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Spectral-diffusion decay in echo experiments

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We calculate the decay of phase memory due to spectral diffusion in certain echo experiments. Local-field fluctuations, at the site of resonant two-level systems, controlled by the spin-lattice relaxation of neighboring spins, cause the spin diffusion. The results generalize those previously obtained which were valid only at high temperature.

I. INTRODUCTION

Often physical systems may be represented exactly, or to good approximation, as assemblies of two-level subsystems. Atomic situations often occur in which a physical system may be divided in a natural way into subsystems for each of which only two energy levels are significant. Nuclei and atoms in magnetic fields, optical transitions of atoms and molecules and, it seems likely, ultrasonic transmission in amorphous materials, all furnish examples where this decomposition is appropriate. When such systems absorb power there will always be broadening of the resonance line. This may be inhomogeneous or homogeneous. The former arises from all factors which cause the long-time average of the energy splitting of the two-level systems to vary from one system to another. Examples are splittings due to crystal strain or spatial inhomogeneity of applied magnetic field in spin resonance. Homogeneous broadening, on the other hand, arises from the mutual interaction of two-level systems or from interaction with an external system (lifetime broadening). It is a dynamical process and causes the irreversible loss of phase coherence in the system as a whole. The standard method of studying this loss of phase coherence is the echo technique which is applicable in various cases as spin,[1] photon,[2] and Raman[3] echo. It is customary to speak of the decay of the echo generated after coherent excitation in terms of a single-phase memory time, T_2. In fact, the form of the decay is usually complicated and not characterized by a single exponential function.

One important contribution to the echo decay, the spectral diffusion,[4-6] comes from the fluctuation of the local field at the site of the resonant two-level system. It is usual to divide systems in which this process is important into two classes, designated as T_1 and T_2 systems. In T_1 samples, the fluctuation of local fields arises from the flipping of neighboring ions by spin-lattice relaxation (described by T_1, the spin lattice relaxation time); in T_2 samples the flipping of the neighbors comes primarily from spin-spin interactions (T_2 being the spin-spin relaxation time).[5] We shall be concerned here exclusively with T_1 systems. The assumptions of the model are simple. The spins are first divided into two classes, A and B, both of them of sufficiently low concentration. The A spins are those whose resonance is being observed. They will be considered to be isolated from one another. The remaining B spins are randomly placed and in thermal equilibrium with the lattice; they flip at a rate which is characterized by T_1, the spin lattice relaxation time. We assume that the resonance frequencies of A and B are so disparate that we need only use the diagonal part of their interaction. For simplicity, we present results for the case of dipolar interaction. If the interaction has a more general dependence upon the orientation of the spins but falls off as the third power of their separation the form of the result is not changed but the definition of the parameters involved will be affected. An interaction of this kind has been shown to exist for certain models of the interaction of two-level systems in glasses.[7] The results may also be generalized to more complicated interactions.

An uncorrelated-sudden-jump model for the systems considered here was previously analyzed by Hu and Hartmann.[6] The present work generalizes the results of that paper and we follow the same notation. However, in the work of Hartmann and Hu it was assumed that the B spins flip from one state to another with equal transition probabilities. This is essentially a high-temperature approximation. We remove this restriction here and obtain exact results for the decay of two- and three-pulse echoes in the general case.

II. TWO-PULSE ECHO AND THREE-PULSE STIMULATED ECHO

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

$$\mathcal{H}_{AB} = \vec{\mu}_A \cdot \vec{\mu}_B / r^3 - 3(\vec{\mu}_A \cdot \vec{r})(\vec{\mu}_B \cdot \vec{r})/r^5 ; \qquad (1)$$

we retain, as mentioned above, only the diagonal part of this interaction. The three-pulse stimulated echo is generated by applying three $\frac{1}{2}\pi$ resonant excitation pulses separated by τ and T. The two-pulse echo is simply a special case of the stimulated echo where $T=0$, i.e., it is generated by a π pulse at time τ after the first $\frac{1}{2}\pi$ pulse. The stimulated-echo amplitude $e(2\tau, T)$ is given by[4-6]:

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

where

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

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 stimulated-echo amplitude as[6]

$$e(2\tau, T) = a\left\langle\left\langle \exp\left[i\sum_\beta \omega_{\alpha\beta}\left(\int_0^\tau h(t)\,dt - \int_{T+\tau}^{T+2\tau} h(t)\,dt \right)\right]\right\rangle\right\rangle_\alpha ,$$

where

$$\omega_{\alpha\beta} = 2\mu_A\mu_B(1-3\cos^2\theta_{\alpha\beta})\hbar^{-1}r_{\alpha\beta}^{-3}.$$

The operator a averages over all B spin-flip histories. 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 unit magnitude and changes sign every time its representative B spin flips. The operator a performs the average over all B spin-flip histories.

The average over all the A spin environments is straightforward and we obtain[5]

$$e(2\tau, T) = \exp\left(-\Delta\omega_{1/2}\, a \times \left| \int_0^\tau h(t)\,dt - \int_{T+\tau}^{T+2\tau} h(t)\,dt \right| \right),$$

where

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

and the above expression is correct to the first order in the concentration of B spins. n is the number density of B spins.

Here we have neglected a term which corresponds to a finite frequency shift due to the unequal number of up and down spins. This is justifiable as long as there exists an appreciable amount of other inhomogeneous broadening of the spin systems.

From the definition of $h(t)$ it is clear that

$$\left| \int_0^\tau h(t)\,dt - \int_{T+\tau}^{T+2\tau} h(t)\,dt \right|$$

can be written $2|\tau_1 - \tau_2|$,[6] where $\tau_1(\tau)$ is the time spent by the B spin in the upper state during the interval $(0, \tau)$ and $\tau_2(\tau)$ is the corresponding quantity for the interval $(\tau+T, 2\tau+T)$.

Given a fixed sequence of successive time intervals, τ, T, and τ, each history has a definite $\tau_1(\tau)$ and $\tau_2(\tau)$, so that it is then sensible to ask for the probability that a given history has an assigned value of $s = \tau_1(\tau) - \tau_2(\tau)$. This probability is clearly a function of τ (and of s and T). To study its dependence upon τ we first suppose the time intervals to run from $-\tau$ to 0, 0 to T and T to $T+\tau$ and compare the situation with one in which they run from $-\tau - d\tau$ to 0, 0 to T and T to $T+\tau+d\tau$. We can always find a history in the second case which exactly duplicates between $-\tau$ and $T+\tau$ a given history of the first case and the relevant probabilities for τ and $\tau + d\tau$ can therefore only change as a result of the behavior of the second case in the intervals $-\tau - d\tau$ to $-\tau$ and $T+\tau$ to $T+\tau+d\tau$. This will depend on the spin state of the system at $-\tau$ and $T+\tau$. We are thus led to define four probabilities $P_{\uparrow\uparrow}(s,\tau)$, $P_{\uparrow\downarrow}(s,\tau)$, $P_{\downarrow\uparrow}(s,\tau)$, and $P_{\downarrow\downarrow}(s,\tau)$, where $P_{\uparrow\uparrow}(s,\tau)$, for example, is the probability that the system is in the upstate at $t=-\tau$ and at $t=T+\tau$ and the difference $\tau_1(\tau) - \tau_2(\tau) = s$. The required average of $|\tau_1 - \tau_2|$ is now

$$f(2\tau, T) = \int_{-\infty}^{+\infty} [P_{\uparrow\uparrow}(s,\tau) + P_{\uparrow\downarrow}(s,\tau) + P_{\downarrow\uparrow}(s,\tau) + P_{\downarrow\downarrow}(s,\tau)]\,|s|\,ds, \tag{4}$$

