

Coherent Averaging Effects in Magnetic Resonance*

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(Received 22 April 1968)

A theory is developed to describe the slow component of the transient decay of transverse spin magnetization, and the central component of the slow-passage absorption spectrum, of a system of spins which is subjected to a periodic and cyclic perturbation. The theory is used to analyze and compare various schemes for high-resolution NMR of solids, including the spinning of the sample about an axis oriented at the "magic angle," the rotating-frame magic-angle experiment of Lee and Goldburg, pulsed versions of the latter, and a number of new pulsed-NMR experiments recently developed in this laboratory. Attention is focused on the factors, both theoretical and practical, which are important in obtaining optimal suppression of static dipole-dipole interactions and quadrupole splittings, and retention of chemical and Knight shifts and scalar spin-spin interactions. Several new experiments are proposed.

INTRODUCTION

A SYSTEM of spins I_i , polarized in a strong magnetic field H_0 and having (weak) internal interactions described by a time-independent Hamiltonian H , gives rise to a well-known magnetic resonance absorption spectrum in the neighborhood of the Larmor frequency $\omega_0 = \gamma H_0$. The structure of this spectrum depends on \mathcal{H} , and its width may be roughly characterized by a frequency $T_2^{-1} \sim \|\mathcal{H}\|$, where by $\|\mathcal{H}\|$ we mean the "size" of the internal Hamiltonian (in units of angular frequency).

If \mathcal{H} is not static, but changes over a time scale τ , the structure of the spectrum is altered. If the variations are periodic (e.g., because the sample is rotated in an inhomogeneous field¹), the spectrum develops sidebands at frequencies $\Delta\omega_n = n/\tau$. When the sidebands have become well resolved because $\tau \ll T_2$, the structure of the central component ($n=0$) becomes describable by a time-independent effective Hamiltonian $\bar{\mathcal{H}}$, which is an average of \mathcal{H} over the modulation.¹⁻³ If, on the other hand, the variations of \mathcal{H} are random (e.g., because of random atomic motion), characterized by a correlation time τ_c , the sidebands are no longer distinct. However, for $\tau_c \ll T_2$ the residual central absorption component again becomes describable by a time-independent Hamiltonian $\bar{\mathcal{H}}$ which is an average over the motion.⁴ In general $\|\bar{\mathcal{H}}\| < \|\mathcal{H}\|$, and one speaks, perhaps inelegantly, of "motional narrowing."

Recently we have developed a class of transient

NMR experiments⁵⁻⁹ in which \mathcal{H} , while in fact static, can be made in a sense to appear time-dependent. The time dependence is introduced through the application of a train of intense magnetic field pulses. As the characteristic repetition period τ of the pulses becomes small compared to T_2 , the spin system again comes to behave over long times as though under the exclusive influence of a time-independent average Hamiltonian. This average is under the control of the experimenter through his manipulation of the intensities, directions, and timing of the pulses, so that a wide variety of effects can be achieved. It is our aim in this paper to put these pulse experiments into a consistent theoretical context with the other sorts of averaging effects just mentioned. We concentrate for emphasis on the practically useful goal of achieving averaging which is selective in the sense of removing the part of \mathcal{H} which corresponds to direct dipole-dipole interactions (\mathcal{H}_d) while retaining the often much smaller effects of resonance shifts \mathcal{H}_c (chemical shifts, Knight shifts, inhomogeneous broadening) and scalar spin-spin coupling (\mathcal{H}_j). That is, our aim is to seek experimental methods for accomplishing "high-resolution" NMR of solids.

ELEMENTARY THEORY OF THE PULSE EXPERIMENTS

We begin by clarifying, in an idealized context, the remark made above that the effective spin Hamiltonian in pulse experiments can be made to appear time-dependent in a controlled way, whereas the ac-

* This work was supported in part by the Joint Services Electronics Program under Contract No. DA-28-043-AMC-02536, and in part by the National Science Foundation.

† Stipendiat of the Deutsche Forschungsgemeinschaft.

¹ F. Bloch, *Phys. Rev.* **94**, 496 (1954).

² E. R. Andrew, A. Bradbury, and R. G. Eades, *Arch. Sci. (Geneva)* **11**, 223 (1958).

³ I. J. Lowe, *Phys. Rev. Letters* **2**, 285 (1959).

⁴ A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. X.

⁵ E. D. Ostroff and J. S. Waugh, *Phys. Rev. Letters* **16**, 1097 (1966).

⁶ J. S. Waugh and C. H. Wang, *Phys. Rev.* **162**, 209 (1967).

⁷ J. S. Waugh and L. M. Huber, *J. Chem. Phys.* **47**, 1862 (1967).

⁸ J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, *J. Chem. Phys.* **48**, 662 (1968).

⁹ J. S. Waugh, L. M. Huber, and U. Haebleren, *Phys. Rev. Letters* **20**, 180 (1968).

tual Hamiltonian is static. Imagine that a δ -function pulse of magnetic field, P_1 , is applied at time t_0 to a spin system initially in the quantum state $|t_0\rangle$. The system then develops freely in the rotating frame under the influence of its internal Hamiltonian \mathcal{H} for a time τ_1 , after which it receives a second pulse P_2 , perhaps different from the first, develops freely for a further interval τ_2 , etc. The pulses, being arbitrarily narrow and intense, have effects which can be represented by the instantaneous transformations

$$P_k = \exp(-i\theta_k \mathbf{n}_k \cdot \mathbf{I}), \quad (1)$$

where θ_k is the angle through which the resultant spin \mathbf{I} of the system is rotated and \mathbf{n}_k is a unit vector denoting the direction of the field pulse in the rotating frame. Immediately before the $(n+1)$ st pulse, the quantum state of the system is

$$|t_0 + \sum_{k=1}^n \tau_k\rangle = \left\{ \prod_{k=1}^n [\exp(-i\mathcal{H}\tau_k) P_k] \right\} |t_0\rangle, \quad (2)$$

where it is understood that, in writing out the indicated product, k increases toward the left. By repeated use of the identity $P_k P_k^{-1} = 1$, Eq. (2) can be rewritten as

$$|t_0 + \sum_{k=1}^n \tau_k\rangle = \left\{ \prod_{m=1}^n P_m \right\} \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_k \tau_k) \right\} |t_0\rangle, \quad (3)$$

where

$$\mathcal{H}_k = \left(\prod_{l=1}^k P_l \right)^{-1} \mathcal{H} \left(\prod_{l=1}^k P_l \right). \quad (4)$$

Equation (3) expresses the time development in a time-dependent interaction representation in which the effective Hamiltonian $\tilde{\mathcal{H}}(t)$ is time-dependent: $\tilde{\mathcal{H}}(t) = \mathcal{H}_1, \mathcal{H}_2, \dots$.

Now suppose that for some value of n the pulses have the property that

$$\prod_{m=1}^n P_m = 1. \quad (5)$$

Such a sequence will be called a *cycle* and its duration

$$\sum_{k=1}^n \tau_k = t_c$$

will be called the *cycle time*. (This notation is deliberately chosen to suggest the correlation time τ_c familiar in problems involving random motions.) We then have

$$|t_0 + t_c\rangle = \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_k \tau_k) \right\} |t_0\rangle = \mathcal{L}(t_c) |t_0\rangle. \quad (6)$$

Suppose in addition that the pulse train is periodic, with period t_c or smaller. Then after N cycles,

$$|t_0 + Nt_c\rangle = [\mathcal{L}(t_c)]^N |t_0\rangle. \quad (7)$$

Now, by expanding $\mathcal{L}(t_c)$ in powers of t_c , raising to

the N th power, and regrouping terms, it is possible to show⁸ that as t_c/T_2 is made arbitrarily small the system develops over long times Nt_c according to a time-independent average Hamiltonian $\bar{\mathcal{H}}$:

$$\lim_{\substack{t_c/T_2 \rightarrow 0 \\ N \rightarrow \infty \\ Nt_c = t}} [\mathcal{L}(t_c)]^N = \exp(-i\bar{\mathcal{H}}Nt_c), \quad (8)$$

$$\bar{\mathcal{H}} = \sum_{k=1}^n \mathcal{H}_k(\tau_k/t_c). \quad (9)$$

Equation (8) is just the time-development operator which would be used to calculate the Bloch decay of a spin system whose static Hamiltonian was $\bar{\mathcal{H}}$. According to the Lowe-Norberg theorem,¹⁰ the unsaturated slow-passage absorption spectrum of the same fictitious system can be obtained from this Bloch decay through a Fourier transformation.

A particularly interesting feature of (9) is that a great deal of control over the form of $\bar{\mathcal{H}}$ can be exercised by the experimenter through judicious choice of the pulses P_k employed and their timing τ_k . Thus one can expect to achieve a wider variety of effects than are obtained by, e.g., rotating the sample or allowing nature to modulate \mathcal{H} through random molecular motion. We have discussed some of these possibilities elsewhere.^{8,9}

Because of the periodicity of the pulse trains, one expects strong periodicities of the actual magnetization signal, corresponding to a distinct sideband structure in the spectrum obtained by Fourier transformation. By restricting our attention to instants of time separated by t_c in Eqs. (7) and (8), in effect we suppress these periodicities, which amounts to selecting the central component of the slow-passage absorption spectrum. It is helpful to make this selection experimentally as well as theoretically by sampling the observed transient induction signal at intervals of t_c .

The preceding discussion clarifies the general outlook we have taken toward the design of pulse experiments. It is, however, somewhat incomplete from the viewpoint of an experimenter, who does not have ideal δ -function pulses at his disposal and who cannot reach the mathematical limit $t_c/T_2 \rightarrow 0$ expressed in (8). Effects of finite pulse width and finite t_c are in fact very important in experimental design, as we shall see. Therefore, in the next section we proceed to generalize the above framework to include the possibility of quite general time variations of the applied magnetic field.

THEORY

We describe the system by its spin density matrix $\rho(t)$. In addition to its static internal Hamiltonian

¹⁰ I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957); see also Ref. 4, Chap. IV.

ian \mathcal{H} , the system is subject to time-dependent external fields which generate an explicitly time-dependent Hamiltonian $\mathcal{H}_1(t)$. $\mathcal{H}_1(t)$ in general will not commute with itself for different values of t . The time evolution of ρ from some arbitrary initial time $t=0$ is given by

$$\rho(t) = L(t)\rho(0)L^\dagger(t), \quad (10)$$

with

$$L(t) = T \exp\left(-i \int_0^t [\mathcal{H} + \mathcal{H}_1(t')] dt'\right), \quad (11)$$

where T is the Dyson time-ordering operator.

