HIGH RESOLUTION NMR IN SOLIDS

by

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ABSTRACT

Two approaches to the problem of high resolution NMR in solids are described. The first involves modulation of the nuclear magnetic dipole-dipole interaction by resonance offset fields in multiple-pulse NMR. A simple treatment of zero order effects is presented which shows that if the resonance offset frequency is smaller than the inverse multiple-pulse cycle time, but larger than the linewidth, then the average dipolar Hamiltonian is just the dipolar Hamiltonian truncated along some average axis in the rotating frame. This is shown to have potential applications to line-narrowing, time-reversal, spin-locking and nuclear double resonance.

The second approach involves the observation of dilute spins (S) in a reservoir of abundant "unlike" spins (I). The problem of dipolar broadening by the I spins is overcome by spin-decoupling and the reduced sensitivity is enhanced by employing a double-resonance procedure due to Hartmann and Hahn. The approach involves "cross-polarization" of the S spins by the I reservoir and observation of the S free induction decay while decoupling the I spins. This is repeated ~ N_I/N_S times until the I polarization is depleted and the S signals are co-added to yield a markedly enhanced sensitivity over conventional Fourier techniques. Some illustrative results on chemical shielding and relaxation of ^13C in solids are presented and references are given to results of other experiments both published and in progress. Alternative versions of the experiment employing both direct and indirect detection are discussed briefly.

An important requirement for these experiments is timing flexibility. A description of the computer interface which provides this is given together with circuit and software details.
Finally, a discussion of solid state spin echoes is presented in the form of a paper reprint entitled "Time-Reversal Experiments in Dipolar-Coupled Spin Systems", by W-K. Rhim, A. Pines and J.S. Waugh. It is demonstrated that the spin-temperature hypothesis (which actually forms the basis for a large part of this thesis) must be employed with caution. The effects of cycle symmetry and applications to high resolution NMR in solids are discussed briefly.

Thesis Supervisor: John S. Waugh
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Chairman

Thesis Supervisor
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CHAPTER I

QUANTITATIVE ASPECTS OF COHERENT AVERAGING. SIMPLE TREATMENT OF RESONANCE OFFSET PROCESSES IN MULTIPLE-PULSE NMR
I. INTRODUCTION

The problem of calculating the response of a coupled spin system to an arbitrary radiofrequency excitation is, in general, an extremely complex one. It is well known, however, that if the excitation fulfills certain conditions of periodicity and duration, an enormous simplification ensues, taking the form of what we have called "coherent averaging" (1). This theory has formed a powerful tool for the description and design of a variety of effects in pulsed nmr, including spin locking (2-4), line narrowing and high resolution nmr in solids (5-7), spin echoes (8), steady-state behavior (9), and scaling of inhomogeneous shifts (10).

It was noticed in several of these experiments that when pulse trains were applied with the r.f. carrier frequency substantially displaced from the Larmor frequency of the spin system, i.e., with a "resonance offset", a new phenomenon manifested itself in the form of additional averaging, for example enhanced line-narrowing. This phenomenon has recently been explained and, in fact, has been shown to possess a number of useful properties (11).

Basically, what happens, in qualitative terms, is the following: in the presence of r.f. excitation, the coupling between the spins becomes modulated with a period equal to that of the excitation itself, in an appropriate reference frame (1,12). In the limit of strong modulation we perform
a time average of this time-dependent coupling and obtain an average coupling which effectively governs the response of the spin system. The process of "truncation" of the dipolar interaction in the presence of a large static external field (13-16), for example, is a particular case of this approach (11). Now consider what happens if there is a large resonance offset. In the rotating frame, this appears as a static magnetic field and, as in the case of truncation just mentioned, this field will provide an additional modulation of the coupling, which may be averaged in the appropriate limit (1). Thus, the behavior of pulsed nmr experiments near and far from resonance should be distinctly different, as has indeed been observed (11).

In this communication, we wish to present a simple treatment of this phenomenon in a form more amenable to an intuitive understanding and quantitative application to a variety of nmr experiments than that of our previous work. This presentation is warranted by the fact that these multiple-pulse techniques are becoming increasingly useful in studies of chemical problems, and resonance offset effects form an integral component in their usefulness and in their understanding.

The approach here is simple in the sense that only zero order (1) averaging effects are considered, and insofar as is possible the notation and tools used should be quite familiar. Higher order effects are more conveniently treated in terms
of irreducible tensor operators, since we are interested in the transformations of such operators under the rotations induced by the r.f. excitation. This will be deferred to a later detailed exposition of these experiments.

In section II a brief review of pertinent theory is presented and a general description of averaging due to resonance offset fields is derived. In section III this is applied to some simple multiple-pulse sequences and some of its uses and limitations are discussed. Details on the exact steps involved in the calculations of average Hamiltonians in various representations are not given, since this has been presented several times. The procedure is simply mentioned and the results written down directly.
II. GENERAL THEORY

A. HAMILTONIAN AND FRAME OF REFERENCE

We begin by writing down a Hamiltonian for the system. We select as an example of a spin coupling the dipolar interaction, since this is the most important and widely encountered for solids of interest to chemists. The results are easily generalized, as we shall see. We write the Hamiltonian in the laboratory frame in frequency units:

\[ H_L(t) = H_0 + H_1(t) + H_d \] (1)

\[ H_0 \] is the Zeeman interaction with applied static field along the z axis

\[ H_0 = -\omega_0 I_z \] (2)

\[ H_1(t) \] the applied r.f. excitation

\[ H_1(t) = -2\omega_1(t) I_x \cos(\omega t + \phi(t)) \] (3)

where \( \omega_1(t) \) and \( \phi(t) \) describe the amplitude and phase modulation of the r.f. excitation applied at frequency \( \omega \), and

\[ H_d = -\sum_{i,j} \frac{\gamma^2 \mu}{r_{ij}^3} \left\{ \frac{3(I_i \cdot r_{ij})(I_j \cdot r_{ij})}{r_{ij}^2} - I_i \cdot I_j \right\} \] (4)

is the dipolar interaction.
We now perform the customary transformation to a coordinate system rotating at frequency $\omega$ about the z axis. An average is then performed over a time period of $2\pi/\omega$ and this removes the time dependent terms in $H_1(t)$ and $H_d$ in this frame. All this is well known -- it corresponds to discarding the counter-rotating component of the r.f. field and the "nonsecular terms" of the dipolar interaction (or truncation) and is just a special case of coherent averaging. It is clearly legitimate whenever $H_0$ is much larger than $H_1$ and $H_d$. Our Hamiltonian in the rotating frame thus assumes the form

$$H_R^0(t) = H_\Delta + H_1(t) + H_d^0$$ (5)

where $R$ indicates the rotating frame.

$H_\Delta$ is the resonance offset

$$H_\Delta = -\Delta \omega I_z; \quad \Delta \omega = (\omega_0 - \omega);$$ (6)

$$H_1(t) = -\omega_1(t) \cdot I_z,$$ (7)

$$H_d^0 = \sum_{i<j} b_{ij} (3 I_{iz} I_{jz} - I_i \cdot I_j); \quad b_{ij} = \frac{-\gamma I_{ij}^2}{r_{ij}^3} P_z (\cos \theta_{ij}).$$ (8)

The form $\omega_1(t)$ depends on the particular experiment at hand. Note that for brevity we sometimes use the same
notation for terms of $H$ in different frames to conform with accepted practice - the frame will always be specified if this is done. The $^0$ superscript indicates a truncation or zero order average of the particular term.

If the spin system is initially described in the rotating frame by the density matrix $\rho_R(0) = \rho_L(0)$, then at a time $t$ it has evolved to a state described by

$$\rho_R(t) = U_R^0(t,0) \rho_R(0) U_R^{0\dagger}(t,0) \tag{9}$$

here $U_R^0(t,0)$ is the effective time development operator in the rotating frame, given by

$$U_R^0(t,0) = T \exp(-i \int_0^t H_R^0(t') dt') \tag{10}$$

and $T$ is a time ordering operator. It is an expansion of $U$ in which we shall be interested.

B. COHERENT AVERAGING EFFECTS

We now prepare to take account of the modulation that the first two terms in (5) produce in the third. To this end we assume (i) $H_1(t)$ is cyclic and periodic with period $t_c$, and $t$ is restricted to integer values of $t_c$, $t = N t_c$

(ii) $t_c \ll t_\Delta$, $T_2$; $t_\Delta = 2\pi/\Delta\omega$ , \( \tag{11} \)
(i) has been discussed in detail\(^{(1)}\) and (ii) will allow us to perform a factorization of (10) in two steps.

Employing the conditions above we obtain to a good approximation, factoring out \(H_1(t)\) in a straightforward application of the theory:

\[
U_R^0(t,0) = \overline{U}_{TR}^0(t,0) = \exp(-it\overline{H}_{TR}^0), \quad (12)
\]

where

\[
\overline{H}_{TR}^0 = \frac{1}{t_c} \int_0^{t_c} U_1^+(t,0) [H_d + H_\Delta] U_1(t,0) dt = \overline{H}_d^0 + \overline{H}_\Delta = \overline{H}_d^0 - \overline{\Delta \omega} \ I_\mu; \ U_1(t,0) = T \exp(-i \int_0^t H_1(t') dt'). \quad (13)
\]

Note that restriction \([11(i)]\) applies to calculations involving time evolution as Eq. (12) and not, of course, to calculations of expansion terms as in Eq. (13). \(\overline{H}_{TR}^0\) is the average Hamiltonian; \(T\) stands for "toggling" (12) since \(\overline{H}_{TR}^0\) is precisely the average Hamiltonian in an interaction (toggling) frame defined by \(H_1(t)\), (due to restriction 11(i), \(U_{TR}^0\) is thus the effective evolution operator in the rotating frame).

\(\overline{\mu}\) refers symbolically to the average direction \(\overline{\mu}\) in the rotating frame along which the spins are quantized (12). This is easily visualized by taking a unit spin vector \(\mu\) along the \(z\) axis and applying \(H_1(t)\) in the rotating frame. Then we define

\[
\overline{\mu} = \frac{\int_0^{t_c} U_1^+(t,0) \mu U_1(t,0) dt}{\int_0^{t_c} |U_1^+(t,0) \mu U_1(t,0) dt|}. \quad (14)
\]
Figure 1

Pictorial description of resonance offset averaging under the pulse sequence of figure 2(a). The pulses are imagined to be δ-pulses \( t_w = 0 \) and are depicted by arrows along \( x \) and \(-x\) which nutate the unit magnetization vector \( \vec{u} \) alternately by angles \( \theta^0 \) and \(-\theta^0\). Thus \( \vec{u}(t) \) switches between positions 1 and 2 and its average direction is given by the unit vector \( \vec{u} \). The average offset field \( \overline{\Delta \omega} = \cos(\theta/2)\Delta \omega \) points along \( \vec{u} \) and thus any magnetization \( M \) will precess on the average about this axis with frequency \( \overline{\Delta \omega} \). This gives rise to the scaling of chemical and inhomogeneous shifts. The factor \( \overline{P(\vec{u} \cdot \vec{y}(t))} \) in equations (23), (24) is simply evaluated for this sequence as \( P_2(\cos\theta/2) \), so the average dipolar interaction is scaled by \( \overline{P_2(\vec{u} \cdot \vec{y}(t))} = P_2(\cos\theta/2) \).
For example if \( \omega_1(t) \) consists of 90° phase alternated \( \delta \)-pulses along the x axis then \( \mu = \frac{1}{\sqrt{2}} (\hat{j} + \hat{k}) \). This is illustrated in Figure 1. \( \overline{\Delta \omega} \) is analogously the average resonance offset over this cycle:

\[
\overline{\Delta \omega} = \frac{\Delta \omega}{t_c} \left| \int_0^{t_c} \mu(t) \, dt \right|.
\] (15)

We now add to (11) the further restriction

\[
(iii) \ t_\Delta \ll T_2; \ t_\Delta = \frac{2\pi \overline{\Delta \omega}^{-1}}{1}.
\] (11)

This allows us, exactly as above, to factor the operator in (12) and then take an average over one cycle of the interaction with the static field \( -\Delta \omega I \mu \). What we are doing is in fact a truncation of the average dipolar interaction \( \overline{H^0_d} \) due to the presence of a large static field along the \( \mu \) axis. To a good approximation then

\[
\overline{U}_{TR}(t,0) = \overline{U}_\Delta(t,0) \overline{U}_{DTR}(t,0)
\] (16)

where

\[
\overline{U}_\Delta(t,0) = \exp(-it \overline{H}_\Delta)
\] (17)

\[
\overline{U}_{DTR}(t,0) = \exp(-it \overline{H}^0_{DTR})
\] (18)

\[
\overline{H}^0_{DTR} = \overline{H}^0_d = \frac{1}{t_\Delta} \int_0^{t_\Delta} \overline{U}_\Delta(t,0) \overline{H}_d \overline{U}_\Delta(t,0) \, dt.
\] (19)
Here the additional D subscript stands for "doubly rotating" - \( H_{DTR}^{0,0} \) is precisely the average Hamiltonian in a frame which now rotates about the \( \bar{u} \) axis at frequency \( \bar{\omega} \) (12). Superscript \(^{0,0}\) indicates the double averaging or truncation.

Now using equations (13) and (19) and changing the order of integration over \( t_c \) and \( t_\Delta \) we have

\[
\bar{H}_{DTR}^{0,0} = \frac{1}{t_c t_\Delta} \int_0^{t_c} dt'' \int_0^{t_\Delta} dt' \bar{U}_\Delta^+(t',0) U_1^+(t'',0) H_d^0 U_1(t'',0) \bar{U}_\Delta(t',0),
\]

but using (13) and (17) it is easily found that

\[
\frac{1}{t_\Delta} \int_0^{t_\Delta} dt' \bar{U}_\Delta^+(t',0) U_1^+(t'',0) H_d^0 U_1(t'',0) \bar{U}_\Delta(t',0) = H_{\bar{d}_\mu}^{0,0} P_2(\bar{\mu} \cdot \mu(t''))
\]

where

\[
H_{\bar{d}_\mu}^{0,0} = \sum_{i<j} b_{ij} (3 I_i \bar{I}_i - I_j \bar{I}_j - I_i \cdot I_j).
\]

\( H_{\bar{d}_\mu}^{0,0} \) is of course just the "secular" part of \( H_d^0 \), the part that commutes with \( \bar{H}_\Delta \). With this notation, for example, \( H_d^0 \equiv H_{dz}^0 \). Thus we obtain finally for the average Hamiltonian (excluding \( \bar{H}_\Delta \)) putting (21) into (20):
\[ \overline{H}_{DTR}^{0,0} = \overline{H}_{d}^{0,0} = \overline{H}_{d\mu}^{0} \cdot P_2 (\overline{\nu} \cdot \overline{\nu}(t)). \]  

(23)

As usual the bar denotes an average over the r.f. cycle:

\[ \overline{P}_2 (\overline{\nu} \cdot \overline{\nu}(t)) = \frac{1}{t_c} \int_0^{t_c} P_2 (\overline{\nu} \cdot \overline{\nu}(t)) dt \]  

(24)

where \( \overline{\nu} \) is defined as (14) and \( \overline{\nu}(t) \) is the integrand. We prefer to leave (23) in the rotating frame since normal detection methods correspond to measurements in this frame and not in the more suitable tilted frame along \( \overline{\nu} \).

C. DISCUSSION

Equation (23) expresses a simple yet remarkable result. It says that no matter how complicated the cycle of r.f. excitation, if it is applied with a resonance offset fulfilling conditions 11(i) - (iii) then the average dipolar Hamiltonian is just the truncated Hamiltonian itself along an average axis in the rotating frame. This is depicted pictorially in Figure 1. Obviously in a frame tilted with its z axis along \( \overline{\nu} \), \( \overline{H}_{d}^{0,0} \) is exactly proportional to (8). In order to calculate this average Hamiltonian it is thus not necessary to calculate \( \overline{H}_{TR}^{0} \) in the intermediate step - we need only (i) find \( \overline{\nu} \) and write down \( \overline{H}_{d\mu}^{0} \) immediately, (ii) calculate \( \overline{P}_2 \) as in (24), so no manip-
ulations are necessary on the spin variables. This fact, although rather obvious with a little reflection, is obscured in the original work\(^{(11)}\) and with complicated cycles the manipulation of spin operators becomes unwieldy. The form of (23) allows a simple understanding of these experiments and permits us to draw more general conclusions (as we shall see for example in the discussion of spin locking). Of course in the event that we wish to enquire about the behavior at resonance \((\Delta \omega = 0)\) this treatment is not valid and \(\mathcal{H}^0_{TR}\) must be calculated separately.

These results are easily generalized. If our interaction is not dipolar but is given, say, by a Hamiltonian \(H^0_n\) whose effective spin part transforms like an \(n\)'th rank irreducible tensor in the rotating frame, then under the same conditions

\[
\mathcal{H}^0_n = H^0_n - \frac{P_n}{p} (\mathbf{\mu}(t)).
\]

(25).

For example, the isotropic chemical shift treated by Ellett and Waugh\(^{(10)}\) has a spin part which transforms like a first rank irreducible tensor, and indeed their average Hamiltonian is a special case of our results. There, however, \(\mathcal{H}^0_{TR}\) commutes with \(\overline{H}_\Delta\) (since \(I\) transforms like \(\mathbf{\mu}\)) and thus the result is independent of resonance offset.

One nice feature of (23) is that it allows a quantitative comparison with experiment as, for example, in the work of Lee and Goldberg\(^{(15)}\). In the case of irradiation at resonance, \(\mathcal{H}^0_d\) usually has some form different from \(\mathcal{H}^0_d\) and line-
shape comparisons are difficult to reconcile with theory. Thus we have to date mostly satisfied ourselves with qualitative or semiquantitative conclusions, except in special cases. In the present case, however, arguments can be made more precise and quantitative.

Note that this treatment is not applicable to resonance offset experiments such as those of Lee and Goldberg (15) and Barnaal and Lowe (16), since there, requirement 11(ii) is violated ($t_c \sim t_\Delta$). In these cases the first transformation must be made not by $U_1(t,0)$ as in our case, but by the full effective field (14).

$$U_e(t,0) = \exp(-it(H_1 + H_\Delta))$$

In the present case the fact that $H_1$ is not exactly perpendicular to $H_0$ would be accounted for by correction terms in the expansion of $\overline{U}_R^0$, which are not considered here.
III. REPRESENTATIVE PULSE SEQUENCES

It now remains for us to specify the form of $\omega_1(t)$ in (7) and to write down some representative results. We select only simple examples to illustrate the general approach to application of the theory. Other examples will undoubtedly be investigated for fun by the interested reader.

A. TWO-PULSE CYCLE

Figure 2(a) shows the form of $\omega_1(t)$ for a phase alternated two-pulse sequence. By inspection (see Figure 1) we find immediately that $\overline{\nu}$ is in the $y$-$z$ plane and makes an angle $\theta/2$ with the $z$ axis. Defining the duty cycle $\delta$ by

$$\delta = \frac{2t_w}{t_c}$$

and using equation (23) we find trivially for a pure dipolar interaction

$$H^0_{\delta} = 3p_{\delta}(\theta) + 1$$

$$p_{\delta}(\theta) = (1-\delta) \cos \theta + \delta \frac{\sin \theta}{\theta}.$$ (27)

If there is an inhomogeneous or chemical shift term in the rotating frame Hamiltonian

$$H_0^c = \sum_i \sigma_{iz} I_{iz}$$ (28)
Figure 2

Pulse sequences discussed in the text. Although not carried out here, these sequences may be symmetrized by a redefinition of the cycle to eliminate some correction terms to the average Hamiltonian.
where $H^0_C$ is again a truncated form of the full chemical shift $H_C$, then $\tilde{H}^{0,0}_{\text{DTR}}$ will contain another term given by

\[ \tilde{H}^{0,0}_C = H^{0}_{\text{CU}} p_\delta (\theta/2) \]  \hspace{1cm} (29)

with $p_\delta$ defined in (27); this is in agreement with previous results (10).

B. LINE NARROWING

Figure 3 shows a calculated plot of $\frac{3p_\delta (\theta) + 1}{4}$ as a function of $\theta$ for several values of the duty factor $\delta$. For $\delta < 0.75$ we see that $\tilde{H}^{0,0}_d$ can be made to vanish by an appropriate selection of $\theta$ and thus leads to a simple technique for line narrowing. For $\delta = 0$, i.e. $\delta$-pulses we need $\theta = \theta_t$ where $\theta_t$ is the tetrahedral angle (109°28'); this is just the previously described PAT sequence (11). However, the present analysis shows that even for $\delta > 0$ the coupling can be made to vanish with $\theta > \theta_t$, thus eliminating the term in equation (21) of reference (11).

The fact that $\theta = \theta_t$ explains the limited line narrowing in Figure 2 of the above work. With careful adjustment of $\theta > \theta_t$ decay times exceeding 1 msec for the $^{19}$F nuclei in CaF$_2$ have actually been attained for this experiment (18). Interestingly, it appears from Figure 2 that employing $\delta \sim 0.75$ should be superior to the PAT experiment, since the region of line narrowing is then markedly less sensitive
Plot of the dipolar scale factor $\tilde{P}_2(\mu \cdot \nu(t)) = 1/4(3p_\delta(\theta) + 1)$ vs. $\theta$ for several values of the duty factor $\delta$ in the phase alternated pulse sequence (figure 2(a)). The sequence produces line narrowing and is applicable for high resolution nmr in solids when $\overline{P}_2 = 0$, e.g. at 109.5° for $\delta = 0$ (the phase alternated tetrahedral experiment). For $\overline{P}_2 < 0$ the Hamiltonian becomes "negative" yielding the conditions for time-reversal.
to any inhomogeneities in the r.f. field. However, in this range $\Delta \omega$ is also reduced so there is no large gain in cycle time. An experimental check of the full curves in Figure 2 will be interesting and should provide an additional verification of this simple theory. Note that for any solution of $\tan \theta = \theta$, e.g. $\theta = 257.5^\circ$, the line narrowing is predicted to be independent of the duty factor $\delta$.

C. MAGIC ECHOES

Magic echoes, which appear after homogeneous free induction decay in solids, were first reported by Rhim, Pines and Waugh\(^{(8)}\). To remind the reader, magic echoes are produced in the following way: following the decay of magnetization due to $H^0_d$, a strong r.f. perturbation is applied under which the effective Hamiltonian is given by $kH^0_d$ with $k < 0$. This induces a negative time development which recalls the previous history of the spin system and produces an echo. See Chapter V for details.

Looking at Figure 2, we see that for small $\delta$, we can make $3P_\delta(\theta) + 1 < 0$, i.e. $H^0_d$ "negative", thus yielding the necessary conditions for time reversal. The observation of magic echoes should provide verification for this aspect of the theory. These could be produced simply by applying a train of phase alternated pulses "sandwiched" between a pair of phase shifted $\xi$ and $-\xi$ pulses as in the analogous on resonance experiments\(^{(8)}\).
Note that this is another manifestation of the simple form taken by the average Hamiltonian $\mathcal{H}_{DTR}^{0,0}$. In a general pulse experiment, say an on resonance phase alternated sequence, the effective Hamiltonian has some other form except for special cases like 90° pulses\(^{(3)}\) (vide infra) and time reversal becomes much more restricted.

D. SPIN LOCKING

The form of $\mathcal{H}_{DTR}^{0,0}$ allows another general conclusion. Since

$$[I_\mu, \mathcal{H}_{DTR}^{0,0}] = 0 \tag{30}$$

we have all the prerequisites for spin locking of the \(\bar{\mu}\) component of magnetization. We point out that (30) is the correct criterion to employ for spin locking -- the presence of an average or mean $H_1$ field is neither sufficient nor a necessary condition as is still sometimes erroneously assumed.

We see then that the observation of $T_{\parallel}$ and $T_{\perp}$ (20) should be a general phenomena in any resonance offset multiple-pulse experiment. If we start with the magnetization along an arbitrary axis in the rotating frame we may separate it into components perpendicular to and parallel to $\bar{\mu}$. The perpendicular component will then precess about $\bar{\mu}$ and decay by spin-spin processes with a time constant $T_{\perp} = \bar{F}_2^{-1}T_2$; when $\bar{F}_2$ + 0 the decay will of course be dominated by correction terms. The parallel component will be spin locked.
and will change only by spin-lattice relaxation in the rotating frame \((12,14,21-24)\). The effects of spin-lattice relaxation are very interesting in these experiments and will be treated in detail elsewhere.

If the effective field along \(\vec{e}_z\), i.e. in \(\vec{H}_\Delta\), is inhomogeneous (for example from an inhomogeneous \(H_0\) or from inhomogeneous shifts as in a polycrystalline solid) then \(T_L\) may be dominated by this inhomogeneity if \(\vec{P}_2\) is small. This effect can be demonstrated quite dramatically by production of inhomogeneous rotary spin echoes\(^{(25)}\) when \(\vec{e}_z\) is at the magic angle (i.e. \(\vec{P}_2 = 0\)) as in the experiments of Rhim and Kessemeyer\(^{(26)}\) and Pines, Rhim and Waugh\(^{(27)}\). In the latter experiment, the nature of the two components of magnetization is shown quite clearly using the off resonance four-pulse technique\(^{(5)}\).

The simple behavior we have outlined above is a peculiar characteristic of the resonance offset experiment. If we enquire into the behavior of the spin system under the pulse sequence of figure 2(a) at resonance (\(\Delta \omega = 0\)) we find from (13)

\[
\vec{H}_d^0 = - \frac{1}{2} \mu_0 \frac{d}{dx} + \frac{3}{2} \vec{P}_0(\theta) \sum_{i<j} b_{ij} \{ \cos \theta (I_{iz}I_{jz} - I_{iy}I_{jy}) \\
- \sin \theta (I_{iz}I_{jy} + I_{iy}I_{jz}) \},
\]

(31)
In this case an analysis of the spin system response is difficult and comparison with the normal unperturbed behavior can be made only on the basis of moments of the decays. For example, the second moments defined by (28)

\[ <\omega^2> \mu = \frac{\text{Tr}[H_0^d, I_\mu]^2}{\text{Tr}I_\mu^2} \quad (32) \]

are given for (31) by:

\[ <\omega^2>_x = p_\delta^2(\theta) <\omega^2>_0 \quad (33) \]

\[ <\omega^2>_y = \frac{1}{4}(p_\delta^2(\theta) + 2\cos\theta p_\delta(\theta) + 1)<\omega^2>_0 \quad (34) \]

\[ <\omega^2>_z = \frac{1}{4}(p_\delta^2(\theta) - 2\cos\theta p_\delta(\theta) + 1)<\omega^2>_0 \quad (35) \]

where \(<\omega^2>_0\) is the normal high field truncated second moment

\[ <\omega^2>_0 = \frac{\text{Tr}[H_0^d, I_x]^2}{\text{Tr}I_x^2} . \quad (36) \]

For \(\theta = 90^\circ\), \(\delta \sim 0\) we have the experiment of Waugh and Huber (29) which produces a prolonged decay only along the \(x\) axis as expected from (33). As we have seen though, this picture changes drastically as we go off resonance.

We take this opportunity to note that (33) also gives the second moment of spin echo decays (with constant \(\delta\)) produced by a 90\(_x\) pulse followed by a 90\(_y\) pulse since this
is one cycle of the appropriate pulse sequence. This important problem will be dealt with in the near future\(^{(9)}\).

E. IDEAL 90° PULSES

Since the simple properties of 90° δ-pulses have a special appeal and in fact most proponents of multiple pulse nmr have been primarily obsessed with such pulses, we enquire here into the possibility of using them for experiments similar to those mentioned above. A general two-pulse sequence composed of such pulses is shown in figure 2(b) with α variable from 0 through 1. It is trivial to show that if this sequence is applied with the appropriate resonance offset then from (23)

\[
\hat{H}_{d}^{0°} = \hat{H}_{d}^{0°} \left( 1 - \frac{3}{2} \frac{\alpha(1-\alpha)}{\alpha^2 + (1-\alpha)^2} \right)
\]

(37)

where \( \bar{\mu} \) is in the yz plane and

\[
\bar{\mu} \cdot \bar{y} = \frac{\alpha}{\sqrt{\alpha^2 + (1-\alpha)^2}}
\]

(38)

and therefore \( \hat{H}_{d}^{0°} \) cannot be made to vanish for any real α.

Thus using only 90° δ-pulses we conclude that we must resort to a cycle containing more than two pulses to achieve line-narrowing. It is interesting that the maximal line narrowing of 0.25 occurs at \( \alpha = 1/2 \) which gives just the pulse sequence of Waugh and Huber\(^{(29)}\).
F. FOUR-PULSE CYCLE

There are many possible four-pulse cycles. The most well known to pulsed NMR spectroscopists is the four-pulsed four-phase WAHUHA cycle\(^{(5)}\). Here we treat a four-pulse cycle employing only two phases shown in figure 2(c). Defining \(\delta\) as in (26) we find again using (23),

\[
\overline{H}_{d}^{00} = H_{d}^{0} \left\{ \frac{1}{2}(1-\alpha)(1-\delta) + \frac{1}{4}(1+\alpha)(1-\delta)(3\cdot\cos^2\theta - 1) + \right.
\]

\[
\frac{\delta}{4}(1 + \frac{3}{\delta}\frac{\sin\theta \cos\theta}{}) \} \quad (39)
\]

which reduces for \(\theta = \pi/2\) to

\[
\overline{H}_{d}^{00} = H_{d}^{0} \left( 1 - \frac{3\alpha(1-\delta)}{4} \right). \quad (40)
\]

For ideal \(\delta\)-pulses, \(\delta = 0\), we see that we can achieve an effective line narrowing, \(\overline{H}_{d}^{00} = 0\), for \(\alpha = 1/3\); this yields precisely the same timing as that of the WHH cycle and has been verified experimentally yielding decay times of 2 msec on the \(^{19}\text{F}\) spins of CaF\(_{2}\). Just as in this latter cycle the effects of finite pulse width can be compensated for. If we wish to retain 90° pulses then this is easily done by varying \(\alpha\) (as long as \(\delta < 2/3\)) using (40). The change in effective decay time going off resonance is quite marked for this pulse sequence. Magic echoes may be produced just as in the two pulse cycle by making \(\overline{H}_{d}^{00}\) "negative".
IV. SUMMARY

We have attempted to present a clear picture of the additional averaging effects produced by resonance offset fields in multiple-pulse nmr, and have illustrated this with some simple examples. In particular, the theory shows that behavior at, and far from resonance may be distinctly different, and that calculations made disregarding the resonance offset field, lead to erroneous results\(^{(30)}\). In addition, several uses of this phenomenon including line narrowing, spin locking, and magic echoes have emerged.

We conclude by pointing out two other possible applications of this phenomenon in the future.

(i) Design of more efficient pulse sequences for line narrowing and magic echoes. The discussion in this paper has centered on zero order effects, but there are equally profound higher order effects which can be accounted for by the theory. These effects may in some cases outweigh the conclusions drawn from symmetry considerations alone in designing multiple-pulse experiments\(^{(7,8,27,31,32)}\).

(ii) This type of experiment provides a simple means of producing effective static fields in the rotating frame with arbitrary directions and magnitudes, and with modified dipolar interactions, while being able
to observe the magnetization between pulses. These facts give it an appealing potential for application to double-resonance experiments\(^{(33,34)}\) which have stirred up some interest among chemists since their recent adaptations to high resolution nmr of dilute spins in solids\(^{(35-37)}\).

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REFERENCES AND FOOTNOTES


20. $T_\parallel$ and $T_\perp$ refer to the two components of magnetization respectively parallel and perpendicular to the effective field in the rotating frame.


30. This is similar to the trouble encountered when there are microscopic inhomogeneities stronger than the spin-spin interactions. The effects of the inhomogeneities on the spins cannot be accounted for independently, but modulate the spin-spin interactions, making additional truncation or averaging of these interaction terms a necessity: D. Hone, V. Jaccarino, T. Ngwe and P. Pincus, *Phys. Rev.*, 186, 291 (1969).


32. This fact probably explains the observation by us that there is no increase in line narrowing efficiency going from the four-pulse cycle of Ref. 5 to the symmetrical four-pulse cycle of Ref. 8b.


CHAPTER II

HIGH RESOLUTION NUCLEAR DOUBLE RESONANCE

OF DILUTE SPINS IN SOLIDS
I. INTRODUCTION

Although high resolution NMR in liquids is established as a powerful tool for structural and dynamical studies of chemical systems,\(^1\) analogous experiments on solids have enjoyed a more limited prosperity. The reason is readily traceable: whereas the direct nuclear magnetic dipole-dipole interaction is averaged to zero in liquids due to rapid rotational and translational diffusion, no such motion prevails in rigid solids, leaving the above interaction as an annoying source of spectral broadening. If we consider that spectral structure due to chemical shifts and spin-spin couplings requires resolution of \(~\) several Hz, while dipolar broadening is normally of \(~\) several kHz, it is clear that we are faced with an awesome problem if we wish to bring solids into the realm of conventional high resolution NMR.

In many instances, it is precisely the dipolar interaction in a solid which is at the center of attention (or its presence is a crucial factor). Such is the case, for example, in studies of lineshapes,\(^2\) spin-diffusion,\(^3\) spin-temperature,\(^4\) etc. In addition, it can be used to good advantage in both structural and dynamical studies, as exemplified by wideline dipolar structure\(^5\) and by second moment and spin-lattice relaxation studies of motion.\(^6\) It is clear, however, that a considerable increase
in information could be attained if it were possible to suppress
the dipolar broadening and extract details on other interactions
such as chemical shifts and indirect nuclear spin-spin couplings.
The type of information from solids should be valuable, since the
restriction of molecular reorientation preserves any anisotropy
(e.g. chemical shielding anisotropy) which is averaged to zero
in liquid systems and may show up only indirectly through spin
relaxation effects.

