Spin Echoes with Four Pulses—An Extension to n Pulses

T. P. DAS AND D. K. ROY
Institute of Nuclear Physics, Calcutta, India

(Received June 7, 1954; revised manuscript received August 12, 1954)

Following Das and Saha's method, the response of a nuclear spin system to four rf pulses has been analyzed by using the classical Bloch equations. The calculations enable one to obtain a recursion formula for the number of echoes to be expected with n pulses. Besides, the calculations also yield several other results important from the experimental view. Thus, they provide a method for obtaining T_1, the spin-lattice relaxation time, from primary echo measurements alone, and also give an idea of the order of correction necessary in a measurement of T_2, the "spin-spin relaxation time," by observation of primary echoes with successive paired pulses of gradually changing intervals.

I. INTRODUCTION

HAHN[1] first gave the mathematical theory for the occurrence of free-induction and spin-echo signals when the rf field is applied in the form of short pulses. Das and Saha[2] subsequently showed that in estimating the damping effects of diffusion on these signals, the frequency difference and phase shift accumulated by a certain "isochromatic" group in any free-precession interval, by virtue of diffusion, could be regarded as independent of those accumulated in the previous intervals. Hence they can be averaged independently after collecting all the terms that are of even parity in all the variables involved. We have followed this procedure in our calculations with four pulses, the results of which we present in Sec. II. In Sec. III, we have interpreted the various terms obtained in Sec. II in terms of the primary and stimulated echo mechanisms between applied pulses and between echoes and applied pulses. One term remains unexplained after applying this mode of explanation. It appears to be characteristic of four pulses alone and follows a new law of combination of intervals as regards its position. We call it a quaternary echo; subsequent calculations with five and six pulses also show that we have similar "pentanary" and "hexanary" echoes occurring with five and six pulses respectively. Using this idea, we establish a recursion formula for the number of echoes to be expected in general with n pulses. In Sec. IV, we discuss the corrections to be applied to primary and stimulated echo envelope measurements with successive groups of two and three pulses respectively when the intervals between these successive groups are only fractions of T_1. A possible method for obtaining T_1, by measurements on primary echo envelopes alone, is suggested.

II. RESULTS WITH FOUR PULSES

As shown in Fig. 1, we take four rf pulses of equal width. The angle of nutation during each pulse is therefore given by

$$\xi=\omega_1 t_w.$$

We follow the same terminology and notation as in I. Thus, we denote the frequency drifts undergone by the constituents of a certain isochromatic group in the first three free-precession intervals by η_{10}, η_{21}, and η_{32} respectively, while we denote the phase shifts in these three intervals and in the interval following the fourth pulse by ϕ_{10}, ϕ_{21}, ϕ_{32}, and ϕ_{t3} respectively. The distribution functions for these are given by Eqs. (31) and (33) of I. Also, for completeness, and to enable us to draw conclusions about the number of echoes to be expected with n pulses, we assume that the following conditions hold regarding the lengths of the different free-precession intervals:

$$\tau_3>2\tau_2 \quad \text{and} \quad \tau_2>2\tau_1. \tag{1}$$

If these conditions do not hold, then as we shall presently obtain by our calculations, some of the echoes will not be observed.

To obtain the conditions after the passage of the fourth pulse, we have to proceed as in I, by solving the Bloch equations during and after a pulse, and tabulating the solutions at the different stages of passage of pulses. For our present purpose, we shall need, besides the solutions tabulated in I, *viz.*, those at A, B, C, D, F, G, and H, also those at I, J, and K. Following an exactly similar procedure as in I, we can then obtain the value of V after the passage of four pulses, *viz.*, $V(K)$. It will be seen to consist of 22 terms, whose positions and the different parts of the amplitudes, *viz.*, trigonometric, diffusion damping, and relaxation damping parts are tabulated in Table I. The terminology for the different terms will be explained in Sec. III.

III. DISCUSSION OF THE VARIOUS TERMS IN TABLE I; THE RECURSION FORMULA FOR n PULSES

We shall now explain the terminology used for the different terms in Table I and interpret them physically.

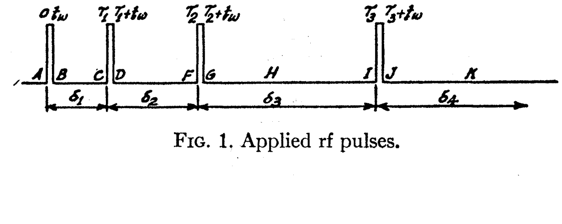

FIG. 1. Applied rf pulses.