and the amplitude of the stimulated echo is

$$e(2\tau, T) = \exp[-2\Delta\omega_{1/2} f(2\tau, T)]. \tag{5}$$

By comparing the states of the system for intervals τ and $\tau - dt$ we may derive partial differential equations satisfied by the P's. Consider, for example, $P_{\uparrow\uparrow}(s,\tau)$. If the system is to be in the upstate at start and finish with $\tau_1(\tau) - \tau_2(\tau) = s$, then at $\tau - d\tau$ it was in one of four conditions: (i), up at $-\tau - d\tau$, up at $T+\tau-d\tau$, s unchanged; (ii), up at $-\tau+d\tau$, down at $T+\tau-d\tau$, s replaced by $s-O(d\tau)$; (iii), down at $-\tau+d\tau$, up at $T+\tau-d\tau$, s replaced by $s+O(d\tau)$; (iv), down at $-\tau+d\tau$, up at $T+\tau-d\tau$, s unchanged. To the first order in $d\tau$ we have

$$P_{\uparrow\uparrow}(s,\tau) = P_{\uparrow\uparrow}(s,\tau-d\tau)(1-2w_1 d\tau) + P_{\uparrow\downarrow}(s,\tau)w_2 d\tau + P_{\downarrow\uparrow}w_2\, d\tau \tag{6}$$

or

$$\frac{\partial P_{\uparrow\uparrow}(s,\tau)}{\partial\tau} = -2w_1 P_{\uparrow\uparrow}(s,\tau) + w_2[P_{\uparrow\downarrow}(s,\tau)+P_{\downarrow\uparrow}(s,\tau)]\,. \tag{7a}$$

w_1 and w_2 are, respectively, the probability of jumping from the upper and lower state. Similarly one may derive

$$\frac{\partial P_{\downarrow\downarrow}}{\partial\tau} = -2w_2 P_{\downarrow\downarrow} + w_1(P_{\uparrow\downarrow}+P_{\downarrow\uparrow})\,, \tag{7b}$$

$$\frac{\partial P_{\uparrow\downarrow}}{\partial\tau} + \frac{\partial P_{\downarrow\uparrow}}{\partial s} = -(w_1+w_2)P_{\uparrow\downarrow} + w_1 P_{\uparrow\uparrow} + w_2 P_{\downarrow\downarrow}\,, \tag{7c}$$

$$\frac{\partial P_{\downarrow\uparrow}}{\partial\tau} - \frac{\partial P_{\downarrow\uparrow}}{\partial s} = -(w_1+w_2)P_{\downarrow\uparrow} + w_1 P_{\uparrow\uparrow} + w_2 P_{\downarrow\downarrow}\,. \tag{7d}$$

We define $\hat{P}_{\uparrow\uparrow}(s,\sigma) = \int_0^\infty e^{-\sigma\tau} P_{\uparrow\uparrow}(s,\tau)\,d\tau$ and similar expressions for the other P's. Then we find

$$(\sigma+2w_1)\hat{P}_{\uparrow\uparrow} - w_2(\hat{P}_{\uparrow\downarrow}+\hat{P}_{\downarrow\uparrow}) = P_{\uparrow\uparrow}(s,0)\,, \tag{8a}$$

$$(\sigma+2w_2)\hat{P}_{\downarrow\downarrow} - w_1(\hat{P}_{\uparrow\downarrow}+\hat{P}_{\downarrow\uparrow}) = P_{\downarrow\downarrow}(s,0)\,, \tag{8b}$$

$$\left(\frac{\partial}{\partial s}+\sigma+w_1+w_2\right)\hat{P}_{\uparrow\downarrow} - w_1\hat{P}_{\uparrow\uparrow} - w_2\hat{P}_{\downarrow\downarrow} = P_{\uparrow\downarrow}(s,0)\,, \tag{8c}$$

$$\left(\frac{\partial}{\partial s}+\sigma+w_1+w_2\right)\hat{P}_{\downarrow\uparrow} - w_1\hat{P}_{\uparrow\uparrow} - w_2\hat{P}_{\downarrow\downarrow} = P_{\downarrow\uparrow}(s,0)\,. \tag{8d}$$

