obtained at helium temperature, 19.2 eV.[8] It is thus concluded that Keyes' theory of the electronic contribution to the elastic constants for degenerate material accounts quantitatively for the effects here observed.

In the interpretation of this experiment, it has been assumed that the density of states in the neighborhood of the Fermi level is parabolic, so that in Eq. (3) one may insert a constant effective mass. Keyes has shown[2] that a study of the temperature dependence of δC_{44} and/or δC_{456} can provide m^* directly. Such a study for different doping levels might then permit direct determination of the energy dispersion of the conduction band to substantial energies above the band edge point. A study of the temperature dependence of the elastic constants of samples I and III is now in progress.

[8] H. Fritzsche, Phys. Rev. 115, 336 (1959).

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Multiple-Pulse Nuclear Magnetic Resonance Transients in Solids*

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The response of a spin system is calculated when a pair of 90° rf pulses is applied to a set of static identical interacting nuclei, initially polarized in an external static magnetic field. For pulse spacings the order of the spin-spin relaxation time, a "solid echo" is predicted. This effect is strongly dependent on the relative phasing of the two pulses and is maximized for a 90° phase shift. Extending the work of Powles and Strange, it is shown that the second moment of the nuclear resonance absorption line can be obtained from the solid echo in a straightforward manner, and to a predictable accuracy. A general expression is derived for the principal error term arising in the estimation of the second moment by the solid-echo technique and is applicable to a system of static interacting nuclei of any spin I. Preliminary experimental data shows the presence of solid echoes in powdered aluminum ($I=\frac{5}{2}$). An experimental estimate of the second moment gives $\Delta M_2 = 9.5\pm0.2$ G^2 at 297°K. The effect of two closely spaced rf 90° pulses has also been calculated for a system of static interacting spins composed of two magnetic species. The rf pulses are assumed to interact with one species only. Some new and interesting effects are predicted, especially in the case when the two pulses are coherent. Unlike a single-spin species where this pulse combination would give zero signal, the presence of the second magnetic ingredient gives rise to a signal the initial slope of which is proportional to the second-moment contribution of the nonresonant spins. Direct measurement of this "cross second moment" should be very valuable, particularly when scalar interactions are present as well as the dipolar interaction. The automatic removal of the resonant spin contribution to the total second moment would tend to increase the accuracy of a scalar coupling constant determination, particularly if the resonant spin term were dominant. Preliminary experiments on a single crystal of NaF show general qualitative agreement with the predictions. Also calculated is the double-pulse response of a single magnetic species with half-integral spin which has both a dipolar and quadrupolar interaction. The system treated is one of well resolved quadrupole satellites. The rf is assumed to interact with the central transition only. Kambe and Ollom have calculated the second moment of the steady-state absorption line of the central transition due to dipolar broadening in the case of well-resolved quadrupole structure. In the present work, it is shown that, as might be expected, the second moment as derived from the free induction decay, when the central line only is pulsed, is in agreement with that of Kambe and Ollom. If a second pulse is applied to the system, in phase with the first, a nonzero signal is predicted, even though this is a single-spin species. It is shown that the growth of this signal is characterized by only part of the dipolar interaction, and a second moment which can be extracted is analogous to the "cross second moment" of a two-spin-species system. When a scalar interaction is present as well as the dipolar term, the nontrivial fact is shown that for two pulses the interaction measured is no longer a simple fraction of the steady-state second moment. The scalar coupling constants and the dipolar lattice sums are shown to be combined in a different way in each case, so that a double-pulse experiment will yield new information on the spin system. This should certainly help in estimating the scalar coupling constants further than just nearest neighbors.

I. INTRODUCTION

IT has been shown previously[1] that if two short 90° rf pulses are applied within a time of order T_2 and at the Larmor frequency, to a variety of polarized protonous solids, the system gives rise to a "solid echo" following the second pulse. The echo maximum can rise almost to the full free induction decay amplitude

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[1] P. Mansfield, Ph.D. thesis, London University, 1962 (unpublished).

and is found to be dependent on the relative phasing of the two rf pulses.

The formation of this echo is contrasted to the more familiar "spin echoes" of Hahn.[2] These are usually produced in liquids and rely upon an external magnetic-field gradient for their formation.

In solids, the rigid-lattice magnetic dipolar field is usually considerably greater than the external magnetic-field inhomogeneity over the sample. Typically for metals, the absorption linewidth is a few gauss, giving $T_2\sim100$ μsec. The field inhomogeneity over a 1-cc volume for a standard magnet may be ~20 mG, so that nuclei are effectively in a uniform external static field.

It has been shown that the "solid echoes" arise through the effect of the dipolar interaction. An exact calculation has been performed in the case of isolated static proton pairs. This was shown to predict the correct behavior in the case of the hydrate protons in a single crystal of gypsum.[3]

In the study of solid materials, the even moments[4] of the steady-state absorption line shape are of considerable interest. In principle, these moments can be obtained directly from the free induction decay signal following a single 90° pulse, since the signal is the Fourier transform of the steady-state line.[5] For the second moment, a measure of the second time derivative is required at zero time, i.e., immediately following the pulse. It is well known, however, that experimentally it becomes extremely difficult to get the resolution time of pulse equipment very short, and considerable effort has been expended to this end.[6,7]

Recently, Powles and Strange[8] have demonstrated that, as expected, for very close pulse spacings the solid half-echo shape of the proton resonance is practically the same as the Bloch decay over the whole signal envelope in a number of solid polymers. They have also considered the general case of n interacting static spins $\frac{1}{2}$, and they have shown both theoretically and experimentally that the second and fourth moments can be obtained directly and rapidly from the solid echo.

In a two-pulse experiment of close pulse spacing, all the information concerning the even moments is contained in the region of the solid-echo maximum, as well as the Bloch decay following the first pulse. Since by careful choice of pulse spacing, the echo maximum can be made to fall just *outside* the equipment resolution time, information that is normally inaccessible through equipment limitations can be made available with relatively modest pulse apparatus.

The present work extends the solid-echo calculations to include n identical interacting dipoles of any spin I. In Sec. II.A, an expression is given for the principle error term arising in the evaluation of the second moment.

Also calculated is the effect of two or more rf pulses on solids containing two magnetic ingredients. It is predicted that for certain pulse sequences, which for a single-spin species would normally give zero signal, transient signals are obtained which are neither solid echoes in the forgoing sense nor Fourier transforms of the steady-state line shape. It is shown that measurements of these signals should lead to a direct estimate of the second-moment contribution of the nonresonant spins. This cannot be done either by steady-state absorption *or* "conventional" solid-echo studies; although there is a class of double irradiation and cross relaxation experiments,[9,10] which could, in principle, measure this quantity. These experiments, however, require a rather complicated theory with which to extract the result and are by no means as direct as here. We are thus able essentially to isolate the cross-coupling terms between the two magnetic species arising in the dipolar Hamiltonian and look at the effect of this alone.

A phenomenological explanation of the signal formation is obtained if we consider the nonresonant S spins as providing an effective static local field through the $C_{k\beta}I_{zk}S_{z\beta}$ interaction or cross-coupling term. This is seen to have the same rotational symmetry as a single-spin interaction with external inhomogeneity, provided the pulses interact with the resonant spins only. Immediately following an rf phase-coherent pair of 90° pulses with spacing less than T_2, the net transverse magnetization is zero. Classically, the y magnetization, say, is composed of two equal and opposite components of magnetization which evolved during the free induction decay following the first 90° pulse. These two equal and opposite components of magnetization are free to precess in the local S spin field, and thus a signal growth might be expected, not unlike the classical Hahn spin-echo formation. The time to reach the maximum signal amplitude is not expected to be equal to the pulse spacing, so in that sense this effect is not a solid echo.

In Sec. II.C, the applicability of solid-echo studies is considered in the case of a quadrupolar broadened system. Kambe and Ollom,[11] in an earlier paper, have calculated the second moment of the central absorption line due to dipolar broadening in quadrupolar broadened systems of half integral spin.

The present work considers the effect of pulse irradiating the central transition of a well-resolved quadrupolar broadened system of half integral spin. In the case of a single 90° pulse, it is shown that the second time derivative of the free induction decay envelope at zero time yields the second moment of the central absorption line, in agreement with Kambe and Ollom.

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[2] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[3] J. G. Powles and P. Mansfield, Phys. Letters **2**, 58 (1962).
[4] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
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[8] J. G. Powles and J. H. Strange, Proc. Phys. Soc. (London) **82**, 6 (1963).
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[10] F. M. Lurie and C. P. Slichter, Phys. Rev. **133**, A1108 (1964).
[11] K. Kambe and J. F. Ollom, J. Phys. Soc. Japan **11**, 50 (1956).

An expression is also given to first order in time for the transverse magnetization when the central transition only is irradiated by a pair of coherent 90° pulses. It is rather surprising that a signal should appear at all in this system, since we are dealing with a single magnetic species. The interesting consequences of this fact, particularly when scalar interactions are present, is discussed.

II. THEORETICAL TREATMENT

A. Single Magnetic Species, Any Spin I

The pulse response of a spin system is easily calculated using the density matrix formulation.[12] Let

$$\rho(0)=\frac{\exp-\hbar\mathcal{H}/kT}{\mathrm{Tr}(\exp-\hbar\mathcal{H}/kT)}$$

be the initial thermal equilibrium density matrix, where $\hbar\mathcal{H}$ is the total Hamiltonian of the system, k is the Boltzmann constant, and T is the absolute temperature. Here Tr denotes the trace or diagonal sum. We take the spin dependent part in the high-temperature approximation and put

$$\rho(0)\simeq\hbar\omega_0 I_z/kT\ \mathrm{Tr}[1]=aI_z.$$

If the spin system is perturbed by an external agency, the equation of motion of the density matrix is

$$d\rho(t)/dt=-i[\mathcal{H},\rho] \quad (1)$$

with solution

$$\rho(t)=(\exp-i\mathcal{H}t)\rho(0)(\exp i\mathcal{H}t). \quad (2)$$

$\hbar\mathcal{H}$ includes the perturbing Hamiltonian.

Where possible, the square bracket is reserved to denote the commutator of two operators.

The macroscopic observables of the quantum mechanical operators are calculated using

$$\langle A\rangle=\mathrm{Tr}\{\rho A\}, \quad (3)$$

where A is an arbitrary operator. During the application of an rf pulse $(-H_p\sin\omega t,\ -H_p\cos\omega t,\ 0)$, the total Hamiltonian for the system is

$$\hbar\mathcal{H}=(\mathcal{H}_0+\mathcal{H}_p+\mathcal{H}_1^{\mathrm{Tot}})\hbar, \quad (4)$$

where $\mathcal{H}_0$ is the Zeeman term.

