Spin Echoes from Broad Resonance Lines with High Turning Angles

W. B. MIMS
Bell Telephone Laboratories, New York, New York

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The generation of spin-echo signals in wide resonance lines for which the rf field intensity $H_1 \ll$ linewidth is discussed. Particular attention is given to the case in which the spins turn by angles greater than 360° during the rf pulses. Inhomogeneities in H_1 lead to a considerable simplification of the expressions used to compute the echo wave form. Experimental wave forms obtained for electron spins in (Ca,Nd)WO_4 are compared with calculated results.

A FEW years ago Itoh *et al.*[1] reported experiments in which nuclear spin echoes are used as a means of plotting out broad inhomogeneous resonance lines. In such experiments the rf field intensity H_1 is very much smaller than the linewidth, and the echo signals are generated by sample portions of the line rather than by the whole resonance line, as in the more familiar case when narrow lines are being studied. Some workers using the echo technique for the study of nuclear resonance in metals have remarked on the curious shape of the echo wave forms[2] which are sometimes observed, and on their critical dependence on the power level and on the duration of the two applied rf pulses. It has been suggested to the author that an attempt should be made to reproduce some of the experimental conditions in an electron echo apparatus,[3] in the hope of finding out how far the phenomena are characteristic of spin systems in general and are independent of the particular material being studied.

The behavior of the echo wave form as a function of power level and pulse duration can be described in terms of the following experiments. The times concerned are denoted in Fig. 1, and the detection apparatus is assumed to respond to the absolute magnitude of the rf field generated in the echo. Initially the two rf pulses are made exactly equal in length, i.e., $t_1=t_3=t_p$. As the rf power is gradually increased the first echo signal to appear is a smooth wave form of about the same width as the applied pulses. The timing of this echo signal is such that the centers of the applied pulses and of the echo are almost equally spaced in time, i.e., the center of the echo appears at $t\simeq\frac{1}{2}t_p$ which is $\frac{1}{2}t_p$ later than in the narrow-line case. As the power level is increased the echo signal rises to a maximum, then falls and changes shape. At the maximum itself a small bump is visible in the foot at the beginning of the wave form. About 3 dBs above this power level the echo consists of two equal peaks, and for further increases in power a variety of complicated wave forms can be observed. At a level about 20 dB higher there is a striking simplification in the echo wave form. A double peak which is several times higher and narrower than the wave forms observed at the first maximum appears. This echo is timed so that the interval from the end of pulse II to the center of the echo is equal to the interval between the end of pulse I and the beginning of pulse II, i.e., the center of the echo is now at $t=0$ and occurs at the same time as it would in the narrow-line case. If at this power level the two rf pulses are made slightly unequal it is possible to obtain a single sharp peak in place of the double peak, but this signal is critically dependent on the relative length of the two pulses and falls to a considerably lower amplitude if t_1-t_3 is increased to more than a few percent of the pulse durations. These signals correspond to very high turning angles of the spins in the rf field. Such turn angles are easily obtained for nuclei in ferromagnetic metals because of the enhancement of the interaction between the spins and the rf field, and the signals themselves may on account of their height and clarity appear to be the optimum echoes obtainable with a particular apparatus.

In order to parallel these conditions in electron resonance it was necessary to ensure that H_1 was less than the linewidth and to adjust the pulse length so that $\gamma H_1 t_p$ (where γ is the gyromagnetic ratio) could be made several times as large as 360°. The first condition was easily satisfied. In electron echo experiments it is quite usual to find lines wider than the field intensities H_1 which correspond to convenient values of t_p. Echo wave forms such as those described above for the lower power levels are readily observed, and their origin has been discussed elsewhere[3]; the first maximum occurs when $\gamma H_1 t_p \simeq 120°$, and the two equal peaks are obtained at $\gamma H_1 t_p = 180°$. The second condition $\gamma H_1 t_p \gg 360°$ could not be attained under the normal operating conditions of the electron echo apparatus with

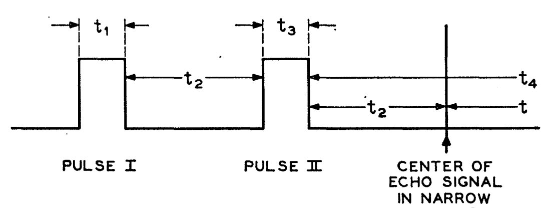

FIG. 1. A spin-echo sequence showing the times used in the calculations. Echoes appear at $t=0$ or at $t\simeq\frac{1}{2}t_p$ according to the experimental conditions.