[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[2] T. P. Das and A. K. Saha, Phys. Rev. **93**, 749 (1954). We shall refer to this paper henceforth as I.

These terms can evidently be divided into the following categories.

(*a*) *Free induction terms.*—The symbol used for any one of these is in general F_n, representing the free induction signal following the nth pulse. In the case of four applied pulses there are thus four such terms designated by F_1, F_2, F_3, and F_4.

(*b*) *Terms arising from a primary echo mechanism between any two of the applied pulses.*—A typical one is denoted by $P_{(mn)}$, which represents the primary echo arising from a pair of rf pulses respectively applied at instants τ_m and τ_n. The interval between the first pulse of the pair and the echo is $2(\tau_n-\tau_m)=2\delta_{nm}$, δ_{nm} representing the interval between the pair of pulses. There

TABLE I. Amplitudes of the different free induction and echo terms for four pulses.[a]

Term	Position of maximum	Trigonometric part of amplitude	Diffusion damping of the amplitude[b]	Relaxation damping of the amplitude
F_1	0	$-\sin\xi\cos^6(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_1+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
F_2	τ_1	$-W(C)\sin\xi\cos^4(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_1+\sum_r^{2,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t-\tau_1}{T_2}\right)$
F_3	τ_2	$-\sin\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_2+\sum_r^{3,4}\delta_r^3\right)\right]$	$\left\{1-[1-W(C)\cos\xi]\exp\left(-\frac{\delta_2}{T_1}\right)\right\}\times\exp\left(-\frac{t-\tau_2}{T_2}\right)$
F_4	τ_3	$\sin\xi$	$\exp\left[-\frac{k}{3}(f_3+\delta_4^3)\right]$	$\left\{1-(1-\cos\xi)\exp\left(-\frac{\delta_3}{T_1}\right)-\cos\xi[1-W(C)\cos\xi]\times\exp\left(-\frac{\tau_3-\tau_1}{T_1}\right)\right\}\exp\left(-\frac{t-\tau_3}{T_2}\right)$
$P_{(12)}$	$2\tau_1$	$\frac{1}{4}\sin^3\xi\cos^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_1+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{(13)}$	$2\tau_2$	$\frac{1}{4}\sin^3\xi\cos^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_4+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{(23)}$	$2\tau_2-\tau_1$	$\frac{1}{4}W(C)\sin^3\xi$	$\exp\left[-\frac{k}{3}\left(f_4+\sum_r^{2,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t-\tau_1}{T_2}\right)$
$P_{(14)}$	$2\tau_3$	$\frac{1}{4}\sin^3\xi\cos^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_5+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{(24)}$	$2\tau_3-\tau_1$	$\frac{1}{4}W(C)\sin^3\xi$	$\exp\left[-\frac{k}{3}\left(f_5+\sum_r^{2,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t-\tau_2}{T_2}\right)$
$P_{(34)}$	$2\tau_3-\tau_2$	$\sin\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_6+\sum_r^{3,4}\delta_r^3\right)\right]$	$\left\{1-[1-W(C)\cos\xi]\exp\left(-\frac{\delta_2}{T_1}\right)\right\}\times\exp\left(-\frac{t-\tau_2}{T_1}\right)$

[a] Here, $\delta_1=\tau$, $\delta_2=\tau_2-\tau_1$, $\delta_3=\tau_3-\tau_2$, $\delta_4=t-\tau_3$,

$$f_1=3(t-\tau_1)^2\tau_1+3(t-\tau_2)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_2=3(t-\tau_2)^2\tau_1+3(t-\tau_2)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_3=3(t-\tau_3)^2\tau_1+3(t-\tau_3)^2(\tau_3-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_4=3(t-2\tau_2+\tau_1)^2\tau_1+3(t-\tau_2)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_5=3(t-2\tau_3+\tau_1)^2\tau_1+3(t-2\tau_3+\tau_2)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_6=3(t-2\tau_3+\tau_2)^2\tau_1+3(t-2\tau_3+\tau_2)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_7=3(t-2\tau_3+2\tau_2-\tau_1)^2\tau_1+3(t-2\tau_3+\tau_2)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2),$$
$$f_8=3(t-\tau_3-\tau_2+\tau_1)^2\tau_1+3(t-\tau_3)^2(\tau_2-\tau_1)+3(t-\tau_3)^2(\tau_3-\tau_2).$$

[b] By $\sum_r^{m,n}\delta_r^3$ we mean $\delta_m^3+\delta_{m+1}^3+\cdots+\delta_n^3$.