Several approaches have been made to this important problem.
They may be discussed in terms of the Hamiltonian for a "truncated"
dipolar interaction\(^{(7)}\) between like spins which we write as:

\[
\mathcal{H}_d^0 = -\gamma^2 h^2 \sum_{i<j} \frac{1}{r_{ij}^3} p_2(\cos \theta_{ij}) (3 I_{i z} I_{j z} - I_i \cdot I_j)
\]

(1)

The techniques differ in which part of (1) they choose to affect.
In the magic-angle sample-spinning experiment\(^{(8-10)}\) it is \(\theta_{ij}\) which
is modulated rapidly giving \(<p_2(\cos \theta_{ij})> = 0\). In multiple-
pulse NMR,\(^{(11-14)}\) in an appropriate reference frame, it is \(I\) that
is modulated, giving \(<3 I_{i z}(t) I_{j z}(t) - I_i \cdot I_j> = 0\). These have
met with considerable success. The sample-spinning, however,
requires high rotation speeds (\(\geq 10\) kHz) making it difficult for
rigid solids. In addition it removes any anisotropy in the chemi-
cal shift. The multiple-pulse techniques, on the other hand,
require high r.f. phase and amplitude stability, and despite the
promise of enhanced resolution through the use of symmetry,
resonance-offset effects\(^{(20,21)}\) and computer-aided adjustments,\(^{(22)}\) they are difficult to perform routinely.

In the present paper we discuss a different approach which we find to be rather simple and widely applicable, and which has produced a significant flux of preliminary experimental results since its recent institution.\(^{(23)}\) The basic premise is remarkably simple. Looking at (1), we see that the "size" of \(\kappa_d^0\) could be reduced by simply increasing the magnitude of the \(r_{ij}\). How can we do this? At least one solution presents itself immediately: if the nuclear spins of interest are of an isotope having a low natural abundance, or if they are chemically dilute, then of course the average \(r_{ij}\) is increased. Precisely this thinking motivated the experiment of Lauterbur on \(\text{CaCO}_3\) and those of Pines, Rhim and Waugh on \(\text{CaCO}_3\) and \(\text{CS}_2\).\(^{(25)}\) \(\text{C}^{13}\) and \(\text{N}^{15}\) constitute ideal nuclei for such studies since they have both low magnetogyric ratios and low isotopic abundance. Their importance in chemical and biological systems goes without saying.

The alert reader will no doubt take issue with the above remarks which appear to be somewhat naïve on two counts:

(a) dipolar broadening by abundant unlike spins

(b) low sensitivity.

Both objections are clearly legitimate. Note that in \(\text{CaCO}_3\) and \(\text{CS}_2\), \(\text{C}^{13}\) is the only significantly active nucleus. In the general, more interesting case, other "unlike" nuclei (for example 'H)
will be present in high abundance and cause a severe dipolar broadening of the rare spins under study. The problem would thus appear to revert to that encountered normally in abundant spin systems.

The problem raised in (b) is no less critical. An obvious price which we must pay for the attenuation of dipolar interaction between the spins is a reduction of the number of resonant spins in the sample and a consequent reduction in the sensitivity of NMR detection. The problem of sensitivity is a well known one in liquid studies of rare isotopes, and Fourier-transform and signal averaging techniques are employed to their full extent. \(^{(26)}\) In solids, where resolution is lower and spin-lattice relaxation times may be very long, the problem becomes much more acute, making conventional techniques essentially useless.

Lest the reader despair and turn to simpler experiments such as molecular beam studies of radical reactions, \(^{(27)}\) we remark that both problems mentioned above can be solved with surprising facility. Dipolar broadening by unlike spins is removed by strong irradiation of these spins at their resonance frequency. \(^{(28,29)}\) As in the case of J-coupling in liquids, this induces a "spin-decoupling". \(^{(30)}\) The power requirements in the solid case are much greater due to the strength of the dipolar interaction relative to J-coupling. It might appear that this spin-decoupling should be as difficult as the removal of dipolar interactions between like spins making it similar to multiple-pulse experiments.
However, it is actually much simpler due to the simpler transformation properties of the resonant spin operators, and the stability requirements on r.f. phase and amplitude are considerably less stringent.

The sensitivity problem is similarly approached using an idea established by Hartmann and Hahn. \(^{(31)}\) In the Hartmann-Hahn experiment, a system of rare spins (S) is detected by observing its accumulative effects on an abundant spin system. The language of spin thermodynamics \(^{(4,32)}\) is ideally suited to a discussion of these phenomena (see Figure 1). Basically, the experiment works as follows: the I spin system is brought into equilibrium with the lattice at a temperature \(T^L\). Normally, a large magnetization \(\gamma M <I> \sim 1/T^L\) could now be observed. Instead, the I spins are now brought into contact with the S spins which are imagined to have no spin order, i.e. an infinite spin-temperature. The contact can be established in many ways some of which will be discussed later in this paper. The simplest to visualize is the application of two strong r.f. fields, \(H_{1I}\) and \(H_{1S}\), at the I and S resonance frequencies. The former is arranged by one of several methods to spin-lock \(^{(20,21,33,34)}\) the I magnetization.

If the Hartmann-Hahn condition is satisfied, i.e.:

\[
\gamma I H_{1I} = \gamma S H_{1S}
\]  

(2)

then mutual I and S spin flips via the I-S dipolar interaction become energy conserving and cause the system to proceed rapidly
Figure 1

Simple thermodynamical picture for double-resonance. $T_{1S}$ and $T_{1T}$ are nuclear spin lattice relaxation times which are imagined to be very long, and $T_{IS}$ is a cross-relaxation time. The two energy reservoirs of I and S spins are at spin-temperatures $T^I$ and $T^S$. In the classical indirect detection method, the I spins are cooled by allowing them to equilibrate for $\sim T_{1I}$ with the lattice. The S spins are detected by bringing them into contact with the I spin reservoir and keeping them hot by one of several techniques. Energy flows at a rate of $\sim \epsilon / T_{IS}$ from the S to the I spin reservoir (where $\epsilon$ is the ratio of S to I heat capacities) causing a cumulative heating and destruction of the I spin order. Subsequent observation of a reduced I signal indicates the S resonance. The sensitivity demands that I spin order be maintained for long times $\sim T_{IS} / \epsilon$.

In the direct detection method, the I spin reservoir is used only as a source of polarization and is not observed. Following an I-S contact (the S spins are not kept hot here), the S spins are observed directly, and the signals coadded $\sim 1 / \epsilon$ times to yield a markedly enhanced S spectrum within one $T_{1I}$. 
to internal equilibrium. The result is a cooling of the S spin system by the establishment of an S spin order (in the form of a magnetization along $H_{1S}$) and a small heating of the I spin reservoir (a small decrease in the I magnetization). The effect on the I spins is very small since the S spins are rare. The process may be repeated by destroying the S spin order and again bringing them into contact with the I spins. The destruction can be performed in several ways—in the Lurie-Slichter\textsuperscript{(35)} experiment it is done by simply removing the $H_{1S}$ field and allowing $<S>$ to decay to zero.

If the cycle is repeated many times, the net effect is a substantial heating of the I spin reservoir; subsequent observation of the I magnetization yields a considerably reduced signal, leading to a greatly enhanced sensitivity in the detection of the S spin resonance.

For application to our problem, this experiment suffers from poor resolution. The I and S spins cannot be decoupled as described before since it is precisely their mutual interaction which constitutes the thermal link between their reservoirs and is necessary for the sensitive detection. We therefore make use of the I spin reservoir only as a source of polarization, and instead of detecting the S spins indirectly via the I spins, we observe them directly. The experiment is then exactly the same as the Lurie-Slichter version\textsuperscript{(35)} (of the Hartmann-Hahn experiment\textsuperscript{(31)})
described above, except that the S, and not the I magnetization is observed. Following the I-S contact (in the direct detection method we call this "cross-polarization"), the S spin decay is observed. Spin-decoupling, and thus high resolution, is achieved by the I spin irradiation used for the spin-locking. The cycle is repeated and the S signals accumulated until the I magnetization is depleted. This yields of course a large sensitivity enhancement over a conventional S free induction decay; we have therefore made some recognizable progress in our attack on problem (b), making the present approach an attractive one for high resolution NMR in solids.

The indirect detection methods can also be modified to yield better resolution. Two approaches have been proposed and used in preliminary experiments. We shall see later that depending on circumstances, these may or may not have advantages over our direct detection.

The next section describes our direct detection method, "proton-enhanced nuclear induction spectroscopy", in more detail, with reference to one typical version. Section III gives relevant experimental details and Section IV some exemplary results. In section V we discuss briefly alternative versions of our experiment and finally, compare them with the indirect detection methods.
II. DESCRIPTION OF TECHNIQUE

In this section we present a more detailed account of our direct detection method. Since both the spin-decoupling and double-resonance procedures are not new, only the aspects relevant to the present experiments are discussed. Excellent quantitative details on the double-resonance phenomena can be found in several papers. \(^{(31,35,36)}\) We indicate only how they are employed in a novel way for our purposes.

As mentioned in the introduction there are many variants to the experiment since the spin-decoupling and cross-polarization can be done in several ways. These will be discussed in Section V. For the present we have chosen to illustrate one simple version in order to make our presentation concrete for the reader inexperienced in these matters. We shall see later that this may not be the best solution from the view of technical efficiency. Since the purpose of the experiment is to provide an enhanced sensitivity and resolution, we wish to compare with conventional techniques; this is done next, following a brief theoretical digression.

A. BASIC THEORY

We consider the following system in a large external magnetic field: an abundant I spin system with a resonance frequency \(\omega_{0I}\) is dipolar coupled to a rare S spin system with resonance
frequency $\omega_{0S}$. Two strong r.f. fields with rotating components $H_{1I}$ and $H_{1S}$ are applied at frequencies of $\omega_{0I}$ and $\omega_{0S}$, respectively. This is illustrated in Figure 2a. The full Hamiltonian has the form:

$$H = \mathcal{H}_0 + \mathcal{H}_{dII} + \mathcal{H}_{dIS} + \mathcal{H}_{dSS} + \mathcal{H}_{1I}(t) + \mathcal{H}_{1S}(t)$$  \tag{3}

where $\mathcal{H}_0$ is the Zeeman interaction of I and S spins with the external field, $\mathcal{H}_d$ is the dipolar interaction and $\mathcal{H}_{1I}(t)$ and $\mathcal{H}_{1S}(t)$ describe the coupling of the I and S spins to the r.f. excitation. As shown by Redfield, it is convenient to transform to a rotating frame in which the r.f. fields are stationary. In this case we need a double rotating frame induced by the transformation:

$$R = \exp [-it(\omega_{1I}z + \omega_{1S}z)]$$  \tag{4}

In this frame, the Hamiltonian has transformed to:

$$H = \mathcal{H}_0 + \mathcal{H}_{dII} + \mathcal{H}_{dIS} + \mathcal{H}_{dSS} + \mathcal{H}_{1I} + \mathcal{H}_{1S}$$  \tag{5}

+ time-dependent terms

where $\mathcal{H}_0$ and $\mathcal{H}_d$ have the form of equation (1), and

$$\mathcal{H}_{dII} = \sum_i S_{iz} \sum_j b_{ij} I_{jz}$$

$$b_{ij} = \left(-\frac{2\gamma_I \gamma_S \hbar}{r^3} p_2(\cos \theta_i)\right) \frac{1}{i}$$  \tag{6}
Figure 2

Double rotating frame transformation. In the laboratory frame (a) the rotating components of the I and S rf have amplitudes $H_{1I}$, $H_{1S}$, and angular frequencies $\omega_I$, $\omega_S$. A rotating frame transformation, equation (4) is performed which rotates the I spins at $\omega_I$ and the S spins at $\omega_S$ about z. In this frame (b) we can effectively view the I spins in their rotating frame experiencing a static field $H_{1I}$ along z and the S spins in their rotating frame experiencing $H_{1S}$ along X. The effects of $H_{1S}$ on I spins and $H_{1I}$ on S spins can be neglected if $\omega_I - \omega_S$ is much larger than the S and I spectral widths, as is normally the case.
LABORATORY FRAME

H_I(t)

H_S(t)

\omega_I

\omega_S

(a)

DOUBLE ROTATING FRAME

I SPINS

H_{II}

S SPINS

H_{IS}

(b)
\[ \mathcal{H}_{II} = -\gamma_I H \sum_i I_{ix} \]  
\[ \mathcal{H}_{IS} = -\gamma_S H \sum_i S_{ix} \]  

The phase of the rotation is chosen to put \( H_{II} \) and \( H_{IS} \) along the \( x \) axes in the I and S rotating frames as in Figure 2b. Since we are not interested in calculating spin-lattice effects, we may discard the time dependent terms; all this is well known.

Thermodynamics can now be applied in the rotating frame since the Hamiltonian is effectively time-independent.\(^{(32b)}\)

The two terms \( \mathcal{H}_{II} \) and \( \mathcal{H}_{IS} \) are considered as reservoirs of Zeeman energy which exchange energy via the dipolar coupling with which they do not commute. The dipolar reservoir should also be included in the thermodynamics but we shall neglect it for the present since we assume that \( H_{II} \) is very large compared to internal local fields. Following Redfield, we assume that the system ultimately approaches a state of full internal equilibrium in the rotating frame described by the density matrix:

\[ \rho_{eq}^R = \frac{\exp(-\mathcal{H}_R/kT)}{\text{Tr}[\exp(-\mathcal{H}_R/kT)]} \]  

which for high temperatures and large fields is given to a good enough approximation for our purposes by:

\[ \rho_{eq}^R = \frac{1}{Z} [1 + \frac{1}{kT} (\mathcal{H}_{II} + \mathcal{H}_{IS})] \]  

where \( Z = \text{Tr} \{1\} \)
As pointed out by Hartmann and Hahn, the rate at which this single spin temperature is approached depends strongly on the magnitudes of $H_{1I}$ and $H_{1S}$. In general, each reservoir can be in internal equilibrium with a different spin temperature:

$$\rho_R = \frac{1}{Z} \left[ 1 + \frac{\gamma_{1I}}{kT_I} + \frac{\gamma_{1S}}{kT_S} \right]$$

and the two subsystems come to equilibrium in a time $T_{IS}$ (Figure 1) which depends on $\gamma_{1I} - \gamma_{1S}$. When condition (2) is fulfilled, the rate is maximal as we shall see.

The quantities of interest to us are the energy, entropy and magnetization. The Zeeman energy of the system in a state described by (11) is given by:

$$E = -\text{Tr} \left\{ \rho_R \mathcal{H} \right\} = E_I + E_S = -\frac{C_{1I}H_{1I}^2}{T_I} - \frac{C_{1S}H_{1S}^2}{T_S}$$

where $C_I$ and $C_S$ are Zeeman spin heat capacities given by:

$$C_I = \frac{\gamma_{1I}^2}{3k} \frac{I(I+1)}{N_I}$$

and similarly for $C_S$. $N_I$ and $N_S$ are the numbers of I and S spins.

The $x$ component of the magnetization in the rotating frame (i.e. along the $H_1$ field) is given by:

$$M_I = \gamma_I \mathcal{H}_I \langle \mathcal{I}_x \rangle = \gamma_I \mathcal{H}_I \text{Tr} \left\{ \rho_R \mathcal{I}_x \right\} = \frac{C_{1I}H_{1I}}{T_I}$$

and similarly for $\gamma_S \mathcal{H}_S \langle \mathcal{S}_x \rangle = M_S$. 
Finally, the entropy is given by:

\[
S = -k \text{Tr}\{\rho_R \log \rho_R\} = \text{const} - \frac{C_{II}^{11}}{2T^{I2}} - \frac{C_{S}^{1S}}{2T^{S2}} \quad (15)
\]

We now turn to an analysis of the experiments using these equations.

B. FREE INDUCTION DECAY

Figure 3 shows how we would obtain a high resolution \( S \) spectrum by conventional techniques. The rare \( S \) system is allowed to equilibrate with the lattice in the external field \( H_0 \) for \( T_{1S} \) at temperature \( T_L \), yielding, from (14), a magnetization:

\[
M_S^{(0)} = \frac{C_{S}^{H_0}}{T_L^S} \quad (16)
\]

This is observed in a free induction decay following a 90° pulse on the \( S \) spins\(^{(37,38)}\). The r.f. field on the \( I \) spins serves to decouple them, and Fourier transformation of the \( S \) decay yields a high resolution NMR spectrum. Before this can be repeated we must wait \( T_{1S} \) again; in solids \( T_1 \)'s can be extremely long and thus sensitivity enhancement by signal-averaging is rather painful. Since the \( S \) spins are rare, the signals are small; for \( S = ^{13}C \) at low temperatures we might on occasion obtain tolerable signals, but if there are many lines, or if we are dealing with a less favorable isotope such as \( ^{15}N \), then this approach becomes prohibitively difficult.
Conventional high resolution S free induction decay with I spin-decoupling. \( \theta_\mu \) indicates a \( \theta^\circ \) pulse about the \( \mu \) axis of the appropriate rotating frame and \( H_{1\mu} \) continuous irradiation along \( \mu \). The S spins are polarized every \( \sim T_{1S} \) and then observed following a \( 90^\circ \) pulse while continuously irradiating the I spins. For the purposes of the analysis in the text it is imagined that \( T_{1S} \gg T_{2S}^* \). \( S(\tau) \) is the normalized free induction decay.
I

\[ H_{lx} \]

\[ \sim T_{2S} \]

\[ \sim T_{1S} \]

H_{lx}

S

90\(\gamma\)

\[ M_s^{(o)} S(t) \]

90\(\gamma\)

\[ M_s^{(o)} S(t) \]
One particularly simple version of proton-enhanced nuclear induction spectroscopy, using $I-S$ cross-polarization. After polarization of the $I$ spins in $\sim T_{1I}$, the $I$ magnetization is spin-locked at resonance along $H_{1I}$ in the $I$ rotating frame (see Figure 5). The $S$ spins are brought into contact with the $I$ reservoir by applying a resonant $H_{1S}$ such that the Hartmann-Hahn condition, equation (2), is satisfied. The spin systems comes rapidly to equilibrium causing a small decrease in $M_I$ and a growth of $M_S$ along their $H_1$ fields. This is indicated schematically in the figure by the curves inside the $H_1$ irradiation blocks. The $H_{1S}$ field is then removed and the $S$ free induction decay observed while continuing the $I$ irradiation for spin decoupling. This is repeated $N$ times and the $S$ signals coadded until $M_I$ is reduced to $\sim 0$. For the purposes of analysis in the text it is imagined that $T_{10I}, T_{11} \gg N(T_{2S} + T_{1S})$. 

**Figure 4**
Figure 5

One version of spin-locking. Following a 90° pulse (a) bringing $M_{I}^{(0)}$ along $x$, the rf is phase shifted to come along $M_{I}^{(0)}$ and kept on continuously (b). The magnetization $M_{I}^{(0)}$ which would normally decay by spin-spin processes is spin-locked and decays by spin-lattice relaxation in a time $T_{1\rho}$. 
C. CROSS-POLARIZATION

As we mentioned in the introduction, the S spin signal can be enhanced by using the abundant I spin reservoir. The analysis follows exactly that due to Lurie and Slichter \(^{(35)}\) except that we shall be enquiring into the accumulated S signal.

The experiment is illustrated in Figure 4. In this case, the I spins are allowed to equilibrate with the lattice, yielding a magnetization:

\[
M^{(0)}_I = \frac{C_{II}H_0}{T_L} \tag{17}
\]

This is now spin-locked along the x axis in the I rotating frame by application of a 90\(^{\circ}\) pulse followed by a long phase-shifted pulse of amplitude \(H_{II}\). This is one of several ways of producing a spin-locked state and is illustrated in Figure 5.

Since the I and S systems are mutually isolated we have:

\[
\rho^{(0)}_R = \frac{1}{Z} \left( 1 + \frac{3C_{II}}{kT^{(0)}} \right) \tag{18}
\]

and from (14):

\[
M^{(0)}_I = \frac{C_{II}H_{II}}{T^{(0)}} \tag{19}
\]

which is an operational definition of \(T^{(0)}\), the I Zeeman spin-temperature in the rotating frame. From (17) and (18):

\[
T^{(0)} = T_L \frac{H_{II}}{H_0} \tag{20}
\]

so this corresponds to a cooling of the I spin system. The S
spins are now coupled to the I by turning on an r.f. field of amplitude $H_{ls}$ along the $x$ axis in the $S$ rotating frame (see Figure 2b). The magnitude of $H_{ls}$ is arranged to fulfill the Hartmann-Hahn condition (2) so that the I and S systems come rapidly ($\sim T_{IS}$) to equilibrium at a common spin-temperature $T^{(1)}$, i.e.:

$$\rho^{(1)}_R = \frac{1}{2} \left[ 1 + \frac{1}{kT^{(1)}} (\mathcal{K}_{II} + \mathcal{K}_{ls}) \right]$$

(21)

Since energy must be conserved in the equilibration process (spin-lattice relaxation times are long), we have using (12), (18) and (21):

$$\frac{C_{II}H_{II}^2}{T^{(1)}} + \frac{C_{ls}H_{ls}^2}{T^{(1)}} = \frac{C_{II}H_{II}^2}{T^{(0)}}$$

(22)

Putting (2) into (22) and rearranging we find:

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(0)}} \frac{1}{1 + \varepsilon}$$

(23)

where

$$\varepsilon = \frac{\gamma^2 C_S}{\gamma^2 C_I} = \frac{S(S+1)N_S}{I(I+1)N_I}$$

(24)

and from (14), the S magnetization following this first thermal contact is:

$$M^{(1)}_S = \frac{C_{ls}H_{ls}}{T^{(1)}} = \frac{C_S \gamma_I H_{II}}{\gamma_S T^{(1)}}$$

(25)
Using equations (20) and (23) we find from (25):

\[
M_S^{(1)} = \frac{\gamma_I}{\gamma_S} \frac{1}{1+\epsilon} \frac{C_S H_0}{T^L}
\]

or since \(\epsilon \ll 1\), to an excellent approximation

\[
M_S^{(1)} = \frac{\gamma_I}{\gamma_S} (1-\epsilon) \frac{C_S H_0}{T^L}
\] (26)

Recall from B that if we had allowed the \(S\) spins to equilibrate directly with the lattice then from (16) we would have

\[
M_S^{(0)} = \frac{C_S H_0}{T^L} ; \text{ so looking at (26), we see that even in a single cross-polarization we have gained a factor of } \frac{\gamma_I}{\gamma_S} (1-\epsilon).
\]

This is \(\sim 4\) for \(I = ^1H, \ S = ^13C\) and \(\sim 10\) for \(I = ^1H, \ S = ^15N\).

The \(H_L\) field is now removed and the decay of \(M_S^{(1)}\) is observed. Then contact is established again, and going through the same procedure, we find after \(N\) such steps:

\[
M_S^{(N)} = \frac{\gamma_I}{\gamma_S} (1-\epsilon)^n M_S^{(0)}
\]

or again to a good approximation:

\[
M_S^{(N)} = \frac{\gamma_I}{\gamma_S} e^{-N\epsilon} M_S^{(0)}
\] (27)

If the signals are added then the total cross-polarization signal after depletion of the \(I\) magnetization is:

\[
M_S^{(CP)} = \frac{\gamma_I}{\gamma_S} M_S^{(0)} \sum_{n=1}^{\infty} e^{-n\epsilon}
\]
which is to a good approximation:

\[
\frac{M_{\text{CP}}}{M} = \frac{\gamma_i}{\gamma_s} \frac{1}{\epsilon} M^{(0)}_s
\]

or \( \frac{\gamma_i}{\gamma_s} \frac{1}{\epsilon} \) times the single shot normal equilibrium signal.

**D. SIGNAL TO NOISE CONSIDERATIONS**

The calculation leading to (28) is naive in that we have neglected one important fact: the signal is necessarily measured in the presence of noise. It is the signal/noise or more precisely the data rate (S/N per unit time) in which we should be interested; obviously when N gets large enough we shall be accumulating mostly noise and degrading the signal/noise.

We assume that the noise voltage in our detector bandwidth for a given point \( S(t) \) on the \( S \) free induction decay is given by \( v_{ns} \), and that the signal voltage is given by \( K_s M_s \) when the initial magnetization is \( M_s \). The accumulated power signal to noise for this point after \( N \) steps of the cross-polarization is then

\[
\frac{(S/N)_{\text{CP}}}{(S/N)_{\text{CP}}} = \left( \frac{\gamma_i}{\gamma_s} \frac{K_s}{\sqrt{N}} \frac{M_s^{(0)}}{v_{ns}} \sum_{n=1}^{N} e^{-n \epsilon^2} \right)
\]

since the signals add coherently and the noise adds incoherently. The optimal value of \( N \) is that which maximizes (29) and is found to be given by:
Inserting this into (29) then gives us to a good approximation for optimal power signal/noise in ~ $T_{ll}$:

$$\left(\frac{S}{N}\right)_{CP} = 0.41 \left(\frac{\gamma_I}{\gamma_S}\right)^2 \frac{1}{\varepsilon} \left(\frac{K_S M_S^{(0)}}{V_{nS}}\right)^2$$

(31)

It is convenient to express the efficiency of an experiment in terms of a data rate, $Q$, the extracted signal/noise per unit time. For the cross-polarization procedure this is given by:

$$Q_{CP} = \frac{1}{T_{ll}} \left(\frac{S}{N}\right)_{CP}$$

(32)

An analogous calculation for the same point $S(t)$ on the conventional free induction decay in Section B gives us in ~ $T_{ls}$:

$$\left(\frac{S}{N}\right)_{FID} = \left(\frac{K_S M_S^{(0)}}{V_{nS}}\right)^2$$

(33)

and a data rate:

$$Q_{FID} = \frac{1}{T_{ls}} \left(\frac{S}{N}\right)_{FID}$$

(34)

Finally, combining (31) to (34) we summarize the sensitivity enhancement as:

$$Q_{CP} = Q_{CP} Q_{FID}$$

(35)

where
\[ G_{CP} = \frac{0.41}{\epsilon} \left( \frac{\gamma_I}{\gamma_S} \right)^2 \frac{T_{1S}}{T_{1I}} \]  

(36)

We remark that the whole analysis is based on \( T_1 \) and \( T_{1\rho} \) for the I spins being long enough for the duration of the full cross-polarization. If this is not so, the enhancement expressed by (36) is reduced.

For \( I = 'H \ S = ^{13}C \) in typical organic compounds, \( G_{CP} \sim 10^3 \) if \( T_{1S} \sim T_{1I} \); for \( I = 'H \ S = ^{15}N \), \( G_{CP} \sim 10^5 - 10^6 \). These get larger if \( T_{1S} > T_{1I} \) which is generally the case. In fact at low temperature, paramagnetic or chemical doping would shorten \( T_{1I} \) much more than \( T_{1S} \) due to the more efficient spin diffusion amongst the I spins.

E. ADIABATIC TRANSFER

Here we compare (36) with the most efficient process possible, namely an adiabatic one. We assume as in Figure 6 that we can somehow transfer adiabatically (and thus reversibly) all the polarization from the I to the S spin reservoir. How this can be done does not interest us at present since we wish only to calculate a figure of merit for the above experiment. Suffice it to say that the process is indeed feasible \(^{(39)}\) and will be discussed in detail elsewhere.

Before the transfer, all the polarization is in the I system and we assume the density matrix is given by (18). At
Figure 6

Schematic representation of a complete adiabatic transfer of I spin order into S spin order and observation of the S signal. This is the most efficient process possible; magnetization can be calculated by imposing conservation of entropy. For the purposes of analysis it is assumed that $T_{1I} \gg T_{AD}$. 
the end of the transfer, the $S$ spins only are polarized and thus:

$$\rho_{AD} = \frac{1}{Z} \left( 1 + \frac{\chi_{LS}}{kT_{AD}} \right) \quad (37)$$

Since we postulate that the process is adiabatic we invoke conservation of entropy. Using equation (15) this tells us:

$$\frac{C_I H_{II}^{2}}{T(0)^2} = \frac{C_S H_{LS}^{2}}{T_{AD}^{2}} \quad (38)$$

Plugging equations (16), (17) and (24) into (38) and rearranging, we find for the final $S$ magnetization:

$$\frac{M_{AD}}{M_{S}} = \frac{\gamma_I}{\gamma_S} \frac{1}{\sqrt{\varepsilon}} M_S^{(0)} \quad (39)$$

which gives us for the data rate of our fixed point in exactly the same way as before:

$$Q_{AD} = G_{AD} Q_{FID} \quad (40)$$

where:

$$G_{AD} = \frac{1}{\varepsilon} \left( \frac{\gamma_I}{\gamma_S} \right)^2 \frac{T_{LS}}{T_{II}} \quad (41)$$

Thus, looking at (36), we have lost only a factor of 0.41 in the cross-polarization technique. Considering the simplicity of our approach, this is certainly not a great price to pay.
III. EXPERIMENTAL

The basic features of the pulsed NMR spectrometer used in these experiments have been described in detail elsewhere, (40-42) Changes were made to accommodate the double-resonance facilities, and these, together with the relevant experimental details are described in this section. We also make some comparisons between spectrometer requirements for these experiments and those for multiple-pulse experiments.

A. SPECTROMETER

A schematic diagram of the spectrometer is shown in Figure 7. The external magnetic field for our experiments was 22.8 KG provided by an Oxford Instruments superconducting solenoid. The configuration shown is for $^1H$ (97.2 MHz) and $^{13}C$ (22.4 MHz). Two synthesizers provide the basic rf for the two frequencies. Operation is superheterodyne; the intermediate frequency of 30 MHz is split into four channels by a quadripole network. (43) Three of these, with relative phases of 0°, 90° and 180° are gated by the 'H gating network, controlled by the pulse programmer, to produce the 'H pulse sequence. Transmission of 97.2 MHz is from an amplified signal from the single sideband (lower) generator. This is necessary since the 'H transmitter is a wideband device (44) and power considerations are crucial.
Figure 7

Block diagram of double-resonance spectrometer shown in configuration for $^{13}$C-$^1$H operation with $^{13}$C detection.
Figure 8

Low temperature double-resonance probe adapted to geometry of superconducting solenoid. The crossed coil geometry is shown in more detail in Figure 9.
Crossed coil geometry for double-resonance experiments. Diameter of the inner coil is ~0.6 cm and length ~1.5 cm. Support is provided by a ~1 mm pyrex tube between the two coil systems. Care is taken to mount the coils orthogonally to reduce mutual coupling and leakage into the low frequency detection system.
Since the final $^{13}$C stage is tuned, SSB operation is not required for the 24.4 MHz and this is obtained directly from 54.4 MHz and the fourth 30 MHz channel. We do not go into a detailed discussion of power requirement, since these vary greatly from experiment to experiment. As an example, for the high Q, 5 mm sample coils used in most of our $^{13}$C work, ~200 watts of rf power has been found to suffice for both final stages.

Reception of the 24.4 MHz signal is made with a tuned preamplifier (several have been used) and dual phase detection produces quadrature free induction decay signals for processing by complex Fourier transformation. (40,45) One problem in reception for these experiments is that of isolating the high-power 'H frequency which leaks into the $^{13}$C receiving system and produces large (bias) voltages at the preamplifier input. This is solved in several stages:

(a) orthogonal sample coils
(b) 97.2 MHz trap filter in the $^{13}$C receiver line.

Without these precautions, detecting the small $^{13}$C signals while irradiating the 'H spins (decoupling) with high power rf is exceedingly difficult.

B. PROBE

The low temperature double-resonance probe, depicted in Figure 8, is designed for operation in the superconducting solenoid geometry. A double coil is used; the inner one is a
horizontal solenoid of diameter ~0.6 cm and length ~1.5 cm
wound around the sample tube and used for the low frequency
transmission and reception. The outer is of Helmholtz geometry,
insulated from the inner one by ~1 mm of pyrex dielectric, and
provides the high power 'H fields. Figure 9 shows in more detail
the double coil geometry.

Matching and tuning of these coils is accomplished by stan-
dard techniques; the $^{13}$C system can be tuned in situ by means
of the variable capacitor which consists of two concentric copper
tubes with a glass dielectric. The 'H coil is connected via a
$\lambda/2$ coaxial cable and tuning and impedance matching are done
remotely. The coaxial cables depicted contain high temperature
resistant teflon dielectric, since conventional materials are
prone to melting on extended application of high power rf.(46)

Temperature control is achieved in a standard way by passing
dry nitrogen gas through a cooled copper coil and then into the
sample chamber through evacuated transfer lines.

Samples were prepared in cylindrical pyrex ampules with o.d.
0.5 cm and sealed under vacuum.

C. TIMING AND SIGNAL PROCESSING

An important consideration for the initial period of experi-
mentation for the double resonance was timing flexibility. Sev-
eral versions of the experiment are possible and each has
advantages and disadvantages which are strong functions of the
circumstances. In the present spectrometer, timing is provided by a homelbuilt pulse programmer (41) under control of an on-line minicomputer (PDP 12). This provides variable pulse widths and delays for the four rf channels, and extremely flexible counting facilities. Pulse programs are entered through the computer from magnetic tape storage. This leads to very convenient interchangeability of programs and makes the experimentation with new revisions and sequences a simple matter.

In addition to supervising the timing, the computer is also responsible for signal processing. After each cross-polarization, the free induction decay is digitized and stored directly in computer core. Subsequent processing includes signal averaging, Fourier transformation, apodization and digital smoothing, plotting, mass storage, etc. The spectrometer operates with a dual phase detector and advantage can be taken of this by using complex Fourier transformation which extends the effective spectral bandwidth by a factor of two.