When $\tau=0$, clearly s can only be zero so the initial P's all contain a factor $\delta(s)$. The remaining factor [in $P_{\uparrow\downarrow}(s,0)$, for example] is just the probability of finding the system in the upstate at the start and the down state at the end of an interval of length T. We assume the initial probabilities to be those of an equilibrium distribution, namely $w_2/(w_1+w_2)$ for the up state and $w_1/(w_1+w_2)$ for the down state. The initial P's are now readily found to be

$$P_{\uparrow\uparrow}(s,0) = \delta(s)[w_2/(w_1+w_2)^2] \times (w_2 + w_1 e^{-(w_1+w_2)T})\,, \tag{9a}$$

$$P_{\uparrow\downarrow}(s,0) = \delta(s)[w_2/(w_1+w_2)^2] \times (w_1 - w_1 e^{-(w_1+w_2)T})\,, \tag{9b}$$

$$P_{\downarrow\uparrow}(s,0) = \delta(s)[w_1/(w_1+w_2)^2] \times (w_2 - w_2 e^{-(w_1+w_2)T})\,, \tag{9c}$$

$$P_{\downarrow\downarrow}(s,0) = \delta(s)[w_1/(w_1+w_2)^2] \times (w_1 + w_2 e^{-(w_1+w_2)T})\,. \tag{9d}$$

Note that $P_{\uparrow\downarrow}(s,0) = P_{\downarrow\uparrow}(s,0)$.

From Eqs. (8), we may find an equation satisfied by $\hat{P}_{\uparrow\downarrow}+\hat{P}_{\downarrow\uparrow} = \Sigma$. This is

$$\left(\frac{d^2}{ds^2} - k^2(\sigma)\right)\Sigma = -A\,\delta(s)\,, \tag{10}$$

where

$$k^2(\sigma) = (\sigma+w_1+w_2)^2\,\frac{\sigma(\sigma+2w_1+2w_2)}{(\sigma+2w_1)(\sigma+2w_2)} \tag{11}$$

and

$$A = 2\left(\frac{w_1 w_2}{(w_1+w_2)^2}\right)\frac{(\sigma+w_1+w_2)^2}{(\sigma+2w_1)(\sigma+2w_2)} \times[(\sigma+2w_1+2w_2) - \sigma e^{-(w_1+w_2)T}]\,. \tag{12}$$

The equation for Σ has the solution

$$\Sigma = \begin{cases} \dfrac{A}{2k(\sigma)}\,e^{-|k(\sigma)|s}, & s>0\,, \\[2mm] \dfrac{A}{2k(\sigma)}\,e^{|k(\sigma)|s}, & s<0\,. \end{cases} \tag{13}$$

For $T = \hat{P}_{\uparrow\uparrow}+\hat{P}_{\downarrow\downarrow}+\hat{P}_{\uparrow\downarrow}+\hat{P}_{\downarrow\uparrow}$ we now have

$$T = \Sigma + \frac{P_{\uparrow\uparrow}(s,0)+w_2\Sigma}{\sigma+2w_1} + \frac{P_{\downarrow\downarrow}(s,0)+w_1\Sigma}{\sigma+2w_2}\,. \tag{14}$$

The $\delta(s)$ terms in the $P_{\uparrow\uparrow}(s,0)$ and $P_{\downarrow\downarrow}(s,0)$ will contribute nothing to the integral $\int_{-\infty}^{+\infty} T(s,\sigma)|s|\,ds$ and we have

$$\int_{-\infty}^{+\infty} T(s,\sigma)|s|\,ds = \left(1+\frac{w_2}{\sigma+2w_1}+\frac{w_1}{\sigma+2w_2}\right)\frac{A}{2k(\sigma)}\int_{-\infty}^{+\infty}|s|\,e^{-k(\sigma)|s|}\,ds = \left(1+\frac{w_2}{\sigma+2w_1}+\frac{w_1}{\sigma+2w_2}\right)\frac{A}{k^3(\sigma)}$$

$$= \frac{2w_1w_2}{(w_1+w_2)^2}\,\frac{(\sigma+2w_1+2w_2) - \sigma e^{-(w_1+w_2)T}}{[(\sigma+2w_1+2w_2)(\sigma+2w_1)(\sigma+2w_2)\sigma^3]^{1/2}}\,. \tag{15}$$

