ITERATIVE SCHEMES FOR BROAD-BAND AND NARROW-BAND POPULATION INVERSION IN NMR

R. TYCKO and A. PINES
Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

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We derive iterative schemes for generating rf pulse sequences that invert nuclear spin populations over either broad or narrow ranges of resonance offsets and rf amplitudes. The schemes employ only phase shifting and concatenation operations. Iterative application of a scheme produces a series of pulse sequences with successive improvements in population inversion performance.

1. Introduction

Broad-band excitation of spins or two-level systems by coherent radiation is a problem that has attracted attention in nuclear magnetic resonance (NMR) [1–11] and coherent optics [12], due to both its intrinsic interest and its practical importance. With some exceptions [2,7], work in NMR has centered on the design of sequences of contiguous, phase-shifted radiofrequency (rf) pulses to replace the traditional single $\pi/2$ and π pulses. Called composite pulses, such sequences perform some or all of the functions of single pulses, but produce uniform excitation over larger ranges of resonance offsets [1–8], rf amplitudes [1–3, 6, 8, 9] or spin couplings [10,11].

Recently, iterative schemes for generating composite pulses have appeared [13,14]. In general, an iterative scheme is an operation that is applied repetitively to some initial pulse sequence S_0, producing a series of iterates S_1, S_2, S_3, etc., with increasingly desirable properties. Iterative schemes have been used previously in multiple-quantum NMR [15] and in heteronuclear decoupling techniques [5,16,17]. In this Letter, we introduce a new class of iterative schemes that generate pulse sequences for spin population inversion over large ranges of rf amplitudes and resonance offsets, simultaneously. A variant of that class produces sequences for narrow-band population inversion which may be employed in a method for spatially localizing NMR signals in an rf field gradient [18].

2. Theory of schemes for broad-band population inversion

The net effect of any rf pulse sequence S_i acting on an isolated spin is to produce a rotation R_i in the space of spin angular momentum vector operators $\boldsymbol{I}$. In other words, the propagator for S_i can be written:

$$R_i = \exp(-\mathrm{i}\boldsymbol{\alpha}_i \cdot \boldsymbol{I}) , \tag{1}$$

where $\boldsymbol{\alpha}_i$ is a vector whose direction is the net rotation axis and whose magnitude is the net rotation angle. $\boldsymbol{\alpha}_i$ is a function of the rf amplitude ω_1 and the resonance offset $\Delta\omega$. If all the rf pulses in S_i are phase-shifted by ϕ, $\boldsymbol{\alpha}_i$ is rotated by φ about the static magnetic field direction, or z axis. A class of iterative schemes may be defined by the following operation:

(1) Form N phase-shifted versions of S_i, with phase shifts $\phi_1, \phi_2, ..., \phi_N$. N is taken to be an odd integer.

(2) Concatenate the N versions in order from 1 to N. The result is a new sequence S_{i+1} that is N times longer than S_i.

Iterative schemes of this type have been used by Warren et al. [15] for the selective excitation of multiple-quantum coherences. We describe such a scheme with the notation $[\phi_1, \phi_2, ..., \phi_N]$.

Population inversion can be viewed as a rotation of the spin density operator from its equilibrium condition of I_z to $-I_z$, or as a rotation of a magnetization vector from $+z$ to $-z$. A sequence that produces complete population inversion for some values of ω_1 and $\Delta\omega_1$ must have an overall propagator that produces a rotation by π about an axis in the xy plane. To focus on the problem of broad-band inversion, the propagator for S_i can be written with intact generality in an alternative form:

$$R_i = \exp[-i(I_x \cos\gamma + I_y \sin\gamma)\pi] \exp(-i\boldsymbol{\varepsilon}\cdot\boldsymbol{I}) , \quad (2)$$

where $\boldsymbol{\varepsilon}$ has a z component of zero. Thus, the effect of S_i appears as the product of two rotations about axes in the xy plane, the first by an angle $|\boldsymbol{\varepsilon}|$ and the second by π. If S_i produces complete population inversion for some combination of rf amplitude and resonance offset, $\boldsymbol{\varepsilon} = 0$. If the inversion is nearly complete, $\boldsymbol{\varepsilon}$ is small. Applying the iterative scheme, we generate a sequence S_{i+1} whose propagator to first order in $|\boldsymbol{\varepsilon}|$ is:

$$R_{i+1} = \exp[-i(I_x \cos\phi_T + I_y \sin\phi_T)\pi] \exp(-i\boldsymbol{\varepsilon}_T\cdot\boldsymbol{I}) , \quad (3)$$

where

$$\phi_T = \gamma + \sum_{n=1}^{N} (-1)^{n+1}\phi_n$$

and

$$\boldsymbol{\varepsilon}_T = \sum_{n=1}^{N} (\epsilon_x \cos\Gamma_n - \epsilon_y \sin\Gamma_n , \; (-1)^{n+1}\epsilon_y \cos\Gamma_n + (-1)^{n+1}\epsilon_x \sin\Gamma_n , 0).$$

