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Mathematical Analysis of the Hahn Spin-Echo Experiment

T. P. DAS AND A. K. SAHA
Institute of Nuclear Physics, Calcutta, India
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It was felt that the averaging procedures employed by Hahn in his theory of the "Spin-echoes" requires modification in several respects. A more satisfactory averaging procedure has been introduced here, and gives substantially the same results as those obtained by Hahn.

INTRODUCTION

THE powerful free-induction technique has been introduced into the field of nuclear induction quite recently by Hahn.[1] In contrast to the usual methods of observation, where the motion of magnetic nuclei is studied in the *presence* of a steady or pulsed rf field, the free-induction method confines itself to a study of the motion in the *absence* of the rf field, or rather in the interval following the application of the rf field, which is applied in the form of rectangular pulses of short duration. A theory of the "free induction" process and of a further extension of it, termed the "spin-echo" process, was also given by Hahn,[1] starting from the conventional Bloch equations.[2] Besides taking account of the effects of natural relaxation processes and field inhomogeneity, Hahn has also considered the effect of diffusion processes within the periods of observation. In trying to follow his theory, we found that his arguments regarding the diffusion damping of the free induction and the echo signals did not appear quite convincing. We therefore repeated his calculations using what appeared to us a more satisfactory averaging procedure. We give below the details of our calculations and compare our results with those obtained by Hahn.

THE FUNDAMENTAL EQUATIONS

In the analysis of the spin-echo phenomena, the basic Bloch equations and their solutions, in the presence and absence of the applied rectangular rf-field pulses, are applied successively. However, the following two modifications are introduced:

(a) First, because of the inhomogeneity of the steady magnetic field in the Z direction, the sample under study may be broken up into small groups of nuclei, each characterised by a particular value of ω_z, the angular Larmor frequency about the Z direction. The inhomogeneity of the magnetic field causes a distribution in ω_z and hence in $\Delta\omega=\omega_z-\omega$ (ω being the applied rf frequency) among the groups; and we may call this breakup into groups a division into "isochromatic" groups. We shall then have one set of Bloch equations[2] for each isochromatic group, and in this we shall have to use the natural spin-spin relaxation time T_2 instead of the net transverse relaxation time T_2^*, including the effect of the field inhomogeneity.[3] The effect of the magnetic field inhomogeneity is taken care of by the splitting into isochromatic groups. It will be assumed that $g(\Delta\omega)$, representing the distribution in $\Delta\omega$ among the groups, is Gaussian with a root-mean-square value $1/T_2^*$, and is thus symmetrical about $\Delta\omega=0$.

(b) Secondly, the "self-diffusion" effect has to be introduced. This takes account of the fact that by virtue of the random motion of the molecules carrying the nuclei, especially in liquid samples, each isochromatic group moves into different inhomogeneous parts of the field, so that ω_z is a random function of time and may be written

$$\omega_z(t)=\omega_z(t')+\eta_{tt'}.$$

$\eta_{tt'}$ represents the change in Larmor frequency by diffusion in the interval $t-t'$, so that $\Delta\omega$ is now also a function of time; i.e.,

$$\Delta\omega(t)=\Delta\omega(t')+\eta_{tt'}. \qquad (1)$$

When we write $\Delta\omega$ without specifying the time, we shall mean the value at time $t=0$. Thus $\Delta\omega(t')=\Delta\omega+\eta_{t'0}$. Thus, the modified Bloch equations for a isochromatic group $\Delta\omega$ may, for the interval t' to t, be written as

$$\begin{aligned} dU/dt+[\Delta\omega(t')+\eta_{tt'}]V&=-U/T_2,\\ dV/dt-[\Delta\omega(t')+\eta_{tt'}]U&=-(V/T_2)-\omega_1W, \qquad (2)\\ dW/dt&=\omega_1V+((1-W)/T_1),\end{aligned}$$

where UM_0, VM_0, and WM_0 are the X, Y, and Z components, respectively, of the magnetic moment vector $\mathbf{M}(\Delta\omega)$ of a nucleus, in the group under study, in a coordinate system rotating with the rf field $\mathbf{H}_1$, with frequency equal to the frequency of the rf field, and with $\mathbf{U}$ in the direction of $\mathbf{H}_1$.[2] M_0 corresponds to the intrinsic magnetic moment of the nucleus under study. T_1 and T_2 represent the spin-lattice and spin-spin relaxation times, respectively, because of natural relaxation processes, and $\omega_1=\gamma H_1$, γ being the gyromagnetic ratio of the nucleus under study. Here $\Delta\omega(t')$ has been used instead of $\Delta\omega$ because there will be a spectrum of Larmor frequencies in the originally homogeneous isochromatic group $\Delta\omega$ at the instant t' as a result of the fact that the members of the group will on account of diffusion spread out to different positions.

[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[2] F. Bloch, Phys. Rev. **70**, 460 (1946).
[3] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

$\eta_{tt'}$ represents the further shift of Larmor frequency of the cluster $\Delta\omega+\eta_{t'0}$ in the interval $t-t'$.

