

Optimal control in NMR spectroscopy: Numerical implementation in SIMPSON

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ABSTRACT

We present the implementation of optimal control into the open source simulation package SIMPSON for development and optimization of nuclear magnetic resonance experiments for a wide range of applications, including liquid- and solid-state NMR, magnetic resonance imaging, quantum computation, and combinations between NMR and other spectroscopies. Optimal control enables efficient optimization of NMR experiments in terms of amplitudes, phases, offsets etc. for hundreds-to-thousands of pulses to fully exploit the experimentally available high degree of freedom in pulse sequences to combat variations/limitations in experimental or spin system parameters or design experiments with specific properties typically not covered as easily by standard design procedures. This facilitates straightforward optimization of experiments under consideration of rf and static field inhomogeneities, limitations in available or desired rf field strengths (e.g., for reduction of sample heating), spread in resonance offsets or coupling parameters, variations in spin systems etc. to meet the actual experimental conditions as close as possible. The paper provides a brief account on the relevant theory and in particular the computational interface relevant for optimization of state-to-state transfer (on the density operator level) and the effective Hamiltonian on the level of propagators along with several representative examples within liquid- and solid-state NMR spectroscopy.

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1. Introduction

In the recent few years optimal control [1–3] has found its way into nuclear magnetic resonance as a powerful tool for efficient design and optimization of experiments for applications in imaging [4–7], liquid-state NMR [8–13], solid-state NMR [14–20], quantum computation [21–26], and dynamic nuclear polarization/electron-nuclear interactions [27–31]. This method, originally being introduced for optimizations in engineering and economy, is very attractive for optimization problems dealing with complex internal Hamiltonians and a large number of external manipulation parameters. Opposed to the small space of variables typically associated with standard non-linear optimization methods [32], optimal control is capable of handling hundreds-to-thousands of free variables within an optimization and provides an optimal solution much fas-

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ter than standard optimization procedures in such cases. This opens up interesting new possibilities for performing experiment design which takes into account all typically available information on (i) the relevant nuclear spin systems (size, typical nuclear spin interaction parameters, and variations in these), (ii) the available experimental manipulations (external magnetic field, rf fields, limitations and inhomogeneities in these), and (iii) relevant experimental conditions (sample spinning, dynamics).

Using optimal control, it is possible to extend the numerical design and optimization of NMR methods [33,34] to fully exploit the available experimental degrees of freedom to reach the optimal experiment, as for example expressed in terms of universal bounds on spin dynamics [35–39]. The outcome of numerical optimizations with optimal control may not only provide optimum experiments for direct applications, but may also provide new insight into, e.g., the maximal possible transfer efficiencies, which then may be used (i) as an evaluation of whether there is room for improvements of state-of-the-art experiments and (ii) to provide new inspiration to alternative design strategies, for example based on average (or effective) Hamiltonian theory [40–43]. As an example of the latter, it became clear from optimal control design of heteronuclear coherence transfer schemes in solid-state NMR [14]

that optimal control can increase the efficiency of so-called γ -encoded dipolar recoupling experiments [44] by compensating more efficiently for spread in another crystallite orientation angle (β) leading to the concept of COMpensation for Beta (COMB) composite refocusing [45]. This led to an analytical single-spin optimization strategy for improved dipolar recoupling, which in a subsequent phase was feeded back to fast optimal control single-spin numerical optimizations of two-spin dipolar recoupling experiments [20]. Another option is to use optimal control directly as a means to analytically design optimal experiments [46–53].

In this paper, we address software implementation of optimal control for easy conduction of experiment optimizations for specific applications, to improve robustness towards the parameters that are essential for the intended experiments or simply to obtain a test on the maximum possible efficiency of an experiment to compare with existing methods. The paper serves as a description of (and manual for) an extension of the powerful and widely used simulation package SIMPSON [54] to include optimal control applications [14]. The combined software is released as open source software in a new version of SIMPSON. The paper is organized as follows. First the relevant theory is discussed briefly with reference to the original literature for a more detailed account. Subsequently, we introduce the novel features relevant for SIMPSON optimal control calculations, and finally provide a few relevant examples illustrating these features and demonstrating some of the flexibility of an optimal control numerical tool for NMR experiment design and optimization.

2. Theory

The spin dynamics of NMR experiments is typically expressed in terms of the evolution of density operators as expressed by the Liouville-von-Neuman equation

$$\dot{\rho}(t) = -i[H(t), \rho(t)] \quad (1)$$

addressing cases without relaxation. In general terms, the Zeeman frame Hamiltonian may be described as

$$H(t) = H_{\text{int}}(t) + H_{\text{rf}}(t), \quad (2)$$

$$H_{\text{rf}}(t) = \sum_i \omega_{\text{rf}}^{ix}(t) I_{ix} + \omega_{\text{rf}}^{iy}(t) I_{iy}, \quad (3)$$