For odd n, Γ_n is given by:

$$\Gamma_n = \phi_n + \sum_{m=1}^{n-1} (-1)^{m+1} 2\phi_m .$$

For even n, Γ_n is given by:

$$\Gamma_n = \phi_n - 2\gamma + \sum_{m=1}^{n-1} (-1)^{m} 2\phi_m .$$

If $\boldsymbol{\varepsilon}_T$ can be made to vanish by the proper choice of phase shifts, then the first-order deviation from complete population inversion in S_i will be removed in S_{i+1}. Thus, beginning with an initial pulse sequence S_0, it should be possible to generate a series of iterates S_1, S_2, S_3, etc., that invert spin populations essentially completely over increasingly large ranges of ω_1 and $\Delta\omega$, i.e. with increasing inversion bandwidths. For $N = 5$, $\boldsymbol{\varepsilon}_T$ vanishes when the following conditions hold to within an even multiple of π:

$$\Gamma_3 = \Gamma_1 + 2\pi/3 , \quad \Gamma_4 = \Gamma_2 + \pi , \quad \Gamma_5 = \Gamma_1 + 4\pi/3 . \quad (4)$$

In general, ϕ_1 can be taken to be zero, since a nonzero ϕ_1 merely adds overall phase shifts to the series of iterates. Then eq. (4) is satisfied by any iterative scheme of the form $[0, \phi_2, 2\phi_2 + 2\pi/3, 3\phi_2 + \pi/3, 4\phi_2 + 2\pi/3]$. Two specific examples are [0, 0, 120, 60, 120] and [0, 330, 60, 330, 0], with the phase shifts indicated in degrees.

3. Broad-band population inversion results

Taking a single π pulse as the initial sequence, the iterative schemes of section 2 should generate pulse sequences of 5^i phase-shifted π pulses with increasingly large inversion bandwidths. This prediction is born out in figs. 1 and 2, which show experimental data and simulations of population inversion as a function of $\Delta\omega$ and ω_1, respectively, for 5-, 25-, 125-, and 625-pulse sequences. Inversion is defined as the negative of the final z component of spin angular momentum, or magnetization, normalized to one. In figs. 1 and 2, ω_1^0 represents the nominal rf amplitude, used to establish the length of a single π pulse. For clarity, the rf phases of the individual pulses that comprise the 5-, 25-, and 125-pulse sequences are listed in table 1.

Fig. 3 shows a contour plot of the inversion as a function of both ω_1 and $\Delta\omega$ for the 25-pulse sequence. Essentially complete population inversion is produced for all rf amplitude and resonance offset combinations in a region defined approximately by $0.75\omega_1^0 < \omega_1 < 1.25\omega_1^0$ and $-0.5\omega_1^0 < \Delta\omega < 0.5\omega_1^0$. Larger regions are covered by the longer sequences.

The fact that the iterates generated by our scheme produce broad-band population inversion with respect to both the rf amplitude and the resonance offset simultaneously is a consequence of the theoretical approach. The two parameters are treated identically,

