Optimal Ensemble Control of Open Quantum Systems with a Pseudospectral Method

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Abstract— In this paper, we extend our previous results concerning the application of the Legendre pseudospectral method to optimal pulse design problems for open quantum systems. We now consider the more realistic case in which systems are characterized by variations in parameter values, such as relaxation rates and coupling constants. Such dispersions in system parameters motivate us to consider an ensemble of systems, each member distinct due to distinct parameter values. We demonstrate the method with systems from nuclear magnetic resonance (NMR) spectroscopy in liquid. In particular, we highlight the flexibility and robustness of the pseudospectral method approach by developing pulses that minimize the energy or total duration of the pulse sequence.

I. INTRODUCTION

Much of scientific research in the control of quantum systems makes assumptions neglecting the interactions that the studied quantum system has with the environment. While these assumptions are often valid for the cases considered, as we look to close the gap between theoretical prediction and experimental outcome, the models describing these systems must become increasingly more accurate and, thus, include such contributions. In addition, there are many quantum systems for which environmental interaction cannot be neglected and these open quantum systems are characterized by relaxation to the environmentally-induced equilibrium state [1]. This relaxation causes signal degradation and, therefore, experimental losses in signal.

Furthermore, either due to lack of information regarding the system or to environmental interactions within the system that perturb the known values, the parameters that characterize quantum system dynamics are prone to variation. To accurately represent a system with parameter variation, we consider an ensemble of systems, each with unique parameter values, however, all driven by the same input [2]. Developing robust control pulses to produce desired evolutions while reducing the impact of relaxation and exhibiting insensitivity to parameter variations is both an important topic for optimal quantum control and a challenging problem in optimal pulse design.

Within, we formulate the pulse design objective as a new type of optimal ensemble control problem based on open quantum systems for which state feedback is either difficult or impossible to attain. This is a general characterization that can be used throughout all areas of open-loop quantum control from NMR, as illustrated in this paper, to quantum optics. We then present and demonstrate a computational method based on pseudospectral approximations and optimal sampling in the parameter domain that effectively discretizes the optimal ensemble control problem.

In Section II, we present the methodology behind the numerical algorithm and the corresponding transformation of the optimal control problem. In Section III, we use two open quantum systems to highlight the flexibility and effectiveness of the pseudospectral method. These systems, without parameter variation, have been well studied and there are analytic expressions of the optimal control sequences for the single system case within existing literature [3], [4].

II. METHODS

We apply the pseudospectral method for solving optimal control problems to a class of nonunitary (open) quantum systems for which the Markovian approximation applies. Under this assumption, the environment is approximated by an infinite thermostat which remains unaltered despite interaction with the quantum system. The state of the system, a density matrix, evolves according to Lindblad's formula [5],

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

where $H(t)$ is the time-dependent system Hamiltonian, which represents the non-interacting, or unitary, evolution of the system while the term $L(\rho)$ models relaxation (nonunitary dynamics) [7]. A typical control problem in such systems is a point-to-point state transfer, guiding the system from an initial state $\rho(0)$ to (or as close as possible to) a desired final state $\rho(T)$ at the terminal time $t = T$. The evolution in (1) can be expressed in terms of expectation values,

$$\dot{x} = \left[\mathcal{H}_d + \sum_{i=1}^{m} u_i(t) \mathcal{H}_i \right] x , \qquad (2)$$

where $x = (x_1, \ldots, x_n)^T \in \mathbb{R}^n$ is the state vector and $\mathcal{H}_d, \mathcal{H}_i \in \mathbb{R}^{n \times n}$ are square matrices representing $H(t)$ and L [6]. The analogous problem on this transformed system is to design inputs $u_i(t)$, $i = 1, \ldots, m$, starting from an initial state $x(0)$, that maximize $x_n(T)$ subject to the dynamics given in (2) [8]. We can then describe the pulse design

