ESR SATURATION AND DOUBLE RESONANCE IN LIQUIDS

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XVIII.1. INTRODUCTION TO SATURATION: A SIMPLE LINE

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:

\[
\tilde{M}_y = \frac{\gamma H_1 I_2}{1 + (E_2 \Delta \omega)^2 + \gamma^2 H_1^2 I_1 I_2} \cdot M_0
\]

(1)

with \( M_0 \) the equilibrium magnetization. When we switch to a quantum mechanical description, we can calculate:

\[
M_\pm = M_x \pm iM_y = (\tilde{M}_x \pm i\tilde{M}_y) e^{i\omega t}
\]

(2)

statistically from its associated quantum mechanical operator

\[
M_\pm = \mathcal{N} h \gamma S_\pm
\]

(3)

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

\[
M_\pm(t) = \mathcal{N} h \gamma \text{Tr}[\sigma(t) S_\pm]
\]

(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. VII-20, and we shall neglect effects of higher order than \( R^{(2)} \).
We have from Eq. VIII-20a, that when $\mu_1(t) = 0$, so $R = 0$,

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

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 $\omega_0 = \omega_{ab}$ where $a$ and $b$ are the $M_B = \pm \frac{1}{2}$ and $-\frac{1}{2}$ levels, and there are no other spin levels. Then

$$\langle b | S_- | a \rangle = \langle a | S_+ | b \rangle = 1$$

and

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

with

$$\sigma_{ba}(t) = \exp\left(-i\omega_{ba}t + R_{ba,ba}t\right) \sigma_{ba}(0).$$

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

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

which is the interaction of the spin with a rotating field $B_1'$ = $B_1 (\cos \omega t \hat{\mathbf{i}} + \sin \omega t \hat{\mathbf{j}})$. Then for our simple line the $ \langle b | - | a \rangle$ matrix element of eq. VIII-20 is:

$$\sigma_{ba} = (i \omega_o + R_{ba,ba}) \sigma_{ba} - i d(\sigma_{bb} - \sigma_{aa}) e^{i\omega t}$$

where

$$d = \frac{1}{2} \gamma_e B_1$$

Now the power absorbed from the rotating field is just:

$$P = \omega \hbar \tilde{M}_y = \frac{-\hbar \omega_1 i}{2} [M_+ e^{-i\omega t} - M_- e^{i\omega t}]$$

where from eq. 4 $M_\pm = \text{Tr}_\sigma [\sigma(t)S_{\pm}]$ 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

$$\sigma_{ba} = Z e^{i\omega t}$$

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

$$(\Delta \omega + i R_{ba,ba})Z = d(\sigma_{bb} - \sigma_{aa})$$
where \((\sigma_{bb} - \sigma_{aa})\) is the population difference in the two states.

Now note that \(\sigma\) is Hermitian, so \(\sigma_{ab}^* = \sigma_{ba}\) and

\[
\sigma_{ab}^* = Z^* e^{-i\omega t}.
\]  \(15\)

Thus

\[
P \propto \text{Im} Z = Z' .
\]  \(16\)

We may begin to suspect that \(Z\) plays the role of \(\tilde{M}_r\) (while \(Z^\ast\) is \(\tilde{M}_\perp\)). Also

\[
R_{ba,ba} = -(1/T_b)_{ba} = -(1/T_\perp)_{ab}.
\]

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

\[
\dot{\sigma} = -i[\sigma_o + \epsilon(t),\sigma] + R\sigma .
\]  \(17\)

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

\[
R_{aa,aa} \sigma_{aa} + R_{aa,bb} \sigma_{bb} = d_1(Z - Z^\ast) = -2d\text{Im} Z .
\]  \(18a\)

\[
R_{bb,aa} \sigma_{aa} + R_{bb,bb} \sigma_{bb} = 2d\text{Im} Z .
\]  \(18b\)

Note that

\[
R_{aa,bb} = R_{bb,aa} = 2J_{ab,ab} = W_{ab} = W_{ba} .
\]  \(19a\)

while

\[
R_{aa,aa} = \sum_{\gamma \neq a} W_{a\gamma} .
\]  \(19b\)

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 \(\gamma = b\) only, (i.e., our simple line). Then we have

\[
W_{ab}(\chi_a - \chi_{by}) = 2d\xi^\prime
\]  \(20\)

where we have made the ad hoc replacements:

\[
\sigma_{aa} \rightarrow \chi_a = \sigma_{aa} - \sigma_{oaa} .
\]  \(21a\)

\[
\sigma_{bb} \rightarrow \chi_b = \sigma_{bb} - \sigma_{obb} .
\]  \(21b\)

so that the effects of the \(W_{ab}\), etc. is to lead to thermal equilibrium in the absence of \(\epsilon(t)\). \(\sigma_o\) is the equilibrium value of \(\sigma\). Now eq. 14 is rewritten as:
\[(\Delta \omega - i T_a^{-1})Z + d(\chi_a - \chi_b) = q \omega_0 d\]  \hspace{1cm} (22)

where the high temperature approximation: \(1, 2\)

\[
\sigma_{oaa} - \sigma_{obb} = \frac{e^{-E_a/kT} - e^{-E_b/kT}}{\sum_{\alpha} e^{-E_{\alpha}/kT}} \approx \frac{-h \omega_{ab}}{kTA} \approx -q \omega_0
\]  \hspace{1cm} (23)

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

\[
\begin{pmatrix}
\Delta \omega & T_a^{-1} & d \\
-T_a^{-1} & \Delta \omega & 0 \\
0 & -2d & \gamma_{ab}
\end{pmatrix}
\begin{pmatrix}
Z' \\
Z'' \\
(\chi_a - \chi_b)
\end{pmatrix}
= \begin{pmatrix}
q \omega_0 d \\
0 \\
0
\end{pmatrix}
\]  \hspace{1cm} (24)

