

# Broadband population inversion in solid state NMR

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We present theory, simulations and experimental demonstrations of composite  $\pi$  pulses for population inversion in coupled spin systems such as occur in solid state NMR. The composite  $\pi$  pulses are phase-shifted rf pulse sequences designed to invert spins over a larger range of dipole or quadrupole couplings than a conventional  $\pi$  pulse, for a given rf power. We discuss a previously proposed theory for constructing composite pulses, in the specific context of solids. Two particular sequences  $45_0 180_{90} 90_{180} 180_{90} 45_0$  and  $180_0 180_{120} 180_0$  are examined in detail. Their performance in coupled spin systems of various sizes is evaluated in simulations. Experiments are performed on two solid compounds,  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{C}_4\text{O}_4\text{H}_2$ . The results reveal markedly less spectral distortion after composite pulse inversion than after conventional  $\pi$  pulse inversion at low rf powers.

## I. INTRODUCTION

A universal problem in pulsed nuclear magnetic resonance (NMR) is that of exciting a system of nuclear spins with a broad spectrum of resonant frequencies using only a single frequency of radio frequency (rf) radiation. Two types of excitation are of particular importance, namely the creation of coherence between spin states and the creation of a population inversion. Both of these can be accomplished with single rf pulses, the familiar  $\pi/2$  and  $\pi$  pulses, respectively. If the pulse power is such that the resulting Rabi frequency is  $\omega_1$ , however, uniform excitation can only be achieved with single pulses over a spectral width  $\Delta\omega$  satisfying the condition  $\Delta\omega \ll \omega_1$ . The precise limits on the inequality depend on the specific application, but the problem is severe enough that much effort has been devoted to improvements on the basic  $\pi/2$  and  $\pi$  pulses over the past several years.

The idea of replacing single rf pulses with sequences of pulses with phase-shifts between them and with a constant amplitude for broadband excitation was first proposed by Levitt and Freeman. Such sequences were given the name "composite pulses." A pulse sequence designed to replace a single  $\pi$  pulse is called a composite  $\pi$  pulse; one designed to replace a single  $\pi/2$  pulse is called a composite  $\pi/2$  pulse. Attention was originally directed towards liquid state NMR, where the spectral width is primarily the result of chemical shifts. Consequently, most of the work on composite pulses has been devoted to constructing sequences that can excite spins uniformly over a range of chemical shifts.<sup>1-4</sup> In addition, composite pulses have been suggested for uniform excitation in the presence of inhomogeneity in the rf field strength.<sup>1-3,5</sup> A common feature of the chemical shift and the rf inhomogeneity problems is that they are both single-spin problems. They are therefore easily described by the Bloch vector model, allowing geometric arguments and intuitions to be used and allowing definitive computer simulations of the pulse sequence to be made. Most of the progress in the development of composite pulses for liquid state NMR has depended on exactly that combination of geometric pictures and computer simulations. Quite recently, though, al-

ternate, and perhaps more sophisticated, routes to the design of composite pulses have been explored. One of these is the generation of pulse sequences as approximations to continuously phase-modulated pulses with demonstrated broadband excitation properties.<sup>6,7</sup> This approach is well suited to constructing long sequences that excite spins over a very large spectral width. A second recent approach is the use of iterative schemes to produce successive improvements on a basic sequence unit.<sup>8-10</sup> Again, this approach generates long sequences with very large excitation bandwidths.

A third approach to constructing composite pulses,<sup>11</sup> and the one that is the focus of this paper, is the use of the Magnus expansion<sup>12,13</sup> in a manner similar to the coherent averaging theory that is of central importance to many techniques in the NMR of solids, liquid crystals, and liquids.<sup>14-16</sup> The Magnus expansion approach is in principle the most general method proposed to date in that it can be applied to both composite  $\pi$  and composite  $\pi/2$  pulses in a system of an arbitrary number of spins in which the spectral width results from any type of interaction. It reduces the problem of finding a composite pulse to that of solving a specific set of equations. This can then be done analytically or numerically, depending on the complexity of the equations. All of this generality is achieved at the expense of the appealing geometric pictures that characterize earlier approaches. However, in a general, coupled many-spin system, such as occurs in the NMR of anisotropic materials, the Bloch vector model does not apply anyway (the system is not describable by only three coordinates).

Levitt *et al.* have recently extended some liquid-state composite pulse results to solid-state deuterium NMR,<sup>17</sup> where fictitious spin-1/2 formalisms provide a modified vector model.<sup>18-20</sup> But, as it is presented, that work is limited to isolated quadrupolar spin-1 nuclei or pairs of dipole coupled spin-1/2 nuclei. In Ref. 11, we proposed composite  $\pi$  and composite  $\pi/2$  pulses for dipolar or quadrupolar spin systems of any size. It is the purpose of this paper to describe in more detail the application of the Magnus expansion approach to the design of composite pulses for solid state NMR. We present simulations and experimental demon-

strations of the performance of composite  $\pi$  pulses on spin systems of various sizes.

The paper is organized as follows: Sec. II contains the theory along with details as to how the formalism is put into practice. Specific composite  $\pi$  pulses are introduced. Advantages of the approach are discussed. Section III contains the results of simulations and experiments demonstrating the effectiveness of composite  $\pi$  pulses on two-spin systems. Simulations and experiments on many-spin systems are presented in Sec. IV. Section V contains conclusions. In an Appendix, we present a proof regarding the symmetry of the response of a coupled spin system to a composite pulse with respect to a change in the overall sign of the coupling constants.

## II. THEORY

### A. Formalism

The essential points of the theory have been presented in Ref. 11. In this section, we concentrate on the particular problem of constructing a pulse sequence for excitation over a spectrum that results from quadrupole or dipole couplings.

We begin by considering the Hamiltonian for the spin system in the rotating frame during rf irradiation to be the sum of two parts:

$$\mathcal{H} = \mathcal{H}_{\text{rf}} + V, \quad (1)$$

$$\mathcal{H}_{\text{rf}} = \omega_1 [I_x \cos \phi(t) + I_y \sin \phi(t)]. \quad (2)$$

$\mathcal{H}_{\text{rf}}$  is the interaction of the spin system, with total angular momentum vector operator  $\mathbf{I}$ , with the rf field of constant magnitude  $\omega_1$  (rad/s) and varying phase  $\phi(t)$ . In the rotating frame, the carrier frequency oscillations do not appear, so that  $\phi(t)$  during a pulse sequence is a piecewise-constant function of time. If the sequence consists of  $N$  pulses, then  $\phi(t)$  has the value of  $\phi_n$  during the  $n$ th pulse, with  $1 \leq n \leq N$ . The  $n$ th pulse has a duration  $\tau_n$ . The pulse sequence is then completely specified by the  $N$  phases  $\phi_n$  and the  $N$  pulse lengths  $\tau_n$ . However, as a result of the usual high-field condition  $[V, I_z] = 0$ , the bandwidth of excitation of the sequence will not be changed by adding a constant to all phases. Therefore, we can take  $\phi_1 = 0$ , leaving  $2N - 1$  variables to characterize the sequence.

