i/T_e] Z_e + d_e(\chi_a - \chi_{a'}) + d_n Z_{b'a} = q\omega_e d_e \tag{65a}$$

$$[\Delta_n - i/T_n] Z_n + d_n(\chi_{a'} - \chi_{b'}) - d_e Z_{b'a} = q\omega_n d_n \tag{65b}$$

$$[\Delta_e + \Delta_n - i/T_{b'a}] Z_{b'a} - d_e Z_n + d_n Z_e = 0 \quad . \tag{65c}$$

Note the appearance of

$$\chi_{b'a} = Z_{b'a} e^{i(\omega_e + \omega_n)t} \equiv Z_x e^{i(\omega_e + \omega_n)t} \quad . \tag{66}$$

This is an overtone term: a 2 quantum effect. Also:

$$\sum_{\alpha \neq a} W_{a\alpha}(\chi_a - \chi_\alpha) = 2d_e Z''_{a'a} \tag{67a}$$

$$\sum_{\alpha \neq a'} W_{a'\alpha}(\chi_{a'} - \chi_\alpha) = -2d_e Z''_{a'a} + 2d_n Z''_{b'a'} \tag{67b}$$

$$\sum_{\alpha \neq b} W_{b\alpha}(\chi_b - \chi_\alpha) = 0 \tag{67c}$$

$$\sum_{\alpha \neq b'} W_{b'\alpha}(\chi_{b'} - \chi_\alpha) = -2d_n Z''_{b'a'} \quad . \tag{67d}$$

Again we may write these equations in the matrix form given by eqs. 48 with the formal solution given by eqs. 50 and 51. Note that the K or coherence matrix is:

$$K = \begin{pmatrix} \Delta_e & 0 & d_n \\ 0 & \Delta_n & -d_e \\ d_n & -d_e & \Delta_e + \Delta_n \end{pmatrix} \quad . \tag{68}$$

and is no longer diagonal. Also intensities are proportional to

$$Q = q\begin{pmatrix} \omega_e d_e \\ \omega_n d_n \\ 0 \end{pmatrix} , \tag{69}$$

but because $\frac{\omega_e}{\omega_n} \sim \frac{1}{660}$ for protons, we may usually set

$$Q \cong q\begin{pmatrix} \omega_e d_e \\ 0 \\ 0 \end{pmatrix} , \tag{69a}$$

which amounts to neglecting the analogue of effect 1 in the ENDOR case.

Neglect of Coherence Effects. The coherence effects arise from the off-diagonal elements in the K matrix or in other words the contribution from Z_x. Consider the case of exact resonance, when $\Delta_e = \Delta_n = 0$, since this is the condition under which double-resonance effects will be maximized. Equations 65-67 and 50-51 then yield:

$$Z'^r_e = Z'^r_n = Z''^r_x = 0 \tag{70a}$$

$$Z''^r_e = \frac{q\omega_e d_e T_e}{1+d_e^2(\Omega_e-\xi_e^r)T_e+d_n^2 T_x T_e} \tag{70b}$$

where

$$\xi_e^r = \frac{T_n d_n^2 (T_x+|\Omega_{e,n}|)^2}{1+d_n^2\Omega_n T_n+d_e^2 T_x T_n} \tag{70c}$$

Thus from eq. 70b when

$$1+d_e^2\Omega_e T_e \gg d_n^2 T_x T_e \tag{71}$$

$$(\text{and } \xi_e^r \not\ll \Omega_e)$$

the coherence effect on Z''^r_e may be neglected. ξ_e^r leads to an enhancement of a saturated ESR signal, since it effectively reduces the saturation parameter Ω_e. Now when

$$1+d_n^2\Omega_n T_n \gg d_e^2 T_x T_e \tag{72}$$

it follows from eq. 70c that the ratio ξ_e/Ω_e will not be affected

by d_e, and further if

$$|\Omega_{e,n}| \gg T_x \tag{73}$$

we may completely neglect the coherence effects.

If there is appreciable saturation and

$$d_e^2 \sim d_n^2 \tag{74}$$

then we can replace eqs. 71-73 with the simpler set of conditions:

$$\Omega_e, \Omega_n, |\Omega_{e,n}| \gg T_x \tag{75}$$

for the neglect of coherence effects. The inequalities of eq. 75 are fulfilled if the T_1's or saturation parameters are much larger than the T_2's or inverse linewidths.