We wish to separate out the part of the motion of the system which is due to the external fields alone. This is accomplished by means of an interaction representation, which must be time-dependent because \mathcal{H}_1 depends on the time.¹¹ We write

$$L(t) = L_1(t)\mathcal{L}(t), \quad (12)$$

where

$$L_1(t) = T \exp\left(-i \int_0^t \mathcal{H}_1(t') dt'\right). \quad (13)$$

Then, from (11)-(13),

$$\mathcal{L}(t) = T \exp\left(-i \int_0^t \tilde{\mathcal{H}}(t') dt'\right), \quad (14)$$

where

$$\tilde{\mathcal{H}}(t) = L_1^{-1}(t)\mathcal{H}L_1(t). \quad (15)$$

The derivation of Eqs. (14) and (15), which have been given by Evans and Powles,¹² would be trivial if the operator exponentials could be factorized. However, they cannot since the operators do not commute. We indicate a proof of (14) and (15) as follows: From (11) and (12),

$$\begin{aligned} dL(t)/dt &= -i[\mathcal{H} + \mathcal{H}_1(t)]L(t) \\ &= \frac{dL_1(t)}{dt}\mathcal{L}(t) + L_1(t)\frac{d\mathcal{L}(t)}{dt}. \end{aligned}$$

From (13), $dL_1(t)/dt = -i\mathcal{H}_1(t)L_1(t)$, so that

$$-i\mathcal{H}L_1(t)\mathcal{L}(t) = L_1(t)d\mathcal{L}/dt$$

or, using (15), which defines $\tilde{\mathcal{H}}(t)$,

$$d\mathcal{L}/dt = -i\tilde{\mathcal{H}}(t)\mathcal{L}(t),$$

whose formal integral is Eq. (14).

We now choose $\mathcal{H}_1(t)$ to be both *periodic* and *cyclic* over a time t_c :

$$\mathcal{H}_1(t + Nt_c) = \mathcal{H}_1(t), \quad (16)$$

$$L_1(Nt_c) = T \exp\left(-i \int_0^{Nt_c} \mathcal{H}_1(t) dt\right) = 1. \quad (17)$$

We note in passing that in some cases (17) may be satisfied over a shorter time than t_c . The experiment of Waugh, Huber, and Haebleren⁹ is such a case. When this occurs we shall speak of *subcycles* of duration t_s .

By satisfying (16) and (17) we ensure that

$$\tilde{\mathcal{H}}(t + Nt_c) = \tilde{\mathcal{H}}(t). \quad (18)$$

That is, the periodicity of $\mathcal{H}_1(t)$ is transferred to $\tilde{\mathcal{H}}(t)$. Also

$$\rho(Nt_c) = \mathcal{L}(Nt_c)\rho(0)\mathcal{L}^\dagger(Nt_c) \quad (19)$$

and

$$\mathcal{L}(Nt_c) = [\mathcal{L}(t_c)]^N, \quad (20)$$

which is a consequence of (14) and (18).

To describe the state of the system at any integer multiple of the cycle time t_c it is thus sufficient to calculate the *short-time* evolution over 1 cycle. The 1-cycle propagator $\mathcal{L}(t_c)$ is then raised to the N th power. To obtain the result in the form of a single exponential it is convenient to apply the Magnus formula¹³ to $\mathcal{L}(t_c)$ as given by (14).

$$\begin{aligned} \mathcal{L}(t_c) &= \exp(-iFt_c) \\ &\equiv \exp\{-it_c(\tilde{\mathcal{H}} + \tilde{\mathcal{H}}^{(1)} + \tilde{\mathcal{H}}^{(2)} + \dots)\}. \end{aligned} \quad (21)$$

Proofs of the Magnus formula have been given by a number of authors,¹⁴⁻¹⁹ and it has been exploited in magnetic resonance problems by Evans,¹⁹ whose treatment differs from the present one mainly in that it does not explicitly exploit the periodic and cyclic properties mentioned above.

Using (20), and recalling that F is a time-independent operator,

$$\begin{aligned} \mathcal{L}(Nt_c) &= \exp(-iFNt_c) \\ &= \exp\{-iNt_c(\tilde{\mathcal{H}} + \tilde{\mathcal{H}}^{(1)} + \tilde{\mathcal{H}}^{(2)} + \dots)\} \end{aligned} \quad (22)$$

or, if it is understood that the real time t is restricted to integer multiples of t_c following some initial condition,

$$\mathcal{L}(t) = \exp(-iFt). \quad (23)$$

$\tilde{\mathcal{H}}$ is the (zero-order) average Hamiltonian of (8). When t_c is finite, $\tilde{\mathcal{H}}$ is to be supplemented by the first-, second-, ... order average Hamiltonians $\tilde{\mathcal{H}}^{(1)}$, $\tilde{\mathcal{H}}^{(2)}$, ... It is important to note that all of these are *independent of time*. They depend only on the

¹¹ J. D. Macomber and J. S. Waugh, Phys. Rev. **140**, A1494 (1965); J. Chem. Phys. **45**, 985 (1966).

¹² W. A. B. Evans and J. G. Powles, Proc. Phys. Soc. (London) **92**, 1046 (1967).

¹³ W. Magnus, Commun. Pure Appl. Math. **7**, 649 (1954).

¹⁴ G. H. Weiss and A. A. Maradudin, J. Math. Phys. **3**, 771 (1962).

¹⁵ D. W. Robinson, Helv. Phys. Acta **36**, 140 (1963).

¹⁶ K. Kumar, J. Math. Phys. **6**, 1928 (1965).

¹⁷ P. Pechukas and F. C. Light, J. Chem. Phys. **44**, 3897 (1966).

¹⁸ R. M. Wilcox, J. Math. Phys. **8**, 962 (1967).

¹⁹ W. A. B. Evans (to be published).

parameter t_c . $\bar{\mathcal{H}}$ and the correction terms are given by¹⁹

$$\bar{\mathcal{H}} = t_c^{-1} \int_0^{t_c} \tilde{\mathcal{H}}(t) dt, \quad (24)$$

$$\bar{\mathcal{H}}^{(1)} = \frac{-i}{2t_c} \int_0^{t_c} dt_2 \int_0^{t_2} dt_1 [\tilde{\mathcal{H}}(t_2), \tilde{\mathcal{H}}(t_1)], \quad (25)$$

$$\begin{aligned} \bar{\mathcal{H}}^{(2)} = & (6t_c)^{-1} \int_0^{t_c} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \\ & \times \{ [\tilde{\mathcal{H}}(t_3), [\tilde{\mathcal{H}}(t_2), \tilde{\mathcal{H}}(t_1)]] \\ & + [\tilde{\mathcal{H}}(t_1), [\tilde{\mathcal{H}}(t_2), \tilde{\mathcal{H}}(t_3)]] \}, \quad (26) \end{aligned}$$

etc. Each of these terms is Hermitian.¹⁷ If $\tilde{\mathcal{H}}(t)$ commuted with itself at different times, $\bar{\mathcal{H}}$ (which we shall continue to call "the average Hamiltonian") alone would suffice to describe the time development of the system. Such is sometimes the case, e.g., when \mathcal{H} is an inhomogeneous shift Hamiltonian describing a distribution of isochromats and $\mathcal{H}_1(t)$ consists of a regular train of 180° pulses (Carr-Purcell method B^{20}). One then has $\bar{\mathcal{H}} = \bar{\mathcal{H}}^{(1)} = \bar{\mathcal{H}}^{(2)} = \dots = 0$ over a cycle of two pulses, and the magnetization at integral cycle times (e.g., echo maxima) does not decay at all. More often, however, $\tilde{\mathcal{H}}(t)$ does not behave so simply and the higher-order average Hamiltonians must be included. In a sense they can be thought of as quantum corrections to a "classical" theory.

To get a rough idea of their relative importance, consider first the particularly unfavorable case in which $\bar{\mathcal{H}}$, $\bar{\mathcal{H}}^{(1)}$, etc., exhibit no averaging but $\bar{\mathcal{H}}$ is of the same order of magnitude as \mathcal{H} itself. Then from the form of (24)–(26) we expect the decay time associated with $\bar{\mathcal{H}}^{(n)}$ to be of the order of $T_2(T_2/t_c)^n$, which becomes rapidly long with increasing n as t_c/T_2 is made appreciably smaller than unity. A more favorable situation exists if we can arrange that $\bar{\mathcal{H}} = \bar{\mathcal{H}}^{(1)} = \dots = \bar{\mathcal{H}}^{(n-1)} = 0$. We then find

$$\begin{aligned} \bar{\mathcal{H}}^{(n)} = & (-i)^n t_c^{-1} \int_0^{t_c} dt_n \int_0^{t_n} dt_{n-1} \dots \\ & \times \int_0^{t_2} dt_1 \tilde{\mathcal{H}}(t_n) \tilde{\mathcal{H}}(t_{n-1}) \dots \tilde{\mathcal{H}}(t_1) \quad (27) \end{aligned}$$

and, since the volume of integration in (27) is $t_c^{n+1}/(n+1)!$, the first nonvanishing correction $\bar{\mathcal{H}}^{(n)}$ will lead to a decay time not shorter than

$$T_{\text{decay}} \sim T_2(n+1)!(T_2/t_c)^n,$$

which grows quite rapidly with increasing n for $t_c/T_2 < 1$. These considerations have been discussed in greater detail by Waugh and Wang⁵ and Evans¹⁹ with reference to a specific pulsed-NMR experiment, and can be made more precise by means of a formal

cumulant expansion²¹ of the expectation value of the magnetization.

We now wish to apply these considerations to a number of NMR experiments, old and new, whose primary aim is to eliminate static dipolar line broadening in solids but to retain the structure arising from interaction of nuclear spins with electrons. In particular we shall be concerned with the truncated dipolar and chemical shift Hamiltonians as contributors to $\bar{\mathcal{H}}$:

$$\begin{aligned} \bar{\mathcal{H}}_D^{(z)} = & \sum_{i < j} \sum b_{ij} (\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{zi} I_{zj}), \\ b_{ij} = & \gamma^2 \hbar r_{ij}^{-3} P_2(\cos \theta_{ij}), \quad (28) \end{aligned}$$

$$\bar{\mathcal{H}}_C^{(z)} = \omega_0 \sum_i \sigma_{zzi} I_{zi}. \quad (29)$$

The reason for writing the superscript (z), which refers to the z -component spin operators appearing in (28) and (29), will appear later. The quantity σ_{zzi} is the zz component of the chemical shift tensor of spin i in laboratory coordinates, where \mathbf{H}_0 is along the z axis. In terms of the principal-axis system (XYZ) of the chemical shift tensor, related to the laboratory system (xyz) by the Eulerian angles θ, ϕ, ψ ,

$$\sigma_{zz} = \sin^2 \theta \cos^2 \phi \sigma_{XX} + \sin^2 \theta \sin^2 \phi \sigma_{YY} + \cos^2 \theta \sigma_{ZZ}. \quad (30)$$

Introducing the anisotropy $\Delta\sigma$ and asymmetry parameter η of the chemical shift by

$$\begin{aligned} \sigma_{XX} = & -\Delta\sigma(1 - \frac{1}{2}\eta) + \frac{1}{3}\text{Tr}\sigma, \\ \sigma_{YY} = & -\Delta\sigma(1 + \frac{1}{2}\eta) + \frac{1}{3}\text{Tr}\sigma, \\ \sigma_{ZZ} = & 2\Delta\sigma + \frac{1}{3}\text{Tr}\sigma, \end{aligned}$$

one has

$$\begin{aligned} \sigma_{zz} = & \Delta\sigma(\frac{1}{3}\pi)^{1/2} \{ 4Y_{2,0}(\theta, \phi) \\ & + \eta(\sqrt{\frac{2}{3}}) [Y_{2,2}(\theta, \phi) + Y_{2,-2}(\theta, \phi)] \} + \frac{1}{3}\text{Tr}\sigma. \quad (31) \end{aligned}$$

The introduction of the spherical harmonics Y_{2m} is useful when considering the behavior of σ_{zz} under rotations, as we shall do presently.

