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Multipole Theory of Composite Pulses

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From the results for a pure pulse from the multipole theory of nuclear magnetic resonance, it is possible to obtain general analytical expressions for the decomposition of a single pulse into a product of a number of constituent pulses. These pulses, which are represented as Wigner rotation matrices, have the angles as functions of the off-resonance frequency and the rf amplitude. By multiplying 3×3 matrices n times it is possible to generate the analytical expressions for n composite pulses which describe the three components of the magnetization vector. These are exact for all off-resonance conditions and for any spin magnitude. Our theoretical results agree with experimental data presented here and elsewhere. © 1987 Academic Press, Inc.

INTRODUCTION

Composite pulses have been found to be useful in a number of experimental applications where it is necessary to overcome instrumental shortcomings. These pulse sequences have been developed to compensate for rf inhomogeneity, off-resonance effects, and phase distortion (*1*). In this paper we will show that the multipole theory (*2, 3*) generates analytical expressions which agree exactly with other theoretical approaches and with experiment. We use some composite pulse sequences given in the literature to test our theory.

Since a hard pulse causes the magnetization vector to rotate through an angle, and since any rotation can be written as a product of rotations, then a product of pulses can be treated as a product of rotations. One difficulty that arises is when one attempts to determine which angles and phases the composite pulses should take with the goal of retaining unchanged the overall effect of the total pulse on the resonance spins. In essence one seeks the conditions which render the off-resonance spins insensitive to their offset. An example of a composite pulse sequence with a clear physical picture of why off-resonance spins should be rotated like resonance spins is the inversion pulse, $90^\circ_x\ 180^\circ_y\ 90^\circ_x$ (*4*). Unfortunately, it is not possible to carry these physical pictures very far since the visualization becomes too complicated and, alternatively, numerical simulation sacrifices physical insight. Hence, an exact analytical description would facilitate the understanding and development of composite pulses. Blümich and Spiess (*4*) have noted quarternions may be used to determine the net rotation angle and the effective rotation axis of a composite pulse sequence. Counsell *et al.* (*5*) have modified the quarternion approach by eliminating matrix multiplication which is tractable up to three pulses. Use of the multipole theory gives a simple analytical solution which

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allows for the calculation of the net magnetization and phase distortion as a result of any number of composite pulses (any angle and phase) at any resonance offset and for any spin magnitude. For a few composite pulses, the rotation matrices can be explicitly evaluated in terms of sines and cosines. We prefer, however, to consider the rotation matrices as the essential functions since these have well known properties which can be exploited.

THEORY OF A PURE PULSE

Using the standard Hamiltonian for pure pulses, which are the same as hard or delta pulses,

$$\mathscr{H} = \hbar\omega_0 \hat{I}_z + \omega_1 \hbar \cos(\omega t + \phi)\hat{I}_x - \omega_1 \hbar \sin(\omega t + \phi)\hat{I}_y \quad [1]$$

the objective is to solve the quantum Liouville equation for the density matrix

$$i\hbar \frac{\partial \sigma}{\partial t} = [\mathscr{H}, \sigma]_- \quad [2]$$

for any spin I at any initial condition. At this point there is a considerable divergence of the two main methods used. One method, in popular use, is to exponentiate the Hamiltonian and calculate the series of commutators

$$\sigma(t) = T\left\{\exp\left[-i\int_0^t \mathscr{H}(t)/\hbar\, dt\right]\right\}\sigma(0)T\left\{\exp\left[i\int_0^t \mathscr{H}(t)/\hbar\, dt\right]\right\}. \quad [3]$$

Although this is a valid approach it becomes tedious to evaluate so many commutators, especially as the spin magnitude increases. To circumvent this difficulty, one simplification in this approach is to consider the initial condition as $\sigma(0) = I_z$ rather than the more general products of spin operators.