Now our solutions for Δ_e, $\Delta_n \approx 0$ are:

$$Z_e'' = \frac{q\omega_e d_e T_e}{1+(\Delta_e T_e)^2 + (\Omega_e - \xi_e)T_e d_e^2} \tag{76a}$$

$$\xi_e = \frac{d_n^2 (\Omega_{e,n})^2 T_n}{1+(\Delta_n T_n)^2 + d_n^2 T_n \Omega_n} \quad . \tag{76b}$$

If the ENDOR spectrum is monitored after subtraction of the ESR signal; then for $\Delta_e = 0$ and $\Omega_e T_e d_e^2 \gg 1$ we have

$$Z_{ENDOR}''^{r} - Z_{ESR}''^{r} = q\omega_e d_e \left(\frac{\Omega_{e,n}}{\Omega_e}^2\right) \frac{d_n^2 T_n}{1+(\Delta_n T_n)^2 + \left[1-\frac{\Omega_{e,n}^2}{\Omega_e \Omega_n}\right] T_n \Omega_n d_n^2} \quad . \tag{77}$$

Thus the signal strength is proportional to $(\Omega_{e,n}/\Omega_e)^2$ and the shape is a Lorentzian of width T_n^{-1} and (modified) saturation parameter:

$$\Omega_n \left(1 - \frac{\Omega_{e,n}^2}{\Omega_n \Omega_e}\right) \quad . \tag{78}$$

The percent enhancement of an ESR line due to ENDOR is then, from eq. 77,

$$\% \text{ enh} = \frac{Z_{ENDOR}'' - Z_{ESR}''}{Z_{ENDOR}''} = \frac{\xi_e}{\Omega_e - \xi_e} \frac{d_n^2 \to \infty}{\Delta_n \to 0} \left[\frac{\Omega_n \Omega_e}{\Omega_{e,n}^2} - 1\right]^{-1} \quad . \tag{79}$$

XVIII.4. GENERAL APPROACH

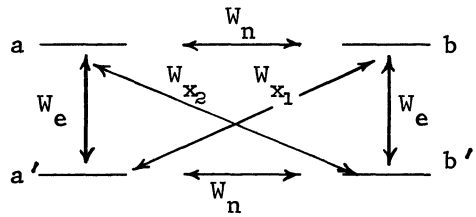
One finds that, in general, multiple-resonance, ESR experiments in liquids may be expressed in the matrix form eq. 48 with formal solution given by eqs. 51-53.[1] In this formal solution, $\bar{Z}$ is a vector in the space of all induced transitions and $\bar{\chi}$ is a vector in the space of all spin eigenstates. The only requirement is that a raising convention apply. This is the requirement that all induced transitions in the space of $\bar{Z}$ are those in which there is (are) increase(s) in spin quantum number but no decrease(s) in spin quantum number.[5] This requirement is often met for ENDOR and ELDOR experiments, but it sometimes requires neglect of some multiple quantum transitions. If it is not met, then a somewhat more complex form of eqs. 48 and 51-53 could become necessary. Also, in summary, the validity of the general relaxation eq. 17 for well separated hyperfine lines requires, that,

$$|\gamma_e B_o|,\ |\gamma_i B_o|,\ |\gamma_e \bar{a}_i|,\ \tau_c^{-1},\ \gg \epsilon(t),\ |R| \tag{80}$$

where τ_c refers to the relevant correlation time(s).

XVIII.5. TRANSITION PROBABILITIES

Consider now the general 4-level system with all types of spin-lattice relaxation transitions:



We can solve for C_{ii} and $C_{ij,kl}$ the cofactors and double cofactors of the $\bar{W}$ matrix to obtain all the $\Omega_{ij,kl}$.

A. ELDOR— Generalized No Saturation of Observing Mode.

We have from eq. 61 that the signal reduction is given by:

$$R \equiv \frac{\%\ \text{reduction}}{100} = \frac{\Omega_{o,p}}{\Omega_p} = \frac{W_n^2 - W_{x_1} W_{x_2}}{W_e(2W_n + W_{x_1} + W_{x_2}) + (W_n + W_{x_1})(W_n + W_{x_2})} \,. \tag{81}$$

Clearly if $W_n^2 > W_{x_1} W_{x_2}$ one has a reduction in signal, while if $W_n^2 < W_{x_1} W_{x_2}$ there will be an enhancement.

a. Let $W_{x_1} = W_{x_2} = 0$ (i.e., only pseudosecular dipolar terms important). Then

$$R = \frac{W_n}{2W_e + W_n} = \frac{b}{2 + b} \text{ where } b \equiv \frac{W_n}{W_e}$$

or a reduction.

b. Let $W_{x_1} = W_n = 0$ (i.e., isotropic hyperfine modulation). Then $R = 0$ i.e., no effect.

c. Let $W_{x_2} = 4W_n$, $W_{x_1} = \frac{2}{3}W_n$ (dipolar, extreme narrowing). Then

$$R = -\frac{b}{4+5b}$$

or an enhancement.