[1] J. Itoh, K. Asayama, and S. Kobayashi, J. Phys. Soc. Japan **18**, 455, 458 (1963).
[2] J. I. Budnick and N. Kaplan (private communication).
[3] The apparatus used in the experiments reported here have been described by W. B. Mims in Rev. Sci. Instr. **36**, 1472 (1965).

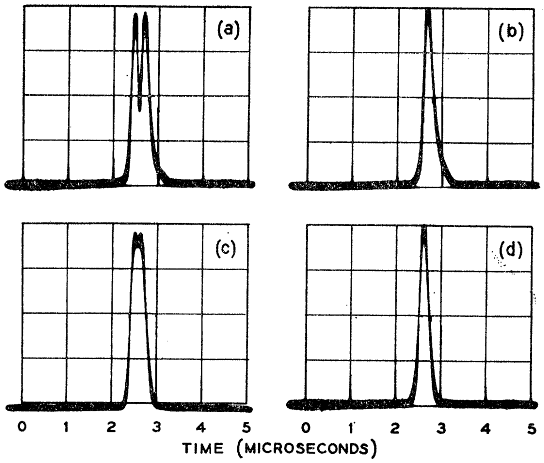

FIG. 2. Electron echo wave form obtained in (Ca,Nd)WO_4 when the turning angle of the spins during the rf pulses is large. (a) $t_1=t_3=t_p=2.5$ msec, $\gamma H_1 t_p=2540°$, (b) same as (a) but with t_3 about 3% less than t_1, (c) $t_1=t_3=t_p=2.5$ msec, $\gamma H_1 t_p=5070°$, (d) same as (c) but with t_3 slightly less than t_1. The echo wave form is limited by the bandwidth of the detector in (c) and (d).

$t_p=0.2$ msec. In order to examine high-turn-angle phenomena t_p was changed to 2.5 msec, and a material with a phase memory time of convenient length was placed in the microwave cavity.[4] The microwave power level was increased from zero until the first maximum had been passed and the echo wave form consisted of two equal peaks. This served to identify the setting of the microwave attenuator giving $\gamma H_1 t_p=180°(\gamma H_1/2\pi=0.2$ Mc/sec). The power level was then increased by a further 23 dB to give $\gamma H_1 t_p=2540°(\gamma H_1/2\pi=2.8$ Mc/sec), and the wave form in Fig. 2(a) was observed. Pulse II was made $\simeq 3\%$ shorter than pulse I, and the echo wave form changed to that shown in Fig. 2(b). [The amplifier gain used in obtaining Fig. 1(b) was about 60% of that used in obtaining Fig. 1(a).] A wave form similar to that in Fig. 1(b) was observed when pulse II was $\simeq 3\%$ longer than pulse I, but larger discrepancies between the pulse durations gave smaller echo signals, the echo amplitude varying periodically with t_1-t_3. A repetition of these tests at a 6 dB higher power level ($\gamma H_1 t_p=5070°$, $\gamma H_1/2\pi=5.6$ Mc/sec) gave the traces shown in Figs. 2(c) and 2(d). These traces show the limiting effect of the detector bandwidth (8 Mc/sec) and will be discussed later.

The generation of spin echoes in broad inhomogeneous lines under the condition that $\gamma H_1 \ll$ linewidth has been discussed by Bloom, who gives an expression for the contribution of each spin packet to the precessing magnetization which generates the echo.[5] If ΔM_0 is the static magnetization of a spin packet and ΔM_p is its contribution to the precessing moment, then the ratio $E=dM_p/dM_0$ is given by

$$E=-\sin^3\theta\,\sin bt_1\,\sin^2\tfrac{1}{2}bt_3\,\cos\omega t-\sin 2\theta\,\sin^2\theta\,\sin^2(\tfrac{1}{2}bt_1)\,\sin^2(\tfrac{1}{2}bt_3)\,\sin\omega t,$$