The operator  $V$  in Eq. (1) is the quadrupole or dipole coupling term, which we will call  $V_Q$  or  $V_D$ :

$$V_Q = \omega_Q (I_z^2 - \frac{1}{3} I^2), \quad (3)$$

$$V_D = \sum_{i>j} d_{ij} (I_{zi} I_{zj} - \frac{1}{3} \mathbf{I}_i \cdot \mathbf{I}_j), \quad (4)$$

$\omega_Q$  is the quadrupole coupling constant.  $d_{ij}$  is the dipole coupling constant between spins  $i$  and  $j$ ; the sum in Eq. (4) is over all pairs of coupled spins in the system.

The Hamiltonian of Eq. (1) brings about an evolution of the spin system given by the propagator  $U(t)$ , which is conveniently written using the Dyson time-ordering operator  $T$  as

$$U(t) = T \exp - i \int_0^t dt' \mathcal{H}(t'). \quad (5)$$

An exact separation of  $U(t)$  can be made as follows:

$$U(t) = U_{\text{rf}}(t) U_V(t), \quad (6)$$

$$U_{\text{rf}}(t) = T \exp - i \int_0^t dt' \mathcal{H}_{\text{rf}}(t'), \quad (7)$$

$$U_V(t) = T \exp - i \int_0^t dt' \tilde{V}(t'), \quad (8)$$

$$\tilde{V}(t) = U_{\text{rf}}(t)^{-1} V U_{\text{rf}}(t). \quad (9)$$

$\tilde{V}(t)$  is the complete Hamiltonian in the interaction representation defined by  $\mathcal{H}_{\text{rf}}(t)$ . In the "delta-function pulse" limit commonly encountered in coherent averaging theory in solid-state NMR, the interaction representation would be the "toggling frame". Here we are explicitly dealing with weak pulses, so that the situation is the same as the one that occurs in the windowless pulse sequences for line narrowing proposed by Burum *et al.*<sup>21</sup>

$U_{\text{rf}}$  is the propagator for the interaction of the individual spins with the applied radiation alone. Since  $\mathcal{H}_{\text{rf}}(t)$  is piecewise-constant, Eq. (7) can be written:

$$U_{\text{rf}}(t) = \exp [ -i\omega_1 I_{\phi_n} (t - \tau_{n-1} - \dots - \tau_1) ] \\ \dots \exp [ -i\omega_1 I_{\phi_2} \tau_2 ] \exp [ -i\omega_1 I_{\phi_1} \tau_1 ], \\ \tau_1 + \dots + \tau_{n-1} \leq t \leq \tau_1 + \dots + \tau_n, \quad (10)$$

$$I_{\phi} = I_x \cos \phi + I_y \sin \phi. \quad (11)$$

Each of the exponential operators in Eq. (10) is simply a rotation in the spin vector space by an angle  $\omega_1 \tau_i$  about an axis in the  $xy$  plane making an angle  $\phi_i$  with the  $x$  axis.  $U_{\text{rf}}(t)$  is then a product of rotations, which is itself always a rotation.

If the couplings in Eqs. (3) or (4) were negligibly small compared to  $\omega_1$ , the total propagator  $U$  would be equal to  $U_{\text{rf}}$ , i.e., a pure rotation. Assuming the usual equilibrium initial condition for the spin system describable by a density operator proportional to  $I_z$ , the creation of a population inversion corresponds to a rotation of the density operator to  $-I_z$ , in other words to a rotation by an angle  $\pi$  about any axis in the  $xy$  plane. A condition that must be satisfied by any composite  $\pi$  pulse of total length  $\tau$  is therefore:

$$U_{\text{rf}}(\tau) I_z U_{\text{rf}}(\tau)^{-1} = -I_z. \quad (12)$$

The problem that we are trying to solve, though, is one in which the couplings are not negligible. Still, if we could make  $U_V(\tau)$  in Eq. (8) approximately the identity operator for some range of couplings by choosing the proper pulse sequence, and simultaneously satisfy Eq. (12), then we would achieve uniform population inversion over that range of couplings. A straightforward way to accomplish this is to make a Magnus expansion<sup>12,13</sup> of  $U_V(\tau)$ :

$$U_V(\tau) = \exp [ -i(V^{(0)} + V^{(1)} + \dots) \tau ], \quad (13)$$

$$V^{(0)} = \frac{1}{\tau} \int_0^\tau dt \tilde{V}(t), \quad (14)$$

$$V^{(1)} = \frac{-i}{2\tau} \int_0^\tau dt_1 \int_0^{t_1} dt_2 [\tilde{V}(t_1), \tilde{V}(t_2)]. \quad (15)$$

Discussions of the Magnus expansion and of its applications in NMR have been given elsewhere.<sup>14-16</sup> The  $n$ th term in the Magnus expansion,  $V^{(n+1)}$ , is a sum of  $n+1$ -fold integrals of  $n$ -fold commutators of  $\tilde{V}(t)$  with itself, evaluated at different times. Thus, if the size of  $V$  is characterized by a parameter like  $\omega_Q$  in Eq. (3), the Magnus expansion is a pow-

er series in that parameter. We call a pulse sequence for which  $V^{(n)} = 0$  for  $0 < n < M$  an  $M$ th-order composite pulse. As  $M$  increases, the range of couplings for which uniform excitation is achieved also increases.<sup>11</sup>

The procedure for finding an  $M$ th order composite pulse is as follows. As explained earlier, a sequence of  $N$  pulses is described by  $2N - 1$  variables. Through Eqs. (9)–(11) and (14) and (15),  $V^{(n)}$  is a function of those variables. The pulse sequence must satisfy Eq. (12) in addition to the  $M + 1$  equations  $V^{(n)} = 0$ . Therefore, we choose a value of  $N$  large enough that a simultaneous solution to the required equations exist. Each equation is an operator equation, and therefore has more than one component. In addition, the equations are nonlinear so that there is no obvious relationship between the number of equations and the number of variables needed for a simultaneous solution to exist. Experience shows, however, that a solution can usually be found when the number of variables approximately equals the number of component equations. Often the solutions correspond to composite pulses with experimentally favorable pulse lengths and phases, as well.

Composite pulses are often most easily found by solving the desired equations numerically. A computer program is written that evaluates  $U_{\text{rf}}(\tau) I_z U_{\text{rf}}(\tau)^{-1}$  and the required  $V^{(n)}$ . Criteria are established for the precision to which the equations are to be solved. A search for solutions is then conducted over a set of possible pulse length and phase combinations. Typically, more than one solution is found. In such cases, simulations of the performance of the composite pulses on model spin systems are used to select the best composite pulse. Differences in the performance of composite pulses of the same order may be attributed to properties of higher terms in the Magnus expansion that are not set to zero.

