Iterative Maps for Bistable Excitation of Two-Level Systems

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Iterative maps on SO(3) with two stable fixed points are described. These generate bistable spectroscopic excitation sequences for isolated two-level systems. From such sequences, tailored population inversion over specific ranges of parameters such as the resonance frequency or radiation amplitude can be obtained. The ideas developed here suggest ways of designing tailored excitation sequences useful in spatially selective NMR, spin decoupling, *nk*-quantum selective multiple-quantum NMR, and isotope-selective zero-field NMR.

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Excitation sequences have recently been developed for nuclear magnetic resonance (NMR) and optical spectroscopy which are effective over very broad[1–8] or very narrow[6,9] ranges of transition frequencies and radiation amplitudes. Of the methods conceived for deriving these sequences, an iterative approach based on the use of sequence-refining algorithms has proven particularly useful. By treatment of these algorithms as iterative maps,[10–12] it has been shown that stable fixed points lead to sequences with broad-band properties, while unstable fixed points produce sequences which exhibit narrow-band properties.[8] This Letter reports the first example of iterative maps for pulse sequences with more than one stable fixed point. From such maps, sequences for excitation over sharply defined, preselected ranges of parameters, e.g., frequencies or amplitudes, can be obtained. This provides the first experimental approach to the long-desired goal of tailored excitation of nonlinear spectroscopic responses in spin and optical systems. The implementation of this pass-band response has applications in several areas in spectroscopy, including spatially selective NMR,[13] selective *n*-quantum pumping of multiple-quantum transitions,[14] heteronuclear zero-field NMR,[15] and optical information storage.[16]

The sequences demonstrated here selectively invert the equilibrium populations of uncoupled two-level systems depending on the amplitude (commonly denoted ω_1) of the resonant radio-frequency (rf) radiation at the nuclear-spin position. This general technique can, in fact, be used to select one or several discrete ranges of rf amplitudes for specific excitation.

For the analysis of these sequences, we employ a formalism drawn from the theory of iterative maps and their fixed points.[10] The effect of a pulse sequence on some system is represented by its time development operator, or propagator, U. Usually a specific propagator $\bar{U}$ is desired, for example, one which corresponds to an inversion of the equilibrium populations. This can be achieved with an iterative algorithm which prescribes the transformation that must be performed on a pulse sequence for its propagator U to converge to the desired form $\bar{U}$. This iterative procedure can be summarized by the equation

$$U_{n+1} = F(U_n). \qquad (1)$$

The dynamics of such iterative maps are influenced by their fixed points,[10–12] which are defined by the rela-

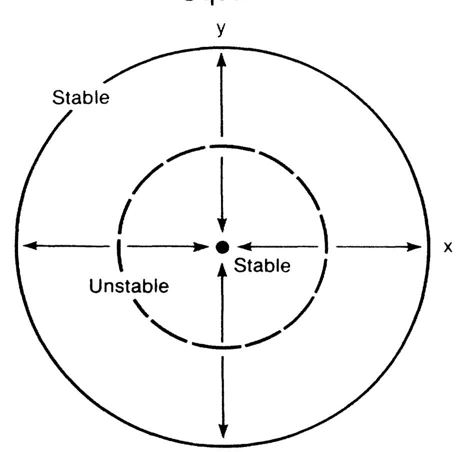
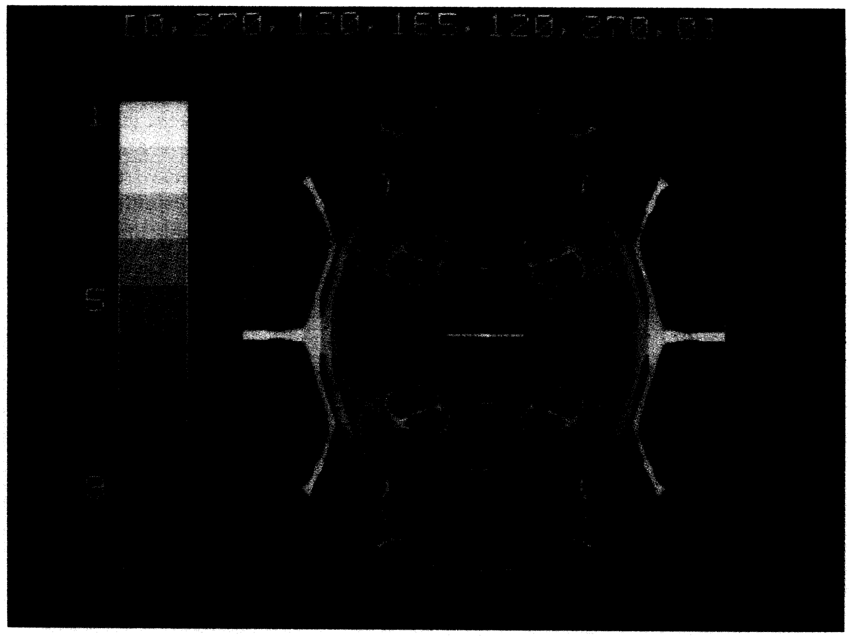