Thus, we arrive at the expression

$$f(2\tau,T)=\frac{2w_1w_2}{(w_1+w_2)^2}\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}e^{\sigma\tau}\frac{(\sigma+2w_1+2w_2)-\sigma e^{-(w_1+w_2)T}}{[(\sigma+2w_1+2w_2)(\sigma+2w_1)(\sigma+2w_2)\sigma^3]^{1/2}}\,d\sigma\,,$$

where c is real and the path of integration lies to the right of all the singularities of the integrand. If we write

$$x=(w_1+w_2)\tau\,, \tag{16}$$

$$\xi=(w_1-w_2)/(w_1+w_2)\,, \tag{17}$$

and

$$g=\sigma/(w_1+w_2)+1\,, \tag{18}$$

we obtain

$$\begin{aligned}f(2\tau,T)&=\frac{2w_1w_2}{(w_1+w_2)^3}\frac{e^{-x}}{2\pi i}\int_{c'-i\infty}^{c'+i\infty}e^{gx}\frac{(g+1)-(g-1)e^{-(w_1+w_2)T}}{[(g^2-\xi^2)(g+1)(g-1)^3]^{1/2}}\,dg\\&=\frac{2w_1w_2}{(w_1+w_2)^3}\frac{e^{-x}}{2\pi i}\int_{c'-i\infty}^{c'+i\infty}e^{gx}\frac{2+(g-1)(1-e^{-(w_1+w_2)T})}{(g^2-\xi^2)^{1/2}(g^2-1)^{1/2}(g-1)}\,dg\end{aligned} \tag{19}$$

with the path again to the right of the singularities. Carrying out the inverse Laplace transforms,[8] we find

$$f(2\tau,T)=\frac{2w_1w_2}{(w_1+w_2)^3}\times[F(\xi;x)+(1-e^{-(w_1+w_2)T})G(\xi;x)]\,, \tag{20}$$

where

$$F(\xi;x)=2e^{-x}\int_0^x I_0[\xi(x-x')]\times x'[I_0(x')+I_1(x')]\,dx' \tag{21}$$

and

$$G(\xi;x)=e^{-x}\int_0^x I_0[\xi(x-x')]I_0(x')\,dx'\,. \tag{22}$$

I_0 and I_1 are modified Bessel functions of order zero and one. Note that $\partial F(\xi;x)/\partial x=2G(\xi;x)$.[5]

In terms of the functions $F(\xi;x)$ and $G(\xi;x)$ the amplitudes of the two-pulse and three-pulse stimulated echoes, $e(2\tau)$ and $e(2\tau,T)$, are given by

$$e(2\tau)=\exp\left(-\Delta\omega_{1/2}\frac{4w_1w_2}{(w_1+w_2)^3}\times F[\xi;(w_1+w_2)\tau]\right) \tag{23}$$

and

$$e(2\tau,T)=\exp\{-\Delta\omega_{1/2}[4w_1w_2/(w_1+w_2)^3]\times[F(\xi;(w_1+w_2)\tau)+(1-e^{-(w_1+w_2)T})G(\xi;(w_1+w_2)\tau)]\}\,, \tag{24}$$

where $\Delta\omega_{1/2}$ and ξ are defined by Eqs. (3) and (17).

When $w_1=w_2$, the high temperature limit, we have $\xi=0$ and the functions F and G reduce to

$$F(0,x)=2e^{-x}\int_0^x x'[I_0(x')+I_1(x')]\,dx'$$

and

$$G(0,x)=e^{-x}\int_0^x I_0(x')\,dx'\,.$$

These results agree with those derived by Hu and Hartmann[6] by another procedure for this special case.

There are a number of ways of expressing the function $G(x,\xi)$ which may be useful for computation. One of these is

$$G(x,\xi)=e^{-x}\sum_{n=0}^{\infty}\frac{x^{2n+1}}{(2n+1)!}\xi^nP_n\left(\frac{1+\xi^2}{2\xi}\right)\,, \tag{25}$$

where P_n is the Legendre polynomial of order n. For small ξ this reduces to

$$G(x,\xi)=e^{-x}\sum_{n=0}^{\infty}\frac{x^{2n+1}}{2^{2n}(n!)^2(2n+1)}\times\left(1+\frac{n}{2n-1}\xi^2+O(\xi^4)\right)\,. \tag{26}$$