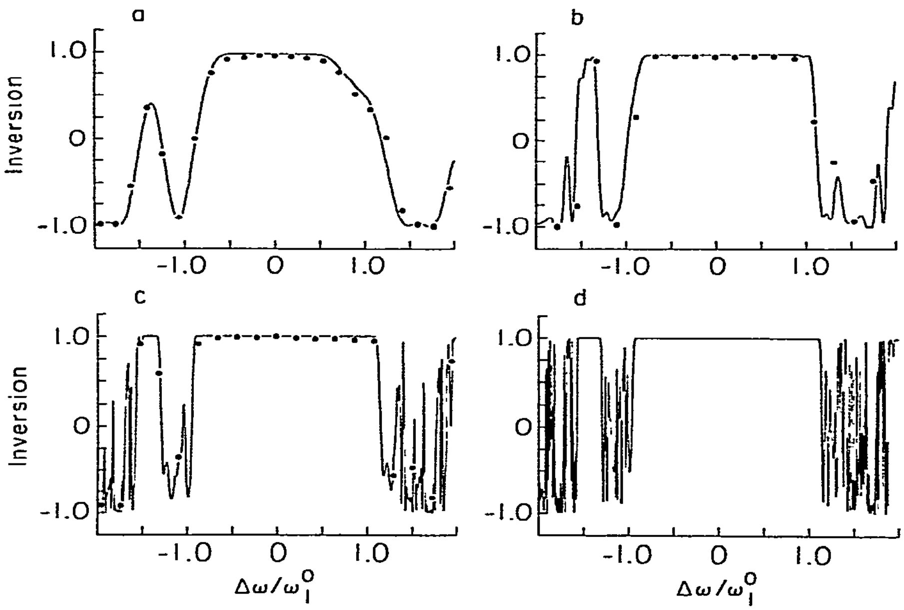

Fig. 1. The extent of population inversion as a function of the ratio of the resonance offset Δω to the radiofrequency (rf) field amplitude ω_1^0 for pulse sequences generated iteratively according to the scheme [0, 0, 120, 60, 120]. An inversion value of 1 corresponds to complete population inversion; a value of −1 corresponds to equilibrium populations. From (a) to (d), the pulse sequences are composed of 5, 25, 125, and 625 phase-shifted π pulses, with the phase shifts given in table 1. Computer simulations appear in the solid line. Experimental results, from ^{1}H NMR on a $H_2O(\ell)$ sample, appear in dots. The results apply to isolated spins or to two-level systems in general.

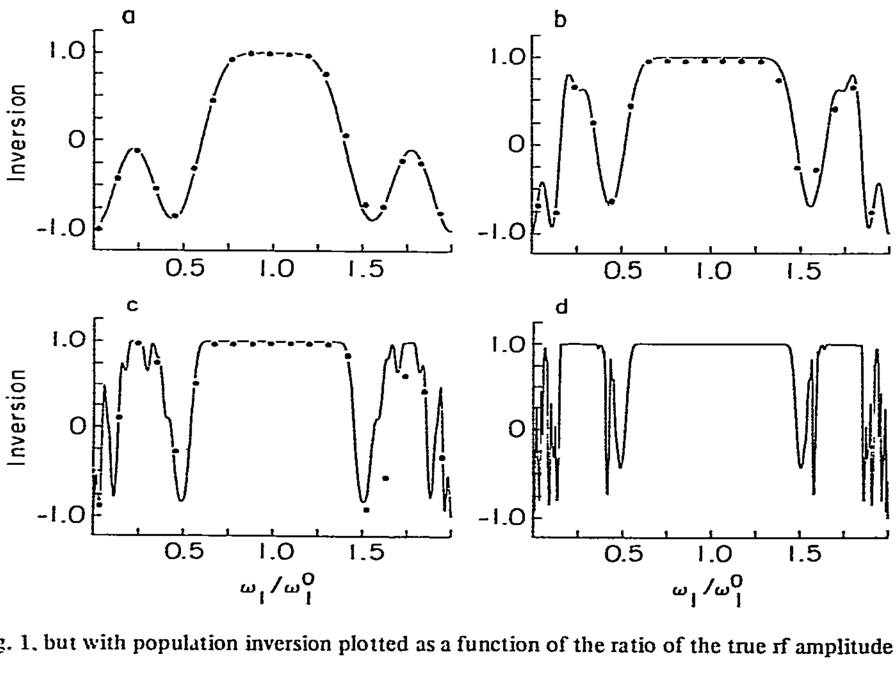

Fig. 2. Same as fig. 1, but with population inversion plotted as a function of the ratio of the true rf amplitude ω_1 to the nominal amplitude ω_1^0.

