

# Theory of saturation and double resonance in ESR spectra. V. The average ENDOR and ELDOR lines\*

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The general theory for the analysis of saturation and double resonance effects in the ESR spectra of dilute solutions of free radicals developed in the earlier papers in this series, has been solved approximately to obtain relatively simple formulas for the general case of free radicals with many nuclei. The solution is based on an expansion linear in  $b \equiv W_n/W_e$  (where  $W_n$  and  $W_e$  are, respectively, the lattice-induced pure nuclear-spin and electron-spin flip relaxation rates), but it is asymptotically valid for Heisenberg and (polarized) chemical exchange processes. Also, coherence effects are neglected. The resulting expressions for ENDOR take the simple form of a single average (saturated) Lorentzian for each distinct ENDOR line obtained from a particular group of equivalent nuclei; while for ELDOR one similarly obtains an average ELDOR line shape. Expressions are given for the average saturation parameters that are needed in terms of the various relaxation mechanisms. The range of validity of these solutions is analyzed and discussed. In the case of equivalent nuclei of spins of  $1/2$ , an interesting result is that the relative ENDOR enhancement of the ESR signal is in lowest order, approximately directly proportional to the number of equivalent spins ( $I=1/2$ ) under certain conditions such as when the NMR resonance is not significantly saturated. This result, when applicable, can prove quite useful for analytical purposes. It is, however, no longer valid for ENDOR signals from groups of equivalent nuclei for which  $I > 1/2$ , and it must be modified, even for  $I=1/2$ , if lattice-induced cross transitions involving combined electronic and nuclear spin transitions are more important than pure  $W_n$ , and these considerations are discussed. Effects of having equivalent nuclei which are not completely equivalent are also discussed. Details regarding the structure and simplifying symmetry considerations of the general solutions are also given.

## I. INTRODUCTION

Over the last several years a detailed general theory has been developed for the analysis of saturation and double resonance effects in the ESR spectra of dilute solutions of free radicals.<sup>1-6</sup> These have included explanations for the experiments of ENDOR and ELDOR, which result from saturation effects. The analysis depends critically on the magnitudes of the lattice-induced spin-relaxation transitions such as:  $W_e$  (electron spin flips),  $W_n$  (nuclear spin flips), and  $\omega_{EX}$  (Heisenberg and/or chemical exchange frequencies). While the latter two are useful ELDOR mechanisms,  $W_n$  (and not  $\omega_{EX}$ ) is a useful ENDOR mechanism.

We have, in these laboratories, conducted extensive experiments to test the validity and range of applicability of this theory with primary emphasis on ENDOR,<sup>7-9</sup> but including saturation<sup>5,7-9</sup> and ELDOR<sup>10</sup> as well. There has recently been a growing application of these techniques in many laboratories, and the recent literature for studies in liquids has been reviewed.<sup>11</sup> Much of the work in ENDOR has been as an analytical tool, although Allendoerfer and Maki<sup>12</sup> offer a simple phenomenological treatment of some of their ENDOR results.

It is clear from the recent experimental work<sup>7-9,11,12</sup> that a primary problem of importance in the application of these techniques is in the intensities associated with the ENDOR and ELDOR signals. Thus, for example,

in ENDOR, an understanding of the relative intensities of the signals from different groups of nuclear spins having different splittings would be very useful in assigning the splittings properly. In general, these intensities are complex functions of the different relaxation terms noted above. While the general theory<sup>1-6</sup> is, in principle, fully applicable to a complicated case involving multiple resonance spectra from radicals with many magnetic nuclei, only actual results for some simple cases of radicals with only a few magnetic nuclei have been given. The more complicated cases may be handled by obtaining appropriate computer solutions<sup>7</sup> of the general matrix expressions which involve superpositions of coupled (saturated) resonance transitions. However, a separate computer solution is required for each situation, and even it becomes unwieldy as the number of nuclei increases.

It therefore appeared desirable to develop approximate analytical expressions for the general case of many nuclei, which, however, would necessarily have a limited range of applicability. The expansion parameter found most convenient theoretically and also most useful experimentally is  $b \equiv W_n/W_e$ . (This parameter  $b$  is more carefully defined in Sec. III.) The latter is because, in many experimental situations of free radicals in liquids, one expects  $b \ll 1$ . That is,  $W_n$  usually results from rotational modulation of electron-nuclear dipolar (END) interactions,<sup>1-6</sup> and these are often much smaller than  $W_e$  terms, such as spin-rotational or  $g$ -

tensor interactions,<sup>2,7,8</sup> in normal liquids. These points are particularly relevant with respect to methyl protons, because their internal rotational motion averages the END terms to be significantly smaller than, e.g., a ring proton<sup>7</sup>; and furthermore the existence of several methyl groups in the radical renders even a computer solution somewhat unwieldy.

It has been shown in the analysis of ENDOR<sup>1-3,6</sup> that values of  $b \sim 1$  (as defined in this section) give optimum ENDOR signals. However, one often observes ENDOR under much less than favorable circumstances. In our laboratories, for example, ENDOR signals of enhancements as low as 0.1% in the absence of Heisenberg exchange and 0.01% in the presence of exchange may be observed fairly routinely.<sup>7-9</sup> The requirement of our treatment, that  $b \ll 1$ , still allows for the possibility of enhancements even greater than 1%, as will be seen.

When an expansion of the general solution is carried out to lowest order terms in  $b$  (i.e., linear terms), it is possible to derive relatively simple expressions which yield what we call "average-ENDOR" and "average-ELDOR" lines. These are lines that have a simple (saturated) Lorentzian appearance, and are characterized by a single average width and saturation parameter. This result is, in a sense, a generalization of the concept of an average unsaturated ESR width<sup>13-16</sup> to the realm of saturation and double resonance phenomena.

In Sec. II the general solutions are briefly reviewed, some matrix transformations needed to simplify their analysis are discussed, and the approximations leading to average ENDOR are developed. The approximations needed for obtaining the saturation parameters conveniently are developed in Sec. III. Average ELDOR is discussed in Sec. IV. The effects of having equivalent nuclei which are not completely equivalent are discussed in Sec. V. A summary is given in Sec. VI. General properties of the transition moment and saturation matrices needed both for average ENDOR and ELDOR and for more general solutions are given in Appendix A, and the effects of cross transitions  $W_x$  (mutual electron-nuclear spin flips) are discussed from the viewpoint of average ENDOR and ELDOR in Appendix B.

## II. GENERAL EXPRESSIONS AND AVERAGING: ENDOR

We start with the matrix equations which define steady-state saturation and multiple resonance experiments<sup>1-6</sup>:

$$(\mathbf{K} + i\mathbf{R})\mathbf{Z} = \mathbf{d}\mathbf{X} + \mathbf{Q} \quad (2.1)$$

and

$$\mathbf{W}\mathbf{X} = -2\mathbf{d}^{\text{tr}}\mathbf{Z}'', \quad (2.2)$$

where  $\mathbf{Z} = \mathbf{Z}' + i\mathbf{Z}''$  as well as the normalization condition

$$\text{Tr}\mathbf{X} = 0, \quad (2.3)$$

which is needed because the transition probability

matrix  $\mathbf{W}$  is always singular. The solution to these equations may be written as

$$\mathbf{Z}'' = \mathbf{M}^{-1}(-\mathbf{R}^{-1})\mathbf{Q}, \quad (2.4)$$

$$\mathbf{Z}' = (-\mathbf{R}^{-1})\mathbf{K}\mathbf{Z}'', \quad (2.5)$$

with

$$\mathbf{M} = \mathbf{1} + (\mathbf{R}^{-1}\mathbf{K})^2 + (-\mathbf{R}^{-1})\mathbf{S} \quad (2.6)$$

and

$$\mathbf{S} = [2\mathbf{d}(\mathbf{W}^i)^{-1}\mathbf{d}^{\text{tr}i}]. \quad (2.7)$$

In Eqs. (2.1)-(2.7),  $\mathbf{K}$  is the coherence matrix,  $\mathbf{R}$  the relaxation, or linewidth matrix,  $\mathbf{S}$  is the saturation matrix,  $\mathbf{d}$  is the matrix of transition moments (note that in Papers I-IV the symbol  $\mathbf{D}$  has been used),  $\mathbf{Z}$  is a vector which includes the induced transitions, while the vector  $\mathbf{X}$  includes all the spin eigenstates. Their definitions and descriptions are given in some detail in I-IV and to some extent below. It is usually advantageous to redefine the  $\mathbf{X}$  vector as follows.<sup>5</sup> Let  $X_{\lambda,+}$  and  $X_{\lambda,-}$  correspond to the  $m_s = +$  and  $-$  states corresponding to the  $\lambda$ th transition with degeneracy index  $j$ . Then let  $\hat{X}_{\lambda,j} \equiv X_{\lambda,+} - X_{\lambda,-}$  and  $\tilde{X}_{\lambda,j} \equiv X_{\lambda,+} + X_{\lambda,-}$ . We may then rewrite Eq. (2.2) as partitioned matrices:

$$\begin{pmatrix} \hat{\mathbf{W}} & \mathfrak{B} \\ \mathfrak{B}^{\text{tr}} & \tilde{\mathbf{W}} \end{pmatrix} \begin{pmatrix} \hat{\mathbf{X}} \\ \tilde{\mathbf{X}} \end{pmatrix} = -2 \begin{pmatrix} \hat{\mathbf{d}}^{\text{tr}} \\ \tilde{\mathbf{d}}^{\text{tr}} \end{pmatrix} \mathbf{Z}''. \quad (2.8)$$

Note that we can define an orthogonal matrix  $\mathbf{O}_x$  by

$$\begin{pmatrix} \hat{\mathbf{X}} \\ \tilde{\mathbf{X}} \end{pmatrix} = \sqrt{2}\mathbf{O}_x\mathbf{X} \quad (2.9)$$

which represents the transformation between  $\mathbf{X}$  vectors, and may be used to transform  $\mathbf{W}$  and  $\mathbf{d}^{\text{tr}}$  as well. This transformation is particularly useful when the matrix elements of  $\mathbf{W}$  (a symmetric matrix in the high temperature approximation) obey

$$W_{\alpha\pm,\beta\mp} = W_{\alpha\mp,\beta\pm} \quad (2.10a)$$

and

$$W_{\alpha\pm,\beta\pm} = W_{\alpha\mp,\beta\mp} \quad (2.10b)$$

(where  $\alpha$  and  $\beta$  represent any nuclear-spin configurations and the  $\pm$  signs refer to  $m_s$ ) for then it is easy to show  $\mathfrak{B}$  in Eq. (2.8) is zero.<sup>5</sup> Thus, when Eqs. (2.10) apply, we can rewrite Eq. (2.7) as

$$\begin{aligned} \mathbf{S} &= 4 \begin{bmatrix} \hat{\mathbf{W}}^{-1} & 0 \\ 0 & \tilde{\mathbf{W}}^{-1} \end{bmatrix} \begin{bmatrix} \hat{\mathbf{d}}^{\text{tr}} \\ \tilde{\mathbf{d}}^{\text{tr}i} \end{bmatrix} \\ &= 4[\mathbf{d}\hat{\mathbf{W}}^{-1}\hat{\mathbf{d}}^{\text{tr}} + \tilde{\mathbf{d}}(\mathbf{W}^i)^{-1}\tilde{\mathbf{d}}^{\text{tr}i}], \end{aligned} \quad (2.11)$$

where  $\hat{\mathbf{W}}$  and  $\tilde{\mathbf{W}}$  may be separately inverted. The singularities in  $\mathbf{W}$  now appear in  $\tilde{\mathbf{W}}$ , so it must be modified by incorporation of Eq. (2.3) for each subgroup of eigenstates whose sum of probabilities remains a constant. Equations (2.4)-(2.6) with Eq. (2.11) replacing (2.7) give the solution.

Further simplifications accrue from recognizing that, when there are completely equivalent nuclei (labeled the  $r$ th set) one may average over degenerate states as well as degenerate transitions labeled by  $\kappa$  corresponding to a particular set of values of the  $\{J_r\}$  and  $\{M_r\}$ , where  $J_r = \sum_{i \text{ in } r} J_{r_i}$  and  $M_r = \sum_{i \text{ in } r} M_{r_i}$  and the sum is over the individual equivalent spins. The curly brackets refer to the collection of  $J_r$  and  $M_r$  values, respectively, for all the different sets of completely equivalent nuclei. (In the case of a particular NMR transition we, of course, mean an  $M_r \leftrightarrow M_r \pm 1$  transition.) Thus we define

$$Z_{\lambda}^{\text{av}} \equiv \sum_{\kappa} Z_{\lambda_{\kappa}} \quad (2.12)$$

and

$$X_{\lambda_{\pm}}^{\text{av}} = \sum_{\kappa} X_{\lambda_{\kappa \pm}} \quad (2.13)$$

which are, respectively, sums over the  $Z$  components for the  $\lambda$ th degenerate transition, Eq. (2.12), and the diagonal density-matrix elements (actually their deviations from thermal equilibrium value) for the states between which these transitions occur. More specifically we note that Eq. (2.13) may be written as

$$\hat{X}_{\lambda}^{\text{av}} = \sum_j \hat{X}_{\lambda_j} \quad (2.13')$$

and

$$\tilde{X}_{\lambda}^{\text{av}} = \sum_j \tilde{X}_{\lambda_j} \quad (2.13'')$$

Then the solutions become

$$\mathbf{Z}'^{\text{av}} = (\mathbf{M}^{\text{av}})^{-1} (-\mathbf{R}^{\text{av}})^{-1} \mathbf{D} \mathbf{Q}^{\text{av}}, \quad (2.14)$$

$$\mathbf{Z}^{\text{av}} = (-\mathbf{R}^{\text{av}})^{-1} \mathbf{K}^{\text{av}} \mathbf{Z}'^{\text{av}}, \quad (2.15)$$

with

$$\mathbf{M}^{\text{av}} = \mathbf{1} + [(\mathbf{R}^{\text{av}})^{-1} (\mathbf{K}^{\text{av}})]^2 + (-\mathbf{R}^{\text{av}})^{-1} \mathbf{S}^{\text{av}} \quad (2.16)$$

and

$$\mathbf{S}^{\text{av}} = 4\mathbf{D}[\hat{\mathbf{d}}^{\text{av}}(\hat{\mathbf{W}}^{\text{av}})^{-1}\hat{\mathbf{d}}^{\text{av},\text{tr}} + \tilde{\mathbf{d}}^{\text{av}}(\tilde{\mathbf{W}}^{\text{av},i})^{-1}\tilde{\mathbf{d}}^{\text{av},\text{tr}}] \quad (2.17)$$

where "av" indicates the matrices in the reduced subspaces defined by Eqs. (2.12), (2.13'), and (2.13''). (The  $\mathbf{W}^{\text{av}}$  elements are defined in terms of the  $X_{\lambda_{\pm}}^{\text{av}}$ 's as opposed to the  $X_{\lambda_{\pm}}^{\text{av}'}$ 's.) Here  $\mathbf{D}$  is a diagonal matrix, such that  $D_{\lambda,\eta} = D(\lambda)\delta_{\lambda,\eta}$  gives the degeneracy of the  $\lambda$ th transition [cf. Eq. (2.12)] as well as the degeneracy of the  $\lambda$ th eigenstate pair [cf. Eqs. (2.13') and (2.13'')].