The other method, used here, is the differential equation approach. The solution is easily obtained because the operator basis is chosen to be tensors irreducible under the rotation group. These tensor operators change their orientation by unitary transformations which are represented as Wigner rotation matrices. We express the spin density operator in a basis of irreducible tensor operators,

$$\sigma(t) = \frac{1}{2I+1}\sum_{kq} \phi_q^k(t)\mathscr{Y}^{kq}(\mathrm{I}) \quad [4]$$

where the operators obey the normalization

$$\mathrm{Tr}\{\mathscr{Y}^{kq\dagger}(\mathrm{I})\mathscr{Y}^{k'q'}(\mathrm{I})\} = \delta_{kk'}\delta_{qq'}(2I+1). \quad [5]$$

These tensor operators have been extensively discussed by one of the authors (*2*) and in numerous books on angular momentum theory (*7*). Using the differential equation approach, the one commutator in Eq. [2] is evaluated, and the resulting set of coupled differential equations is solved. In this way one calculates the coefficients $\phi_q^k(t)$ in Eq. [4] which once known, completely determines the density operator and the state, and hence solves the problem. In the case at hand, the solution is particularly simple being valid for any spin magnitude from any initial condition, and is given by (*3*)

$$\hat{\phi}_q^k(t) = \sum_{q'} \mathcal{D}_{qq'}^k(\alpha + \phi, \beta, \alpha - \phi + \pi)\phi_{q'}^k(0) \qquad [6]$$

where the angles are defined below and the hat refers to the rotating frame of the applied radiation

$$\hat{\phi}_q^k(t) = e^{i\omega q t}\phi_q^k(t). \qquad [7]$$

Equation [6] expresses the well known effect of a pulse: that is, the spin states are rotated from one orientation to another. Although rotation matrices exist in solutions of the state space problem, the rotation matrices in that case are $\mathcal{D}^I$ and not $\mathcal{D}^k$. Consequently, this approach is more appealing than the state space problem since the spin magnitude does not appear in the exact result. Hence, the pure pulse functions for *any* spin magnitude is given by Eq. [6]. As noted by Morajana, the angles through which spin I operators rotate as the result of a pulse are functionally all the same. The only difference between a spin $\frac{1}{2}$ and a spin I is that there are more operators available as the magnitude of the spin increases. If we are treating the magnetization vector, $k = 1$, then the results are equally valid for all spins.

We have solved and reported earlier (*3*) the angles which appear in the Wigner rotation matrices. These are given by

$$\cos\beta = \frac{1}{\Omega^2}[\Delta\omega^2 + \omega_1^2\cos(\Omega t)] \qquad [8]$$

$$\sin\beta = \frac{2\omega_1}{\Omega}\sin(\Omega t/2)\cos(\beta/2) \qquad [9]$$

$$\sin\alpha = -\frac{\cos(\Omega t/2)}{\cos(\beta/2)} \qquad [10]$$

$$\cos\alpha = -\frac{\Delta\omega}{\Omega}\frac{\sin(\Omega t/2)}{\cos(\beta/2)} \qquad [11]$$

where

$$\Delta\omega = \omega - \omega_0 \qquad [12]$$

and

$$\Omega = \sqrt{\Delta\omega^2 + \omega_1^2}. \qquad [13]$$

In using these expressions it can be seen from Eq. [6] that if a pulse is applied at equilibrium, the z component of the magnetization is proportional to $\phi_0^1(0)$ and explicitly one obtains,

$$\hat{\phi}_x(t) = -\cos(\alpha - \phi + \Delta\omega t)\sin\beta\,\phi_0^1(0) \qquad [14a]$$

$$\hat{\phi}_y(t) = -\sin(\alpha - \phi + \Delta\omega t)\sin\beta\,\phi_0^1(0) \qquad [14b]$$

$$\hat{\phi}_z(t) = \cos\beta\,\phi_0^1(0). \qquad [14c]$$

At resonance one can show that $\alpha = -\pi/2$ and $\beta = \omega_1 t$. As an example, if the pulse is applied about the y axis, then

$$\hat{\phi}_x(t) = \sin \omega_1 t\, \phi_0^1(0) \quad [15a]$$

$$\hat{\phi}_y(t) = 0 \quad [15b]$$

$$\hat{\phi}_z(t) = \cos \omega_1 t\, \phi_0^1(0). \quad [15c]$$

Comparison between Eq. [14] and Eq. [15] shows the difference between resonance and off-resonance. In particular, the major difference is due to phase distortion (8) through α.

