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Design and application of robust rf pulses for toroid cavity NMR spectroscopy

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ABSTRACT

We present robust radio frequency (rf) pulses that tolerate a factor of six inhomogeneity in the B_1 field, significantly enhancing the potential of toroid cavity resonators for NMR spectroscopic applications. Both point-to-point (PP) and unitary rotation (UR) pulses were optimized for excitation, inversion, and refocusing using the gradient ascent pulse engineering (GRAPE) algorithm based on optimal control theory. In addition, the optimized parameterization (OP) algorithm applied to the adiabatic BIR-4 UR pulse scheme enabled ultra-short (50 μs) pulses with acceptable performance compared to standard implementations. OP also discovered a new class of non-adiabatic pulse shapes with improved performance within the BIR-4 framework. However, none of the OP-BIR4 pulses are competitive with the more generally optimized UR pulses. The advantages of the new pulses are demonstrated in simulations and experiments. In particular, the DQF COSY result presented here represents the first implementation of 2D NMR spectroscopy using a toroid probe.

1. Introduction

Practical NMR applications require pulses that provide robust performance with respect to experimental limitations, such as resonance offset effects and rf inhomogeneity. A simple rectangular pulse delivered with a perfectly homogeneous rf amplitude of 20 kHz (pulse length 12.5 μs) transforms M_z to M_x with a fidelity of 99% over an offset range of only ±2.8 kHz. Miscalibration or inhomogeneity of the B_1 field exceeding ±9% reduces M_x on resonance below the desired fidelity.

Increased tolerance to offset and/or rf inhomogeneity can be achieved using composite [1,2] and shaped [3] pulses. More recently, efficient pulse design using optimal control theory [4] has made it possible to establish physical limits to pulse performance [5–14]. Short (100 μs), broadband, PP excitation pulses (98% fidelity) have been optimized that achieve bandwidth to peak rf ratios of 2 with a ±10% tolerance to rf inhomogeneity applicable to modern high resolution NMR probes [8]. In an extreme case study of dual compensation, a 1 ms pulse was found that provides excellent broadband excitation over an offset range of 50 kHz for miscalibration of the B_1 field anywhere in the range 10–20 kHz [10]. Much larger spatial variations of the B_1 field limit applications involving, e.g., surface coils, ex situ NMR, and high field imaging.

Here we focus on toroid cavity probes [15–17], which can be built to tolerate high rf amplitude, high pressure, and high temperature, but at the price of large rf field inhomogeneity. A toroid cavity detector is a unique NMR resonator with a wide range of potential applications for in situ reaction studies at high-pressure and/or high temperature [18]. Whereas the defined B_1 field gradient of the coil is an advantage for some applications (for example, rotating frame NMR imaging on the micrometer scale [19]), it is a serious problem in spectroscopic applications, severely limiting the potential of toroid NMR. For the toroid probe designs considered here, the ratio between the minimum and maximum B_1 field in the sample volume is a factor of six. Other detector geometries produce even larger inhomogeneities [17].

We present efficient point-to-point (PP) and unitary rotation (UR) pulses optimized for toroid probe applications using the GRAPE algorithm [20]. PP pulses transform one specified initial state to a desired target state, whereas UR pulses rotate any orientation of the initial magnetization about a defined axis. While composite PP pulses developed specifically for toroid detectors exist, [22], no UR pulses, which are crucial for multi-dimensional NMR, have been developed previously for these probes. The performance of individual toroid pulses is characterized both theoretically and experimentally in Section 3. We demonstrate the performance and relevance of the new pulses for toroid probe NMR in a DQF COSY experiment, where significant gains in signal amplitude are found compared to experiments using conventional pulses.

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2. Toroid probes

The first use of toroid coils in NMR spectroscopy was reported in 1983 [15,23]. Toroid rf coils and toroid cavities provide excellent signal-to-noise ratio compared to conventional Helmholtz or saddle coils, and very high rf amplitudes on the order of 100 kHz can be reached. In toroid cavity autoclaves [18,24], pressures of up to 300 bar and temperatures of up to 250 °C are attainable, making it possible, e.g., to investigate in situ reaction dynamics of homogeneously catalyzed reactions, such as the cobalt-catalyzed hydroformylation process [25–28].

In a typical toroid probe with cylindrical symmetry, the sample is located between a minimum radius r_{min} (given by the radius of the central conductor) and a maximum radius r_{max}. The B_1 field for a toroidal geometry varies inversely with radial distance r as detailed more fully in [17,29,30]. Hence, the corresponding rf amplitude, $\nu_{rf}(r) = \gamma B_1(r)/(2\pi)$, can be expressed relative to its smallest value at r_{max} as $\nu_{rf}(r) \propto \nu_{rf}(r_{max})/r$ to obtain

$$\nu_{rf}(r) = \frac{r_{max}}{r}\nu_{rf}(r_{max}). \tag{1}$$

The time dependence of the rf pulse can then be written simply in terms of an amplitude modulation function $0 \leqslant a(t) \leqslant 1$ as

$$\nu_{rf}(r,t) = a(t)\nu_{rf}(r) \tag{2}$$

applied to the rf spatial profile at any position r in the toroid.

For the toroid probe used here, r_{min} = 1 mm and r_{max} = 6 mm. A conventional rectangular pulse thus rotates spins near the central conductor by a flip angle that is six times larger than the flip angle experienced by spins near the outer wall of the toroid resonator. This large and well-defined rf inhomogeneity of toroid probes can be exploited, e.g., in spatially resolved diffusion measurements and imaging [19,31–33]. However, the large rf inhomogeneity has limited spectroscopic applications of toroid probes to relatively simple experiments. In the following, we remove this limitation by developing pulses with the necessary high tolerance to rf inhomogeneity.

