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Amplitudes of Superhyperfine Frequencies Displayed in the Electron-Spin-Echo Envelope

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Some of the calculations presented in a previous paper [W. B. Mims, Phys. Rev. B 5, 2409 (1972)] have been extended in order to make it easier to find the amplitudes of the superhyperfine-frequency components in two- and three-pulse envelopes when $I>\frac{1}{2}$. A simple recipe is given for deriving the stimulated-echo result from the two-pulse-echo result. The suppression of frequency components in the stimulated-echo envelope is also considered.

I. INTRODUCTION

Some of the calculations presented in a previous paper[1] (henceforth denoted as I) have been extended in order to make it easier to derive the amplitudes of the superhyperfine-structure (shfs) components in two- and three-pulse-echo envelopes for cases not covered by the explicit formulas given in I. The suppression of shfs frequencies in the three-pulse-echo envelope which occurs for certain values of τ is also considered.

II. EXPANSION OF TRACE EXPRESSIONS

Writing Eq. (38) of I with the appropriate Hermitian conjugate and normalizing to unity at zero time τ between the pulses, we have the two-pulse envelope modulating function

$$E_{\text{mod}}(\tau)=\left(\frac{1}{2(2I+1)}\right)\text{Tr}(Q_\tau^\dagger M^\dagger P_\tau^\dagger M Q_\tau M^\dagger P_\tau M+\text{H. c.}) , \quad (1)$$

where I is the spin of the nucleus giving rise to the shfs and H. c. stands for Hermitian conjugate. P_τ and Q_τ are diagonal $(2I+1)\times(2I+1)$ matrices describing the evolution of the upper (α) and lower (β) manifold of shfs states during the free precession intervals. They consist of elements $(P_\tau)_{ii}\equiv P_{ii}=e^{i\omega_i^{(\alpha)}\tau}$ and $(Q_\tau)_{kk}\equiv Q_{kk}=e^{i\omega_k^{(\beta)}\tau}$. M is a $(2I+1)\times(2I+1)$ unitary matrix which describes the coupling between α and β manifolds caused by the microwave resonance pulses and is defined in I, Eq. (34).[2]

By expanding Eq. (1) and rearranging terms we obtain

$$E_{\text{mod}}(\tau)=\left(\frac{1}{2(2I+1)}\right)\sum_{i,j,k,n}[(P_{ii}P_{jj}^*Q_{kk}Q_{nn}^*)\times(M_{ik}^*M_{in}M_{jn}^*M_{jk})+\text{c. c.}] , \quad (2)$$

where c. c. stands for complex conjugate. This expression can be broken down into a "dc term," terms involving shfs frequencies $\omega_{ij}^{(\alpha)}=\omega_i^{(\alpha)}-\omega_j^{(\alpha)}$ belonging to the upper manifold, terms involving frequencies $\omega_{kn}^{(\beta)}=\omega_k^{(\beta)}-\omega_n^{(\beta)}$ belonging to the lower manifold, and terms involving sums and differences of frequencies belonging to both manifolds. Thus, if we group together products for which $j=i$ and $n=k$, we obtain the dc term

$$\chi_0=\left(\frac{1}{2I+1}\right)\sum_{i,k}|M_{ik}|^4 . \quad (3)$$

Products for which $n=k$ yield terms

$$\sum_{i,j}^{i\neq j}{}' \chi_{ij}^{(\alpha)}\cos\omega_{ij}^{(\alpha)}\tau ,$$

where

$$\chi_{ij}^{(\alpha)}=\left(\frac{2}{2I+1}\right)\sum_k |M_{ik}|^2|M_{jk}|^2 . \quad (4)$$

By setting $j=i$ we obtain terms

$$\sum_{k,n}^{k\neq n}{}' \chi_{kn}^{(\beta)}\cos\omega_{kn}^{(\beta)}\tau ,$$

where

$$\chi_{kn}^{(\beta)} = \left(\frac{2}{2I+1}\right)\sum_i |M_{ik}|^2 |M_{in}|^2 . \quad (5)$$