TABLE I (*continued*).

Term	Position of maximum	Trigonometric part of amplitude	Diffusion damping of the amplitude[b]	Relaxation damping of the amplitude
$P_{((12)3)}$	$2\tau_2-2\tau_1$	$-\frac{1}{4}\sin^3\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_4+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{((12)4)}$	$2\tau_3-2\tau_1$	$-\frac{1}{4}\sin^3\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_5+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{((13)4)}$	$2\tau_3-2\tau_2$	$-\frac{1}{4}\sin^3\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_7+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{((23)4)}$	$2\tau_3-2\tau_2-\tau_1$	$-W(C)\sin\xi\sin^4(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_7+\sum_r^{2,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t-\tau_1}{T_2}\right)$
$P_{(((12)3)4)}$	$2\tau_3-2\tau_2+2\tau_1$	$\sin\xi\sin^6(\xi/2)$	$\exp\left[-\frac{k}{3}\left(f_7+\sum_r^{1,4}\delta_r^3\right)\right]$	$\exp\left(-\frac{t}{T_2}\right)$
$P_{(123)}$	$\tau_2+\tau_1$	$\frac{1}{2}\sin^3\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}(f_2+\delta_1^3+\delta_3^2+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_2+\tau_1}{T_2}-\frac{\delta_2}{T_1}\right)$
$P_{(134)}$	$\tau_3+\tau_2$	$-\frac{1}{2}\sin^3\xi\cos^2(\xi/2)$	$\exp\left[-\frac{k}{3}(f_8+\delta_1^3+\delta_2^3+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_3+\tau_2}{T_2}-\frac{\delta_3}{T_1}\right)$
$P_{(124)}$	$\tau_3+\tau_1$	$-\frac{1}{2}\sin^3\xi\cos\xi$	$\exp\left[-\frac{k}{3}(f_3+\delta_1^3+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_3+\tau_1}{T_2}-\frac{\tau_3-\tau_1}{T_1}\right)$
$P_{(234)}$	$\tau_3+\tau_2-\tau_1$	$-\frac{1}{4}W(C)\sin^3\xi$	$\exp\left[-\frac{k}{3}(f_8+\delta_2^3+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_3+\tau_2-\tau_1}{T_2}-\frac{\delta_3}{T_1}\right)$
$P_{((123)4)}$	$2\tau_3-(\tau_2+\tau_1)$	$-\frac{1}{2}\sin^3\xi\cos^2(\xi/2)$	$\exp\left[-\frac{k}{3}(f_7+\delta_1^3+\delta_3^3+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_2+\tau_1}{T_2}-\frac{\delta_2}{T_1}\right)$
$P_{((12)34)}$	$\tau_3+\tau_2-2\tau_1$	$\frac{1}{2}\sin^3\xi\sin^2(\xi/2)$	$\exp\left[-\frac{k}{3}(f_8+\delta_1^3+\delta_2^3+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_3+\tau_2}{T_2}-\frac{\delta_3}{T_1}\right)$
$P_{(1234)}$	$2\tau_3-\tau_2+\tau_1$	$-\frac{1}{2}\sin^3\xi\cos^2(\xi/2)$	$\exp\left[-\frac{k}{3}(f_8+\delta_1^3+\delta_3^3+\delta_4^3)\right]$	$\exp\left(-\frac{t-\tau_2+\tau_1}{T_2}-\frac{\delta_2}{T_1}\right)$

are six such echoes in the case of four applied pulses as seen from Table I, and the above law for finding their positions is seen to give their positions correctly.

