

Theory of Saturation and Double-Resonance Effects in ESR Spectra

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A theory of saturation in the electron spin resonance spectra of dilute solutions of free radicals has been developed in terms of the general Boltzmann equation for the density matrix given by Bloch and Redfield. It is shown, in contrast to the earlier theories, that, in general, a composite line arising from a set of degenerate nuclear spin states must be described by a generalized (matrix) saturated Lorentzian rather than a single line of over-all saturated Lorentzian shape. The general properties of this solution are discussed in detail for the case when electron-nuclear dipolar interactions are the only important nuclear-spin-dependent relaxation mechanism. A particularly simple situation exists when similar nuclei are completely equivalent. Then each composite line consists of a superposition of saturated Lorentzians, and the linewidths and saturation parameters of each component depend only on the values of the total spin and of the z component of spin of the associated configuration of the completely equivalent nuclei. Thus it would be possible to saturate some components to a greater extent than others. These simple components may become coupled together in a complex fashion when the time-dependent fluctuations of the dipolar interactions for equivalent nuclei are no longer identical, which is often the case for aromatic-ring protons. Further coupling may be expected from the effects of nuclear-quadrupole interactions and from intermolecular-exchange phenomena and are only qualitatively discussed. In the absence of saturation the present theory reduces to the linewidth theory of Freed and Fraenkel.

Detailed expressions are obtained for steady-state electron-nuclear double-resonance (ENDOR) effects on radicals containing completely equivalent sets of nuclei. The saturating fields can lead to coherence and induced-transition effects. It is shown how the latter, under appropriate conditions, can result in enhancement of saturated ESR spectra. It appears necessary for enhancements that lattice-induced nuclear spin transitions should be comparable in magnitude to the lattice-induced electron spin transitions, or else cross transitions involving both nuclear and electron spins must be important in the relaxation process. Coherence effects involving both electron and nuclear spin transitions should be unimportant when the main contribution to the ESR linewidths results from secular processes and is nuclear spin independent. This is also the condition for NMR linewidths to be significantly narrower than ESR linewidths. Complications still arise from the coherence and linewidth coupling effects of the different nuclear transitions being excited. A brief discussion of enhancement by a transient "heating" effect is also given.

1. INTRODUCTION

IN a number of recent theoretical and experimental studies,¹⁻⁷ many detailed properties of the unsaturated line shapes of electron spin resonance of free radicals have been elucidated, and it has been shown that such studies can often yield useful information about dynamical molecular processes such as molecular tumbling motions, internal rotations, solvent complexing, etc. These processes modulate the molecular spin systems and thus lead to spin relaxation effects which determine the line shapes. Since these mechanisms also determine the saturation behavior of the spectra, saturation studies represent another method by which information may be obtained about them. The recent successful experiments of Hyde and Maki⁸ with elec-

tron-nuclear double resonance (ENDOR) suggest that this technique would also be useful in relaxation studies.

The recent theory of linewidths of Freed and Fraenkel¹ deals in detail with the unsaturated line shapes of ESR spectra with well-resolved hyperfine structure. It was shown that in such situations degenerate (or multiple) hyperfine lines will be described by superpositions of unsaturated Lorentzian lines which may in general have different widths. This prediction is contrary to the earlier theory of Kivelson⁹ which, based on the general Kubo-Tomita theory,¹⁰ assumed a degenerate hyperfine line to be a single Lorentzian with an averaged width. The necessity for introducing superpositions of lines is demonstrated quite clearly in the interpretation of alternating linewidth phenomena which can arise from solvent or internal-rotation induced modulations of the hyperfine splittings.^{1,3,5,7} Careful measurements on the spectrum of the tetracyanoethylene anion,⁴ where the widths are strongly dependent on molecular tumbling modulations of the electron-nuclear dipolar interaction, demonstrated that the degenerate hyperfine lines did in fact have different shapes a result incompatible with an assumption of averaged Lorentzians. The importance of considering unsaturated Lorentzians as superpositions must of course carry over to the treatment of saturation effects in ESR spectra.

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² J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **40**, 1815 (1964).

³ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962); **41**, 699 (1964); J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *ibid.* **37**, 1881 (1962).

⁴ J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **41**, 949 (1964).

⁵ J. H. Freed and G. K. Fraenkel, *J. Am. Chem. Soc.* **86**, 3477 (1964).

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⁸ (a) J. S. Hyde and A. H. Maki, *J. Chem. Phys.* **40**, 3117 (1964); (b) J. S. Hyde, *Bull. Am. Phys. Soc.* **9**, 568 (1964).

⁹ D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960).

¹⁰ R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).

Earlier theoretical and experimental work on ESR saturation by Lloyd and Pake¹¹ was concerned only with the nondegenerate hyperfine lines of peroxyamine disulfonate, and while Stephen and Fraenkel^{12,13} developed a theory for degenerate hyperfine lines which was utilized in saturation studies by Schreurs and Fraenkel,¹⁴ theirs takes as its starting point the assumption that each degenerate hyperfine line is a simple average Lorentzian, whose saturation behavior is represented by a single saturation parameter. In this paper we are concerned, in part, with extending the treatment of the linewidth theory in I involving superpositions of Lorentzians to conditions when saturation effects become appreciable. The earlier saturation theories¹¹⁻¹³ assume at the outset that a master equation can be written solely in terms of populations of the spin eigenstates, i.e., one may neglect off-diagonal elements of the density matrix. A detailed demonstration of the effects of degeneracies requires, however, a more general approach, and it can be seen that the simplified master equation used in the earlier theories is not always correct. It is also useful to have a formulation in which the correct unsaturated linewidths appear in the results, so there will be no ambiguity about the detailed shape of the saturated hyperfine lines, and this also requires the correct evaluation of off-diagonal density-matrix elements. The theory in I, while rigorous for degenerate lines, was based on the Kubo-Tomita¹⁴ analysis of a linear response to an applied oscillatory field and is thus not applicable to saturation problems. In this paper the general Boltzmann equation for the density matrix as developed by Bloch¹⁵ and modified by Redfield¹⁶ and Abragam¹⁷ is utilized. It contains the oscillatory field explicitly in the Hamiltonian and readily permits an analysis of saturation effects.

The detailed application of the general theory is in general quite complex. However, the emphasis is on the special conditions applicable to the ESR of well-resolved hyperfine lines where intermolecular exchange effects are small (these effects are not readily handled in terms of the Bloch formulation), and this permits a number of simplifying assumptions. Nevertheless, many of the interesting effects which one may hope to note experimentally are based upon further rather specific properties of the relaxation mechanisms, and we try to elucidate what a few of them are as well as conditions under which they may be realized. The present treatment is also applicable to the case where more than one oscillatory field is applied, and this permits a discussion of steady-state ENDOR experiments.

¹¹ J. P. Lloyd and G. E. Pake, *Phys. Rev.* **94**, 579 (1954).

¹² M. J. Stephen and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1435 (1960).

¹³ M. J. Stephen, *J. Chem. Phys.* **34**, 484 (1961).

¹⁴ (a) J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.* **34**, 756 (1961); (b) J. W. H. Schreurs, G. E. Blomgren, and G. K. Fraenkel, *ibid.* **32**, 1861 (1960).

¹⁵ (a) F. Bloch, *Phys. Rev.* **102**, 104 (1956); (b) R. K. Wangness and F. Bloch, *ibid.* **89**, 728 (1953).

¹⁶ A. G. Redfield, *IBM J. Res. Develop.* **1**, 19 (1957).

¹⁷ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

2. THEORY OF SATURATION

A. General Theory

i. Hamiltonian

A spin system is described by a spin Hamiltonian of the form

$$\hbar\mathcal{H}(t) = \hbar\mathcal{H}_0 + \hbar\mathcal{H}_1(t) + \hbar\epsilon(t), \quad (2.1)$$

where, in the high-field approximation,¹⁸

$$\hbar\mathcal{H}_0 = \bar{g}_e \beta_e B_0 S_z - \hbar \sum_i \gamma_i I_{zi} B_0 - \hbar \gamma_e \sum_i \bar{a}_i S_z I_{zi}; \quad (2.2a)$$

is the time-independent Hamiltonian, from which zero-order energy levels as well as transition frequencies may be predicted. Here β_e is the Bohr magneton; B_0 is the externally applied dc magnetic field assumed to be along the z axis; $\gamma_e = -|\gamma_e|$ and γ_i are, respectively, the magnetogyric ratios of the electron and the i th nucleus; \bar{g}_e and \bar{a}_i are averaged values (see I) of the g -tensor and isotropic hyperfine interactions (in gauss), respectively. The summations are over all magnetic nuclei in the radical. Only radicals with a single unpaired electron ($S = \frac{1}{2}$) will be considered. It will also be assumed that the ESR consists of well-separated hyperfine lines which are, in general, degenerate. $\mathcal{H}_1(t)$ in Eq. (2.1) includes the terms which are randomly modulated by the lattice and lead to line broadening and relaxation. It may be formally written in terms of irreducible tensors as

$$\mathcal{H}_1(t) = \sum_{L,m,\mu,i} F_{\mu,i}{}^{(L,m)}(t) A_{\mu,i}{}^{(L,-m)}, \quad (2.2b)$$

where $F_{\mu,i}{}^{(L,m)}$ is a random lattice function and $A_{\mu,i}{}^{(L,-m)}$ contains only spin operators. The different types of perturbations in $\mathcal{H}_1(t)$ are distinguished by the subscript μ and the different nuclei in the radical by i . The rank and component of the tensors are given by L and m , respectively. In Eq. (2.1) $\epsilon(t)$ represents the interaction of the spins with a time-dependent magnetic field which is assumed to be made up of one or more monochromatic oscillatory fields.

ii. Density Matrix Equation of Motion¹⁶⁻¹⁷

One may define a density matrix σ_s for a spin system. It obeys the equation of motion

$$\dot{\sigma}_s = -i[\mathcal{H}(t), \sigma_s]. \quad (2.3)$$

Due to the random nature of $\mathcal{H}_1(t)$, it is necessary to consider a statistical ensemble of systems described by the average density operator: $\sigma = \bar{\sigma}_s$. It is shown in the general theories¹⁵⁻¹⁷ that when

$$\langle |\mathcal{H}_1(t)|^2 \rangle_{av} \ll \tau_c^{-1}, \quad (2.4a)$$

where τ_c is a correlation time for the random motions leading to relaxation and the pointed brackets indicate

¹⁸ This equation neglects the $\bar{a}_i S_z I_{zi}$ terms on the assumption that they will lead to frequency shifts which are small compared to the observed linewidths. But see R. W. Fessenden, *J. Chem. Phys.* **32**, 747 (1962); also, G. K. Fraenkel, *ibid.* **42**, 4275 (1965).

an ensemble average, only terms to second order in $\mathcal{H}_1(t)$ affect the relaxation. Furthermore, when

$$|\epsilon(t)| \ll \tau_c^{-1}, \quad (2.4b)$$

any effects of the rf field on the relaxation terms are negligible.

One obtains in the high-temperature approximation:

$$\dot{\sigma} = -i[\mathcal{H}_0 + \epsilon(t), \sigma] - \Gamma(\sigma - \sigma_0), \quad (2.5)$$

where σ_0 is the equilibrium density matrix given by

$$\sigma_0 \equiv \frac{\exp(-\hbar\mathcal{H}_0/kT)}{\text{Tr}[\exp(-\hbar\mathcal{H}_0/kT)]} \cong N^{-1}(1 - q\mathcal{H}_0). \quad (2.6)$$

N is equal to the number of eigenstates of \mathcal{H}_0 and $q = \hbar/kT$. Since $|\epsilon(t)|$ is assumed small compared to $\mathcal{H}_0(t)$ (see below), it has been omitted from Eq. (2.6). Also,

$$-[\Gamma(\sigma - \sigma_0)]_{\alpha\alpha'} = \sum_{\beta\beta'}' R_{\alpha\alpha'\beta\beta'}(\sigma_{\beta\beta'} - \sigma_{0\beta\beta'}), \quad (2.7)$$

where the relaxation effects of $\mathcal{H}_1(t)$ are contained in the relaxation matrix $R_{\alpha\alpha'\beta\beta'}$, given by¹⁹

$$R_{\alpha\alpha'\beta\beta'} = 2J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha\beta}) - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\alpha\gamma\beta\gamma}(\omega_{\gamma\beta}) - \delta_{\alpha\beta} \sum_{\gamma} J_{\gamma\alpha'\gamma\beta'}(\omega_{\beta'\gamma}) \quad (2.8a)$$

and

$$J_{\alpha\beta\alpha'\beta'}(\omega) = \sum_{L, \mu, \nu, i, j} j_{ij}^{(\mu, \nu; L)}(\omega) \sum_q [A_{\mu, i}^{(L, q)}]_{\alpha\beta} \cdot [A_{\nu, j}^{(L, q)}]_{\alpha'\beta'}^*. \quad (2.8b)$$

Here $A_{\alpha\beta}$ is a shorthand notation for the α, β matrix element of A . The spectral densities $j_{ij}^{(\mu, \nu; L)}(\omega)$ are the Fourier transforms of correlation functions, $g_{ij}^{(\mu, \nu; L)}(\tau)$:

$$j_{ij}^{(\mu, \nu; L)}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} g_{ij}^{(\mu, \nu; L)}(\tau) \exp(-i\omega\tau) d\tau. \quad (2.8c)$$

These correlation functions are determined by the properties of the $F_{\mu, i}^{(L, m)}(t)$. They are given in detail in I and in Ref. 6 for electron-nuclear-dipolar, g -tensor, and quadrupolar interactions.

The prime on the summation of Eq. (2.7) indicates that it is restricted by the condition

$$\omega_{\alpha\alpha'} - \omega_{\beta\beta'} = 0, \quad (2.7')$$

where the angular frequencies $\omega_{\alpha\beta}$ are defined by $\hbar\omega_{\alpha\beta} = -\hbar\omega_{\beta\alpha} = E_{\alpha} - E_{\beta}$ and E_{α} represents the energy of the α th eigenstate of $\hbar\mathcal{H}_0$. The restriction of Eq. (2.7') on Eq. (2.7) is applicable provided that the energy difference between any pair of eigenlevels, given by $\omega_{\alpha\beta}$, as well as any double difference $\omega_{\alpha\alpha'} - \omega_{\beta\beta'}$, may either be taken as zero or large compared to $|\epsilon(t)|$

and $|\Gamma(\sigma - \sigma_0)|$.¹⁶ Thus from an examination of Eqs. (2.2a) and (2.4), we obtain the conditions

$$|\gamma_e B_0|, \quad |\gamma_i B_0|, \quad |\gamma_e \bar{a}_i| \gg |\epsilon(t)|, \quad |\Gamma(\sigma - \sigma_0)|, \quad (2.9)$$

and we assume no accidental near equalities of any of the three kinds of terms on the left of Eq. (2.9). Conditions given by Eq. (2.9) are equivalent to saying that all the lines in the spectrum (both for electron spin and for nuclear spin transitions) are either well separated in the presence of relaxation and saturation effects or they are degenerate. It implies, furthermore, that $\epsilon(t)$ must have a frequency component lying close to that of a particular spin transition if it is to have any appreciable effect on the spectrum, and then it will excite no other spin transitions which are not actually degenerate with the first.

iii. Power Absorption

We consider a single rotating rf field

$$\mathbf{B}_1(t) = B_1(\cos\omega t \mathbf{i} + \sin\omega t \mathbf{j}) \quad (2.10)$$

whose frequency lies near that of an ESR transition frequency. It induces a magnetic moment $\mathbf{M}(t)$ in a macroscopic sample. (This field may be thought of as one of the components of a linear field $\mathbf{B}_x = 2B_1 \cos\omega t \mathbf{i}$.) The power absorbed by the paramagnetic spins may be expressed as²⁰

$$P = -\mathbf{M} \cdot d\mathbf{B}_1(t)/dt = -\omega B_1 i / 2 [M_+ \exp(-i\omega t) - M_- \exp(+i\omega t)], \quad (2.11)$$

where $M_{\pm}(t) = M_x(t) \pm iM_y(t)$.

Now $M_{\pm}(t)$ may be calculated statistically from its associated quantum-mechanical operator

$$\mathfrak{M}_{\pm} = \mathfrak{N} \hbar \gamma_e S_{\pm} \quad (2.12a)$$

by

$$M_{\pm}(t) = \mathfrak{N} \hbar \gamma_e \text{Tr}[\sigma(t) S_{\pm}], \quad (2.12b)$$

where \mathfrak{N} is the concentration of electron spins. Equation (2.9) assumes an assembly of noninteracting spin systems, that are well represented by Boltzmann statistics. Since this equation represents a trace over all spin states, it will be invariant to a choice of zero-order basis functions.

B. Transitions and Relaxation Matrix

i. Basis Functions and Transitions

A convenient set of basis functions used in I may be abbreviated by

$$|\gamma^{\pm}\rangle \equiv |\pm\rangle; \{J_{r_u}^{(\kappa)} M_{r_u}\} \\ \equiv |m_s = \pm \frac{1}{2}\rangle \prod_{r_u} |J_{r_u}^{(\kappa)} M_{r_u}\rangle, \quad (2.13)$$

¹⁹ There are small imaginary terms in $R_{\alpha\alpha'\beta\beta'}$ which are neglected in the present discussion. They are sometimes important and methods for including them in the absence of saturation effects are discussed by G. K. Fraenkel, Ref. 18.