If the rf field be applied for an interval t_w, very small compared with T_1 and T_2, so that the relaxation processes and diffusion processes have little time to be effective, then we can neglect the terms involving these effects, and the solutions of Eqs. (2) for a isochromatic group $\Delta\omega$ during the pulse are given by

$$\begin{aligned} U(t)&=[\Delta\omega(t')/\Omega]aQ+U(t'),\\ V(t)&=a\sin(\Omega t+\psi),\\ W(t)&=-(\omega_1/\Omega)aQ+W(t'), \end{aligned} \tag{3}$$

where t' refers to the start of the rf-field pulse, and

$$\begin{aligned} a&=\{[V(t')]^2+[U(t')\cdot\cos\Theta-W(t')\cdot\sin\Theta]^2\}^{\frac{1}{2}},\\ \psi&=\tan^{-1}\left(\frac{V(t')}{U(t')\cdot\cos\Theta-W(t')\sin\Theta}\right),\\ \Delta\omega(t')&=\Delta\omega+\eta_{t'0},\\ \cot\Theta&=\Delta\omega(t')/\omega_1,\\ Q&=\cos[\Omega(t-t')+\psi]-\cos\psi,\\ \Omega&=\{\omega_1^2+[\Delta\omega(t')]^2\}^{\frac{1}{2}}. \end{aligned} \tag{4}$$

If we further have the condition that

$$\omega_1\gg(\Delta\omega)_{\frac{1}{2}}, \tag{5}$$

where $(\Delta\omega)_{\frac{1}{2}}$ is the half-width of the distribution in $\Delta\omega$ and is proportional to $1/T_2^*$, then we can write the solutions at the end of the pulse approximately as

$$\begin{aligned} U(t'+t_w)&=U(t'),\\ V(t'+t_w)&=V(t')\cos\xi-W(t')\sin\xi,\\ W(t'+t_w)&=V(t')\sin\xi+W(t')\cos\xi, \end{aligned} \tag{6}$$

with $\xi=\omega_1 t_w$ representing the angle of nutation of the magnetic moment vector about the direction of the rf field.[1] The rf pulse may be referred to by specifying the angle ξ. Thus in Purcell's qualitative explanation [Sec. III(B) of Hahn's paper[1]] of the spin-echo phenomena, a 90° pulse was used.

In the absence of the rf field pulse, $\omega_1=0$, and the Eqs. (2) reduce to

$$\begin{aligned} dU/dt+[\Delta\omega(t'')+\eta_{tt''}]V&=-U/T_2,\\ dV/dt-[\Delta\omega(t'')+\eta_{tt''}]U&=-V/T_2,\\ dW/dt&=(1-W)/T_1, \end{aligned} \tag{7}$$

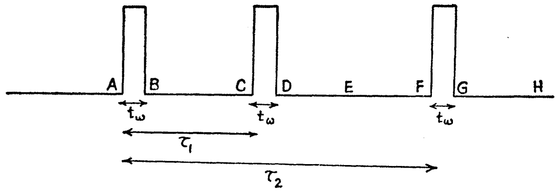

FIG. 1. Applied radio-frequency pulses.

where t'' refers to the instant when the previous rf pulse was cut off and free precession started. From the first two equations of (7) we get, putting $f=U+iV$, (compare Jacobsohn and Wangsness[4])

$$f(t)=f(t'')\cdot\exp\left[-\frac{t-t''}{T_2}+i\left\{\Delta\omega(t'')\cdot(t-t'')+\int_{t''}^{t}\eta_{t'''t''}dt'''\right\}\right]. \tag{8}$$

Separating (8) into real and imaginary parts, we have

$$\begin{aligned} U(t)&=\exp\left(-\frac{t-t''}{T_2}\right)\\ &\quad\times[U(t'')\cos\{\Delta\omega(t'')\cdot(t-t'')+\phi_{tt''}\}\\ &\quad-V(t'')\sin\{\Delta\omega(t'')\cdot(t-t'')+\phi_{tt''}\}],\\ V(t)&=\exp\left(-\frac{t-t''}{T_2}\right)\\ &\quad\times[V(t'')\cos\{\Delta\omega(t'')\cdot(t-t'')+\phi_{tt''}\}\\ &\quad+U(t'')\sin\{\Delta\omega(t'')\cdot(t-t'')+\phi_{tt''}\}]. \end{aligned} \tag{9}$$

From the third equation of (7), we have

$$W(t)=1+\{W(t'')-1\}\exp\left(-\frac{t-t''}{T_1}\right). \tag{10}$$

Now, in (9), we have a phase factor involved, *viz.*,

$$\phi_{tt''}=\int_{t''}^{t}\eta_{t'''t''}dt''', \tag{11}$$

giving the phase accumulation by the precessing group owing to the random diffusion process. Now, because of the random nature of this diffusion process we have to average over the different possible $\phi_{tt''}$ values. For this purpose we need a distribution function in $\phi_{tt''}$, which we may denote by

$$P[\phi_{tt''},t-t'']. \tag{12}$$

This has been evaluated by Slichter (see reference 1), and is shown in the appendix to be

$$P[\phi_{tt''},t-t'']=\frac{1}{\left[\frac{4\pi}{3}k(t-t'')^3\right]^{\frac{1}{2}}}\times\exp\left(-\frac{3\phi_{tt''}^2}{4k(t-t'')^3}\right), \tag{13}$$

where $k=(\gamma G)^2D$; G refers to the field gradient, assumed constant over the sample, and D is the self-

[4] B. A. Jacobsohn and R. K. Wangsness, Phys. Rev. **73**, 942 (1948).

diffusion coefficient of the liquid containing the nuclei. There is an important difference between our method of averaging over ϕ and that of Hahn. This point will be taken up later and leads to results somewhat different in nature from those of Hahn. Furthermore, to average over the Larmor frequency shift $\eta_{t''t'''}$, we need a distribution function in $\eta_{t''t'''}$, *viz.*, $P[\eta_{t''t'''}, t''-t''']$, which is shown in the appendix to be

$$P[\eta_{t''t'''}, t''-t''']=\frac{1}{[4\pi k(t''-t''')]^{\frac{1}{2}}}\times\exp\left[-\frac{\eta_{t''t'''}^2}{4k(t''-t''')}\right]. \quad (14)$$