Timing requirements vary from experiment to experiment. Cross-polarization times vary in the range ~ 0.1 – 1 msec when condition (2) is satisfied. The decoupling time (~T2S*) depends of course on the resolution achievable or desirable in the experiment. Ideally, this should approach the pure S-S dipolar broadening which for 13C is expected to be of the order of ~10 Hz. (47) In practice, other limitations are inherent in
our experiments, including magnetic field inhomogeneities and incomplete spin-decoupling. Routinely we have operated with ~ 60 Hz linewidths (as evidenced from rigid single crystal studies) but have on occasion reduced linewidths to ~ 20 Hz in favorable cases. For $^{15}$N, there is considerable broadening by the abundant $^{14}$N isotope (~ 200 Hz) and data collection requires only ~ 10 msec per contact. Of course these requirements may change as auxiliary techniques such as sample-spinning are implemented.

In favorable cases, where $T_{1\text{I}}$ is not too long a single cross-polarization can be useful. One then obtains a single free induction decay per $T_{1\text{I}}$ with $\gamma_I/\gamma_S$ enhancement. Many of our $^{13}$C experiments were done in this way since the sensitivity is sufficient and sample heating by prolonged irradiation is avoided. For the less abundant isotopes, like $^{15}$N, multiple contact was found to be essential.

D. ADDITIONAL COMMENTS

We make some final remarks concerning the stability requirements for these experiments as compared to the multiple-pulse techniques. In multiple-pulse experiments, phase and amplitude stability are of crucial importance since the process requires long term coherent excitation of the spins. Any instabilities will cause accumulative precessional phase lags between the spins and a subsequent rapid destruction of the magnetization.
In addition, phase transients occur with the turn-on and turn-off of the rf pulses and these must either be minimized by using low Q probe circuits or a tedious amount of tuning must be performed to eliminate their effects. Since we are dealing in the dilute spin case, with heteronuclear decoupling the requirements are considerably less stringent on several counts:

(i) power: both experiments require sufficient rf field strengths to decouple spins interacting with strong dipolar couplings. However, in the double-resonance experiment decoupling is continuous (since observation is at a different frequency); this means that multiple-pulse experiments require $\frac{1}{\delta}$ times the power to produce the same average $H_1$ field (where $\delta$ is the duty cycle), since power is proportional to $H_1^2$. An additional advantage is indicated in consideration (iii) below.

(ii) stability: neither the spin-locking nor the spin-decoupling require extraordinary stability of phase or amplitude of the rf. Only if quantitative cross-relaxation studies are the purpose of the research do stability requirements assume any importance, since $T_{1S}$ is sensitive to the $H_1$'s.

(iii) probe Q: it is advantageous for the purposes of producing large $H_1$ fields and enhancing the sensitivity of signal detection to use high Q probe circuits. In multiple-pulse work this cannot be done indiscriminately since the magnetization must be sampled between closely spaced pulses, and receiver
dead-time due to probe ringing becomes an important consideration. In the double-resonance experiments, of course, there is no such problem and high Q circuits like those used in liquid studies, can be implemented. In fact our initial experiments have utilized circuits with $Q \sim 100$ at 24 MHz which is far greater than one is accustomed to in solid state multiple-pulse NMR.

Finally we remark that the above considerations are not intended to imply that double-resonance always constitutes a wiser selection than multiple-pulse NMR, since both are relevant to different conditions. For abundant spins such as $^1H$, $^{19}F$, the double-resonance procedure is irrelevant and one must resort to the more challenging technical requirements of multiple-pulse NMR. We think that the two techniques will probably find their ultimate usefulness working in concert on the same systems--the multiple pulse approach on the abundant spins ($^1H$, $^{19}F$) and the cross-polarization on the dilute spins ($^{13}C$, $^{15}N$).
IV. RESULTS

In this section we present a discussion and some exemplary results to illustrate the utility and scope of the technique. We do not present a detailed and quantitative account of the experiments and results—these have been dealt with elsewhere and detailed references to them will be made where appropriate.

A. POLYCRYSTALLINE SAMPLES

Our main interest in the preliminary experiments has been the measurement of chemical shielding anisotropies \(^{(48)}\) which are not available from liquid measurements. This information should be extremely valuable since it is related to molecular structure and is a much more severe test of chemical shielding theories than is the isotropic shift alone.

To remind the reader, the chemical shift is a second rank tensor \((\sigma)\) which transforms under a rotation from \((x,y,z)\) to \((x',y',z')\) as:

\[
\sigma'_{ik} = \sum_{j,l} R_{ij} R_{kl} \sigma_{jl} \tag{42}
\]

In high field, only \(\sigma_{zz}\) in the laboratory system of coordinates is of interest; \(^{(49)}\) if \(R(\phi,\theta,\psi)\) is the transformation from the principal axes \((1,2,3)\) of \(\sigma\) to the laboratory system \((x,y,z)\) in terms of the Euler angles \(\phi,\theta,\psi\) then the observed shift \(\sigma = \sigma_{zz}\) is given by:
\[ \sigma = \sin^2 \theta \cos^2 \phi \sigma_{11} + \sin^2 \theta \sin^2 \phi \sigma_{22} + \cos^2 \theta \sigma_{33} \quad (43) \]

where \( \sigma_{11}, \sigma_{22}, \sigma_{33} \) are eigenvalues of \( \sigma \) and we adopt the convention:

\[ \sigma_{11} \leq \sigma_{22} \leq \sigma_{33} \quad (44) \]

In a polycrystalline sample, the effective chemical shift \( \sigma_{zz} \) must be weighted according to the probability of \( (\theta, \phi) \), yielding the following absorption lineshape derived by Bloembergen and Rowland:

\[
I(\sigma) \propto \begin{cases} 
\left( \frac{\sigma_{33}-\sigma_{11}}{\sigma-\sigma_{11}} \right)^{\frac{1}{2}} K(\sin \alpha) & \text{for } \sigma_{22} < \sigma < \sigma_{33} \\
\left[ \frac{(\sigma_{33}-\sigma_{11})(\sigma_{33}-\sigma_{22})}{(\sigma_{33}-\sigma)(\sigma_{22}-\sigma_{11})} \right]^{\frac{1}{2}} K\left( \frac{1}{\sin \alpha} \right) & \text{for } \sigma_{11} < \sigma < \sigma_{22} \\
0 & \text{elsewhere}
\end{cases} \quad (45)
\]

where:

\[
\sin^2 \alpha = \frac{(\sigma_{22}-\sigma_{11})(\sigma_{33}-\sigma)}{(\sigma_{33}-\sigma_{22})(\sigma-\sigma_{11})} \quad (46)
\]

and \( K(k) \) is the complete elliptic integral of the first kind:

\[
K(k) = \int_{0}^{\pi/2} (1 - k^2 \sin^2 \gamma)^{-\frac{1}{2}} d\gamma \quad (47)
\]

This lineshape is depicted in Figure 10(a). \( \sigma_{11}, \sigma_{22} \) and \( \sigma_{33} \) may be read off directly from the lineshape. For a tensor
Absorption lineshapes for polycrystalline samples with (a) axially asymmetric, and (b) axially symmetric chemical shielding tensor $\tilde{\sigma}$. The lineshapes are given by equations (45) and (48). The principal values $\sigma_{11}$, $\sigma_{22}$, $\sigma_{33}$ ($\sigma_{11} = \sigma_{22} = \sigma_{\perp}, \sigma_{33} = \sigma_{||}$ in (b)) can be read off directly.
Proton-enhanced $^{13}$C spectra of polycrystalline compounds containing carbonyl groups. The low field peaks are from the C=O and the high field ones from CH$_3$. The spectra were obtained using the sequence in Figure 4 with various values of N, typically in minutes. Temperatures were all close to liquid nitrogen. Note the sensitivity of $\sigma_{22}$ to substituents. The horizontal axis is calibrated in ppm relative to an external reference of liquid benzene (23°C).
Proton-enhanced $^{13}$C spectra of polycrystalline methanol and dimethyl disulfide. Note how $\sigma_{11}$ and $\sigma_{22}$ change when we go from O-CH$_3$ to S-CH$_3$ whereas $\sigma_{33}$ remains relatively unperturbed. The horizontal axis is in ppm relative to external liquid benzene (23°C).
DIMETHYL DISULFIDE
-186 °C

METHANOL
-186 °C
with uniaxial symmetry the lineshape simplifies to:

\[
I(\sigma) \propto \begin{cases} 
(\sigma - \sigma_\perp)^{-\frac{1}{2}} & \text{for } \sigma_\perp < \sigma < \sigma_\parallel \\
0 & \text{elsewhere}
\end{cases}
\]  

(48)

where we have taken the case:

\[
\sigma_{11} = \sigma_{22} = \sigma_\perp \quad \sigma_{33} = \sigma_\parallel
\]  

(49)

This is shown in Figure 10(b).

Although this is all well known, it is very seldom that such lineshapes have been observed in NMR; except in unusual favorable cases (examples are given in references 51-55)\(^{(25,51-55)}\) or where multiple pulse techniques are applicable,\(^{(56)}\) they are normally obscured by the strong dipolar broadening.

Figure 11 shows proton-enhanced \(^{13}\text{C}\) spectra in some polycrystalline organic compounds at low temperatures. The low field absorption is due to the carbonyl carbon in each compound. The lineshapes conform to those in figure 10 and the elements of \(\tilde{\sigma}\) are read off with facility. Note the extreme sensitivity of \(\sigma_{22}\) to substituents. Methyl group \(^{13}\text{C}\) shielding (e.g. the high field absorption figure 11) displays somewhat smaller anisotropies; an interesting feature in this case is that \(\sigma_{33}\) remains relatively unperturbed while \(\sigma_{11}\) and \(\sigma_{22}\) are very sensitive to
substituent. An example of this is shown in Figure 12 which
compares CH$_3$ bonded to oxygen and CH$_3$ bonded to sulphur.

In this way we have determined the elements of $\sigma$ for several
low abundance nuclei in a variety of compounds in polycrystalline
form. These include:

(a) $^{13}$C: An extensive list of chemical shielding para-
parameters illustrating different functional groups and
substituents has been reported for organic com-
ounds.\textsuperscript{(58,59)} More recent measurements include
acetonitrile, nitromethane, oxalates, glycine,
ethylenes and organometallic materials.\textsuperscript{(60)}

(b) $^{29}$Si: Chemical Shielding parameters have been repor-
ted for a number of organo-silicon compounds.\textsuperscript{(61)}

(c) $^{15}$N: Chemical shielding parameters were obtained
for ($\text{NH}_4$)$_2$SO$_4$, NH$_4$NO$_3$ and glycine;\textsuperscript{(62)} more recently
some additional compounds have been studied includ-
ing acetonitrile, nitromethane, dimethylformamide,
etc.\textsuperscript{(60)}

Conditions for these experiments varied. Typically, for
the $^{13}$C and $^{29}$Si work high frequency $H_1$ was $\sim$ 12 G and low
frequency $H_1$ was $\sim$ 40-50 G. For the $^{15}$N work, the corresponding
values were $\sim$ 5 G and $\sim$ 40-50 G.

\textsuperscript{†} These are reproduced in Table I which follows.
TABLE I

\[ ^{13}\text{C} \text{ Shielding parameters in some organic compounds} \]
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<tr>
<th>Carbon Type</th>
<th>Compound</th>
<th>Formula</th>
<th>T(°C)</th>
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Note: The table above lists various organic compounds along with their chemical formulas, boiling points (T), and some other properties (σ₁₁, σ₂₂, σ₃₃, σ, σ₁). The values represent specific properties of each compound, with T denoting the boiling point in °C.
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B. MOTIONAL EFFECTS

The type of spectra we have seen above may be severely modified in the presence of motion. Three types of motion are particularly relevant:

(i) macroscopic sample rotation
(ii) molecular reorientation
(iii) molecular conformational changes

In the case that (i) is performed about an axis inclined at the magic angle (54° 44') to $\mathbf{H}_0$, it is easy to show that the average shift $\bar{\sigma} = \bar{\sigma}_{zz}$ over one cycle of rotation becomes independent of orientation and is given by the isotropic shift $\sigma_i$:

$$\sigma_i = \text{Tr} \bar{\sigma} \approx \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (10)$$

This means that in a polycrystalline sample only a single sharp line will be observed, for each inequivalent nucleus, at $\sigma_i$, if the above rotation is performed rapidly compared to the anisotropy spread $\sigma_{33} - \sigma_{11}$. This provides a convenient means of retaining the sensitivity of the cross-polarization and eliminating the broadening due to chemical shielding anisotropy where the latter is of no interest or difficult to evaluate due to overlapping peaks. It would certainly be a valuable accessory in the use of these techniques for structural studies in the solid state. (63)

The motion mentioned in (ii) may also manifest itself in
these experiments and indeed may on occasion serve some useful purpose. A trivial case is that of rapid isotropic or nearly isotropic molecular reorientation in the solid. In this case the chemical shielding anisotropy is averaged to zero and we should expect to see a sharp line at $\sigma_i$. Since the intramolecular I-S dipole-dipole coupling is also averaged away, the proton-enhancement cross-polarization proceeds entirely through the average intermolecular dipole-dipole coupling. A simple example of this phenomenon was provided by our early spectrum of adamantane using this technique.\(^{23b}\) As is well known, adamantane undergoes rapid ($t_C \sim 10^{-11}$ sec) molecular rotation at 300 K.\(^{64}\) and indeed two sharp lines were obtained in the solid $^{13}\text{C}$ spectrum.

An additional example is afforded by another "roundish" molecule, camphor, whose solid state $^{13}\text{C}$ spectrum is shown in Figure 13. Eight lines are resolved and the spectrum compares well with the high resolution spectrum in solution.\(^{65}\)

Other molecules have been found to behave similarly including TMS, neopentane, cyclohexane, etc. In all these cases the requirements for proton $^1H$ fields are much less stringent in decoupling since the average dipolar interactions are reduced by the motion. Fields of $\sim 3G$ were found to produce acceptable resolution.

A more interesting case is that of very anisotropic molecular
Proton-enhanced $^{13}$C spectrum of solid polycrystalline camphor. In this case, no anisotropy of the $^{13}$C chemical shift is observed since the molecules undergo rapid reorientation more or less isotropically. The spectrum is similar to that obtained in solution; the resolution is worse, but the sensitivity of detection substantially greater. Spectra such as these can be obtained in seconds. The reference is again external liquid benzene.
solid camphor
23°C
motion, for example restricted rotation about one axis in the molecule. When this is rapid a partial averaging of shielding tensor ensues. Again, the rotation may be described by the operator $R(\alpha, \beta, \gamma(t))$ in terms of the Euler angles $\alpha, \beta, \gamma(t)$ in the principal axes system; this is illustrated in Figure 14. If an average is performed over $\gamma(t)$ we find for the effective shielding tensor $\bar{\sigma}$ the principal values:

$$
\bar{\sigma}_{33} = \bar{\sigma}_{11} = \sin^2 \beta \cos^2 \alpha \sigma_{11} + \sin^2 \beta \sin^2 \alpha \sigma_{22} + \cos^2 \beta \sigma_{33}
$$

$$
\bar{\sigma}_{11} = \bar{\sigma}_{22} = \bar{\sigma}_\perp = \frac{1}{2} (3 \sigma_i - \sigma_{33})
$$

(51)

So the average shielding tensor displays (as expected) axial symmetry about the rotation axis. This may be very helpful in polycrystalline samples for assigning $\sigma_{11}$ to the molecular frame if something is known or assumed about the motion. On the other hand, where the orientation information is available from other sources (see below) this may be used to learn a great deal about the nature of the motion.

We have reported a striking example of such behavior in polycrystalline hexamethylbenzene. The low temperature aromatic region of the $^{13}$C spectrum exhibits an axial asymmetry and at high temperatures, with the onset of molecular motion the spectrum displays pseudoaxial symmetry, with
Coordinate systems describing anisotropic molecular reorientation about one axis in the molecule. \((1, 2, 3)\) are the principal axes of \(\vec{\gamma}_\text{z}\), \((\overline{1}, \overline{2}, \overline{3})\) are the rotating system about \(\overline{3}\). When rotation is rapid, an average over \(\gamma(t)\) is taken and one finds the average shielding tensor \(\overline{\vec{\sigma}}\) to be axially symmetric about \(\overline{3}\). In the text is is shown how this may be used to learn about the orientation of \((1, 2, 3)\) in the molecule.
\[ \overline{\sigma} = \sigma_{33} \]
\[ \overline{\sigma} = \frac{1}{2} (\sigma_{11} + \sigma_{22}) \]  \hspace{1cm} (52)

This shows that \( \beta = 0 \) in (51); i.e. rotation is about the molecular axis 3 corresponding to \( \sigma_{33} \). Since it is known that the motion in hexamethylenobenzene, like that in benzene, consists of reorientation about the \( C_6 \) axis, this immediately assigns \( \sigma_{33} \), the most shielded component, to the \( C_6 \) axis. The enhanced shielding of the ring carbons perpendicular to the aromatic plane has subsequently been verified in single crystal experiments.

Finally, we mention that the motion indicated in (iii), molecular conformational change, may also be studied using these techniques. Solid state \(^{13}\)C NMR should provide a powerful means of treating conformational processes in solids, just as conventional NMR has served a vital role in studying these processes in liquids. The information content in solid state spectral changes should be greater due to the orientational information contained in the chemical shielding anisotropy.

C. SINGLE CRYSTAL STUDIES

Although the principal values of \( \sigma \) are of great interest, valuable additional information could be obtained from the orientation of the principal axes in the molecular frame, thus specifying the full shielding tensor. In polycrystalline spectra this
information is generally, but not always, lost. There are several ways to approach this problem the most direct and clear cut of which is by working with single crystals, where these are available.

If we denote, as before, the laboratory coordinate system as \((x,y,z)\), the principal axis system of \(\sigma \approx \) as \((1,2,3)\) and some axes fixed in the crystal as \((X,Y,Z)\), then the elements of \(\sigma \approx \) in the \((XYZ)\) system can be obtained by rotating the crystal about three independent axes and recording the chemical shift \(\sigma (= \sigma_{zz}\) as mentioned before) vs. rotation angle. Computation is simplified if the rotations are about orthogonal axes, say \(X\ Y\) and \(Z\). For example, a rotation about \(X\) perpendicular to \(H_0\) with \(Z\) along \(H_0\) (= \(z\)) for \(\theta = 0\) yields:

\[
\sigma(\theta) = \frac{1}{2} (\sigma_{yy} + \sigma_{zz} - \frac{1}{2} (\sigma_{yz} + \sigma_{zy}) \sin 2\theta
\]

\[+ \frac{1}{2} (\sigma_{zz} - \sigma_{yy}) \cos 2\theta
\]

\[= A + B \sin 2\theta + C \cos 2\theta \tag{53}
\]

and similarly with permutations, for rotations about \(Y\) and \(Z\). \(A, B\) and \(C\) are determined by least-squares fitting of \((53)\) to the experimental rotation plot and from three such plots, nine equations are obtained for the six elements of the (symmetric part of) \(\sigma \approx \) in the crystal frame:

\[
\sigma_{xx'}, \sigma_{yy'}, \sigma_{zz'}, \frac{1}{2} (\sigma_{xz} + \sigma_{zx}), \frac{1}{2} (\sigma_{xy} + \sigma_{yx}), \frac{1}{2} (\sigma_{yz} + \sigma_{zy}) \tag{54}
\]
These are again solved by least-squares fitting. In the more general case that the rotations are not about orthogonal axes, then the rotations in (53) contain all six elements of (54) and a more general least-squares fitting is used. Once the elements of (54) have been obtained, the tensor is diagonalized, yielding the eigenvalues $\sigma_{11}^r$, $\sigma_{22}^r$, $\sigma_{33}^r$, and the corresponding eigenvectors; the eigenvectors give the orientation of $(1,2,3)$ in $(X,Y,Z)$. If the molecular orientation in the crystal is known, say from x-ray studies, then $(1,2,3)$ may be related to the molecular geometry, yielding the fullest possible information on $\sigma$.

We have undertaken such studies in several crystalline compounds. Two initial systems to be studied, contain aromatic and carbonyl groups. In the former case, a study of $^{13}\text{C}$ in single crystal durene (1,2,4,5-tetramethylbenzene) shows the most shielded element, $\sigma_{33}^r$, for the aromatic carbon to be perpendicular to the plane of the molecule.\(^{(68)}\) In addition, the methyl groups present substantial perturbations and the chemical shielding anisotropy is markedly different for ring carbons with and without methyl groups; this was not evident from the powder spectra.\(^{(59)}\) In the second case, single crystals of ammonium oxalate and glycine show the $^{13}\text{C}$ $\sigma_{33}$ to be perpendicular to the COO\textsuperscript{−} plane. Results on these and other experiments will be presented in detail elsewhere.\(^{(71)}\)
We mention briefly, in passing, that even when single crystals are not available, a substantial amount of orientational information may be extracted by auxiliary experiments. One possibility already mentioned is that of molecular motion. Another is to utilize dipolar splitting by a third nucleus (like or unlike S, unlike I). For $^{13}\text{C} - ^{1}\text{H}$, the third nucleus could be $^{13}\text{C}$, $^{2}\text{H}$, $^{14}\text{N}$ etc. From the lineshape in a polycrystalline sample, information can be obtained on the mutual orientation of the principal axes of $\sigma$ and the dipolar interaction tensor. Since the latter have a well defined orientation in the molecule this is a useful way of assigning $\sigma$ to the molecular frame. An additional possibility is the study of cross-polarization times (see below). A study of the differential cross-polarization times for different regions of the S spectrum should yield additional information on $\sigma$ since these are also related to geometry through the orientation-dependent I-S dipolar interactions. Studies of both these types are in progress for several compounds from which crystals cannot be grown with facility.

D. CROSS-POLARIZATION DYNAMICS

The theoretical discussion in Section II assumed that the cross-polarization step (Figure 4) proceeded to full equilibrium between I and S. It is possible to learn a lot about orientation and motion in solids by interrupting this step after a time $\tau$ and observing the high resolution S spectrum as a function of
\[ \tau. \text{ This would measure the I-S cross relaxation times for different lines or portions of the S spectrum in much the same spirit that high resolution } T_1 \text{ measurements are made in liquids.} \]

We do not go into a detailed discussion of the cross-relaxation since we have performed no quantitative experiments. We point out only the principal aspects of the theory relevant to our experiments and mention the possible potential in structural and dynamical studies.

If we assume that the coupling term \( \mathcal{K}_{dI}^0 \) in (5) is a perturbation on the large reservoir terms \( \mathcal{K}_{lI} \) and \( \mathcal{K}_{lS} \), then we can arrive at an exponential form for the flow of energy between the I and S systems:

\[ \frac{d}{dt} \left( \frac{1}{T_I} - \frac{1}{T_S} \right) = - \frac{1}{T_{IS}} \left( \frac{1}{T_I} - \frac{1}{T_S} \right) \]  

(55)

The cross-relaxation time \( T_{IS} \) is calculated by the density matrix perturbation approach used by McArthur, Hahn and Walstedt. For the case of the resonant spin-locking version (Figure 4) which we have discussed, we find:

\[ \frac{1}{T_{IS}} = \frac{1}{2} \langle \Delta \omega^2 \rangle_{IS} \int_0^\infty f(\tau) \cos \Delta \omega \tau d\tau \]  

(56)

where:

\[ \Delta \omega = \gamma_{lI} - \gamma_{lS} \]  

(57)
\[ <\Delta \omega >_{IS} \] is the S second moment due to I-S dipolar interactions

\[ <\Delta \omega >_{IS} = - \frac{\text{Tr}[K_{\text{dis}}^0 \sum_i S_{i\text{ix}}]^2}{\text{Tr}[(\sum_i S_{i\text{ix}})^2]} \] (58)

and \( f(\tau) \) is the autocorrelation function of \( K_{\text{dis}}^0 \) modulated by \( K_{\text{dii}}^0 \)

\[ f(\tau) = \frac{\text{Tr}(\sum_i b_i I_{i\text{ix}}) \exp(-\frac{i}{2\hbar} K_{\text{dii}}^0 \tau) (\sum_i b_i I_{i\text{ix}}) \exp(\frac{i}{2\hbar} K_{\text{dii}}^0 \tau)}{\text{Tr}[(\sum_i b_i I_{i\text{ix}})^2]} \] (59)

\( K_{\text{dii}}^0, K_{\text{dis}}^0 \) and \( b_i \) are given in equations (1) and (6). The form of \( f(\tau) \) can be determined experimentally by measuring its Fourier transform \( \frac{1}{T_{IS}} \) vs. \( \Delta \omega \) (since it is practically impossible to calculate \( f(\tau) \) exactly) as in the work of McArthur, Hahn and Walstedt.\(^{36}\) We have not done this but for the present assume that the behavior in our case is also exponential i.e.:

\[ \frac{1}{T_{IS}} \propto \exp(\Delta \omega \tau) \] so:

\[ f(\tau) = \frac{1}{1 + \frac{\tau^2}{\tau_c^2}} \] (60)

The exact form of \( f(\tau) \) is not crucial for the purposes of our discussion where the Hartmann-Hahn condition \(^{31}\) (2) is satisfied, \( \Delta \omega = 0 \). The correlation time \( \tau_c \) is given, comparing (56) and (60), by:
\[ \frac{1}{\tau_c^2} = -\frac{1}{8} \frac{\text{Tr} \left[ K_0^{dII', \sum b_i I_{ix}^i} \right]^2}{\text{Tr}(\sum_i b_i I_{ix})^2} \] (61)

Plugging this into (56) and taking the case that \( \Delta w_1 = 0 \) we get:

\[ \frac{1}{T_{IS}} = C_{IS} <\Delta w^2>_{IS} <\Delta w^2>_{II}^{\frac{1}{4}} \] (62)

where \( <\Delta w^2>_{II} \) is the normal high field truncated second moment:

\[ <\Delta w^2>_{II} = -\frac{\text{Tr} \left[ K_0^{dII', \sum I_{ix}^i} \right]^2}{\text{Tr}(\sum_i I_{ix})^2} \] (63)

\( C_{IS} \) is a lumped constant given by:

\[ C_{IS} = 3\pi \left( \frac{\sum_i a^2_{ij} \sum b^2_i}{N_i \sum_{i+j} a^2_{ij} \left[ (2b_i + b_j)^2 + (b_i + 2b_j)^2 \right]} \right)^{\frac{1}{4}} \] (64)

and \( a_{ij} \) is the geometrical factor in (1) for I spins

\[ a_{ij} = \frac{-\gamma_i^2 \hbar^2 p_2(\cos \theta_{ij})}{r_{ij}^3} \] (65)

From (62) we see that the dependence of \( T_{IS} \) on geometry is contained predominantly in \( <\Delta w^2>_{IS} \) and to a lesser extent in the remaining factors. Typical values of \( <\Delta w^2>_{IS} \), \( <\Delta w^2>_{II} \) and \( C_{IS} \) indicate that \( T_{IS} \) should range from \( \sim 0.1-1 \) msec for \(^{13}\text{C} - ^1\text{H} \) as we have indeed observed.
A good example of this behavior is exhibited by the $^{13}$C NMR of solid polycrystalline benzene. Figure 15(b) shows the normal proton-enhanced spectrum with full cross-polarization. The spectrum displays an axial symmetry due to rapid reorientation about the C$_6$ axis, as discussed in Section IV.A. The line-shape is that of equation (48) (Figure 10(b)) with $\sigma$ given by:

$$\frac{\sigma - \sigma_\perp}{\sigma_\parallel - \sigma_\perp} = \cos^2 \beta$$

(66)

where $\beta$ is the angle between the C$_6$ axis and $H_0$ as shown in Figure 15(a). Figures 15(c), (d), show the effects of cross-relaxation. For $^{13}$C, the main contribution to $\langle \Delta \omega^2 \rangle_{IS}$ is intramolecular and is given by:

$$\langle \Delta \omega^2 \rangle_{IS} = \langle \Delta \omega^2 \rangle_0 \left( P_2(\cos \beta) \right)^2$$

(67)

where $\langle \Delta \omega^2 \rangle_0$ is the intramolecular second moment for $\beta = 0$, since the dipolar interaction is proportional to $P_2(\cos \beta)$. This predicts that the cross-relaxation should be strongly inhibited at the magic angle ($54^\circ 44'$) where $P_2(\cos \beta) = 0$, i.e.

$$\frac{\sigma - \sigma_\perp}{\sigma_\parallel - \sigma_\perp} = \frac{1}{3}$$

(68)

This is indeed observed in Figure 15 in agreement with the result obtained using indirect detection by Yannoni and Bleich. Note, however, that the distortion due to cross-relaxation is a
Effects of incomplete cross-relaxation in proton-enhanced $^{13}$C NMR of solid polycrystalline benzene at -50°C. The molecule is undergoing rapid reorientation about the $C_6$ axis which makes an angle $\beta$ with $H_0(a)$. The spectra are obtained from a single-contact version of Figure 4 (N=1) with variable $\tau$. For long $\tau > T_{1S}$ (b) we see a fully relaxed $^{13}$C spectrum. For short $\tau$, we see that $^{13}$C in molecules with $P_2(\cos \beta) \sim 0$ (i.e. $rac{\sigma_+ - \sigma_0}{\sigma_+ - \sigma_-} \sim \frac{1}{3}$) cross-polarize very slowly as expected from theory.
(a) 

(b) \( \tau_{mix} = 10 \text{msec} \)

(c) \( \tau_{mix} = 2 \text{msec} \)

(d) \( \tau_{mix} = 1 \text{msec} \)

\[
\frac{\sigma - \sigma_\perp}{\sigma_\parallel - \sigma_\perp}
\]
necessary consequence of the latter technique, whereas it is an option in our direct detection method.

A quantitative study would necessitate a calculation of the intra- and intermolecular contributions to $<\Delta w^2>_{\text{IS}}$ and $<\Delta w^2>_{\text{II}}$ from the crystal structure. It is known, for example, that in benzene both contributions are about equal for $<\Delta w^2>_{\text{II}}$. In addition, from the experimental point of view, a calibration of the $H_1$'s would be essential—in our case this was not done due to a rather large instability in the amplitudes of the rf. Thus at present no quantitative discussion is pertinent and only the relative behavior discussed above is meaningful. A full quantitative study of this system (including the case $\Delta w_1 = 0$ to check the form of $f(\tau)$ in (59)) would be very interesting.

Another case which we have studied is solid adamantane at room temperature. There, both sharp $^{13}$C lines are found to cross-polarize at the same rate ($\sim 1$ msec for the conditions of our experiment). This is in line with the isotropic motion notion which wipes out the anisotropy in $<\Delta w^2>$. Cross-relaxation proceeds purely by intermolecular dipolar coupling. If there was no motion, the carbon with two protons bonded would be expected to cross-polarize more rapidly than that with one.

Preliminary results have also been reported for $^{13}$C spin-lattice relaxation in solid benzene. This is a useful additional experiment to the cross-relaxation, and also fits in with
accepted model of anisotropic motion. (67) In adamantane, spin-lattice relaxation does distinguish the two carbons, that with two protons relaxing more rapidly (as expected for dipolar relaxation) as in solution. (77) Full details on these experiments will be presented separately.
V. ALTERNATIVE VERSIONS

The discussion so far has centered on one particular version of the double-resonance experiment. This has served, we hope, to illustrate the main features of the technique. In this section we wish to point out that many versions are possible and that each one, or some combinations thereof may be more advantageous in different circumstances. We first talk about alternative direct detection methods and then mention briefly some high resolution modifications of the direct detection.

A. DIRECT DETECTION

For the purposes of this discussion it is convenient to reduce the direct detection methods to four major steps depicted schematically in Figure 16. Step 1, preparation, is usually the polarization of I spins to full magnetization in $H_0$. The hold period is that during which the I spin order must be maintained. In the version we have discussed, this is done in the I rotating frame by spin-locking. Mix constitutes the transfer of spin order from the I to S spin systems which was done by transfer of polarization from $H^I_{1I}$ in the I rotating frame to $H^S_{1S}$ in the S rotating frame. Finally, in the observe step the S signal is observed and recorded—the I spins may be decoupled if we desire high resolution S spectra, or remain undecoupled if we are interested in broad line S spectra.
Figure 16

Schematic general representation of direct detection double-resonance such as proton-enhanced NMR. Examples of options for the various steps are presented in the text.
In our preceding version, decoupling was performed continuously by the I spin-locking field.

The following is not intended to be an encyclopaedia of all the methods available as alternatives for the above steps. We wish only to point out illustrative examples. Many others will surely occur to the reader. Which one or which combination is best suited to the particular experiment at hand is largely a matter of the experimenter's discretion and may be the result, in some cases, of trial and error. We shall also indicate a few combinations suited for general application.

1. Prepare. (a) polarize I by spin-lattice relaxation in $H_0$
   (b) dynamically polarize I by optical polarization
   (c) polarize I using polarized quadrupolar nucleus with short spin-lattice relaxation time

2. Hold. (a) hold $M_I$ along $H_0$ in laboratory frame
   (b) spin-lock $M_I$ along $H_{II}$ in rotating frame
   (c) hold I order in dipolar state in laboratory or rotating frame.

3. Mix. (a) Hartmann-Hahn; matched or unmatched
   (b) Solid effect in laboratory or rotating frames
4. Observe. 
(a) undecoupled $I$
(b) continuous $I$ spin-decoupling\(^{(28)}\)
(c) pulsed $I$ spin-decoupling\(^{(29)}\)

The nature of these phenomena has been discussed in detail in the references cited. Matched and unmatched Hartmann-Hahn mixing refer to mixing satisfying, or not satisfying, equation (2) respectively. More generally, $H_{1I}$ would be replaced by $\overline{H}_{1I}$ where $\overline{H}_{1I}$ is either the average $H_1$ over a pulse train or a local dipolar field.\(^{(82,83)}\)

An important consideration in these experiments is sample heating. In the version we talked about in Section II, long continuous irradiation of the $I$ system is required and this may lead to unacceptable average power dissipation in the probe. This is the purpose of the hold period--to allow a cooling of the sample and probe while maintaining the $I$ spin order. A particularly useful option in this respect, mentioned in 2(c) is the dipolar state which we discuss now in a little more detail. This presents a means of storing $I$ order in the rotating frame without the need for strong spin-locking fields.