²⁰ See Ref. 17, p. 48.

that is, the product of an electron spin wavefunction $|m_s\rangle$ with the products of nuclear spin functions $|J_{r_u}^{(\kappa)} M_{r_u}\rangle$. Here r_u represents the u th completely equivalent subgroup of nuclei of the r th group of equivalent nuclei. {Nuclei are said to be equivalent if they are identical in $\mathcal{H}_0 + \epsilon(t)$ and completely equivalent only if identical in $\mathcal{H}_1(t)$ as well, [see Eq. (2.1)].²¹} Defining the operator

$$J_{r_u} = \sum_{i \text{ in } r_u} I_i,$$

then $|J_{r_u} M_{r_u}\rangle$ represents the eigenfunction of $J_{r_u}^2$ and J_{r_u} with eigenvalues $J_{r_u}(J_{r_u}+1)$ and M_{r_u} , respectively. The superscript κ denotes the different degenerate states of the same value of J_{r_u} . The term in braces $\{J_{r_u}^{(\kappa)} M_{r_u}\}$ thus corresponds to a particular configuration of nuclear spin states.

It is useful to relate the different eigenstates and their matrix elements to the particular ESR hyperfine lines to which they contribute. Let $|a_j^-\rangle$ and $|a_j^+\rangle$ denote two eigenstates which contribute to the λ th line, such that

$$|a_j^\pm\rangle = |\pm\frac{1}{2}; \{J_{r_u}^{(\kappa)} M_{r_u}\} \lambda_j\rangle, \quad (2.14)$$

i.e., they have the same combination of nuclear spin functions but differ only in their value of m_s . The subscript j ranges in value from 1 to D_λ . (Note that $N = 2 \sum_\lambda D_\lambda$.) Now the matrix elements of any operator, O , involving only the $|a_j^\pm\rangle$ may be written as follows when it is desired to order them according to the transi-

²¹ Further details on equivalence versus complete equivalence are given in I. When equivalent nuclei differ only slightly in $\mathcal{H}_1(t)$, then it is useful to consider them as completely equivalent and then to introduce a simple first-order correction. That is, if the r th equivalent group is composed of two completely equivalent subgroups r_u, r_v , and if $g_{r_u r_v}^{(\mu; \nu; L)} = g_{r_r}^{(\mu; \nu; L)} + \Delta_r^{(\mu; \nu; L)}$, where

$$|\Delta_r^{(\mu; \nu; L)} / g_{r_r}^{(\mu; \nu; L)}| \ll 1 \quad (\text{for all } \mu, \nu, \text{ and } L),$$

then using Eqs. (2.8)

$$\begin{aligned} & \sum_{i, j \text{ in } r_u, r_v} g_{ij}^{(\mu, \nu, L)}(\tau) [A_{\mu, i}^{(L, \vartheta)}]_{\alpha\beta} [A_{\nu, j}^{(L, \vartheta)}]_{\alpha'\beta'}^* \\ &= g_{r_r}^{(\mu, \nu, L)} [A_{\mu, r}^{(L, \vartheta)}]_{\alpha\beta} [A_{\nu, r}^{(L, \vartheta)}]_{\alpha'\beta'}^* \\ &+ \Delta_r^{(\mu, \nu, L)} \{ [A_{\mu, r_u}^{(L, \vartheta)}]_{\alpha\beta} [A_{\nu, r}^{(L, \vartheta)}]_{\alpha'\beta'}^* \\ &+ [A_{\mu, r_v}^{(L, \vartheta)}]_{\alpha\beta} [A_{\nu, r_u}^{(L, \vartheta)}]_{\alpha'\beta'}^* \}, \end{aligned}$$

where

$$A_{\mu, r}^{(L, \vartheta)} = \sum_{i \text{ in } r_u, r_v} A_{\mu, i}^{(L, \vartheta)}$$

and the term in $\Delta_r^{(\mu, \nu, L)}$ is a small correction to be added to those $R_{\alpha\alpha'\beta\beta'}$ matrix elements for which the term in $g_{r_r}^{(\mu, \nu, L)}$ is nonvanishing. In the case of the linewidth matrix, this amounts to a neglect of the small off-diagonal elements compared to the large (corrected) diagonal terms. For the transition-probability matrix, this amounts to a neglect of weak pseudotransitions (see Sec. 4). If it is desired to calculate the error involved in such approximations, it is better to use the representation of products of the two equivalent groups rather than their coupled representation, as the calculation of off-diagonal matrix elements is much more difficult in the latter representation. (Note that the theory given in I is treated in full detail with the former representation.)

tions to which they are related:

$$O_{\lambda_{jk}} \equiv O_{a_j^- a_k^+} = O_{a_k^+ a_j^-}^{\text{tr}} = O_{\lambda_{kj}}^{\text{tr}}, \quad (2.15a)$$

where $O_{\lambda_{jk}}$ is referred to as the matrix element for the λ_{jk} th transition, and we sometimes use

$$O_{\lambda_{jk}} \equiv O_{a_j^\pm a_k^\pm} = O_{a_k^\pm a_j^\pm}^{\text{tr}}, \quad (2.15b)$$

where the superscript tr stands for transpose. When $j=k$ in Eqs. (2.15), the second subscript is dropped (i.e., $O_{\lambda_{jj}} = O_{\lambda_j}$), and whenever it does not result in ambiguity the forward arrows are also dropped. When ω lies close to the resonant frequency ω_λ of the λ th hyperfine line which is well separated from the other lines in the spectrum, then the trace of Eq. (2.12b) need only be taken over those states which contribute to the λ th line. Furthermore, from the nature of the S_\pm operator this trace need only be taken over all pairs of states $|a_j^-\rangle$ and $|a_j^+\rangle$ obeying Eq. (2.14). By definition they also obey

$$E_{\lambda_j^+} - E_{\lambda_j^-} = \hbar\omega_\lambda. \quad (2.16)$$

We neglect accidental degeneracies of hyperfine lines for simplicity (although the formulation can readily be extended to include them). Thus the λ th composite ESR hyperfine line is assumed to arise only because $E_{\lambda_j^\pm} = E_{\lambda_k^\pm}$ for all values of j and k . It then follows from Eq. (2.2a) that the relation

$$M_{r^\lambda} \equiv \sum_{u \text{ in } r} M_{r_u}^{\lambda_j} = M_{r^\lambda} \quad (2.17)$$

must be obeyed independent of j and for all r .

ii. Steady-State Equations

It is convenient to study the deviation of the density matrix from its equilibrium values given by

$$\chi \equiv \sigma - \sigma_0. \quad (2.18)$$

Steady-state solutions for the χ_{λ_j} will be obtained where

$$\chi_{\lambda_j} = Z_{\lambda_j} \exp(i\omega t) \quad (2.19)$$

with Z_{λ_j} time independent.

Then the λ th hyperfine line leads to a power absorption

$$P_\lambda = \mathfrak{R} \hbar \omega \gamma_e B_1 \sum_j (S_{-\lambda_j} Z_{\lambda_j}'''), \quad (2.20)$$

where

$$Z_{\lambda_j} = Z_{\lambda_j}' + i Z_{\lambda_j}'''. \quad (2.21)$$

Expressions for the Z_{λ_j} are obtained from Eq. (2.5). In the present case of a rotating rf field given by Eq. (2.10) which excites only electron spin transitions we may take:

$$\hbar\epsilon(t) = \frac{1}{2} \hbar \gamma_e B_1 [S_+ \exp(-i\omega t) + S_- \exp(+i\omega t)]. \quad (2.22)$$

Let

$$\frac{1}{2} \gamma_e B_1 S_{-\lambda_j} = d_{\lambda_j} = d. \quad (2.23)$$

Then taking the $\langle a_j^- || a_j^+ \rangle$ matrix element of Eq. (2.5) gives

$$\omega_\lambda Z_{\lambda_j} - i \exp(-i\omega t) [\Gamma(\chi)]_{\lambda_j} + d(\chi_{\lambda_j^+} - \chi_{\lambda_j^-}) = q\omega_\lambda d, \tag{2.24}$$

where $\Delta\omega_\lambda = \omega - \omega_\lambda$ and $\chi_{\lambda_j^\pm}$ are the departures of the populations of states $|a_i^\pm\rangle$, etc., from their thermal equilibrium values. They are taken as time-independent in the steady-state solution, and must obey the condition $\sum_i \chi_i = 0$ which follows from the normalization $\sum_i \sigma_{0i} = \sum_i \sigma_i = 1$. Oscillatory terms have been neglected in Eq. (2.24) as they have zero time average values.¹⁵

It may be shown from I that, in the present notation,

$$\exp(-i\omega t) [\Gamma(\chi)]_{\lambda_j} = \sum_{kl} R_{\lambda_j, \lambda_{kl}} Z_{\lambda_{kl}}, \tag{2.25}$$

where k and l need not be equal. Thus, while there are only D_λ distinct Z_{λ_j} needed for Eq. (2.20), there are D_λ^2 distinct $Z_{\lambda_{kl}}$ which may be coupled by Eqs. (2.24) and (2.25). The general expression for all the $D_\lambda^2, Z_{\lambda_{kl}}$ is

$$\Delta\omega_\lambda Z_{\lambda_{jk}} - i \sum_{l,m} R_{\lambda_{jk}, \lambda_{lm}} Z_{\lambda_{lm}} + (d\chi_{\lambda_{jk}^+} - d\chi_{\lambda_{jk}^-}) = q\omega_\lambda d \delta_{jk}, \tag{2.26}$$

where δ_{jk} is the Kroenecker delta function. The $\chi_{\lambda_{jk}^\pm}$ when $j \neq k$ are called pseudodiagonal density matrix elements, since they connect degenerate basis states. In general, then, the coupled Eqs. (2.26) must be solved to obtain the absorption.

iii. Weak Fields—No Saturation

When the applied rf field is very weak, the $\chi_{\lambda_{jk}^\pm}$ will be very small and their product with d_{λ_j} , etc., will be higher order in the rf field, so they may be neglected in Eq. (2.26). One then obtains

$$\Delta\omega_\lambda Z_{\lambda_{jk}} - i \sum_{l,m} R_{\lambda_{jk}, \lambda_{lm}} Z_{\lambda_{lm}} = q\omega_\lambda d \delta_{jk}. \tag{2.27}$$

The “normal-modes” solution of Eq. (2.27) may be obtained by first diagonalizing the $R_{\lambda_{jk}, \lambda_{lm}}$ matrix. The detailed form of this matrix is given in I, and since the solution of Eq. (2.27) is readily shown to be equivalent to the linewidth formulation given there, it is not pursued here except to note that the degenerate hyperfine line is given by a superposition of Lorentzians. This superposition may, of course, be obtained quite simply when the $R_{\lambda_{jk}, \lambda_{lm}}$ matrix is automatically diagonal (i.e., $R_{\lambda_{jk}, \lambda_{lm}} = R_{\lambda_{jk}, \lambda_{jk}} \delta_{\lambda_{jk}, \lambda_{lm}}$). Then Eq. (2.27) yields

$$Z_{\lambda_j} = q\omega_\lambda d T_{\lambda_j} [(\omega - \omega_\lambda) T_{\lambda_j} + i] / [1 + (\omega - \omega_\lambda)^2 T_{\lambda_j}^2], \tag{2.28}$$

for each of the λ_j^\pm pairs of states. Here $T_{\lambda_j} = -(R_{\lambda_j, \lambda_j})^{-1}$ is the transverse relaxation time for the λ_j th transition, and the Lorentzian form of Z_{λ_j} is apparent.

iv. Relationships between Transition Probabilities and Linewidths

While detailed expressions have been given in I for the terms in the $R_{\lambda_{jk}, \lambda_{lm}}$ matrix (i.e., the linewidth matrix for the λ th hyperfine line), it is useful to relate these terms to the lattice-induced transition probabilities which are important in saturation phenomena. It may readily be shown (see Appendix A, I, and Ref. 17) that the diagonal terms are given by

$$-R_{\lambda_{jk}, \lambda_{jk}} = T'_{\lambda_{jk}}^{-1} + \frac{1}{2} \left(\sum_{\gamma \neq a_j^-} W_{a_j^-, \gamma} + \sum_{\gamma \neq a_k^+} W_{a_k^+, \gamma} \right), \tag{2.29}$$

where $W_{\beta\gamma}$ is the transition probability from the β th to the γ th state and $|a_j^\pm\rangle = |\lambda_j^\pm\rangle$. There is an important physical distinction between lattice-induced transitions in which $\Delta m_s = \pm 1$ (nonsecular transitions) and those where there is a change in nuclear spin quantum numbers but $\Delta m_s = 0$ (pseudosecular transitions). The dependence of the nonsecular terms on the relevant τ_c is given to a good approximation by the usual Debye-type function $\tau_c / (1 + \omega_n^2 \tau_c^2)$, where

$$\omega_n = \hbar^{-1} \bar{g}_n \beta_e B_0,$$

while that of the pseudosecular terms is

$$\tau_c / (1 + \omega_n^2 \tau_c^2) \cong \tau_c,$$

since the condition $\omega_n \tau_c \ll 1$ (where ω_n represents a nuclear Larmor frequency) is almost always obeyed in liquids (see Appendix A) even when $\omega_0 \tau_c \gg 1$. (For protons $\omega_n / \omega_0 = \frac{1}{1836}$.) The $T'_{\lambda_{jk}}^{-1}$ in Eq. (2.29) represent only secular line-broadening effects (i.e., effects from modulations of energies of the spin states). Now, the only kinds of off-diagonal terms which can appear (except when quadrupole effects are important) using the set of basis functions given by Eq. (2.13) are of form $R_{\lambda_{ij}, \lambda_{ik}}$ and $R_{\lambda_{ij}, \lambda_{ki}}$ where, for example,

$$-R_{\lambda_{ij}, \lambda_{ik}} = \frac{1}{2} \sum_{\gamma \neq a_j^+, a_k^+} W_{\gamma, (a_j^+, a_k^+)} \quad j \neq k. \tag{2.30}$$

The $W_{(\alpha_j, \alpha_k), \gamma}$ are pseudotransition probabilities given by:

$$W_{(\alpha_j, \alpha_k), \gamma} = 2J_{\alpha_j \alpha_k \gamma}(\omega_{\alpha_j \gamma}), \tag{2.31a}$$

where α_j and α_k are any degenerate pair of eigenstates.

Note that when $j = k$ one obtains the normal transition probabilities

$$W_{(\alpha_j, \alpha_j), \gamma} \delta_{jk} = W_{\alpha_j \gamma} = 2J_{\alpha_j \alpha_j \gamma}(\omega_{\alpha_j \gamma}). \tag{2.31b}$$

The pseudotransition probabilities imply an uncertainty in the appropriate degenerate set of zero-order states from which transitions occur due to the random fluctuations of $\mathcal{H}_1(t)$. It follows from the assumed stationary Markoff time variation of $\mathcal{H}_1(t)$ as well as its Hermitian character that the pseudotransition probabilities obey the relations

$$W_{(\alpha_j, \alpha_k), \gamma} = W_{\gamma, (\alpha_k, \alpha_j)} = W_{\gamma, (\alpha_j, \alpha_k)}^* = W_{(\alpha_k, \alpha_j), \gamma}^* \tag{2.32a}$$

It follows from the detailed forms of the terms in $\mathcal{H}_1(t)$ (given by Table I and Eq. (4.19a) of I that

$$W_{(\alpha_j, \alpha_k), \gamma} = W_{(\alpha_j, \alpha_k), \gamma}^* \quad (2.32b)$$

A list of the nuclear spin-dependent transition probabilities arising from the dipolar and g -tensor terms are given in Appendix A. These transition probabilities may be seen to have the properties that they are zero between degenerate states or states having different values for the $\{J_{r_u}\}$. (These results are no longer correct when quadrupole terms become important since they will connect states of different J_{r_u} .) These properties are a simple consequence of the nature of the basis functions Eq. (2.13) and the fact that the only nuclear spin-dependent terms in $\mathcal{H}_1(t)$ which are being considered are the dipolar terms and they involve either J_{r_u} or $J_{r_u}^\pm$ operators. Furthermore, it is always possible to order the degenerate $\{J_{r_u}^{(\kappa)} M_{r_u}\}$ states so that the value of κ (as well as the value of J_{r_u}) will be preserved in a transition. This conclusion may be expected from general group-theoretic considerations.²² Furthermore,

²² The above nuclear functions correspond to eigenfunctions of the operator $J_{r_u}^2 + bJ_{r_u}$, where b is arbitrary. The eigenfunctions corresponding to each eigenvalue of this operator must transform irreducibly under \mathfrak{H} (apart from accidental degeneracy), where \mathfrak{H} is the group of all possible symmetry transformations of this operator, i.e., each set of m degenerate eigenfunctions forms a basis for a unique m -dimensional irreducible representation of this group. Further, it is possible to order the partner basis functions of a particular basis set by the index κ , such that they are not only orthogonal to all other basis functions corresponding to different irreducible representations, but they are also orthogonal to basis functions of the same irreducible representation but different values of this index κ . Now if an operator O commutes with all the members of the group \mathfrak{H} , it can only have matrix elements between functions belonging to the same irreducible representation and having the same index number κ . The operator $\mathcal{H}_1(t)$, is, by definition, invariant to all the permutations of the r_u th group of completely equivalent nuclei. In the case where these nuclei have $I = \frac{1}{2}$, the group \mathfrak{H} may be taken as this permutation group. This follows from the fact that all the simple-product nuclear spin basis functions [which appear as linear combinations in our representation Eq. (2.13)] corresponding to each value of M_{r_u} may be obtained from one another by the permutation operators. E. P. Wigner in *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959), Chap. 13, shows that this last condition leads to the result that all the functions, which in the present discussion correspond to $M_{r_u} = l$ (where $l = J_{r_u}, J_{r_u} - 1, \dots, 0$) include all the irreducible representations (of the permutation group) contained in the functions corresponding to $M_{r_u} = l + 1$ (where $l < J_{r_u}$) plus one new and distinct irreducible representation of dimensionality $D(n, M_{r_u} = l) - D(n, M_{r_u} = l + 1)$ [where $D(n, M_{r_u})$ refers to the degeneracy of nuclear states for n spins giving a particular value of M_{r_u}]. It is readily seen that such a breakdown into irreducible representations is equivalent to the breakdown into eigenfunctions of the operator $J_{r_u}^2 + bJ_{r_u}$.