CONDITIONS AT SUCCESSIVE STAGES OF APPLICATIONS TO THE PULSES

Using these results, we pass on to an analysis of the nature of nuclear signals to be expected when the rf field is applied in the form of successive pulses of the type indicated in Fig. 1. The pulses satisfy the following conditions regarding the intervals between the first and second and between the second and third pulses:

$$\tau_1 \gg t_w, \quad \tau_1 \gg T_2^*, \quad \text{and} \quad \tau_2 > 2\tau_1, \quad (15)$$

together with the following conditions regarding the width and amplitude:

$$t_w \ll T_2, T_1 \quad \text{and} \quad \omega_1 \gg 1/T_2^*. \quad (16)$$

Using Eqs. (6), (9), and (10), we shall now tabulate the values of U, V, and W for a group, at successive stages of application of the pulses, *viz.*, at A, B, C, D, F, G, and H (see Fig. 1). The equations at E are obtained from those at F by writing t in place of τ_2. In this connection, it is to be noted that at A, as well as at B, the isochromatic group has its precessing frequency equal to $\Delta\omega$. In the first free precession interval, i.e., from B to C, diffusion occurs; and a phase accumulation ϕ_{10}, given by $\int_0^{\tau_1}\eta_{t'''0}dt'''$, and with a distribution given by Eq. (31), takes place in the U and V terms, W remaining independent of the diffusion. At C, the isochromatic group $\Delta\omega$ breaks up into clusters, each with a Larmor frequency $\Delta\omega+\eta_{10}$, whose spectrum is given by (33). In the second free precession interval, i.e., from D to F, a further phase accumulation ϕ_{21}, equal to $\phi_{\tau_2\tau_1}$, occurs in U and V, and the cluster $\Delta\omega+\eta_{10}$ again breaks up at F into further clusters of Larmor frequencies $\Delta\omega+\eta_{10}+\eta_{21}$. The quantity W, belonging to the isochromatic group $\Delta\omega$, still remains unaffected by the diffusion at the end of the second free precession interval, as is apparent from the equations in Table I. On this point we disagree with Hahn, who expected a spectrum in W at this stage depending on η. Finally, as the positions reached by the cluster at C and again at F, starting from C, are quite independent of each other, η_{10} and η_{21} will be independent of each other and may be separately averaged by using the probability that a cluster may collect a Larmor frequency shift η_{10} in the interval between 0 and τ_1, and

TABLE I. Values of U, V, and W at instants A, B, C, D, F, G, and H.

Instant	$0(A)$	$t_w(B)$	$\tau_1(C)$	$\tau_1+t_w(D)$	$\tau_2(F)$	$\tau_2+t_w(G)$	$t>\tau_2+t_w(H)$
Lamor frequency	$\Delta\omega$	$\Delta\omega$	$\Delta\omega+\eta_{10}$	$\Delta\omega+\eta_{10}$	$\Delta\omega+\eta_{10}+\eta_{10}$	$\Delta\omega+\eta_{10}+\eta_{21}$	$\Delta\omega+\eta_{10}+\eta_{21}+\eta_{t2}$
U	0	0	$\sin\xi\sin(\Delta\omega\tau_{10}+\phi_{10})\times\exp(-\tau_{10}/T_2)P(\phi_{10},\tau_{10})$	$U(C)$	$[U(D)\cos\{(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}\}-V(D)\sin\{(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}\}]\times\exp(-\tau_{21}/T_2)P(\phi_{21},\tau_{21})P(\eta_{10},\tau_{10})$	$U(F)$	$[U(G)\cos\{(\Delta\omega+\eta_{10}+\eta_{21})(t-\tau_2)+\phi_{t2}\}-V(G)\sin\{(\Delta\omega+\eta_{10}+\eta_{21})(t-\tau_2)+\phi_{t2}\}]\times\exp\left(-\frac{t-\tau_2}{T_2}\right)P(\phi_{t2},t-\tau_2)P(\eta_{21},\tau_{21})$
V	0	$-\sin\xi$	$-\sin\xi\cos(\Delta\omega\tau_{10}+\phi_{10})\times\exp(-\tau_{10}/T_2)P(\phi_{10},\tau_{10})$	$V(C)\cos\xi-W(C)\sin\xi$	$[U(D)\sin\{(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}\}+V(D)\cos\{(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}\}]\times\exp(-\tau_{21}/T_2)P(\phi_{21},\tau_{21})P(\eta_{10},\tau_{10})$	$V(F)\cos\xi-W(F)\sin\xi$	$[U(G)\sin\{(\Delta\omega+\eta_{10}+\eta_{21})(t-\tau_2)+\phi_{t2}\}+V(G)\cos\{(\Delta\omega+\eta_{10}+\eta_{21})(t-\tau_2)+\phi_{t2}\}]\times\exp\left(-\frac{t-\tau_2}{T_2}\right)P(\phi_{t2},t-\tau_2)P(\eta_{21},\tau_{21})$
W	1	$\cos\xi$	$1+(\cos\xi-1)\exp(-\tau_{10}/T_1)$	$V(C)\sin\xi+W(C)\cos\xi$	$1+\{W(D)-1\}\exp(-\tau_{21}/T_1)$	$V(F)\sin\xi+W(F)\cos\xi$	$1+\{W(G)-1\}\exp\left(-\frac{t-\tau_2}{T_1}\right)$

η_{21} in the interval $\tau_2-\tau_1$, *viz.*, $P(\eta_{10},\tau_{10})\cdot P(\eta_{21},\tau_{21})$ given by Eqs. (38) and (39). After the third pulse, free precession starts again and we use ϕ_{t2} to denote the phase difference accumulated in U and V between G and H, the latter corresponding to instant $t>\tau_2+t_w$. It is our aim to calculate $V(t)$ explicitly in the second and third free precession intervals, because the signal expected will only depend on V.