(*c*) *Terms which can be explained by a primary-echo mechanism between primary echoes due to previous applied rf pulses and subsequent rf pulses.*—A typical one is denoted by $P_{((mn)p)}$, which gives the primary echo due to primary-echo interaction between the primary echo $P_{(mn)}$ and the applied pulse at τ_p. The interval between the echo $P_{((mn)p)}$ and the echo $P_{(mn)}$ is given by $2\delta_{p,(mn)}$, where $\delta_{p,(mn)}$ is the interval between the applied rf pulse at τ_p and the primary echo $P_{(mn)}$, the position of the latter being found by the combination rule given in the previous paragraph. This rule gives correctly the positions of the maxima of four such terms occurring in Table I with four applied rf pulses. There is one more echo in Table I which comes into this category, *viz.* $P_{(((12)3)4)}$, which represents the primary echo due to interaction between the primary echo $P_{((12)3)}$ and the fourth applied pulse. We can make a general notation $P_{(((mn)p)q)}$ for this type of echo. The rule for finding its position is that it is at an interval $2\delta_{q,((mn)p)}$ away from the echo $P_{((mn)p)}$ with $\delta_{q,((mn)p)}$ representing the interval between the pulse at τ_q and the echo $P_{((mn)p)}$; the position of the latter is found by the combination rule given in the first part of this paragraph. A similar interpretation may be given to terms like $P_{(((\cdots(mn)p)\cdots)\cdots))}$ which may arise with more than four applied rf pulses.

(*d*) *Terms which may be explained by a "stimulated" echo mechanism between three applied pulses.*—A typical one we denote by $P_{(mnp)}$, arising out of the three applied pulses at τ_m, τ_n and τ_p; the rule for finding its position is that it is situated an interval $(\tau_n-\tau_m)+(\tau_p-\tau_m)$, i.e., $\delta_{pn}+2\delta_{nm}$ away from the first of the trio. There are clearly four such echo terms in Table I, and the above law of combination evidently gives the positions of their maxima correctly.

(*e*) *Terms which can be explained as arising from a primary echo mechanism between a stimulated echo due to three previous rf pulses and a subsequent rf pulse.*—A typical one is denoted by $P_{((mnp)q)}$, arising out of a primary echo—mechanism between the stimulated echo $P_{(mnp)}$ and the applied pulse at τ_q. The law of combination of intervals for finding the position of this echo is that it is an interval $2\delta_{q,(mnp)}$ away from the stimulated echo $P_{(mnp)}$, $\delta_{q,(mnp)}$ representing the interval between τ_q and the echo $P_{(mnp)}$, the position of the latter being given by the rule in the preceding paragraph. There is evidently one such echo in Table I for four applied rf pulses, *viz.* $P_{((123)4)}$, and the above rule is seen to give its position correctly.

(*f*) *Terms which can be explained as arising out of a "stimulated-echo" mechanism between an echo (primary or stimulated) and two subsequent pulses.*—A typical one is denoted by $P_{((lmn)pq)}$ or $P_{((mn)pq)}$, according as the previous echo contributing to the "stimulated echo" mechanism in question is the "stimulated echo" $P_{(lmn)}$ or the primary echo $P_{(mn)}$ respectively, the rule for finding the position being easily found by a combination of the different rules given in the previous paragraphs. We have only one such echo, *viz.* $P_{((12)34)}$ in the case of four pulses tabulated in Table I.

(*g*) *Final term.*—Finally we have one echo which we have denoted by $P_{(1234)}$, with a maximum occurring at $2\tau_3-\tau_2+\tau_1$, which we cannot explain by the mechanism discussed in the above paragraphs. It appears to be due to a new type of combination of intervals which we call "quaternary," characteristic of four pulses, and analogous to the "primary" combination with two pulses, and the "stimulated" combination with three pulses. The rule for finding its position when written in terms of the interval between the pulses is also interesting; it is at an interval $2\delta_3+\delta_2+2\delta_1$ (see Fig. 1) away from the first pulse as compared to $\delta_2+2\delta_1$ for the stimulated and $2\delta_1$ for the primary echo mechanisms. We have also carried out calculations with five and six applied rf pulses, when "pentanary" and "hexanary" mechanisms following the combination rules $\delta_4+2\delta_3+\delta_2+2\delta_1$ and $2\delta_5+\delta_4+2\delta_3+\delta_2+2\delta_1$ are found as well. Hence we find that there is a new law of combination giving rise to a special type of echo, coming in with every extra applied pulse. Of course, all these can be explained by the rotating vector models developed by Hahn.[1,3] In general, the law of combination involving n pulses, giving the interval of the echo in question from the first pulse of the group, will thus be given by

$$\begin{aligned}&2(\delta_{n-1}+\delta_{n-3}+\cdots+\delta_1)+(\delta_{n-2}+\delta_{n-4}+\cdots+\delta_2), \quad \text{for } n \text{ even},\\ &(\delta_{n-1}+\delta_{n-3}+\cdots+\delta_2)+2(\delta_{n-2}+\delta_{n-4}+\cdots+\delta_1) \quad \text{for } n \text{ odd}.\end{aligned} \tag{2}$$

[3] For a specially simplified picture for explaining the origin of these mechanisms, we can consider rotating models with a 90° pulse followed by 180° pulses, as discussed by H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).