The case where $I > \frac{1}{2}$ is more complex, and \mathfrak{H} must then contain more members than just the group of permutations of equivalent nuclei. Calculations for the cases $n \leq 4$ and $I = 1$ show that a set of degenerate eigenfunctions of $J_{r_u}^2 + bJ_{r_u}$ will in general be reducible under just the permutation group. However, the irreducible representations that are then obtained are different and distinct, and this is sufficient for our purposes.

If one attempts to use group-theoretic techniques in dealing with equivalent but not completely equivalent nuclei, one is immediately confronted with the obstacle of incoherent time variations in $\mathcal{H}_1(t)$ of the terms corresponding to the different equivalent sets, as well as the tedious problem of evaluating the terms in Eqs. (2.8b) in basis sets different from Eq. (2.13).

the pseudotransition probabilities also are seen to have the property of only connecting States α_j, α_k , and γ where the values of $\{J_{r_u}^{(\kappa)}\}$ and $\{J_{r_u}^{(\omega)}\}$ remain unchanged.²² When this conclusion along with Eq. (2.30) is applied to Eqs. (2.24) to (2.26), it is seen that a separate coupled equation of form (2.26) may be written for each set of states corresponding to the same value of all the $\{J_{r_u}^{(\kappa)}\}$. Of course, the properties of each set corresponding to the same $\{J_{r_u}\}$ but different κ are identical. The above remarks will lead to other simplifications when saturation effects become important.

C. Saturation

In the event that the rf field is strong enough that the $\chi_{\lambda_j, \pm}$ must be retained in Eq. (2.26), it is necessary to obtain the matrix elements $\langle \lambda_j^\pm || \lambda_k^\pm \rangle$ of Eq. (2.5). Thus

$$[\Gamma(\chi)]_{\lambda_j^+} = 2dZ_{\lambda_j}'' \quad (2.33a)$$

$$[\Gamma(\chi)]_{\lambda_j^-} = -2dZ_{\lambda_j}'' \quad (2.33b)$$

where $j = 1, 2, \dots, D_\lambda$.

Also

$$[\Gamma(\chi)]_{\beta\beta} = 0 \quad (2.33c)$$

where β refers to all eigenstates except $|\lambda_j^\pm\rangle$, and there are $N - 2D_\lambda$ such states. Now Eqs. (2.7) lead to

$$[\Gamma(\chi)]_{\alpha_j \alpha_i} = \sum_{k \text{ in } \alpha, \gamma_l} W_{(\alpha_k \alpha_i), \gamma_l} \chi'_{\alpha_k \alpha_i} - \sum_{\gamma_k, \gamma_l} W_{\alpha_j(\gamma_l, \gamma_m)} \chi'_{\gamma_l \gamma_m} \quad (2.34)$$

where Eqs. (2.31) have been used. Note that in Eq. (2.34), γ_l refers to the l th member of the γ th set of degenerate levels, while α_j refers to the α th set. The transition probabilities in Eq. (2.34) are subject to the conditions discussed in the previous section. Thus the summations in Eq. (2.34) need only be taken over states $|\alpha_k\rangle, |\gamma_l\rangle, |\gamma_m\rangle$ which have the same $\{J_{r_u}^{(\omega)}\}$ as the particular state $|\alpha_j\rangle$. Note that only the real parts of the "pseudodiagonal" elements of χ are involved in the coupled equations.

i. Completely Equivalent Sets of Nuclei

Before considering the general solution of the saturation problem, the case where pseudotransition probabilities are unimportant, i.e., $W_{(\alpha_j, \alpha_k), \gamma_l} = W_{\alpha_k, \gamma_l} \delta_{jk}$ is treated. This is, of course, the case when all equivalent groups of nuclei are also completely equivalent. Then Eq. (2.34) takes the particularly simple form:

$$[\Gamma(\chi)]_{\alpha_j \alpha_i} = \sum_{\gamma_k} W_{\alpha_j \gamma_k} (\chi_{\alpha_j} - \chi_{\gamma_k}), \quad (2.35)$$

and Eq. (2.26) is also simplified [cf. Eq. (2.30)] and becomes

$$Z_{\lambda_j} = (V_{\lambda_j}/d)[q\omega_\lambda - (\chi_{\alpha_j^+} - \chi_{\alpha_j^-})][q\omega_\lambda T_{\lambda_j} + i], \quad (2.36)$$

where

$$V_{\lambda_j} = d^2 T_{\lambda_j} / [1 + (T_{\lambda_j} \Delta\omega_\lambda)^2], \quad (2.36')$$

TABLE I. Saturation factors for sets of completely equivalent nuclei.

M_J	J	$\phi(J, M_J)^{a,b}$	D_J^c						
			$\phi(J, M_J)^{a,b}$			$I = \frac{1}{2}$		$I = 1$	
			$b \ll 1$	$b = 1$	$b \gg 1$	$n=1;$	$n=2;$	$n=3;$	$n=4$
$\pm \frac{3}{2}$	$\frac{3}{2}$	$\frac{2+17b+33b^2+9b^3}{2+20b+54b^2+36b^3}$	1	0.5446	0.2500	1			
$\pm \frac{1}{2}$	$\frac{1}{2}$	$\frac{2+b}{2+2b}$	1	0.750	0.5000	1	2		
	$\frac{3}{2}$	$\frac{2+13b+21b^2+9b^3}{2+20b+54b^2+36b^3}$	1	0.4018	0.2500	1			
± 2	2	$\frac{1+18b+95b^2+150b^3+32b^4}{1+20b+127b^2+288b^3+180b^4}$	1	0.4805	0.2000			1	1
± 1	1	$\frac{1+3b+b^2}{1+4b+3b^2}$	1	0.6250	0.3333	1	3		1 1
	2	$\frac{1+15b+65b^2+96b^3+32b^4}{1+20b+127b^2+288b^3+180b^4}$	1	0.3393	0.2000			1	1
0	0	1	1	1.000	1.0000	1	2		1
	1	$\frac{1+2b+b^2}{1+4b+3b^2}$	1	0.5000	0.3333	1	3		1 1
	2	$\frac{1+14b+61b^2+84b^3+32b^4}{1+20b+127b^2+288b^3+180b^4}$	1	0.3117	0.2000			1	1

^a See Eq. (3.1). ^b $b = W_n/W_e$. ^c Degeneracies of states for n equivalent nuclei of spin I_i , for a particular value of $J = \sum_i I_i$.

and Eqs. (2.33) and (2.35) become,

$$\sum_{\gamma_i} W_{\alpha_i^+ \gamma_i} (\chi_{\alpha_i^+} - \chi_{\gamma_i}) = 2V_{\lambda_i} [q\omega_{\lambda} - (\chi_{\alpha_i^+} - \chi_{\alpha_i^-})] \equiv U_{\lambda_i}, \tag{2.37a}$$

$$\sum_{\gamma_i} W_{\alpha_i^- \gamma_i} (\chi_{\alpha_i^-} - \chi_{\gamma_i}) = -2V_{\lambda_i} [q\omega_{\lambda} - (\chi_{\alpha_i^+} - \chi_{\alpha_i^-})] \equiv -U_{\lambda_i}, \tag{2.37b}$$

$$\sum_{\gamma_i} W_{\beta_i \gamma_i} (\chi_{\beta_i} - \chi_{\gamma_i}) = 0, \tag{2.37c}$$

and

$$\sum_{\gamma_i} \chi_{\gamma_i} = 0, \tag{2.37d}$$

where Subscript j now indicates the j th set of functions corresponding to the same value for the $\{J_{r_u}^{(k)}\}$. The restricted sums (indicated by primes) are only over States γ_j where j is always the same. Note that $|\beta_j\rangle \neq |a_j\rangle$. There are in fact

$$A(J_{r_u}^{(k)}) \equiv 2 \prod_{r_u} (2J_{r_u} + 1),$$

states corresponding to $\{J_{r_u}^{(k)}\}$, so

$$N = \sum_{k, J_{r_u}} A(J_{r_u}^{(k)}) = \sum_{J_{r_u}} D(J_{r_u}) A(J_{r_u}^{(k)}), \tag{2.38}$$

where $D(J_{r_u})$ is the degeneracy of the states of a particular set of values of $\{J_{r_u}, M_{r_u}\}$, and is the same for all values of $\{M_{r_u}\}$.

a. Transition probability matrix. Equations (2.37) may be written in matrix notation as

$$\mathbf{W}\boldsymbol{\alpha} = \mathbf{U}. \tag{2.39}$$

\mathbf{W} is a singular $A \times A$ matrix (where the particular subscript has been dropped). When the rank of \mathbf{W} is $A-1$, then a replacement of any of the A [Eqs. (2.37a)-(2.37c)] by Eq. (2.37d) leads to a nonsingular matrix and Eqs. (2.37a)-(2.37c) become:

$$\boldsymbol{\alpha} = (\mathbf{W}^i)^{-1} \mathbf{U}^i, \tag{2.40}$$

where the superscript on W^i indicates the matrix formed by replacing the i th row of \mathbf{W} by ones and \mathbf{U}^i indicates the i th component of \mathbf{U} has been replaced with a zero. Let C_{ij} be the cofactor of W_{ij} ; C_{ij}^k be the cofactor of W_{ij}^k ; and $C_{ik,jl}$ the kl th cofactor of C_{ij} . Several useful relations follow in part from the property of \mathbf{W} , that the n th row (column) is equal to the negative of the sum of all the other $A-1$ rows (columns).

They are

$$\begin{aligned}
 (1) \quad & C_{ij} = C_{ii} = C_{jj} = C && \text{for all } i, j; \\
 (2) \quad & C_{jl}^i = -C_{il}^j = C_{jk}^i - C_{ik}^j && i \neq j \neq k; \\
 (3) \quad & C_{ki}^l - C_{kj}^l = AC_{kl,ij} && l \neq k; i \neq j; \\
 (4) \quad & C_{ik,ij} - C_{il,ij} = C_{lk,ij} && l \neq k; i \neq j, k, l; \\
 (5) \quad & C_{kl,ij} = -C_{lk,ij} = C_{lk,ji} = C_{ij,kl} && l \neq k; i \neq j.
 \end{aligned}
 \tag{2.41}$$

It may be shown, utilizing a theorem of Ledermann,²³ that C_{ii} , the diagonal double cofactors $C_{ij,ij}$, and also $C_{ij,ik}$ are always positive. The signs of the $C_{ij,kl}$ however, depend in general on the relative values of the W_{ij} .

It follows that

$$\chi_i = \sum_k (C_{ki}^l / AC) U_k^l, \tag{2.42a}$$

where l is arbitrary and

$$(\chi_{\alpha_i^+} - \chi_{\alpha_i^-}) = \sum_k \Omega_{\alpha_i^+ \alpha_i^-, kl} U_k^l / 2, \tag{2.42b}$$

where

$$\Omega_{ij,kl} \equiv 2C_{ij,kl} / C. \tag{2.42c}$$

[Note that the relation $\sum_k C_{ik} = AC$ has been used in Eq. (2.42a).] Thus for the present case when only one rf field is present, Eq. (2.42b) yields

$$(\chi_{\alpha_i^+} - \chi_{\alpha_i^-}) = \Omega_{\lambda_j} V_{\lambda_j} [q\omega_\lambda - (\chi_{\alpha_i^+} - \chi_{\alpha_i^-})], \tag{2.43}$$

where $\Omega_{\lambda_j} = \Omega_{\lambda_j, \lambda_j}$ is the saturation parameter for the λ_j th transition.

b. Line shapes. Now Eqs. (2.36) and (2.43) yield

$$Z_{\lambda_j} = dT_{\lambda_j} q\omega_\lambda (\Delta\omega_\lambda T_{\lambda_j} + i) / [1 + (\Delta\omega_\lambda T_{\lambda_j})^2 + d^2 T_{\lambda_j} \Omega_{\lambda_j}]. \tag{2.44}$$

When this equation is substituted into Eq. (2.14), it is seen that the saturated absorption from a multiple hyperfine line is given as a superposition of saturated Lorentzians and each component, corresponding to a different set of values of the $\{J_{r,u}\}$, will in general have a different width T_{λ_j} , and a different saturation parameter Ω_{λ_j} . If, for two components, $T_{\lambda_j} \Omega_{\lambda_j} \gg T_{\lambda_k} \Omega_{\lambda_k}$, then it will be possible to saturate the j th component without saturating the k th.

Suppose, however, that all the T_{λ_i} as well as the Ω_{λ_i} are nearly equal for each value of λ . Then it is useful to define

$$T_\lambda^{-1} = D_\lambda^{-1} \sum_{j \text{ in } \lambda} T_{\lambda_j}^{-1} \tag{2.45a}$$

and

$$\Omega_\lambda^{-1} = D_\lambda^{-1} \sum_{j \text{ in } \lambda} \Omega_{\lambda_j}^{-1}. \tag{2.45b}$$

Also let

$$T_{\lambda_j}^{-1} = T_\lambda^{-1} + \epsilon_j \tag{2.46a}$$

and

$$\Omega_{\lambda_j}^{-1} = \Omega_\lambda^{-1} + \delta_j, \tag{2.46b}$$

where ϵ_j and δ_j measure the small deviations from the average, so

$$\sum_{j \text{ in } \lambda} \epsilon_j = \sum_{j \text{ in } \lambda} \delta_j = 0.$$

Then from Eq. (2.44) one obtains

$$\begin{aligned}
 Z_{\lambda_j}'' = & \frac{dq\omega_\lambda T_\lambda}{1 + (\Delta\omega_\lambda T_\lambda)^2 + d^2 T_\lambda \Omega_\lambda} \\
 & \times \frac{(1 + \epsilon_j T_2)(1 + \delta_j T_1)}{1 + \{Q_{\lambda_j} / [1 + (\Delta\omega_\lambda T_\lambda)^2 + d^2 T_\lambda \Omega_\lambda]\}}, \tag{2.47}
 \end{aligned}$$

where

$$\begin{aligned}
 Q_{\lambda_j} = & \epsilon_j T_\lambda (2 + \epsilon_j T_\lambda + 2\delta_j \Omega_\lambda + \delta_j \Omega_\lambda \epsilon_j T_\lambda) + \delta_j \Omega_\lambda \\
 & + (\Delta\omega_\lambda)^2 \delta_j \Omega_\lambda T_\lambda^2 + d^2 \epsilon_j \Omega_\lambda T_\lambda^2. \tag{2.47'}
 \end{aligned}$$

If the right-hand factor in Eq. (2.47) is expanded in powers of $\epsilon_j T_\lambda$ and $\delta_j \Omega_\lambda$ then to first order in these terms we obtain from Eq. (2.20)

$$P_\lambda = 2\mathcal{N}\hbar\omega d^2 q\omega_\lambda D_\lambda T_\lambda / [1 + (\Delta\omega_\lambda T_\lambda)^2 + d^2 T_\lambda \Omega_\lambda], \tag{2.48}$$

i.e., a single saturated Lorentzian with an average T_λ and Ω_λ . Corrections to Eq. (2.48) may be obtained by including quadratic terms in expanding Eq. (2.47) but the results are quite complex for the case of appreciable saturation.²⁴

ii. Coupled Saturated Hyperfine Lines

In the event that pseudotransition probabilities given by Eq. (2.31a) make important contributions to the unsaturated linewidths and to the spin-lattice relaxation, the coupled equations (2.26), (2.33), and (2.34) must be solved. It is then necessary to generalize Eqs. (2.33) to

$$[\Gamma(\chi)]_{\lambda_j k^*} = \pm d(Z_{\lambda_k^*}^* - Z_{\lambda_j k^*}), \tag{2.49}$$

where both j and k can take on any of D_λ values. Also

$$[\Gamma(\chi)]_{\beta_i \beta_m} = 0, \tag{2.50}$$

where β_i and β_m refer to all pairs of degenerate states which are not included in the λ th set of transitions.

The more general form of Eq. (2.34) is

$$\begin{aligned}
 [\Gamma(\chi)]_{\alpha_i \alpha_k} = & + T_{\alpha_i \alpha_k}^{-1} \chi_{\alpha_i \alpha_k} \\
 & - \frac{1}{2} \sum_{l \text{ in } \alpha, \gamma_m} (W_{(\alpha_k \alpha_i), \gamma_m} \chi_{\alpha_i \alpha_l} + W_{(\alpha_i \alpha_l), \gamma_m} \chi_{\alpha_l \alpha_k}) \\
 & + \sum_{\beta_i, \beta_m} W_{(\alpha_i \alpha_k), (\beta_i \beta_m)} \chi_{\beta_i \beta_m}, \tag{2.51}
 \end{aligned}$$

²⁴ D. Kivelson [J. Chem. Phys. **41**, 1904 (1964)] gives the quadratic correction term for the case of no saturation. Note that, to first order in $\epsilon_j T_\lambda$ and $\delta_j \Omega_\lambda$, the definitions $T_\lambda = D_\lambda^{-1} \sum_{j \text{ in } \lambda} T_{\lambda_j}$ and $\Omega_\lambda = D_\lambda^{-1} \sum_{j \text{ in } \lambda} \Omega_{\lambda_j}$ are equivalent to Eqs. (2.45).

