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Envelope Modulation in Spin-Echo Experiments

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Expressions have been obtained for the envelope-modulation effect in spin-echo experiments of the two- and three-pulse type by partitioning the matrices which describe the evolution of the quantized system. The initial results are quite general and may be applied to a variety of systems. Simplified expressions are derived for the case of an electron spin transition split by small nuclear hyperfine interactions. The results are given in matrix product form. The problem of computing the envelope-modulation parameters in specific instances is discussed. Algebraic results are given for $S=\frac{1}{2}$, $I=\frac{1}{2}$ and $S=\frac{1}{2}$, $I=1$.

I. INTRODUCTION

In spin-echo experiments a periodic variation of amplitude or "modulation" associated with small splittings of the resonance line is sometimes observed in the envelope of echoes.[1] This modulation effect has been used to measure splittings which could not be seen by cw methods because they were too small to be resolved in the presence of inhomogeneous line broadening. Examples in the field of nuclear resonance are the measurement of the $\mathcal{J}\vec{I}_1\cdot\vec{I}_2$ coupling[2,3] in organic molecules and in metals,[4] and the measurement of nuclear quadrupole coupling.[5,6] Here we shall be primarily concerned with electron spin echoes, where modulation effects are due to coupling between electron spins and nuclei in the host lattice, i.e., to the superhyperfine structure (shfs) of the resonance. Such modulation effects are a common feature of electron spin-echo experiments.[7–9]

In Secs. II and III the modulation phenomenon is discussed from a general standpoint without reference to any specific system. This helps to focus attention on the origins of the effect, and makes it possible to derive results for two- and three-pulse echoes (stimulated echoes) without undue mathematical complexity. The method of analysis follows closely that which is used in the treatment of a simple two-level system. The basic formulas can be applied in a wide variety of cases covering both nuclear and optical echo phenomena.[10]

The general results are applied to the special case of an electron resonance with shfs splitting in Secs. IV and V. The matrix expressions derived in Sec. IV can be used either to obtain a plot of the echo envelope or to find the amplitudes of the frequency components which appear in it. A procedure for performing the necessary calculations is suggested in Sec. VI. Explicit formulas for coupled systems with $S=\frac{1}{2}$, $I=\frac{1}{2}$ and $S=\frac{1}{2}$, $I=1$

are derived in Secs. VII and VIII (see also Acknowledgments).

Envelope-modulation experiments may sometimes provide a convenient alternative to electron-nuclear double-resonance (ENDOR) studies, in particular when the shfs splitting is small and conventional ENDOR experiments are difficult to perform. Two-pulse and stimulated-echo sequences can both be used in this way. The two-pulse echo envelope contains sum and difference frequencies as well as the ENDOR frequencies themselves. A display of the ENDOR frequencies without such combinations can however be obtained by performing a stimulated-echo experiment and plotting the echo amplitude as a function of the time between pulses II and III.

II. GENERAL EXPRESSIONS FOR ENVELOPE MODULATION WITH TWO-PULSE ECHOES

Figure 1 shows a set of energy levels which interact with a pulsed resonance field. The diagram is used here to represent the transferred hyperfine structure associated with two electron spin states $|\alpha\rangle$ and $|\beta\rangle$. Only those levels of the over-all quantized system for which the transition $|\alpha_i\rangle \rightleftarrows |\beta_j\rangle$ has a significant amplitude are shown. Levels corresponding to electron intervals which are off resonance, and therefore not influenced appreciably by the pulses, are omitted from the diagram. It will be noted that transitions are shown connecting each $|\alpha_i\rangle$ to more than one $|\beta_j\rangle$. This "branching" of the transitions is essential if envelope modulation is to be observed, and is implicitly assumed in the matrix calculations which follow. The reason lies in the pattern of coherence induced by the pulses. In the absence of branching the resonance pulses cause the appropriate pairs of states $|\alpha_i\rangle$ and $|\beta_j\rangle$ to become coherent and hence to generate signal amplitudes which add constructively to form a spin echo, but the effect is the same as if each $|\alpha_i\rangle$, $|\beta_j\rangle$ pair belonged to an independent quantized system forming part of an inhomogeneous line. The superhyperfine splitting is then merely an additional source of inhomogeneous broadening. When branching transitions occur, the resonant pulses induce coherent relationships within the α and β manifolds as well as between states in opposite manifolds. This leads to interference effects in the spin echo and hence to the modulation of the envelope.

The evolution of the α and β states during the successive periods of nutation and free precession which make up a spin-echo sequence (see Fig. 2) can be followed by means of the density-matrix formalism. If ρ stands for the density matrix and $\mathcal{H}$ for the Hamiltonian, then the equation of motion is

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, \mathcal{H}] . \tag{1}$$

In order to calculate the echo signal, Eq. (1) must be integrated to give the final density ρ_E (corresponding to the time of appearance of the echo) in terms of the initial density ρ_0. The echo signal E is then proportional to $\mathrm{Tr}(\rho\mathcal{H}_1)$ where $\mathcal{H}_1$ is the portion of the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 , \tag{2}$$

which describes the interaction with the resonance field. Thus we have

$$E = \eta\, \mathrm{Tr}(\rho\mathcal{H}_1) , \tag{3}$$

where η is a constant of proportionality depending in part on the experimental arrangements. It may be noted that two summations must be performed to obtain $\mathrm{Tr}(\rho\mathcal{H}_1)$: a sum over the $|\alpha_i\rangle$ and $|\beta_j\rangle$ states of each quantized system and a sum over the systems which make up the inhomogeneous line. If the distribution of values of $\mathcal{H}_0$,

$$\mathcal{H}_{0,k} = \mathcal{H}_{0,\mathrm{av}} + \Delta\mathcal{H}_{0,k} , \tag{4}$$

about a mean value $\mathcal{H}_{0,\mathrm{av}}$ is such that the spread in the inhomogeneous shifts $\Delta\mathcal{H}_{0,k}$ is large compared with the intervals in the α and β manifolds, then the two summations can be factored out, the first sum giving the envelope-modulation function and the second sum the form of the spin-echo signal. We shall assume that this factorization can be made. We shall also assume that $\Delta\mathcal{H}_{0,k}$ only varies the spacing between the α and β manifolds and does not lead to an inhomogeneous distribution of intervals within each manifold. [11]

Equation (1) can easily be integrated for the free-

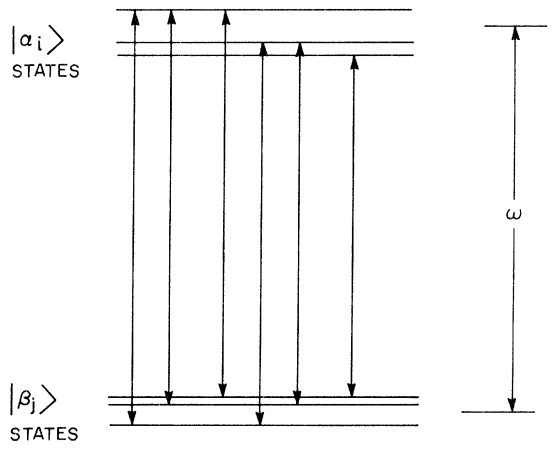

FIG. 1. Energy levels of a quantized system and transitions involved in the generation of spin-echo signals. The resonance field at frequency ω is able to induce transitions in all intervals $\omega_{\alpha i} - \omega_{\beta j}$ provided that the corresponding matrix elements are not zero. It is essential that transitions should occur from any given state $|\alpha_i\rangle$ to more than one state $|\beta_j\rangle$ if envelope-modulation effects are to be observed.

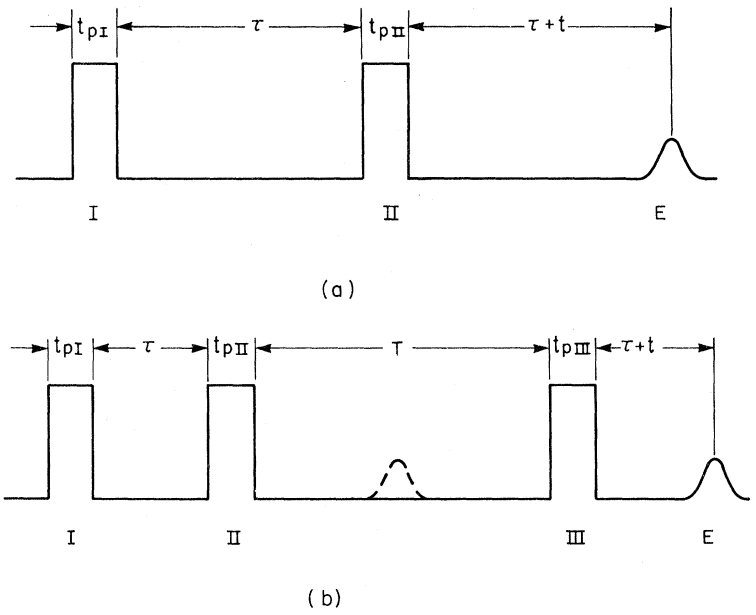

FIG. 2. (a) Two-pulse spin-echo sequence. In the idealized 90°-180° sequence the peak of the echo appears at a time τ after the end of pulse II. In some other situations it occurs at a time $\tau+t$ after pulse II, where $t \sim \frac{1}{2} t_p$. The envelope-modulation function $E_{\mathrm{mod}}(\tau)$ is obtained by plotting the amplitude of the echo E against the pulse separation τ. (b) Three-pulse or stimulated-echo sequence. (The two-pulse echo after pulse II will also be present unless pulses I and II are ideal 90° pulses.) It is most useful here to obtain the envelope-modulation function $E_{\mathrm{mod}}(\tau, T)$ by plotting the amplitude of the echo E against the time T. Since T may often be made much longer than τ, the modulation periods can be determined more precisely from $E_{\mathrm{mod}}(\tau, T)$.