PRIMARY ECHO

Using the solutions in Table I, we shall now investigate the conditions after passage of the second pulse at $t=\tau_1$. In this case, we have to consider the solutions at E for U and V, which can be obtained, as pointed out before, from the solutions at F, by substituting t for τ_2, with $\tau_1+t_w<t<\tau_2$. It has, of course, to be remembered that since we shall ultimately integrate over a Gaussian distribution in $\Delta\omega$, we need only retain the terms with even parity with respect to $\Delta\omega$. In this respect, the U term at E may easily be seen to be entirely of odd parity with respect to $\Delta\omega$, and so it does not contribute to the total signal from the sample under study. And even in the V term, we have to retain only that part which is even with respect to $\Delta\omega$.

In this connection we need the even terms in x in products of the form $\sin(ax+p)\sin(bx+q)$ and $\cos(ax+p)\cos(bx+q)$, and it may be easily seen that, in these products, the parts even with respect to x are given by:

$$[\sin(ax+p)\sin(bx+q)]_{\text{even}}=\sin ax\,\sin bx\,\cos p\,\cos q+\cos ax\,\cos bx\,\sin p\,\sin q.$$

$$[\cos(ax+p)\cos(bx+q)]_{\text{even}}=\cos ax\,\cos bx\,\cos p\,\cos q+\sin ax\,\sin bx\,\sin p\,\sin q. \quad (17)$$

Now, at E, we find, substituting the values of U, V, and W in previous instants, the total signal to be proportional to

$$V(E)=\int\int_{-\infty}^{\infty}\int\int\Big[\sin\xi\,\sin(\Delta\omega\tau_{10}+\phi_{10})\times\exp\left(-\frac{\tau_{10}}{T_2}\right)\sin\{(\Delta\omega+\eta_1)(t-\tau_1)+\phi_{t1}\}+\Big\{-\sin\xi\cos(\Delta\omega\tau_{10}+\phi_{10})\times\exp\left(-\frac{\tau_{10}}{T_2}\right)\cos\xi-W(c)\sin\xi\Big\}\times\cos\{(\Delta\omega+\eta_{10})(t-\tau_1)+\phi_{t1}\}\Big]\times\exp\left(-\frac{t-\tau_1}{T_2}\right)P(\phi_{10},\tau_{10})P(\phi_{t1},t-\tau_1)\times P(\eta_{10},\tau_{10})g(\Delta\omega)d\phi_{10}d\phi_{t1}d\eta_{10}d(\Delta\omega).$$

Since the distributions over η_{10} and ϕ_{10} are Gaussian, we have to retain only that part of V which is even in η_{10} and ϕ_{10}. Applying the symmetry conditions (17) we have, for the part of the integrand which is of even parities in $\Delta\omega$, η_{10} and ϕ_{10},

$$[\sin\xi\{\sin^2\tfrac{1}{2}\xi\cos\Delta\omega(t-2\tau_1)\cos(\phi_{t1}-\phi_{10})-\cos^2\tfrac{1}{2}\xi\cos\Delta\omega t\cos(\phi_{t1}+\phi_{10})\}\times\cos\eta_1(t-\tau_1)\exp(-t/T_2)-W(C)\sin\xi\cos\Delta\omega(t-\tau_1)\cos\phi_{t1}\times\cos\eta_1(t-\tau_1)\exp\{-(t-\tau_1)/T_2\}]\times P(\phi_{10},\tau_{10})P(\phi_{t1},t-\tau_1)P(\eta_{10},\tau_{10})g(\Delta\omega). \quad (19)$$

Using for $g(\Delta\omega)$ the normalized Gaussian distribution,

$$g(\Delta\omega)=\frac{T_2^*}{(2\pi)^{\frac{1}{2}}}\exp\left[-\frac{(\Delta\omega T_2^*)^2}{2}\right], \quad (20)$$

and using Eqs. (31), (33), and (34) of the appendix, we get the total signal at E proportional to

$$V(E)=\sin\xi\,\sin^2\frac{\xi}{2}\exp\left[-\frac{t}{T_2}-\frac{(t-2\tau_1)^2}{2T_2^{*2}}\right]\times\exp\left[-\frac{k}{3}\{(t-\tau_1)^3+\tau_1^3+3\tau_1(t-\tau_1)^2\}\right]-\sin\xi\,\cos^2\frac{\xi}{2}\exp\left[-\frac{t}{T_2}-\frac{t^2}{2T_2^{*2}}\right]\times\exp\left[-\frac{k}{3}\{(t-\tau_1)^3+\tau_1^3+3\tau_1(t-\tau_1)^2\}\right]-W(c)\sin\xi\exp\left[-\frac{t-\tau_1}{T_2}-\frac{(t-\tau_1)^2}{2T_2^{*2}}\right]\times\exp\left[-\frac{k}{3}\{(t-\tau_1)^3+3\tau_1(t-\tau_1)^2\}\right]. \quad (21)$$

This equation may be compared with the corresponding Eq. (17) of Hahn's paper. The first and third terms give, respectively, the *primary echo* at $t=2\tau_1$, and the *free-induction signal* following the second pulse. The middle term is a continuation of the *free-induction signal* following the first pulse and, on account of the smallness of T_2^*, is almost zero in the second free precession interval. There is complete agreement between our results and those of Hahn regarding the trigonometric part of the amplitude of the various terms, the damping due to the natural relaxation processes, and the position of the maxima. But, there is disagreement in the diffusion terms. We compare our diffusion terms with those of Hahn, in Table II.

SECONDARY ECHOES

In this case, we have to consider the conditions at H, after the passage of the third pulse. Here again we need

TABLE II. Our diffusion damping terms for the primary echo, compared with those of Hahn.