Finally, the products remaining in (2) after the removal of (3)–(5) correspond to the sum and difference frequency terms

$$\sum_{i,j}^{i\neq j}{}' \sum_{k,n}^{k\neq n}{}' \chi_{ij,kn}^{(\alpha,\beta)} [\cos(\omega_{ij}^{(\alpha)} + \omega_{kn}^{(\beta)})\tau + \cos(\omega_{ij}^{(\alpha)} - \omega_{kn}^{(\beta)})\tau] ,$$

where

$$\chi_{ij,kn}^{(\alpha,\beta)} = \left(\frac{2}{2I+1}\right)\mathrm{Re}[M_{ik}^* M_{in} M_{jn}^* M_{jk}] . \quad (6)$$

The notation $\sum'$ is used to indicate that any given pair of indices i, j or k, n is to be assigned in one order only, and any given frequency is to be considered once only in the sum. The appearance of pairs of identical terms in the sum (for example, $\chi_{ij}^{(\alpha)} \cos\omega_{ij}^{(\alpha)}\tau$ and $\chi_{ji}^{(\alpha)} \cos\omega_{ji}^{(\alpha)}\tau$) has been taken into account in arriving at the normalizing factors $2/(2I+1)$.

Some general properties of $E_{\mathrm{mod}}(\tau)$ could be inferred more or less directly from (1). The function is even in τ, as may be verified by setting $P_\tau \to P_\tau^\dagger$, $Q_\tau \to Q_\tau^\dagger$ and by applying the theorem $\mathrm{Tr}(ABC) = \mathrm{Tr}(BCA)$. Also it is real and will therefore contain cosine terms only. Likewise, it can be shown by setting $P_\tau \to P_\tau^\dagger$ (or $Q_\tau \to Q_\tau^\dagger$) that the coefficient of a sum frequency is the same as the coefficient of the corresponding difference frequency.

A relationship which is useful for checking results in the more complicated cases exists between the summed amplitudes $S^{(\alpha)}$, $S^{(\beta)}$ of the electron-nuclear-double-resonance frequencies belonging to the upper and lower manifolds, the sum $S^{(\alpha,\beta)}$ of the amplitudes of all the combination frequencies and the dc term χ_0. We find that

$$S^{(\alpha)} = S^{(\beta)} = -S^{(\alpha,\beta)} = 1 - \chi_0 . \quad (7)$$

The equation $S^{(\alpha)} = 1 - \chi_0$ follows readily from the fact that M is a unitary matrix. Substituting from Eq. (4), we obtain

$$S^{(\alpha)} = \frac{1}{2}\sum_{i,j}^{i\neq j} \chi_{ij}^{(\alpha)} = \left(\frac{1}{2I+1}\right)\sum_{i,j}^{i\neq j} |M_{ik}|^2 |M_{jk}|^2$$

$$= \left(\frac{1}{2I+1}\right)\left(\sum_{i,j,k} |M_{ik}|^2 |M_{jk}|^2 - \sum_{i,j} |M_{ik}|^4\right)$$

In this expression the sum

$$\sum_{i,j,k} |M_{ik}|^2 |M_{jk}|^2 = \sum_{i,k} |M_{ik}|^2 \sum_j |M_{jk}|^2$$

$$= \sum_{i,k} |M_{ik}|^2 = 2I+1 .$$

The sum $[1/(2I+1)]\sum_{i,j}|M_{ik}|^4$ is the term χ_0 in (3). Similarly, it can be shown that $S^{(\beta)} = 1 - \chi_0$. The remainder of (7) follows from the normalization of the echo envelope to unity at $\tau = 0$, i.e., from the equation $\chi_0 + S^{(\alpha)} + S^{(\beta)} + S^{(\alpha,\beta)} = 1$.

