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FREE NUCLEAR INDUCTION

By E. L. Hahn

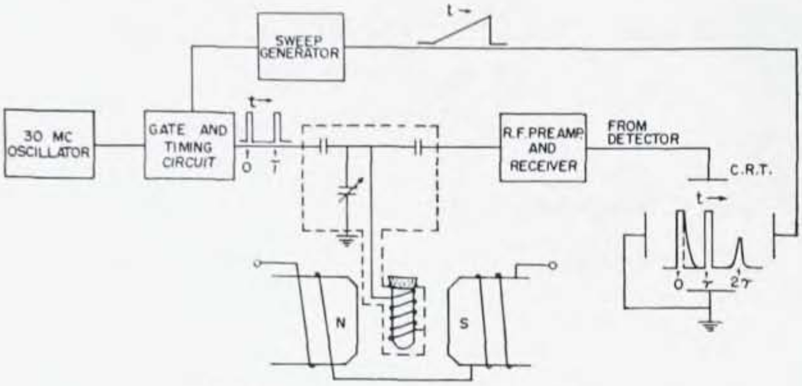

Fig. 1. Arrangement for obtaining spin echoes.

Unusually clear measurements of the time precession of nuclear magnetic moments and other properties of nuclei have become possible with the development of the free induction "spin echo" technique in the still new science of nuclear magnetic resonance.

THE STUDY of nuclear magnetic resonance or nuclear induction, a recent field of research for which F. Bloch [1] and E. M. Purcell [2] have been awarded the Nobel Prize, has been carried out by a variety of techniques. The usual approach has been to observe the nuclear resonance of an ensemble of nuclear moments in a large static magnetic field as a function of a slow change in this field. Meanwhile, a small radio-frequency field is applied continuously to the nuclear sample in a direction perpendicular to the large field. An alternative method to this steady state or "slow passage" technique is one by which the radio-frequency energy is applied to the sample in the form of short, intense pulses, and nuclear signals are observed after the pulses are removed. The effects which result can be compared to the free vibration or "ringing" of a bell, a term often applied to the free harmonic oscillations of a shocked inductive-capacitive (LC) circuit. The circuit is first supplied with electrical energy from some source, and the supply of energy is suddenly removed. The LC circuit then remains for a time in the "excited state", and the energy is gradually dissipated into heat, mostly in the circuit resistance. Similarly the atom or nucleus in the excited state can store energy for a time before it is completely dissipated, and in the case discussed here, the free oscillation or precession of an ensemble of nuclear spins in a large static field provides the ringing process.

It appears that the topic of free nuclear precession or "spin echoes", as it will be called here, can be classified under one of the following two approaches to the study of excited states: (a) A study can be made of the absorption or emission of radiation by a system. The system gains or loses radiation (or particles), and the experiment involves a measurement of the energy and intensity of radiation. (b) The behavior of some systems can be studied, not by observing directly whether they gain or lose radiation, but by detecting their mode of motion under the influence of applied *static* electric and magnetic fields. While observing such motion it is possible to infer whether or not the system has gained or lost radiation in the past.

It is well known that the latter approach is involved in the Rabi molecular beam technique [3] in which molecules and atoms are deflected in space. Also, this approach applies to the free nuclear precession or induction effect. The viewpoint of the experiment has been particularly emphasized by Bloch,[1] and is very much like the scheme for detecting the ringing of a tuned LC circuit. A pickup loop can be coupled to the magnetic flux about the inductance and a voltage of induction is measured. In the actual experiment the magnetic induction is provided by the precession of an ensemble of nuclear moments in a static magnetic field after the moments are "shocked" into a coherent state of precession by one or more pulses of radio-frequency magnetic field. One might classify this measurement under (a) above, and deduce that here the ringing of the system is measured by detecting the stored magnetic energy which the system dissipates. Certainly some radio-frequency (rf) energy is consumed by the loop which couples to the ringing LC circuit, but this can be made