$\mathcal{H}_p$ is the interaction between the applied rf pulse and spin system and is equal to

$$\gamma H_p e^{i\omega t I_z} I_y e^{-i\omega t I_z}.$$

$\mathcal{H}_1^{\mathrm{Tot}}$ is the total dipolar interaction. Transforming the density matrix according to

$$\rho^*(t)=(\exp i\mathcal{H}_0 t)\rho(t)(\exp-i\mathcal{H}_0 t)$$

and substituting into the equation of motion this gives at resonance

$$d\rho^*(t)/dt=-i[\gamma H_p I_y + (\exp i\mathcal{H}_0 t)\mathcal{H}_1^{\mathrm{Tot}}(\exp-\mathcal{H}_0 t),\ \rho^*]. \quad (5)$$

In the present work, we assume that $\mathcal{H}_p\gg\mathcal{H}_1^{\mathrm{Tot}}$, so that during the rf pulse, the dipolar interaction may be ignored. In this case, it is seen that the perturbing pulse acts as a simple rotation operator R, about I_y, so that $R^\dagger\rho(0)R\simeq aR^\dagger I_z R=a(I_z\cos\omega_p t+I_x\sin\omega_p t)$; and for the special case of a 90° pulse considered here we have $R^\dagger I_z R=I_x$, and in a similar manner one obtains $R^\dagger I_x R=-I_z$ and $R^\dagger I_y R=I_y$, where

$$R=e^{i\omega_p t I_y}$$

and $R^\dagger$ is the Hermitian adjoint. Immediately following the pulse, the spin-system Hamiltonian is

$$\hbar\mathcal{H}=\hbar(\mathcal{H}_0+\mathcal{H}_1^{\mathrm{Tot}}).$$

($\mathcal{H}_1^{\mathrm{Tot}}$ is the rigid-lattice dipolar interaction, any lattice vibrations being ignored.) Since, in the present work $\mathcal{H}_0\gg\mathcal{H}_1^{\mathrm{Tot}}$, there is no energy exchange between the Zeeman and dipole energies, we take that part of $\mathcal{H}_1^{\mathrm{Tot}}$ which commutes with $\mathcal{H}_0$, i.e., $[\mathcal{H}_0,\mathcal{H}_1]=0$. $\mathcal{H}_1$ is the truncated dipolar Hamiltonian[4] given by

$$\mathcal{H}_1=\sum_{k>j} A_{jk}\mathbf{I}_j\cdot\mathbf{I}_k+B_{jk}I_{zj}I_{zk}, \quad (6)$$

where for a pair of spins jk of internuclear distance r_{jk}, and with the vector $\mathbf{r}$ making an angle θ_{jk} with the applied static field $\mathbf{H}_0$,

$$A_{jk}=-\tfrac{1}{2}\gamma^2\hbar((1-3\cos^2\theta_{jk})/r_{jk}^3),$$
$$B_{jk}=\tfrac{3}{2}\gamma^2\hbar((1-3\cos^2\theta_{jk})/r_{jk}^3).$$

The normalized x component of the free induction decay signal following a 90° pulse is thus

$$\langle I_x\rangle=\frac{a}{\mathrm{Tr}\{I_x^2\}}\mathrm{Tr}\{(\exp-i\mathcal{H}_0 t)(\exp-i\mathcal{H}_1 t)\times I_x(\exp i\mathcal{H}_1 t)(\exp i\mathcal{H}_0 t)I_x\}$$
$$=\frac{a\cos\omega_0 t}{\mathrm{Tr}\{I_x^2\}}\mathrm{Tr}\{(\exp-i\mathcal{H}_1 t)I_x(\exp i\mathcal{H}_1 t)I_x\}. \quad (7)$$

In all the calculations presented here, $\langle I_y\rangle=0$. This formulation is extended to the case of two rf pulses, the second of which is applied at a time τ later and is represented by a second rotation operator $R_{(2)}$. We obtain for the transverse free induction signal

$$\langle I_x\rangle=\frac{a\cos\omega_0 t}{\mathrm{Tr}\{I_x^2\}}\mathrm{Tr}\{(\exp-i\mathcal{H}_1 t')R_{(2)}^\dagger(\exp-i\mathcal{H}_1\tau)I_x \times(\exp i\mathcal{H}_1\tau)R_{(2)}(\exp i\mathcal{H}_1 t')I_x\}. \quad (8)$$

[12] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961). See also for introduction to the density matrix, D. ter Haar, *Elements of Statistical Mechanics* (Holt, Rinehart and Winston, Inc., New York, 1954). The general methods of calculation used in this work are those used by I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

For two 90° pulses separated by time τ and which have an rf phase difference θ, we use the notation $90°\text{-}\tau\text{-}90°_\theta$. We now consider the special case where $\theta = 90°$.

1. $90°\text{-}\tau\text{-}90°_{90°}$ Pulse Sequence

By cyclic rearrangement within the trace, and putting $R_{(2)}^\dagger \mathcal{H}_1 R_{(2)} = \mathcal{H}_1'$ and $R_{(2)}^\dagger I_x R_{(2)} = I_x$, Eq. (8) can be expanded as a double series of commutators using the expression

$$e^{+iBt}Ae^{-iBt} = A + i[B,A]t + i^2[B,[B,A]](t^2/2!) + \cdots. \quad (9)$$

Finally, after some manipulation, the transverse magnetization Eq. (8) reduces to

$$\langle I_x\rangle = a\cos\omega_0 t\{1 - M_2(\tau - t')^2/2! + M_4(\tau-t')^4/4! + \cdots + (6/4!)M_{4\epsilon}\tau^2 t'^2 + \cdots\}, \quad (10)$$

where M_2, M_4, $\cdots$ are the Van Vleck moments of the absorption line shape in appropriate angular frequency units, and $M_{4\epsilon}$ is an error term, correct to fourth power in time, which gives the loss in signal of the echo maximum at $t' = \tau$ and is a measure of the irreversibility of the transverse decay. The precise form of the error term is

$$M_{4\epsilon} = (-M_4 + [1/\mathrm{Tr}(I_x^2)]\,\mathrm{Tr}\{[\mathcal{H}_1',[\mathcal{H}_1',I_x]] \times [\mathcal{H}_1,[\mathcal{H}_1,I_x]]\}) \quad (11)$$

and has been calculated previously,[8] for the special case of spin $\frac{1}{2}$. It is zero for a pair of spins $\frac{1}{2}$; this is implicit in the exact calculation of Powles and Mansfield.[5]

It is seen from Eq. (10) that the second time derivative of the transverse signal envelope at $\tau = t'$ yields the second moment plus a small correction factor. Higher moments can also be obtained but, strictly speaking, would require the evaluation of correction terms to higher powers of time. For the present, we limit ourselves to a discussion of the applicability of the method of solid echoes to the measurement of second moments in materials of any spin I, and thereby justify the termination of the expansions used to fourth powers in time.

Calculation of $M_{4\epsilon}$. Using the truncated dipolar interaction Hamiltonian Eq. (6) to evaluate the commutators occurring in Eq. (11), we obtain

$$[\mathcal{H}_1,[\mathcal{H}_1,I_x]] = \sum_{k>j}\{(jk)+(kj)\} + \sum_{l>k>j}\{(jkl)+(klj)+(ljk)\}, \quad (12)$$

where

$$(jk) = B_{jk}^2 I_{xj}I_{zk}^2 + A_{jk}B_{jk}(-I_{zj}I_{xk}I_{zk} + I_{yk}I_{yj}I_{xj} - I_{yj}^2 I_{xk} + I_{xj}I_{zk}^2)$$

and

$$(jkl) = 2B_{jk}B_{kl}I_{zj}I_{xk}I_{zl} + (-B_{jl}A_{jk} + B_{kl}A_{jk} - B_{jl}A_{kl} + B_{jk}A_{kl}) \times (I_{zj}I_{xk}I_{zl} - I_{yj}I_{xk}I_{yl}).$$

A similar expression is obtained using $\mathcal{H}_1'$.

These two commutators are multiplied together and summed over all suffices. The trace of this product is evaluated using the well-known trace relations which are written here for convenience.

$$\begin{aligned}
&\mathrm{Tr}\{I_{xj}^2\} = \tfrac{1}{3}I(I+1)(2I+1)^N,\\
&\mathrm{Tr}\{I_{xj}I_{yj}I_{zj}\} = \tfrac{1}{6}iI(I+1)(2I+1)^N,\\
&\mathrm{Tr}\{I_{xj}^4\} = \tfrac{1}{5}[I^2(I+1)^2 - \tfrac{1}{3}I(I+1)](2I+1)^N,\\
&\mathrm{Tr}\{I_{xj}^2 I_{yj}^2\} = \tfrac{1}{5}[\tfrac{1}{3}I^2(I+1)^2 + \tfrac{1}{6}I(I+1)](2I+1)^N,\\
&\mathrm{Tr}I_{xj}I_{xk} = \mathrm{Tr}I_{xj} = \mathrm{Tr}I_{xj}^3 = \mathrm{Tr}I_{xj}^2 I_{yj} = 0 \quad (j\neq k);
\end{aligned} \quad (13)$$

N here is the total number of spins in the system. After much algebra, we obtain the result

$$\begin{aligned}
M_{4x} &= (1/\mathrm{Tr}(I_x^2))\,\mathrm{Tr}\{[\mathcal{H}_1',[\mathcal{H}_1',I_x]][\mathcal{H}_1,[\mathcal{H}_1,I_x]]\}\\
&= \sum_{l>k>j}\{-12B_{jk}B_{kl}[A_{jk}(B_{kl}-B_{jl}) + A_{kl}(B_{jk}-B_{jl})] - 6[A_{jk}(B_{kl}-B_{jl}) + A_{kl}(B_{jk}-B_{jl})]^2 + 6B_{kj}^2B_{kl}^2\}(\tfrac{1}{3}I(I+1))^2\\
&\quad + 2\sum_{k>j}\{B_{jk}^4[\tfrac{1}{5}I(I+1)+\tfrac{1}{2}] + B_{jk}^3A_{jk}\tfrac{1}{5}[-4I(I+1)+3] + B_{jk}^2A_{jk}^2\tfrac{1}{5}[-6I(I+1)+\tfrac{9}{2}]\}(\tfrac{1}{3}I(I+1)).
\end{aligned} \quad (14)$$

If we use the fact that $\sum_{l>k>j} = \frac{1}{6}\sum_{l\neq k\neq j}$ and make the simplifying assumption that there is no exchange interaction, i.e., $A_{jk} = -B_{jk}/3$, then Eq. (14) reduces to

$$M_{4x} = \frac{1}{N}\sum_{l\neq k\neq j}[\tfrac{1}{3}B_{jk}^2(B_{kl}-B_{jl})^2 + B_{kl}^2B_{kj}^2] \times [\tfrac{1}{3}I(I+1)]^2 + \frac{1}{N}\sum_{k\neq j}B_{jk}^4[\tfrac{1}{3}I(I+1)]^2. \quad (15)$$

Subtracting from Eq. (15) the expression for the fourth moment,[4] we get finally for Eq. (11)[13]

$$\begin{aligned}
M_{4x} = [&-(3/N)(\textstyle\sum_{k\neq j}B_{jk}^2)^2\\
&+ (2/3N)\textstyle\sum_{l\neq k\neq j}[B_{jk}^2(B_{jl}-B_{kl})^2 + \tfrac{3}{2}B_{jk}^2B_{kl}^2]\\
&+ (1/N)\textstyle\sum_{k\neq j}\tfrac{1}{5}B_{jk}^4(13+3/2I(I+1))] \times [\tfrac{1}{3}I(I+1)]^2.
\end{aligned} \quad (16)$$