In the case of solids, one can also examine ELDOR enhancements for forbidden ESR transitions.[6]

B. ENDOR—Limiting Enhancements.

We have from eq. 79 that the % enhancement E is given by:

$$1 + E^{-1} = \frac{\Omega_n \Omega_e}{\Omega_{e,n}^2} =$$

$$[W_n(2W_e+W_{x_1}+W_{x_2})+(W_e+W_{x_1})(W_e+W_{x_2})] \times$$

$$[W_e(2W_n+W_{x_1}+W_{x_2})+(W_n+W_{x_1})(W_n+W_{x_2})] \times$$

$$[W_{x_2}(W_e+W_n+W_{x_1})+W_eW_n]^{-2} \quad . \tag{82}$$

a. Let $W_{x_1} = W_{x_2} = 0$ (i.e., only pseudo-secular dipolar terms important). Then

$$E = \frac{1}{2[2 + b + b^{-1}]} \qquad \begin{array}{l} \xrightarrow{b \gg 1} \frac{1}{2}b^{-1} \\ \xrightarrow{b \ll 1} \frac{1}{2}b \\ \xrightarrow{b=1} \frac{1}{8} \end{array}$$

b. Let $W_{x_1} = W_n = 0$ (i.e., isotropic hyperfine modulation). Then

$$E = \frac{W_{x_2}}{W_e} \quad .$$

This would theoretically be a most effective ENDOR mechanism if W_{x_2} were large.

c. Case b but now the a↔b ENDOR transition is saturated. Then $E = 0$.

d. Let $W_{x_2} = 4W_n$, $W_{x_1} = \frac{2}{3}W_n$ (dipolar, extreme narrowing).

$$E = \frac{b[22.5 + 60b + 40b^2]}{6 + b[25 + 34b + 15b^2]} \qquad \begin{array}{ll} \xrightarrow{b\gg 1} & (8/3)b \\ \xrightarrow{b\ll 1} & 3.75b \\ \xrightarrow{b=1} & 1.53 \end{array}$$

This is also a very effective ENDOR mechanism if $b>1$.

e. Case d but now the a↔b ENDOR transition is saturated

$$E = \frac{b[2.5 + 10b + 10b^2]}{6 + b[45 + 84b + 45b^2]} \qquad \begin{array}{ll} \xrightarrow{b\gg 1} & 2/9 \\ \xrightarrow{b\ll 1} & (5/12)b \\ \xrightarrow{b=1} & 1/8 \end{array}$$

C. Expressions for Transition Probabilities.[1]

We assume a single set of completely equivalent nuclei with total nuclear spin quantum number J and total z component M. (We do not explitly indicate the distinction between degenerate states of the same values of J and M. Note that there will often be degenerate states for a given set of values of J and M. However, it is possible for dipolar terms (but not quadrupolar terms) to order the degenerate states according to a parameter K or $J^{(K)}$ such that the values of J and K are preserved.[1] We do not explicitly indicate K in the equations below.)

i. Nuclear-Spin Transitions

a. Dipolar:

$$W_{(M_S, M) \rightarrow (M_S, M\pm 1)} = \tfrac{1}{2} j^D(0)[J(J+1)-M(M\pm 1)] \tag{83}$$

where the electron-nuclear dipolar spectral density $j^D(0)$ is:

$$j^D(0) = \frac{1}{5}\gamma_e^2\gamma_n^2\hbar^2\sum_m |D^m|^2\tau_R \tag{84}$$

with τ_R the rotational correlation time, and it is assumed $|\omega_n\tau_R| \ll 1$. The dipolar coefficients are:[7]

$$D^{(m)} = \left(\frac{6\pi}{5}\right)^{\frac{1}{2}} \langle \psi_e | r'^{-3} Y_{2,m}(\theta', \varphi') | \psi_e \rangle \tag{85}$$

where θ', and φ' and r' are spherical polar co-ordinates which define the position of the unpaired electron with respect to a

nucleus in the molecular co-ordinate frame.

