Theory of spectral diffusion decay using an uncorrelated-sudden-jump model*

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The decay behavior of the one-pulse free-induction, two-pulse echo, and three-pulse stimulated-echo signals is calculated for a system of A spins, isolated from each other, whose local field fluctuates because of the uncorrelated flipping of a system of B spins randomly located. The decay behavior is obtained in closed form and is valid for all time. We find that the dipolar line shape, which is the Fourier transform of the free-induction decay, is always narrowed by the flipping of the B spins. The two-pulse echo first decreases as the B-spin-flip rate W increases and then increases as W is further increased. Except for the free-induction decay our formulas coincide in the limits of very short and very long times with those calculated by Klauder and Anderson and by Mims.

I. INTRODUCTION

One of the most intriguing effects in the study of both spin resonance and the transient excitation of optical resonance is the relaxation behavior of the signals generated.[1-3] Although one speaks freely of the decay in terms of a single-phase memory time the decay is usually not characterized by a simple exponential function. One important mechanism is the so-called spectral diffusion[4] which is caused by the fluctuation of the local field at the site of the resonance ions. The local field at an atomic site has many contributions of different origin: strain fields, dipolar fields, hyperfine fields, etc. For a material containing unpaired atomic spins which interact strongly either with each other or with the lattice vibrations of the sample, the source of the fluctuating local field will be the flipping of those unpaired spins.

The problem of spectral diffusion decay in spin resonance has been studied by many workers.[4,5] For simplicity, the samples are usually classified into two kinds. Those in which the flipping of the neighboring ions is mainly caused by a spin-lattice interaction are called T_1 samples (T_1 is the spin-lattice relaxation time), and those in which the flipping is caused by a spin-spin interaction are called T_2 samples (T_2 is the spin-spin relaxation time). Obviously a T_1 sample is simpler to treat and this is the case that we restrict ourself to in this paper.

Two models have been proposed. In the model presented by Klauder and Anderson,[4] the fluctuation of the local field is described by means of a stochastic model, and wide classes of both Markoffian and non-Markoffian distributions are used to predict the results of transient electron-spin-resonance experiments. In the particular case where the local field is due to neighboring magnetic dipoles, the conditional distribution for the spin precessional frequency is argued to be Lorentzian in the short-time limit. This distribution function leads to a spin-echo behavior which is in good agreement with experiment.[2]

The other model, utilized by Mims,[5] is called the Gauss-Markoffian model. The echo amplitude is obtained as a double average over (i) an ensemble of A spins having identical spatial B-spin environments and (ii) all possible such environments (A environments). The second average is calculated assuming random placement, while it is argued that the first average is effected by assuming that the z component of the B-spin dipole moment is a Gaussian random variable and its correlation function is Markoffian. The echo amplitude is calculated for arbitrary excitation pulse separation but it is stressed that only the long-time results are physically valid.

Our model is elementary. Our essential assumptions are only the following.

(i) The spin placement is random.

(ii) The A spins, whose signal we observe, are isolated from each other.

(iii) The fluctuating field at the A-spin sites is due to the dipolar field of the B spins which are flipping between two quantum states at random, at an average rate W.

(iv) The A and B spins can be treated as spin-$\frac{1}{2}$ systems. By averaging first over all spin configurations we express the free-induction or echo amplitude in terms of a sum over all possible B-spin-flip sequences which we evaluate to obtain a result which is valid for all time. Our model is such that it corresponds realistically to what one would expect when using a T_1 sample. Our results coincide exactly with those of Klauder and Anderson in the case of two- and three-pulse echoes in the short-time limit and with Mims for the two-pulse echo in the long-time limit.

Our calculations involve isolated A spins interacting with B spins which are flipping. In practice the A-spin resonance is further broadened by other spin species, crystal field strains, etc. As long as the additional broadening is static (inhomogeneous) the effect on all our results is elementary. For the free-induction decay, an additional static inhomogeneity would have the effect of multiplying our result by the Fourier transform of that inhomogeneity line shape. There is no effect of the additional inhomogeneity on the echo-amplitude calculations since we restrict ourselves to calculating the amplitude of the echo at τ_e, the time the echo is expected under idealized conditions.[6] The static inhomogeneity modifies the shape of the echo by attenuating it for times other than τ_e. The static inhomogeneity thereby serves to sharpen and better define the echo; it does not change its value at τ_e.

In Sec. II we begin by writing the expression for the free-induction signal amplitude for a single A spin interacting with a single B spin. The B spin flips at random at an average rate W. A formal expression for the general free-induction signal is obtained by summing over all B spins and by averaging over all possible A environments. Our result is expressed in terms of a sum over all possible B-spin-flip sequences. The leading terms involving zero or just one spin flip are calculated explicitly and show that the initial effect of B-spin flipping is to lengthen the free-induction decay. We recast the general spin-flip term by a reordering procedure and reduce it to an elementary integral, enabling us to sum over all spin-flip terms. Our result is in terms of modified Bessel functions of zero and first order and shows that the effect of the B-spin flips is always to lengthen the free-induction decay.

In Sec. III we calculate the two-pulse echo amplitude. We proceed as in Sec. II and obtain our result in terms of a sum over all B-spin-flip sequences. By evaluating the leading term explicitly we obtain a short-time result which is identical to the result of Klauder and Anderson. We evaluate the general spin-flip term for an odd number of spin flips by demonstrating an equivalence with the general spin-flip term evaluated in Sec. II. We evaluate the long-time limit by recognizing that it is only necessary to evaluate the term corresponding to the average number of flips $2W\tau$ that one would expect in the time 2τ between the first excitation pulse and echo. Our result agrees with the work of Mims. The general spin-flip term, corresponding to an even number of spin flips, is evaluated by obtaining a differential equation which relates the even and odd spin-flip terms. This differential equation is derived in Appendix A. The sum over all spin-flip terms is evaluated in terms of modified Bessel and Struve functions and it is demonstrated that in both the short- and long-time limits it reduces to results previously obtained.

In Sec. IV we evaluate the three-pulse stimulated-echo decay amplitude. This calculation is straightforward as we are able to utilize the results of Sec. II and III directly.

The last section (Sec. V) is the discussion. All our results are expressed in terms of two generalized dimensionless functions $G(z)$ and $K(z)$ with dimensionless arguments z. We plot and tabulate these functions and discuss all our results in terms of their behavior. We explain why one should always expect line narrowing for our model. We give a physical explanation for the dipping of the two-pulse spin-echo relaxation time.[7,8]

We obtain a rather large signal amplitude (the word echo might be misleading) at the normal position of the stimulated echo, in the case where $WT \gg 1$, when T is the time between the second and third excitation pulses even when the only contribution to the local field is due to the flipping B spins. We explain how this arises in a natural way.

II. FREE-INDUCTION DECAY

We start by considering an A and a B spin, with dipole moment operators $\vec{\mu}_A$ and $\vec{\mu}_B$ and separated by a distance $\vec{r}$, which interact through the dipolar interaction:

$$\mathcal{H}_{AB} = \vec{\mu}_A \cdot \vec{\mu}_B / r^3 - 3\vec{\mu}_A \cdot \vec{r}\vec{\mu}_B \cdot \vec{r}/r^5 , \qquad (2.1)$$

and we assume that their resonance frequencies are so large and disparate that we need only use the diagonal part of this interaction. We apply a 90° excitation pulse, the effect of which is to take an A spin initially in the ground state $\psi_{\downarrow}^{(A)}$, and put it into a linear superposition of the A-spin ground $\psi_{\downarrow}^{(A)}$ and excited $\psi_{\uparrow}^{(A)}$ states. We write the resulting A-spin wave function in a frame of reference at resonance with the average A-spin frequency, i.e.,

$$\psi^{(A)}(\tau) = (1/\sqrt{2}) \{\exp[-\tfrac{1}{2}i \int_0^{\tau} \omega(t)\, dt]\} \psi_{\uparrow}^{(A)} + (1/\sqrt{2}) \{\exp[\tfrac{1}{2}i \int_0^{\tau} \omega(t)\, dt]\} \psi_{\downarrow}^{(A)}, \qquad (2.2)$$

where

$$\omega(t) = 2\mu_A \mu_B(t)(1 - 3\cos^2\theta)\hbar^{-1} r^{-3} . \qquad (2.3)$$

The angle between the static applied magnetic field and $\vec{r}$ is given by θ. In the expression for $\omega(t)$ the magnetic moment μ_A is constant in time while μ_B jumps between the values $\pm \mu_B$, at random, at a rate W.

The free-induction-decay amplitude is then the matrix element of the dipole moment operator in the state $\psi^{(A)}(\tau)$ and is

$$f(\tau, r, \theta, \omega(t)) = \exp[i \int_0^\tau \omega(t)\, dt], \tag{2.4}$$

where it is to be understood that we take the real part of the exponential term.[4]

The many-spin solution is obtained from the two-spin solution by averaging over all A- and B-spin sites. We must also average over all B-spin-flip histories. We incorporate these operations into our notation by writing the free-induction amplitude as

$$F(\tau) = \underline{\mathfrak{a}} \left\langle\!\!\left\langle \exp\left[i \sum_\beta \omega_{\alpha,\beta} \int_0^\tau h(t) dt \right] \right\rangle\!\!\right\rangle_\alpha, \tag{2.5}$$

where

$$\omega_{\alpha,\beta} = 2\mu_A \mu_B (1 - 3\cos^2\theta_{\alpha,\beta}) \hbar^{-1} r^{-3}_{\alpha,\beta} \tag{2.6}$$

and the subscripts α and β refer to A- and B-spin sites, respectively. The bracket $\langle\langle\ \rangle\rangle_\alpha$ represents the operation of averaging over A-spin sites. We have defined $h(t)$ through $\mu_B(t) = \mu_B h(t)$, so that $h(t)$ has unity magnitude and changes sign every time its representative B spin flips. The operator $\underline{\mathfrak{a}}$ performs the average over all B-spin-flip histories.