Various other contributions to $\bar{\mathcal{H}}$ could be included as well. As we have shown earlier,⁷ a first-order quadrupole splitting $\bar{\mathcal{H}}_Q$ has the same space and spin symmetry as $\bar{\mathcal{H}}_D$, so that whatever conclusions we draw about the latter will be true of the former as well. Electron-coupled spin-spin interactions will appear through their scalar parts $\bar{\mathcal{H}}_J^{(ij)} = J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$ only.⁷ Since this operator is invariant to rotations in coordinate or spin space, it will be unaffected by any of the averaging schemes we shall discuss. Because of these simplifications we will not sacrifice much generality by confining our specific attention of $\bar{\mathcal{H}}_D$ and $\bar{\mathcal{H}}_C$. It is important to keep in mind, however, that coupling effects among different parts of $\bar{\mathcal{H}}$ may

²⁰ H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

²¹ R. Kubo, J. Phys. Soc. Japan **17**, 1100 (1962); C. H. Wang, Ph.D. thesis, M.I.T., 1967 (unpublished).

occur in the higher-order average Hamiltonians $\bar{\mathcal{H}}_C^{(1)}$, $\bar{\mathcal{H}}_C^{(2)}$, etc.

ROTATING SAMPLE EXPERIMENT

For some years it has been known that the effects of dipolar interactions could be removed by rotating the (solid) sample at a sufficiently high angular velocity ω about an axis making the "magic angle" $\tan^{-1}\sqrt{2}$ with \mathbf{H}_0 .^{2,3} The behavior of the time-dependent magnetization has recently been treated in detail by Evans and Powles¹² for short times and by Clough and McDonald²² and Evans¹⁹ for long times. The

well-known results are easily rederived by use of the present theory. We content ourselves with making a few points which will form the basis of contrasts with other types of experiments.

Of course, in the rotating sample experiments the *spatial* parts of the Hamiltonian are made explicitly time-dependent, and there is no need of an interaction representation of the type introduced in the previous section. Therefore we drop the tildes (\sim) on the time-dependent operators for the present. The cycle time becomes just the period of rotation: $t_c = 2\pi/\omega$. We have

$$\bar{\mathcal{H}}_D(t) = \sum_{i < j} \sum b_{ij}(t) (I_i \cdot I_j - 3I_{zi}I_{zj}), \quad (32)$$

$$b_{ij}(t) = \frac{1}{2}(\gamma^2\hbar) r_{ij}^{-3} [\sqrt{2} \sin(2\alpha_{ij}) \cos(\beta_{ij} + \omega t) + \sin^2\alpha_{ij} \cos(2\beta_{ij} + 2\omega t)], \quad (33)$$

where α_{ij} and β_{ij} specify the *initial* orientation of \mathbf{r}_{ij} . Also

$$\bar{\mathcal{H}}_C(t) = \omega_0 \sum_i I_{zi} \frac{1}{3} \text{Tr} \sigma_i + \text{terms oscillating with } \omega \text{ and } 2\omega. \quad (34)$$

From the definition of the average Hamiltonian we immediately have that

$$\bar{\mathcal{H}}_D = 0, \quad (35)$$

$$\bar{\mathcal{H}}_C = \omega_0 \sum_i I_{zi} \frac{1}{3} \text{Tr} \delta_i. \quad (36)$$

Equations (35) and (36) state that the average Hamiltonian has the same form as in a liquid.

Inserting (33) into (25) one finds

$$\bar{\mathcal{H}}_D^{(1)} = -\frac{1}{2}i \sum_{i < j} \sum_{i' < j'} \sum \sum [(I_i \cdot I_j - 3I_{zi}I_{zj}), (I_{i'} \cdot I_{j'} - 3I_{z i'}I_{z j'})] t_c^{-1} \int_0^{t_c} dt_2 \int_0^{t_2} dt_1 b_{ij}(t_2) b_{i'j'}(t_1) \neq 0. \quad (37)$$

This form can be used to obtain the leading (second-moment) term in the Bloch decay $G_e(t)$ of a spinning sample. One obtains

$$G_e(t) = 1 - \frac{1}{2}t^2 \frac{I^2(I+1)^2}{N} \sum_i \sum_{j \neq j'} \sum \left(t_c^{-1} \int_0^{t_c} dt_2 \int_0^{t_2} dt_1 [b_{ij}(t_2) + b_{ij'}(t_2)] b_{jj'}(t_1) \right)^2 + \dots \quad (38)$$

Equation (38) reduces to a result of Clough and McDonald²² [their Eq. (41)], which they obtain by a generalization of the method of Lowe and Norberg,¹⁰ if we insert $I = \frac{1}{2}$ and assume that all spins are in equivalent positions. Evans and Powles¹² have criticized this result on the ground that it applies only to the envelope $(0, t_c, 2t_c, \dots)$ of the actual signal. The same criticism, of course, applies to our formalism. However, it misses the point if in fact the experiment is performed to measure chemical shifts in solids: if this is to be done one must choose $t_c < T_2$, and the slow beat arising from the chemical shifts will necessarily be well defined by the large number of points for which the theory is valid.

MAGIC-ANGLE EXPERIMENTS IN THE ROTATING FRAME

1. Lee-Goldburg Experiment

In this (LG) experiment²³ a strong steady rf field $2H_1 \cos \omega t$ is applied to a sample shifted off resonance by ΔH_0 , so that in the rotating frame the spins experience a field $H_e = (H_1^2 + \Delta H_0^2)^{1/2}$ which makes an angle $\xi = \tan^{-1}(H_1/\Delta H_0)$ with the z axis. The perturbing Hamiltonian, in the tilted rotating frame,²⁴ takes the form

$$\mathcal{H}_1(t) = \omega_e I_z; \quad \omega_e = -\gamma H_e, \quad (39)$$

which leads to a cyclic behavior for $t_c = 2\pi/\omega_e$. Per-

²² S. Clough and I. R. McDonald, Proc. Phys. Soc. (London) **86**, 833 (1965).

²³ M. Lee and W. I. Goldburg, Phys. Rev. **140**, A1261 (1965).

²⁴ A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

forming the transformations prescribed by (15) one obtains in the rotating frame

$$\begin{aligned} \tilde{\mathcal{H}}_D(t) = \sum_{i < j} b_{ij} \{ & (3I_{zi}I_{zj} - \mathbf{I}_i \cdot \mathbf{I}_j) P_2(\cos\xi) \\ & - (I_{xi}I_{zj} + I_{zi}I_{xj}) 3 \sin\xi \cos\xi \cos\omega_e t \\ & + (I_{yi}I_{zj} + I_{zi}I_{yj}) 3 \sin\xi \cos\xi \sin\omega_e t \\ & + (I_{xi}I_{xj} - I_{yi}I_{yj}) \frac{3}{2} \sin^2\xi \cos 2\omega_e t \\ & - (I_{xi}I_{yj} + I_{yi}I_{xj}) \frac{3}{2} \sin^2\xi \sin 2\omega_e t \} \end{aligned} \quad (40)$$

and

$$\begin{aligned} \tilde{\mathcal{H}}_C(t) = \omega_0 \sum_i \sigma_{zzi} \\ \times \{ I_{zi} \cos\xi - (I_{xi} \cos\omega_e t - I_{yi} \sin\omega_e t) \sin\xi \}. \end{aligned} \quad (41)$$

By satisfying the magic-angle condition $\tan\xi = \tan\xi_m = \sqrt{2}$, one obtains in the tilted rotating frame

$$\tilde{\mathcal{H}}_D = 0, \quad (42)$$

$$\tilde{\mathcal{H}}_C = 3^{-1/2} \omega_0 \sum_i \sigma_{zzi} I_{zi}. \quad (43)$$

To this degree of approximation the dipolar interactions are eliminated and the chemical shifts reduced by the common scale factor $\sqrt{3}$.

Note that, unlike the rotating sample experiment, the LG method preserves the full spatial anisotropy of the chemical (or Knight) shift. We shall find the same to be true of a number of pulse experiments to be discussed shortly. This distinction arises because the vanishing of \mathcal{H}_D in the rotating sample experiment depends on exploiting the transformation properties of \mathcal{H}_D under rotations in space, whereas the rotating-frame methods exploit corresponding transformation properties of \mathcal{H}_D under rotations in spin space. The famous magic angle ξ_m , for which $P_2(\cos\xi_m) = 0$, arises in both because \mathcal{H}_D is a second rank spherical tensor operator with respect to both spatial and spin coordinates.

The anisotropy of the shifts contains useful information, and could be regarded as making the various rotating-frame experiments potentially more fruitful than the high-resolution NMR spectra of liquids. There may be situations, particularly when the sample is complex and not a single crystal, when the extra information constitutes an embarrassment of riches. In such a case one could suppress the shift anisotropy by performing one of the rotating-frame experiments and simultaneously spinning the sample at the magic angle, preferably making the spinning period an integral multiple of the cycle time t_c . Note that the spinning rate need not ordinarily be so extremely large as in the pure rotating sample experiments: The rotating-frame experiment is relied upon to suppress the dipolar broadening, leaving only the (usually smaller) anisotropy of the chemical shift to be re-

moved by sample spinning. We shall make this assertion more concrete in a later section.

The first-order correction to the average Hamiltonian, $\tilde{\mathcal{H}}_D^{(1)}$, is obtained straightforwardly from (25), putting $t_c = 2\pi/\omega_e$. One recovers just what LG, in their paper,²³ call the "nonsecular" dipolar effects \mathcal{H}_s , which are important if H_1 is not very large. It is this term which limits at present the degree to which dipolar effects can in practice be suppressed. Note that the critical expansion parameter $t_c/2\pi T_2 = H_{10c}/H_e$, where the local field $H_{10c} = (\gamma T_2)^{-1}$.

Another important practical problem, to which LG paid a good deal of experimental attention, is associated with inhomogeneity of H_1 , which arises from rf currents in a coil whose dimensions are not very large compared to the sample. An inhomogeneity of H_1 has two effects:

(i) It leads to a nonuniformity in the magnitude of H_e , and thus to a spreading of isochromats which were in phase at the beginning of the experiment. The importance of this effect can be seen in liquid samples, where other sources of decay are absent.