By rearranging the terms in ξ as power series in $s=1-\xi^2$ and resumming one obtains the expansion

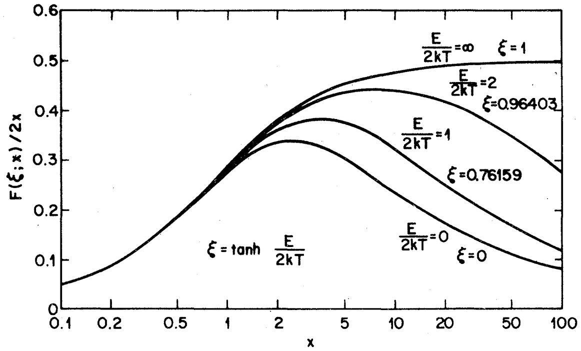

FIG. 1. Function $F(\xi\,;x)/2x$ vs x for different values of ξ.

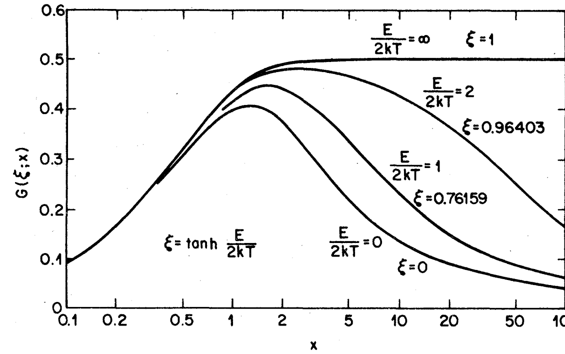

FIG. 2. Function $G(\xi\,;x)$ vs x for different values of ξ.

$$G(x,\xi)=e^{-x}\sum_{p=0}^{\infty}\frac{(-1)^p\frac{1}{2}\times\frac{3}{2}\cdots\times\frac{1}{2}(2p-1)}{(p!)^2}\,s^p\frac{x^{2p}}{2p}\left(\frac{d}{dx}\frac{1}{x}\right)^p\sinh x$$

$$=e^{-x}\{\sinh x-\tfrac{1}{4}s\,(x\cosh x-\sinh x)+\tfrac{3}{64}s^2[(x^2+3)\sinh x-3x\cosh x]$$

$$-\tfrac{5}{768}s^3[(x^3+15x)\cosh x-(6x^2+15)\sinh x]+\cdots\}\,. \qquad (27)$$

Any of these expressions may be integrated term by term to yield $F(x,\xi)=2\int_0^x G(x',\xi)\,dx'$. For large values of sx, $G(x,\xi)\sim\frac{1}{2}e^{-sx/4}I_0(\frac{1}{4}sx)$ and there is a rather cumbersome expansion;

$$G(x,\xi)=\tfrac{1}{2}\sum\frac{(-1)^p}{p!}\left(\frac{s}{8}\right)^p\left(z\frac{d}{dz}+p+\tfrac{1}{2}\right)$$

$$\times\left(z\frac{d}{dz}+p+\tfrac{3}{2}\right)\cdots\left(z\frac{d}{dz}+2p-\tfrac{1}{2}\right)$$

$$\times\left(\frac{d}{dz}\right)^p[e^{-z}I_0(z)]\,, \qquad (28)$$

where $z=\frac{1}{4}sx$.

In Figs. 1 and 2, we have shown the function $F(\xi,x)/2x$ and $G(\xi,x)$ on a semilog plot for different values of ξ. For small values of x, i.e., $x\equiv(w_1+w_2)\tau\ll 1$, there is hardly any dependence on the value of ξ. This is easily understood because this corresponds to a situation where the probability of flipping in the time interval τ is small and we only have to take into account single flips. For larger values of x, where multiple flippings in the time interval τ become important, the dependence on ξ is quite drastic. In Fig. 3, we have shown the echo decay as a function of $\Delta\omega_{1/2}\tau$ for different values of the parameter $\eta\equiv 2\Delta\omega_{1/2}/(w_1+w_2)$. The decay behavior is quite different for $\eta=0.2$ to 2 as is evident in the figure.