The average[9] over all spin sites is particularly simple, as we assume that both the A and B spins have equal probability of being located in any point in space and that the A-spin environments are uncorrelated with each other. This average is obtained by factoring the exponential into a product of terms corresponding to a fixed A spin and all the B spins in the system. We then average each B-spin position over space. The result is independent of which A spin we pick as a reference. We indicate the above operation in the expression for the free-induction decay as[9,10]

$$F(\tau) = \prod_{\beta=1} \underline{\mathfrak{a}} \left\langle \exp\left[i\omega_{\alpha,\beta} \int_0^\tau h(t) dt \right] \right\rangle, \tag{2.7}$$

where

$$\langle Q_{\alpha,\beta} \rangle = (2\pi/V) \int_0^\infty r^2_{\alpha,\beta} dr_{\alpha,\beta} \int_0^\pi \sin\theta_{\alpha,\beta} d\theta_{\alpha,\beta} Q_{\alpha,\beta}, \tag{2.8}$$

N is the number of B spins in the sample, and V is the volume of the sample.

We note that $\underline{\mathfrak{a}} \cdot 1$ represents the average of unity over all spin-flip histories and therefore must itself be unity. We can therefore write

$$F(\tau) = \{1 - (1/N) N \underline{\mathfrak{a}} \times \langle 1 - \exp[i\omega_{\alpha,\beta} \int_0^\tau h(t) dt] \rangle\}^N . \tag{2.9}$$

Since $N\langle Q_{\alpha,\beta}\rangle$ is independent of N [Eq. (2.9)] for large N, $F(\tau)$ becomes

$$F(\tau) = \exp\{N \underline{\mathfrak{a}} \langle 1 - \exp[i\omega_{\alpha,\beta} \int_0^\tau h(t)\, dt] \rangle\}. \tag{2.10}$$

We complete the operations of averaging over spin sites by using

$$\int_{-\infty}^{\infty} (1 - e^{iCx}) x^{-2}\, dx = \pi |C|$$

and

$$\int_{-1}^{1} |1 - 3\cos^2\theta|\, d(\cos\theta) = 8/3\sqrt{3}$$

to obtain[5,9,10]

$$F(\tau) = \exp[-\Delta\omega_{1/2} \underline{\mathfrak{a}} \mid \int_0^\tau h(t) dt \mid], \tag{2.11}$$

where[11]

$$\Delta\omega_{1/2} = [16\pi^2/(9\sqrt{3})] n \mu_\alpha \mu_\beta \hbar^{-1}.$$

Here, n ($=N/V$) is the number density of B spins.

It will be convenient for what follows to use a more compact notation. We define

$$\mathfrak{a}^{(h)}(\tau) = \underline{\mathfrak{a}} \mid \int_0^\tau h(t)\, dt \mid, \tag{2.12}$$

then

$$F(\tau) = \exp[-\Delta\omega_{1/2} \mathfrak{a}^{(h)}(\tau)]. \tag{2.13}$$

The operator $\underline{\mathfrak{a}}$ averages over all B-spin-flip histories; it is an average over the probability that a B spin does not flip, that it flips only once, that it flips only twice, etc. We call the B-spin flip rate W so that the probability that the B spin does not flip in a time τ is $e^{-W\tau}$. The probability that it flips just once in the time τ and that the flip occurs in the interval between t_1 and $t_1 + dt_1$ is $e^{-W\tau} W\, dt_1$. The probability that it flips just twice in the time τ, once in the time inverval t_1 to $t_1 + dt_1$ and then once again in the later time interval t_2 to $t_2 + dt_2$, is $e^{-W\tau} W\, dt_1\, W\, dt_2$ and so on. The operator $\underline{\mathfrak{a}}$ is therefore a sum of operators; accordingly we define $\underline{\mathfrak{a}}_\gamma$ through the equation

$$\underline{\mathfrak{a}} = \sum_{\gamma=0}^{\infty} \underline{\mathfrak{a}}_\gamma, \tag{2.14}$$

so that $\underline{\mathfrak{a}}_\gamma$ gives the γ-flip contribution to $\underline{\mathfrak{a}}$. In a similar manner we define

$$\mathfrak{a}^{(h)}(\tau) = \sum_{\gamma=0}^{N} \mathfrak{a}_\gamma^{(h)}, \tag{2.15}$$

where we have suppressed the dependence of $\mathfrak{a}_\gamma^{(h)}$ on τ.

The quantity $\underline{\mathfrak{a}}_\gamma \cdot 1$ is just the probability that there will be a total of γ B-spin flips and is

$$\underline{\mathfrak{a}}_\gamma \cdot 1 = e^{-W\tau} W^\gamma \int_0^\tau dt_1 \int_{t_1}^\tau dt_2 \cdots \int_{t_{\gamma-1}}^\tau dt_\gamma = e^{-W\tau} (W\tau)^\gamma / \gamma!, \tag{2.16}$$

so that

$$\underline{\mathfrak{a}} \cdot 1 = e^{-W\tau} \sum_{\gamma=0}^{\infty} \frac{(W\tau)^\gamma}{\gamma!} = 1,$$

as we argued earlier.

The operator $\underline{\mathfrak{A}}_\gamma$ on $|\int_0^\tau h(t)dt|$ puts restrictions on $h(t)$ which we make explicit in writing

$$\mathfrak{A}_\gamma^{(h)} = \underline{\mathfrak{A}}_\gamma \left| \int_0^\tau h(t)dt \right|$$

$$= e^{-W\tau} W^\gamma \int_0^\tau dt_1 \int_{t_1}^\tau dt_2 \cdots \int_{t_{\gamma-1}}^\tau dt_\gamma \left| \int_0^\tau h_\gamma(t)\, dt \right|, \tag{2.17}$$

where

$$h_\gamma(t) = (\pm)\, 1 \text{ for } t_{\kappa-1} < t < t_\kappa \text{ for } \kappa\binom{\text{odd}}{\text{even}},$$

$$t_0 = 0, \quad t_{\gamma+1} = 2\tau,$$

except that

$$\mathfrak{A}_0^{(h)} = \underline{\mathfrak{A}}_0 = e^{-W\tau}.$$

The problem of evaluating the free-induction-decay amplitude [Eq. (2.13)] comes first in evaluating the general term $\mathfrak{A}_\gamma^{(h)}$ and then from evaluating $\mathfrak{A}^{(h)}(\tau)$ from the sum over all γ. For short times such that $W\tau \ll 1$ the problem is quite trivial since we need only evaluate the leading nonzero terms in the expansion of $\mathfrak{A}_\gamma^{(h)}$. If we restrict ourselves to the first two terms, then

$$F(\tau) = \exp[-\Delta\omega_{1/2}(\mathfrak{A}_0^{(h)} + \mathfrak{A}_1^{(h)})] \tag{2.18}$$

for $W\tau \ll 1$.

We can calculate $\mathfrak{A}_0^{(h)}$ and $\mathfrak{A}_1^{(h)}$ directly. We obtain

$$\mathfrak{A}_0^{(h)} = \mathfrak{A}_0 \left| \int_0^\tau h(t)dt \right|$$

$$= e^{-W\tau} \left| \int_0^\tau h_0(t)dt \right| = e^{-W\tau}\tau,$$

where we have used $h_0(t) = 1$ and

$$\mathfrak{A}_1^{(h)} = \underline{\mathfrak{A}}_0 \left| \int_0^\tau h(t)dt \right| = e^{-W\tau} W \int_0^\tau dt_1 \left| \int_0^\tau h_1(t)\, dt \right|.$$

From the definition of $h_1(t)$,

$$\int_0^\tau h_1(t)dt = t_1 - (\tau - t_1) = 2t_1 - \tau,$$

so that

$$\mathfrak{A}_1^{(h)} = \tfrac{1}{2} e^{-W\tau} W\tau^2$$

and $F(\tau)$ becomes

$$F(\tau) = \exp[-\Delta\omega_{1/2}\, e^{-W\tau}\tau(1 + \tfrac{1}{2}W\tau)], \tag{2.19}$$

or on expanding the exponential inside the brackets

$$F(\tau) = \exp[-\Delta\omega_{1/2}\tau(1 - \tfrac{1}{2}W\tau)] \tag{2.20}$$

for $W\tau \ll 1$.

In lowest order the free-induction-decay signal behaves like a simple exponential, as is well known. The effect of the B-spin flips is to lengthen the free-induction decay. The correction term $\frac{1}{2}W\tau$ in Eq. (2.20) is new.