There is another factor that is often important in the design of composite pulses, namely symmetry. For example, in composite  $\pi$  pulses designed to produce population inversion over a range of chemical shifts, it can be shown that the extent of inversion is independent of the sign of the chemical shift if the rf phase is an even function of time with respect to the middle of the pulse sequence.<sup>5</sup> Such symmetries can be incorporated into our procedure as restrictions on the allowed pulse length and phase combinations.

In the case of a spin system with quadrupole or dipole coupling, symmetry with respect to the sign of the couplings in the response of the spins to an rf pulse sequence is a consequence of the form of the coupling Hamiltonians themselves. We prove this fact in the Appendix. As a result, symmetry restrictions are not required in the composite pulses discussed below.

## B. Zeroth order composite pulses

Zeroth order composite pulses are characterized by  $V^{(0)} = 0$  in Eq. (14). To evaluate  $V^{(0)}$ , it is necessary to calculate  $\tilde{V}(t)$ . For quadrupole and dipole couplings, this is most conveniently done using a basis of second-rank irreducible tensor operators, symbolized by  $T_{2m}$  with  $-2 \leq m \leq 2$ . The  $T_{2m}$  form a closed set under rotations. Their definition and

properties are discussed in many places.<sup>22,23</sup> The coupling Hamiltonians of Eqs. (3) and (4) both have the transformation properties of a  $T_{20}$ . Therefore,  $\tilde{V}(t)$  is always a linear combination of  $T_{2m}$  operators, since it is related to  $V$  by the rotation  $U_{\text{rf}}^{-1}(t)$ :

$$\tilde{V}(t) = \sum_{m=-2}^2 c_m(t) T_{2m}. \quad (16)$$

Additionally,  $\tilde{V}(t)$  must be Hermitian, since  $V$  is Hermitian and  $U_{\text{rf}}(t)$  is unitary. This requires that

$$c_{-m}(t) = (-1)^m c_m^*(t). \quad (17)$$

The coefficients  $c_m(t)$  for an arbitrary pulse sequence, in other words an arbitrary sequence of rotations, are readily calculated using the Wigner rotation matrices<sup>22</sup> or the tables in Ref. 23.

What we need to evaluate  $V^{(0)}$  are the integrals of the  $c_m(t)$  over the pulse sequence, which we denote by the complex numbers  $a_m + ib_m$ . Because of Eq. (17), there are five independent quantities required to specify  $V^{(0)}$ , which we write as the five-dimensional vector  $\mathbf{g} = (a_0, a_1, b_1, a_2, b_2)$ . Thus, the operator equation  $V^{(0)} = 0$  consists of five component equations.

Throughout the remainder of this paper, we will use the standard notation  $(\omega_1 \tau_1)_{\phi_1} (\omega_2 \tau_2)_{\phi_2} \dots (\omega_N \tau_N)_{\phi_N}$  to describe a composite pulse, with all angles in degrees. The quantities  $\omega_i \tau_i$  are the flip angles of individual pulses. In Ref. 11, we proposed the sequence  $45_0 180_{90} 90_{180} 180_{90} 45_0$  as a composite  $\pi$  pulse for coupled spin systems. For this sequence,  $\mathbf{g} = (0, 0, 0, 0, 0)$  exactly. Equation (12) is also exactly satisfied.

A slight variation of the theory is possible when the composite pulse acts on an initial state with a density operator proportional to  $I_z$ . In that case, an alternative to requiring that  $V^{(0)} = 0$  is to require that  $[V^{(0)}, I_z] = 0$ . Then the following relationship will hold for some range of couplings:

$$U(\tau) I_z U^{-1}(\tau) \approx U_{\text{rf}}(\tau) \exp(-iV^{(0)} \tau) I_z \times \exp(iV^{(0)} \tau) U_{\text{rf}}(\tau)^{-1}, \quad (17)$$

$$U(\tau) I_z U^{-1}(\tau) \approx U_{\text{rf}}(\tau) I_z U_{\text{rf}}(\tau)^{-1}. \quad (18)$$

The lowest order effects of the couplings disappear. The condition  $[V^{(0)}, I_z] = 0$  is equivalent to the condition  $V^{(0)} \propto T_{20}$ . A composite  $\pi$  pulse satisfying this condition is the sequence  $180_0 180_{120} 180_0$ , with  $\mathbf{g} = (3\pi/4, 0, 0, 0, 0)$ .

## C. Higher order composite pulses

Higher order composite pulses involve complications that do not appear in the zeroth order composite pulses. In constructing zeroth order composite pulses, no mention need be made of the size of the spin system. This is because the coupling Hamiltonians in Eqs. (3) and (4) have  $T_{20}$  symmetry regardless of the number of coupled spins or the total spin angular momentum quantum number of each individual spin. The  $T_{20}$  symmetry is all that is needed to determine zeroth order composite pulses. Higher order composite pulses must satisfy equations like  $V^{(n)} = 0$  with  $n > 0$ . The term  $V^{(n)}$  in the Magnus expansion involves an  $n$ -fold commutator of  $\tilde{V}(t)$ . It therefore may contain irreducible tensor components up to rank  $n + 2$  in the most general case. How-

ever, the size of the spin system places a limit on the rank of the tensor components that may appear in  $V^{(n)}$ . For example, a system of  $m$  coupled spin-1/2 nuclei will have Magnus expansion terms with irreducible tensor components of rank no greater than  $m$ . Similarly, an isolated quadrupolar nucleus with total angular momentum quantum number  $I$  will have irreducible tensors of rank no greater than  $2I$  in the Magnus expansion. As a result, the number of component equations in the operator equation  $\dot{V}^{(n)} = 0$ , and hence the number of pulses required in the higher order sequence, depends on the size of the spin system. Of course, an upper bound on the number of component equations is set by the above-mentioned fact that  $V^{(n)}$  contains components of rank  $n + 2$  or less.

#### D. Characteristics and advantages of the Magnus expansion approach

There are several aspects of the Magnus expansion approach to constructing composite pulses that are a consequence of the formalism and that distinguish it from other possible approaches. One is that the most uniform excitation is expected to occur in a range of couplings around zero. This results from the power series nature of the Magnus expansion. Approaches that rely heavily on computer simulations may lead to composite pulses that give, for example, better population inversion at large couplings than at small couplings.

The Magnus expansion approach treats the composite pulse in its entirety, rather than requiring a detailed pulse-by-pulse analysis. Pulse-by-pulse analyses, along with computer simulations, have produced important results in the NMR of isotropic liquids. However, it is difficult to see how such an approach would proceed for a coupled spin system of arbitrary size.

The Magnus expansion approach produces composite pulses that are equivalent to constant, pure rotations over a range of couplings. The design of the composite pulse is not geared towards the behavior of a particular initial condition of the spin system. This is an important and unique feature, since the composite pulses may then be suitable for use in various decoupling, line narrowing, echo, multiple quantum, and two-dimensional NMR experiments. In such experiments, rf pulses act on a spin system far from equilibrium. Their function is to produce well-defined rotations in the spin angular momentum vector space.