precession portions of the echo experiment, during which $\mathcal{H}=\mathcal{H}_0$ is a time-independent operator. The density $\rho(t_f)$ at the end of any such period is related to the density $\rho(t_i)$ at the beginning by the similarity transform

$$\rho(t_f)=\exp[-i\mathcal{H}_0(t_f-t_i)/\hbar]\,\rho(t_i)\exp[i\mathcal{H}_0(t_f-t_i)/\hbar]\,. \tag{5}$$

If we adopt the $\mathcal{H}_0$ representation {in which the matrices $\exp[i\mathcal{H}_0(t_f-t_i)/\hbar]$ are diagonal, with elements $\exp[i\omega_{\alpha i}(t_f-t_i)]$, $\exp[i\omega_{\beta j}(t_f-t_i)]$} this transform merely multiplies the off-diagonal elements of ρ by phase factors $\exp[i(\omega_{\alpha i}-\omega_{\beta j})(t_f-t_i)]$.

The evolution of the system during the pulses is harder to describe. In order to formulate the problem in a concise manner, we partition the matrix for $\mathcal{H}_1$ into four submatrices consisting of the $\alpha_i\alpha_{i'}$, $\alpha_i\beta_j$, $\beta_j\alpha_i$, and $\beta_j\beta_{j'}$ arrays of matrix elements. The resonance field interaction

$$\mathcal{H}_1=\mathcal{H}_N e^{i\omega t}+\mathcal{H}^{-i\omega t} \tag{6}$$

can then be written down in the form

$$\mathcal{H}_1=\begin{array}{c} \\ (\alpha\text{ states}) \\ (\beta\text{ states}) \end{array}\begin{array}{c} \begin{array}{cc} (\alpha\text{ states}) & (\beta\text{ states}) \end{array} \\ \begin{bmatrix} 0 & \mathcal{H}_N e^{-i\omega t/2} \\ \mathcal{H}_N^{\dagger} e^{-i\omega t/2} & 0 \end{bmatrix} \end{array}, \tag{7}$$

where ω is the frequency of the oscillating field and $\mathcal{H}_N$ is a time-independent Hermitian operator which connects α states with β states, but which has no elements making connections within the α or β manifolds. The partitioning procedure indicated above will be used throughout the remaining calculations.

The time dependence can be removed from $\mathcal{H}_1$ by means of the transformation

$$\mathcal{H}_1=e^{i\omega\Sigma_z t/2}\,\mathcal{H}_1\,e^{-i\omega\Sigma_z t/2}\,, \tag{8}$$

where (in submatrix form)

$$\Sigma_z=\begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}. \tag{9}$$

We therefore have

$$\hat{\mathcal{H}}_1=\begin{bmatrix} 0 & N \\ N^{\dagger} & 0 \end{bmatrix}, \tag{10}$$

where N consists of the elements $\langle\alpha_i^*|\mathcal{H}_N|\beta_j\rangle$. By making the analogous transformations

$$\hat{\mathcal{H}}_0=e^{i\omega\Sigma_z t/2}\,\mathcal{H}_0\,e^{-i\omega\Sigma_z t/2}, \tag{11}$$

$$\hat{\rho}=e^{i\omega\Sigma_z t/2}\,\rho e^{-i\omega\Sigma_z t/2} \tag{12}$$

for the other operators we can restate the problem in a frame of reference[12] in which the equation of motion can always be solved by an expression of the form (5). Thus

$$\frac{d\hat{\rho}}{dt}=\frac{i}{\hbar}[\hat{\rho},\hat{\mathcal{H}}] \tag{13}$$

and

$$\hat{\rho}(t_f)=\exp[-i\hat{\mathcal{H}}(t_f-t_i)/\hbar]\,\rho(t_i)\exp[i\hat{\mathcal{H}}(t_f-t_i)/\hbar], \tag{14}$$

where $\hat{\mathcal{H}}=\hat{\mathcal{H}}_0+\hat{\mathcal{H}}_1$ or $\hat{\mathcal{H}}_0$ according to whether the period t_f-t_i is one of nutation or free precession. The final result

$$E=\eta\,\mathrm{Tr}(\hat{\rho}_E\hat{\mathcal{H}}_1) \tag{15}$$

will of course be expressed in the transformed coordinate system and will correspond to the amplitude of an oscillation taking place at the frequency ω.

Let us denote the exponential operators appropriate to the nutation and free-precession periods in the two-pulse spin-echo sequence [Fig. 2(a)] as follows:

$$R_{N\,\mathrm{I}} = \exp\left[i(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1)\, t_{p\,\mathrm{I}}/\hbar\right], \tag{16}$$

$$R_{N\,\mathrm{II}} = \exp\left[i(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1)\, t_{p\,\mathrm{II}}/\hbar\right], \tag{17}$$

$$R_\tau = \exp\left[i\hat{\mathcal{H}}_0\, \tau/\hbar\right]. \tag{18}$$

Then the final density is related to $\rho_0 (= \hat{\rho}_0)$ by the transformation

$$\hat{\rho}_E = R^{-1}\rho_0 R = R^\dagger \rho_0 R, \tag{19}$$

where

$$R = R_{N\,\mathrm{I}} R_\tau R_{N\,\mathrm{II}} R_{\tau+t}\,. \tag{20}$$

R^{-1} can be replaced by $R^\dagger$ since $\hat{\mathcal{H}}_0$ and $\hat{\mathcal{H}}_1$ are Hermitian and the exponential operators (16)–(18) are unitary.

The calculations can be carried out in terms of submatrices. $\hat{\mathcal{H}}_1$ is given in (10) and we can denote the remaining operators by

$$\rho_0 = \begin{bmatrix} A & 0 \\ 0 & B \end{bmatrix}, \tag{21}$$

$$R_\tau = \begin{bmatrix} P_\tau & 0 \\ 0 & Q_\tau \end{bmatrix}, \tag{22}$$

$$R_{N\,\mathrm{I}} = \begin{bmatrix} T_{\mathrm{I}} & U_{\mathrm{I}} \\ V_{\mathrm{I}} & W_{\mathrm{I}} \end{bmatrix} \tag{23}$$

(with similar matrices for $R_{\tau+t}$, $R_{N\,\mathrm{II}}$). Performing the multiplication (20) we have

$$R = \begin{bmatrix} (T_{\mathrm{I}} P_\tau T_{\mathrm{II}} P_{\tau+t} + U_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_{\tau+t}) & (T_{\mathrm{I}} P_\tau U_{\mathrm{II}} Q_{\tau+t} + U_{\mathrm{I}} Q_\tau W_{\mathrm{II}} Q_{\tau+t}) \\ (V_{\mathrm{I}} P_\tau T_{\mathrm{II}} P_{\tau+t} + W_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_{\tau+t}) & (V_{\mathrm{I}} P_\tau U_{\mathrm{II}} Q_{\tau+t} + W_{\mathrm{I}} Q_\tau W_{\mathrm{II}} Q_{\tau+t}) \end{bmatrix}. \tag{24}$$