We now calculate the free-induction decay $F(\tau)$ without restrictions. We require $\mathfrak{A}^{(h)}(\tau)$, which is a sum over the $\mathfrak{A}_\gamma$'s. The term $\mathfrak{A}_\gamma^{(h)}$ involves γ spin flips and is expressed through Eqs. (2.12), (2.14), and (2.15) as

$$\mathfrak{A}_\gamma^{(h)} = \underline{\mathfrak{A}}_\gamma \left| \int_0^\tau h(t)dt \right|$$

$$= e^{-W\tau} W^\gamma \int_0^\tau dt_1 \int_{t_1}^\tau dt_2 \cdots \int_{t_{\gamma-1}}^\tau dt_\gamma \left| \int_0^\tau h_\gamma(t)dt \right|, \tag{2.21}$$

where $h_\gamma(t)$ is defined in Eq. (2.17).

For $\gamma = 5$ we illustrate $h_\gamma(t)$ in Fig. 1(a), counting that part above the zero line as positive and the other part as negative. The total shaded area represents $\int_0^\tau h_5(t)\, dt$. We note that an integration over the t_α's is equivalent to an integration over the spin-flip intervals. Consequently we can reorder the t_α's so that all the intervals in which $h_\gamma(t)$ is positive come first and the other intervals come later just as shown in Fig. 1(b). This defines a new $h_\gamma^*(t)$ [see Fig. 1(b)] such that

$$h_\gamma^*(t) = +1, \quad 0 < t < t_\kappa$$

$$h_\gamma^*(t) = -1, \quad t_\kappa < t < \tau$$

where $\kappa = \mu$ if $\gamma = 2\mu$ or if $\gamma = 2\mu + 1$ (μ is an integer) and we have relabeled the t variable. We do not change notation with respect to the t variable since it is a dummy variable.

But now

$$\int_0^\tau h_\gamma^*(t)dt = 2t_\kappa - \tau,$$

therefore

$$\mathfrak{A}_\gamma^{(h)} = e^{-W\tau} W^\gamma \int_0^\tau dt_1 \int_{t_1}^\tau dt_2 \cdots \int_{t_{\gamma-1}}^\tau dt_\gamma \left| 2t_\kappa - \tau \right|. \tag{2.22}$$

This integral is simple if we integrate over the variable t_κ last. Then,

$$\mathfrak{A}_\gamma^{(h)} = e^{-W\tau} W^\gamma \int_0^\tau dt_\kappa \left(\int_0^{\tau_\kappa} dt_1 \int_{t_1}^{\tau_\kappa} dt_2 \cdots \int_{t_{\kappa-2}}^{\tau_\kappa} dt_{\kappa-1} \right)$$

$$\times \left(\int_{t_\kappa}^\tau dt_{\kappa+1} \int_{t_{\kappa+1}}^\tau dt_{\kappa+2} \cdots \int_{t_{\gamma-1}}^\tau dt_\gamma \right) \left| 2t_\kappa - \tau \right| \tag{2.23}$$

or

$$\mathfrak{A}_\gamma^{(h)} = e^{-W\tau} W^\gamma \int_0^\tau dt_\kappa P_\gamma(t_\kappa) \left| 2t_\kappa - \tau \right|.$$

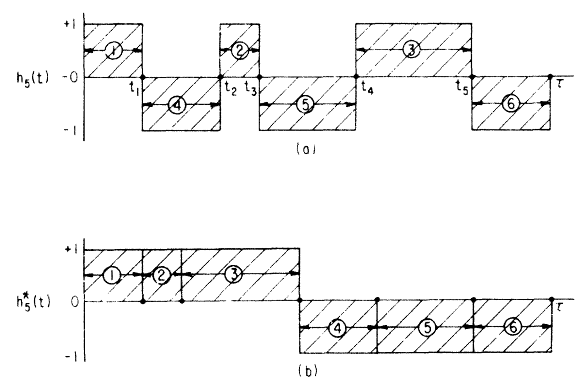

FIG. 1. Reordering of spin-flip intervals to simplify calculation of $\mathfrak{A}_\gamma^{(h)}$: (a) illustration of $h_\gamma(t)$ for $\gamma = 5$ with B-spin flips at t_1, t_2, ..., t_5; (b) reordering spin-flip intervals of (a) to generate the simplified function $h_\gamma^*(t)$.

The evaluation of $P_\gamma(t)$ is elementary; the result is

$$P_{2\eta}(t) = t^\eta(\tau - t)^{\eta-1}/\eta!(\eta-1)!,$$
$$P_{2\eta+1}(t) = t^\eta(\tau - t)^\eta/\eta!\eta! . \qquad (2.24)$$

The remaining integration is just over t_κ. We obtain

$$\mathfrak{a}_{2\eta}^{(h)} = e^{-W\tau}\tau\frac{(W\tau/2)^{2\eta}}{(\eta!)^2},$$
$$\mathfrak{a}_{2\eta+1}^{(h)} = e^{-W\tau}\tau\frac{(W\tau/2)^{2\eta+1}}{\eta!(\eta+1)!} . \qquad (2.25)$$

The quantity of interest $\mathfrak{a}^{(h)}(\tau)$ is the sum over all η. These sums we recognize in terms of the expansion of the modified Bessel functions $I_\nu(z)$:

$$I_\nu(z) = e^{-i\pi\nu/2}(\tfrac{1}{2}e^{i\pi/2}z)^\nu \sum_{\mu=0}^{\infty}\frac{(\frac{1}{2}z)^{2\mu}}{\mu!(\mu+\nu)!} \qquad (2.26)$$

for integral ν.[12] We obtain

$$\mathfrak{a}_{\text{even}}^{(h)} = \sum_{\eta=0}^{\infty}\mathfrak{a}_{2\eta}^{(h)} = e^{-W\tau}\tau I_0(W\tau), \qquad (2.27)$$

$$\mathfrak{a}_{\text{odd}}^{(h)} = \sum_{\eta=0}^{\infty}\mathfrak{a}_{2\eta+1}^{(h)} = e^{-W\tau}\tau I_1(W\tau), \qquad (2.28)$$

and $F(\tau)$ [Eq. (2.13)] becomes

$$F(\tau) = \exp\{-\Delta\omega_{1/2}\tau e^{-W\tau}[I_0(W\tau) + I_1(W\tau)]\} . \qquad (2.29)$$

As a check we use Eq. (2.26) in the limit $W\tau \ll 1$ to write

$$I_0(W\tau) + I_1(W\tau) = 1 + \tfrac{1}{2}W\tau, \qquad (2.30)$$

so that we recover Eq. (2.20). In the limit $W\tau \gg 1$ we can use[12]

$$I_\nu(z) = (2\pi z)^{-1/2}e^z[1 - (4\nu^2 - 1)/8z + \cdots], \qquad (2.31)$$

which is independent of ν in lowest order and which is good for $z \gg 1$. We obtain, in lowest order,

$$F(\tau) = \exp[-(2/\pi)^{1/2}\Delta\omega_{1/2}W^{-1/2}\tau^{1/2}] \qquad (2.32)$$

for $W\tau \gg 1$.

III. TWO-PULSE ECHO

The two-pulse echo is obtained by applying a 180° excitation pulse at a time τ after a 90° excitation pulse is applied. The effect of the second 180° pulse is to interchange the ground- and excited-state spin-wave functions so that at a time 2τ the wave function, which was Eq. (2.2) just prior to the excitation pulse, is

$$\psi^{(A)}(2\tau) = (1/\sqrt{2})\{\exp[-\tfrac{1}{2}i\int_0^{2\tau}s(t)\omega(t)\,dt]\}\psi_\uparrow^{(A)} + (1/\sqrt{2})\{\exp[\tfrac{1}{2}i\int_0^{2\tau}s(t)\omega(t)\,dt]\}\psi_\downarrow^{(A)}, \qquad (3.1)$$

where the function[4]

$$s(t) = +1 \text{ if } t < \tau,$$
$$s(t) = -1 \text{ if } t > \tau. \qquad (3.2)$$

The echo amplitude is then the matrix element of the dipole moment operator for the state $\psi^{(A)}(2\tau)$ and is[4,5]

$$e(2\tau, r, \theta, \omega(t)) = \exp[i\int_0^{2\tau}s(t)\omega(t)dt]; \qquad (3.3)$$

again it is understood that we are to take the real part of Eq. (3.3).

The many-spin solution is obtained as in Sec. II. The equations corresponding to Eqs. (2.11)–(2.13) are

$$E(2\tau) = \exp[-\Delta\omega_{1/2}\,\underline{\mathfrak{a}}\,|\int_0^{2\tau}s(t)h(t)\,dt|], \qquad (3.4)$$

$$\mathfrak{a}^{(sh)}(2\tau) = \underline{\mathfrak{a}}\,|\int_0^{2\tau}s(t)h(t)\,dt|, \qquad (3.5)$$

$$E(2\tau) = \exp\{-\Delta\omega_{1/2}\mathfrak{a}^{(sh)}(2\tau)\}, \qquad (3.6)$$

and as in Eq. (2.15) we define

$$\mathfrak{a}^{(sh)}(2\tau) = \sum_{\gamma=0}^{\infty}\mathfrak{a}_\gamma^{(sh)}, \qquad (3.7)$$

where again we suppress the τ dependence of $\mathfrak{a}_\gamma^{(sh)}$.

For short times such that $W\tau \ll 1$ we can evaluate $E(2\tau)$ directly. We need only calculate the first nonzero term in the expansion of $\mathfrak{a}^{(sh)}(2\tau)$. As we will see, the leading term is $\mathfrak{a}_1^{(sh)}$ so that

$$E(2\tau) = \exp(-\Delta\omega_{1/2}\mathfrak{a}_1^{(sh)}) \qquad (3.8)$$

for $W\tau \ll 1$.