FIG. 1. Cross section of SO(3) through the *xy* plane indicating the movement of points in this plane as an algorithm designed to produce a bistable band-pass sequence is iterated. The origin and equator are stable fixed sets of this mapping with an unstable fixed circle between them. The position of the unstable set defines the effective bandwidth of the excitation. Points initially in the *xy* plane remain in this plane even after iteration of the algorithm as a result of the symmetry of the sequence.

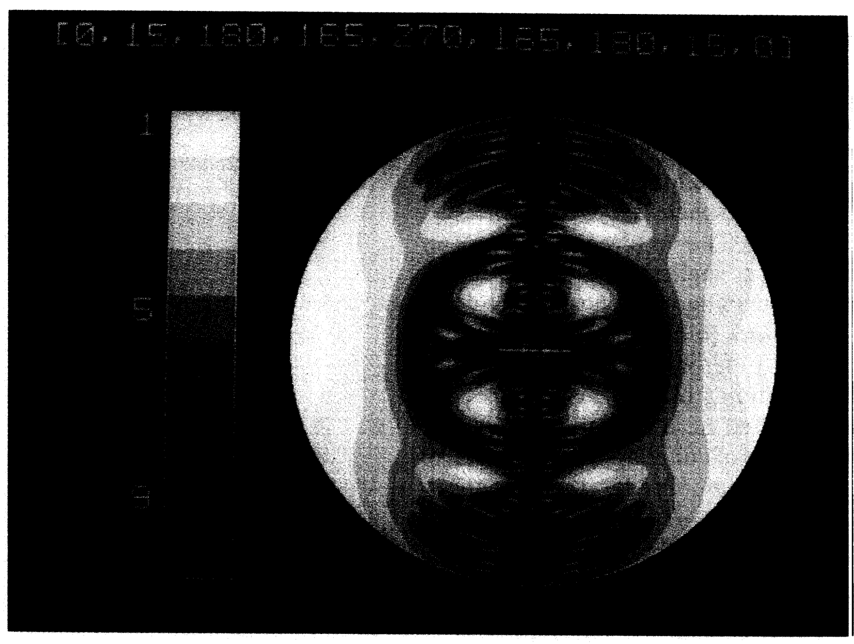
tion

$$\bar{U} = F(\bar{U}). \tag{2}$$

The consequences of fixed points and their stability on the behavior of iterative pulse-sequence maps have already been discussed in detail.[8] Briefly, it was shown that pulse-sequence algorithms could be considered as maps on a quantum-mechanical propagator space, with fixed points corresponding to the desired propagators $\bar{U}$.



(a)



(b)

FIG. 2. Basin images for the maps generated by the algorithms [0,270,120,165,120,270,0] and [0,15,180,165,270,165,180,15,0] showing a cross section of SO(3) containing the z axis. The number of iterations of the algorithm required to map a point in SO(3) to one of the two stable fixed sets is given by the density key to the left of the image.

In the absence of couplings, any propagator U, including the effects of pulse sequences, is describable as a simple rotation of the spin-density operator.[17,18] It follows that only a subspace of the entire propagator space need be considered in the analysis, namely the space of pure rotations, commonly designated SO(3),[19] which can be visualized as a solid sphere of radius π. Every rotation is uniquely defined in this space by a unit vector drawn from the origin (corresponding to the axis of the rotation) and a radius (corresponding to the angle of the rotation).

In general, the convergence of a map to its fixed points depends on the initial condition U_0 and the stability of the fixed points in various directions. The initial condition U_0 can itself be a function of several parameters, designated here as $\{\lambda_i\}$, such as the resonance frequency or the rf amplitude ω_1. In the devising of a sequence effective over broad ranges of λ_i, the objective is to make a single fixed point stable for as wide a range of the parameter λ_i as possible. For narrow-band sequences, the aim is to specify a single fixed point which is unstable over the parameter λ_i. For the present case of bistable pass-band sequences, however, two stable fixed points are required, so that for some values of λ_i, U converges to one fixed point $\bar{U}_1$, while for other values of λ_i, U converges to the other fixed point $\bar{U}_2$.