$$H_{\text{int}}(t) = H_{\text{CS}}(t) + H_J(t) + H_D(t) + H_Q(t). \quad (4)$$

$H_{\text{rf}}(t)$ expresses external manipulations in terms of rf irradiation, here expressed as a summation over x - and y -phase contributions for the involved spins (or spin species) through continuous functions in time t . In numerical calculations the pulses are for practical reasons represented in digitized form as a train of pulses appropriately reflecting the time variation. $H_{\text{int}}(t)$ collects contributions from internal nuclear spin interactions, including chemical shifts, scalar (J) couplings, dipole–dipole couplings, and quadrupolar couplings. The internal Hamiltonian for the various interactions may typically be cast in the form of a Fourier series

$$H_\lambda(t) = \sum_{m=-2}^2 \omega_\lambda^{(m)} e^{im\omega_r t} O_\lambda, \quad (5)$$

where time dependencies, e.g., due to sample spinning with angular frequency ω_r , is expressed through the exponentials. Expressions for the angular frequencies of the isotropic and anisotropic (i.e., orientation dependent) internal nuclear spin interactions $\omega_\lambda^{(m)}$ as well as the associated spin operators O_λ for typical solid- and liquid-state NMR applications can be found in Ref. [54].

For a generalized pulse sequence consisting of a train of N pulses acting consecutively on the initial spin density operator $\rho(0)$ from time 0 to time $t_N = T$, the density operator at the end of the pulse sequence takes the form

$$\rho(T) = U_N(t_N, t_{N-1}) \dots U_2(t_2, t_1) U_1(t_1, 0) \rho(0) \quad (6)$$

$$U_1^\dagger(t_1, 0) U_2^\dagger(t_2, t_1) \dots U_N^\dagger(t_N, t_{N-1})$$

with each propagator defined as $U(t_{k+1}, t_k) = \hat{T} \exp\{-i \int_{t_k}^{t_{k+1}} H(t) dt\}$ using the Hamiltonian in Eq. (2) and the Dyson time-ordering operator \hat{T} . The aim of the optimization is to adjust the external manipulation parameters, which are the instantaneous rf field amplitudes $\omega_{\text{rf}}^{ix}(t_k)$ and $\omega_{\text{rf}}^{iy}(t_k)$ in Eq. (3), to provide the best performance of the experiment. This amounts to systematic variation of the amplitudes in Fig. 1 to obtain the optimal experiment.

The performance may be evaluated as the highest transfer efficiency transferring a given initial state operator, e.g., $\rho(0) = A$ to a desired destination spin operator C as expressed by the density operator at time T , $\rho(T) = c_{\text{max}} C + B$, where the coefficient c_{max} is maximized and B contains all residual operator terms. Henceforth, we will refer to this situation as *state-to-state transfer*. In cases of transfer between *Hermitian operators* this amounts to optimization of the overlap between C and the transformed operator $\rho(T) = U\rho(0)U^\dagger$ as expressed in terms of a standard inner product between the operators

$$\Phi_{\text{fin}} = \langle C | \rho(T) \rangle = \text{Tr}\{C^\dagger U\rho(0)U^\dagger\}. \quad (7)$$

In cases of transfer between *non-Hermitian operators*, the transfer function defined in Eq. (7) is complex valued in general and can not be used directly. In this case there are several possible replacements for Φ_{fin} , for example just evaluating the real part or the norm squared of the transfer function. For implementation within SIMPSON, we have chosen the latter case:

$$\Phi_{\text{fin}} = |\langle C | \rho(T) \rangle|^2 = \left| \text{Tr}\{C^\dagger U\rho(0)U^\dagger\} \right|^2. \quad (8)$$

We note that this cost function leads to a multitude of solutions, as discussed previously in the context of unitary bounds on spin dynamics [36,38].

For other applications, it is relevant to optimize the *effective Hamiltonian* H_{eff} (or the effective propagator U_{eff}) to a desired effective Hamiltonian H_D (or the desired propagator U_D) which amounts to optimization of

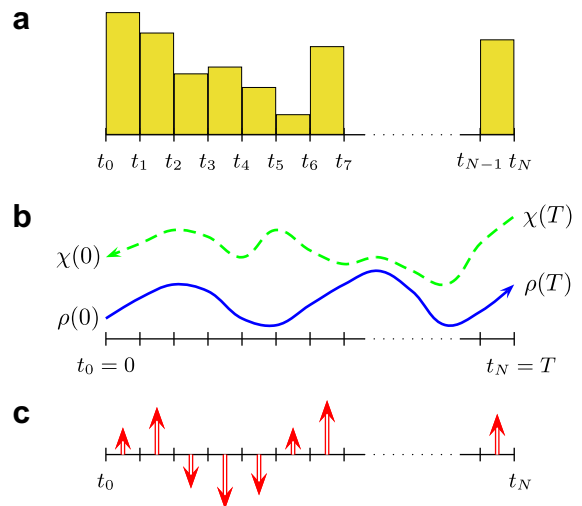


Fig. 1. Schematic illustration of optimal control design of multiple-pulse experiments. (a) The pulse sequence consists of many short pulses with variable amplitude and phase. (b) The effect of the pulse sequence is monitored by forward and backward evolution of initial state $\rho(0)$ and the target state $\chi(T)$, respectively. (c) Utilizing the fact that the two paths are different, corrections to pulse parameters are calculated in terms of a gradient.

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