$\delta_1, \delta_2, \cdots$, representing the intervals between successive pulses starting from the first one.

These considerations enable us to obtain a recursion formula for the number of echoes, y_n, to be expected with n pulses.

(*a*) Number of primary echoes due to interaction directly between the nth pulse and any of the previous pulses $=\binom{n-1}{1}$.

(*b*) Number of primary echoes due to interaction between nth pulse and previous echoes $=y_{n-1}+y_{n-2}+\cdots+y_1$.

(*c*) Number of stimulated echoes between nth pulse and any two of the previous pulses $=\binom{n-1}{2}$.

(*d*) Number of stimulated echoes between nth and $(n-1)$th pulses and a previous echo $=y_{n-2}+y_{n-3}+\cdots+y_1$.

(*e*) Number of quaternary mechanism echoes between nth pulse and three previous pulses $=\binom{n-1}{3}$.

(*f*) Number of quaternary mechanism echoes between the previous echoes and last three pulses $=y_{n-3}+y_{n-4}+\cdots+y_1$.

(*g*) Number of $(n-1)$-mechanism echoes between nth pulse and $(n-2)$ previous pulses $=\binom{n-1}{n-2}$.

(*h*) Number of $(n-1)$-mechanism echoes between the last pulses and previous echoes $=y_2+y_1$.

(*i*) Number of n-mechanism echoes $=\binom{n-1}{n-1}=1$.

We therefore have

$$\begin{aligned}y_n&=\binom{n-1}{1}+\binom{n-1}{2}+\cdots+\binom{n-1}{n-1}\\&\quad+[y_{n-1}+2y_{n-2}+\cdots+ry_{n-r}+\cdots\\&\qquad+(n-2)y_2+(n-1)y_1]\\&=(2)^{n-1}-1+[y_{n-1}+2y_{n-2}+\cdots+ry_{n-r}+\cdots\\&\qquad+(n-2)y_2+(n-1)y_1].\end{aligned} \tag{3}$$

By using $y_1=0$, the formula (3) gives $y_2=1$, $y_3=4$, $y_4=13$, $y_5=39$, $y_6=112$, in agreement with the results of direct calculations with 2, 3, 4, 5 and 6 pulses, respectively. The laws of combination giving rise to the different echoes with four pulses are shown in Fig. 2, where a horizontal line is drawn to represent the mode of combination for each echo, the dots representing the parent pulses and the crosses the echoes obtained from them.

Of course it is to be remembered that the recursion formula (3) holds only under the conditions:

$$\left.\begin{aligned}&\tau_n>2\tau_{n-1}, \quad \tau_{n-1}>2\tau_{n-2}, \quad \text{etc.};\\ &\text{or, in terms of } \delta,\\ &\delta_{n-1}>\delta_{n-2}>\delta_{n-3}>\cdots>\delta_1.\end{aligned}\right\} \tag{4}$$