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optimal control problem with the following formulation,

$$\min \quad \varphi(T, x(T)) + \int_0^T \mathcal{L}(x(t), u(t))dt$$

$$\text{s.t.} \quad \dot{x} = \left[\mathcal{H}_d + \sum_{i=1}^m u_i(t)\mathcal{H}_i\right]x \qquad (3)$$

$$e(x(0), x(T)) = \mathbf{0}$$

$$g(x(t), u(t)) \leq \mathbf{0},$$

where φ and $\mathcal{L}$ are the terminal and running cost terms of the general objective function, respectively, e represents endpoint constraints (specifying initial and final state values), and g denotes path constraints, which is a constraint that holds for all $t \in [0, T]$. In the typical problem mentioned above, the cost function would be chosen as $\varphi(T, x(T)) = -x_n(T)$ and $\mathcal{L} = 0$. The general formulation in (3), however, allows us to design other practical pulses, such as those that complete the desired transfer while minimizing the input energy or minimizing the duration of the pulse.

A. Pseudospectral Method

In general, the nonlinear optimal control problem (3) is difficult, if not impossible, to solve analytically. As the complexity of the problems in quantum control increases, such as considering the ensemble control case, researchers look to find reliable numerical methods to solve the problem given in (3). We present a method to convert this continuous optimal control problem into a constrained algebraic minimization problem on a finite dimensional vector space for which there are numerous mature numerical solvers. The pseudospectral method was originally developed to solve problems in fluid dynamics and since then has been successfully applied to many areas of science and engineering [9], [10], [11]. Pseudospectral discretization methods use expansions of orthogonal polynomials to approximate the states of the system and thereby inherit the spectral accuracy characteristic of orthogonal polynomial expansions (the kth coefficient of the expansion decreases faster than any inverse power of k) [12]. Through special properties, derivatives of these orthogonal polynomials can be expressed in terms of the polynomials themselves, making it possible to accurately approximate the differential equation that describes the dynamics with an algebraic relation imposed at a small number of discretization points. An appropriate choice of these discretization points, or nodes, facilitates the approximation of the states as well as ensuring accurate numerical integration through Gaussian quadrature. We expand upon these ideas below.

In order to expand the state trajectories in terms of the orthogonal polynomials, we first transform the original problem from the time domain $t \in [0, T]$ to the rescaled domain $t \in [-1, 1]$ on which the polynomials are defined. Here we use the Legendre polynomials, which are orthogonal, as evaluated by the weighted L^2 inner product, with respect to the weight, $w(t) = 1$ [13]. This choice of orthogonal polynomial family suggests we compute the integral term of the cost function using Legendre-Gauss-Lobatto (LGL) quadrature, in which the integral is approximated by a weighted summation of the integrand evaluated at a specific set of nodes,

$$\int_{-1}^1 f(t)dt \approx \sum_{i=1}^N f(t_i)w_i, \qquad w_i = \int_{-1}^1 \ell_i(t)dt, \qquad (4)$$

where N is the order of polynomial approximation, w_i are discrete weights, and $\ell_i(t)$ is the ith Lagrange polynomial, discussed below [14]. Lobatto in LGL refers to the inclusion of the endpoints as nodes, which is necessary to discretize optimal control problems in order to enforce initial and terminal conditions. In particular, if the integrand $f \in \mathbb{P}_{2N-1}$ and the nodes $t_i \in \Gamma^{LGL}$, the integral approximation is exact, where $\mathbb{P}_{2N-1}$ denotes the set of polynomials of degree $2N - 1$ or less and where $\Gamma^{LGL} = \{t_i : \dot{L}_N(t)|_{t_i} = 0, i = 1, \ldots N - 1\} \bigcup \{-1, 1\}$ are the $N+1$ LGL nodes determined by the derivative of the Nth order Legendre polynomial, $\dot{L}_N(t)$, and the interval endpoints [12].