III. DERIVATION OF STIMULATED-ECHO ENVELOPE

Writing Eq. (39) of I complete with Hermitian conjugate and appropriate normalizing factor, we have the envelope function

$$E_{\mathrm{mod}}(\tau, T) = \left(\frac{1}{4(2I+1)}\right)\mathrm{Tr}[Q_\tau^\dagger M^\dagger (P_T^\dagger P_\tau^\dagger) M Q_\tau M^\dagger (P_T P_\tau) M + (Q_T^\dagger Q_\tau^\dagger) M^\dagger P_\tau^\dagger M (Q_T Q_\tau) M^\dagger P_\tau M + \mathrm{H.\ c.}] . \quad (8)$$

The quantities in parentheses $P_T P_\tau$, etc., are diagonal matrices containing elements of the form $\exp i\omega_i^{(\alpha)}(T+\tau)$.

It may be noted that (8) can be obtained from (1) by writing (1) twice, once with $P_T P_\tau$ substituted for P_τ and once with $Q_T Q_\tau$ substituted for Q_τ and halving the result. This suggests the following recipe by means of which the expansion of (8) can be derived from the expansion of (1) without the need for a new *ab initio* calculation.

(i) Expand (1) in such a way that $\cos\omega_{ij}^{(\alpha)}\tau$ (from P_τ) and $\cos\omega_{kn}^{(\beta)}\tau$ (from Q_τ) appear as separate factors. [This merely involves replacing $\cos(\omega_{ij}^{(\alpha)} + \omega_{kn}^{(\beta)})\tau + \cos(\omega_{ij}^{(\alpha)} - \omega_{kn}^{(\beta)})\tau$ in (6) with $2\cos\omega_{ij}^{(\alpha)}\tau \cos\omega_{kn}^{(\beta)}\tau$.]

(ii) Write the expression with $\cos\omega_{ij}^{(\alpha)}\tau$ changed to $\cos\omega_{ij}^{(\alpha)}(T+\tau)$.

(iii) Write the expression again with $\cos\omega_{kn}^{(\beta)}\tau$ changed to $\cos\omega_{kn}^{(\beta)}(T+\tau)$.

(iv) Add the results of steps (ii) and (iii) and renormalize by dividing by 2.

Applying this recipe, we have

$$E_{\mathrm{mod}}(\tau, T) = \chi_0 + \frac{1}{2}\sum_{i,j}^{i\neq j}{}' \chi_{ij}^{(\alpha)}[\cos\omega_{ij}^{(\alpha)}\tau + \cos\omega_{ij}^{(\alpha)}(T+\tau)] + \frac{1}{2}\sum_{k,n}^{k\neq n}{}' \chi_{kn}^{(\beta)}[\cos\omega_{kn}^{(\beta)}\tau + \cos\omega_{kn}^{(\beta)}(T+\tau)] + \sum_{i,j}^{i\neq j}{}' \sum_{k,n}^{k\neq n}{}' \chi_{ij,kn}^{(\alpha,\beta)}[\cos\omega_{ij}^{(\alpha)}(T+\tau)\cos\omega_{kn}^{(\beta)}\tau + \cos\omega_{ij}^{(\alpha)}\tau\cos\omega_{kn}^{(\beta)}(T+\tau)] , \quad (9)$$

where the coefficients are as given in (3)–(6).

IV. PARTIAL SUPPRESSION OF FREQUENCIES IN STIMULATED-ECHO ENVELOPE

It is usually convenient to perform experiments by setting τ to a fixed value and allowing T to vary in order to trace out a stimulated-echo envelope. The amplitudes of the observed frequency components will, however, depend partly on the choice of τ and may vanish entirely for certain values of τ. Factoring out $\cos\omega_{ij}^{(\alpha)}(T+\tau)$ and $\cos\omega_{kn}^{(\beta)}(T+\tau)$ in Eq. (9), and dropping terms not governed by these factors, we have

$$E_{\mathrm{mod},\tau}(T)=\sum_{i,j}^{i\neq j}{}'\cos\omega_{ij}^{(\alpha)}(T+\tau)\left(\tfrac{1}{2}\chi_{ij}^{(\alpha)}+\sum_{k,n}^{k\neq n}{}'\chi_{ij,kn}^{(\alpha,\beta)}\cos\omega_{kn}^{(\beta)}\tau\right)+\sum_{k,n}^{k\neq n}{}'\cos\omega_{kn}^{(\beta)}(T+\tau)\left(\tfrac{1}{2}\chi_{kn}^{(\beta)}+\sum_{i,j}^{i\neq j}{}'\chi_{ij,kn}^{(\alpha,\beta)}\cos\omega_{ij}^{(\alpha)}\tau\right). \quad (10)$$

The amplitudes of any frequency in the α manifold will thus be a periodic function involving τ and the frequencies in the β manifold and vice versa. The partial suppression of frequencies in the stimulated-echo envelope is obviously closely related to the appearance of sum and difference frequencies in the two-pulse-echo envelope. Both properties can be useful experimentally in deciding whether two shfs frequencies belong to the same or to opposite electron-spin manifolds.