Evaluating (19) and using the result in (15) we find that

$$\begin{aligned} E = \eta\, \mathrm{Tr}\,[&(Q^\dagger_{\tau+t} U^\dagger_{\mathrm{II}} P^\dagger_\tau T^\dagger_{\mathrm{I}} + Q^\dagger_{\tau+t} W^\dagger_{\mathrm{II}} Q^\dagger_\tau U^\dagger_{\mathrm{I}})\, A\, (T_{\mathrm{I}} P_\tau T_{\mathrm{II}} P_{\tau+t} + U_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_{\tau+t})\, N \\ &+ (Q^\dagger_{\tau+t} U^\dagger_{\mathrm{II}} P^\dagger_\tau V^\dagger_{\mathrm{I}} + Q^\dagger_{\tau+t} W^\dagger_{\mathrm{II}} Q^\dagger_\tau W^\dagger_{\mathrm{I}}) \\ &\times B\, (V_{\mathrm{I}} P_\tau T_{\mathrm{II}} P_{\tau+t} + W_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_{\tau+t})\, N + (P^\dagger_{\tau+t} T^\dagger_{\mathrm{II}} P^\dagger_\tau T^\dagger_{\mathrm{I}} + P^\dagger_{\tau+t} V^\dagger_{\mathrm{II}} Q^\dagger_\tau U^\dagger_{\mathrm{I}})\, A\, (T_{\mathrm{I}} P_\tau U_{\mathrm{II}} Q_{\tau+t} + U_{\mathrm{I}} Q_\tau W_{\mathrm{II}} Q_{\tau+t})\, N^\dagger \\ &+ (P^\dagger_{\tau+t} T^\dagger_{\mathrm{II}} P^\dagger_\tau V^\dagger_{\mathrm{I}} + P^\dagger_{\tau+t} V^\dagger_{\mathrm{II}} Q^\dagger_\tau W^\dagger_{\mathrm{I}})\, B\, (V_{\mathrm{I}} P_\tau U_{\mathrm{II}} Q_{\tau+t} + W_{\mathrm{I}} Q_\tau W_{\mathrm{II}} Q_{\tau+t})\, N^\dagger\,]\,. \end{aligned} \tag{25}$$

Equation (25) contains a number of terms which will not in fact contribute to the spin echo. To see this let us consider what will happen when the trace is summed over the inhomogeneous line. The diagonal matrices P, Q, $P^\dagger$, $Q^\dagger$ consist of elements $\exp[\pm i(\omega_{\alpha i} - \frac{1}{2}\omega)\tau]$, $\exp[\pm i(\omega_{\beta j} + \frac{1}{2}\omega)\tau]$, which contain, as part of the frequencies $\omega_{\alpha i}$ and $\omega_{\beta j}$, the shifts generated by the inhomogeneous broadening $\Delta\mathcal{H}_{0,k}$ [Eq. (4)]. In the submatrix notation this broadening term becomes

$$\Delta\mathcal{H}_{0,k} = \Delta\hat{\mathcal{H}}_{0,k} = \tfrac{1}{2}\hbar\,\Delta\omega_k \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}. \tag{26}$$

Thus, by Eqs. (18) and (22), it introduces scalar factors $e^{i\Delta\omega_k\tau/2}$, $e^{-i\Delta\omega_k\tau/2}$ into P_τ and Q_τ. Only those products in Eq. (25) for which such scalar factors cancel out will contribute to the echo. When the sum is made over the inhomogeneous line, the remaining products will be associated with factors of the form $\sum_k e^{i\Delta\omega_k\tau/2}$ and will correspond to the free-induction signals appearing only for relatively short times τ after the pulses. Eliminating these unwanted terms, and making use of the fact that A, B are real diagonal matrices, we thus have, in place of Eq. (25),

$$\begin{aligned} E = 2\eta\, \mathrm{Tr}\,(&Q^\dagger_{\tau+t} U^\dagger_{\mathrm{II}} P^\dagger_\tau T^\dagger_{\mathrm{I}} A U_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_{\tau+t} N \\ &+ Q^\dagger_{\tau+t} U^\dagger_{\mathrm{II}} P^\dagger_\tau V^\dagger_{\mathrm{I}} B W_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_{\tau+t} N)\,. \end{aligned} \tag{27}$$

[In simplifying (25) we obtain the terms in the parentheses above and their Hermitian conjugates; hence the factor of 2 in front of the trace.] Exact cancellation of the phase factors associated with inhomogeneous broadening will occur when $t \simeq 0$, i.e., when the two pulses and the echo are approximately equally spaced. (Small discrepancies in the timing may arise from phase factors $\sim e^{\pm\Delta\omega_k t_p/2}$ contained in the nutation operators.[13])

The echo envelope can be derived from the Hamiltonian by calculating the following quantities: (a) the initial densities A and B (i.e., the occupation probabilities for the states in the α and β manifolds), (b) the eigenfrequencies $\omega_{\alpha i}$, $\omega_{\beta j}$ which enter into P and Q, and (c) the nutation submatrices T, U, V, W from $\hat{\mathcal{H}}_1$ and t_p and by summing (27) over all ensembles for a range of values of $\Delta\mathcal{H}_{0,k}$. A procedure for making these calculations is suggested in Sec. VI. In practice it is sometimes pos-

sible to simplify the calculations by assuming that[14] $\hat{\mathcal{H}}_0 < \hat{\mathcal{H}}_1$. Since $R_N \simeq e^{i\hat{\mathcal{H}}_1 t/\hbar}$, the inhomogeneous broadening term $\Delta\mathcal{H}_{0,k}$ then appears only in the free precession matrices P, Q and can be taken outside the trace [see Eq. (26)] which need only be computed once. The condition $\hat{\mathcal{H}}_0 < \hat{\mathcal{H}}_1$ is analogous to the common assumption that "$\gamma\mathcal{H}_1$ is larger than the linewidth." It may, however, be harder to justify since there are a number of different matrix elements in $\mathcal{H}_1$ to be considered, some of them perhaps small because of the partially forbidden nature of the transitions concerned. In Sec. IV we show that when $\mathcal{H}_1 \gg \mathcal{H}_0$, and when certain additional conditions are met, the nutation matrices R_N can be written down at once from $\hat{\mathcal{H}}_1$.

If $\hat{\mathcal{H}}_0 \gtrsim \hat{\mathcal{H}}_1$, or if the assumptions in Sec. IV cannot be made, it is possible to obtain the nutation matrices by the following straightforward, if somewhat tedious, method. The Hamiltonian is first diagonalized by the unitary transformation $U_D^\dagger(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1) U_D = \hat{\mathcal{H}}_D$. In the new representation of the (diagonal) nutation matrix $R_N' = e^{i\mathcal{H}_D t_p/\hbar}$ is written down using the elements of $\mathcal{H}_D$. The inverse transformation $U_D R_N' U_D^\dagger$ is then applied to obtain R_N in the $\mathcal{H}_0$ representation. This is equivalent to the procedure sometimes used in two-level problems where nutations are described as taking place about an "effective field" made up of the resonance field and a portion of the original Zeeman field.

III. GENERAL EXPRESSIONS FOR ENVELOPE MODULATION IN STIMULATED-ECHO SEQUENCE

The pulse sequence required for the generation of a stimulated-echo signal is shown in Fig. 2(b). The echo amplitude for this sequence can be calculated by the methods already outlined by setting

$$R = R_{N\,\mathrm{I}} R_\tau R_{N\,\mathrm{II}} R_T R_{N\,\mathrm{III}} R_{\tau+t} \tag{28}$$

in place of the operator defined in Eq. (20). R_T here describes the free precession of the system between pulses II and III and may be written in terms of submatrices P_T and Q_T as in Eq. (22).

The calculation of the final density ρ_E can be simplified by taking account of the effects of inhomogeneous broadening of the resonance. As was pointed out earlier, the diagonal matrices P_τ, Q_τ, P_T, Q_T, etc., contain phase factors $e^{\pm i\Delta\omega_k \tau/2}$, $e^{\pm i\Delta\omega_k T/2}$, where $\Delta\omega_k$ varies according to the position in the resonance line. When calculating the echo, we need only retain those products of submatrices for which these phase factors approximately cancel. If the density matrix corresponding to the end of pulse II is written schematically in the form

$$\rho_{\mathrm{II}} = \begin{bmatrix} X_{11} & X_{12} \\ X_{21} & X_{22} \end{bmatrix} \tag{29}$$

it is easily verified (by finding $R_{\mathrm{II},E}^\dagger \rho_{\mathrm{II}} R_{\mathrm{II},E}$ where $R_{\mathrm{II},E} = R_T R_{N\,\mathrm{III}} R_{\tau+t}$) that the off-diagonal submatrices X_{21}, X_{12} do not contribute to the echo and may be discarded at this stage of the problem. The residual portion of ρ_{II} is a Hermitian matrix consisting of the elements

$$\begin{aligned} X_{11} &= (T_{\mathrm{II}}^\dagger P_\tau^\dagger T_{\mathrm{I}}^\dagger + V_{\mathrm{II}}^\dagger Q_\tau^\dagger U_{\mathrm{II}}^\dagger) A (T_{\mathrm{I}} P_\tau T_{\mathrm{II}} + U_{\mathrm{I}} Q_\tau V_{\mathrm{II}}) \\ &\quad + (T_{\mathrm{II}}^\dagger P_\tau^\dagger V_{\mathrm{I}}^\dagger + V_{\mathrm{II}}^\dagger Q_\tau^\dagger W_{\mathrm{I}}^\dagger) B (V_{\mathrm{I}} P_\tau T_{\mathrm{II}} + W_{\mathrm{I}} Q_\tau V_{\mathrm{II}}) , \\ X_{22} &= (U_{\mathrm{II}}^\dagger P_\tau^\dagger T_{\mathrm{I}}^\dagger + W_{\mathrm{II}}^\dagger Q_\tau^\dagger U_{\mathrm{I}}^\dagger) A (T_{\mathrm{I}} P_\tau U_{\mathrm{II}} + U_{\mathrm{I}} Q_\tau W_{\mathrm{II}}) \\ &\quad + (U_{\mathrm{II}}^\dagger P_\tau^\dagger V_{\mathrm{I}}^\dagger + W_{\mathrm{II}}^\dagger Q_\tau^\dagger W_{\mathrm{I}}^\dagger) B (V_{\mathrm{I}} P_\tau U_{\mathrm{II}} + W_{\mathrm{I}} Q_\tau W_{\mathrm{II}}) . \end{aligned} \tag{30}$$

