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Iterative Carr–Purcell Trains

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Iterative schemes have provided a new way to devise complex sequences of RF pulses. In broadband spin decoupling they offer a significant reduction in RF power deposition for a given operating bandwidth (*1, 2*) and much better tolerance of instrumental imperfections (*3, 4*). New composite pulses for broadband, narrowband, or band-pass inversion (*5–8*) or excitation (*9, 10*) have also been discovered. An iterative scheme defines an entire family of composite pulses at once, since many possibilities exist for the starting sequence and the iterative procedure can be terminated at different stages. It is, of course, necessary to terminate the procedure at some stage to obtain a composite pulse of finite duration.

In this communication we show that iterative schemes can also be interleaved with data acquisition as multiple-pulse sequences and, as an example, discuss an iterative version of the Carr–Purcell train (*11*). Unlike the Meiboom–Gill modification (*12*), our sequences stabilize long-term behavior of *both* components of transverse magnetization under the sequence of 180° refocusing pulses. This multiple-pulse scheme defines an entire family of echo trains depending on the nature of the inversion pulse and degree of iteration; we demonstrate the technique using conventional 180° pulses.

Neglecting relaxation, physical transport of the spins, and any time-dependent fluctuations in field, frequency, or amplitude, each 180° pulse in the echo train can be characterized by a unitary operator R and the pulses are identical except for the choice of RF phase. Pulses of different phase differ by a rotation about the z axis of the rotating reference frame, e.g.,

$$\bar{R} = \exp(-i\pi I_z)R\exp(i\pi I_z) \quad [1]$$

denotes phase inversion of R. The only information the iterative scheme uses is that each pulse is imperfect in exactly the same way.

We can factor the imperfect inversion pulse into an ideal part and an additional small rotation:

$$R = R_0 R_\delta, \quad [2]$$

where R_0 is a perfect 180° pulse (which we can assume to be along the x axis) and $R_\delta = \exp(-i\delta\mathbf{n}\cdot\mathbf{I})$ represents an error rotation due to pulse imperfections. The nature of the imperfection is unimportant: it could arise from a misadjustment of the pulse amplitude or duration, frequency mismatch caused by chemical shift or the imposition

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of static B_0 gradients, reproducible phase transients due to hardware limitations, or any combination of these factors.

Windowless sequences of inversion pulses have been extensively studied in the context of spin decoupling (*1–4*). In particular, the MLEV sequences (*1*) are an iterative way to construct sequences of 2^n inversion pulses such that the overall propagator for the sequence approaches the identity operator if δ is sufficiently small. In this case convergence is essentially geometric; that is, successive powers of δ are removed at each iteration. The overall length of the sequence grows geometrically as well, expanding by a factor of two at each stage. To the accuracy that the propagator is the identity operator, such a sequence of pulses should periodically return the density operator to its initial state. Transverse magnetization is therefore preserved under such a sequence.

Suppose each 180° pulse is sandwiched between equal delays τ. The propagator over a single element in the echo train becomes

$$\exp(-i\phi I_z)R\,\exp(i\phi I_z) = R_0\exp(i\phi I_z)R_\delta\exp(-i\phi I_z), \qquad [3]$$

where $\phi = \tau\Delta$ describes the free precession of the spins at resonance offset Δ during the time τ and we have made use of the property that R_0 inverts I_z. Equation [3]

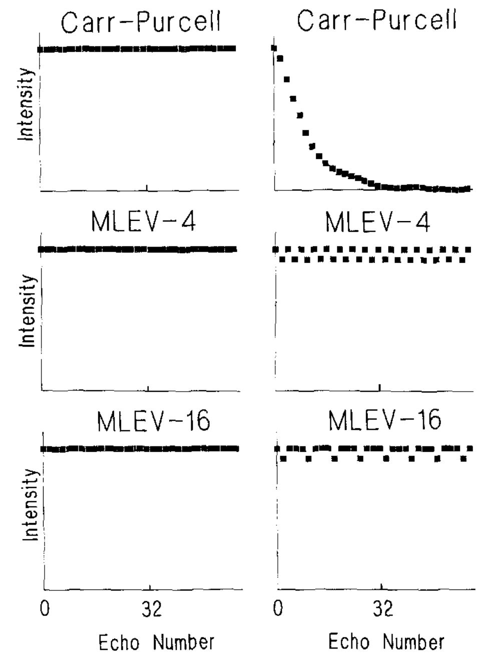

FIG. 1. Simulated time-domain signals resulting from various multiple-echo trains at exact resonance. Relaxation is neglected. The initial density matrix is $\rho(0) = I_y$, and the y magnetization is sampled once at what would be the apex of each even-numbered echo (if the 180° pulses were ideal). In each case, conventional 180° pulses are used to stimulate the spin echoes, and the overall phase of the refocusing pulses is y for the left-hand series and x for the right-hand series. In the conventional Carr–Purcell method all the pulses have the same phase (top), whereas, in the iterative Carr–Purcell trains, 180° phase shifts are applied to some of the refocusing pulses according to the MLEV iterative scheme. The very slight modulation of the signal when the Carr–Purcell method is applied with phase x is due to the finite sampling of the RF distribution function.

