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Optimal control design of constant amplitude phase-modulated pulses: Application to calibration-free broadband excitation

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Abstract

An optimal control algorithm for generating purely phase-modulated pulses is derived. The methodology is applied to obtain broadband excitation with unprecedented tolerance to RF inhomogeneity. Design criteria were transformation of $I_z \rightarrow I_x$ over resonance offsets of ±25 kHz for constant RF amplitude anywhere in the range 10–20 kHz, with a pulse length of 1 ms. Simulations transform I_z to greater than 0.99 I_x over the targetted ranges of resonance offset and RF variability. Phase deviations in the final magnetization are less than 2–3° over almost the entire range, with sporadic deviations of 6–9° at a few offsets for the lowest RF (10 kHz) in the optimized range. Experimental performance of the new pulse is in excellent agreement with the simulations, and the robustness of the excitation pulse and a derived refocusing pulse are demonstrated by insertion into conventional HSQC and HMBC-type experiments.

Keywords: BEBOP; Broadband excitation; Optimal control theory; Phase modulation; PM pulses

1. Introduction

Although dual compensation for RF inhomogeneity/miscalibration and chemical-shift offset effects in excitation has been difficult to achieve [1–13], broadband excitation by optimized pulses (BEBOP) [14–17] has been shown to be an effective solution for RF tolerance of 10–15%, which is typical of calibrated pulses output by high-quality RF probes. Broadband in this context refers to a pulse capable of uniformly exciting the entire ^{13}C chemical-shift range at field strengths of 800–900 MHz, requiring a bandwidth of 40–50 kHz.

Broadband pulses which tolerate an even higher degree of RF inhomogeneity could also be useful. NMR-spectroscopy on natural products is one potential application. For example, calibration of ^{13}C-pulses is extremely difficult for natural abundance samples at very low concentration. Moreover, significant variations in pulse length can be caused by varying salt concentrations. Sufficient RF tolerance would remove the need for painstakingly accurate pulse calibrations, which are also important for optimal sensitivity of many complex multidimensional experiments or the automated acquisition of a large number of strongly differing samples.

Encouraged by the success of optimal control theory in designing broadband pulses with outstanding performance, we therefore consider a problem which has been resistant to a successful solution: nearly calibration-free broadband excitation. To accommodate the majority of ^{13}C probes in

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use, the pulse should operate equally well for a peak RF output anywhere in the range 10–20 kHz (25–12.5 μs pulse width).

In addition, while the BEBOP pulses obtained to date exhibit nearly ideal performance, their rapid and extreme amplitude jumps can require some monitoring and adjustment of system hardware, primarily with regard to amplifier linearity and accurate output of the waveform generators. We have demonstrated that this is not a problem for modern NMR-consoles with linearized amplifiers and fast amplitude and phase switching times. For NMR-spectrometers equipped with non-linearized amplifiers, however, constant amplitude pulses would be more convenient.

For a given bandwidth and tolerance to RF variability, an optimal control algorithm which allows amplitude/phase modulation and limits the maximum RF amplitude produces a purely phase-modulated pulse when the pulse length is reduced below a certain level [16]—the algorithm pins the RF to its maximum allowed value at all times during the pulse in attempting to optimize pulse performance. For longer pulse lengths, the algorithm is able to converge to a solution using lower, time-variable values of the amplitude without having to consider larger RF values. Instead of reducing pulse length by trial-and-error until constant amplitude pulses are found, it is more efficient to derive them directly, which is the topic of the next section. The results of the new procedure for deriving phase-modulated pulses and their applications in HSQC and HMBC-type experiments are discussed in a following section.

2. Theory and methods

Details of the optimal control procedure, as it relates to broadband excitation in NMR, and the algorithms developed so far are discussed in [14,15,17]. More general information on broadband excitation [1–13], optimal control theory [18–21], and its use in NMR [22–25] can be found in the references. In this section, we derive the modifications to our previous treatment that are required to maximize the performance of a pulse modulated only in phase.