To clarify the last point, suppose a composite  $\pi$  pulse is constructed with the only requirement being that it convert an initial condition of  $I_z$  to a final condition of  $-I_z$  for some desired range of couplings. This may be done, for example, by relying on computer simulations of the population inversion properties alone. The resulting composite pulse then must have an overall propagator given approximately by

$$U(\tau) = e^{-i\pi I_x A}, \quad (19)$$

where  $[A, I_z] = 0$ , but where  $A$  may be a function of the coupling strength. An arbitrary initial condition will not be transformed in a constant way. In general, this results in nonuniform excitation and spectral phase distortions. In fa-

vorable cases, phase distortions may be overcome with multiple composite pulses.<sup>3,24</sup>

On the other hand, an  $M$ th order composite  $\pi$  pulse constructed using the Magnus expansion with the requirement  $V^{(n)} = 0$  for  $n < M$  has an overall propagator approximately equal to  $U_{rf}(\tau)$ , i.e., a constant rotation, over its effective range of couplings. The transformation of an arbitrary initial condition will be independent of the coupling strength.

### III. APPLICATION TO TWO-SPIN SYSTEMS

#### A. Simulations

In Fig. 1, we show computer simulations of the inversion performance as a function of dipolar coupling strength in a system composed of a pair of equivalent spin-1/2 nuclei for the composite  $\pi$  pulses presented in Sec. II B. For reference, the inversion performance of a normal, single  $\pi$  pulse is depicted as well. The inversion  $W$  is defined by

$$W = \frac{-\text{Tr}[I_z U(\tau) I_z U(\tau)^{-1}]}{\text{Tr}[I_z^2]}. \quad (20)$$

$W$  is therefore the negative of the final  $z$  component of spin angular momentum after applying the composite pulse to a spin system with an initial  $z$  component of  $+1$ .

It is apparent from Fig. 1 that both the sequence  $45_0 180_{90} 90_{180} 180_{90} 45_0$  and the sequence  $180_0 180_{120} 180_0$  provide substantial improvements in inversion performance over a single  $\pi$  pulse. Good inversion is accomplished with couplings that are as large as  $2\omega_1$ . These results apply identically to the inversion of a quadrupolar spin-1 nucleus, substituting  $2\omega_Q/\omega_1$  for  $d/\omega_1$  on the abscissa of Fig. 1.

An interesting feature of Fig. 1 is that  $180_0 180_{120} 180_0$ , derived by the variant of the Magnus expansion approach discussed in Sec. II B, gives slightly better inversion for small couplings than  $45_0 180_{90} 90_{180} 180_{90} 45_0$ . It is possible that the presence of a nonzero  $V^{(0)}$  term in Eq. (13), with the requirement  $[V^{(0)}, I_z] = 0$ , truncates the higher order terms

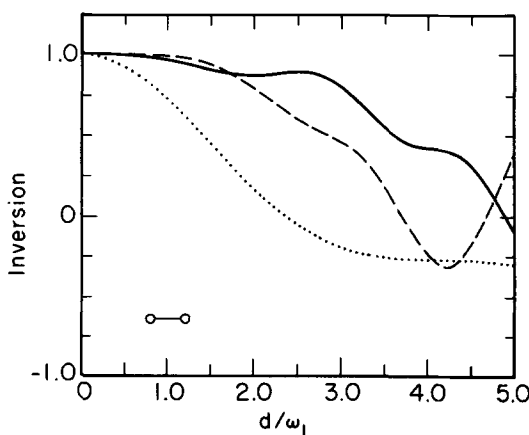


FIG. 1. Simulation of inversion for a system of two dipole coupled spin-1/2 nuclei as a function of the ratio of the coupling constant  $d$  to the applied rf amplitude  $\omega_1$ . Inversion is defined by Eq. (20) of the text as the final projection of spin angular momentum onto the  $-z$  axis. Initially, the spin angular momentum is aligned with the  $+z$  axis and has unit length. Results are shown for a single  $\pi$  pulse (dotted line), a  $45_0 180_{90} 90_{180} 180_{90} 45_0$  composite  $\pi$  pulse (solid line), and a  $180_0 180_{120} 180_0$  composite  $\pi$  pulse (dashed line).

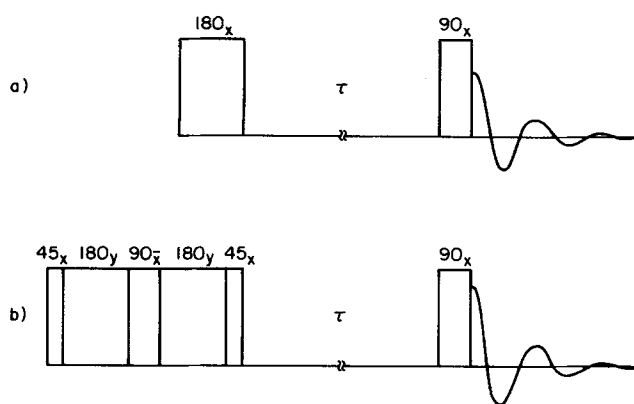


FIG. 2. Schematic representation of the pulse sequences used in the simulations of Fig. 3 and the experiments of Figs. 4, 5, and 9. (a) Spins are inverted by a  $\pi$  pulse. Single quantum and higher coherences, which are created at low rf amplitudes, dephase during a delay of length  $\tau$ . The FID signal after the final  $\pi/2$  pulse is digitized and Fourier transformed to give a spectrum that reflects the inversion efficiency of the initial  $\pi$  pulse. (b) Same as (a), but with a  $45_x 180_y 90_x 180_y 45_x$  composite  $\pi$  pulse in place of the single  $\pi$  pulse. A  $180_0 180_{120} 180_0$  composite  $\pi$  pulse may be used as well.

in the expansion. For example, if  $V^{(0)}$  is much larger than  $V^{(1)}$ , then only those components of  $V^{(1)}$  that commute with  $V^{(0)}$  will significantly affect the inversion. Such an effect is reminiscent of the "second averaging" technique commonly employed in multiple pulse line-narrowing experiments in solid state NMR.<sup>15,25</sup>

Figure 2 illustrates pulse sequences used to experimentally contrast the inversion performance of composite  $\pi$  pulses against that of a single  $\pi$  pulse. Spins initially at equilibrium are (partially) inverted by a  $\pi$  [2(a)] or composite  $\pi$  [2(b)] pulse. During a delay  $\tau$ , coherences other than zero quantum dephase, leaving the spin system in a state describable by a density operator that commutes with  $I_z$ . The free induction decay (FID) signal is then collected following a  $\pi/2$  pulse and Fourier transformed to give the spectrum. Spectral distortions at low rf power reflect imperfect inversion. The sequence of Fig. 2(a) is commonly used to study spin lattice relaxation.<sup>26</sup> Figure 2(b) represents the analogous experiment employing a composite  $\pi$  pulse.

