turbation calculation. We have carried through such calculations for $\omega_1 t_w = \pi/2$ in Hahn's notation[1] (spins turned through $\pi/2$ by the radiofrequency pulses) and $\omega_1 \gg \delta\Omega$, $\delta\omega$. We find the echo envelope is proportional to

$$|1+\cos\delta\omega\tau+(1-\cos\delta\omega\tau)\cos\delta\Omega\tau|.$$

This agrees with the results of Hahn and Maxwell.[6]

In addition, our calculation explains the echo asymmetries in the following manner. We consider separately the two spin groups 1 and 2 whose Larmor frequencies are chemically shifted relative to one another. At time $t=2\tau$ there is a resultant magnetization of group 1 and of group 2. The echo amplitude and asymmetry result from the following: (a) The length of the magnetization vectors is a function of τ. (b) The relative spatial orientation of the vectors at $t=2\tau$ depends on τ. Feature (b) accounts for the asymmetry, since if the vectors are not in phase at $t=2\tau$, their different precession frequencies cause a more perfect alignment at times either before or after $t=2\tau$. For example, the vectors might reach alignment on the leading edge of the echo, but not on the trailing edge with the result that the leading edge would be stronger than the trailing edge. The analysis shows that when $\delta\Omega\tau = n\pi$, where n is an integer, the vectors are in phase at $t=2\tau$, and the echo is symmetrical. This result is in agreement with the experimental facts mentioned earlier since these values of τ are the ones for which the envelope has a maximum or a minimum.

* Supported by the ONR.

[1] E. L. Hahn, Phys. Rev. **80**, 58 (1950).
[2] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. (to be published.)
[3] Gutowsky, McCall, and Slichter, Phys. Rev. **84**, 589 (1951).
[4] W. C. Dickinson, Phys. Rev. **81**, 717 (1951); W. G. Proctor and F. C. Yu, Phys. Rev. **81**, 20 (1951).
[5] In a letter to HSG, E. L. Hahn stated he had found proton slow beats only in compounds having a fine structure in chemically shifted lines.
[6] E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951). We are indebted to Dr. Hahn for sending us a copy of their letter in advance of publication.

Chemical Shift and Field Independent Frequency Modulation of the Spin Echo Envelope*

E. L. Hahn† and D. E. Maxwell
Stanford University, Stanford, California
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FURTHER investigation of the echo envelope modulation effect[1] has been carried out and related to measurements made by slow passage nuclear resonance methods.[2,3] According to the echo method, two short, intent pulses of radiofrequency power are applied to the spin ensemble at the nuclear resonance condition, and are separated by time interval τ. The echo appears with a given maximum amplitude at time 2τ. At the onset of the first radiofrequency pulse the spin system is at thermal equilibrium. For each setting of τ the maximum of the echo signal is measured and plotted as a function of increasing τ. If the spin ensemble consists of magnetic moments located in equivalent chemical environments [i.e., protons in H_2O or $(CH_3)_2O$], a monotonic decay in the echo envelope is obtained.

The envelope modulation effect is observed in molecules in which nuclear magnetic dipoles have neighboring nuclear dipoles in nonequivalent chemical environments. Examples are dichloroacetaldehyde ($CHCl_2CHO$), 1-fluoro-1,2,2 trichloro-ethane ($CFClH-CCl_2H$), and ethyl alcohol (C_2H_5OH), where H and F^{19} are the resonant nuclei concerned. In general these molecules may fall into either of two classes which contain resonant nuclear moments in the following arrangements: A resonant nucleus (or chemically equivalent nuclei) may have one or more neighboring dipole nuclei which are (1) identical with the resonant one, but chemically nonequivalent, or (2) not identical.

In molecules such as $CHCl_2CHO$, C_2H_5OH,[1] and $CCl_3(CHCl)_3$-CCl_3, two distinct modulation frequencies appear on the echo envelope: (1) One frequency corresponds to the difference in chemical shift,[4,5] δ, between two nonequivalent spin groups, which is measured by the slow passage method as a frequency difference between peaks of resonance signals.[2,3] (2) A second frequency, J, appears which is generally smaller than the frequency due to the chemical shift. This frequency is observed to be independent of the dc magnetic field H_0. In cases where it can be resolved[6] by the slow passage method[3,7] it is measured by the splitting of resonance lines belonging to equivalent spin groups.

