

Theory of Linewidths in Electron Spin Resonance Spectra*

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A general theory of the linewidths in the electron spin resonance spectra of dilute solutions of free radicals has been developed in terms of the relaxation-matrix theory of Bloch, Redfield, and Ayant. In contrast to previous theories, it is shown that a composite line arising from a set of degenerate nuclear-spin states should, in general, consist of a sum of superimposed lines of Lorentzian shape with different widths rather than a single line with an over-all Lorentzian shape. A single Lorentzian line is still obtained, however, as a limiting case when the variation of the widths of the different components of a composite line is small compared to the average width. Although the non-Lorentzian shape of a composite line is often difficult to observe experimentally, a number of other observable properties are predicted by the present development that are outside the scope of the previous theories. For example, linewidth effects resulting from differences in the widths of the separate components of a composite line are predicted that explain the alternation in the linewidths from one hyperfine line to another recently observed in the ESR spectra in certain free radicals. The detailed form of the relaxation matrix is presented for intramolecular anisotropic and isotropic electron-nuclear dipolar interactions, quadrupole interactions, and g -tensor relaxations. Modulations of the spin density and hyperfine splittings are included, as are internal motions, and a number of cross terms between the different relaxation mechanisms arise. In general the relaxation matrix of a composite line contains significant off-diagonal elements, and the determination of the linewidths requires the evaluation of the eigenvalues of the matrix. Problems involving rapid chemical exchange, or modulation by jumps to a small number of sites, can be treated by the relaxation-matrix theory and, under special restrictions, by either the modified Bloch equations or the Anderson theory of motional narrowing. When applicable, these latter procedures can be used over the entire range of exchange rates, while the relaxation-matrix theory is limited to fast rates only.

I. INTRODUCTION

THE first theoretical analysis of magnetic-resonance linewidths was presented by Bloembergen, Purcell, and Pound (BPP),¹ but early studies² of the electron-spin resonance spectra of free radicals in solution indicated that this theory was not sufficiently general to account for the experimental observations. Subsequently a general theory was developed by Kubo and Tomita³ which was then used by Kivelson⁴ to obtain a theory for the linewidths in ESR spectra. Kivelson's results were in general agreement with the experimental observations.⁵⁻⁷ The saturation behavior of free radicals was also investigated,^{5,6,8-10} and the theoretical account was in adequate agreement with most of the experimental findings.

Recently a number of ESR spectra have been reported which exhibited a new type of phenomenon:

the linewidth was found to alternate in magnitude from one hyperfine component to another. This alternating linewidth was observed in the spectrum of the dihydroxydurene (1,4-dihydroxy-2,3,5,6-tetramethylbenzene) cation,^{11,12} the dinitrodurene (1,4-dinitro-2,3,5,6-tetramethylbenzene) anion,¹³⁻¹⁶ the dinitromesitylene (2,4-dinitro-1,3,5-trimethylbenzene) anion,¹⁴⁻¹⁶ and the *m*-dinitrobenzene anion,¹⁷ as well as several other radicals.¹⁸ These linewidth variations could not be explained by the Kivelson-Kubo-Tomita theory, and we were therefore led to a re-examination of the theory of linewidths in ESR spectra.

It is well known that the BPP theory of linewidths is not generally satisfactory^{3,19-21}; but there are two particular problems which make it unsuitable for application to the ESR spectra of free radicals in solution. The first problem arises even if there is only a single nucleus interacting with the unpaired electron. Here the BPP theory breaks down because it does not provide a means of taking into account the nuclear-spin

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relaxations which cause transitions between different hyperfine components. The Kivelson-Kubo-Tomita theory handles this situation without difficulty. The second problem arises in the presence of several equivalent nuclei because of the degeneracy of the nuclear-spin states. The degeneracy causes special complications, and as will be shown in the following, it is this part of the theory that requires modification.

Several authors¹⁹⁻²³ have presented an alternative to the general theory of magnetic resonance relaxation developed by Kubo and Tomita. These treatments utilize an approximate form of the equation of motion for the density matrix of the spin system in terms of what may be called a relaxation matrix. Since this theory can be applied to the ESR spectra of free radicals in a straightforward way which eliminates any ambiguity in handling the degeneracies of the hyperfine components, it has been employed throughout in the following.

In Sec. II, the general formulation of the relaxation-matrix theory is outlined, and in Sec. III it is shown that a degenerate ESR line may consist in general of a superposition of several Lorentzian lines of different widths. Section IV is devoted to a detailed specification of the form of the relaxation matrix for the most important types of relaxation processes, and much of the development in this section, as well as in Sec. II, is presented in general form for use in subsequent work.²⁴ Simple applications are then made to problems involving modulation of the isotropic hyperfine interaction (Secs. V and VI) and a theory is developed to account for the alternating linewidth phenomenon. In Sec. VII, the problems encountered with nondiagonal relaxation matrices are discussed, and in Sec. VIII a comparison is made between the relaxation-matrix theory and the application of either the modified Bloch²⁵⁻²⁸ equations or the Anderson theory of motional narrowing²⁹ to problems involving chemical exchange and jump-type modulations.

II. GENERAL THEORY

In this section we briefly outline that part of the theory of magnetic resonance line shapes and widths which is required to treat the ESR spectra of free radicals in solution. The general theory is due to Bloch,¹⁹ Redfield,²² and Ayant,²⁰ and for the most part we use the development of Abragam.²¹ For brevity, no derivations are given in the following, and only those

results needed for defining the notation or for subsequent applications are presented. The system is described by a Hamiltonian $\hbar\mathcal{H}$, is of volume V , and at temperature T . When an rf field of frequency $\omega/2\pi$ is applied to the system, the magnetic absorption is determined by the imaginary part of the magnetic susceptibility which can be shown to be given by^{3,21}

$$\chi''(\omega) = \frac{\omega V}{kT} \cdot \frac{1}{\text{Tr}[\mathcal{E}]} \int_0^\infty \cos\omega t \text{Tr}[M_x(t)M_x] dt, \quad (2.1)$$

where M_x is the operator for the x component of the macroscopic magnetization of the sample,

$$M_x(t) = \exp(i\mathcal{H}t) M_x \exp(-i\mathcal{H}t), \quad (2.2)$$

and \mathcal{E} is the unit operator in the vector space spanned by \mathcal{H} . Equation (2.1) is valid to first order in the amplitude of the rf field (no saturation), and at high temperatures [$(\hbar\mathcal{H}/kT) \ll 1$].

For most of our purposes, we can use a semiclassical formulation in which the total Hamiltonian of the spin system is divided into two parts,^{3,4,21,22}

$$\hbar\mathcal{H} = \hbar\mathcal{H}_0 + \hbar\mathcal{H}_1(t). \quad (2.3)$$

The zero-order Hamiltonian $\hbar\mathcal{H}_0$ is time independent and gives rise to a sharp-line spectrum, while $\hbar\mathcal{H}_1(t)$ is a fluctuating time-dependent perturbation which causes relaxation and line broadening. The operator $\mathcal{H}_1(t)$ is a stationary random function with a time-average value of zero. It includes the effects of the random molecular tumbling motions of the radical resulting from collisions with the solvent, internal rotation and vibration, and the disturbances introduced by fluctuating complexes between the radical and solvent. By "solvent" we mean the major constituent of the solution and also all solutes other than the radicals themselves. Some of the solutes, such as, for example, alkali-metal cations and oxidized or reduced forms of the radicals, may have specific interactions with the radicals. The molecular tumbling modulates the anisotropic intramolecular dipolar interaction, the effects of the anisotropic spectroscopic-splitting-factor tensor (g tensor), and the quadrupole interaction. The internal rotation and vibration, and the fluctuating solvent complexes, may change both the geometry of the molecule and the distribution of pi-electron spin density, and thus modulate the isotropic hyperfine interactions, the anisotropic intramolecular dipolar interactions, the principal values (and perhaps direction) of the g tensor, and the quadrupole interactions. Dipolar interactions between the solvent and the radical, and chemical exchange between the radical and other species, can also be included in the theory, but we specifically restrict our considerations to solutions with sufficiently dilute concentrations of the radicals to permit the neglect of radical-radical perturbations such as intermolecular

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dipolar interactions and quantum mechanical exchange effects.^{4,30}

The time variation of $\mathcal{H}_1(t)$ is assumed to be described by a stationary Markoff process³¹ so that the random motions are described by only two probability distributions. For any random process $y(t)$, these distributions are the probability $W(y)dy$ of finding y in the range $(y, y+dy)$, and the joint probability $W_2(y_1; y_2\tau)dy_1dy_2$ of finding y in the range (y_1, y_1+dy_1) at any time t_1 and in the range (y_2, y_2+dy_2) at a time t_2 , where, because of the stationary nature of the process, W_2 depends on the time interval $\tau=t_2-t_1$, not on t_1 or t_2 separately. The joint probability $W_2dy_1dy_2$ can be expressed in terms of the conditional probability $P(y_1 | y_2, \tau)dy_2$ that given y_1 at an initial time, one finds y in the range (y_2, y_2+dy_2) at a time τ later by the relation

$$W_2(y_1; y_2\tau) = W(y_1)P(y_1 | y_2, \tau). \quad (2.4)$$

The average of a function $f(y) = f[y(t)] = f(t)$ is thus

$$\langle f(t) \rangle = \int W(y)f(y)dy. \quad (2.5)$$

The only other average required is the correlation function $g_{12}(\tau)$ of two functions $f_1(t)$ and $f_2(t)$, defined by

$$g_{12}(\tau) = \langle f_1(t)f_2^*(t+\tau) \rangle \\ = \int dy_1W(y_1)f_1(y_1) \int dy_2P(y_1 | y_2, \tau)f_2^*(y_2). \quad (2.6)$$

It follows from the usual assumptions of the theory of random functions that^{21,31}

$$g_{12}(\tau) = g_{12}(-\tau) = g_{21}^*(\tau). \quad (2.7)$$

A sufficient condition for the general formulation of the theory is that the motions be rapid in the sense that^{3,21,22}

$$[\langle |\mathcal{H}_1|^2 \rangle_{\text{av}} \tau_c^2]^{\frac{1}{2}} \ll 1, \quad (2.8)$$

where τ_c is a correlation time characteristic of the motion. Thus the present theory is applicable to the jumping of an electron from one molecule to another, as in the naphthalene-naphthalenide exchange reactions studied by Weissman,³² only in the limit of rapid jump rates. Similarly, changes in geometrical conformation or spin-density distribution must be rapid in the sense of Eq. (2.8).

The zero-order spin Hamiltonian is given by

$$\mathcal{H}_0 = \bar{g}_s \beta_e \mathbf{S} \cdot \mathbf{B}_0 - \hbar \sum_i \gamma_i \mathbf{I}_i \cdot \mathbf{B}_0 - \hbar \sum_i \bar{a}_i \mathbf{I}_i \cdot \mathbf{S}, \quad (2.9)$$

where β_e is the Bohr magneton; \mathbf{B}_0 is the external applied magnetic field; $\gamma_e = -|\gamma_e|$ and γ_i are the magnetogyric ratios of the electron and the i th nucleus, respectively; and the summations are over all magnetic nuclei in the radical. The $\bar{a}_i = \langle a_i(t) \rangle$ are the values of the isotropic hyperfine interactions (in gauss) averaged over internal motions and fluctuating solvent interactions. The quantity \bar{g}_s is the average value of the g tensor and is given by

$$\bar{g}_s = \frac{1}{3}(\bar{g}_1 + \bar{g}_2 + \bar{g}_3), \quad (2.10)$$

where the $\bar{g}_i = \langle g_i(t) \rangle$, $i=1, 2, 3$, are the principal values of the g tensor of the radical averaged over internal motions and fluctuating solvent interactions. We restrict our considerations to radicals with a single unpaired electron ($S=1/2$). The high-field approximation is assumed, and thus certain second-order shifts are neglected.^{33,34} A line in the spectrum may be degenerate, with degeneracy D_k , but each line is assumed to be well separated from adjacent lines.

It is convenient to introduce the correlation function of the electron-spin angular momentum,

$$G(t) = \text{Tr}[S_x(t)S_x], \quad (2.11)$$

where S_x is the x component of the electron-spin angular momentum of a single radical and $S_x(t)$, which is an ensemble average, is given in terms of S_x by an equation analogous to Eq. (2.2). The trace is taken over the spin states of the electron and nuclei of a single radical. This correlation function is a real and even function²¹ of t . The imaginary part of the susceptibility can then be rewritten as

$$\chi''(\omega) = (\pi\chi_0\omega/2 \sum D_k) I(\omega), \quad (2.12)$$

where χ_0 is the static susceptibility and

$$I(\omega) = \frac{4}{\pi} \int_0^\infty G(t) \cos\omega t dt \quad (2.13)$$

is the spectrum normalized so that for a line of angular frequency ω_k and degeneracy D_k (see Sec. III),

$$\int_0^\infty I_k(\omega) d\omega = D_k. \quad (2.14)$$

The correlation function $G(t)$ is evaluated by solving the differential equation²¹

$$\frac{d}{dt} \langle \alpha | S_x^\dagger(t) | \alpha' \rangle = \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \langle \beta | S_x^\dagger(t) | \beta' \rangle \quad (2.15)$$

for the ensemble average of the matrix elements of the x component of the electron-spin angular momentum in the interaction representation,

$$S_x^\dagger(t) = \exp(-i\mathcal{H}_0 t) S_x(t) \exp(i\mathcal{H}_0 t). \quad (2.16)$$

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In Eq. (2.15), $R_{\alpha\alpha'\beta\beta'}$, the relaxation matrix, is given by

$$R_{\alpha\alpha'\beta\beta'} = 2J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha\beta}) - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\alpha\gamma\beta\gamma}(\omega_{\gamma\beta}) - \delta_{\alpha\beta} \sum_{\gamma} J_{\gamma\alpha'\gamma\beta'}(\omega_{\beta'\gamma}), \quad (2.17)$$

where

$$J_{\alpha\beta\alpha'\beta'}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} \langle \mathcal{H}_1(t)_{\alpha\beta} \mathcal{H}_1^*(t+\tau)_{\alpha'\beta'} \rangle \times \exp(-i\omega t) d\tau \quad (2.18)$$

and $\mathcal{H}_1(t)_{\alpha\beta}$ is a short-hand notation for the α, β matrix element of $\mathcal{H}_1(t)$, i.e., $\mathcal{H}_1(t)_{\alpha\beta} = \langle \alpha | \mathcal{H}_1(t) | \beta \rangle$. The angular brackets in Eq. (2.18) signify an average over the random motion. Equation (2.17) is subject to a restriction among the energies,

$$E_{\alpha} - E_{\alpha'} = E_{\beta} - E_{\beta'}. \quad (2.19)$$

Each index α, β, \dots refers to a particular state, and in general several states may have the same energy, i.e., the energy levels may be degenerate. The angular frequencies are defined by $\hbar\omega_{\alpha\beta} = -\hbar\omega_{\beta\alpha} = E_{\alpha} - E_{\beta}$, and it follows from Eqs. (2.7) and the Hermitian character of $\mathcal{H}_1(t)$ that the spectral densities $J(\omega)$ satisfy the relations

$$J_{\alpha\beta\alpha'\beta'}(\omega) = J_{\beta'\alpha'\beta\alpha}(\omega) = J_{\alpha\beta\alpha'\beta'}(-\omega) = J_{\beta\alpha\beta'\alpha'}^*(\omega). \quad (2.20)$$

Imaginary terms in the relaxation matrix which give rise to small second-order shifts of the line positions^{21,22} have been omitted from Eq. (2.17).

There are thus several steps in calculating the spectrum $I(\omega)$. These include, first, the computation of the spectral densities $J_{\alpha\alpha'\beta\beta'}(\omega)$. The relaxation matrix $R_{\alpha\alpha'\beta\beta'}$ is then evaluated from the spectral densities. The differential equation for $S_x^{\dagger}(t)$ must be solved in order to calculate the correlation function $G(t)$, and finally $I(\omega)$ can then be obtained from the Fourier transform of $G(t)$. Before proceeding to these detailed calculations, some general conclusions about the line shape are first discussed (Sec. III).