This gives:

\[
Z' = \Delta \omega T_a Z''
\]  \hspace{1cm} (24a)

\[
Z'' = \frac{q d \omega_0 T_a}{1 + \Delta \omega ^2 T_a^2 + 4d ^2 T_a T_1}
\]  \hspace{1cm} (24b)

where \(T_1 = (2 \omega_e)^{-1}\) and

\[
(\chi_a - \chi_b) = q \omega_0 d^2 \frac{T_a T_1}{1 + \Delta \omega ^2 T_a^2 + 4d ^2 T_a T_1}.
\]  \hspace{1cm} (24c)

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

\[
2M_o = q \omega_0 = \frac{h \omega_0}{kT} = \sigma_{oaa} - \sigma_{obb}
\]  \hspace{1cm} (25a)

\[
T_a = (T_a)_{ab}, \ T_1 = (T_1)_{ab}
\]  \hspace{1cm} (25b)

\[
\gamma \vec{H} = -\omega_0 \vec{k} + 2d [\hat{t} \cos \omega t + \hat{j} \sin \omega t]
\]  \hspace{1cm} (25c)

\[
Z' = \vec{H}_x, \ Z'' = \vec{H}_y, \ Z = \vec{H}_z
\]  \hspace{1cm} (25d)

\[
\chi_a - \chi_b = 2(M_o - M_z)
\]  \hspace{1cm} (25e)

The above treatment is based on the high field approximation \(|B_o| >> |B_1|\), as well as the fast motional condition \(|\omega_1| T_c << 1\).
It also requires that $|\gamma_{E_1}|\tau_c \ll 1$ 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,

$$E(t) = H_0 + \varepsilon(t)$$

we must define a new interaction representation:

$$\sigma^\pm = U(t)\sigma(t)U^{-1}(t) \quad (26a)$$

$$K^\pm_1(t) = U(t)K_1(t)U^{-1}(t) \quad (26b)$$

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

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

with $U(t_0, t_0) = 1$ and $U(t-\tau,0) = U(t,0)U(t-\tau,t)$. Its solution is the time-ordered exponential:

$$U(t,0) = \exp_o \left( \int_0^t iE(t')dt' \right) \quad (28)$$

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

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

Then we have in the interaction representation:

$$\sigma^\pm = -iK^\pm_1 \sigma^\pm \quad (30)$$

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:

$$\hat{\sigma}^\pm \approx \int_0^\infty d\tau \langle K^\pm_1(t)K^\pm_1(t-\tau) \rangle_c \sigma^\pm(t)$$

$$= -U(t) \int_0^\infty \{ \langle K_1(t)^X [U(t-\tau,t)K_1(t-\tau)U^{-1}(t-\tau,t)^X_c] \rangle \} \, d\tau U^{-1}(t) \quad (31)$$

Then

$$\dot{\sigma} = -i[H(\varepsilon(t),\sigma) - \int_0^\infty d\tau \langle K_1(t)^X [U(t-\tau,t)K_1(t-\tau)U^{-1}(t-\tau,t)]^X \rangle_c \sigma(t) \quad (32)$$
Now the integral in eq. 32 is non-negligible only for $\tau \leq \tau_c$, but since $|c|\tau_c \ll 1$ we can in this interval write
\[ U(t-\tau) = e^{-i\omega \tau} + O(t) \approx e^{-i\omega \tau} \]
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:

![Diagram of spin transitions](image)

Then we have:
\[ \sum_{\alpha \neq \beta} W_{\alpha\beta} (\chi_{\alpha} - \chi_{\beta}) = 2d\text{Im}Z \] (34a)
\[ \sum_{\alpha \neq \beta} W_{\alpha\beta} (\chi_{\alpha} - \chi_{\beta}) = -2d\text{Im}Z \] (34b)

And, for $\alpha \neq a, b$ we get $A-2$ equations:
\[ \sum_{\alpha} W_{\alpha\beta} (\chi_{\alpha} - \chi_{\beta}) = 0 \quad \beta \neq \alpha \] (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:
\[ \text{Tr} \sigma = \text{Tr} \sigma_0 = 1, \text{ or } \text{Tr} \chi = 0 \] (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:
\[ \tilde{W} \tilde{\chi} = \tilde{U} \] (36)
When the rank of $\tilde{W}$ is $A-1$, then replacement of any one equation by eq. 35 yields the matrix $\tilde{W}^{-1}$, which is now non-singular, and we have:

$$\tilde{\chi} = (\tilde{W}^{-1})^{-1} \tilde{U}^{-1}$$  \hspace{1cm} (36a)

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

$$(\chi_a - \chi_b) = \Omega_{ba,ba} v_{ba} [q_w - (\chi_a - \chi_b)]$$  \hspace{1cm} (37)

and from eq. 34

$$dz'' = v_{ba} [q_w - (\chi_a - \chi_b)]$$  \hspace{1cm} (38)

where

$$v_{ba} = 2d^2 T_a (1 + T_a^2 A w^2)$$  \hspace{1cm} (39)

and

$$\Omega_{ba,ba} = 2 C_{ba,ba} / C$$  \hspace{1cm} (40)

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

$$\Omega_{\alpha\beta,\gamma\delta} = 2 C_{\alpha\beta,\gamma\delta} / C$$  \hspace{1cm} (40a)

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

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

$$T_1 \rightarrow \frac{1}{2} \Omega_{ba,ba} = \frac{1}{2} \Omega_{ba}$$  \hspace{1cm} (41)

where $\Omega_{ba}$ is the saturation parameter for the $b \rightarrow a$ 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 $\tilde{W}$ matrix).