A low temperature dipolar-ordered state may be obtained by transforming Zeeman order into dipolar order by one of several techniques, e.g.\(^{(84)}\)

(i) adiabatic demagnetization in the rotating frame \(\text{ADRF}\)\(^{(85)}\) following spin-locking.
(ii) ADRF by adiabatic fast passage with a small \( H_1 \) into resonance, and removal of \( H_1 \).

(iii) 90\( \gamma \)-45\( \gamma \) two pulse transfer \( ^{86} \) --this is not adiabatic but is a simple and rapid way to make a \( \sim 50\% \) efficiency transfer.

Following such a conversion, the high temperature density matrix assumes the form:

\[
\rho_{\text{dip}} = \frac{1}{Z} \left( 1 + \frac{k_0}{k_T \text{dip}} \right) \quad (69)
\]

with \( T_{\text{dip}} \) depending on the initial spin temperature and the technique used. The thermodynamical discussion in Section II is still valid if \( H_{1L} \) is replaced by \( H_L' \), the local dipolar field defined by:

\[
\frac{C_I H_L'^2}{T_{\text{dip}}} = \text{Tr} \left\{ \rho_{\text{dip}} k_0 \text{dII} \right\} \quad (70)
\]

to make the analogy with the Zeeman field \( H_{1II} \) in the expression for the Zeeman energy in (12). \( H_L' \) is given by:

\[
H_L'^2 = \frac{1}{3\gamma_1^2} \langle \Delta \omega \rangle_{II}^2 \quad (71)
\]

where \( \langle \Delta \omega \rangle_{II} \) appears in (63). This is all well known and will not be enlarged on here. The main point is that this order may still be transferred from the I to the S spins by application
of an $S$ field $H_{1S}$ in the $S$ rotating frame. The dynamics of this process have been treated in detail by McArthur, Hahn and Walstedt\textsuperscript{36} for the case of $^{43}\text{Ca}^{19}\text{F}$ double-resonance.

Assume as in Section II.C that we begin again with the $I$ spins polarized at the lattice temperature, and perform an ADRF. The density matrix is then given to a good approximation, in analogy to (18), by:

$$\rho_R^{(0)} = \frac{1}{Z} \left( 1 + \frac{\mathcal{K}_0}{kT(0)} d_{II} \right)$$

(72)

where this time it is easily seen:

$$T(0) = T_0 \frac{H_L'}{H_0}$$

(73)

We now turn on an $S$ field $H_{1S}$ at exact resonance such that:

$$\gamma_S H_{1S} = \alpha \gamma_I H_L'$$

(74)

The $I$ and $S$ spins now come to equilibrium with:

$$\rho_R^{(1)} = \frac{1}{Z} \left[ 1 + \frac{1}{kT(1)} (\mathcal{K}_0 d_{II} + \mathcal{K}_{1S}) \right]$$

(75)

yielding, using exactly the same considerations as those leading to (23) and (26):

$$M_S^{(1)} = \frac{\gamma_I}{\gamma_S} \frac{\alpha}{1 + \alpha^2 \epsilon} M_S^{(0)}$$

(76)

with $M_S^{(0)}$ given by (16). The spin-locking case we treated before corresponds to $H_L' \rightarrow H_{1I}$ and $\alpha = 1$ (Hartmann-Hahn condition). The
cross-relaxation time \( T_{IS} \) for this type of experiment calculated by McArthur, Hahn and Walstedt is:

\[
\frac{1}{T_{IS}} = \frac{\Delta w^2}{\delta w_L} \int_{0}^{\infty} a(\tau) \cos \omega_L' \tau \, d\tau
\]  

(77)

where \( \omega_L' = \gamma L \) is constant and \( a(\tau) \) is the same as \( f(\tau) \) in (59) with \( I_{ix} \) replaced by \( I_{iz} \). The above authors measured an exponential dependence of \( T_{IS} \) on \( \alpha \), i.e. \( \frac{1}{T_{IS}} = \alpha \exp(- \alpha \omega_L' \tau_c) \). If we assume this to be generally true then we can use equation (17) of their work:

\[
\frac{1}{T_{IS}} = \frac{\pi}{2} \Delta w^2 \exp(- \alpha \omega_L' \tau_c)
\]  

(78)

with \( \tau_c \) given by (61) and \( I_{ix} \) replaced by \( I_{iz} \).

Two interesting cases arise:

(i) \( \alpha \sim 1 \). In this case \( T_{IS} \) can still be short and one obtains after \( N \) cycles of transfer a magnetization \( M_S^{(N)} \) given by (27) exactly as before. The signals from \( M_S^{(K)} \) are again co-added yielding \( \sim \) the same sensitivity as before. Several versions of this approach are illustrated in Figure 17 which also shows some permissible combinations of decoupling sequences.

(ii) \( \alpha \gg 1 \). In this case we can obtain, looking at (76), a large S polarization in one shot. The maximal value of \( M_S^{(1)} \) occurs for

\[
\alpha \sqrt{\epsilon} = 1
\]  

(79)

whence:
Examples of high resolution cross-polarization experiments using an I dipolar state in the rotating frame. The I dipolar state in each case is produced by an adiabatic demagnetization in the rotating frame (ADRF). The mixing in each case is between the I spins in the dipolar state and the S spins with field $H_{1X}$. The hold period is to allow the probe and sample to cool. Several mixing steps may be used for each holding one until heating is excessive. (a) The I spins are decoupled while in the dipolar state. The 90° pulses cause a "spin-locking" of the I dipolar state (magic sandwich). Direct irradiation would cause a 75% destruction. (b) An adiabatic remagnetization in the rotating frame (ARRF) brings back the I magnetization along $H_{1X}$ and it is spin- locked and decoupled during S observation. (c) The I spins are maintained in the dipolar state and decoupled with 180° pulses. Since $H_{dII}^0$ is invariant to a 180° rotation this does not affect the spin order. (d) Here the decoupling is done with 90° pulses (to which $H_{dII}^0$ is not invariant), so the system must be spin-locked by 90° pulses. This is a pulsed version of (a). Many other versions are possible. (e) S spin irradiation for mixing and observation; $\gamma_{SH_{1S}}$ may be larger than $\gamma_{SH_{1I}}$ to provide even mixing of all the S spins.
Scheme for high-resolution study of S spin-lattice relaxation. The I spins are prepared in a dipolar state by ADRF. Cross-polarization of the S spins is achieved with $\gamma_S H_{1S} > \gamma_I H_{1I}$ which gives a large S polarization (albeit more slowly, as explained in the text). This is placed along the z axis and allowed to relax for a time $\tau$. Subsequent observation with I spin-decoupling gives a high resolution partially relaxed S spectrum. Again, many other versions are possible.
or one half the polarization from an adiabatic transfer in (39). Adiabatic transfers are also possible as mentioned in Section II.E and will be discussed in detail elsewhere.

The above looks like a very profitable venture since we obtain a massive ($\epsilon << 1$) S polarization in one shot. Note however, from (78) that $T_{IS}$ gets longer as $\alpha$ is increased and may become prohibitively long. This is especially bad since $H_{1S}$ is then large and sample heating may become a problem. The form of $a(\tau)$ also becomes crucial—Gaussian behavior, as some authors have assumed, would make things even worse if $\frac{\omega L c}{\sqrt{\epsilon}} >> 1$ as would usually be the case for small $\epsilon$. In any case, the final sensitivity or data rate is about the same as in the multiple contact version ($\alpha \sim 1$) if $T_{1\Pi}$ is long.

There is at least one case where (ii) above may clearly offer a considerable advantage, namely in $T_1$ measurements of the S spin system as discussed by McArthur, Hahn and Walstedt. (36) In this case a single-shot large S polarization is very useful since there is no analogy to the co-addition of many S signals from a single I polarization if $T_{1S}$ is long. It is thus worthwhile to put $\alpha >> 1$ and accept the long $T_{IS}$ (the sample heating may be alleviated by periodically putting $M_S$ along $H_0$). Figure 18 shows how we adapt this approach to high resolution $T_1$ studies in
our direct detection scheme. This is similar to $T_1$ studies in liquids \( \text{(72,73) } \) except for the enhanced sensitivity.

Finally, note that the unmatched Hartmann-Hahn experiment 
\( (\gamma_S^H \gamma_I^H = \alpha \gamma_I^H \gamma_I^I) \) may be used to obtain large \( M_S^{(1)} \) even in the spin-locking version of Section II. There however the equation (62) for $T_{IS}$ would read:

\[
\frac{1}{T_{IS}} = C_{IS} <\Delta w^2>_{IS} <\Delta w^2>_{II}^{-\frac{1}{2}} \exp \left[-(\alpha-1)\omega_{II}^Tc\right] \tag{81}
\]

and we see that since $\omega_{II}^c$ is large, this becomes much more sensitive to the unmatching.

B. INDIRECT DETECTION

Two modifications of the normal Hartmann-Hahn indirect detection method have been proposed for high resolution. \( \text{(87,88) } \) An obvious appeal of these techniques is that it is the abundant I spins which are observed making the signals much larger (due to number and frequency) than that of the direct S detection. This is not the whole story, however, since the indirect detection methods, signal strength not withstanding, involve a mapping of the S spectrum point by point and thus require long times to acquire the whole S spectrum. Thus, although the sensitivity may be very good, it may in some cases be too good, requiring long times, and making the rapid S detection, where the whole spectrum is obtained immediately, preferable. In this section
we discuss one of the above two techniques. Both are similar -- one involves a direct mapping of the $S$ absorption spectrum; the second involves a mapping of the $S$ free induction decay. We discuss the latter since it is easier to compare to our direct detection scheme. However, the sensitivity is similar in both and thus the conclusions we draw from the comparison should be generally useful.

Figure 19 shows the high resolution modification of the $T_2$ experiment of McArthur, Hahn and Walstedt$^{(36)}$ used by Mansfield and Grannell.$^{(88)}$ The mixing and decoupling steps are performed through spin-locking in the same way as for our direct detection scheme. Following the mixing step the $S$ spins are allowed to undergo a decoupled (high resolution) free induction decay for a time $\tau$, and the mixing performed again. If the normalized free induction decay is $S(t)$ as in II.D and the above cycle is performed $N$ times then an accumulative destruction of the $I$ magnetization ensues. Considerations similar to those used in Section II yield:

$$M_{I}^{(N)} = M_{I}^{(0)} \exp (- N \varepsilon (1 - S(\tau)))$$  \hspace{1cm} (82)

where $M_{I}^{(0)}$ is given by (17).

To prevent distortion of the signal it is necessary that

$$N \varepsilon = \lambda \ll 1$$  \hspace{1cm} (83)

for which:
Adaptation (reference (88)) of indirect detection techniques to high resolution. In this case, the I spins are observed. Following an I-S contact (cross-polarization) the S magnetization is allowed to decay, while decoupling I, for a time τ. This is performed N times with fixed τ, and the final I magnetization recorded. From the dependence of the I magnetization destruction on τ, the S free induction decay \( S(\tau) \) may be extracted with very high sensitivity.
\[ M^{(0)}_I - M^{(N)}_I = \lambda M^{(0)}_I (1 - S(\tau)) \] (84)

So the destruction is proportional to \( S(\tau) \). The \( S \) free induction decay can therefore be mapped out by plotting the destruction vs. \( \tau \). For each point it is necessary to wait \( \lambda T_{1I} \) for repolarization of the \( I \) spins. If \( \lambda \approx 1 \) this can still be performed but a correction for distortion must be made.

Assume now that the voltage produced by \( M^{(0)}_I \) is \( K_{II} M^{(0)}_I \) and that like in Section II.D the noise voltage in the \( I \) detector bandwidth is \( V_{nI} \). The data rate for our fixed point \( S(\tau) \) on the \( S \) free induction decay by the \( I \) detection is then

\[ Q^{(n)}_{\text{IND}} \sim \frac{1}{\lambda T_{1I}} \left( \frac{\sqrt{2} V_{nI}}{\lambda K_{II}} \right)^2 \] (85)

Since the power \((S/N)\) involves the destruction \( \lambda \) for the \( I \) magnetization and the noise voltage involves a difference \((\sqrt{2})\).

We now note one important difference between the direct and indirect detection methods. In the former, within one \( T_{1I} \) it is the full free induction decay, not just the point \( S(\tau) \) that is obtained. In the latter only one point is obtained per \( \sim \lambda T_{1I} \). Assume then that the number of points required on the free induction decay is given by

\[ M = \frac{\Delta S}{\delta S} \] (86)
where $\Delta_s$ and $\delta_s$ are the spectral bandwidth and requisite resolution of the $S$ spectrum. To compare the data rate of (85) with the direct detection for the full free induction decay we must then write:

$$Q_{\text{IND}} \sim \frac{\delta_s}{\Delta_s} \frac{1}{\lambda T_{1I}} \left( \frac{\lambda K_{IM}^{(0))}}{\sqrt{2} v_{nI}} \right)^2$$ (87)

Since we are interested only in a general semiquantitative comparison of the techniques, we do not take into account details such as sampling widths which depend on factors such as $T_{2I}$ etc. These effects will usually be of order unity if $\Delta_s \sim T_{2I}^{-1}$ which is normally a realistic estimate. For comparison then, (87) can finally be written:

$$Q_{\text{IND}} = \mathcal{G}_{\text{IND}} Q_{\text{FID}}$$ (88)

where

$$\mathcal{G}_{\text{IND}} = \frac{\delta_s T_{1S} \lambda}{2 \Delta_s T_{1I}} \left( \frac{K_{IM}^{(0))}}{K_{SM}^{(0))} \frac{v_{nS}}{v_{nI}} \right)^2$$ (89)

Comparing this with the analogous expression from the direct cross-polarization technique (36) we find:

$$\frac{\mathcal{G}_{\text{CP}}}{\mathcal{G}_{\text{IND}}} = \mu \sim 1 \frac{1}{\varepsilon} \left( \frac{v_{IM}}{v_{IS}} \right)^2 \frac{\Delta_s}{\lambda \delta_s} \left( \frac{K_{SM}^{(0))}}{K_{IM}^{(0))}} \frac{v_{nI}}{v_{nS}} \right)^2$$ (90)

where $\mu$ is a measure of the relative efficiency of the two experiments in terms of long term data rate. It can be shown that the relative power $(S/N)$ for $I$ and $S$ spins due to difference
in \( \gamma \)'s and number of spins is given by:

\[
\frac{K_S M_S^{(0)} V_{nI}}{K_I M_I^{(0)} V_{nS}} \sim \varepsilon^2 \left( \frac{\gamma_S}{\gamma_I} \right)^5
\]  

(91)

This assumes that both systems operate with the same unloaded Q and that detector noise is similar. Using this ratio, (91) assumes the form:

\[
\mu \sim \varepsilon \left( \frac{\gamma_S}{\gamma_I} \right)^3 \frac{\Delta S}{\lambda \delta S}
\]  

(92)

C. COMPARISON

Although the above analysis is terribly simplistic it does allow some general conclusions:

(a) In terms of long term data rate \( T > n_\lambda T_\lambda \) on which the above analysis is based, the indirect detection method appears to gain when \( \varepsilon \) and \( \frac{\gamma_S}{\gamma_I} \) get smaller. For \(^{1}H\)–\(^{13}C\) \( \gamma_S = 0.25 \) and typical values of \( \varepsilon \) and \( \frac{\Delta S}{\delta S} \) are \( \sim 0.5 \times 10^{-2} \) and \( \sim 10^3 \) respectively. Taking \( \lambda \sim 1 \) (which gives good S/N but produces a distortion according to (82)), we see \( \mu \sim 10^{-1} \) so the indirect detection approach appears to be superior. For \(^{15}N\) the difference becomes even greater.

(b) By adaptation of steady state techniques \((83,87,89)\) the sensitivity of the indirect detection can be enhanced even further. In this approach, the I magnetization is not allowed
to decay but is spin-locked off resonance with a pulse train and observed between the pulses. Both the frequency and time domain indirect experiments can benefit from this, and yield an enhancement in sensitivity of $\sim \frac{T_{1p}}{T_2}$ for the I spins. In the present context we do not feel that a detailed discussion of this is warranted, but mention that the method does produce a gain in sensitivity but suffers from spectral distortion due to cross-relaxation effects.

(c) The conclusions above might superficially lead one to suspect the merit of the direct direction methods that we have so laboriously outlined in this paper, despite their evident success in terms of preliminary experimental showing. That this would be foolish is made transparent by the following observations:

(i) the technique is simple and requires no serious modification of conventional Fourier transform spectrometers. The indirect detection requires rather more elaborate automation and timing and an effort must be expended to eliminate spectral distortion.

(ii) in many cases the cross-polarization, direct detection experiment will yield a sufficient S/N ratio from one polarization of the I spins. In this case, the whole long term analysis above breaks down and, in general, the direct detection
will be vastly superior to the indirect one if $T_{II}$ is very long. This is because the latter requires $\sim T_{II}$ per point and even though the final $S/N$ may be tremendous, the time expended in collecting it is unrealistically long. The direct method yields sufficient $S/N$ in a short time. Modifications could be introduced to aid the direct detection approach in this respect but they deduct from the straightforwardness and simplicity of the experiment.

Finally, we mention that similar remarks can be made about the modification of Bleich and Redfield.\(^{(87)}\) We feel that both direct and indirect detection will prove valuable; the former should be more useful in routine applications to $^{13}\text{C}$ spectroscopy, whereas the latter should find its potential in applications to very dilute spin such as $^{15}\text{N}$ in biologically interesting systems.
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REFERENCES AND FOOTNOTES


44. Instruments for Industry, Inc., Farmingdale, N.Y., Model M404P.


46. A. Pines, unpublished results.


49. The terms containing other elements are non-secular in high field (oscillate rapidly) and cause only small second order shifts.


57. This is in line with recent theoretical calculations on $^{13}\text{C}$ shielding using gauge increment orbitals: R. Ditchfield, (private communication).


59. J. S. Waugh, M. G. Gibby, S. Kaplan, and A. Pines, Colloque Ampère, Turku, Finland, 1972 (to be published). References 58 and 59 report measurements on the following compounds: benzene, hexamethylbenzene, toluene, durene, hexafluorobenzene, acetaldehyde, acetone, acetic acid, thioacetic acid, silver acetate, acetic anhydride, methyl formate, methyl acetate, dimethyl carbonate, dimethyl oxalate, silver trifluoroacetate, trifluoroacetic anhydride, dimethyl acetylene, methanol, ethanol, diethyl ether, dimethyl dimethoxy silane, tetramethoxy silane, dimethyl disulfide, dimethylsulfoxide, octamethyl cyclotetrasiloxane, hexamethyl disiloxane, hexamethyl Dewar benzene, carbon disulfide.


63. (a) J. Schaeffer, presented at the Thirteenth Experimental NMR Conference, Asilomar, California, 1972.
    (b) J. Schaeffer, S. H. Chin and S. I. Weissman, (to be published).


78. K. H. Hausser and D. Stehlik, (private communication).


80. Reference 4(c), chapter 7.

81. Reference 4(c), chapter 6.


84. An excellent discussion with leading references is given in reference 4(c), chapters 2 and 3.


CHAPTER III

HARDWARE
1. PULSE PROGRAMMER OPERATION

A. INTRODUCTION

The complexity of pulse experiments in our laboratory has increased appreciably in recent years. Previously, the implementation of new pulse experiments invariably necessitated the time consuming design and construction of specific logic circuits. To overcome this obstacle we therefore set out to produce a more versatile and generally powerful pulse programmer, and the end result of our endeavor is described in the following sections. The device contains an independent memory unit of its own which carries all the information necessary for the execution of an arbitrary pulse sequence, and is preloaded and otherwise serviced by an on-line computer. The realization of new pulse experiments is thus essentially reduced to a computer software problem--a considerable advance over previous methods--and recent experiments have already utilized this facility with promising efficiency. A schematic diagram of the programmer is shown in Fig. 1. Components include mostly homemade circuits and currently available TTL and DTL logic.

Section B describes the basic operation including the memory, cycling, and addressing. Sections C-G describe the different units involved in the production of a pulse sequence, and Section H elaborates on the points of access and function of the
Figure 1

Functional schematic diagram of computer-controlled pulse programmer. 12 refers to the PDP 12 computer.
computer in servicing the instrument. Section I gives a sample pulse program.

B. BASIC OPERATION

The heart of the programmer is an extendable 384 bit flip-flop memory organized as sixteen words of 24 bits each. Each word is assigned an address in the memory and contains an instruction to be executed by the programmer. The assignment of bits within each word is depicted in the schematic diagram. Here we give a brief description of the function of these bits, the basic cycling of the instrument and addressing of the memory. More specific details on the different units involved are presented in later sections.

The cycling of the instrument is achieved very simply. Each instruction contains several basic pieces of information: (i) the function to be performed (pulse output, sampling, counting, etc.), (ii) address of the next instruction, and (iii) the delay until execution of the next instruction. The main operating unit is the major state generator. This emits 2 pulses called TPl and TP2 about 0.1 μsec apart. TPl triggers the execution of the current instruction and the specified delay and TP2 then selects the next word specified by the next address (NA) bits in the memory. The major state generator is then retriggered at the end of the delay through the end-delay gate and the next instruction is executed. In this way cycling is
maintained and we see that the cycle time is redetermined at each instruction and is normally not clock-controlled as in previous devices.

Summarizing, the basic chain of events is: (i) end of previous delay triggers major state generator, (ii) TP1 triggers execution of instruction and next delay, and (iii) TP2 selects next instruction. The function of the memory bits is as follows:

(i) N1 N2 N3 N4—Next address. There are sixteen words coded in binary with addresses 0000-1111. The addressing of a selected word is done in "x-y" fashion. One of four "x" lines and one of four "y" lines specify which one of the sixteen words is to be accessed. This memory location may be written into by the computer in loading or read by the programmer during operation. To understand the addressing more explicitly let us assume that the programmer is just executing the instruction in word 0010 and the NA bits N1-N4 of this word contain 0011 as the next address. (This next address may or may not be modified at the adder as explained later in this section.) In any case, TP1 transfers the number 0011 or the modified address to the NA register whence TP2, after execution of instruction 0010, then transfers it to the current address register where it becomes the new current address. The decoders use the 4 bits from the current address register as two sets of two, each of which is decoded to 1 of 4 lines, the x and y sets mentioned above. These are used, by driving them with current-sinking transistors, to
select the corresponding word 0011 (or modification) in the memory.

(ii) $X, \overline{X}, Y, \overline{Y}, V, \overline{V}$ and $H$. These bits specify whether or not a pulse is to be produced in any of the six output channels. For every bit that is set to logic 1 a pulse will be produced in the corresponding output channel. $X, \overline{X}, Y, \overline{Y}$ designate the 4 channels used to gate the 4-phase box described in Section C. $V, \overline{V}$ are auxiliary outputs which may be used for producing video pulses, double resonance pulses, or for general triggering purposes.

Bit $H$, the hold bit, extends the capabilities of the pulse output. If $H$ is set to 0 we obtain normal pulsed output. If $H$ is set to 1 the specified output channels are held open for the duration of the present delay, i.e., until the execution of the next instruction where they may be closed or, of course, held open. All this is discussed further in Section F.

(iii) $C$, $D_1$, $D_2$, $D_3$. These bits specify the delay. $D_1$ and $D_2$ and $D_3$ specify one of 8 available codes for analog delays (Section D) and a recycle delay (Section D) and $C$ specifies a clocked delay using a crystal clock with computer-controlled timing (Section D).

(iv) $S$-Sample bit. When set to 1 the sample-and-hold is triggered and the magnetization sampled. (See Section G).

(v) $SB$, $BC$, $DC$. Counter bits: These control three
counters called the subburst, burst, and decade counters. When any of these bits is set to 1 the corresponding counter is incremented until overflow occurs at some specified count (either set manually or under computer control) and the advance decoder then modifies the next address by adding to it some number dependent on which counters have overflowed. This allows us to accomplish skipping and branching in the pulse program after a specific preset number of instructions or groups of instructions. A more complete discussion of this facility appears in Section E. 

It is often useful to step through a pulse program one instruction at a time in order to examine the contents of the programmer memory or to check the program's operation. This can be done using the single instruction switch. In normal operation this is set to allow triggering of the major state generator through the end-delay gate. In single-step operation the end of a delay will not trigger the next instruction. Instead each instruction is triggered manually through the execute switch which produces a pulse from the corresponding pulse generator. All pushbutton switches of this sort are equipped with circuits to prevent multiple triggering due to contact bounce.

A little thought, together with the example at the end, will convince the reader that most feasible pulse sequences require very few of the sixteen available memory locations. Thus another switch, the memory bank switch, enables us to store and use two pulse programs each of less than eight words. The switch allows
the programmer to operate in either the lower memory bank, locations 0-7, or in the upper bank, locations 8-15. For longer pulse sequences the whole memory may of course be used as one unit.

C. RECYCLING AND INITIALIZATION

During an experiment one usually wishes to repeat the pulse sequence periodically; for example, in order to make adjustments or perform some averaging. The experiment is thus composed of a major cycle consisting of what we call a "burst" during which the pulses are emitted and the signal observed, and a "recycle delay" during which the spin system returns to full equilibrium before initiation of the next burst. During the recycle delay the data may also be manipulated and the programmer serviced if necessary.

The recycle delay is one of the 8 possible delays selected with each instruction. When its code is encountered by TPL, a 1 KHz astable multivibrator is activated. The output of this is fed into two channels, in one of which the frequency is divided by 1000. One or the other channel, selected by a manual switch is fed to a 12 bit ripple counter. The overflow bit of the counter is selected on the front panel giving us recycle times of $1 - 2^{11}$, in powers of 2, with msec or sec units. The end of the recycle delay does not trigger the execution of the next instruction as with other delays. Instead it is sensed by the initializer (consisting of three monostables) which prepares for
initialization and triggering of the next burst. First, a clear pulse is emitted (output 1 of initializer), which after current amplification by a driver clears all the registers in the programmer. This includes the various counter registers, the current address register, the clock counter, and all skip and interrupt flags connected to the computer. Clearing may also be accomplished manually using the clear pushbutton. About 1 usec later a second pulse "BG" (output 2) is sent to the mode select switch from which it may be directed to one of several places depending on the mode selected. The available modes and subsequent operation are:

(i) Normal Operation. In this mode the retriggering is automatic. The pulse BG (output 1 of mode select) enters the end delay gate which then triggers the first instruction through the major state generator.

(ii) Computer Control. Here the pulse BG (output 2) is channeled to the computer and continuation is thus computer controlled, the triggering of a new burst being initiated through input 2 of the end delay. This is discussed further in Section H.

(iii) Bloch Decay. This mode is used if one wishes at any time to look at a single pulse, or a Bloch decay of the sample, independent of the contents of the programmer memory. There are six positions in this mode, X, \( X \), \( \ldots \), \( \bar{v} \), and for the one selected a single corresponding output pulse is produced by
hardwiring of the appropriate bit and disabling of the memory (symbolized by output 4). BG (output 3) is channeled to trigger the main pulse generators (see Section F) and retrigger the recycle delay. Thus recycling here is automatic and a single pulse is repeated with a recycle delay period.

(iv) Off. The pulse BG is unused, there is no retriggering of the burst, and programmer operation ceases.

The initial cycling of the computer is activated by the start pushbutton switch, after loading a new pulse program or after cessation of operation for any number of reasons. This activates the pulse generator and simulates the end of a recycle delay, thus performing the necessary initialization and starting operation in the selected mode.

D. DELAYS

The 8 available delay codes are used as follows:

(i) Four Variable Analog Delays. Each analog delay consists of two identical monostable multivibrators (type 9601) with RC time constants controllable manually. The first monostable is triggered by a pulse from the delay decoder when its code is encountered by TPl. The end of the pulse triggers the second monostable and the end of the pulse from this triggers the major state generator through the end-delay gate and the next instruction is then executed. The use of two cascaded monostables is an artifice for insuring that the same delay can be immediately
retriggered if this is called for by the next instruction.

These delays cover different ranges. Two produce delays varying from 0.2 to 8 μsec to 1 msec. These may also be multiplied by one of the counters available (Section E) so that any practically useful delay is accessible.

(ii) One Fixed Analog Delay. This is the same as above except not controllable on the front panel. Normally it is set at about 1 μsec and is useful when one wishes to generate an instruction immediately on termination of a 90° pulse without using one of the variable delays.

(iii) Recycle Delay. This was described in detail in Section C.

(iv) Two are unused. One is available for extension and one remains open to be used when the crystal clock is requested and we want no extra delay triggered simultaneously.

In addition to these delays we have available a crystal clock. When bit C is set to 1 a gate is opened and a 1 MHz crystal clock counts into a series of 6 decade counters providing us with 7 selectable channels with counting units of 1 μsec to 1 sec. The desired channel is selected manually or by the computer and the clock register then fills at the corresponding frequency. The latter is a 12 bit ripple counter which can be preloaded and read by the computer. This opens up two modes of operation for the clock: (i) To produce a clocked delay the
clock counter is preloaded by the computer with the complement of the desired delay. This is useful for experiments where computer-controlled timing of pulses is necessary; for example, in $T_1$ measurements. (ii) In order to measure the length of a burst the clock counter is preloaded with 0 by the computer. The clock gate is then opened at the beginning of the burst and is automatically shut when a recycle delay is requested. The real time of the burst may then be read by the computer.

E. COUNTERS

Clearly, for most conceivable pulse experiments it is necessary to be able to count—we may need to produce a certain number of pulses or cycles of pulses, or to sample a fixed number of times, and so on. Three counters in the programmer provide this facility; called the subburst counter, burst counter, and decade counter they count respectively from 1 to $2^7$ in powers of 2, from $2^5$ to $2^{11}$ in powers of 2, and from 1 to 1000 continuously, and all have either manual or computer-controlled selection.

When a counter memory bit is encountered by TP1 the corresponding counter control looks at the counter register to see if it has overflowed at the preselected bit. If not, the register will then be incremented by TP2. If it has overflowed, i.e., the count is over, the register will be cleared by TP2 in preparation for recounting. When overflow has occurred at some
instruction, the next instruction is modified and branching of the pulse program can occur. Modification of the address is simple—the next address (see Section B) enters a 4 bit binary adder as one addend. The other addend is a decoded 4 bit binary number with 3 bits from a decoder and 1 from the memory bank switch (Section B). The decoder will present a number different from 0 in the selected memory bank only if an overflow has occurred in one or more of the counter registers. The number there presented will add to the next address 1 for a subburst overflow, 2 for a burst overflow, and 4 for a decade overflow, thus permitting separate branching for each of these counters inside the selected memory bank. Obviously, the counters may also be used as multipliers, specifically to create long pulses or delays and provide a convenient extension of their ranges.

The sample pulse program in Section I demonstrates some uses of these counters.

F. PULSE OUTPUT

A major feature of most pulse experiments is the necessity for very sensitive pulse width adjustments. There are six pulse output channels in the programmer and these are divided into 2 groups labeled $X \bar{X} Y \bar{Y}$ and $V \bar{V}$. The first four provide gating for the 4 phase box described later. The other two provide separate gating, for example, for a second frequency in double resonance experiments or video current pulses in tilted coil
experiments. The pulse output is produced quite simply. TPl triggers two pulse generators—the rf and V main pulse generators. These are monostable multivibrators with RC time constants selectable manually, from 0 to 4 μsec. They are fed respectively into 4 and 2 channels which are then gated by 6 pulse selection gates. We now differentiate again between the modes of operation described in Section C.

(i) Normal Operation or Computer Control. The gates are controlled by the 6 appropriate bits in the memory.

(ii) Bloch Decay. The gates are controlled by bits set from the mode select switch and the memory is disabled totally.

For every bit that is 1 the corresponding gate is open and the main pulse passes through to the pulse generators and triggers a pulse from one of 6 monostables with RC constants again determined manually and with sensitive continuous selection of 0-4 μsec. The output from the pulse generators is thus a pulse for each pulse bit set to 1 either by the memory or the mode select switch, with each pulse separately controllable. Now we introduce the possibility for an overall pulse width control—this is done separately for the two groups of pulses at the pulse trimmer gates as described for pulse programmer A.†

The last manipulation that the pulses undergo occurs at the final pulse gates. These provide another useful facility described in Section B, namely, the possibility of holding open a

pulse gate until the next instruction occurs. This is necessary when the desired output is not short pulses but long ones or continuous rf bursts with or without phase switching as employed in some recent experiments. This is determined by bit H in the memory. If set to 0, the trimmed pulses pass straight through the final gates and form the final output. If set to 1, the selected pulse channels are not closed at the end of the trimmed pulse and are kept open until the end of the current delay or more if necessary (by keeping H and the pulse bit set to 1). Clearly this also extends the range of accessible pulse widths by having them set with the delays. If the mode of operation is Bloch decay then the hold function is suspended and only pulsed output is possible.

A switch which opens the final driver gates (disable spectrometer switch) enables us to disconnect the logic from the rf circuitry, thus avoiding burning out the transmitter with excessive duty cycles when new pulse sequences are being tested.