In the special case $I = \frac{1}{2}$, the error term reduces to

$$M_{4x} = -(1/9N)\textstyle\sum_{l\neq k\neq j}(\tfrac{3}{8}B_{jk}^2B_{jl}^2 + \tfrac{3}{4}B_{jk}^2B_{jl}B_{kl})$$

[13] This expression has been obtained independently by J. H. Strange (private communication).

in agreement with Powles and Strange. If the further assumption is made of equivalent nuclear sites, i.e., a cubic lattice, then Eq. (16) reduces to

$$M_{4\epsilon}=[-3(\sum_k B_{jk}^2)^2 + (2/3N)\sum_{l\neq k\neq j}[B_{jk}^2(B_{jl}-B_{kl})^2+\tfrac{3}{2}B_{jk}^2B_{kl}^2] + \sum_k \tfrac{1}{5}B_{jk}^4(13+3/2I(I+1))][\tfrac{1}{3}I(I+1)]^2. \quad (17)$$

Equation (17) has been evaluated explicitly for a simple cubic lattice with lattice constant d and for the static magnetic field along the [100] direction. Only the pure dipolar interaction is considered. We use the lattice sums given by Van Vleck.[4] The result is

$$M_{4\epsilon}=3M_2^2[-0.46+0.021/I(I+1)],$$

where the second moment

$$M_2=(36.8/d^6)\gamma^2\hbar[1-0.187]\tfrac{1}{3}I(I+1).$$

Comparison with the expression given by Van Vleck for the fourth moment shows that, in general, $-M_{4\epsilon}<M_4$, and if taken to be the principal error term, the second moment can be estimated from the solid echo to a predictable accuracy.

If the exchange interaction is included in Eq. (14), then the A_{jk} are replaced by $A_{jk}+\tilde{A}_{jk}$, the B_{jk} terms are unchanged. Thus, in this case, measurement of $M_{4\epsilon}$ and M_4 could, at least in principle, lead to a separation of the exchange coupling constant from the dipolar term. However, because of the rather complex form for M_4 and $M_{4\epsilon}$, it is doubtful if any tractable method of untangling the two interactions is possible. This point is discussed in more detail below, in connection with quadrupole broadened systems.

2. 90°-τ-90°$_{0°}$ Pulse Sequence

This case corresponds to the transverse magnetization being tipped down into the $-z$ direction, and is easily shown to give zero free induction signal following the second 90° pulse for any τ.

B. Two Spin Species *I*, *S*—Irradiate *I* But Not *S*

We now consider the case of two magnetic ingredients with spin I for the resonant and S for the nonresonant species. The truncated dipolar Hamiltonian for this case[4] is

$$\mathcal{H}_1=\sum_{k>j}A_{jk}\mathbf{I}_j\cdot\mathbf{I}_k+B_{jk}I_{z_j}I_{z_k}+\sum_{\beta>\alpha}a_{\alpha\beta}\mathbf{S}_\alpha\cdot\mathbf{S}_\beta + b_{\alpha\beta}S_{z_\alpha}S_{z_\beta}+\sum_{k,\beta}C_{k\beta}I_{z_k}S_{z_\beta}, \quad (18)$$

where A_{jk}, etc., is as given previously, and

$$C_{k\beta}=\tilde{A}_{k\beta}+\gamma_I\gamma_S[\hbar(1-3\cos^2\theta_{k\beta})/r_{k\beta}^3].$$

Because of the different rotational symmetry of

$$\sum_{k,\beta}C_{k\beta}I_{z_k}S_{z_\beta},$$

Eq. (10) cannot be used to calculate the transverse decay response to two 90° pulses. Instead, we must return to Eq. (8) and consider the actual expansion coefficients of $\langle I_x\rangle$, term by term.

1. 90°-τ-90°$_{90°}$ Pulse Sequence

Expanding Eq. (8) using the operator expansion Eq. (9), we get for the transverse decay following two 90° pulses correct to the fourth power in time:

$$\langle I_x\rangle=(a/\mathrm{Tr}\{I_x^2\})\,\mathrm{Tr}\{I_x^2+i^2([\mathcal{H}_1',[\mathcal{H}_1',I_x]]I_x(\tau^2/2!)-[\mathcal{H}_1',I_x][\mathcal{H}_1,I_x]t'\tau+I_x[\mathcal{H}_1,[\mathcal{H}_1,I_x]](t'^2/2!)) + i^4([\mathcal{H}_1',[\mathcal{H}_1',[\mathcal{H}_1',[\mathcal{H}_1',I_x]]]]I_x(\tau^4/4!)-[\mathcal{H}_1',[\mathcal{H}_1',[\mathcal{H}_1',I_x]]][\mathcal{H}_1,I_x](t'\tau^3/3!)-[\mathcal{H}_1',[\mathcal{H}_1',I_x]] \times[\mathcal{H}_1,[\mathcal{H}_1,I_x]](t'^2\tau^2/4)-[\mathcal{H}_1',I_x][\mathcal{H}_1,[\mathcal{H}_1,[\mathcal{H}_1,I_x]]](t'^3\tau/3!) + I_x[\mathcal{H}_1,[\mathcal{H}_1,[\mathcal{H}_1,[\mathcal{H}_1,I_x]]]](t'^4/4!))+\cdots\}. \quad (19)$$

The traces of the coefficients of $t'^n\tau^m$ for $n+m$ odd are easily shown to be zero, so we do not include them above.

Now in this case, $\mathcal{H}_1'=R_{(2)}^\dagger\mathcal{H}_1R_{(2)}$ and $R_{(2)}^\dagger I_zR_{(2)}=I_y$; also, $R_{(2)}^\dagger I_yR_{(2)}=-I_z$ and $R_{(2)}^\dagger I_xR_{(2)}=I_x$. Using these operators, together with Eq. (18), we find in contrast to the single-spin species case that $[\mathcal{H}_1',I_x]\neq-[\mathcal{H}_1,I_x]$ because of the cross term

$$\sum_{k,\beta}C_{k\beta}I_{z_k}S_{z_\beta}.$$

This makes the evaluation of the traces in Eq. (19) more tedious since more of the commutator coefficients of the fourth power in time are unequal; also the coefficients of the second power in time are no longer all equal to the total second moment. Explicit evaluation of Eq. (19) gives

$$\langle I_x\rangle=a\cos\omega_0t\{1-[(M_{2II}+M_{2IS})(t'-\tau)^2/2! + M_{2IS}t'\tau]+[(M_{4II}+M_{4IS})(t'-\tau)^4/4! + M_{4\epsilon_1}(t'\tau^3/3!)+M_{4\epsilon_2}(t'^2\tau^2/4) + M_{4\epsilon_3}(t'^3\tau/3!)]+\cdots\}. \quad (20)$$

Here

$$M_{2II}=(\tfrac{2}{3}I(I+1)/N_I)\sum_{k>j}B_{jk}^2,$$
$$M_{2IS}=(\tfrac{1}{3}S(S+1)/N_I)\sum_{k,\beta}C_{k\beta}^2,$$

and N_I is the number of resonant I spins. $M_{2II}+M_{2IS}$ is, of course, the total Van Vleck second moment for a spin system composed of two magnetic ingredients. M_{4II} is the fourth moment of the resonant spin only,

M_{4IS} is the fourth moment contribution from the nonresonant spins.

The error terms arising in Eq. (20) are defined below but not evaluated explicitly.

$$M_{4\epsilon_1}=M_{4II}+M_{4IS}-\mathrm{Tr}\{[\mathcal{H}_1',[\mathcal{H}_1',[\mathcal{H}_1',I_x]]][\mathcal{H}_1,I_x]\}, \quad (21a)$$

$$M_{4\epsilon_2}=-(M_{4II}+M_{4IS})+\mathrm{Tr}\{[\mathcal{H}_1',[\mathcal{H}_1',I_x]][\mathcal{H}_1,[\mathcal{H}_1,I_x]]\}, \quad (21b)$$

$$M_{4\epsilon_3}=M_{4II}+M_{4IS}-\mathrm{Tr}\{[\mathcal{H}_1',I_x][\mathcal{H}_1,[\mathcal{H}_1,[\mathcal{H}_1,I_x]]]\}. \quad (21c)$$

For short times τ and for $t'\sim\tau$, the dominant terms in Eq. (20) can be rearranged as

$$\langle I_x\rangle\propto[1-M_{2II}(t'-\tau)^2/2!-M_{2IS}(t'^2+\tau^2)/2!+\cdots].$$

If $M_{2II}\gg M_{2IS}$, the second term dominates and a definite echo results. The maximum amplitude of the echo will be decreased by the third term as well as higher $M_{4\epsilon}$-type terms. If, on the other hand, $M_{2II}\ll M_{2IS}$, as happens in some ionic crystals, no measurable solid echo may be observed. Solid echoes may be discernible for larger τ, however, since the fourth moment terms will become increasingly effective in increasing the signal.

Taking the second time derivative of the signal envelope Eq. (20) at $t'=\tau$,

$$\frac{d^2\langle I_x\rangle}{dt^2}\propto\left[-(M_{2II}+M_{2IS})+\frac{2M_{4\epsilon_2}}{4}\tau^2+\frac{6M_{4\epsilon_3}}{3!}\tau^2\cdots\right]. \quad (22)$$

It is seen that the procedure for evaluating second moments from the solid echo at $t=2\tau$ is still valid in the case of two spin species, for short τ. In this case, however, the error term may be slightly larger than for a single magnetic ingredient. From the foregoing discussion, one might guess that the half-echo shape when an echo arises should deviate more severely from the free induction decay shape than is the case for a single-spin system.