The fact that $\mathfrak{a}_0^{(sh)}$ is zero is evident from

$$\mathfrak{a}_0^{(sh)} = \mathfrak{a}_0\,|\int_0^{2\tau}s(t)h(t)\,dt| = e^{-2W\tau}\,|\int_0^{2\tau}s(t)\,dt| = 0,$$

where we have used the condition $h_0(t) = 1$.

We evaluate $\mathfrak{a}_1^{(sh)}$ explicitly

$$\mathfrak{a}_1^{(sh)} = \underline{\mathfrak{a}}_1\,|\int_0^{2\tau}s(t)h(t)\,dt| = e^{-2W\tau}\,|\int_0^{2\tau}dt_1\,|\int_0^{2\tau}s(t)h(t)\,dt|.$$

From the definition of $s(t)$ and $h_1(t)$ [see Eqs. (3.2) and (2.17)],

$$\int_0^{2\tau}s(h)h(t)\,dt = \int_0^{\tau}h_1(t)\,dt - \int_\tau^{2\tau}h_1(t)dt$$
$$= 2t \quad \text{for } t \le \tau$$
$$= 2(2\tau - t) \quad \text{for } t \ge \tau,$$

so that

$$\mathfrak{a}_1^{(sh)} = 2W\tau^2 \qquad (3.9)$$

and

$$E(2\tau) = \exp(-2W\Delta\omega_{1/2}\tau^2) \qquad (3.10)$$

for $W\tau \ll 1$.

The quantity $2W$ corresponds to the $R=T_1^{-1}$ of Klauder and Anderson[4] and Mims.[5] Setting $R=2W$ we recover the Klauder-Anderson result.[13]

In the limit $W\tau \gg 1$ the expression for $E(2\tau)$ simplifies inasmuch as it is sufficient to regard each B spin as flipping exactly $2W\tau$ times. The expression for $E(2\tau)$ then involves only one term in the expansion of $\mathcal{A}^{(sh)}(2\tau)$. We write the echo amplitude in this limit as

$$E(2\tau)=\exp(-\Delta\omega_{1/2}\mathcal{A}_\gamma^{(sh)}/\underline{\mathcal{A}}_\gamma^{(sh)}\cdot 1), \qquad (3.11)$$

with $\gamma=2W\tau$.

The term $\underline{\mathcal{A}}_\gamma^{(sh)}\cdot 1$ provides the proper normalization since the number of spin flips is fixed at $\gamma=2W\tau$ and $\underline{\mathcal{A}}_\gamma^{(sh)}\cdot 1$ is the probability that there are just $\gamma=2W\tau$ spin flips. From Eq. (2.16) of Sec. II we have, on replacing τ with 2τ,

$$\underline{\mathcal{A}}_\gamma^{(sh)}\cdot 1=e^{-2W\tau}\frac{(2W\tau)^\gamma}{\gamma!}.$$

The general formula for $\mathcal{A}_\gamma^{(sh)}$ is obtained from (3.5) and (3.7) and is

$$\mathcal{A}_\gamma^{(sh)}=\underline{\mathcal{A}}_\gamma\left|\int_0^{2\tau}s(t)h(t)\,dt\right|. \qquad (3.12)$$

The essential difference between $\mathcal{A}_\gamma^{(sh)}$ and the term $\mathcal{A}_\gamma^{(h)}$ [Eq. (2.17)] is the function $s(t)$. Whereas $\mathcal{A}_\gamma^{(h)}$ was readily evaluated for γ, even or odd, we are only able to obtain a simple derivation for $\mathcal{A}_\gamma^{(sh)}$ when γ is odd.

Consider $\gamma=7$. We show in Fig. 2(a) the possible function $h(t)=h_7(t)$. We have chosen to illustrate the case in which four spin flips take place before the time τ and three spin flips take place after τ. The integrand we must consider is $s(t)h_7(t)$, which we show in Fig. 2(b). The value of the integrand is the sum of the shaded area (area is positive or negative depending whether it is above or below the zero reference line). But we must perform an integration over all possible spin-flip times which correspond to four spin flips on the left and three flips on the right. This is equivalent to integrating over all possible intervals indicated by the circled numbers in Fig. 2(a). This being so we can reorder to obtain the sequence shown in Fig. 2(b), which is equivalent to a new function $h_7^{**}(t)$ [see Fig. 2(c)] for which the time τ occurs between the fourth and fifth spin flip, and there are a total of seven spin flips. Our point is that the function $h_7^{**}(t)$ of Fig. 2(d), constructed as we have indicated and used in Eq. (3.12) with the function $s(t)$ replaced by unity, is equivalent to using the function $h_7(t)$ of Fig. 2(a) in Eq. (3.12). A parallel argument holds if there are an odd number of spin flips before τ and an even number after. We can now, when γ is odd, reexpress $\mathcal{A}_\gamma^{(sh)}$ of Eq. (3.12) in the form

$$\mathcal{A}_{2\eta+1}^{(sh)}=\underline{\mathcal{A}}_{2\eta+1}\left|\int_0^{2\tau}h(t)\,dt\right|, \qquad (3.13)$$

which corresponds to Eq. (2.17) of Sec. II. From Eq. (2.25) of Sec. II we obtain on replacing τ with 2τ

$$\mathcal{A}_{2\eta+1}^{(sh)}=2e^{-2W\tau}\tau\frac{(W\tau)^{2\eta+1}}{\eta!(\eta+1)!}. \qquad (3.14)$$

The parallel argument for $\mathcal{A}_\gamma^{(sh)}$ when γ is even does not work because it fails when there are an even number of flips before and after τ.

We now evaluate $E(2\tau)$ [Eq. (3.11)] using Eqs. (3.12) and (3.14):

$$E(2\tau)=\exp\left(-2\frac{\Delta\omega_{1/2}}{W}\frac{W\tau}{2^{2\eta+1}}\frac{(2\eta+1)!}{(\eta+1)!\eta!}\right), \qquad (3.15)$$

with the conditions that $2\eta+1=2W\tau$ and $W\tau\gg 1$.

Since the arguments of the factorials are large we can use Stirling's approximation to simplify. Stirling's approximation is[12]

$$\Gamma(z)\cong(2\pi)^{1/2}\exp[(z-\tfrac{1}{2})\ln z-z]$$

for $z\gg 1$. We use $\Gamma(z+1)=z!$ for integral $z\geq 0$. It follows that

$$\frac{(2\eta+1)!}{(\eta+1)!\eta!}\cong\frac{1}{\sqrt{2\pi}}\exp[(2\eta+2)\ln 2-\tfrac{1}{2}\ln(2\eta+2)]$$

$$\cong\frac{1}{\sqrt{2\pi}}2^{2\eta+2}(2\eta+2)^{-1/2}.$$

On setting $2W\tau=2\eta+1$ we obtain

$$E(2\tau)=\exp[-2(1/\pi)^{1/2}W^{-1/2}\Delta\omega_{1/2}\tau^{1/2}] \qquad (3.16)$$

for $W\tau\gg 1$, which for $2W=R$ recovers the result first obtained by Mims.[14]

To go beyond the limiting expressions for $E(2\tau)$ it is necessary to sum the $\mathcal{A}_\gamma^{(sh)}$ over all γ. Part of this sum we can do directly, as it corresponds to a sum we performed in Sec. II.

We define

$$\mathcal{A}_{\text{odd}}=\sum_{\eta=0}^{\infty}\mathcal{A}_{2\eta+1}^{(sh)}$$

and (3.17)

$$\mathcal{A}_{\text{even}}=\sum_{\eta=0}^{\infty}\mathcal{A}_{2\eta+2}^{(sh)},$$

so now

$$\mathcal{A}^{(sh)}(2\tau)=\mathcal{A}_{\text{even}}+\mathcal{A}_{\text{odd}}.$$

Just as in Sec. II, Eqs. (3.17), (3.14), and (2.26) lead to

$$\mathcal{A}_{\text{odd}}=2e^{-2W\tau}\tau I_1(2W\tau). \qquad (3.18)$$

The corresponding expansion for $\mathcal{A}_{\text{even}}$ is not as easily identified. However, as is shown in Appendix A there is a simple relationship between $\mathcal{A}_{\text{odd}}$ and $\mathcal{A}_{\text{even}}$, which is

$$\frac{d}{d\tau}e^{2W\tau}\mathcal{A}_{\text{even}}=2We^{2W\tau}\mathcal{A}_{\text{odd}}. \qquad (3.19)$$

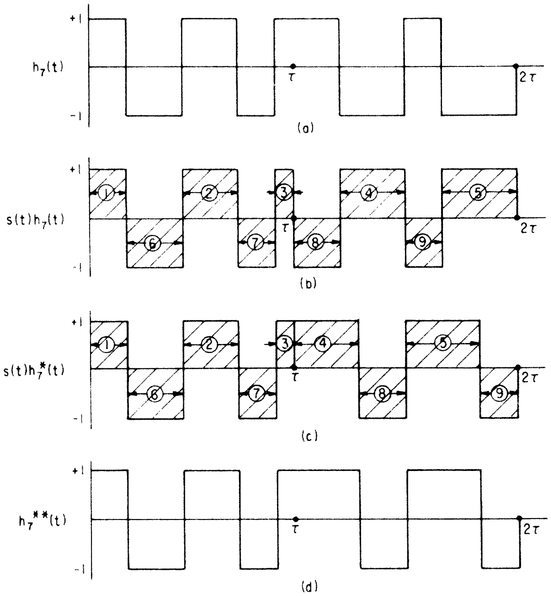

FIG. 2. Reordering of spin-flip intervals to demonstrate an equivalence between the $\mathfrak{A}_\gamma^{(h)}$ and $\mathfrak{A}_\gamma^{(sh)}$ terms for γ odd: (a) illustration of $h_\gamma(t)$ for $\gamma = 7$ with four B spin flips before τ and three B spin flips after τ; (b) illustration of $s(t)h_\gamma(t)$ for case (a); (c) reordering in second interval to generate an $h_\gamma^*(t)$ which is equivalent to $h_\gamma(t)$; (d) illustration of $h_\gamma^{**}(t)$ obtained from (c) which is equivalent to $h_\gamma(t)$ when $s(t)$ is replaced by unity.