The construction of the  $\mathbf{W}^{\text{av}}$  and  $\mathbf{R}^{\text{av}}$  matrices is discussed for several special cases in papers II and IV. Those involved averaging over all transitions, etc., corresponding to a particular hyperfine line regardless of differences in  $\{J_r\}$  value between components of that line, so they are necessarily approximate (i.e., END terms were neglected). The present summation over only components of the same  $\{J_r\}$  value is exact, since

one may write

$$R_{\lambda_i, \lambda_j} = R_{\lambda, \lambda}^{\text{d}} \quad \text{all } j \text{ in } \lambda, \quad (2.18a)$$

$$R_{\lambda_i, \eta_k} = R_{\lambda, \eta}^{\text{non}} \quad \lambda_j \neq \eta_k, \quad (2.18b)$$

where superscripts d and non refer, respectively, to diagonal and nondiagonal matrix elements in transition space. We assume completely equivalent nuclei in Eqs. (2.18), so the only off-diagonal elements in  $\mathbf{R}$  [Eq. (2.18b)] come from exchange terms. The specific expressions for  $\mathbf{R}$  which include END and exchange terms are given by Ref. 13, I, and II. In the  $\mathbf{K}$  matrix, the off-diagonal terms come from the  $d_{\lambda_i}$  coupling transitions corresponding to the same partner functions of a given  $\{J_r\}$  value (cf. I). Then

$$K_{\lambda_i, \eta_k} = K_{\lambda, \eta} \delta_{j, k} \quad (2.18c)$$

(i.e., while the  $\lambda$ th and  $\eta$ th transitions may be different, only the partner functions of the same spin permutation symmetry may be coupled). Similarly, one has for the  $\mathbf{W}$  matrix

$$\hat{W}_{\lambda_i, \lambda_j} = \hat{W}_{\lambda, \lambda}^{\text{d}} \quad \text{all } j \text{ in } \lambda, \quad (2.18d)$$

while for the off-diagonal elements we write separately for the exchange and END contributions

$$\hat{W}(\text{ex})_{\lambda_i, \eta_k} = \hat{W}(\text{ex})_{\lambda, \eta} \quad \lambda_j \neq \eta_k, \quad (2.18e)$$

$$\hat{W}(\text{END})_{\lambda_i, \eta_k} = \hat{W}(\text{END})_{\lambda, \eta} \delta_{j, k} \quad \lambda \neq \eta. \quad (2.18f)$$

The form of  $\mathbf{S}^{\text{av}}$  given by Eq. (2.17) is that of a nonsymmetric matrix due to the presence of  $D(J)$ . One finds that if  $\mathbf{R}^{\text{av}}$  has nondiagonal elements, it also may be nonsymmetric. The nonsymmetric character of these matrices is introduced only if there are off-diagonal elements between transitions (or states) corresponding to different  $\{J_r\}$  values. The presence of exchange processes will lead to such matrix elements. The  $\mathbf{K}^{\text{av}}$  matrix remains symmetric because its elements preserve selection rules dependent on  $\{J_r\}$  values.

One can symmetrize the solutions, Eqs. (2.14)–(2.17), by introducing a similarity transformation  $\mathbf{D}^{1/2}$  defined by  $D_{\lambda, \eta}^{1/2} = [D(\lambda)]^{1/2} \delta_{\lambda, \eta}$ . Then

$$(\mathbf{D}^{1/2})_{\lambda, \eta}^{-1} \equiv (D^{-1/2})_{\lambda, \eta} = [D(\lambda)]^{-1/2} \delta_{\lambda, \eta}. \quad (2.19)$$

Then if we let a symmetrized operator such as  $\mathbf{M}$  be  $\mathbf{M}^{\text{s}} \equiv \mathbf{D}^{-1/2} \mathbf{M}^{\text{av}} \mathbf{D}^{1/2}$  and a vector such as  $\mathbf{Z}^{\text{s}} \equiv \mathbf{D}^{-1/2} \mathbf{Z}^{\text{av}}$ , we have<sup>16</sup>

$$\mathbf{Z}^{\text{s}'} = (\mathbf{M}^{\text{s}})^{-1} (-\mathbf{R}^{\text{s}})^{-1} \mathbf{Q}^{\text{s}} \quad (2.20)$$

with

$$\mathbf{M}^{\text{s}} = \mathbf{1} + [\mathbf{R}^{\text{s}} \mathbf{K}^{\text{s}}]^2 + (-\mathbf{R}^{\text{s}})^{-1} \mathbf{S}^{\text{s}} \quad (2.21)$$

and

$$\mathbf{S}^{\text{s}} = 4\hat{\mathbf{d}}(\hat{\mathbf{W}}^{\text{s}})^{-1}\hat{\mathbf{d}}^{\text{tr}} + 4\tilde{\mathbf{d}}(\tilde{\mathbf{W}}^{\text{s},i})^{-1}\tilde{\mathbf{d}}^{\text{tr},i}. \quad (2.22)$$

Note that the symmetrized saturation parameter  $\Omega_{\lambda_i, \eta_k}^{\text{s}}$  is given by

$$S_{\lambda_i, \eta_k}^{\text{s}} = d_{\lambda_i} d_{\eta_k} \Omega_{\lambda_i, \eta_k}^{\text{s}}. \quad (2.22')$$

An alternative way to derive Eqs. (2.20)–(2.22) is to start with Eqs. (2.4)–(2.7) before averaging. Then

introduce an orthogonal transformation  $\mathbf{U}$  by the requirement that

$$\begin{aligned}
 (\mathbf{UZ}')_{\lambda_1, \nu} &= \{1/[D(\lambda)]^{1/2}\} Z_{\lambda}''^{\nu} \\
 &= \{1/[D(\lambda)]^{1/2}\} \sum_j Z_{\lambda_j}'' \quad (2.23)
 \end{aligned}$$

so

$$U_{\lambda_1, \nu, \lambda_j} = 1/[D(\lambda)]^{1/2} \quad (2.23')$$

while the other  $U_{\lambda_i, \nu, \lambda_j}$  represent the coefficients of the  $i$ th linear combination of the  $Z_{\lambda_j}$  which is orthonormal to the other linear combinations (l.c.'s) in the  $\lambda$ th subspace spanned by the degenerate transitions  $Z_{\lambda_j}$ . Thus

$$\begin{aligned}
 \sum_j U_{\lambda_i, \nu, \lambda_j} U_{\lambda_j, \lambda_k, \nu}^{\text{tr}} &= \delta_{\lambda_i, \nu, \lambda_k, \nu} \\
 &= \{1/[D(\lambda)]^{1/2}\} \sum_j U_{\lambda_j, \lambda_k, \nu}^{\text{tr}}. \quad (2.24)
 \end{aligned}$$

An orthogonal matrix  $\mathbf{V}$  with similar characteristics to  $\mathbf{U}$  may be introduced by

$$(\mathbf{V}\hat{\mathbf{X}})_{\lambda_1, \nu} = \{1/[D(\lambda)]^{1/2}\} X_{\lambda}^{\nu} \quad (2.25)$$

with equations similar to Eqs. (2.23') and (2.24), where we are taking linear combinations of the  $\lambda$ th set of eigenstate pairs.

Note that from Eq. (2.18) utilizing Eq. (2.24) we obtain, after some manipulation for  $R_{\lambda_i, \nu, \eta}^{\nu}$ ,

$$\begin{aligned}
 R_{\lambda_i, \nu, \eta}^{\nu} &= \sum_{j \text{ in } \lambda, k \text{ in } \eta} U_{\lambda_i, \nu, \lambda_j} R_{\lambda_j, \eta} U_{\eta k, \nu}^{\text{tr}} \\
 &= \{(R_{\lambda, \lambda}^{\text{d}} - R_{\lambda, \lambda}^{\text{non}}) \delta_{\lambda, \eta} \\
 &\quad + R_{\lambda, \eta}^{\text{non}} [D(\lambda)D(\eta)]^{1/2} \delta_{i, 1}\} \delta_{i, l}. \quad (2.26)
 \end{aligned}$$

This equation shows that the  $\lambda_1^{\nu}$  sum mode only couples to other sum modes  $\eta_1^{\nu}$ , which is, of course,

expected. Similarly we obtain for the  $\mathbf{K}$  matrix

$$K_{\lambda_i, \nu, \eta_i, \nu}^{\nu} = K_{\lambda, \eta} \delta_{i, l}, \quad (2.27)$$

while for  $\hat{\mathbf{W}}^{\nu}$  we obtain<sup>17</sup>

$$\begin{aligned}
 \hat{W}_{\lambda_i, \nu, \eta_i, \nu}^{\nu} &= [\{\hat{W}_{\lambda, \lambda}^{\text{d}} - \hat{W}(\text{ex})_{\lambda, \lambda}\} \delta_{\lambda, \eta} + \hat{W}(\text{ex})_{\lambda, \eta} \\
 &\quad + \hat{W}(\text{ex})_{\lambda, \eta} [D(\lambda)D(\eta)]^{1/2} \delta_{i, 1} + \hat{W}(\text{END})_{\lambda, \eta}\} \delta_{i, l}. \quad (2.28)
 \end{aligned}$$

In all these cases the completely symmetric l.c.  $\lambda_1^{\nu}$  only couples to other completely symmetric l.c.'s  $\eta_1^{\nu}$ .

### A. A Single Set of Completely Equivalent Nuclei

There is another transformation of importance. This is the one which transforms all the  $D(M)$  degenerate ESR transitions belonging to the  $M$ th hyperfine line. Its function is to transform all the  $Z_J(\kappa)_{,M}$  into linear combinations (l.c.'s) which are symmetry functions belonging to the permutation group of  $D(M)$  identical objects. The most important l.c. is the totally symmetric function (symmetry  $\Gamma_1$ )

$$\begin{aligned}
 Z_M &= \{1/[D(M)]^{1/2}\} \sum_{\kappa, J} Z_J(\kappa)_{,M} \\
 &= \{1/[D(M)]^{1/2}\} \sum_J Z_{J, M}^{\nu}, \quad (2.29)
 \end{aligned}$$

which gives the total absorption of the  $M$ th line, and the most important property of the other l.c.'s is that they are orthogonal to this one.

Since we have already seen that it is sufficient to consider only the  $Z_{J, M}^{\nu}$ , it is only necessary to consider the subset of dimension equal to all the different  $J$  values for a given  $M$  of symmetry functions which are l.c.'s of these  $\{1/[D(J)]^{1/2}\} Z_{J, M}^{\nu}$ . Call this orthogonal transformation  $\mathbf{O}$ . Then one need only operate in this subspace as  $\mathbf{O}D^{-1/2}Z''^{\nu}$ , to obtain  $Z_M$ , and one may conveniently transform Eqs. (2.20)–(2.22) by  $\mathbf{O}$ . For example, for the  $M=0$  line for a system containing four equivalent protons we have

$$\begin{matrix} J=2 & J=1 & J=0 \\ \Gamma_1 & \begin{pmatrix} 6^{-1/2} & 2^{-1/2} & 3^{-1/2} \\ -6^{-1/2} & 2^{-1/2} & -3^{-1/2} \\ (2/3)^{1/2} & 0 & -3^{-1/2} \end{pmatrix} \\ \mathbf{O} = \Gamma_2 & \\ \Gamma_3 & \end{matrix} = [D(M=0)]^{-1/2} \begin{pmatrix} D(J=2)^{1/2} & D(J=1)^{1/2} & D(J=0)^{1/2} \\ -D(J=2)^{1/2} & D(J=1)^{1/2} & -D(J=0)^{1/2} \\ 2D(J=2)^{1/2} & 0 & -D(J=0)^{1/2} \end{pmatrix}, \quad (2.30)$$

where  $D(J=2)=1$ ,  $D(J=1)=3$ ,  $D(J=0)=2$  and  $D(M=0)=6$ . In general, then  $M$ :

$$\begin{aligned}
 O_{\Gamma_{1eJ}}(M) &= [\sum_{J \text{ in } M} D(J)]^{-1/2} D(J)^{1/2} \\
 &= D(M)^{-1/2} D(J)^{1/2} \quad (2.31a)
 \end{aligned}$$

and

$$O_{\Gamma_{1eJ}}^{-1}(M) = O_{eJ \Gamma_1}^{\text{tr}} = O_{\Gamma_{1eJ}}. \quad (2.31b)$$

Note that  $\mathbf{O}$  is an operator on only the subspace of electron-spin transitions summed over degeneracies in  $J^{(k)}$ . It may be regarded as a unit matrix on the subspace of nuclear-spin transitions (which have also been summed over degeneracies in  $J^{(k)}$ ).

We now assume that the simplified form of ENDOR is applicable,<sup>1</sup> i.e.,

(1)  $\mathbf{K}^{\nu}$  is diagonal—the rf and microwave powers

are weak enough that coherence effects are negligible, and

(2)  $\mathbf{R}^s$  is diagonal (except for exchange coupling of degenerate transitions)—i.e., (a) the END terms are not a very large component of the ESR or ENDOR linewidths and (b) the chemical or Heisenberg exchange, which may be present, still leaves the different ESR lines well separated.