This $\Omega_{ba}$ may be regarded as a steady-state self-impedance representing the response of the $b \rightarrow a$ transition to the application
of an rf field. I.e., we rewrite eqs. 37 and 38 as:

$$\langle \chi_a - \chi_b \rangle = \Omega_{ba} \cdot (dZ')$$

(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 $\Omega_{ba}$.

\[ \text{XVIII.2. ELDOR}^{3} \]

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

Now we have

$$\mathcal{E}(t) = \frac{1}{\hbar} \gamma_e B_0 \left[ S_e \exp(-i\omega_o t) + S_e \exp(+i\omega_o t) \right]$$

$$+ \frac{1}{\hbar} \gamma_e B_p \left[ S_e \exp(-i\omega_p t) + S_e \exp(+i\omega_p t) \right] .$$

(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

$$|\gamma_{e \rightarrow o}|, |\gamma_{e \rightarrow p}|, |R| \ll |\omega_{aa}, - \omega_{bb}| \sim |a| ,$$

(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:

$$\sigma'_a = \chi'_a = Z_a \exp(i\omega_o t) \equiv Z_o \exp(i\omega_o t)$$

$$\sigma'_b = \chi'_b = Z'_b \exp(i\omega_p t) \equiv Z_p \exp(i\omega_p t)$$

(45a)

(45b)

We obtain from eq. 17:

$$[\Delta \omega_o - 1/T_{a, o}] Z_o + d_o (\chi_a - \chi_b) = q_{aa} d_o \equiv q_{ew} d_o$$

(46a)
\[ [\Delta w_p - iT_2, p] Z_p + d_p (\chi_b - \chi_b^r) = q w_{bb} / d_p \approx q w_e / d_p \]  \tag{46b}

Also, the analogues of eqs. 34 are now:

\[ \sum_{\alpha \neq \alpha'} W_{a \alpha} (\chi_a^r - \chi_{\alpha'}) = 2d_o Z_o^r \]  \tag{47a}

\[ \sum_{\alpha \neq b} W_{a \alpha} (\chi_a^r - \chi_{\alpha}) = -2d_o Z_o^r \]  \tag{47b}

\[ \sum_{\alpha \neq \alpha'} W_{a \alpha} (\chi_a^r - \chi_{\alpha'}) = 2d P_o^r \]  \tag{47c}

\[ \sum_{\alpha \neq \alpha'} W_{a \alpha} (\chi_b^r - \chi_{\alpha'}) = -2d P_o^r \]  \tag{47d}

These equations may be rewritten in matrix form as:

\[ (\bar{K} + i\bar{R}) \bar{Z} = \bar{D} \bar{X} + \bar{Q} \]  \tag{48a}

\[ \bar{w}^j (\chi) = -2d^{trj} \bar{Z} \]  \tag{48b}

where

\[ \bar{Q} \equiv q w_e / d_p \]  \tag{49a}

\[ K = \begin{pmatrix} \Delta w_b & 0 \\ 0 & \Delta w_p \end{pmatrix} \]  \tag{49b}

\[ R = \begin{pmatrix} -1 & 0 \\ 0 & T_2, p \end{pmatrix} \]  \tag{49c}

\[ D = \begin{pmatrix} d_o & -d_o & 0 & 0 \\ 0 & d_p & -d_p \end{pmatrix} \]  \tag{49d}

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

\[ \bar{Z}^r = M^{-1} (-R^{-1}) \bar{Q} \]  \tag{50a}

\[ \bar{Z}' = (-R^{-1}) \bar{D} \bar{X} \]  \tag{50b}

\[ \bar{D} \bar{X} = -\bar{Z} \bar{Z}^r \]  \tag{50c}
where
\[
M = 1 + (\bar{R}^{-1})^2 + (-\bar{R}^{-1})S
\] (51a)

and
\[
S = 2 [\bar{D}(W^1)^{-1} tr \bar{J}] .
\] (51b)

Suppose \( d = 0 \). One recovers the single-line, simple saturation result and by comparison, we find
\[
S_{o, o} = d_o^2 \Omega_{a'o}, a'a' = d_o^2 \Omega_{o, o}
\] (52)

One finds more generally:
\[
S_{i, j} = d_i d_j \Omega_{i, j}
\] (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 \( \alpha \rightarrow \beta \) being the \( i \)th transition and \( \gamma \rightarrow \sigma \) the \( j \)th transition.]

Thus eq. 50c is a generalization of eq. 42 for the single resonance case. In fact it gives
\[
(X_{a'} X_{a'}) = d_o^2 \Omega_{o, o} Z'' + d_p \Omega_{o, p} Z''
\] (54a)
\[
(X_{b'} X_{b'}) = d_p \Omega_{p, p} Z'' + d_o \Omega_{p, o} Z''
\] (54b)

with an electrical circuit analogy similar to that of eq. 42. It follows from eqs. 49-53 that:
\[
M = \begin{pmatrix}
1 + \Delta w_o^2 T_o, o^2 + d_o^2 T_o, o & d_o d_p \Omega_{o, p} T_a, o \\
d_p d_o \Omega_{p, o} T_a, p & 1 + \Delta w_p^2 T_p, o + d_p \Omega_{p, o}
\end{pmatrix},
\] (55)

where we have let \( \Omega_{o, o} = \Omega_o \) and \( \Omega_{p, p} = \Omega_p \). Then from eq. 50a:
\[
Z''_o = q_w T_o, o d_o \frac{1 - \varepsilon_o / \Omega_{p, o}}{1 + \Delta w_o^2 T_o, o^2 + \Omega_o - \varepsilon_o}
\] (56a)

with
\[
\varepsilon_o = d_p^2 T_p, p \Omega_{p, o} \Omega_{o, o} / (1 + \Delta w_p^2 T_p, o^2 + \Omega_p) .
\] (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:

$$d^2_T T_{pp} \gg 1.$$  \hspace{1cm} (57)

Then:

$$g_0^r (d^2 \rightarrow \infty) = \frac{\Omega_{o,p} \Omega_p \omega_o}{\Omega_p} \hspace{1cm} (58)$$

which is just relaxation determined. We now let $T_s, p = T_p'$, etc.