²³ W. Ledermann, Proc. Cambridge Phil. Soc. **46**, 581, (1950).

where it is again assumed that $E_\beta, E_\gamma \neq E_\alpha$. In Eq. (2.51)

$$-T_{\alpha_j \alpha_k}^{-1} = [2J_{\alpha_j \alpha_j \alpha_k \alpha_k}(0) - J_{\alpha_j \alpha_j \alpha_j \alpha_j}(0) - J_{\alpha_k \alpha_k \alpha_k \alpha_k}(0)] \quad (2.52)$$

and is a "secular linewidth" between Degenerate States α_j and α_k resulting from instantaneous differences in the time-dependent energy fluctuations of these states.²⁵ Also

$$W_{(\alpha_j \alpha_k), (\beta_l \beta_m)} = 2J_{\alpha_j \beta_l \alpha_k \beta_m}(\omega_{\alpha\beta}). \quad (2.53)$$

The terms of Eq. (2.53), for which States $\alpha_j \neq \alpha_k \neq \beta_j \neq \beta_k$, do not have the usual lifetime effect on the linewidths, although the $W_{(\alpha_j \alpha_k), \gamma}$ terms do.

It is convenient to define symmetrized matrix elements

$$\tilde{Z}_{\lambda_j \lambda_k} = \frac{1}{2}(Z_{\lambda_j \lambda_k} + Z_{\lambda_k \lambda_j}) \quad (2.54)$$

and

$$[\Gamma(\tilde{\chi})]_{\alpha_j \alpha_k} = \frac{1}{2}[\Gamma(\chi)]_{\alpha_j \alpha_k} + \frac{1}{2}[\Gamma(\chi)]_{\alpha_k \alpha_j}. \quad (2.55)$$

It follows from the Hermitian character of χ that

$$\tilde{\chi}_{\alpha_j \alpha_k} = \chi'_{\alpha_j \alpha_k} = \chi'_{\alpha_k \alpha_j}. \quad (2.56)$$

Then Eq. (2.49) may be rewritten as:

$$[\Gamma(\tilde{\chi})]_{\lambda_j \lambda_k} = \pm 2d\tilde{Z}'_{\lambda_j \lambda_k} \quad (2.57)$$

and it may be shown from Conditions (2.27) that $[\Gamma(\tilde{\chi})]_{\lambda_j \lambda_k}$ is given by Eq. (2.51) with the $\chi_{\alpha_j \beta_l}$, replaced by $\chi'_{\alpha_j \beta_l}$, etc. From Eq. (2.26) we obtain

$$\Delta\omega_\lambda \tilde{Z}_{\lambda_j \lambda_k} - (i/2) \sum_{l,m} (R_{\lambda_j \lambda_k \lambda_l m} + R_{\lambda_k \lambda_j \lambda_l m}) Z_{\lambda_l m} + d(\chi'_{\lambda_j \lambda_k} - \chi'_{\lambda_k \lambda_j}) = q\omega_\lambda d\delta_{jk}. \quad (2.58)$$

Now $R_{\lambda_j \lambda_k \lambda_l m}$ is nonzero only if $j=l$ and/or $k=m$.¹ Then it may be shown that

$$R_{\lambda_j \lambda_k \lambda_l l} = R_{\lambda_k \lambda_j \lambda_l l} \quad (2.59)$$

by recognizing that only the nuclear spin functions are permuted by $\lambda_{jk} \rightarrow \lambda_{kj}$, etc. One need only permute the nuclear spin-dependent terms in Eqs. (4.46) to (4.48) of I, neglecting small frequency changes in the spectral densities which are negligible under the usual conditions that $\omega_n \ll \tau_c^{-1}, \omega_0$. The off-diagonal elements given by Eq. (2.30) may also be seen to yield the desired conditions under this approximation. It follows from Eq. (2.59) that the second term on the left in Eq. (2.58) becomes:

$$-i \sum_{l,m} R_{\lambda_j \lambda_k \lambda_l m} \tilde{Z}_{\lambda_l m} \quad (2.58')$$

where $l=j$ and/or $m=k$ and only the symmetrized matrix elements given by Eqs. (2.54) to (2.56) need be considered in the solution.

²⁵ This term will become important if, for example, an alternating linewidth is present, since this phenomenon results from large instantaneous energy differences of degenerate zero-order states. When nuclei are completely equivalent, then this term must vanish. (See Appendix A.)

Equations (2.58) may be written in matrix notation as:

$$(\Delta\omega_\lambda \mathbf{1} - i\mathbf{R}) \tilde{\mathbf{Z}} = \tilde{\mathbf{D}} \tilde{\mathbf{X}} + \tilde{\mathbf{Q}} \quad (2.60)$$

and Eq. (2.57) with the symmetrized form of Eqs. (2.51) becomes:

$$\tilde{\mathbf{W}} \mathbf{X} = -2\tilde{\mathbf{D}} + \tilde{\mathbf{Z}}'. \quad (2.61)$$

It is useful to order the vector \mathbf{X} so that it may be divided into a principal part of dimension N given by $\boldsymbol{\chi}$ and including all diagonal elements χ_{α_j} and the remainder including all the pseudodiagonal $\chi'_{\alpha_j \alpha_k}$, where $j \neq k$, i.e.,

$$\mathbf{X} = \begin{pmatrix} \boldsymbol{\chi} \\ \boldsymbol{\chi}'^P \end{pmatrix}.$$

The rows and columns of $\tilde{\mathbf{W}}$ may then be ordered in a consistent fashion so that it appears as the partitioned matrix

$$\tilde{\mathbf{W}} = \begin{pmatrix} \mathbf{W} & \mathbf{W}_1 \\ \mathbf{W}_2 & \mathbf{W}_{12} \end{pmatrix}, \quad (2.62)$$

where \mathbf{W} is an $N \times N$ matrix which corresponds to the matrix defined in Eq. (2.37). If N' is the number of different degenerate pairs of states, then $\mathbf{W}_{12}, \mathbf{W}_1$, and \mathbf{W}_2 are $N' \times N', N \times N'$, and $N' \times N$ dimensional, respectively.

The first N equations of Eq. (2.61) (which involve \mathbf{W} and \mathbf{W}_1) are linearly dependent since, using Eq. (2.34), it follows that

$$\sum_{\alpha_j} \Gamma(\chi)_{\alpha_j \alpha_j} = 0. \quad (2.63)$$

Thus one of these equations must be replaced by

$$\sum_{\alpha_j} \chi_{\alpha_j} = 0 \quad (2.63')$$

in order to carry out the solution. [This replacement will again be indicated by a superscript j in \mathbf{W} and \mathbf{D}^w in Eq. (2.61).] Note, however, that in general

$$\sum_{\alpha_j, \alpha_k} \Gamma(\chi)_{\alpha_j \alpha_k} \neq 0. \quad (2.64)$$

It is also true that the first N columns of $\tilde{\mathbf{W}}$ (which include \mathbf{W} and \mathbf{W}_2) are also linearly dependent. This may be shown by rewriting Eq. (2.51) as

$$[\Gamma(\tilde{\chi})]_{\alpha_j \alpha_k} = \sum_{\gamma m} (W_{\alpha_j \alpha_k \gamma m}) [\chi_{\gamma m} - \frac{1}{2}(\chi_{\alpha_j} + \chi_{\alpha_k})] + \text{terms in } \chi'_{\gamma m \gamma n} \quad (m \neq n), \quad (2.65)$$

and by noting that for the $\alpha_j \alpha_k$ th row the sum of all the coefficients of the components of $\boldsymbol{\chi}$ equals zero. Thus Eqs. (2.41) and (2.42), which applied to \mathbf{W} when \mathbf{W}_1 and \mathbf{W}_2 were negligible, will still apply to cofactors of elements of \mathbf{W} when \mathbf{W}_1 and \mathbf{W}_2 are no longer negligible, but these cofactors must be obtained in terms of the full $\tilde{\mathbf{W}}$ matrix. The solution to Eqs. (2.60) and

(2.61) becomes

$$[(\Delta\omega_\lambda)^2\mathbf{R}^{-1}+\mathbf{R}+\tilde{\mathbf{S}}]\tilde{\mathbf{Z}}''=\mathbf{Q} \quad (2.66a)$$

where

$$\tilde{\mathbf{S}}=2\tilde{\mathbf{D}}(\tilde{\mathbf{W}}^j)^{-1}\tilde{\mathbf{D}}^{+j}. \quad (2.66b)$$

It may be shown by using Eqs. (2.41), (2.42), and the general form of \mathbf{D} that

$$\tilde{S}_{\lambda_j\lambda_k}=d^2\tilde{\Omega}_{\lambda_j\lambda_k}, \quad (2.66c)$$

where $\tilde{\Omega}_{\lambda_j\lambda_k}$ is the appropriate generalization of $\Omega_{\lambda_j\lambda_k}$, which was defined by Eq. (2.42). Note that for $j \neq k$, states corresponding to the λ_j th and λ_k th transitions must be coupled in some fashion via the lattice-induced (pseudo-) transition probabilities if $\tilde{\Omega}_{\lambda_j\lambda_k}$ is to be non-vanishing. The matrix elements of $\tilde{\mathbf{S}}$ involving pseudo-transitions λ_jk are more difficult to calculate from Eq. (2.66b) since Eqs. (2.41) and (2.42) are directly applicable only to the cofactors of \mathbf{W} . However the calculation of $\tilde{\mathbf{S}}$ from Eq. (2.66b) must still be independent of which of the N rows of \mathbf{W} is taken as j . The real part of $\tilde{\mathbf{Z}}$ is obtained from

$$\mathbf{R}\tilde{\mathbf{Z}}'=\Delta\omega_\lambda\tilde{\mathbf{Z}}''. \quad (2.67)$$

Equation (2.66a) has the form of a generalized (matrix) saturated Lorentzian shape for the vector $\tilde{\mathbf{Z}}''$. The "normal modes" solution, in the presence of appreciable saturation, is now seen to involve the diagonalization of the matrix

$$(\Delta\omega_\lambda^2\mathbf{R}^{-1}+\mathbf{R}+\tilde{\mathbf{S}})$$

which for $\tilde{\mathbf{S}}$ negligible would just require diagonalization of \mathbf{R} . The absorption spectrum will, however, depend only on the transitions $\sum_j Z_{\lambda_j}''$ [see Eq. (2.20)]. The solution for \mathbf{z} is obtained by a matrix inversion of Eq. (2.61). The detailed solution of Eqs. (2.66) is greatly simplified by recognizing that only those states (and transitions) are coupled which correspond to a particular set of values of the $\{J_{r_u^{(k)}}\}$ as long as only the relaxation terms discussed in Appendix A are important.²⁶ Further simplifications based on other symmetries are discussed in the example given in Sec. 3.B.

3. ILLUSTRATIONS OF THE SATURATION THEORY

A. Completely Equivalent Sets of Nuclei

i. Electron Spin vs Nuclear Spin Transitions

We treat some simple examples which illustrate the theory and show how composite hyperfine lines are affected by saturation. The easiest situations to discuss

²⁶ Note that the selection rules on $\mathcal{H}_1(t)$ discussed in Sec. B.iv and Eq. (2.34) show that only those $W_{(\alpha j\alpha k),(\beta l\beta m)}$, for which the subscripts $j, k, l,$ and m refer to the same $\{J_{r_u^{(k)}}\}$ have any effect on the $\chi_{\alpha j\alpha j}$. Thus the inclusion of these new terms does not affect the separation of the terms and states depending on their values of $\{J_{r_u^{(k)}}\}$.

are those for which pseudotransition probabilities are negligible (i.e., all equivalent nuclei are completely equivalent), so this case is treated first. It is further assumed that there is only a single set of such nuclei in the radical. Let us also neglect cross-relaxation effects given by Eqs. (A3) and (A4) as well as dipolar terms in Eq. (A2). Such approximations will be valid in (1) the slow tumbling region where $\omega_0\tau_c \gg 1$, so that the pure nuclear spin-flip terms in Eq. (A1) are the dominant nuclear spin-dependent terms, and also the nuclear spin-independent terms in Eq. (A2) must be large; or (2) when $\omega_0\tau_c \ll 1$ and the dominant relaxation terms are the last two terms in Eq. (A2).²⁷ (It is also being assumed that isotropic spin-density fluctuations have no important relaxation effects.) Case (1) is more interesting because it leads to coupled relaxation of the different hyperfine lines. These approximations mean that all the electron spin transition probabilities W_e are independent of nuclear spin, although the nuclear spin transitions depend upon the value of J and M_J as given in Eq. (A1), but let $\frac{1}{2}j_{nn^{(D)}}(0) \equiv W_n$.

Now for λ_j corresponding to a particular set of J and M_J

$$\Omega_{\lambda_j}=\Omega_{J,M_J}=2W_e^{-1}\phi(J,M_J), \quad (3.1)$$

where the $\phi(J, M_J)$ must be calculated using Eq. (2.42c). The results are given in Table I for several different values of J and M_J . Note that these results are applicable whether the identical particles are $I=\frac{1}{2}$ (protons); $I=1$ (e.g., ^{14}N nuclei), etc. All that is changed is the degeneracy of the different components of the hyperfine line corresponding to a particular value of M_J . The values of $\phi(J, M_J)$ are also given for the special cases $W_n \ll W_e$, $W_n = W_e$, and $W_n \gg W_e$. In the first case $\phi(J, M_J)$ is always unity because this implies that nuclear spin transitions are negligible. Thus the pair of states contributing to the λ_j th transition is essentially isolated from all the other states. The case $W_n \gg W_e$ is seen to yield $\phi(J, M_J) = (2J+1)^{-1}$. This is easily understood as resulting from the fact that the $2J+1$ pairs of states corresponding to a particular value of $J^{(k)}$ are "shorted" together by a large W_n , and to use the analogy with an equivalent electrical circuit,^{15b} we then have $2J+1$ "conductances" of equal magnitude in parallel, through which excited electron spins ($m_s = +\frac{1}{2}$) can return to their unexcited states ($m_s = -\frac{1}{2}$). When $W_n \approx W_e$ the situation is more complex, but since there are more relaxation or "conductance" paths than just the λ_j th, the $\phi(J, M_J)$ lie somewhere between the two extremes. Note also from Table I that the components of a line corresponding to a particular M_J but different J will have different saturation parameters, and, in general, the components corre-

²⁷ M. J. Stephen and G. K. Fraenkel assumed, in their calculations, a fast exchange, i.e., $\omega_0\tau_c \ll 1$ although this required an unusually short $\tau_c < 10^{-11}$ sec. They included *all* terms equivalent to Eqs. (A1)-(A4) except isotropic ones, but could set the $j(\omega_0) \approx j(0)$.

sponding to the lower values of J will saturate more readily.

ii. Predictions from Experimentally Measured Spectral Densities: Para-Dinitrobenzene

The condition that $W_n \gtrsim W_e$, which leads to more complex relaxation processes, appears to be a possible physical situation for ESR experiments on sharp, well-resolved spectra. For such cases the rotational correlation time τ_c often obeys the condition $\omega_0 \tau_c \gg 1$ and exchange effects may be negligible. The dipolar terms in Eq. (A2) are small as a result of the slow tumbling approximation and we may expect that other mechanisms must dominate in W_e , such as the effect of a g -tensor anisotropy as well as intermolecular interactions of the electron spin.

It is possible, from the low-temperature (-55°C) linewidth study of *para*-dinitrobenzene,² to estimate many of the terms contributing to W_e and W_n for this radical by using the relations between linewidths and transition probabilities as given by Eqs. (2.29), as well as the expressions in Appendix A. We find as the intramolecular contributions to $W_e(\Delta m_s = \pm 1, \Delta m_I = 0)$,²⁸ with $\tau_c = 2.01 \times 10^{-10}$ sec, to be in seconds⁻¹

$$\begin{aligned} W_e^{(G_2)} &= 13.4 \times 10^2, \\ W_e^{(DN G_2)} &= -12.7 \times 10^2 M_N, \\ W_e^{(DH G_2)} &= 2.12 \times 10^2 M_H, \\ W_e^{(DN)} &= 5.92 \times 10^2 M_N^2, \\ W_e^{(DH)} &= 0.758 \times 10^2 M_H^2, \\ W_e^{(DNH)} &= -2.08 \times 10^2 M_N M_H, \end{aligned}$$

where the subscripts N and H refer to the ¹⁴N and proton nuclei, respectively, while D and G_2 refer to dipolar and G -tensor terms.

The contributions to $W_n(\Delta m_I = \pm 1, \Delta m_s = 0)$ are^{28,29}

$$\begin{aligned} W_N^{(D)} &= 166 \times 10^2 J^2 (J_N, \pm M_N), \\ W_H^{(D)} &= 25.7 \times 10^2 J^2 (J_H, \pm M_H). \end{aligned}$$

The residual (nuclear spin-independent and presumably partly intermolecular) contributions to W_e are difficult to estimate. The residual contributions to the linewidths in *para*-dinitrobenzene were estimated experimentally to be of the order of $0.4 \times 10^6 \text{ sec}^{-1}$. If it is assumed that

²⁸ $W_e^{(DH)}$ and $W_H^{(D)}$ are estimated from the theoretical calculation given in Ref. 2 for $j_H^{(D)}(0)$ and not from the anomalous experimental result reported there.