Now Condition 2a will mean that the ESR linewidths for the unsaturated components of the  $M$ th degenerate line are nearly equal despite differences in their  $J$  values.

Therefore, we have  $\mathbf{OR}^s\mathbf{O}^{-1}$  becoming essentially diagonal, and let

$$-\sum_J O_{\Gamma_{1eJ}}(M) R_{ii}^s O_{eJ\Gamma_1}^{-1}(M) \equiv T_{2,e}^{-1} \\ = -[1/D(M)] \sum_{J \text{ in } M} R_{J,M}^s D(J). \quad (2.32)$$

Condition 2a with respect to the ENDOR linewidth is usually equivalent to having  $b \ll 1$ , and, when this is the case, the symmetrized saturation parameters  $\Omega_{eJ,M}^s$  for the  $M$ th degenerate line are nearly the same as are the off-diagonal  $\Omega_{eJ,M eJ',M}^s$ . Then we may define

$$d_e^2 \Omega_e(M) \equiv \sum_{J,J' \text{ in } M} O_{\Gamma_{1eJ}}(M) S_{eJ,eJ'}^s O_{eJ'\Gamma_1}^{-1}(M) = [d_e^2/D(M)] \left\{ \sum_{J \text{ in } M} D(J) \Omega_{eJ}^s + \sum_{J \neq J'} [D(J)D(J')]^{1/2} \Omega_{eJ,eJ'}^s \right\} \quad (2.33)$$

and this transformation approximately diagonalizes  $S_{eJM,eJ',M}^s$ . The diagonalization is exact if  $b=0$ . (Note that if the basis for  $O$  includes any degenerate symmetry species  $\Gamma_d$  then only block diagonalization may be achieved, but this is unimportant to us, since  $\Gamma_1$ , the totally symmetric mode, has been approximately uncoupled from all others.)

Then the absorption given by  $[D(M)]^{1/2} Z''_M$  becomes<sup>18</sup> utilizing a Cauchy expansion on  $OM^sO^{-1}$

$$[D(M)]^{1/2} Z''_M \approx \frac{D(M) q \omega_e d_e T_{2,e}(M)}{1 + [T_{2,e}(M) \Delta \omega_e(M)]^2 + [\Omega_e(M) - \xi_e(M)] d_e^2 T_{2,e}(M)}, \quad (2.34)$$

where

$$d_e^2 \xi_e(M) = \sum_{\substack{n_i, n_j = \text{induced} \\ \text{nuclear transitions}}} (M^s O^{-1})_{n_i, \Gamma_1} (OM^s)_{\Gamma_1, n_j} F_{n_i n_j} / F, \quad (2.35)$$

where  $F$  is the determinant of elements  $f_{n_i n_j}$  formed from  $(OR^s O^{-1})(OM^s O^{-1})$  (with  $OR^s O^{-1}$  essentially diagonal) by considering only the subspace of nuclear transitions,<sup>19</sup> and  $F_{n_i n_j}$  is the  $n_i n_j$ th cofactor of  $F$ . Now

$$(OM^s)_{\Gamma_1, n_i} = [1/D(M)]^{1/2} \sum_{J \text{ in } M} D(J)^{1/2} S_{eJ, n_i}^s \\ = [d_e/D(M)]^{1/2} \sum_{J \text{ in } M} d_{n_i} D(J)^{1/2} \Omega_{eJ, n_i}^s \quad (2.36a)$$

and

$$(M^s O^{-1})_{n_i, \Gamma_1} = (OM^s)_{\Gamma_1, n_i}. \quad (2.36b)$$

For the  $i$ th and  $j$ th nuclear transitions one has

$$f_{n_i, n_j} = [T_{2, n_i}^{-1} + T_{2, n_i} (\Delta \omega_{n_i})^2] \delta_{i,j} + d_{n_i} d_{n_j} \Omega_{n_i, n_j}^s. \quad (2.37)$$

One finds that if (1) the NMR transitions are only weakly saturated or (2)  $b \ll 1$  (see Sec. III) then

$$d_{n_i} d_{n_j} \Omega_{n_i, n_j}^s \ll T_{2, n_i}^{-1} + T_{2, n_i} (\Delta \omega_{n_i})^2 + d_{n_i}^2 \Omega_{n_i}^s \quad \text{any } i, j, \quad (2.38)$$

and the diagonal elements of  $F$  are much greater than the off-diagonal elements.<sup>20</sup> Then, by using an expansion on diagonal elements [cf. Eqs. (3.8) and (3.9) of Sec. III] one has to lowest order

$$\xi_e(M) \approx \sum_{n_j} [d_{n_j}^2 \Omega_{\Gamma_1, n_j}^s T_{2, n_j} / (1 + T_{2, n_j}^2 \Delta \omega_{n_j}^2 + d_{n_j}^2 \Omega_{n_j}^s T_{2, n_j})], \quad (2.39a)$$

where

$$\Omega_{\Gamma_1, n_j} \equiv D(M)^{-1/2} \sum_{J \text{ in } M} D(J)^{1/2} \Omega_{eJ, n_j}^s. \quad (2.39b)$$

Now Condition 2a means that

$$T_{2, n_j} = \langle T_{2, n} \rangle + \epsilon_{n_j} \quad (2.40a)$$

with

$$|\epsilon_{n_j}| \ll \langle T_{2, n} \rangle, \quad (2.40b)$$

where  $\langle T_{2,n} \rangle$  is an appropriate average over nuclear transitions. When Eq. (2.38) follows because of weak NMR saturation, then for

$$T_{2,n_i}' \equiv T_{2,n_i} (1 + d_{n_i}^2 T_{2,n_i} \Omega_{n_i}^s)^{-1/2} \equiv T_{2,n_i} Y_{n_i}^{-1/2} \quad (2.41)$$

one easily finds that

$$Y_{n_i} = \langle Y_n \rangle + \delta_{n_i} \quad (2.42a)$$

with

$$|\delta_{n_i}| \ll \langle Y_n \rangle \quad (2.42b)$$

with  $\langle Y_n \rangle$  an average quantity. [One can also see that Eqs. (2.42) follow for  $b \ll 1$  from the form of  $\Omega_{n_i}^s$ , cf. Appendix A.] Under these conditions it is possible to replace the weighted sum in Eq. (2.39a) over saturated NMR Lorentzians by a single NMR Lorentzian (cf. Ref. 13 and Paper I for parallel discussions of average ESR lines):

$$\xi_e(M) \approx \langle J_-^2 \rangle d_n^2 \langle \Omega_{e,n}^s(M) \rangle \langle T_{2,n}(M) \rangle / \{ 1 + [\Delta\omega_n \langle T_{2,n}(M) \rangle]^2 + \langle J_-^2 \rangle d_n^2 \langle \Omega_n^s(M) \rangle \langle T_{2,n}(M) \rangle \}, \quad (2.43)$$

where

$$\langle J_-^2 \rangle \equiv \sum_{n_i} (J_{n_i}^-)^2 = \sum_{n_i} [J_{n_i} (J_{n_i} + 1) - M_{n_i} (M_{n_i} + 1)] \quad (2.44)$$

and the sums in Eq. (2.44) are over all induced nuclear transitions, while  $M_{n_i}$  refers to the lower value for the  $n_i$ th induced nuclear transition. Also,

$$\langle \Omega_{e,n}^s(M) \rangle = \sum_{n_i} J_{n_i}^-^2 \langle \Omega_{\Gamma_1, n_i}^s \rangle^2 / \langle J_-^2 \rangle, \quad (2.45a)$$

$$\langle T_{2,n}(M) \rangle = \sum_{n_i} J_{n_i}^-^2 \langle \Omega_{\Gamma_1, n_i}^s \rangle^2 T_{2,n_i} / \langle J_-^2 \rangle \langle \Omega_{e,n}^s(M) \rangle, \quad (2.45b)$$

$$\langle \Omega_n^s(M) \rangle = \sum_{n_i} J_{n_i}^-^4 \langle \Omega_{\Gamma_1, n_i}^s \rangle^2 \Omega_{n_i}^s / \langle J_-^2 \rangle^2 \langle \Omega_{e,n}^s(M) \rangle. \quad (2.45c)$$

In Eq. (2.43) one has<sup>1</sup>

$$d_{n\pm} = (\gamma_n B_n / 2) [1 \pm (\gamma_e / \gamma_n) (a_n^{\text{av}} / 2B_0)], \quad (2.46)$$

where the sign depends on whether  $m_e = \pm \frac{1}{2}$  for the nuclear transitions excited, and  $a_n^{\text{av}}$  is the (average) hyperfine interaction in gauss. One then finds that, for the ENDOR signal,

$$\begin{aligned} E &\equiv (Z_{\text{ENDOR}}'' - Z_{\text{ESR}}'') / Z_{\text{ESR}}'' \\ &\approx d_n^2 \langle J_-^2 \rangle \langle \Omega_{e,n}^s(M) \rangle \langle T_{2,n} \rangle [\Omega_e(d_e^{-1}, M)]^{-1} / \{ 1 + (\Delta\omega_n \langle T_{2,n} \rangle)^2 + d_n^2 \langle J_-^2 \rangle \langle T_{2,n} \rangle \{ \langle \Omega_n^s \rangle - \langle \Omega_{e,n}^s \rangle [\Omega_e(d_e^{-1}, M)]^{-1} \} \}, \end{aligned} \quad (2.47a)$$

where

$$\Omega_e(d_e^{-1}, M) \equiv \Omega_e(M) + \{ 1 + [\Delta\omega_e T_{2,e} d_e^2]^2 \} / (T_{2,e} d_e^2). \quad (2.47b)$$

Equations (2.47) follow exactly from the approximate form, Eq. (2.43).

Actually one normally employs field modulation and observes the derivative ESR signal. That is, Eq. (2.34) should be differentiated with respect to  $\Delta\omega_e$ . (It is not necessary to consider the field modulation of  $\Delta\omega_n$ , since, by virtue of  $\gamma_n / \gamma_e = 1/660$  for protons and  $\gamma_n / \gamma_e \ll 1$  in general, when  $\gamma_e B_{\text{mod}} \lesssim T_{2,e}^{-1}$ , then  $\gamma_n B_{\text{mod}}$  is at least 100 times smaller than  $T_{2,n}^{-1}$ .) One then obtains

$$\begin{aligned} E(\text{deriv}) &= \frac{\xi_e T_{2,e} d_e^2}{1 + (\Delta_e T_{2,e})^2 + (\Omega_e - \xi_e) T_{2,e} d_e^2} \left( 1 + \frac{1 + (\Delta\omega_e T_{2,e})^2 + \Omega_e T_{2,e} d_e^2}{1 + (\Delta\omega_e T_{2,e})^2 + (\Omega_e - \xi_e) T_{2,e} d_e^2} \right) \\ &\cong \frac{2\xi_e T_{2,e} d_e^2}{1 + (\Delta\omega_e T_{2,e})^2 + (\Omega_e - \xi_e) T_{2,e} d_e^2} = 2E, \end{aligned} \quad (2.48)$$

where  $E$  is defined by Eq. (2.47a), while  $E(\text{deriv})$  is equivalently defined for derivative signals. The approximate equality in Eq. (2.48) follows because usually  $\xi_e \ll \Omega_e$ . When performing the actual experiment, generally one adjusts the dc magnetic field to a single peak of the first derivative ESR line, while sweeping the NMR frequency  $\omega_n$ . That is, one sets  $(\Delta\omega_e T_{2,e})^2 \approx \frac{1}{3}$  in Eqs. (2.47a) or (2.48), and the ENDOR enhancement of the derivative ESR line is given by  $2E$  with  $E$  given by the rhs of Eq. (2.47a). This  $E(\text{deriv})$  as a function of  $\omega_n$  is seen to be a single saturated Lorentzian. (Note that one usually sets  $\Omega_e T_{2,e} d_e^2 \sim 1$  for a maximum ENDOR signal.)

### B. Several Sets of Completely Equivalent Nuclei

We now assume that there are several sets of completely equivalent nuclei, and each set has a sufficiently different NMR frequency from the others to give a distinct ENDOR signal. Providing conditions 1 and 2 of Sec. II.A apply to each set, one may again define an average (saturated) ESR signal analogous to Eq. (2.34) and an average ENDOR enhancement analogous to Eq. (2.43). The primary change that results is to replace the degeneracy factors and the averaging over the degenerate ESR line. Specifically a given ESR hyperfine line is now characterized by the set of  $\{M_r\}$  and its degeneracy is given by

$$D\{M_r\} \equiv \prod_r D(M_r), \quad (2.49)$$

where  $D(M_r)$  is the degeneracy of the  $r$ th set having quantum number  $M_r$ . The changes in Eqs. (2.31)–(2.36) then involve the replacements

$$D^p(M) \rightarrow D^p\{M_r\} \quad (2.50a)$$

and

$$D^p(J) \rightarrow \prod_r D^p(J_r), \quad (2.50b)$$

where  $p=1$  or  $\frac{1}{2}$  and in general

$$\sum_{J_r \text{ in } M_r} D(J_r) = D(M_r). \quad (2.51)$$

Then, for example, the averaging of a quantity  $R_{J,M}^s$  analogous to Eq. (2.32) becomes

$$D(M)^{-1} \sum_{J \text{ in } M} R_{J,M}^s D(J) \rightarrow (D\{M_r\})^{-1} \sum_{(J_r) \text{ in } \{M_r\}} \prod_r D(J_r) R^s\{J_r, M_r\}. \quad (2.52)$$

If now  $R^s\{J_r, M_r\}$  depends only on the  $v$ th set so that we may write  $R_{J,M}^s$  (or else if  $R^s\{J_r, M_r\}$  may be expanded in a linear combination of such terms), then

$$(D\{M_r\})^{-1} \sum_{(J_r) \text{ in } \{M_r\}} \prod_r D(J_r) R_{J,M}^s = D(M_v)^{-1} \sum_{J_v \text{ in } M_v} D(J_v) R_{J_v, M_v}^s, \quad (2.53)$$

which is equivalent to the expression we have for a single set of nuclei. One thus finds that Eq. (2.34) is again appropriate, but with  $D(M) \rightarrow D\{M_r\}$ ,  $T_{2,e}(M) \rightarrow T_{2,e}\{M_r\}$ ,  $\Omega_e(M) \rightarrow \Omega_e\{M_r\}$ , and  $\xi_e(M) \rightarrow \xi_e\{M_r, v\}$ , where the calculation of  $T_{2,e}\{M_r\}$  is discussed in detail elsewhere,<sup>13,15</sup> and  $\Omega_e\{M_r\}$  is discussed in the next section. The expressions for  $\xi_e\{M_r, v\}$  now depend on the particular set ( $v$ th set) of equivalent nuclei yielding the ENDOR signal. One thus obtains in place of Eq. (2.43)

$$\xi_e\{M_r, v\} \approx \langle J_{v-2} \rangle d_{n_v}^2 \langle \Omega_{n_v}^s \rangle \langle \xi_e\{M_r, v\} \rangle \times \frac{\langle T_{2,n_v}\{M_r\} \rangle}{1 + (\Delta\omega_{n_v} \langle T_{2,n_v}\{M_r\} \rangle)^2 + \langle J_{v-2} \rangle d_{n_v}^2 \langle \Omega_{n_v} \rangle \langle T_{2,n_v}\{M_r\} \rangle}, \quad (2.54)$$

where

$$\langle J_{v-2} \rangle = \sum_{n_i \text{ in } v} (J_{v, n_i - 2}) = \sum_{n_i \text{ in } v} [J_{v, n_i} (J_{v, n_i} + 1) - M_{v, n_i} (M_{v, n_i} + 1)] \quad (2.55)$$

and the sums are over all induced nuclear transitions, which only involve the  $v$ th set. Equations (2.45)–(2.48) are equivalently modified.