Then

$$Z^2 = qu_T \frac{(\Omega_p - \Omega_{o,p})/\Omega_p}{1 + T_0^2 \omega_o^2 + d^2_T (\Omega_o \Omega_p - \Omega_{o,p} \Omega_p \omega_o)/\Omega_p}.$$  \hspace{1cm} (59)

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

$$d^2_T (\Omega_o \Omega_p - \Omega_{o,p} \Omega_p \omega_o)/\Omega_p \ll 1 \hspace{1cm} (60)$$

one has the simple result that:

$$Z^2 = qu_T \frac{1}{1 + \omega_o^2 T_0^2} \left[ 1 - \frac{\Omega_{o,p}}{\Omega_p} \right] \hspace{1cm} (61)$$

Since $\Omega_p$ is always positive, 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:

<table>
<thead>
<tr>
<th>$a$</th>
<th>$W_n$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_o$</td>
<td>$W_n$</td>
<td>$W_p$</td>
</tr>
</tbody>
</table>

is easily understood. Let $P_i$ be the population of the $i^{th}$ state. Then saturation by $W_p$ 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 Overhauser 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:

\[
\begin{align*}
\epsilon(t) = & \frac{1}{2} \gamma_e \beta_e \left[ S_+ \exp(-i\omega_e t) + S_- \exp(i\omega_e t) \right] \\
& + \frac{1}{2} \gamma_n \beta_n \left[ I_+ \exp(-i\omega_n t) + I_- \exp(i\omega_n t) \right] \\
& + \frac{1}{2} \gamma_e \beta_e \left[ S_+ \exp(-i\omega_e t) + S_- \exp(i\omega_e t) \right] \\
& + \frac{1}{2} \gamma_n \beta_n \left[ I_+ \exp(-i\omega_n t) + I_- \exp(i\omega_n t) \right].
\end{align*}
\] (62)

In eq. 62, the microwave field at frequency \( \omega_e \) is to induce electron-spin flips, while the rf field at frequency \( \omega_n \) 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:

[Diagram of a four-level system with transitions labeled by energies and magnetic quantum numbers.]

Let us assume the following four-level system:
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with

\[ \Delta_e \equiv w_e - w_{ea} \approx 0 \]  

\[ \Delta_n \equiv w_n - w_{an} \approx 0 \]  

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

\[ \chi_{a_a} = z_{a_a} e^{i\omega_a t} = z_e e^{i\omega_e t} \]  

\[ \chi_{b_a} = z_{b_a} e^{i\omega_n t} = z_n e^{i\omega_n t} \]  

We obtain the series of equations:

\[ [\Delta_e - i/T_e] z_e + d_e (\chi_a - \chi_a') + d_n z_{b_a} = q_w d_e \]  

\[ [\Delta_n - i/T_n] z_n + d_n (\chi_a - \chi_b') - d_e z_{b_a} = q_w d_n \]  

\[ [\Delta_e + \Delta_n - i/T_n] z_{b_a} - d_e z_n + d_n z_e = 0 \]  

Note the appearance of

\[ \chi_{b_a} = z_{b_a} e^{i(\omega_e + \omega_n)t} = z_x e^{i(\omega_e + \omega_n)t} \]  

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

\[ \sum_{\alpha \neq a} w_{a \alpha} (\chi_{a \alpha} - \chi_{\alpha}) = 2d e z_{a a}' \]  

\[ \sum_{\alpha \neq a} w_{a \alpha} (\chi_{a \alpha} - \chi_{\alpha}) = -2d e z_{a a}' + 2d n z_{a b}' \]  

\[ \sum_{\alpha \neq \beta} w_{\beta \alpha} (\chi_{\beta \alpha} - \chi_{\alpha}) = 0 \]  

\[ \sum_{\alpha \neq \beta} w_{\beta \alpha} (\chi_{\beta \alpha} - \chi_{\alpha}) = -2d n z_{a b}' \]  

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:

\[ K = \begin{pmatrix} \Delta_e & 0 & d_n \\ 0 & \Delta_n & -d_e \\ d_n & -d_e & \Delta_e + \Delta_n \end{pmatrix} \]
and is no longer diagonal. Also intensities are proportional to

\[
Q = q \begin{pmatrix}
\omega_d e \\
\omega_n d \\
0
\end{pmatrix}
\]

but because \( \frac{\omega_e}{\omega_n} \approx 1 \) for protons, we may usually set

\[
Q \approx q \begin{pmatrix}
\omega_d e \\
0 \\
0
\end{pmatrix}
\]

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 \( \Omega_n = \Omega_n = 0 \), since this is the condition under which double-resonance effects will be maximized. Equations 65-67 and 50-51 then yield:

\[
Z^x = Z^x = Z^x = 0
\]

\[
Z^x_{e e} = \frac{q \omega_d T}{1 + d^2 T^e T_n + e^2 T_n T_n}
\]

where

\[
\xi^x_e = \frac{T_n x + |\Omega_n^e|}{1 + d^2 T^e T_n + e^2 T_n T_n}
\]

Thus from eq. 70b when

\[
1 + d^2 \Omega^e_{e e} \gg d^2 T^e T_n
\]

(\( \xi^x_e \approx \Omega^e_{e e} \))

the coherence effect on \( Z^x \) may be neglected. \( \xi^x_e \) leads to an enhancement of a saturated ESR signal, since it effectively reduces the saturation parameter \( \Omega^e_{e e} \). Now when

\[
1 + d^2 \Omega^e_{n n} \gg d^2 T^e T_n
\]

it follows from eq. 70c that the ratio \( \xi^x_e / \Omega^e_{e e} \) will not be affected
by \( \Delta e' \) and further if

\[
|\Omega_{e,n}| \gg T_x
\]  

(73)

we may completely neglect the coherence effects.