LGL quadrature requires we know the integrand values at the LGL nodes, however, the Nth order Legendre expansions

$$x(t) \approx P_N x(t) = \sum_{k=0}^N \tilde{x}_k L_k(t), \qquad (5)$$

$$u(t) \approx P_N u(t) = \sum_{k=0}^N \tilde{u}_k L_k(t), \qquad (6)$$

do not directly give us a way to discretize the states and controls at these nodes, i.e. the expansions coefficients $\tilde{x}_k$ and $\tilde{u}_k$ have no direct physical meaning. To overcome this, we approximate these Legendre expansions with interpolating polynomials, which, by definition, are equal to the Legendre expansions at the interpolation nodes. Because any interpolating polynomial can be represented by Lagrange polynomials we can represent the state and control as,

$$P_N x(t) \approx I_N x(t) = \sum_{k=0}^N \bar{x}_k \ell_k(t), \qquad (7)$$

$$P_N u(t) \approx I_N u(t) = \sum_{k=0}^N \bar{u}_k \ell_k(t), \qquad (8)$$

where the coefficients $\bar{x}_k$ and $\bar{u}_k$ are the values of the state and control Legendre expansions evaluated at the kth interpolation node, respectively, i.e., $P_N x(t_k) = I_N x(t_k) = \bar{x}_k$ and $P_N u(t_k) = I_N u(t_k) = \bar{u}_k$. The coefficients have this property because the kth Lagrange polynomial is characterized by taking unit value at the kth interpolation node and zero value at all other nodes such that $\ell_k(t_i) = \delta_{ki}$, where δ_{ki} is the Kronecker delta function [13]. Therefore, using this second approximation we can compute the integrand of the cost function integral at the LGL nodes and $\bar{x}_k$ and $\bar{u}_k$ become the decision variables of the subsequent discrete problem.

Furthermore, the selection of LGL nodes, which are non-uniform on $[-1, 1]$ with quadratic spacing towards the endpoints, as interpolation nodes suppresses the spurious oscillations between nodes that can be present when using uniformly spaced nodes, called the Runge phenomena [15]. Although a closed form for the optimal nodes has not been achieved in the literature, the LGL nodes have been shown to be *close to optimal* [16]. In addition, the LGL nodes permit us rewrite the Lagrange polynomials in terms of the Legendre polynomials, which is critical to inherit the special derivative and spectral accuracy properties of the

orthogonal polynomials despite using Lagrange interpolating polynomials. Given $t_k \in \Gamma^{LGL}$, we can express the Lagrange polynomials as [17],

$$\ell_k(t) = \frac{1}{N(N+1)L_N(t_k)} \frac{(t^2-1)\dot{L}_N(t)}{t-t_k}. \qquad (9)$$

The derivative of (7) at $t_j \in \Gamma^{LGL}$ is then,

$$\frac{d}{dt}I_N x(t_j) = \sum_{k=0}^{N} \bar{x}_k \dot{\ell}_k(t_j) = \sum_{k=0}^{N} D_{jk}\bar{x}_k, \qquad (10)$$

and using (9) with the Legendre property that

$$\frac{d}{dt}[(1-t^2)\dot{L}_N(t)] = -N(N+1)L_N(t) ,$$

D is the constant matrix with elements given by [18],

$$D_{jk} = \begin{cases} \frac{L_N(t_j)}{L_N(t_k)}\frac{1}{t_j - t_k} & j \neq k \\ -\frac{N(N+1)}{4} & j = k = 0 \\ \frac{N(N+1)}{4} & j = k = N \\ 0 & \text{otherwise.} \end{cases} \qquad (11)$$

We are now in a position to write the discretized optimal control problem using equations (4), (7), (8), and (10). We transform the continuous-time problem in (3) to the constrained minimization problem

$$\min \quad \varphi(T, \bar{x}_N) + \frac{T}{2}\sum_{i=0}^{N} \mathcal{L}(\bar{x}_i, \bar{u}_i)w_i$$

$$\text{s.t.} \quad \sum_{k=0}^{N} D_{jk}\bar{x}_k = \frac{T}{2}\Big[\mathcal{H}_d + \sum_{i=1}^{m} \bar{u}_{ij}\mathcal{H}_i\Big]\bar{x}_j,$$
$$e(\bar{x}_0, \bar{x}_N) = 0,$$
$$g(\bar{x}_j, \bar{u}_j) \leq 0, \quad \forall j \in \{0, 1, \ldots, N\},$$

where $\bar{u}_{ij}, i = 1, \ldots, m$, are components of the vector $\bar{u}_j$ denoting the value of the control function u_i at the jth LGL node t_j, namely, $\bar{u}_j = (\bar{u}_{1j}, \ldots, \bar{u}_{mj})^T = (u_1(t_j), \ldots, u_m(t_j))^T$.