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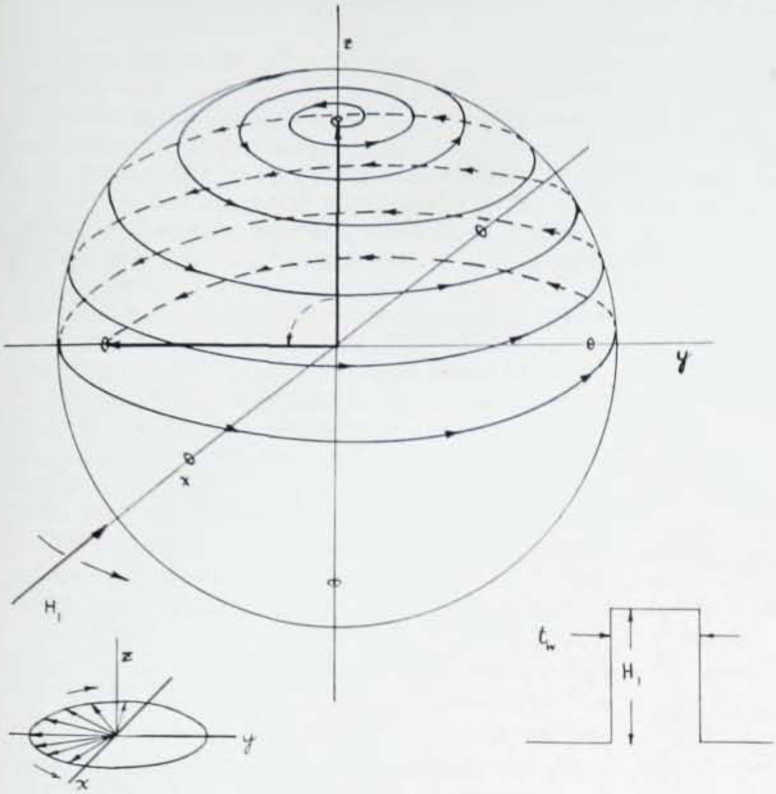
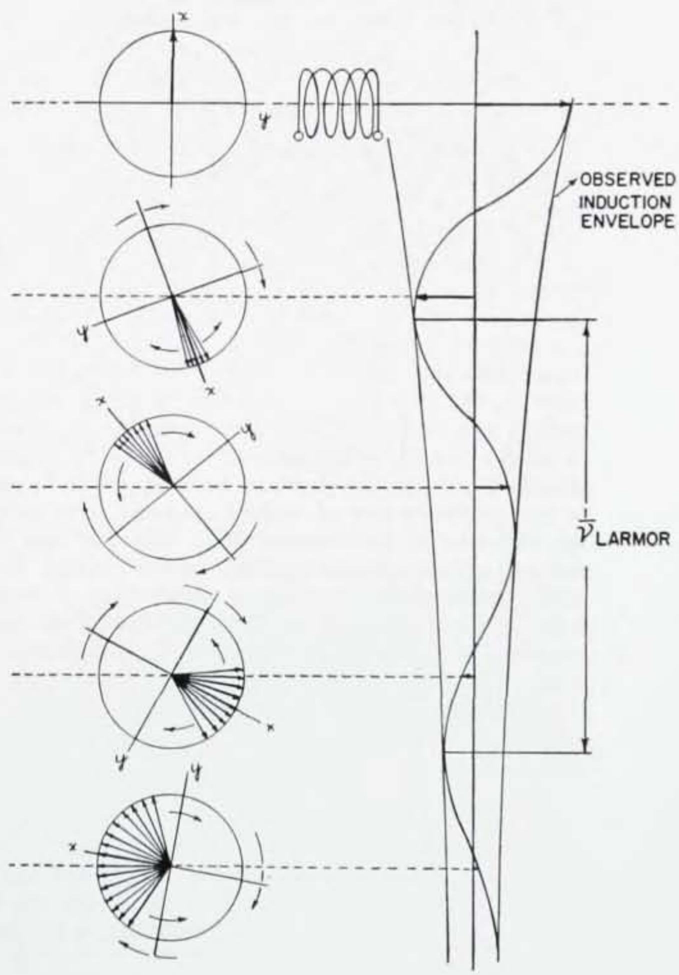