If either of these frequencies is zero the modulation is absent. Many molecules exist (i.e., CH_3COOH) which have a chemical shift between nonequivalent nuclei as measured by the slow passage method. This shift, however, does not always appear on the echo envelope, but will only appear in those molecules in which these nuclei are sufficiently close neighbors. For these molecules the frequency J becomes finite, which in turn makes possible the appearance of the chemical shift on the echo envelope. For the special case involving two nonequivalent nuclei in CCl_2HCHO[8,9] these properties and the shape of the echo envelope can be predicted if the empirical Hamiltonian operator

$$\mathcal{H} = -\hbar[\gamma\sigma_{1z}(H_0+h_1)+\gamma\sigma_{2z}(H_0+h_2) + J(\sigma_{1x}\sigma_{2x}+\sigma_{1y}\sigma_{2y}+\sigma_{1z}\sigma_{2z})] \quad (1)$$

is chosen to describe the system. h_1 and h_2 are the absolute chemical shifts in gauss of the nuclei 1 and 2, respectively, and $\gamma(h_1-h_2)=\delta$. γ is the gyromagnetic ratio and $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$ are Pauli spin operators. The eigenvalues and the splitting which results in the stationary state are shown by the Zeeman level diagram in Fig. 1. The top and bottom levels are pure triplet states and each of the two closely spaced levels is a linear combination of singlet and triplet states. For $\delta\to 0$ the mixed state with the energy eigenvalue $J+(4J^2+\delta^2/4)^{\frac{1}{2}}$ now becomes a pure singlet state. The J splitting therefore disappears because transitions to and from the pure singlet state are forbidden. This supports the fact in the case of two equivalent nuclei that no J splitting is observed.[2,3,10]

The time-dependent population coefficients of each state have been evaluated under the initial conditions imposed by the application of two radiofrequency pulses. Each pulse at H_1 gauss maximum amplitude lasts for t_w seconds, where $t_w \ll \tau$ and $1/t_w$, $\gamma H_1 (=\omega_1) \gg \gamma\Delta H$, δ, J. ΔH is the magnitude of the external field inhomogeneity over the sample. For the case $\delta \gg J$ the expression for the observed echo amplitude (excluding damping due to relaxation) is given by

$$V = M_0|\sin^2(\omega_1 t_w/2)\sin(\omega_1 t_w)\cos(4J\tau)\sin^2(\delta\tau/2) - \cos(\omega_1 t_w)\cos^2(\delta\tau/2)+\tfrac{1}{2}\sin^3\omega_1 t_w\cos^2(\delta\tau/2)|, \quad (2)$$

where M_0 is the macroscopic magnetic moment. For $\omega_1 t_w = \pi/2$ the observed plot of the envelope due to protons in CCl_2HCHO is given in Fig. 2. The plot agrees with (2) within experimental error when normalized to unity in order to correct for damping due to T_2 (total relaxation time) and molecular diffusion.[1] A generalized form of the Hamiltonian operator (1) containing terms with more than two spin operators is now being used to calculate the shape of the echo envelope. The results thus obtained will be

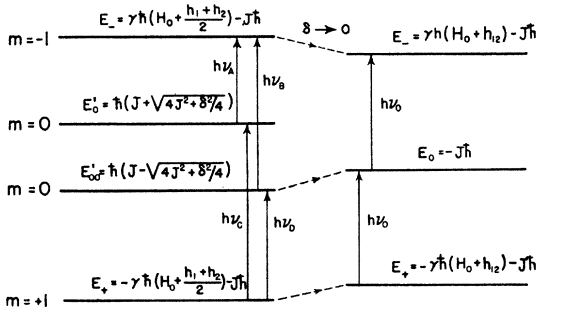

FIG. 1. Zeeman energy level diagram for a nonequivalent two spin system (for each spin, $I=\frac{1}{2}$). For $\delta\to 0$ the magnitude of $h_{12}=h_1=h_2$ chosen is arbitrary. For $\delta\sim J$ the intensities of the transitions indicated are determined by the particular transition probabilities between the given states as well as by their statistical weights. For δ finite, two pairs of resonance lines results where $h(\nu_C-\nu_B)=h(\nu_D-\nu_A)=4J\hbar$ is the separation between lines in each pair, and $h(\nu_B-\nu_A)=h(\nu_C-\nu_D)=2\hbar(4J^2+\delta^2/4)^{\frac{1}{2}}$.