B. Optimal Ensemble Sampling

In this paper, we are interested in considering the more practical case in which the matrices $\mathcal{H}_d$ and $\mathcal{H}_i$ in (2), and therefore, the states are indexed by certain parameters within the dynamics which is due to environmental effects, for example relaxation rate dispersion. This introduces another dimension (or dimensions) of continuity that must be discretized to fit within the constrained minimization method. Consider the d-dimensional parameter $s \in I_1 \times I_2 \times ... \times I_d$, such that each s_i exists within a known interval $I_i = [a_i, b_i] \subset \mathbb{R}$, then the corresponding ensemble dynamical equation for (2) is

$$\dot{x}(t,s) = \Big[\mathcal{H}_d(s) + \sum_{i=1}^{m} u_i(t)\mathcal{H}_i(s)\Big]x(t,s) . \qquad (12)$$

Note that ensemble systems are characterized by extra degrees of continuity without additional (partial) derivative relations (i.e. $\nabla_s x = \mathbf{0}$) describing their impact on the system. The lack of dynamics associated with the parameters allows us to extend the pseudospectral method to sample these parameters in a straightforward manner. Consider now the ensemble extension of the interpolation approximation in (7) with a single parameter variation, i.e., $d = 1$ and $s \in [a, b]$,

$$x(t,s) \approx I_{N \times N_s} x(t,s) = \sum_{k=0}^{N} \bar{x}_k(s)\ell_k(t)$$
$$\approx \sum_{k=0}^{N} \left(\sum_{r=0}^{N_s} \bar{x}_{kr}\ell_r(s)\right)\ell_k(t). \qquad (13)$$

and the ensemble extension of the approximate derivative from (10) at $t_i \in \Gamma^{LGL}$ and $s_j \in \Gamma_{N_s}^{LGL}$,

$$\frac{d}{dt}I_{N \times N_s}x(t_i, s_j) = \sum_{k=0}^{N} D_{ik}\left(\sum_{r=0}^{N_s} \bar{x}_{kr}\ell_r(s_j)\right)$$
$$= \sum_{k=0}^{N} D_{ik}\bar{x}_{kj}, \qquad (14)$$

where $\bar{x}_{kj} = x(t_k, s_j)$. In (13) and (14) we have effectively used a two dimensional interpolating grid at the $N+1$ and $N_s + 1$ LGL nodes in time and the parameter, respectively. Using these equations in conjunction with the LGL quadrature rule, we construct the ensemble pseudospectral discretization of the optimal ensemble control problem as

$$\min \quad \frac{b-a}{2}\sum_{r=0}^{N_s}\Big[\varphi(T, \bar{x}_{Nr}) + \frac{T}{2}\sum_{i=0}^{N} \mathcal{L}(\bar{x}_{ir}, \bar{u}_i)w_i^N\Big]w_r^{N_s}$$

$$\text{s.t.} \quad \sum_{k=0}^{N} D_{jk}\bar{x}_{kr} = \frac{T}{2}\Big[\mathcal{H}_d^r + \sum_{i=1}^{m} \bar{u}_{ij}\mathcal{H}_i^r\Big]\bar{x}_{jr},$$
$$e(\bar{x}_{0r}, \bar{x}_{Nr}) = 0,$$
$$g(\bar{x}_{jr}, \bar{u}_j) \leq 0, \quad \forall \begin{array}{l} j \in \{0, 1, \ldots, N\} \\ r \in \{0, 1, \ldots, N_s\} \end{array}, \qquad (15)$$

where $\bar{u}_{ij}$ is the value of the control function u_i at the jth LGL node t_j.