In Fig. 3, we show simulations of powder pattern spectra resulting from the sequence of Fig. 2(a) applied to an isotropic orientational distribution of pairs of spin-1/2 nuclei. The usual Pake pattern results from the  $3 \cos^2 \theta - 1$  dependence of the dipolar coupling constant on the angle between the constant, applied magnetic field and the internuclear displacement vector. Here the maximum coupling is taken to be  $d/2\pi = 80$  kHz. Clearly, the characteristic spectral features are lost as the rf amplitude is reduced.

In Fig. 3, we also show simulated spectra resulting from the sequence of Fig. 2(b). We have merely substituted a composite  $\pi$  pulse for the normal  $\pi$  pulse. The spectral distortion is dramatically reduced at low rf amplitudes. Using the composite  $\pi$  pulse  $180_0 180_{120} 180_0$  gives essentially the same results.

The slight asymmetry in the spectrum in Fig. 3(f) resulting from the composite  $\pi$  pulse requires some explanation, since it is generally assumed that the spectrum of a quadrupolar or dipolar spin system must be symmetric.<sup>27</sup> Suppose we start with a coupled spin system described by a density

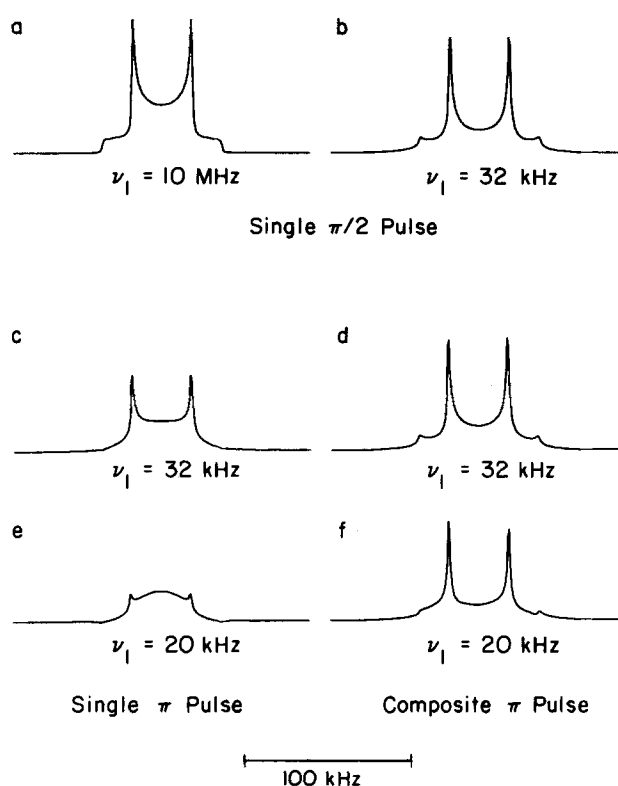


FIG. 3. Simulated NMR spectra of an isotropic orientational distribution of pairs of dipole-coupled, spin-1/2 nuclei. The maximum coupling is  $d_{\max}/2\pi = 80$  kHz. 1 kHz line-broadening is added. (a) Spectrum after a single  $\pi/2$  pulse, with  $\omega_1/2\pi = \nu_1 = 10\,000$  kHz. Since  $\omega_1 \gg d_{\max}$ , the spectrum is undistorted. (b) Spectrum after a single  $\pi/2$  pulse, with  $\nu_1 = 32$  kHz, illustrating the distortion resulting from a  $\pi/2$  pulse alone at low rf amplitudes. (c) Spectrum resulting from sequence a of Fig. 2 with  $\nu_1 = 32$  kHz. (d) Spectrum resulting from sequence b of Fig. 2 with  $\nu_1 = 32$  kHz. (e) Spectrum from sequence a with  $\nu_1 = 20$  kHz. (f) Spectrum from sequence b with  $\nu_1 = 20$  kHz. The characteristic features of the spectrum, which are lost by a single  $\pi$  pulse at low rf amplitudes, are preserved by a composite  $\pi$  pulse.

operator  $I_z$ . When a weak pulse sequence is applied to the spin system, the presence of the couplings interferes with the action of the applied rf in such a way that the magnitude of the expectation value of the spin angular momentum actually changes. In other words, the magnetization shrinks. The density operator evolves into not only a linear combination of  $I_x$ ,  $I_y$ , and  $I_z$ , but also into multiple quantum coherence, zero quantum coherence (including dipolar order), and non-observable single quantum coherence. Therefore, the density operator for the spin system immediately before the final weak  $90_0$  pulse contains a component of dipolar order.<sup>28</sup> It is this dipolar order which produces the asymmetry in the spectrum in Fig. 3(f).

The asymmetry is absent in the spectra resulting from a single  $\pi$  pulse. We can understand this by proving that there can be no dipolar order produced by a  $180_0$  pulse, regardless of the rf amplitude. Dipolar order implies that the density operator contains a component proportional to  $V_D$  in Eq. (4). The amount of dipolar order is proportional to  $D$ , where

$$D = \text{Tr}[V_D U(\tau) I_z U(\tau)^{-1}]. \quad (21)$$

$U(\tau)$  is the propagator for the pulse resulting from the Hamiltonian of Eqs. (1), (2), and (4), with  $\phi(t) = 0$  in Eq. (2). Since the trace is invariant to a unitary transformation, we can

rotate all the operators on the right side of Eq. (21) by an angle  $\pi$  about the  $x$  axis without changing the validity of that equation. Since that rotation changes  $I_z$  to  $-I_z$  and leaves all the other operators unchanged we have  $D = -D$ , or  $D = 0$ . The proof may be extended to show that no dipolar order is created by any pulse sequence in which the rf phase only takes on the values  $\phi$  and  $\phi + \pi$ .

## B. Experimental results

In Fig. 4, we show proton NMR spectra of  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  powder obtained with the sequences of Fig. 2 applied at two different rf amplitudes. The delay  $\tau$  in Fig. 2 is here taken to be 5 ms. As predicted by the simulations, the spectral distortion with weak rf is quite obviously reduced by the use of a composite  $\pi$  pulse.