²⁹ Note that in *para*-dinitrobenzene there are two pairs of equivalent protons which are not completely equivalent. Thus from Footnotes 21 and 2,

$$|\Delta_H^{(D)}/g_H^{(D)}| = 0.31,$$

which amounts to appreciable differences in the calculation of proton spin transitions. We do, however, neglect the differences in the protons for the present order-of-magnitude estimates. More accurate calculations of transition probabilities would require the methods of Sec. 2.C.ii (or the approximation in Footnote 21 when $W_H \ll W_e$).

exchange-type effects may be neglected (see Sec. V) and the remaining relaxation effects (such as dipolar coupling of the electron spin to the nuclear spins of solvent molecules) are governed by a relaxation time of roughly the order of magnitude as that for intramolecular effects,³⁰ then, because of the slow tumbling condition the secular effects dominate the nonsecular effects in the linewidths, so an order-of-magnitude estimate of $W_e^{(\text{residual})}$ may then be obtained as

$$(0.4 \times 10^6) / \omega_0^2 \tau_c^2 = 30 \times 10^2 \text{ sec}^{-1},$$

which is of the order of $W_e^{(G_2)}$ and $W_H^{(D)}$.³¹ These estimates are only meant to be suggestive, and indicate that at least in the region $\omega_0^2 \tau_c^2 \gtrsim 100$, it is possible that W_H might be of the order of magnitude of W_e , and nuclei such as ¹⁴N with large dipolar terms might even have $W_N > W_e$. The calculation of Ω in the previous section would then not be very good for the ¹⁴N nuclei, since the nuclear spin-dependent terms in W_e , i.e., $W_e^{(DN)}$ and $W_e^{(DN G_2)}$ would be appreciable. This also means that the combined electron-nuclear spin-flip transitions Eqs. (A3) and (A4) would also become important. (The effects of modulation of isotropic hyperfine interactions, which have been neglected in the present discussion, can become important for nuclei having large isotropic splittings.³)

Arguments similar to the above indicate that even when $W_H \sim W_e$, the hyperfine linewidths need *not* have large contributions from terms depending on M_H , which is, of course, the experimental result in Ref. 2. Then variations in saturation behavior of the different hyperfine components for proton containing radicals will be due primarily to the variations in the $\Omega_{J,M}$ rather than the $T_{J,M}$. In fact, it is clear from Table I that as long as $W_H \sim W_e$ the variations in $\Omega_{J,M}$ can be considerable. A final point to note is that the complicating effects of incompletely equivalent nuclei may well become important in determining $\Omega_{J,M}$ when $W_H \sim W_e$ even when these effects play a negligible role in the $T_{J,M}$.

B. Coupled Saturated Hyperfine Lines

As an example of a calculation employing coupled saturated hyperfine lines we will consider the simplest problem, that of two protons which are symmetrically equivalent but not completely equivalent. The unsaturated case was treated in I, Sec. VII. In the extension

³⁰ It should, however, be noted that, if intermolecular correlation times are involved and are associated primarily with translational diffusion, then the Stokes formula gives $\tau_{\text{trans}} = 9\tau_{\text{rot}}$ (Ref. 17, p. 302). A discussion of intermolecular effects that are expected to be important is given by Stephen and Fraenkel (Ref. 12), assuming $\tau_{\text{trans}} \omega_0 \ll 1$. For long correlation times, $\tau_{\text{trans}} \omega_0 \gg 1$, the spectral densities $j(\omega_0)$ depend on the microscopic diffusion process. Nevertheless, reasonable models (Ref. 17, p. 462) indicate that an order-of-magnitude estimate of $j(\omega_0)$ will be given by $j(o)/(\omega_0 \tau_{\text{trans}})^2$ in this limit.

³¹ Note however that Schreurs and Fraenkel [Ref. 14(a)] obtained a considerably larger estimate (about $30 \times 10^4 \text{ sec}^{-1}$) of the remaining contribution to the saturation parameters from their room-temperature experimental data on the *b*-benzosemiquinone anion. They could not account for such large values

to saturation one must invert the $\tilde{\mathbf{W}}$ matrix, a 10×10 matrix in the present case. Since the simplifications inherent in Eqs. (2.41) and (2.42) are no longer fully applicable, we do not attempt to perform this operation in detail. The notation we employ is given in Fig. 1. There will be eight diagonal elements $\chi_a, \chi_{a'}, \chi_b, \chi_{b'}, \chi_c, \chi_{c'}, \chi_d, \chi_{d'}$ and two off-diagonal elements $\chi'_{b'c'}$ and χ'_{bc} which are coupled according to Eq. (2.61). When the $+1$ (-1) transition is excited only Z_{+1} (Z_{-1}) has a nonvanishing value. Thus Eq. (2.66a) becomes

$$[(\Delta\omega_{+1})^2 + (R_{+1,+1})^2 + R_{+1,+1}\tilde{S}_{+1,+1}]Z''_{+1} = R_{+1,+1}q\omega_{+1}d. \quad (3.2)$$

$R_{+1,+1}$ is readily obtained from Eqs. (4.46) to (4.48) of I, and $\tilde{S}_{+1,+1} = d^2\tilde{\Omega}_{+1,+1}$. A similar expression may be written for Z''_{-1} , so each of the ± 1 transitions are given as simple saturated Lorentzians, although their saturation parameters include effects of pseudotransition probabilities. The center line, however, is doubly degenerate. This line will include nonvanishing matrix elements $Z_0, Z_{0'}$, and $Z_{00'}$. It is clear from symmetry that

$$\begin{aligned} Z_0 &= Z_{0'} \equiv \hat{Z}_0, \\ \chi_b &= \chi_c \equiv \hat{\chi}_b, \\ \chi_{b'} &= \chi_{c'} \equiv \hat{\chi}_{b'}. \end{aligned} \quad (3.3)$$

[These relations follow in detail by first noting from Eq. (7.5) of I that $R_{00} = R_{0',0'} = (A+B)$; $R_{0,00'} = R_{0',00'} = C$ and $R_{00',00'} = B$ are the only nonvanishing matrix elements of \mathbf{R} . Then one may use the fact that all of the (pseudo)transition probabilities from a state b to any other state γ are equal to those from c to the same state γ . (The same remark is true for States b' and c' .) Equations (3.3) are then obtained from the expressions for $\Gamma(\chi)_{bb} - \Gamma(\chi)_{cc}$, $\Gamma(\chi)_{b'b'} - \Gamma(\chi)_{c'c'}$, and $Z_0 - Z_{0'}$.] These symmetry relations permit one to reduce the order of the simultaneous equations to be solved to the two equations

$$[\Delta\omega_\lambda - i(A+B)]\hat{Z}_0 - 2iC\hat{Z}_{00'} = d(\hat{\chi}_b - \hat{\chi}_{b'}) + q\omega_\lambda d, \quad (3.4a)$$

$$[\Delta\omega_\lambda - iB]\hat{Z}_{00'} - 2iC\hat{Z}_0 = d(\hat{\chi}_{bc} - \hat{\chi}_{b'c'}), \quad (3.4b)$$

which are obtained from Eq. (2.58). Equations (2.61) may be reduced by using sums of the b th and c th rows and of the b' th and c' th rows. Then $\tilde{\mathbf{W}}$ becomes a 8×8 matrix and $\tilde{\mathbf{X}}$ an eight-dimensional vector, etc.³²; it is necessary to replace $\tilde{\mathbf{D}}^{\text{tr}}$ in Eqs. (2.61) and (2.66) by $\hat{\mathbf{D}}^{\text{tr}}$, which differs from the former only in that $\hat{D}_{bb}^{\text{tr}} = 2\tilde{D}_{bb}^{\text{tr}}$ and $\hat{D}_{b'0'}^{\text{tr}} = 2\tilde{D}_{b'0'}^{\text{tr}}$. The solutions expressed by Eqs. (2.66) may now be applied in the revised two-dimensional transition space and the eight-dimensional space of the (pseudo)eigenstates. Equation (2.66a) is

$$\begin{pmatrix} A+B(1+Y) + 2d^2\tilde{\Omega}_{0,0} & 2C(1-Y) + \tilde{S}_{0,00'} \\ 2C(1-Y) + 2\tilde{S}_{00',0} & (A+B)Y + B + \tilde{S}_{00',00'} \end{pmatrix} \begin{pmatrix} \hat{Z}_0 \\ \hat{Z}_{00'} \end{pmatrix} = \begin{pmatrix} q\omega_\lambda d \\ 0 \end{pmatrix}, \quad (3.5)$$

where

$$Y = (\Delta\omega_\lambda)^2 / [(A+B)B - 4C^2], \quad (3.6)$$

and the matrix elements of $\tilde{\mathbf{S}}$ in Eq. (3.4) are those defined by Eq. (2.66b). Letting the 2×2 matrix of Eq. (3.5) be represented by \mathfrak{R} , then the shape of the central line may be obtained from

$$Z_0 + Z_{0'} = 2q\omega_\lambda \mathfrak{R}_{22} / \det |\mathfrak{R}| \quad (3.7)$$

and will depend in detail on the saturation terms of $\tilde{\mathbf{S}}$.

The result expressed by Eqs. (3.5) may be compared to the calculation involving two completely equivalent spins of $\frac{1}{2}$ as given in Table I. The present results indicate a breakdown of the selection rules for completely equivalent spins which prevented any connection between the $J=0$ and $J=1$ degenerate components of the center line. Thus $\tilde{\Omega}_{0,0}$ involves spin-lattice transition-induced couplings between degenerate zero-order states (which are now expressed in the simple product representation). These effects also lead to a coupling of the degenerate, microwave-induced transitions which appear in the form of the off-diagonal matrix elements of $\tilde{\mathbf{S}}$ in Eqs. (3.5). Lastly, there is a coupling of the linewidths given by the term C (and discussed in more detail in I).

4. DOUBLE-RESONANCE EFFECTS

A rotating rf field lying close to a resonant frequency for nuclear spins may modify the microwave signal being monitored in several ways. The rf field, by virtue of its coherence, can cause a change in the eigenstates seen by the microwave field. The rf field will also demonstrate the characteristic of inducing transitions between coupled states, and this effect will appear to be most useful for studying free radicals in solution. An Overhauser-type effect, which would be important if nuclear resonance frequencies were being monitored, is not expected to be important in ESR studies (see below). These different effects are most simply illustrated in the case of a free radical with $S = \frac{1}{2}$ and one nucleus with $I = \frac{1}{2}$, so this case is discussed first. A number of complications arise when both signals are very strong and comparable in magnitude making a detailed analytical solution somewhat difficult. But because of the successful Hyde and Maki experiment, it

³² The simple symmetry features of the present example may be generalized to more complicated situations in a manner analogous to that outlined in Sec. 7 of I for the unsaturated case. One need only note which sets of $\tilde{Z}_{\lambda i}$ and corresponding sets of $\tilde{X}_{\lambda i}$; \pm must be equal by symmetry and solve for corresponding sums over the equivalent members of each set.

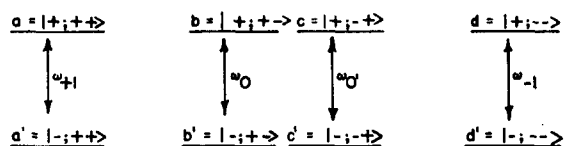


FIG. 1. Notation for product spin representation and ESR transitions of radical with two equivalent protons.

is of interest to see how enhancement of a saturated ESR line could be brought about by such a technique.³³

A. Four-Level System: $S = \frac{1}{2}$; $I = \frac{1}{2}$

In this case the rf frequency, ω_n , lies close to one of the resonance frequencies of a single spin $I = \frac{1}{2}$, interacting with the electron spin. From Fig. 2 and Eq. (2.2), they are

$$\omega_{ab} = |\gamma_n B_0 + \frac{1}{2} \gamma_e \bar{a}_n|, \quad (4.1a)$$

$$\omega_{a'b'} = |\gamma_n B_0 - \frac{1}{2} \gamma_e \bar{a}_n|. \quad (4.1b)$$

For purposes of the present calculation it is not necessary to assume that this is the only interacting magnetic nucleus but only that there are no other nuclei equivalent to the one under consideration. Then States a , a' , b , and b' in Fig. 2 represent a particular configuration of all the other nuclei. Let us further assume that the microwave frequency ω_e of strength B_e lies close to $\omega_{aa'}$, while ω_n is close to $\omega_{a'b'}$, i.e.,

$$\begin{aligned} \Delta_e &\equiv \omega_e - \omega_{aa'} \approx 0, \\ \Delta_n &\equiv \omega_n - \omega_{a'b'} \approx 0. \end{aligned} \quad (4.2)$$

Now Eq. (2.22) must be replaced by

$$\begin{aligned} \epsilon(t) &= \frac{1}{2} \gamma_e B_e [S_+ \exp(-i\omega_e t) + S_- \exp(+i\omega_e t)] \\ &+ \frac{1}{2} \gamma_n B_n [I_+ \exp(-i\omega_n t) + I_- \exp(+i\omega_n t)]. \end{aligned} \quad (4.3)$$

The applied fields may be expected to generate steady-state density-matrix elements:

$$\chi_{a'a} = Z_{a'a} \exp(i\omega_e t), \quad (4.4a)$$

and

$$\chi_{b'a'} = Z_{b'a'} \exp(-i\omega_n t). \quad (4.4b)$$

It follows from Eq. (2.9) that \bar{a}_n is large enough so that Matrix Elements $\chi_{bb'}$ and χ_{ab} will be negligible. Note, however, that the two rotating fields, taken together, couple States a and b' and lead to a nonvanishing "overtone" term

$$\chi_{b'a} = Z_{b'a} \exp[i(\omega_e + \omega_n)t]. \quad (4.4c)$$

³³ Double-irradiation techniques are frequently employed in NMR experiments. However, effects common to nuclear magnetic double resonance such as spin decoupling are precluded in the present case by the condition of Eq. (2.9) ($\gamma_e \bar{a}_i \gg |\epsilon_{\text{NMR}}(t)|$, where the subscript indicates the rotating field close to an NMR frequency (cf. Ref. 17). If the opposite condition, $\gamma_e \bar{a}_i \ll |\epsilon(t)|$, held for any particular \bar{a}_i , then by exciting the resonance of such nuclei $\epsilon(t)$ one would expect to remove any effect such nuclei might have on the ESR spectrum.

Utilizing Eqs. (2.5) and 4.3), one obtains the matrix elements

$$[\Delta_e - (i/T_{a'a})]Z_{a'a} + d_e(\chi_a - \chi_{a'}) + d_n Z_{b'a} = q\omega_{aa'} d_e, \quad (4.5a)$$

$$[\Delta_n - (i/T_{b'a'})]Z_{b'a'} + d_n(\chi_{a'} - \chi_{b'}) - d_e Z_{b'a} = q\omega_{a'b'} d_n, \quad (4.5b)$$

$$[\Delta_e + \Delta_n - (i/T_{b'a})]Z_{b'a} - d_e Z_{b'a'} + d_n Z_{a'a} = 0, \quad (4.5c)$$

which show that $Z_{a'a}$ and $Z_{b'a'}$ may be expected to be coupled via the presence of $Z_{b'a}$. Here $T_{b'a}^{-1}$ is the linewidth which is associated with the transition $a \leftrightarrow b'$ while d_e is equal to d in Eq. (2.23), and d_n is the equivalent term for the nuclear transition.³⁴

The equations (2.33) and (2.35) for the diagonal elements become

$$\sum_{\alpha \neq a} W_{a\alpha}(\chi_a - \chi_\alpha) = 2d_e Z''_{a'a}, \quad (4.6a)$$

$$\sum_{\alpha \neq a'} W_{a'\alpha}(\chi_{a'} - \chi_\alpha) = -2d_e Z''_{a'a} + 2d_n Z''_{b'a'}, \quad (4.6b)$$

$$\sum_{\alpha \neq b} W_{b\alpha}(\chi_b - \chi_\alpha) = 0, \quad (4.6c)$$

$$\sum_{\alpha \neq b'} W_{b'\alpha}(\chi_{b'} - \chi_\alpha) = -2d_n Z''_{b'a'}, \quad (4.6d)$$

with equations like (2.37c) for the $(A-4)$ other levels and

$$\sum_{\alpha} \chi_\alpha = 0. \quad (4.6e)$$

Equations (4.6a) and (4.6b) differ from Eqs. (2.37a) and (2.37b) in the appearance of a term in $Z''_{b'a'}$ which leads to the induced transitions and to Overhauser effects of the nuclear resonance upon the levels a and a' .

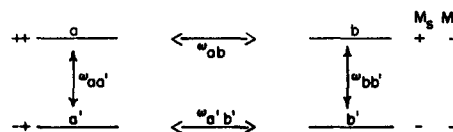


FIG. 2. Transitions and eigenstates for double resonance in a radical with $S = \frac{1}{2}$ and $I = \frac{1}{2}$.

³⁴ In the calculation of d_n it is important to recognize that Eq. (4.3) omits the term $\frac{1}{2} \gamma_e B_n (S_+ e^{-i\omega_n t} + S_- e^{+i\omega_n t})$. Its effect depends on a departure from the high-field approximation, even though the assumption in Footnote 18 is valid. Thus, if the high-field wavefunctions are corrected to first order in $\bar{a}_n S_{\pm} I_{\mp}$ and the aforementioned term is then included, it is found that d_n^0 (i.e., in the high-field limit) becomes $d_{n\pm}$, where $d_{n\pm} = d_n^0 [1 \pm (\gamma_e/\gamma_n) (\bar{a}_n/2B_0)]$ and the signs depend on whether $m_s = \pm \frac{1}{2}$. For protons, $|\gamma_e/\gamma_n| = 660$ and when $B_0 = 3300$ G, $d_{n\pm} = d_n^0 [1 \pm (\bar{a}_n/10)]$, and the effect is not negligible. We are indebted to D. H. Whiffen for calling this to our attention. Since the sign of $d_{n\pm}$ is obvious in the discussion, it has not been explicitly included.