III. EXAMPLES & RESULTS

Open quantum systems, such as those in NMR of liquids, exhibit several known parameter variations. The relaxation rate, the rate at which the system dissipates by interacting with the environment, can have uncertainty or variation. Coupled spin systems are modeled as two separate systems with a coupling constant that determines the interaction and is also prone to variation [7], [19]. In this section we consider two ensemble systems that have been studied analytically as well as by the pseudospectral method for the single valued case (i.e. without considering variation) [3], [4], [8]. The analytic results allow us to compare the performance of the ensemble pseudospectral to a known criteria.
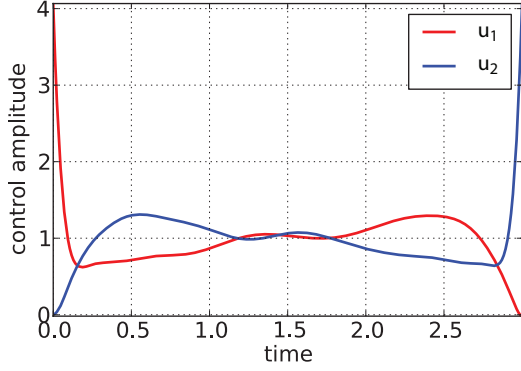
(a) Ensemble Pseudospectral Optimized Pulse
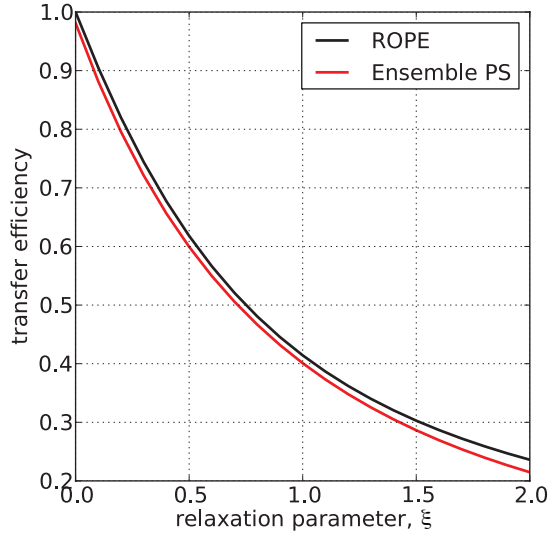
(b) Transfer Efficiency over the Ensemble

Fig. 1. The ensemble optimal control pulse (a) effectively compensates for all variations of ξ on the interval $[0, 2]$ with only minor losses in transfer efficiency (b) when compared to each analytic ROPE [3] efficiency for a single value of ξ. This optimal ensemble pulse was developed by maximizing average transfer efficiency and minimizing energy with $N = 28$ and $N_\xi = 8$ and free terminal time.

A. Spin Pair without Cross-Correlated Relaxation

We first consider a polarization transfer between two heteronuclear spins. It has been shown that this problem can be reduced to maximizing $x_4(T)$ subject to the initial condition $x(0) = (1, 0, 0, 0)^T$ and obeying the governing dynamics

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \\ \dot{x}_4 \end{bmatrix} = \begin{bmatrix} 0 & -u_1 & 0 & 0 \\ u_1 & -\xi & -J & 0 \\ 0 & J & -\xi & -u_2 \\ 0 & 0 & u_2 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix}, \quad (16)$$

where x_i are expectation values of the original spin components, $\xi \in [\xi_1, \xi_2]$ is the relaxation parameter, $J \in [1 - \delta, 1 + \delta]$, $0 \leq \delta \leq 1$, is the spin-spin coupling constant, and $u_1(t)$ and $u_2(t)$ are the applied controls [8], [3]. We first focus on variations in the relaxation parameter alone, developing a pulse robust to all $\xi \in [\xi_1, \xi_2]$ while fixing $J = 1$. The