(ii) If H_0 is relatively homogeneous, it leads to a failure to satisfy the magic-angle condition everywhere in the sample, so that $\mathcal{H}_D \neq 0$. An element of sample for which $\xi = \xi_m - \delta$, $\delta \ll 1$ has

$$\tilde{\mathcal{H}}_D = \sqrt{2} \delta \mathcal{H}_D^{(2)},$$

which leads to a decay time of the order of $T_2/(\sqrt{2}\delta)$. For a sample with mean square inhomogeneity described by $\langle \delta^2 \rangle_{av}$, one expects

$$T_{decay} \sim T_2 / (\sqrt{2} \langle \delta^2 \rangle_{av})^{1/2}.$$

2. Tilted Coil Modification

The second type of inhomogeneity effect can be ameliorated by deriving ΔH_0 and H_1 from suitable currents in one and the same coil.⁹ Suppose the coil is tilted so that its axis makes an angle α with the direction of \mathbf{H}_0 , which is set on exact resonance. The coil is now excited simultaneously by a dc current I_{dc} and an oscillating rf current I_{rf} , which give rise to proportional magnetic fields H_{dc} and H_{rf} . These lead to *secular* Zeeman interactions in the rotating frame corresponding to a longitudinal field $H_z = H_{dc} \cos\alpha$ and a transverse field $H_x = \frac{1}{2} H_{rf} \sin\alpha$. It is H_z and H_x which must be adjusted to obtain the magic-angle condition. This can be done by satisfying

$$(H_{rf}/2H_{dc}) \tan\alpha = \sqrt{2}. \quad (44)$$

Since H_{dc} and H_{rf} have the same geometrical inhomogeneity over the sample, the magic-angle condition (44) is everywhere maintained. (Note, however, that only variations in the magnitude, but not in the direction, of the coil field are fully compensated.)

3. Pulsed Analog of the LG Experiment

We recently suggested,^{8,25} and have since carried out, an experiment which is identical to the tilted coil modification of the LG experiment except that H_e is periodically pulsed. The pulsed version has the practical advantage that the free precession signal can be observed "continuously" in the gaps between the pulses, thus making the entire history of the magnetization available in one shot, as it were. It is easily verified, for cycles of three or more pulses and any repetition rate, that $\tilde{\mathcal{H}}$ is the same as in the steady LG experiment. $\tilde{\mathcal{H}}^{(1)}$ depends on the details of the cycle. The values of $\tilde{\mathcal{H}}^{(1)}$ for the LG and a three-pulse cycle can be compared as follows in terms of the operators $\tilde{\mathcal{H}}^{(i)}$ defined by Lee and Goldberg:

$$\begin{aligned} \tilde{\mathcal{H}}^{(1)}(\text{LG}) &= (t_c/36\pi) \{ [\tilde{\mathcal{H}}^{(1)}, \tilde{\mathcal{H}}^{(-1)}] + \frac{1}{4} [\tilde{\mathcal{H}}^{(2)}, \tilde{\mathcal{H}}^{(-2)}] \}, \\ \tilde{\mathcal{H}}^{(1)}(3 \text{ pulse}) &= t_c(36 \times 3\sqrt{3})^{-1} \{ [\tilde{\mathcal{H}}^{(1)}, \tilde{\mathcal{H}}^{(-1)}] + \frac{1}{2} [\tilde{\mathcal{H}}^{(-2)}, \tilde{\mathcal{H}}^{(2)}] \\ &\quad + (1/\sqrt{2}) ([\tilde{\mathcal{H}}^{(2)}, \tilde{\mathcal{H}}^{(1)}] + [\tilde{\mathcal{H}}^{(-1)}, \tilde{\mathcal{H}}^{(-2)}]) \}. \end{aligned}$$

A detailed calculation of the comparative effects on the decay time of the induction signal for finite t_c seems unwarranted. A consideration of the orders of magnitude of the matrix elements which contribute to the second moment suggests that the decay times resulting from $\tilde{\mathcal{H}}^{(1)}$ should be very nearly the same for the two experiments. The effect of $\tilde{\mathcal{H}}^{(1)}$ is expected to depend strongly on t_c but not on the number of pulses contained in a cycle. This means that the importance of the "nonsecular" correction $\tilde{\mathcal{H}}^{(1)}$ depends on the *average* value of H_e . In the pulsed experiment using pulses of width t_w and repetition time τ one must then increase the peak pulse field by the factor τ/t_w over that in the steady LG experiment in order to obtain comparable results. Since the power required to maintain a field H_e is proportional to H_e^2 , the average transmitter power then becomes proportional to τ/t_w .

Figure 1(a) shows the Bloch decay (^{19}F resonance) of a single crystal of CaF_2 , observed following a 90° pulse of 60-G rotating field at 54.0 MHz. Figure 1(b) shows the decay observed during the application of a train of 120° pulses ($t_w=1.6 \mu\text{sec}$, $\tau=14 \mu\text{sec}$) applied along the magic-angle direction. These conditions correspond to an average effective field

$$\langle H_e \rangle_{\text{av}} = 2\pi/3\gamma t = 6.0 \text{ G.}$$

which is only slightly less than the steady field $H_e \approx 6.4 \text{ G}$ employed by Lee and Goldberg,²³ also on a sample of CaF_2 . The decay time exhibited in Fig. 1(b) is therefore nearly as long as theirs (LG, Fig. 2).

²⁵ J. S. Waugh, L. M. Huber, and E. D. Ostroff, Phys. Letters 26A, 211 (1968).

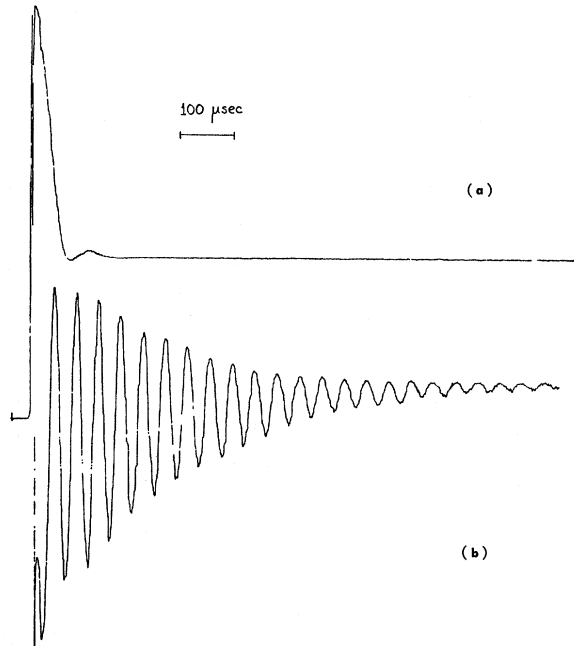


FIG. 1 (a) Bloch decay of the ^{19}F resonance in a single crystal of CaF_2 . (b) Smoothed envelope of sampled magnetization in a pulsed analog of the Lee-Goldburg experiment using the tilted coil method.

In this experiment we employed the scheme outlined in subsection 2 to compensate the inhomogeneity of H_1 , which was produced in a coil only 6 mm in diameter and 1 cm in length. As each rf pulse was applied to the coil by a 100-W transmitter, a video current pulse of the same width was simultaneously applied by a Hewlett-Packard 214A pulse generator. The pulser was prevented from loading the rf transmitter by placing a 54.0-MHz notch filter in the line between the pulser and the coil. The orientation α [cf. Eq. (44)] of the coil in the Zeeman field was adjusted to meet the magic-angle condition and was roughly 45° .

The traces of Fig. 1 were obtained using a phase-sensitive receiver followed by a sample-and-hold circuit which captured the induction signal following each pulse and held it through the next one. The output of this device was filtered with a time constant $\sim \tau$ to smooth the staircase signal obtained. The transient was then digitized in a Fabritek Model 952/1062 averager and read out on an XY plotter.

4. Magic-Angle Cycles with Periodic Reversal of H_e

Consider a situation like that of Subsec. 3, except that at the end of each cycle the direction of H_e in the rotating frame is reversed. For simplicity imagine that the original cycle (now a subcycle) consisted of three equally spaced 120° pulses, although any larger number would do. The full cycle now consists of six pulses, as diagrammed in Fig. 2. If H_e is chosen

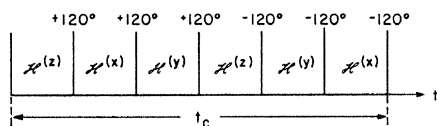


FIG. 2. Pulse cycle for a pulsed analog of the Lee-Goldburg experiment, employing periodic reversal of the effective field. Each pulse rotates the magnetization by 120° about the (111) direction in the rotating frame. Instead of a three-pulse subcycle of 120° pulses, a four-pulse subcycle of 90° pulses, etc., could have been used. The symbols $\mathcal{H}^{(z)}$, etc., between the pulses denote the transformed effective Hamiltonians $\tilde{\mathcal{H}}$ which can be thought of as acting during the indicated intervals, and whose average is $\bar{\mathcal{H}}$.

along the (111) and $(\bar{1}\bar{1}\bar{1})$ directions of the rotating frame, the effective Hamiltonian $\tilde{\mathcal{H}}$ takes on a succession of algebraically simple forms, denoted by $\mathcal{H}^{(x)}$, $\mathcal{H}^{(y)}$, and $\mathcal{H}^{(z)}$, and indicated in the appropriate intervals in Fig. 2. The superscript notation is a shorthand for the transformations induced by the pulses: a 120° pulse along the (111) direction,

$$P_{111} = \exp[-(2i\pi/3\sqrt{3})(I_x + I_y + I_z)],$$

induces the transformation $I_x \rightarrow I_y$, $I_y \rightarrow I_z$, $I_z \rightarrow I_x$ on every spin operator in \mathcal{H} . The original Hamiltonian of Eqs. (28) and (29), written with component operators I_x to denote space quantization along the \mathbf{H}_0 , is abbreviated $\mathcal{H}^{(z)}$ to indicate that fact. The transformed versions $\tilde{\mathcal{H}}_k$ are correspondingly labeled $\mathcal{H}^{(x)}$ or $\mathcal{H}^{(y)}$. We shall make use of this notation extensively.

From an examination of Fig. 2 it is clear that $\tilde{\mathcal{H}}_D$ vanishes, inasmuch as $I_{xi}I_{xj} + I_{yi}I_{yj} + I_{zi}I_{zj} = \mathbf{I}_i \cdot \mathbf{I}_j$. The chemical shifts do not:

$$\begin{aligned} \bar{\mathcal{H}}_C &= \frac{1}{3} \{ \mathcal{H}^{(x)} + \mathcal{H}^{(y)} + \mathcal{H}^{(z)} \} \\ &= \frac{1}{3} \omega_0 \sum_i \sigma_{zzi} (I_{xi} + I_{yi} + I_{zi}). \end{aligned} \quad (45)$$

Equation (45) is more easily interpreted if transformed to a tilted frame with its z axis along the (111) direction. In this frame

$$\bar{\mathcal{H}}_C' = 3^{-1/2} \omega_0 \sum_i \sigma_{zzi} I_{zi}. \quad (46)$$

This corresponds to an apparent precession of the spins about the (111) direction of the rotating frame, each at a rate corresponding to its chemical shift field reduced by the factor $\sqrt{3}$.