where

$$b^2=\omega_1^2+\omega^2,\quad \tan\theta=\omega_1/\omega,\quad \omega_1=\gamma H_1,\quad t=t_4-t_2, \tag{1}$$

and ω is the difference between the rf frequency and the Larmor frequency of the spin packet under consideration. θ is the angle between the Zeeman field axis and the effective field in the rotating coordinate system, and b gives the rate of precession about the effective field vector. The echo signal can be obtained by integrating ΔM_p numerically over all the spin packets in the resonance line. If $S(\omega)\Delta\omega$ represents the static magnetization due to spin packets in the interval from ω to $\omega+\Delta\omega$ away from exact resonance, the precessing magnetization which generates the echo is given by

$$W_p(t)=\int_{-\infty}^{+\infty} S(\omega)E(\omega)d\omega. \tag{2}$$

Noting the common factor of $\sin^3\theta$ in E one can see that the major contribution to M_p arises from spin packets in the range $-\omega_1<\omega<\omega_1$. If $S(\omega)$ does not vary greatly in this range we may take it outside the integral and write

$$W_p(t)=S(\omega)\int_{-\infty}^{+\infty} E(\omega)d\omega. \tag{3}$$

Computations of the quantity $-\{M_p(t)\}$ divided by $\{\omega_1 S(\omega)\}$ for the case $t_1=t_3=t_p$ and for $\omega_1 t_p=90°$, 120°, 180°, and 240°, have been made in the course of some earlier work and the absolute magnitudes are shown graphically in Fig. 6 of Ref. 3. Similar computations have been repeated here for values of $\omega_1 t_p$ taken every 60° from 1080° to 1500°, and two typical results are shown in Figs. 3(a) and 3(b). None of these wave forms in this high tuning angle range had a simple shape approximating to that found experimentally. It became clear, however, that a fractional variation in ω_1 which was small enough to be unimportant at low values of $\omega_1 t_p$, could lead to major changes in the computed wave form at high values of $\omega_1 t_p$. This suggested that an average over ω_1 should be made in order to obtain a realistic prediction of the wave form under the conditions of a large turning angle. An average from $\omega_1 t_p=1080°$ to $\omega_1 t_p=1500°$ is shown in Fig. 3(c). The absolute magnitude of this wave form may be compared with the experimental result of Fig. 2(a).[6]

If there is a sufficiently wide distribution in ω_1 and in the dependent quantities bt_1 and bt_3 it becomes possible to make some important simplifications in the

[4] The material was (Ca,Nd)WO_4 at 4.2°K with the Zeeman field at an angle of 45° to the c axis.

[5] A. L. Bloom, Phys. Rev. **98**, 1105 (1955). Equation (28) in this reference appears as Eq. (1) in the present paper with the following alterations: ω has been written in place of $\Delta\omega$, t in place of t_4-t_2, and the first factor on the right-hand side has been corrected to $\sin^3\theta$.

[6] The apparatus gives a wave form proportional to the absolute magnitude of $M_p(t)$. The structure observed in the computed average wave form at $t\sim\pm 0.8$ may possibly arise from the coarseness in the intervals chosen for $\omega_1 t_p$.