shows that, aside from a strong frequency-dependent phase shift of the error rotation, a Carr–Purcell train can be analyzed in the same way as the corresponding windowless sequence. Provided the phase shift ϕ remains constant throughout the echo train (fixed resonance offset) it does not interfere in any way with the desired cancellation of the R_δ rotations, which are allowed to be arbitrary in the first place. Accordingly, we can use sequences such as MLEV-4, MLEV-16, or MLEV-64 to stabilize the echo train.

Figure 1 shows a simulation comparing a conventional Carr–Purcell sequence with two iterative Carr–Purcell sequences derived from the MLEV decoupling sequences. The nominal value of the B_1 field is 10 kHz, giving a 50 μs 180° pulse, and we have set τ = 10 ms. A single resonance offset is assumed (Δ = 0), but the effects of spatial inhomogeneity of the RF field during the echo train are included by summing over a distribution of fields. Almost any reasonable distribution function will show similar qualitative behavior. We chose a Lorentzian distribution purely for convenience. The nuclear spin magnetization is initially aligned along the y axis of the rotating frame by a perfectly homogeneous 90° pulse and the various schemes are applied either with a relative phase of y (left-hand series) or x (right-hand series). A single data point is acquired at the top of *the even-numbered echoes,* for clarity, although the same considerations hold if the apex of each echo or each entire echo is sampled. Since relaxation is neglected, the ideal response is a perfect dc signal, indicating that the y magnetization is fully restored at each sampling. The Carr–Purcell train falls far short of this ideal

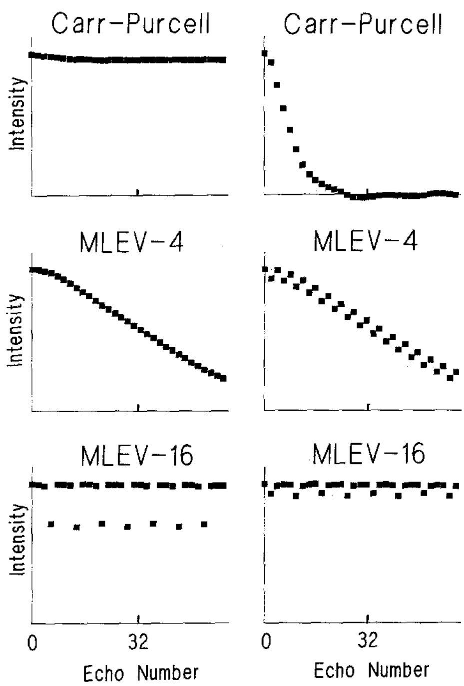

FIG. 2. Simulations carried out under the same conditions as those in Fig. 1 except that a resonance offset of 2 kHz has been assumed. The RF field strength is 10 kHz. The iterative Carr–Purcell trains show compensation when applied with phase x or phase y, whereas the conventional Carr–Purcell train dephases the magnetization quite rapidly when applied with relative phase x.

when applied with relative phase x, the inhomogeneity of the RF field resulting in a rapid decay of the signal. When applied with relative phase y (the Meiboom–Gill modification) the propagator describing the echo train commutes with the initial state of the spins and so a dc signal is obtained. The iterative Carr–Purcell sequences, on the other hand, show compensation for *both* components, as evidenced by the much longer decays. This compensation can be understood as a generalization of the Meiboom–Gill approach: the identity propagator commutes with *any* initial state of the spins.

Even the first stage of compensation, using the MLEV-4 scheme, shows much improved performance when applied with relative phase x. A pure dc signal is not obtained with the iterative Carr–Purcell trains because the compensation is most effective at the end of a certain number of 180° pulses; the minor modulation of the echo envelope is entirely analogous to that which produces "cycling sidebands" in broadband decoupling experiments (*4*) and does not interfere with the measurement of the width of the centerband resonance.