If these conditions do not hold, some of the echoes

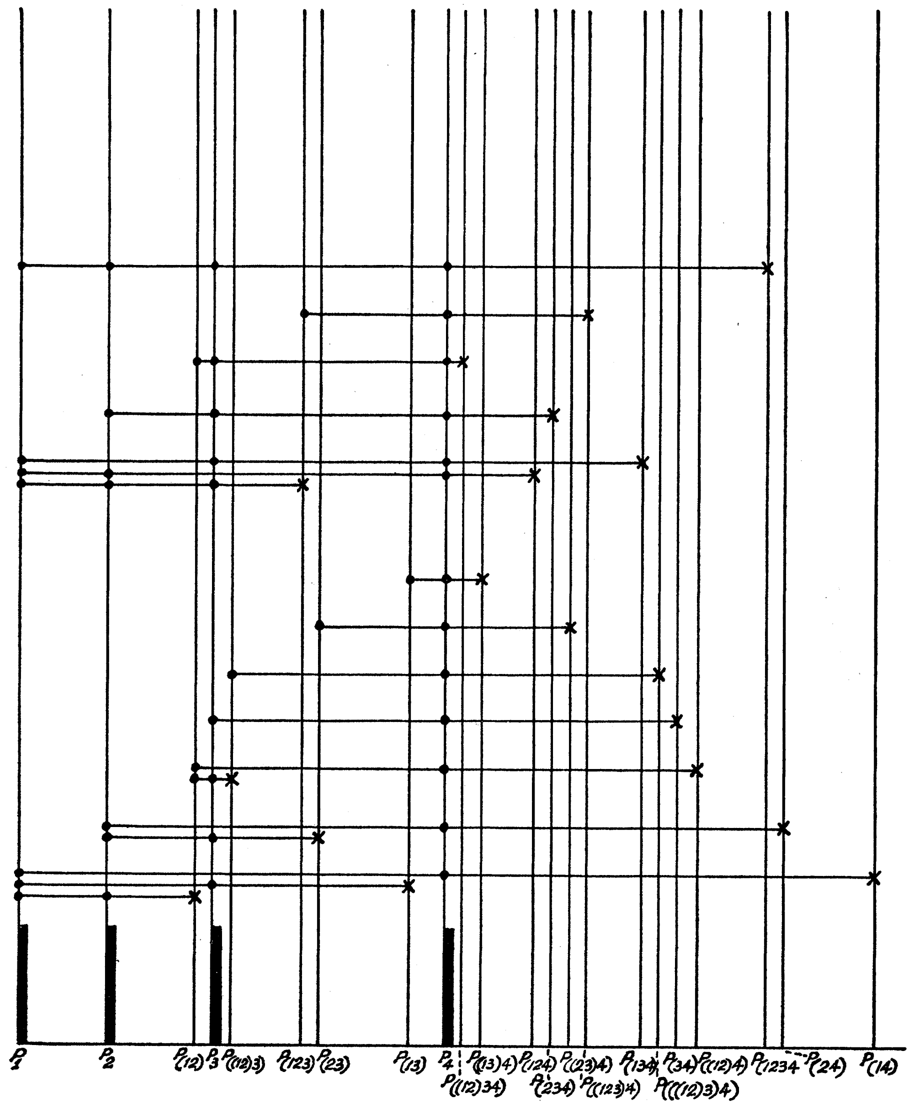

FIG. 2. Diagram illustrating the mode of formation of the echoes with 4 pulses.

predicted by (3) will not be observed. Moreover, one may enquire why we do not observe all these echoes discussed above when we apply successive pairs of pulses of increasing intervals, as in primary-echo envelope measurements.[1] The reason is that in such measurements, the pulse intervals do not evidently satisfy the conditions (4) so that some of the echoes discussed above do not occur. Further, it is to be expected that since the applied pulses now consist of pairs of pulses with fairly large gaps between successive pairs, all the echoes arising out of pulses belonging to different pairs will be heavily damped and so disappear in noise. Only the primary echoes between pulses within a pair will have significant amplitude and will be observed.

The aforementioned analysis for echoes with four pulses has an important practical application. Thus, it is difficult to set the angle of nutation $\xi=\omega_1 t_w$ at exactly $\pi/2$, because $\omega_1=\gamma H_r$, and H_r, the rf field amplitude cannot be measured accurately by a direct method. But the present investigation gives us a way to attain this end. Thus we see that the stimulated echo due to the first, second, and fourth pulses has an amplitude given by

$$P_{(124)}=-\tfrac{1}{2}\sin^3\xi\cos\xi\left(\exp-\frac{5k\tau_1^3}{3}-k\tau_1^2\tau_3\right)\times\exp\left(-\frac{2\tau_1}{T_2}-\frac{\tau_3-\tau_1}{T_1}\right). \quad (5)$$

Thus if a circuit be arranged to give four successive rf pulses with intervals satisfying (1) and also such that the diffusion and relaxation dampings are small, and then the groups of pulses be repeated at a rate faster than that necessary for persistence of vision, the full

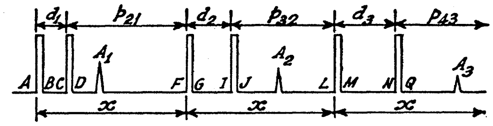

FIG. 3. Arrangements of rf pulses for Hahn primary-echo experiment.

echo pattern can be seen, from which the particular echo of interest, *viz.* $P_{(124)}$, may be chosen from its position. Now, keeping the pulse-width t_w constant, the rf voltage from the oscillator may be varied till this echo vanishes. The value of H_r when this occurs is the value necessary for making $\xi=\omega_1 t_w=\pi/2$.