Table 1
rf phases (degrees) of individual π pulses in the broad-band inversion sequences S_1, S_2, and S_3 generated by the iterative scheme [0, 0, 120, 60, 120]

S_1:	0, 0, 120, 60, 120
S_2:	0, 0, 120, 60, 120, 0, 0, 120, 60, 120, 120, 120, 240, 180, 240, 60, 60, 180, 120, 180, 120, 120, 240, 180, 240
S_3:	0, 0, 120, 60, 120, 0, 0, 120, 60, 120, 120, 120, 240, 180, 240, 60, 60, 180, 120, 180, 120, 120, 240, 180, 240, 0, 0, 120, 60, 120, 0, 0, 120, 60, 120, 120, 120, 240, 180, 240, 60, 60, 180, 120, 180, 120, 120, 240, 180, 240 120, 120, 240, 180, 240, 120, 120, 240, 180, 240, 240, 240, 0, 300, 0, 180, 180, 300, 240, 300, 240, 240, 0, 300, 0, 60, 60, 180, 120, 180, 60, 60, 180, 120, 180, 180, 180, 300, 240, 300, 120, 120, 240, 180, 240, 180, 180, 300, 240, 300, 120, 120, 240, 180, 240, 120, 120, 240, 180, 240, 240, 240, 0, 300, 0, 180, 180, 300, 240, 300, 240, 240, 0, 300, 0

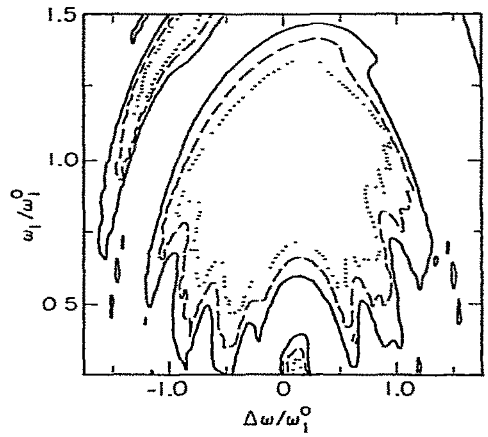

Fig. 3. A calculated contour plot of the population inversion performance of the 25-pulse sequence of figs. 1b and 2b, illustrating broad-band inversion with respect to the resonance offset $\Delta\omega$ and the rf amplitude ω_1 simultaneously. In the region enclosed by the dotted line, the inversion is greater than 0.99. Contours corresponding to an inversion of 0.90 (dashed line) and 0.50 (solid line) are shown as well.

merely as a source of the error ε in eq. (2). Similarly, the effects of certain other experimental imperfections, including phase transients and deviations from square pulse envelopes, are eliminated by iteration. The only requirement for the error introduced by an imperfection to cancel is that it transform under a phase shift as a rotation about the z axis. The cancellation of experimental imperfections probably contributes to the good agreement between the experimental results and the simulations in figs. 1 and 2, particularly for the 125-pulse sequence.

4. Experimental method

The pulse sequences in figs. 1 and 2 require rf phase shifts in all multiples of $\pi/3$. Consequently, a home-built NMR spectrometer, which normally operates with two independent quadrature phase generation circuits, was modified to combine the outputs of six rf gates. The relative phases of rf pulses from the various gates were measured with a vector voltmeter and adjusted with phase trimmers and delay cables. The amplitudes of the pulses were balanced with an oscilloscope. No tune-up sequences were used to adjust the phases and amplitudes.

The experiments were performed at 180 MHz on a small $H_2O(\ell)$ sample. The population inversion produced by a sequence S was measured as the signal amplitude resulting from S–τ–$\pi/2$, where τ stands for a delay during which transverse magnetization dephases. The signal amplitude following a single $\pi/2$ pulse alone was used for normalization. For fig. 1, S was applied off resonance, while the $\pi/2$ pulse was applied on resonance. As a matter of experimental convenience, the changes in ω_1 in fig. 2 were replaced by changes in the pulse lengths in S. On resonance, variations in ω_1 and in the pulse lengths are equivalent, since the rotation produced by a pulse is proportional to its area.

5. Narrow-band population inversion

The scheme [0, 120, 240] generates pulse sequences with narrow-band inversion properties [18]. Fig. 4 contains experimental data and simulations of population inversion as a function of ω_1 for 3-, 9-, 27-,