The spectrum of  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  reflects the fact that individual  $\text{H}_2\text{O}$  molecules are essentially isolated from one another, giving a Pake pattern characteristic of pairs of protons. The experimental pattern is somewhat distorted from the ideal pattern assumed in the simulations by two factors. The first of these is the presence of couplings between  $\text{H}_2\text{O}$  molecules. Such intermolecular couplings have the effect of broadening each individual transition, as reviewed in Ref. 29. The second factor is the presence of chemical shift anisotropy. The proton chemical shift anisotropy for  $\text{H}_2\text{O}$  in ice has been measured to be about 34 ppm.<sup>30</sup> We attribute the

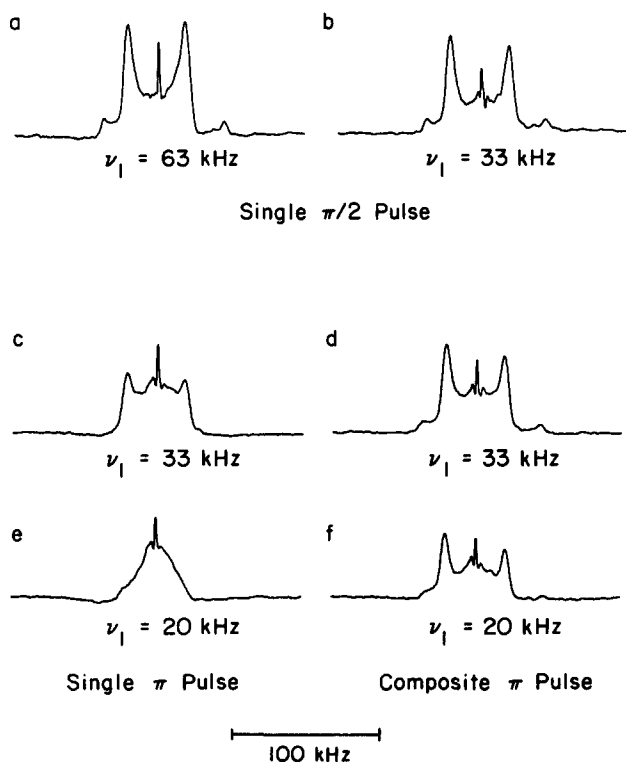


FIG. 4. Experimental proton NMR spectra of  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  powder. All spectra are the averages of 60 scans, with a recycle delay of 30 s. (a) Spectrum after a single  $\pi/2$  pulse with  $\nu_1 = 63$  kHz. (b) Spectrum after a single  $\pi/2$  pulse with  $\nu_1 = 33$  kHz. (c) Spectrum from sequence a of Fig. 2 with  $\nu_1 = 33$  kHz. (d) Spectrum from sequence a of Fig. 2 with  $\nu_1 = 33$  kHz. (e) Spectrum from sequence a with  $\nu_1 = 20$  kHz. (f) Spectrum from sequence b with  $\nu_1 = 20$  kHz. The principal features of the simulations of Fig. 3 are reproduced.

sharp peak in the center of the  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  spectra to residual protons and to  $\text{H}_2\text{O}$  molecules that are free to reorient rapidly and isotropically.

The delay  $\tau$  of 5 ms was chosen to be long compared to the dephasing time of transverse magnetization ( $T_2$ ) but short compared to the spin-lattice relaxation time ( $T_1$ ).  $T_1$  in  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  at room temperature is approximately 10 s. Measurements of  $T_{1d}$ , the relaxation time for dipolar order, using the Jeener-Broekaert technique,<sup>28</sup> indicate that  $T_{1d}$  is about equal to  $T_1$ . Hence, we expect to see a slight asymmetric distortion in the composite  $\pi$  pulse spectra in Fig. 4 at low rf amplitudes, as discussed in Sec. III A. This is observed.

Similar experimental results to those in Fig. 4 were obtained using the  $180_0 180_{120} 180_0$  sequence. All experiments were performed on a homebuilt NMR spectrometer operating at a proton frequency of 362 MHz.<sup>31</sup> The spectrometer is capable of giving rf pulses with four adjustable phases. Pulse gating and phase generation occur at an IF frequency of 30 MHz. Phase adjustments were done with a HP8405A vector voltmeter. No elaborate tune-up procedures were used to refine the phase or amplitude settings of the four pulse channels. Pulse lengths were calibrated by searching for a null in the FID signal from a small  $\text{H}_2\text{O}_{(l)}$  sample following a train of four equal pulses. This technique allows pulse lengths corresponding to flip angles of any multiple of  $\pi/4$  to be set.

## C. Compensation for rf inhomogeneity

Unless we use a sample that is much smaller than the excitation coil of the NMR probe, the sample sees a spatial distribution of rf amplitudes. In addition, the technique for setting pulse lengths described above involves changing from one sample to another. For both reasons, it is difficult to set the lengths for the individual pulses in a composite pulse accurately; it is important that the composite pulse be

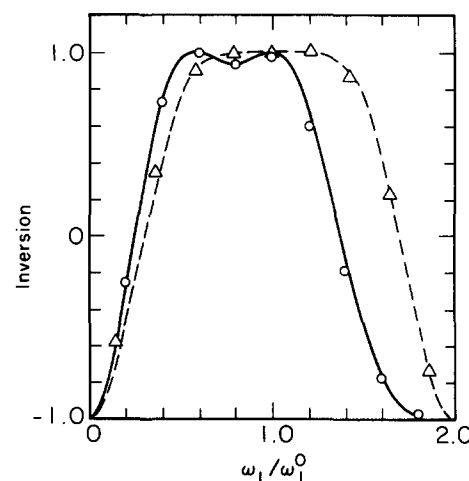


FIG. 5. Inversion for an isolated nucleus as a function of the ratio of the actual rf amplitude  $\omega_1$  to its nominal value  $\omega_1^0$ . This illustrates the principal effect of rf inhomogeneity or of miscalibrated pulse lengths on the performance of composite  $\pi$  pulses. Results are shown for  $45_0 180_0 90_0 180_0 45_0$  (simulations in solid line, experiments in circles) and for  $180_0 180_{120} 180_0$  (simulations in dashed line, experiments in triangles). Experimental data was taken using sequence b of Fig. 2, with the pulse lengths in the composite  $\pi$  pulse deliberately misset to mimic rf inhomogeneity. A small  $\text{H}_2\text{O}_{(l)}$  sample was used. Inversion was measured from the peak height in the NMR spectrum.

insensitive to pulse length errors, or equivalently to rf inhomogeneity.

We have previously reported that the sequence  $180_0 180_{120} 180_0$  compensates for rf inhomogeneity to zeroth order, in addition to its performance as a composite  $\pi$  pulse in coupled spin systems.<sup>11</sup> The  $45_0 180_{90} 90_{180} 180_{90} 45_0$  sequence also proves to be insensitive to rf inhomogeneity, particularly when the rf amplitude is less than its nominal value. Experimental data for the inversion performance of the two sequences as a function of the ratio of actual pulse lengths to nominal pulse lengths are presented in Fig. 5.

The data in Fig. 5 were obtained with a  $\text{H}_2\text{O}_{(l)}$  sample, i.e., with no couplings. Thus, we see the effect of rf inhomogeneity alone on the inversion performance. The interaction of rf inhomogeneity with couplings is a higher order effect which we do not consider here.