If there is appreciable saturation and

\[
d^2_e \sim d^2_n
\]  

(74)

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

\[
\Omega_{e,n} \gg T_x
\]  

(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 \( \Delta e', \Delta n \approx 0 \) are:

\[
Z^e = \frac{q\omega_d^e}{1+(\Delta T_e)^2 + (\Omega_{e,n} - \xi_e)^2 T_e^2} d^2_e
\]  

(56a)

\[
\xi_e = \frac{d^2_n (\Omega_{e,n})^2 T_n}{1+(\Delta T_n)^2 + d^2_n T_n \Omega_n}
\]  

(56b)

If the ENDOR spectrum is monitored after subtraction of the ESR signal; then for \( \Delta e = 0 \) and \( \Omega_{e,n} d^2_e \gg 1 \) we have

\[
Z^e_{\text{ENDOR}} - Z^e_{\text{ESR}} = q\omega_d^e \left( \frac{\Omega_{e,n}^2}{\Omega_e^2} \right) \left( \frac{d^2_T n}{1+(\Delta T_n)^2 + \left[ 1 - \frac{\Omega_{e,n}^2}{\Omega_e^2} \right] T_n \Omega_n d^2_n} \right)
\]  

(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:

\[
\Omega_n \left( 1 - \frac{\Omega_{e,n}^2}{\Omega_e \Omega_n} \right)
\]  

(78)

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

\[
\% \text{enh} = \frac{Z^e_{\text{ENDOR}} - Z^e_{\text{ESR}}}{Z^e_{\text{ENDOR}}} = \frac{\xi_e d n^2}{\Omega_{e,n} \Omega_e - \xi_e \Delta n} \left[ \frac{\Omega_{e,n} \Omega_e}{\Omega_{e,n}} \right]^{-1}
\]  

(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. In this formal solution, $\overline{Z}$ is a vector in the space of all induced transitions and $\overline{\chi}$ 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 $\overline{Z}$ are those in which there is (are) increase(s) in spin quantum number but no decrease(s) in spin quantum number. 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,

$$|\gamma_{e_{1}}^{B_{1}}|, \quad |\gamma_{1}^{B_{1}}|, \quad |\gamma_{e_{1}}^{a_{1}}|, \quad \tau_{c}^{-1}, \quad \gg \epsilon(t), \quad |R| \tag{80}$$

where $\tau_{c}$ 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:

![Diagram of a 4-level system with transition probabilities](image)

We can solve for $C_{i1}$ and $C_{ij,k1}$ the cofactors and double cofactors of the $\widetilde{W}$ matrix to obtain all the $\Omega_{i,j,k1}$.

A. ELDOR—Generalized No Saturation of Observing Mode.

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

$$R \equiv \% \text{ reduction} = \frac{\Omega_{p1}}{\Omega_{p}} = \frac{W_{n}^{2}W_{x_{1}}W_{x_{2}}}{W_{e}^{2}W_{n}^{2}W_{x_{1}}W_{x_{2}} + (W_{e}W_{n}W_{x_{1}})(W_{e}W_{n}W_{x_{2}})} \quad (81)$$
Clearly if \( W_n^2 > W_n W_{x_1} W_{x_2} \) one has a reduction in signal, while if \( W_n^2 < W_n W_{x_1} W_{x_2} \) there will be an enhancement.

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

\[
R = \frac{W_n}{2 W_e + W_n} = \frac{b}{2 + b} \quad \text{where} \quad b = \frac{W_n}{W_e}
\]

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

\[
R = -\frac{b}{4 + 5b}
\]

or an enhancement.

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

B. ENDOR—Limiting Enhancements.

We have from eq. 79 that the \( Z \) enhancement \( E \) is given by:

\[
1 + E^{-1} = \frac{\Omega_{n,e}}{\Omega_{e,n}} = \frac{[W_n (2W_n + W_{x_1} + W_{x_2}) + (W_n + W_{x_1} + W_{x_2}) (W_n + W_{x_1} + W_{x_2})] x}{[W_n (2W_n + W_{x_1} + W_{x_2}) + (W_n + W_{x_1} + W_{x_2}) (W_n + W_{x_1} + W_{x_2})] x} \times \frac{[W_{x_2} (W_n + W_{x_1} + W_{x_2}) + W_n W_{x_1} W_{x_2}]^2}{W_{x_2} (W_n + W_{x_1} + W_{x_2}) + W_n W_{x_1} W_{x_2}}
\]

(82)

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

\[
E = \frac{1}{2 [2 + b + b^{-1}]} \quad \text{for} \quad b \gg 1, \quad b \gg 1 \quad \text{and} \quad b \ll 1 \quad \text{and} \quad b = 1 \rightarrow \frac{1}{6}
\]

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

\[
E = \frac{W_{x_2}}{W_e}
\]

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 $W_2 = 4W_n$, $W_1 = \frac{2}{3}W_n$ (dipolar, extreme narrowing).

$$E = \frac{b[22.5 + 60b + 40b^2]}{6 + b[25 + 34b + 15b^2]} \quad \text{with} \quad b \gg 1 \rightarrow (\frac{8}{3})b$$

$$b \ll 1 \rightarrow 3.75b$$

$$b = 1 \rightarrow 1.53$$

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

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

$$E = \frac{b[2.5 + 10b + 10b^2]}{6 + b[45 + 84b + 45b^2]} \quad \text{with} \quad b \gg 1 \rightarrow \frac{2}{9}$$

$$b \ll 1 \rightarrow (\frac{5}{12})b$$

$$b = 1 \rightarrow 1/8$$

C. Expressions for Transition Probabilities

We assume a single set of completely equivalent nuclei with total nuclear spin quantum number $J$ and total z component $M$. (We do not explicitly 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. We do not explicitly indicate $K$ in the equations below.)

i. Nuclear-Spin Transitions

a. Dipolar:

$$W(M_s, M) \rightarrow (M_s, M+1) = \frac{1}{2} \langle J \rangle J^{(0)}[J(J+1)-M(M+1)]$$

(83)

where the electron-nuclear dipolar spectral density $J^{(0)}$ is:

$$J^{(0)} = \frac{1}{5} \gamma_e^2 \gamma_n^2 \hbar^2 \sum_m D_m^2 |\tau_R|^2$$

(84)

with $\tau_R$ the rotational correlation time, and it is assumed $|w_n|\tau_R| < 1$. The dipolar coefficients are:

$$D_m^2 = \left( \frac{6\pi}{5} \right)^3 \langle \psi_e | r^{-3} \gamma_2, m(\theta', \varphi') | \psi_e \rangle$$