We prefer, however, to abandon the use of sines and cosines and represent the effects of a pulse in terms of the Wigner rotation matrices. We do this in order to display the separate effects of rf phase, ϕ, and effective off-resonance flip angle, Ω, and to use the properties of rotation matrices. Rotation matrices arise naturally from the effective field (or tilted) frames, which differ with resonance offset. In these forms the polarizations $\psi_{\bar{q}}^k(t)$ simply precess according to,

$$\tilde{\psi}_{\bar{q}}^k(t) = e^{i\Omega \bar{q} t} \psi_{\bar{q}}^k(0) \quad [16]$$

where these are related to the laboratory rotating frame polarizations, $\hat{\phi}_q^k(t)$, by

$$\tilde{\psi}_{\bar{q}}^k(t) = \sum_q e^{iq\phi} d_{\bar{q}q}^k(\theta) \hat{\phi}_q^k(t) \quad [17]$$

with

$$\cos\theta = \Delta\omega/\Omega. \quad [18]$$

This leads to the useful expression,

$$\hat{\phi}_q^k(t) = \sum_{q'} \mathcal{D}_{qq'}^k(\alpha+\phi, \beta, \alpha-\phi+\pi)\hat{\phi}_{q'}^k(0) = \sum_{\bar{q}} e^{-iq\phi} d_{q\bar{q}}^k(\theta) e^{i\bar{q}\Omega t} d_{\bar{q}q'}^k(\theta) e^{-iq'\phi} \hat{\phi}_{q'}^k(0) \quad [19]$$

which is in terms of Wigner rotation matrices.

THEORY OF COMPOSITE PULSES

Rotations form a group and hence the product (matrix multiplication) of two rotations is again a rotation. This group property is expressed by

$$\mathscr{D}^k(\omega_{12}) = \mathscr{D}^k(\omega_2)\mathscr{D}^k(\omega_1) \quad [20]$$

and hence repeating the process gives also

$$\mathscr{D}^k(\omega) = \prod_{i=1}^{n} \mathscr{D}^k(\omega_i). \quad [21]$$

A composite pulse is understood to be the replacement of one pulse (LHS), which usually has a desired effect upon spins at resonance, by composite pulses (RHS) which have overall exactly the same effect as the LHS at resonance, but which, if chosen judiciously, will minimize the effects giving rise to the spectral width of the system such as resonance offset.

Therefore, using Eq. [6] and Eq. [21], the effect of two composite pulses $(\beta_2)_{\phi_2}(\beta_1)_{\phi_1}$, can be written as

$$\phi_q^1(t) = \sum_{q'} \mathcal{D}_{qq'}^1(\alpha_2+\phi_2, \beta_2, \alpha_2-\phi_2+\pi)\mathcal{D}_{qq'}^1(\alpha_1+\phi_1, \beta_1, \alpha_1-\phi_1+\pi)\phi_q^1(0). \quad [22]$$

In terms of sines and cosines where $\beta_i = \omega_i t_i$ and ϕ_i are the pulse phases, the result is given by

$$\tilde{\phi}_x(t) = \cos(\alpha_2 + \pi - \phi_2)\{\sin\beta_1\cos\beta_2 + \cos\beta_2\sin\beta_1\cos\alpha\} - \sin(\alpha_2 + \pi - \phi_2)\{\sin\beta_1\sin\alpha\} \quad [23]$$

$$\tilde{\phi}_y(t) = \cos(\alpha_2 + \pi - \phi_2)\{\sin\beta_1\sin\alpha\} + \sin(\alpha_2 + \pi - \phi_2)\{\sin\beta_1\cos\beta_2 + \cos\beta_1\sin\beta_1\cos\alpha\} \quad [24]$$

and

$$\tilde{\phi}_z(t) = \cos\beta_1\cos\beta_2 - \sin\beta_1\sin\beta_2\cos(\alpha + \pi) \quad [25]$$

where

$$\alpha = \alpha_1 + \alpha_2 + \phi_2 - \phi_1 \quad [26]$$

and the pulses are applied on the equilibrium state $\phi_0^1(0) = 1$. Imposing the resonance condition again, these equations, for $\phi_1 = \phi_2 = \pi/2$, reduce to

$$\tilde{\phi}_x(t) = \sin(\omega_1(t_1 + t_2))$$

$$\tilde{\phi}_y(t) = 0$$

$$\tilde{\phi}_z(t) = \cos(\omega_1(t_1 + t_2)) \quad [27]$$

as expected (cf. Eq. [15]). The results for only two pulses in terms of sines and cosines Eqs. [23]–[25] are not easily visualized and visualization becomes more difficult for higher tensor ranks and more composite pulses. Therefore, the exact result for n composite pulses is better left in the form

$$\tilde{\phi}_q^k(t) = \sum_{q_1 q_2 \cdots q_n} \mathcal{D}_{qq_n}^k(\Omega)\mathcal{D}_{q_n q_{n-1}}^k(\Omega_{n-1}) \cdots \mathcal{D}_{q_2 q_1}^k(\Omega_1)\phi_{q'}^k(0). \quad [28]$$