From this we obtain

$$\mathfrak{A}_{\text{even}} = 4e^{-2W\tau}W^{-1}\int_0^{W\tau} uI_1(2u)\,du\,. \tag{3.20}$$

This integral is standard and given by[15]

$$\int_0^v uI_1(u)\,du = \tfrac{1}{2}\pi v[I_1(v)L_0(v) - L_1(v)I_0(v)]\,, \tag{3.21}$$

where $I_\nu(v)$ and $L_\nu(v)$ are the modified Bessel and Struve functions of order ν. The value of $\mathfrak{A}_{\text{even}}$ is then

$$\mathfrak{A}_{\text{even}} = \pi e^{-2W\tau}\,\tau[I_1(2W\tau)L_0(2W\tau) - L_1(2W\tau)I_0(2W\tau)]\,. \tag{3.22}$$

The expression for the echo amplitude for arbitrary $W\tau$ is now obtained using Eq. (3.6) with Eqs. (3.20) and (3.22):

$$E(2\tau) = \exp(-2\Delta\omega_{1/2}\,e^{-2W\tau}\,\tau\{I_1(2W\tau) + \tfrac{1}{2}\pi[I_1(2W\tau)L_0(2W\tau) - L_1(2W\tau)I_0(2W\tau)]\})\,. \tag{3.23}$$

As a check on our work we evaluate $E(2\tau)$ [Eq. (3.23)] for the limiting conditions using the appropriate expansions for $I_\nu(2W\tau)$ and $L_\nu(2W\tau)$.

For small z we represent $I_\nu(z)$ by its expansion in z [Eq. (2.26)] and $L_\nu(z)$ by its expansion in z:

$$L_\nu(z) = \sum_{\eta=0}^{\infty} \frac{\frac{1}{2}z^{\nu+2\eta+1}}{\Gamma(\eta+\frac{3}{2})\Gamma(\nu+\eta+\frac{3}{2})}\,, \tag{3.24}$$

so that after rearrangement we obtain the useful expression

$$E(2\tau) = \exp\left[-\Delta\omega_{1/2}e^{-2W\tau}\,\tau\left(\sum_{\eta=1}^{\infty} C_\eta\cdot(2W\tau)^\eta\right)\right]\,, \tag{3.25}$$

where the C_η's can be deduced from the recurrence relationship

$$C_{\eta+1} = \frac{\eta+1}{2\eta+4}\,\frac{C_\eta}{(\eta+1) - \frac{1}{2}[1+(-1)^\eta]}\,, \tag{3.26}$$

with $C_1 = 1$. In lowest order, the above expression recovers Eq. (3.10) for $W\tau \ll 1$.

For large z we use Eq. (2.31) for $I_\nu(z)$; for the modified Struve functions we use[13]

$$\begin{aligned} L_0(z) &\cong I_0(z) - (2/\pi)z^{-1}\,,\\ L_1(z) &\cong I_1(z) - (2/\pi)\,. \end{aligned} \tag{3.27}$$

The echo amplitude $E(2\tau)$ [Eq. (3.23)] then becomes identical, in lowest order, with Eq. (3.16).

IV. THREE-PULSE STIMULATED ECHO

The stimulated echo is generated by applying three 90° excitation pulses separated by τ, T.[16] We assume that there is either a large enough static inhomogeneity or that τ is long enough so that there is appreciable dephasing when the second excitation pulse is applied. If that is the case then the contribution to the stimulated echo amplitude from a pair of A and B spins is given by[4]

$$e_s(2\tau, T, r, \theta, \omega(t)) = \exp\left[-i\int_0^\tau \omega(t)\,dt + i\int_{T+\tau}^{T+2\tau}\omega(t)\,dt\right]\,. \tag{4.1}$$

We proceed as in Sec. II and list the equations for the many-spin system corresponding to Eqs. (2.11)–(2.13):

$$E_s(2\tau, T) = \exp\left[-\Delta\omega_{1/2}\underline{\mathfrak{A}}\left|\int_0^\tau h(t)\,dt - \int_{T+\tau}^{T+2\tau}h(t)\,dt\right|\right]\,, \tag{4.2}$$

$$\mathfrak{A}^{(hh)}(2\tau, T) = \underline{\mathfrak{A}}\left|\int_0^\tau h(t)\,dt - \int_{T+\tau}^{T+2\tau}h(t)\,dt\right|\,, \tag{4.3}$$

$$E_s(2\tau, T) = \exp[-\Delta\omega_{1/2}\,\mathfrak{A}^{(hh)}(2\tau, T)]\,. \tag{4.4}$$

We define a term $\mathfrak{A}_\gamma^{(hh)}$ according to

$$\mathfrak{A}^{(hh)}(2\tau, T) = \sum_{\gamma=0}^{\infty}\mathfrak{A}_\gamma^{(hh)}\,, \tag{4.5}$$

which is to mean that γ is the total number of spin flips in the intervals 0 to τ and $T+\tau$ to $T+2\tau$. We are to assume that a sum over all possible number of spin flips in the interval between τ and $T+\tau$ has been included. If the number of spin flips in the time interval T is even then $h(\tau) = h(\tau+T)$, whereas if the number is odd then $h(\tau) = -h(\tau+T)$. It follows then that

$$\mathfrak{A}_\gamma^{(hh)} = \underline{\mathfrak{A}}_\gamma \left| \int h(t)\,dt \right| \left(e^{-W\tau} \sum_{\eta=0}^{\infty} W^{2\eta+1} \int_\tau^{T+\tau} dt_1 \int_{t_1}^{T+\tau} dt_2 \cdots \int_{t_{2\eta}}^{T+\tau} dt_{2\eta+1} \right)$$

$$+ \underline{\mathfrak{A}}_\gamma \left| \int_0^{2\tau} s(t)h(t)\,dt \right| \left(e^{-W\tau} \sum_{\eta=0}^{\infty} W^{2\eta} \int_\tau^{T+\tau} dt_1 \int_{t_1}^{T+\tau} dt_2 \cdots \int_{t_{2\eta-1}}^{T+\tau} dt_{2\eta} \right). \quad (4.6)$$

The quantity $\underline{\mathfrak{A}}_\gamma | \int_0^{2\tau} h(t)dt |$ corresponds to $\mathfrak{A}_\gamma^{(h)}$ [Eq. (2.17)] with τ replaced by 2τ, whereas $\underline{\mathfrak{A}}_\gamma | \int_0^{2\tau} s(t)h(t)\,dt |$ is exactly $\mathfrak{A}_\gamma^{(sh)}$ [Eq. (3.12)]. The integral factors on the right-hand side of Eq. (4.6) correspond to the functions $\frac{1}{2}(1 - e^{-2WT})$ and $\frac{1}{2}(1 + e^{-2WT})$. We can therefore obtain $\mathfrak{A}^{(hh)}(2\tau, T)$ directly from Eqs. (2.27), (2.28), (3.18), and (3.22). Thus,

$$\begin{aligned}\mathfrak{A}^{(hh)}(2\tau, T) &= e^{-2W\tau}\,\tau([I_0(2W\tau) + I_1(2W\tau)](1 - e^{-2WT}) \\ &\quad + \{I_1(2W\tau) + \tfrac{1}{2}\pi[I_1(2W\tau)L_0(2W\tau) \\ &\quad - L_1(2W\tau)I_0(2W\tau)]\}(1 + e^{-2WT})),\end{aligned} \quad (4.7)$$

which yields $E_s(2\tau, T)$ through Eq. (4.4)

Using the limiting expressions from Secs. II and III we find that

$$E_s(2\tau, T) = \exp[-2\Delta\omega_{1/2}\tau(W\tau + WT)] \quad (4.8)$$

for $W\tau \ll 1$ and $WT \ll 1$.

This corresponds exactly to the result of Klauder and Anderson.