(85)

where $\theta'$, and $\varphi'$ 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 1):

\[
W(M_s, M) \rightarrow (M_s, M \pm 1) = 2J^Q(0)\left[I(I+1) - M(M \pm 1)\right]^{1/2} (86a)
\]

\[
W(M_s, M) \rightarrow (M_s, M \pm 2) = 2J^Q(0)\left[I(I+1) - M(M \pm 1)\right]^{1/2} (M+1)(M+2)\right] (86b)
\]

where

\[
j^Q(0) = \frac{r^2}{80} \frac{e^2 Q^2}{h^2} \frac{1}{(2I - 1)} \sum_{m} |\psi_e(m)|^2 (87)
\]

with electric-field-gradient irreducible-tensor components:

\[
\psi_e(0) = -\left(\frac{3}{2}\right)^{1/2} \psi_e \left|V_{ZZ}^f\right| \psi_e (88a)
\]

\[
\psi_e(\pm 1) = \pm \left(\psi_e \left|V_{XX}^f \pm i V_{YY}^f\right| \psi_e (88b)
\]

\[
\psi_e(\pm 2) = \pm i \left(\psi_e \left|V_{XY}^f \pm i V_{YX}^f\right| \psi_e (88c)
\]

ii. Electron-Spin Transitions

\[
W(\pm, M) \rightarrow (\pm, M) = 2J^D(0)M^2 + 4J^D(G_2)\left(\omega_o B_o M^2 \right. + 2J^D(G_2)\left(\omega_o B_o^2 + \omega_e\right) + X (89)
\]

\[
W(\pm, M) \rightarrow (\pm, M) = 2J^D(0)\left[1 + \omega_o^{-2} \right] \tau_R^{-1} (90)
\]

The g-tensor spectral density is:

\[
j^D(G_2)\left(\omega_o^2 = \frac{1}{20} \frac{B_o^2}{h^2} \left(\frac{3}{\sum_{k=1}^3 (g_k)^2 - 3g_2^2}\right) \frac{\tau_R}{1 + \omega_o^2 \tau_R} (91)
\]

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

\[
j^D(G_2)\left(\omega_o^2 = \frac{1}{10} \frac{B_o Y_o Y_n}{\sum D(m) g(m)} \frac{\tau_R}{1 + \omega_o^2 \tau_R} (92)
\]

with \n g^{(0)} = \frac{3}{2} \left[2g_2^f - \left(g_x^f + g_y^f\right) \right] and g^{(\pm 2)} = \frac{3}{2} \left(g_x^f - g_y^f\right). The spin-rotational contribution to \n W_e is in a semi-classical treatment:

\[
W_{SR} = \frac{\hbar^2 C^2}{\hbar^2} \left(\frac{\tau_J}{1 + \omega_o^2 \tau_J} (93)
\]
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 $\tau_J$ is the correlation time for the angular momentum, (cf. Atkins, Ch. XI). In liquids, usually $\tau_J \ll \tau_R$, $w_o^{-1}$. One has for a Stokes-Einstein model

$$\tau_R = \frac{4\pi \eta a^3}{3kT}$$  \hspace{1cm} (94a)

$$\tau_J = \left[6kT\tau_R\right]^{-1}$$  \hspace{1cm} (94b)

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

$$W^C_e = \sum_i (g_i - g_e)^2/40\tau_R \quad \text{(for } w_o^2 \tau R^2 \gg 1)$$  \hspace{1cm} (95a)

$$W_{e}^{SR} = \sum_i (g_i - g_e)^2/18\tau_R$$  \hspace{1cm} (95b)

If these are the dominant terms in $W_e$, then:

$$W_e \propto \tau_R^{-1}$$  \hspace{1cm} (96a)

or

$$W_e = A T/\eta$$  \hspace{1cm} (96b)

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

$$W_n \propto \tau_R$$

or

$$W_n = B \eta/T$$

Then

$$b = \left(\frac{B}{A}\right)^{2} \left(\frac{1}{T}\right)^{2}$$  \hspace{1cm} (97)

If we let

$$\eta \propto T e^{W/kT} \quad W > 0$$

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


(Cross-Relaxation)

$$W_{M_g,M_s+1}^{M_\pm 1,M_\pm 1} = \left[\frac{1}{2}j^D(w_o) + \frac{1}{2}j^I(w_o)\right] x [J(J+1) - M(M+1)].$$  \hspace{1cm} (98)
\[ W_{M_s, M \rightarrow M_s \pm 1, M \pm 1} = 2 \beta^D(\omega_0) \left[ J(J+1) - M(M+1) \right] . \]  

(99)

The isotropic dipolar spectral density is:

\[ j^I(\omega_0) = \gamma_e^2 \frac{2}{1+\omega_0^2} \frac{\tau_c}{\gamma_e^2} \]  

(100)

Note that \( j^D(\omega_0) << j^D(0) \) (and small \( j^I(\omega_0) \)) \( W_x \ll W_n \) 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 \( \tau_2 \) and \( \tau_1 \) respectively, and with density matrices \( \rho \) and \( \sigma \) respectively. The equations of motion are then:

\[ i\dot{\rho} = \kappa_T^{(1)} \rho + \frac{2}{\tau_2} \text{Tr}_s \sigma - \frac{2}{\tau_2} \rho \]  

(101)

\[ i\dot{\sigma} = \kappa_T^{(2)} \rho + \kappa_T^{(1)} \rho + \kappa_J \sigma - i\tau_1^{-1} (\sigma \rho \times \rho) \]  

(102)

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

\[ H_J = J S^{(1)} \cdot S^{(2)} \]  

(103)

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

\[ |J|, \tau_1^{-1} \gg |a_1|, \omega_1 \]  

(104)

Eq. 101 is well approximated by:

\[ i\dot{\rho} = \kappa_T^{(1)} \rho + i\omega_{HE} \left[ \text{Tr}_s (\rho \rho \times \rho \rho) - \rho \right] \]  

(105)

where

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

(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., Ap ≈ 1 + ρ' with |ρ'| ≪ 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 $S = \frac{1}{2}$:

$$\mathcal{H}_J^X = \frac{1}{2} J P^X$$  \hfill (107)

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

$$\tau_2^{-1} = 4 \pi D f R$$  \hfill (108a)

$$\tau_1^{-1} = (6D/d^2) f e^u$$  \hfill (108b)

where $\mathcal{R}$ is the density of radicals, the diffusion coefficient is
$D = kT/6 \pi \eta d$, 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 pro-
cesses for which the well-known Kaplan-Alexander 10 method applies.