b. Quadrupolar. (For this case only we consider a single nucleus of Spin I):

$$W_{(M_S, M) \to (M_S, M\pm1)} = 2j^Q(0)\,[I(I+1) - M(M\pm1)][2M\pm1]^2 \tag{86a}$$

$$W_{(M_S, M) \to (M_S, M\pm2)} = 2j^Q(0)\,[I(I+1) - M(M\pm1)][I(I+1) - (M+1)(M\pm2)] \tag{86b}$$

where

$$j^Q(0) = \frac{\tau_R}{80}\frac{e^2Q^2}{\hbar^2 I^2(2I-1)^2}\sum_m |\nabla\epsilon^{(m)}|^2 \tag{87}$$

with electric-field-gradient irreducible-tensor components:[7]

$$\nabla\epsilon^{(0)} = -\left(\frac{3}{2}\right)^{\frac{1}{2}}\langle\psi_e|V'_{ZZ}|\psi_e\rangle \tag{88a}$$

$$\nabla^{\epsilon(\pm1)} = \pm\langle\psi_e|V'_{XZ}\pm iV'_{YZ}|\psi_e\rangle \tag{88b}$$

$$\nabla\epsilon^{(\pm2)} = -\tfrac{1}{2}\langle\psi_e|V'_{XX}-V'_{YY}\pm 2iV'_{XY}|\psi_e\rangle \quad . \tag{88c}$$

ii. Electron-Spin Transitions

$$W_{(\mp, M) \to (\pm, M)} = 2j^D(0)M^2 + 4j^{(DG_2)}(\omega_o)B_oM + 2j^{(G_2)}(\omega_o)B_o^2 + W_e^{SR} + X \quad . \tag{89}$$

Here

$$j^D(\omega_o) = j^D(0)\,[1+\omega_o^2\tau_R^2]^{-1} \quad . \tag{90}$$

The g-tensor spectral density is:

$$j^{(G_2)}(\omega_o) = \frac{1}{20}B_o^2\hbar^{-2} \times \left\{\sum_{k=1}^{3}(g_k)^2 - 3g_s^2\right\}\frac{\tau_R}{1+\omega_o^2\tau_R^2} \quad . \tag{91}$$

The g-tensor-dipolar cross-term spectral density is:

$$j^{(DG_2)}(\omega_o) = -\frac{1}{10}\gamma_e B_o \gamma_n \sum_m D^{(m)}g^{(m)}\frac{\tau_R}{1+\omega_o^2\tau_R^2} \tag{92}$$

with $g^{(0)} = 6^{-\frac{1}{2}}[2g_z' - (g_x' + g_y')]$ and $g^{(\pm2)} = \frac{1}{2}(g_x' - g_y')$. The spin-rotational contribution to W_e is in a semi-classical treatment:

$$W_e^{SR} = \frac{IkTC^2}{\hbar^2}\left(\frac{\tau_J}{1+\omega_o^2\tau_J^2}\right) \tag{93}$$

where I is the moment of inertia, C is the spin-rotational constant of the radical (and we have assumed both to be isotropic), and τ_J is the correlation time for the angular momentum, (cf. Atkins, Ch. XI). In liquids, usually $\tau_J \ll \tau_R$, ω_o^{-1}. One has for a Stokes-Einstein model

$$\tau_R = 4\pi\eta a^3/3kT \tag{94a}$$

$$\tau_J = [6IkTr_R]^{-1} \tag{94b}$$

More generally (Atkins Ch. XI) $\overline{C} \cong -2\overline{A}\Delta\overline{g}$ where A is the inverse moment of inertia tensor and $\Delta\overline{g} = \overline{g} - 2.00231$. Then we have (for axially symmetric $\overline{A}$):

$$W_e^G \cong \sum_i (g_i - g_s)^2/40\tau_R \quad (\text{for } \omega_o^2\tau_R^2 \gg 1) \tag{95a}$$

$$W_e^{SR} \cong \sum_i (g_i - g_e)^2/18\tau_R \ . \tag{95b}$$

If these are the dominant terms in W_e, then:

$$W_e \propto \tau_R^{-1} \tag{96a}$$

or

$$W_e \equiv A\ T/\eta \tag{96b}$$

Usually $\tau_R > \omega_o^{-1}$ for free radicals in liquids below room temperature since at X-band $\omega_o^{-1} \cong 1.7 \times 10^{-11}$ sec. Then pseudo-secular dipolar terms dominate in ELDOR or ENDOR. So, from eqs. 83 and 84:

$$W_n \propto \tau_R$$

or

$$W_n \equiv B\ \eta/T \ .$$

Then

$$b = \left(\frac{B}{A}\right)\left(\frac{\eta}{T}\right)^2 \ . \tag{97}$$

If we let

$$\eta \propto Te^{W/kT} \qquad W > 0$$

we get b increasing significantly with decreasing T. This usually leads to better ELDOR and ENDOR signals at reduced temperatures.

iii. Combined Electron-Spin-Nuclear-Spin Transitions.
(Cross-Relaxation)

$$W_{M_s, M \to M_s \pm 1,\ M \mp 1} = \left[\tfrac{1}{3}j^{(D)}(\omega_o) + \tfrac{1}{2}j^{I}(\omega_o)\right] \times [J(J+1) - M(M \mp 1)]. \tag{98}$$

$$W_{M_s, M \to M_s \pm 1,\ M \pm 1} = 2 j^{(D)}(\omega_o)\,[J(J+1) - M(M \pm 1)] \quad . \tag{99}$$

The isotropic dipolar spectral density is:

$$j^{I}(\omega_o) = \gamma_e^2 [\langle a(t)a(t+\tau)\rangle - \bar{a}^2] \frac{\tau_c}{1+\omega_o^2 \tau_c^2} \tag{100}$$

Note that for $j^{D}(\omega_o) \ll j^{D}(0)$ (and small $j^{I}(\omega_o)$) $W_x \ll W_n$ and pseudo-secular terms dominate as noted above.

XVIII.6. HEISENBERG SPIN EXCHANGE AND CHEMICAL EXCHANGE

Heisenberg spin exchange is a very important radical-concentration dependent relaxation mechanism in normal liquids. It is probably the dominant one for $S = \frac{1}{2}$. It may be analyzed by a simple model which also serves as a simple example of the stochastic Liouville approach.[8] We assume radicals exist either as well separated "monomers" or as interacting pairs or "dimers" each with mean lifetimes τ_2 and τ_1 respectively, and with density matrices ρ and σ respectively. The equations of motion are then:

$$i\dot{\rho} = \mathcal{H}_T^{(1)\times} \rho + i \frac{2}{\tau_2} \mathrm{Tr}_s \sigma - i \frac{2}{\tau_2} \rho \tag{101}$$

$$i\dot{\sigma} = (\mathcal{H}_T^{(1)\times} + \mathcal{H}_T^{(2)\times} + \mathcal{H}_J^{\times})\sigma - i\tau_1^{-1}(\sigma - \rho \times \rho) \tag{102}$$

where $\mathcal{H}_T^{(1)}$ is the spin Hamiltonian and $\mathrm{Tr}_s \sigma = \frac{1}{2}(\mathrm{Tr}_1 \sigma + \mathrm{Tr}_2 \sigma)$ is a symmetrized trace over each of the two components of the interacting dimer. Also

$$H_J = J\, S^{(1)} \cdot S^{(2)} \tag{103}$$

where J is twice the exchange integral. One obtains a steady-state solution for σ in the rotating frame. It is then possible to show that when:

$$|J|,\ \tau_1^{-1} \gg |a_i|,\ \omega_1 \tag{104}$$

Eq. 101 is well approximated by:

$$i\dot{\rho} = \mathcal{H}_T^{(1)\times} \rho + i\omega_{HE}[\mathrm{Tr}_s(P\rho \times \rho P) - \rho] \tag{105}$$

where

$$\omega_{HE} = \frac{1}{\tau_2}\left[\frac{J^2 \tau_1^2}{1 + J^2 \tau_1^2}\right] \tag{106}$$

is the Heisenberg exchange frequency. In eq. 105 we have neglected a frequency shift term which is readily shown to be zero in the high temperature approximation, (i.e., $A\rho \cong 1 + \rho'$ with $|\rho'| \ll 1$, cf. eq. 23). Here P is the operator which permutes electron spins. The derivation of eq. 105 is based on the fact that for spins $S = \frac{1}{2}$:

$$H_J^{\times} = \tfrac{1}{2}JP^{\times} \quad . \tag{107}$$

For simple Brownian diffusion of the radicals in solution we have:

$$T_2^{-1} = 4\pi Df\mathfrak{N} \tag{108a}$$

$$T_1^{-1} = (6D/d^2)fe^u \tag{108b}$$

where $\mathfrak{N}$ is the density of radicals, the diffusion coefficient is $D = kT/6\pi a\eta$, and d is the interaction distance for exchange. The factors f and fe^u are introduced for charged radicals to take account of Coulombic and ionic atmosphere effects.[8,9]