In the limit $W\tau \gg 1$ we use Eqs. (2.31) and (3.29) to obtain

$$E_s(2\tau, T) = \exp[-2(1/\pi)^{1/2} W^{-1/2} \Delta\omega_{1/2} \tau^{1/2}] = E(2\tau) . \quad (4.9)$$

V. DISCUSSION

A. Free-induction decay

The behavior of the free-induction-decay signal $F(\tau)$ [Eq. (2.29)] is conveniently analyzed by expressing it in terms of the universal function

$$G(z) = e^{-z}[I_0(z) + I_1(z)], \quad (5.1)$$

so that

$$F(\tau) = \exp[-\Delta\omega_{1/2}\tau G(W\tau)] . \quad (5.2)$$

We plot and tabulate $G(z)$ in Fig. 3 and Table I, respectively. It approaches unity at small z as $1 - \frac{1}{2}z$. As z increases $G(z)$ decreases and approaches the function $(2/\pi)^{1/2} z^{-1/2}$ for large z. From the form of Eq. (5.2) we can regard $F(\tau)$ as a function of the two variables $W/\Delta\omega_{1/2}$ and $\Delta\omega_{1/2}\tau$, i.e.,

$$F(\tau) = \exp\left[-\Delta\omega_{1/2}\tau G\left(\frac{W}{\Delta\omega_{1/2}}\Delta\omega_{1/2}\tau\right)\right]. \quad (5.3)$$

In Fig. 4 we plot $F(\tau)$ as a function of $\Delta\omega_{1/2}\tau$ for several values of $W/\Delta\omega_{1/2}$. In the limit $W/\Delta\omega_{1/2} = 0$ the decay of $F(\tau)$ is a simple exponential,

$$F(\tau) = e^{-\Delta\omega_{1/2}\tau}, \quad (5.4)$$

since $G(z)$ is constant. The rate of decay of $F(\tau)$ decreases as $W/\Delta\omega_{1/2}$ increases. This is always true since $G(z)$ is a monotonically decreasing function of z. As $W/\Delta\omega_{1/2}$ is increased, the free-induction-decay signal is *always* lengthened. This behavior is to be expected on the grounds that any spin precessing at some frequency other than exactly at the central resonance frequency is more likely to be shifted, when a B spin flips, toward the central resonance frequency rather than to be shifted in the other direction. This argument is transparent in the artificial situation where each A spin interacts with a *single* isolated B spin. Then when a B spin flips, the associated A-spin resonance frequency jumps to its symmetric position on the other side of the resonance line and narrows it. But we can argue precisely. If a B spin flips, its effect on the free-induction amplitude at any instant is the same as if it had not flipped but had its moment reduced to its time-average value up to that instant. This obviously lengthens the free-induction-decay signal and reduces the effective linewidth. This is a kind of motional narrowing.[7,8]

For larger $W/\Delta\omega_{1/2}$ the free-induction decay follows the asymptotic form of Eq. (2.32), i.e.,

$$F(\tau) = \exp[-(2/\pi)^{1/2}\Delta\omega_{1/2} W^{-1/2} \tau^{1/2}] \quad (5.5)$$

for all values of $\Delta\omega_{1/2}\tau$ above that at which $W\tau \gg 1$. The accuracy of the asymptotic form may be seen

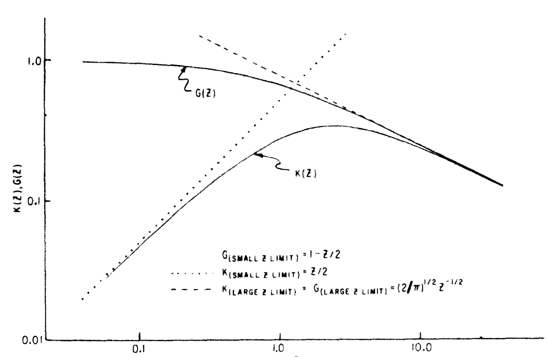

FIG. 3. Generalized functions $K(z)$ and $G(z)$ are plotted as a function of their dimensionless argument z. Asymptotic limits are shown as a dashed and dotted line. The limit of $G(z)$ at small z is unity.

TABLE I. Generalized functions $G(z)$ and $K(z)$.

z	$G(z)$	$K(z)$	z	$G(z)$	$K(z)$	z	$G(z)$	$K(z)$
0.04	0.980	0.0195	0.4	0.834	0.155	4	0.386	0.323
0.05	0.976	0.0242	0.5	0.801	0.182	5	0.348	0.305
0.06	0.971	0.0288	0.6	0.772	0.206	6	0.319	0.287
0.08	0.962	0.0379	0.8	0.719	0.245	8	0.278	0.258
0.10	0.952	0.0468	1.0	0.674	0.274	10	0.249	0.236
0.13	0.939	0.0597	1.3	0.618	0.304	13	0.219	0.210
0.16	0.926	0.0720	1.6	0.572	0.323	16	0.198	0.191
0.20	0.909	0.0878	2.0	0.524	0.336	20	0.177	0.173
0.25	0.888	0.1063	2.5	0.477	0.340	25	0.159	0.156
0.30	0.870	0.1236	3.0	0.440	0.338	30	0.145	0.143

in Fig. 4 where we have plotted Eq. (5.5) as a dotted curve.

B. Resonant contribution from nonresonant B spins

The analysis presented above is valid until $\omega_{0A}W^{-1}$, where ω_{0A} is the resonance frequency of the A spins, becomes less than or of the order of unity. After $\omega_{0A}W^{-1}\lesssim 1$, then, there will be appreciable noise power at ω_{0A} generated by the flipping B spins. It has been shown, however, under the conditions studied in this paper, where the A system is so dilute that the A spins do not interact, that the effect is to cause a spin-lattice relaxation where the approach to equilibrium is of the same form as Eq. (5.5).[17] To obtain the exact form of spin-lattice relaxation function we use Eq. (12) of Tse and Hartmann[17] but with their τ_1^{-1} obtained from the noise field in the laboratory frame rather than in the rotating frame. From Eqs. (A27) and (A28) of Lowe and Tse[18] we note that this means a reduction of $\tau_1^{1/2}$ by the factor

$$\frac{(\frac{1}{3})^{1/2}\int_{-1}^{1}|1-3x^2|\,dx}{(3)^{1/2}\int_{-1}^{1}(1-x^2)x^2\,dx}=\frac{20}{3\sqrt{3}}\,,$$

with the result that the spin-lattice-relaxation function [Eq. (12) of Ref. 17] becomes (in our notation)

$$S(t)=\exp[-(5/3\sqrt{3})(2/\pi)^{1/2}\Delta\omega_{1/2}W^{-1/2}\tau^{1/2}]\,.$$

But $(5/3\sqrt{3})\approx 1$ so that the effect of spin-lattice relaxation is identical to the effect of spectral diffusion when Eq. (5.5) applies.

C. Two-pulse echo

As an aid in analyzing the two-pulse echo behavior we define the universal function

$$K(z)=e^{-z}\{I_1(z)+\tfrac{1}{2}\pi[I_1(z)L_0(z)-L_1(z)I_0(z)]\},\qquad(5.6)$$

whereupon the echo amplitude [Eq. (3.23)] becomes

$$E(2\tau)=\exp[-2\Delta\omega_{1/2}\tau K(2W\tau)]\,.\qquad(5.7)$$

We plot and tabulate $K(z)$ in Fig. 3 and Table I, respectively; it falls off as $(2/\pi)^{1/2}z^{-1/2}$ at large z and as $\frac{1}{2}z$ at small z and has a maximum value of approximately $\frac{1}{2}\pi^{-1/3}$. The form of $K(z)$ complicates the behavior of $E(2\tau)$ somewhat. For ease of analysis it is customary to define a relaxation time $2\tau=T_M$ for which $E(2\tau)$ is down by a factor of e.[5] This occurs at

$$\Delta\omega_{1/2}T_M K(WT_M)=1$$

or

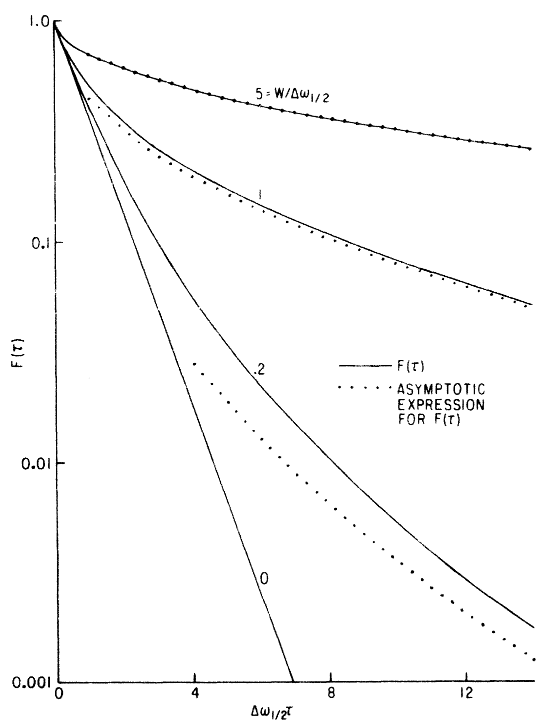

FIG. 4. Free-induction amplitude $F(\tau)$ is plotted as a function of $\Delta\omega_{1/2}\tau$ for several values of $W/\Delta\omega_{1/2}$. The asymptotic limit, valid for large values of $W\tau$, is shown as a dotted line.