Equations (4.5) and (4.6) may be written in matrix notation as

$$(\mathbf{K} - i\mathbf{T}^{-1})\mathbf{Z} = \mathbf{D}\boldsymbol{\chi} + \mathbf{Q}, \quad (4.7a)$$

and

$$(\mathbf{W}^j)(\boldsymbol{\chi}) = -2\mathbf{D}^{\text{tr}j}\mathbf{Z}''. \quad (4.7b)$$

Note that these matrices span two different spaces, which, in the present case consists of the three-dimensional space of the relevant transitions and the A -dimensional space of the relevant eigenstates. Here \mathbf{T}^{-1} is a 3×3 diagonal matrix whose elements are the inverse relaxation times $T_{\alpha\beta}$; \mathbf{K} is a 3×3 matrix; \mathbf{D} a $3 \times 2A$ matrix and \mathbf{D}^{tr} is the transpose of \mathbf{D} where the superscripted j has the same meaning as in Eq. (2.40); \mathbf{Z} is a 3×1 column vector equal to $\mathbf{Z}' + i\mathbf{Z}''$; etc. The matrix elements are readily obtained by inspection. The formal solution to Eqs. (4.7) is

$$[\mathbf{KTK} + \mathbf{T}^{-1} + \mathbf{S}]\mathbf{Z}'' = \mathbf{Q} \quad (4.8a)$$

and

$$\mathbf{Z}' = \mathbf{TKZ}'', \quad (4.8b)$$

where \mathbf{Z}'' may be obtained by matrix inversion in Eq. (4.8a). Here $\mathbf{T} = (\mathbf{T}^{-1})^{-1}$. \mathbf{S} is given in a form similar to Eq. (2.66b):

$$S_{\lambda_j, \eta_k} = [2\mathbf{D}(\mathbf{W}^j)^{-1}\mathbf{D}^{\text{tr}j}]_{\lambda_j, \eta_k} = d_{\lambda_j} d_{\eta_k} \Omega_{\lambda_j, \eta_k}, \quad (4.9)$$

where the subscripts indicate the different transitions. Equation (4.9) is seen to be quite general applying to larger spin systems and more induced transitions than the example with which we are presently concerned.

It will be sufficient for our present purposes to solve the simpler equations for exact resonance, when $\Delta_s = \Delta_p = 0$, since this is the condition under which double-resonance effects will be maximized. Equations (4.8) and (4.9) yield

$$Z''_{b'a'} = Z'_{a'a'} = Z'_{b'a'} = 0 \quad (4.10a)$$

and

$$[d_n^2 T_{b'a} + T_{a'a}^{-1} + \Omega_{a'a}] Z''_{a'a'} + d_e d_n (\Omega_{a'a, b'a'} - T_{b'a}) Z''_{b'a'} = q\omega_{aa'} d_e, \quad (4.10b)$$

$$[d_e^2 T_{b'a} + T_{b'a}^{-1} + \Omega_{b'a'}] Z''_{b'a'} + d_e d_n (\Omega_{a'a, b'a'} - T_{b'a}) Z''_{a'a'} = q\omega_{a'b'} d_n, \quad (4.10c)$$

$$Z'_{b'a} = T_{b'a} (d_n Z''_{a'a'} - d_e Z''_{b'a'}). \quad (4.10d)$$

Equation (4.10a) is a special consequence of the condition of exact resonance. The terms in $T_{b'a}$ arise from the effects of the coherence of the oscillating fields while those involving $\Omega_{a'a, b'a'}$ represent coupling of $Z''_{a'a}$ and $Z''_{b'a'}$ due to the induced transitions of the oscillating fields. [Note that $\Omega_{a'a, b'a'}$ is always negative. See Sec. 2 after Eqs. (2.41).] From Eqs. (4.10) we get

$$Z''_{a'a'} = \frac{q\omega_{aa'} d_e T_{a'a}}{1 + d_e^2 (\Omega_{a'a} - \xi_{a'a'}) T_{a'a} + d_n^2 T_{b'a} T_{a'a}}, \quad (4.11a)$$

where

$$\xi_{a'a'} = \frac{T_{b'a} d_n^2 (T_{b'a} + |\Omega_{a'a, b'a'}|)^2}{1 + d_n^2 \Omega_{b'a'} T_{b'a} + d_e^2 T_{b'a} T_{b'a'}}. \quad (4.11b)$$

A term in $q\omega_{b'a'} d_n$ representing an Overhauser effect on $Z''_{a'a'}$ is neglected in Eq. (4.11a) since $\omega_{a'b'}/\omega_{aa'} \sim \frac{1}{8} \frac{v}{v_0}$. When $d_n^2 \sim 0$, then $\xi_{a'a'} \sim 0$ and $Z''_{a'a'}$ assumes its proper resonance value for the case of only one saturating oscillatory field [see Eq. (2.44)]. When $d_e^2 \sim 0$, then Eq. (4.11a) becomes

$$Z''_{a'a'(d_e^2 \rightarrow 0)} = q\omega_{aa'} d_e T_{a'a} / (1 + d_n^2 T_{b'a} T_{a'a}). \quad (4.12)$$

The decrease in $Z''_{a'a'(d_e^2 \rightarrow 0)}$ when d_n increases results from the fact that the coherence effect of the applied NMR field leads to a splitting of the ESR line into two shifted components. [If $T_{a'a} = T_{b'a} = T_2$, then it is easy to show from Eq. (4.8a) that Eq. (4.12) arises from two Lorentzians of width T_2^{-1} at $\Delta\omega_e = \pm d_n$ which replace the original line.] Now when

$$1 + d_e^2 \Omega_{a'a} T_{a'a} \gg d_n^2 T_{b'a} T_{a'a}, \quad (4.13a)$$

this coherence effect on $Z''_{a'a'}$ may be neglected compared to the normal saturation effect (barring an accidental equality $\Omega_{a'a} \cong \xi_{a'a}$ which is not likely to occur: See below). Now $\xi_{a'a}$ leads to an enhancement of the signal, since it effectively reduces the saturation parameter $\Omega_{a'a}$. If $\xi_{a'a}/\Omega_{a'a}$ is not to depend on the magnitude of d_e^2 , the condition

$$(1 + d_n^2 \Omega_{b'a'} T_{b'a'}) \gg d_e^2 T_{b'a} T_{b'a'} \quad (4.13b)$$

must hold. This is equivalent to neglecting the coherence effect on $Z''_{b'a'}$ resulting from the ESR field as compared to the saturation of $Z''_{b'a'}$ by the NMR field. A further condition,

$$|\Omega_{a'a, b'a'}| \gg T_{b'a}, \quad (4.13c)$$

leads to a complete neglect of coherence effects, but is not necessary for obtaining an enhancement. When coherence effects are appreciable and Eqs. (4.13a) and (4.13b) are not applicable, then detailed evaluation of the relaxation terms is required in order to determine whether there will be an enhancement or an attenuation of $Z''_{a'a'}$. It is readily seen that when there is appreciable saturation and

$$d_e^2 \sim d_n^2, \quad (4.14a)$$

then Conditions (4.13) are satisfied when

$$\Omega_{a'a}; \Omega_{b'a'}; |\Omega_{a'a, b'a'}| \gg T_{b'a}. \quad (4.14b)$$

Let us assume that Eqs. (4.14) hold in a particular situation. Then $\xi_{a'a'}$ is a maximum as $d_n^2 \rightarrow \infty$ where $\xi_{a'a'(d_n^2 \rightarrow \infty)} = (\Omega_{a'a, b'a'})^2 / \Omega_{b'a'}$. A measure of the relative enhancement is given by the quantity

$$E = \{1 - [(\Omega_{a'a, b'a'})^2 / \Omega_{a'a} \Omega_{b'a'}]\}^{-1} \quad (4.15)$$

TABLE II. Values of the enhancement factor E for several sets of values of transition probabilities when the $\omega_{aa'}$ and $\omega_{a'b'}$ transitions are excited.^a

	$\frac{a}{W_{x1} \sim W_{x2} = W_x}$	$\frac{b}{W_x = W_{x1} \gg W_{x2}}$	$\frac{c}{W_x = W_{x2} \gg W_{x1}}$
(1) $W_e \sim W_n \sim W_x$	4/3	25/24	25/16
(2) $W_e \gg W_n \sim W_x$	1	1	1
(3) $W_n \gg W_e \sim W_x$	1	1	1
(4) $W_x \gg W_e \sim W_n$	$W_x/2(W_e + W_n)$	1	$W_x/(W_e + W_n)$
(5) $W_n \sim W_x \gg W_e$	3/2	1	2
(6) $W_e \gg W_x \gg W_n$	1	1	1
(7) $W_e \sim W_n \gg W_x$	9/8	9/8	9/8

^a See Fig. 2.

as compared to unity, and for large d_e^2 ,

$$Z''_{a'a'}(\bar{a}_n, \bar{d}_e^2 \rightarrow \infty) = (q\omega_{aa'}/d_e\Omega_{a'a})E. \quad (4.16)$$

It is of interest to see what kinds of mechanisms can yield an enhancement factor E greater than unity. We consider transition probabilities as given by Eqs. (A1)–(A4). For simplicity let $W_{aa'} = W_{bb'} = W_e$, $W_{ab} = W_{a'b'} = W_n$, $W_{a'b} = W_{x1}$, and $W_{a'b'} = W_{x2}$ and neglect any terms involving other nuclei in the molecule. We may then study the limiting conditions which depend on the relative values of these four quantities. The results are given in Table II. The largest values of E may be obtained by Condition (4), i.e., when W_x is the strongest relaxation mechanism. An examination of Eqs. (A1)–(A4) shows that this is highly unlikely unless the isotropic dipolar mechanism is very important in which case only Conditions (4b) may be realized, where no enhancement would be expected. However, if the ω_{ab} nuclear transition is excited instead of the $\omega_{a'b'}$ transition, then the results for Conditions b and c are interchanged, and a significant enhancement could result. If the $\omega_{bb'}$ ESR transition were being studied, then the $\omega_{a'b'}$, instead of the ω_{ab} frequency, would give enhancement.³⁵

The other situations where enhancements may be obtained are given by (1), (5), and (7) in Table II. The remarks about (4) also apply to (5) and most likely to (1) as well, but these conditions would also probably require slow tumbling and/or intermolecular exchange effects (see Sec. V). Condition (7) is the only one for which enhancement may be obtained in

³⁵ It may at first glance be thought that an effect of this sort could predict the sign of \bar{a}_n . However, it turns out [see Eq. (2.2)] that the low-field ESR line (corresponding to $\omega_{aa'}$ if \bar{a}_n is positive and $\omega_{bb'}$ if \bar{a}_n is negative) will be enhanced by the higher NMR frequency if γ_n is negative and by the lower NMR frequency for positive γ_n independent of the sign of \bar{a}_n . This preferential enhancement effect could, however, be useful in studying isotropic splitting-constant fluctuations when they lead to large transition probabilities. These remarks also apply to the two outside lines arising from any set of n completely equivalent nuclei.

the absence of appreciable cross relaxation. Using the slow-tumbling approximations discussed in Sec. 3.A and setting $W_e = W_n$, we readily see that Eqs. (4.14b) follow for the case of protons. More specifically, the saturation factors in Eq. (4.14b) are all comparable to $T_{b'a'}$ but greater than $T_{a'a}$ and $T_{b'a}$.³⁶ It is found for (7) that E is a maximum when $W_e = W_n$. Physically, the enhancement arises for this case because the rf-induced transitions between States a' and b' "short" out the lattice-induced $W_{a'b'}$, thereby increasing the effectiveness of the relaxation path for the $a \rightarrow a'$ transition via States $a \rightarrow b \rightarrow b' \rightarrow a'$. The maximum when $W_e = W_n$ follows because if (1) $W_n \ll W_e$ then W_{ab} is still very small, while if (2) $W_e \ll W_n$ then $W_{bb'}$ is the rate-controlling transition no matter whether $W_{b'a'}$ is shorted.

B. Completely Equivalent Nuclei

When several completely equivalent nuclei are present (and/or when $I > \frac{1}{2}$), the nuclear transitions, Eqs. (4.1), are degenerate with all the other nuclear transitions between states corresponding to the same value of m_s and obeying the selection rule $\Delta M_J = \pm 1$. It is expected that the appropriate generalization of Eqs. (4.13) will still lead to a neglect of coherence effects on the ESR transition being excited. But now there are "overtone" off-diagonal density matrix elements between pairs of states for which $\Delta m_s = 0$ but $\Delta M_J = \pm 2, \pm 3, \dots$. Furthermore the relaxation matrix for the NMR linewidths is not diagonal [see Eqs. (B4)], and this will lead to a further coupling of transitions for which $\Delta M_J = \pm 2, \Delta m_s = 0$. These effects may be studied for the $J=1$ states arising from two completely equivalent nuclei of $I = \frac{1}{2}$ (this, of course, corresponds to the problem of one nucleus of $I=1$). The $J=0$ states will be unaffected by the oscillatory field ω_n . Equations equivalent to Eqs. (4.5)–(4.7) may be written down, but since \mathbf{T}^{-1} is no longer diagonal, \mathbf{T} must be replaced by $(\mathbf{T}^{-1})^{-1}$ in Eqs. (4.8). When the equivalent of Eqs. (4.13) are applicable, then only four $Z_{\alpha\beta}$ terms need be considered in \mathbf{Z} . That is, let ESR transition $|+, - \rangle \leftrightarrow |-, - \rangle$, be excited giving

³⁶ The linewidths for the $\Delta m_s = \pm 1$ transitions are found from Eqs. (4.46) and (4.47) of I to be (assuming slow tumbling)

$$T_{a'a}^{-1} = T_{b'a}^{-1} + \frac{1}{4}[j^I(0) + (8/3)j^D(0)] + \frac{1}{2}[j^{IG}(0) + (16/3)j^{DG}(0)]B_0,$$

$$T_{b'a}^{-1} = \frac{1}{2}j^D(0) + [j^{G_0}(0) + (8/3)j^{G_2}(0)]B_0^2 + X' + X,$$

where $X' \sim (1 + \omega_0^2 \tau_e^2)X$ [see Eq. (A2) and Sec. 3.A.i] and, from Appendix B,

$$T_{b'a}^{-1} = \frac{1}{4}j^I(0) + (7/6)j^D(0) + X.$$

Also $\Omega_{b'a'} = (1/W_n)[(1+2b)/(1+b)]$, where $b = W_n/W_e$, and

$$|\Omega_{a'a,b'a'}| = (W_e + W_n)^{-1},$$

$$W_e = 2j^{G_2}(\omega_0)B_0^2 + X,$$

and

$$W_n = \frac{1}{2}j^D(0).$$

It is assumed that $g^{G_0}(0)B_0^2$ and X' are the largest terms.

$Z_{\bar{e}}$ and NMR transitions $|-, -\rangle \leftrightarrow |-, 0\rangle$ giving Z_a ; $|-, 1\rangle \leftrightarrow |-, +\rangle$ giving Z_b ; then the $|-, -\rangle \leftrightarrow |-, +\rangle$ overtone transition giving Z_c must also be considered. The notation used is $|m_s; M_J\rangle$. The resulting value of $Z''_{\bar{e}}{}^r$ is

$$Z''_{\bar{e}}{}^r = q\omega_{\bar{e}}d_e T_{\bar{e}}/[1 + d_e^2(\Omega_{\bar{e}} - \xi_{\bar{e}}) T_{\bar{e}}], \quad (4.17)$$

where

$$\xi_{\bar{e}}{}^r = \frac{d_n^2}{2} \left[\frac{(\Omega_{\bar{e},a} - \Omega_{\bar{e},b})^2}{(T_n^{-1} - T_{a,b}^{-1}) + d_n^2(2T_c + \Omega_a - \Omega_{a,b})} + \frac{(\Omega_{\bar{e},a} + \Omega_{\bar{e},b})^2}{(T_n^{-1} + T_{a,b}^{-1}) + d_n^2(\Omega_a + \Omega_{a,b})} \right] \quad (4.18)$$

and $d_a^2 = d_b^2 = d_n^2$. Also $T_a = T_b = T_n$, $T_{a,b}^{-1}$, and T_c are given by $-R_a^{-1}$, $-R_{a,b}^{-1}$, and $-R_c^{-1}$, respectively, which may be obtained from Eqs. (B1)–(B3).³⁷ In the presence of saturation, conditions equivalent to Eq. (4.14) for the neglect of coherence effects among the nuclear levels are found to be given by Eq. (4.14a) and

$$T_c \ll \Omega_a, \Omega_b, \Omega_{a,b}. \quad (4.19)$$

But when $W_e \sim W_n$, Eq. (4.19) will not be the case. T_c should, in fact, be comparable to the saturation parameters.³⁷ Thus a quantitative calculation of the parameter $\xi_{\bar{e}}{}^r$ must include the coherence terms. Note, however, that for large d_n , T_n , and $T_{a,b}$ have a negligible effect on $\xi_{\bar{e}}{}^r$ although they will help determine a double-resonance spectrum width when ω_n is varied. The equivalent expression for the center component of the ESR line corresponding to $J=1$ is given by replacing \bar{e} with e^0 in Eq. (4.18). But $\Omega_{e^0,a} = -\Omega_{e^0,b}$ by symmetry and sign considerations, (when the assumptions in Sec. 3.A.i of the neglect of transition probability terms linear in M_J may be utilized), so the equivalent of the second term in Eq. (4.18) vanishes. However, because of the complications introduced by the coherence and linewidth couplings of the nuclear levels, it seems worthwhile to attempt a first approximation to the double-resonance spectrum without considering their effects in detail.