### III. APPROXIMATING THE SATURATION PARAMETERS

We now wish to develop simple approximations for the required saturation parameters. As is seen from Eqs. (2.22), one must first obtain expressions for the transition probabilities. These are given in I, II, and IV and we summarize them below as matrix elements of  $\hat{W}^s$  [utilizing Eq. (2.28)]. The diagonal elements are

$$\begin{aligned} \hat{W}^s\{J_r, M_r\}, \{J_r, M_r\} &= 2W_e\{0\} \\ &\times (1 + \delta\{M\} + (N/2 - D\{J\})b'' \\ &+ \sum_r b_r [J_r(J_r + 1) - M_r^2]) \end{aligned} \quad (3.1)$$

while the off-diagonal elements are

$$\begin{aligned} \hat{W}^s\{J_r, M_r\}, \{J_v, M_v \rightarrow M_v \pm 1\} &= -W_e\{0\} \\ &\times (2D\{J\}b'' + b_v [J_v(J_v + 1) - M_v(M_v \pm 1)]) \end{aligned} \quad (3.2)$$

and otherwise

$$\hat{W}^s\{J_r, M_r\}, \{J_r', M_r'\} = -2W_e\{0\} (D\{J\}D\{J'\})^{1/2} b''. \quad (3.3)$$

Equation (3.2) applies for a transition between the eigenstate pair of nuclear configuration  $\{J_r, M_r\}$  and that of configuration  $\{J, M_r'\}$ , where  $\{M_r'\}$  differs from  $\{M_r\}$  only in that for the particular  $v$ th set  $M_v' = M_v \pm 1$ . Equation (3.3) applies in all other cases. In these equations  $W_e\{0\}$  is the dominant portion of the electron-spin relaxation rate usually taken as that for the center line of the spectrum with all  $M_r = 0$  or more generally as the nuclear-spin-independent portion of  $W_e\{J_r, M_r\}$ . Thus

$$W_e\{0\} = W_e^{\text{SR}} + 2j^{(G2)}(\omega_0) B_0^2 + X, \quad (3.4)$$

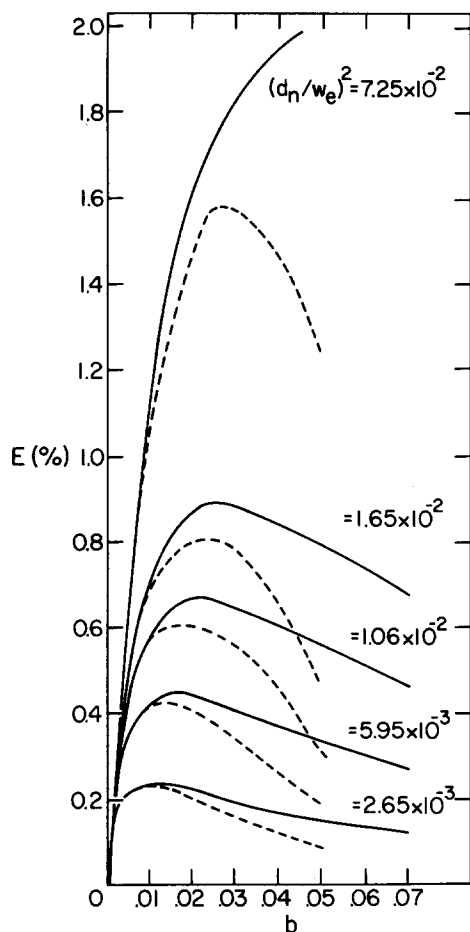


FIG. 1. Comparison of the percent enhancements predicted by the average-ENDOR approximation (dashed lines) and by the exact solution (solid lines) for the case of four equivalent spins of  $I = \frac{1}{2}$  given as a function of  $b$  for different values of  $[(d_n/w_e(0))^2]$ . The  $M=0$  ESR line is saturated, and  $b''=0$ ,  $\Delta\omega_e = \Delta\omega_n = 0$ , and  $d_e^2 T_{2,e}(M)\Omega_e(M) = 1$ .

where  $W_e^{\text{SR}}$  is the spin-rotational contribution to  $W_e$ ,<sup>2</sup> the second term is the  $g$ -tensor contribution (cf. I), and  $X$  represents all other contributions. Also

$$W_e\{M_r\} \equiv [1 + \delta\{M_r\}]W_e\{0\} \\ = W_e\{0\} + 4 \sum_r j_r^{DG_2}(\omega_0) B_0 M_r \\ + \sum_{r,s} 2j_{rs}^{(D)}(\omega_0) M_r M_s. \quad (3.5)$$

The second and third terms of Eq. (3.5) are, respectively, the  $g$ -tensor-dipolar cross terms and dipolar contributions to  $W_e$  (cf. I). One also has

$$b_r = \frac{1}{2} j_{rr}^D(0)/W_e\{0\}, \quad (3.6)$$

where  $j_{rr}^D(0)$  is the spectral density for the  $r$ th set of nuclei available for pure nuclear-spin-flip transitions; and

$$b'' = \omega_{\text{EX}}/NW_e\{0\}, \quad (3.7)$$

where  $\omega_{\text{EX}}$  is the exchange frequency [a sum of Heisenberg and (polarized) chemical exchange], and  $N$  is the total number of spin eigenstates.<sup>18</sup>

In order to develop simple approximations, we require that the  $b_r \ll 1$  (i.e., the END terms are small). We also assume at first that exchange terms are small as well. It is then clear from Eqs. (3.1)–(3.7) that the diagonal terms [Eq. (3.1)] are much larger than the off-diagonal terms.

Thus, in calculating the  $\det \hat{W}^s$  and its cofactors  $\det \hat{W}_{mm}^s$  as needed for  $S^s$ , we may expand about the diagonal elements keeping only terms to lowest order in off-diagonal elements, or

$$\det \hat{W}^s = \prod_k \hat{W}_{kk} [1 - \sum_{i < j} (\hat{W}_{ij} \hat{W}_{ji} / \hat{W}_{ii} \hat{W}_{jj}) + \dots], \quad (3.8)$$

$$\det \hat{W}_{mm}^s = \prod_{k \neq m} \hat{W}_{kk} \\ \times [1 - \sum_{i < j, i, j \neq m} (\hat{W}_{ij} \hat{W}_{ji} / \hat{W}_{ii} \hat{W}_{jj}) + \dots], \quad (3.9)$$

$$\det \hat{W}_{nn}^s = -[\hat{W}_{nm} \prod_{k \neq n, m} \hat{W}_{kk}] \\ \times [1 - \sum_{i \neq m, n} (\hat{W}_{ni} \hat{W}_{im} / \hat{W}_{nm} W_{ii}) \\ - \sum_{i < j, i, j \neq m, n} (\hat{W}_{ij} \hat{W}_{ji} / \hat{W}_{ii} \hat{W}_{jj}) + \dots]. \quad (3.10)$$

Then, to first order in  $b$  and  $Nb''/2$  we have for inverse matrix elements

$$(\hat{W}^s)^{-1}\{J_r, M_r\}\{J_r, M_r\} \\ \approx [\hat{W}^s\{J_r, M_r\}, \{J_r, M_r\}]^{-1} \\ \approx [2W_e\{0\}]^{-1} \times (1 - \delta\{M_r\} - (N/2 - D\{J_r\})b'' \\ - \sum_r b_r [J_r(J_r + 1) - M_r^2]), \quad (3.11)$$

$$(\hat{W}^s)^{-1}\{J_r, M_r\}\{J_v, M_v \rightarrow M_v \pm 1\} \\ \approx -\hat{W}^s\{J_r, M_r\}, (J_v, M_v \rightarrow M_v \pm 1) / \hat{W}^s\{J_r, M_r\} \\ \times \hat{W}^s\{J_r, M_r', M_v \pm 1\}\{J_r, M_r', M_v \pm 1\} \\ \approx [2W_e\{0\}]^{-1} (D\{J_r\}b'' + \frac{1}{2}b_v [J_v(J_v + 1) - M_v(M_v \pm 1)]) \quad (3.12)$$

and

$$(\hat{W}^s)^{-1}\{J_r, M_r\}\{J_r', M_r'\} \\ \approx [2W_e\{0\}]^{-1} b'' (D\{J_r\}D\{J_r'\})^{1/2} \quad (3.13)$$

otherwise. However, in the absence of any END terms (i.e.,  $b_r = 0$ ), the solutions for all orders of  $b''$  are known (cf. IV); and we may write for symmetrized matrix elements

$$(\hat{W}^s)^{-1}_{ii} = (2W_e\{0\})^{-1} [(1 + D_i b'')/h(b'')] \quad (3.14)$$

and

$$(\hat{W}^s)^{-1}_{ij} = (2W_e\{0\})^{-1} (D_i D_j)^{1/2} b'' / h(b'') \quad \text{for } i \neq j, \quad (3.15)$$



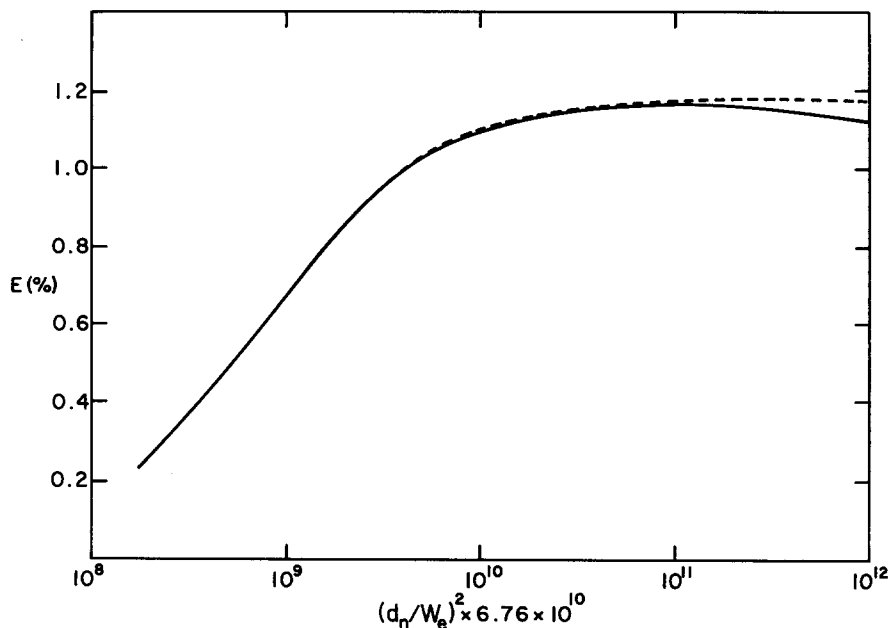


FIG. 2. Comparison of the percent enhancements predicted by the average-ENDOR approximation (dashed line) and by the exact solution (solid line) for the case of four equivalent spins of  $I = \frac{1}{2}$  showing the discrepancy between them due to the neglect of rf coherence effects in the approximate solution. The  $M = 0$  line is saturated and  $b = 0.01$ ,  $b'' = 0.00$ ,  $\Delta\omega_e = \Delta\omega_n = 0$ , and  $d_e^2 T_{2,e}(M)\Omega_e(M) = 1$ . Abscissa based on nominal  $W_e = 2.6 \times 10^6 \text{ sec}^{-1}$ .