We let

$$\Phi_H(\chi) \equiv \omega_{\text{HE}} \left[ T_2 (\mathcal{R} \chi \times \mathcal{R} \chi) - \sigma \right]$$  \hfill (109)

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

$$T_2^{-1}_2, \text{HE (ESR, } \lambda) = \left( \frac{A - 2D_\lambda}{A} \right) \omega_{\text{HE}}$$  \hfill (110)

$$T_2^{-1}_2, \text{HE (NMR)} = \frac{1}{2} \omega_{\text{HE}}$$  \hfill (111)

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

$$\frac{1}{2} \omega_{\text{HE}} \left[ (\chi_{\chi} \mp \chi_{\chi}) + (\chi_+ - \chi_-) \right]$$  \hfill (112)

where

$$\chi_{\pm} = \frac{2}{A} \sum_{\gamma} \chi_{\gamma \pm}$$  \hfill (113a)

and

$$\chi_+ + \chi_- = 0$$  \hfill (113b)
The notation \( \alpha \pm \) in eqs. 112 and 113 refers to the \( \alpha \)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 \( \frac{\omega_{\alpha^-}}{\omega_{\alpha^+}} \) 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.

We now consider the \( \tilde{W} \) matrix including eq. 112. Note first that

\[
\begin{align*}
[\Phi_{HE}(\chi)]_{\alpha^+} &+ [\Phi_{HE}(\chi)]_{\alpha^-} - \omega_{HE}(\chi)_{\chi\chi^+} = [\Phi_{HE}(\chi)]_{\chi\chi^+} + \chi_+ \\
+ [\Phi_{HE}(\chi)]_{\chi\chi^-} + \chi_- \end{align*} \tag{115}
\]

so that each pair of rows of \( \tilde{W} \) labeled \( \alpha^+ \) and \( \alpha^- \) are linearly dependent. Thus, while \( \tilde{W}^{HE} \) is an \( \Lambda \times \Lambda \) matrix, it is of rank \( \Lambda/2 \), i.e., HE does not act to change \( \chi_{\alpha^+} \) but rather to equate all \( \chi_{\alpha^+} \). One must add \( \tilde{W}_n \) or \( \tilde{W}_x \) 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 \( \tilde{W}_e \), \( \tilde{W}_n \) or \( \tilde{W}_x \)-type (i.e., no \( \tilde{W}_x \)).
2. a. \( \tilde{W}(+, M) = \tilde{W}(-, M) \to (+, M) \)
   b. \( \tilde{W}(+, M) = \tilde{W}(-, M) \to (+, M\pm 1) \)

Then we may define a \( \Lambda \) dimensional square matrix \( \tilde{W} \) (which is usually non-singular or readily separated into non-singular components) according to

\[
[\tilde{W}^\Lambda_\chi]_{\lambda} = [\tilde{W}^\Lambda_x]_{\lambda^+} - [\tilde{W}^\Lambda_x]_{\lambda^-} \tag{116}
\]

This reduced eigenstate space is found to include only the \( \chi_\lambda \).
\[ \chi_\lambda^+ - \chi_\lambda^- \] which are closely related to pure ESR transitions.

Then if only ESR transitions are induced, we find

\[ S_{\lambda, \eta} = 4 d_\lambda d_\eta \left( W^{-1} \right)_{\lambda, \eta} = d_\lambda d_\eta \Omega_{\lambda, \eta} \]  \hspace{1cm} \text{(117)}

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

\[ \Omega_\lambda = \frac{2}{W_\lambda} \frac{1 + D_\lambda b^\prime}{1 + \frac{D_\lambda b^\prime}{2} \Delta_\lambda} \]  \hspace{1cm} \text{(118)}

with

\[ b^\prime = \frac{\mu_{\text{HE}}}{\Delta W_e} \]  \hspace{1cm} \text{(118a)}

and

\[ T_{1, \lambda} = \frac{1}{2} (D_\lambda \Omega_\lambda) \]  \hspace{1cm} \text{(119)}

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

\[ R = \frac{Z_{\text{ESR}} - Z_{\text{ELDOR}}}{Z_{\text{ESR}}} \]  \hspace{1cm} \text{(121)}

is (for \( \Delta w_0 = 0 \) and the no-saturation condition of eq. 60):

\[ R^{-1} = \frac{\Omega_p}{\Omega_{o, p}} + \frac{\left( 1 + \Delta w_p^2 \right)}{T_p \Omega_{o, p}} \]  \hspace{1cm} \text{(122)}

and

\[ R^{-1}_\infty = \frac{\Omega_p}{\Omega_{o, p}} \frac{1 + D_{o, p} b^\prime}{D_{o, p} b^\prime} = (D_{o, p} b^\prime)^{-1} + 1 \]  \hspace{1cm} \text{(123)}

Here \( R_\infty \) is defined in the same manner as the asymptotic \( R \) of Eq. 81. Equation 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 \( W_K = 0 \) one has
\[ \Omega_e = \frac{1}{W_e} \frac{[2W_e + (W_n + \frac{u_{HE}}{2})]}{W_e + (W_n + \frac{u_{HE}}{2})} \]  