Term	Position of maximum	Hahn's results: Value of the diffusion term	Hahn's results: Value of the diffusion term at echo maximum	Our results: Value of the diffusion term	Our results: Value of the diffusion term at echo maximum
Primary echo	$2\tau_1$	$\exp(-\frac{1}{3}kt^3)$	$\exp\left(-\frac{8k\tau_1^3}{3}\right)$	$\exp\left[-\frac{k}{3}\{(t-\tau_1)^3+\tau_1^3+3\tau_1(t-\tau_1)^2\}\right]$	$\exp\left(-\frac{5k\tau_1^3}{3}\right)$
Free induction signal following second pulse	τ_1	$\exp\left[-\frac{k}{3}(t-\tau_1)^3\right]$		$\exp\left[-\frac{k}{3}\{(t-\tau_1)^3+3\tau_1(t-\tau_1)^2\}\right]$	

consider only the terms even in $\Delta\omega$, and the U term may again be seen to have no contribution to the total signal. Further, we have also to find the terms in V even in $\Delta\omega$. For this purpose, in addition to conditions (17) we need the terms even in x from the products

$$\sin(ax+p\,\sin(bx+q)\,\cos(cx+r)$$

and

$$\cos(ax+p)\,\cos(bx+q)\,\cos(cx+r).$$

Thus,

$$\begin{aligned}[\sin(ax+p)\,\sin(bx+q)\,\cos(cx+r)]_{\text{even}} &= \sin ax\,\sin bx\,\cos cx\,\cos p\,\cos q\,\cos r\\ &\quad -\sin ax\,\sin bx\,\sin cx\,\cos p\,\sin q\,\sin r\\ &\quad -\cos ax\,\sin bx\,\sin cx\,\sin p\,\cos q\,\sin r\\ &\quad +\cos ax\,\cos bx\,\cos cx\,\sin p\,\sin q\,\cos r.\\ [\cos(ax+p)\,\cos(bx+q)\,\cos(cx+r)]_{\text{even}} &= \cos ax\,\cos bx\,\cos cx\,\cos p\,\cos q\,\cos r\\ &\quad +\cos ax\,\sin bx\,\sin cx\,\cos p\,\sin q\,\sin r\\ &\quad +\sin ax\,\cos bx\,\sin cx\,\sin p\,\cos q\,\sin r\\ &\quad +\sin ax\,\sin bx\,\cos cx\,\sin p\,\sin q\,\cos r. \qquad (22)\end{aligned}$$

From the solutions for V at H, we get, after applying the values of U, V, and W at previous instants A, B, C, D, F, and G, the total signal, as proportional to

$$\begin{aligned}V(H)=\int\int\int_{-\infty}^{\infty}\int\int\int\Big[&\sin\{(\Delta\omega+\eta_{10}+\eta_{21})(t-\tau_2)+\phi_{t2}\}\\ &\times\Big(\cos\{(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}\}\,\sin\xi\,\sin(\Delta\omega\tau_{10}+\phi_{10})\\ &\times\exp\left(-\frac{\tau_{10}}{T_2}\right)P(\phi_{10},\tau_{10})\\ &-\sin\{(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}\}.\\ &\times\Big\{-\cos\xi\,\sin\xi\,\cos(\Delta\omega\tau_{10}+\phi_{10})\\ &\times\exp\left(-\frac{\tau_{10}}{T_2}\right)P(\phi_{10},\tau_{10})-\sin\xi W(C)\Big\}\Big)\\ &\times\exp\left(-\frac{\tau_{21}}{T_2}\right)P(\phi_{21},\tau_{21})P(\eta_{10},\tau_{10})\\ &+\cos\{(\Delta\omega+\eta_{10}+\eta_{21})(t-\tau_2)+\phi_{t2}\}\\ &\times\Big(\cos\xi\sin[(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}]\\ &\times\sin\xi\,\sin(\Delta\omega\tau_{10}+\phi_{10})\,\exp\left(-\frac{\tau_{10}}{T_2}\right)\\ &\times P(\phi_{10},\tau_{10})+\cos[(\Delta\omega+\eta_{10})\tau_{21}+\phi_{21}]\\ &\times\Big\{-\cos^2\xi\,\sin\xi\,\cos(\Delta\omega\tau_{10}+\phi_{10})\\ &\times\exp\left(-\frac{\tau_{10}}{T_2}\right)P(\phi_{10},\tau_{10})-\sin\xi\,\cos\xi W(C)\Big\}\\ &\times\exp\left(-\frac{\tau_{21}}{T_2}\right)P(\phi_{21},\tau_{21})P(\eta_{10},\tau_{10})\\ &-\sin\xi-\sin\xi\,\exp\left(-\frac{\tau_{21}}{T_1}\right)\\ &\times\Big\{-1-\sin\xi\,\sin\xi\,\cos(\Delta\omega\tau_{10}+\phi_{10})\\ &\times\exp\left(-\frac{\tau_{10}}{T_2}\right)P(\phi_{10},\tau_{10})+\cos\xi W(C)\Big\}\Big)\Big]\\ &\times\exp\left(-\frac{t-\tau_2}{T_2}\right)P(\phi_{t2},t-\tau_2)P(\eta_{21},\tau_{21})g(\Delta\omega)\\ &\times d\phi_{10}d\phi_{21}d\eta_{10}d\phi_{t2}d\eta_{21}d(\Delta\omega). \qquad (23)\end{aligned}$$