C. Simplified Version of Double Resonance

It is assumed that all the off-diagonal elements in $(\mathbf{K} - i\mathbf{T}^{-1})$ of Eq. (4.7a) (which is now applied to the

³⁷ The saturation parameters, using the equivalent of Condition (7) in Table II are:

$$\Omega_e = (1/N)W_n^2(4W_e^2 + 12W_eW_n + 4W_n^2),$$

$$\Omega_b = \Omega_a = (1/N)W_eW_n(W_e^2 + 6W_eW_n + 6W_n^2),$$

$$\Omega_{\bar{e},b} = (1/N)2W_eW_n^2,$$

$$\Omega_{\bar{e},a} = (1/N)2W_eW_n^2(W_e + 2W_n),$$

$$\Omega_{a,b} = -(1/N)W_e^2W_n^2,$$

$$N = W_eW_n^2(2W_e^2 + 8W_eW_n + 6W_n^2).$$

Both W_n and W_e contribute to T_c via Eqs. (B2) and (B3), respectively. The secular contribution, given by Eq. (B1) is comparable in magnitude to Eq. (B2).

case of a set of completely equivalent nuclei) are negligible, so that separate, uncoupled equations may be written for each of the $Z_{\alpha\beta}$ that are generated by the applied oscillating fields. Then the formal solution, Eqs. (4.8a) becomes

$$(\mathbf{T}' + \mathbf{T}^{-1} + \mathbf{S})\mathbf{Z}'' = \mathbf{Q} \quad (4.20a)$$

and

$$\mathbf{Z}' = \mathbf{T}'\mathbf{Z}'', \quad (4.20b)$$

where \mathbf{S} is given by Eq. (4.9); \mathbf{T}' and \mathbf{T}'' are both diagonal matrices given by

$$T''_{\lambda_j} = K_{\lambda_j}T'_{\lambda_j} = K_{\lambda_j}T_{\lambda_j}^{-1}K_{\lambda_j}. \quad (4.21)$$

It is assumed that the T_{λ_j} corresponding to the λ th degenerate nuclear transition is independent of j and is given by Eqs. (B1)–(B3). Note that \mathbf{K} contains only the Δ_i terms. Thus all the coupling, between the different $Z_{\alpha\beta}$'s, appear as a result of a nondiagonal \mathbf{S} —the effect of induced transitions. The solution to the $S = \frac{1}{2}$, $I = \frac{1}{2}$, single-nucleus case neglecting the Overhauser effect on the electrons on letting $a' \leftrightarrow a = e$ and $b' \leftrightarrow a' = n$ becomes

$$Z'' = q\omega_e d_e T_e/[1 + (\Delta_e T_e)^2 + (\Omega_e - \xi_e) T_e d_e^2], \quad (4.22a)$$

where

$$\xi_e = d_n^2(\Omega_{e,n})^2 T_n/[1 + (\Delta_n T_n)^2 + d_n^2 T_n \Omega_n]. \quad (4.22b)$$

It is readily seen that when $\Delta_e = \Delta_n = 0$, Eqs. (4.22) become Eqs. (4.11) (neglecting coherence effects). If the ENDOR spectrum is monitored after subtracting off the ESR signal,³⁸ then for $\Delta_e = 0$ and $\Omega_e T_e d_e^2 \gg 1$:

$$\begin{aligned} \frac{P}{2\Omega\hbar\omega_e} &= d_e(Z''_{\text{ENDOR}} - Z''_{\text{ESR}}) \\ &= \frac{q\omega_e d_n^2 \Omega_n}{\Omega_e} (1 - E^{-1}) \frac{T_n}{1 + (\Delta_n T_n)^2 + E^{-1} T_n \Omega_n d_n^2}. \end{aligned} \quad (4.22c)$$

That is, a saturated Lorentzian of width T_n and saturation parameter Ω_n/E is obtained and the signal strength is proportional to $(1 - E^{-1})$. The extension to where m degenerate (or nondegenerate) nuclear transitions are induced is [from Eqs. (4.20) neglecting effects on the ESR] again Eq. (4.22a), but now

$$d_e^2 \xi_e = \sum_{i,j}^m S_{i,e} S_{e,j} \frac{F_{ij}}{F}, \quad (4.23a)$$

where F is the $m \times m$ determinant with elements

$$(f_{ij})^{-1} = T_i/(1 + \Delta_i^2 T_i^2 + T_i S_i), \quad (4.23b)$$

$f_{ij} = S_{i,j}$ for $i \neq j$ [where $S_{i,j}$ is defined by Eq. (4.9)], and F_{ij} is the cofactor of f_{ij} . Note that $f^{ii}(d_n \rightarrow \infty) = S_i$, and a generalized enhancement factor is given by

$$E \equiv \{1 - [\xi_e^r(d_n \rightarrow \infty)/\Omega_e]\}^{-1}. \quad (4.23c)$$

³⁸ J. S. Hyde (private communication) has developed such a technique.

Equations (4.23) are related to a result given by Stephen,¹³ who, however, treated a multiple hyperfine line as an averaged line. We have also given the explicit dependence on the nuclear line-shape factors, Eq. (4.23b), and have retained double cofactor terms S_{ij} instead of his diagrammatic approach.³⁹

For the two nuclei $J=1$ case, the e^\pm lines and the e^0 line, have enhancement factors E of $\frac{3}{2}\frac{\Omega}{\omega_0}$ and $\frac{\Omega}{\omega_0}$, respectively, in the slow-tumbling approximation when $2W_n$ is set equal to W_e . The central component, where $J=0$, will not be enhanced (i.e., $E=1$). Somewhat greater enhancements are predicted for radicals containing larger numbers of nuclei both equivalent and inequivalent since there will be more relaxation paths whose "effective resistances" will be decreased by the applied NMR field.

In the absence of favorable conditions for a steady-state ENDOR experiment [e.g., Conditions (2), (3), or (6) of Table II] it might be possible to utilize other techniques. Thus, for example, if $W_e \gg W_n \sim W_x$ a triple resonance technique in which both NMR frequencies, Eqs. (4.1), are simultaneously excited may be expected to lead to signal enhancements. On the other hand, if $W_n \gg W_e, W_x$, a double-ESR technique, where both the ESR transitions (in Fig. 2, for example) are simultaneously excited, could be useful.

D. Transient Effects

In the Hyde and Maki ENDOR experiment,⁸ the NMR field is pulsed. This raises the question of the importance of transient effects. The appropriate equations including transient effects may be obtained by taking matrix elements of Eq. (2.5), where $\epsilon(t)$ is given by Eq. (4.3), and then integrating with the initial condition on σ that it be the steady-state solution when B_n in Eq. (4.3) is zero. Then the resulting Z_{λ_i} defined by Eq. (2.19), which would now be time dependent, may be substituted into Eq. (2.20) to obtain the time-dependent power absorption. For times long compared to the T_{λ_i} and Ω_{λ_i} , the steady-state solutions discussed above should be obtained. Because of the complexity of the transient equations, no attempt has been made to solve them. However, we can make a very crude estimate of some of the effects of such a transition from one steady state to another if we regard this as an exponential decay process without any excessive oscillations. During this period there will be (1) power absorption due to the transfer of energy from the microwave field via the spins to the lattice, and the rate of this transfer is shifting from one steady-state value to another; (2) a net absorption or emission of energy depending on whether there is a net increase

³⁹ A direct comparison of this result with Stephen's¹³ leads to the relations $\Omega_\lambda = 2\Omega_\lambda^{(S)}$ and $\Omega_{\lambda_i}^2 = (\Omega_\lambda \Omega_n - 4\Omega_{\lambda_i}^{(S)})$ where the superscripts S refer to the terms given by Stephen. Thus the Ω_i and $\Omega_{i,j}$ needed in Eqs. (4.26) and (4.27) can be calculated using Stephen's diagram method. [See discussion after Eqs. (2.41) for the signs of the Ω_{λ_i} .]

or decrease of radicals with $m_e = \pm \frac{1}{2}$ when the NMR field is on, i.e., a possible "heating" of the electron spins. If there is a predicted enhancement in the final steady state, then the effect of (1) should be increasing steadily to this value (averaging over oscillations). The total energy change from (2) is for the four-level system in Fig. 2:

$$E_2 = \hbar\omega_e(\Delta\chi_a + \Delta\chi_b), \quad (4.24)$$

where $\Delta\chi_a = \chi_a^\infty - \chi_a^0$, etc., where the superscripts refer, respectively, to $d_n \rightarrow \infty$ and $d_n \rightarrow 0$. If it is assumed that Eqs. (4.14) apply and that $W_x \sim 0$, then Eq. (4.24) is a maximum (indicating net absorption) for $d_e \rightarrow \infty$ where:

$$\Delta\chi_a + \Delta\chi_e = \frac{1}{2} [W_e W_n / (W_e + W_n) (2W_e + W_n)] q\omega_0 \equiv \bar{\Omega} q\omega_0. \quad (4.25)$$

This result, which is obtained from Eq. (4.7b), is independent of which of the two nuclear transitions of Eq. (4.1) are excited. Assuming that the steady-state enhancement is small (e.g., $\sim 10\%$), then for large powers, the absorption due to (1) is approximately proportional to Eq. (4.6) with $E \sim 1$. Then using Eq. (2.20), the ratios of the absorption by (1) to that by (2), when averaged over the length of the pulse t is approximated by

$$P_2/P_1 \cong \bar{\Omega} \Omega_{aa'} / 2t. \quad (4.26)$$

Using the expression for $\Omega_{aa'}$ obtained from Table I, the maximum is found to occur for $W_e = W_n$, where $[P_2/P_1]_{\max} = 1/16(W_e t)^{-1}$. Thus for pulse times $t \sim W_e^{-1} = \frac{2}{3}\Omega_{aa'}$ the effect of "heating up" the spin systems could lead to a nonnegligible enhancement of the signal. Note that for $W_e = W_n$, $d_e \rightarrow \infty$; $\chi_a^0 = -\chi_a^0 = \frac{1}{2}$, $\chi_b^0 = -\chi_b^0 = +\frac{1}{6}$; $\chi_a^\infty = \frac{5}{8}$, $\chi_a'^\infty = \chi_b'^\infty = -\frac{3}{8}$, $\chi_b^\infty = \frac{1}{8}$ in units of $q\omega_0$, where the approximation $\omega_{aa'} \cong \omega_{bb'} \cong \omega_0$ has been used.

Any more accurate estimates await a detailed solution of the proper transient equations.

5. SOME REMARKS ON EXCHANGE EFFECTS AND SATURATION

The general theory presented in this paper is applicable when both chemical and quantum-mechanical exchange effects are negligible compared with other relaxation mechanisms. It is of interest, however, to take note of the effects that significant exchange processes will have on the applicability of the theory. A rigorous development of this problem would require a theory recast to include intermolecular exchanges, such as given by Kaplan,⁴⁰ Alexander,⁴¹ or Currin,⁴² as well as to include the relaxation effects discussed in the present paper. We outline a simple, intuitive approach and are concerned only with the case of well-separated hyperfine

⁴⁰ J. I. Kaplan, J. Chem. Phys. **28**, 278 (1958); **29**, 462 (1958).

⁴¹ S. Alexander, J. Chem. Phys. **37**, 966, 974 (1962).

⁴² J. D. Currin, Phys. Rev. **126**, 1995 (1962).

lines affected by incipient exchange effects, i.e., dilute solutions. In a simple model we may assume strong collisions which destroy the original memory of the colliding particles but short enough that no effective relaxation occurs during a collision. Thus, in chemical exchange, a collision between a radical and a parent molecule with a different nuclear spin configuration will transfer the electron spin to a different environment with a probability of $\frac{1}{2}$. The effect on each of the unsaturated well-separated hyperfine lines is then an uncertainty in lifetime broadening proportional to the exchange frequency and to the sum of the statistical weights of all the other lines,⁴³ since the latter reflects the number of nuclear spin states of the radical to which effective (nondegenerate) transitions may be made. In other words, in the slow exchange limit, chemical exchange effects look like nuclear spin transitions of the radical system where the unpaired spin is being transferred to different nuclear sites. In the presence of saturation, then, chemical exchange effects should appear as enhanced rates of nuclear spin flips. In an ENDOR experiment a very large rate of lattice-induced nuclear spin flips will cause the added effect of the NMR field to be unimportant although moderate rates could be helpful. (See Table II for further details.) It may be shown from the appropriate steady-state rate equations that the chemical exchange mechanism in fact tries to equalize the populations of radicals having different nuclear spin configurations but the same sign of the electron spin.

Heisenberg exchange effects when looked at in the same manner will be important only when two radicals of opposite electron spin and of different nuclear spin configurations collide. When they separate, there is a 50% probability that the up and down electron spins have exchanged nuclear environments. Thus the broadening of any particular hyperfine line is again proportional to the exchange rate as well as to the statistical weights of all the other lines (as predicted more rigorously by Currin⁴²). In this case the exchange acts to equalize the ratios of the populations of electron spins $+\frac{1}{2}$ to electron spins $-\frac{1}{2}$ for each of the nuclear configurations. This is again equivalent to "shorting" out nuclear spin transitions, i.e., electron spin excitations due to the resonant field are transmitted to other nuclear configurations, so that for the relaxation to be complete there still must be an accompanying lattice-induced downward electron spin flip.

This discussion has so far neglected any considerations of the effects of degeneracies, which must be properly treated in a manner that will be invariant to a choice of degenerate states and degenerate transitions as in Sec. 2. However, it is worthwhile to note that the modified Bloch equations, in the absence of saturation, predict that when transitions connect degenerate hyperfine components which have different linewidths, then

the lines will experience a lifetime broadening effect when the transition rate is smaller than the differences in linewidths, but, when the transition rate becomes greater, the degenerate lines will appear to merge into a single line with an average linewidth.⁴⁴ This consideration thus has important consequences for the theory presented in the present paper and for the theory in I. A detailed analysis and justification of these remarks awaits a rigorous theoretical formulation.

6. SUMMARY AND CONCLUSIONS

A general theory of saturation in the electron spin resonance spectra of dilute solutions of free radicals has been formulated in terms of the general density-matrix equations of motion due to Bloch, Redfield, and Abragam. This theory predicts a saturation behavior for a composite hyperfine line that is different from the earlier theory of Stephen and Fraenkel which assumed (1) that such a line in the absence of saturation is a simple Lorentzian and (2) transition probabilities to (and from) degenerate zero-order basis states may be averaged over these degenerate states in rate equations which describe the populations of the different basis states. Thus, while Stephen and Fraenkel obtained a single linewidth (T^{-1}) and saturation parameter (Ω) for each composite line, the present theory shows that in general more than one T and Ω will be required. In fact T and Ω become matrices in the space of all transitions whose frequencies are nearly equal to that of the exciting field. A particularly simple situation arises when all equivalent nuclei are also completely equivalent, and the only significant nuclear spin-dependent transitions arise from intramolecular electron-nuclear-dipolar interactions. Then, if the wavefunction of each such completely equivalent group is written in the coupled representation corresponding to particular values of $J^{(\kappa)}$ and M [where (κ) is a degeneracy index], it follows that each degenerate component of the multiple line corresponding to a particular M but a different $J^{(\kappa)}$ will behave as a separate, saturated Lorentzian with its own T and Ω . Then, the greater the value of J for a component, the smaller will be its value of T_J and Ω_J , so that this component will saturate less readily. Predictions based on the experiments and calculations of linewidths in *para*-dinitrobenzene anion suggest that in the slow-tumbling region (viz., $\omega_0^2\tau_c^2 \gg 1$) obtained at below room temperatures (where intermolecular exchange effects appear to be negligible), it might be possible for the dipolar-induced rate of proton spin transitions to be comparable in magnitude to the rate of electron spin flips, while the ^{14}N rate could even be greater. This remark must be strongly qualified by the considerable present uncertainty about the nuclear spin-independent relaxation mechanisms. It is under such conditions that the Ω_J for a particu-

⁴³ P. J. Zandstra and S. I. Weissman, J. Chem. Phys. **35**, 757 (1961).

⁴⁴ A related calculation is discussed in Sec. III of J. H. Freed, J. Chem. Phys. **41**, 7 (1964).

lar value of M are expected to differ markedly. It is frequently the case that protons, which are equivalent in $\mathcal{H}\mathcal{C}_0$ are not completely equivalent in $\mathcal{H}\mathcal{C}_1(t)$. This is true for the electron-nuclear-dipolar interaction of the ring protons in *p*-dinitrobenzene. Such an inequivalence complicates the description of saturation behavior by destroying the selection rules for the dipolar-induced transitions which lead to the above simple picture of superpositions of saturated Lorentzians. Specific degenerate components of a composite hyperfine line may then be coupled via these transitions, and this will result in further coupling through the saturating microwave fields as well as through their linewidths (this latter phenomenon is discussed fully in I). The resulting multiple line may now be described as a generalized (matrix) saturated Lorentzian from which the detailed line shape can be calculated by standard matrix techniques. Appropriate symmetry considerations such as those employed in the example of two not completely equivalent protons can be used to simplify these calculations. In the absence of saturation, the present theory reduces to the linewidth theory presented in I. It is important to note that while, in the absence of saturation, these coupling effects may make very small contributions via the linewidths, they can become important in the presence of saturation via their effect on the saturation parameter. Such might well be the case for the protons in *p*-dinitrobenzene in the slow tumbling region. The electron-proton dipolar interaction was found experimentally to have a very small effect on the linewidth compared to contributions from proton-spin-independent and presumably secular mechanisms. But if this proton-dipolar interaction is the dominant mechanism inducing proton spin flips, and if they occur at a rate comparable to or greater than electron spin flips, then "pseudotransitions" involving degenerate states will become important. The theory given here does not include the detailed effects of quadrupole terms. They represent another mechanism for lattice-induced nuclear spin transitions. However, they are expected to couple (degenerate) states of different J . Incipient chemical and Heisenberg exchange effects have only been discussed qualitatively. They may be expected to serve as mechanisms for nuclear spin transitions, but they should also effectively couple together *all* degenerate components of a multiple hyperfine line.