In Fig. 4, we have shown the decay of the stimulated echo signal. The decay is always of the form $\exp[-c(1-e^{-(w_1+w_2)T})]$, the only difference being the values of c for different values of ξ. Again it is shown that the dependence of c on ξ is only observable for $\Delta\omega_{1/2}\tau>1$.

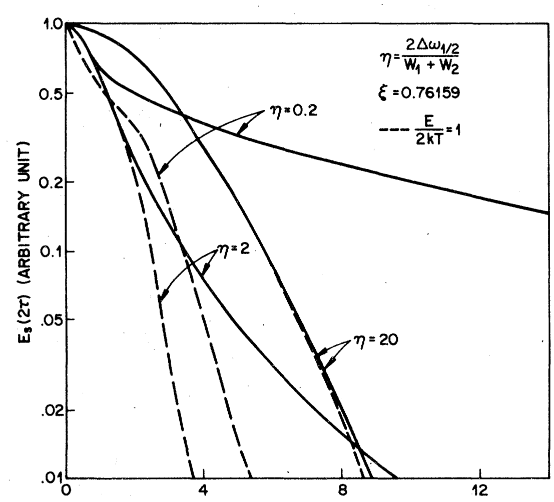

FIG. 3. Echo decay as a function of $\Delta\omega_{1/2}\tau$ for different values of $\eta\equiv 2\,\Delta\omega_{1/2}\tau/(w_1+w_2)$.

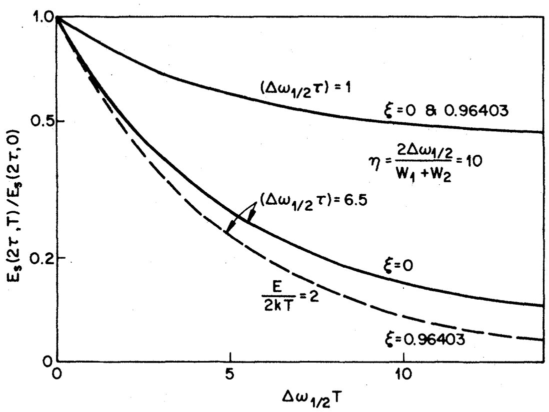

FIG. 4. Stimulated echo decay as a function of $\Delta\omega_{1/2}\tau$ for different values of $\eta \equiv 2\Delta\omega_{1/2}\tau/(w_1+w_2)$.

III. CONCLUSION

Using an uncorrelated sudden jump model, we have presented here a calculation of the phase memory time involved in a typical echo experiment. Though this paper is essentially an extension of the previous work by Hu and Hartmann,[6] the mathematical approach is different and more general. This allows us in a natural way to take into account the fact that the B spins may flip from one state to another with unequal transition probabilities. For application to electron spin resonance, our results provide a necessary correction to the previous work in the cases of high frequency and in the low-temperature domain. However, in most experiments done up to now, and, where the comparisons have been made with the theory,[9-11] the correction is quite small and negligible. This is because at lower temperatures the experiments are in the region of $(w_1+w_2)\tau \leq 1$ and for higher temperatures, though $(w_1+w_2)\tau \geq 1$ the value of $E/2kT$ is correspondingly decreased.

Spectral diffusion in NMR, of course, has been studied earlier.[4] Although, in that case, the decay mechanisms and the distribution of B spins are quite different from those considered here, the echo decay curves show many qualitative similarities.

An interesting and direct application of present theory has already been applied by us to the study of phonon echo decay[12,13] in glasses at very low temperatures. As we pointed out there, the results indicate that more extended observation of the echo would enable one to verify the prediction of the tunnelling model. Another simple extension of our present work will be the application of our theory to the study of spin coherence in photoexcited triplet state under the influence of vibronic relaxation, e.g., in parabenzoquinone and liquinone.[14,15] In these and other experiments,[16] the temperature dependence of the linewidth can be studied in addition to the echoes. It is straightforward to extend our calculation to find the linewidth. It is noted that in the special case of equal flipping probability, this is the well-known linewidth problem first solved by Archer and by Anderson.[17]

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