IV. APPLICATIONS TO HAHN'S MEASUREMENTS ON PRIMARY AND SECONDARY ECHOES

The aforementioned analysis with four applied pulses also has interesting applications in experimental measurements on primary and stimulated echoes, with groups of two and three pulses respectively. Thus, it gives us a possible method of obtaining T_1 from primary echo measurements alone, and also a correction to measurement of T_2 from observations on primary echoes. Hahn,[1] in his experiments on the primary echo, applies paired pulses (Fig. 3) with intervals $d_1, d_2, d_3, \cdots$, respectively between members of successive pairs, the intervals between the last member of the $(n-1)$th pair and the first member of the nth pair being denoted by $p_{n,(n-1)}$. The interval between the first pulses of successive pairs is denoted by x, which is usually kept constant.

From Table I, we get the primary echo amplitude due to the first pair of pulses as

$$A_1=\sin\xi\,\sin^2(\xi/2)\,\exp\left(-\frac{2d_1}{T_2}-\frac{5kd_1^3}{3}\right).$$

The primary echo amplitude due to the second pair of pulses is given by

$$A_2=\sin\xi\,\sin^2(\xi/2)\left\{1+[W'(D)-1]\exp\left(-\frac{p_{21}}{T_1}\right)\right\}\times\exp\left(-\frac{2d_2}{T_2}-\frac{5kd_2^3}{3}\right),$$

where $W'(D)$ represents that part of $W(D)$ which is contributed by the W's of the previous instants. The term

$$C=1+\{W'(D)-1\}\exp(-p_{21}/T_1) \tag{6}$$

gives the effect, on the primary-echo amplitude, of the memory retained by the spin system regarding the conditions established by the previous pair of pulses, and is a consequence of the fact that thermal equilibrium is not attained in the interval between the two successive pairs of pulses. Similar calculations with a third pair of pulses gives the primary-echo amplitude due to these as

$$A_3=\sin\xi\,\sin^2(\xi/2)\left\{1+[W'(J)-1]\exp\left(-\frac{p_{32}}{T_1}\right)\right\}\times\exp\left(-\frac{2d_3}{T_2}-\frac{5kd_3^3}{3}\right).$$

If we now use pulses with $\xi=\pi/2$, then the C term for the primary echo due to the nth pair of pulses will have the general form

$$[1-\exp(-p_{n,n-1}/T_1)].$$

This factor we shall call the "memory damping" factor in the primary-echo experiment. This "memory damping" effect provides us with a method of obtaining T_1 from primary-echo measurements alone. Thus, from Fig. 3, we have

$$p_{n,n-1}=x-d_{n-1}.$$

Hence the amplitude of the primary echo due to the nth pair of pulses will be given by

$$A_n=\sin\xi\,\sin^2(\xi/2)\,\exp\left(-\frac{2d_n}{T_2}-\frac{5k}{3}d_n^3\right)\times\left[1-\exp\left(-\frac{x-d_{n-1}}{T_1}\right)\right].$$

If now the d_n's be kept constant and the interval between the successive pairs of pulses be varied, then the primary-echo envelope will be given by

$$A_n\propto\left[1-\exp\left(-\frac{x-d}{T_1}\right)\right]. \tag{7}$$

Thus, we can arrange a circuit to give us paired pulses with equal intervals between the members of each pair, but with gradually decreasing intervals x between successive pairs, starting from a value of x large compared to T_1, corresponding to attainment of thermal equilibrium between successive pairs of pulses, till x is of the order of T_1 or even smaller. By taking multiple exposures we shall then get the echo envelope giving by (7), and by taking a log-plot of this envelope we can then evaluate T_1 directly.