Pulse sequences which excite a pass-band population inversion in ω_1 can be obtained from maps which have the origin and the equator of SO(3) in the xy plane as stable fixed sets of points. These points correspond to the identity operator and the set of π rotations which take $+z$ to $-z$, respectively. The significance of this bistability can be appreciated by referring to Fig. 1. This figure shows schematically that maps with the origin and the equator of SO(3) as fixed sets stable in the xy plane necessarily possess an unstable circle of points also in the xy plane. Points in SO(3) inside this circle move towards the origin upon iteration of the algorithm, while points outside the circle move towards the equator.

Two algorithms derived to satisfy these stability conditions are

$$[0, 270, 120, 165, 120, 270, 0], \qquad \text{(a)}$$

$$[0, 15, 180, 165, 270, 165, 180, 15, 0]. \qquad \text{(b)}$$

Following the notation of Ref. 8, these algorithms are comprised of two basic operations, a series of phase shifts, shown in the brackets, followed by concatenation of the phase-shifted parts. Figure 2 depicts the basin images[8] of the two algorithms. The regions of SO(3) that are convergent to the stable fixed sets are known collectively as the basin of the map, and appear as the light areas of the image. The images in this instance are cross sections of SO(3) containing the z axis. Since algorithms comprised of simple phase shifts exhibit axial symmetry around the z axis, no information is lost in displaying a single cross section.

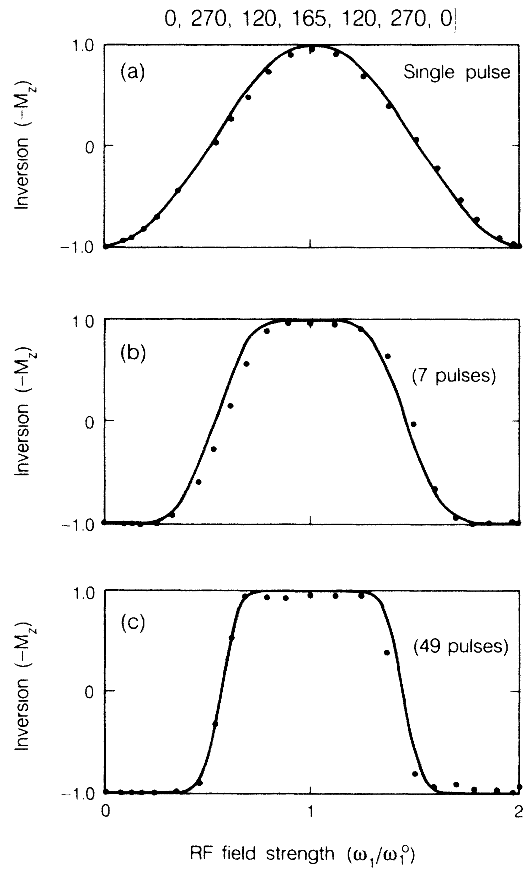


FIG. 3. Extent of nuclear-spin population inversion as a function of normalized on-resonance rf field amplitude for (a) a single π pulse, (b) one iteration of the indicated algorithm, and (c) two iterations of the algorithm. -1 on the y axis denotes the normalized equilibrium spin population (bulk magnetization aligned with the magnetic field), $+1$ denotes the normalized population-inverted state (magnetization antiparallel to the magnetic field). The effect of iteration is seen to sharpen the pass band of the response function. Such a bistable response can be tailored to different regions of ω_1. Experimental data were obtained from the proton resonance of a distilled-water sample at a Larmor frequency of 180 Mhz.

One conspicuous difference between the two images displayed is the size of their respective basins. The reason for this is that the nine-shift algorithm (b) was designed so that the equator would be stable in all directions. The seven-shift algorithm (a), however, is not stable at the equator for points off the xy plane. The basin for the nine-shift algorithms is therefore larger and exhibits a more intricate structure than does the seven-shift sequence. A consequence of this additional stability is that the nine-shift algorithm is broad band over resonance frequencies.