Fig. 2a. As seen in the laboratory frame of reference the classical magnetic moment precesses toward the *xy* plane in a spiral motion due the torque effect of the rf field H_1 at nuclear resonance. In the frame of reference rotating with H_1 the magnetic moment appears to precess in a plane perpendicular to H_1.

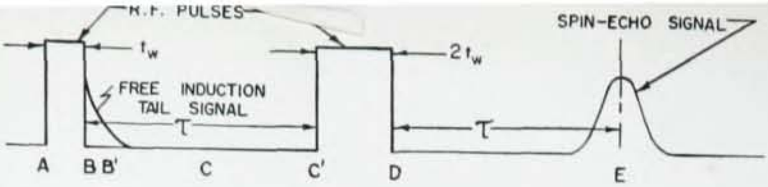
Fig. 2b. Following the orientation of the total magnetic moment into the *xy* plane by a 90° pulse the spectrum of moment vectors provides a free nuclear induction signal. The precessional motion relative to the moving and fixed frames of reference is indicated.



negligibly small by using a loop of high-circuit impedance. In the free precession experiment, a sample of nuclei is placed in a pickup loop comprising the inductance of an LC circuit tuned to the Larmor precession frequency. A low voltage of induction (about a millivolt at most due to protons) is produced across the inductive coil by the nuclear spins, and the current which flows in the coil produces a weak rf magnetic field throughout the volume of the sample. This field does react upon the nuclear spins, but causes only a negligibly small rate of induced emission. The ringing oscillator, in this case the nuclear moments, is again very weakly loaded by the pickup coil.

If any clear distinction can be made between the terms "nuclear magnetic resonance absorption" and "nuclear induction", it can be made in the free precession experiment. Nuclear resonance absorption belongs under heading (a) above. Radio-frequency energy in the form of pulses, absorbed by the nuclear moments, prepares the moments for the ringing process which is observed only by nuclear induction under heading (b).

A qualitative description of the experiment involves many of the basic features of nuclear resonance techniques. A large constant magnetic field H_0 must be available in which polarization and precession of the nuclear spins take place. In practice this field is never perfectly homogeneous for all of the nuclei throughout the volume of the sample. Instead the field varies throughout space in a manner which is determined by the inhomogeneity of the magnet or also by local magnetic fields in the lattice of the sample. In liquids and gases, however, except for certain special but small molecular effects, any local magnetic field in the lattice