where

$$h(b'') = 1 + \frac{1}{2}Nb''.$$

This suggests that Eqs. (3.11)–(3.13) be modified, so they might agree asymptotically for all values of  $b''$  with Eqs. (3.14) and (3.15), while being correct for small values of  $Nb''/2$ . When we compare with the exact results for a single nuclear spin of  $I = \frac{1}{2}$ ,<sup>21</sup> we may write

$$\langle \hat{W}^s \rangle^{-1} \{J_r, M_r\} \{J_r, M_r\} \approx A [1 - \delta \{M_r\} - \sum_r b_r [J_r(J_r+1) - M_r^2] / h(b'') + D \{J_r\} b''], \quad (3.16)$$

$$\langle \hat{W}^s \rangle^{-1} \{J_r, M_r\} (J_v, M_v \rightarrow M_v \pm 1) \approx A (D \{J_r\} b'' + b_v [J_v(J_v+1) - M_v(M_v+1)] / h(b'')), \quad (3.17)$$

and

$$\langle \hat{W}^s \rangle^{-1} \{J_r, M_r\} \{J_r', M_r'\} \approx A (D \{J_r\} D \{J_r'\})^{1/2} b'' \quad (3.18)$$

otherwise. Here

$$A^{-1} = 2W_e \{0\} h(b'').$$

The calculation of the  $\mathbf{S}^s$  matrix elements in terms of these approximate  $\langle \mathbf{W}^s \rangle^{-1}$  is discussed in Appendix A. It is then possible to determine the average parameters given by Eqs. (2.45) [or their equivalent needed for Eqs. (2.54)–(2.55)]. In particular, one notes from Eqs. (A13)–(A15) for  $\Omega_{e,n}$ -type parameters that to terms linear in  $b$ , one need only sum over nuclear transitions satisfying Eq. (A13) [since Eqs. (2.45) all involve  $(\Omega_{r_1, n_i})^2$  making the contribution from Eq. (A14) quadratic in  $b$ ]. These averages are conveniently obtained once the averages

$$\langle J_r(J+1) - M_r^2 \rangle_{M_r} \equiv D(M_r)^{-1} \times \sum_{J \text{ in } M_r} D(J_r) [J_r(J_r+1) - M_r^2] \quad (3.19)$$

and

$$\langle [J_r(J_r+1) - M_r^2]^2 \rangle_{M_r} \equiv D(M_r)^{-1} \times \sum_{J_r \text{ in } M_r} D(M_r) [J_r(J_r+1) - M_r^2]^2 \quad (3.20)$$

are found. For  $n_r$  spins of  $I = \frac{1}{2}$  (e.g., protons), these averages take a particularly simple form. In this case Fraenkel<sup>14</sup> has shown

$$\langle J_r(J_r+1) - M_r^2 \rangle_{M_r} = n_r/2 \quad (3.21)$$

and by a similar procedure one finds

$$\langle [J_r(J_r+1) - M_r^2]^2 \rangle_{M_r} = (n_r^2/2) - M_r^2. \quad (3.22)$$

The case for  $I > \frac{1}{2}$  is not so simple. [Fraenkel<sup>15</sup> gives a table of results for  $\langle J_r(J_r+1) - M_r^2 \rangle_{M_r}$  for  $I = 1$  and  $n_r \leq 4$ .] One then obtains for spins of  $I = \frac{1}{2}$ <sup>21</sup>

$$\langle \Omega_e \{M_r\} \rangle \approx 4A [(1 - \delta \{M_r\}) + D \{M_r\} b'' - \sum_r n_r b_r / 2h(b'')], \quad (3.23)$$

$$\langle J_{v-2} \rangle \langle \Omega_{e, n_v} \{M_r\} \rangle \approx 4n_v A^2 (1 - 2\delta \{M_r\} - [b_v/h(b'')]) \times (3n_v - 4M_v^2/n_v) - \sum_{r \neq v} n_r b_r / h(b''), \quad (3.24)$$

$$\langle J_{v-2} \rangle \langle \Omega_{n_v} \{M_r\} \rangle \approx [b_v W_e \{0\}]^{-1} [1 + n_v b_v / h(b'')], \quad (3.25)$$

$$\langle T_{2, n_v} \{M_r\} \rangle \approx 2A (1 - (2\delta \{M_r\} + \delta \{M_r', M_v + 1\} + \delta \{M_r', M_v - 1\}) / 4h(b'') - [b_v/h(b'')]) (2n_v + \frac{1}{2}) - \sum_{r \neq v} n_r b_r / h(b'') - \frac{1}{4} j_{v,v}^I(0) W_e \{0\}. \quad (3.26)$$

The complete solution for average ENDOR then involves substitution of the results, Eqs. (3.23)–(3.26), into expressions such as Eq. (2.47a) [or (2.48) and see Eq. (2.45)] for the enhancements  $E$ .<sup>22</sup> While it is possible

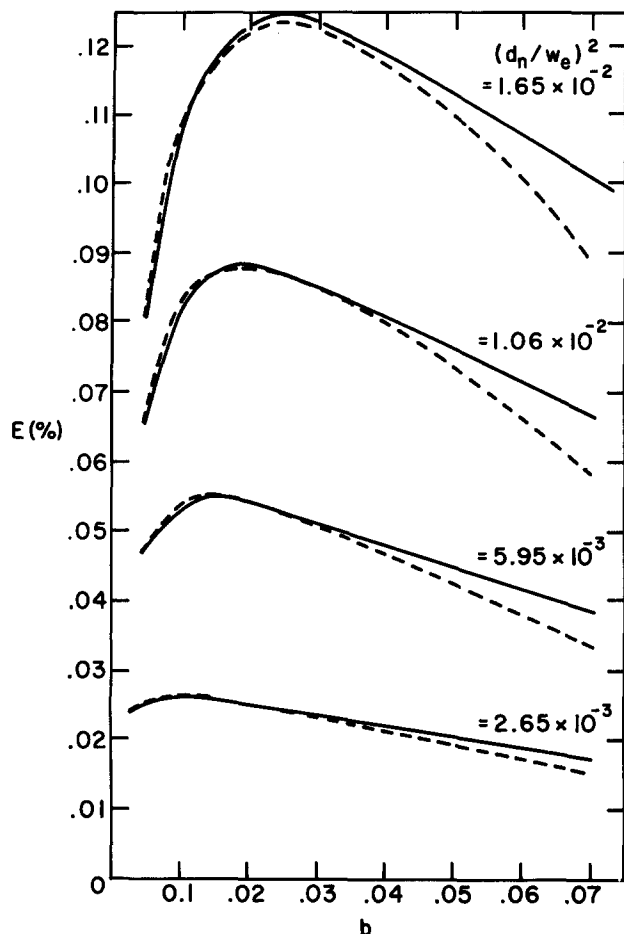


FIG. 3. Comparison of the percent enhancements predicted by the average-ENDOR approximation (dashed lines) and by the exact solution (solid lines) for the case of four equivalent spins of  $I = \frac{1}{2}$  given as a function of  $b$  for different values of  $[(d_n/W_e(0))^2]$ . The  $M=0$  ESR line is saturated, and  $b''=0.08$ ,  $\Delta\omega_e = \Delta\omega_n = 0$ , and  $d_e^2 T_{2,e}(M)\Omega_e(M) = 1$ .

to measure these enhancements,<sup>7-9</sup> in most cases, it is the relative enhancements, i.e., the ratios of the intensities of the ENDOR signals from the different sets of equivalent nuclei, which are most conveniently observed in an experiment. One should saturate a particular ESR line while sweeping NMR frequency  $\omega_n$ , keeping  $B_n$  constant. Then if all the  $b_r$  are small, the relative enhancements depend in lowest order (for  $I = \frac{1}{2}$ ) on

$$\frac{\frac{1}{2}n_v d_{n_v}^2}{1 + d_{n_v}^2/b_v h(b'')W_e\{0\}}$$

for the ENDOR maximum from the  $v$ th set of equivalent protons. Thus, if the NMR transitions are not saturated, i.e.,  $d_{n_v}^2 \ll b_v h(b'')W_e$ , the ratios of the ENDOR peak heights vary as  $n_v d_{n_v}^2$ . By correcting these ratios for the dependence of  $d_{n_v}^2$  on  $a_{n_v}$ ,<sup>av</sup> according to Eq. (2.46), one may obtain adjusted ratios of ENDOR peak heights which depend essentially on

the relative numbers of protons contributing to each ENDOR line. This is a particularly useful result for assigning the ENDOR transitions. [This result is a direct consequence of Eq. (3.21), and it therefore does *not* simply generalize for nuclear spins of  $I > \frac{1}{2}$ .] It amounts to the fact that the "average" transition moment is properly given by  $n_v d_{n_v}^2$  when  $I = \frac{1}{2}$ .] Since it is possible that some, if not all, of the NMR transitions are at least partially saturated, one should first extrapolate the relative enhancements to a lower power level where all the ENDOR signals are simply linear in  $B_n^2$ .<sup>8,9</sup> When there is significant saturation of the ENDOR signals (with respect to  $B_n^2$ ), an extrapolation (of inverse relative enhancements) to infinite  $B_n^2$  yields, to lowest order, asymptotic relative enhancements in the ratio of  $n_v b_v$ . Once the ENDOR lines have been assigned, this result provides a first approximation to the ratios of the spectral densities  $j_{v,v}^D(0)$  for the different sets of nuclei. One sees that, for small  $b_v$ , the actual magnitude of each  $j_{v,v}^D(0)$  is obtained from an ENDOR saturation experiment,<sup>7-9</sup> in which the ENDOR width is studied as a function of  $B_n^2$ , in a manner analogous to an ESR cw saturation measurement.<sup>5,10</sup> The unsaturated ENDOR width

$$\langle\langle T_2, n_v \{M_r\} \rangle\rangle \approx [W_e\{0\}h(b'')]^{-1} \text{ in lowest order}$$

would also be obtained.

Since the whole analysis has been based on keeping only terms linear in the  $b_r$ , and since

$$\langle\Omega_{e,n_v}^2 \{M_r\} \rangle \langle J_{v-}^2 \rangle d_n^2$$

plays a dominant role in determining ENDOR enhancements, one may discern from Eq. (3.24) that a better estimate of the limit of validity of our results is given by

$$3n_v b_v / h(b'') \ll 1. \quad (3.27)$$

It is very difficult from our analysis, where the quadratic terms in  $b_r$  come in in many complex ways, to attempt a more careful estimate of the range of validity of our results. We have therefore compared with the results obtained from an exact and rigorous solution to Eqs. (2.14)-(2.17) (including coherence effects dependent on  $d_n$ ) for the nontrivial case of a single set of four equivalent protons. The exact solution is complex enough to require computer simulation.<sup>7</sup>

Typical results on  $E$  are shown in Figs. 1-3. Figures 1 and 2 are given for  $b''=0$ . One sees in Fig. 1 that the "average-ENDOR" expressions agree very well with the exact results for  $b < 0.015$  with moderate agreement for  $b < 0.025$ . This is consistent with Eq. (3.27). For  $b > 0.025$  the "average-ENDOR" results decrease much more rapidly with  $b$  than do the exact results. This suggests that the neglected quadratic (and higher order terms) in  $b$  tend to cancel out somewhat the effects of the terms linear in  $b$ . In Fig. 2 the effects of increasing  $d_n^2$  for the case of  $b=0.01$  is shown. Here  $E$  obtained by both methods agrees very well until coherence effects

begin to set in at  $d_n^2 > 10^{11} \text{ sec}^{-2}$ . It is seen in Fig. 2 that values of  $E$  as high as 1% (for small  $b_r$ ) may be predicted satisfactorily by the average results. One sees in Fig. 3 the effects of a substantial  $b''$  set at 0.08, or  $1-g(b'')=N/2=1.28$ . The values of  $E$  are greatly decreased, but the agreement between the two methods persists to much higher values of  $b$ , in accordance with Eq. (3.27).

The values of  $\langle T_{2,n}(M) \rangle$  obtained from Eq. (3.26) and from extrapolating the computer solutions to  $d_n^2=0$  agree over a wider range than do the values of  $E$ . Thus for the data of Fig. 1 ( $b''=0$ ), for  $b \leq 0.025$  they agree within about 2%, while for  $b=0.05$ , the discrepancy is  $\sim 15\%$  with the average value being lower. The effect of a finite  $b''(=0.08)$  again improves the agreement, so for  $b=0.07$  the average result is only  $\sim 7\%$  lower.

It is clear from an analysis of Eqs. (2.54), (2.47a), and Eqs. (3.23)–(3.26) that exchange acts only to reduce ENDOR enhancements  $E$  (cf. II). However, the observed ENDOR signal depends on  $E$  times the ESR signal, and increased concentration of course improves the ESR signal. One can obtain the optimum concentration which maximizes the ENDOR signal from these expressions. Let  $\omega_{HE}=[R]k$  where  $[R]$  is the radical concentration and  $k$  the bimolecular rate constant.<sup>5</sup> Under the conditions that (1)  $\omega_{HE}$  makes a small contribution to  $T_{2,e}\{M_r\}$ ; (2)  $d_e^2 T_{2,e}\{M_r\} \times \langle \Omega_e\{M_r\} \rangle = \text{const}$  (usually  $\sim 1$ )<sup>7,8</sup> independent of concentration; then if (a) the NMR is not saturated, the optimum  $[R] \cong 2W_e\{0\}/k$  [or  $(N/2)b'' \cong 1$ ]; while if (b) the NMR is strongly saturated [cf. denominator of Eq. (2.54)] the optimum  $[R]$  is obtained asymptotically for  $[R] \gg 2W_e\{0\}/k$ .