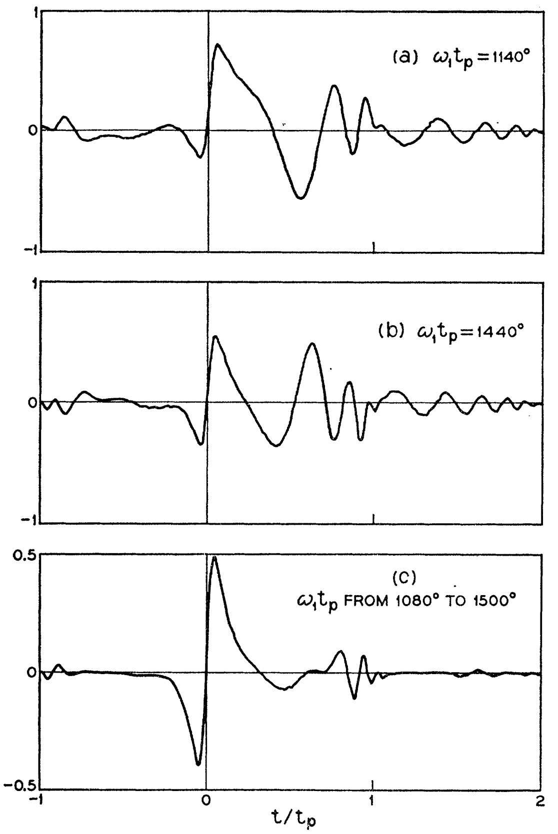

FIG. 3. Wave forms computed using Eq. (1). The ordinate gives $\{M_p(t)\}$ divided by $\omega_1 S(\omega)$ where $M_p(t)$ is the precessing magnetization, $\omega_1=\gamma H_1$, and $S(\omega)\Delta\omega$ is the static magnetization in a portion of the resonance line $\Delta\omega$ wide. The turn angles during the pulse for exactly resonant spins are (a) 1140°, (b) 1440°. (c) shows an average of wave forms computed for $\omega_1 t_p=1080°$ to $\omega_1 t_p=1500°$ at intervals of 60°.

calculation of the echo wave form. Firstly, let us write in place of Eq. (2)

$$M_p(t)=\int_{-\infty}^{+\infty}d\omega_1\int_{-\infty}^{+\infty}S'(\omega_1,\omega)E(\omega_1,\omega)d\omega\,, \qquad (4)$$

where $S'(\omega_1,\omega)\Delta\omega_1\Delta\omega$ denotes the static magnetization due to those spin packets in the spectral interval ω to $\omega+\Delta\omega$ away from exact resonance which are located in the rf field in such a way that γH_1 ranges from ω_1 to $\omega_1+\Delta\omega_1$. Let us again suppose that the resonance line is wide, and, to simplify the discussion, let us assume that the distribution of values of ω_1 is the same throughout the sample and is given by $g(\omega_1)$ where

$$\int_{-\infty}^{+\infty}g(\omega_1)d\omega_1=1\,.$$

Equation (4) then becomes

$$W_p(t)=S(\omega)\int_{-\infty}^{+\infty}d\omega_1\int E(\omega_1,\omega)g(\omega_1)d\omega\,, \qquad (5)$$

where $S(\omega)$ has the same meaning as in Eq. (3). Trigonometrical manipulation of Eq. (1) gives $E(\omega_1,\omega)$ in the form

$$E=\tfrac{1}{4}\sin^3\theta\,\{\sin b(t_1+t_3)+\sin b(t_1-t_3)-2\sin bt_1\}\cos\omega t$$
$$-\tfrac{1}{8}\sin 2\theta\sin^2\theta\{2-2\cos bt_1+\cos b(t_1+t_3)+\cos b(t_1-t_3)\}\sin\omega t. \qquad (6)$$

For high values of $\omega_1 t_1$, $\omega_1 t_3$, a spread in values of ω_1 will cause the terms with arguments bt_1, bt_3, $b(t_1+t_3)$ to average to zero leaving

$$E=\tfrac{1}{4}\sin^3\theta\sin b(t_1-t_3)\cos\omega t$$
$$-\tfrac{1}{8}\sin 2\theta\sin^2\theta\{2+\cos b(t_1-t_3)\}\sin\omega t. \qquad (7)$$

For the special case of $t_1=t_3=t_p$ the first term in (7) vanishes leaving

$$E=-\tfrac{3}{8}\sin 2\theta\sin^2\theta\sin\omega t. \qquad (8)$$

Expressing this in terms of ω, ω_1 and substituting in (5) we have

$$W_p(t)=-\tfrac{3}{4}S(\omega)\int_{-\infty}^{+\infty}d\omega_1\int_{-\infty}^{+\infty}\frac{(\omega/\omega_1)g(\omega_1)\sin\omega t}{\{1+(\omega/\omega_1)^2\}^2}d\omega \qquad (9)$$

$$=-S(\omega)\int_{-\infty}^{+\infty}(3\pi/8)\omega_1^2 te^{-\omega_1|t|}g(\omega_1)d\omega_1. \qquad (10)$$