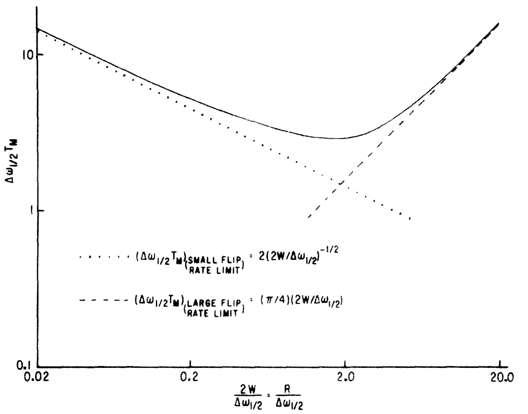

FIG. 5. Behavior of the relaxation time T_M is illustrated by plotting $\Delta\omega_{1/2}T_M$ as a function of $2W/\Delta\omega_{1/2}$.

$$\Delta\omega_{1/2}T_M K\left(\frac{1}{2}\,\frac{2W}{\Delta\omega_{1/2}}\,\Delta\omega_{1/2}T_M\right)=1\,. \qquad (5.8)$$

In Fig. 5 we plot $\Delta\omega_{1/2}T_M$ as a function of $2W/\Delta\omega_{1/2}$. When the B-spin flip rate W is approximately equal to $\Delta\omega_{1/2}$ we have a "resonance" and the relaxation time T_M is a minimum.[19] For higher spin flip rates the effect of the B-spin flips averages out.[7,8] At lower spin flip rates the echo is not much attenuated, as the time-averaged A-spin local field does not change much in the time intervals $\pm\tau$ centered about the time of the second excitation pulse. In these limits we obtain

$$(\Delta\omega_{1/2}T_M)=2(2W/\Delta\omega_{1/2})^{-1/2} \text{ (small-flip rate limit)} \qquad (5.9)$$

and

$$(\Delta\omega_{1/2}T_M)=\tfrac{1}{4}\pi(2W/\Delta\omega_{1/2}) \text{ (high-flip-rate limit)}\,. \qquad (5.10)$$

We next consider the form of $E(2\tau)$. The echo decay behavior is readily appreciated if we first plot the asymptotic form of $E(2\tau)$. The asymptotic forms of $E(2\tau)$ are Eqs. (3.10) and (3.16), which we rewrite as

$$E(2\tau)=\exp\left[-2W/\Delta\omega_{1/2}(\Delta\omega_{1/2}\tau)^2\right] \qquad (5.11)$$

for $W\tau\ll 1$ and

$$E(2\tau)=\exp\left[-2(2/\pi)^{1/2}\left(\frac{2W}{\Delta\omega_{1/2}}\right)^{-1/2}(\Delta\omega_{1/2}\tau)^{1/2}\right] \qquad (5.12)$$

for $W\tau\gg 1$. The exact $E(2\tau)$ is always larger than either of the two asymptotic forms. One may say that Eq. (5.11) underestimates the tendency for the effect of the flipping B spins to average out, while Eq. (5.12) underestimates the correlation between local-field values in the rephasing interval and those in the dephasing interval. Both of these expressions are valuable as estimates of $E(2\tau)$ and, in their respective limits, will accurately represent $E(2\tau)$. They have been obtained earlier: in the lower limit [Eq. (3.10)] by Klauder and Anderson, and in the higher limit [Eq. (3.16)] by Mims.

The lower limit to the correct $E(2\tau)$ is obtained by either Eq. (5.11) or Eq. (5.12), whichever is largest. In Fig. 6 we give this plot. The locus of points for which the two asymptotic forms intersect occurs [equating Eqs. (3.10) and (3.16)] for

$$W\tau=\pi^{-1/3}$$

and is represented by the function

$$E_1=\exp(-2\pi^{-1/3}\Delta\omega_{1/2}\tau)\,, \qquad (5.13)$$

which we plot as a dotted line in Fig. 6.

We next plot in Fig. 7 the exact decay behavior [Eq. (5.7)] for the same set of parameters as in Fig. 6, using the same scale. We note the correspondence between the two figures and close agreement for values of $\Delta\omega_{1/2}\tau$ far away from the cusps in Fig. 6. For example, for large values of $\Delta\omega_{1/2}\tau$ the curves corresponding to $2W/\Delta\omega_{1/2}=5$ are identical, whereas for $2W/\Delta\omega_{1/2}=0.25$ the curves become identical at the lower values of $\Delta\omega_{1/2}\tau$. In the intermediate regions there is a significant departure from the asymptotic behavior.

A lower limit to $E(2\tau)$ is obtained by replacing $K(2W\tau)$ with its maximum value. We calculate

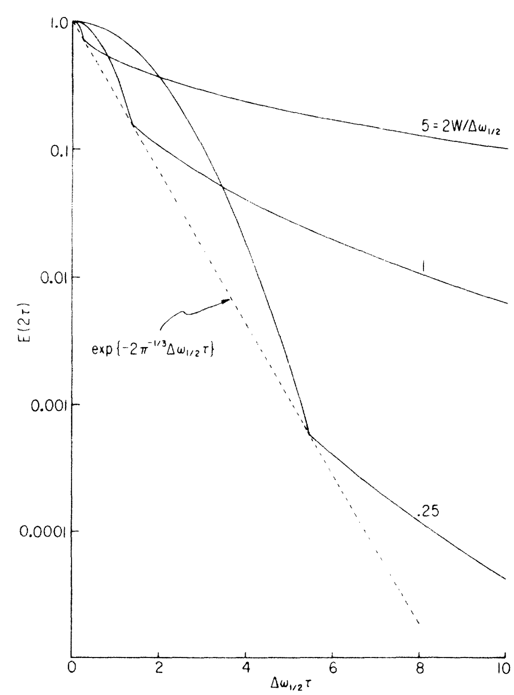

FIG. 6. Asymptotic limits to the echo amplitude is plotted as a function of $\Delta\omega_{1/2}\tau$ for several values of $2W/\Delta\omega_{1/2}$.

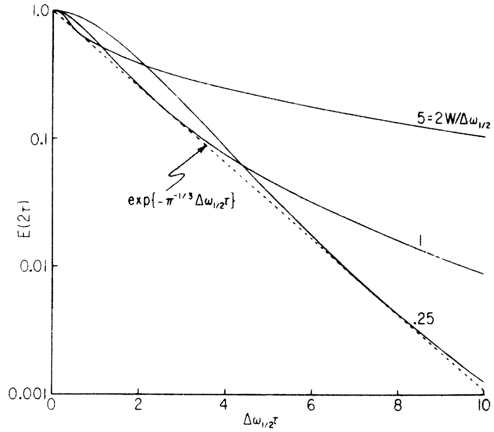

FIG. 7. Echo amplitude $E(2\tau)$ is plotted as a function of $\Delta\omega_{1/2}\tau$ for several values of $2W/\Delta\omega_{1/2}$. A simple lower limit to $E(2\tau)$ is plotted as a dashed line.

that $K_{max} = \frac{1}{2}\eta\pi^{-1/3}$ with $\eta \cong 0.998 \simeq 1$. A useful limit is therefore

$$E_{limit}(2\tau) = \exp(-\pi^{-1/3}\Delta\omega_{1/2}\tau), \qquad (5.14)$$

which we plot as a dashed curve in Fig. 7.

D. Stimulated echo

We express the stimulated-echo decay function [see Eqs. (4.4) and (4.7)] in terms of $G(z)$ and $K(z)$ as

$$E_s(2\tau, T) = \exp\{-\Delta\omega_{1/2}\tau[(1-e^{-2WT})G(2W\tau) + (1+e^{-2WT})K(2W\tau)]\}, \qquad (5.15)$$

which on rearranging becomes

$$E_s(2\tau, T) = \exp[-2\Delta\omega_{1/2}\tau K(2W\tau)] \times \exp\{-\Delta\omega_{1/2}\tau[G(2W\tau) - K(2W\tau)] \times (1-e^{-2WT})\}. \qquad (5.16)$$

But, the first factor is exactly the two-pulse-echo decay amplitude $E(2\tau)$; therefore

$$E_s(2\tau, T) = E(2\tau)\exp\{-\Delta\omega_{1/2}\tau[G(2W\tau) - K(2W\tau)] \times (1-e^{-2WT})\}. \qquad (5.17)$$

The stimulated-echo amplitude is just the product of (i) the two-pulse decay amplitude and (ii) a factor which depends in an instructive way on τ and on T, the time separation between the second and third excitation pulses.

The stimulated-echo amplitude $E_s(2\tau, T)$ never increases as T increases since $G(z) > K(z)$ for all z, as can be seen from Fig. 3.

For $W\tau \ll 1$ and $WT \ll 1$ we use $G(z) = 1 - \frac{1}{2}z$ and $K(z) = \frac{1}{2}z$ and write Eq. (5.15) as

$$E_s(2\tau, T) = \exp[-2\Delta\omega_{1/2}\tau(W\tau + WT)], \qquad (4.8)$$

which is identical to the result of Klauder and Anderson.

For large values of WT the stimulated echo amplitude $E_s(2\tau, t)$ becomes independent of T. In this limit the B-spin orientation configuration is completely rerandomized when the third excitation pulse is applied.