Retaining, as before, the part of the integrand which is of even parity in $\Delta\omega$, η_{10}, η_{21}, ϕ_{10}, ϕ_{21}, and ϕ_{t2}, we get, using Eqs. (31), (33), and (34) of the appendix,

$$
\begin{aligned}
V(H)=&\frac{\sin^3\xi}{2}\exp\left[-(\tau_2-\tau_1)\left(\frac{1}{T_1}-\frac{1}{T_2}\right)-\frac{t}{T_2}\right]\\
&\times\exp\left[-\frac{\{t-(\tau_2+\tau_1)\}^2}{2T_2^{*2}}\right]\exp[-\tfrac{1}{3}k\{(t-\tau_2)^3\\
&+\tau_1^3+3\tau_1(t-\tau_1)^2+3(\tau_2-\tau_1)(t-\tau_2)^2\}]\\
&+\sin\xi\,\sin^4\frac{\xi}{2}\exp\left[-\frac{t}{T_2}\right]\\
&\times\exp\left[-\frac{\{t-(2\tau_2-2\tau_1)\}^2}{2T_2^{*2}}\right]\\
&\times\exp[-\tfrac{1}{3}k\{(t-\tau_2)^3+(\tau_2-\tau_1)^3+\tau_1^3\\
&+3\tau_1(t-2\tau_2+\tau_1)^2+3(\tau_2-\tau_1)(t-\tau_2)^2\}]\\
&+W(c)\sin\xi\,\sin^2\frac{\xi}{2}\exp\left[-\frac{t-\tau_1}{T_2}\right]\\
&\times\exp\left[-\frac{\{t-(2\tau_2-\tau_1)\}^2}{2T_2^{*2}}\right]\\
&\times\exp[-\tfrac{1}{3}k\{(t-\tau_2)^3+(\tau_2-\tau_1)^3\\
&+3\tau_1(t-2\tau_2+\tau_1)^2+3(\tau_2-\tau_1)(t-\tau_2)^2\}]\\
&+\frac{\sin^3\xi}{4}\exp\left[-\frac{t}{T_2}\right]\exp\left[-\frac{\{t-2\tau_2\}^2}{2T_2^{*2}}\right]\\
&\times\exp[-\tfrac{1}{3}k\{(t-\tau_2)^3+(\tau_2-\tau_1)^3+\tau_1^3\\
&+3(\tau_2-\tau_1)(t-\tau_2)^2+3\tau_1(t-2\tau_2+\tau_1)^2\}].\quad(24)
\end{aligned}
$$

We have not included in the above equation those terms which represent the continuations of the primary echo and the free induction terms arising in the previous free precession intervals, because these will be almost totally damped out in the interval H. The first term in (24) represents the *stimulated echo* occurring at the instant $t=\tau_2+\tau_1$. The remaining terms represent the *secondary echoes* occurring, respectively, at $t=2(\tau_2-\tau_1)$, $2\tau_2-\tau_1$, $2\tau_2$. Our results agree again with those of Hahn [reference 1, Eqs. (22-A) to (22-D)] for the positions, trigonometric dependence on ξ, and damping due to natural relaxation processes. But there appears again a discrepancy in the diffusion damping terms. We tabulate in Table III our results, together with those of Hahn for comparison.

DISCUSSION

The physical picture explaining the mechanism of formation of the various echoes has been given in great detail by Hahn.[1] We shall here confine ourselves mainly to a discussion on the origin and magnitude of the discrepancies between Hahn's diffusion terms and ours.

The origin of the discrepancy is in the different procedures used for averaging over ϕ and η. Hahn applies the averaging procedure for η merely to the W term as indicated in his Eq. (14). For the U and V terms [see reference 1, Eq. (11-A)], he collects the phase difference accumulated in the interval $t-t''$, *viz.*, $\phi(t)-\phi(t'')$, and in the term $\exp[i\{\phi(t)-\phi(t'')\}]$ he applies the averaging procedure to $\phi(t)$, regarding $\phi(t'')$ as a constant and with $\phi(t)$ now representing the phase difference accumulated in the interval from t to the start. Our method, on the other hand, is somewhat different. In our procedure terms like $\phi(t)$ and $\phi(t'')$, by themselves, have no meaning; only terms like $\phi_{tt''}$, representing the phase difference accumulated by diffusion in the interval t to t'', are important. This is because, as mentioned before, we divide the entire interval of application of pulses, into successive free precession intervals. Starting with a single isochromatic group characterized by $\Delta\omega$, we take account both of the entire Larmor frequency shifts for calculations of U, V, and W, and the phase differences that U and V undergo in the successive intervals, applying suitable distribution functions for these (given in appendix); ultimately, at the position of formation of the echoes, as in Eqs. (18) and (23),

TABLE III. Our diffusion damping terms for the secondary echoes, compared with those of Hahn.

	Hahn's results			Our results	
Term	Position of echo maximum	Value of the diffusion term	Value of the diffusion term at echo maximum	Value of the diffusion term	Value of the diffusion term at echo maximum
Stimulated echo	$\tau_2+\tau_1$	$-\frac{1}{3}k[\tau_1^3+(t-\tau_2)^3+3\tau_1^2(\tau_2-\tau_1)]$	$-\frac{1}{3}k(3\tau_1^2\tau_2-\tau_1^3)$	$-\frac{1}{3}k[(t-\tau_2)^3+\tau_1^3+3\tau_1(t-\tau_2)^2+3(\tau_2-\tau_1)(t-\tau_2)^2]$	$-\frac{1}{3}k(3\tau_1^2\tau_2+2\tau_1^3)$
First secondary echo	$2\tau_2-2\tau_1$	$-\frac{1}{3}kt^3$	$-(8k/3)[\tau_2^3-3\tau_2^2\tau_1+3\tau_1^2\tau_2-\tau_1^3]$	$-\frac{1}{3}k[(t-\tau_2)^3+(\tau_2-\tau_1)^3+\tau_1^3+3\tau_1(t-2\tau_2+\tau_1)^2+3(\tau_2-\tau_1)(t-\tau_2)^2]$	$-\frac{1}{3}k[5\tau_2^3-23\tau_1^3+39\tau_1^2\tau_2-29\tau_1\tau_2^2]$
Second secondary echo	$2\tau_2-\tau_1$	$-\frac{1}{3}k(t-\tau_1)^3$	$-(8k/3)(\tau_2-\tau_1)^3$	$-\frac{1}{3}k[(t-\tau_2)^3+(\tau_2-\tau_1)^3+3(\tau_2-\tau_1)(t-\tau_2)^2+3\tau_1(t-2\tau_2+\tau_1)^2]$	$-\frac{1}{3}k[5(\tau_2-\tau_1)^3]$
Third secondary echo	$2\tau_2$	$-\frac{1}{3}kt^3$	$-(8k/3)\tau_2^3$	$-\frac{1}{3}k[(t-\tau_2)^3+\tau_1^3+(\tau_2-\tau_1)^3+3(\tau_2-\tau_1)(t-\tau_2)^2+3\tau_1(t-2\tau_2+\tau_1)^2]$	$-\frac{1}{3}k[5\tau_2^3-6\tau_1\tau_2^2+3\tau_1^2\tau_2+3\tau_1^3]$