G. SAMPLING

At any instruction where we wish to sample the magnetization the S bit is set to 1, opening the sample gate. TPl then triggers the integrate and hold described elsewhere and the magnetization is sampled a manually variable time later. In addition to this a sample register is incremented. The output of this 10 bit ripple counter is connected to the computer direct
address lines and one higher order bit is provided from the sample and hold unit. The latter bit selects one of two buffers in computer core for the deposit of real and imaginary digitized data from the dual phase detector. The sample register increments the address within each buffer thus providing sequential storage of digitized data in computer core whence it may be displayed and otherwise manipulated by the computer.

H. COMPUTER ACCESS

The great versatility in programming experiments and in signal processing is provided by the computer and this has several points of access to the programmer, all provided by standard interface techniques. The more important of these access points are symbolized in the schematic diagram by a "12" (for PDP 12). The computer has two main functions, namely, servicing the pulse programmer, and storing and processing data. Here we describe the more important aspects of these two functions.

(i) Servicing the Pulse Programmer. This includes loading in pulse programs, setting the counter registers for preset counts, selecting the clock decade, preloading and reading the clock counter, triggering and controlling the operation of some auxiliary external devices, and triggering the bursts when in computer control mode. All of these are carried out either when the programmer is at a standstill or just at the end of a recycle delay during operation.
Loading is carried out simply: Assuming the program is in computer core, either from the teletype or from tape, the computer steps through the programmer memory by incrementing the current address register and reads in the pulse program through the I/O bus. Programs may be read in and changed at any time during operation--this is entirely determined by the available computer software. Our library of pulse programs currently contains about 150 entries.

Servicing is initiated when the computer is interrupted by the BG pulse at the end of a recycle delay (Section C). The service functions mentioned above are then performed and the computer then triggers a new burst through input 2 of the end-delay gate.

(ii) During the burst data are stored in computer core. The end of the burst interrupts the computer through the recycle delay request. During the recycle delay, processing of the data occurs. This may include, for example, displaying and plotting, storing on tape, averaging, fourier transformation, counter and clock time readout, etc. The end of the recycle delay is sensed by the computer which then enters a service routine as in (i). If signal processing has not been completed the computer may choose, under software control, to lengthen the recycle delay. All in all, operation is extremely flexible and a variety of service and signal processing routines have been used for different experiments. The last section shows an example of one such simple experiment.
I. EXAMPLE

Pulse programs are written in a format closely related to the organization of the pulse programmer memory described previously. Table I shows

| CA | X | X | Y | Y | V | V | H | C | D1 | D2 | D3 | S | SB | B | DC | N1 | N2 | N3 | N4 |
|----|---|---|---|---|---|---|---|---|----|----|----|---|----|---|----|----|----|----|
| 0000| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0  | 1  | 1  | 0 | 0  | 0 | 1  | 0  | 0  |    |
| 0001| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0  | 1  | 0  | 0 | 0  | 0 | 1  | 0  | 0  |    |
| 0010| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0  | 1  | 1  | 0 | 0  | 0 | 1  | 0  | 0  |    |
| 0011| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1  | 1  | 1  | 0 | 0  | 0 | 0  | 0  | 0  |    |
| 0100| 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1  | 0  | 0  | 0 | 0  | 0 | 1  | 0  | 1  |    |
| 0101| 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0  | 1  | 0  | 0 | 0  | 0 | 1  | 1  | 0  |    |
| 0110| 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1  | 0  | 0  | 1 | 1  | 0 | 0  | 0  | 0  | 1   |

the pulse program used for the present four-pulse experiment. N1-DC represent the instruction bits described in detail in Section A and CA depicts the location of this instruction in the pulse programmer's memory. The program is entered in octal form into the computer (see Fig. 2) whence it may be stored on magnetic tape for future use or loaded into the pulse programmer. Operation can then begin under control of the computer. It may easily be verified that this pulse program will produce the following pulse sequence:
Figure 2

PPMOD computer program display for making new pulse programs. These are typed in octal format as explained in the text and may then be stored on tape or read into the pulse programmer. In the latter case they may be retrieved by an updated version of GOLEM.
**Pulse Programme**

Type in Pulse Programme & Strike LF

<table>
<thead>
<tr>
<th>Address</th>
<th>Word (Octal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40038200</td>
</tr>
<tr>
<td>1</td>
<td>40038200</td>
</tr>
<tr>
<td>2</td>
<td>40038200</td>
</tr>
<tr>
<td>3</td>
<td>80128000</td>
</tr>
<tr>
<td>4</td>
<td>20040240</td>
</tr>
<tr>
<td>5</td>
<td>10020300</td>
</tr>
<tr>
<td>6</td>
<td>04042848</td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>
\[(x, \tau_1', -x, \tau_2', y, \tau_1', -y, \tau_2')_n \], \text{ RD}

where \(x\) denotes an \(x\) pulse, etc. and \(\tau_1\) and \(\tau_2\) are the analog delays called for by the delay codes (001) and (010). \(\text{RD}\) denotes a recycle delay called for by code (111). Sampling is initiated through the \(S\) bit between the \(x\) and \(-x\) pulses, and \(n\), the number of four-pulse cycles, is determined by the burst counter. The sampling frequency is decided by the subburst counter; when the latter is set to \(m\), the magnetization is sampled every \(m\) cycles. At the end of the recycle delay the pulse train is automatically reinitialized at address (0000) by the computer. During this delay, data sampled in the pulse train is displayed and Chapter IV demonstrates how it may be accumulated and averaged, transformed, plotted, or stored on tape.
A. PULSE PROGRAMMER CARD LAYOUT

The functional blocks described in the previous section are handwired on Digital Equipment Corporation (DEC) cards and housed in H803 blocks mounted in an H925 module drawer. The accessories are all described in DEC's logic handbook (1969 version was used). Table II shows the card layout in the available slots. Detailed schematics of the cards are shown in Section III and detailed wiring lists for block pin connections in Section IV.E.

B. SELECTED MNEMONICS

<table>
<thead>
<tr>
<th>MNEMONIC</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>master pulse</td>
</tr>
<tr>
<td>MPA</td>
<td>master pulse allowed</td>
</tr>
<tr>
<td>XMP</td>
<td>MPA &amp; specific pulse (X, X ...)</td>
</tr>
<tr>
<td>CCL</td>
<td>crystal clock</td>
</tr>
<tr>
<td>AD</td>
<td>analog delay</td>
</tr>
<tr>
<td>S</td>
<td>sample</td>
</tr>
<tr>
<td>H</td>
<td>hold</td>
</tr>
<tr>
<td>ESB</td>
<td>enable sub-burst counter</td>
</tr>
<tr>
<td>SSB</td>
<td>skip on sub-burst overflow</td>
</tr>
<tr>
<td>EBC</td>
<td>enable burst counter</td>
</tr>
<tr>
<td>SBL</td>
<td>skip on burst overflow</td>
</tr>
<tr>
<td>CA</td>
<td>current address register</td>
</tr>
<tr>
<td>LDM</td>
<td>load memory</td>
</tr>
<tr>
<td>ED</td>
<td>end of delay</td>
</tr>
<tr>
<td>MS</td>
<td>major state</td>
</tr>
<tr>
<td>BD</td>
<td>block decay</td>
</tr>
<tr>
<td>NO</td>
<td>normal operation</td>
</tr>
<tr>
<td>CC</td>
<td>computer control</td>
</tr>
<tr>
<td>ND</td>
<td>no delay</td>
</tr>
<tr>
<td>PC</td>
<td>pulse codes</td>
</tr>
<tr>
<td>EPC</td>
<td>enable pulse codes</td>
</tr>
<tr>
<td>PS</td>
<td>pulse select</td>
</tr>
<tr>
<td>ESP</td>
<td>enable spectrometer</td>
</tr>
</tbody>
</table>
TABLE II

Pulse Programmer Card Layout

Cards such as M624, M103, M111, K681, M908 and M903 refer to standard DEC modules. The card schematics appear in Section III and are referenced by the slot numbers in this table.
<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PDP12 M9032 N15</td>
<td>PDP12 M9031 N14</td>
<td>PDP12 M9035 N18</td>
<td>BIOMATION</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>M624-6</td>
</tr>
<tr>
<td>3</td>
<td>PDP12 M9036 N13</td>
<td>PDP12 M9033 N16</td>
<td>PDP12 M9034 N17</td>
<td>M624 3</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>M624 1</td>
</tr>
<tr>
<td>5</td>
<td>ADC 1</td>
<td>ADC 2</td>
<td>SAMPLE</td>
<td>M624 2</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>GATE</td>
<td>ADC DATA</td>
<td>M624 4</td>
</tr>
<tr>
<td>7</td>
<td>ADC 3</td>
<td>ADC 4</td>
<td>P.I.</td>
<td>M624 5</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>V P GATES</td>
<td>M111 1</td>
</tr>
<tr>
<td>9</td>
<td>SKIP</td>
<td>B C</td>
<td></td>
<td>M103 6</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>Y P GATES</td>
<td>M103 5</td>
</tr>
<tr>
<td>11</td>
<td>SBC</td>
<td>SBC</td>
<td></td>
<td>M103 4</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td>X P GATES</td>
<td>M103 3</td>
</tr>
<tr>
<td>13</td>
<td>ADDRESS ADV.</td>
<td>ADDRESS ADV.</td>
<td></td>
<td>M103 1</td>
</tr>
<tr>
<td>14</td>
<td>MO 19,20</td>
<td></td>
<td>DRIVERS</td>
<td>M103 2</td>
</tr>
<tr>
<td>15</td>
<td>MO 17,18</td>
<td>MO 1,2,3,4</td>
<td>DRIVERS</td>
<td>M111 2</td>
</tr>
<tr>
<td>16</td>
<td>MO 15,16</td>
<td>MO 5,6</td>
<td>COMPUTER Light</td>
<td>M103-7</td>
</tr>
<tr>
<td>17</td>
<td>MO 13,14</td>
<td>MO 7,8</td>
<td>DELAY DECODE</td>
<td>M103-8</td>
</tr>
<tr>
<td>18</td>
<td>MO 11,12</td>
<td>MO 9,10</td>
<td>BIOMATION</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>CLOCK DECADE</td>
<td>CLOCK DECADE</td>
<td>CLOCK COUNTER</td>
<td>CRYSTAL CLOCK</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td>V M P GEN</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>MODE</td>
<td>MODE</td>
<td>Y M P GEN</td>
<td>K 681 6</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td>X M P GEN</td>
<td>K681 5</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>---</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>23</td>
<td>MAJOR STATE GEN</td>
<td>MAJOR STATE GEN</td>
<td>END DELAY</td>
<td>K681 4</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td>K681 3</td>
</tr>
<tr>
<td>25</td>
<td>RECYCLE DELAY</td>
<td>RECYCLE DELAY</td>
<td>MPA GEN</td>
<td>K681 2</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td>K681 1</td>
</tr>
<tr>
<td>27</td>
<td>M908 4</td>
<td>M908 7</td>
<td>M908 1</td>
<td>M908 8</td>
</tr>
<tr>
<td>28</td>
<td>M908 2</td>
<td>M908 3</td>
<td>M908 5</td>
<td>M908 6</td>
</tr>
</tbody>
</table>

FRONT
SBC - sub-burst counter  PI - program interrupt
BC  - burst counter     WE - write enable
RD  - recycle delay    SC - sampling counter
SIPB - single instruction pushbutton
PB  - pushbutton       CCBG - computer controlled begin
CL  - clear            AC - accumulator
BG  - begin            INL - initialize
NA  - next address register  SI - single instruction
PLT - plot             NC - not connected
GND - ground           MEM - memory
EX  - execute          ERD - end recycle delay
BCO - burst counter overflow
EADα - end analog delay α  VDMP - video main pulse
RFMP - RF main pulse   MOα - memory cell α

C. DEVICE SELECTOR ASSIGNMENTS

M1031 (30IOP - load memory)

30IOP1  - WE1 to pulse programmer memory
30IOP2  - WE2 to pulse programmer memory

30IOP4  - address advance clock pulse

M1032 (30IOP - initialize)

31IOP1  - SBC selection strobe
BC selection strobe

clock decade selection strobe

---

3IOP2 - clear SC register

---

3IOP4 - CCBG (computer controlled begin) to MS generator

M103 3 (32IOP - clock and SC)

---

32IOP1 - strobe SC into AC

---

32IOP2 - strobe final time from clock register to AC

---

32IOP4 - strobe initial time into clock register from AC

M103 4 (33IOP - plotter and RD)

---

33IOP1 - enable plotter (flip-flop → 0

---

33IOP2 - check RD PI-flag

---

33IOP4 - disable plotter (FF → 1)

M103 5 (34IOP - check flags)

---

34IOP1 - check LDM PI flag

---

34IOP2 - check INL PI flag

---

34IOP4 - check PLT PI flag

M103 6 (35IOP - clear flags)

---

35IOP1 - clear LDM PI flag
351OP2 - clear PLT PI flag

351OP4 - clear INL PI flag

D. XY PLOTTER INTERFACE

PLOTTER SIDE - Hewlett Packard 7004A X-Y Recorder with 17173A
Null Detector

1. Null Detector

<table>
<thead>
<tr>
<th>Pin No.</th>
<th>Signal</th>
<th>Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>- polarity seek pulse</td>
<td>NC</td>
</tr>
<tr>
<td>2</td>
<td>+ polarity seek pulse</td>
<td>C7U1 (EPLT) on pulse programmer</td>
</tr>
<tr>
<td>3</td>
<td>high current ground</td>
<td>blue and gray</td>
</tr>
<tr>
<td>4</td>
<td>complete plot pulse</td>
<td>pulse programmer</td>
</tr>
<tr>
<td>5-9</td>
<td></td>
<td>NC</td>
</tr>
</tbody>
</table>

2. Plotter

<table>
<thead>
<tr>
<th>Pin NO.</th>
<th>Signal</th>
<th>Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+Y</td>
<td>NC</td>
</tr>
<tr>
<td>2</td>
<td>-Y</td>
<td>white</td>
</tr>
<tr>
<td>6</td>
<td>ground</td>
<td>black</td>
</tr>
<tr>
<td>14</td>
<td>+X</td>
<td>yellow</td>
</tr>
<tr>
<td>15</td>
<td>-X</td>
<td>violet</td>
</tr>
</tbody>
</table>

* colors correspond to connections on following page.
PDP 12 SIDE - via Blue 26-B96 Female Connector on Front Panel

<table>
<thead>
<tr>
<th>Pin No.</th>
<th>Signal</th>
<th>Wire Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Channel Select</td>
<td>yellow</td>
</tr>
<tr>
<td>2</td>
<td>NC</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Shield chassis ground</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Intensify pulse</td>
<td>green--to C7D2 (PI)on pulse programmer</td>
</tr>
<tr>
<td>5</td>
<td>NC</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Shield chassis ground</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>X high Q ground</td>
<td>blue</td>
</tr>
<tr>
<td>8</td>
<td>X deflection</td>
<td>violet</td>
</tr>
<tr>
<td>9</td>
<td>Shield chassis ground</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Y high Q ground</td>
<td>gray</td>
</tr>
<tr>
<td>11</td>
<td>Y deflection</td>
<td>white</td>
</tr>
<tr>
<td>12</td>
<td>Shield chassis ground</td>
<td></td>
</tr>
<tr>
<td>13-18</td>
<td>NC</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>503 intensify</td>
<td></td>
</tr>
<tr>
<td>20-24</td>
<td>NC</td>
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E. CRYSTAL CLOCK DECADE CODE

<p>| | | | | |</p>
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<tr>
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<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>μsec</td>
<td>100</td>
<td>10 μsec</td>
<td></td>
</tr>
<tr>
<td>001</td>
<td>100 msec</td>
<td>101</td>
<td>sec</td>
<td></td>
</tr>
<tr>
<td>010</td>
<td>100 μsec</td>
<td>110</td>
<td>not used</td>
<td></td>
</tr>
<tr>
<td>011</td>
<td>10 msec</td>
<td>111</td>
<td>msec</td>
<td></td>
</tr>
</tbody>
</table>
III. SCHEMATIC DIAGRAMS

A. WIRING CONVENTION

1. signal mnemonic
2. C indicates pin number on card according to my convention. See the correspondence with DEC convention on next page.
3. pin number
4. pin number connected on integrated circuit
5. device number.

B. CARD PIN NUMBER INTERCONVERSION

<table>
<thead>
<tr>
<th>Mine</th>
<th>DEC</th>
<th>Mine</th>
<th>DEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A2</td>
<td>19</td>
<td>V1</td>
</tr>
<tr>
<td>2</td>
<td>B2</td>
<td>20</td>
<td>U1</td>
</tr>
<tr>
<td>3</td>
<td>C2</td>
<td>21</td>
<td>T1</td>
</tr>
<tr>
<td>4</td>
<td>D2</td>
<td>22</td>
<td>S1</td>
</tr>
<tr>
<td>5</td>
<td>E2</td>
<td>23</td>
<td>R1</td>
</tr>
<tr>
<td>Mine</td>
<td>DEC</td>
<td>Mine</td>
<td>DEC</td>
</tr>
<tr>
<td>------</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>6</td>
<td>F2</td>
<td>24</td>
<td>Pl</td>
</tr>
<tr>
<td>7</td>
<td>H2</td>
<td>25</td>
<td>N1</td>
</tr>
<tr>
<td>8</td>
<td>J2</td>
<td>26</td>
<td>M1</td>
</tr>
<tr>
<td>9</td>
<td>K2</td>
<td>27</td>
<td>L1</td>
</tr>
<tr>
<td>10</td>
<td>L2</td>
<td>28</td>
<td>K1</td>
</tr>
<tr>
<td>11</td>
<td>M2</td>
<td>29</td>
<td>J1</td>
</tr>
<tr>
<td>12</td>
<td>N2</td>
<td>30</td>
<td>H1</td>
</tr>
<tr>
<td>13</td>
<td>P2</td>
<td>31</td>
<td>F1</td>
</tr>
<tr>
<td>14</td>
<td>R2</td>
<td>32</td>
<td>E1</td>
</tr>
<tr>
<td>15</td>
<td>S2</td>
<td>33</td>
<td>D1</td>
</tr>
<tr>
<td>16</td>
<td>T2</td>
<td>34</td>
<td>C1</td>
</tr>
<tr>
<td>17</td>
<td>U2</td>
<td>35</td>
<td>B1</td>
</tr>
<tr>
<td>18</td>
<td>V2</td>
<td>36</td>
<td>A1</td>
</tr>
</tbody>
</table>

Figures 3-36 show the schematics for the pulse programmer cards. The detailed pin wiring can be found in the next section (IV).
Figure 3—Figure 36

Schematic diagrams of the main computer interface and pulse programmer cards. The signal names are for cross-referencing. Detailed pin connections are given in the wiring lists (next section). Schematics of the standard DEC modules (e.g. M103) are not presented—they may be found in DEC's logic handbook, and connections are in the wiring lists. The names for the cards are related to their function as described in the operation section. A convenient index for locating them is in the layout—Section II.A of this chapter.
Figure 3: Memory Cells  A15-18  
Bl16-18

*WEI OR WE2 IN WIRING LIST. SEE LOADING INSTRUCTIONS.
Figure 4: Memory Address

* WE1 OR WE2 IN WIRING LIST - SEE LOADING INSTRUCTIONS
Figure 5: Address Advance
Figure 6: Line Drivers  C14, C15
Figure 7: MPA Generators

RFMPC3
XCC5
\overline{\text{YCC8}}
\overline{\text{XCC2}}
\text{YCC6}

C4 \overline{\text{XMPA}}
C9 \overline{\text{YMPA}}
C1 \overline{\text{XMPA}}
C7 \overline{\text{YMPA}}

VDMPC25
VC C13
\overline{\text{VC C11}}

C12 \overline{\text{VMPA}}
C10 \overline{\text{VMPA}}

C14
C15

C16

T.I.
SN 7400N
T.I.
SN 7400N
T.I.
SN 7400N
T.I.
SN 7400N
Figure 8: XMP Generators  C20-22
Figure 9: X Pulse Gates C8, C10, C12

(Y, V) XMP C4

C1 X0

(CLC16)

H C10

(Y, V) XC C7

SW 948-2P

GND

Vcc

(CARD C12 = X PULSE GATES)
(CARD C10 = Y PULSE GATES)
(CARD C8 = V PULSE GATES)

(TPI C14)

(XMP C5)

(XC C8)

SN7400N

C2 X0

SW 948-2P

GND

XO = XMP + H
Figure 10: MS Generator  AB23
Figure 12: Burst Counter
Figure 14: Clock decade
Figure 15: Clock Counter
Figure 16: Delay Decoder
Figure 20: Sample C5
Figure 21: Program Interrupt
Figure 22: Computer Light
Figure 23: RFMP and VDMP Generator Switches
Figure 24: AD1, AD2 Switches
Figure 25: Mode Switch

BG
INL
OPEN
IA
PA
LBG

Vcc
GND
OPEN
IB
PB
EPC

OPEN
OPEN
OPEN
IC
PC
GRAYHILL 5003-9

OPEN
3C
4C
5C
6C
7C
8C
9C
XB
XB
YB
YB
VB
VB
GND
Figure 26: (a) Clock Switch, (b) Recycle Delay Switch
Figure 27: (a) Subburst Switch, (b) Burst Switch
Figure 28: (a) SI Switch, (b) Execute Switch
Figure 29: (a) RD Units Switch, (b) DIS PDPI2 Switch

(a)

(b)
Figure 30: (a) Top/Bot. Mem. Switch
(b) Dis. Spectr. Switch

(a) OPEN \rightarrow IA \rightarrow NO \rightarrow V_{cc} \rightarrow PA \rightarrow MEM

V_{cc} \rightarrow IC \rightarrow NO \rightarrow 2C \rightarrow OPEN

OPEN \rightarrow ID \rightarrow NO \rightarrow 2D \rightarrow V_{cc} \rightarrow L2 \rightarrow GND

(b) OPEN \rightarrow IA \rightarrow NO \rightarrow 2A \rightarrow V_{cc} \rightarrow PA \rightarrow SPECTR

V_{cc} \rightarrow IC \rightarrow NO \rightarrow 2C \rightarrow V_{cc} \rightarrow L2 \rightarrow GND

LAMP \rightarrow L1
LAMP \rightarrow L3
Figure 31: Start Switch, (b) Stop Switch

(a)

(b)
Figure 32: (a) Clear Switch, (b) Load Switch

(a)

(b)
Figure 33: Gate
Figure 34: ADC4: Data Multiplexer and Break Request B7
Figure 35: ADC3: data timing circuit
Figure 36: ADC Data: Gray/Binary Converter

[Diagram of a circuit with labeled components and connections, including SN7400N and N8242A ICs, with a binary comparator on the right.]
IV. WIRING

A. GENERAL PIN CARDS

Wire list convention is the following:

\[
\begin{array}{c|cc}
  + & XD1 & a \\ 
  \uparrow & Bl4 & 1 \\
  \uparrow & A2 & 2 \\
  \uparrow & - & 3 \\
  \uparrow & C14D1 & 4 \\
\end{array}
\]

1. + incoming signal name
   - outgoing signal name
   † bussed or multiply-connected incoming signal
   = bussed or multiply-connected outgoing signal
   a bar on the signal indicates active LOW.

2. Signal mnemonic

3. (a) card slot number for this card in the pulse programmer
   (b) pin number (DEC convention)

4. Same as 3--pin 3 is connected to pin 4.

B. PANEL CONNECTOR CARDS

Same as above but with wire connection to panel indicated.
Wire numbering corresponds to the panel connector pin number.
C. ROTARY SWITCHES

1. Same as 1 and 2 of A.
2. Switch name (usually mnemonic for function).
3. Number of switch position. P stands for pole.
4. Switch deck number. For the rotary switches corresponding to pulses (x y etc) and analog delays 3 and 4 are replaced by something like

\[ \begin{align*}
&\text{Q} \quad 3 \\
&3' \quad 4'
\end{align*} \]

3' indicates switch connection (my labelling)
4' connection number

5. Connector card wire or pin number connected.

D. PUSHBUTTON SWITCHES

1. Same as 1 and 2 of A
2. Switch name
3. Position of single-pole double-throw switch

   C: pole

   NC: normally connected

   NO: normally off

4. Deck of switch    5. Connection

   For pushbutton switches L1, L2, L3 indicate light connections
   on the switch:

   L1 - top lamp

   L2 - common (connected to ground)

   L3 - bottom lamp

E. WIRING LISTS

   Detailed wiring lists follow in this section. The pins are
   named according to the conventions in Sections A-D. The lists
   are labelled in alphabetical order for easy access and may be
   cross-referenced to the schematic diagrams and card layout dia-
   gram in Section II of this chapter.
5 e min shorter along different paths from corresponding vertex to VC generator.
### 38A

**Connections**

<table>
<thead>
<tr>
<th>+18 Vcc</th>
<th>224 A2 - NC</th>
<th>1. Empty lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>92 - NC</td>
<td>2. DC lamp</td>
</tr>
<tr>
<td></td>
<td>C1 - NC</td>
<td>3. EM lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>4. SB lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>5. END BUS WIRE</td>
</tr>
<tr>
<td>72</td>
<td>92 - A1K4</td>
<td>6. A lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>7. 31 lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>8. 32 lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>9. 31 lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>10. 32 lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>11. 31 lamp</td>
</tr>
</tbody>
</table>

### 42A

**Connections**

<table>
<thead>
<tr>
<th>+18 Vcc</th>
<th>D13 A2 - NC</th>
<th>1. End lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80 - NC</td>
<td>2. Rearview lamp</td>
</tr>
<tr>
<td></td>
<td>C2 - NC</td>
<td>3. Clock lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>4. Compass lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>5. END BUS WIRE</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>6. Empty lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>7. Empty lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>8. Open</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>9. Open</td>
</tr>
</tbody>
</table>

### 38B

**Connections**

<table>
<thead>
<tr>
<th>+18 Vcc</th>
<th>315 A2 - NC</th>
<th>1. C lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>92 - NC</td>
<td>2. K lamp</td>
</tr>
<tr>
<td></td>
<td>92 - NC</td>
<td>3. T lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>4. Y lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>5. END BUS WIRE</td>
</tr>
<tr>
<td>72</td>
<td>92 - A1K4</td>
<td>6. Y lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>7. Y lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>8. Y lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>9. Y lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>10. Y lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - NC</td>
<td>11. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>12. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>13. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>14. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>15. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>16. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>17. X lamp</td>
</tr>
<tr>
<td>92</td>
<td>92 - A1K4</td>
<td>18. X lamp</td>
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</table>
### Clock Switch

<table>
<thead>
<tr>
<th>LA</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>A800</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A819</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A818</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A817</td>
<td>A8702 Wire</td>
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<tr>
<td>A816</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A815</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A814</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A813</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A812</td>
<td>A8702 Wire</td>
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<tr>
<td>A811</td>
<td>A8702 Wire</td>
</tr>
<tr>
<td>A810</td>
<td>A8702 Wire</td>
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</tbody>
</table>

### Node Switch

<table>
<thead>
<tr>
<th>LA</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPEN</td>
<td>OPEN</td>
</tr>
<tr>
<td>LA</td>
<td>MC</td>
</tr>
<tr>
<td>OPEN</td>
<td>OPEN</td>
</tr>
<tr>
<td>2A</td>
<td>3A Wire</td>
</tr>
<tr>
<td>2B</td>
<td>4A Wire</td>
</tr>
<tr>
<td>2C</td>
<td>5A Wire</td>
</tr>
<tr>
<td>2D</td>
<td>6A Wire</td>
</tr>
<tr>
<td>2E</td>
<td>7A Wire</td>
</tr>
<tr>
<td>2F</td>
<td>8A Wire</td>
</tr>
<tr>
<td>2G</td>
<td>9A Wire</td>
</tr>
<tr>
<td>2H</td>
<td>10A Wire</td>
</tr>
<tr>
<td>2I</td>
<td>11A Wire</td>
</tr>
<tr>
<td>2J</td>
<td>12A Wire</td>
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</tbody>
</table>

### Operate Switch

<table>
<thead>
<tr>
<th>LA</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>A2081 Wire</td>
</tr>
<tr>
<td>2A</td>
<td>A2581 Wire</td>
</tr>
<tr>
<td>3A</td>
<td>A2881 Wire</td>
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<tr>
<td>4A</td>
<td>A2582 Wire</td>
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<tr>
<td>5A</td>
<td>A2583 Wire</td>
</tr>
<tr>
<td>6A</td>
<td>A2584 Wire</td>
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<tr>
<td>7A</td>
<td>A2585 Wire</td>
</tr>
<tr>
<td>8A</td>
<td>A2586 Wire</td>
</tr>
<tr>
<td>9A</td>
<td>A2587 Wire</td>
</tr>
<tr>
<td>10A</td>
<td>A2588 Wire</td>
</tr>
<tr>
<td>11A</td>
<td>A2589 Wire</td>
</tr>
<tr>
<td>12A</td>
<td>A2590 Wire</td>
</tr>
<tr>
<td>13A</td>
<td>A2591 Wire</td>
</tr>
</tbody>
</table>

### Node Switch

<table>
<thead>
<tr>
<th>LA</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>A2701 Wire</td>
</tr>
<tr>
<td>2A</td>
<td>A2702 Wire</td>
</tr>
<tr>
<td>3A</td>
<td>A2703 Wire</td>
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<tr>
<td>4A</td>
<td>A2704 Wire</td>
</tr>
<tr>
<td>5A</td>
<td>A2705 Wire</td>
</tr>
<tr>
<td>6A</td>
<td>A2706 Wire</td>
</tr>
<tr>
<td>7A</td>
<td>A2707 Wire</td>
</tr>
<tr>
<td>8A</td>
<td>A2708 Wire</td>
</tr>
<tr>
<td>9A</td>
<td>A2709 Wire</td>
</tr>
<tr>
<td>10A</td>
<td>A2710 Wire</td>
</tr>
<tr>
<td>11A</td>
<td>A2711 Wire</td>
</tr>
<tr>
<td>12A</td>
<td>A2712 Wire</td>
</tr>
</tbody>
</table>
CHAPTER IV

SOFTWARE
I. INTRODUCTION

The spectrometer is controlled by an expandable executive routine known as GOLEM 2. The layout of this program in the 8 fields (8k) of core in our PDP 12 is as follows:

<table>
<thead>
<tr>
<th>Field</th>
<th>Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>1</td>
<td>Alphanumeric display</td>
</tr>
<tr>
<td>2</td>
<td>Real average</td>
</tr>
<tr>
<td>3</td>
<td>Imaginary average</td>
</tr>
<tr>
<td>4</td>
<td>Spectrometer control routines</td>
</tr>
<tr>
<td>5</td>
<td>Phase correction</td>
</tr>
<tr>
<td>6</td>
<td>Real input</td>
</tr>
<tr>
<td>7</td>
<td>Imaginary input</td>
</tr>
</tbody>
</table>

A list of commands follows in the next section and immediately after this is a listing of the program.

Additional commands can be added to GOLEM 2 very simply:

(a) write subroutine for command execution somewhere in free core space. Exit from subroutine to BURST in Segment 4.

(b) assign two letter code and add at the end of INDEX and with suffix AD at the end of TABLE

(c) make table entry the name of first location for subroutine.
The operation of GOLEM 2 is self-explanatory from the listing (with detailed comments). The only instructions not included in the PDP 12 list are some I/O commands (6xxx). These are the instructions which service the peripherals (pulse programmer, plotter); they are coded and explained under device selection codes in the hardware section of this thesis. Further details may be understood by appealing to the detailed schematics.

The command pointer is an *. After execution of any command the executive routine is reentered and this displays the contents of the data buffer until a new command is received from the teletype. Typing rubout at any stage will cause an immediate re-initialization of the command buffer as indicated by an*. GOLEM2 may be restarted at any time by putting the PDP12 in LINK mode, setting the left switches to (10200) and pressing start left switches. Alternatively if it has been destroyed in core, the load and go option of DIAL may be used to fetch it from magnetic tape.

An additional program used in spectrometer control is PPROM: this creates, files and loads new pulse programs. This is not detailed here--an updated version and description is maintained by Mr. S. Kaplan.

I am grateful to Dr. W.E. Good Jr. for his assistance in writing the programs.
## II. GOLEM2 COMMANDS

### A. LISTING

<table>
<thead>
<tr>
<th>COMMAND</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL</td>
<td>Call &quot;Dial&quot;</td>
</tr>
<tr>
<td>RS</td>
<td>Run spectrometer, display input</td>
</tr>
<tr>
<td>RA</td>
<td>Run with averaging, display average</td>
</tr>
<tr>
<td>$\text{RA,} \alpha_1 \alpha_2 \alpha_3 \alpha_4$</td>
<td>Run with averaging $(\alpha_1 \alpha_2 \alpha_3 \alpha_4)$ times $\alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_8$</td>
</tr>
<tr>
<td>CA</td>
<td>Continue - averaging</td>
</tr>
<tr>
<td>$\text{CA,} \alpha_1 \alpha_2 \alpha_3 \alpha_4$</td>
<td>Average another $(\alpha_1 \alpha_2 \alpha_3 \alpha_4)$ times $\alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_8$</td>
</tr>
<tr>
<td>DI</td>
<td>Display input</td>
</tr>
<tr>
<td>DA</td>
<td>Display average</td>
</tr>
<tr>
<td>PD</td>
<td>Plot data</td>
</tr>
<tr>
<td>CL</td>
<td>Clear data buffers</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transform average</td>
</tr>
<tr>
<td>IT</td>
<td>Inverse transform average</td>
</tr>
<tr>
<td>$\text{SD,} \alpha_1 \alpha_2 \alpha_3 \alpha_4$</td>
<td>Save average as no. $(\alpha_3 \alpha_4)$ on tape 1</td>
</tr>
<tr>
<td>$\text{CD,} \alpha_1 \alpha_2 \alpha_3 \alpha_4$</td>
<td>Call data no. $(\alpha_3 \alpha_4)$ from tape 1 into average buffer</td>
</tr>
<tr>
<td>ST</td>
<td>Stop; this exits from all other commands</td>
</tr>
<tr>
<td>MX</td>
<td>Phase mix average; angle determined by POT 7.</td>
</tr>
<tr>
<td>AD</td>
<td>Add constant to average up to cursor; const $\equiv$ POT 3.</td>
</tr>
<tr>
<td>$\text{SM,} \alpha_1 \alpha_2 \alpha_3 \alpha_4$</td>
<td>Smooth average $(\alpha_3 \alpha_4)$ times $\alpha_3 \alpha_4 \alpha_8$</td>
</tr>
<tr>
<td>RUBOUT</td>
<td>Return command pointer (*)</td>
</tr>
</tbody>
</table>
### DISPLAY OPTIONS

<table>
<thead>
<tr>
<th>SENSE SWITCH</th>
<th>POTENTIOMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - expanded display</td>
<td>0-move, 1-horizontal expand, 2-vertical expand</td>
</tr>
<tr>
<td>1 - data buffer, real or imag.</td>
<td></td>
</tr>
<tr>
<td>2 - display every second point</td>
<td></td>
</tr>
<tr>
<td>3 - alfanumeric + cursor</td>
<td>5-coarse cursor 6 - fine cursor</td>
</tr>
</tbody>
</table>

### B. DESCRIPTION OF COMMANDS

We present only a brief description of some of the commands. The operation will be referenced to the discussion of the pulse programmer operation in the hardware section.