2. 90°-τ-90°$_{0°}$ Pulse Sequence

We use Eq. (8) but with the rotation operators defined as $R_{(2)}^\dagger I_zR_{(2)}=I_x$, $R_{(2)}^\dagger I_xR_{(2)}=-I_z$, and $R_{(2)}^\dagger I_yR_{(2)}=I_y$. The dipolar Hamiltonian is again Eq. (18). Following the procedure outlined above and evaluating the traces, we find in contrast to the single spin case, the nontrivial fact that not all of the time coefficients vanish. The expansion up to the fourth power in time is

$$\langle I_x\rangle=-a\{M_{2IS}t'\tau+M_{4IS_1}(\tau^3t'/3!)+M_{4IS_2}(\tau^2t'^2/4)+M_{4IS_3}(\tau t'^3/3!)+\text{higher terms}\}, \quad (23)$$

where

$$M_{2IS}=(1/N_I)\textstyle\sum_{k,\beta}\frac{1}{3}S(S+1)C_{k\beta}^2, \quad (24a)$$

$$\begin{aligned}M_{4IS_1}=&(1/N_I)\textstyle\sum_\beta\sum_{k>j}\{3B_{jk}^2(C_{j\beta}^2+C_{k\beta}^2)+2A_{jk}^2(C_{j\beta}-C_{k\beta})^2+3B_{jk}A_{jk}(C_{j\beta}-C_{k\beta})^2\}\frac{1}{3}I(I+1)\frac{1}{3}S(S+1)\\&-(1/N_I)\textstyle\sum_j\sum_{\beta>\alpha}\{2a_{\alpha\beta}^2(C_{j\beta}-C_{j\alpha})^2+6C_{j\alpha}^2C_{j\beta}^2\}[\frac{1}{3}S(S+1)]^2\\&-(1/N_I)\textstyle\sum_{j,\beta}C_{j\beta}^4\frac{1}{5}\{S^2(S+1)^2-\frac{1}{3}S(S+1)\}, \quad (24b)\end{aligned}$$

$$\begin{aligned}M_{4IS_2}=&(1/N_I)\textstyle\sum_\beta\sum_{k>j}\{2A_{jk}^2(C_{k\alpha}-C_{k\beta})^2-8B_{kj}^2C_{k\beta}C_{j\beta}+4B_{kj}A_{jk}(C_{j\beta}-C_{k\beta})^2\}\frac{1}{3}I(I+1)\frac{1}{3}S(S+1)\\&-(1/N_I)\textstyle\sum_k\sum_{\beta>\alpha}2a_{\alpha\beta}^2(C_{k\alpha}-C_{k\beta})^2[\frac{1}{3}S(S+1)]^2, \quad (24c)\end{aligned}$$

$$\begin{aligned}M_{4IS_3}=&-(1/N_I)\textstyle\sum_\beta\sum_{k>j}\{2A_{jk}^2(C_{k\beta}-C_{j\beta})^2-3B_{jk}^2(C_{j\beta}^2+C_{k\beta}^2)+B_{jk}A_{jk}(C_{j\beta}-C_{k\beta})^2\}\frac{1}{3}I(I+1)\frac{1}{3}S(S+1)\\&-(1/N_I)\textstyle\sum_k\sum_{\beta>\alpha}\{2a_{\alpha\beta}(C_{k\alpha}-C_{k\beta})^2+6C_{j\beta}^2C_{j\alpha}^2\}[\frac{1}{3}S(S+1)]^2\\&-(1/N_I)\textstyle\sum_{j,\beta}C_{j\beta}^4\frac{1}{5}\{S^2(S+1)^2-\frac{1}{3}S(S+1)\}. \quad (24d)\end{aligned}$$

M_{2IS} is the Van Vleck second-moment contribution of the nonresonant spins. It is emphasized that M_{4IS_1}, M_{4IS_2}, and M_{4IS_3} are not fourth-moment contributions of the nonresonant spins but related quantities which include an error term.

The signal following the second 90° pulse given by Eq. (23) has the general character of a derivative free induction decay, but characterized by the cross-coupling interaction of the two spin species only. This is only approximately true since $M_{4IS_3}\neq M_{4IS}$ and there are additional terms in t' and t'^2. Taking the first time derivative of Eq. (23) evaluated at $t'=0$, we obtain

$$(d/dt')\langle I_x\rangle_{t'=0}=-a[M_{2IS}\tau+M_{4IS_1}(\tau^3/3!)+\cdots]. \quad (25)$$

Using Eq. (24b), M_{4IS_1} can be simplified in terms of the fourth-moment contribution of the nonresonant spins, i.e.,

$$M_{4IS_1}=-M_{4IS}+\sum_\beta\sum_{k>j}\{3B_{jk}^2(C_{j\beta}^2+C_{k\beta}^2)+B_{jk}A_{jk}(C_{j\beta}-C_{k\beta})^2\}\tfrac{1}{3}I(I+1)\tfrac{1}{3}S(S+1). \quad (26)$$

Measurement of the initial slope of the signal for fairly short τ should yield a direct estimate of the cross second moment. We briefly mention a slightly different approach which yields the same result as Eq. (25). The quantity of interest, namely $d\langle I_x\rangle/dt'$ evaluated at $t'=0$, can be calculated in a rather more direct manner, showing the τ dependence in a clearer way. From the equation of motion of the density matrix Eq. (1), we have in the rotating frame

$$(d\rho^*/dt')_{t'=0}=-i[\mathcal{H}_1,\rho^*(\tau)] \tag{27}$$

but

$$\rho^*(\tau)=(\exp-i\mathcal{H}_1'\tau)-aI_z(\exp i\mathcal{H}_1'\tau)\,.$$

Expanding this, using Eq. (9) and substituting into Eq. (27), we find

$$(d/dt')\langle I_x\rangle_{t'=0}=\frac{ai}{\mathrm{Tr}(I_x^2)}\,\mathrm{Tr}\left\{\left[\mathcal{H}_1,\left(I_z-[\mathcal{H}_1',I_z]i\tau+[\mathcal{H}_1'[\mathcal{H}_1',I_z]]\frac{i^2\tau^2}{2!}+\cdots\right)\right]I_x\right\}\,. \tag{28}$$

The first term and the coefficients of the even powers of τ vanish on taking the trace, thus yielding Eq. (25). We see, however, that the function $(d/dt')\langle I_x\rangle|_{t'=0}$ is itself an odd function of τ. This has the form of a free induction decay derivative. Integration of this function gives an even function of τ which is similar to a transverse decay signal but characterized by the cross-coupling interaction, i.e.,

$$\int_\tau^\infty \frac{d}{dt'}\langle I_x\rangle_{t'=0}d\tau=G(\tau) \tag{29}$$

and

$$(d^2/d\tau^2)G(\tau)|_{\tau=0}=-aM_{2IS}\,. \tag{30}$$

The fourth derivative of $G(\tau)$ yields M_{4IS_1}, which from Eq. (26) is generally less than the true fourth moment contribution of the nonresonant spins.

Cross second moments which are derived from Eq. (29) and Eq. (30) should be more accurate since their calculation involves using all the experimental points on the $(d/dt')\langle I_x\rangle_{t'=0}$ versus τ plot. This method amounts to an averaging technique and is rather less sensitive to the values of signal slopes for short τ.

A possible experimental difficulty may arise with the foregoing double pulse technique. The finite resolution time of a pulse apparatus may make the estimation of the initial slope of the signal after the second pulse difficult, although it should be easier and more accurate than the estimate of the second time derivative in the case of a single-pulse free induction decay. The reason is that in the latter case, one does not know the maximum signal amplitude, and often guesses have to be made about the actual shape of the decay signal within the receiver dead time. In the present case, however, we know that immediately following the pulse the signal is zero. Provided the signal shows a maximum outside the second-pulse dead time, a reasonable value of slope should be obtainable. The modulus of the expected signals is sketched in Fig. 1. We now propose a further experiment which may overcome to some extent the objection raised above.

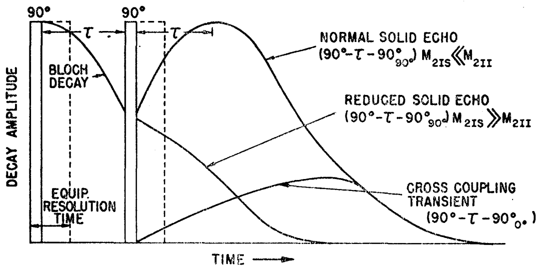

FIG. 1. Sketch of the modulus of the expected signals in a two spin system in response to two rf 90° pulses spaced a time τ apart. When the second pulse phase is shifted by 90° with respect to the first one, we expect the normal solid echo provided the dipolar coupling between the two spin species is small compared with the total dipolar interaction. This case approaches a single species spin system. If the cross coupling term dominates, then the same pulse sequence may not give rise to a well-defined echo for short pulse separations. If the two pulses are phase coherent, we expect a different effect, antiphase to the normal echo, and characterized mainly by the dipolar coupling between the two spin species.

3. 90°-τ_1-90°$_{0°}$-τ_2-180°$_{0°}$ Pulse Sequence

The expression for the transverse signal Eq. (8) is extended to include a third 180° rf pulse in phase with the first two 90° pulses as follows:

$$\begin{aligned}\langle I_x\rangle=a\cos\omega_0t\,\mathrm{Tr}\{&(\exp-i\mathcal{H}_1t')R_{(3)}{}^\dagger(\exp-i\mathcal{H}_1\tau_2)R_{(2)}{}^\dagger\\&\times(\exp-i\mathcal{H}_1\tau_1)I_x(\exp i\mathcal{H}_1\tau_1)R_{(2)}\\&\times(\exp i\mathcal{H}_1\tau_2)R_{(3)}(\exp i\mathcal{H}_1t')I_x\}\,.\end{aligned} \tag{31}$$

Using the same notation as in the previous section, we put

$$R_{(3)}\mathcal{H}_1R_{(3)}{}^\dagger=\mathcal{H}_1''=\sum_{k>j}A_{jk}\mathbf{I}_j\cdot\mathbf{I}_k+B_{jk}I_{z_j}I_{z_k}+\sum_{\beta>\alpha}a_{\alpha\beta}\mathbf{S}_\alpha\cdot\mathbf{S}_\beta+b_{\alpha\beta}S_{z_\alpha}S_{z_\beta}-\sum_{k,\beta}C_{k\beta}I_{z_k}S_{z_\beta}\,, \tag{32}$$

since

$$R_{(3)}I_xR_{(3)}{}^\dagger=-I_x\quad\text{and}\quad R_{(3)}I_zR_{(3)}{}^\dagger=-I_z\,.$$

Rearranging Eq. (31) and substituting the above operators, we obtain

$$\begin{aligned}\langle I_x\rangle=(a\cos\omega_0t/\mathrm{Tr}\{I_x^2\})\,\mathrm{Tr}\{&(\exp-i\mathcal{H}_1'\tau_1)\\&\times(-I_z)(\exp i\mathcal{H}_1'\tau_1)(\exp i\mathcal{H}_1\tau_2)(\exp i\mathcal{H}_1''t')\\&\times(-I_x)(\exp-i\mathcal{H}_1''t')(\exp-i\mathcal{H}_1\tau_2)\}\,.\end{aligned} \tag{33}$$

The cross-coupling term $\sum_{k,\beta}C_{k\beta}I_{z_k}S_{z_\beta}$ does not commute, in general, with the rest of the dipolar interaction. The total dipolar Hamiltonian is divided into two parts as follows:

$$\mathcal{H}_1=P+Q\quad\text{and}\quad\mathcal{H}_1''=P-Q\,,$$

where

$$P=\sum_{k>j} A_{jk}\mathbf{I}_j\cdot\mathbf{I}_k+B_{jk}I_{zj}I_{zk}+\sum_{\beta>\alpha} a_{\alpha\beta}\mathbf{S}_\alpha\cdot\mathbf{S}_\beta+b_{\alpha\beta}S_{z\alpha}S_{z\beta}$$

and

$$Q=\sum_{k,\beta} C_{k\beta}I_{zk}S_{z\beta}.$$

In order to break down the exponential operator products $(\exp i\mathcal{H}_1\tau_2)(\exp i\mathcal{H}_1't')$, etc., arising in Eq. (33), we use the well-known separation formula for exponential operators,[14]

$$e^{(P+Q)\tau}=e^{P\tau}\exp\int_0^\tau e^{-Pt}Qe^{Pt}dt. \tag{34}$$

The product

$$(\exp i\mathcal{H}_1\tau_2)(\exp i\mathcal{H}_1''t')$$
$$=e^{P\tau_2}\left(\exp\int_0^{\tau_2} e^{-Pt}Qe^{Pt}dt\right)$$
$$\times e^{-Qt'}\left(\exp\int_0^{t'} e^{+Qt}Pe^{-Qt}dt\right). \tag{35}$$

For short times τ_2 and t', a first-order approximation gives

$$\exp i\mathcal{H}_1\tau_2 \exp i\mathcal{H}_1''t'\simeq e^{P\tau_2}e^{-Q(\tau_2-t')}e^{Pt'}. \tag{36}$$

Using Eq. (36) in Eq. (33), it is easily seen that for $t'=\tau_2$, $\langle I_x\rangle=0$. The gradient of the signal at $t'=\tau_2$ is from Eq. (33) and Eq. (36):

$$(d/dt')\langle I_x\rangle_{t'=\tau_2}\simeq(a\cos\omega_0 t/\mathrm{Tr}(I_x^2))\,\mathrm{Tr}\{(\exp-i\mathcal{H}_1'\tau_1)$$
$$\times I_z(\exp i\mathcal{H}_1'\tau_1)\exp iP2\tau_2[\mathcal{H}_1'',I_x]$$
$$\times\exp-iP2\tau_2\}, \tag{37}$$

which is, in general, nonzero. For small τ_2, the dominant term in Eq. (37) reduces to Eq. (28), except for a change in sign of the cross term. The modulus of the expected signals is sketched in Fig. 2.