Some further terms which do not lead to the cancellation of the line inhomogeneity factors $e^{i\Delta\omega_k \tau/2}$ (i.e., terms which correspond to free-induction effects) can be relinquished in the final expression for ρ_E. We thus obtain the expression

$$\begin{aligned} E_{\mathrm{stim}} = 2\eta\,\mathrm{Tr}\,(&Q_{\tau+t}^\dagger U_{\mathrm{III}}^\dagger P_T^\dagger T_{\mathrm{II}}^\dagger P_\tau^\dagger T_{\mathrm{I}}^\dagger A U_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_T T_{\mathrm{III}} P_{\tau+t} \\ &+ Q_{\tau+t}^\dagger U_{\mathrm{III}}^\dagger P_T^\dagger T_{\mathrm{II}}^\dagger P_\tau^\dagger V_{\mathrm{I}}^\dagger B W_{\mathrm{I}} Q_\tau V_{\mathrm{II}} P_T T_{\mathrm{III}} P_{\tau+t} \\ &+ Q_{\tau+t}^\dagger W_{\mathrm{III}}^\dagger Q_T^\dagger U_{\mathrm{II}}^\dagger P_\tau^\dagger T_{\mathrm{I}}^\dagger A U_{\mathrm{I}} Q_\tau W_{\mathrm{II}} Q_T V_{\mathrm{III}} P_{\tau+t} \\ &+ Q_{\tau+t}^\dagger W_{\mathrm{III}}^\dagger Q_\tau^\dagger U_{\mathrm{II}}^\dagger P_\tau^\dagger V_{\mathrm{I}}^\dagger B W_{\mathrm{I}} Q_\tau W_{\mathrm{I}} Q_T V_{\mathrm{III}} P_{\tau+t}) . \end{aligned} \tag{31}$$

It should be noted that by discarding the off-diagonal submatrices in ρ_{II}' we have not ceased to consider all free-precession effects during the interval T but merely those free-precession effects associated with the resonance interval ω. Phase relationships within the α and β manifolds are still accounted for by the off-diagonal elements belonging to the submatrices X_{11} and X_{22}. If, as we have so far assumed, the intervals within these manifolds are not subject to inhomogeneous broadening at all, then the modulation effects associated with the time evolution of X_{11} and X_{22} will continue to be visible for as long as it is possible to detect stimulated-echo signals. Actually some broadening (i.e., ENDOR broadening) will be present, and, since the phase factors which result from this broadening are not cancelled out in the stimulated-echo sequence, the modulation will eventually be erased.[15]

IV. NUCLEAR MODULATION OF ELECTRON SPIN-ECHO ENVELOPE

We now specialize to the case of an electron nuclear system described by the Hamiltonian

$$\mathcal{H}_0 = \mathcal{H}_S + \mathcal{H}_I + \mathcal{H}_{SI} . \tag{32}$$

The electron term $\mathcal{H}_S$ generates a level scheme from which we select the two levels α and β defining an interval $\simeq \hbar\omega$. (Other levels not defining resonance intervals can be ignored.) The nuclear term $\mathcal{H}_I$ and the electron nuclear coupling term $\mathcal{H}_{SI}$ are both small and give rise to the superhyperfine split-

ting.

Since the resonance field interacts mainly with the electron spin, $\hat{\mathcal{H}}_1$ can be written in the $\mathcal{H}_S + \mathcal{H}_I$ representation in the form

$$\hat{\mathcal{H}}_1 = \tfrac{1}{2}\hbar\omega_N \begin{bmatrix} 0 & I \\ I & 0 \end{bmatrix} . \tag{33}$$

The transformation to the $\mathcal{H}_0$ representation can then be made by operating on the α and β state vectors separately with unitary matrices M_α and M_β, which describe the state mixing caused by $\mathcal{H}_{SI}$ in the α and β manifolds. In this way we obtain

$$\hat{\mathcal{H}}_1 = \tfrac{1}{2}\hbar\omega_N \begin{bmatrix} 0 & M \\ M^\dagger & 0 \end{bmatrix} , \tag{34}$$

where $M = M_\alpha^\dagger M_\beta$ is also unitary. This transformation by means of submatrices derived from the shfs terms $\mathcal{H}_{SI} + \mathcal{H}_I$ only is permissible here because $\mathcal{H}_{SI}$ is too small to cause any significant mixing of the eigenstates of $\mathcal{H}_S$.

The form (34) for $\hat{\mathcal{H}}_1$ leads to major simplifications in the nutation matrices and in the final results. Let us suppose that $\hat{\mathcal{H}}_1 \gg \hat{\mathcal{H}}_0$. Then $R_N = e^{i\hat{\mathcal{H}}_1 t_p/\hbar}$ and can be expanded to give

$$R_N = \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix} \cos\tfrac{1}{2}\omega_N t_p + i \begin{bmatrix} 0 & M \\ M^\dagger & 0 \end{bmatrix} \sin\tfrac{1}{2}\omega_N t_p . \tag{35}$$

The two-pulse-echo result (27) reduces to

$$\begin{aligned} E(\tau) = {} & \tfrac{1}{2} i\hbar\omega_N \eta \sin\omega_N t_{p\,\mathrm{I}} \sin^2\tfrac{1}{2}\omega_N t_{p\,\mathrm{II}} \\ & \times \mathrm{Tr}(Q_{\tau+t}^\dagger M^\dagger P_\tau^\dagger A M Q_\tau M^\dagger P_{\tau+t} M \\ & - Q_{\tau+t}^\dagger M^\dagger P_\tau^\dagger M B Q_\tau M^\dagger P_{\tau+t} M) \end{aligned} \tag{36}$$

and the stimulated-echo result (31) to

$$\begin{aligned} E_{\mathrm{stim}}(\tau, T) = {} & \tfrac{1}{8} i\hbar\omega_N \eta \sin\omega_N t_{p\,\mathrm{I}} \sin\omega_N t_{p\,\mathrm{II}} \sin\omega_N t_{p\,\mathrm{III}} \\ & \times \mathrm{Tr}(Q_{\tau+t}^\dagger M^\dagger P_T^\dagger P_\tau^\dagger A M Q_\tau M^\dagger P_T P_{\tau+t} M \\ & - Q_{\tau+t}^\dagger M^\dagger P_T^\dagger P_\tau^\dagger M B Q_\tau M^\dagger P_{\tau+t} M \\ & + Q_{\tau+t}^\dagger Q_T^\dagger M^\dagger P_\tau^\dagger A M Q_\tau Q_T M^\dagger P_{\tau+t} M \\ & - Q_{\tau+t} Q_T^\dagger M^\dagger P_\tau^\dagger M B Q_\tau Q_T M^\dagger P_{\tau+t} M) . \end{aligned} \tag{37}$$

If, in addition, we assume that $A \simeq aI$ and $B \simeq bI$ (i.e., that the initial Boltzmann populations of all the α sublevels are the same and likewise for the β sublevels), then

$$\begin{aligned} E(\tau) = {} & \tfrac{1}{2}(a-b)\,(i\hbar\omega_N\eta) \sin\omega_N t_{p\,\mathrm{I}} \sin^2\tfrac{1}{2}\omega_N t_{p\,\mathrm{II}} \\ & \times \mathrm{Tr}(Q_{\tau+t}^\dagger M^\dagger P_\tau^\dagger M Q_\tau M^\dagger P_{\tau+t} M) \end{aligned} \tag{38}$$

and

$$\begin{aligned} E_{\mathrm{stim}}(\tau, T) = {} & \tfrac{1}{8}(a-b)\,(i\hbar\omega_N\eta) \sin\omega_N t_{p\,\mathrm{I}} \sin\omega_N t_{p\,\mathrm{II}} \\ & \times \sin\omega_N t_{p\,\mathrm{III}} \mathrm{Tr}(Q_{\tau+t}^\dagger M^\dagger P_T^\dagger P_\tau^\dagger M Q_\tau M^\dagger P_T P_{\tau+t} M \\ & + Q_{\tau+t}^\dagger Q_T^\dagger M^\dagger P_\tau^\dagger M Q_\tau Q_T M^\dagger P_{\tau+t} M) . \end{aligned} \tag{39}$$