#### IV. AVERAGE ELDOR

One may develop expressions for average ELDOR in a similar manner to ENDOR as long as the  $b_r$  are small. In fact the rigorous expressions needed when the  $b_r=0$  have already been given in Paper IV. There are some differences compared to ENDOR which actually tend to simplify the case of ELDOR. (1) The observing and pumping transition moments  $d_o$ , and  $d_p$ , respectively, are the same for all the components of observing and pumping modes. (2) It is necessary to transform both observing and pumping modes into their respective completely symmetric linear combinations according to the  $\mathbf{O}$  transformation described by Eqs. (2.31a). It is this transformation, which will exactly diagonalize  $\mathbf{R}$  and  $\mathbf{S}$  (hence  $\mathbf{M}$ ) when  $b=0$ , and will approximately diagonalize  $\mathbf{M}$  for small  $b$ . These transformations then lead to an average ELDOR expression given by

$$Z_o''\{M_r\} \approx \frac{q\omega_e \langle T_{2,o}\{M_r\} \rangle d_o D_o\{M_r\} [1 - (D_p\{M_r'\}/D_o\{M_r\})^{1/2} \xi_o\{M_r, M_r'\} / \langle \Omega_{p,o^s}\{M_r, M_r'\} \rangle]}{1 + \Delta\omega_o^2 \langle T_{2,o}\{M_r\} \rangle^2 + d_o^2 \langle T_{2,o}\{M_r\} \rangle \langle \Omega_o^2\{M_r\} \rangle - \xi_o\{M_r, M_r'\}}, \quad (4.1)$$

$$\xi_o\{M_r, M_r'\} \approx d_p^2 \langle T_{2,p}\{M_r'\} \rangle \langle \Omega_{o,p^s}\{M_r, M_r'\} \rangle \langle \Omega_{p,o^s}\{M_r', M_r'\} \rangle / [1 + \Delta\omega_p^2 \langle T_{2,p}\{M_r'\} \rangle^2 + d_p^2 \langle T_{2,p}\{M_r'\} \rangle \langle \Omega_{p^s}\{M_r'\} \rangle]. \quad (4.2)$$

Here  $\{M_r, M_r'\}$  refer to the  $\{M_r\}$  set of quantum numbers characterizing the observing mode and to the  $\{M_r'\}$  set for the pumping mode. The averaging procedure in this case obeys

$$\langle \Omega_{e_i, e_i^s}\{M_{r_i}, M_{r_i'}\} \rangle = (D\{M_{r_i}\} D\{M_{r_i'}\})^{-1/2} \sum_{J_{r_i} \text{ in } M_{r_i}, J_{r_i'} \text{ in } M_{r_i'}} (D\{J_{r_i}\} D\{J_{r_i'}\})^{1/2} \Omega_{eJ_{(r_i)}, eJ_{(r_i')}}\{J_{r_i}, M_{r_i}; J_{r_i'}, M_{r_i'}\} \quad (4.3)$$

for the  $i$ th and  $j$ th hyperfine lines with quantum numbers  $\{M_{r_i}\}$  and  $\{M_{r_i'}\}$ , respectively. The  $\langle T_{2,o}\{M_r\} \rangle$  and  $\langle T_{2,p}\{M_r'\} \rangle$  are the usual average widths,<sup>13–15</sup> also  $\langle \Omega_o^s\{M_r\} \rangle$  and  $\langle \Omega_{p^s}\{M_r'\} \rangle$  are given by Eq. (3.23) for nuclear spins of  $I=\frac{1}{2}$ . From Eq. (4.3) and Eqs. (A10)–(A12) one has

$$\langle \Omega_{o,p^s}\{M_r, M_r'\} \rangle = \langle \Omega_{p,o^s}\{M_r', M_r\} \rangle \approx 2A (D_o\{M_r\}/D_p\{M_r'\})^{1/2} \times (2D_p\{M_r'\} b'' + \sum_v [b_v/h(b'')]) [(J_v(J_v+1) - M_v^2 + M_v)_{M_r, \delta_{M_r', M_r-1}} + (J_v(J_v+1) - M_v^2 - M_v)_{M_r, \delta_{M_r', M_r+1}}], \quad (4.4)$$

where for  $I=\frac{1}{2}$

$$\langle J_r(J_r+1) - M_r^2 \pm M_r \rangle_{M_r} = n_r/2 \pm M_r. \quad (4.5)$$

The  $\delta_{M_r', M_r \pm 1}$  terms in Eq. (4.4) are taken as nonzero only for combinations of  $\{M_r\}$  and  $\{M_r'\}$  such that only the  $v$ th set of equivalent nuclei differ in the observing and pump spin configurations by  $\Delta M_v = \pm 1$ , and all other sets of equivalent nuclei have the same  $M_r$  values. This configuration corresponds to an ELDOR "fundamental line."

Usually an ELDOR experiment is performed by saturating the pump mode, while the observing mode is not saturated.<sup>4,10</sup> If the pump mode resonant frequency is swept, keeping the observing mode constant, one notes from Eqs. (4.1), (4.2), and (4.4) that a single saturated Lorentzian characteristic of the pumped ESR line is obtained.

More specifically, one may define a reduction factor  $R^{4,10}$  as

$$R \equiv \frac{Z_{\text{ESR}}'' - Z_{\text{ELDOR}}''}{Z_{\text{ESR}}''} \rightarrow \frac{(D_p\{M_r'\}/D_o\{M_r\})^{1/2} \xi_o\{M_r, M_r'\}}{\langle \Omega_{p,o}^s\{M_r, M_r'\} \rangle}, \quad (4.6)$$

where the arrow implies that the ESR observing mode is not saturated. A convenient experimental technique is to extrapolate  $R^{-1}$  to infinite  $d_p^2$ .<sup>4,10</sup> Then one has from Eq. (4.6)

$$R(d_p^2 \rightarrow \infty) \cong \frac{(D_p\{M_r'\}/D_o\{M_r\})^{1/2} \langle \Omega_{o,p}^s\{M_r, M_r'\} \rangle}{\langle \Omega_p^s\{M_r'\} \rangle} \quad (4.7)$$

for the maximum in  $R$  obtained at  $\Delta\omega_p^2=0$ . Then to lowest order in the  $b_r$ , and for  $I=\frac{1}{2}$ , one has from Eqs. (4.4) and (3.23)

$$R(d_p^2 \rightarrow \infty) \cong (D_p\{M_r'\} b'' + \frac{1}{2} \sum_v [b_v/h(b'')] [(n_v/2 + M_v) \delta_{M_r', M_v-1} + (n_v/2 - M_v) \delta_{M_r', M_v+1}]). \quad (4.8)$$

If spin exchange is the predominant ELDOR mechanism, then it follows from Eq. (4.8) that the ELDOR reduction will depend simply on  $D_p\{M_r'\}$ , the degeneracy of the pumped line (times  $b''$ ), and there are no selection rule restrictions upon which lines are observed or pumped. In this instance the relative (asymptotic) ELDOR signal strengths obtained by sweeping the pump mode should be useful in assigning the spectrum. When END terms are important, then one must consider the terms in  $b_v$  in Eq. (4.4) or Eq. (4.8). We have already noted that since our results are derived only to terms in  $b_r$  (since  $b_r$  is assumed to be small), then Eq. (4.4) [hence Eq. (4.8)] includes only the effects of the END terms for observing and pump lines separated by  $\Delta M_v = \pm 1$ , i.e., a fundamental. Overtone ELDOR lines, wherein the  $\{M_r'\}$  of the pump line differs more significantly from the  $\{M_r\}$  of the observing line, would yield reductions, which come in in higher powers of the  $b_r$  and are thus insignificant for  $b_r/h(b'') \ll 1$ . When Eq. (4.8) is applicable, and when exchange is not important, then the asymptotic reductions obtained for each fundamental observed by sweeping the pump will be essentially given by  $\frac{1}{2} b_v (n_v/2 \pm M_v)$ , in the case of protons (and generally proportional to  $b_v$  even for  $I_v > \frac{1}{2}$ ). If the source of each fundamental is known, then this may be used to extract a first approximation to the important relaxation quantities  $b_v$  from a complex spectrum.

In general, when both END and exchange terms are contributing to the ELDOR signal, then their respective contributions may be separated out by studying fundamental vs overtone ELDOR lines, once they have been distinguished. This distinction could, if needed, be made by monitoring the ELDOR reductions either for samples of low enough concentration to remove exchange effects (and at temperatures where  $b_r$  are reasonably small) or by cooling samples of moderate concentration to enhance the END contribution relative to the exchange<sup>4</sup> (but still keeping the  $b_r$  reasonably small).

Again one should note that usually a derivative ESR (and ELDOR) is observed. The discussion of an  $R$ - (deriv) proceeds in a manner similar to that given

above for  $R$ , and this is discussed in Ref. 10 in a form that can be directly applied to our present average-ELDOR discussion, i.e., one still gets Eq. (4.7) in the  $d_p^2 \rightarrow \infty$  asymptotic limit.

## V. EQUIVALENT NUCLEI WHICH ARE NOT COMPLETELY EQUIVALENT

It is often the case that equivalent nuclei are not completely equivalent. These are nuclei characterized by identical average hyperfine splittings, so that they resonate at the same frequency of the NMR field, but their relaxation properties are not identical. This situation may be due to out-of-phase correlations of fluctuations in isotropic hyperfine interactions or may simply be due to relative orientational considerations of their respective END interactions. It is the latter which are important when an END mechanism is the dominant for ENDOR or ELDOR. Such effects greatly complicate the calculation of saturation and double resonance spectra

One may note that equivalent nuclei are completely equivalent with respect to rf-induced NMR transitions. This consideration is of primary importance for ENDOR, so (especially when the  $b \ll 1$ ) one should still calculate the ENDOR spectra in the coupled representation of all equivalent nuclei. Only the  $\mathbf{R}$  and  $\mathbf{W}$  matrices are significantly affected by the lack of complete equivalence. (The  $\mathbf{K}$  and  $\mathbf{d}$  matrices are unchanged.) One must now allow for relaxation transitions which mix up the degenerate eigenstates and transitions, and this will, in general, increase the dimensions of  $\mathbf{R}$  and  $\mathbf{W}$ . These matrices must be calculated in a product representation of spins which belong to different completely equivalent subsets of the same equivalent set, and methods for their calculation are given elsewhere.<sup>1,13,15</sup>

The case of ELDOR is actually easier to consider than that of ENDOR, since it is not necessary to obtain  $\mathbf{R}$  and  $\mathbf{W}$  in the coupled representation of all equivalent-nuclei. One may obtain satisfactory results, especially for "average ELDOR," from the uncoupled representa-

tion. An analysis equivalent to that of Sec. III may be given for the approximate saturation parameters, recognizing that in Eq. (3.1) the sum over  $r$  becomes replaced by a sum over  $r_u$  (i.e., including the  $u$ th completely equivalent subset of the  $r$ th equivalent set) representing all the allowed nuclear-spin transition probabilities in the uncoupled representation. Similarly Eq. (3.2) merely requires  $v \rightarrow v_u$ . There are now "pseudo-diagonal eigenstates" included in the proper  $\mathbf{W}$  matrix which, however, do not affect the average results, because (1) they are not directly involved in any allowed ESR transition, and (2) their effects are higher order in both  $b_{r_u, r_u} \equiv b_{r_u} = b_r$  and  $b_{r_u, r_w}$  and therefore negligible.<sup>23</sup> Here  $b_{r_u, r_w} \equiv \frac{1}{2} j_{r_u, r_w}^D(0) / W_e \{0\}$ . One again needs averages like Eqs. (2.32) and (2.33) [with averaging like Eqs. (2.54) and (2.55)] and Eq. (4.3), where the sums are now generalized to be over the completely equivalent subsets. However, since<sup>14</sup>

$$\begin{aligned} & \langle J_{r_u}(J_{r_u}+1) - M_{r_u}^2 \rangle_{M_r} \\ & \equiv D(M_r)^{-1} \sum_{M_{r_u} J_{r_u}} D(J_{r_u}) [J_{r_u}(J_{r_u}+1) - M_{r_u}^2] \\ & = \langle J_r(J_r+1) - M_r^2 \rangle_{M_r}, \end{aligned} \quad (5.1)$$

the average results given by Eq. (4.4) and Eq. (3.23) are actually *unaffected* [except for letting  $r \rightarrow r_u$  and  $s \rightarrow s_w$  in Eq. (3.5) for the definition of  $\delta\{M_{r_u}\}$ ]. That is, for average saturated ESR or ELDOR saturation parameters one may treat each equivalent group of nuclei as being a completely equivalent group whether or not it really is. One need only use the  $b_r$  values in Eqs. (4.4) and (3.23). The average ESR linewidths for these cases are discussed in detail elsewhere.<sup>13,15,24</sup>

The case of ENDOR is more difficult to treat, as noted, involving the need to obtain  $\mathbf{R}$  and  $\mathbf{W}$  in the coupled representation. For this reason, and because the actual magnitude of the END contributions (which are a usual source of the distinction between equivalent and completely equivalent nuclei) do not play a crucial role in "average-ENDOR" intensities in lowest order, we have not carried out a general analysis of the "average-ENDOR" results. We have, however, analyzed in detail the simplest nontrivial case of two equivalent nuclear spins of  $I = \frac{1}{2}$  for its instructional value.<sup>25</sup> One first obtains  $\mathbf{R}$  and  $\mathbf{W}$  in the uncoupled representation, and then transforms to the coupled representation by use of generalized unitary transformations. In this case one obtains

$$\begin{aligned} & \langle J_-^2 \rangle \langle \Omega_{e,n}(M=0) \rangle = W_e(0)^{-2} \\ & \times [1 - 2\delta(M=0) - 3(b_{1,1} + b_{1,2}) - (b_{1,1} - b_{1,2})] \end{aligned} \quad (5.2)$$

and

$$\langle J_-^2 \rangle \langle \Omega_n(M=0) \rangle = W_e(0)^{-1} [y b_{11}^{-1} + 2b_{11}], \quad (5.3)$$

where  $y = (17b_{11} + 3b_{12}) / (14b_{11} + 6b_{12})$ . The expressions Eqs. (5.2) and (5.3) are seen to be equivalent to Eqs. (3.24) and (3.25) for two completely equivalent

nuclei, if  $b_{1,2} = b_{1,1}$  as they should. One again notes the relatively minor role played by  $b_{1,1}$  and  $b_{1,2}$  in Eq. (5.2) and the form suggests that for two subsets of equivalent but not completely equivalent nuclei it may be sufficient just to let  $b_r$  in Eq. (3.24) be replaced by  $\frac{1}{2}(b_{r_1, r_1} + b_{r_1, r_2})$ . One sees from Eq. (5.3) that  $\langle \Omega_n \rangle$  is hardly affected by the lack of complete equivalence. Similar comments apply to  $\langle T_{2,n} \rangle$  which is given by

$$\begin{aligned} \langle T_{2,n}(M=0) \rangle & \cong W_e(0)^{-1} \{ 1 - \frac{1}{4} [2\delta(M=0) + \delta(M=1) \\ & + \delta(M=-1)] - (\frac{1}{3} b_{1,1} + b_{1,2}) \}. \end{aligned} \quad (5.4)$$

## VI. SUMMARY AND CONCLUSIONS

The concept of average-ENDOR and average-ELDOR is found to be a useful one when the END interactions are small [i.e., Eq. (3.27) is fulfilled]. When this is so, and the ENDOR lines are not significantly saturated, the intensity of an "average-ENDOR" line for spins of  $I = \frac{1}{2}$  (e.g., protons) is in lowest order predicted to be directly proportional to the number of equivalent nuclei ( $n_r$ ) contributing to it. (This statement must be modified if lattice-induced cross transitions involving combined electronic- and nuclear-spin transitions are more important than the pure nuclear-spin transitions, cf. Appendix B.) This permits the possibility of assigning the ENDOR lines of a single ENDOR spectrum (obtained from saturating a single ESR line) to the different equivalent groups of protons in terms of their intensity ratios. The relative enhancement in lowest order is approximately proportional to

$$\frac{n_r}{2} \left( \frac{d_{n_r}}{W_e(1 + \omega_{\text{EX}}/2W_e)} \right)^2$$

when the ENDOR line is not significantly saturated, while for significant NMR saturation it goes in lowest order as

$$\frac{(n_r/2)b_r}{(1 + \omega_{\text{EX}}/2W_e)}.$$

The proportionality constant depends on the degree of ESR saturation [cf. Eqs. (2.47a) and (2.47b)].