4. *90°-τ-180°$_{0°\text{ or }90°}$ Pulse Sequences*

Unlike the single-spin case discussed elsewhere,[1] with two magnetic ingredients, one would expect a small signal growth superimposed on a transverse decay for both zero and 90° phase shifts. This arises because of the difference in rotational symmetry of the $\sum_{j,\beta}C_{j\beta}I_{zj}S_{z\beta}$ to the remainder of the dipolar Hamiltonian. This case is quite straightforward to evaluate by using the foregoing techniques and is not discussed further.

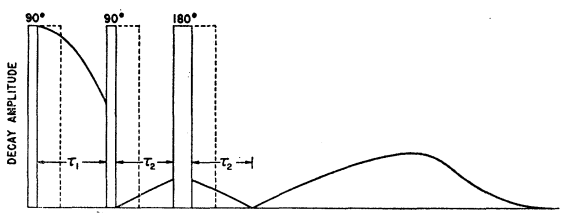

FIG. 2. Sketch of the modulus of the expected signals in a two spin system in response to three coherent rf pulses. The first two are 90° pulses and the third is a 180° pulse. The zero following the third pulse is expected to fall at about $\tau_1+2\tau_2$ from the time origin.

[14] R. Feynman, Phys. Rev. 84, 108 (1951).

C. Echoes in Quadrupolar Broadened Systems

We now consider the case of a single magnetic species with half-integral spin I and quadrupole moment Q. For simplicity, we take the case where all nuclei are equivalent and in a fixed electric field gradient q. The case of a distribution of q's is a simple generalization of the calculation in this section and is not presented here. In what follows, we consider the quadrupole satellites to be well resolved from the central line, i.e., $\nu_Q>\nu_{\mathrm{dip}}$, so that irradiation of the central line does not interfere with the satellites.

The technique used to calculate the effect of various pulse sequences is essentially the same as Sec. 2.A, with the added complexity, however, that now we have to discard certain matrix elements arising in the spin operators. In view of the added complexity, the expansions are evaluated to the second power in time only. Since we will be interested only in the expansions around zero time, the results will predict the gross effects, higher order time terms entering as small corrections.

The present work differs from the well-known quadrupole multiple echoes in solids of Solomon[15] in the following way. We have specifically included the dipolar interaction, which is responsible for the echo formation. Solomon ignores the dipolar interaction entirely, the echoes being formed through a distribution of quadrupolar splittings throughout the sample. Essential in his case also is a very short 90° pulse such that $\gamma H_p/2\pi\gg\nu_Q$, which ensures that initially the whole of the resonance spectrum is turned over—a condition that often cannot be met in many solids where the quadrupole splittings may be many megacycles. The expressions developed here are the result of first-order quadrupole splitting. Second-order effects, which produce shifts in the central transition, are entirely neglected. This is valid if $\nu_Q^2/\nu_0\ll\nu_{\mathrm{dip}}$, where ν_0 is the Larmor frequency. Except for extreme broadening, this approximation has a wide applicability. For single crystals with one crystalline field axis, we can always orient the crystal in the static magnetic field such that the second-order effects vanish.

1. *Free Induction Decay*

The total Hamiltonian for the spin system in the presence of the rf pulse and with a quadrupole inter-

[15] I. Solomon, Phys. Rev. 110, 61 (1958).

action is

$$\hbar\mathcal{H}=\hbar(\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_p+\mathcal{H}_Q), \quad (38)$$

where $\mathcal{H}_Q$ is the quadrupolar contribution, the other parts have their previous meaning. We take the electric-field gradient to have cylindrical symmetry. If θ is the angle between the principal axis of the electric field gradient tensor eq and the static magnetic field vector $\mathbf{H}_0$, we write $\mathcal{H}_Q$ to first order as

$$\mathcal{H}_Q=[e^2qQ/8I(2I-1)\hbar](3\cos^2\theta-1)\times[3I_z^2-I(I+1)]$$
$$=\omega_Q[3I_z^2-I(I+1)]. \quad (39)$$

We transform the density matrix to a rotating frame at the applied frequency according to $\rho^*(t)=e^{-i\omega_R I_z t}\times\rho(t)e^{i\omega_R I_z t}$ such that $\mathcal{H}_0+\mathcal{H}_Q=\omega_R I_z$. $\mathcal{H}_1$ is neglected during the rf pulse, i.e., assume that $\mathcal{H}_p\gg\mathcal{H}_1$. The equation of motion of the transformed density matrix then becomes, using Eqs. (1) and (38),

$$d\rho^*/dt=-i[\mathcal{H}_0+\mathcal{H}_Q+\mathcal{H}_p^*+\omega_R I_z,\rho^*], \quad (40)$$

where

$$\mathcal{H}_p^*=\omega_1 I_y \quad\text{and}\quad \omega_1=\gamma H_p.$$

The solution of Eq. (40) is

$$\rho^*(t)=[\exp-i(\mathcal{H}_0+\mathcal{H}_Q+\mathcal{H}_p^*+\omega_R I_z)t]\times\rho^*[\exp i(\mathcal{H}_0+\mathcal{H}_Q+\mathcal{H}_p^*+\omega_R I_z)t]. \quad (41)$$

Using the explicit forms for the Hamiltonian, we obtain from Eq. (41) in general form

$$\rho^*(t)=\sum_{\substack{m,n\\m',n'}}\exp i\{(m'-m)[\Delta\omega+3\omega_Q(m+m')]+(n'-n)[\Delta\omega+3\omega_Q(n+n')]\}t$$
$$\times\left\langle m,n\right|\left(\exp-i\int_0^t\mathcal{H}_p'(t')dt'\right)\rho^*\times\left(\exp i\int_0^t\mathcal{H}_p'(t')dt'\right)\left|m',n'\right\rangle, \quad (42)$$

for a pair of spins with individual magnetic quantum numbers m, n. Here

$$\mathcal{H}_p'(t')=(\exp i\{\Delta\omega I_z+\omega_Q[3I_z^2-I(I+1)]\}t')\omega_1 I_y\times(\exp-i\{\Delta\omega I_z+\omega_Q[3I_z^2-I(I+1)]\}t'), \quad (43)$$

and $\Delta\omega=\omega_R-\omega_0$, ω_0 is the Zeeman resonance angular frequency of the central transition. We see from Eq. (42) that the effect of an rf pulse at the central line frequency on the equilibrium density matrix is to leave the diagonal matrix elements of $\rho(0)$ for $|m|$, $|n|>\frac{1}{2}$ undisturbed, provided, of course, $\omega_Q\gg\omega_1$. Only the $\pm\frac{1}{2}$ m states are changed. The ρ^* is left with a diagonal z component of elements $\langle m,n|I_z|m,n\rangle$ for $|m|$ or $|n|>\frac{1}{2}$ only, plus a z' component for $m,n=\pm\frac{1}{2}$. Also, of course, an x' component with matrix elements $\langle m,\pm\frac{1}{2}|I_x'|m,\mp\frac{1}{2}\rangle$ and $\langle\pm\frac{1}{2},m|I_x'|\mp\frac{1}{2},m\rangle$ only. The latter can be seen from a consideration of the Zeeman energies in the presence of a quadrupole splitting. As expected, the applied rf pulse serves to connect only energy states whose total magnetic quantum numbers differ by one, i.e., $\Delta M=\Delta m+\Delta n=\pm1$ with Δm, $\Delta n=\pm1$, 0. Since the static I_z component commutes with the dipolar Hamiltonian and also does not contribute to the transverse x signal, we do not need to consider this further.

The I_z' and I_x' referred to above are *not*, of course, the matrix components of the total spin I, since we are irradiating the central transition only. The following is a simple example: If we consider spin I and calculate the effect on the initial equilibrium density matrix of pulse irradiating the $\pm\frac{1}{2}$ levels for a *single* spin using Eq. (42), by simple matrix multiplication it is easily shown that

$$R^\dagger\rho(0)R=\sum_{|m|>\frac{1}{2}}\langle m|I_z|m\rangle+I_z'\cos\alpha\omega_1 t+I_x'\sin\alpha\omega_1 t, \quad (44)$$

where R is the pulse rotation operator, $I_z'=\frac{1}{2}\hbar\sigma_z$, $I_x'=\frac{1}{2}\hbar\sigma_x$ and σ_x, σ_z are the components of the Pauli spin matrix; also $\omega_1=\gamma H_1$ and $\alpha=(I(I+1)+\frac{1}{4})^{1/2}=\frac{1}{2}(2I+1)$. So, in this case, we see that for a given applied H_1 the nutation of the 2×2 submatrix is actually α times as fast as that of a real spin $\frac{1}{2}$. In the following calculation, we assume 90° nutations, so that $\alpha\gamma H_1 t=\frac{1}{2}\pi$, making the z' component vanish. The x component of the free induction decay following a 90° pulse is given by Eq. (7) with the modifications mentioned above, i.e.,

$$\langle I_x\rangle=(a\cos\omega_0 t/\mathrm{Tr}\{I_x'I_x\})\,\mathrm{Tr}\{(\exp-i\mathcal{H}_1 t)I_x'\times(\exp i\mathcal{H}_1 t)I_x\}. \quad (45)$$

Because of the quadrupole splitting, some of the original degeneracy of the Zeeman levels is lifted, so that now the dipolar interaction has to be further truncated, since spin-spin interactions connect only degenerate states of the same total M.[16] Expansion of Eq. (45) to the second power in time gives

$$\langle I_x\rangle=a\cos\omega_0 t\left[1-\frac{\mathrm{Tr}\{-[\mathcal{H}_1,I_x'][\mathcal{H}_1,I_x]\}}{\mathrm{Tr}\{I_x'I_x\}}\frac{t^2}{2!}+\cdots\right]. \quad (46)$$

We now wish to evaluate the coefficient of t^2 in Eq. (46) above which we denote as M_2, but subject to the restrictions imposed by the presence of the quadrupole interaction. Kambe and Ollom in an earlier paper,[11] have calculated the second moment of the central absorption line due to dipolar broadening in a quadrupolar broadened system of half-integral spins. Following

[16] C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row Publishers, Inc., New York, 1963).

their notation, we write the dipolar interaction as

$$\mathcal{H}_1=\sum_{k>j}\mathcal{H}_{jk}=\sum_{k>j}(\tilde{A}_{jk}+A_{jk}')I_{zj}I_{zk}+\tfrac{1}{2}(\tilde{A}_{jk}-\tfrac{1}{2}A_{jk}')(I_{+j}I_{-k}+I_{-j}I_{+k}),\quad(47)$$

where $\tilde{A}_{jk}$ is the scalar coupling coefficient, as defined previously, and $A_{jk}'=\gamma^2\hbar[(1-3\cos^2\theta_{jk})/r_{jk}^3]=-2A_{jk}$ in the previous notation and $I_\pm$ are the usual displacement operators.