The result, eq. 105 means that Heisenberg exchange appears as a simple exchange process analogous to chemical exchange processes for which the well-known Kaplan-Alexander[10] method applies. We let

$$\Phi_H(\chi) \equiv \omega_{HE}[Tr_s(P\sigma \times \sigma P) - \sigma] \tag{109}$$

and add this relaxation term to eq. 17. One then finds that for well separated hyperfine lines the T_2 contributions are:

$$T_{2,HE}^{-1}(ESR,\lambda) = \left(\frac{A-2D_\lambda}{A}\right)\omega_{HE} \tag{110}$$

$$T_{2,HE}^{-1}(NMR) = \tfrac{1}{2}\omega_{HE} \quad . \tag{111}$$

Here D_λ is the degeneracy of the λ^{th} transition, and the $T_2^{-1}(NMR)$ is the width contribution to a well-resolved ENDOR line. The diagonal elements of eq. 109 yield:

$$\tfrac{1}{2}\omega_{HE}[(\chi_{\alpha\mp} - \chi_{\alpha\pm}) + (\chi_+ - \chi_-)] \tag{112}$$

where

$$\chi_\pm = \frac{2}{A}\sum_\gamma \chi_{\gamma\pm} \tag{113a}$$

and

$$\chi_+ + \chi_- = 0 \tag{113b}$$

The notation $\alpha\pm$ in eqs. 112 and 113 refers to the α^{th} nuclear-spin configuration and $M_s = \pm$.

The steady-state solution of eq. 112 in eq. 17 is:

$$\chi_{\alpha+} - \chi_{\alpha-} = 2\chi_+ \tag{114}$$

i.e., differences in population between all pairs of levels differing only in M_s are equal. The unlinearized rate equations yield the s.s. result that all the ratios $\frac{\sigma_{\alpha-}}{\sigma_{\alpha+}}$ are equal.

If in chemical exchange (CE) (i.e., electron transfer), the predominant NMR relaxation of the diamagnetic radical precursors is the CE process, then CE appears to be just like HE in magnetic resonance experiments on the radicals.[4]

We now consider the $\bar{W}$ matrix including eq. 112. Note first that

$$[\Phi_{HE}(\chi)]_{\alpha+\alpha+} + [\Phi_{HE}(\chi)]_{\alpha-\alpha-} = \omega_{HE}\left\{[\tfrac{1}{2}(\chi_{\alpha-} - \chi_{\alpha+}) + \chi_+] + [\tfrac{1}{2}(\chi_{\alpha+} - \chi_{\alpha-}) + \chi_-]\right\} = 0 \tag{115}$$

so that each pair of rows of $\bar{W}$ labeled α^+ and α^- are linearly dependent. Thus, while $\bar{W}^{HE}$ is an A x A matrix, it is of rank A/2, i.e., HE does not act to change $(\chi_{\alpha+} + \chi_{\alpha-})$ but rather to equate all $(\chi_{\alpha+} - \chi_{\alpha-})$. One must add W_n or W_x terms to reduce this high order singularity.

One may alternatively employ another method. Sufficient conditions for this method are:

1. All spin-flip relaxation transitions are of W_e, W_n or ω_{HE}-type (i.e., no W_x).

2.a. $W_{(+,M)\to(-,M)} = W_{(-,M)\to(+,M)}$

b. $W_{(+,M)\to(+,M\pm1)} = W_{(-,M)\to(-,M\pm1)}$

Then we may define a $\pm$A dimensional square matrix W (which is usually non-singular or readily separated into non-singular components) according to

$$[\hat{W}\hat{\chi}]_\lambda \equiv [W\chi]_{\lambda+} - [W\chi]_{\lambda-} \quad . \tag{116}$$

This reduced eigenstate space is found to include only the $\hat{\chi}_\lambda \equiv$

$\chi_{\lambda+} - \chi_{\lambda-}$, which are closely related to pure ESR transitions.