While the effects of exchange act to reduce relative ENDOR enhancements, the absolute ENDOR enhancements are maximized by adjusting the concentrations to set  $\omega_{\text{HE}} \approx 2W_e$ , when the ENDOR lines are not significantly saturated and for large NMR saturation require  $\omega_{\text{HE}} \gg 2W_e$ .

In the case of "average ELDOR," the END terms, even in lowest order, play an important role. If one has equivalent nuclei, which are not completely equivalent in the relaxation properties of their END terms, it does not affect the calculation of the "average-ELDOR" signals. When exchange terms are dominant, then the asymptotic reductions observed for very large pump powers and small observing mode powers are just in the ratio of  $D_p$ , the degeneracy of the pump line; while

if END terms are dominant, they go in lowest order for the fundamental ELDOR lines as  $\frac{1}{2}b_r(n_r/2 \pm M_r)$ , where  $M_r$  is the nuclear-spin configuration of the observing mode for the  $r$ th set of nuclei. (Again cross transitions require modification of these statements, cf. Appendix B.)

As the END terms become larger [i.e., Eq. (3.27) no longer valid] the analysis presented here in terms of averaging is no longer sound, and one has to appeal to the general theory in terms of superpositions of coupled (saturated) resonance transitions in order to obtain correct results.

### APPENDIX A: PROPERTIES OF THE $\mathbf{d}$ AND $\mathbf{S}$ MATRICES

The  $\mathbf{d}$  matrix is obtained from the diagonal and pseudodiagonal spin matrix elements of the commutator  $[\epsilon(t), \chi]$ , where  $\epsilon(t)$  is the interaction of the radiation field with the spins, and  $\chi = \sigma - \sigma_0$ , where  $\sigma$  is the spin density matrix and  $\sigma_0$  its equilibrium value. In the case of two rotating rf fields where one lies close to  $\omega_e$ , a (degenerate) ESR transition resonance, and the other close to  $\omega_n$ , a (degenerate) NMR transition resonance,

$$\epsilon(t) = d_e[S_+ \exp(-i\omega_e t) + S_- \exp(i\omega_e t)] + d_n[J_{r+} \exp(-i\omega_n t) + J_{r-} \exp(i\omega_n t)]. \quad (\text{A1})$$

A diagram method may be developed for the elements of the  $\mathbf{d}$  matrix or the  $\hat{\mathbf{d}}$  and  $\tilde{\mathbf{d}}$  submatrices. It is similar to that described for the  $\mathbf{K}$  matrix in III. Let an arrow be drawn between each pair of states for which the energy difference  $\hbar\omega_{\lambda_i}$  is nearly resonant with an applied radiation field and for which a transition moment  $d_{\lambda_i}$  exists. Each arrow should point to the state of increasing spin quantum number.

Now let  $\alpha$  and  $\beta$  each refer to a particular nuclear spin configuration, so that it is equivalent to the eigenstate pair differing only in  $m_s$  [cf. Eqs. (2.10) and (2.11)]. The elements of  $\hat{d}_{\lambda_i, \alpha}$  are as follows:

$$\begin{aligned} \hat{d}_{\lambda_i, \alpha} &= d_e && \text{if } \lambda_i = \alpha \\ &= \pm (d/2) \lambda_i && \text{if } \lambda_i \text{ contains only one state of the } \alpha\text{th eigenstate pair (i.e., } \lambda_i \text{ is a nuclear transition);} \\ &&& \text{the } - (+) \text{ sign is affixed when the arrow representing the } \lambda_i \text{ transition points toward} \\ &&& \text{(away from) the } \alpha\text{th eigenstate pair} \\ &= 0 && \text{if } \lambda_i \text{ contains no states of the } \alpha\text{th eigenstate pair.} \end{aligned} \quad (\text{A2})$$

Similarly one may describe the elements of  $\tilde{d}_{\beta, \lambda_k}^{trj}$ . The superscript  $j$  implies the inclusion of equations of type (2.3) in Eq. (2.11). One has

$$\begin{aligned} \tilde{d}_{\beta, \lambda_k}^j &= \pm d_{\lambda_k}/2 && \text{if } \lambda_k \text{ contains only one state of the } \beta\text{th eigenstate pair, (i.e., } \lambda_k \text{ is a nuclear transition);} \\ &&& \text{the } - (+) \text{ sign is affixed as for } \hat{d}_{\lambda_i, \alpha} \\ &= 0 && \text{(a) if } \lambda_k = \beta \\ &&& \text{(b) if } \lambda_k \text{ contains no states of the } \beta\text{th eigenstate pair} \\ &&& \text{(c) if } \beta = j, \text{ i.e., if the } \beta\text{th eigenstate is identical to (one of) the eigenstate pair(s) which} \\ &&& \text{was replaced by zero in } \tilde{d}^{trj}. \end{aligned} \quad (\text{A3})$$

[Case (c) in Eq. (A3) does not apply for  $\tilde{d}_{\beta, \lambda_k}$  without the superscript  $j$ .] Given these rules and Eq. (2.11), it is possible to give rules for  $\mathbf{S}$ , or equivalently  $\mathbf{S}^s$  in terms of  $\mathbf{W}^s$ . We write them without the superscript  $s$ , but they are the same for the symmetrized forms, Eqs. (2.20)–(2.22) which include degeneracies. We use the symbols  $\lambda_i \rightarrow e_i$ ,  $n_i$  to indicate the  $i$ th ESR and NMR transitions, respectively. One has

$$S_{e_i, e_j} = 4d_{e_i} d_{e_j} W_{e_i, e_j}^{-1}, \quad (\text{A4})$$

$$S_{e_i, n_j} = 2d_{e_i} d_{n_j} (\hat{W}_{e_i, \alpha(n_j)}^{-1} - \hat{W}_{e_i, \beta(n_j)}^{-1}), \quad (\text{A5})$$

where  $\alpha(n_j)$  and  $\beta(n_j)$  refer to the eigenstate pairs containing the eigenstate of the  $n_j$ th transition from which and to which, respectively, the arrow, representing this transition, points. In similar notation one has

$$S_{n_i, n_j} = \hat{S}_{n_i, n_j} + \tilde{S}_{n_i, n_j}, \quad (\text{A6a})$$

where

$$\hat{S}_{n_i, n_j} = d_{n_i} d_{n_j} (\hat{W}_{\alpha(n_i), \alpha(n_j)}^{-1} + \hat{W}_{\beta(n_i), \beta(n_j)}^{-1} - \hat{W}_{\alpha(n_i), \beta(n_j)}^{-1} - \hat{W}_{\beta(n_i), \alpha(n_j)}^{-1}) \quad (\text{A6b})$$

and  $\tilde{S}_{n_i, n_j}$  is the same as that for  $\hat{S}_{n_i, n_j}$  except with  $\hat{W}_{\alpha, \beta} \rightarrow \tilde{W}_{\alpha, \beta}^j$ , etc., and those  $\tilde{W}_{\alpha, \beta}^{-1}$  for which either  $\alpha$  or  $\beta = j$  are set equal to zero.

Actually, the  $\tilde{\mathbf{S}}$  matrix elements are found to have a very simple form. First we note that  $\tilde{\mathbf{W}}$  contains only the END terms [i.e., the pure nuclear-spin transitions when Eqs. (2.10) apply], and  $\tilde{\mathbf{W}}$  may be obtained from  $\hat{\mathbf{W}}$  by setting all other terms (i.e.,  $W_e$  and  $b''$ ) in that matrix equal to zero. This matrix  $\tilde{\mathbf{W}}$  then has the simple property

characteristic of typical complete  $\mathbf{W}$  matrices (in the high temperature approximation)<sup>26</sup> that the sum of all elements in a row (or column) is equal to zero. One is then able to use general relations for the cofactors and double cofactors of such matrices as given in Paper I [Eq. (2.41)]. One then may readily show that

$$\tilde{S}_{n_i, n_i} = d_{n_i} d_{n_i} C_{\alpha(n_i)\beta(n_i), \alpha(n_i)\beta(n_i)} / C, \quad (\text{A7})$$

where  $C$  is any cofactor of  $\tilde{W}$  (they are all equal) and  $C_{kl, mn}$  is a double cofactor (i.e., the  $l$ ,  $n$ th cofactor of the cofactor  $C_{km}$ ). Now if one takes the determinant representing  $C_{\alpha(n_i), \alpha(n_i)}$  and sums all rows on the  $\beta(n_i)$ th one obtains

$$C_{\alpha(n_i), \alpha(n_i)} = \tilde{W}_{\alpha(n_i), \beta(n_i)} C_{\alpha(n_i)\beta(n_i), \alpha(n_i)\beta(n_i)}, \quad (\text{A7}')$$

where we have set  $C_{\alpha(n_i)\beta(n_i), \alpha(n_i)\beta(n_i)} \equiv C_{n_i, n_i}$ . It is also easy to show that  $C_{n_i, n_i} = 0$  if  $i \neq j$ . Thus one has

$$\tilde{S}_{n_i, n_j} = d_{n_i}^2 \tilde{W}_{n_i}^{-1} \delta_{i, j}, \quad (\text{A8})$$

where if  $n_i$  refers to the transition  $J_r, M_r \rightarrow J_r, M_r \pm 1$  has

$$\tilde{W}_{J_r, M_r \rightarrow J_r, M_r \pm 1} = -b_r W_e(0) [J_r(J_r+1) - M_r(M_r \pm 1)]. \quad (\text{A9})$$

For  $b_r \ll 1$ ,  $\tilde{S}_{n_i, n_i}$  contributes the dominant term to  $S_{n_i, n_i}$ .

*The approximate saturation-matrix elements.* One may now use the approximate Eqs. (3.16)–(3.18) to calculate  $S^s$ , and one obtains

$$S_{e, e}^s \{J_r, M_r\} \{J_r, M_r\} \approx 4A d_e \{J_r, M_r\}^2 (1 - \sum_r b_r [J_r(J_r+1) - M_r^2] / h(b'') + D\{J_r\} b'' - \delta\{M_r\}), \quad (\text{A10})$$

$$S_{e, e}^s \{J_r, M_r\} (J_v M_v \rightarrow M_v \pm 1) \approx 4A d_e \{J_r, M_r\} d_e \{J_v, M_v \rightarrow M_v \pm 1\} (\frac{1}{2} b_v [J_v(J_v+1) - M_v^2] / h(b'') + D\{J_r\} b''), \quad (\text{A11})$$

with

$$S_{e, e}^s \{J_r, M_r\} \{J_r', M_r'\} \approx 4A d_e \{J_r, M_r\} d_e \{J_r', M_r'\} (D\{J_r\} D\{J_r'\})^{1/2} b'' \quad (\text{A12})$$

otherwise.

$$|S_{e, n}^s \{J_r, M_r\} (J_v, M_v \rightarrow M_v \pm 1)| \approx 2A d_e \{J_r, M_r\} d_n (J_v, M_v \rightarrow M_v \pm 1) \times (1 - \delta\{M_r\} - \frac{3}{2} b_v [J_v(J_v+1) - M_v^2 \mp \frac{1}{3} M_v] / h(b'') - \sum_{r \neq v} b_r [J_r(J_r+1) - M_r^2] / h(b'')), \quad (\text{A13})$$

$$|S_{e, n}^s \{J_r, M_r\} (J_v, M_v \pm 1 \rightarrow M_v \pm 2)| \approx 2A d_e \{J_r, M_r\} d_n (J_v, M_v \pm 1 \rightarrow M_v \pm 2) \times \frac{1}{2} b_v [J_v(J_v+1) - M_v(M_v \pm 1)(M_v \pm 2)], \quad (\text{A14})$$

with

$$S_{e, n}^s \{J_r, M_r\}, (J_v', M_v' \rightarrow M_v' \pm 1) \approx 0 \quad (\text{A15})$$

otherwise.

$$S_{n, n}^s (J_v, M_v \rightarrow M_v \pm 1), (J_v, M_v \rightarrow M_v \pm 1) \approx d_n^2 [b_v W_e(0) h(b'')]^{-1} \{1 + b_v [(J_v+1) - M_v(M_v \pm 1)] / h(b'')\}, \quad (\text{A16})$$

$$S_{n, n}^s (J_v, M_v \rightarrow M_v \pm 1), (J_v, M_v \pm 1 \rightarrow J_v, M_v \pm 2) \approx -d_n (J_v, M_v \rightarrow M_v \pm 1) d_n (J_v, M_v \pm 1 \rightarrow M_v \pm 2) / 2W_e(0) h(b''), \quad (\text{A17})$$

with

$$S_{n, n}^s (J_v, M_v \rightarrow M_v \pm 1), (J_v' M_v' \rightarrow M_v' \pm 1) \approx 0 \quad (\text{A18})$$

otherwise.