The normalizing factor for the envelope-modulation function (i.e., the envelope amplitude when $\tau \to 0$ and $T \to 0$) can be found by setting $P = Q = I$ in the above expressions. In (38) it is

$$\tfrac{1}{2}(a-b)\,(i\hbar\omega_N\eta) \sin\omega_N t_{p\,\mathrm{I}} \sin^2\tfrac{1}{2}\omega_N t_{p\,\mathrm{II}} \mathrm{Tr}(I)$$

and in (39) it is

$$\tfrac{1}{4}(a-b)\,(i\hbar\omega_N\eta) \sin\omega_N t_{p\,\mathrm{I}} \sin\omega_N t_{p\,\mathrm{II}} \sin\omega_n t_{p\,\mathrm{III}} \mathrm{Tr}(I) ,$$

where I has the dimensions of the submatrices P, Q, M. *The normalized modulation functions* $E_{\mathrm{mod}}(\tau)$ *and* $E_{\mathrm{mod}}(\tau, T)$ *are therefore given by the trace expressions divided by the number of* shfs *levels in the two-pulse case or by twice the number of* shfs *levels in the stimulated-echo case.* As was pointed out earlier, it is essential that $\hat{\mathcal{H}}_1$ should be able to induce branching transitions between the α_i and β_j states. Otherwise $M = I$ (or can be put into this form by a rearrangement of rows and columns) and, as may easily be verified, the trace in Eqs. (38) and (39) becomes $\propto \mathrm{Tr}(I)$, indicating no envelope modulation. The same thing happens if the frequencies in either of the α or β manifolds become degenerate, i.e., if $P = e^{i\omega_\alpha t} I$ or $Q = e^{i\omega_\beta t} I$.

Two different kinds of numerical computation may be performed with the trace expressions derived here and in the previous sections, one yielding the time development of the modulation function and the other the amplitudes of the various frequency components. The first computation proceeds along obvious lines. The trace is evaluated for a series of values of τ or T extending over the experimental interval, and the modulation function is multiplied by some suitable function representing the decay of signal intensity. To see how the frequency amplitudes may be extracted instead, let us consider the following example. We take the product $Q_\tau^\dagger M^\dagger P_\tau^\dagger M Q_\tau M^\dagger P_\tau M$ from (38) and insert unity for the diagonal elements $e^{i\alpha_i\tau}$, $e^{i\beta_j\tau}$, $e^{-i\alpha_{i'}\tau}$, $e^{-i\beta_{j'}\tau}$ in P_τ, Q_τ, $P_\tau^\dagger$, $Q_\tau^\dagger$. All other elements in these matrices are set equal to zero. When the trace is computed with these values the resulting number is the coefficient $c_{ii'jj'}$ of the term $c_{ii'jj'} \times \exp[i(\omega_{\alpha i} - \omega_{\alpha i'} + \omega_{\beta j} - \omega_{\beta j'})\tau]$. The coefficient $c_{i'ij'j}$ of the complex conjugate term can be found by inserting unity for $e^{i\alpha_{i'}\tau}$, $e^{i\beta_{j'}\tau} e^{-i\alpha_i\tau}$, and $e^{-i\beta_j\tau}$ in the same four submatrices. The amplitudes and phases of frequency components belonging to the α manifold only are derived by evaluating the sums of the form $\sum_j c_{ii'jj'}$, amplitudes and phases of frequency components belonging to the β manifold only by evaluating $\sum_i c_{iijj'}$. The constant term is derived from $\sum_{ij} c_{iijj}$. Stimulated-echo results can be treated in the same way. For example, by inserting unity for the elements $e^{i\alpha_i\tau}$, $e^{i\beta_j\tau}$, $e^{-i\alpha_k T}$, $e^{-i\alpha_i\tau}$, $e^{-i\beta_{j'}\tau}$, $e^{-i\alpha_{k'}T}$, and 0 for the remaining elements of P_τ, Q_τ, P_T, $P_\tau^\dagger$, $Q_\tau^\dagger$, $P_T^\dagger$ in the first matrix product in Eq. (39) and taking the trace we find the

coefficient $c_{ii'jj'kk'}$ of the term in $\exp\{i[(\omega_{\alpha i}-\omega_{\alpha i'})+(\omega_{\beta j}-\omega_{\beta j'})]\tau\}\exp[i(\omega_{\alpha k}-\omega_{\alpha k'})T]$.

A frequency analysis may be more economical than a time development of the modulation function when the experimental times are long. It has also the merit of affording a better insight into the way in which the amplitudes in the modulation envelope are related to the shfs transitions. In this connection it is worth noting that the T-dependent factors in the stimulated-echo envelope will contain either a frequency $\omega_{\alpha k}-\omega_{\alpha k'}$ from the α manifold or a frequency from the β manifold but not sum and difference frequencies from both manifolds. For this reason (as well as because of the longer times which are generally available) a stimulated-echo sequence may be more convenient if the modulation function is to be used to measure shfs frequencies.

V. COUPLING WITH SEVERAL NUCLEI

Simultaneous coupling of an electron spin with N nuclei leads to submatrices of dimension $(2I+1)^N$. Fortunately, however, the dimensions can usually be reduced to $(2I+1)$, as we show by means of the following example. Let us consider the eight states associated with an electron transition coupled to two nuclei of $I=\frac{1}{2}$. The free-precession Hamiltonian is

$$\mathcal{H}_0=\mathcal{H}_S+\mathcal{H}_{I_1}+\mathcal{H}_{I_2}+\mathcal{H}_{S,I_1}+\mathcal{H}_{S,I_2}+\mathcal{H}_{I_1,I_2}\ . \tag{40}$$

The resonance field Hamiltonian $\hat{\mathcal{H}}_1$ can be obtained as before by writing it down in the $\mathcal{H}_S+\mathcal{H}_{I_1}+\mathcal{H}_{I_2}$ representation [in which it contains two off-diagonal 4×4 unit submatrices located as in Eq. (33)] and transforming to the $\mathcal{H}_0$ representation by a suitable unitary operator. If we ignore the small term $\mathcal{H}_{I_1,I_2}$ we can make this transformation by means of the tensor products $M_\alpha=M_{1\alpha}\times M_{2\alpha}$ and $M_\beta=M_{1\beta}\times M_{2\beta}$. The subscripts 1, 2 indicate that the matrices operate on the states of nuclear spins I_1 and I_2, and are derived from $\mathcal{H}_{I_1}+\mathcal{H}_{SI1}$ and $\mathcal{H}_{I_2}+\mathcal{H}_{SI_2}$, respectively.[16] Thus M may be factored as the tensor product $M=M_1\times M_2$, where $M_1=M_{1\alpha}^{\dagger}M_{1\beta}$, etc. Factoring the remaining matrices as tensor products we can obtain the over-all products in Eqs. (38) and (39) in the form $Y=Y_1\times Y_2$. Then, using the theorem $\mathrm{Tr}(Y)=(\mathrm{Tr}_1 Y_1)(\mathrm{Tr}_2 Y_2)$ we can proceed at once to the result

$$E_{I_1I_2}=E_{I_1}E_{I_2} \tag{41}$$

for the two-pulse envelope-modulation function and to a similar result in the case of stimulated echoes. For N nuclear neighbors Eq. (41) becomes

$$E_N=\Pi_i E_i\ . \tag{42}$$

Equation (42) holds good for nuclei with $I>\frac{1}{2}$ and for systems in which an electron is coupled to several different types of nuclei. As will be apparent from the product form of the answer, frequencies which are combinations (or multiples) of the ENDOR frequencies due to a single nuclear spin may be present in the modulation envelope, these frequencies representing the energy differences between the various levels in the α and β manifolds. In any practical situation some caution should be used in applying the product formula (42) in conjunction with expressions such as (38) and (39) which are based on the assumption $\hat{\mathcal{H}}_1>\hat{\mathcal{H}}_0$. This assumption can easily fail for some of the transitions when the level scheme describes an interaction with many nuclear neighbors.

VI. PROCEDURE FOR MAKING DETAILED CALCULATIONS

We consider the case for which $\hat{\mathcal{H}}_1\gg\hat{\mathcal{H}}_0$ and $\mathcal{H}_S\gg\mathcal{H}_{SI}+\mathcal{H}_1$. The interaction of the resonance field with the nuclear moment is neglected, so that $\hat{\mathcal{H}}_1$ can be written down as in Eq. (33) in the $\mathcal{H}_S+\mathcal{H}_I$ representation. [These are the assumptions used in deriving Eqs. (38) and (39) in Sec. IV.] The aim here is to obtain values for the eigenfrequencies which appear in the free-precession matrices, P, Q and to find the elements of the unitary matrix M which determines the amplitudes of the various frequency components in the echo envelope.