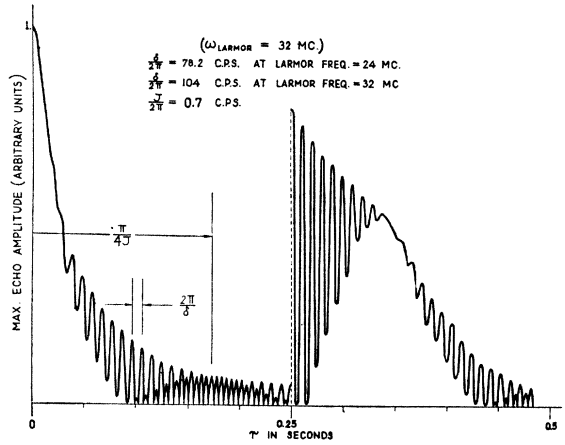

FIG. 2. Echo envelope plot for protons in dichloroacetaldehyde. The break in the plot at $\tau = 0.25$ sec indicates continuation of the plot in the region of small echo amplitude, but multiplied by a factor in order to make the plot readable.

compared with experiment. Apart from explaining the shape of the echo envelope, its consistency with observations made by the slow passage method also remains to be established.

We are not prepared, at present, to propose a detailed mechanism which can explain the observed effects.[11] It is well known that the direct nuclear dipole-dipole coupling averages out completely due to the rapid and random rotations of a molecule in a liquid.[12] We wish to point out, however, that any anisotropy effects would prevent a complete averaging out of this coupling, and, for reasons of rotational invariance, could indeed be expected to lead to a Hamiltonian of the form (1).[13]

The authors are grateful to Professor F. Bloch for his valuable advice and suggestions. The authors are grateful to Gutowsky, McCall, and Slichter[3] for sending them a copy of their letter in advance of publication to which was later added (while in press) the suggestion, arrived at independently, that the J splitting depends on the interaction $\sigma_1 \cdot \sigma_2$. One of us (E. L. H.) wishes to thank the National Research Council for Fellowship support during the course of this research.

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† National ResearchCouncil Post doctoral Fellow.
[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[2] Arnold, Dharmatti, and Packard, J. Chem. Phys. **19**, 507 (1951).
[3] H. S. Gutowsky and D. W. McCall, Phys. Rev. **82**, 748 (1951); Gutowsky, McCall, and Slichter, Phys. Rev. **84**, 589 (1951).
[4] W. G. Proctor and F. C. Yu, Phys. Rev. **77**, 717 (1950).
[5] W. C. Dickinson, Phys. Rev. **77**, 736 (1950).
[6] For long relaxation times the echo method has the advantage of being able to resolve frequencies of the order of 1 cps even though the external field inhomogeneity over the sample produces a spread in Larmor frequencies much greater than this.
[7] J. T. Arnold and M. E. Packard, Phys. Rev. **83**, 210 (1951).
[8] The rapid transfer between possible structural isomers of $CHCl_2CHO$ causes an averaging into two definite chemical shifts, one for each proton. This will result when the lifetimes in each isomeric state (obtained from known chemical potential barriers) are much shorter than the period associated with the observed frequency difference between chemical shifts (104 cps at a Larmor frequency of 32 Mc).
[9] Because of electric quadrupole broadening, the magnetic moments of the Cl^{35}, Cl^{37} nuclei are assumed to be ineffective because their quantum states have lifetimes short compared to the relaxation time of the protons and $1/J$.
[10] In references 3 it is observed that the J splitting depends upon the statistical weights of possible orientations of nonequivalent neighbors and the magnitude of their magnet moments.
[11] The operator (1) is formally obtained if one considers that two nonequivalent protons mutually exchange positions in the molecule by quantum mechanical exchange. Because of mass considerations, the exchange hypothesis is excluded since F^{19} nuclei are observed to exhibit the J splitting as well as protons.
[12] Bloembergen, Pound, and Purcell, Phys. Rev. **73**, 679 (1948).
[13] As a possible source of anisotropy we have considered that caused by the electron configuration. Gutowsky, McCall, and Slichter have also suggested that a coupling takes place via the electrons (see reference 3). This would be similar to the pseudo-quadrupole effect for a single nucleus, discussed by H. M. Foley, Phys. Rev. **72**, 504 (1947). This effect is also related, in its origin, to Ramsey's proposal [N. F. Ramsey, Phys. Rev. **78**, 699 (1950)] for explaining chemical shifts. It seems, however, difficult to reconcile the orders of magnitude of J to be thus expected with the experimental values.