III. LINE SHAPE

The spectrum, and therefore the line shape, can be specified in general terms by obtaining a formal solution of Eq. (2.15) for $S_x^{\dagger}(t)$. Only the D_k -dimensional subspace of the relaxation matrix $R_{\alpha\alpha'\beta\beta'}$ which contains all the states $|\alpha\rangle$ and $|\alpha'\rangle$ for which

$$E_{\alpha} - E_{\alpha'} = \hbar\omega_k \quad (3.1)$$

are needed to determine the correlation function $G_k(t)$ for the line with angular frequency ω_k , and the formal solution of Eq. (2.15) is obtained by diagonalizing this part of the R matrix.²¹ In the appropriate subspace, the matrix elements $\langle \alpha | S_x | \alpha' \rangle$ are taken

as the components $X_j^{(k)}$ of a D_k -dimensional vector $\mathbf{X}^{(k)}$. Let $\mathbf{U}^{(k)}$ be the unitary transformation which diagonalizes the relaxation matrix $\mathbf{R}^{(k)}$ in the subspace,

$$\left([\mathbf{U}^{(k)}]^{-1} \mathbf{R}^{(k)} \mathbf{U}^{(k)} \right)_{ij} = \sum_{m,n=1}^{D_k} [\mathbf{U}^{(k)}]_{im}^{-1} R_{mn}^{(k)} U_{nj}^{(k)} = \lambda_i^{(k)} \delta_{ij}, \quad (3.2)$$

where the $\lambda_i^{(k)}$ are the eigenvalues of $R_{mn}^{(k)}$; and let $Y_i^{(k)}$ be the components of a vector $\mathbf{Y}^{(k)}$ obtained from $\mathbf{X}^{(k)}$ by the inverse of the transformation $\mathbf{U}^{(k)}$:

$$Y_i^{(k)} = \sum_{j=1}^{D_k} [\mathbf{U}^{(k)}]_{ij}^{-1} X_j^{(k)}. \quad (3.3)$$

Then it can be shown that²¹

$$G_k(t) = 2 \cos \omega_k t \sum_{i=1}^{D_k} |Y_i^{(k)}|^2 \exp(\lambda_i^{(k)} t) \quad (3.4)$$

and, since on physical grounds the $\lambda_i^{(k)}$ must be negative, one obtains

$$I_k(\omega) = (4/\pi) \sum_{i=1}^{D_k} |Y_i^{(k)}|^2 \frac{T_{2,i}^{(k)}}{1 + [T_{2,i}^{(k)}]^2 (\omega - \omega_k)^2}, \quad (3.5)$$

where we have set $[-\lambda_i^{(k)}]^{-1} = T_{2,i}^{(k)}$, the transverse relaxation time for the i th component of the line with angular frequency ω_k .

The spectrum given by Eq. (3.5) is the sum of lines of Lorentzian shape and different widths,^{21,35} and thus in general the shape of a composite line is not Lorentzian. On the other hand, the Kubo and Tomita theory,³ as applied to the linewidths of free radicals by Kivelson,⁴ predicts that a composite line should have an over-all Lorentzian shape. Some examples of this discrepancy between the two theories are discussed in Sec. V. If all the $T_{2,i}^{(k)}$ are equal, Eq. (3.5) gives a single Lorentzian line. To obtain the spectrum we note that the matrix elements $X_i^{(k)} = \langle \alpha | S_x | \alpha' \rangle$ have the value $X_i^{(k)} = \frac{1}{2}$ for D_k of the matrix elements and zero for the remaining $D_k(D_k - 1)$. This follows because in the high-field approximation each state can be represented by a wavefunction which is a product of an electron-spin wavefunction and one function from a set of D_k orthonormal nuclear-spin wavefunctions. From Eq. (3.3),

$$\sum_i |Y_i^{(k)}|^2 = \sum_i |X_i^{(k)}|^2,$$

and thus

$$I_k(\omega) = \frac{D_k}{\pi} \frac{T_2^{(k)}}{1 + [T_2^{(k)}]^2 (\omega - \omega_k)^2}, \quad (3.6)$$

A single Lorentzian line is also obtained if the different eigenvalues $\lambda_i^{(k)}$ of the part of the relaxation

³⁵ The lines are, of course, not Lorentzian in the wings. See Ref. 3 and 21.

matrix $\mathbf{R}^{(k)}$ related to the line of angular frequency ω_k do not differ appreciably from one another. Thus, we write

$$\lambda_i = \lambda + \delta_i \quad (3.7)$$

with

$$\delta_i \ll \lambda,$$

(where the superscript k has been omitted for brevity). Now the only important contribution of $G_k(t)$ to the spectrum $I_k(\omega)$ is in the time interval $0 < t \sim |\lambda_i|^{-1}$, and since $|\delta_i| \ll |\lambda|$, $|\delta_i t| \ll 1$ in this time interval. Equation (3.4) can thus be written

$$\begin{aligned} G_k(t) &\cong 2 \cos \omega_k t \exp(\lambda t) \sum_i |Y_i|^2 (1 + \delta_i t) \\ &\cong 2 \cos \omega_k t \exp(\lambda t) \sum_i |Y_i|^2 (1 + \bar{\delta} t) \\ &\cong 2 \cos \omega_k t \exp[(\lambda + \bar{\delta})t] \sum_i |Y_i|^2, \end{aligned} \quad (3.8)$$

where

$$\bar{\delta} = [\sum_i |Y_i|^2 \delta_i] / \sum_i |Y_i|^2. \quad (3.9)$$

This $G_k(t)$ leads to the spectrum $I_k(\omega)$ of Eq. (3.6), i.e., a single Lorentzian, with a transverse relaxation time given by

$$\begin{aligned} 1/T_2^{(k)} &\cong -(\lambda^{(k)} + \bar{\delta}^{(k)}) = -(4/D_k) \sum_{i,j=1}^{D_k} X_i^{(k)*} R_{ij}^{(k)} X_j^{(k)} \\ &= -(1/D_k) \sum_{i,j} R_{ij}^{(k)}, \end{aligned} \quad (3.10)$$

where the prime is used to indicate that the last summation contains only terms in the D_k -dimensional subspace for which neither $X_i^{(k)}$ nor $X_j^{(k)}$ vanish. As is shown in Sec. IV, it is always possible (in the absence of appreciable quadrupole interactions) to choose a representation by inspection for which off-diagonal elements of $\mathbf{R}^{(k)}$ in this subspace vanish [see discussions following Eqs. (4.45) and (4.50) in Sec. IV] and thus

$$1/T_2^{(k)} \cong -(1/D_k) \sum_i R_{ii}^{(k)}. \quad (3.11)$$

Equation (3.11) is equivalent to Kivelson's result,⁴ but it is clear that a single Lorentzian will not be obtained in general. Equations (3.7) are, of course, only a sufficient condition for obtaining a line with over-all Lorentzian shape.

Although the foregoing theory shows that in general a composite line will not have a Lorentzian shape, shape-dependent parameters such as the linewidth and the relative amplitude of a hyperfine component are much more readily studied experimentally than the shape itself. Line-shape investigations are notoriously difficult because the wings must be carefully examined, and in the typical ESR spectra of interest the wings are obscured by too small a signal-to-noise ratio and too great a degree of overlapping of adjacent components. One of the problems in detecting that a line is a

superposition of Lorentzians rather than a single Lorentzian may be illustrated by plotting the curve resulting from two superimposed Lorentzian lines of the same statistical weights (intensities) with linewidths differing by a factor of 2. Inspection of the computed curve for the first derivative (and comparable conclusions are obtained from the absorption curve) shows that a single Lorentzian-shaped curve can be fitted to the maximum deflection and the width so as to reproduce this curve for the superimposed line extremely well in the central portion. The single Lorentzian line has too small an integrated intensity, but differences in the amplitudes of the multiple and single Lorentzians are only evident in regions greater than several linewidths from the center of the spectrum.³⁶ As a second example with quite different properties, let us consider two superimposed lines of the same statistical weight which differ in widths by a larger factor. For definiteness, we take one line to have a width of 0.1 G and the other a width of 0.5 G. Then the amplitudes of the derivative maxima, which are inversely proportional to the square of the widths, would be 100 and 4, respectively, in arbitrary units. Thus the broader of the two lines would be barely detectable, and the line actually observed would have a Lorentzian shape. In contrast, a single Lorentzian line with the average width of 0.3 G and of the same total integrated intensity, corresponding to the spectrum predicted by the Kivelson theory, would have an amplitude of $11 \times 2 = 22$ in the same units. Thus even though in many instances the experimental limitations involved in line-shape studies may prevent the observation of non-Lorentzian shapes, the present treatment predicts striking variations in the linewidths and amplitudes which are outside the scope of the previous theories.

IV. RELAXATION MATRIX

In this section we obtain the explicit form of the relaxation matrix for dilute solutions of free radicals. Radical-radical and radical-solvent dipolar interactions are neglected. The small intramolecular nuclear-nuclear dipolar perturbations are also not included. We first summarize the procedure for averaging over the molecular tumbling, and then give the form of the perturbations and the correlation functions for the interactions of interest. The different types of "equivalent" nuclei and the appropriate basis functions are discussed next. Finally, before presenting the detailed expressions for the R matrix, the different types of transition frequencies, and the importance of their contributions, are summarized. Some of the expressions obtained in this section are not needed for the problems treated in the present work, but are included for completeness and for use in subsequent applications.^{23,24}

³⁶ J. Gendell (private communication).

A. Perturbing Hamiltonian and the Correlation Functions

The perturbing Hamiltonian $\hbar\mathcal{H}_1(t)$ which we consider contains contributions from the isotropic ($\mathcal{H}^{(I)}$) and anisotropic ($\mathcal{H}^{(D)}$) intramolecular dipolar interactions, the g tensor ($\mathcal{H}^{(G)}$), and the quadrupolar interaction

$$\hbar\mathcal{H}_1(t) = \hbar\mathcal{H}^{(I)}(t) + \hbar\mathcal{H}^{(D)}(t) + \hbar\mathcal{H}^{(G)}(t) + \hbar\mathcal{H}^{(Q)}(t). \quad (4.1a)$$

It is convenient to write $\mathcal{H}_1(t)$ in the form

$$\mathcal{H}_1(t) = \sum_{L,m,\mu,i} F_{\mu,i}{}^{(L,m)}(t) A_{\mu,i}{}^{(L,-m)}, \quad (4.1b)$$

where $F_{\mu,i}{}^{(L,m)}(t)$ is a function of all the spatial variables, and is thus a randomly varying function of the time, and $A_{\mu,i}{}^{(L,-m)}$ contains only the spin operators. In this second equation, the different types of perturbations which contribute to $\mathcal{H}_1(t)$ are distinguished by the subscript μ , and the subscript i refers to the different nuclei in the radical. The interactions are expressed as irreducible (spherical) tensors with L denoting the rank and m the component. The only perturbations of interest here have $L=0$ or 2. The prime signifies that the interactions are written in molecule-fixed axes, and in particular it is convenient to use the axes of the (average) principal values of the g tensor. The transformation from molecule-fixed to space-fixed axes is readily carried out with the Wigner rotation matrices³⁷⁻³⁹ $\mathcal{D}_{mm'}{}^{(L)}(\alpha\beta\gamma)$, where α , β , and γ are the Euler angles relating the two systems of axes, giving

$$A_{\mu,i}{}^{(L,-m)} = \sum_{m'} \mathcal{D}_{-m,m'}{}^{(L)}(\alpha\beta\gamma) A_{\mu,i}{}^{(L,m')}, \quad (4.2)$$

where the A 's without a prime refer to space-fixed axes. When averaged over the Euler angles, the Wigner rotation matrices obey the orthogonality conditions³⁸

$$\langle \mathcal{D}_{m_1,q_1}{}^{(L_1)*}(\alpha\beta\gamma) \mathcal{D}_{m_2,q_2}{}^{(L_2)}(\alpha\beta\gamma) \rangle_{\alpha\beta\gamma} = (2L_1+1)^{-1} \delta_{L_1 L_2} \delta_{m_1 m_2} \delta_{q_1 q_2}. \quad (4.3)$$

The correlation function which appears in the spectral density $J(\omega)$ of Eq. (2.18) can thus be written

$$\begin{aligned} & \langle \mathcal{H}_1(t)_{\alpha\beta} \mathcal{H}_1^*(t+\tau)_{\alpha'\beta'} \rangle \\ &= \sum_{L,L'} \sum_{m,m'} \sum_{\mu,\nu} \sum_{i,j} \langle F_{\mu,i}{}^{(L,m)}(t) F_{\nu,j}{}^{(L',m')}*(t+\tau) \rangle \\ & \quad \times \sum_{q,q'} \langle \mathcal{D}_{-m,q}{}^{(L)}(t) \mathcal{D}_{-m',q'}{}^{(L')*}(t+\tau) \rangle_{\alpha\beta\gamma} \\ & \quad \times [A_{\mu,i}{}^{(L,q)}]_{\alpha\beta} [A_{\nu,j}{}^{(L',q')}]_{\alpha'\beta'}^*. \quad (4.4) \end{aligned}$$

³⁷ E. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959).

³⁸ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

³⁹ A. K. Saha and T. P. Das, *Nuclear Induction* (Saha Institute of Nuclear Physics, Calcutta, India, 1957).

We have assumed in writing Eq. (4.4) that the molecular tumbling is independent of the internal motions and fluctuating solvent interactions, and vice versa; and the quantity $\langle F'(t) F'(t+\tau)^* \rangle$ is an average over these latter motions only. The tensors with $L=0$ are independent of the Euler angles, and we assume that for $L=2$ the molecular tumbling is described by a single correlation time τ_R . We can thus write^{1,21} (with $d\Omega'$ as the normalized volume element in $\alpha'\beta'\gamma'$ space)

$$\begin{aligned} & \int d\Omega' \mathcal{D}_{-m',q'}{}^{(2)*}(\alpha'\beta'\gamma') P(\alpha\beta\gamma | \alpha'\beta'\gamma'; \tau) \\ &= \mathcal{D}_{-m',q'}{}^{(2)*}(\alpha\beta\gamma) \exp(-|\tau|/\tau_R). \quad (4.5) \end{aligned}$$

Applying Eqs. (4.3) and (4.5) to Eq. (4.4) gives

$$\begin{aligned} & \langle \mathcal{H}_1(t)_{\alpha\beta} \mathcal{H}_1^*(t+\tau)_{\alpha'\beta'} \rangle = \sum_L \sum_{\mu,\nu} \sum_{i,j} g_{ij}{}^{(\mu\nu;L)}(\tau) \\ & \quad \times \sum_q [A_{\mu,i}{}^{(L,q)}]_{\alpha\beta} [A_{\nu,j}{}^{(L,q)}]_{\alpha'\beta'}^*, \quad (4.6) \end{aligned}$$

where

$$\begin{aligned} g_{ij}{}^{(\mu\nu;2)}(\tau) &= \frac{1}{5} \exp(-|\tau|/\tau_R) \\ & \quad \times \sum_m \langle F_{\mu,i}{}^{(2,m)}(t) F_{\nu,j}{}^{(2,m)*}(t+\tau) \rangle \quad (4.7) \end{aligned}$$

with a similar expression for $g_{ij}{}^{(\mu\nu;0)}(\tau)$ except that the factor preceding the summation sign is equal to unity. Finally, we write for $J(\omega)$ in Eq. (2.18)

$$\begin{aligned} J_{\alpha\beta\alpha'\beta'}(\omega) &= \sum_L \sum_{\mu,\nu} \sum_{i,j} j_{ij}{}^{(\mu\nu;L)}(\omega) \\ & \quad \times \sum_q [A_{\mu,i}{}^{(L,q)}]_{\alpha\beta} [A_{\nu,j}{}^{(L,q)}]_{\alpha'\beta'}^*, \quad (4.8) \end{aligned}$$

where

$$j_{ij}{}^{(\mu\nu;L)}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} g_{ij}{}^{(\mu\nu;L)}(\tau) \exp(-i\omega\tau) d\tau. \quad (4.9)$$

The perturbations of interest are listed in Table I in the form in which they will be used for substitution in Eqs. (4.6)–(4.9). The operators $A_{\mu,i}{}^{(L,q)}$ are given in space-fixed axes and the functions of spatial variables $F_{\mu,i}{}^{(L,m)}(t)$ in the molecule-fixed axes of the (average) principal values of the g tensor, x' , y' , z' . Much of the notation is defined in the discussion of Eqs. (2.9) and (2.10). The expectation values in the $D_i^{(m)}(t)$ and $[\nabla \mathbf{E}(t)]_i^{(m)}$ are over the electronic wavefunction ψ . The $Y_{2m}(\theta_i', \phi_i')$ are the surface harmonics of order two (Condon and Shortley definition⁴⁰), and r_i' , θ_i' , and ϕ_i' are spherical polar coordinates which define the position of the unpaired electron with respect to the i th nucleus in the x' , y' , z' axis system. In the quadrupole terms, Q_i is the quadrupole moment of the i th nucleus, $V(i)$ is the electrostatic potential at the i th nucleus, and the subscripts x , y , etc., indicate the

⁴⁰ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

TABLE I. Terms in the perturbation $\mathfrak{H}_1(t)$.^a

		Dipolar	
		Isotropic (<i>I</i>)	Anisotropic (<i>D</i>)
$A_{\mu,i}^{(L,q)}$	$q=0$	$-\mathbf{I}_i \cdot \mathbf{S}$	$-2(\frac{2}{3})^{\frac{1}{2}}[I_{iz}S_z - \frac{1}{2}(I_{i+}S_{-} + I_{i-}S_{+})]$
	$q=\pm 1$	0	$\pm(I_{i+}S_z + I_{iz}S_{\pm})$
	$q=\pm 2$	0	$-I_{i\pm}S_{\pm}$
$F_{\mu,i}^{(L,m)}(t)$		$\gamma_e[a_i(t) - \bar{a}_i]\delta_{m0}$	$(-1)^m \gamma_e \gamma_j \hbar D_i^{(m)}(t)$ $D_i^{(m)}(t) = (6\pi/5)^{\frac{1}{2}} \langle \psi r_i'^{-3} Y_{2m}(\theta_i', \phi_i') \psi \rangle$
		<i>g</i> Tensor	
		Isotropic (G_0)	Anisotropic (G_2)
$A_{\mu,i}^{(L,q)}$	$q=0$	$-B_0 S_z$	$-2(\frac{2}{3})^{\frac{1}{2}} B_0 S_z$
	$q=\pm 1$	0	$\pm B_0 S_{\pm}$
	$q=\pm 2$	0	0
$F_{\mu,i}^{(L,m)}(t)$		$-\beta_e \hbar^{-1} [g_s(t) - \bar{g}_s] \delta_{m0}$	$-\frac{1}{2} (-1)^m \beta_e \hbar^{-1} g^{(m)}(t)$ $g^{(0)}(t) = 6^{-\frac{1}{2}} \{2g_3(t) - [g_1(t) + g_2(t)]\}$ $g^{(\pm 1)}(t) = 0$ $g^{(\pm 2)}(t) = \frac{1}{2} [g_1(t) - g_2(t)]$
		Quadrupolar (<i>Q</i>) ^b	
		Anisotropic	
$A_{\mu,i}^{(L,q)}$	$q=0$		$-(\frac{2}{3})^{\frac{1}{2}} [3I_{iz}^2 - I_i(I_i+1)]$
	$q=\pm 1$		$\pm(I_{i\pm}I_{iz} + I_{iz}I_{i\pm})$
	$q=\pm 2$		$-I_{i\pm}^2$
$F_{\mu,i}^{(L,m)}(t)$			$(-1)^m \{eQ_i \hbar^{-1} [4I_i(2I_i-1)]^{-1} [\nabla \mathfrak{E}(t)]_i^{(m)}\}$ $[\nabla \mathfrak{E}(t)]_i^{(0)} = -(\frac{2}{3})^{\frac{1}{2}} \langle \psi V_{zz'}(i) \psi \rangle$ $[\nabla \mathfrak{E}(t)]_i^{(\pm 1)} = \pm \langle \psi V_{xz'}(i) \pm i V_{yz'}(i) \psi \rangle$ $[\nabla \mathfrak{E}(t)]_i^{(\pm 2)} = -\frac{1}{2} \langle \psi V_{xx'}(i) - V_{yy'}(i) \pm 2i V_{xy'}(i) \psi \rangle$

^a The expressions for the $A_{\mu,i}^{(L,q)}$ are given in space-fixed axes while those for the $F_{\mu,i}^{(L,m)}(t)$ are in the molecule-fixed axes coinciding with the principle values of the *g* tensor.