**DL:** Brings the PDPl2 linctape operating system "DIAL MS" into core.

**RS:** Runs the spectrometer when the pulse programmer is in CC (Computer Control) mode. The end of a RD is sensed by the computer (6342) and it then initializes by clearing flags and counters in the pulse programmer and initializes a new burst through CCBG to the MS generator (6314). Now, while data is being received via data break into fields 6 and 7 the computer waits in a loop. The RD request causes a PI which returns GOLEM2 to the spectrometer service routine.

**RA:** Data from fields 6 and 7 is stable averaged into fields 2 and 3. The remainder of the operation is the same
as for RS. Averaging is performed at the end of the RD for all 1024 complex points and takes ~ 250 msec so is not suited to ultra rapid data acquisition. This may easily be streamlined. The stable average algorithm is due to Hewlett-Packard. If $\bar{S}_N$ is the average after $N$ passes and $S_n$ the input at pass $n$ then:

$$\bar{S}_N = \frac{1}{N} \sum_{n=1}^{N} S_n$$  \hspace{1cm} (1)

This may be written

$$\bar{S}_N = \frac{N-1}{(N-1)N} \sum_{n=1}^{N-1} S_n + \frac{1}{N} S_{N-1}$$

$$\bar{S}_N = \frac{N-1}{N} \bar{S}_{N-1} + \frac{1}{N} S_{N-1}$$

or finally

$$\bar{S}_N = \bar{S}_{N-1} + \frac{S_{N-1} - \bar{S}_{N-1}}{N}$$  \hspace{1cm} (2)

This expression is exact. It may now be made operationally very convenient for a computer by introducing the approximation

$$\bar{S}_N = \bar{S}_{N-1} + \frac{S_{N-1} - \bar{S}_{N-1}}{2^k}$$  \hspace{1cm} (3)

where $k$ is an integer satisfying

$$2^{k-1} < N < 2^k + 1$$  \hspace{1cm} (4)

This is an excellent approximation and easily implemented in
the program: the current average is subtracted from incoming data, the result is shifted by \( k \) and added to the current average to give the next average.

CA: continues averaging if \( RA_1, a_2, a_3, a_4 \) was not sufficient. May be done after some intermediate commands (FT) as well.

DI: displays input buffer (fields 6 and 7)

DA: displays average buffer (fields 2 and 3)

PD: data is plotted on the Hewlett-Packard plotter (see hardware section) from exactly what is viewed on the PDPl2 screen. This therefore benefits from all the display options described above. Plotting is very efficient, in that the plotter runs at a speed compatible with the distance between points, by generating signals to the PDPl2 when each point is plotted. This is sensed (6344) by the computer, which clears the flag (6354) and plots the next point. The plotter is driven by X-Y signals from the PDPl2 scope display and the scope intensify pulse. The plotter can be enabled and disabled (6331 and 6334) to prevent jitter during normal, un-plotted display of CCLEM 2.

FT: performs a fast Fourier transform (FFT) on 1024 complex 12 bit words in the average buffer (fields 2 and 3). The transform is placed into the average buffer.
Transformation is accomplished in approximately 5 seconds. The size of the transform may be decreased by changing N and NU on the first page of the sub-routine. The sine table is used as a general lookup table for both the FFT and the phase mixing routine.

**IT:** Same as FT but performs inverse transform.

**SD:** data in the field under display (2, 3, 6, or 7) is stored on magnetic tape UNIT 1. If the data number requested is \( 00XY \) then the data will take up blocks \( (00XY + 4) \times 10 \) on magnetic tape. This uses up only one half of the storage space—the remainder can be used to store pulse programs.

**MX:** this performs a phase correction of data in the average buffer. The correction is on line with the display, and the angle \( \alpha (-90^\circ \text{ to } +90^\circ) \) is determined by potentiometer 7. The routine performs the operation

\[
(\text{real})_{\text{corr}} = \cos \alpha \cdot \text{real} + \sin \alpha \cdot \text{imag} \\
(\text{imag})_{\text{corr}} = -\sin \alpha \cdot \text{real} + \cos \alpha \cdot \text{imag}
\]

**AD:** a constant determined by potentiometer 3 is added to the data. If we are not in alphanumeric display option (sense switch 3) then all the data in the displayed field are affected. If the alphanumeric option is activated then only points up to and including the cursor are affected. The display may be restabilized
by typing ST.

SM: a three point quadratic \((0.25 N-1 + 0.5 N + 0.25 N+1)\) smoothing of data in the average buffer is performed. It can be shown easily that smoothing with this algorithm in one domain, say time, is equivalent to filtering in the other (frequency) with a transfer function:

\[
g(\omega) = \frac{1}{2} (1 + \cos \omega \Delta t) \tag{5}
\]

where \(\Delta t\) is the time domain sampling period. For this to be effective, the input should be band-limited by a filter with cutoff frequency equal to the Nyquist frequency

\[
\omega_F = \frac{\pi}{\Delta t} \tag{6}
\]

since (5) does not eliminate noise folded over into this band. For repeated smoothings, \((\alpha_1 \alpha_2 \alpha_3 \alpha_4)\) large, it is easily shown that the smoothing approaches Gaussian. (Gaussian filtering in the other domain). Smoothing is frequency domain accomplishes what one normally calls "apodization" of the time domain signal by a function of the form of (5).

DISPLAY: the alphanumeric option (switch 3) will produce a cursor by brightening one of the displayed data points.
The cursor position is controlled by coarse and fine potentiometers (5 and 6). The coordinates of this point will appear at the top right hand corner of the screen. The top number is the (decimal) location of the selected point in the displayed buffer (0-1023). The lower one is the contents of that location as scaled for the screen display (vertical coordinate).

III. PROGRAM LISTING

A computer printout of the source program follows.
GOLEM2, I LN=1

SEGMENT 4
/
*1 /*FLAGS POINTERS COUNTERS AND
REGISTERS
/
BFLAG, 0 /*BUFFFER
AFLAG, 0 /*AVERAGE
RFLAG, 0 /*RUN
PFLAG, 0 /*PLOT
X, 0 /*DATA
Y, 0 /*DATA
EFLAG, 0 /*EXPAND
CPINT, 0 /*COMMAND
TPINT, 0 /*TABLE
IPINT, 0 /*INDEX
ACOUNT, 0 /*AVERAGE
DIV, 0 /*DIVISION
MXFLAG, 0 /*MIX
ANFLAG, 0 /*ALFANUMERIC
/
SEGMENT 0
/
*40 /*FOR PROGRAM INTERRUPT (PI)
/
0
108
6031 /*WAS IT TELETYPewriter (TTY)?
JMP .+3 /*NO - THEN ASSUME IT WAS RECYCLE
DELAY (RD)
LIF 4 /*YES
JMP TTY
LIF 4
JMP CHKAVE /*AND CONTINUE
/
SEGMENT 4
/
*20
/
ENTER, LDA I
252
I0B
6046 /*WRITE *
SET I ACOUNT 0 /*SET AVERAGE COUNTER
SET I BFLAG 1 /*AVERAGE BUFFER
SET I AFLAG 0 /*AVERAGE FLAG OFF
SET I RFLAG 0 /*RUN FLAG OFF
SET I PFLAG 0 /*PLOT FLAG OFF
SET I MXFLAG 0 /*MIX FLAG OFF
SET I ANFLAG 0 /*ALFANUMERIC FLAG OFF
JMP BUFF
GOLEM2,2 LN=71

*100
/

BUFF,  LDA
BFLAG
AZE
JMP .+7  /AVERAGE BUFFER
SNS I 1  /INPUT BUFFER
JMP .+3
LDF 6   /REAL INPUT
JMP .+10 /IMAG INPUT
LDF 7   
JMP .+6
SNS I 1
JMP .+3
LDF 2   /REAL AVERAGE
JMP .+2
LDF 3   /IMAG AVERAGE
CHKALF, SAM 5  /ALPHANUMERIC
ADA I
1000  /MAKE POSITIVE
BCL 1
7   /TO PREVENT JITTER - COARSE
STC SAMREG  /FOR ALPHANUM AND ADDITION ROUTINES
SAM 6   /FINE CURSOR ADJUSTMENT
SCR 4
ADA
SAMREG
STC SAMREG
COORD,  SET I X
       0
SET I Y
3777
SET I EFLAG
0   /EXPAND FLAG OFF
SNS I 0  /MOVE AND EXPAND?
JMP MOVE  /YES
DISPLY, JMP FPLOT  /GO CHECK PLOT FLAG
SNS 0
JMP .+12  /NORMAL DISPLAY
SAM 2   /VERTICAL SCALING
COM
SCR 7
BCL I
777A
ADA I
SCR
STC VERT
JMP .+4
LDA I
SCR 3  /NORMAL VERTICAL SCALE
STC VERT
LDA I Y
VERT,  0   /SCALE
DIS X   /DISPLAY
SNS 3  /ALPHANUMERIC?
JMP NOALF  /NO
GOLEM2.3 LN=162

LDA
Y
BCL I
2000  
SAE I
/STRIP OFF DATA FIELD INDEX
SAMREG, 0  
/JMP NOALF+3
/LDA
/YES - BRIGHTEN
VERTI
STC VERTI
LDA Y
VERTI, 0  
/DIS X
/DIS X
/DIS X
/DIS X
/DIS X
/DIS X
/DIS X
/DIS X
/DIS X
/DIS X
/Scale
ALFNUM, LDA
/SAMREG
/Prepare to Display Alphanumeric
ADDRESS
LIF 1
/JMP 20
/GO To Subroutine OCTDEC For Octal
- Decimal Conversion Of Address
LDA I
340  
/LIF 1
/JMP 200  
/YCOORDINATE
/GO To DISCHR For Address Display
(Decimal)
LDA Y  
/Prepare To Display Alphanumeric
Contents
LIF 1
/JMP 20  
/GO To OCTDEC
LDA I
300  
/LIF 1
/JMP 200  
/YCOORDINATE
/JMP NOALF+3
/GO To DISCHR
NOALF, LDA I
1777
STC SAMREG  
/For SNS3=0 - SAMREG Has 1777
XSK I X  
/Increment X
NOP
SNS 2  
/Concentrated Display?
/JMP +3
/NO
XSK I Y  
/YES - Display Every Second Data
POINT
NOP
LDA
EFLAG
AZE  
/Expand?
G0LEM2.4  LN=246

JMP EXPAND  /YES
LDA
X
ROL 2
AP0 I  /DISPLAY REACHED END OF PDP SCORE?
JMP DISPLAY  /NO
LDA  /YES
PFLAG:
AZE I  /DID WE JUST PLOT?
JMP .+6  /NO
I0B
6344
JMP .-2  /YES - SO WAIT FOR LAST POINT TO BE PLOTTED
I0B
6357  /CLEAR DEVICE FLAGS
SET I PFLAG
0  /PLOT FLAG OFF
JMP TTY  /GO CHECK TTY
/

FPLOT, LDA  /SUBROUTINE TO CHECK IF POINT SHOULD BE PLOTTED. IF SO IT WAITS UNTIL PLOTTER READY
0
STC SUBPLT  /FOR EXIT
LDA
PFLAG
AZE I  /PLOT FLAG ON?
JMP 0  /NO - GO DISPLAY
I0B
6344
JMP .-2  /YES - WAIT FOR COMPLETE PLOT PULSE
I0B
6357  /CLEAR DEVICE FLAGS
I0B
6331  /REENABLE PLOTTER
JMP SUBPLT  /EXIT
/

SUBPLT, 0
/

MOVE, SAM 0
BCL I
7008
ROL 1
XSK I Y
NQP
ADM
Y
SET I EFLAG
1  /TURN ON EXPAND FLAG
JMP 0  /EXIT
/

EXPAND, SAM 1
BCL I
7000
SCR 3
ADM
GOLEM2.S  LN=335

X
      JMP @  /EXIT

TTY,
   SET I CPOINT
   COMM /COMMAND BUFFER
   IOB
   6031 /TTY READ FLAG ON?
   SKP /NO
   JMP READ-3 /YES

CHKMIX, LDA
   MXFLAG
   AZE I /IN PHASE MIXING LOOP?
   JMP *+3 /NO - CONTINUE
   LIF @ /YES GO TO MIX ROUTINE
   JMP 201

CHKADD, LDA
   ANFLAG
   AZE I /IN ADDITION LOOP?
   JMP *+2 /NO - CONTINUE
   JMP DOADD /YES - GO ADD

RD,    IOB
   6342 /END OF RD?
   JMP BUFF /NO
   LDA /YES
   RFLAG
   AZE I /RUN FLAG ON?
   JMP BUFF /NO

BURST, PDP /YES
   PMODE
   CLA
   6042 /CLEAR TTY WRITE FLAG TO PREVENT PI
   ION
   LINC
   LMODE
   IOB
   6357 /CLEAR DEVICE FLAGS
   IOB
   6312 /CLEAR SAMPLE COUNTER
   NOP
   NOP
   NOP
   IOB
   5314 /INITIALIZE BURST
   NOP
   JMP *-1 /WAIT FOR PI (FROM RD)

CHKAVE, LDA
   AFLAG
   AZE /AVERAGE FLAG ON?
   JMP STAVE /YES
   JMP BUFF /NO

STAVE, LDA
   AFLAG
GOLEM2, 6 LN=426

SAE 1
2

COMMAND?
JMP +4 /ARE WE ON FIRST AVERAGE PASS OF RA
SET I AFLAG /NO - AVERAGE
I
/YES - DO NOT AVERAGE. FOR CASE RD

NOT >> T1
JMP BUFF
LDA ACOUNT /AVERAGE COUNTER
SAE
NAVE /REACHED PRESET COUNT?
JMP +6 /NO
SET I AFLAG /YES
0
/CREASED FLAG OFF
SET I RFLAG 0
/RUN FLAG OFF
JMP BUFF /

AGO, XSK I ACOUNT /INCREMENT AVERAGE COUNTER
NQP
LDA ACOUNT
JMP INCR /GO SEE IF AVERAGED ANOTHER 2000

TIMES STC ACOUNT /IF SO STORE MODIFIED AVERAGE COUNT
(+2000)
SET I DIV 0
JMP POWER /POWER OF TWO FOR AVERAGE DIVISION

INCR, STC STORE /STORE AVERAGE COUNT
LDA 0
STC SUBINC
LDA STORE
BCL I 6000
AZE /IS AVERAGE COUNT MULTIPLE OF 2000?
JMP +6 /NO
LDA STORE
ADA I 2000 /TRANSFER TO NEXT 2000
JMP SUBINC /EXIT
LDA STORE
JMP SUBINC /NO MODIFICATION OF AVERAGE COUNT

STORE, 0 /EXIT
SUBINC, 0

POWER, LDA ACOUNT
SCR +1
BCL I 4000 /IN CASE AVERAGE COUNT WAS >3777
GOLEM2,7 LN=512

OThERWISE SCALE NEVER REACHES 0
AZE I /FOUND POWER OF TWO FOR AVERAGE
COUNT?
JMP +4 /YES
XSK I DIV /NO - INCREMENT POWER OF TWO
NOP
JMP POWER+2 /AND GO SCALE AGAIN
LDA
DIV
ADA I
SCR
STC SHFT /FOR DIVISION
SET I X
1777 /DATA COUNTER
SET I Y
3777 /DATA POINTER
SET I EFLAG
0 /EFLAG USED AS BUFFER INDICATOR
LDA I /SET UP DATA FIELD COMMANDS FOR

AVE,
CLR /START AVERAGING
D1,
0 /AVERAGE BUFFER

D2,
0 /INPUT BUFFER
LDA Y
STC SHFT-2

PDP /DO TWO'S COMPLEMENT ARITHMETIC

SINCE DIGITIZER INPUT IS IN THIS FORM
P'MODE
TAD AVB
CIA
TAD INB /IN-AVE ==> AC
JMP +3

INB,
0
AVB,
0
LINC
LMODE
SHFT,
0 /DIVIDE - SCALE BY K WHERE
2^POWER(K-1)<C(ACCOUNT)<2^POWER(K)+1
PDP
P'MODE
TAD AVB /(IN-AVE)/K + AVE ==> AC
LINC
LMODE
D3,
0 /AVERAGE BUFFER
STA Y /(IN-AVE)/K + AVE ==> AVE
GOLEM2,10 LN=577

XSK I X /DONE 2000 POINTS?
JMP AVE /NO
LDA /YES
EFLAG
AZE
JMP BUFF /YES
SET I EFLAG I /JUST DONE IMAGINARY DATA?
I
LDA I /NO
LDF 3
STA
D1
STA
D3
LDA I
LDF 7
STA
D2
SET I X
1777 /RESET DATA COUNTER
SET I Y
3777 /RESET DATA POINTER
JMP AVE /GO AVERAGE IMAG DATA
/
CLR
10B
6044 /DUMMY WRITE TO SET ITY WRITE FLAG
/
READ,
LDA I
7707
STA
COMM+1
STA
COMM+2 /PUT 7777 IN NUMBER PART OF COMMAND
BUFFER SO WE SMOOTH OR AVERAGE 8000 TIMES IF NO PRESET COUNT IS SPECIFIED
JMP RTT /GO READ ITY
JMP CHKRRUB /SEE IF RUB
JMP WRT /NO - ECHO
SHT CPQINT /SAVE FIRST HALF
JMP RTT
JMP CHKRRUB
JMP WRT
SHT I 10
SHTD I 10 /SAVE IT
INCREMENT HALF WORD
NOP
LDA
CPQINT
SAE I
COMM+2 /ON LETTER (XX) OR NUMBER (AAAA)
PART OF COMMAND?
SKP
JMP READ+6 /LETTER

CHAR,
JMP RTT /NUMBER
JMP CHKRRUB /GET NEXT CHARACTER
SAE I
GOLEM2,11 LN=665

254 /COMMA?
JMP +3 /NO
JMP WRT /YES
JMP READ /ECHO AND GO GET NEXT CHARACTER
SAE I
215 /CR?
JMP CHAR /NO - GO TRY AGAIN FOR LEGAL

CHARACTER (RUB,COMMA,CR)
JMP WRT /YES - ECHO
LDA I
212
JMP WRT /WRITE LF
LDA I
252
JMP WRT /WRITE *
SET I CPOINT
COMM /RESET COMMAND POINTER
JMP CNTRL /

RTT,  PDP /READ TTY
PMODE
6031
JMP -.1 /WAIT FOR TTY READ FLAG
6036 /CLEAR FLAG AND READ
LINC
LMODE
JMP @ /EXIT /

WRT,  PDP /WRITE ON TTY
PMODE
6041
JMP -.1 /WAIT FOR TTY WRITE FLAG
6046 /CLEAR FLAG AND WRITE
LINC
LMODE
JMP @ /EXIT /

CHKRUB, SAE I
377 /RUB OUT?
JMP @ /NO
JMP RUB /YES /

RUB,  SET I CPOINT /RUB OUT COMMAND
COMM /RESET COMMAND POINTER
LDA I
215
JMP WRT /WRITE CR
LDA I
212
JMP WRT /WRITE LF
LDA I
252
JMP WRT /WRITE *
JMP READ /RETURN /

CNTRL,  SET I TPOINT
TABLE-1
**GOLEM2,12 LN=755**

```
SET I IPOINT
INDX-1
CMPAR, XSK I IPOINT /ADVANCE IN TABLE
XSK I IPOINT /ADVANCE IN INDEX
LDA
IPOINT
SAE I
COUNT /COMMAND NOT IN INDEX?
SKP
JMP READ /NO
LDA CPOINT
SAE IPOINT /FOUND COMMAND IN INDEX?
JMP CMPAR /NO
LDA TPOINT /YES
ADA I
JMP
STC EXEC
/
EXEC, 0 /GO EXECUTE COMMAND
/
COMM, 0

/ST - STOP
/RS - RUN SPECTROMETER
/RA - RUN WITH AVERAGING
/CA - CONTINUE AVERAGING
/DI - DISPLAY INPUT
/DA - DISPLAY AVERAGE
/MD - PLOT DATA
/CL - CLEAR BUFFERS
/FT - FOURIER TRANSFORM AVERAGE
/IT - INVERSE TRANSFORM AVERAGE
/SD - SAVE DATA ON TAPE
/CD - CALL DATA FROM TAPE
/MP - MAKE PULSE PROGRAM
```
GOLEM2,13 LN=1046

1420 /LP - LOAD PULSE PROGRAM
1530 /MX - PHASE MIX AVERAGE
0104 /AD - ADD CONSTANT TO DATA
0414 /DL - CALL DIAL
2315 /SM - SMOOTH DATA
/
COUNT, 0 /INDICATES END OF INDEX
/
TABLE, STAD /COMMAND EXECUTE ADDRESSES
RSAD
RAAD
CAAD
DIAD
DAAD
FDAD
CLAD
FTAD
ITAD
SDAD
CDAD
MPAD
LPAD
MXAD
ADAD
DLAD
SMAD
/
STAD, SET I AFLAG /STOP
0
SET I RFLAG 0
SET I PFLAG 0
SET I MXFLAG 0
SET I ANFLAG 0
JMP BUFF
/
RSAD, SET I BFLAG /RUN SPECTROMETER
0
SET I AFLAG 0
SET I PFLAG 0
SET I RFLAG 1
SET I MXFLAG 0
SET I ANFLAG 0
JMP BURST
/
RAAD, SET I PFLAG /RUN WITH AVERAGING
0
SET I BFLAG 1
GOLEM2.14  LN=1137

SET I AFLAG 2
SET I RFLAG 1
SET I MXFLAG 0
SET I ANFLAG 0
SET I ACOUNT 0  /*RESET AVERAGE COUNTER*/
JMP ACOMM
JMP BURST  /*RETURN*/

ACOMM, NOP

SET I CPQINT  /*NOW TAKE NUMBER PART OF COMMAND*/
BUFFER (COMM+1 AND COMM+2) REPACK AS A SINGLE NUMBER AND STORE IN NAVE
COMM+1
LDH CPQINT  /*GET FIRST DIGIT FROM NUMBER PART*/

OF RA COMMAND
BCL I 7770
ROL 11
STC TEMM1
LDH I CPQINT  /*SECOND DIGIT*/
BCL I 7770
ROL 6
STC TEMM2
LDH I CPQINT  /*THIRD DIGIT*/
BCL I 7770
ROL 3
STC TEMM3
LDH I CPQINT  /*FOURTH DIGIT*/
BCL I 7770
ADD TEMM1  /*PACK FOUR DIGITS*/
ADD TEMM2
ADD TEMM3
STC NAVE  /*STORE IN PRESET AVERAGE COUNT*/

REGISTER
SET I CPQINT
COMM
JMP 0  /*RETURN*/

NAVE, 0
TEM1, 0
TEM2, 0
TEM3, 0

CAAD, SET I PFLAG  /*CONTINUE AVERAGING*/

0
SET I BFLAG 1
SET I AFLAG 2
SET I RFLAG
GOLEM2,15  LN=1224

1
SET I MXFLAG
0
SET I ANFLAG
0
JMP ACOMM  /GO READ NUMBER OF REQUESTED
AVERAGE
PASSES
JMP BURST  /GO AVERAGE
DIAD,
SET I BFLAG  /DISPLAY INPUT
0
JMP BUFF
/DAAD,
SET I BFLAG  /DISPLAY AVERAGE
1
JMP BUFF
/PDAD,
SET I AFLAG  /PLOT DATA
@\nSET I RFLAG
@\nSET I PFLAG
1
SET I MXFLAG
0
SET I ANFLAG
0
1GB  A/ENABLE PLOTTER
6331
CLR
DIS PFLAG  /DUMMY PLOT OF POINT (0,0) TO GIVE
PLOT COORDINATES ORIGIN AND TO SEND OUT FIRST COMPLETE PLOT
PULSE
JMP BUFF
/CLAD,
LDF 2  /CLEAR DATA BUFFERS
SET I Y
3777
SCL,
CLR
STA Y
XSK I Y
JMP SCL
LDA
CLAD
SAE I
LDF 3  /CLEARED AVERAGE BUFFER?
JMP ./+5  /NO
LDA I  /YES
LDF 6
STC CLAD  /SWITCH TO INPUT BUFFER
JMP CLAD
SAE I
LDF 7  /CLEARED ALL?
JMP ./+5  /NO
LDA I
LDF 2
STC CLAD  /RESET CLAD
JMP BUFF  /YES
GOLEM 2, 16  LN=1312

ADA I
  I
STC CLAD
JMP CLAD

FTAD, SET I AFLAG
  0
/INCREMENT DATA FIELD
SRT I RFLAG
  0
SET I BFLAG
  I
SET I MXFLAG
  0
SET I ANFLAG
  0
LDF 2
  /SET DATA FIELD FOR FT
LIF 0
JMP 20

ITAD, SET I AFLAG
  0
/INVERSE TRANSFORM AVERAGE
SRT I RFLAG
  0
SET I BFLAG
  I
SET I MXFLAG
  0
SET I ANFLAG
  0
LDF 2
  /SET DATA FIELD FOR IT
LIF 0
JMP 30

SDAD, SET I AFLAG
  0
/SAVE DATA ON TAPE
SRT I RFLAG
  0
SET I MXFLAG
  0
SET I ANFLAG
  0
JMP PACK
  /GO GET DATA NUMBER
R0L 3
  /X10
ADA I
3004
STC STAP
  715
/WRITE
STAP, 0
  /READ BLOCKS FROM CURRENT DATA FIELD
ONTO TAPE STARTING AT BLOCK NUMBER (10 X DATA NUMBER) + 4
JMP BUFF

CDAD, SET I AFLAG
  0
/CALL DATA FROM TAPE
SRT I RFLAG
  0
SET I MXFLAG
  0
GOLEM2,17 LN=1402

0
SET I ANFLAG
0
JMP PACK       /GO GET DATA NUMBER
RCL 3          /X10
ADA I
3004
STC CTAP
711            /READ
CTAP, 0        /4 BLOCKS FROM TAPE ADDRESS (10 X DATA NUMBER)+4 INTO CURRENT DATA FIELD
JMP BUFF
/
PACK, SET I CPONIT
COMM+2         /PACKS THIRD AND FOURTH DIGITS OF NUMBER PART OF SD CD MP LP SM COMMANDS
LDH CPONIT     /GET THIRD DIGIT
BCL I
7770
RCL 3
STC TEMMI
LDH I CPONIT   /GET FOURTH DIGIT
BCL I
7770
ADD TEMMI      /PACK
JMP 0          /EXIT
/
MPAD, JMP BUFF
LPAD, JMP BUFF
/
ADAD, SET I AFLAG       /FOR ADDING CONSTANT TO DATA IN AVE
BUFFER
0
SET I RFLAG
0
SET I MXFLAG
0
SET I ANFLAG
1
JMP SMSTRT       /GO TRANSFER DATA TO INPUT BUFFER
DQADD, SET I Y
3777
SAM 3            /ADDITION CONSTANT
BCL I
1               /TO PREVENT JITTER
SAE
ADADDRG         /CONSTANT SAME AS BEFORE?
JMP +2         /NO - GO ADD
JMP 100       /YES - RETURN TO CONTROL AND DISPLAY
STC ADDADDRG   /STORE NEW CONSTANT
ADSTRT, SNS 1   /REAL OR IMAGINARY DATA?
JMP +3        /IMAG
LDF 7          
SKP
LDF 6          /
LDA I Y
ADA I
GOLEM2.20  LN=1470

ADREG, 0
SNS 1 /ADD CONSTANT
JMP +3
LDF 3 /REAL OR IMAGINARY DATA?
SKP
LDF 2 /IMAG
STA Y
LDA Y
BCL I
2000 /STORE NEW VALUE
SAE
SAMREG
/REAL

POINT FOR SNS3=1 AND HAS 1777 FOR SNS3=0
JMP ADSTRT
/JMP ADSTRT /NO - GO DO NEXT POINT
JMP D0ADD /YES - GO CHECK FOR CHANGE OF

CONSTANT
/

MXAD,
SET I MXFLAG
1
SET I ANFLAG
0
JMP SMAD+14 /ADDED TO ALL REQUESTED POINTS?
CLR
LIF 0
JMP 200
/STRIP OFF DATA FIELD INDEX
SAE
SAMREG
/ADD TO ALPHANUMERIC

SNS 1

JMP ADSTRT
/JMP ADSTRT /NO - GO DO NEXT POINT
JMP D0ADD /YES - GO CHECK FOR CHANGE OF

CONSTANT
/

DLAD,
SET I EFLAG /ADDED TO ALL REQUESTED POINTS?
2015
LDF 2
LDA I
701
/AVG BUFFER ==> INPUT BUFFER
STA I EFLAG
LDA I
7300
STA I EFLAG
LIF 2
LDF 3
JMP 16

SMAD,
SET I AFLAG
0
SET I RFLAG
0
SET I MXFLAG
0
SET I ANFLAG
0
JMP PACK /AVERAGE BUFFER ==> INPUT BUFFER
STC NAVE
LDA ACCOUNT
STC TMCOUNT
/ADD TO ALPHANUMERIC

PASSES
SET I ACOUNT
0 /FOR SMOOTHING COUNT
SMSTR, SET I X
3777
SMD1, LDF 2 /MAY BE LDF 3
LDA X
SMD2, LDF 6 /MAY BE LDF 7
STA X /AVERAGE BUFFER ==> INPUT BUFFER
XSK I X /TRANSFERRED 2000 POINTS?
JMP SMD1 /NO
LDA /YES
SMD1
SAE I
LDF 3 /TRANSFERRED IMAG DATA?
SKP
JMP *.10 /YES
LDA I /NO - SET UP FOR IMAG
LDF 3
STC SMD1
LDA I
LDF 7
STC SMD2
JMP SMSTR
LDA I /RESET TO REAL
LDF 2
STC SMD1
LDA I
LDF 6
STC SMD2
LDA MXFLAG
AZE I /WAS THIS DATA TRANSFER FOR MIXING?
JMP *.2 /NO - CONTINUE
JMP MXAD+5 /YES - RETURN TO MIXING ROUTINE
LDA ANFLAG
AZE I /WAS THIS DATA TRANSFER FOR ADDITION?
JMP *.2 /NO - CONTINUE
JMP DQADD /YES - RETURN TO ADDITION ROUTINE
SMOOTH, SET I X
3777
JMP SMD3 /SMOOTH NEXT POINT
SDONE, LDA /DONE 2000 POINTS
SMD4
SAE I
LDF 3 /SMOOTHED IMAG DATA?
JMP SMIMAG /NO - GO DO IMAG
LDA I /YES - RESET FOR REAL
LDF 2
STC SMD4.
LDA I
LDF 6
STC SMD3
XSK I ACOUNT /INCREMENT SMOOTHING COUNTER
NOP
LDA
ACOUNT
SAE
GOLEM2,22 LN=1646

NAVE /SMOOTHED PRESET COUNT?
JMP SMSRST /NO - G0 SMOOTH AGAIN
LDA
TMCONT
STC ACOUNT /RESTORE AVERAGE COUNTER
SET I PFLAG 0
SET I RFLAG 0
SET I AFLAG 0
SET I BFLAG 1
JMP BUFF /RETURN
SMIMAG, LDA I /SET FOR IMAGINARY
LDF 3
STC SMD4
LDA I
LDF 7
STC SMD3
JMP SMOOTH
SMD3, LDF 6 /MAY BE LDF 7
LDA X
SCR 2
STC STMEM1 /0.25C(X-1)
LDA I X
SCR 1
STC STMEM2 /0.5C(X)
LDA I X
SCR 2 /0.25C(X+1)
PDP /FOR TQMS COMPLEMENT
PMODE
TAD STMEM1
TAD STMEM2 /0.25C(X-1) + 0.5C(X) + 0.25C(X+1)
FOR @<X<1777
JMP .+4
STMEM1, 0
STMEM2, 0
STMEM3, 0
LINC
LMODE
SMD4, LDF 2 /MAY BE LDF 3
STC STMEM3
LDA X
SAE I 2000 /DONE 2000 POINTS?
JMP .+2 /NO
JMP .+5 /YES - STORE LAST POINT AND RETURN
ADA I -1
STC X
JMP .+10
LDA I 3777
STC X
LDA
GOLEM2.23 LN=1736