In Hahn's primary-echo experiment to measure T_2, on the other hand, x is kept constant and d is varied. In such a case, unless $x\gg d$, there will be a correction due to the "memory damping" factor. Thus, considering the primary echoes due to the second and third pairs of pulses, we have

$$\frac{A_2}{A_3}=\frac{1-\exp[-(x-d_1)/T_1]}{1-\exp[-(x-d_2)/T_2]}\cdot\frac{\exp(-2d_2/T_2)}{\exp(-2d_3/T_2)}.$$

If we had neglected the momemory damping factor, we would have had

$$\frac{A_2}{A_3}=\frac{\exp(-2d_2/T_2')}{\exp(-2d_3/T_2')},$$

T_2' representing the uncorrected value of T_2. Then, putting

$$d_2-d_1=d_3-d_2=\cdots=d_n-d_{n-1}=\beta$$

as employed in Hahn's experiment,[1] we get

$$\frac{1}{T_2}=\frac{1}{T_2'}-\frac{1}{2\beta}\log_e\left[1-\exp\left(-\frac{x}{T_1}\right)\frac{\beta}{T_1}\right]. \quad (8)$$

Of course, in general, the correction will be small, because, for T_1 large, β/T_1 is small and for T_1 small x/T_1 can be made large. A similar correction for "memory damping" will apply to stimulated echo measurement with groups of three pulses also.

ACKNOWLEDGMENT

The authors are very grateful to Professor M. N. Saha for his keen interest in their work. They are also thankful to Dr. A. K. Saha for guidance and encouragement.

PHYSICAL REVIEW VOLUME 98, NUMBER 2 APRIL 15, 1955

Dirac Bracket Transformations in Phase Space*

PETER G. BERGMANN AND IRWIN GOLDBERG
Department of Physics, Syracuse University, Syracuse, New York
(Received December 22, 1954)

The purpose of this paper is twofold. One is to analyze the group-theoretical significance of the Dirac bracket and to examine, in particular, the apparent ambiguities in the presence of both first-class and second-class constraints. The other is to prepare the ground for the utilization of the Dirac bracket for the quantization of generally covariant theories. It is shown that the Dirac bracket represents the commutator of infinitesimal transformations in phase space which are not canonical but form a group, in that they are the only transformations that preserve the form of all the constraints of a theory as well as the canonical form of the equations of motion. This group of transformations possesses an invariant subgroup: those transformations that correspond to coordinate transformations, gauge transformations and the like. From this subgroup, we can construct the factor group. All members of the original group have generators, but the generators of the invariant subgroup are zero. There is, then, a one-to-one correspondence between the nonvanishing generators and the members of the factor group. The Dirac bracket is uniquely defined for all dynamical variables that can serve as generators; excluded are variables that have no invariant significance (such as the divergence of the electromagnetic vector potential). If it is possible to identify all these permissible generators, then the theory can be reformulated in terms of these and will be free of constraints. It is proposed to adopt the set of generators and the Dirac brackets between them as the point of departure for the formulation of covariant quantum theories.

1. INTRODUCTION

IT is well known that the quantization of a given classical field theory is not a straightforward unique process. The replacement of classical Poisson brackets by commutators between operators cannot be carried out simultaneously for all conceivable dynamical variables without leading to internal inconsistencies. Ordinarily, the formulation of commutators is therefore restricted at first to a certain class of variables, such as the canonical coordinates of the theory,[1] all other commutators being obtained subsequently by calculations from this primary set. But a given classical field theory may be set up in terms of any set of canonically conjugate variables; the transition from Poisson brackets to operator commutators then leads to different quantum theories depending on the canonical coordinate system chosen. Hence the usual prescription is ambiguous unless we can single out a particular canonical coordinate system for the transition to quantum theory.

This situation is somewhat less ambiguous in quantum mechanics. There the rule is to carry out the quantization in Cartesian (or Lorentzian) coordinates and to go over to other coordinate systems only after quantization. This rule can be transferred to field theories that are "essentially linear." An essentially linear theory is one whose Lagrangian can be split naturally into a "free field" part and an "interaction" part, such as the Lagrangian of electrodynamics. This separation of the Lagrangian into two components, of which the former is purely quadratic in the field variables, remains preserved under linear-homogeneous variable transformations. There is, then, a set of privileged and identifiable canonical coordinate systems, any one of which may be adopted as the point of departure for quantization. The resulting theories are all equivalent to each other, except for terms that are readily identified as so-called zero-point energy terms. Such terms can be subtracted from a given Lagrangian or Hamiltonian without serious consequences. There is some doubt about the ultimate justification for such a procedure, especially in the event of strong coupling, but we shall not concern ourselves with that question here.

Generally covariant theories are not essentially linear. Moreover, the most convenient canonical coordinates of such a theory, i.e., the initial field variables

* This work was supported by the Office of Naval Research.
[1] R. E. Peierls, Proc. Roy. Soc. (London) A214, 143 (1952).