So far everything is the same as in the simpler three-pulse experiment of Subsec. 3. An important difference appears, however, when we calculate the first-order correction to $\bar{\mathcal{H}}$. This is easily done from the definition (25) with reference to Fig. 3, which shows the domain of integration. The result, for the dipolar effects alone, is

$$\begin{aligned} \bar{\mathcal{H}}_D^{(1)} &= (-it_c/36) [(\mathcal{H}_D^{(x)} + \mathcal{H}_D^{(y)}), \mathcal{H}_D^{(z)}] \\ &= (-it_c/12) [\bar{\mathcal{H}}_D, \mathcal{H}_D^{(z)}] = 0. \end{aligned} \quad (47)$$

Thus, for nonzero pulse spacing, this experiment is

expected to be much better than the cw or pulsed LG experiments at getting rid of dipolar broadening.

If chemical shifts are present, $\bar{\mathcal{H}}^{(1)}$ retains a coupling term between \mathcal{H}_D and \mathcal{H}_C :

$$\bar{\mathcal{H}}^{(1)} = -\frac{1}{12} (it_c) [\bar{\mathcal{H}}_C, \mathcal{H}_C^{(z)}]. \quad (48)$$

For the usual case in which $\|\mathcal{H}_C\| \ll \|\mathcal{H}_D\|$ this correction will be relatively small. To eliminate it from importance in comparison to $\bar{\mathcal{H}}$, one need only make τ sufficiently small compared to some precession period $T_2\sigma$ in the chemical shift field, not to the precession period T_2 in the dipolar local field.

The second-order average Hamiltonian $\bar{\mathcal{H}}^{(2)}$ does not vanish. Its dominant dipolar part is

$$\bar{\mathcal{H}}_D^{(2)} = (t_c^2/1296) [(\mathcal{H}_D^{(x)} - \mathcal{H}_D^{(y)}), [\mathcal{H}_D^{(x)}, \mathcal{H}_D^{(y)}]]. \quad (49)$$

Whether (49) or (48) will dominate the observed decay depends, of course, upon the relative magnitudes of the dipolar and chemical shift fields and upon the pulse spacing which can be achieved.

Another contrast between the present experiment and the preceding ones lies in the fact the net precession angle of a spin after one full cycle is zero, even if the pulses are not perfect 120° pulses, so long as they are all alike in intensity. Thus the first type of effect of H_1 inhomogeneity (cf. Subsec. 1)—the spreading of isochromats—is cancelled. The situation can be likened to the contrast between the Carr-Purcell experiment²⁰ and its modification by Meiboom and Gill.²⁶ The second type of effect—failure to maintain the magic-angle condition throughout the sample—can be corrected as outlined in Subsec. 2.

When the pulses have finite width, the situation between the pulses is still the same as if they had been infinitely sharp, and $\bar{\mathcal{H}}$ is the same as given in (45). During the pulses we have exactly the LG situation, with the same type of average Hamiltonian. An experiment with finite pulses thus has no new properties. The cancellation of $\bar{\mathcal{H}}_D^{(1)}$ and the avoidance of dephasing of the isochromats can in fact be achieved in a cw experiment of the LG type, if the direction of \mathbf{H}_e is reversed at intervals of $n2\pi/\omega_e$. This can be accomplished either by reversing \mathbf{H}_e directly, as outlined above, or by reversing the phase

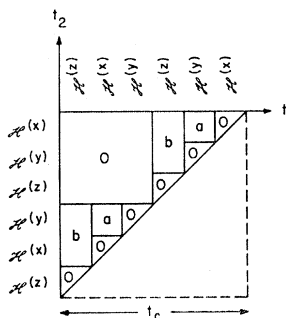


FIG. 3. Domain of integration for evaluation of $\bar{\mathcal{H}}^{(1)}$ under the conditions of Fig. 2. Contributions from regions labeled 0 vanish identically. Contributions from the two regions labeled a cancel, as do those from the two regions labeled b [cf. Eq. (47)].

²⁶ S. Meiboom and D. Gill, Rev. Sci. Instr. 29, 688 (1958).

of the rf field H_1 and simultaneously changing the spectrometer frequency from between two values which lie below and above resonance by $\pm\Delta\omega = \pm\gamma\Delta H_0$. The two frequencies $\pm\Delta\omega$ could be conveniently obtained as the two possible selectable single sidebands of a balanced-mixer suppressed carrier modulator.

MULTIPLE 90° rf PULSES

We consider here a type of experiment which has the convenience that only pure rf pulses are required to eliminate dipolar effects. Out of the many possibilities, we restrict ourselves to the special situation in which (i) all pulses are 90° pulses; (ii) each is applied along the $\pm x$ or $\pm y$ axis of the rotating frame, i.e., a maximum of four carrier phases, each differing by 90° from its neighbors, need be provided in the laboratory; (iii) there are 2^n pulses in a full cycle, n being an integer; (iv) each 2^n -pulse cycle contains 2^{n-1} 2-pulse subcycles.

The reason for restriction (iv) is an experimental one. For every pulsed-NMR spectrometer there exists some minimum pulse spacing t_s for which it is possible to detect the free-induction signal between the pulses. The minimum is set by a variety of technical limitations, including rise and fall times and widths of the pulses and recovery time of the sensing system. The more pulses are contained in a cycle, the longer the cycle time must therefore be. We have seen that the criterion for unimportance of the higher-order average Hamiltonians is that t_c/T_2 be small. Therefore it would appear that there is little to be gained by using long and elaborate cycles, however desirable they might appear from the viewpoint of their properties for fixed t_c . If, however, the full cycle possesses subcycles having "useful" properties, it again becomes advantageous to work with long and sophisticated cycles. To see this, consider a simple case in which a cycle, having the properties

$$\bar{\mathcal{C}} = \bar{\mathcal{C}}^{(1)} = 0,$$

$$\bar{\mathcal{C}}^{(2)} \sim t_c^{-1} \int_0^{t_c} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \tilde{\mathcal{C}}(t_3) \tilde{\mathcal{C}}(t_2) \tilde{\mathcal{C}}(t_1), \quad (50)$$

and made up of n subcycles of equal duration $t_s = t_c/n$, such that over a *subcycle*

$$\bar{\mathcal{C}}_s = 0, \quad \bar{\mathcal{C}}_s^{(1)} \neq 0. \quad (51)$$

The domain of integration of $\bar{\mathcal{C}}^{(2)}$ is shown in Fig. 4 for $n=3$: its volume is $\frac{1}{6}t_c^3$. Without the existence of the subcycles having the property (51), we would estimate the decay time $T_2^{(2)}$ of the magnetization due to $\bar{\mathcal{C}}^{(2)}$ to be of the order of

$$T_2^{(2)} \sim T_2 \times 6(T_2/t_c)^2. \quad (52)$$

Now the integration volume of Fig. 4 is made up of cubes, prisms of types a and b, and tetrahedra

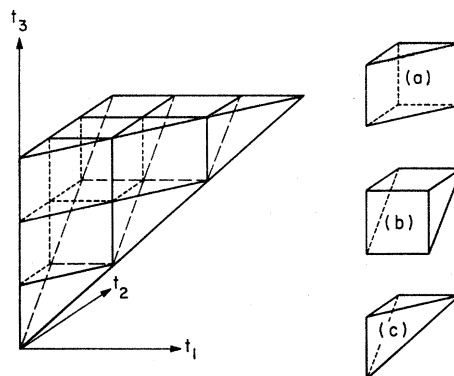


FIG. 4. Domain of integration of $\bar{\mathcal{C}}^{(2)}$ in an illustrative cyclic experiment containing three subcycles of equal length (see text).

of type c. The triple integrals (50) over all cubes and prisms contain at least one factor of the type

$$t_s^{-1} \int_{vt_s}^{(v+1)t_s} \tilde{\mathcal{C}}(t) dt = \bar{\mathcal{C}}_s = 0, \quad (53)$$

leaving a nontrivial integration volume of

$$nt_s^3/6 = t_c^3/6n^2,$$

leading to a revised estimate of the decay time $T_{2s}^{(2)}$ of

$$T_{2s}^{(2)} \sim T_2 \times 6(T_2/t_s)^2 = n^2 T_2^{(2)}, \quad (54)$$

which is longer than the estimate of (52). It is likewise longer than the decay time

$$T_2^{(1)} \sim T_2 \times 2(T_2/t_s), \quad (55)$$

which would have been obtained by repetition of the subcycle alone, as long as $t_s < T_2$.

One can say roughly that, even though the subcycle does not itself give optimum narrowing, it does achieve a partial narrowing, or increased decay time $T_2^{(1)}$. The criterion for efficacy of the full cycle then becomes $t_c < T_2^{(1)}$ rather than $t_c < T_2$. One can thus envision long cycles which build up their effects stepwise through a cascade of sub-subcycles, subcycles, etc.

1. Two-Pulse Cycles

It is easy to see (cf. Fig. 5) that there is no two-pulse cycle which assures $\bar{\mathcal{C}}_D = 0$. For an arbitrary pulse, the form of $P_1^{-1}\bar{\mathcal{C}}_D P_1$ can be written down explicitly. It is then clear that no choice of the direction \mathbf{n}_1 or rotation angle θ_1 of the pulse [cf. Eq. (1)] will make $\bar{\mathcal{C}}_D^{(2)}$ and $P_1^{-1}\bar{\mathcal{C}}_D^{(2)}P_1$ cancel.

The best that can be done is to use a train of equally spaced 90° pulses, alternately along the $+x$ and $-x$ directions of the rotating frame⁷ (WH experiment). Then $[\bar{\mathcal{C}}_D, I_x] = 0$. If the x component of magnetization is observed, the leading (second-moment) term a_2 in the decay

$$G_e(t) = 1 + a_2 t^2 + a_4 t^4 + \dots$$

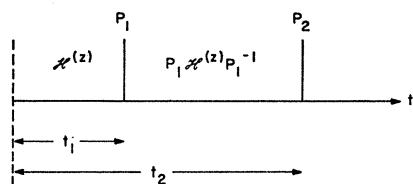


FIG. 5. General two-pulse cycle.

does not contain any dipolar contribution. If there are chemical shifts, the decay time is lengthened until the beat corresponding to the largest shift difference becomes apparent, but essentially no further.^{7,8,25}

2. Four-Pulse Cycles

An experiment of this type (WHH) has recently been reported,⁹ using 90° pulses in the $-x$, $+x$, y , $-y$ directions successively (cf. Fig. 6). Note that the $-x$, $+x$ and y , $-y$ pulse pairs constitute subcycles of the type discussed above. From (24) we obtain

$$\bar{\mathcal{C}} = \bar{\mathcal{C}}_D + \bar{\mathcal{C}}_C,$$

$$\bar{\mathcal{C}}_D = t_c^{-1} \{ \mathcal{C}_D^{(z)}(t_1 + t_3) + \mathcal{C}_D^{(x)} t_2 + \mathcal{C}_D^{(y)} t_4 \}, \quad (56)$$

which vanishes if

$$t_1 + t_3 = t_2 = t_4 = \frac{1}{3} t_c = t_s. \quad (57)$$

Under the last condition,

$$\bar{\mathcal{C}}_C = \frac{1}{3} \omega_0 \sum_k \sigma_{zzk} (I_{zk} + I_{yk} + I_{xk}), \quad (58)$$

which is the same result obtained in the LG experiment and its pulsed modifications. The effective shifts are scaled down by a factor of $\sqrt{3}$.