Since the dipolar Hamiltonian is the sum of two-body interactions, it is sufficient to consider just two spins j, k in evaluating the second moment.

Of the matrix elements of Eq. (47), the above considerations show that the terms to be retained are

$$\langle m,n|\mathcal{H}_{jk}|m,n\rangle=(\tilde{A}_{jk}+A_{jk}')mn,\quad(48\text{a})$$

$$\langle m,m-1|\mathcal{H}_{jk}|m-1,m\rangle=\langle m-1,m|\mathcal{H}_{jk}|m,m-1\rangle=(\tfrac{1}{2}\tilde{A}_{jk}-\tfrac{1}{4}A_{jk}')(I+m)\times(I-m+1).\quad(48\text{b})$$

The matrix elements of the x components of spin are

$$\langle m,\pm\tfrac{1}{2}|I_x|m,\mp\tfrac{1}{2}\rangle=\langle\pm\tfrac{1}{2},m|I_x|\mp\tfrac{1}{2},m\rangle=\tfrac{1}{4}(2I+1)\quad(49\text{a})$$

and

$$\langle m,\pm\tfrac{1}{2}|I_x'|m,\mp\tfrac{1}{2}\rangle=\langle\pm\tfrac{1}{2},m|I_x'|\mp\tfrac{1}{2},m\rangle=\tfrac{1}{4}(2I'+1)=\tfrac{1}{2}.\quad(49\text{b})$$

I' means reduced or fictitious spin $\frac{1}{2}$. The calculation of the traces is straightforward but more tedious than for the case with no quadrupole splitting and is the principal reason for terminating the series in t^2. The resulting coefficient of t^2 in Eq. (46) becomes

$$M_2=\left[\frac{I(I+1)}{3}+\frac{2I^2(I+1)^2-3I(I+1)+\frac{1}{8}}{2(2I+1)}\right]\frac{2}{N}\sum_{k>j}\tilde{A}_{jk}^2+\left[-\tfrac{4}{3}I(I+1)+\frac{4I^2(I+1)^2+7/4}{2(2I+1)}\right]\frac{2}{N}\sum_{k>j}\tilde{A}_{jk}\frac{A_{jk}'}{2}+\left[\tfrac{4}{3}I(I+1)+\frac{2I^2(I+1)^2+3I(I+1)+13/8}{2(2I+1)}\right]\frac{2}{N}\times\sum_{k>j}\frac{A_{jk}'^2}{4}.\quad(50)$$

As expected, this result agrees with Kambe and Ollom's second moment for the central absorption line and shows that the latter can be obtained from the second derivative at zero time of the free induction decay envelope. We now apply the above ideas to the calculation of the effect of a second effective 90° pulse which is coherent with the first one and again irradiates the central transition only in a time short compared with the free induction decay. This pulse inverts the populations of the $\pm\frac{1}{2}$ energy levels.

2. 90°-τ-90°$_{0°}$ Pulse Sequence, Irradiating the Central Transition Only

We follow the procedure used in Sec. II.B, Eq. (19), but with the modifications expressed in Eq. (45). Thus, for an effective 90°-τ-90°$_{0°}$ pulse sequence, we obtain for the transverse component of magnetization following the second pulse applied at time τ after the first

$$\langle I_x\rangle=\frac{a\cos\omega_0 t}{\mathrm{Tr}\{I_xI_x'\}}\mathrm{Tr}\{(\exp-i\tilde{\mathcal{H}}_1'\tau)I_z^*(\exp i\tilde{\mathcal{H}}_1'\tau)\times(\exp i\mathcal{H}_1't')I_x(\exp-i\mathcal{H}_1't')\}.\quad(51)$$

The prime denotes here that we are dealing with the modified dipolar interaction, the matrix elements of which are given in Eq. (48). Although formally the same as Eq. (8), there are some subtle differences. We see from Eq. (44), that I_z^* is now essentially the total I_z component, but with the populations of the *central transition only* reversed. Expanding Eq. (51) and considering terms up to the second power in time, we get

$$\langle I_x\rangle=(a\cos\omega_0t/\mathrm{Tr}\{I_x'I_x\})\,\mathrm{Tr}\{I_z^*I_x-i[\tilde{\mathcal{H}}_1',I_z^*]I_x\tau+iI_z^*[\mathcal{H}_1',I_x]t'+i^2[\tilde{\mathcal{H}}_1',[\tilde{\mathcal{H}}_1',I_z^*]]I_x(\tau^2/2!)-i^2[\tilde{\mathcal{H}}_1',I_z^*][\mathcal{H}_1',I_x]t'\tau+i^2I_z^*[\mathcal{H}_1',[\mathcal{H}_1',I_x]]\times(t'^2/2!)+\cdots\}.\quad(52)$$

The trace of the first term is obviously zero. To evaluate higher terms, we must consider carefully the matrix $\tilde{\mathcal{H}}_1'$. Now,

$$\tilde{\mathcal{H}}_1'=R_{(2)}^\dagger\mathcal{H}_1'R_{(2)}.\quad(53)$$

By considering the effect of a 90° pulse on the central transition of the z component of a single spin, the matrix elements of the diagonal terms of $\mathcal{H}_1'$, Eq. (47) which we denote as $\mathcal{H}_{jk\mathrm{D}}'$, become

$$\langle m,n|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|m,n\rangle=(\tilde{A}_{jk}+A_{jk}')mn\quad\text{for}\quad|m|,|n|>\tfrac{1}{2},\quad(54\text{a})$$

$$\langle m,\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle=\langle\pm\tfrac{1}{2},m|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|\mp\tfrac{1}{2},m\rangle=(\tilde{A}_{jk}+A_{jk}')m\tfrac{1}{4}(2I'+1)\quad\text{for}\quad|m|>\tfrac{1}{2},\quad(54\text{b})$$

$$\langle+\tfrac{1}{2},\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|-\tfrac{1}{2},\mp\tfrac{1}{2}\rangle=\langle-\tfrac{1}{2},\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|+\tfrac{1}{2},\mp\tfrac{1}{2}\rangle=(\tilde{A}_{jk}+A_{jk}')\tfrac{1}{4}(I'(I'+1)+\tfrac{1}{4}).\quad(54\text{c})$$

The further subscript D used here and OD referred to below denote the diagonal and off-diagonal parts of $\mathcal{H}_1$ in Eq. (47), i.e.,

$$\tilde{\mathcal{H}}_1'=\sum_{k>j}\tilde{\mathcal{H}}_{jk}'=\sum_{k>j}\tilde{\mathcal{H}}_{jk\mathrm{D}}'+\tilde{\mathcal{H}}_{jk\mathrm{OD}}'.$$

For the effect of the pulse on the off-diagonal terms, we again note that the rf connects only the $\pm\frac{1}{2}$ m states of a single spin, so that the matrix elements for $|m|>\frac{1}{2}$ remain unchanged.

The matrix elements for $m=\pm\frac{1}{2}$ *do* interact with the rf field operator, and this case requires a treatment similar to Eq. (42) for the effect of an rf pulse on I_x when irradiating the central transition. For the effect of a pulse on the x component of a single spin I, we obtain

$$R^\dagger I_x R=\sum_{|m|>\frac{1}{2}}\langle m|I_x|m-1\rangle+\langle m-1|I_x|m\rangle +\tfrac{1}{2}\alpha\hbar\sigma_x\cos\alpha\omega_1 t+\tfrac{1}{2}\alpha\hbar\sigma_z\sin\alpha\omega_1 t. \quad (55)$$

We must now consider the effect of the 90° pulse on the off-diagonal term in the dipolar interaction in Eq. (47), which is

$$\begin{aligned}\tilde{\mathcal{H}}_{jk\mathrm{OD}}'&=\tfrac{1}{4}(2\tilde{A}_{jk}-A_{jk}')R^\dagger[I_{+j}I_{-k}+I_{-j}I_{+k}]R\\&=\tfrac{1}{2}(2\tilde{A}_{jk}-A_{jk}')R^\dagger[I_{xj}I_{xk}+I_{yj}I_{yk}]R. \quad (56)\end{aligned}$$

The $I_{y_j}I_{y_k}$ term commutes with the rotation operator about I_y so it remains unchanged. Using Eq. (55) with $\alpha\omega_1 t=\frac{1}{2}\pi$, we obtain for the matrix elements of Eq. (56).

$$\begin{aligned}&\langle m,m-1|\tilde{\mathcal{H}}_{jk\mathrm{OD}}'|m-1,m\rangle\\&=\langle m-1,m|\tilde{\mathcal{H}}_{jk\mathrm{OD}}'|m,m-1\rangle\\&=[\tfrac{1}{2}\tilde{A}_{jk}-\tfrac{1}{4}A_{jk}'](I+m)(I-m+1)\\&\qquad\text{for}\quad |m|>\tfrac{1}{2}, \quad (57a)\end{aligned}$$

$$\langle m,m'|\tilde{\mathcal{H}}_{jk\mathrm{OD}}'|m,m'\rangle=\tfrac{1}{2}(2\tilde{A}_{jk}-A_{jk}')\alpha^2 mm' \quad \text{for}\quad m,m'=\pm\tfrac{1}{2}, \quad (57b)$$

$$\begin{aligned}&\langle +\tfrac{1}{2},\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{OD}}'|-\tfrac{1}{2},\mp\tfrac{1}{2}\rangle\\&=-\langle -\tfrac{1}{2},\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{OD}}'|+\tfrac{1}{2},\mp\tfrac{1}{2}\rangle\\&=\left(\frac{2\tilde{A}_{jk}-A_{jk}'}{2}\right)\left(\frac{2I+1}{4}\right)^2. \quad (57c)\end{aligned}$$

We now have all the relevant matrix elements of $\mathcal{H}_1'$, $\tilde{\mathcal{H}}_1'$, I_x, and I_z^*, and the traces in Eq. (52) can now be evaluated. In striking analogy with the case of a spin system composed of two magnetic species discussed in Sec. II.B, we find the surprising fact that the coefficient of $t'\tau$ is nonzero. All other terms in the expansion up to $t'^n\tau^m$ for $n+m=2$ vanish on taking the trace. A short proof of this is given in the Appendix.