## APPENDIX B: CONTRIBUTIONS FROM CROSS TRANSITIONS

When one includes the effects of cross transitions (i.e., combined electron–nuclear spin flips), the  $\mathfrak{B}$  of Eq. (2.8) are no longer nonzero, because these transitions do not fulfill Eqs. (2.11). The analysis of  $\mathbf{S}$  therefore becomes somewhat more complex. Instead of carrying this out directly, we take advantage of the simplifying effects of keeping these terms only in lowest order. One first makes the observation that the results of Eqs. (A10)–(A18) (where only terms lowest order in  $b_r$ , i.e., in the pure nuclear-spin-flip transitions, were kept) included only those lattice-induced nuclear-spin-flip transitions and rf-induced NMR transitions involving an eigenstate that is included in a particular (degenerate) ESR transition which is being saturated. That is, for a single set of completely equivalent nuclei, wherein the  $M$ th ESR line is being saturated, one need only focus on the set of six ESR eigenstates and transitions given in Fig. 4. The ENDOR consists in inducing the  $\omega_n$ – or  $\omega_{n+}$  transitions. The  $W_{x_1}$  transitions are the  $\Delta m_s = \pm 1$ ,  $\Delta M = \pm 1$  type while the  $W_{x_2}$  transitions involve  $\Delta m_s = \pm 1$ ,  $\Delta M = \mp 1$ , and these transition probabilities

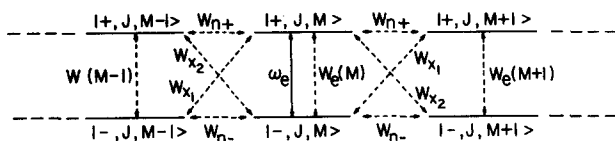


FIG. 4. Eigenstates and transitions of importance for determining approximate saturation parameters associated with the  $|\pm, J_r, M_r\rangle$  states when nuclear-spin-flip-inducing transitions are small.

are given in Paper I. One may solve for the subspace of eigenstates in Fig. 4 utilizing the standard methods of Papers I-III. The results are similar to those of Sec. III, the primary differences simply reflect the asymmetry caused by having  $W_{x1} \neq W_{x2}$ . We give the equivalent Eqs. (3.23)-(3.27) for one completely equivalent set of spins of  $I = \frac{1}{2}$  to illustrate this:

$$\langle \Omega_e(M) \rangle \approx 4A \{ [1 - \delta(M)] + D(M)b'' - ns/2h(b'') \}, \quad (B1)$$

$$\langle J_{-2} \rangle \langle \Omega_{e,n}^{s2} \rangle \approx nA^2 (r_1^2 + r_2^2) [1 - 2\delta(M)] \left[ 1 - 2M\epsilon \left( \frac{r_1^2 - r_2^2}{r_1^2 + r_2^2} \right) / n \right] - \frac{s}{h(b'')} \left[ \left( 3n - \frac{4M^2}{n} \right) - 4M\epsilon \left( \frac{r_1^2 - r_2^2}{r_1^2 + r_2^2} \right) \right], \quad (B2)$$

$$\langle J_{-2} \rangle \langle \Omega_n^s(M) \rangle \approx \left[ \frac{1}{2} t W_e(0) \right]^{-1} [1 + n(t-s)/h(b'')], \quad (B3)$$

$$\langle T_{2,n}(M) \rangle \approx \langle T_{2,n}^{\text{sec}} \rangle + \langle T_{2,n}^{\text{pseudosec}}(M) \rangle + \langle T_{2,n}^{\text{nonsec}}(M) \rangle, \quad (B4)$$

where  $\langle T_{2,n}^{\text{sec}}(M) \rangle + \langle T_{2,n}^{\text{pseudosec}}(M) \rangle$  are given by Eq. (3.26) and

$$\langle T_{2,n}^{\text{nonsec}}(M) \rangle = -2A \left\{ \frac{4}{3} b [j^D(\omega_0)/j^D(0)] \left[ \frac{1}{2} n + 3(M^2 - \frac{1}{2}\epsilon) + (6\epsilon - 7)M^2 \right] + \frac{1}{4} j^I(\omega_0) W_e\{0\} [2n + 1 - 2\epsilon M - 2M(M + \epsilon)/n] \right\}. \quad (B5)$$

In these equations

$$r_i = 2(b + c_i)/t, \quad (B6)$$

$$s = 2(b + c_1)(b + c_2)/t, \quad (B7)$$

$$t = 2b + c_1 + c_2, \quad (B8)$$

where  $c_1$  and  $c_2$  are proportional to the spectral densities needed for  $W_{x1}$  and  $W_{x2}$ , respectively:

$$c_1 = 2j_{rr}^{(D)}(\omega_0)/W_e(0), \quad (B9a)$$

$$c_2 = \left[ \frac{1}{3} j_{rr}^{(D)}(\omega_0) + \frac{1}{2} j_{rr}^{(I)}(\omega_0) \right] / W_e(0). \quad (B9b)$$

Also  $\epsilon = \pm 1$  for ENDOR frequency  $\omega_{n\pm}$  (i.e.,  $m_e = \pm 1$ ). These results are easily generalized to several groups of completely equivalent nuclei, where for  $\langle J_{v-2} \rangle \langle \Omega_{e,n}^s \{M_r\}^2 \rangle$  the leading term is given by

$$n_v A^2 (r_{1,v}^2 + r_{2,v}^2) \left( 1 - 2M_v \epsilon \frac{r_{1,v}^2 - r_{2,v}^2}{r_{1,v}^2 + r_{2,v}^2} / n_v \right).$$

This has the required property that if  $c_{1,v} = 0$  (pure isotropic spectral density) then for  $M_v = \mp n_v$  the  $\omega_{n\pm}$  ENDOR induces no enhancements.<sup>1</sup> Also when  $c_{1,v}, c_{2,v} \rightarrow 0$ ,  $r_{1,v} = r_{2,v} = b_v$  and the expression becomes equivalent to Eq. (3.24). But, when  $c_{1,v} \neq c_{2,v}$  and  $c_{1,v}, c_{2,v} \gtrsim b_v$ , the relative intensities of the ENDOR lines from the different equivalent sets of protons can be affected, in lowest order, by the values of these dimensionless parameters. Note that the results of Eqs. (B1)-(B3) may be applied to spins of  $I > \frac{1}{2}$  by reverse application of Eqs. (3.21) and (3.22).

One may deal with the ELDOR effects in a similar manner. One finds that in Eq. (4.4) one needs only to let  $b_v \rightarrow (b_v^2 - c_{1,v}c_{2,v}) / [b_v + \frac{1}{2}(c_{1,v} + c_{2,v})]$ . Thus if  $c_{1,v}c_{2,v} > b_v^2$  (and  $b''$  is negligible), an enhancement, rather than a reduction, is seen for the  $v$ th set of nuclei.

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<sup>6</sup>J. H. Freed, *ESR Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Chap. 18.

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<sup>16</sup>Note that in Eq. (2.22) we also utilize the matrix  $\mathbf{D}$  as an operator on  $\hat{W}$ , etc., hence on eigenstate-pair space which is, in general, of different dimension than the space of induced transitions. However, one finds that  $\mathbf{D}_i \hat{d} = \hat{d} \mathbf{D}_i$  (and  $\mathbf{D}_i \hat{d} = \hat{d} \mathbf{D}_i$ ), where  $\mathbf{D}_i$  and  $\mathbf{D}_e$  are specifically operators in transition and eigenstate space, respectively. [This equality follows because the degeneracy of a transition is the same as the degeneracy of the eigenstate(s) (pairs) to which it is related.] Because of this equality, which is utilized in obtaining Eq. (2.22), it is not really necessary to specify the subscript, since the required space and dimension is always clear.

<sup>17</sup>Note that the matrix  $\hat{W}^s$  given here is related to the  $\hat{W}^{av}$ -type matrix used in II and IV by  $\hat{W}^s = D^{-1/2} \hat{W}^{av} D^{1/2}$ .

<sup>18</sup>The definitions of these terms are discussed in detail in papers I-III and Ref. 6. We summarize them as follows:

$\Delta\omega_e = \omega_e - \omega$ , and  $\Delta\omega_n = \omega_n - \omega_n$  are the deviations of the ESR and NMR resonant fields from the respective Larmor frequencies of the induced transitions;  $d_e = (1/2)\gamma_e B_e$  and  $d_n = 1/2\gamma_n B_n$  where  $B_e$  and  $B_n$  [see Eq. (2.46) for  $d_n$ ] are the strengths of the radiation fields rotating at frequencies  $\omega_e$  and  $\omega_n$  respectively. Also,  $d_n = [J_n(J_n + 1) - M_n(M_n + 1)]d_n$ ;  $q = \hbar / NkT$ , where  $N$  is the total number of eigenstates.

<sup>19</sup>In general the sum in Eq. (2.35) should include terms  $(OM'O^{-1})_{\Gamma_i, \Gamma_j}$ ,  $(OM'O^{-1})_{\Gamma_i, \Gamma_j} F_{\Gamma_i, \Gamma_j} / F$ , where  $i, j \neq 1$  and the  $\Gamma_i, \Gamma_j$  refer to the various linear combinations of induced ESR transitions. But the approximate diagonalization of  $OM'O^{-1}$  means that  $(OM'O^{-1})_{\Gamma_i, \Gamma_j}$  are of order  $d_n d_e b / W_e$  (see Sec. III), so these terms appear as quadratic in  $b$ . Thus they may be neglected at our level of approximation. These terms simply tend to lead to an "effective"  $\Omega_e(M)$  which is a little smaller than that computed from Eq. (2.35). They would have no direct ENDOR effect in lowest order.

<sup>20</sup>We are also assuming that off-diagonal elements  $f_{\Gamma_i, \Gamma_j}$  for  $i \neq j$  given by  $d_n d_e (O \Omega_{\Gamma_i, \Gamma_j}^s)$  for  $i \neq j$  are much smaller than typical diagonal elements. One may show that they are of order  $d_n d_e b / W_e$  (see Sec. III) and thus negligible (cf. Ref. 19).

<sup>21</sup>The saturation parameters for a single nuclear spin of  $I = 1/2$  are  $\Omega_e = 2W_e^{-1}[(1+b''+1/2b)/(1+2b''+b)]$ ,  $|\Omega_{e,n}| = W_e^{-1}(1+2b''+b)^{-1}$ ,  $\Omega_n = (bW_e)^{-1}[(1+2b''+2b)/(1+b+2b'')]$ . The average results of Eqs. (3.23)-(3.25) for  $n=1$  become equal to these expressions as  $b \rightarrow 0$ .

<sup>22</sup>These results for "average ENDOR" appear to be

independent of  $b$ , to lowest order. Note, however, that if  $b, = 0$ , the saturation term in the denominator of Eq. (2.47) would become infinite and  $E \rightarrow 0$ . The peculiarity of  $\langle \Omega_{e,n}^2 \{M_r\} \rangle$  seeming to be virtually independent of  $b$ , for  $b, \ll 1$  is really a consequence of having set  $W_{n,+} = W_{n,-}$  [cf. Eq. (2.10b)], i.e., the nuclear spin transitions for lower and upper electron-spin states are equal, as should be the case for an END mechanism in liquids. If we allow for  $W_{n,+}$  and  $W_{n,-}$  to be different, then for a single spin of  $I = 1/2$  one has  $|\Omega_{e,n\pm}| = 2W_{n\mp} / Y$ , while  $\Omega_{n\pm} = 2(W_e + 2W_{n\mp}) / Y$ , where  $Y = W_e(W_{n\pm} + W_{n\mp}) + 2W_{n\pm}W_{n\mp}$  as compared to the case for  $W_{n,+} = W_{n,-}$  given in Ref. 21. Thus, if one induces the  $n+$  NMR transitions and  $W_{n,-} \rightarrow 0$ , with  $W_{n,+}$  remaining finite, then  $\Omega_{e,n+} \rightarrow 0$  (while  $\Omega_{n+}$  remains finite), and there would be no ENDOR enhancement,  $E = 0$ . Related comments apply if the dominant relaxation is  $W_{X_1}$  and  $W_{X_2}$  instead of  $W_{n\pm}$  (cf. paper I and Appendix B).

<sup>23</sup>The basis of the analysis of the  $\mathbf{W}$  matrix is Eq. (2.51) of I. Since there are some errors in sign in it, we give it correctly here:  $[\Gamma(X)]_{a_j a_k} = T_{a_j a_k}^{-1} X_{a, a_k} + 1/2 \sum_l \text{in } a, \gamma_m (W_{(a_k a_l)} \gamma_m^X a_k a_l + W_{(a_j a_l)} \gamma_m^X a_j a_k) - \sum_{\beta l, \beta m} W_{(a_j a_k)(\beta l \beta m)} X_{\beta l, \beta m}$ . One notes from this equation that the diagonal elements of  $\mathbf{W}$  [i.e.,  $(W)_{a_j a_j a_j a_j}$ ] do not include any pseudotransition probabilities (e.g.,  $W_{(a_k a_l) \gamma_m}$ ,  $k \neq l$ ) which would have involved  $b_{n, \gamma_m}$ -type terms.

<sup>24</sup>Note that for the average widths the forbidden transitions involving the pseudodiagonal eigenstates again play no role. One considers only the subspace of allowed ESR transitions.<sup>13</sup>

<sup>25</sup>We have found some interesting simplifications in this case of two  $I = 1/2$  spins in the coupled rep. (1) In the  $\mathbf{W}$  matrix, although there are transition probabilities between  $|1,0\rangle$  and  $|0,0\rangle$  states, there are no pseudotransition probabilities, i.e.,  $W_{(a_j a_k) \gamma} = 0$  for  $j \neq k$ . (2) The  $\mathbf{R}$  matrix for the NMR transitions does not couple any transitions involving  $|J, M\rangle = |1,0\rangle$  with those involving  $|0,0\rangle$ . (3) The  $\mathbf{R}$  matrix for the ESR transitions does not mix in the forbidden ESR transitions  $|\pm; 1,0\rangle \leftrightarrow |\mp; 0,0\rangle$  with the allowed transitions  $|+; 1,0\rangle \leftrightarrow |-; 1,0\rangle$  and  $|+; 0,0\rangle \leftrightarrow |-; 0,0\rangle$  although the latter two are coupled. We have not determined if any of these observations are more general.

<sup>26</sup>It was pointed out in Paper II that Heisenberg spin exchange (utilized in its linearized form) is not symmetric, so Eqs. (2.41) of I do not apply. This followed from the form of Eq. (2.18) of II. It is possible to take advantage of the relation  $X_+ + X_- = 0$  [cf. Eq. (2.19a) of II] to rewrite this equation as  $[W_{EX} X]_{a\pm} = (\omega_{EX}/2) [(X_{a\mp} - X_{a\pm}) + (X_+ - X_-)] = (-\omega_{EX}/2) [(1-2/N)\hat{X}_\alpha - \Sigma \gamma \pm \alpha (2/N)\hat{X}_\gamma]$  and in this form the sum of all elements in a row (as well as in a column) yields zero. This relation is closely related to the form of Eq. (B7) in IV for  $\hat{W}_{EX}$ .