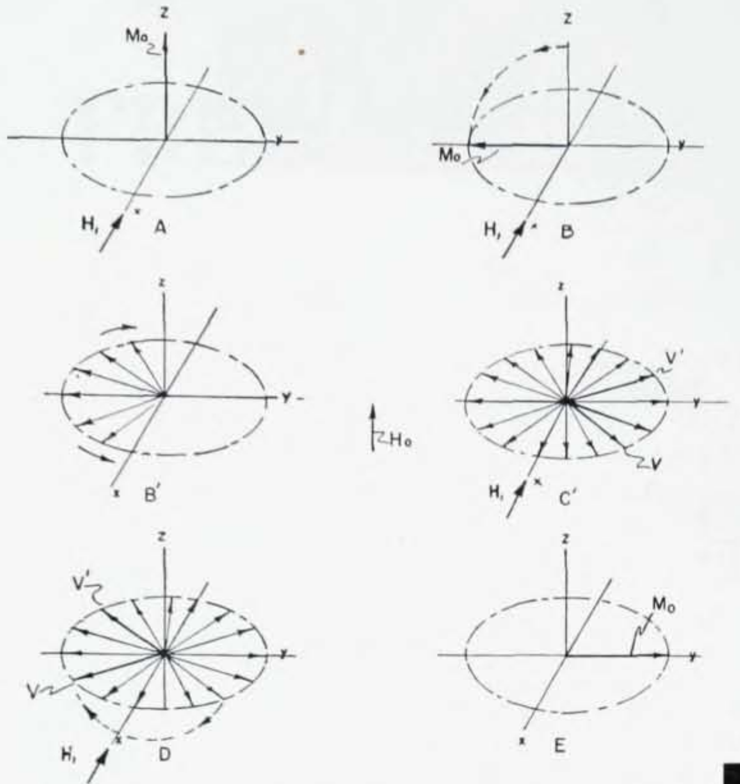


Fig. 3. Vector schematic of the spin echo formation.

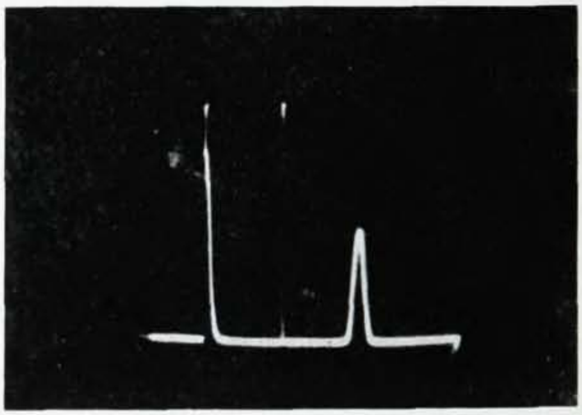


Fig. 4. Oscillographic display of the spin echo due to protons in glycerine. The rf pulse widths are narrow compared to the duration of the signals.

which a given nuclear moment sees as a result of its neighbors will average completely to zero over a Larmor period. This happens because the tumbling and translational frequencies common to liquid molecules at normal temperatures, for example, are extremely large compared to the Larmor frequency of precession (greater by a factor of 10^4 to 10^5). During one Larmor period of precession the field caused by a neighboring dipole does not remain at a given value long enough to influence the rate of precession determined by the externally applied field H_0. It becomes possible, therefore, to ascribe to each volume element of the liquid an isochromatic or classical magnetic moment, which is due to the preponderance of nuclear moments pointing in the direction of the external field. This field can be assigned as homogeneous over the volume element. The entire liquid sample provides a distribution of magnetic moments according to how much volume of spin sample is assigned to each value of H_0 as it varies in space. Such a spectrum may be described by some symmetric distribution, where the maximum number of nuclear moments may be subject to a field of 7000 gauss, for example, and fewer moments see values of H_0 smaller or greater than this average value.

At thermal equilibrium the net magnetic moment M_0 which is aligned with the field can be compared to the "sleeping" mechanical top that spins with its axis along the direction of the gravitational field. If the top is perturbed by applying torque perpendicular to its spin axis, it will precess in a certain direction at a given frequency for any angle θ which exists between the spin axis and the direction of the gravitational field. The nuclear magnetic top has a torque exerted upon it by the magnetic field H_0 in place of gravity, and when it is tipped away from the H_0 or z axis direction by rotating rf magnetic fields in the xy plane, it consequently precesses about the z axis at the Larmor frequency given by $\omega_0 = \gamma H_0$ after the xy perturbing field is removed. The constant γ is the gyromagnetic ratio defined by $\gamma = \mu / I\hbar$, where μ is the magnetic moment and $I\hbar$ is the nuclear spin angular momentum. The time that the induction signal due to a classically precessing $\overline{M}_0$ vector can persist is also the time for which constituent nuclear spins precess in phase before damping effects due to the lattice become appreciable. This coherence time is given by T_2, often referred to as the "transverse relaxation time". Another relaxation time of importance, which determines in part the value of T_2, is the longitudinal or thermal relaxation time T_1, the time in which a precessing spin remains in the magnetically excited state regardless of its phase. In liquids both of these relaxation times may vary from fractions of milliseconds to several seconds.