we average over the entire frequency shift and phase difference accumulated. This procedure has been accepted by Dr. Hahn as more rigorous.[5]

The magnitude of the discrepancies is apparently serious, when we consider the expressions for any general time t. But we must remember that the damping of the echoes is primarily determined by T_2^*, which is usually very short, so that we have to evaluate these expressions by taking the values of t near the echo maxima. The discrepancy now appears less serious, and the qualitative dependence pointed out by Hahn, *viz.*, that the stimulated echo is much less damped than the others, is also clearly borne out, as the stimulated echo only involves τ_2 and the others involve τ_2^3. For the special condition of experiment, *viz.*, $\tau_2 \gg \tau_1$ (in fact in his experiment for measuring the damping of the stimulated echo, Hahn uses $\tau_2/\tau_1 \approx 50$), we get the diffusion term for the stimulated echo by both Hahn's method and our method to be $\exp(k\tau_1^2\tau_2)$. Thus, the experimental result, *viz.*, the linear dependence of the diffusion damping of the stimulated echo on τ_1^2 (see Fig. 8 of reference 1), also receives support from our calculations.

However, a uniform discrepancy appears in the damping effect because of diffusion for the other terms. For $\tau_2 \gg \tau_1$, Hahn's treatment gives $\exp[-(8/3)k\tau_2^3]$ for all the other secondary echoes, while ours gives $\exp[-(5/3)k\tau_2^3]$. An exactly similar discrepancy occurs in the primary echo. Unfortunately, Hahn has published no exact quantitative measurements on the damping effect due to diffusion of the other echoes. Of course, this numerical coefficient is quite unimportant in measurements of k, and therefore of γ, G, and D by comparison methods, but we feel that the above analysis puts the interpretation of the echoes on a firmer footing.

We are grateful to Dr. E. L. Hahn for pointing out to us that Carr[6] has arrived at results in agreement with ours for the primary echo. We have not yet had the opportunity to procure a copy of Carr's work. The authors are indebted to Professor M. N. Saha for his constant interest during the progress of the work.

APPENDIX

The distribution functions $P[\phi_{tt''}, t-t'']$ may be evaluated as follows. If we assume that there is a field gradient G outwards from the center of the magnet, then if $\Delta\omega(t'')$ refers to the start of the self-diffusion process, then at instant t''' we shall have in its place, $\Delta\omega(t'')+\gamma G[l(t''')-l(t'')]=\Delta\omega(t'')+\gamma G l_{t'''t''}$, where $l_{t'''t''}$ represents the displacement in the direction of the field-gradient $t'''-t''$ (because the change in field involved in the diffusion process $=G[l(t''')-l(t'')]$). Therefore,

$$\eta_{t'''t''}=\gamma G l_{t'''t''},$$

and

$$\phi_{tt''}=\gamma G\int_{t''}^{t} l_{t'''t''}dt''';\qquad (25)$$

[5] E. L. Hahn (private communication).

[6] H. Carr, thesis, Harvard University, 1952 (unpublished).

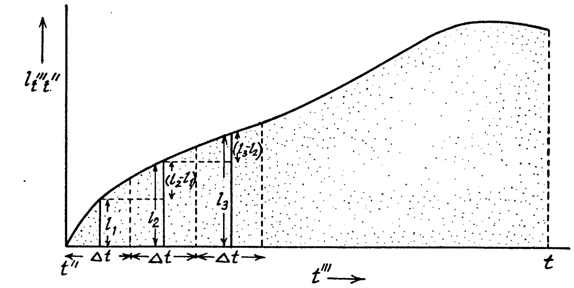

FIG. 2. Area covered in the $l-t$ plane.

i.e., $\phi_{tt''}$ depends on the area covered by the $l_{t'''t''}$ *versus* t''' curve. Now, the distribution in $l_{t'''t''}$ is well known to be given by the expression

$$P[l(t'''),t''';l(t''),t'']=\frac{1}{[4\pi D(t'''-t'')]^{\frac{3}{2}}}\exp\left[-\frac{l_{t'''t''}^2}{4D(t'''-t'')}\right],\qquad (26)$$

D referring to the coefficient of self-diffusion. Therefore, mean square value of $l_{t'''t''}$ is given by

$$\langle l_{t'''t''}^2\rangle_{\text{Av}}=\int_0^\infty\int_0^\pi\int_0^{2\pi}\frac{1}{[4\pi D(t'''-t'')]^{\frac{3}{2}}}\times\exp\left[-\frac{l^2}{4D(t'''-t'')}\right]l^4\sin\theta d\theta d\phi dl$$

$$=6D(t'''-t'').$$

As we are interested in only the component of the displacement along the field gradient direction,

$$\langle l_{t'''t''}^2\rangle_{\text{Av}}=(6D/3)(t'''-t'')=2D(t'''-t'').\qquad (27)$$