We now evaluate the coefficient of $t'\tau$, in Eq. (52), i.e.,

$$\mathrm{Tr}\{[\tilde{\mathcal{H}}_1',I_z^*][\mathcal{H}_1',I_x]\}.$$

Since we require the diagonal sum, we see from Eqs. (A6) and (A7) contained in the Appendix that we require all matrix elements like

$$\begin{aligned}&\langle m,\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle\langle m,\mp\tfrac{1}{2}|I_z^*|m,\mp\tfrac{1}{2}\rangle\\&\times\langle m,\mp\tfrac{1}{2}|\mathcal{H}_{jk}|m,\mp\tfrac{1}{2}\rangle\langle m,\mp\tfrac{1}{2}|I_x|m,\pm\tfrac{1}{2}\rangle\\&\qquad\text{for}\quad |m|>\tfrac{1}{2}.\end{aligned}$$

There are no matrix elements of $[\mathcal{H}_1',I_x]$ which couple with those of Eq. (A7) to give diagonal terms, so we may disregard them from further consideration. Now from Eq. (48a) and Eq. (49a), we get

$$\begin{aligned}&\langle m,\mp\tfrac{1}{2}|\mathcal{H}_{jk}|m,\mp\tfrac{1}{2}\rangle\langle m,\mp\tfrac{1}{2}|I_x|m,\pm\tfrac{1}{2}\rangle\\&-\langle m,\mp\tfrac{1}{2}|I_x|m,\pm\tfrac{1}{2}\rangle\langle m,\pm\tfrac{1}{2}|\mathcal{H}_{jk}|m,\pm\tfrac{1}{2}\rangle\\&=2(\tilde{A}_{jk}+A_{jk}')\tfrac{1}{4}(2I+1)m(\mp\tfrac{1}{2}), \quad (58)\end{aligned}$$

and from Eq. (A6) we obtain

$$\begin{aligned}&\langle m,\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle\langle m,\mp\tfrac{1}{2}|I_z^*|m,\mp\tfrac{1}{2}\rangle\\&-\langle m,\pm\tfrac{1}{2}|I_z^*|m,\pm\tfrac{1}{2}\rangle\langle m,\pm\tfrac{1}{2}|\tilde{\mathcal{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle\\&=2(\tilde{A}_{jk}+A_{jk}')\tfrac{1}{4}(2I'+1)m(\pm\tfrac{1}{2}). \quad (59)\end{aligned}$$

Multiplying the two commutators and summing over the m states and all particles, the total trace is

$$\mathrm{Tr}\{[\tilde{\mathcal{H}}_1',I_z^*][\mathcal{H}_1',I_x]\}=-\sum_{\substack{m>\frac{1}{2}\\n}}\sum_{k>j}4(\tilde{A}_{jk}+A_{jk}')^2 \times\tfrac{1}{4}(2I+1)\tfrac{1}{4}(2I'+1)(\tfrac{1}{2})^2m^2n_m. \quad (60)$$

n_m is simply the number of matrix elements like $\langle m,\pm\frac{1}{2}||m,\mp\frac{1}{2}\rangle$ or $\langle\pm\frac{1}{2},m||\mp\frac{1}{2},m\rangle$ for $|m|>\frac{1}{2}$. This is 8, independent of m.

Returning to Eq. (52), we obtain the central result of our calculation, namely, that the transverse signal following an effective 90°-τ-90°$_{0°}$ pulse sequence evaluated to the second power in time is

$$\langle I_x\rangle=-a\cos\omega_0 t\left\{\frac{2(2I'+1)}{(2I+1)^2}\left[\frac{I(I+1)(2I+1)}{2.3}-\frac{1}{4}\right]\times\frac{2}{N}\sum_{k>j}(\tilde{A}_{jk}+A_{jk}')^2t'\tau-\cdots\right\}. \quad (61)$$

The precise meaning of this result is the following. The application of two closely spaced coherent 90° rf pulses to the central transition of a resolved quadrupolar broadened nuclear system of half-integral spin I gives rise to a nuclear signal following the second 90° pulse. The calculation is correct in powers of time as far as $n+m=2$ in $t'^n\tau^m$.

According to Eq. (61), the signal should be zero initially after the second 90° pulse and will increase as a function of time antiphase to the free induction signal. Higher order terms, the calculation of which are not presented here, will doubtless limit the maximum build-up and ultimately average the signal to zero for long times t'.

We emphasize that the presence of this signal is due entirely to the quadrupole interaction, and removal of the quadrupole term would cause the signal to vanish. This case would then simply reduce to the single-spin species case dealt with earlier in Sec. II.A.

The appearance of the signal is a direct manifestation of a quadrupole interaction, and thus we have a new way of detecting the *presence* of a quadrupole interaction without actually measuring it or, more important, without locating the actual satellites.

Measurements on the signal cannot in any simple way yield information on the quadrupole interaction itself.

Comparison of Eq. (61) with the case of two magnetic ingredients, Eq. (23), shows that we have an analogous situation in which the first derivative with respect to t' evaluated at $t'=0$ should yield a slope which for short pulse spacings is proportional to τ. Measurement of this slope will yield an experimental value of

$$M_2^*=\frac{2(2I'+1)}{(2I+1)^2}\left[\frac{I(I+1)(2I+1)}{2.3}-\frac{1}{4}\right]\frac{2}{N}\times\sum_{k>j}(\tilde{A}_{jk}+A_{jk}')^2.$$

If the exchange coupling is zero, M_2^* is a simple fraction of the central-line second-moment M_2. Some values of this ratio are given in Table I.

TABLE I. Theoretical ratios of M_2^*/M_2 for various spin I, when the scalar interaction is zero.

Spin I	Moment ratio M_2^*/M_2
$\frac{1}{2}$	0
$\frac{3}{2}$	0.22
$\frac{5}{2}$	0.14

An interesting consequence arises when $\tilde{A}_{ij}$ is nonzero. Comparison with the true second moment, Eq. (50), shows that the coefficients of the sums are different, i.e.,

$$\begin{aligned} M_2&=A\sum_{k>j}\tilde{A}_{jk}^2+B\sum_{k>j}\tilde{A}_{jk}A_{jk}'+C\sum_{k>j}A_{jk}'^2,\\ M_2^*&=D\{\sum_{k>j}\tilde{A}_{jk}^2+2\sum_{k>j}\tilde{A}_{jk}A_{jk}'+\sum_{k>j}A_{jk}'^2\},\end{aligned}\qquad(62)$$

so that some degree of separation of the two types of interaction is now possible. For example, if we take $ABCD$ and A_{jk}' as known, then we get a number for

$$\sum_{k>j}\tilde{A}_{jk}^2$$

and

$$\sum_{k>j}\tilde{A}_{jk}A_{jk}'.$$

From this information, one might be able to get the individual $\tilde{A}_{jk}$, particularly if the series are strongly convergent, and hence get a better picture of the scalar interaction wave functions.

III. CONCLUSIONS

For a single nuclear magnetic species of any spin I, solid echoes are predicted in the case of a $90°$-τ-$90°_{90°}$ rf pulse sequence. From the second time derivative at $t'=2\tau$, experimental values of second moment are possible within a predictable accuracy. An expression is given for the principal error term.

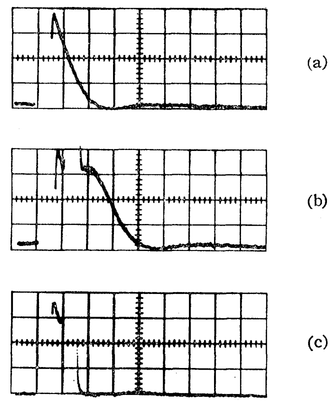

FIG. 3. Photographs of transient signals in powdered aluminum at 297°K. (a) Bloch decay following a single 90° rf pulse. (b) Solid echo following a $90°$-τ-$90°_{90°}$ pulse sequence with $\tau=50$ μsec. (c) Zero signal following a $90°$-τ-$90°_{0°}$ pulse sequence. The 90° pulse length was 12 μsec in these experiments and the Larmor frequency 10 Mc/sec. The horizontal time base sweep is 50 μsec/div.

Experimental studies of solid echoes in powdered Al^{27} ($I=\frac{5}{2}$) indicate a value of the second moment $\Delta M_2=9.5\pm0.2$ G^2 at 297°K (see Fig. 3). This is to be compared with the rigid-lattice theoretical value of 7.5 G^2. The rather large discrepancy between theory and experiment seems unaccountable in terms of experimental errors. The experimental value, however, is in good agreement with earlier second moments derived from absorption line measurements on powdered aluminum.[17,18]

In the case of two magnetic ingredients, it is shown that a $90°$-τ-$90°_{90°}$ pulse sequence should yield an estimate of the total second moment of the resonant and nonresonant spins. The expressions derived for the transverse signal following the second pulse indicate that the actual shape of the signal can be changed considerably by the "cross" terms in the dipolar interaction. For example, when this interaction is much greater than that of like spins, a discernable echo may not appear for close pulse spacings. In this case, the expression for the evolution of the signal from time 2τ onwards indicates a larger deviation from the free induction decay shape than would be the case for a normal solid echo of a single-spin species. Explicit evaluation of the correction terms has not been done.

An example of the absence of a solid echo for the $90°$-τ-$90°_{90°}$ pulse sequence has been observed experimentally in a single crystal of NaF [Fig. 4(b)].

For the $90°$-τ-$90°_{0°}$ pulse sequence, some new solid transient effects are predicted which should lead to a direct measurement of the second-moment contribution of the nonresonant spins. These effects have been ob-

[17] H. S. Gutowsky B. R. and McGarvey, J. Chem. Phys. **20**, 1472 (1952).
[18] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

served in a single crystal of NaF oriented with the [110] direction along H_0 [Fig. 4(c)]. The modulus of the initial slope of the solid transient signal has been measured as a function of the pulse spacing τ. These results are shown in Fig. 5. The general shape of the curve follows Eq. (25) and is seen to substantiate the gross predictions of the theory. Details of this work will be published elsewhere.[19]

The last part of this paper considers the applicability of double pulse response studies when applied to single species spin systems of half-integral spin, having a dipolar interaction and a resolved quadrupolar splitting. The specific case studied is when the central line only is pulsed with effective 90° rf pulses. It is shown that the second time derivative at zero time of the free induction decay envelope following one 90° pulse is proportional to the second moment of the central absorption line shape. When a second pulse is applied with the same rf phase as the first, a signal is predicted, the initial slope of which is simply related to the central line second moment when there is only a dipolar broadening. If a scalar interaction is also present, it is shown that the dipolar lattice sums and the sums of the scalar coupling constants combine in different proportions to that of the true central-line second moment. Thus these measurements will lead to new information about the spin system. In particular, it would appear that the separation of the scalar coupling constants is possible, and it is reasonable to suppose that evaluation of individual $\tilde{A}_{jk}$ to further than just nearest neighbors is possible.