#### IV. APPLICATION TO MANY-SPIN SYSTEMS

##### A. Simulations

The results of Sec. III indicate that zeroth order composite  $\pi$  pulses can produce  $\pi$  rotations over a much larger range of couplings than a single  $\pi$  pulse in two-spin systems. This is important because, even in a many-spin system, the strongest couplings may be arranged in pairs, for example as methylene groups in an organic solid. The fact that the two-

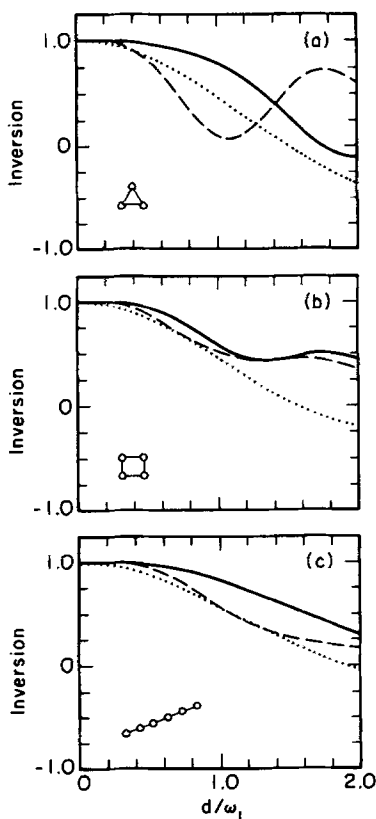


FIG. 6. Simulations of inversion as a function of the ratio of the nearest-neighbor dipole coupling constant  $d$  to the rf amplitude  $\omega_1$  for three possible systems of coupled spin-1/2 nuclei. Results are shown for a single  $\pi$  pulse (dotted lines), a  $45_0 180_{90} 90_{180} 180_{90} 45_0$  composite  $\pi$  pulse (solid lines), and a  $180_0 180_{120} 180_0$  composite  $\pi$  pulse (dashed lines). (a) Three spins in an equilateral triangle. (b) Four spins in a square. (c) Six spins in a row. Coupling constants are taken to be proportional to  $r_{ij}^{-3}$ , where  $r_{ij}$  is the distance between nuclei  $i$  and  $j$ .

spin results apply identically to quadrupolar spin-1 nuclei makes the composite  $\pi$  pulses of obvious importance in deuterium and  $^{14}\text{N}$  NMR as well.

Coupled spins occur in other configurations, however. For composite  $\pi$  pulses to be of general use in solid state NMR, they should provide an advantage over a single  $\pi$  pulse in an arbitrary coupled system. Therefore, we investigate the inversion performance of composite  $\pi$  pulses in systems of more than two coupled spin-1/2 nuclei.

In Fig. 6, we present the results of computer simulations of the inversion performance of the  $45_0 180_{90} 90_{180} 180_{90} 45_0$  and  $180_0 180_{120} 180_0$  composite  $\pi$  pulses, as well as that of a single  $\pi$  pulse, in three different spin systems. The spin system of Fig. 6(a) consists of three spin-1/2 nuclei arranged in an equilateral triangle perpendicular to the applied constant magnetic field so that all dipole coupling constants are equal. Figure 6(b) represents a system of four spin-1/2 nuclei in a square, again perpendicular to the applied field. The coupling constants are taken to be proportional to  $r_{ij}^{-3}$ , where  $r_{ij}$  is the distance between nucleus  $i$  and nucleus  $j$ . The spin system of Fig. 6(c) is a straight row of six, equally spaced spin-1/2 nuclei. Again, the coupling constants are proportional to  $r_{ij}^{-3}$ .

In all cases considered, both composite  $\pi$  pulses give better inversion than a single  $\pi$  pulse over some range of couplings. Generally speaking, the  $45_0 180_{90} 90_{180} 180_{90} 45_0$  sequence is the more effective of the two. Note that the range of nearest-neighbor couplings over which good inversion is achieved is substantially smaller than in the two-spin case, for the single  $\pi$  as well as the composite  $\pi$  pulses.

##### B. Experimental results

Experimental spectra resulting from the sequences of Fig. 2 applied to a single crystal squaric acid ( $\text{C}_4\text{O}_4\text{H}_2$ ) sample are shown in Fig. 7. In the crystal, squaric acid molecules are arranged in planes in such a way that the hydrogen nuclei, or protons, form chains perpendicular to the molecular planes. The spacing between adjacent protons in a chain is known to be 2.636 Å.<sup>32</sup> Squaric acid has been the subject of NMR<sup>33,34</sup> and other studies,<sup>35</sup> in particular due to the observation of a structural phase transition at 370 K which exhibits critical behavior suggestive of a two-dimensional system. We chose squaric acid for demonstration purposes because it is a true many-spin solid, yet there is resolved structure in its proton NMR spectrum.

As shown in Fig. 7, spectra resulting from the sequence of Fig. 2(b) have greater overall intensity at low rf amplitudes than those resulting from the sequence of Fig. 2(a). This supports the conclusion of Sec. IV A that the  $45_0 180_{90} 90_{180} 180_{90} 45_0$  sequence produces better inversion in a many-spin, coupled system than a single  $\pi$  pulse.

We emphasize that the spectra in Fig. 7 are from a single crystal, although they superficially resemble a powder pattern. In a powder pattern, as in Fig. 4, the features of the spectrum furthest from the center result from spins with the largest couplings. Therefore, those features are lost first due to poor inversion at low rf amplitudes. The squaric acid spectrum, on the other hand, is the product of an essentially infinite network of coupled spins, with the strongest cou-

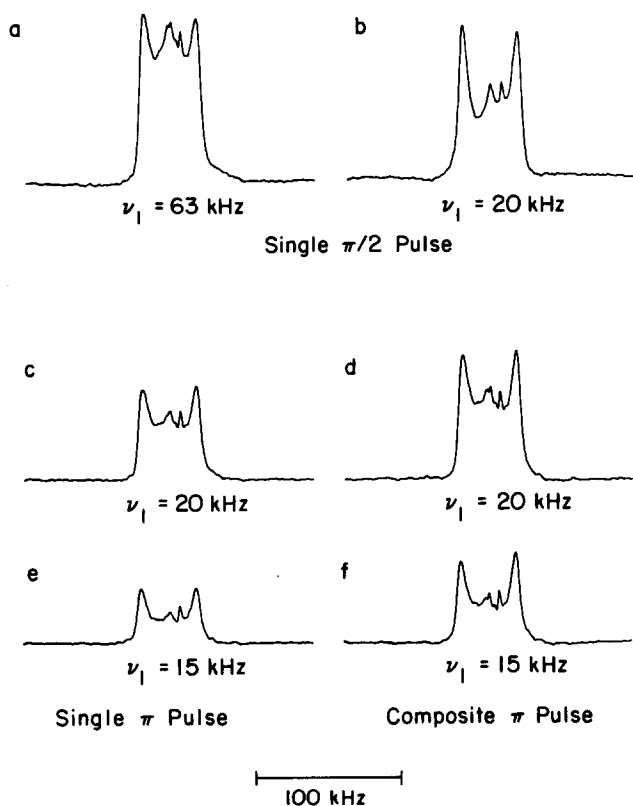


FIG. 7. Experimental proton NMR spectra of a squaric acid crystal. All spectra are the averages of 20 scans, with a recycle delay of 30 s. The narrow peak to the right of center of each spectrum results from residual protons. Its displacement from the center is due to the large chemical shift of squaric acid, approximately 20 ppm with respect to TMS at this orientation. (a) Spectrum after a single  $\pi/2$  pulse with  $\nu_1 = 63$  kHz. (b) Spectrum after a single  $\pi/2$  pulse with  $\nu_1 = 20$  kHz. Low rf amplitude results in a loss of intensity from the center of the spectrum. (c) Spectrum from sequence *a* of Fig. 2 with  $\nu_1 = 20$  kHz. (d) Spectrum from sequence *b* of Fig. 2 with  $\nu_1 = 20$  kHz. (e) Spectrum from sequence *a* with  $\nu_1 = 15$  kHz. (f) Spectrum from sequence *b* with  $\nu_1 = 15$  kHz. Use of the composite  $\pi$  pulse results in greater overall intensity, reflecting a more complete inversion.