After a few preliminary definitions, we shall impose special experimental conditions for purposes of clearly explaining the echo nuclear induction effect. An inductive driving coil which surrounds the nuclear sample is tuned to the Larmor frequency $\omega = \omega_0'$ where ω_0' is the average angular Larmor frequency of a sample of nuclear moments. rf pulses applied to the tuned LC circuit each last for t_w seconds during which time approximately $\omega_0' t_w$ Larmor oscillations take place. The effective rf magnetic field is referred to as the $\bar{H}_1$ Gauss vector which precesses in the direction that $\bar{M}_0$ precesses, and is the vector which remains essentially perpendicular to the plane defined by $\bar{M}_0$ and $\bar{H}_0$ (see Fig. 2). In a coordinate system which rotates with frequency $\omega_0'/2\pi$ about the z axis, the $\bar{M}_0$ vector will then appear to precess about $\bar{H}_1$ through angle $\theta = \gamma H_1 t_w$ from the time $\bar{H}_1$ is turned on. This $\bar{H}_1$ field is one of two circularly polarized field components which sum to provide the alternating magnetic field $2H_1$ along the axis of the inductive coil. The other $\bar{H}_1$ field component, rotating in the opposite direction, can be ignored because its torque acting upon $\bar{M}_0$ is alternately positive and negative, and averages to zero for all practical purposes. We shall assume that $\bar{H}_1$ is turned on infinitely fast, and that it shall be removed after t_w seconds infinitely fast. During the time t_w, all isochromatic moments, initially aligned along $\bar{H}_0$, will be turned away from the z axis toward the xy plane. The driving radiofrequency pulses may be transmitted by the same coil used for receiving signals, or two separate coils perpendicular to each other may be used, one for transmitting and one for receiving. If $\bar{H}_1$ rotates in the xy plane at a frequency ω, all those isochromatic moments which are tuned to Larmor frequency ω_0, different from ω, will, strictly speaking, not precess exactly in a plane perpendicular to the direction of $\bar{H}_1$. However, $\bar{H}_1$ is chosen to be sufficiently intense so that most of the isochromatic moments are rotated toward the xy plane in a time short compared to the time in which they would get out of phase with $\bar{H}_1$ (i.e. they would scarcely deviate from the plane defined by $\bar{M}_0$ and $\bar{H}_0$, perpendicular to $\bar{H}_1$). Therefore all the isochromatic moments are substantially in phase at the time t_w when they have reached the xy plane. At this time t_w the field $\bar{H}_1$ is suddenly removed. A nuclear induction signal in the receiver or pickup coil will persist after the field $\bar{H}_1$ is removed, but will finally die out because each isochromatic moment is now free to precess at its natural frequency. Since these frequencies differ for each isochromatic moment, the moments will, after a time, get out of phase and their inductive effects will interfere or cancel among themselves.[4] The time required for this loss of a net observed induced output signal is usually determined by the inhomogeneity of the magnet. After such a time, the isochromatic moment vectors are uniformly distributed about the z axis, but the original magnitudes of these isochromatic moments are preserved if it is assumed that there are no relaxation effects. Although