Steady-state solutions when both electronic and nuclear spin transitions are excited by separate oscillatory fields (ENDOR) have been obtained for several cases. The simplest case of $S = \frac{1}{2}$ and a single $I = \frac{1}{2}$ is discussed in detail. The nuclear rf field is an effective means of inducing transitions between nuclear spin levels but it also can mix the nuclear states by virtue of its coherence. While the former effect could enhance a saturated ESR signal, the latter could reduce the signal strength. This coherence effect becomes unimportant in the presence of appreciable saturation by both fields (whose interactions with the spin systems are

set to be comparable in magnitude), when T for the overtone transition resulting from the combined nuclear and electron spin transitions generated by the applied fields is much smaller than the saturation parameters for these transitions [see Eqs. (4.14)]. Such a situation may be realized for slow tumbling when secular nuclear spin-independent line-broadening mechanisms should dominate the ESR linewidths. The enhancement effect of the induced transition mechanism can be significant when (1) cross-relaxation effects involving a simultaneous nuclear and electronic transition play a dominant role in the relaxation or (2) lattice-induced nuclear transitions (W_n) are comparable to the electronic transitions (W_e). (1) may be achieved for example by large fluctuations of the isotropic hyperfine interactions with a correlation time comparable to ω_0 , while (2) may be achieved when there is slow tumbling and an absence of large exchange effects. It is found, in extending the treatment to a set of completely equivalent nuclei, that the states corresponding to different M_J but the same $J^{(k)}$ can still exhibit coherence effects, because of the multiple rf-induced transitions between them, and also because of couplings via the linewidths for these transitions. However, if these effects are neglected, a simplified expression for ENDOR enhancement is obtained, where, again, components of the same M_J but $J^{(k)}$ exhibit independent behavior. The effects of noncompletely equivalent nuclei and/or exchange phenomena are expected to lead to complications such as those already mentioned for the case of saturation with a single (microwave) field.

Careful experimental studies would be required to determine the relative importance of the kinds of effects discussed here.

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APPENDIX A: LATTICE-INDUCED TRANSITION PROBABILITIES

The lattice-induced transition probabilities given here are based on the relaxation terms discussed in I, where the various spectral densities are given. Emphasis is on the dipolar and g -tensor terms. It is assumed that $\omega_n \tau_c \ll 1$ for all nuclei and that the important remaining terms are nuclear spin independent.^{12,45}

Transition Probabilities

i. Nuclear Spin Transitions

$$W_{\alpha, \gamma \pm} = \frac{1}{2} j_{r_u r_u}^{(D)}(0) [J_{r_u}(J_{r_u} + 1) - M_{r_u}(M_{r_u} \pm 1)], \quad (A1)$$

⁴⁵ If first-order corrections are made to the high-field wavefunctions,^{18,34} it is found, for example, that the g -tensor terms can affect $W_{\alpha, \gamma \pm}$ for nuclear spin transitions leading to a replacement of $j_{r_u r_u}^{(D)}(0)$ in Eq. (A1) by $[j_{r_u r_u}^{(D)}(0) \pm 2(\bar{a}_{r_u}/B_0)j_{r_u}^{(Dg_2)}(0)B_0 + (\bar{a}_{r_u}/B_0)^2 j_{r_u}^{(Dg_2)}(0)B_0^2]$, where the signs correspond to $m_S = \pm \frac{1}{2}$. This will not be important unless the g -tensor terms are very much greater than the dipolar terms. For the *para*-dinitrobenzene case discussed in Sec. 3 the effect is readily found to be negligible.

where

$$|\gamma_{\pm}\rangle = |\alpha\rangle(|J_{r_u}^{(k)}, M_{r_u}\pm 1\rangle/|J_{r_u}^{(k)}, M_{r_u}\rangle). \quad (\text{A1}')$$

ii. Electron Spin Transitions

$$W_{\alpha, \gamma_{\pm}} = \sum_{r_u, s_v} 2j_{r_u s_v}^{(D)}(\omega_0) M_{r_u} M_{s_v} + \sum_{r_u} 4j_{r_u}^{(DG2)}(\omega_0) B_0 M_{r_u} + 2j^{(D2)}(\omega_0) B_0^2 + X, \quad (\text{A2})$$

where X includes all remaining terms

$$|\gamma_{\pm}\rangle = |\alpha\rangle(|m_s\pm 1\rangle/|m_s\rangle)\delta_{m_s, \mp \frac{1}{2}}. \quad (\text{A2}')$$

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

$$(a) W_{\alpha, \gamma_{\pm}} = [\frac{1}{3}j_{r_u r_u}^{(D)}(\omega_0) + \frac{1}{2}j_{r_u r_u}^{(I)}(\omega_0)] \times [J_{r_u}(J_{r_u}+1) - M_{r_u}(M_{r_u}\mp 1)], \quad (\text{A3})$$

where

$$|\gamma_{\pm}\rangle = |\alpha\rangle \frac{|m_s\pm 1\rangle |J_{r_u}^{(k)}, M_{r_u}\mp 1\rangle}{|m_s\rangle |J_{r_u}^{(k)}, M_{r_u}\rangle} \delta_{m_s, \mp \frac{1}{2}}; \quad (\text{A3}')$$

$$(b) W_{\alpha, \gamma_{\pm}} = 2j_{r_u r_u}^{(D)}(\omega_0) [J_{r_u}(J_{r_u}+1) - M_{r_u}(M_{r_u}\pm 1)], \quad (\text{A4})$$

where

$$|\gamma_{\pm}\rangle = |\alpha\rangle \frac{|m_s\pm 1\rangle |J_{r_u}^{(k)}, M_{r_u}\pm 1\rangle}{|m_s\rangle |J_{r_u}^{(k)}, M_{r_u}\rangle} \delta_{m_s, \mp \frac{1}{2}}. \quad (\text{A4}')$$

Pseudotransition Probabilities

i. Nuclear Spin Transitions

$$W_{(\alpha_i, \alpha_k^{\pm}), \gamma_{\pm}} = \frac{1}{2}j_{r_u r_u}^{(D)}(0) f(J_{r_u}\mp M_{r_u}) f(J_{r_u}\pm M_{r_u}), \quad r_u \neq r_v, \quad (\text{A5})$$

where

$$|\alpha_{k\pm}\rangle = |\alpha_j\rangle \frac{|J_{r_u}^{(k)}; M_{r_u}\pm 1\rangle |J_{r_u}^{(j)}; M_{r_u}\mp 1\rangle}{|J_{r_u}^{(k)}; M_{r_u}\rangle |J_{r_u}^{(j)}; M_{r_u}\rangle} \quad (\text{A5}')$$

and

$$|\gamma_{\pm}\rangle = |\alpha_{k\pm}\rangle (|J_{r_u}^{(k)}; M_{r_u}\rangle/|J_{r_u}^{(k)}; M_{r_u}\pm 1\rangle) \quad (\text{A5}''')$$

or

$$= |\alpha_{k\pm}\rangle (|J_{r_u}^{(j)}; M_{r_u}\rangle/|J_{r_u}^{(j)}; M_{r_u}\mp 1\rangle). \quad (\text{A5}''')$$

$$\text{Also } f(J, \pm M) = [(J\pm M)(J\mp M+1)]^{\frac{1}{2}}.$$

ii. Combined Electron-Spin-Nuclear-Spin Transitions

$$(a) W_{(\alpha_i, \alpha_k^{\pm}), \gamma_{\pm}} = [\frac{1}{3}j_{r_u r_u}^{(D)}(\omega_0) + \frac{1}{2}j_{r_u r_u}^{(I)}(\omega_0)] \times f(J_{r_u}\mp M_{r_u}) f(J_{r_u}\pm M_{r_u}), \quad r_u \neq r_v, \quad (\text{A6})$$

where $|\alpha_{k\pm}\rangle$ is given by Eq. (A5'), and

$$|\gamma_{+}\rangle = |\alpha_{k+}\rangle \frac{|m_s\mp 1\rangle |J_{r_u}^{(j)}; M_{r_u}\rangle}{|m_s\rangle |J_{r_u}^{(j)}; M_{r_u}-1\rangle} \delta_{m_s, \pm \frac{1}{2}} \quad (\text{A6}')$$

$$|\gamma_{-}\rangle = |\alpha_{k-}\rangle \frac{|m_s\mp 1\rangle |J_{r_u}^{(k)}; M_{r_u}\rangle}{|m_s\rangle |J_{r_u}^{(k)}; M_{r_u}-1\rangle} \delta_{m_s, \pm \frac{1}{2}}; \quad (\text{A6}''')$$

$$(b) W_{(\alpha_i, \alpha_k^{\pm}), \gamma_{\pm}} = 2j_{r_u r_u}^{(D)}(\omega_0) f(J_{r_u}\mp M_{r_u}) f(J_{r_u}\pm M_{r_u}), \quad r_u \neq r_v, \quad (\text{A7})$$

where $|\alpha_{k+}\rangle$ is given by Eq. (A5'), and

$$|\gamma_{+}\rangle = |\alpha_{k+}\rangle \frac{|m_s\pm 1\rangle |J_{r_u}^{(k)}; M_{r_u}\rangle}{|m_s\rangle |J_{r_u}^{(k)}; M_{r_u}+1\rangle} \delta_{m_s, \mp \frac{1}{2}}, \quad (\text{A7}')$$

$$|\gamma_{-}\rangle = |\alpha_{k-}\rangle \frac{|m_s\pm 1\rangle |J_{r_u}^{(j)}; M_{r_u}\rangle}{|m_s\rangle |J_{r_u}^{(j)}; M_{r_u}+1\rangle} \delta_{m_s, \mp \frac{1}{2}}. \quad (\text{A7}'')$$

The terms given by Eq. (A1) will contribute to the pseudosecular line broadening given by Eq. (4.47) of I; those given by Eqs. (A2), (A3), and (A4) contribute to the nonsecular line broadening, Eq. (4.48) of I. Equation (A5) leads to Eq. (4.52) of I, while Eqs. (A6) and (A7) give Eqs. (4.53) of I. The off-diagonal linewidth terms in I are ambiguous as written (since, while summations are implied, they are not given explicitly). They may be rewritten as follows (where the summations have been performed). Equation (4.52a) of I becomes

$$-R_{\alpha_i, \alpha_k^{\pm}, \alpha_i^{\pm}, \text{nonsec}} = \frac{1}{2}j_{r_u r_u}^{(D)}(\omega_r) f(J_{r_u}\pm M_{r_u}) f(J_{r_u}\pm M_{r_u}),$$

and Eq. (4.53) of I becomes

$$-R_{\alpha_i, \alpha_k^{\pm}, \alpha_i^{\pm}, \text{pseudosec}} = [\frac{1}{4}j_{r_u r_u}^{(I)}(\omega_0) + \frac{1}{8}j_{r_u r_u}^{(D)}(\omega_0)] \times f(J_{r_u}\mp M_{r_u}) f(J_{r_u}\pm M_{r_u}), \quad r_u \neq r_v,$$

where $|\alpha_{k\pm}\rangle$ is given by Eq. (A5'). Equivalent expressions may be written in place of Eqs. (4.52b) and (4.53b) of I.

Equation (2.52) may be written as

$$T'_{\alpha_i, \alpha_k}^{-1} = \sum_{r_u, s_v} [j_{r_u s_v}^{(I)}(0) + \frac{8}{3}j_{r_u s_v}^{(D)}(0)] \times \frac{1}{4}[M_{r_u, i} - M_{r_u, k}][M_{s_v, i} - M_{s_v, k}].$$

The expressions for $W_{(\alpha_i, \alpha_k), (\beta_l, \beta_m)}$ may also be obtained for the pseudo- and nonsecular terms discussed in I. They will include the effects represented by X in Eq. (A2).

APPENDIX B: LINEWIDTHS FOR NUCLEAR TRANSITIONS

We consider only a completely equivalent set of nuclei. In dilute solution, when exchange effects are unimportant, the dominant relaxation mechanisms will be the effect of dipolar interactions with the unpaired electron as well as all other lattice-induced electron spin transitions. (The quadrupole interactions are again being neglected.) However, any secular interactions in $\mathcal{H}_1(t)$ that are nuclear spin independent cannot affect the linewidths of the nuclear transitions, because of the commutation of such terms with both \mathcal{H}_0 and J_{\pm} (that is, such terms cause no transitions from eigenstates of \mathcal{H}_0 , and their induced energy fluctuations cancel out just as the static electron spin Zeeman energy does in the nuclear transition). Let α and α' represent two states of the same m_s and $J^{(k)}$ but

different values of M_J , then

$$-R_{\alpha\alpha',\alpha\alpha'}^{\text{sec}} = \frac{1}{4}[j_{rr}^{(I)}(0) + \frac{3}{8}j_{rr}^{(D)}(0)][M_\alpha - M_{\alpha'}]^2 \quad (\text{B1})$$

$$-R_{\alpha\alpha',\alpha\alpha'}^{\text{pseudosec}} = \frac{1}{2}j_{rr}^{(D)}(0)[2J(J+1) - (M_\alpha^2 + M_{\alpha'}^2)] \quad (\text{B2})$$

$$\begin{aligned} -R_{\alpha\alpha',\alpha\alpha'}^{\text{nonsec}(\pm)} &= \frac{1}{8}j_{rr}^{(D)}(\omega_0) \\ &\times [14J(J+1) - (M_\alpha^2 + M_{\alpha'}^2) \mp 5(M_\alpha + M_{\alpha'})] \\ &+ \frac{1}{4}j_{rr}^{(I)}(\omega_0)[2J(J+1) - M_\alpha(M_\alpha \mp 1) - M_{\alpha'}(M_{\alpha'} \mp 1)] \\ &+ 2j_r^{(DG_2)}(\omega_0)[M_\alpha + M_{\alpha'}] + 2j^{(G_2)}(\omega_0)B_0^2 + X. \quad (\text{B3}) \end{aligned}$$

The superscripted plus and minus signs on the R -matrix elements in Eq. (B3) refer to the sign of m_s . There are also off-diagonal R -matrix elements which arise from the first term of Eq. (2.8a):

$$-R_{M,M+1,M+1,M+2}^{\text{pseudosec}} = -\frac{1}{2}j_{rr}^{(D)}(0)\{f(J, -M)f(J, -[M+1])\} \quad (\text{B4a})$$

and

$$-R_{M-1,M,M,M+1}^{\text{pseudosec}} = -\frac{1}{2}j_{rr}^{(D)}(0)\{f(J, M)f(J, [M+1])\}, \quad (\text{B4b})$$

where the subscripts on R indicate the values of M_J of the states being coupled. When the nonsecular terms in Eq. (B3) involving dipolar interactions are negligible (e.g., in the slow-tumbling region), one may show, using the equivalent of Eqs. (2.20), (2.22), and (2.27) for the nuclear magnetic resonance, that in the absence of saturation, the degenerate NMR line one obtains (corresponding to each of the two values of m_s) is a single Lorentzian with linewidth:

$$T^{-1} = \frac{1}{4}j_{rr}^{(I)}(0) + \frac{7}{8}j_{rr}^{(D)}(0) + 2j^{(G_2)}(\omega_0)B_0^2 + X. \quad (\text{B5})$$

One must perform the sum equivalent to Eq. (2.20) for each value of J to obtain this result. However, when the dipolar terms in Eqs. (B3) are important, the composite line shape becomes considerably more complex. In a steady-state ENDOR experiment, the NMR transitions are monitored in a fashion that is different from a conventional NMR experiment (viz., each transition affects a different part of the relaxation paths for the ESR spectrum), so that, in general, the terms in Eqs. (B1) to (B4) will have a different effect on the ENDOR spectrum.

Proton Dynamics in Hydrogen-Bonded Ferroelectrics

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A comparison between infrared absorption and neutron inelastic-scattering measurements indicates the existence of a broad low-energy (around 400 cm^{-1}) protonic level in KH_2PO_4 above the Curie point. This level is only weakly discerned in the ir but is seen quite clearly in neutron scattering. The mode is explained as resulting from splitting of the ground level of the proton in a slightly asymmetric double minimum potential well where tunneling of the proton takes place. The asymmetry is caused by the interaction between the different protons, and it changes slowly with time as the result of the collective motions of the protons. Prominent changes in ir spectra in the 400-cm^{-1} range were found on cooling through the Curie point, indicating the disappearance of the tunneling mode.

† This picture allows a simplified treatment of the system, leading to the existence of two correlated phase transition points, and a negative thermal expansion coefficient of the H bond at temperatures between these points. The two transition points are identified as the Curie point and the melting or dissociation point of the crystal. The theory also suggests an increase in the dielectric constant as the melting point is approached, corresponding to the Curie-Weiss behavior as the Curie point is approached.

1. INTRODUCTION

IN KH_2PO_4 -type crystals it is known that the motion of the protons is responsible for the ferroelectric transition. The involvement of the protons is seen for example from the large shift in the Curie point upon deuteration.¹ Moreover, the hydrogen bond, being the weakest bond in the crystal, is probably also responsible² for the low melting point of these crystals (e.g.,

253°C for KH_2PO_4 as against 1340°C for K_3PO_4). The neutron-diffraction data of Pease and Bacon³ on KH_2PO_4 show a symmetrical elongated proton distribution along the axis of the hydrogen bond above the Curie temperature, and a more concentrated distribution below it. There are several ways of explaining their results above the Curie point: the proton might be located asymmetrically near one of the oxygens, but be statistically disordered in the crystal sites, or

¹ F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, London, 1962).

² Y. Imry and I. Pelah, *Israel A.E.C. Report IA-861* (1963).

³ R. S. Pease and G. E. Bacon, *Proc. Roy. Soc. (London)* **A220**, 397 (1953); **A236**, 359 (1955).