3. Pulse optimizations and applications

The GRAPE algorithm for pulse optimization is discussed in detail in [20]. Further details of its application can be found in the cited references on optimal control [5–14,34,36]. A quality factor, Φ, for pulse performance is defined which, in turn, provides an efficiently calculated gradient for iterative improvement of pulse performance. Most generally, the quality factor is a quantitative comparison between the state of the system and some desired target state. The gradient therefore also depends on the system state—in the present case, the magnetization **M**. Modifications in the basic algorithm that are required for the large and well-defined rf spatial inhomogeneity in toroid probes requires some elaboration.

3.1. Simulating pulse performance in a toroid

For a general rf pulse, each combination of offset, ν_{off}, and rf amplitude, $\nu_{rf}(r)$, produces a potentially different transformation of the initial magnetization. The goal of pulse optimization is to find a particular rf pulse that produces the same transformation for all the scalings of the rf amplitude due to spatial inhomogeneity and all the desired offsets. A gradient giving the proportional adjustment to make in the rf pulse components to improve performance at each ν_{off} and $\nu_{rf}(r)$ can be efficiently calculated for point-to-point (PP) pulses [5,20] and for unitary rotation (UR) pulses [20]. The total gradient is obtained by averaging these constituent gradients over offset and rf inhomogeneity.

For the small volumes and relatively small deviations from homogeneity seen in standard NMR probes, giving equal weight to different possible spatial values of the rf is sufficient to provide accurate simulations of pulse performance relative to experiment. In a toroid probe, the effect of the large and well-defined spatial inhomogeneity on both the spatial dependence of the transformed magnetization and the spatially dependent detection sensitivity must be considered.

The signal from the toroid cavity depends on the total contribution from spins at each radius. Signal is proportional to the detection sensitivity per spin times the number of spins within a cylindrical sample slice of height h, inner radius r, and outer radius $r + \delta r$. The slice volume $\delta V = 2\pi r\, h\delta r$ (and, thus, the corresponding number of spins in the slice) increases linearly with r. By the principle of reciprocity [21], the detection sensitivity is proportional to ν_{rf} and hence proportional to $1/r$ (c.f. Eqs. (1) and (2)). Therefore, the signal from a cylindrical slice volume δV is *independent* of r, and we can define an effective magnetization vector representing the sample in a toroid probe as

$$\mathbf{M}^{eff}(t) = \frac{1}{r_{max} - r_{min}} \int_{r_{min}}^{r_{max}} \mathbf{M}(r,t)\mathrm{d}r \tag{3}$$

with equal weighting at each radius. The (x,y) components of the detected signal are proportional to the (x,y) components of $\mathbf{M}^{eff}(t)$, respectively. The magnetization vector $\mathbf{M}(r,t)$ in Eq. (3) resulting from the applied rf is calculated starting from thermal equilibrium $\mathbf{M}_0 = (0,0,1)$ using the rf amplitude $\nu_{rf}(r)$ given in Eq. (1).

In the numerical simulations, the integration in Eq. (3) is approximated by a discrete sum. For each offset, the gradient (which depends on **M**) is averaged over the range of rf spatial variation by one of the two methods outlined in Appendix A. The first method samples $\mathbf{M}(r,t)$ at equally spaced r. Since ν_{rf} varies as $1/r$, this has the effect of coarsely digitizing the rf for small values of r and sets the stepsize Δr required for accurate simulations of rf inhomogeneity in the toroid. At large r, however, Δr is more accurate than necessary. Alternatively, the second method samples $\mathbf{M}[\nu_{rf}(r),t]$ at equally spaced ν_{rf}, multiplied by the proper weight for each rf frequency that accurately represents the nonlinearity of $\nu_{rf}(r)$, as derived in Appendix A. The gradients resulting from either procedure, averaged over the range of rf spatial variation for each individual offset, are subsequently averaged with equal weight over the range of offsets ν_{off} to give the overall gradient for the performance factor Φ.

Optimizations for a range of experimental parameters obtained efficient and robust pulses for ratios r_{max}/r_{min} as high as 100, which is significant for extending the present results to additional toroid applications. An experimental upper limit $\nu_{rf}^{max} = 25\,\mathrm{kHz}$ on $\nu_{rf}(r_{max})$ for our toroid cavity resonator (r_{min} = 1 mm, r_{max} = 6 mm) limited the time-dependent pulse amplitude at r_{max} to the range $0 \leqslant \nu_{rf}(r_{max}, t) \leqslant \nu_{rf}^{max}$ in the optimizations. We consider offsets ν_{off} in the range ±1.5 kHz, corresponding to a 15 ppm ^{1}H chemical shift at a spectrometer frequency of 200 MHz. Different experimental settings are accommodated by expressing frequencies relative to the limit ν_{rf}^{max}. In these relative frequency units, the current experimental setting corresponds to an offset range of $-0.06 \leqslant \nu_{off}/\nu_{rf}^{max} \leqslant 0.06$. Pulses were optimized starting from a set of random initial pulses. Each pulse was digitized in time steps of 0.5 µs duration and, at each time step t_j, the rf amplitude modulation function $a(t_j)$ and the phase $\phi(t_j)$ were optimized.

3.2. Point-to-point (PP) pulses

Point-to-point transformations rotate one specified initial state to a desired target state. For example, a PP pulse for the transformation $M_z \to M_x$ will not in general rotate any other component