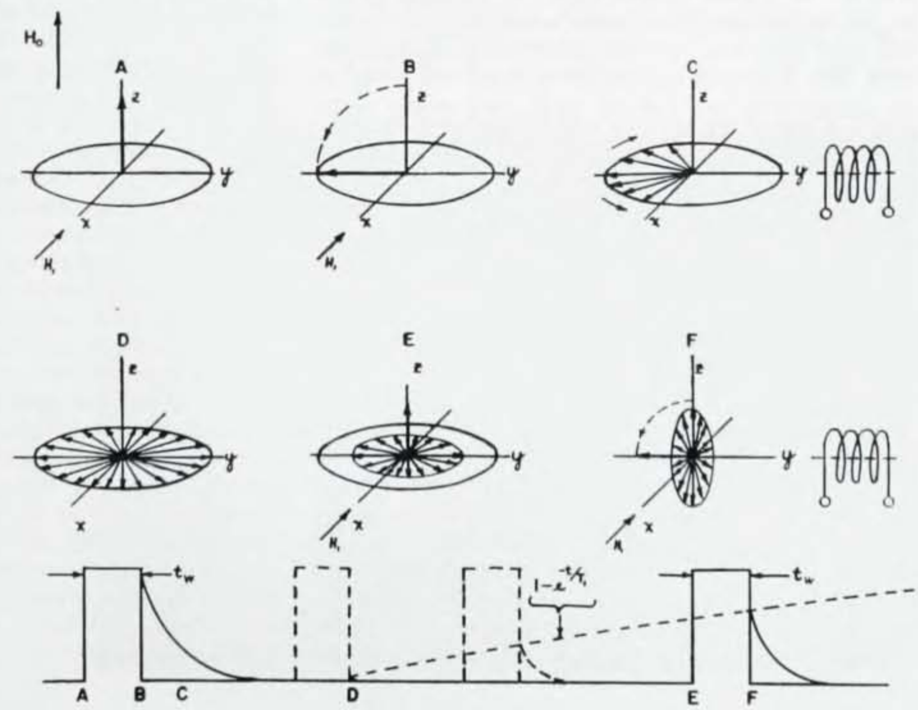


Fig. 5. Scheme for measurement of T_1. The sequence from A through D is the same as in Fig. 3. At the time a pulse is applied at time E a fraction of the total nuclear magnetism has returned to thermal equilibrium along the z axis. Following this pulse at F a free induction signal results which is proportional to this magnetism.

these isochromatic moment vectors do not provide a resultant moment, they do have definite phase relations among themselves, and each vector occupies a position which has been determined by its past history. If at a time τ after cessation of the first pulse, a second pulse is transmitted to the driving coil, this past history is manifested in what is called the "spin echo".

The echo effect [5] can be explained from a very simple analogy. Let a team of runners with different but constant running speeds start off at a time $t = 0$ as they would do at a track meet (see the cover of this issue). At some time T these runners will be distributed around the race track in apparently random positions. The referee fires his gun at a time $t = \tau > T$, and by previous arrangement the racers quickly turn about-face and run in the opposite direction with their original speeds. Obviously, at a time $t = 2\tau$, the runners will return together precisely at the starting line. This will happen once and only once, just as it will be shown in the case of two rf pulses and the echo. From this analogy, one can see that if even more than two pulses are applied to the ensemble, a pattern of echoes or constructive interference events will occur which will uniquely be related to the pulses which were applied in the past. For example, if the referee again fired his gun for a third time after the racers came together at the starting point and fanned out again around the track, and the runners again repeated the about-face procedure, they would again come back to the starting line.

For the purpose of simplifying the description of the actual echo formation, as shown in Fig. 3, the second pulse is made either of the same intensity and twice as long as the first pulse or twice as intense with the same duration as the first pulse. From the time $\bar{H}_1$ appears again in the xy plane, each isochromatic moment vector precesses in a cone whose axis is the direction of $\bar{H}_1$. At the instant the second pulse is removed, all vectors will have been rotated from whatever xy plane quadrants they happened to have been in (at the onset of the second pulse) on one side of $\bar{H}_1$ to a mirror image position on the opposite side of $\bar{H}_1$. The second pulse, so to speak, has flipped the "pancake" of isotropically distributed moments by 180°. When this flip has occurred it can be seen that if we refer to the central average isochromatic moment, each isochromatic moment which lay ahead of this average moment by a given angle before the second pulse now lies behind it by the same angle. Furthermore, each isochromatic moment which lay behind the average isochromatic moment by a given angle will lie ahead by the same angle. Now if these isochromatic moments continue to precess as before, those behind the reference vector or average isochromatic moment will be catching up and those ahead will be falling back. Hence, at time τ beyond the second pulse, all the moment vectors will be back in phase and the echo of the first pulse will occur at time 2τ where τ is the time between the first pulse and the second or reversing pulse. This can be seen by tracing the history of a pair of vectors from the figure. At the onset of the first pulse, the moments M_0 lie on the z axis at thermal equilibrium at A. Following a rotation of 90°, completed at B by the first pulse, the isochromatic moments spread out as shown in B'. During this time, an induction signal forms as a "tail" following the first pulse. At C and C' the tail is absent because the isochromatic moments are evenly distributed in the xy plane. Follow, for example, the precessional motion of isochromatic moment vectors V and V' shown at C'. Here they happen to be oriented in positions indicated at the onset of the second pulse, which now rotates them and the whole array in the xy plane by 180°, as shown at D. After the pulse is removed at D, the vectors V and V' will proceed to precess through angles in the xy plane again in a time τ as they did after the first pulse. They obviously must coincide at the time of the echo at E. This argument holds for every pair of vectors in the ensemble for the special case given here. The spin echo has a shape which grows and dies out symmetrically in the time it takes for the isochromatic moments to get in phase and then out of phase.