Condition (57) still leaves some latitude in the pulse spacing. However, we readily deduce that

$$\bar{\mathcal{C}}^{(1)} = -\frac{1}{6} i \{ 3t_s [\mathcal{C}^{(x)}, \bar{\mathcal{C}}_C] + [\mathcal{C}^{(y)}, \mathcal{C}^{(z)}] (2t_1 - t_s) \}. \quad (59)$$

The last commutator, and with it all terms quadratic in \mathcal{C}_D , drops out if $t_1 = t_3 = \frac{1}{2} t_s$. It was this timing that was employed in the WHH experiment.⁹ What remains of (59) is precisely the same as the expression obtained for $\bar{\mathcal{C}}^{(1)}$ in the six-pulse magic angle experiment (Subsec. 4 of the preceding section). Moreover,

$$\bar{\mathcal{C}}_D^{(2)} = (t_s^2/72) [(\mathcal{C}_D^{(x)} - \mathcal{C}_D^{(y)}), [\mathcal{C}_D^{(y)}, \mathcal{C}_D^{(x)}]], \quad (60)$$

which is—apart from a factor $\frac{1}{2}$ and a change of sign—also the same as in the magic-angle experiment. The discussion given there thus applies to the present case.

An important difference appears, however, when we consider the possibility of finite pulse width t_w . Consider, for example, a 90° pulse in the $-x$ direction, having

$$\mathcal{C}_1(t) = \gamma H_1 I_x, \quad 0 \leq t < t_w. \quad (61)$$

The calculation of $\bar{\mathcal{C}}_D(t)$ during the pulse is easily done from (15). The result is conveniently expressed as a correction $C_D(-x)$ which represents the difference between the average of the true $\bar{\mathcal{C}}_D$ during the pulse and the average that would have been obtained over the time t_w if the pulse had been a δ -function at $t=0$:

$$C_D(-x) = \sum_{i < j} \sum b_{ij} \left\{ \frac{3}{2} (I_{yi} I_{yj} - I_{zi} I_{zj}) + (3/\pi) (I_{zi} I_{yj} + I_{yi} I_{zj}) \right\}. \quad (62)$$

The corresponding correction terms for the other pulses ($+x$, $+y$, $-y$) used in the cycle are obtained from (62) by replacing all the I_y operators by $-I_y$, $+I_x$, $-I_x$, respectively. In calculating $\bar{\mathcal{C}}$ for the whole cycle we must recall, however, that the Hamiltonian, and so also the correction terms, must be further transformed by all pulse operators preceding them in the cycle [cf. Eq. (4)]. Thus

$$\begin{aligned} \bar{\mathcal{C}}_D = (t_w/t_c) \{ & C_D(-x) \\ & + P_1^{-1} C_D(+x) P_1 + P_1^{-1} P_2^{-1} C_D(+y) P_2 P_1 \\ & + P_1^{-1} P_2^{-1} P_3^{-1} C_D(-y) P_3 P_2 P_1 \}. \end{aligned} \quad (63)$$

Performing the indicated transformations, and remembering the subcycle property $P_2 P_1 = 1$, we have

$$\begin{aligned} \bar{\mathcal{C}}_D = (t_w/t_c) (6/\pi) \sum_{i < j} \sum b_{ij} \\ \times [I_{zi} (I_{xj} + I_{yj}) + I_{zj} (I_{xi} + I_{yi})]. \end{aligned} \quad (64)$$

A similar calculation for the chemical shifts gives

$$\begin{aligned} \bar{\mathcal{C}}_C = \frac{1}{3} \omega_0 \sum_i \sigma_{zzi} \{ [1 + (3t_w/t_c) (4/\pi - 1)] \\ \times (I_{xi} + I_{yi} + I_{zi}) + (3t_w/t_c) (4/\pi - 1) I_{zi} \}. \end{aligned} \quad (65)$$

The result of (65) represents harmless changes of the scaling factor away from its ideal value of $\sqrt{3}$, and of the axis of the chemical shift precession away from its ideal (111) direction. However, the damping represented by (64) would be very serious were it not for the fact that a correction mechanism exists consisting of an adjustment of the pulses away from the "ideal" 90° condition. Suppose that we have

$$\gamma H_1 t_w = \alpha = \frac{1}{2} \pi + \epsilon, \quad \epsilon \ll 1.$$

The calculation of $\bar{\mathcal{C}}_D$ is entirely straightforward

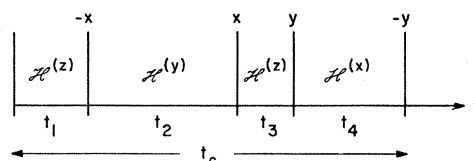


FIG. 6. General four-pulse cycle containing two two-pulse subcycles, not necessarily of equal length. All pulses are 90° pulses.

and gives

$$\begin{aligned} \bar{\mathcal{H}}_D &= \mathcal{H}_D^{(2)} \cos^2 \alpha + \frac{1}{2} \sin 2\alpha \\ &\times \sum_{i < j} \sum b_{ij} \{ I_{zi}(I_{yj} + I_{xj}) + I_{zj}(I_{yi} + I_{xi}) \} \\ &\approx \mathcal{H}_D^{(2)} \epsilon^2 + \epsilon \sum_{i < j} \sum b_{ij} \\ &\times \{ I_{zi}(I_{xj} + I_{yj}) + I_{zj}(I_{xi} + I_{yi}) \}. \end{aligned} \quad (66)$$

By proper choice of ϵ ,

$$\epsilon = -(6/\pi) t_w/t_c, \quad (67)$$

the term in (66) linear in ϵ can be made to cancel the effects of finite pulse width. For our experiments⁹ with $t_w \sim 1 \mu\text{sec}$, $t_c = 36 \mu\text{sec}$, this corresponded to use of about an 87° pulse. The adjustment is quite critical.

If the rf field H_1 is inhomogeneous, the necessary adjustment cannot be made for every part of the sample. The result is a superposition of different decays for different parts of the sample. Those parts for which the correction is not made decay relatively rapidly, leaving progressively slower decays for those parts for which \mathcal{H}_D lies progressively closer to zero. When the complete decay is Fourier transformed, the result is a line shape with a sharp peak and broad skirts, reminiscent of an exchange-narrowed line shape. This behavior was evident in our original experiments.⁹

The above considerations put a great premium on homogeneity of H_1 —a premium which runs counter to the desirability of high filling factor and large rf fields. One wonders whether there is not some more direct way of removing the effects embodied in (64) and (66) without resorting to trickery to make them cancel one another. The fact that the operators I_x and I_y enter linearly in (64) and (66) in fact suggests a way of accomplishing this aim by use of an eight-pulse cycle composed of two complementary WHH cycles.

3. Eight-Pulse Cycles

Consider the eight-pulse cycles of Fig. 7 (the HW cycles), each made up of a four-pulse subcycle followed by a similar one in which all rf carrier phases have been reversed. As before each four-pulse subcycle consists in turn of two two-pulse subcycles. Since, for each four-pulse subcycle, $\bar{\mathcal{H}}_D = \mathcal{H}_D^{(1)} = 0$, the same is true of the eight-pulse cycle as a whole.

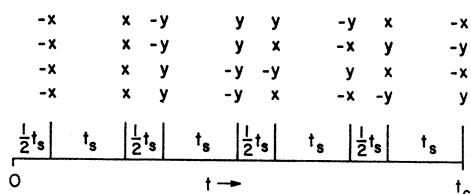


FIG. 7. The HW cycles. The labels $\pm x$, $\pm y$ above the (90°) pulses refer to their directions in the rotating frame. Four independent ways of choosing the sequence are indicated.

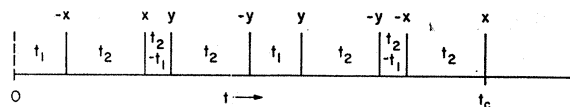


FIG. 8. An eight-pulse cycle having three different spacings. The version with $t_1/t_2 = \frac{2}{3}$, suggested by Evans (see Ref. 27), eliminates the second-order average dipolar coupling.

Similarly, since $\bar{\mathcal{H}}_D^{(2)}$ has the same value for each four-pulse subcycle, Eq. (60) also gives the correct result for the full cycle.

The average shift Hamiltonian is somewhat changed, however. One easily finds

$$\begin{aligned} \bar{\mathcal{H}}_C &= \frac{1}{6} (\mathcal{H}_C^{(x)} - \mathcal{H}_C^{(y)} + \mathcal{H}_C^{(y)} - \mathcal{H}_C^{(x)} + 2\mathcal{H}_C^{(z)}) \\ &= \frac{1}{3} \mathcal{H}_C^{(z)} = \frac{1}{3} \omega_0 \sum_i \sigma_{zzi} I_{zi}, \end{aligned} \quad (68)$$

which is reduced from that in the WHH experiment by a further factor of $\sqrt{3}$. Offsetting this disadvantage is a cancellation of effects of finite pulse width and inhomogeneity of H_1 , mentioned above in Subsec. 2. The only remaining inhomogeneity term is the one quadratic in ϵ . One expects

$$\langle \bar{\mathcal{H}}_C^{(z)} \rangle_{\text{av}} = \langle \epsilon^2 \rangle_{\text{av}} \mathcal{H}_C^{(z)}. \quad (69)$$

We now turn to a different eight-pulse cycle, shown in Fig. 8, which contains the same two-pulse subcycles as before. The effects of finite t_w and H_1 inhomogeneity do *not* disappear, but

$$\bar{\mathcal{H}}_D^{(2)} \propto [(\mathcal{H}_D^{(x)} - \mathcal{H}_D^{(y)}), [\mathcal{H}_D^{(y)}, \mathcal{H}_D^{(x)}]] [3(t_1/t) - 2], \quad (70)$$

which vanishes if $t_1/t = \frac{2}{3}$. This version of the cycle has been suggested by Evans.²⁷ For it $\bar{\mathcal{H}}_C$ takes the same form as for the WHH cycle, i.e., the reduction factor for the shifts is restored to $\sqrt{3}$.

4. Sixteen-Pulse Cycles

Again we are prompted to seek an expanded cycle which combines the advantages of the HW cycles (cancellation of t_w and H_1 effects) with those of Evan's cycle (vanishing of $\bar{\mathcal{H}}_D^{(2)}$). It will not surprise the reader at this point to learn that this can be done by means of a 16-pulse cycle (cf. Fig. 9). The properties of this cycle are easily derived from the properties of the two-, four-, and eight-pulse subcycles which it contains, and we shall simply summarize the results:

(i) $\bar{\mathcal{H}}_D = 0$ over every four-pulse subcycle, (ii) $\bar{\mathcal{H}}_D^{(1)} = \bar{\mathcal{H}}_D^{(2)} = 0$ over every eight-pulse subcycle (note that $\bar{\mathcal{H}}_D^{(1)} \neq 0$ over the four-pulse subcycle, so that the present situation may in fact be a step backward!), (iii) effects of finite t_w and H_1 inhomogeneity are cancelled, but only over the full 16-pulse cycle, (iv) $\bar{\mathcal{H}}_C = \frac{1}{3} \mathcal{H}_C$ as in the HW cycles.