SMT EM3
STA X
JMP SDONE
LDA
SMT EM3
STA X

/* SMOOTHED POINT ==> AVERAGE BUFFER */
JMP SMOOTH+2

TMCONT, 0

/*
*/

SEGMENT 0

/*
*/

*20
PDP

/* MODE */
JMS I DOFFT
JMS I SORT
LINC
LMODE
LIF 4
JMP 100

/* RETURN TO BUFF */

/*
*/

/*30
PDP

/* MODE */
JMS I DOIFFT
JMS I SORT
LINC
LMODE
LIF 4
JMP 100

/* RETURN TO BUFF */

/*
*/

/*
*/

/*50 */

/* FFTS, COMPLEX */
/

/* TABLE PARAMETERS */
N, 2000 / NUMBER OF POINTS
NU, 12 / LOG(BASE 2) N

L, 0
S, 0 / GIVE SPACING BETWEEN NODES PAIRS IN LTH ARRAY
F, 0 / USED FOR SCALING NODE POSITION TO GET NUMBERS IN NODES

NOVER4, 0 / STORAGE FOR N/4
MAXNU, BIGSNU / LARGEST TABLE SIZE (POWER OF 2)
MNOVR2, 0 / STORAGE FOR -N/2

/* INDEXING VARIABLES */
QR, 0 / POINTER TO REAL PART OF X(Q)
QI, 0 / POINTER TO IMAG PART OF X(Q)
PR, 0 / POINTER TO REAL PART OF X(P)
PI, 0 / POINTER TO IMAG PART OF X(P)
Q, 0 / NUMERICAL INDEX Q(=0,...,N-1)
P, 0 / NUMERICAL INDEX P(=0,...,N-1)
GOLEM2.24  LN=2025

K,  0  /NUMBER IN THE NODE BEING OPERATED ON
/LOOP DELIMITERS
C,  0  /INTERUPTS COMPUTATION OF LTH ARRAY EVERY
S PASSES
/DATA VARIABLES
ADD2,  0  /USED BY SUBROUTINE ADDR AS DATA (ADDEND)
TEMPR,  0  /TEMPORARY STORAGE REGISTER FOR REAL PARTS
SIN,  0  /TEMP STORAGE FOR SIN(2*PI*K/N)
COSINE,  0  /TEMP STORAGE FOR COS(2*PI*K/N)
GR,  0  /REL PART OF PRODUCT BWK*X(P)
GI,  0  /IMAG PART OF (WK)*X(P)
/SUBROUTINE CALL LIST
ADDER, ADDR /ADD C(AC) TO C(ADD2) AND SCALE RIGHT
SORT, SORTX /BIT INVERTED BUFFER SORTED
INVERT, INVRT /WORD IN AC OF NU BITS IS BIT INVERTED
MULTI,MULTI
GETRIG, TRIGET /FETCH SIN AND COS OF 2*PI*C(AC)/N
DQFFIT, FFT /DO FOURIER TRANSFORM ON DATA IN BUFFER
DOIFFIT, IFFT /DO INVERSE OF THE BUFFER
/DATA TABLES
SINLOC, SINTAB /TABLE OF SIN(2*PI*I/N) FOR I=0,...,N-1
XRLOC, XRTAB /INPUT BUFFER AND TABLE OF ARRAYS (REAL
DATA)
XLDCF, XITAB-XRTAB /DIFFERENCE IN ADDRESSES OF REAL
AND IMAG TABLES
/PSEUDO FLOATING POINT FORMAT FLAGS
SCALE, 0 /PSEUDO EXPONENT OF FOURIER COEFFICIENTS
SHFLAG, I /IF =1, ADD WITH SHIFT, IF=0, ADD WITHOUT
SHIFT
SHFCHK, 0 /INDICATES IF ALL X IN AN ITERATION ARE
LESS THAN .5
/DATA FOR SIN TABLE LOOK UP
SHIFT1, 0 /NUMBER OF SHIFTS ,NEGATIVE
SHIFT2, SHF /SHIFT COUNTER
*400
FFT, 0
CLA IAC CLL
DCA L
DCA SCALE
IAC
   DCA SHFLAG
   DCA SHFCHK
   TAD N
   CLL RTR
   DCA NOVER4
   TAD NU
   CIA
   TAD MAXNU
CMA
DCA SHIFT1
TAD SHIFT1
DCA I SHIFT2
NOP
   TAD N
   CLL RAR
   DCA S
   TAD S
CIA
DCA MNOVR2
   CMA
   TAD S
   TAD XRLQ
   DCA QR
   TAD NU
   CIA
   IAC
   DCA F
LOOP1, TAD QR
   TAD S
DCA PR
   TAD QR
   TAD XLOCDF
   DCA Qi
   TAD PR
   TAD XLOCDF
   DCA PI
   TAD I Qi
   DCA ADD2
   TAD I PI
   JMS I ADDER
   DCA TEMPR
   TAD I Qi
   DCA ADD2
   TAD I PI
   CIA
   JMS I ADDER
   DCA I PI
   TAD TEMPR
   DCA I Qi
   TAD I QR
   DCA ADD2
   TAD I PR
   JMS I ADDER
   DCA TEMPR
   TAD I QR
   DCA ADD2
   TAD I PR
   CIA
   JMS I ADDER
   DCA I PR
   TAD TEMPR
   DCA I QR
   TAD XRLQ
   CIA
   TAD QR
   SPA SNA CLA
   JMP CHKPT
   CMA
   TAD QR
   DCA QR
   JMP LOOP1
/PAGE 3
CHKPT, TAD L
CIA
TAD NU
SNA CLA
JMP I FFT
TAD SHFCHK
DCA SHFLAG
TAD SHFCHK
SNA CLA
ISZ SCALE
DCA SHFCHK
ISZ L
TAD S
CLL RAR
DCA S
ISZ F
NOP
CMA
TAD N
TAD XRL0C
DCA PR
SETG, CLA IAC
DCA C
BUILD, TAD PR
TAD XLOCDF
DCA PI
TAD XRL0C
CIA
TAD PR
DCA P
TAD F
CIA
LINC
LMODE
BSE I
SCR I
STC *.+2
ADD P
@ PDP
PMODE
/PAGE 4
JMS I INVERT
TAD MNQVR2
JMS I GETRIG
ADJSGN, NOP
DCA SINE
TAD I PR
JMS I MULT
COSINE
DCA ADD2
TAD I PI
JMS I MULT
SINE
TAD ADD2
DCA GR
/ FOR IMAGINARY
TAD I PI
JMS I MULT
COSINE
DCA ADD2
TAD I PR
JMS I MULT
SINE
CIA
TAD ADD2
DCA GI
TAD S
CIA
TAD PR
DCA QR
TAD QR
TAD XLOCDF
DCA GI
TAD I QR
DCA ADD2
TAD GR
CIA
JMS I ADDER
DCA I PR
TAD I QI
DCA ADD2
TAD GI
CIA
JMS I ADDER
DCA I PI
TAD I QR
DCA ADD2
TAD GR
JMS I ADDER
DCA I QR
TAD I QI
DCA ADD2
TAD GI
/PAGE 5
JMS I ADDER
DCA I QI
CMA
TAD P
DCA P
CMA
TAD PR
DCA PR
TAD C
CIA
TAD S
SZA CLA
JMP CNOTS
TAD P
CMA
TAD S
SNA CLA
JMP I RECHK
TAD S
CIA
TAD PR
GOLEM2,30  LN=2364

DCA PR
JMP I RESETC
CNOTS, ISZ C
JMP I RBUILD
RBUILD, BUILD
RESETC, SETC
RECHK, CHKPT
/PAGE 6
SORTX, 0
CMA
TAD N
DCA Q
REVERS, TAD 0
JMS I INVERT
DCA P
TAD P
CIA
TAD Q
SPA SNA CLA
JMP SWAPED
TAD P
TAD XRLOC
DCA PR
TAD Q
TAD XRLOC
DCA QR
TAD PR
TAD XLOCDF
DCA PI
TAD QR
TAD XLOCDF
DCA QI
TAD I PR
DCA TEMPR
TAD I QR
DCA I PR
TAD TEMPR
DCA I QR
TAD I PI
DCA TEMPR
TAD I QI
DCA I PI
TAD TEMPR
DCA I QI
SWAPED, TAD Q .
SNA CLA
JMP I SORTX
CMA
TAD Q
DCA Q
JMP REVERS
/PAGE 7, INVERSE TRANSFORM
IFFT, 0
CLA CLL
TAD CCIA
DCA I SGNADJ
JMS I DOFFT
GOLEM2,31 LN=2455

TAD CNOP
DCA I SGNADJ
JMP I IFFT
SGNADJ, ADJSGN
CCIA, CIA
CNOP, NOP
*1000
MULTI,0
   CLL
SPA
TAD M1
   DCA TEM1   /PUT AWAY MULTIPLIER
TAD I MULTI
   DCA TEM2   /SAVE IT
   TAD I TEM2   /GET MULTIPLICAND
SPA
TAD M1
ISZ MULTI
   LINC
LMODE
SCR I
   MUL   /MULTIPLY
   TEM1+4000   /AS A FRACTION
LZE   /IS RESULT NEGATIVE?
COM   /YES, MAKE IT POS
   SCR 12   /SHIFT IT INTO MQ
GAC   /BRING IT BACK WITH ANOTHER BIT
GLZ   /DOES NEXT BIT=1?
ADD ONE   /YES, ROUND UP
PDP
PMODE
SZL
CIA
JMP I MULTI
TEM1, 0
TEM2, 0
ONE, 1
M1, -1
   /PAGE 9
INVRT, 0
DCA WORD
DCA WORDP
TAD NU
CIA
DCA FLIPCT
FLIP, TAD WORD
CLL RAR
DCA WORD
TAD WORDP
RAL
DCA WORDP
ISZ FLIPCT
JMP FLIP
TAD WORDP
JMP I INVRT
WORD,0
WORDP,0
GOLEM2.32  LN=2546

FLIPCT,0
/PAGE 10
TRIGET,0
DCA K
TAD K
CLL CIA
TAD NOVERA
DCA NO4MIK
SZL
JMP QUAD1
QUAD2, TAD NO4MIK
CIA
JMS SHIFT
TAD I INDEX
CIA
DCA COSINE
TAD NO4MIK
TAD NOVERA
JMP SINRET
QUAD1, TAD NO4MIK
JMS SHIFT
TAD I INDEX
DCA COSINE
TAD K
SINRET, JMS SHIFT
TAD I INDEX
JMP I TRIGET
SHIFT,0
SKP
CLL RAL
ISZ SHF
JMP -2
TAD SINLOC
DCA INDEX
TAD SHIFT1
DCA SHF
JMP I SHIFT
SHF,0
NO4MIK,0
INDEX,0
/PAGE 11
ADDR,0
DCA ADD1
TAD SHFLAG
SNA CLA
JMP ADDWOS
TAD ADD1
LINC
LMODE
SCR 1
STC ADD1
ADD ADD2
SCR 1
STC ADD2
QAC
RDP
RMODE
GOLEM2, 33  LN=2637

RTL
CMA CML
SMA SNL CLA
IAC
ADDDWOS, TAD ADD1
TAD ADD2
DCA XSUM
TAD XSUM
SPA
CIA
RAL
SMA CLA
JMP NOTNOR
IAC
DCA SHFCHK
NOTNOR, TAD XSUM
JMP I ADDR
ADD1, 0
XSUM, 0
SINTAB, 0000
 0015
 0031
 0046
 0062
 0077
 0113
 0130
 0144
 0161
 0176
 0212
 0227
 0243
 0260
 0274
 0311
 0325
 0342
 0356
 0373
 0407
 0424
 0440
 0455
 0471
 0505
 0522
 0536
 0553
 0567
 0583
 0620
 0634
 0650
 0664
 0701
 0715
GOLEM2,34 LN=2730

0731
0745
0762
0776
1012
1026
1042
1056
1072
1106
1123
1137
1153
1166
1202
1216
1232
1246
1262
1276
1312
1325
1341
1355
1370
1404
1420
1433
1447
1462
1476
1511
1525
1540
1554
1567
1602
1616
1631
1644
1657
1672
1705
1720
1734
1747
1761
1774
2007
2022
2035
2050
2062
2075
2110
2122
2135
GOLEM2,36  LN=3112

3155
3164
3174
3203
3212
3222
3231
3240
3247
3256
3265
3274
3302
3311
3320
3326
3335
3343
3351
3360
3366
3374
3402
3410
3416
3424
3432
3440
3445
3453
3460
3466
3473
3501
3506
3513
3520
3525
3532
3537
3544
3551
3556
3562
3567
3573
3600
3604
3610
3614
3621
3625
3631
3635
3640
3644
3650
G0LEM2,37  LN=3203

3653
3657
3662
3666
3671
3674
3700
3703
3706
3711
3713
3716
3721
3724
3726
3731
3733
3735
3740
3742
3744
3746
3750
3752
3754
3755
3757
3761
3762
3764
3765
3766
3767
3770
3771
3772
3773
3774
3775
3776
3776
3777
3777
3777
3777
3777
3777

XRTAB=4000
XITAB=6000
BIGSNU=12

/    /    /
/    /    /
LMODE
/    /
SEGMENT 0
*200
/

PHMIX,  STC MXANGL  /FIRST ANGLE=0
FND,  SET I 2  
3777  /FOR DATA
CLR
SAM 7  /READ NEW ANGLE
SCR 1  /SCALE FOR SIN TABLE
BCL I 1  /TO PREVENT JITTER
SAE
MXANGL  /ANGLE SAME AS BEFORE?
JMP .+3  /NO - GO MIX
LIF 4  /YES RETURN TO CONTROL FOR DISPLAY
JMP 100
STA
MXANGL  /STORE NEW ANGLE
PDP PMODE
SPA  /IS IT NEGATIVE?
CGL CML CMA  /YES - CHANGE SIGN AND SET LINK
LINC
LMODE
STA
NWANGL  /POSITIVE ANGLE
ADA I
SINTAB  /MAKE POINTER
STC PNTR  /SAVE
LDA PNTR  /GET VALUE FOR SIN
LZE  /WAS ARGUMENT NEGATIVE?
COM  /YES - MAKE SIN NEGATIVE
STC SIN  /SAVE
CLR  /CLEAR LINK
ADD NWANGL
COM  /FOR COS
ADA I
SINTAB.+400
STC PNTR
LDA PNTR  /GET VALUE FOR COS
STC COS  /SAVE

PMIX,  LDF 7  /IMAG DATA
LDA I 2  /GET IMAGINARY COEFFICIENT
APO  /NEGATIVE?
ADD MM1  /YES - ONES COMPLEMENT
STA I

IM,  0
LDF 6  /REAL DATA
LDA 2  /GET REAL COEFFICIENT
APO  /NEGATIVE?
ADD MM1  /YES - ONES COMPLEMENT
STA I

RE,  0
MUL
SIN.+4000  /AS FRACTION TIMES SIN
COM  /CHANGE SIGN
STC SAVMX
ADD RE  /GET REAL COEFFICIENT AGAIN
GOLEM2.41 LN=3365

MUL
COS+4000 /X COS
STC RE /SAVE FIRST PART
ADD IM /GET IMAGINARY COEFFICIENT
MUL
SIN+4000 /X SIN
ADD RE /ADD FIRST PART
APO /NEGATIVE?
ADD ONE1 /YES - TWO'S COMPLEMENT
LDF 2
STA 2 /STORE PHASE CORRECTED VALUE
CLR
ADD IM /GET IMAGINARY COEFFICIENT AGAIN
MUL
COS+4000 /X COS
ADA 1
SAVMX, 0 /ADD OTHER RESULT
AP0 /NEGATIVE?
ADD ONE1 /YES - TWO'S COMPLEMENT
LDF 3
STA 2 /STORE
XSK 2 /LAST POINT?
JMP PMIX /NO - GO DO NEXT ONE
JMP FND /YES - CHECK FOR ANGLE CHANGE

PRTR=3
SIN, 0
COS, 0
MMI, -1
ONE1, 1
MXANGL, 0
NWANGL, 0

/ SEGMENT 1 /

*20 /HERE WE HAVE OCTAL-DECIMAL
CONVERSION AND CHARACTER DISPLAY /

OCTDEC, PDP
PMODE
DCA DWORD
DCA DECREG /IN DECREG-DECREG+4 ARE STORED SIGN
AND 4 BCD DIGITS
DCA DECREG+1
DCA DECREG+2
DCA DECREG+3
DCA DECREG+4
TAD DWORD
SPA /CHECK FOR SIGN
JMP NWRD /NEGATIVE
CLA CLL
TAD TENS
DCA DECREG /POSITIVE - SO PUT 12 (BLANK) IN

DECREG
JMP VWRD
NWRD, CLA CLL
  TAD NEG
  DCA DECRG /SO PUT 13 (-) IN DECREG
  TAD DWORD
  CIA
  DCA DWORD /AND MAKE POSITIVE
VWRD, TAD DWORD
IREG1, TAD THOSC /-1000 DECIMAL
  SPA /FOUND THOUS?
  JMP VVWRD /YES
  ISZ DECRG+1
  JMP IREG1 /NO - SUBTRACT ANOTHER THOUS
VVWRD, TAD THOS /+1000 DECIMAL
IREG2, TAD HUNDC /-100 DECIMAL
  SPA /FOUND HUNDR?
  JMP VVWRD /YES
  ISZ DECRG+2
  JMP IREG2 /NO - SUBTRACT ANOTHER HUNDR
VVVWRD, TAD HUND /+100 DECIMAL
IREG3, TAD TENCSC /-10 DECIMAL
  SPA /FOUND TENS?
  JMP FWRD /YES
  ISZ DECRG+3
  JMP IREG3 /NO - SUBTRACT ANOTHER TEN
FWRD, TAD TENS /+10 DECIMAL
  DCA DECRG+4 /UNITS
ODEND, LINC LMODE
  LIF 4
  JMP @ /RETURN
THOS, 1750 /1000
HUND, 144 /100
TENS, 12 /10
THOSC, 6030 /-1000
HUNDC, 7634 /-100
TENCSC, 7766 /-10
NEG, 13 /-
DWORD, 0
DECRG, 0
0
0
0
0
0
0
0
0
0

/*

NC, 620 /XCOORDINATE FOR CHARACTER DISPLAY
CY, 0 /YCOORDINATE
ALFPNT, 0 /POINTER TO INPUT CHAR BUFFER
NUMREG, 0 /POINTER TO CHARACTER PATTERN TABLE

*/
DISCHR, STC 2 /VERTICAL COORD
SET I ALFPNT
DECREG-1
LDA
Ø
STC SUBCHR
JMP DISDIG /

NUMTAB, 4136
3641
2101
0177
4523
2151
4122
2651
2414
0477
5172
0651
1506
4225
4443
6050
5126
2651
5122
3651
0000
/BLANK
0000
0404
/-
0404

DISDIG, LDA I ALFPNT
ROL 1
/×2
ADA I
NUMTAB
/=CHARACTER DISPLAY PATTERN
STC NUMREG
LDA
YC
DSC NUMREG
/=DISPLAY FIRST HALF CHARACTER
DSC I NUMREG
/=DISPLAY SECOND HALF
LDA I
4
ADM
XC
/=TO MAKE SPACE BETWEEN CHARACTERS
LDA
ALFPNT
SAE I
DECREG+4
/=DISPLAYED 5 CHARACTERS?
JMP DISDIG
/NO - DISPLAY NEXT
SET I XC
620
/=YES - RESET XCOORDINATE
LDA
SUBCHR
STC 0
LIF 4
JMP 0

SUBCHR, 0
CHAPTER V

TIME-REVERSAL EXPERIMENTS IN DIPOLAR-
COUPLED SPIN SYSTEMS
CHAPTER V

TIME-REVERSAL EXPERIMENTS IN DIPOLAR-COUPLER SPIN SYSTEMS
Time-Reversal Experiments in Dipolar-Coupled Spin Systems*

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By applying a suitable sequence of strong rf fields, a system of dipolar-coupled nuclear spins can be made to behave as though the sign of the dipolar Hamiltonian had been reversed. The system then appears to develop backward in time, and states of nonequilibrium magnetization can be recovered in systems which would superficially appear to have decayed to equilibrium. This behavior is consistent with dynamical and thermodynamical principles, but shows that the spin-temperature hypothesis must be employed with caution. The theory of the time-reversal phenomenon is discussed, including the practical limitations on the accuracy with which it can be achieved. Various echo experiments in the laboratory and in the rotating frame are reported. The application of repeated time reversals to the problem of high-resolution NMR in solids is discussed.

I. INTRODUCTION

One’s first impression on seeing a spin echo tends to be of having witnessed a spontaneous fluctuation of an apparently disordered system into an ordered (magnetized) state. Actually, of course, the system was by no means as disordered as it seemed to be: It had to be prepared from a magnetized state in a special way, such that its microscopic dynamical equations guaranteed a return to the magnetized state; and the name “echo” of course expresses just this fact. The importance of a dynamical, as opposed to thermodynamical, interpretation is particularly transparent in the case of the Hahn echo.1–3 There the spin Hamiltonian is inhomogeneous, i.e., it represents a sum over uncoupled spins or isochromats interacting with fixed local fields. One is not dealing with a “many-body” system at all, and the formation of an echo is easily understood by superposing the quantum-
mechanical (or classical) motion of individually precessing magnetic moments. The same is true of quadrupole echoes, though a purely classical picture is not quite so convenient there, and also of photon echoes, whose interpretation follows the same lines as the Hahn echo if a fictitious spin is suitably introduced.

One feels intuitively that the situation ought to be different in the case of interacting particles, such as the nuclear spins in a rigid solid. There "spin diffusion" prevents one's using pictures based on isochromats moving in local fields. Moreover, there is no known way to integrate the microscopic dynamical equations even approximately over times much longer than $T_1$, the time which characterizes the decay of transverse magnetization from an initially coherent state. Under these circumstances recourse is made to the "spin-temperature" hypothesis, which asserts that the system approaches a state which is adequately described as one of internal equilibrium (sometimes called semi-equilibrium, to emphasize that the spin system can be considered isolated from the surrounding lattice only for a certain time $T_1$, usually much greater than $T_2$).

A particularly simple internal equilibrium state is obtained by first polarizing the system for a long time in a very strong external field $H_0 \gg H_{loc}$, where $\gamma H_{loc} \ll T_1^{-1}$. The state of the system is then assumed to belong to a canonical ensemble characterized by the lattice temperature $T_1$:

$$\sigma_4(0) = (1/Z)e^{-\mathcal{H}_0/kT_1},$$

$$\mathcal{H}_0 = -\gamma H_0 I_x + O(\gamma H_{loc}).$$

We shall henceforth speak in terms of the reduced density matrix

$$\rho_4(0) = 1 + \gamma H_0 I_x/kT_1$$

appropriate to the high-temperature approximation and to the removal of $Z = (2I + 1)^N$. A 90° pulse of resonant rf field is now applied to bring the magnetization along the $y$ direction:

$$\rho_4(0) = 1 + \gamma H_0 I_y/kT_1.$$  

The magnetization $\gamma L_y$ now precesses about $H_0$ because $[\rho_4(0), \mathcal{H}_0] = 0$ and decays to zero because $[\rho_4(0), \mathcal{H}_{stat}] = 0$, where $\mathcal{H}_{stat}$ is the Hamiltonian of the spin-spin interactions. If the system approaches internal equilibrium, it is then to be described by

$$\rho(\infty) = 1 - \mathcal{H}_0/kT_2.$$  

Since Zeeman energy must be conserved under the time-independent Hamiltonian acting during the decay,

$$E(\infty) = E(0) = \text{Tr}[\rho_4(0) \mathcal{H}_0] = 0,$$

one must set the spin temperature $T_2 = \infty$ in (4). Thus $\rho(\infty) = 1$. It is now clear that no echo phe-nomena can be evoked by applying any external fields: The Hamiltonian representing their interactions with the system commutes trivially with $\rho(\infty)$.

To be sure, some echo phenomena are known in solids. However, these echoes can be evoked only by interrupting the development of $\rho_4(0)$ before the system has had an opportunity to approach the postulated equilibrium state, and they are weaker the longer that decay is permitted to proceed before interruption.

In this paper, we shall describe a form of echo which can be made to occur even after $\rho_4(0)$ has been allowed to develop for a time much greater than $T_2$. Its occurrence shows that the spin-temperature hypothesis in the simple form employed above is not correct. Of course, no violation of the second law of thermodynamics is implied, and the spin-temperature hypothesis retains its utility in describing most NMR experiments in solids. We shall return to this point later.

Briefly, the experiments depend on the fact that the time development of the system is dynamically reversible in a microscopic sense, whereas it may behave irreversibly on a thermodynamic scale. The apparent conflict between these manifestations is sometimes called Loschmidt's paradox. We shall find it useful to introduce the concept of a "Loschmidt demon" who is able to reverse the dynamical behavior of a system, thereby retracing a path which seemed to be irreversible. The Loschmidt demon differs from the familiar Maxwell demon in that he accomplishes the reversal by changing the sign of the system Hamiltonian rather than by exercising control over microscopic dynamical variables. Since the state of the system obeys the Schrödinger equation

$$\psi(t) = e^{-i\mathcal{H}_0 t} \psi(0),$$

such a sign reversal is clearly equivalent to a reversal of the time coordinate.

In Sec. II, we show how this is done, and dispel any doubts about its conflict with thermodynamic principles. In Sec. III, we give the results of several experiments. The theory is expanded in Sec. IV, and Sec. V describes an important extension and application of this phenomenon.

II. SIMPLE TREATMENT

A. Theory

The spin Hamiltonian in which we will be mainly interested is the dipole-dipole coupling $\mathcal{H}_d$ in a rigid lattice of like spins $I_x$, or, more precisely, the truncated form of this interaction $\mathcal{H}_d$ appropriate to the reference frame $R$ which rotates at the spectrometer frequency $\omega$ about a very strong Zeeman field $H_0 = \omega_0/\gamma$ in the $z$ direction. We have
\[
x_0^2 = \sum_{i<j} b_{ij} (\mathbf{T}_i \cdot \mathbf{T}_j - 3 I_{i1} I_{j1}) ,
\]
\[
b_{ij} = \gamma^2 k \chi_0 P_2 (\cos \theta_{ij}) .
\]

The Loschmidt demon will convert \( x_0^2 \) into
\( k \chi_0^2 \), with \( k \) a negative number, so that the system retraces its previous normal dipolar development and departs from what appears to be a state of equilibrium, as mentioned in Sec. I. This conversion cannot be made in a literal sense, but its effects can be simulated through the agency of suitable external forces.\(^{15}\) Suppose a strong rf field \( (2 \omega_1/\gamma) \cos \omega t \) is applied in the \( x \) direction with \( |\omega_0 - \omega| \ll \omega_0 \). The Hamiltonian in the rotating frame now includes in addition to (6), the Zeeman effect due to the field

\[
(\omega_0 - (\omega_0 - \omega)) \mathbf{K} / \gamma .
\]

As Redfield has shown,\(^{16}\) it is convenient to view the system from the vantage point of the doubly (tilted) rotating frame (DTR), defined by the transformations
\[
\rho_{\text{DTR}} = \text{DTR} \rho_{\text{LAB}} (\text{DTR})^{-1} ,
\]
\[
R = e^{i \omega t / \gamma} ,
\]
\[
T = e^{i \xi / \gamma} ; \tan \xi = \omega_1 / (\omega_0 - \omega) ,
\]
\[
D = e^{-i \omega t / \gamma} ; \quad \omega_0 = \left[ \omega_0^2 - (\omega_0 - \omega)^2 \right]^{1/2} .
\]

In this frame the density matrix obeys the Liouville equation
\[
\frac{\partial}{\partial t} \rho_{\text{DTR}} = -i [\chi_{\text{DTR}}, \rho_{\text{DTR}}] ,
\]
with
\[
\chi_{\text{DTR}} = \chi_0 P_2 (\cos \xi) - \chi_{\text{ns}} ,
\]
\[
\chi_{\text{ns}} = \frac{1}{2} \sin \xi \cos \xi \sum_{i<j} b_{ij}
\]
\[
\times \left[ I_{i1} I_{j1} - I_{i1} I_{j1} \right] e^{i \omega t} - \text{c. c.}
\]
\[
- \frac{1}{2} \sin^2 \xi \sum_{i<j} b_{ij} \left( I_{i1} I_{j1} e^{-2i \omega t} - \text{c. c.} \right) .
\]

When \( \omega_0 \) is large (\( \omega_0 T_2 \gg 1 \)), the oscillatory part \( \chi_{\text{ns}} \) can be removed for purposes of calculating the secular development of the system. Just as one truncates the ordinary rotating frame Hamiltonian \( x_0 \) to obtain (6) when \( \omega_0 T_2 \gg 1 \). We will discuss this step more fully later. Assuming it to be valid, we see that (9) has the desired form \( k \chi_0^2 \), with \( k \) adjustable between 1 and \(- \frac{1}{2} \) at the experimenter’s discretion.

Remember, however, that this result refers to observations made in the DTR frame, and does not by itself embody a means of reversing the time development of \( \rho_{\text{DTR}} \) in the rotating frame. In fact, the full effect on \( \rho_{\text{DTR}} \) of applying a burst of effective field \( \omega_0 / \gamma \) for a time \( T_2 \) is more complicated:

\[
\rho_{\text{DTR}} (t_1 + T_2) = T_2^{-1} D^{-1} \exp[- i \gamma k \chi_0^2 P_2 (\cos \xi)] DT \rho_{\text{DTR}} (t_1)
\]
\[
\times T_2^{-1} D^{-1} \exp[i \gamma k \chi_0^2 P_2 (\cos \xi)] DT .
\]

It can be simplified by modifying the experiment in the following two ways:

(a) Make the duration of the burst by a resonant number of periods of the precession about \( \omega_0 \) : \( \omega_0 T_2 = 2 \pi \), then \( D = D^{-1} \) in (11).

(b) Immediately precede the burst by a resonant rf pulse chosen to rotate any magnetization present through an angle \( \xi \) about the \( y \) axis of the rotating frame (i.e., the rf carrier in the pulse is in phase quadrature to that in the burst), and terminate it by a similar pulse rotation through \(- \xi \). The effects of these pulses can be represented by \( e^{i \xi / \gamma} = T_2^{\xi / \gamma} \) acting on \( \rho_{\text{DTR}} \) which annihilate the transformations \( T, T_2^{-1} \) in (11).

The effect of this treatment is then simply
\[
\rho_{\text{DTR}} (t_1 + T_2) = \exp[- i \gamma k \chi_0^2 P_2 (\cos \xi)] \rho_{\text{DTR}} (t_1)
\]
\[
\times \exp[i \gamma k \chi_0^2 P_2 (\cos \xi)] ,
\]
and the Loschmidt demon has been realized if we choose \( \xi \) such that \( P_2 (\cos \xi) \ll 0 \). Just this procedure for interconversion between reference frames has been employed by Jeener et al.\(^{17}\) but not for the same purpose. It is if to be used for time reversal over reasonably long times it suffers from a severe practical limitation: Any appreciable inhomogeneity in the applied field, especially the rf field, will result in failure to satisfy condition (a) above in all parts of the sample. The result is a quick destruction of the coherence of the inverse time development and failure of the experiment. This difficulty can be circumvented by adding the further condition:

(c) Periodically reverse the direction of \( \omega_0 \) (i.e., the rf carrier phase and the offset from resonance, \( \omega_0 - \omega \)). By this means the dephasing of isochromatics caused by field inhomogeneity is prevented from accumulating. (There are theoretical benefits to be gained by this procedure even if the fields are homogeneous, as we will see later.) The reversal should be made as often as possible, but at integral multiples of the period expressed in (10). For the general case, a reversal could be made every \( 2 \pi / \omega_0 \) sec. For the special case of exact resonance (\( \xi = \frac{1}{2} \pi \)), the first term of (10) vanishes, and the reversal can be made twice as often if desired, i.e., the burst consists of a train of contiguous phase-alternated 180° pulses. From now on we restrict ourselves to the exact resonance case (\( \xi = \frac{1}{2} \pi \)), as this was the one adopted for the majority of our experiments.

In summary, the free dipolar time development of the spin system which occurred at a time \( t \) can be reversed by applying for a time \( 2t \) a special
sequence consisting of a pair of 90° pulses along the +y and −y axes of the rotating frame, enclosing an even number of contiguous n\(_x\) pulses which alternate between the +x and −x axes: Calling this sequence B\((t_b)\) we have the equivalence
e\(\exp\left(-i\frac{\omega}{2}t_b\right)\) \(\equiv B\((t_b)\)\.

\(B\((t_b)\)\) is depicted in Fig. 1(a). All this evidently holds for any interaction with the same transformation properties as \(X_0^0\). We now present a simple pictorial representation of these equations and apply it to a well-known experiment.\(^{13}\)

B. Simple Picture

The normal inhomogeneous spin echo\(^{11,12}\) is very conveniently described in terms of the evolution of spin isochromats which precess at different frequencies about an external inhomogeneous magnetic field. The behavior of dipolar-coupled spins, on the other hand, is normally not amenable to such a simple “hand-waving” description. However, even for these systems, the simple picture of inhomogeneously perturbed noninteracting spins is sometimes valuable, and if employed carefully, allows a simple understanding of many experiments as well as facilitating further extensions and predictions.\(^{13,14}\)

We describe here the use of such a model which is appropriate for some of our experiments and utilizes Eqs. (7)–(9) with \(\xi = 90°\) as a guideline for its construction. The discussion takes place in the reference frame rotating at frequency \(\omega_0\) about the \(z\) axis. With no rf applied we adopt the well-known picture of spin isochromats in an inhomogeneous field in the \(z\) direction. There is a distribution between fast to slow isochromats (labeled 1 and 2 in Fig. 2) which precess, respectively, clockwise and anticlockwise about the \(z\) axis. During an rf burst along the \(x\) axis we use a similar picture with the following differences: The inhomogeneous field is now along the \(x\) axis and the sense of precession of the isochromats about this axis is opposite to that about \(z\). Further, the rate of precession is reduced by a factor of 2. 90° pulses are treated as usual, whereas the system is invariant to 180° pulses. These stipulations incorporate pictorially the main features of Eqs. (7)–(9): (i) The rf burst converts the effective Hamiltonian from \(X_0^0\) in the rotating frame to \(-\frac{1}{2}X_0^0\) in the tilted rotating frame [taking account of (iii)]. (ii) 90° \(y\) pulses transform the density matrix to and from the above frames. (iii) Our time scale during the burst is limited to integral cycle times of the rf field.