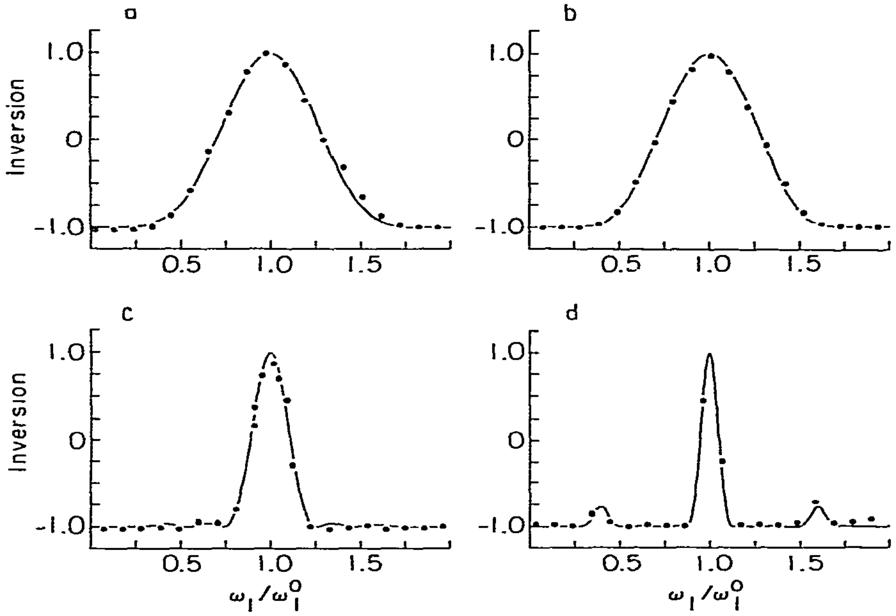

Fig. 4. The extent of population inversion as a function of the ratio of the true rf amplitude ω_1 to the nominal amplitude ω_1^0 for pulse sequences generated by the iterative scheme [0, 120, 240]. From (a) to (d), the pulse sequences are composed of 3, 9, 27, and 81 phase-shifted π pulses. Pulse sequences resulting from [0, 120, 240] exhibit narrow-band inversion.

and 81-pulse sequences that are the iterates of a single π pulse. The development of a narrow inversion profile by iteration is explained by considering the propagator for a sequence S_i in the form of eq. (1). If [0, 120, 240] is applied to generate S_{i+1}, the x and y components of α_{i+1} will vanish to first order in $|\alpha_i|$. Thus, if S_i produces a small rotation for some combination of $\Delta\omega$ and ω_1, S_{i+1} will produce a rotation about the z axis, leaving spin populations uninverted. On the other hand, if S_i already produces complete population inversion for some other combination, then so will S_{i+1}. Thus, referring to fig. 4, the complete inversion at $\omega_1 = \omega_1^0$ is preserved while the ranges of ω_1 over which populations are uninverted increase.

6. Discussion

In practical terms, the advantage of the iterative schemes for broad-band population inversion presented in this Letter over the schemes suggested by Levitt and Ernst [13] and by Shaka and Freeman [14] lies in their simultaneous broad-band properties with respect to the resonance offset and the rf amplitude. The previous schemes depend on the formation of inverse sequences, that is sequences S_i^{-1} that produce the inverse rotation of S_i. If resonance offsets are present, there is no exact, general prescription for forming inverse sequences, although an approximate method has been proposed [13]. Since resonance offsets and rf amplitude inhomogeneity are both significant experimental factors, simultaneous broad-band inversion is important.

Iterative schemes for generating pulse sequences may be analyzed according to a general theory that treats the schemes in this Letter as functions acting on rotation vectors α_i as in eq. (1). To the series of pulse sequences S_0, S_1, S_2, etc., there corresponds a series of vectors α_0, α_1,α_2, etc. These vectors are the iterates of α_0. They are generated by a function F, with $\alpha_n = F^n(\alpha_0)$. The particular form of F depends on the choice of phase shifts $\phi_1, \phi_2, ..., \phi_N$.

Certain vectors are fixed points of F, meaning that $\alpha = F(\alpha)$. Regardless of the choice of phase shifts, the vector $\boldsymbol{\alpha} = 0$ and the set of vectors of the form $\boldsymbol{\alpha} = (\pi \cos \gamma, \pi \sin \gamma, 0)$ are fixed. A fixed point is called stable if the iterates of points in the neighborhood of the fixed point converge to the fixed point. The stability of fixed points may be manipulated by varying the rf phase shifts that define an iterative scheme. Broad-band population inversion sequences are produced when vectors of the form $\boldsymbol{\alpha} = (\pi \cos \gamma, \pi \sin \gamma, 0)$ are stable as in section 2; narrow-band population inversion sequences are produced when the vector $\boldsymbol{\alpha} = 0$ is stable with respect to displacements in the x and y directions as in section 5.

Algebraic and numerical methods for analyzing the fixed-point properties of F have been developed. These methods may be used to select an initial pulse sequence whose iterates exhibit inversion bandwidths even larger than those shown in figs. 1 and 2. The methods of analysis will be presented in a later publication, along with full details of the general fixed-point theory.

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