(124a)

\[ \Omega_n = \frac{1}{W_n} \frac{[2W_n + (W_e + \frac{u_{HE}}{2})]}{W_e + \frac{u_{HE}}{2} + W_n} \]  

(124b)

\[ \Omega_{e,n} = (W_e + W_n + \frac{u_{HE}}{2})^{-1} \]  

(124c)

and

\[ \frac{W_n}{[2W_n + W_e + \frac{u_{HE}}{2}] [W_e + W_n + \frac{u_{HE}}{2}]} \]  

(125)

In general if \( W_n = 0 \) and \( W_e = 0 \), \( \xi_e^{R}(d \rightarrow \infty) = 0 \) even for more than one magnetic nucleus. Thus Heisenberg exchange is not 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**

This work was supported in part by the Advanced Research Projects Agency and by the National Science Foundation.
| Table I |
| ESR Linewidth and Relaxation Mechanisms |

<table>
<thead>
<tr>
<th>Linewidths</th>
<th>Saturation-(n)</th>
<th>ELDOR</th>
<th>ENDOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear spin dependence</td>
<td>Field-frequency dependence</td>
<td>Temperature-viscosity</td>
<td>Activity</td>
</tr>
<tr>
<td>1) G-Isotropic Secular Only</td>
<td>None</td>
<td>Quadratic</td>
<td>As $\tau_c$</td>
</tr>
<tr>
<td>2) Dipole-Isotropic</td>
<td>a) Secular</td>
<td>$n^2$</td>
<td>None</td>
</tr>
<tr>
<td>b) Non-secular</td>
<td>$n^2$</td>
<td>Quadratic</td>
<td>As $\tau_c$</td>
</tr>
<tr>
<td>3) Isotropic G-Dipole X-Term Secular Only</td>
<td>Linear</td>
<td>As $\tau_c$</td>
<td>None</td>
</tr>
<tr>
<td>4) G-Anisotropic a) Secular</td>
<td>None</td>
<td>Quadratic</td>
<td>$\tau_R = \frac{\pi}{2}$</td>
</tr>
<tr>
<td>b) Non-secular</td>
<td>$n^2$</td>
<td>Quadratic</td>
<td>$\tau_R = \frac{\pi}{2}$</td>
</tr>
<tr>
<td>5) Dipole-Anisotropic a) Secular ($S_{z\perp}$)</td>
<td>None</td>
<td>None</td>
<td>Quadratic</td>
</tr>
<tr>
<td>b) Pseudo-secular ($S_{z\perp}$)</td>
<td>$n^2$</td>
<td>None</td>
<td>Quadratic</td>
</tr>
<tr>
<td>c) Non-secular</td>
<td>None</td>
<td>Quadratic</td>
<td>$\tau_R = \frac{\pi}{2}$</td>
</tr>
<tr>
<td>1) $S_{z\perp}$</td>
<td>$n^2$</td>
<td>Quadratic</td>
<td>$\tau_R = \frac{\pi}{2}$</td>
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<tr>
<td>2) $S_{z\perp} S_{\perp} S_{\perp}$</td>
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<td>Quadratic</td>
<td>$\tau_R = \frac{\pi}{2}$</td>
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<tr>
<td>6) Anisotropic G-Dipole Z-Term a) Secular</td>
<td>Linear</td>
<td>As $\tau_c$</td>
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<tr>
<td>b) Non-secular</td>
<td>$n^2$</td>
<td>Quadratic</td>
<td>As $\tau_c$</td>
</tr>
</tbody>
</table>

Notes:
- ELDOR and ENDOR activities may depend on additional parameters not listed.
- Enhancement factors may vary depending on experimental conditions.
- $n$: electron spin quantum number.
- $\tau_R$: relaxation time.
- $\tau_c$: correlation time.
- $W$: linewidth contribution.
<table>
<thead>
<tr>
<th>7) Quadrupolar a) Secular</th>
<th>No width contribution</th>
<th>$\tau_R$</th>
<th>None</th>
<th>None</th>
<th>None</th>
<th>None</th>
<th>Yes</th>
<th>$W_n$</th>
<th>Yes</th>
<th>$W_n/W_n &lt; 1$</th>
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<tbody>
<tr>
<td>b) Pseudo-secular</td>
<td>$H^2$ and $H^6$</td>
<td>$\tau_R$</td>
<td>$W_n$</td>
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<td>$W_n$-Reduction</td>
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<tr>
<td>8) Spin-rotation a) Secular</td>
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<td>$\tau_j = \gamma/\eta$</td>
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<td>None</td>
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<td>None</td>
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<td>None</td>
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<tr>
<td>b) Non-secular</td>
<td>None</td>
<td>$\tau_j = \gamma/\eta$</td>
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<td>9) Intramolecular spin-orbit processes a) Secular</td>
<td>None</td>
<td>Independent</td>
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<td>None</td>
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<td>None</td>
<td>None</td>
<td>None</td>
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<tr>
<td>b) Non-secular</td>
<td>None</td>
<td>Independent</td>
<td>$W_\sigma$-type</td>
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<td>10)Zero-Field Splitting $${\Delta g}$$ a) Secular</td>
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<td>$W_\sigma$</td>
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<td>b) Non-secular</td>
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<td>$(1 + \eta^2 \Delta g^2)^{-1}$</td>
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<td>$W_\sigma$-type</td>
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<td>INTRAMOLECULAR</td>
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<tr>
<td>11) Heisenberg Spin Exchange (Electron Transfer)</td>
<td>Symmetric Dependence on $N_H$</td>
<td>$\tau_j = \gamma/\eta$</td>
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<td>12) Dipole-dipole a) Secular</td>
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<tr>
<td>b) Pseudosecular $\bullet - \bullet$ alike</td>
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<tr>
<td>c) Nonsecular $\bullet - \bullet$ unlike</td>
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<td>$W_\sigma$</td>
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<td>---</td>
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</tbody>
</table>
References