These quantities can be found from $\mathcal{H}_0$ in the following four steps:

(i) The $(2S+1)$-dimensioned matrix for $\mathcal{H}_S$ is written down in a convenient representation. The term

$$\mathcal{H}_{SI}/\hbar=\sum_{ij}a_{ij}S_iI_j\quad(i,j=x,y,z)$$

is factored to give

$$\mathcal{H}_{SI}/\hbar=I_x\textstyle\sum_i a_{ix}S_i+I_y\sum_i a_{iy}S_i+I_z\sum_i a_{iz}S_i\ ,$$

and the coefficients of I_x, I_y, I_z are written down in the representation used for $\mathcal{H}_S$.

(ii) $\mathcal{H}_S$ is diagonalized by making the unitary transformation $U_S^{\dagger}\mathcal{H}_S U_S=D_S$. The same transformation is applied to each of the matrices $\sum_i a_{ix}S_i$, etc., only the diagonal elements being retained.

(iii) The three sets of diagonal elements derived from $\mathcal{H}_{SI}$ in this way are treated as numerical coefficients of the operators I_x, I_y, I_z. The coefficients corresponding to the electron states α and β are then selected and are used with the appropriate nuclear operators and with $\mathcal{H}_I$ to form two new Hamiltonians $\mathcal{H}_\alpha$ and $\mathcal{H}_\beta$ operating on the α and β shfs manifolds. Thus we have

$$\begin{aligned}\mathcal{H}_\alpha/\hbar&=a'_{x,\alpha}I_x+a'_{y,\alpha}I_y+a'_{z,\alpha}I_z+\mathcal{H}_I\ ,\\ \mathcal{H}_\beta/\hbar&=a'_{x,\beta}I_x+a'_{y,\beta}I_y+a'_{z,\beta}I_z+\mathcal{H}_I\ .\end{aligned} \tag{43}$$

(iv) The $(2I+1)$-dimensional matrices $\mathcal{H}_\alpha$ and $\mathcal{H}_\beta$ are now written down and diagonalized. The eigenvalues give the frequencies $\omega_{\alpha i}$, $\omega_{\beta j}$ which appear

in the free-precession matrices P, Q. The eigenvectors are assembled to form the columns of the matrices $M_\alpha^\dagger$ and $M_\beta^\dagger$ which are required in order to evaluate $M = M_\alpha^\dagger M_\beta$.

Separate diagonalization of $\mathcal{H}_S$ and of the nuclear Hamiltonians can only be justified when the off-diagonal elements derived from $\mathcal{H}_{SI}$ in step (ii) can be ignored, and when $\mathcal{H}_I$ has a negligible effect on the composition of the electron spin states (as implied by the condition $\mathcal{H}_S > \mathcal{H}_{SI} + \mathcal{H}_I$). If large electron nuclear couplings, such as those which frequently exist between an electron spin and a nucleus belonging to the same paramagnetic ion, are present, they should be included in $\mathcal{H}_S$, leaving $\mathcal{H}_{SI} + \mathcal{H}_I$ to specify small shfs couplings only.

The transition matrix element between the α and β eigenstates of $\mathcal{H}_S$ does not affect the form of the envelope function and need not be calculated here. It is factored out in the parameters η [Eq. (3)] and ω_N [Eq. (36)] and merely serves to determine the experimental conditions required in order to generate satisfactory spin-echo signals.

It is easy to see that $M \simeq I$ (and hence that there is no envelope modulation) when $\mathcal{H}_{SI} \ll \mathcal{H}_I$. The two matrices $\mathcal{H}_\alpha$, $\mathcal{H}_\beta$ then become identical, $M_\alpha \to M_\beta$ and $M = M_\alpha^\dagger M_\beta \to I$. A similar result may also be obtained in certain cases when $\mathcal{H}_{SI} \gg \mathcal{H}_I$. For example, if $\mathcal{H}_S$ describes a Kramers doublet ($S' = \frac{1}{2}$), the diagonalization prescribed in step (ii) can be performed by rotating the Cartesian axes of S in such a way as to make S_z a good quantum number. The coefficients a_{ij} will be transformed to a'_{ij} giving in Eq. (43) the operators

$$\langle \alpha | S_z | \alpha \rangle (\textstyle\sum_j a'_{zj} I_j) \quad \text{and} \quad \langle \beta | S_z | \beta \rangle (\textstyle\sum_j a'_{zj} I_j) \, .$$

Both these operators are the same except for the scalar factors $\langle \alpha | S_z | \alpha \rangle$, $\langle \beta | S_z | \beta \rangle$ and can be diagonalized by a single unitary matrix $U_{SI} = M_\alpha = M_\beta$.

VII. FOUR-LEVEL ELECTRON NUCLEAR SYSTEM

When $I = \frac{1}{2}$ the unitary matrix M has the simple form

$$M = \begin{bmatrix} v & u \\ -u^* & v^* \end{bmatrix} \tag{44}$$

and the normalized-echo envelope functions derived from Eqs. (38) and (39) are

$$E_{\mathrm{mod}}(\tau) = |v|^4 + |u|^4 + |v|^2 |u|^2 [2\cos\omega_{\alpha\beta}\tau + 2\cos\omega_{cd}\tau - \cos(\omega_{ab} - \omega_{cd})\tau - \cos(\omega_{ab} + \omega_{cd})\tau] \tag{45}$$

and

$$E_{\mathrm{mod}}(\tau, T) = |v|^4 + |u|^4 + |v|^2 |u|^2 [\cos\omega_{ab}\tau + \cos\omega_{cd}\tau + 2\sin^2\tfrac{1}{2}\omega_{cd}\tau \cos\omega_{ab}(\tau + T) + 2\sin^2\tfrac{1}{2}\omega_{ab}\tau \cos\omega_{cd}(\tau + T)] \, . \tag{46}$$

The frequencies ω_{ab}, ω_{cd} denote the intervals between states $|a\rangle$, $|b\rangle$ and $|c\rangle$, $|d\rangle$, respectively. The parameters

$$|u| = |\langle a^* | \hat{\mathcal{H}}_1 | b \rangle| / (\tfrac{1}{2}\hbar\omega_N)$$

and

$$|v| = |\langle a^* | \hat{\mathcal{H}}_1 | c \rangle| / (\tfrac{1}{2}\hbar\omega_N)$$

describe the extent to which the branching transitions are allowed or forbidden (see Fig. 3). If one transition is fully allowed and the other fully forbidden, then either $|v| = 0$ or $|u| = 0$ and there will be no modulation. Equation (46) illustrates how the individual shfs frequencies, without their sum and difference frequencies, may be measured in a stimulated-echo experiment by plotting the echo amplitude as a function of T at constant τ. (This holds good in the more general case as well, see note at the end of Sec. IV.)

If the two-electron levels belong to a Kramers doublet ($S' = \frac{1}{2}$), the transformations required in order to find $|u|$ and $|v|$ can be described as rotations of the electron and nuclear coordinate systems. As pointed out in Sec. VI, the diagonalization in step (ii) is equivalent to the rotation of the electron z axis along the direction of quantization of the electron spin. [In the special case of an axial site, the new z axis is at an angle θ_S to this c axis, where $\sin\theta_S = (g_\perp/g)\sin\theta_H$, where θ_H is the angle of the Zeeman field, and $g = (g_\parallel^2 \cos^2\theta_H + g_\perp^2 \times \sin^2\theta_H)^{1/2}$.] This change of axes transforms $\mathcal{H}_{SI}$

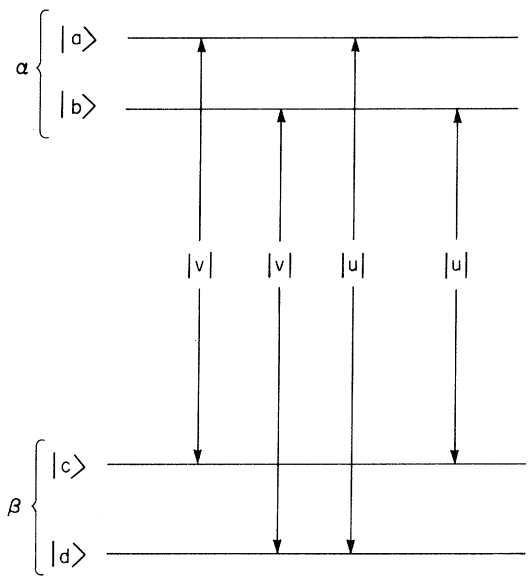

FIG. 3. Four-level scheme obtained when two-electron levels α and β are split by coupling with a nucleus of $I = \frac{1}{2}$. The transition matrix elements connecting $|a\rangle \rightleftarrows |b\rangle$ and $|c\rangle \rightleftarrows |d\rangle$ have magnitudes $i\hbar\omega_N |v|$; the corresponding elements connecting $|a\rangle \rightleftarrows |d\rangle$ and $|b\rangle \rightleftarrows |c\rangle$ have magnitudes $i\hbar\omega_N |u|$.