The implications of applying an algorithm described by a bistable map to a single nominal π pulse appear in Fig. 3. This figure shows that such algorithms, in this case the seven-shift algorithm, produce sequences which display distinctive pass-band characteristics in the ω_1 domain. This implies that only spins that lie within specified bandwidths in ω_1 will be inverted by these sequences. Spins outside these bands remain in their initial equilibrium state. The result is a pulse sequence which is highly amplitude selective in inverting nuclear spins. Moreover, as the algorithm is iterated, the pass band becomes sharper and more pronounced, indicating the refinement of the sequence by iteration. The experimental points on this curve demonstrate the practical feasibility of these algorithms for obtaining ω_1-selective inversion of the magnetization. Generalized tailoring of the population inversion can be achieved across a range of ω_1 values with the appropriate choice of an initial sequence. Sequences which favor certain basins in SO(3), or cross from one basin to another, create this kind of tailored response. Extensions of this approach are currently being undertaken for iterative mappings with multiple fixed points to allow general nonlinear excitation.

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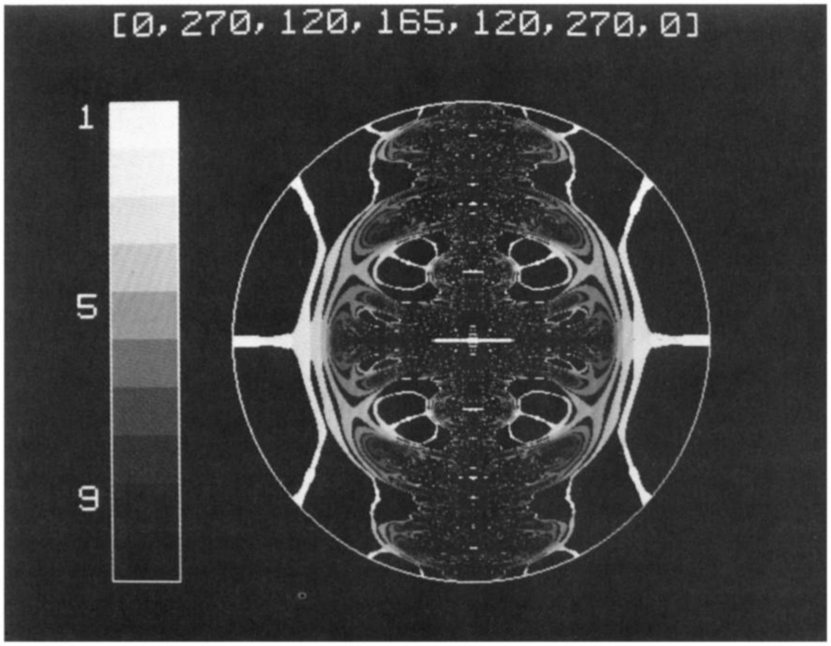
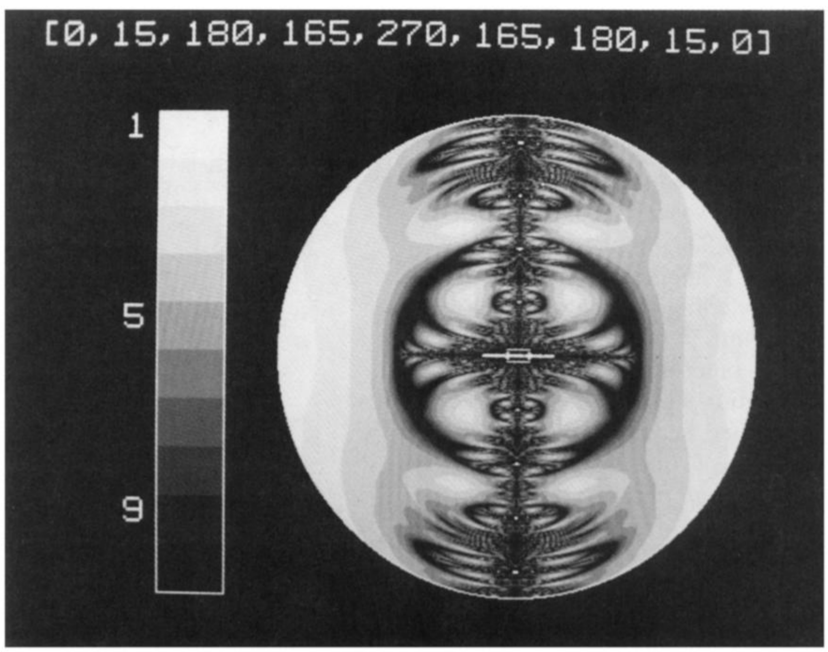


(a)



(b)

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