²⁷ W. A. B. Evans (private communication).

PULSE EXPERIMENTS IN THE PRESENCE OF MOTION OF THE SPINS

1. WHH Experiment with Sample Spinning

We have mentioned several times the usefulness of subcycles which by themselves accomplish partial removal of dipolar broadening. There is no need for the full cycle and its subcycles to belong to the same class of experiments: One could, for example, superpose a relatively slow Carr-Purcell train of 180° pulses on any of the experiments mentioned above, and thereby remove chemical shifts and inhomogeneity effects. Perhaps more interestingly, as mentioned earlier, the anisotropy $\Delta\sigma$ of the chemical shift could be removed by rotating the sample about the magic-angle direction while at the same time performing, say, a WHH experiment to remove the main part of the dipolar broadening. We proceed to analyze that experiment, both for its intrinsic interest and for the insight it provides to the situation where there is *random* motion of the spins.

Denote the duration of the WHH cycle by t_c and the period of rotation by $t_r = 2\pi/\omega_r$. For the sake of simplicity we shall assume the longer of these times to be an integral multiple of the shorter, although this is not really essential. Regardless of the relative magnitudes of t_r and t_c , $\mathcal{H}_1(t)$ is always periodic *modulo* t_c , and the nuclear signal can be conveniently detected at intervals of t_c . $\mathcal{H}(t)$, however, is periodic only over the longer of the two times, which becomes the full cycle time. $\tilde{\mathcal{H}}$ can be found by combining Eq. (33) and the form of $\tilde{\mathcal{H}}$ for the WHH experiment as indicated in Fig. 6. Restricting ourselves to purely

dipolar interactions and using the abbreviations

$$Z_{ij} = \mathbf{I}_i \cdot \mathbf{I}_j - 3I_{zi}I_{zj}, \text{ etc.}, \quad (71)$$

$$X_{ij} + Y_{ij} + Z_{ij} = 0, \quad (72)$$

we obtain

$$\tilde{\mathcal{H}}_D(t) = \sum_{i < j} \sum b_{ij}(t) Q_{ij}(t), \quad (73)$$

with

$$\begin{aligned} Q_{ij} &= Z_{ij}, t_k \leq t < t_k + \tau \\ &= Y_{ij}, t_k + \tau \leq t < t_k + 3\tau \\ &= Z_{ij}, t_k + 3\tau \leq t < t_k + 4\tau \\ &= X_{ij}, t_k + 4\tau \leq t < t_k + 6\tau. \end{aligned}$$

Here $\tau = \frac{1}{6}t_c$ and t_k is the starting time of the k th WHH cycle. $b_{ij}(t)$ is given by Eq. (33).

We wish now to examine $\tilde{\mathcal{H}}_D(t)$ averaged over both t_c and t_r . The average over the longer time will give the average Hamiltonian $\bar{\mathcal{H}}_D$. Where necessary we shall also examine the first correction $\bar{\mathcal{H}}_D^{(1)}$. We distinguish three cases: (i) $t_r = nt_c$, $n > 1$; (ii) $t_r = t_c$; (iii) $t_c = mt_r$, $m > 1$. Notice that $b_{ij}(t)$ as given by (33) consists of two linearly independent terms, one associated with $\cos(\beta_{ij} + \omega_r t)$ and the other with $\cos(2\beta_{ij} + 2\omega_r t)$. To keep the algebra as compact as possible we shall drop the second of these. Whatever general conclusions we can reach about the behavior of the system for a specific value of t_c/t_r will also hold for $2t_c/t_r$.

a. Slow Spinning and Rapid Pulsing: $t_r = nt_c$

The average of $\tilde{\mathcal{H}}(t)$ over the subcycle time t_c depends on t_k and will be denoted by $\bar{\mathcal{H}}(k)$. From Eqs. (72) and (73),

$$\begin{aligned} \bar{\mathcal{H}}_D(k) &= t_c^{-1} \sum_{i < j} \left[Y_{ij} \left(\int_{t_k + \tau}^{t_k + 3\tau} b_{ij}(t) dt - \int_{t_k}^{t_k + \tau} b_{ij}(t) dt - \int_{t_k + 3\tau}^{t_k + 4\tau} b_{ij}(t) dt \right) \right. \\ &\quad \left. + X_{ij} \left(\int_{t_k + 4\tau}^{t_k + 6\tau} b_{ij}(t) dt - \int_{t_k}^{t_k + \tau} b_{ij}(t) dt - \int_{t_k + 3\tau}^{t_k + 4\tau} b_{ij}(t) dt \right) \right]. \quad (74) \end{aligned}$$

The integrals in (74) are of the type

$$\begin{aligned} \frac{\gamma^2 \hbar}{2^{1/2} r_{ij}^3 t_c} \sin 2\alpha_{ij} \int_{t_k + \mu\tau}^{t_k + \nu\tau} \cos(\beta_{ij} + \omega_r t) dt \\ = a_{ij} (n/2\pi) \sin[\tfrac{1}{2}(\nu - \mu)\phi] \{ \cos\eta_{ijk} \cos[\tfrac{1}{2}(\mu + \nu)\phi] - \sin\eta_{ijk} \sin[\tfrac{1}{2}(\mu + \nu)\phi] \}, \quad (75) \end{aligned}$$

with

$$\begin{aligned} \eta_{ijk} &= \beta_{ij} + \omega_r t_k, \\ \phi &= \omega_r \tau = \pi/3n, \\ a_{ij} &= 2^{1/2} \gamma^2 \hbar r_{ij}^{-3} \sin 2\alpha_{ij}. \end{aligned}$$

The only quantity characteristic of the WHH cycle is $\phi = \pi/3n$. For $n \gg 1$ the largest contribution to

$\bar{\mathcal{H}}_D(k)$ arises from the X_{ij} terms:

$$\bar{\mathcal{H}}_D(k) = \frac{\pi}{3n} \sum_{i < j} a_{ij} \sin\eta_{ijk} X_{ij} + O(1/n^2). \quad (76)$$

Thus $\bar{\mathcal{H}}_D(k)$ does not vanish as in the pure WHH experiment, but is smaller than \mathcal{H}_D itself by a factor of the order of n . Over the full cycle t_r the average Hamiltonian does vanish. This is a consequence of

the fact [cf. Eq. (75)] that

$$\sum_{k=0}^{n-1} \cos \eta_{ijk} = \sum_{k=0}^{n-1} \sin \eta_{ijk} = 0, \quad n > 1. \quad (77)$$

According to Eq. (76) the decay of magnetization is slowed by the pulsing alone, and the criterion for full removal of dipolar broadening becomes

$$t_r \ll nT_2 \quad (78a)$$

rather than $t_r \ll T_2$ as in the pure sample spinning experiment. The chemical shifts, while scaled down by the customary factor of $\sqrt{3}$, are not otherwise affected by the pulse cycle. To remove their anisotropy $\Delta\sigma$ (whose range of values may be characterized by a decay time T_{2c}), one must choose

$$t_r \ll T_{2c}. \quad (78b)$$

Conditions (78) may not be difficult to achieve in samples whose linewidth is dominated by dipolar interactions.

Since satisfaction of (78) sends $\bar{\mathcal{F}}_D$ to zero, we must investigate $\bar{\mathcal{F}}_D^{(1)}$ to learn about the limiting decay time of the nuclear signal. A conclusion as to its order of magnitude can be reached with the aid of Fig. 10. The value of

$$\bar{\mathcal{F}}_D^{(1)} = \frac{-i}{2t_r} \int_0^{t_r} dt_2 \int_0^{t_2} dt_1 [\tilde{\mathcal{F}}_D(t_2), \tilde{\mathcal{F}}_D(t_1)]$$

is thought of as made up of contributions from the various zones shown in the figure. The contribution from each square of side $t_c = t_r/n$ does not vanish, since it depends on t_k . In order of magnitude it is

$$\left| \iint [\tilde{\mathcal{F}}_D(t_2), \tilde{\mathcal{F}}_D(t_1)] dt_2 dt_1 \right| \approx t_c^2 \|\tilde{\mathcal{F}}_D(k)\|^2 \approx t_c^2/n^2 \|\mathcal{F}_D\|^2.$$

The nontrivial area of integration is $\frac{1}{4}t_r^2$, so we have

$$\|\bar{\mathcal{F}}_D^{(1)}\| \sim (1/2t_r) \frac{1}{4}t_r^2 (1/n^2) \|\mathcal{F}_D\|^2 = \|\mathcal{F}_D\|^2 t_c / 8n.$$

Setting $\|\mathcal{F}_D\| = T_2^{-1}$, this leads to a decay time of the order of

$$T_2^{(1,n)} \sim T_2 (8nT_2/t_c),$$

which is to be compared with the decay time for the pure WHH experiment

$$T_2^{(2)} \sim T_2 (T_2/t_c)^2.$$

We conclude that spinning the sample does not de-

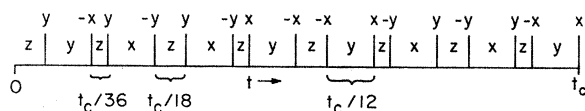


FIG. 9. Sixteen-pulse cycle of 90° pulses, composed of two eight-pulse subcycles of the type of Fig. 8 with all rf phases reversed in the second subcycle.

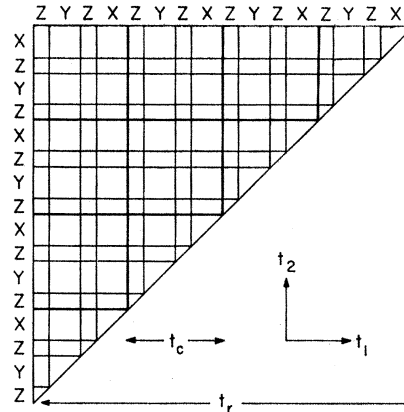


FIG. 10. Domain of integration of $\bar{\mathcal{F}}_D^{(1)}$ for $n=4$ in an experiment for which the sample is rotated once about the magic direction for each four cycles of a four-pulse experiment. The spin part of $\tilde{\mathcal{F}}_D(t)$ is indicated for each interval in the notation of Eq. (73). The spatial part of \mathcal{F}_D changes continuously.

grade the WHH experiment as long as, roughly speaking,

$$n > T_2/t_c; \quad t_r > T_2. \quad (78c)$$

That is, the experiment is best suited to a situation in which $\Delta\sigma$ is small enough compared to the dipolar line width that it can be removed by a relatively slow rotation, whose period contains many WHH cycles.

$$b. \quad t_c = t_r$$

For this special situation $\bar{\mathcal{F}}_D$ does not vanish. From Eqs. (74) and (75),

$$\bar{\mathcal{F}}_D = (1/4\pi) \sum_{i < j} (X_{ij} - Y_{ij}) a_{ij} \times (\sqrt{3} \cos \beta_{ij} + 3 \sin \beta_{ij}). \quad (79)$$