$= \hbar\sum_{ij} a_{ij} S_i I_j$ to $\mathcal{H}'_{SI} = \hbar\sum_{ij} a'_{ij} S'_i I_j$ from which we extract the S'_z terms to give

$$\mathcal{H}'_{SI,\alpha} = -\mathcal{H}'_{SI,\beta} = +\tfrac{1}{2}\hbar\sum_j a'_{zj} I_j \ .$$

The a'_{zj} are the projections of the three vectors (a_{xj}, a_{yj}, a_{zj}) along the electron quantization axis.

The coordinate system used to define I need not be the same as that used to define S, and may conveniently be taken so that the nuclear z axis is parallel to the Zeeman field H_0. Then $\mathcal{H}_I$ is diagonal with elements $\pm\frac{1}{2} g_I \beta_I H_0 = \pm\frac{1}{2}\hbar\omega_I$. A rotation of the nuclear xy axes about the nuclear z axis can also be made in order to eliminate the I_y term. (This choice of nuclear x, y, z axes may involve a further transformation of the a'_{zj}.) We thus obtain the Hamiltonians

$$\begin{aligned} \mathcal{H}_\alpha/\hbar &= \omega_I I_z + \tfrac{1}{2}AI_z + \tfrac{1}{2}BI_x \ , \\ \mathcal{H}_\beta/\hbar &= \omega_I I_z - \tfrac{1}{2}AI_z - \tfrac{1}{2}BI_x \ . \end{aligned} \tag{47}$$

The two eigenfrequencies are given by

$$\begin{aligned} \omega_\alpha = \omega_{ab} &= [(\tfrac{1}{2}A + \omega_I)^2 + (\tfrac{1}{2}B)^2]^{1/2} \ , \\ \omega_\beta = \omega_{cd} &= [(\tfrac{1}{2}A - \omega_I) + (\tfrac{1}{2}B)^2]^{1/2} \end{aligned} \tag{48}$$

and the diagonalization is effected by means of the rotation operators $e^{-iI_y\xi}$, $e^{-I_y\eta}$, where

$$\begin{aligned} \tan\xi &= B/(A + 2\omega_I) \ , \\ \tan\eta &= B/(A - 2\omega_I) \ . \end{aligned} \tag{49}$$

The rotation operators $e^{-iI_y\xi}$ and $e^{-iI_y\eta}$ correspond to the transformation matrices M_α, M_β of Sec. IV. We can therefore obtain $M = M_\alpha^\dagger M_\beta$ by writing down $e^{-iI_y(\eta-\xi)}$ in the $\mathfrak{D}_{1/2}$ representation, yielding a 2×2 matrix, as in Eq. (44), with $u = \sin\frac{1}{2}(\eta - \xi)$ and $v = \cos\frac{1}{2}(\eta - \xi)$. The product $|v|^2|u|^2$ is given by

$$4|v|^2|u|^2 = \sin^2(\eta - \xi) = (\omega_I B/\omega_\alpha\omega_\beta)^2$$

and can be used in Eqs. (45) and (46) to obtain the envelope-modulation functions. The results of this calculation can also be expressed in the forms

$$E_{\rm mod}(\tau) = 1 - \frac{2\omega_I^2 B^2}{\omega_{ab}^2\,\omega_{cd}^2}\sin^2\tfrac{1}{2}\omega_{ab}\tau\sin^2\tfrac{1}{2}\omega_{cd}\tau \tag{50}$$

and

$$\begin{aligned} E_{\rm mod}(\tau, T) = 1 - \frac{\frac{1}{2}\omega_I^2 B^2}{\omega_{ab}^2\,\omega_{cd}^2}\{&\sin^2\tfrac{1}{2}\omega_{ab}\tau[1 - \cos\omega_{cd}(\tau + T)] \\ &+ \sin^2\tfrac{1}{2}\omega_{cd}\tau[1 - \cos\omega_{ab}(\tau + T)]\} \ . \end{aligned} \tag{51}$$

VIII. COUPLING WITH $I = 1$ NUCLEI

We consider here the restricted case in which the electron states $|\alpha\rangle$ and $|\beta\rangle$ belong to a Kramers doublet, and in which the nuclear quadrupole interaction is small enough to be ignored when calculating the matrix M which determines the modulation amplitudes.[17] It will be apparent from the results that it is generally better to compute the modulation amplitudes numerically in all but the simplest cases. The algebraic expressions obtained here may however be useful in view of the occurrence of the nuclei H^2 and N^{14} (both having small quadrupole moments) in some commonly studied host materials.

The level diagram is the same as that shown in Fig. 1 with the $|\alpha_i\rangle$ states labeled a, b, c and the $|\beta_i\rangle$ states d, e, f. The Hamiltonians $\mathcal{H}_\alpha$, $\mathcal{H}_\beta$ can be approximated by (47) and give eigenfrequencies ω_α, ω_β as in (48) which can be adjusted to take account of quadrupolar interactions if necessary. We thus have $\omega_{ab} = \omega_\alpha + \Delta$, $\omega_{bc} = \omega_\alpha - \Delta$, $\omega_{cd} = \omega_\beta + \Delta$, and $\omega_{de} = \omega_\beta - \Delta$, where Δ is the appropriate quadrupolar correction. The matrix M is calculated in the same way as in Sec. VII except that it is now necessary to write down the operator $e^{-iI_y(\eta-\xi)}$ in the $\mathfrak{D}_1$ representation. We thus have

$$M = \begin{bmatrix} \frac{1}{2}[1 + \cos(\eta - \xi)] & (-1/\sqrt{2})\sin(\eta - \xi) & \frac{1}{2}[1 - \cos(\eta - \xi)] \\ (1/\sqrt{2})\sin(\eta - \xi) & \cos(\eta - \xi) & (-1/\sqrt{2})\sin(\eta - \xi) \\ \frac{1}{2}[1 - \cos(\eta - \xi)] & (1/\sqrt{2})\sin(\eta - \xi) & \frac{1}{2}[1 + \cos(\eta - \xi)] \end{bmatrix}, \tag{52}$$

where ξ, η are as given in Eq. (49). The normalized envelope-modulation functions are

$$\begin{aligned} E_{\rm mod}(\tau) = {} & (1 - \tfrac{4}{3}k + \tfrac{3}{4}k^2) + (\tfrac{2}{3}k - \tfrac{1}{2}k^2)(\cos\omega_{ab}\tau + \cos\omega_{bc}\tau + \cos\omega_{de}\tau + \cos\omega_{ef}\tau) \\ & - [\tfrac{1}{6}k - \tfrac{1}{6}k^2 + \tfrac{1}{6}k(1 - k^2)^{1/2}][\cos(\omega_{ab} + \omega_{de})\tau + \cos(\omega_{ab} - \omega_{de})\tau + \cos(\omega_{bc} + \omega_{ef})\tau + \cos(\omega_{bc} - \omega_{ef})\tau] \\ & - [\tfrac{1}{6}k - \tfrac{1}{6}k^2 - \tfrac{1}{6}k(1 - k^2)^{1/2}][\cos(\omega_{bc} + \omega_{de})\tau + \cos(\omega_{bc} - \omega_{de})\tau + \cos(\omega_{ab} + \omega_{ef})\tau + \cos(\omega_{ab} - \omega_{ef})\tau] \\ & + \tfrac{1}{4}k^2(\cos\omega_{ac}\tau + \cos\omega_{df}\tau) - \tfrac{1}{24}k^2[\cos(\omega_{ac} + \omega_{df})\tau + \cos(\omega_{ac} - \omega_{df})\tau] \\ & - \tfrac{1}{12}k^2[\cos(\omega_{de} + \omega_{ac})\tau + \cos(\omega_{de} - \omega_{ac})\tau + \cos(\omega_{df} + \omega_{ab})\tau + \cos(\omega_{df} - \omega_{cb})\tau \\ & + \cos(\omega_{df} + \omega_{bc})\tau + \cos(\omega_{df} - \omega_{bc})\tau + \cos(\omega_{ef} + \omega_{ac})\tau + \cos(\omega_{ef} - \omega_{ac})\tau] \ , \end{aligned} \tag{53}$$