COMPARISON WITH OTHER THEORIES AND WITH EXPERIMENT

Levitt (*9*) considers expansions in the smallness of $|\Delta\omega/\omega_1|$ to obtain analytical results. This approach, valid for small resonance offsets, allows him to build up composite pulse sequences which compensate for larger $|\Delta\omega/\omega_1|$. In his calculation, Levitt solves the Schrödinger equation for each $\Delta\omega$ and choice of angles and plots the calculated curves for three composite pulse sequences. In Fig. 1 we plot our results for the same three sequences using Eq. [28]. For small offsets the analytical results agree exactly with Levitt's numerical work. Additionally, we used some of Shaka's composite pulses (*10*) to test our theory. He considers a spin-$\frac{1}{2}$ system and multiplies 2×2 rotation matrices $\mathcal{D}^{1/2}$ to obtain his results. Our calculations are shown in Fig. 2 and agree exactly with Shaka's numerical results. Experimental verification of these composite pulses has not been published at the time of writing, except for $m = 6$, therefore we did the experiments to further support our results (Fig. 3). The calculations and experiments were carried out to offsets beyond the intended performance of the composite pulse sequences to show the agreement between experiment and theory; all the oscillations are faithfully reproduced by the theory. A Fortran program which will accommodate any number of pulses at any offset was used in the calculations. The program takes approximately one-half second to calculate a composite pulse with 30

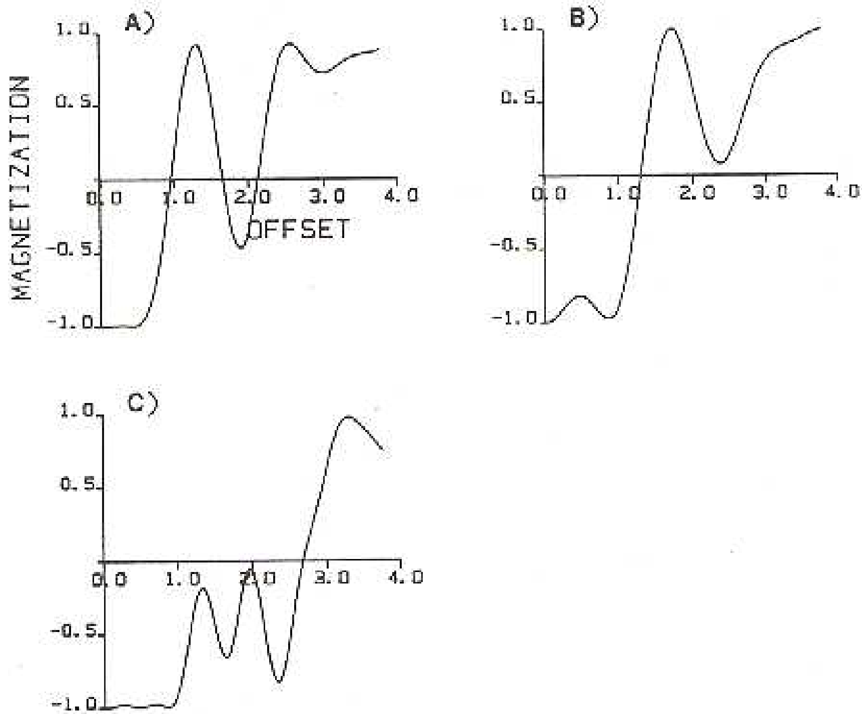

FIG. 1. Exact analytical calculations of inversion composite pulses agree with Levitt's exact numerical results (*9*). (A) Composite pulse $90^\circ_x\ 240^\circ_y\ 90^\circ_x$. (B) Composite pulse $90^\circ_x\ 180^\circ_y\ 90^\circ_x$. (C) Composite pulse $90^\circ_x\ 200^\circ_y\ 80^\circ_{-y}\ 200^\circ_y\ 90^\circ_x$.

elements for each choice of $|\Delta\omega/\omega_1|$ on an IBM-AT and can be used to evaluate any composite pulse sequence designed for single spin systems.