$\bar{\mathcal{F}}_D$ is in fact comparable in size to \mathcal{F}_D itself, so that combining the two experiments results in largely cancelling the benefits of each. That this should be so is not surprising: Either experiment can be regarded as producing a central narrowed spectrum (with which we have been concerned) and a set of sidebands. In the combined experiment the low-order sidebands arising from pulsing coincide and mix with those arising from sample rotation, resulting in regeneration of a secular contribution to the effective Hamiltonian and thus to additional broadening of the central component. We shall return to this point in a later discussion of random molecular motions.

c. Rapid Spinning and Slow Pulsing: $t_c = mt_r$

We restrict our attention to $m \geq 3$, for which the spins remain undisturbed by pulses for a sufficiently long time that $\bar{\mathcal{F}}_D = 0$ from the spinning alone. $\mathcal{F}_D^{(1)}$, which is given in Eq. (37) for the pure spinning experiment, is, however, modified by the pulses. Gen-

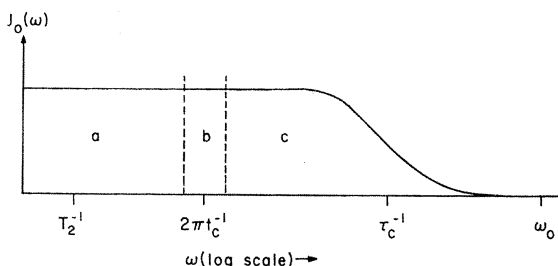


FIG. 11. Schematic power spectrum of fluctuating dipolar interactions in a solid with correlation time τ_c . The case for partial narrowing, $\tau_c < T_{2r} < T_2$ is shown, where T_{2r} is the transverse relaxation time of the rigid solid. The numbered regions correspond roughly to the three cases discussed in the text.

erizing (37) we obtain for $m=3$ (and much the same for larger m)

$$\begin{aligned} \bar{\mathcal{H}}_{\mathcal{D}}^{(1)} &= -\frac{1}{6}i \sum_{i < j} \sum_{i' < j'} \{ [Z_{ij}, Z_{i'j'}] \\ &\quad + [X_{ij}, X_{i'j'}] + [Y_{ij}, Y_{i'j'}] \} \\ &\quad \times t_r^{-1} \int_0^{t_r} dt_2 \int_0^{t_2} dt_1 b_{ij}(t_2) b_{i'j'}(t_1) \\ &= \frac{1}{2}i \sum_{i < j} \sum_{i' < j'} [\mathbf{I}_i \cdot \mathbf{I}_j, \mathbf{I}_{i'} \cdot \mathbf{I}_{j'}] t_r^{-1} \\ &\quad \times \int_0^{t_r} dt_2 \int_0^{t_2} dt_1 b_{ij}(t_2) b_{i'j'}(t_1). \quad (80) \end{aligned}$$

Note that $\bar{\mathcal{H}}_{\mathcal{D}}^{(1)}$, while it does not vanish, commutes with all components of \mathbf{I} and therefore does not lead to any decay. The situation is reminiscent of the experiment of Ostroff and Waugh^{5,6} described earlier. Complications will of course occur if chemical shifts are included in $\bar{\mathcal{H}}_{\mathcal{D}}^{(1)}$, but the resulting effects on the decay of magnetization are of a sufficiently high order that good resolution of the chemical shifts should still be possible.

2. Effects of Random Molecular Motion

The results of the preceding section, where a "monochromatic" molecular motion was superimposed on a pulse experiment, can be used as a guide to the phenomena which can be expected when a random motion having a wide frequency spectrum occurs. We emphasize strongly that the parallel is a crude one, fraught with dangerous analogies, and that the following discussion is to be regarded as merely suggestive. We hope to provide a proper discussion in a future communication.

Figure 11 shows schematically the familiar power spectrum $J_0(\omega)$ of the truncated dipole-dipole Hamiltonian which fluctuates with a characteristic cor-

relation time τ_c . We imagine a situation in which the line is partially narrowed from its rigid-lattice width T_{2r}^{-1} to a value T_2^{-1} by a motion which is relatively rapid ($\tau_c^{-1} > T_{2r}^{-1}$) but the situation of extreme narrowing has not been reached ($\tau_c^{-1} \ll \omega_0$). The value of T_2 is determined by the spectral intensity at zero frequency $J_0(0)$, or, more precisely²⁸ by the integral of $J_0(\omega)$ over a frequency range of the order of T_2^{-1} about $\omega=0$.

Imagine that a multiple-pulse experiment (e.g., a WHH experiment) is performed with cycle length $t_c < T_2$. We divide the frequency scale into three regions, lettered a-c in Fig. 11, and apply the arguments of the preceding section to them as though $J_0(\omega)$ could be regarded as a superposition of independent δ functions, each corresponding to the spinning of the sample at the corresponding frequency.

The part of $J_0(\omega)$ lying in region a, represents dipolar interactions which are effectively static over a time t_c , and are effectively averaged out by the pulse cycle as discussed under case a of Subsec. 1. Note that for this to be true it is required only that $t_c^{-1} \gg T_{2r}^{-1}$, not $t_c^{-1} \gg T_2^{-1}$, since it is only the part of $J_0(\omega)$ lying between 0 and T_2^{-1} which was originally static in the sense of contributing to the linewidth.

Region b, which occupies a width of the order of T_2^{-1} about $\omega = 2\pi t_c^{-1}$, represents motions which defeat the line-narrowing tendencies of the pulse experiment, as discussed under case b above. One can think in terms of part of the power spectrum, in the neighborhood of $\omega = 2\pi t_c^{-1}$, being shifted downward in frequency to the neighborhood of $\omega = 0$, where it contributes to the linewidth, as well as upward in frequency to $\omega = 4\pi t_c^{-1}$. However, an examination of Eq. (79) shows that, as a result of the pulse transformations, the spin operator which takes part in this process is not the ordinary truncated dipolar operator Z_{ij} , but rather the operator $X_{ij} - Y_{ij}$, which can be reexpressed from its definition (71) as

$$X_{ij} - Y_{ij} = -\frac{3}{2}(I_{+i}I_{+j} + I_{-i}I_{-j}). \quad (81)$$

This operator is familiar in the theory of spin-lattice relaxation in the rotating frame at exact resonance.²⁴ One is tempted to say that a Fourier component of $\bar{\mathcal{H}}_{\mathcal{D}}^{(2)}$ in the neighborhood of $2\pi t_c^{-1}$ has much the same effect on the pulse experiment as a secular (zero-frequency) component of $\bar{\mathcal{H}}_{\mathcal{D}}^{(2)} - \bar{\mathcal{H}}_{\mathcal{D}}^{(2)}$, $J_2(0)$, in a cw experiment. Because the pulsing generates an upper as well as a lower sideband, one can think as well in terms of the component $J_2(4\pi t_c^{-1})$ at twice the frequency of the pulse cycle. The decay time is therefore expected to be roughly describable as a rotating-frame spin-lattice relaxation time $T_{1\rho}$, evaluated

²⁸ N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

TABLE I. Summary of the chief properties of various experiments designed to remove dipolar coupling but not resonance shifts or scalar coupling from NMR spectra of solids.

Experiment	Dipolar effects			Shift effects		Compensation of	
	$\overline{\mathcal{H}}_D=0$	$\overline{\mathcal{H}}_D^{(1)}=0$	$\overline{\mathcal{H}}_D^{(2)}=0$	$\sigma_{\text{true}}/\sigma_{\text{eff}}$	$\Delta\sigma?$	finite $t_w?$	nonuniform $H_1?$
Spinning sample	Yes	No	No	1	No
Lee and Goldburg (LG)	Yes	No	No	$\sqrt{3}$	Yes	...	No
Pulsed LG (PLG)	Yes	No	No	$\sqrt{3}$	Yes	Yes	No
LG, PLG, tilted coil	Yes	No	No	$\sqrt{3}$	Yes	Yes	Yes
PLG with H_c reversal	Yes	Yes	No	$\sqrt{3}$	Yes	Yes	Yes
WH	No	No	No	$\sqrt{2}$	Yes
WHH	Yes	Yes	No	$\sqrt{3}$	Yes	Yes	No
HW	Yes	Yes	No	3	Yes	Yes	Yes
Evans	Yes	Yes	Yes	$\sqrt{3}$	Yes	Yes	No
16-pulse	Yes	Yes	Yes	3	Yes	Yes	Yes
WHH+spinning	Yes	Yes	No	$\sqrt{3}$	No	Yes	Yes

at a field strength H^* given by

$$H^* \sim (4\pi/\gamma t_c) = 2 < |H_1| >_{\text{av}}. \quad (82)$$

The second equality, involving the mean absolute value of the rf pulse field, is a consequence of the use of 90° pulses. Of course the ordinary average rf field in the four-pulse experiment vanishes because of the use of opposing phases, so the role of $T_{1\rho}$ would not have been so obvious *a priori*. The above arguments indicate that the limiting frequency resolution to be expected from the multiple pulse experiment in the presence of molecular motion is of the order of the rotating-frame relaxation time in a rotating field of strength H^* . This is a more severe limit than one has in the ordinary NMR of liquids, where it is the laboratory-frame relaxation time T_1 which governs.

The part of $J_0(\omega)$ in region c is already eliminated from any role in line broadening by the molecular motion, as mentioned above. If in fact $t_c < T_{2r}$, the discussion of case c Subsec. 2 applies, and the pulsing produces some additional narrowing by removal of $\overline{\mathcal{H}}_D^{(1)}$. Thus the pulse experiments can be expected to have some benefit in situations where partial narrowing through molecular motion has already occurred. A case in point arises in the NMR spectra of solutions of high molecular weight solutes, such as proteins. It is well known that the rotational correlation times are often long enough to leave a residue of static dipolar broadening ($T_1 > T_2$).²⁹ In such cases, the application of a multiple pulse cycle might well yield an improvement in resolution, at least if the more stringent condition $T_{1\rho} > T_2$ proves to be obeyed.

²⁹ W. D. Phillips (private communication).

SUMMARY

Evidently there are many possible experiments, using applied fields which are suitably modulated in amplitude and direction in the rotating frame, which have desirable properties of one sort or another in connection with the quest for high-resolution NMR of solids. We emphasize that we have considered here only certain simple classes of such experiments, where the field amplitudes are steady or modulated with square pulses, and where phase modulation is restricted to the four points of the compass in the rotating frame. The theoretical framework developed here, and illustrated by application to these experiments, is adapted to more general conditions as well. Doubtless many possibilities will occur to the reader.

Even within the limited compass we explore here we have given scant attention to a number of points of detail. Most obviously one would wish to investigate the cross-coupling effects among dipolar interactions, quadrupole interactions, shifts, and scalar spin coupling which enter all of the average Hamiltonians except the zero-order $\overline{\mathcal{H}}$ itself. The importance of such effects, and the choice among the many experiments to be performed, will quite clearly depend on the sample of interest and upon how small a pulse spacing it is possible to employ.

In Table I we summarize the chief properties of the various experiments discussed in this paper.

ACKNOWLEDGMENTS

We are indebted to L. M. Huber and J. D. Ellett for continuing valuable conversation. We thank W. A. B. Evans for sending us his manuscript before publication, and for a stimulating correspondence.