If the two applied pulses are not exactly equal, the first term in (7) no longer vanishes but reaches a peak value whenever $b(t_1-t_3)$ is an odd multiple of $\pi/2$. In practice the largest contribution is likely to occur at $\pm\pi/2$ since the inhomogeneity in ω_1 is increasingly important at the larger values of $b(t_1-t_3)$ and will tend to cause $\sin[b(t_1-t_3)]$ to average to zero as has already been assumed for terms in $b(t_1+t_3)$, etc. $M_p(t)$ is less amenable to calculation than in the previous case since the argument $b(t_1-t_3)$ is itself a function of θ. We can, however, approximate by assuming that $b(t_1-t_3)\simeq\pi/2$ for all the spin packets which make a significant contribution to $M_p(t)$ when the pulse durations have been adjusted to give a maximum echo signal.[7] With this substitution

$$E=\pm\tfrac{1}{4}\sin^3\theta\cos\omega t-\tfrac{1}{4}\sin 2\theta\sin^2\theta\sin\omega t\,, \qquad (13)$$

the + sign corresponding to the condition $t_1>t_3$. The second term contributes to the precessing magnetization a quantity $\{M_p(t)\}_{\mathrm{II}}$ which is $\frac{2}{3}$ of the amount shown in Eq. (10). The first term, expressed in terms of ω, ω_1 and substituted in (5) gives

$$\{M_p(t)\}_{\mathrm{I}}=\pm\tfrac{1}{4}S(\omega)\int_{-\infty}^{+\infty}d\omega_1\int_{-\infty}^{+\infty}\frac{g(\omega_1)\cos\omega t}{\{1+(\omega/\omega_1)^2\}^{3/2}}d\omega \qquad (14)$$

$$=\pm\tfrac{1}{6}S(\omega)\int_{-\infty}^{+\infty}\omega_1^2|t|K_1(\omega_1|t|)g(\omega_1)d\omega_1. \qquad (15)$$

[7] To illustrate the scope of this approximation let us suppose that the times t_1, t_3 have been adjusted so that $b(t_1-t_3)=\pi/2$ when $\omega=\omega_1$ (i.e., when $b=\sqrt{2}\omega_1$). Then over the range $-2\omega_1<\omega<2\omega_1$ we have $1\geq\sin b(t_1-t_3)>0.82$. From (14) it can be seen that the major contribution of the integrand occurs in this range.