The suppression effect may be illustrated by taking the case of $I=\frac{1}{2}$ as an example. In this case the coefficients are $\chi_{12}^{(\alpha)}=\chi_{12}^{(\beta)}=2|v|^2|u|^2$ and $\chi_{12,12}^{(\alpha,\beta)}=-|v|^2|u|^2$, where v, u are elements of the 2×2 matrix M as in I, Eq. (44). Equation (10) becomes

$$E_{\mathrm{mod},\tau}(T)=|v|^2|u|^2[(1-\cos\omega_\beta\tau)\cos\omega_\alpha(T+\tau)+(1-\cos\omega_\alpha\tau)\cos\omega_\beta(T+\tau)], \quad (11)$$

where ω_α, ω_β are the single shfs frequencies in the α and β manifolds, respectively. When τ corresponds to a whole number of cycles of ω_α, the companion frequency ω_β in the opposite manifold is entirely suppressed and vice versa.

Suppression of frequency components will be harder to detect and to interpret in the more general case when $I>\frac{1}{2}$. Obvious suppression effects may, however, be commoner in practice than Eq. (10) would suggest. Let us for example consider the situation when the transitions between the α and β manifolds are clearly denotable as either allowed or forbidden. The *numbering* of the levels in the two manifolds, is, of course, arbitrary, and one can write the matrix M so that the diagonal elements correspond to the allowed transitions and the off-diagonal elements to the forbidden ones. M can then be approximated by $1+i\epsilon H$, where ϵ is a small number and H is a Hermitian matrix derived from the state mixing terms which give rise to the forbidden transitions. Referring to Eq. (4) we see that the only terms $\simeq\epsilon^2$ in the sum are $|M_{ii}|^2|M_{ji}|^2$ and $|M_{ij}|^2|M_{jj}|^2$. But, since $M\simeq 1+i\epsilon H$, $M_{ij}=-M_{ji}^*$ and $\chi_{ij}^{(\alpha)}\simeq(4/2I+1)|M_{ij}|^2$. From Eq. (6) we likewise find only one term $\chi_{ij,ij}^{(\alpha,\beta)}=(2/2I+1)\,\mathrm{Re}[M_{ij}M_{ji}]\simeq(2/2I+1)|M_{ij}|^2$ which is $\sim\epsilon^2$. Substituting these approximate values in (10), we have

$$E_{\mathrm{mod},\tau}(T)\simeq\left(\frac{2}{2I+1}\right)\sum_{i,j}^{i\neq j}{}'|M_{ij}|^2\times[(1-\cos\omega_{ij}^{(\beta)}\tau)\cos\omega_{ij}^{(\alpha)}(T+\tau)+(1-\cos\omega_{ij}^{(\alpha)}\tau)\cos\omega_{ij}^{(\beta)}(T+\tau)], \quad (12)$$

an expression which is similar to (11). A situation of this kind exists when the shfs states are more or less good eigenstates of I_z slightly admixed by S_xI_x, S_zI_y terms in the electron nuclear Hamiltonian or, conversely, when the $\vec{S}\cdot\vec{I}$ term is the main quantizing term and the nuclear Zeeman term causes the mixing. Some caution must of course be exercised when approximating (10) by (12) to ensure that higher-order terms derived from other matrix elements do not exceed any of the terms in $|M_{ij}|^2$.

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[1]W. B. Mims, Phys. Rev. B 5, 2409 (1972).

[2]A procedure for computing the elements of M is outlined in Ref. 1, Sec. VI.