Now, to get the distribution in ϕ, we have to find the root-mean-square value of $\phi_{t'''t''}$, which we denote by $(\langle\phi_{tt''}^2\rangle_{\text{Av}})^{\frac{1}{2}}$; this depends on the shaded area in Fig. 2. We have to find the mean square value of this shaded area $A_{tt''}$. To do so, we divide the time interval $t-t''$ into n equal parts Δt, where

$$n\Delta t=t-t'',$$

so that if $n\rightarrow\infty$, then $\Delta t\rightarrow 0$. We evidently have from Fig. 2,

$$A_{tt''}=l_1\Delta t+l_2\Delta t+\cdots+l_n\Delta t.$$

Now, l_1 and l_2 are not independent quantities, because

$$l_2=l_1+\Delta l,$$

where Δl refers to the displacement in the interval between Δt and $2\Delta t$, but Δl is itself independent of l_1 and l_2. So, to get $A_{tt''}$ as a sum of independent quantities, we use the relations

$$l_2=l_1+(l_2-l_1),$$
$$l_3=l_1+(l_2-l_1)+(l_3-l_2),$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$l_n=l_1+(l_2-l_1)+(l_3-l_2)+\cdots+(l_n-l_{n-1}).$$

Therefore,

$$A_{tt''}=[nl_1+(n-1)(l_2-l_1)+\cdots+(l_n-l_{n-1})]\Delta t, \quad (28)$$

and so $A_{tt''}$ is now expressed as a sum of independent quantities. Hence, by the standard deviation theorem,[7]

$$\langle A_{tt''}{}^2\rangle_{\text{Av}}=[\langle l_1{}^2\rangle_{\text{Av}}n^2+\langle(l_2-l_1)^2\rangle_{\text{Av}}(n-1)^2+\cdots+\langle(l_n-l_{n-1})^2\rangle_{\text{Av}}](\Delta t)^2.$$

As l_1, l_2-l_1, $\cdots$ all occur in the same time Δt, we have, from (27),

$$\langle l_1{}^2\rangle_{\text{Av}}=\langle(l_2-l_1)^2\rangle_{\text{Av}}=\cdots=\langle(l_n-l_{n-1})^2\rangle_{\text{Av}}=2D\Delta t.$$

Therefore,

$$\begin{aligned}\langle A_{tt''}{}^2\rangle_{\text{Av}}&=2D\Delta t[1^2+2^2+\cdots+n^2]\\&=2D(\Delta t)^3n(n+1)(2n+1)/6\\&\approx\tfrac{2}{3}D(\Delta t)^3n^3\\&\approx\tfrac{2}{3}D(t-t'')^3,\end{aligned} \quad (29)$$

remembering that n is large. Therefore,

$$\begin{aligned}\langle\phi_{tt''}{}^2\rangle_{\text{Av}}&=\gamma^2G^2\langle A_{tt''}{}^2\rangle_{\text{Av}}\\&=\tfrac{2}{3}(\gamma G)^2D(t-t'')^3=\tfrac{2}{3}k(t-t'')^3,\end{aligned} \quad (30)$$

where $k=(\gamma G)^2D$. Hence, assuming a Gaussian distribution for $\phi_{tt''}$ also, we have

$$\begin{aligned}P(\phi_{tt''},t-t'')&=\frac{1}{(2\pi\langle\phi_{tt''}{}^2\rangle_{\text{Av}})^{\frac{1}{2}}}\exp\left[\frac{-\phi_{tt''}{}^2}{2\langle\phi_{tt''}{}^2\rangle_{\text{Av}}}\right]\\&=\left(\frac{3}{4\pi k(t-t'')^3}\right)^{\frac{1}{2}}\exp\left[-\frac{3\phi_{tt''}{}^2}{4k(t-t'')^3}\right].\end{aligned} \quad (31)$$

Further, we need the distribution function in $\eta_{tt''}$. From Eq. (25), we have

$$\begin{aligned}\langle\eta_{tt''}{}^2\rangle_{\text{Av}}&=(\gamma G)^2\langle l_{tt''}{}^2\rangle_{\text{Av}}\\&=2(\gamma G)^2D(t-t'')=2k(t-t'').\end{aligned} \quad (32)$$

Hence, assuming a Gaussian distribution in $\eta_{tt''}$, we have

$$\begin{aligned}P[\eta_{tt''},t-t'']&=\frac{1}{(2\pi\langle\eta_{tt''}{}^2\rangle_{\text{Av}})^{\frac{1}{2}}}\exp\left[-\frac{\eta_{tt''}{}^2}{2\langle\eta_{tt''}{}^2\rangle_{\text{Av}}}\right]\\&=\frac{1}{[4\pi k(t-t'')]^{\frac{1}{2}}}\exp\left[-\frac{\eta_{tt''}{}^2}{4k(t-t'')}\right].\end{aligned} \quad (33)$$

Using these distribution functions for $P[\phi_{tt''},t-t'']$ and $P[\eta_{tt''},t-t'']$, we can evaluate the various integrals over ϕ and η involved in (18) and (23), making suitable substitutions for t and t''. For these integrations as well as those over $\Delta\omega$ we need the standard integrals:

$$\begin{aligned}&\int_{-\infty}^{\infty}\cos ax\exp(-b^2x^2)dx=\frac{\sqrt{\pi}}{b}\exp\left(-\frac{a^2}{4b^2}\right),\\&\int_{-\infty}^{\infty}\sin ax\exp(-b^2x^2)dx=0.\end{aligned} \quad (34)$$

[7] See James V. Uspensky, *Introduction to Mathematical Probability* (McGraw-Hill Book Company, Inc., New York, 1937), p. 270.