2.1. Optimal control theory: application to excitation

We first provide a synopsis describing those aspects of the methodology that are unaffected by the transition to a phase-modulated pulse. During the time interval $[t_0, t_p]$, we seek to transfer initial magnetization $\boldsymbol{M}(t_0) = \hat{\boldsymbol{z}}$ to the target final state $\boldsymbol{F} = \hat{\boldsymbol{x}}$ for a specified range of chemical-shift offsets and a desired degree of tolerance to RF inhomogeneity or miscalibration. The trajectories $\boldsymbol{M}(t)$ are constrained by the Bloch equation

$$\dot{M} = \boldsymbol{\omega}_e \times M. \tag{1}$$

The effective RF field $\boldsymbol{\omega}_e$ in angular frequency units (rad/s) can be written in the rotating frame as

$$\begin{aligned}\boldsymbol{\omega}_e &= \omega_1(t)[\cos\phi(t)\hat{\boldsymbol{x}} + \sin\phi(t)\hat{\boldsymbol{y}}] + \Delta\omega\hat{\boldsymbol{z}} \\ &= \boldsymbol{\omega}_{\rm rf}(t) + \Delta\omega\hat{\boldsymbol{z}},\end{aligned} \tag{2}$$

which encompasses any desired modulation of the amplitude ω_1 and phase ϕ of the pulse.

Constraints on the optimization are incorporated into the formalism using the technique of Lagrange multipliers (see for example, [26]), with a multiplier λ_i for each constraint. The vector Bloch equation thus introduces a vector Lagrange multiplier $\boldsymbol{\lambda}$. Some suitable measure of pulse performance, the cost function Φ, is then defined as the object of the optimization. One then finds that $\boldsymbol{\lambda}$ must also obey the Bloch equation at each time for the cost to be optimized, with its value at the end of the interval given by $\boldsymbol{\lambda}(t_p) = \partial\Phi/\partial\boldsymbol{M}$.

2.1.1. Application to phase modulation

Since optimal control theory is a generalization (e.g., [21]) of the classical Euler–Lagrange formalism, a "hamiltonian" h can be defined in terms of $\boldsymbol{\lambda}$ and the constraints on the possible trajectories as

$$h = \boldsymbol{\lambda}\cdot(\boldsymbol{\omega}_e \times \boldsymbol{M}) = \boldsymbol{\omega}_e\cdot(\boldsymbol{M}\times\boldsymbol{\lambda}). \tag{3}$$

In terms of general controls u_i, the final conditions that are necessary for the cost to be optimal are that

$$\frac{\partial h}{\partial u_i} = 0 \tag{4}$$

at all times throughout the evolution. If Eq. (4) is not equal to zero, it represents a gradient giving the proportional adjustment to make in the controls for a more optimal solution.

In our previous work, the controls were equal to $\boldsymbol{\omega}_e$, giving $\partial h/\partial\boldsymbol{\omega}_e = \boldsymbol{M}\times\boldsymbol{\lambda}$. As noted in the previous section, since very few spectrometers implement frequency modulation directly, the controls were restricted to the transverse, (x, y), components represented by $\boldsymbol{\omega}_{\rm rf}$ in Eq. (2). The z component of $\boldsymbol{M}\times\boldsymbol{\lambda}$ was therefore irrelevant in adjusting the controls.

For a constant amplitude phase-modulated pulse, ω_1 in Eq. (2) is time-independent and the only control is the phase, ϕ. Plugging $\boldsymbol{\omega}_e$ from Eq. (2) into Eq. (3) and setting $\partial h/\partial\phi = 0$ gives, together with the previous conditions on the evolution of $\boldsymbol{M}$ and $\boldsymbol{\lambda}$, the following requirements to optimize the cost:

$$\dot{\boldsymbol{M}} = \boldsymbol{\omega}_e \times \boldsymbol{M}, \qquad \boldsymbol{M}(t_0) = \hat{\boldsymbol{z}} \tag{5}$$

$$\dot{\boldsymbol{\lambda}} = \boldsymbol{\omega}_e \times \boldsymbol{\lambda}, \qquad \boldsymbol{\lambda}(t_p) = \partial\Phi/\partial\boldsymbol{M} \tag{6}$$

$$\boldsymbol{\omega}_{\rm rf}\cdot(\boldsymbol{\lambda}M_z - \boldsymbol{M}\lambda_z) = 0. \tag{7}$$

2.1.2. The cost function

The dot product $\Phi = \boldsymbol{M}(t_p)\cdot\boldsymbol{F}$ is one possible choice for quantifying the degree to which $\boldsymbol{M}(t_p) = \boldsymbol{F}$, which gives $\boldsymbol{\lambda}(t_p) = \boldsymbol{F}$ from Eq. (6) [14–16]. For alternative cost functions see Ref. [17]. For any of the cost functions, the procedure is the same–$\boldsymbol{M}$ and $\boldsymbol{\lambda}$ obey the Bloch equation,