DISCUSSION

Two limiting factors are immediately apparent in composite pulses. First, we note that as a single pulse is replaced by a product of more and more pulses, then the time of the overall pulse sequence becomes longer. Under this condition the pulse may no longer be pure. In other words, the spin system may be governed by more than just the Zeeman Hamiltonian. Second, for any one pulse, as $\Delta\omega$ becomes large, the angle β becomes zero and no rotation occurs. Mathematically this is expressed by the relation

$$\lim_{|\Delta\omega/\omega_1|\to\infty} \mathcal{D}^k(\Omega) = \mathbf{E}^k \quad [29]$$

where Ω denotes the angles described above and $\mathbf{E}^k$ is the identity matrix of order $2k + 1$. Therefore one can conclude that by the method inherent in Eq. [21] no composite pulse sequence can be fully compensatory for all off resonances. We remark, however, that very large off-resonance effects can be accomplished (*10*). Within current spectral

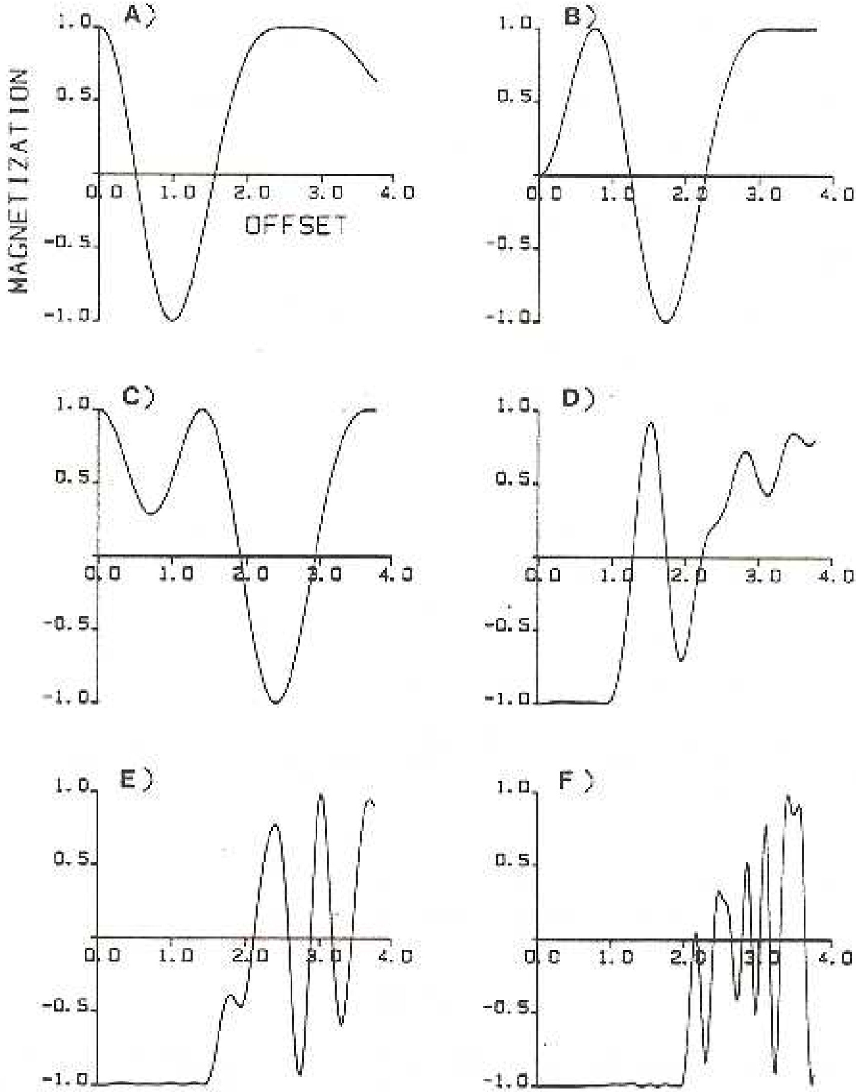

FIG. 2. Exact analytical calculations agree with Shaka's exact numerical results (*10*). (A) Selective composite pulse $127.3^\circ_x\ 127.3^\circ_{-x}$, $|\Delta\omega/\omega_1| = 1.0$. (B) Selective composite pulse $90^\circ_x\ 90^\circ_{-x}\ 90^\circ_x$, $|\Delta\omega/\omega_1| = 1.73$. (C) Selective composite pulse $68.9^\circ_x\ 68.9^\circ_{-x}\ 68.9^\circ_x\ 68.9^\circ_{-x}$, $|\Delta\omega/\omega_1| = 2.41$. (D–I) are inversion composite pulses composed of m pulses with $m = 4, 6, 11, 15, 25, 31$, respectively (see Ref. (*10*) for details).