^b Quadrupole moments are defined in the conventional manner. See, for example, Refs. 4, 21, or 39.

derivatives of $V(i)$ with respect to the x' , y' , z' coordinates. The $F_{\mu,i}^{(L,m)}(t)$ are functions of time through their dependence on the internal motions and the fluctuating solvent interactions, effects which can modify the isotropic interactions $a_i(t)$; the r_i' , θ_i' , ϕ_i' ; $g_i(t)$; the derivatives of $V(i)$; and the electronic wavefunction ψ . The *g* value of the free electron, $g_0 = -(\hbar\gamma_e/\beta_e)$, and the average isotropic *g* value \bar{g}_s , are used interchangeably when they occur as multiplicative factors in $\mathfrak{H}_1(t)$.

The correlation functions, which we write in a somewhat more compact notation than in Eq. (4.7), and with the angular brackets signifying an average over the internal motions and fluctuating solvent interactions only, are as follows.

Isotropic dipolar interaction (hyperfine interaction) (*I*):

$$g_{ij}^{(I)}(\tau) = \gamma_e^2 \langle [a_i(t) - \bar{a}_i][a_j(t+\tau) - \bar{a}_j] \rangle \\ = \gamma_e^2 \langle a_i(t) a_j(t+\tau) \rangle - \bar{a}_i \bar{a}_j. \quad (4.10)$$

Anisotropic dipolar interaction (*D*):

$$g_{ij}^{(D)}(\tau) = \frac{1}{5} \gamma_e^2 \gamma_j \hbar^2 \exp(-|\tau|/\tau_R) \\ \times \sum_m \langle D_i^{(m)}(t) D_j^{(m)*}(t+\tau) \rangle. \quad (4.11)$$

Isotropic *g*-tensor interaction (G_0):

$$g^{(G_0)}(\tau) = \beta_e^2 \hbar^{-2} \langle [g_s(t) g_s(t+\tau) - \bar{g}_s^2] \rangle. \quad (4.12)$$

Anisotropic g -tensor interaction (G_2):

$$g^{(G_2)}(\tau) = \frac{1}{2^0} \exp(-|\tau|/\tau_R) \beta_e^2 \hbar^{-2} \times \sum_m \langle g^{(m)}(t) g^{(m)}(t+\tau) \rangle = \frac{1}{2^0} \exp(-|\tau|/\tau_R) \beta_e^2 \hbar^{-2} \times \left\{ \sum_{k=1}^3 \langle g_k(t) g_k(t+\tau) \rangle - 3 \langle g_s(t) g_s(t+\tau) \rangle \right\}. \quad (4.13)$$

Quadrupolar interaction (Q):

$$g_{ij}^{(Q)}(\tau) = \frac{1}{8^0} \exp(-|\tau|/\tau_R) \times \{ e^2 Q_i Q_j \hbar^{-2} [I_i(2I_i-1) I_j(2I_j-1)]^{-1} \} \times \sum_m \langle [\nabla \mathcal{E}(t)]_i^{(m)} [\nabla \mathcal{E}(t+\tau)]_j^{(m)*} \rangle. \quad (4.14)$$

There are also cross terms between the different interactions with the same value of L :

Isotropic dipolar- g -tensor interaction (IG_0):

$$g_i^{(IG_0)}(\tau) = \bar{g}_i \beta_e^2 \hbar^{-2} [\langle a_i(t) g_s(t+\tau) \rangle - \bar{a}_i \bar{g}_s]. \quad (4.15)$$

Anisotropic dipolar- g -tensor interaction (DG_2):

$$g_i^{(DG_2)}(\tau) = -\frac{1}{1^0} \gamma_e \beta_e \gamma_i \exp(-|\tau|/\tau_R) \times \sum_m \langle D_i^{(m)}(t) g^{(m)}(t+\tau) \rangle. \quad (4.16)$$

Anisotropic dipolar-quadrupolar interaction (DQ):

$$g_{ij}^{(DQ)}(\tau) = \frac{1}{2^0} \exp(-|\tau|/\tau_R) \gamma_e \gamma_i \{ e Q_j [I_j(2I_j-1)]^{-1} \} \times \sum_m \langle D_i^{(m)}(t) [\nabla \mathcal{E}(t+\tau)]_j^{(m)*} \rangle. \quad (4.17)$$

Anisotropic g -tensor-quadrupolar interaction (G_2Q):

$$g_i^{(G_2Q)}(\tau) = -\frac{1}{4^0} \exp(-|\tau|/\tau_R) \beta_e \hbar^{-2} \times \{ e Q_i [I_i(2I_i-1)]^{-1} \} \times \sum_m \langle g^{(m)}(t) [\nabla \mathcal{E}(t+\tau)]_i^{(m)*} \rangle. \quad (4.18)$$

The correlation functions for the cross terms obey the relation

$$g_{ij}^{(\mu\nu)}(\tau) = g_{ji}^{(\nu\mu)*}(\tau) = g_{ji}^{(\nu\mu)}(\tau), \quad (4.19a)$$

and they contribute a term to the summation over μ, ν, i, j , and L in Eq. (4.6) of the form

$$\frac{1}{2} g_{ij}^{(\mu\nu, L)}(\tau) \sum_{\rho} \{ [A_{\mu, i}^{(L, \rho)}]_{\alpha\beta} [A_{\nu, j}^{(L, \rho)}]_{\alpha'\beta'}^* + [A_{\nu, j}^{(L, \rho)}]_{\alpha\beta} [A_{\mu, i}^{(L, \rho)}]_{\alpha'\beta'}^* \}. \quad (4.19b)$$

The principal axes x', y', z' of the g tensor do not, in general, coincide with the principal axes of the dipolar interaction for a particular nucleus. In terms of the principal axes of this interaction for the i th

nucleus, x_i'', y_i'', z_i'' , with Hamiltonian

$$\hbar \mathcal{H}_i^{(D)} = -|\gamma_e| \gamma_i \hbar^2 [d_{i,1} I_{ix}'' S_z'' + d_{i,2} I_{iy}'' S_y'' + d_{i,3} I_{iz}'' S_z''], \quad (4.20)$$

the $D_i^{(m)}$ (Table I) are given by

$$D_i^{(m)} = -\frac{1}{2} \sum_{m'} (-1)^{m'} d_{i, m'}^{(2)} \mathcal{D}_{m, m'}^{(2)}(\alpha_i'', \beta_i'', \gamma_i''), \quad (4.21)$$

where

$$d_i^{(2)} = d_i^{(-2)} = \frac{1}{2} (d_{i,1} - d_{i,2}), \\ d_i^{(\pm 1)} = 0, \\ d_i^{(0)} = \left(\frac{3}{2}\right)^{1/2} d_{i,3}, \quad (4.22)$$

and $\alpha_i'', \beta_i'', \gamma_i''$ are the Euler angles of the x', y', z' axes with respect to the x_i'', y_i'', z_i'' axes. As pointed out by Schreurs,⁴¹⁻⁴³ even for two nuclei i and j that are at equivalent positions (in the sense that the symmetry operations of the molecule transform one position into the other), $D_i^{(m)}$ is not necessarily equal to $D_j^{(m)}$. This difficulty arises because the x_i'', y_i'', z_i'' and x_j'', y_j'', z_j'' axes may not have the same orientation. For planar radicals, $\beta_i'' = \gamma_i'' = 0$, and

$$\mathcal{D}_{mm'}^{(2)}(\alpha_i'', 0, 0) = \exp(-im\alpha_i'') \delta_{mm'}, \quad (4.23)$$

so that

$$D_i^{(\pm 2)} = -\frac{1}{2} d_i^{(2)} \exp(\mp 2i\alpha_i''), \\ D_i^{(\pm 1)} = 0, \\ D_i^{(0)} = -\frac{1}{2} d_i^{(0)}. \quad (4.24)$$

Thus in general $D_i^{(\pm 2)} \neq D_j^{(\pm 2)}$ for nuclei i and j at equivalent positions, although if nucleus i can be transformed into j by a twofold rotation about the axis perpendicular to the plane of the molecule and passing through its center, $D_i^{(\pm 2)} = D_j^{(\pm 2)}$. Another especially simple and frequently occurring case arises when there is a twofold symmetry axis lying in the plane of the molecule, since then nuclei which are transformed into each other by this twofold rotation have coefficients that obey the relation $D_i^{(\pm 2)} = D_j^{(\mp 2)}$. For computational purposes, the wavefunction ψ in pi-electron radicals is conveniently written as a linear combination of atomic pi orbitals ϕ_κ , and to a first approximation the contribution of each orbital can be calculated separately. The principal axes and principal values of the dipolar interaction at the i th nucleus arising from each of the κ orbitals are in general different, and each set must be transformed from the x_{ik}'' ,

⁴¹ J. W. H. Schreurs, thesis, Free University of Amsterdam, Amsterdam, 1962.

⁴² J. W. H. Schreurs and D. Kivelson, J. Chem. Phys. **36**, 117 (1962).

⁴³ Similar observations have been made by A. Carrington and H. C. Longuet-Higgins, Mol. Phys. **5**, 447 (1962). See, however, Ref. 45.

γ_{ik}'', z_{ik}'' axes to the x', y', z' axes. Writing

$$\psi = \sum_{\kappa} c_{\kappa} \phi_{\kappa},$$

$$D_i^{(\pm 2)} = -\frac{1}{2} \sum_{\kappa} \rho_{\kappa}^{\pi} d_{ik}^{(2)} \exp(\mp 2i\alpha_{ik}''), \quad (4.25)$$

$$D_i^{(\pm 1)} = 0,$$

$$D_i^{(0)} = -\frac{1}{2} \sum_{\kappa} \rho_{\kappa}^{\pi} d_{ik}^{(0)}, \quad (4.26)$$

where $\rho_{\kappa}^{\pi} = |c_{\kappa}|^2$ is the pi-electron spin density associated with orbital ϕ_{κ} , and the $d_{ik}^{(m)}$ are related to the principal values $d_{ik,n}$, $n=1, 2, 3$, by relations analogous to Eqs. (4.22). Formulas for calculating the $d_{ik,n}$ have been given by McConnell and Strathdee.⁴⁴ Similar considerations apply to the quadrupolar interaction.

B. Equivalent Nuclei, Basis Functions, and Frequency Dependence of the R Matrix

The proper formulation of the relaxation matrix requires that careful distinctions be drawn between the different types of environments of the nuclei in a radical. We shall also find that although in general the R matrix is not diagonal, there are certain natural representations for the eigenstates of \mathcal{H}_0 which lead to the simplest form for the matrix. In addition, the frequency dependence of the perturbations is helpful in determining the importance of the off-diagonal elements. In this subsection the definitions of "equivalent" nuclei, the choice of basis functions, and the frequency dependence, are discussed in detail.

1. Types of "Equivalent" Nuclei

We say two nuclei i and j are *equivalent* if the zero-order Hamiltonian \mathcal{H}_0 in Eq. (2.9) is symmetric with respect to the interchange of i and j , which implies that $\gamma_i = \gamma_j$, $I_i = I_j$, and $\bar{a}_i = \bar{a}_j$. Usually two nuclei are equivalent in this sense only if they are located at symmetrically equivalent positions in the radical, but this definition also includes as equivalent those nuclei which are not at symmetrically related positions provided that they have the same magnetic properties and average isotropic splitting constants. We call these two cases *symmetrical* and *accidental equivalence*, respectively. For accidental equivalence, two splitting constants may be considered to be the same if their difference is small compared to the linewidth. It is common practice to use the terms "equivalent" or "accidentally equivalent" if $\bar{a}_i = \bar{a}_j$, even though $\gamma_i \neq \gamma_j$ or $I_i \neq I_j$, but for simplicity this rather special situation will be excluded from the general treatment and we define two nuclei i and j to be *nonequivalent* if any of the equalities $\gamma_i = \gamma_j$, $I_i = I_j$, or $\bar{a}_i = \bar{a}_j$, does not hold.

It does not follow that two nuclei which are equivalent with respect to \mathcal{H}_0 are also equivalent with respect to the perturbation \mathcal{H}_1 . For example, even if the

average values of the isotropic hyperfine interactions for two nuclei are the same ($\bar{a}_i = \bar{a}_j$), the instantaneous values $a_i(t)$ and $a_j(t)$ may not be equal, or the coefficients in the dipolar interaction, $D_i^{(\pm 2)}$ and $D_j^{(\pm 2)}$, in Eq. (4.24), may be different. We use the term *completely equivalent* for two nuclei i and j if the perturbing Hamiltonian $\mathcal{H}_1(t)$ is symmetric with respect to the interchange of i and j . The nuclei can thus be divided into sets r, s, \dots of *equivalent* groups, containing n_r, n_s, \dots nuclei, respectively, and within each equivalent group they can be subdivided into sets r_u, r_v, \dots of *completely equivalent* subgroups, containing n_{r_u}, n_{r_v}, \dots nuclei, respectively, with $n_r = \sum_u n_{r_u}$.

For any nucleus i in the *completely equivalent* subgroup r_u , and any nucleus j in the *completely equivalent* subgroup r_v ,

$$g_{ij}^{(\mu, \nu; L)}(\tau) = g_{r_u r_v}^{(\mu, \nu; L)}(\tau). \quad (4.27a)$$

Thus if the nuclei i and j are in the *same* completely equivalent subgroup r_u ,

$$g_{ii}^{(\mu, \nu; L)}(\tau) = g_{jj}^{(\mu, \nu; L)}(\tau) = g_{ij}^{(\mu, \nu; L)}(\tau) = g_{r_u r_u}^{(\mu, \nu; L)}(\tau). \quad (4.27b)$$

For any two *completely equivalent* subgroups r_u and r_v in a *symmetrically equivalent* group r ,

$$g_{r_u r_u}^{(\mu, \nu; L)}(\tau) = g_{r_v r_v}^{(\mu, \nu; L)}(\tau) = g_{rr}^{(\mu, \nu; L)}(\tau), \quad (4.27c)$$

but

$$g_{r_u r_v}^{(\mu, \nu; L)}(\tau) \neq g_{rr}^{(\mu, \nu; L)}(\tau) \quad (4.27d)$$

if r_u and r_v are different subgroups. It also is important to note that $g_{r_u r_v}^{(\mu, \nu; L)}(\tau)$ is not in general independent of the indices u and v specifying the completely equivalent subgroups of different groups r and s , i.e.,

$$g_{r_u r_v}^{(\mu, \nu; L)}(\tau) \neq g_{rs}^{(\mu, \nu; L)}(\tau).$$

For a *completely equivalent* subgroup r_u , we can write

$$\sum_{i, j \text{ in } r_u} g_{ij}^{(\mu, \nu; L)}(\tau) [A_{\mu, i}^{(L, q)}]_{\alpha\beta} [A_{\nu, j}^{(L, q)}]_{\alpha'\beta'}^* \\ = g_{r_u r_u}^{(\mu, \nu; L)}(\tau) [A_{\mu, r_u}^{(L, q)}]_{\alpha\beta} [A_{\nu, r_u}^{(L, q)}]_{\alpha'\beta'}^*, \quad (4.28)$$

where

$$A_{\mu, r_u}^{(L, q)} = \sum_{i \text{ in } r_u} A_{\mu, i}^{(L, q)}, \quad (4.29)$$

for the contribution of the nuclei in subgroup r_u to the μ, ν, L, q term of Eq. (4.6). Except for the quadrupolar terms, the nuclear-spin operators in the $A_{\mu, r_u}^{(L, q)}$ can thus be written as the appropriate component of \mathbf{J}_{r_u} , the operator for the total nuclear spin in the *completely equivalent* subgroup r_u ,

$$\mathbf{J}_{r_u} = \sum_{i \text{ in } r_u} \mathbf{I}_i. \quad (4.30)$$

If there is no accidental equivalence in the group r , $g_{r_u r_u}^{(\mu, \nu; L)}(\tau) = g_{rr}^{(\mu, \nu; L)}(\tau)$ in Eq. (4.28), but because of Eq. (4.27d), the different completely equivalent

⁴⁴ H. M. McConnell and J. Strathdee, Mol. Phys. 2, 129 (1959).

subgroups are collected separately in Eqs. (4.29) and (4.30).