plings occurring along chains. Each of the individual, unresolved transitions that make up the spectrum is a transition of the spin system as a whole, so that it should not be expected that the outer spectral features would be attenuated at low rf amplitudes.

For the squaric acid experiments, we used a  $\tau$  of 5 ms. The crystal was doped with chromium to reduce the proton  $T_1$  to approximately 10 s. The crystal was oriented with the *b* axis<sup>31</sup> parallel to the static magnetic field. In this orientation, the proton chains are parallel to the field, giving the strongest possible couplings.

## V. CONCLUSION

We have demonstrated that the Magnus expansion provides a useful means for constructing composite pulses for solid state NMR. The  $45_0 180_{90} 90_{180} 180_{90} 45_0$  and  $180_0 180_{120} 180_0$  composite  $\pi$  pulses both yield significantly better population inversion at low rf amplitudes than a single  $\pi$  pulse in two-spin systems; the  $45_0 180_{90} 90_{180} 180_{90} 45_0$  sequence also provides an advantage in many-spin systems.

An obviously important application of the composite  $\pi$  pulses presented above is in inversion-recovery measure-

ments of spin-lattice relaxation.<sup>1,26</sup> Complete population inversion is crucial, particularly if the relaxation time is extracted with the null point method. Techniques for obtaining two-dimensional, dipolar-chemical shift spectra in solids<sup>27,36,37</sup> may profit from composite  $\pi$  pulses as well. Composite  $\pi$  pulses may also be applied to the generation of indirectly induced spin echoes,<sup>38</sup> or as refocussing pulses in solid state multiple quantum NMR experiments.<sup>39</sup>

We have given examples of zeroth order composite pulses only. As presented in Sec. II C, the derivation of higher order composite pulses for solids is a large computational problem which will require more sophisticated numerical methods than we have yet employed. It is possible that symmetry conditions can be found that cause some of the component equations to be satisfied identically, reducing the size of the problem.

The approach discussed in this paper may be used to construct composite  $\pi/2$  pulses for solid state NMR as well. Composite  $\pi/2$  pulses and their applications are currently being investigated.

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## APPENDIX

In this Appendix, we discuss the symmetry of the response of a coupled spin system to a pulse sequence with respect to the overall sign of the coupling constants. We make use of the time reversal operator  $K$  whose properties are extensively discussed in many texts.<sup>40</sup>  $K$  is an example of an antilinear, unitary operator. The properties of  $K$  that are of relevance here are

$$KiK^{-1} = -i, \quad (\text{A1})$$

$$KI_jK^{-1} = -I_j, \quad j = x, y, z, \quad (\text{A2})$$

$$\langle n | (K | m \rangle) = [(\langle n | K | m \rangle)]^*. \quad (\text{A3})$$

Note that Eq. (A3) implies that the parentheses in the inner product can not be disregarded, as they can for a linear operator.

The significance of  $K$  in the problem of symmetry is apparent from a consideration of the following equation:

$$KU(t)K^{-1} = T \exp -i \int_0^t dt' (\mathcal{H}_{\text{rf}} - V), \quad (\text{A4})$$

where  $U(t)$  is the propagator in Eq. (5) of Sec. II. Here we rely on the fact that  $\mathcal{H}_{\text{rf}}$  is a linear function of angular momentum operators, while the coupling Hamiltonian  $V$  is bilinear. Thus, the time reversal transformation has the effect of



changing the sign of all coupling constants without changing the applied radiation.

The response of a spin system may be calculated in the form of traces of products of linear operators. It is well known that the trace of a linear operator is unchanged by a linear, unitary transformation. For antilinear, unitary transformations such as  $K$ , the trace is converted to its complex conjugate. We prove this by writing the trace of a transformed linear operator  $A$  in the following way:

$$\text{Tr}(KAK^{-1}) = \sum_n \langle n | (KAK^{-1}) | n \rangle. \quad (\text{A5})$$

The summation on the right-hand side of Eq. (A5) is over any complete, orthonormal basis of states  $|n\rangle$ . Using the completeness of that basis and Eq. (A3) we get

$$\text{Tr}(KAK^{-1}) = \sum_{n,m,p} [(\langle n | K | m \rangle \langle m | A | p \rangle \langle p | (K^{-1}) | n \rangle)]^*. \quad (\text{A6})$$

Rearranging the order of the factors, and again using Eq. (A3) and the orthonormality and completeness of the basis, the right-hand side of Eq. (A6) becomes

$$\sum_{m,p} [\langle m | A | p \rangle \delta_{m,p}]^* = [\text{Tr}(A)]^*. \quad (\text{A7})$$

This is the desired result.

We are specifically concerned with expressions for expectation values of the form

$$\text{Tr}[B\rho(t)] = \text{Tr}[BU(t)\rho(0)U(t)^{-1}], \quad (\text{A8})$$

where  $B$  is a Hermitian operator.  $\rho(0)$  is the initial density operator, describing the spin system before the pulse sequence contained in  $U(t)$  is applied. Since  $\rho(t)$  is also Hermitian, the trace in Eq. (A8) is a real number. Then

$$\text{Tr}[B\rho(t)] = \text{Tr}\{[KBK^{-1}][KU(t)K^{-1}] \times [K\rho(0)K^{-1}][KU(t)^{-1}K^{-1}]\}. \quad (\text{A9})$$

This equation contains the symmetry information. In the most common case,  $\rho(0) = I_z$ . Equation (A9) then states that the expectation value of any spin angular momentum component after any applied pulse sequence is unchanged by a change of the overall sign of the spin couplings, as a result of Eqs. (A2) and (A4). Similarly, the expectation value of any bilinear function of angular momentum components does change sign when the overall sign of the couplings is changed. No special symmetry restrictions need be placed on the applied pulse sequence.

Obviously, the foregoing discussion applies to an arbitrary

sequence of rf pulses and delays, not merely to composite pulses. The only requirement is a bilinear internal Hamiltonian.

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