Figure 2 demonstrates the application of this simple picture to the echo experiment described previously\(^{13}\) and referred to again in Sec. III. We see that most of the qualitative features of the experiment are incorporated neatly in this description, but we emphasize that this should not be taken too seriously and serves only as a useful pictorial accessory when used in conjunction with the appropriate equations. The reader will no doubt appreciate the trivial extension to multiple echoes described briefly in Secs. III and V.

C. Remarks on Statistical Mechanics

For an echo of magnitude \(M_\theta\) to occur at time \(t = 0\) in an isolated system of energy \(E_0\), the representative point of the system must lie in some region \(s(0)\) of the phase space. This region is much smaller than the total constant-energy surface \(S_0\), expressing the fact that the magnetized state is one of low entropy. Every possible representative point in \(s(0)\) arrived there from a sequence of earlier locations, completely determined by the system Hamiltonian through the microscopic equations of motion. That is, a knowledge of \(W\) specifies a sequence of mappings of \(s(0)\) onto the precursor regions \(s(-t)\). The problem confronting an experimenter who wishes to produce an echo at time \(t = 0\) is how to prepare a system which is known to be in \(s(-t_0)\).

This is a more subtle task than to prepare the system in \(s(0)\). The latter can be accomplished, for example, by bringing the spins to equilibrium with a lattice in a strong field and then applying a
macroscopic variables alone but requires a knowledge of *all* the dynamical variables and how they change over a time \( t_0 \) under the influence of the equations of motion. The necessary knowledge and ability of selection characterize the Maxwell demon, who violates the second law of thermodynamics in playing his role.

The Loschmidt demon needs no such microscopic control. Beginning with a system prepared in \( S(0) \) as described above, he changes the sign of the Hamiltonian function of the system. After a time \( t_0 \), \( K \) is returned to its normal form. The change is to be accomplished by external means which make no reference to the dynamical state of the system. An analogy is useful here to a gas of molecules interacting according to a potential \( U(r) \):

\[
K = \sum_{i=1}^{N} \frac{1}{2m_i} \mathbf{p}_i \cdot \mathbf{p}_i + \sum_{i<j} U(\mathbf{r}_{ij})
\]

A second kind of Maxwell demon exploits the apparent possibility of recalling the previous history of the gas by reversing the signs of all \( \mathbf{p}_i \) at some instant. It might seem that such a reversal would require a knowledge of the dynamical state at that instant (although Hahn has pointed out in discussion a case of two dimensions in which it apparently does not). Note also that the sign of \( K \) is not changed. The Loschmidt demon, as we define him, might instead change the signs of all the \( m_i \) and \( U_{ij} \). Such an action certainly requires no knowledge of the dynamical state. It implies a degree of control over the nature of the system which may be difficult to credit in the case of gas dynamics but which clearly can be exercised, as we have seen, in certain restricted spin systems. The question of the class of Hamiltonians for which a Loschmidt demon is in principle realizable is an interesting but unsolved one.

How does the spin-temperature hypothesis fit into this discussion? In its strong form it would claim that a distribution \( \rho(0) \) uniformly occupying \( S(0) \) at the beginning of a Bloch decay would come to fill the much larger region \( \delta_0 \) uniformly after several times \( T_2 \). However, Liouville’s theorem tells us that the total volume of \( S(t) \) is conserved. The fact is that \( S(t) \) may come to fill \( \delta_0 \) in a coarse-grained sense only. \( S(0) \) is relatively compact, but \( S(t > T_2) \) is complicated and has a large surfaceto-volume ratio, as it were, especially if forces are present between the particles of the system. Thus, for many purposes the distribution may be treated as though it filled \( \delta_0 \) uniformly. However one must be on guard against performing manipulations which inadvertently exploit the dynamical history of the system to bring \( S(t) \) into a condition characterized by “nonequilibrium” values of the macroscopic observables. It is worth noting that some of the experiments of Jeener et al., 17 which

90° pulse: It requires only the ability to establish specified values of the macroscopic variables \( M \) and \( E \), since \( S(0) \) includes by definition all dynamical states consistent with these values. \( S(-t_0) \), on the other hand, cannot be specified by
seemed to verify the spin-temperature hypothesis, might well have done the contrary, had their experimental conditions been adjusted somewhat differently.

Finally, we remind the reader that our experiments on solids do not actually involve a reversal in sign of $\mathcal{K}$: During the rf burst the representative point appears to move under a Hamiltonian $-\frac{1}{2} \mathcal{K}^2 \sigma$ from the viewpoint of a phase space which is accelerated with respect to the “ordinary” one, the net effect upon conclusion of the time-reversing sequence being to bring the system into $\delta (-\delta)$. The language one uses to describe the motion of the system depends, as always, on the representation in which the motion is viewed.

III. EXPERIMENTS

In this section we describe some experiments based on the properties of the time-reversing sequence described in Sec. II. All experiments were performed at the exact $^{19}$F resonance frequency of 54 MHz on a single crystal of CaF$_2$ oriented approximately along the (110) direction. The peak $H_1$ field was $\sim 100$ G and our pulses had rise and fall times of $\sim 150$ nsec. The apparatus is to be described in more detail elsewhere.

A trivial experiment is one in which $B(t_g)$ is applied to the spin system initially in equilibrium with the lattice in a field $H_0$. $B(t_g)$ reverses the (nonexistent) time development of the $z$ component of the magnetization, leaving the system in its original state.

A more interesting case is the reversal of the time development of the $x, y$ components. Assume, therefore, that we apply the pulse sequence of Fig. 1(b) with $n = 1$, consisting of a time-reversing sequence preceded by a $90_x$ pulse. (Note that this pulse is immediately negated by the leading $90_y$ pulse of the time-reversing sequence. In practice we simply omit both from the experiment.) During the burst the system undergoes a reversed dipolar development with Hamiltonian $-\frac{1}{2} \mathcal{K}^2 \sigma$ corresponding to a normal rotary free induction decay at resonance, treated for example by Goldburg and Lee. At time $t_B$ the system reverts to normal dipolar development and should return to the initial state at $\tau = \frac{1}{2} t_B$ as indicated by the appearance of an echo. This sequence is formed by stages (i)-(j) of Fig. 2. The result of the experiment is shown in Fig. 3. The open circles depict the magnetization along the $y$ axis during the burst and were obtained by observing the signal immediately following the receiver dead time of about 2 $\mu$s without the final $90_y$ pulse, while the number of $(x, -x)$ pulse pairs was varied. The oscillations were introduced deliberately for this part of the data by misadjusting the pulse widths during the burst and having $x$ pulses of nutation angle $\pi - \alpha$ with $\alpha \approx 25^\circ$. This introduces a slow accumulative precession of frequency $\omega_1 \alpha / \pi$ which leads to the observed oscillations, and the free induction decay envelope can be extracted simply by inspection as indicated in the figure. This is necessary because any slower oscillations due to small misadjustments, which are almost unavoidable, would make extraction of the envelope a much less certain proposition. The full circles show the observed echo whose maximum comes at $\frac{1}{2} t_B$, as expected. The shape of the rotary free induction decay is the same as that of the normal free induction decay except stretched by a factor of 2, as observed previously.

In the experiment of Fig. 4 (which is the one described by the simple picture of Fig. 2), we first apply a $90_x$ pulse after which we see a normal free induction decay. The time-reversing sequence with $n = 1$ is then applied as in Fig. 1(c) such that $t_B = 4t_D$, and at time $\tau = t_D$ we see the expected echo. Figure 5 shows the initial decay (full circles) and also the magnetization during the burst (open circles) with the data collected as before by misadjusting the $\pi$ pulse widths and omitting the final $90_\gamma$ pulse. The envelope shows a rotary spin echo (which is of course entirely different in character from the inhomogeneous rotary spin echo observed by Solomon$^{21}$). The width is stretched by a factor of 2 and we see that the

![Figure 3](image-url)  
**Fig. 3.** Transient magnetization of $^{19}$F nuclei in CaF$_2$ observed along the $y$ axis of the rotating frame using the pulse sequence of Fig. 1(b). The closed circles depict the echo obtained in this experiment with a rf burst of $\sim 120$ nsec. In order to see the evolution of the magnetization during the burst the final $90_\gamma$ pulse was omitted and the number of pairs of $(x, -x)$ pulses was varied, leading to the data recorded as open circles. The oscillations were introduced deliberately for this part of the experiment as explained in the text, and the envelope is drawn by inspection. Note the characteristic beat structure in the rotary free induction decay.
shape and beat structure are again preserved by our phase-alternation technique.

In this experiment, we have obtained substantial echoes for burst lengths of up to 650 μsec, meaning a recovery of the magnetization after about 1 msec from the first 90° pulse. The reasons for decay of the echo amplitude are discussed later and are probably dominated by machine instabilities and errors. Figure 6 demonstrates that the same effect may be obtained by using a train of narrow phase-alternated 90° pulses in the time-reversing sequence instead of the contiguous 90° pulses, since the secular part of the Hamiltonian is the same for both. A nice feature of this experiment is the direct observation of the rotary echo during the pulse train. The efficiency of this pulse train for longer bursts, however, is lower than that of 1(a) if compared using the same average rf power. This point is brought up again in Sec. V.

$t_1 = 2t_0$ corresponds to the peak of the rotary echo and Fig. 7 shows the signal observed in an experiment where the burst is terminated soon after this point without the final 90° pulse. We see a large recovery of the magnetization with $t_0 = 133$ μsec, which is substantially larger than $T_1$. (The negative signal is due to a peak negative value in the oscillation caused by a pulse width misadjustment or by change of the nutation angle due to rf power droop during the burst.)

Figure 8 shows that if we apply an additional time-reversing sequence at $\tau = 2t_0$ another echo appears, and this may of course be extended to multiple echoes in a manner analogous to that of Carr and Purcell. 23 The efficiency with which these echoes are summoned suggests that such echo trains might form the basis of a powerful approach to the problem of line narrowing in solids. This is treated briefly in Sec. V.

As a final demonstration of a simple application of the time-reversing sequence, let us look at the experiment of Fig. 9 which employs the pulse sequence in Fig. 1(c) with $\theta = 60°$. The first 90° pulse following the free induction decay produces the well-known "solid

![Figure 4](image4.png)

**FIG. 4.** Oscilloscope trace of the $^{18}$F transient magnetization in CaF$_2$ using the pulse sequence of Fig. 1(c). Following the initial free induction decay a time-reversing burst ($B$) is applied at the noise-free section of the trace and an echo then appears, $t_0 = 88$ μsec, $t_0 = 350$ μsec. This is the experiment described by the simple picture of Fig. 2.

![Figure 5](image5.png)

**FIG. 5.** Experiment designed to show the evolution of the magnetization during the rf burst in an experiment like that of Fig. 4. This is done as in Fig. 3 by omitting the final 90° pulse from the pulse train which follows the free induction decay (closed circles) and plotting the magnetization immediately following the burst vs burst length (open circles). The oscillations were again introduced deliberately as explained in the text. The envelope shows the "rotary echo" and note again the intact beat structure characteristic of the $^{18}$F signal in CaF$_2$.

![Figure 6](image6.png)

**FIG. 6.** Pulsed version of the experiment in Figs. 4 and 5. In this experiment, the time-reversing sequence ($B$) in pulse sequence 1(c) was modified by replacing the contiguous $|+\rangle$ and $|-\rangle$ pulses with a train of alternate 90° and 90° pulses spaced 5 μsec apart. In addition to the free induction decay and echo, observed as in Fig. 4, we see the "rotary echo" of Fig. 5 during the "windows" in the pulse train.
FIG. 7. Oscilloscope trace of magnetization in an experiment like that of Fig. 4. In this case, the time-reversing sequence terminated near the peak of the rotary echo of Fig. 5 and we see a normal free induction decay. The parameters are $t_B = 133\ \mu\text{sec}$, $t_0 = 345\ \mu\text{sec}$. The fact that the second signal has a negative value is explained in the text.

echo. By sequentially using the properties of the time-reversing sequence we see that the first half of the burst brings the system back to its initial state, and the second half produces a rotary free induction decay and corresponding "rotary solid echo." Thus, on terminating the burst we see a normal time-development solid echo and the final $90^\circ$ pulse brings the system back again to the initial state. In this way the effects of any number of pulses may be reversed. This experiment vividly demonstrates the more efficient nature of our echoes as compared to the solid echoes. This matter is referred to again in Secs. IV and V. For $\theta = 45^\circ$, we obtain an anal-

gous reversal of Jeener and Brackaert's pulse sequence showing that their postulated dipolar state is not an adequate description of the system for this type of experiment.

IV. NONIDEALITIES

A. General Framework

The ideal treatment in Sec. II was based on the assumption that the effect of a time-reversing sequence could be represented by replacing $\mathcal{H}_0$ with $-\frac{i}{2}\mathcal{H}_0^*$ as the effective Hamiltonian during the burst (for the case $\xi = \frac{1}{2} \pi$). Here we investigate the validity of this assumption and discuss the effect and extent of various nonidealities encountered in practice.

We begin by writing the time development during the burst as

$$
\rho_B(t_B) = U_B^*(t_B) \rho_B(0) U_B(t_B),
$$

(13)

$$
U_B(t_B) = \exp\left[-it_B\left(-\frac{i}{2}\mathcal{H}_0^* + \lambda V\right)\right],
$$

where $V$ is some correction to $\mathcal{H}_{CT, R}$ whose matrix elements are of order $T_2^\text{d}$, and $\lambda$ is a small parameter. No generality is lost at this stage by insisting that $V$ be time independent; it may depend parametrically on $t_B$ but in most cases to be discussed it will not have even that indirect time dependence.

The nature and origin of $\lambda V$ will be discussed later; at present we simply investigate the consequences of (13).

It is easily shown that

$$
U_B(t_B) = e^{ix^2t_B/2t} \exp\left[-i\lambda \int_0^{t_B} V(t) dt\right],
$$

(14)

FIG. 8. Double-echo version of the experiment in Fig. 4 using pulse sequence 1(d) with $t_B = 180\ \mu\text{sec}$. This shows that an extension of our echoes analogous to that of Carr and Purcell is possible.

FIG. 9. Time reversal of a two-pulse experiment, using the pulse sequence in Fig. 1(d) with $\theta = 90^\circ$. The first two pulses bring about a free induction decay and "solid echo." The following rf burst reverses this total sequence and then propagates it further backwards in time leading to the ensuing "mirror image" of the "solid-echo" experiment when the burst is terminated. The negative value of the "mirror image" is explained in the text. For this experiment $2t_B + t_0 = 342\ \mu\text{sec}$, corresponding to the noise-free portion of the trace.
where \( T \) is a time-ordering operator and \( V(t) = e^{-\frac{i\dot{\omega}}{2}t^2} V e^{\frac{i\dot{\omega}}{2}t^2} \).

For the condition
\[
\lambda t_B \ll T_2 \tag{16}
\]
we may expand the exponential in (14) to first order:
\[
U_B(t_B) = e^{\frac{i\dot{\omega}}{2}t_B^2} U(t_B) e^{-\frac{i\dot{\omega}}{2}t_B^2} \tag{17}
\]

Now we consider the general situation in which the burst is preceded and followed by unperturbed dipolar developments of duration \( t_1 \) and \( t_2 \). The total propagator is
\[
U(t_1 + t_2 + t_B) = e^{-i\frac{1}{2}t_B^2} U(t_B) e^{-i\frac{1}{2}t_B^2} \tag{18}
\]

Combining this with (17) and rearranging a little we find
\[
U(t_1 + t_2 + t_B) = U(\frac{1}{2}t_B + \tau) = e^{-i\frac{\dot{\omega}}{2}t_B^2} e^{-i\frac{\dot{\omega}}{2}t_B\bar{\tau}} \tag{19}
\]
where \( \tau = t_1 + t_2 - \frac{1}{2}t_B \) and \( \bar{\tau} \) is given by
\[
\bar{\tau} = \int_{-t_B}^{t_B} V(t) dt \tag{20}
\]

If the initial magnetization of the system was along the \( \mu \) axis in the rotating frame, \( \langle I_\mu(0) \rangle \), then its final value is
\[
\langle I_\mu(\frac{1}{2}t_B + \tau) \rangle = \text{Tr} \left( e^{-i\frac{\dot{\omega}}{2}t_B^2} e^{-i\frac{\dot{\omega}}{2}t_B\bar{\tau}} \tilde{P} e^{i\frac{\dot{\omega}}{2}t_B^2} e^{i\frac{\dot{\omega}}{2}t_B\bar{\tau}} \tilde{P} \right) \tag{21}
\]

We now introduce the notation
\[
\{a\cdot \cdot \cdot, b\cdot \cdot \cdot \} = \text{Tr} \left( [a, \ldots, \{a, I_\mu\}, \ldots] \langle b, \ldots, \{b, I_\mu\}, \ldots \rangle \right) \tag{22}
\]
where \( a \) and \( b \) appear \( n \) and \( m \) times, and
\[
\{a\cdot \cdot \cdot, 1\} = \{1, a\cdot \cdot \cdot \} = \{a\cdot \cdot \cdot \} \tag{23}
\]
where the last is the bracket introduced by Waugh and Wang. \(^{21}\) Using this and expanding (21) in \( \tau \) and \( \lambda t_B \) we obtain
\[
\langle I_\mu(\frac{1}{2}t_B + \tau) \rangle = \sum_{n=0}^{\infty} M_n \frac{\tau^n}{n!} \tag{24}
\]
where \( M_n \) are the moments of the echo, given by
\[
M_n = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \frac{(\lambda t_B)^k}{(2k)!} \langle \{\tilde{P}^k\} \rangle \tag{25}
\]

B. Lifetime of Echo

The time \( \tau = 0 \) corresponds to the expected position of the echo maximum from the discussion in Sec. II. Substituting \( \tau = 0 \) in (24) and (25) we obtain
\[
\langle I_\mu(t_B) \rangle = \sum_{k=0}^{\infty} (-1)^k \frac{(\lambda t_B)^{2k}}{(2k)!} \langle \{\tilde{P}^{2k}\} \rangle \tag{26}
\]

the odd powers all vanishing, as is well known. \(^{28}\)

Assuming now that \( \|\tilde{P}\| = T_2^2 \) and remembering condition (16) we see that (26) expresses a recovery of the magnetization with an attenuation of order \( \frac{1}{2}(\lambda t_B/T_2)^2 \). Thus we expect the magnetization to recover to an appreciable extent for burst lengths that satisfy condition (16) for fixed \( T_2 \) and \( \lambda \). In order to estimate this, we now inquire into the sources and nature of \( V \) and the size of \( \lambda \). The first place it occurs to us to look is at the truncation of \( \mathcal{K}_{\text{DTR}} \) carried out in Sec. II. Since \( \mathcal{K}_{\text{DTR}} \) of (9) is periodic and the burst contains an integral number of cycles, its effects can be replaced by those of an average Hamiltonian \(^{29}\)
\[
\mathcal{K}_{\text{DTR}} = \sum_{n=0}^{\infty} \mathcal{K}^{(n)}_{\text{DTR}} \tag{27}
\]
whose terms are defined by a Magnus expansion over a single cycle of \( \mathcal{K}_{\mu}(t) \). For Eq. (10) we have the cycle time \( t_c = 2\pi/\omega_c \), and thus
\[
\mathcal{K}^{(0)}_{\text{DTR}} = -\frac{1}{2} \mathcal{K}_{\mu} \tag{28}
\]
Cutting off (27) at this point corresponds to the well-known procedure of “truncation." The next term does not vanish: At this point remember we have not used quite the Hamiltonian of Eq. (9) since we have periodically reversed the direction of \( H_\mu \). Under these conditions it is easily verified that
\[
\mathcal{K}^{(1)}_{\text{DTR}} = 0 \tag{29}
\]
thus leaving \( \mathcal{K}^{(0)}_{\text{DTR}} \) as the leading correction term.

An estimate of this factor shows that it is of the order of \( \frac{1}{2}(t_c/2\pi T_2)^2 \) smaller than \( \mathcal{K}_{\mu} \). Thus for this case we identify \( \lambda' \) with \( \mathcal{K}_{\mu} \) and \( \lambda \) is of order \( \frac{1}{2}(t_c/2\pi T_2)^2 \), which for our experimental condition is about \( 10^{-4} \). Condition (16) is thus satisfied for \( t_B \) of many msecs, and taking only the nonsecular terms into account we might expect the echo to live this long. In fact, we have obtained in the echo experiments of Sec. III a more than 98% recovery of the magnetization for \( t_B \) up to 350 usec and a 75% recovery for \( t_B \) of 500 usec. Some other mechanism could be contributing to the destruction of the echo.

We now turn to some other errors which stem from practical sources. The treatment up till now has assumed that the time-reversing sequence contains a series of contiguous ideal \( (n\pi) \) and \( (n\pi) \) pulses. Evidently, this cannot be realized in practice because of the finite rise and fall times of the pulses which lead to “windows" in the continuous rf irradiation, since the carrier phase of the two pulses differs by \( \pi \). Thus the time-reversing sequence is better represented in practice by the pulse sequence in Fig. 10.

Another source of error is the fact that the pulses may not be exactly of nutation angle \( \pi \), as this is exceedingly difficult to adjust. Accordingly, in Fig. 10 we have indicated this by writing the angles as \( \frac{\pi}{2} + \epsilon \) and \( \frac{\pi}{2} - \epsilon' \), where \( \epsilon \) and \( \epsilon' \) are small error angles. We assume \( |\epsilon| - |\epsilon'| \ll |\epsilon| \) for reasons that will become clear later. We find on calculating the average Hamiltonian \( \mathcal{K}^{(0)}_{\text{DTR}} \) in this case and taking only the first order in \( \epsilon \) and \( \delta \), where \( 1 - \delta \)
FIG. 10. Nonideal time-reversing sequence discussed in Sec. IV.

\[ \frac{(t_{w_1} + t_{w_2})}{t_c} = \left( \frac{\Sigma b_{ij}}{t_{x_i} - t_{y_j}} \right) \left( \frac{\epsilon}{n \pi} \right) \sum_{ij} (U_{xi} - U_{yj}). \]  

(30)

We see that \( \overline{O_{TR}} \) is of the form \(-\frac{1}{2} \Delta \sigma + \lambda V\), where \( \lambda \approx \delta \approx \epsilon / n \pi \). For \( n = 1 \), we have with our apparatus \( \delta = 0.1 \). With \( \epsilon \approx 0 \) this would lead to very short lived echoes since \( \lambda \approx \delta \). However, we see from (30) that by inadvertently adjusting the pulse widths away from \( \pi \), such that \( \delta + \epsilon / n \pi \approx 0 \), this factor can be eliminated to a certain extent. The adjustment is quite critical and requires \( \epsilon < 0 \) as we have indeed observed. A factor limiting this adjustment is the \( H_1 \) inhomogeneity which normally amounts to several percent. Practically, this means that \( \epsilon \) is not constant over the sample and thus the adjustment \( \delta + \epsilon / n \pi \approx 0 \) cannot be made simultaneously over the whole sample. The \( H_1 \) inhomogeneity probably makes a significant contribution to the destruction of the echo for long bursts.

The effect of \( \epsilon \) and \( \delta \) becomes less serious as \( n \) is made larger since \( \epsilon / n \pi \) and \( \delta \) both decrease, but for large \( n \) this may be offset by a harmful increase in phase-switching cycle time.

Other machine errors not treated explicitly here probably make some additional contribution to the destruction of the echo. These include misadjustment of phases, power droop in the pulse transmitter, phase transients, etc.

C. Shape of Echo

We now return to Eq. (24) and investigate \( \langle I_\alpha (\frac{1}{2} t_B + \tau) \rangle \) for \( \tau \neq 0 \), the shape of the echo about its expected maximum. An examination of (25) shows that the first term in the expansion is just the corresponding normal FID moment. The higher terms make a small contribution if condition (16) is fulfilled and lead only to a slight distortion of the echo line shape as compared to the free induction decay. This suggests a useful new means for obtaining moments of the free induction decay when the initial transient is obscured by receiver dead time; we simply produce an echo with \( \lambda \) small enough so that (16) is fulfilled to the desired accuracy with some partic-

ular dead time \( t_d \) [we need \( t_B > 2 t_d \) for pulse sequence 1(b), and \( t_B > 4 t_d \) for 1(c)]. This method has one important advantage over solid echoes. In the latter, assuming a dead time \( t_d \), the terms contributing to the distortion of the echo line shape have some inherent fixed value dependent on powers of \( t_d \). In our case, we have the same distortion in powers of \( \lambda t_B \), not \( t_B \), and this can be made arbitrarily small at least for the \( t_d \) of practical interest. Using pulse sequence 1(b) we have measured some echo line shapes for different burst lengths. These are compared with the free induction decay in Fig. 11 with no adjustable parameters except for normalization of the echo with \( t_B = 110 \mu \text{sec} \). The agreement is very good within experimental error. For \( t_B = 110 \mu \text{sec} \), the onset of some distortion is clearly visible. Comparison with the first part of the free induction decay is of course not possible, but the theory and other experimental evidence indicate no reason why this should not be good too. For \( t_d < 10 \mu \text{sec} \), we need \( t_B \approx 20 \mu \text{sec} \), and this should give us a very accurate representation of the line shape even for moderate \( H_1 \) fields. In any case, the reduction in peak echo amplitude is an indication of the amount of distortion to expect (notwithstanding the remarks below) as we have indeed found in practice.

An interesting feature of Eqs. (24) and (25) as we have seen, is the fact that the first correction term to the peak echo amplitude is in \( (\lambda t_B)^2 \), whereas those to the higher moments are in \( (\lambda t_B) \). This means that distortion of the line shape should occur more rapidly than destruction of the peak echo amplitude might indicate. This is indeed evident in our experiments where for large \( t_B \) the echoes acquire a

FIG. 11. Comparison of the echo line shapes of the experiment in Fig. 3 for various burst lengths. Only the right-hand portion of each echo is depicted, except for burst length 0 (free induction decay) where part of the signal is obscured by receiver dead time. No parameters are involved except the normalization of data for \( t_B = 110 \mu \text{sec} \), where the peak echo amplitude had decreased.
where superscript $B$ denotes the presence of the burst and $\lambda V$ is a correction to the average Hamiltonian. It is easily verified that the total first correction term vanishes, including the dipolar-chemical-shift cross term, so that $\lambda V$ can be associated with the second correction term and $\lambda$ is of order $\frac{1}{T_2} \left( \frac{t_b}{2\pi T_2} \right)^2$.

The average Hamiltonian for the total $\frac{1}{2} t_b$ cycle is

$$\bar{H}_R^{(0)} = \frac{1}{2} \left[ 3C_c + 2C_c^{(B)} \right] + \frac{1}{2} \lambda V.$$

The higher correction terms depend on the symmetry of the circle. For the symmetric cycle in the pulse sequence of Fig. 1(e), we find for the total first correction term

$$\bar{H}_R^{(1)} = 0,$$

again including the dipolar-chemical-shift cross term. The higher-order pure-dipolar correction terms evidently vanish and thus all correction terms are attenuated at least by $\lambda$ or $\Delta$, where the latter is the magnitude of the largest chemical shift. The only nonvanishing second-order term, for example, is found to be attenuated by $\sim 10$ from the magnitude of the usual corresponding pure-dipolar term. The normal requirement of our previous pulse experiments, namely, that we have the cycle time $t_c < T_2$, is therefore not so stringent in this experiment, and much larger cycle times should be tolerable if $\lambda$ and $\Delta$ are small, as we have indeed observed. This is a good example of the exploitation of the properties of subcycles (in this case during the burst) in an effort to increase the efficiency of the full cycle.

Figure 12 shows a preliminary example of the application of this pulse sequence to the $^{19}F$ nuclei of CaF$_2$ with a cycle time of 136 $\mu$sec and using 360 $^\circ$ $x$ and $-x$ pulses ($n=2$). A prolonged decay with an off-resonance beat scaled by $\frac{1}{2} \left[ \bar{H}_c^{(B)} \right] = 0$, is observed: With this cycle time our previous pulse experiments fail completely.

To summarize, we mention briefly several apparent advantages of this new method as compared to some previous line-narrowing techniques. The experiment is essentially continuous wave, except for the 90$^\circ$ pulses, with the magnetization sampling windows forming part of the sequence. We therefore require less power than in our pulsed experiments and do not have to contend to such an extent with the adverse effects of finite pulse width. Further, the experiment does not require the additional video pulses necessary in "magic angle" experiments. An additional advantage is the vanishing of the first-order correction term between dipolar and chemical-shift interactions, and the attenuation in magnitude of the higher-order correction terms. Most important we see that while $t_b$ may be of order $T_2$ or more, the line-narrowing

progressively narrow shape corresponding to a larger destruction of magnetization for $\tau \neq 0$ than for the echo peak.

V. APPLICATION TO LINE NARROWING

A. Multiple Bursts

We have discussed at length elsewhere the possibility of removing the effects of dipolar broadening by repeated application of a suitably chosen cycle of rf perturbations. These cycles have the property that the effective dipolar Hamiltonian in some suitable reference frame, while large, varies during the cycle in such a way that its net effect over a full cycle vanishes to some approximation. The present echo experiments clearly have the same property over a cycle of duration $\frac{1}{2} t_b$: The system behaves as though $\bar{H}_R = \bar{H}_c^{(0)}$ except during the bursts where $\bar{H}_R = -2 \bar{H}_c^{(0)}$ to first order. Thus for a cycle of duration $\frac{1}{2} t_b$ the effective dipolar Hamiltonian is 0 and if the cycle is repeated indefinitely as in Fig. 1(e), the envelope of the magnetization sampled at integral cycle times should generate a very long decay corresponding to an effective line narrowing.

Consider the more interesting case in which the Hamiltonian contains chemical shifts in addition to the dipolar interaction and is given by (31). Removal of the large dipolar broadening is then a necessity if we wish to observe the fine structure associated with the chemical shifts. We have

$$3C_c = 3C_c^{(0)} - 3C_c.$$

(31)

During the burst the effective Hamiltonian is given by

$$\bar{H}_R^{(B)} = -\frac{1}{2} \bar{H}_c^{(0)} + \bar{H}_c^{(B)} - \lambda V,$$

FIG. 12. Multiple-burst line-narrowing sequence (Fig. 1(d)) applied to the $^{19}F$ nuclei of CaF$_2$ with the magnet set slightly off-resonance. The cycle time $\frac{1}{2} t_b$ for this experiment was 136 $\mu$sec, and we observe a prolonged decay with a scaled off-resonance beat. This multiple-echo phenomenon has also been used to observe chemical shifts in solids in an analogous way.
efficiency is determined from (32) essentially by the subcycle time inside the burst, which can be made extremely small since no observation of the magnetization is necessary during this time.

Last, we mention that an analogous experiment employing only 90° rf pulses can be done if the nτ pulses in the time-reversing sequence are replaced by a train of 90° pulses along the ±x directions, but that this would not benefit from all the advantages mentioned above.

B. Symmetric Cycles

We recall from above that the total first-order correction term, including the dipolar-chemical shift cross term, vanished both for the multiple-burst full cycle and the burst subcycle. This is a special case of a more general principle which applies to any symmetric cycle. Adopting the notation in Eq. (15) of Ref. 29, a symmetric cycle is one for which

\[ \tilde{C}(t) = \tilde{C}(t_r - t), \]  

(34)

where \( t_r \) is the pertinent cycle time. It is easily shown for such cycles that the first-order correction term vanishes,

\[ \tilde{C}(1) = 0. \]  

(35)

We see that our cycle and subcycle do indeed have the requisite symmetry, leading to (35). Using (34), other sequences with this property will doubtless occur to the reader, and a general approach to elimination of the first correction term is simply symmetrization of the cycle within the constraints imposed by the requirements of the average Hamiltonian itself. A trivial example is our 4-pulse sequence.30 Preparing the system with a 90° pulse along the y axis, it is

\[ P_y - (\tau - P_x - \tau - P_y - 2\tau - P_y - \tau - P_x - \tau)_n. \]

It is easily verified that (34) holds over a cycle with \( t_r = 6\tau \), and thus (35) is fulfilled. This sequence is simpler than a 6-pulse modification recently proposed by Mansfield,31

\[ P_y - (\tau - P_x - \tau - P_y - 2\tau - P_y - \tau - P_x P_x - \tau)_n, \]

and a 3-dimensional sequence proposed by Silberszyc.32

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BIOGRAPHICAL SKETCH

Alexander Pines, first child of Michael and Neima Pines, was born in Tel-Aviv, Israel on June 22, 1945. He graduated from the Hebrew University of Jerusalem in 1967 and began doctoral studies in Physical Chemistry at the Massachusetts Institute of Technology in September, 1968. He has served as a teaching assistant and has held a Dalton Predoctoral Fellowship while at M.I.T. In August, 1967 he married Ayala Malach and on July 3, 1970 their son, Itai was born. The author has been elected to the Society of Sigma Xi and to Phi Lambda Upsilon, and is a member of the American Physical Society and the American Chemical Society. He has co-authored more than 25 scientific papers.