windows composite pulses may work well and the theoretical limit, Eq. [29], is presently beyond experimental limitations.

It is not the purpose of this article to present new pulse sequences, but rather to give straightforward exact analytical solutions to further the understanding of composite pulses. Insight into composite pulses can be gained by exploiting the properties of Wigner rotation matrices. To give an example of the utility of Eq. [28], consider the

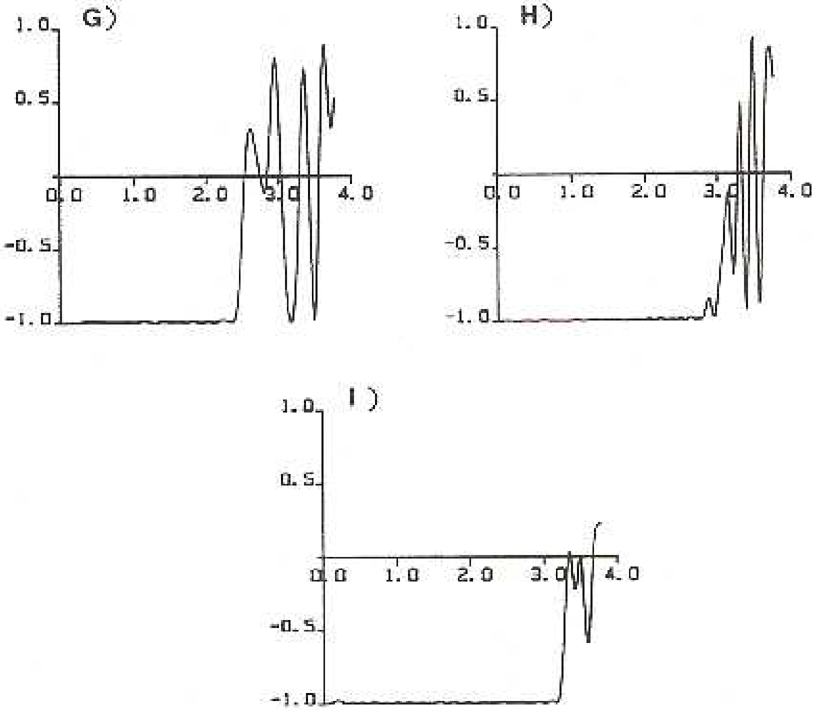

FIG. 2—*Continued.*

inversion of a spin system at a particular off-resonance value $\Delta\omega$ using phase alternating pulses. The off-resonance angle θ appears in Ω as

$$\Omega t = \csc\theta\omega_1 t \qquad [30]$$

and for inversion of the magnetization we assume that $\Omega t = \pi$. The nominal flip angle depends on $\Delta\omega$ via the relation,

$$\omega_1 t = \pi \sin\theta. \qquad [31]$$

By using the relation (7),

$$\sum_{\bar{q}} d^k_{q\bar{q}}(\theta) d^k_{\bar{q}q'}(\theta) = d^k_{qq'}(2\theta) \qquad [32]$$

it can be shown that n pulses give

$$\hat{\phi}^k_q(t) = \sum_{q'} e^{-iq\phi} d^k_{qq'}(2n\theta) e^{iq'\phi} \phi^k_{q'}(0). \qquad [33]$$

Without loss of generality we put $\phi = 0$ (which is a pulse initially along the x axis), and find the effect of n pulses on various off-resonance spins. For example, inversion from the $+Z$ component of the magnetization, $\phi^1_0(0) \propto 1$, to the $-Z$ component, $\phi^1_0(t) = -1$ requires

$$2n\theta = \pi. \qquad [34]$$

Hence for specific off-resonance spins in the effective field direction described by θ, inversion is obtained by n pulses given by the condition in Eq. [34]. For example,