2. Basis Functions

We shall see that the relaxation matrix for a single set of completely equivalent nuclei is diagonal if the eigenstates of \mathcal{H}_0 are chosen to be the eigenfunctions $|JM\rangle$ of J^2 and J_z with eigenvalues $[J(J+1)]^{\frac{1}{2}}$ and M , respectively. This we call the coupled representation. The total wavefunction is written as a product of the electron-spin wavefunction $|m_s\rangle$, with eigenvalues $m_s = \pm(1/2)$ of S_z , and the nuclear-spin function $|JM\rangle$,

$$|\gamma\rangle = |m_s; JM\rangle = |m_s\rangle |JM\rangle. \tag{4.31}$$

For n nuclei of spin I , J takes on the values $nI, nI-1, \dots, 1, 0$ for n even, or n odd and I an integer; or the values $nI, nI-1, \dots, 3/2, 1/2$ for n odd and I a half-odd integer. The number of states with a particular value of J is given by

$$W(n, I, J) = D(n, I, M=J) - D(n, I, M=J+1), \tag{4.32}$$

where $D(n, I, M)$ is the degeneracy of the nuclear-spin states with z component of angular momentum equal to M . The $D(n, I, M)$ can be evaluated from the coefficients of the multinomial expansion. When necessary, we distinguish different degenerate states with the same values of J by the notation $J^{(k)}$. If products of the individual nuclear-spin wavefunctions $|I, m_i\rangle$ are used as the basis for a completely equivalent subgroup instead of the coupled representation, the R matrix is not in general diagonal.

If there is more than one completely equivalent subgroup of nuclei, we shall find that the most convenient basis consists of a product of the wavefunctions of the coupled representations for each completely equivalent subgroup,

$$|\gamma\rangle = |m_s; \{J_{r_u} M_{r_u}\}\rangle = |m_s\rangle \prod |J_{r_u}^{(k)} M_{r_u}\rangle, \tag{4.33}$$

where the expression in the center is a short-hand notation for the product on the right over all completely equivalent subgroups $r_u, r_v, \dots, s_u, s_v, \dots$ in all the different groups r, s, \dots of equivalent nuclei. The bracketed factor $\{J_{r_u}, M_{r_u}\}$ in the expression for $|\gamma\rangle$ indicates that each particular choice of the possible assignments of the set of quantum numbers $J_{r_u}^{(k)}$ and M_{r_u} defines a different state $|\gamma\rangle$. If there is only one nucleus in the subgroup r_u , say nucleus i , the wavefunction $|\{J_{r_u} M_{r_u}\}\rangle$ reduces to the single-nucleus function $|I, m_i\rangle = |m_i\rangle$. The wavefunction in Eq. (4.33) will be called the product of coupled representations or, if each completely equivalent set contains only one nucleus, merely the product representation. We shall find that the matrix is diagonal in this representation if there are no equivalent groups containing more

than one completely equivalent subgroup. A representation in which the wavefunctions of different equivalent groups are coupled together is generally unsuitable.

3. Types of Transition Frequencies

The high-field eigenvalues of the zero-order Hamiltonian, Eq. (2.9), in the state $|\gamma\rangle$ of Eq. (4.33), are

$$E_\gamma = \bar{g}_s \beta_e B_0 m_s - \hbar B_0 \sum_{r=1}^N \gamma_r M_r - \hbar \gamma_e m_s \sum_{r=1}^N M_r \bar{a}_r, \tag{4.34}$$

where

$$M_r = \sum_u M_{r_u} = \sum_{i \text{ in } r} m_i; \tag{4.35}$$

$\gamma_r = \gamma_i, \bar{a}_r = \bar{a}_i$, for i in the set r ; and N is the total number of different equivalent groups. The degeneracy of E_γ is

$$\prod_r D(n_r, I_r, M_r) = \prod_r \{ \sum'_u \prod_u D(n_{r_u}, I_r, M_{r_u}) \}, \tag{4.36}$$

where the prime on the summation indicates that only those terms are included for which the M_{r_u} satisfy Eq. (4.35). We specifically exclude accidental degeneracy in the ESR spectrum, i.e., it is assumed that only one set of values of the M_r leads to the same eigenvalue E_γ , or

$$\sum_{r=1}^N M_r \bar{a}_r \neq \sum_{r=1}^N M_{r'} \bar{a}_{r'} \tag{4.37}$$

if $M_r \neq M_{r'}$ for any r .

In the usual case that the correlation functions $g_{ij}^{(\mu\nu; L)}(\tau)$ depend exponentially on the time, the spectral densities $j_{ij}^{(\mu\nu; L)}(\omega)$ in Eq. (4.9) are proportional to the Debye-type dispersion function $\tau_c/(1+\omega^2\tau_c^2)$, where τ_c is the correlation time for the particular type of motion. Three different groups of frequencies have to be distinguished for the relaxation perturbations listed in Table I. There are first the *secular* terms. These commute with the zero-order Hamiltonian $\hbar\mathcal{H}_0$ (in the high-field approximation), thus giving $\omega=0$, and arise from the spin operators S_z, I_{iz} , and their products, and I_i^2 . The other operators do not commute with \mathcal{H}_0 , and we distinguish between *pseudosecular* terms, which correspond to nuclear-spin transition frequencies, and *nonsecular* terms, which give rise to electron-spin transitions. Pseudosecular transitions are developed by perturbations which contain the operators $I_{i\pm}$ or $I_{i\pm}^2$ but not the operators S_{\pm} , and they obey the selection rules $\Delta m_s = 0$ and $\Delta m_i = \pm 1$ or ± 2 . The angular frequencies for the nuclear-spin transitions involving the i th nucleus are $\omega_{i\pm}$ and $2\omega_{i\pm}$, where

$$\omega_{i\pm} = |\gamma_i B_0 \pm \frac{1}{2} \gamma_e \bar{a}_i| \tag{4.38}$$

and the upper sign applies if $m_s = +\frac{1}{2}$, while the lower sign holds if $m_s = -\frac{1}{2}$. Nonsecular transitions arise from terms containing the operators S_{\pm} , and the different types of combinations are $S_{\pm} I_{iz}, S_{\pm} I_{i\pm},$ or $S_{\pm} I_{i\mp}$. The

selection rules are $\Delta m_s = \pm 1$ and $\Delta m_i = 0, \pm 1$, or ∓ 1 , and the possible angular frequencies are (approximately) ω_0 , $\omega_0 + \omega_{i\pm}$, and $\omega_0 - \omega_{i\pm}$, where $\omega_0 = |\gamma_e| B_0$ is the Larmor frequency for a free electron. Similar definitions of secular, pseudosecular, and nonsecular are used when the total angular momentum operators \mathbf{J}_{r_u} are used instead of the \mathbf{I}_i , and the nuclear transition frequencies $\omega_{r_u\pm} = \omega_{r\pm}$ are given by Eq. (4.38) with the index i replaced by r .

We shall find that in the representations chosen above, the secular terms contribute only diagonal elements to the R matrix. The secular part of the R matrix is also diagonal in a product representation $|I_i m_i\rangle$ over all the nuclei. The pseudosecular and nonsecular terms, however, contribute off-diagonal elements when there is more than one completely equivalent subgroup in a single equivalent group.

When the high-field approximation is valid, the $\omega_{i\pm}$ can be neglected in comparison to ω_0 , and thus we take all the nonsecular transitions to have the same angular frequency ω_0 . For motions with very short correlation times τ_c , $(\omega_0\tau_c)^2 \ll 1$, $(\omega_{i\pm}\tau_c)^2 \ll 1$ (the extreme narrowing case),

$$j(\omega_0) \cong j(\omega_{i\pm}) \cong j(0), \quad (4.39)$$

and the contributions of pseudosecular and nonsecular relaxations are comparable to the secular terms. For intermediate correlation times, $\omega_0\tau_c \cong 1$, $(\omega_{i\pm}\tau_c)^2 \ll 1$,

$$j(\omega_0) < j(\omega_{i\pm}) \cong j(0). \quad (4.40)$$

For longer correlation times, $\omega_{i\pm}\tau_c \cong 1$ [but with τ_c still sufficiently short for Eq. (2.8) to hold], $(\omega_0\tau_c)^2 \gg 1$,

$$j(\omega_0) \ll j(\omega_{i\pm}) < j(0), \quad (4.41)$$

and the nonsecular terms make a negligible contribution. Except in this last case, the nuclear-spin transition frequencies $\omega_{i\pm}$ can be set equal to zero in the expressions for $j(\omega_{i\pm})$.

These considerations show that a particular interaction may have a large effect through its secular and pseudosecular terms, while the nonsecular parts may often be neglected. In many applications, different correlation times τ_c describe the motions associated with different interactions, and since the spectral densities are proportional to τ_c for $(\omega\tau_c)^2 \ll 1$, a perturbation associated with a small value of τ_c may make a small contribution. A motion with a small value of τ_c does not necessarily imply, however, that the associated interaction can be neglected, because the perturbation may be large. If the interaction is large and τ_c is small, Eq. (4.39) implies that the nonsecular, pseudosecular, and secular contributions are equally important. Finally, it should be noted that whenever the intramolecular dipolar interaction makes a significant contribution to the line-broadening mechanisms, the

pseudosecular terms (as distinct from the nonsecular terms) cannot be neglected.⁴⁵

C. Relaxation Matrix

We first consider the relaxation matrix without the quadrupole terms. It is evaluated using the eigenfunctions of Eq. (4.33), taking

$$|\alpha\rangle = |\frac{1}{2}; \{J_{r_u} M_{r_u}\}\rangle, \quad (4.42a)$$

$$|\alpha'\rangle = |-\frac{1}{2}; \{J_{r_u}' M_{r_u}'\}\rangle, \quad (4.42b)$$

$$|\beta\rangle = |\frac{1}{2}; \{J_{r_u}'' M_{r_u}''\}\rangle, \quad (4.42c)$$

$$|\beta'\rangle = |-\frac{1}{2}; \{J_{r_u}''' M_{r_u}'''\}\rangle. \quad (4.42d)$$

If $\{J_{r_u}' M_{r_u}'\} = \{J_{r_u} M_{r_u}\}$, the states $|\alpha\rangle$ and $|\alpha'\rangle$ correspond to the ESR line $|\alpha\rangle \leftrightarrow |\alpha'\rangle$. Equations (4.42) contain the only possible assignment of m_s values for $|\beta\rangle$ and $|\beta'\rangle$ for this transition that satisfies Eq. (2.19). Using these functions in Eq. (4.34), we find that Eq. (2.19) becomes

$$B_0 \sum_r \gamma_r (M_r - M_r' - M_r'' + M_r''') + (\gamma_e/2) \sum_r \bar{a}_r (M_r + M_r' - M_r'' - M_r''') = 0. \quad (4.43)$$

We exclude (as a unique type of accidental degeneracy) special values of B_0 which would cause this equation to be satisfied when the two summations are not separately zero. Equation (4.43) shows that the M 's must satisfy the relations

$$M_r = \sum_u M_{r_u} = \sum_u M_{r_u}'' = M_r'', \quad (4.44a)$$

$$M_r' = \sum_u M_{r_u}' = \sum_u M_{r_u}''' = M_r''', \quad (4.44b)$$

and it can also be shown from Eqs. (2.15) and the general theory⁴⁶ that the only elements of interest in the relaxation matrix are those for which $M_r' = M_r$, so that

$$M_r = M_r' = M_r'' = M_r'''. \quad (4.44c)$$

In addition, the relaxation matrix only contains terms for which $J_{r_u}^{(j)''} = J_{r_u}^{(k)}$ and $J_{r_u}^{(j)'''} = J_{r_u}^{(k)'}$.

Terms with $M_{r_u}' \neq M_{r_u}$ and $J_{r_u}^{(j)'} \neq J_{r_u}^{(k)}$, corresponding to different nuclear-spin functions in the states $|\alpha\rangle$ and $|\alpha'\rangle$, are required in the relaxation matrix even though the correlation function $G(t)$ in Eq. (2.11) depends on matrix elements $\langle\alpha|S_x|\alpha'\rangle$ which vanish if the nuclear-spin functions in $|\alpha\rangle$ and $|\alpha'\rangle$ are different. This complication arises because such terms enter into the calculation of $S_x(t)$ from Eqs. (2.15) and (2.16). On the other hand, if the R

⁴⁵ Carrington and Longuet-Higgins⁴³ neglect the pseudosecular and nonsecular parts of the dipolar interaction. The contribution of the pseudosecular term, however, is comparable to that of the terms they retain.

⁴⁶ See Ref. 21, p. 443, Eq. (39).

matrix is diagonal using the representation with the wavefunctions in Eqs. (4.42), i.e., if

$$R_{\alpha\alpha'\beta\beta'} = R_{\alpha\alpha'\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'},$$

so that $M_{r_u''} = M_{r_u}$ and $M_{r_u'''} = M_{r_u'}$, only terms with $M_{r_u'} = M_{r_u}$ and $J_{r_u}^{(j)'} = J_{r_u}^{(k)}$ affect the spectrum. This last result follows immediately on solving Eq. (2.15) for a diagonal R matrix and making use of the relation $S_x^\dagger(0) = S_x$:

$$\langle \alpha | S_x^\dagger(t) | \alpha' \rangle = \exp(R_{\alpha\alpha'\alpha\alpha'}t) \langle \alpha | S_x | \alpha' \rangle. \quad (4.45)$$

Thus if R is diagonal, the matrix element

$$\langle \alpha | S_x^\dagger(t) | \alpha' \rangle$$

vanishes whenever $|\alpha\rangle$ and $|\alpha'\rangle$ do not have the same nuclear-spin functions, and it is entirely independent of such states. These conclusions can also be obtained readily from the formulation in Sec. III. That part of the R matrix for which

$$\langle \alpha | S_x(0) | \alpha' \rangle = \langle \beta | S_x(0) | \beta' \rangle = \frac{1}{2}$$

we call the *principal part* of the R matrix. In the D_k -dimensional subspace corresponding to the principal part of R , the nuclear-spin functions in $|\alpha\rangle$ and $|\alpha'\rangle$, and also in $|\beta\rangle$ and $|\beta'\rangle$, are the same (although those in $|\alpha\rangle$ need not be the same as those in $|\beta\rangle$), i.e.,

$$\{J_{r_u}^{(j)'}M_{r_u'}\} = \{J_{r_u}^{(k)}M_{r_u}\}$$

and

$$\{J_{r_u}^{(j)'''}M_{r_u}'''\} = \{J_{r_u}^{(k)''}M_{r_u}''\}.$$

Thus only the principal part is needed if the total R matrix is diagonal, and we shall also see that the principal part of R is always a diagonal submatrix [see discussion following Eqs. (4.50) below and Sec. III].