It should be noted at this point that although it has been assumed for the sake of simplicity that the first pulse rotates all the vectors by 90°, and the second pulse rotates them by 180°, these rotations happen to be the ones which give the maximum available echo. Useful results may also be obtained by use of other arbitrary combinations of t_w and H_1 giving different angles of rotation. For example, the second pulse may be of equal length and equal intensity as the first pulse, in which case the array is rotated 90° rather than 180° as described above.

Useful information about the local magnetic fields due to chemical environment about the precessing nucleus can be obtained in certain cases from measurements of shapes and amplitudes of free induction echo signals. Steady state resonance techniques of course can provide the same information, which in some cases is more direct, particularly when a number of closely spaced transitions between stationary states of nuclear Zeeman levels are indicated directly by resonance lines.[6] The equivalent of such small differences in energies of closely spaced Zeeman levels is manifested in the echo method by interference beats [7] between the various components of precessing magnetic moments which precess at different Larmor frequencies in the same sample of spins subjected to a given external H_0. If the maximum echo signal amplitude is measured for increasing values of τ, where for each setting of τ the ensemble is initially at thermal equilibrium, a plot of the echo signal amplitude as a function of τ displays predominantly a monotonic decay. In many cases the decay is exponential and serves as a direct measure of the nuclear spin relaxation parameter T_2, but the decay may also be determined in part by other factors. There are other special ways of studying echo signal plots which do not require that the ensemble be at equilibrium for just a pair of pulses, where the nature of the information obtained is essentially the same.

The decay of the echo may be understood in terms of the race track analogy if it is assumed now that the runners become fatigued after the start of the race. For this reason they may change their speeds erratically or even drop out of the race completely. Consequently, following the second gun shot (the second pulse) some of the racers may return together at the starting line but not all of them. In the nuclear spin system a similar situation prevails: either (1) the nuclear spins return to thermal equilibrium or (2) they lose phase memory of Larmor precession. The effect (1) occurs when the magnetic energy of precession contained by the moment is transferred to a molecule completely in the form of kinetic energy. The time in which this effect occurs is called T_1, the spin-lattice thermal relaxation time. The effect (2) arises when magnetic energy is transferred from spin to spin. One must also add to this the effect due to fluctuating local magnetic fields caused by neighboring moments and paramagnetic substances. The over-all time which relates to processes in the lattice which shorten the phase memory of precession has been denoted by T_2, which includes the effect of T_1 as well.

Another influence which destroys the phase memory of precession is that due to the self diffusion of molecules which contain resonant nuclei. Since there is an established gradient of the magnetic field over the volume of the sample, a molecule whose nuclear moment has been flipped initially in a field H_0, may, in the course of time 2τ, drift by Brownian motion into a randomly differing field H_0. Therefore, as τ is increased, a lesser number of moments participate in the generation of in-phase nuclear radio-frequency signals. The theory of the diffusion effect can be incorporated into the nuclear equations, and a useful expression is obtained by which the self-diffusion coefficient of molecules can be measured from the plotted envelope curve and known parameters.