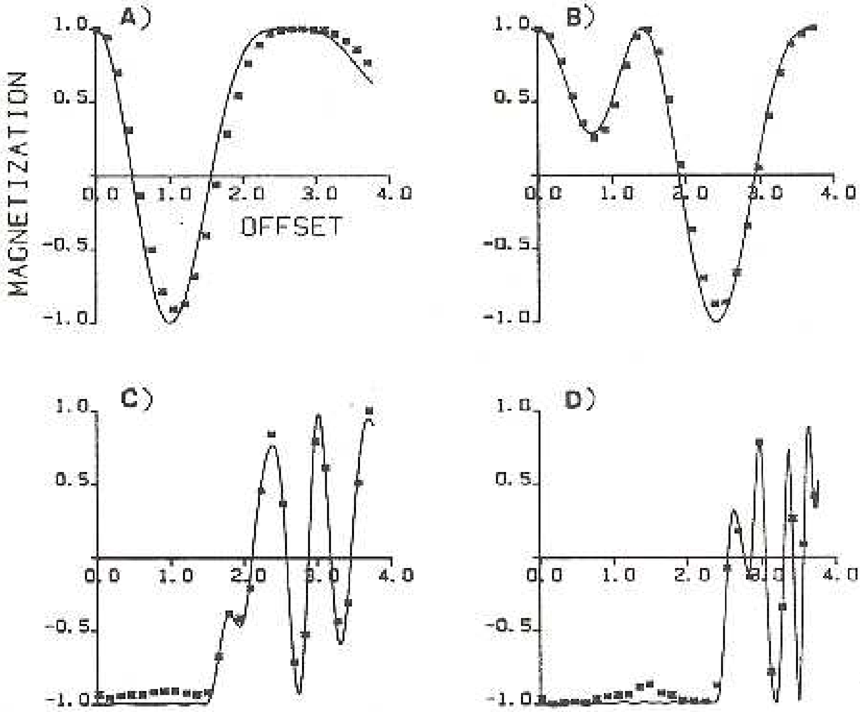

FIG. 3. Experimental points (stars) are compared with the calculated curves. Spectra were obtained on a Varian XL-200 spectrometer using a sample of 10% H_2O in D_2O. The rf field was calibrated and set at 6.8 kHz. The composite pulses were applied at offsets in multiples of 500 Hz. The read pulse was phase cycled and applied at exact resonance. (A) A two-pulse sequence $127.3^\circ_x\ 127.3^\circ_{-x}$, with selective inversion at $|\Delta\omega/\omega_1| = 1.0$. The poor agreement here is probably due to pulse length adjustment. The other composite pulse sequences compensate better for this error. (B) A four-pulse sequence $68.9^\circ_x\ 68.9^\circ_{-x}\ 68.9^\circ_x\ 68.9^\circ_{-x}$, with selective inversion at $|\Delta\omega/\omega_1| = 2.41$. (C) Inversion composite pulse $m = 6$ (*10*). (D) Inversion composite pulse $m = 15$ (*10*).

consider a pulse sequence consisting of two pulses ($n = 2$). In this case $\theta = 45°$ and $|\Delta\omega/\omega_1| = 1$. Hence the pulse sequence $127.3_x\ 127.3_{-x}$ inverts spins at $|\Delta\omega/\omega_1| = 1$. Similarly if $n = 3$, $\theta = 30.12°$ then three phase alternating pulses of 90° will invert spins at off-resonance position $|\Delta\omega/\omega_1| = 1.73$. Likewise four phase alternating pulses of 69° inverts spins at $|\Delta\omega/\omega_1| = 2.41$. This rationalizes the pulse sequences given in Figs. 2A–C (*10*).

CONCLUSION

In this paper we present a simple formula which can be easily investigated analytically, from the properties of rotation matrices, and numerically to test composite pulse sequences. Extension of the experimental data to the oscillatory ranges in Fig. 3 show that the theoretical results can be used to accurately study regions far off resonance. The expressions are valid not only for the magnetization vector, but also for all other polarizations which can occur for spins of higher magnitude where only the Zeeman term dominates.

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Note added in proof. The experimental verification of all the pulse sequences mentioned in Fig. 2 have since been published by Shaka *et al., J. Magn. Reson.* **67**, 580 (1986).

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