Maudsley (*13*) has argued that proper compensation for both the x and the y components of transverse magnetization is of some importance in NMR imaging experiments where, due to the application of phase-encoding gradients, no special relationship exists between the initial phase of the transverse magnetization and the phase of

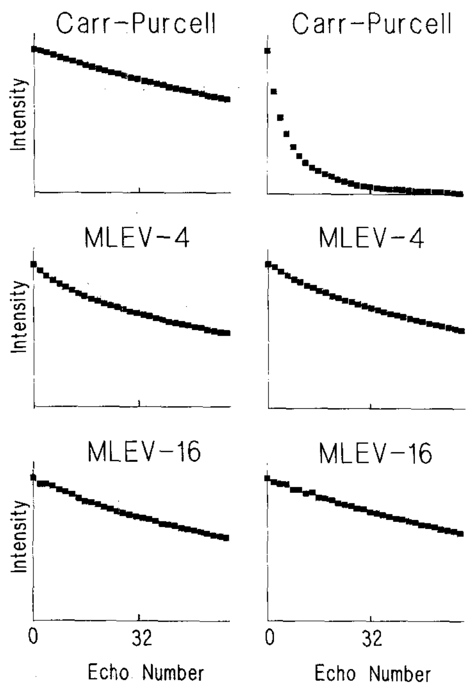

FIG. 3. Results from experiments carried out on a D_2O/H_2O sample. The RF frequency was carefully adjusted to exact resonance and the receiver phase aligned to maximize the signal in one of the quadrature channels. The data points are the measured signal in this channel, acquired at the peak of the even-numbered echoes. The refocusing pulses are applied with either phase y (left) or phase x (right), as in Fig. 1. As expected, the conventional Carr–Purcell train results in an accelerated decay when applied with relative phase x, but the iterative echo trains compensate both components.

the refocusing 180° pulses. In the presence of large field gradients, it may be necessary to consider the influence of resonance offset effects on the stability of the echo train. In Fig. 2 we show a simulation conducted under the same conditions as Fig. 1 except that a resonance offset $\Delta/2\pi = 2$ kHz is assumed. Once again the conventional Carr–Purcell train gives a very rapid decay when applied with relative phase x. With phase y there is an initial slight decay (as the component of the magnetization perpendicular to the effective field dephases) followed by the expected dc behavior. The MLEV-4 modification results in a similar decay time for both components, although the compensation is not effective enough to prevent a significant loss of echo intensity. However, the MLEV-16 echo train delivers a large improvement in the long-term behavior for both components, showing a dc signal as the dominant component. The modulation is deeper than in the on-resonance case because the propagator describing the echo train deviates further away from the identity operator at intermediate times.

Figures 3 and 4 show echo trains from a D_2O/H_2O sample, observed on a Bruker AM-400 spectrometer, at resonance offsets of 0 and 2 kHz, respectively. The RF field strength and interpulse delays match the simulations, and the RF distribution, though not purely Lorentzian, is of a comparable width to that used in the simulations. The phase of the initial 90° pulse and the receiver reference phase were cycled to select only magnetization originating from the first pulse. The major features of the simulations are reproduced by the experiment but a few minor points are worth mentioning. The initial 90° pulse, using a 10 kHz RF field, does not align the magnetization

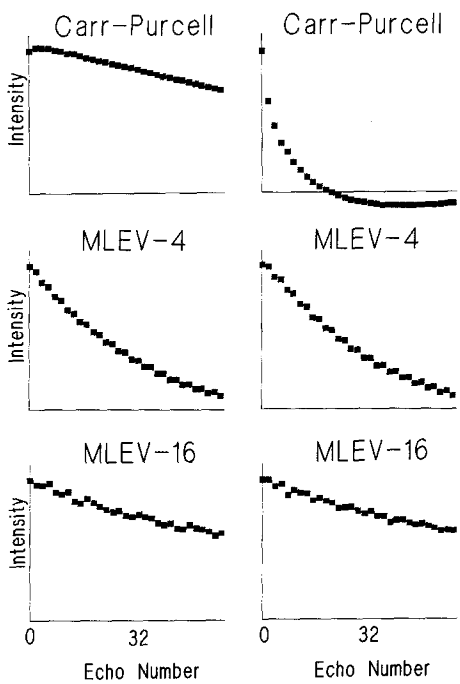

FIG. 4. Results obtained under the same conditions as Fig. 3 except that the transmitter frequency was moved 2 kHz off resonance. At this resonance offset the MLEV-16 scheme compensates pulse imperfections better than the MLEV-4 echo train.

perfectly along the y axis when the resonance offset is 2 kHz. This small phase shift has a relatively minor effect. The experimentally observed modulation is less pronounced than that in the simulations due to the presence of a large number of isochromats with slightly different resonance offsets, because of residual B_0 inhomogeneity. Relaxation and spin diffusion may also play minor parts in the suppression of some of the modulation.

In summary, we have shown how to modify conventional Carr–Purcell echo trains so that they are much less susceptible to the effects of imperfect refocusing pulses. We expect a similar revision of other multiple-pulse techniques is possible and are actively pursuing this line of thought.

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