Then if only ESR transitions are induced, we find

$$S_{\lambda,\eta} = 4d_\lambda d_\eta (\hat{W}^{-1})_{\lambda,\eta} = d_\lambda d_\eta \Omega_{\lambda,\eta} \quad . \tag{117}$$

(This method can also be generalized for ENDOR). Using this method one can then prove:[8]

$$\Omega_\lambda = \frac{2}{W_e D_\lambda} \frac{1 + D_\lambda b''}{1 + \frac{1}{2}Ab''} \tag{118}$$

$$b'' = \frac{\omega_{HE}}{AW_e} \tag{118a}$$

with

$$T_{1,\lambda} = \tfrac{1}{4}(D_\lambda \Omega_\lambda) \tag{119}$$

and

$$\Omega_{i,j} = \frac{2}{W_e} \frac{b''}{1 + \frac{A}{2} b''} \quad i \neq j \quad . \tag{120}$$

Equation 118 illustrates the "shorting-out" effect spin exchange has in coupling the different hyperfine lines (cf. eq. 114) without directly leading to electron-spin flips. It follows from eqs. 56 and 118-120 that

$$R \equiv \frac{Z''_{ESR} - Z''_{ELDOR}}{Z''_{ESR}} \tag{121}$$

is (for $\Delta\omega_o = 0$ and the no-saturation condition of eq. 60):

$$R^{-1} = \Omega_p/\Omega_{o,p} + [(1 + \Delta\omega_p^2 T_p^2)/T_p \Omega_{o,p}]dp^{-2} \tag{122}$$

and

$$R_\infty^{-1} = \Omega_p/\Omega_{o,p} = \frac{1 + D_p b''}{D_p b''} = (D_p b'')^{-1} + 1 \quad . \tag{123}$$

Here R_∞ is defined in the same manner as the asymptotic R of Eq. 81. Eauation 123 shows how Heisenberg spin exchange is effective in enabling significant ELDOR reduction factors.

Now for ENDOR, and a single nucleus of spin $I = \frac{1}{2}$, with $W_x = 0$ one has

$$\Omega_e = \frac{1}{W_e} \frac{[2W_e + (W_n + \omega_{HE}/2)]}{W_e + (W_n + \frac{\omega_{HE}}{2})} \tag{124a}$$

$$\Omega_n = \frac{1}{W_n} \frac{[2W_n + (W_e + \omega_{HE}/2)]}{[W_e + \frac{\omega_{HE}}{2} + W_n]} \tag{124b}$$

$$\Omega_{e,n} = (W_e + W_n + \frac{\omega_{HE}}{2})^{-1} \tag{124c}$$

and

$$\xi_e^r(d_n \to \infty) = \frac{W_n}{[2W_n + W_e + \frac{\omega_{HE}}{2}][W_e + W_n + \frac{\omega_{HE}}{2}]} \tag{125}$$

In general if $W_n = 0$ and $W_x = 0$, $\xi_e^r(d_n \to \infty) = 0$ even for more than one magnetic nucleus. Thus Heisenberg exchange is <u>not</u> an effective ENDOR mechanism, i.e. it is ENDOR "inactive", although it is ELDOR "active".

In conclusion, we note that the characteristic behavior of the various relaxation mechanisms as differently manifested in line width, saturation, ELDOR, and ENDOR is a potentially useful approach to separate out the many possible components of relaxation in a particular paramagnetic system.

We present in the Table a summary of these characteristics. This summary should, however, be used with caution.

XVIII.7. ACKNOWLEDGMENT

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Table I
ESR Linewidth and Relaxation Mechanisms