$\pi^- - p$ Scattering Observed in a Diffusion Cloud Chamber*

R. P. SHUTT, E. C. FOWLER, D. H. MILLER, A. M. THORNDIKE, AND W. B. FOWLER
Brookhaven National Laboratory, Upton, New York
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SCATTERING of 60-Mev negative pions has been observed in a diffusion cloud chamber similar to one previously mentioned,[1] operated in a pion beam at the Columbia University Nevis cyclotron.† The diffusion chamber shown in Fig. 1 was operated with 21 atmos of hydrogen and methanol vapor filling, bottom temperature −65°C and top +20°C. The track-sensitive layer was about 6 cm deep, starting at the bottom. The cyclotron ion source was pulsed every 4 to 6 sec so as to produce about 20 tracks which were photographed stereoscopically. Between pulses a clearing potential of about 1000V was applied while tracks settled out and vapor was replenished.

5600 pictures taken during the first day's operation have been examined. Since the pion beam contains some electrons and μ-mesons,[2] the pion path length was estimated from the fact that 642 $\pi-\mu$ decays in flight were observed with projected $\pi-\mu$ angles $>4°$ in one view. A correction of 30 percent must be applied to obtain the total number of $\pi-\mu$ decays of all angles. From the pion lifetime of 0.029 μsec,[2] pion energy, and hydrogen density, one can calculate that there is one $\pi-\mu$ decay per 2.0 g/cm² of hydrogen traversed, so that the total path length observed is 1670 g/cm².

From the angles, densities of ionization, ranges, and lack of multiple scattering of the tracks involved, $\pi^- - p$ scattering events can be identified with fair certainty. Among beam tracks scatterings of a few degrees that could be identified as electron-electron collisions were fairly numerous, but only three cases have been observed which can be considered to be $\pi^- - p$ scatterings, of which one is doubtful. The three events are very similar in appearance to the one shown in Fig. 2. The angles, measured from the incident pion direction, are: pion 54° and recoil proton 57° in the first case (Fig. 2); pion 70° and proton 44° in the second; pion leaves illuminated region and proton 35° in the third. It is not likely that scattering events were missed in scanning because the heavily ionizing recoil proton makes them more obvious than $\pi-\mu$ decays, and independent repeated scanning indicated an efficiency for observing $\pi-\mu$ decays of about 80 percent.

These data give a cross section of 3 millibarns for the scattering of 60-Mev negative pions by hydrogen, with a large statistical uncertainty. Chedester *et al.* have given a value of 13 millibarns

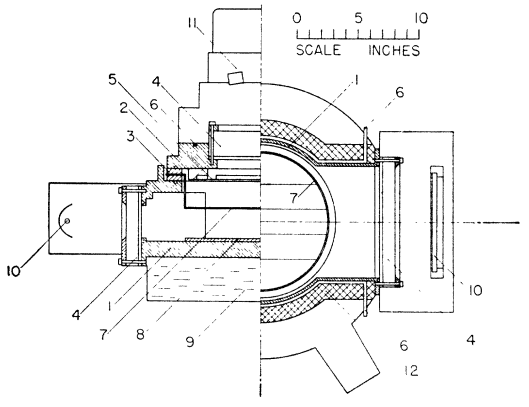

FIG. 1. Diagram of a high pressure diffusion chamber: chamber vessel (1), bottom plate and top flange cold-rolled steel, side walls ½-in. stainless steel, velvet lined; top plate (2), cold-rolled steel; Bakelite ring (3), for thermal insulation; windows (4), inside ½-in. "Allite" to withstand alcohol, outside "Plexiglas"; two concentric alcohol troughs (5), $\frac{1}{16}$-in. copper in thermal contact with (2); heater wires (6); sweeping field wires (7); black "Cararra" glass plate (8); dry ice—alcohol pan (9); light sources (10); stereoscopic camera (11); thermal insulation (12).