It might seem surprising that one would obtain an "echo" (i.e., appreciable signal at $T+2\tau$) in this limit for the case in which the B spins alone provide the inhomogeneous field at the A-spin sites. But consider the case with the additional condition $W\tau \ll 1$, so that no B-spins flip in the time τ. It is just as probable that a particular B-spin orientation in the dephasing interval $0 < t < \tau$ is parallel to its orientation in the rephasing interval $T+\tau < t < T+2\tau$, as that it is antiparallel. But all B spins whose orientation remains parallel will not contribute to the degradation of the echo. Thus, the echo amplitude will be equal to the free-induction amplitude measured at $t = 2\tau$ (recall that $W\tau \ll 1$) and generated in a A-spin environment consisting *only* of B spins whose number density is one-half the actual B-spin density. This is precisely the result one obtains from Eq. (5.15) on setting $G=1$ and $K=0$.

The factor multiplying $E(2\tau)$ in Eq. (5.17) represents the ratios $E_s(2\tau, T)/E_s(2\tau, 0)$, i.e.,

$$E_s(2\tau, T)/E_s(2\tau, 0) = \exp\{-\Delta\omega_{1/2}\tau[G(2W\tau) - K(2W\tau)](1-e^{-2WT})\} = \exp[-A(1-e^{-2WT})], \qquad (5.18)$$

which we have plotted as a function of WT in Fig. 8 for several values of A.[20] In the limiting cases we have

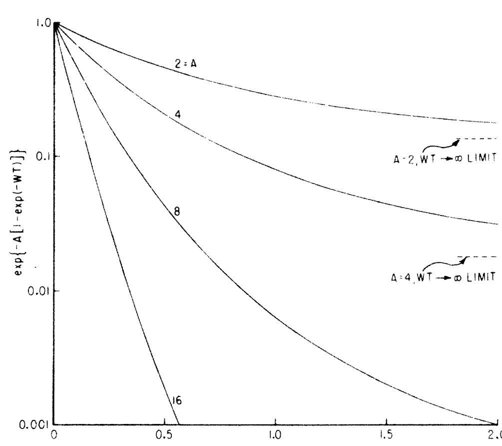

FIG. 8. Behavior of the stimulated-echo amplitude for fixed separation between the first and second excitation pulses is illustrated by its amplitude variation as a function of WT for several values of the parameter A.

$$A = \Delta\omega_{1/2}\tau(1 - 2W\tau) = \Delta\omega_{1/2}\tau\left(1 - \frac{2W}{\Delta\omega_{1/2}}\Delta\omega_{1/2}\tau\right) \quad (5.19)$$

for $W\tau \ll 1$, while for $W\tau \gg 1$ we use

$$G(z) = \frac{1}{(2\pi z)^{1/2}}\left(2 - \frac{1}{4z}\right), \quad K(z) = \frac{1}{(2\pi z)^{1/2}}\left(2 - \frac{5}{4z}\right), \quad (5.20)$$

so that

$$A = (2\pi)^{-1/2}\Delta\omega_{1/2}\tau(2W\tau)^{-3/2} = \tfrac{1}{4}\pi^{-1/2}\left(\frac{2W}{\Delta\omega_{1/2}}\right)^{-3/2}(\Delta\omega_{1/2}\tau)^{-1/2} \quad (5.21)$$

for $W\tau \gg 1$.

E. Closing remark

We have presented a theory valid for all time which is strictly correct only for the idealized T_1 sample (AA- and BB-spin interactions are unimportant). Although considerable experimental work has been performed, this limiting case has not yet been realized fully. The excellent work of Mims[5] studying the behavior of two- and three-pulse-stimulated echoes using the Ce resonance on $CaWO_4$: Ca, Ce, Er [see Figs. 5, 6, and 7 or Ref. 5] is supportive of this present work. However, in order to obtain a significant check of the theory developed, herein, it will be necessary to repeat these experiments over an extended range using more lightly doped samples whose A spins are less tightly coupled to the lattice vibrations.

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APPENDIX A

We present a proof of the identity:

$$\frac{d}{d\tau} e^{2W\tau}\mathfrak{a}_{\text{even}} = 2We^{2W\tau}\mathfrak{a}_{\text{odd}}. \quad (A1)$$

Following the argument which leads from Eq. (2.21) to (2.23) and taking into account that we now have two time intervals 0 to τ and τ to 2τ, we then have

$$e^{W\tau}\mathfrak{a}_{\text{even}} = \sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n}\int_0^\tau du\int_0^\tau dv\, P_{2m}(u)P_{2n}(v)\,|(2u-\tau)-(2v-\tau)|$$
$$+\sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n+2}\int_0^\tau du\int_0^\tau dv\, P_{2m+1}(u)P_{2n+1}(v)\,|(2u-\tau)+(2v-\tau)|, \quad (A2)$$

where the first (second) term in Eq. (A2) arises from the cases where there are even (odd) number of flips in both the time intervals 0 to τ and τ to 2τ. Furthermore just for convenience we have changed the dummy variables in the integration from t_k to u, etc.

We now change the variables u to $\tau - u$ and v to $\tau - v$ in the first term of (A2), but only v to $\tau - v$ in the second term. Furthermore we shall use the following relation:

$$|u-v| = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dp}{p^2}\left(e^{ip(u-v)} + e^{-ip(u-v)}\right), \quad (A3)$$

where $\gamma > 0$. Using the explicit expressions for $P_n(u)$, as given by Eq. (2.24), we then have

$$e^{W\tau}\mathfrak{a}_{\text{even}} = 2\int_0^\tau dv\,|v|\sum_{m=1}^{\infty} W^{2m}\frac{(\tau-v)^m v^{m-1}}{m!(m-1)!} + \int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dp}{p^2}\int_0^\tau du\int_0^\tau dv\left(e^{ip(2u-2v)} + e^{-ip(2u-2v)}\right)$$
$$\times\sum_{\substack{n=1\\m=1}}^{\infty} W^{2m+2n}\frac{(\tau-u)^m u^{m-1}}{m!(m-1)!}\,\frac{(\tau-v)^n v^{n-1}}{n!(n-1)!} + \int_0^\tau du\int_0^\tau dv\left(e^{ip(2u-2v)} + e^{-ip(2u-2v)}\right)$$

$$\times \sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n+2}\,\frac{u^m(\tau-u)^m}{m!\,m!}\;\frac{(\tau-v)^m v^m}{m!\,m!}\quad . \tag{A4}$$

We now take derivative of (A4) with respect to τ. After some straightforward manipulation, we have

$$\frac{d}{d\tau}\,e^{W\tau}\mathfrak{a}_{\text{even}} = 2W\Bigg(\sum_{m=0}^{\infty} W^{2m+1}\int_0^\tau |2\tau-2v|\,\frac{v^m(\tau-v)^m}{m!\,m!} + \sum_{\substack{m=1\\n=0}}^{\infty} W^{2m+2n+1}\int_0^\tau du\int_0^\tau dv\,|2u-2v|\,\frac{u^m(\tau-u)^{m-1}}{m!\,(m-1)!}\;\frac{v^n(\tau-v)^n}{n!\,n!}$$

$$+\sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n+1}\int_0^\tau du\int_0^\tau dv\,|2u-2v|\,\frac{u^m(\tau-u)^{m-1}}{m!\,(m-1)!}\;\frac{v^n(\tau-v)^n}{n!\,n!}\Bigg)$$

$$=4W\Bigg\{\sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n+1}\int_0^\tau du\int_0^\tau dv\;|2u-2v|\,P_{2m}(u)P_{2n+1}(v)\Bigg\}\quad . \tag{A5}$$

We note that an expression similar to (A2) can be easily written down for $e^{W\tau}\mathfrak{a}_{\text{odd}}$, namely,

$$e^{W\tau}\mathfrak{a}_{\text{odd}} = \sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n+1}\int_0^\tau du\int_0^\tau dv\,|(2u-\tau)-(2v-\tau)|\,P_{2m}(u)P_{2m+1}(v)$$

$$+\sum_{\substack{m=0\\n=0}}^{\infty} W^{2m+2n+1}\int_0^\tau du\int_0^\tau dv\,|(2u-\tau)+(2v-\tau)|\,P_{2m+1}(u)P_{2n}(v)\,. \tag{A6}$$

The first (second) term arises from the case where there are even (odd) number of flips in the time interval 0 to τ and odd (even) number of flips in the time interval τ to 2τ. Changing the variable u to $\tau-u$ and then interchanging both the variables u and v and the indices n and m, we have

$$e^{W\tau}\mathfrak{a}_{\text{odd}} = 2\sum_{\substack{m=0\\n=0}}^{\infty}\int_0^\tau du\int_0^\tau dv\,|2u-2v|\,P_{2m}(u)\,P_{2n+1}(v)\,. \tag{A7}$$

Comparing Eq. (A7) with Eq. (A5), we then have the identity (A1).

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[12]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1964).

[13]In Ref. 5 W is mistakenly set equal to R with the result that when the Klauder-Anderson result is rederived in Ref. 5 an extra factor of 2 appears in the coefficient of τ^2 [see line above of Eq. (29a) in Ref. 5].

[14]The apparent disagreement between this and Mim's Eq. (24) arises because we have used the exact value $\sqrt{\pi}$ for $\int_0^\infty dx\,(1-e^{1/x^2})$ [see Ref. 5, p. 374] and have corrected a small numerical error.

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[19]This general behavior has been observed by Mims (Ref. 5) for the Ce resonance in $CaWO_4$: Ca, Ce, Er.

[20]From the character of the curves in Fig. 8, one would expect to obtain a reasonable fit over a moderate interval to a function e^{-BT^x}, where x is a suitable number less than unity. Special care must be taken to differentiate between expected behaviors.