It is possible to measure the thermal relaxation time T_1, independently of all other effects, by measuring signals proportional to the excess population of moments in the z direction at any time, as shown in Fig. 5. This can be done by measuring the amplitude at some arbitrary point on the free induction tail following the second radio-frequency pulse. This is compared to the amplitude at the corresponding point on the free induction tail on the induced signal following the first pulse, which is the amplitude proportional to the maximum available moment M_0. It can be shown that if $\gamma H_1 t_w = \pi/2$ for both pulses, then the tail signal following the second pulse is proportional to the number of gyromagnetic moments which have been thermally relaxed during the time τ. There are alternate methods of measuring T_1, for instance, from the observation of echoes obtained from an application of more than two radio-frequency pulses.

Recently a very interesting phenomenon of a ringing system in the case of an ensemble of molecular electric dipole moments has been demonstrated by R. H. Dicke at Princeton. The principle is very much like the case for pulsed nuclear induction except that a coherent electric field due to molecular rotation induces a signal in a microwave cavity following a strong microwave pulse at resonance. One aim of Dicke's method is to obtain higher resolution in spite of Doppler broadening. Similarly the pulsed echo method permits high resolution where long relaxation times (the equivalent of narrow natural line widths) can be measured in spite of artificial line broadening due to an inhomogeneous magnetic field.

Bibliography

1. F. Bloch, *Physical Review* **70**, 460 (1946).
2. Bloembergen, Purcell, and Pound, *Physical Review* **73**, 679 (1948).
3. Rabi, Millman, Kusch, and Zacharias, *Physical Review* **55**, 526 (1939).
4. E. L. Hahn, *Physical Review* **77**, 297 (1950).
5. E. L. Hahn, *Physical Review* **80**, 580 (1950).
6. H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *Journal of Physical Chemistry* **21**, 279 (1953).
7. E. L. Hahn and D. E. Maxwell, *Physical Review* **88**, 1070 (1952).

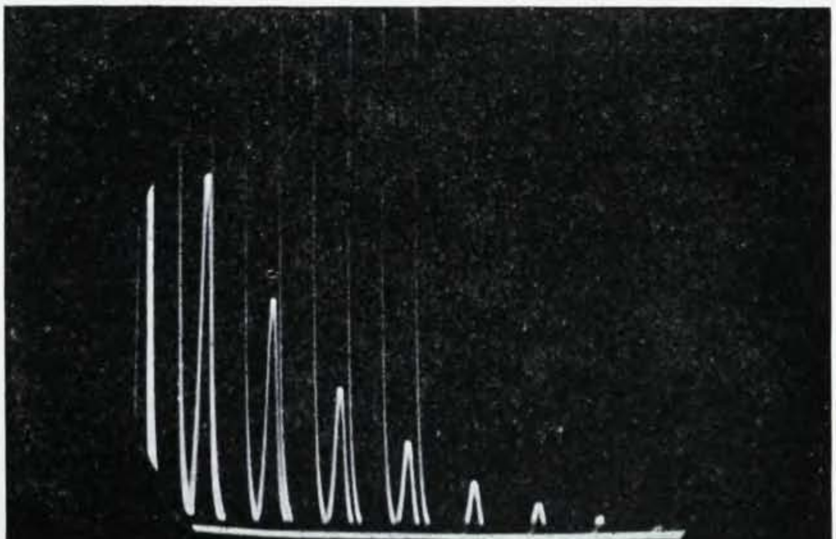


Fig. 6. Multiple exposures of single proton echoes. The first rf pulse occurs at the beginning of the trace and the second pulse is spaced from the origin at equal intervals for each exposure with the sample at thermal equilibrium. The echo envelope provides a measure of the phase coherence parameter T_2.