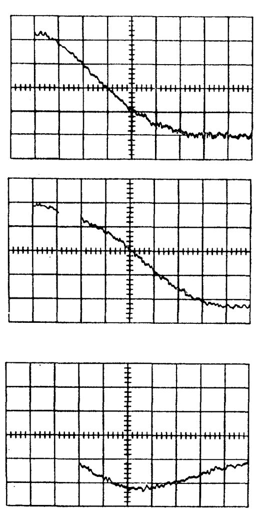

FIG. 4. Photographs of transient signals in a single crystal of NaF oriented with the static magnetic field along the [110] direction. (a) Bloch decay following a single 90° rf pulse. (b) Signal following a 90°-τ-90°$_{90°}$ pulse sequence with τ=30 μsec. Notice the absence of any clear echo formation. (c) Solid transient signal following a 90°-τ-90°$_{0°}$ pulse sequence with τ=30 μsec. The 90° pulse width was approximately 8 μsec, and the horizontal time base sweep is 20 μsec/div.

[19] J. H. Strange (to be published).

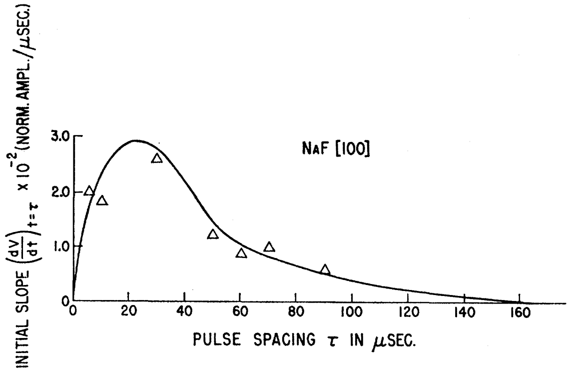

FIG. 5. Preliminary data showing the initial slope versus pulse spacing of the transverse signal following a pair of coherent 90° rf pulses applied to a single crystal of NaF. The static magnetic field is along the [100] direction.

Since the sole action of the quadrupole term is to lift Zeeman degeneracies, explicit information on the electric field gradients is not obtainable from these measurements. The signals described derive entirely from the dipolar and scalar interactions.

A suitable substance to test the theory might well be a pure single crystal of Al_2O_3, since this can be oriented to give zero second-order quadrupole splitting. No quantitative experimental data is available at the present writing, though some preliminary experiments performed on the central line of Al^{27} in a single crystal of ruby have shown the existence of a small signal in the double-pulse experiment.

An interesting material to study which has both a quadrupolar and exchange interaction might be a single crystal of indium. The usual problems of poor signal-to-noise due to low rf penetration can be overcome at low temperatures, but it is not clear how the rf inhomogeneity will affect matters, since in all the expressions derived, we assume a perfectly uniform magnetic field H_p.

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I am also most grateful to Professor J. G. Powles, Professor Rowland, Professor Slichter, and Dr. Strange for reading the manuscript and making a number of valuable suggestions.

APPENDIX

In this Appendix, we wish to calculate the traces of the coefficients of τ, t', τ^2, t'^2, occurring in the expansion of $\langle I_x\rangle$ in Eq. (52) and show that they all vanish. Considering the coefficient of τ, we have by cyclic permutation within the trace that

$$\mathrm{Tr}\{[\tilde{\mathfrak{H}}_1',I_z^*]I_x\}=\mathrm{Tr}\{[I_x,\tilde{\mathfrak{H}}_1']I_z^*\}. \qquad \text{(A1)}$$

The only terms of interest here are the diagonal components of $[I_x,\tilde{\mathfrak{H}}_1']$ since I_z^* is itself diagonal. Inspection of the matrix elements of I_x, Eqs. (49a) and (49b), and $\tilde{\mathfrak{H}}_1'$, Eqs. (54a)–(54c) and (57a)–(57c), show that the only diagonal elements arising come from terms like

$$\begin{aligned}&\langle m,\pm\tfrac{1}{2}|I_x|m,\mp\tfrac{1}{2}\rangle\langle m,\mp\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk\mathrm{D}}'|m,\pm\tfrac{1}{2}\rangle\\&\quad=\langle\pm\tfrac{1}{2},m|I_x|\mp\tfrac{1}{2},m\rangle\langle\mp\tfrac{1}{2},m|\tilde{\mathfrak{H}}_{jk\mathrm{D}}'|\pm\tfrac{1}{2},m\rangle\\&\quad=\tfrac{1}{4}(2I+1)\tfrac{1}{4}(2I'+1)m[\tilde{A}_{jk}+A_{jk}'].\end{aligned} \qquad \text{(A2)}$$

Hence the diagonal elements commute in the expression $[I_x,\tilde{\mathfrak{H}}_1']$, i.e.,

$$[I_x,\tilde{\mathfrak{H}}_1']_{\mathrm{diag}}=0 \quad \text{from above}. \qquad \text{(A3)}$$

We now consider the coefficient of t', and note that there are no diagonal components of $[\mathfrak{H}_1',I_x]$, so that

$$\mathrm{Tr}\{[\tilde{\mathfrak{H}}_1',I_z^*]I_x\tau-I_z^*[\mathfrak{H}_1',I_x]t'\}=0. \qquad \text{(A4)}$$

Turning to the more complex case of evaluating the coefficients of the second power in time, let us consider the coefficient of τ^2 in Eq. (52). We see that

$$\mathrm{Tr}\{[\tilde{\mathfrak{H}}_1',[\tilde{\mathfrak{H}}_1',I_z^*]]I_x\}=-\mathrm{Tr}\{[\tilde{\mathfrak{H}}_1',I_z^*][\tilde{\mathfrak{H}}_1',I_x]\}.$$

We now examine the matrix elements of the commutator $[\tilde{\mathfrak{H}}_1',I_z^*]$. The relevant matrix elements of I_z^* are obtained from Eq. (42). These are

$$\langle m,n|I_z^*|m,n\rangle=m+n \quad \text{for } |m| \text{ and } |n|>\tfrac{1}{2}, \qquad \text{(A5a)}$$

$$\left.\begin{aligned}\langle m,\pm\tfrac{1}{2}|I_z^*|m,\pm\tfrac{1}{2}\rangle&=m\mp\tfrac{1}{2}\\\langle\pm\tfrac{1}{2},m|I_z^*|\pm\tfrac{1}{2},m\rangle&=\mp\tfrac{1}{2}+m\end{aligned}\right\}\quad\text{for } |m|>\tfrac{1}{2}, \qquad \text{(A5b)}$$

and

$$\begin{aligned}&\langle+\tfrac{1}{2},+\tfrac{1}{2}|I_z^*|+\tfrac{1}{2},+\tfrac{1}{2}\rangle\\&\quad=-\langle-\tfrac{1}{2},-\tfrac{1}{2}|I_z^*|-\tfrac{1}{2},-\tfrac{1}{2}\rangle\\&\quad=-(\tfrac{1}{2}+\tfrac{1}{2}).\end{aligned} \qquad \text{(A5c)}$$

In evaluating the commutator, we note from Eqs. (54a), (57b), and (A5a)–(A5c), that all diagonal elements commute, so that we may disregard them further. Terms like

$$\langle m,m-1|\tilde{\mathfrak{H}}_{jk\mathrm{OD}}'|m-1,m\rangle\langle m-1,m|I_z^*|m-1,m\rangle$$

and

$$\langle m,m-1|I_z^*|m,m-1\rangle\langle m,m-1|\tilde{\mathfrak{H}}_{jk\mathrm{OD}}'|m-1,m\rangle$$

are equal from Eqs. (A5b) and (A5c) and Eqs. (54b) and (54c), so that these commutators vanish.

We are left finally with nonzero terms like

$$\begin{aligned}&\langle m,\pm\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle\langle m,\mp\tfrac{1}{2}|I_z^*|m,\mp\tfrac{1}{2}\rangle\\&\quad-\langle m,\pm\tfrac{1}{2}|I_z^*|m,\pm\tfrac{1}{2}\rangle\langle m,\pm\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle\\&\quad=2(\mp\tfrac{1}{2})\langle m,\pm\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk\mathrm{D}}'|m,\mp\tfrac{1}{2}\rangle.\end{aligned} \qquad \text{(A6)}$$

The only other class of nonzero terms arising in the commutator are

$$\left.\begin{aligned}&2\langle+\tfrac{1}{2},+\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk}'|-\tfrac{1}{2},-\tfrac{1}{2}\rangle\\&\qquad\times\langle-\tfrac{1}{2},-\tfrac{1}{2}|I_z^*|-\tfrac{1}{2},-\tfrac{1}{2}\rangle\\&\text{and}\\&2\langle-\tfrac{1}{2},-\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk}'|+\tfrac{1}{2},+\tfrac{1}{2}\rangle\\&\qquad\times\langle+\tfrac{1}{2},+\tfrac{1}{2}|I_z^*|+\tfrac{1}{2},+\tfrac{1}{2}\rangle\end{aligned}\right\}. \qquad \text{(A7)}$$

We now use similar arguments for the commutator $[\tilde{\mathfrak{H}}_1',I_x]$. From the matrix elements of I_x, Eqs. (49a) and (49b), and $\tilde{\mathfrak{H}}_{jk}'$, Eqs. (54) and (57), we see that purely diagonal terms can be dropped since all I_x components are positive. Terms (b) and (c) of Eq. (54) and (a) of Eq. (57) can also be dropped because these are all positive. In fact, the only terms that do not commute are from Eq. (57c) like

$$\begin{aligned}&\langle-\tfrac{1}{2},\pm\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk\mathrm{OD}}'|-\tfrac{1}{2},\pm\tfrac{1}{2}\rangle\langle-\tfrac{1}{2},\mp\tfrac{1}{2}|I_x|-\tfrac{1}{2},\pm\tfrac{1}{2}\rangle\\&\quad-\langle-\tfrac{1}{2},\pm\tfrac{1}{2}|I_x|-\tfrac{1}{2},\mp\tfrac{1}{2}\rangle\langle-\tfrac{1}{2},\mp\tfrac{1}{2}|\tilde{\mathfrak{H}}_{jk\mathrm{OD}}'|-\tfrac{1}{2},\pm\tfrac{1}{2}\rangle\\&\quad=2(\tilde{A}_{jk}-\tfrac{1}{2}A_{jk}')[\tfrac{1}{4}(2I+1)]^2.\end{aligned} \qquad \text{(A8)}$$

We note that these are diagonal terms only, so that in the product of the two commutators there are no diagonal components, i.e.,

$$\mathrm{Tr}\{[\tilde{\mathfrak{H}}_1',[\tilde{\mathfrak{H}}_1',I_z^*]]I_x\}=0. \qquad \text{(A9)}$$

We now wish to consider the coefficient of t'^2, i.e.,

$$\mathrm{Tr}\{I_z^*[\mathfrak{H}_1',[\mathfrak{H}_1',I_x]]\}=-\mathrm{Tr}\{[\mathfrak{H}_1',I_z^*][\mathfrak{H}_1',I_x]\}.$$

It is easily shown from Eqs. (48a), (48b) and Eqs. (A5a)–(A5c) that the commutator $[\mathfrak{H}_1',I_z^*]=0$, so that the trace vanishes, i.e.,

$$\mathrm{Tr}\{I_z^*[\mathfrak{H}_1',[\mathfrak{H}_1',I_x]]\}=0. \qquad \text{(A10)}$$