Straightforward albeit somewhat tedious calculation shows that the secular part of the relaxation matrix is diagonal and can be written

$$\begin{aligned} -R_{\alpha\alpha'\alpha\alpha'}^{sec} = & \sum_{r_u, s_v} [j_{r_u s_v}^{(T)}(0) + \frac{8}{3}j_{r_u s_v}^{(D)}(0)] \\ & \times \frac{1}{2}(M_{r_u} + M_{r_u'})(M_{s_v} + M_{s_v'}) \\ & + \sum_{r_u} [j_{r_u}^{(T(G))}(0) + \frac{8}{3}j_{r_u}^{(D(G))}(0)](B_0)(M_{r_u} + M_{r_u'}) \\ & + [j^{(G)}(0) + \frac{8}{3}j^{(G_2)}(0)]B_0^2. \end{aligned} \quad (4.46)$$

The pseudosecular and nonsecular terms have off-diagonal elements. For the diagonal elements of the pseudosecular part we have

$$\begin{aligned} -R_{\alpha\alpha'\alpha\alpha'}^{pseudosec} = & \sum_{r_u} \frac{1}{2} \{j_{r_u r_u}^{(D)}(\omega_{r_u})[J_{r_u}(J_{r_u}+1) - M_{r_u}^2] \\ & + j_{r_u r_u}^{(D)}(\omega_{r_u-})[J_{r_u}'(J_{r_u}'+1) - M_{r_u'}^2]\}. \end{aligned} \quad (4.47)$$

The diagonal part of the nonsecular contribution (neg-

lecting ω_{r_\pm} compared to ω_0) is

$$\begin{aligned} -R_{\alpha\alpha'\alpha\alpha'}^{nonsec} = & \sum_{r_u} \frac{1}{4} j_{r_u r_u}^{(T)}(\omega_0) [J_{r_u}(J_{r_u}+1) \\ & + J_{r_u}'(J_{r_u}'+1) - (M_{r_u}^2 + M_{r_u'}^2) - (M_{r_u} - M_{r_u}')] \\ & + \sum_{r_u} \frac{1}{8} j_{r_u r_u}^{(D)}(\omega_0) \{7[J_{r_u}(J_{r_u}+1) + J_{r_u}'(J_{r_u}'+1)] \\ & - (M_{r_u}^2 + M_{r_u'}^2) + 5(M_{r_u} - M_{r_u}')\} \\ & + \sum_{r_u \neq s_v} j_{r_u s_v}^{(D)}(\omega_0) [M_{r_u} M_{s_v} + M_{r_u}' M_{s_v}'] \\ & + \sum_{r_u} j_{r_u}^{(D(G_2))}(\omega_0) (2B_0) [M_{r_u} + M_{r_u}'] + j^{(G_2)}(\omega_0) (2B_0^2). \end{aligned} \quad (4.48)$$

Under some circumstances, $j_{r_u s_v}^{(\mu\nu; L)}(\omega)$ is independent of the indices u and v specifying the completely equivalent subgroups [see Eqs. (4.27) and the related discussion], so that

$$j_{r_u s_v}^{(\mu\nu; L)}(\omega) = j_{r_s}^{(\mu\nu; L)}(\omega). \quad (4.49)$$

Using Eq. (4.44c), we can then replace the terms in $(M_{r_u} + M_{r_u}')$ in Eqs. (4.46) and (4.48) by $2M_r$, while the terms in $(M_{r_u} - M_{r_u}')$ in Eq. (4.48) vanish.

There are two types of off-diagonal terms, those for which $|\alpha\rangle = |\beta'\rangle$ but $|\alpha\rangle \neq |\beta\rangle$, $R_{\alpha\alpha'\beta\alpha'}$, and those for which $|\alpha\rangle = |\beta\rangle$ but $|\alpha'\rangle \neq |\beta'\rangle$, $R_{\alpha\alpha'\alpha\beta'}$. For the pseudosecular contributions to the $R_{\alpha\alpha'\beta\alpha'}$ terms, the possible values of $|\beta\rangle$ are

$$|\beta\rangle = |\alpha\rangle \frac{|J_{r_u}, M_{r_u} \pm 1\rangle |J_{r_v}, M_{r_v} \mp 1\rangle}{|J_{r_u} M_{r_u}\rangle |J_{r_v} M_{r_v}\rangle}, \quad r_u \neq r_v \quad (4.50a)$$

while for the $R_{\alpha\alpha'\alpha\beta'}$ terms, the possible values of $|\beta'\rangle$ are

$$|\beta'\rangle = |\alpha'\rangle \frac{|J_{r_u}', M_{r_u}' \pm 1\rangle |J_{r_v}', M_{r_v}' \mp 1\rangle}{|J_{r_u}' M_{r_u}'\rangle |J_{r_v}' M_{r_v}'\rangle}, \quad r_u \neq r_v. \quad (4.50b)$$

In these two equations, a short-hand notation is used in which the denominators on the right-hand sides cancel identical factors that are contained in $|\alpha\rangle$ and $|\alpha'\rangle$, respectively. The contributions from nonsecular perturbations are also given by Eqs. (4.50) if only the *upper* signs are used. These off-diagonal elements occur between all pairs of different completely equivalent subgroups within the same equivalent group (within r_u, r_v, \dots , and within s_u, s_v, \dots , etc.) but not between different equivalent groups (e.g., none between r_u and $s_v, r \neq s$). Equations (4.50) show that there are no off-diagonal elements in the principal part of the R matrix, i.e., in the D_k -dimensional subspace for which

$$\{J_{r_u}^{(j)'}M_{r_u'}\} = \{J_{r_u}^{(k)}M_{r_u}\}$$

and

$$\{J_{r_u}^{(j)'''}M_{r_u}'''\} = \{J_{r_u}^{(k)''}M_{r_u}''\}$$

[see discussion following Eq. (4.45) above, and Sec. III].

Writing

$$f(J, M) = [(J+M)(J-M+1)]^{\frac{1}{2}}, \quad (4.51)$$

the off-diagonal pseudosecular contributions can be expressed as

$$\begin{aligned} -R_{\alpha\alpha'\beta\alpha', \text{pseudosec}} &= \frac{1}{4} j_{r_u r_v}^{(D)}(\omega_{r_+}) f(J_{r_u}, \mp M_{r_u}) f(J_{r_v}, \pm M_{r_v}), \\ & \quad r_u \neq r_v, \quad (4.52a) \end{aligned}$$

and

$$\begin{aligned} -R_{\alpha\alpha'\alpha\beta, \text{pseudosec}} &= \frac{1}{4} j_{r_u r_v}^{(D)}(\omega_{r_-}) f(J_{r_u'}, \mp M_{r_u'}) f(J_{r_v'}, \pm M_{r_v'}), \\ & \quad r_u \neq r_v. \quad (4.52b) \end{aligned}$$

In applying these equations, contributions must be calculated separately for both choices of sign since these correspond to different values of $|\beta\rangle$ or $|\beta'\rangle$ as in Eqs. (4.50). The nonsecular terms are

$$\begin{aligned} -R_{\alpha\alpha'\beta\alpha, \text{nonsec}} &= \frac{1}{4} [j_{r_u r_v}^{(I)}(\omega_0) \\ & \quad + \frac{1}{3} j_{r_u r_v}^{(D)}(\omega_0)] f(J_{r_u}, -M_{r_u}) f(J_{r_v}, M_{r_v}), \\ & \quad r_u \neq r_v, \quad (4.53a) \end{aligned}$$

and

$$\begin{aligned} -R_{\alpha\alpha'\alpha\beta, \text{nonsec}} &= \frac{1}{4} [j_{r_u r_v}^{(I)}(\omega_0) \\ & \quad + \frac{1}{3} j_{r_u r_v}^{(D)}(\omega_0)] f(J_{r_u'}, -M_{r_u'}) f(J_{r_v'}, M_{r_v'}), \\ & \quad r_u \neq r_v. \quad (4.53b) \end{aligned}$$

The quadrupole terms in the relaxation matrix can be treated without difficulty in the product representation

$$|\gamma\rangle = |m_\alpha; m_i\rangle = |m_\alpha\rangle \prod_i |I_i m_i\rangle, \quad (4.54)$$

where the product is over all nuclei, but since the interaction contains the products of two operators acting on the same nucleus, it cannot be evaluated in the coupled representation $|JM\rangle$ without using a procedure equivalent to one involving the Racah coefficients^{38, 47, 48} or the Wigner $6-j$ coefficients.^{43, 49} These procedures are complicated even for two nuclei, and we therefore write the quadrupole terms in the product representation only. A single representation must necessarily be employed for the entire R matrix, and thus the following formulas for the quadrupole contributions can only be used in conjunction with an R matrix for the other contributions that is also written in the product representation, Eq. (4.54), over all the nuclei. Equations

(4.46) to (4.53) are still applicable if the r_u, r_v, \dots are replaced by r_i, r_j, \dots , J_{r_u} by I_r , and M_{r_u} by m_i , etc., but now the pseudosecular and nonsecular parts of the R matrix for a completely equivalent subgroup containing more than one nucleus will never be automatically diagonal.

For the diagonal elements, we have

$$\begin{aligned} -R_{\alpha\alpha'\alpha\alpha', \text{sec}}(xQ) &= \sum_{i,j} \{6j_{ij}^{(Q)}(0)[m_i^2 - m_i'^2][m_j^2 - m_j'^2] \\ & \quad + 4j_{ij}^{(DQ)}(0)[m_i + m_i'] [m_j^2 - m_j'^2]\} \\ & \quad + \sum_i 8j_i^{(G_2Q)} [m_i^2 - m_i'^2] B_0, \quad (4.55) \end{aligned}$$

$$\begin{aligned} -R_{\alpha\alpha'\alpha\alpha', \text{pseudosec}}(xQ) &= \sum_i (2j_{ii}^{(Q)}(\omega_{i+}) \{I_i(I_i+1)[1+4m_i^2] \\ & \quad - 5m_i^2 - 4m_i'^4\} \\ & \quad + 2j_{ii}^{(Q)}(2\omega_{i+}) \{I_i(I_i+1)[I_i(I_i+1) - 2 - 2m_i^2] \\ & \quad + 5m_i^2 + m_i'^4\} + 2j_{ii}^{(DQ)}(\omega_{i+}) m_i [2I_i(I_i+1) - 2m_i^2 - 1]) \\ & \quad + \text{terms in } \{\omega_{i-}, m_i'\}. \quad (4.56a) \end{aligned}$$

The terms in $\{\omega_{i-}, m_i'\}$ are identical to those written out in detail if ω_{i+} is replaced by ω_{i-} and m_i by m_i' , except that the term in $j_{ii}^{(DQ)}$ enters with a minus sign. If $\omega_{i+\tau_c}$ and $\omega_{i-\tau_c}$ are small compared to unity, so that $\omega_{i\pm}$ can be replaced by zero in the spectral densities,

$$\begin{aligned} -R_{\alpha\alpha'\alpha\alpha', \text{pseudosec}}(xQ) &= \sum_i (4j_{ii}^{(Q)}(0) \{I_i(I_i+1) \\ & \quad \times [I_i(I_i+1) - 1 + m_i^2 + m_i'^2] - \frac{3}{2}[m_i^4 + m_i'^4]\} \\ & \quad + 2j_{ii}^{(DQ)}(0) [2I_i(I_i+1) - 1 \\ & \quad - 2(m_i^2 + m_i m_i' + m_i'^2)] (m_i - m_i')). \quad (4.56b) \end{aligned}$$

The secular contribution vanishes if the nuclear-spin states in $|\alpha\rangle$ and $|\alpha'\rangle$ are the same ($m_i = m_i'$), as does the dipolar-quadrupolar cross term in the pseudosecular part. Equation (4.56b) for $m_i = m_i'$ differs by numerical factors in some of the terms from the expression given by Kivelson.⁴ There are no nonsecular quadrupole terms. The off-diagonal elements, which are only pseudosecular, involve transitions analogous to those considered above, and only occur for nuclei within equivalent groups. The possible states $|\beta\rangle$ and $|\beta'\rangle$ in the off-diagonal elements $R_{\alpha\alpha'\beta\alpha'}$ and $R_{\alpha\alpha'\alpha\beta'}$, respectively, are determined by relations analogous to Eqs. (4.50). We designate the wavefunctions of the i th nucleus of the r th group by $|I_r, m_{r_i}\rangle$ and replace the symbols $J_{r_u}, M_{r_u}, J_{r_v}, M_{r_v}$ of Eqs. (4.50) ff. by $I_r, m_{r_i}, I_r, m_{r_j}$, respectively. In addition to transitions $m_{r_i} \rightarrow m_{r_i} \pm 1$, $m_{r_j} \rightarrow m_{r_j} \mp 1$, and similar transitions for m_{r_i}' , etc., double quantum jumps $m_{r_i} \rightarrow m_{r_i} \pm 2$, $m_{r_j} \rightarrow m_{r_j} \mp 2$, etc., are also allowed. The matrix elements for single

⁴⁷ U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

⁴⁸ A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton University Press, Princeton, New Jersey, 1957).

⁴⁹ E. Wigner, as quoted in Ref. 48, pp. 91 ff.

quantum jumps are ($i \neq j$)

$$\begin{aligned}
 & -R_{\alpha\alpha'\beta\alpha'}^{\text{pseudosec}}(xQ; \Delta m = \pm 1) \\
 & = \{j_{r_i r_j}^{(Q)}(\omega_{r_+}) [4m_r m_{r_j} \mp 2(m_{r_i} - m_{r_j}) - 1] \\
 & + j_{r_i r_j}^{(DQ)}(\omega_{r_+}) [2m_{r_i}] \} f(I_r, \mp m_{r_i}) f(I_r, \pm m_{r_j}), \quad (4.57a)
 \end{aligned}$$

while those for double quantum jumps are ($i \neq j$)

$$\begin{aligned}
 & -R_{\alpha\alpha'\beta\alpha'}^{\text{pseudosec}}(xQ; \Delta m = \pm 2) \\
 & = j_{r_i r_j}^{(Q)}(2\omega_{r_+}) f[I_r, (\mp m_{r_i} - 1)] \\
 & \times f[I_r, -(\mp m_{r_i} - 1)] f[I_r, (\pm m_{r_j} - 1)] f[I_r, \\
 & \quad -(\pm m_{r_j} - 1)]. \quad (4.57b)
 \end{aligned}$$

The $R_{\alpha\alpha'\beta\alpha'}$ terms are given by similar expressions with ω_{r_+} and m_{r_i} replaced by ω_{r_-} and m_{r_i}' , respectively, but with a minus sign for the $D-Q$ cross term in Eq. (4.57a).

To recapitulate, we note that in the absence of quadrupole interactions there is a natural way of choosing the nuclear-spin wavefunctions for the determination of the relaxation matrix: completely equivalent subgroups are described in a coupled representation, and products of these coupled representations are used as the wavefunctions for the entire set of nuclei. This product of coupled representations is employed consistently except when quadrupole terms make significant contributions. For a single completely equivalent subgroup of nuclei, the coupled representation leads to a diagonal R matrix, and if every equivalent group contains only one completely equivalent subgroup, a product of the coupled representations for the different equivalent groups also leads to a diagonal matrix. For more than one completely equivalent subgroup in an equivalent group, the pseudosecular and nonsecular terms make nondiagonal contributions, but secular terms always yield diagonal matrix elements if the product of coupled representations is used. Secular terms also give only diagonal matrix elements in a product representation over all the nuclei. Although the nonsecular terms for some of the interactions can often be neglected in comparison to the secular terms, the pseudosecular and secular parts of the anisotropic dipolar interaction are usually comparable in magnitude, and since the pseudosecular terms introduce off-diagonal matrix elements, the determination of the linewidths can become quite complicated (see Sec. VII).

When quadrupole terms make a significant contribution, and there is more than one nucleus in a completely equivalent subgroup, a product representation over all the nuclei may be employed, but the R matrix is necessarily nondiagonal.

V. ILLUSTRATIVE APPLICATION TO ISOTROPIC MODULATION. ALTERNATING LINEWIDTHS IN DINITRO COMPOUNDS

In this section we illustrate the general theory with an application chosen to show that treatments requiring

a multiple line to be of an over-all Lorentzian shape are inadequate. For simplicity, only the secular part of the modulation of the isotropic hyperfine interaction for two nuclei is considered. Some general conclusions are first drawn without using a specific model for the form of the modulation, and it is shown that if the correlation functions satisfy certain special conditions, the linewidths alternate in magnitude from one hyperfine component to another. The theory thus has applications to the experimentally observed alternating linewidths in certain dinitrobenzene anions.^{14,17,18,24} A special model, corresponding to a two-jump interchange of hyperfine splittings between the two nuclei, is then analyzed in detail because it can also be simply treated with the modified Bloch equations²⁵⁻²⁸ (or, with essentially identical results, by the theory of Anderson²⁹). The two-jump interchange model is particularly interesting and instructive because it allows this simple comparison of two rather different theories.

We assume that the two nuclei are symmetrically equivalent [$\bar{a}_1 = \bar{a}_2 = \bar{a}$, $g_{11}^{(I)}(\tau) = g_{22}^{(I)}(\tau)$] but not completely equivalent, so that in general $g_{12}^{(I)}(\tau) \neq g_{11}^{(I)}(\tau)$. For two nuclei of spin I the spectrum consists of $4I+1$ equally spaced lines of degeneracies $D(2, I, M)$, $|M| \leq 2I$. Since the treatment is restricted to only the secular part of the isotropic dipolar interaction, the R matrix is diagonal, and the reciprocal of the transverse relaxation times $[T_{2,k}^{(M)}]^{-1}$ for the k th component of the line with $M = m_1 + m_2$ is equal to the appropriate part of $-R_{\alpha\alpha'\alpha\alpha'}^{\text{sec}}$ in Eq. (4.46). Thus

$$\begin{aligned}
 [T_{2,k}^{(M)}(\text{sec})]^{-1} &= \sum j_{ij} m_i m_j \\
 &= j_{11} M^2 + 2(j_{12} - j_{11}) m_1 m_2, \quad (5.1)
 \end{aligned}$$

where j_{ij} , which is written for $j_{ij}^{(I)}(0)$, is given by Eq. (4.9) with $g_{ij}^{(I)}(\tau)$ from Eq. (4.10) taking $\bar{a}_i = \bar{a}_j = \bar{a}$. The values of T_2^{-1} are listed in Table II for nuclei with spin $I = \frac{1}{2}$, $I = 1$, and $I = \frac{3}{2}$. For an arbitrary relationship between j_{12} and j_{11} , the lines for $I = 1$ with $M = 0$, and $I = \frac{3}{2}$ with $M = 0$ and $M = \pm 1$, consist of several components with different widths. If $j_{12} = j_{11}$, which we call the "in-phase-correlated" case, the two nuclei are completely equivalent, and each line consists of a single Lorentzian with a width which depends quadratically on M : $[T_2^{(M)}(\text{sec})]^{-1} = j_{11} M^2$. On the other hand, if $j_{12} = -j_{11}$ ("out-of-phase-correlated"), or $j_{12} = 0$ ("uncorrelated"), the lines are not all of Lorentzian shape and the width varies in a complex manner from component to component.