	Linewidths			Saturation-(Ω)		ELDOR	ENDOR		
	Nuclear spin Dependence	Field-Frequency Dependence	Temperature-Viscosity	Activity	Nuclear Spin Dependence	Activity	Activity	Linewidth Contribution	%Enhancement (maximum)
1) G-Isotropic Secular Only	None	Quadratic	As τ_c	None	None	None	None	None	None
2) Dipole-Isotropic									
a) Secular	M^2	None	As τ_c	None	——	None	None	Yes	——
b) Non-secular	M^2	$[1+\omega_o^2\tau_c^2]^{-1}$	As $\tau_c[1+\omega_o^2\tau_c^2]^{-1}$	W_{x_1}	Yes	None unless $W_{x_2} \neq 0$	W_{x_1}	Yes	Goes as W_{x_1}/W_e
3) Isotropic G-Dipole X-Term Secular Only	M	Linear	As τ_c	None	——	None	None	None	——
4) G-Anisotropic									
a) Secular	None	Quadratic	$\tau_R \propto \eta/T$	None	——	None	None	None	——
b) Non-secular	None	$\omega_o^2[1+\omega_o^2\tau_R^2]^{-1}$	$\tau_R[1+\omega_o^2\tau_R^2]^{-1}$	W_e	None	W_e	W_e	Yes	W_e
5) Dipole-Anisotropic									
a) Secular (S_ZI_Z)	M^2	None	τ_R	None	——	None	None	Yes	——
b) Pseudo-secular ($S_ZI_\pm$)	M^2	None	τ_R	W_n	Yes	W_n-Reduction	W_n	Yes	$W_n/W_e \sim 1$
c) Non-secular									
i) $S_\pm I_Z$	M^2	$[1+\omega_o^2\tau_R^2]^{-1}$	$\tau_R[1+\omega_o^2\tau_R^2]^{-1}$	W_e	M^2	W_e	W_e	Yes	W_e
ii) $S_\pm I_\pm, S_\pm I_\mp$	M^2	$[1+\omega_o^2\tau_R^2]^{-1}$	$\tau_R[1+\omega_o^2\tau_R^2]^{-1}$	W_{x_1}, W_{x_2}	Yes	W_x-Enhancement	W_{x_1}, W_{x_2}	Yes	Goes as W_x/W_e
6) Anisotropic G-Dipole X-Term									
a) Secular	M	Linear	τ_R	None	——	None	None	None	None
b) Non-secular	M	$\omega_o[1+\omega_o^2\tau_R^2]^{-1}$	$\tau_R[1+\omega_o^2\tau_R^2]^{-1}$	W_e	M	W_e	W_e	Yes	W_e

7) Quadrupolar									
a) Secular	No width contribution	——	τ_R	None	——	None	None	Yes	——
b) Pseudo-secular	M^2 and M^4	None	τ_R	W_x	Yes	W_n-Reduction	W_n	Yes	$W_n/W_e \sim 1$
8) Spin-Rotation									
a) Secular	None	None	$\tau_J \propto T/\eta$	None	——	None	None	None	——
b) Non-secular	None	None	$\tau_J \propto T/\eta$	W_e	None	W_e	W_e	Yes	W_e
9) Intra-molecular spin-orbit processes									
a) Secular	None	None	Independent	None	——	None	None	None	——
b) Non-secular	None	None	Independent	W_e	None	W_e	W_e	W_e	W_e
10) Zero-Field Splitting $S>\frac{1}{2}$									
a) Secular	None	None	τ_R	None	——	None	None	None	——
b) Non-secular	None	$[1+b^2\omega_o^2\tau_t^2]^{-1}$	$\tau_R[1+b^2\omega_o^2\tau_t^2]^{-1}$	W_e-type	None	W_e-type	W_e-type	Yes	W_e-type
INTERMOLECULAR									
11) Heisenberg Spin Exchange (+Electron Transfer)	Symmetric Dependence on D_M	None	$T/\eta[1+(J\tau_1)^2]^{-1}$ $\tau_1 \propto \eta/T$ for HE	ω_{EX}	Some dependence on D_M	ω_{EX}-Reduction	No	Yes	Decreases Enhancements
12) Dipole-Dipole									
a) Secular $S_{1Z}S_{2Z}+S_{1\pm}S_{2\mp}$ like	Symmetric Dependence on D_M	None	τ_t	None	——	None	None	None	——
b) Pseudosecular $S_{1\pm}S_{2\mp}$ unlike	Symmetric Dependence on D_M	None	τ_t	Analagous to ω_{EX}	Some dependence on D_M	Reduction Analagous to ω_{EX}	No	Yes	Decreases Enhancements
c) Nonsecular $S_{1\pm}S_{2Z}+S_{1\pm}S_{2\pm}$	Symmetric Dependence on D_M	$[1+b^2\omega_o^2\tau_t^2]^{-1}$ b = 1 or 2	$\tau_t[1+b^2\omega_o^2\tau_t^2]^{-1}$	W_e	Some dependence on D_M	W_e	W_e	Yes	W_e

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