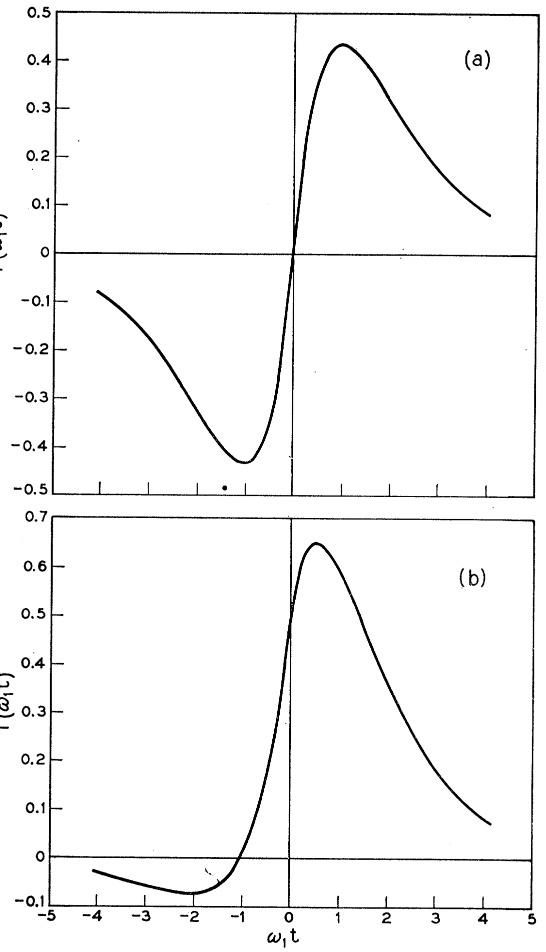

FIG. 4. Functions giving the echo wave form for large turning angles $\omega_1 t_p$ when H_1 is inhomogeneous. If the inhomogeneity is not excessive the ordinate gives $\{M_p(t)\}$ divided by $\bar{\omega}_1 S(\omega)$ where $M_p(t)$ is the precessing magnetization, $\bar{\omega}_1$ is the mean value of ω_1, and $S(\omega)\Delta\omega$ is the static magnetization in a portion of the resonance line $\Delta\omega$ wide. The abscissa is $\omega_1 t$, i.e., it shows t in units of $1/\omega_1$. (a) $f(\omega_1 t) = (3\pi/8)\omega_1 t e^{-\omega_1|t|}$. This gives the echo wave form when both rf pulses are of equal duration. (b) $f(\omega_1 t) = (1/b)\omega_1|t|K_1(\omega_1|t|)+\frac{1}{4}\pi\omega_1 t e^{-\omega_1|t|}$. This gives the echo wave form when t_1 is slightly less than t_3.

The total precessing magnetization

$$M_p(t)=\{M_p(t)\}_{\mathrm{I}}+\{M_p(t)\}_{\mathrm{II}}$$
$$=-S(\omega)\int_{-\infty}^{+\infty}\omega_1\{\mp(\tfrac{1}{6})\omega_1|t|K_1(\omega_1|t|)$$
$$+\tfrac{1}{4}|\pi|\omega_1 t e^{-\omega_1|t|}\}g(\omega_1)d\omega_1. \quad (16)$$

The integrals in Eqs. (10) and (16) correspond to a weighted average of the functions

$$\tfrac{3}{8}\pi\omega_1 t e^{-\omega_1|t|} \quad (17)$$

and

$$\mp\tfrac{1}{6}\omega_1|t|K_1(\omega_1|t|)+\tfrac{1}{4}\pi\omega_1 t e^{-\omega_1|t|}, \quad (18)$$

with weighting factor $\omega_1 g(\omega_1)$. If the range of values of ω_1 is moderate, a mean value $\bar{\omega}_1$ substituted in (17) or (18) will give the approximate form of the quantity $\{M_p(t)\}$ divided by $\bar{\omega}_1 S(\omega)$. The functions 17 and 18 are plotted in Fig. 4.

It may be noted that the echo wave form generated by rf pulses with large turning angles is independent of pulse duration t_p and has a width depending only on ω_1. The full widths at half height of the lobes in Fig. 4(a) and of the peak in Fig. 4(b) are given by t_w where

$$t_w=2.4/\omega_1. \quad (19)$$

The parameter ω_1 measures the width of that portion of the broad resonance line which is sampled by the rf field. Provided that the bandwidth of the detector is adequate to respond to the driving function $M_p(t)$, the peak amplitude of the echo will be directly proportional to ω_1 and the echo duration will be inversely proportional to it. For a wide line driven at high powers it may, however, be possible to excite a range of spin packets which is actually wider than the frequency bandwidth of the detector. Under these conditions an increase in rf field strength will no longer lead to a proportional increase in echo height and a narrowing of the signal.[8] In this limit the apparatus used in the experiments reported here caused the echo signal obtained with slightly unequal pulses to approach a constant height and width [Fig. 2(d)]. The echo obtained with exactly equal pulses [Fig. 2(c)] showed a filling in of the trough in the center because of the inability of circuits following the detector crystal to respond sufficiently rapidly to changes in the wave form. The precise behavior of the echo signal when the detector bandwidth becomes saturated will, of course, differ according to the characteristics of the apparatus used.

ACKNOWLEDGMENTS

The author would like to thank J. I. Budnick of Fordham University and N. Kaplan of Bell Telephone Laboratories, for drawing his attention to the spin-echo phenomena discussed here, and for suggesting that they should be investigated in electron-spin systems.

[8] The value of ω_1 estimated to have been used in obtaining Figs. 2(a), 2(b) was 17.6×10^6 rad/sec. By Eq. (19) the predicted width is therefore 0.14 msec. The observed widths were $\sim$0.2 msec. This discrepancy may be due to the onset of bandwidth limiting in the detector. The 8 Mc/sec bandwidth of the detector corresponds to $3\omega_1$ and would include contributions from packets in the range $-1.5\omega_1<\omega<+1.5\omega_1$.