In the out-of-phase-correlated case, if j_{11} is very large, some of the lines are broad and others are sharp. Thus, for $I = 1$, the component of the $M = 0$ line with statistical weight 2 is broad while the component with statistical weight one is narrow. As a result, in the limit of j_{11} so large that the broad lines would not be ob-

TABLE II. Secular linewidths, isotropic modulation of two nuclei.

I	M	$(m_1, m_2)^a$	D_k	General	$[T_{2,k}^{(m)}(\text{sec})]^{-1}$		
					In-phase correlated $j_{12}=j_{11}$	Out-of-phase correlated $j_{12}=-j_{11}$	Uncorrelated $j_{12}=0$
$\frac{1}{2}$	± 1	$\pm\frac{1}{2}, \pm\frac{1}{2}$	1	$\frac{1}{2}(j_{11}+j_{12})$	j_{11}	0	$\frac{1}{2}j_{11}$
	0	$[\pm\frac{1}{2}, \mp\frac{1}{2}]$	2	$\frac{1}{2}(j_{11}-j_{12})$	0	j_{11}	$\frac{1}{2}j_{11}$
1	± 2	$\pm 1, \pm 1$	1	$2(j_{11}+j_{12})$	$4j_{11}$	0	$2j_{11}$
	± 1	$[\pm 1, 0]$	2	j_{11}	j_{11}	j_{11}	j_{11}
	0	$\pm 1, \mp 1$	2	$2(j_{11}-j_{12})$	0	$4j_{11}$	$2j_{11}$
		0, 0	1	0	0	0	0
$\frac{3}{2}$	± 3	$\pm\frac{3}{2}, \pm\frac{3}{2}$	1	$\frac{3}{2}(j_{11}+j_{12})$	$9j_{11}$	0	$\frac{3}{2}j_{11}$
	± 2	$[\pm\frac{3}{2}, \pm\frac{1}{2}]$	2	$\frac{1}{2}(5j_{11}+3j_{12})$	$4j_{11}$	j_{11}	$\frac{5}{2}j_{11}$
	± 1	$[\pm\frac{3}{2}, \mp\frac{1}{2}]$	2	$\frac{1}{2}(5j_{11}-3j_{12})$	j_{11}	$4j_{11}$	$\frac{5}{2}j_{11}$
		$\pm\frac{1}{2}, \pm\frac{1}{2}$	1	$\frac{1}{2}(j_{11}+j_{12})$	j_{11}	0	$\frac{1}{2}j_{11}$
	0	$[\pm\frac{3}{2}, \mp\frac{3}{2}]$	2	$\frac{3}{2}(j_{11}-j_{12})$	0	$9j_{11}$	$\frac{3}{2}j_{11}$
		$[\pm\frac{1}{2}, \mp\frac{1}{2}]$	2	$\frac{1}{2}(j_{11}-j_{12})$	0	j_{11}	$\frac{1}{2}j_{11}$

* Square brackets indicate that the state specified by (m_1, m_2) and also the state obtained by permutation of 1 and 2, (m_2, m_1) , are both included.

served,⁵⁰ the spectrum for two nuclei with $I=1$ would appear to contain only three lines of equal amplitude corresponding to $M=-2, 0, 2$ with spacing $2\bar{a}$ instead of five lines with intensity ratios 1:2:3:2:1 and spacing \bar{a} . In such a situation, one might erroneously conclude from the spectrum that only one of the two nuclei was exhibiting hyperfine structure, and that the radical was asymmetric. This type of phenomenon has been found experimentally,^{15,16} and other observed anomalies in hyperfine-splitting-constant patterns^{15,16,51} may possibly arise from this mechanism. For j_{11} large, but not so large as to cause the $M=\pm 1$ lines to be unobservable, the spectrum would consist of five equally spaced lines. The $M=\pm 2$ lines would appear sharp, the $M=\pm 1$ lines broad, and the $M=0$ line would consist of a sharp line of statistical weight one superimposed on a broad (and perhaps unobservable) background of statistical weight two. This corresponds to the alternating linewidth phenomena observed in dinitrobenzene anion radicals.^{14,17,18,24} One would expect, from the results for $I=\frac{1}{2}$, that N¹⁵-substituted dinitrobenzenes would show a reverse type of alternating linewidth: the central line would be broad and the outside lines sharp. An analogous type of behavior occurs for $I=\frac{3}{2}$.

These results are very different from those predicted by the Kivelson-Kubo-Tomita theory. Thus, for the out-of-phase-correlated case of two nuclei with $I=1$, the average widths (see Sec. III), which are the values

of the widths predicted by this theory, are $\frac{8}{3}j_{11}, j_{11}$, and 0, respectively, for the $M=0, \pm 1$, and ± 2 lines. In other words, the Kivelson-Kubo-Tomita theory does not predict either an alternating linewidth nor, in the case of extreme broadening, the apparent disappearance from the spectrum of the splitting from one of the nuclei.

A number of different models²⁴ lead to the relation $j_{12}=-j_{11}$, but here we treat only the two-jump interchange case because it can be compared with the Bloch-Anderson procedure. We postulate that the radical can exist in two different states, A and B , and that there is an exchange reaction between the two states. The lifetimes of A and B are assumed to be the same, $\tau_A=\tau_B=\tau_0$, and the time of a jump from one state to the other is assumed to be small compared to τ_0 . We postulate further that each nucleus can have only two different splitting constants, either a_I or a_{II} : in state A nucleus 1 has splitting constant a_I while nucleus 2 has splitting constant a_{II} , and in state B the splitting constants are interchanged. Thus

$$\begin{aligned} a_1(A) &= a_2(B) = a_I, \\ a_2(A) &= a_1(B) = a_{II}. \end{aligned} \quad (5.2)$$

Since the probability of occurrence $W(\mu)$ (with $\mu=A$ or B) is the same for the two states, the average splitting constant is given by

$$\bar{a}_i = \sum_{\mu} W(\mu) a_i(\mu) \quad (5.3a)$$

$$= \frac{1}{2}[a_i(A) + a_i(B)] = \frac{1}{2}(a_I + a_{II}) = \bar{a}, \quad (5.3b)$$

and it is the same for the two nuclei. The conditional

⁵⁰ Note that the amplitude of the first derivative of the absorption is inversely proportional to the square of the width.

⁵¹ R. L. Ward and M. P. Klein, *J. Chem. Phys.* **28**, 518 (1958); R. L. Ward, *ibid.* **30**, 852 (1959); **32**, 410 (1960); *J. Am. Chem. Soc.* **83**, 1296 (1961).

probabilities for finding the system in the states *A* and *B*, respectively, at time $\tau \geq 0$ when the system was in state *A* at time $\tau = 0$ are readily shown to be

$$P(A | A, \tau) = \frac{1}{2}[1 + \exp(-2\tau/\tau_0)],$$

$$P(A | B, \tau) = \frac{1}{2}[1 - \exp(-2\tau/\tau_0)]. \quad (5.4)$$

There are similar expressions with *A* and *B* interchanged when the system is in state *B* at $\tau = 0$. Straightforward calculation using Eqs. (2.6), (4.9), and (4.10) gives

$$j_{11}^{(1)}(0) = -j_{12}^{(1)}(0) = \frac{1}{8}\tau_0\gamma_e^2(a_{1I} - a_{1II})^2, \quad (5.5)$$

and, from Eq. (5.1),

$$[T_{2,k}^{(M)}(\text{sec})]^{-1} = \frac{1}{8}\tau_0\gamma_e^2(a_{1I} - a_{1II})^2(m_1 - m_2)^2. \quad (5.6)$$

To treat this problem in the frame work of the modified Bloch equations²⁵⁻²⁸ or the theory of Anderson,²⁹ we first consider the spectrum in the limit of very long lifetimes for states *A* and *B*. The angular frequencies in the state μ , measured from the center of the spectrum $\omega_0 = |\gamma_e| B_0$, are given by

$$\omega_k(\mu) = \gamma_e \sum_i a_i(\mu) m_i, \quad (5.7)$$

where each value of the index *k* corresponds to a particular choice of the m_i . The spectrum for states *A* and *B* is the same, as shown in the upper part of Fig. 1, but in general the lines $\omega_k(A)$ and $\omega_k(B)$ arising from a particular assignment of m_1 and m_2 occur at different positions. A line with the same position in the two states results from an interchange of the quantum numbers m_1 and m_2 . We assume that the Bloch equations²⁵ are applicable to any line, say the line at position $\omega_k(A)$ in state *A* (see Sec. VIII). Bloch equations with the same relaxation times $T_{1,k}$ and $T_{2,k}$ will then also apply to the line $\omega_k(B)$ which has the same assignment of quantum numbers m_i in state *B* as the m_i for the line $\omega_k(A)$ in state *A*. When exchange is taking place between the two states, the modified Bloch equation²⁶⁻²⁸ can be employed provided only secular effects are important (see Sec. VIII), and in the limit of rapid exchange, the lines $\omega_k(A)$ and $\omega_k(B)$ coalesce to a single line at the mean frequency

$$\bar{\omega}_k = \frac{1}{2}[\omega_k(A) + \omega_k(B)] \quad (5.8a)$$

$$= \frac{1}{2}\gamma_e \sum_i [a_i(A) + a_i(B)] m_i$$

$$= \gamma_e \bar{a} M, \quad (5.8b)$$

where the mean splitting constant \bar{a} is given by Eq. (5.3b). The averaged spectrum is shown in the lower part of Fig. 1 and is, of course, the same as that given by the zero-order Hamiltonian $\hbar\mathcal{H}_0$. The transverse relaxation times (for fast exchange) are given by²⁶

$$[T_{2,k}^{(M)}(\text{sec})]^{-1} = \frac{1}{8}\tau_0[\omega_k(A) - \omega_k(B)]^2 \quad (5.9a)$$

$$= \frac{1}{8}\tau_0\gamma_e^2(a_{1I} - a_{1II})^2(m_1 - m_2)^2 \quad (5.9b)$$

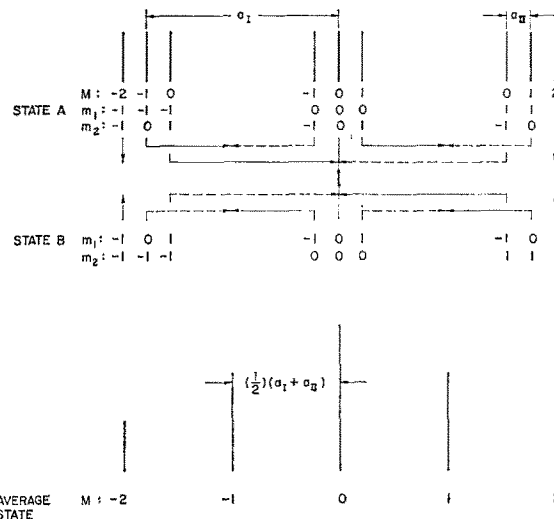


Fig. 1. Spectra for two-jump modulation of isotropic hyperfine interaction. The upper spectrum is for the limit of long lifetimes for the two states (*A* and *B*), and the lower spectrum applies when there is rapid exchange. In state *A*, nucleus 1 (quantum number m_1) has hyperfine splitting a_{1I} and nucleus 2 (quantum number m_2) has splitting a_{1II} , with $a_{1I} > a_{1II}$. In state *B*, the hyperfine splittings are interchanged. Arrows show how lines combine on exchange, with interacting lines in states *A* and *B* that terminate at the same average position being indicated by the same type of arrow (solid horizontal, solid vertical, or dashed horizontal).

which is identical to the expression obtained above by the relaxation-matrix procedure, Eq. (5.6), and leads to the results in the next to last column of Table II.

The arrows shown in the figure indicate in detail how the lines in the individual states *A* and *B* combine to give the average spectrum. Using the notation (m_1, m_2) to identify the lines, we see that only the $(\pm 1, \pm 1)$ and $(0, 0)$ lines are not shifted by the exchange (as shown by the vertical arrows) and, according to Eq. (5.9a), are therefore unbroadened by the exchange mechanism. The $(-1, 0)$ line changes from the position $-\gamma_e a_{1I}$ in state *A* to $-\gamma_e a_{1II}$ in state *B* (shown by the solid arrows) and leads to the average line at $-\gamma_e \bar{a}$ with a width proportional to $[-a_{1I} - (-a_{1II})]^2 = (a_{1I} - a_{1II})^2$. The $(0, -1)$ lines coalesce in the same manner (indicated by the dotted arrows), and similar results are obtained from the $(1, 0)$ and $(0, 1)$ lines on the right-hand side of the spectrum. The $(-1, 1)$ lines in states *A* and *B*, at positions $-\gamma_e(a_{1I} - a_{1II})$ and $\gamma_e(a_{1I} - a_{1II})$, respectively, give one of the three transitions making up the central line of the average spectrum, and have a width proportional to $[-(a_{1I} - a_{1II}) - (a_{1I} - a_{1II})]^2 = 4(a_{1I} - a_{1II})^2$. The $(1, -1)$ lines make an identical contribution, and the third component of the central line is the unbroadened $(0, 0)$ part.

These simple arguments using the modified Bloch equations thus lead to results which are identical to those obtained from the relaxation-matrix theory, and differ from the conclusions of the Kivelson-Kubo-

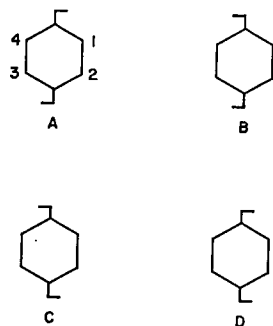


FIG. 2. Schematic structural formulas for four-jump modulation model.

Tomita theory. The Anderson theory also gives identical predictions.²⁹ A comparison of the usefulness and limitations of the Bloch, Anderson, and relaxation-matrix theories is given in Sec. VIII.

A detailed account of the alternating linewidths in dinitrobenzene anions is presented elsewhere.²⁴

VI. FOUR-JUMP ISOTROPIC MODULATION. *Cis-Trans* ISOMERISM

As a second illustration, we consider the linewidth effects arising from modulation of the secular part of the isotropic hyperfine interaction for a system in which a nucleus, or group of completely equivalent nuclei, can exist in four different states. This model has application to the alternating linewidths observed in the dihydroxydurene cation.^{11,12,18}

The four states are designated by *A*, *B*, *C*, and *D*. States *A* and *C* are assumed to be thermodynamically equivalent, as are states *B* and *D*. The interconversion of *A* and *B* is assumed to be governed by the equation



and because of the assumed equivalence there are three similar expressions with the same rate constants, one with *A* replaced by *C*, one with *B* replaced by *D*, and one with *A* replaced by *C* and *B* by *D*. The other interconversion reactions are



and



The probabilities of occurrence of the states are

$$W_A = W_C = \frac{1}{2} [k_1' / (k_1 + k_1')] \quad (6.2a)$$

and

$$W_B = W_D = \frac{1}{2} [k_1 / (k_1 + k_1')]. \quad (6.2b)$$

The conditional probabilities for finding the system in the states *A*, *B*, *C*, or *D* respectively, at time $\tau \geq 0$ if it was in state *A* at time $\tau = 0$ are readily found in terms

of the three relaxation times

$$\begin{aligned} \tau_C &= [2(k_1' + k_4)]^{-1}, \\ \tau_T &= [2(k_1 + k_3)]^{-1}, \\ \tau_{CT} &= [2(k_1 + k_1')]^{-1}, \end{aligned} \quad (6.3)$$

to be

$$\begin{aligned} P(A | A, \tau) &= W_A + W_B \exp(-\tau/\tau_{CT}) + \frac{1}{2} \exp(-\tau/\tau_T), \\ P(A | B, \tau) &= W_B [1 - \exp(-\tau/\tau_{CT})], \\ P(A | C, \tau) &= W_A + W_B \exp(-\tau/\tau_{CT}) - \frac{1}{2} \exp(-\tau/\tau_T), \\ P(A | D, \tau) &= P(A | B, \tau). \end{aligned} \quad (6.4)$$

The conditional probabilities when the system is initially in state *C* can be obtained from Eqs. (6.4) by replacing *A* by *C* and vice versa. When the system is initially in state *B*,

$$\begin{aligned} P(B | A, \tau) &= P(A | B, \tau) (W_A/W_B), \\ P(B | B, \tau) &= W_B + W_A \exp(-\tau/\tau_{CT}) + \frac{1}{2} \exp(-\tau/\tau_C), \\ P(B | C, \tau) &= P(B | A, \tau), \\ P(B | D, \tau) &= W_B + W_A \exp(-\tau/\tau_{CT}) - \frac{1}{2} \exp(-\tau/\tau_C), \end{aligned} \quad (6.5)$$

and similarly, when the system is initially in state *D*, the probabilities are obtained by replacing *B* by *D* in Eqs. (6.5) and vice versa. From Eqs. (2.6) and (4.10), the correlation functions can be shown to be

$$\begin{aligned} \gamma_e^{-2} g_{ij}^{(l)}(\tau) &= W_A W_B \exp(-\tau/\tau_{CT}) [a_i(A) + a_i(C) \\ &\quad - a_i(B) - a_i(D)] [a_j(A) + a_j(C) - a_j(B) - a_j(D)] \\ &\quad + \frac{1}{2} W_A \exp(-\tau/\tau_T) [a_i(A) - a_i(C)] [a_j(A) - a_j(C)] \\ &\quad + \frac{1}{2} W_B \exp(-\tau/\tau_C) [a_i(B) - a_i(D)] [a_j(B) - a_j(D)]. \end{aligned} \quad (6.6)$$

We assume that there are four possible splitting constants for each of the four completely equivalent groups of nuclei and assign them according to the scheme in Fig. 2 and Table III. The figure represents the *cis* and *trans* forms of the terephthalaldehyde anion,⁵² the diacetylbenzene anion,⁵³ or the dihydroxy-

TABLE III. Assignment of splittings $a_i(\mu)$ for four-state *cis-trans* isomerism.