$$E_{\mathrm{mod}}(\tau+T)=(1-\tfrac{4}{3}k+\tfrac{3}{4}k^2)+(\tfrac{1}{3}k-\tfrac{1}{4}k^2)[\cos\omega_{ab}\tau+\cos\omega_{bc}\tau+\cos\omega_{de}\tau$$
$$+\cos\omega_{ef}\tau+\cos\omega_{ab}(\tau+T)+\cos\omega_{bc}(\tau+T)+\cos_{de}(\tau+T)+\cos\omega_{ef}(\tau+T)]$$
$$-[\tfrac{1}{6}k-\tfrac{1}{6}k^2+\tfrac{1}{6}k(1-k^2)^{1/2}][\cos\omega_{ab}\tau\cos\omega_{de}(\tau+T)+\cos\omega_{bc}\tau\cos\omega_{ef}(\tau+T)$$
$$+\cos\omega_{de}\tau\cos\omega_{ab}(\tau+T)+\cos\omega_{ef}\tau\cos\omega_{bc}(\tau+T)]-[\tfrac{1}{6}k-\tfrac{1}{6}k^2-\tfrac{1}{6}k(1-k^2)^{1/2}][\cos\omega_{ab}\tau\cos\omega_{ef}(\tau+T)$$
$$+\cos\omega_{bc}\tau\cos\omega_{de}(\tau+T)+\cos\omega_{de}\tau\cos\omega_{bc}(\tau+T)+\cos\omega_{ef}\tau\cos\omega_{ab}(\tau+T)]$$
$$+\tfrac{1}{8}k^2[\cos\omega_{ac}\tau+\cos\omega_{df}\tau+\cos\omega_{ab}(\tau+T)+\cos\omega_{df}(\tau+T)]+\tfrac{1}{24}k^2[\cos\omega_{ac}\tau\cos\omega_{df}(\tau+T)+\cos\omega_{df}\tau\cos\omega_{ac}(\tau+T)]$$
$$-\tfrac{1}{12}k^2[\cos\omega_{ab}\tau\cos\omega_{df}(\tau+T)+\cos\omega_{df}\tau\cos\omega_{ab}(\tau+T)+\cos\omega_{bc}\tau\cos\omega_{df}(\tau+T)$$
$$+\cos\omega_{df}\tau\cos\omega_{bc}(\tau+T)+\cos\omega_{de}\tau\cos\omega_{ac}(\tau+T)+\cos\omega_{ac}\tau\cos\omega_{de}(\tau+T)$$
$$+\cos\omega_{ef}\tau\cos\omega_{ac}(\tau+T)+\cos\omega_{ac}\tau\cos\omega_{ef}(\tau+T)]\,. \qquad (54)$$

In the above equations $k=\sin^2(\eta-\xi)=(\omega_I B/\omega_\alpha\omega_\beta)^2$. Considerable simplifications may be possible in some experimental situations. For example, if k^2 can be neglected, and if the quadrupole splitting is too small to be taken into account at all, we have

$$E_{\mathrm{mod}}(\tau)=1-\tfrac{16}{3}k\sin^2\tfrac{1}{2}\omega_\alpha\tau\sin^2\tfrac{1}{2}\omega_\beta\tau\,, \qquad (55)$$

$$E_{\mathrm{mod}}(\tau,T)=1-\tfrac{4}{3}k\{\sin^2\tfrac{1}{2}\omega_{\alpha b}\tau\ [1-\cos\omega_\beta(\tau+T)]$$
$$+\sin^2\tfrac{1}{2}\omega_\beta\tau[1-\cos\omega_\alpha(\tau+T)]\}\,. \qquad (56)$$

These last expressions are formally similar to the expressions (50) and (51) obtained for $S=\frac{1}{2}$, $I=\frac{1}{2}$.

IX. SUMMARY

Expressions have been obtained for the modulation effect in spin-echo experiments of the two- and three-pulse type by partitioning the matrices which describe the evolution of the quantized system. The initial results are quite general and cover all cases in which the resonance field interaction has the form

$$\hat{\mathcal{H}}_1=\begin{bmatrix}0 & N\\ N^\dagger & 0\end{bmatrix}.$$

They can be used to find envelope-modulation effects in nuclear, electron, or photon echoes. The $\hat{\mathcal{H}}_1$ matrices for systems containing two or more equal adjacent resonance intervals can, if required, be put into the form above by rearranging the rows and columns.

The general results can be simplified very considerably in the more limited number of cases where the submatrix N is proportional to a unitary matrix. Electron transitions split by small nuclear hyperfine interactions belong in this category. The appropriate envelope-modulation formulas are derived with the additional assumption that $\hat{\mathcal{H}}_1$ is large compared with the superhyperfine splitting.

For experimental reasons envelope-modulation effects are only seen when the splitting of the resonance by nuclear interactions is very small.[18] This condition makes it possible to simplify the matrix calculation by diagonalizing the electron spin Hamiltonian separately. Two Hamiltonians having the dimensions $(2I+1)\times(2I+1)$ of the nuclear system can then be constructed and the quantities in the envelope modulation formulas can be derived from them. The case of $S=\frac{1}{2}$, $I=\frac{1}{2}$ is, as might be expected, an especially simple one and is used here to illustrate the general methods of solution. Detailed calculations have also been made for $S=\frac{1}{2}$, $I=1$.

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[1]The envelope of echoes is the function obtained by plotting the echo amplitude against time τ in Fig. 2(a) [or T in Fig. 2(b)].

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[3]A treatment of envelope modulation due to the $\mathcal{J}\vec{I}_1\cdot\vec{I}_2$ coupling is given by A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., Oxford, England, 1961), p. 498.

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[10]Observations made during photon-echo experiments by N. A. Kurnit, I. D. Abella, and S. R. Hartmann [Phys. Rev. Letters 13, 567 (1964)] were subsequently interpreted in terms of an envelope-modulation effect by D. Grischkowsky and S. R. Hartmann [*ibid.* 20, 41 (1968)].

[11]In the subsequent argument the subscript k will be dropped whenever the inhomogeneous nature of the broadening is not explicitly involved.

[12]This is not the same as adopting the "interaction representation." The interaction representation sets up individual coordinate systems rotating with phase factors $e^{i\mathcal{H}_0 t/\hbar}$ for each of the eigenstates. Here we use common coordinate systems for the α states and for the β states, which rotate with phase factors $e^{i\omega t/2}$ and $e^{-i\omega t/2}$, respectively.

[13]A. L. Bloom, Phys. Rev. 98, 1105 (1955).

[14]The eigenfrequencies of $\hat{\mathcal{H}}_0$ will, of course, be given in the rotating coordinate system. For the α and β manifolds $\hat{\mathcal{H}}_0$ will thus consist of the relatively small diagonal elements $\hbar(\omega_{\alpha i}-\frac{1}{2}\omega)$, $\hbar(\omega_{\beta j}+\frac{1}{2}\omega)$.

[15]This time will generally be long compared with the phase memory time for a two-pulse echo. Modulation effects have been seen for ~100 μsec in the stimulated-echo envelope for a sample of lanthanum magnesium double nitrate doped with Ce^{3+} ions. The two-pulse phase memory in the same sample was ~3 μsec (unpublished observation).

[16]The tensor product $M_{1\alpha}\times M_{2\alpha}$ consists of two 2×2 submatrices $M_{1\alpha}$ and $M_{2\alpha}$ arranged on the diagonal of the 4×4 submatrix M. For a discussion of this formalism and for the theorem used later, see A. Messiah, *Quantum Mechanics* (Interscience, New York, 1961), p. 299.

[17]It is usually easier to detect small differences between the eigenfrequencies than to make a precise experimental measurement of the modulation amplitudes.

[18]It is difficult to generate microwave fields H_1 much in excess of 10 G in the low-Q cavities required for short-pulse experiments. Only those intervals which lie in a range ~$2\gamma H_1$ are effectively in resonance and are therefore able to contribute to the modulation effect.

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Paramagnetic Resonance of $^{155}Gd^{3+}$ in a ThO_2 Single Crystal: Study of the Hyperfine Structure (Allowed and Forbidden Lines)

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The hyperfine structure of $^{155}Gd^{3+}$ ions in Th^{4+} substitutional cubic sites of a single crystal of ThO_2 (fluorite structure) has been studied by means of electron-paramagnetic-resonance techniques. The observation of "forbidden" transitions traditionally labeled by $\Delta m = 1$ or 2 is reported. Theoretical calculations using first-order perturbation theory for the hyperfine structure and nuclear Zeeman terms after a numerical diagonalization of the remaining (electronic Zeeman plus crystal-field terms) spin Hamiltonian are in good agreement with experimental results.

INTRODUCTION

The ground state of ions with half-filled shells (S-state ions) is an orbital singlet. When such ions are put in a crystal field, the spin degeneracy is partially removed. Although the electric field acting alone, regardless of its symmetry, cannot split in first order the S state, group-theory considerations[1] show that, even in a cubic field, the degeneracy will be spiit. Electron-paramagnetic-resonance (EPR) results concerning "cubic" spectra of Gd^{3+} ion ($4f^7$, $^8S_{7/2}$) substituted into tetravalent Th or Ce sites in thorium or cerium dioxydes[2-5] are in good agreement with Bethe's predictions.

Forbidden fine-structure transitions with $|\Delta M| > 1$ were also observed. In the case of Gd^{3+}-doped CeO_2, Bir and Vinokurov[6] gave explicit expressions for the angular dependence of the positions and intensities of various forbidden fine-structure lines using first-order perturbation theory in $a/g\mu_B B$, where a is the constant representing the interaction with the crystal field. They only obtained a satisfactory agreement between theory and experiment for the line positions. Nevertheless, their theoretical formulas gave a correct over-all picture of the angular variation of intensity and of the position of intensity maxima and minima.

Previous experiments were done with natural-