$i \setminus \mu$	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
1	a_{IT}	a_{IC}	a_{IT}	a_{IC}
2	a_{IT}	a_{IC}	a_{IT}	a_{IC}
3	a_{IT}	a_{IC}	a_{IT}	a_{IC}
4	a_{IT}	a_{IC}	a_{IT}	a_{IC}

⁵² A. H. Maki, J. Chem. Phys. **35**, 761 (1961).

⁵³ P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. **37**, 2811 (1962).

durene cation, but other systems in which each nucleus or group of equivalent nuclei can exist in four different magnetic environments would also be schematically represented by this diagram. The table entries contain the values of $a_i(\mu)$, with two possible splittings, I or II , for each conformation, *cis* (C) or *trans* (T). From Eq. (6.6) and Table III, and letting

$$g_C(\tau) = \frac{1}{2}\gamma_e^2 W_B (a_I^C - a_{II}^C)^2 \exp(-\tau/\tau_C)$$

$$g_T(\tau) = \frac{1}{2}\gamma_e^2 W_A (a_I^T - a_{II}^T)^2 \exp(-\tau/\tau_T)$$

$$g_{CT}(\tau) = \gamma_e^2 W_A W_B (a_I^C + a_{II}^C - a_I^T - a_{II}^T)^2 \times \exp(-\tau/\tau_{CT}), \quad (6.7)$$

one can show that $g_{ii}^{(1)}(\tau) = g_{11}^{(1)}(\tau)$, $g_{ij}^{(1)}(\tau) = g_{ji}^{(1)}(\tau)$, and

$$g_{11}^{(1)}(\tau) = g_C(\tau) + g_T(\tau) + g_{CT}(\tau),$$

$$g_{12}^{(1)}(\tau) = g_{34}^{(1)}(\tau) = g_C(\tau) - g_T(\tau) + g_{CT}(\tau),$$

$$g_{13}^{(1)}(\tau) = g_{24}^{(1)}(\tau) = -g_C(\tau) + g_T(\tau) + g_{CT}(\tau),$$

$$g_{14}^{(1)}(\tau) = g_{23}^{(1)}(\tau) = -g_C(\tau) - g_T(\tau) + g_{CT}(\tau). \quad (6.8)$$

The transverse relaxation times are given, as in Eq. (5.1), by

$$[T_{2,k}^{(M)}(\text{sec})]^{-1} = \sum j_{ij} M_i M_j = j_C [2 \sum M_i^2 + 4(M_1 M_2 + M_3 M_4) - M^2] + j_T [2 \sum M_i^2 + 4(M_1 M_3 + M_2 M_4) - M^2] + j_{CT} M^2, \quad (6.9)$$

where $M = \sum M_i$, the summations are over all values of $i = 1, 2, 3, 4$, and the j 's [$=j^{(1)}(0)$] are obtained from the g 's in Eqs. (6.7) and (6.8) by using Eq. (4.9). If $j_{ij} = j_{11}$ for all i and j , the nuclei are completely equivalent, $j_C = j_T = 0$, $j_{11} = j_{CT}$, and the linewidth is proportional to M^2 .

The values of the linewidth from Eq. (6.9) are tabulated in Table IV for the case that (1) each completely equivalent group of nuclei consists of a single proton, and (2) each consists of a methyl group. The last two columns apply when only the *trans* form is present with appreciable probability [$W_A = W_C \cong \frac{1}{2}$, $W_B = W_D \cong 0$], and also apply when only the *cis* form is present if j_C is substituted for j_T . When only the *trans* (or *cis*) form is present, the problem is more simply treated by a two-jump model (Sec. V). In the limit of large j 's when only one form, either *cis* or *trans*, is present, the spectrum for the four-proton case degenerates into three lines corresponding to $M = -2, 0, 2$ with statistical weights 1:4:1 instead of five lines with statistical weights 1:4:6:4:1, while for intermediate values of j , an alternating linewidth variation occurs. The spectrum for the four-methyl group case normally consists of 13 lines with relative intensities 1:12:66:220:495:792:924:792:66:12:1, but when only one form, either *cis* or *trans*, is present, and when the

TABLE IV. Secular linewidths, four-jump isotropic modulation.

	M	D_k	General	<i>Trans</i> only	
			$[T_{2,k}^{(M)}(\text{sec})]^{-1}$	D_k	$[T_{2,k}^{(M)}(\text{sec})]^{-1}$
Four protons	± 2	1	$4j_{CT}$	1	0
	± 1	4	$j_C + j_T + j_{CT}$	4	j_T
	0	2	$4j_C$	2	$4j_T$
		2	$4j_T$	4	0
		2	0		
Four methyl groups	± 6	1	$36j_{CT}$	1	0
	± 5	12	$j_C + j_T + 25j_{CT}$	12	j_T
	± 4	12	$4j_C + 4j_T + 16j_{CT}$	30	$4j_T$
		18	$4j_C + 16j_{CT}$	36	0
		18	$4j_T + 16j_{CT}$		
		18	$16j_{CT}$		
	± 3	4	$9(j_C + j_T + j_{CT})$	40	$9j_T$
		36	$9j_C + j_T + 9j_{CT}$	180	j_T
		36	$j_C + 9j_T + 9j_{CT}$		
		144	$j_C + j_T + 9j_{CT}$		
	± 2	12	$16j_C + 4j_T + 4j_{CT}$	30	$16j_T$
		12	$4j_C + 16j_T + 4j_{CT}$	240	$4j_T$
		18	$16j_C + 4j_{CT}$	225	0
		18	$16j_T + 4j_{CT}$		
		120	$4(j_C + j_T + j_{CT})$		
		108	$4(j_C + j_{CT})$		
	± 1	108	$4(j_T + j_{CT})$		
99		$4j_{CT}$			
12		$25j_C + j_C + j_{CT}$	12	$25j_T$	
12		$25j_T + j_T + j_{CT}$	180	$9j_T$	
36		$9j_C + 9j_T + j_{CT}$	600	j_T	
144		$9j_C + j_T + j_{CT}$			
0	144	$j_C + 9j_T + j_{CT}$			
	444	$j_C + j_T + j_{CT}$			
	2	$36j_C$	2	$36j_T$	
	2	$36j_T$	72	$16j_T$	
	36	$16j_C + 4j_T$	450	$4j_T$	
	36	$16j_T + 4j_C$	400	0	
	36	$16j_C$			
	36	$16j_T$			
216	$4(j_C + j_T)$				
198	$4j_C$				
198	$4j_T$				
164	0				

j 's are large, only the seven lines with $M = \pm 6, \pm 4, \pm 2, 0$ and statistical weights 1:36:225:400:225:... remain. Again, for intermediate values of j , the linewidths alternate. Similar linewidth phenomena result in the general case if j_C and/or j_T are large while j_{CT} is small. In the terephthalaldehyde anion,⁵² and also in the 1,4-diacetylbenzene anion,⁵³ the mean splitting constant in the *cis* form, $\frac{1}{2}(a_I^C + a_{II}^C)$, is approximately equal to the mean splitting constant in the *trans* form, $\frac{1}{2}(a_I^T + a_{II}^T)$, so that for many applications of the present theory j_{CT} is probably small.

The four-proton case is a model for the terephthalaldehyde or 1,4-diacetylbenzene anions, but experimentally both of these radicals exhibit sharp-line spectra arising from a superposition of different spectra from the *cis* and *trans* forms.^{52,53} They thus correspond to the static limit in which the correlation times τ are long, and the zero-order Hamiltonian is best represented by two separate Hamiltonians, one for each of the two rotational isomers.

Similarly, the four-methyl group case may provide a model for the dihydroxydurene cation. This radical does show an alternating linewidth,^{11,12,13} and since the alternation appears on the methyl-proton lines rather than the hydroxyl-proton lines, the phenomenon must be somewhat different from that in the dinitrodurene anion (Sec. V). Bolton and Carrington¹¹ have suggested that a superposition of spectra from the *cis* and *trans* forms of the dihydroxydurene cation, with perhaps some dynamical averaging, could account for the observed linewidth alternation, and indeed the results in Table IV do show an alternating linewidth if the spectral densities j_C and/or j_T are large while j_{CT} is small. Recently Carrington⁵⁴ has obtained results similar to the four-proton example treated above by solving the modified Bloch equations for four sites (see Secs. V and VIII). To make a detailed test of these four-jump models, the magnitude of the spectral densities must be estimated. The spectral densities are proportional to the product of a correlation time and the square of a splitting-constant difference, but unfortunately there is no good basis for estimating either quantity. A correlation time of the order of a microsecond and a splitting-constant difference of the order of 0.1 G would be sufficient, for example, to account for the magnitude of the observed alternating linewidth effects. Splitting-constant differences of about 1 G are observed within each of the *cis* and *trans* isomers in some of the carbonyl anions,⁵³ and the asymmetry of the pi-electron spin-density distribution required to produce this difference has been attributed to the negative charge on the oxygen atoms of the carbonyl groups. It is not clear how large an asymmetry in the spin densities to expect from the hydrogen atom of a hydroxyl group, although it is undoubtedly considerably smaller than for a carbonyl. The theory of the linewidth variations which might arise from the hydroxyl protons, and among the three protons of a methyl group, will be presented elsewhere.²⁴

VII. NONDIAGONAL RELAXATION MATRICES

In this section we consider some of the problems encountered when the relaxation matrix contains off-diagonal elements. In Sec. IV it was shown that the off-diagonal elements arise from the pseudosecular and nonsecular terms between different completely equivalent subgroups within a single group of equivalent

nuclei. Although in many instances the nonsecular terms may be neglected, the pseudosecular terms are in general comparable to the secular contributions, and therefore the proper treatment of the nondiagonal relaxation matrices is of practical importance.

We first treat in detail the simplest problem, that of two protons which are symmetrically equivalent but not completely equivalent. The $M = \pm 1$ states, being nondegenerate, automatically have diagonal R matrices, but the R matrix for the $M = 0$ state is not diagonal. For the four states we use the basis functions

$$\begin{aligned} |a\rangle &= |\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle & |a'\rangle &= |-\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle \\ |b\rangle &= |\tfrac{1}{2}; -\tfrac{1}{2}, \tfrac{1}{2}\rangle & |b'\rangle &= |-\tfrac{1}{2}; -\tfrac{1}{2}, \tfrac{1}{2}\rangle \end{aligned} \quad (7.1)$$

in the notation $|\gamma\rangle = |m_z, m_1, m_2\rangle$. The states $|\alpha\rangle$ in the relaxation-matrix element $R_{\alpha\alpha'\beta\beta'}$ can be either $|a\rangle$ or $|b\rangle$, while $|\alpha'\rangle$ can be $|a'\rangle$ or $|b'\rangle$. We assume that Eq. (4.49) holds, and set the frequencies ω_{\pm} equal to zero in the spectral densities. Equations (4.46) to (4.48) then give, for the diagonal terms,

$$\begin{aligned} R_{aa'aa'} &= R_{bb'bb'} = A + B, \\ R_{ab'ab'} &= R_{ba'ba'} = B, \end{aligned} \quad (7.2)$$

where

$$A = -\tfrac{1}{2}[j_{11}^{(T)}(0) - j_{12}^{(T)}(0)] - \tfrac{1}{4}[j_{11}^{(D)}(0) - j_{12}^{(D)}(0)], \quad (7.3a)$$

$$\begin{aligned} B = & -j_{11}^{(D)}(0) - \tfrac{1}{2}j_{11}^{(T)}(\omega_0) - [\tfrac{1}{8}j_{11}^{(D)}(\omega_0) - j_{12}^{(D)}(\omega_0)] \\ & - [j^{(G_0)}(0) + \tfrac{8}{3}j^{(G_2)}(0) + 2j^{(G_2)}(\omega_0)]B_0^2. \end{aligned} \quad (7.3b)$$

Equations (4.52) and (4.53) give, for the off-diagonal elements, either zero or

$$C = -\tfrac{1}{2}j_{12}^{(D)}(0) - \tfrac{1}{4}[j_{12}^{(T)}(\omega_0) + \tfrac{1}{8}j_{12}^{(D)}(\omega_0)] \quad (7.4)$$

according to the scheme

	aa'	bb'	ab'	ba'
aa'	$A+B$	0	C	C
bb'	0	$A+B$	C	C
ab'	C	C	B	0
ba'	C	C	0	B

(7.5)

It is easy to solve the differential equations [Eq. (2.15)] directly, and we do so rather than diagonalize the R matrix and apply Eq. (3.3). The result is

$$\begin{aligned} \langle a | S_z^\dagger(t) | a' \rangle &= \langle b | S_z^\dagger(t) | b' \rangle \\ &= (1/4D)[(D+A) \exp(\lambda_+ t) + (D-A) \\ &\quad \times \exp(\lambda_- t)], \end{aligned} \quad (7.6)$$

⁵⁴ A. Carrington, *Mol. Phys.* **5**, 425 (1962).

where

$$D = [A^2 + 16C^2]^{1/2}, \tag{7.7a}$$

$$\lambda_{\pm} = \frac{1}{2}[A + 2B \pm D], \tag{7.7b}$$

and use has been made of the initial conditions

$$\langle a | S_x^{\dagger}(0) | a' \rangle = \langle b | S_x^{\dagger}(0) | b' \rangle = \frac{1}{2}, \tag{7.8a}$$

$$\langle a | S_x^{\dagger}(0) | b' \rangle = \langle b | S_x^{\dagger}(0) | a' \rangle = 0. \tag{7.8b}$$

Because of Eq. (7.8b), the ab' and ba' matrix elements do not contribute to the correlation function $G(t)$, Eq. (2.11), or the spectrum, Eq. (2.13). Using the inverse of Eq. (2.16) in these last two equations together with the solution, Eq. (7.6), one obtains (cf. Sec. III),

$$I(\omega) = (1/\pi D) \left[(D+A) \frac{T_{2,1}}{1+T_{2,1}^2(\omega-\omega_0)^2} + (D-A) \frac{T_{2,2}}{1+T_{2,2}^2(\omega-\omega_0)^2} \right], \tag{7.9}$$

where $T_{2,1} = -\lambda_+^{-1}$ and $T_{2,2} = -\lambda_-^{-1}$. The spectrum is thus the superposition of two Lorentzian-shaped lines with different transverse relaxation times $T_{2,1}$ and $T_{2,2}$ and with statistical weights $(D+A)/D$ and $(D-A)/D$, respectively. In the limit of uncorrelated nuclei, [$j_{12}^{(\mu, \nu; L)}(\omega) = 0$], $C=0$, $D=A$, and the spectrum reduces to a single Lorentzian line of width $T_2^{-1} = A+B$ and statistical weight two. This result also holds if the anisotropic dipolar and nonsecular isotropic terms can be neglected. If the nuclei are completely equivalent [$j_{12}^{(\mu, \nu; L)}(\omega) = j_{11}^{(\mu, \nu; L)}(\omega)$], $A=0$, $D=4C$, and the line becomes a superposition of two Lorentzian lines, each with statistical weight one, and widths

$$T_{2,2}^{-1} = [j^{(G_0)}(0) + \frac{2}{3}j^{(G_2)}(0) + 2j^{(G_2)}(\omega_0)]B_0^2$$

$$T_{2,1}^{-1} = T_{2,2}^{-1} + 2j_{11}^{(D)}(0) + j_{11}^{(D)}(\omega_0) + \frac{1}{3}j_{11}^{(D)}(\omega_0), \tag{7.10}$$

in agreement with Eqs. (4.46) to (4.48) for one completely equivalent group with $J^{(1)}=1$, $M=0$, and $J^{(2)}=0$, $M=0$.

In general the order of the relaxation matrix for a line of degeneracy D_k is D_k^2 , and numerical methods must be employed to obtain a solution for the widths. The differential equations can be solved directly or the matrix diagonalized, the two approaches amounting to essentially the same procedure, or the spectrum can be obtained directly by inverting the matrix.^{51,55} For many applications the relaxation matrix has simplifying features resulting from symmetry (or otherwise) which cause certain sets of the time-dependent matrix elements $\langle \alpha | S_x^{\dagger}(t) | \alpha' \rangle$ to have the same value.⁵⁶ A sufficient condition for this simplification can be ob-

tained as follows. To establish a convenient notation, let us classify the matrix elements of $S_x^{\dagger}(t)$ into sets so that within each set the matrix elements have the same value. Let there be $g \leq D_k^2$ sets and n_i matrix elements in the i th set, with $1 \leq n_i \leq D_k^2$ and

$$\sum_{i=1}^g n_i = D_k^2.$$

The j th matrix element of $S_x^{\dagger}(t)$ in the i th set is denoted by $S_{ij}^{\dagger}(t)$ (where the first subscript refers to the set and the second to a particular element of the set). We now show that a set of the matrix elements has the same value, say $S_{ij}^{\dagger}(t) = S_i^{\dagger}(t)$, independent of j , if two conditions are satisfied: (1) the matrix elements $S_{ij}^{\dagger}(0) = S_{ij}(0) = S_i(0)$ at $t=0$ are independent of j ; and (2) the sum of the elements of the relaxation matrix for the j th row of the i th set over all the columns in the m th set is independent of j , i.e.,

$$\sum_n R_{ij;mn} = R_{im} \tag{7.11}$$

is independent of j . It should be noted that condition (1) is a necessary but not sufficient condition for distinguishing between sets, and that the indices $ij; mn$ used here to specify an element of the relaxation matrix refer to a specific grouping of the elements that have not been used elsewhere. To prove this result, we write the formal solution of Eq. (2.15) as

$$S_{ij}^{\dagger}(t) = \sum_{mn} [\exp(Rt)]_{ij;mn} S_{mn}(0). \tag{7.12}$$

The k th term in the series for the exponential is

$$(t^k/k!) \sum_{mn} [R^k]_{ij;mn} S_{mn}(0)$$

$$= (t^k/k!) \sum_{pq \dots mn} R_{ij;pq} R_{pq;rs} \dots R_{rv;mn} S_{mn}(0), \tag{7.13}$$

and since the two conditions defining a set give

$$\sum_n R_{\mu\nu;mn} S_{mn}(0) = R_{\mu m} S_m(0), \tag{7.14}$$

the k th term becomes

$$(t^k/k!) \sum_m [R^k]_{im} S_m(0). \tag{7.15}$$

The solution, Eq. (7.12), can thus be written

$$S_{ij}^{\dagger}(t) = \sum_m [\exp(Rt)]_{im} S_m(0). \tag{7.16}$$

The right-hand side of Eq. (7.16) is independent of j , so that $S_{ij}^{\dagger}(t) = S_i^{\dagger}(t)$ for all j , as was to be proved.

The number of simultaneous differential equations for the matrix elements of $S_x^{\dagger}(t)$ can thus be reduced from D_k^2 to g , i.e., to one equation for each of the different sets. For example, the matrix treated above, Eq. (7.5), can be replaced by the 2×2 matrix obtained from only the first and third rows and columns. In general, however, the reduced relaxation matrix de-

⁵⁵ R. A. Sack, Mol. Phys. 1, 163 (1958).

⁵⁶ We would like to thank R. Bersohn for helpful discussions about the properties of the relaxation matrix.

finer by Eq. (7.11) is no longer a symmetric matrix. In the representations we have employed for evaluating the relaxation matrix in Sec. IV, only D_k of the matrix elements $\langle \alpha | S_x(0) | \alpha' \rangle$, those with the same nuclear spin functions in $|\alpha\rangle$ and $|\alpha'\rangle$, are nonvanishing, as in Eq. (7.8), and the solutions for the $S_x^\dagger(t)$ only have to be obtained for those sets for which $S_i(0) \neq 0$.

As an example of this procedure, we consider the problem of three symmetrically equivalent, but not completely equivalent, protons. The $M = \pm \frac{3}{2}$ lines are nondegenerate, but the $M = \pm \frac{1}{2}$ lines are threefold degenerate and have a 9×9 relaxation matrix. Writing j_{ij} for $j_{ij}^{(\mu\nu;L)}(\omega)$, we have $j_{11} = j_{22} = j_{33}$ because of the symmetrical equivalence, and we assume $j_{12} = j_{23} = j_{31}$ and $j_{ij} = j_{ji}$. After writing down the detailed 9×9 matrix, application of this method shows that it can be reduced to a 2×2 unsymmetric matrix. As a second example, consider two symmetrically equivalent, but not completely equivalent, N^{14} nuclei (spin $I = 1$). The $M = \pm 2$ lines are nondegenerate, the $M = \pm 1$ lines doubly degenerate, and the $M = 0$ line triply degenerate. They have 1×1 , 4×4 , and 9×9 relaxation matrices, respectively. Assuming that $j_{12} = j_{21}$, inspection of the 4×4 matrix shows that it can be reduced to a symmetric 2×2 matrix and, similarly, the 9×9 matrix can be reduced to an unsymmetric 4×4 matrix. Four equivalent protons in two different sets of pairs of completely equivalent protons can be treated in a manner similar to two N^{14} nuclei. We use the coupled representation for each completely equivalent pair, letting $J_1^{(1)} = 0$, $J_1^{(2)} = 1$, and similarly for the second pair. The $M = \pm 2$ lines are nondegenerate. The $M = \pm 1$ lines are fourfold degenerate and thus have 16×16 relaxation matrices. Neither of the states $|J_1 M_1; J_2 M_2\rangle = |1, \pm 1; 0, 0\rangle$ and $|0, 0; 1, \pm 1\rangle$ connect with any other states, and the 16×16 matrix is thus automatically reduced to a 4×4 matrix. This latter matrix is identical to the matrix for $M = \pm 1$ for two N^{14} nuclei, and can be further reduced to a 2×2 matrix. The $M = 0$ line has a 36×36 relaxation matrix. The $|1, 0; 0, 0\rangle$ and $|0, 0; 1, 0\rangle$ states do not contribute any off-diagonal elements, and have the same width, corresponding to that for a nucleus with $I = 1$, $M = 0$. The $|0, 0; 0, 0\rangle$ state does not mix either, and has a width corresponding to that from a radical without any nuclei with magnetic moments. The remaining three states give a 9×9 relaxation matrix identical to the matrix for the $M = 0$ line for two equivalent N^{14} nuclei, and it can be further reduced to an unsymmetric 4×4 matrix. The detailed form of these matrices, and their solutions, will be presented elsewhere.²⁴

These examples show that pseudosecular and nonsecular contributions lead to quite complex relaxation matrices for even rather simple systems. The evaluation of the matrix elements is in itself complicated and tedious, and in general the solutions for the linewidths can only be obtained by numerical methods.

VIII. COMPARISON OF THE RELAXATION-MATRIX AND BLOCH-ANDERSON THEORIES

In Secs. V and VI we saw that problems which can be treated by jump models may be analyzed by either the relaxation-matrix or the Bloch-Anderson theories. It is the purpose of the present section to compare the usefulness and the range of validities of the different theories.

The relaxation-matrix procedure is a completely general method of treating the widths of nonoverlapping lines subject to only one serious limitation: The perturbing Hamiltonian $\hbar \mathcal{H}_1(t)$ which causes line broadening must satisfy the (sufficient) condition that $[\langle |\mathcal{H}_1|^2 \rangle_{Av} \tau_c^2]^{1/2} \ll 1$, where τ_c is a correlation time characteristic of the motion. This restriction means that the rates of exchange or jumping must be fast to be handled by the relaxation-matrix theory. Unlike the other theories, however, it can also be used for nonjump problems.

The Bloch equations²⁵ are formulated in terms of two parameters, the spin-lattice and transverse relaxation times, T_1 and T_2 , and in the modified form²⁶⁻²⁸ can be used to treat chemical exchange, or a situation in which the spectrum changes by jumps from one form to another, without a requirement that the rate of transfer be fast. Problems like those treated in Secs. V and VI, involving jumps between either two or four states, can thus be dealt with over the entire range from the static to the fast-exchange limits.

Unfortunately the Bloch equations are not applicable under many circumstances, and it is only in treating slow and intermediate rates of exchange that the modified equations offer any advantages not contained in the relaxation-matrix theory. The fundamental difficulty in using the Bloch equations for the ESR spectra of free radicals arises when the significant relaxation processes affecting a hyperfine line cause transitions to states belonging to other lines. A line is then not "isolated," and "cross relaxation" as well as "vertical" and secular processes determine the linewidth and saturation behavior. In fact, it is only under rather special conditions²¹ that Bloch-type equations, even those involving more than one set of relaxation times, can be obtained. The cross relaxations between the hyperfine components result from terms in the perturbing Hamiltonian $\hbar \mathcal{H}_1(t)$ which contain the operators I_\pm that cause nuclear-spin transitions. These operators appear in the pseudosecular intramolecular anisotropic dipolar and quadrupolar perturbations, and the nonsecular isotropic and anisotropic dipolar contributions. The isotropic and anisotropic dipolar interactions also contribute to the vertical relaxation processes, as do the g -tensor interactions and intermolecular effects. In typical ESR experiments in solution, the pseudosecular dipolar contribution is comparable to the secular dipolar term, and the nonsecular parts are related to the secular parts by a factor of the form

$(1 + \omega_0^2 \tau_c^2)^{-1}$. It is only when the g -tensor interaction, the intermolecular interactions, and the secular part of the isotropic interaction, are large compared to the cross-relaxation processes that the cross relaxations can be neglected. Some of the problems encountered in trying to use the Bloch equations are exemplified by the results of Sec. VII for the two-proton case. Even if the protons are completely equivalent, there are two different values of T_2 for the central line [Eq. (7.10)], and separate Bloch equations must be used for the $J=1$ and $J=0$ components. If the protons are not completely equivalent but the dipolar and nonsecular terms can be neglected, so that the off-diagonal term C [Eq. (7.4)] is negligible, a single line is obtained and there is no difficulty in employing the Bloch equations. This simple result follows because only secular processes are included. If either the dipolar or any of the nonsecular terms are large, however, the relaxation matrix is not diagonal and the Bloch equations are inapplicable. It should be noted that even if there are no problems about off-diagonal elements, the modified Bloch equations do not properly include nonsecular effects.^{57,58} Essentially similar limitations concerning cross relaxation and nonsecular relaxations apply to the Anderson²⁹ theory of motional narrowing.

In the limit of fast exchange, the relaxation-matrix theory is usually simpler to use, as well as being more versatile and more generally applicable, than either the modified Bloch equations or the Anderson theory. In using the relaxation-matrix theory for many sites, the determination of the conditional probabilities (see Sec. VI) can become quite a complex task, but even greater computational difficulties are encountered with the modified Bloch equations or the Anderson theory. In fact, although Sack⁵⁶ and Pople⁵⁹ have treated the three-state problem with the Anderson theory, it was not until very recently that even a restricted form of the four-jump Bloch equation was explicitly formulated.⁵⁴ In addition, a much wider range of models, not only exchange or jump models, can be treated with the relaxation-matrix theory than with either of the other theories.

It is rather difficult to estimate the limit of validity of the relaxation-matrix theory, i.e., the permissible magnitude of the quantity $[\langle |\mathcal{H}_1|^2 \rangle]_{AV} \tau_c^2$. Since the fast-jump limit of the Bloch-Anderson theory, when applicable, gives the same linewidth as the relaxation-matrix procedure, it is perhaps reasonable to assume that the fast-jump approximation is valid up to the point where the exact solutions of the equations from the Bloch-Anderson theories begin to depart appreciably from the fast-jump approximation. Numerical evaluation of the exact solutions shows that the fast-

jump approximation is good to a few percent if, in the notation of Sec. V, $|\omega_k(A) - \omega_k(B)| \tau_c \lesssim 1$, or $|\gamma_e| |a_I - a_{II}| \tau_c \lesssim 1$.

Kaplan has analyzed the problem of the effect of exchange on a simple NMR spectrum by a more rigorous procedure than that employed in the conventional modifications of the Bloch equations.⁵⁷ This treatment is formulated in terms of the density matrix for the exchanging system, and includes the nonsecular contributions which become important for fast exchange rates. Unfortunately, however, no complete treatment of the equation of motion for the density matrix has been carried out when both exchange and a rapidly varying perturbation are present.

IX. CONCLUSIONS

A general theory of the linewidths in the electron-spin resonance spectra of dilute solutions of free radicals has been formulated in terms of the relaxation matrix for the spin system. The results differ in a number of ways from those obtained earlier by Kivelson using the linewidth theory of Kubo and Tomita. The most important qualitative difference is the prediction from the relaxation-matrix theory that a composite line arising from several degenerate nuclear-spin states should in general consist of a sum of superimposed Lorentzian lines of different widths rather than a single line with an over-all Lorentzian shape. A single Lorentzian line is still obtained, however, as a limiting case when the variation in the widths of the different components of a composite line is small compared to the average width. The Kivelson theory is also not altered in a fundamental way when only one nucleus is present.

Although in many instances experimental limitations make it impossible to detect the predicted non-Lorentzian shape of a composite line from actual studies of the line shape itself, the present treatment indicates that an ESR spectrum may exhibit striking variations in linewidths and amplitudes which are outside the scope of the predictions from the previous theories. The relaxation-matrix theory thus gives an explanation, for example, of the alternation in linewidths observed in the ESR spectra of the dihydroxydurene cation and several dinitrobenzene anions.

The types of linewidth variations in a spectrum depend critically on whether or not different nuclei in a radical have the same instantaneous electron-nuclear interactions and on the dynamical correlations between their motions and hyperfine splittings. Nuclei are classified according to the invariance, with respect to the interchange of their positions, of the zero-order Hamiltonian \mathcal{H}_0 and the relaxation-inducing perturbing Hamiltonian $\mathcal{H}_1(t)$. A set of nuclei is said to be *completely equivalent* if the total Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$ is invariant with respect to interchanges

⁵⁷ J. I. Kaplan, J. Chem. Phys. **28**, 278 (1958); **29**, 462 (1958).

⁵⁸ I. Solomon and N. Bloembergen, J. Chem. Phys. **25**, 261 (1956).

⁵⁹ J. A. Pople, Mol. Phys. **1**, 168 (1958).

within the set, while a set is said to be *equivalent* if \mathcal{H}_0 is invariant but \mathcal{H}_1 is not. No new linewidth phenomena are predicted if each equivalent group of nuclei contains one and only one completely equivalent subgroup, but if there is more than one completely equivalent subgroup within an equivalent group, alternating linewidths and similar effects may result.

The linewidths of the different components of a composite line are given by the eigenvalues of the relaxation matrix, and in general, since this matrix is not diagonal, the diagonalization of the matrix (or some equivalent procedure) must be carried out to obtain the widths. When quadrupole terms are neglected and there is one and only one completely equivalent subgroup in each equivalent group, a representation for the nuclear-spin states can always be chosen *ab initio* that yields a diagonal matrix. The matrix for any collection of nuclei is also automatically diagonal in a suitable representation if only secular processes (those which involve neither electron- nor nuclear-spin transitions) make important contributions. It should be noted that even if the matrix is diagonal, however, a degenerate line will in general consist of a superposition of Lorentzians of different widths. Non-diagonal matrix elements arise from nuclear-spin transitions when there is more than one completely equivalent subgroup in a single equivalent group. These transitions are caused by the pseudosecular interactions and some of the nonsecular interactions. The former induce only nuclear-spin transitions, and the latter (in part) also involve electron-spin transitions. The pseudosecular terms from the anisotropic intramolecular dipolar interaction are comparable in magnitude to the secular terms, and thus if the dipolar relaxation process makes a significant contribution, the pseudosecular part cannot be neglected and the relaxation matrix contains significant off-diagonal elements. The most suitable representation for the nuclear-spin wavefunction (in the absence of large quadrupole effects) has been shown to be one in which each completely equivalent subgroup is written in a coupled representation and the total wavefunction as a product of these coupled functions over all the different subgroups. If the relaxation matrix is not diagonal using this representation, the spectrum of a composite line may have components with relative intensities that are not in the ratio of whole numbers.

Kivelson was able to obtain expressions for the linewidths of the hyperfine components in an ESR spec-

trum in closed form, but this is now not possible for the general case since there is no obvious representation which causes the relaxation matrix to be diagonal. Even if the matrix is diagonal, so that the widths of the individual components are given directly by the negative of the elements of the relaxation matrix, the determination of the apparent over-all width resulting from a superposition of Lorentzian lines requires numerical evaluation of the total shape function. Thus it is only in rather simple cases that the width can be given by an expression in closed form.

The relaxation-matrix theory provides a very general method for computing linewidths in ESR spectra that can be employed to analyze the effects of a variety of relaxation mechanisms. It has been used to describe modulations involving spin-density fluctuations and internal motions in the radicals as well as the over-all tumbling motion caused by solvent collisions. Only the over-all tumbling was included in Kivelson's treatment. Some models for spin-density fluctuations and internal motions can be analyzed by assuming the radical exists in several different states which are undergoing exchange reactions with each other, but when applied to these chemical exchange or jump phenomena, the relaxation-matrix theory is restricted to the fast-exchange limit. The modified Bloch equations, or the Anderson theory of motional narrowing, can also be applied to jump problems, but these theories do not properly take into account pseudosecular and nonsecular interactions. As indicated above, in many instances such processes cannot be neglected. When they are applicable, these two procedures can be used over the entire range of jump rates, not just in the fast-exchange limit. In the limit of fast jump rates, however, the relaxation-matrix theory is both more general and easier to employ than the other two procedures.

A general theory simultaneously applicable to both rapid, random, relaxation perturbations and slow chemical exchange has not been developed. The present modifications in the linewidth theory alter the theory of saturation in ESR spectra, but the formulation of a new theory of saturation has also not yet been attempted.

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