new control objective is to maximize $\int_{\xi_1}^{\xi_2} x_4(T, \xi) d\xi$ given $x(0, \cdot) = (1, 0, 0, 0)^T$. The single ξ, single J valued case has been analyzed analytically and corresponding analytic pulse, denoted ROPE [3], achieves the optimal transfer given by the relation

$$\eta = \sqrt{\left(\frac{\xi}{J}\right)^2 + 1} - \frac{\xi}{J} . \quad (17)$$

Therefore, the ROPE pulse generates a new pulse solution $(u_1(t), u_2(t))$ for each choice of ξ and J, whereas the ensemble pulse is a single pulse solution that can be used for all values of $\xi \in [\xi_1, \xi_2]$ simultaneously.

We used the ensemble pseudospectral method to solve this problem over the ensemble interval $\xi \in [0, 2]$. The optimization was implemented in the AMPL modeling language and then handed to the nonlinear solver KNITRO from Ziena Optimization. The pseudospectral method, due to the use of orthogonal polynomials, is characterized by low numbers of discretization and sampling. In the case presented in Fig. 1, time was discretized by $N = 28$ nodes and the relaxation parameter was sampled by $N_\xi = 8$ nodes. The transfer efficiency corresponding to the ensemble pseudospectral optimized pulse in Fig. 1a is plotted (red) in Fig. 1b against and compares favorably to the single ξ, single J valued optimal ROPE efficiency (black). The pulse in Fig. 1a was achieved using a free terminal time as well as a combined maximum transfer efficiency and normalized minimum energy objective function,

$$\max \ \mathcal{J} = \underbrace{\frac{1}{N_\xi} \sum_{i=0}^{N_\xi} x_4(T, \xi_i)}_{\varphi, \text{ efficiency transfer}} - \overbrace{\frac{1}{A^2 T}}^{\text{max energy}} \int_0^T \underbrace{u_1^2(t) + u_2^2(t)}_{\mathcal{L}, \text{ energy}} dt$$

where A is the maximum allowed amplitude and the ξ_i were sampled at the $N_\xi + 1$ LGL nodes mapped to the domain $[0, 2]$. The choice of cost function can have a dramatic influence on the performance of the optimization so the ability to easily switch between and conglomerate different cost functions and constraints highlights one of the major advantages of using the pseudospectral method over the current state-of-the-art algorithms in pulse design. In addition, there is no time dedicated to the tedious offline calculation of the gradient $(\partial \mathcal{J}/\partial u_1, \partial \mathcal{J}/\partial u_2)^T$, where $\mathcal{J}$ is the cost function. Customizing the pseudospectral implementation to a specific system is as straightforward as writing down the optimal control problem, as in (15).

We extend this example further to include the possible variation in the coupling strength, $J \in [1 - \delta, 1 + \delta]$. The problem becomes a multidimensional sampling problem in both ξ and J to develop a pulse that is robust to both parameter variations. Adapting the previous optimization code to incorporate the variation in the spin-spin coupling is straightforward and does not require any additional offline computation or analysis. Fig. 2 depicts such a two-dimensional ensemble solution for $N = 24$, $N_\xi = 8$, and $N_J = 4$. The control pulse in Fig. 2a simultaneously
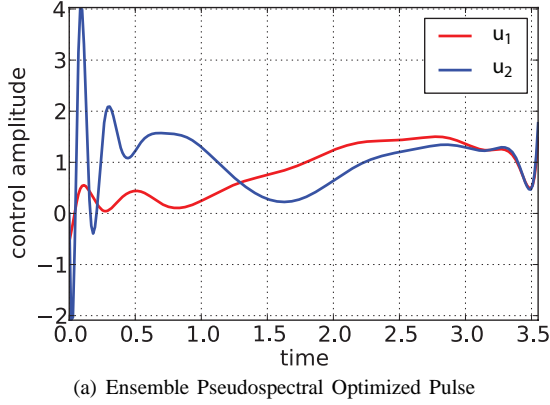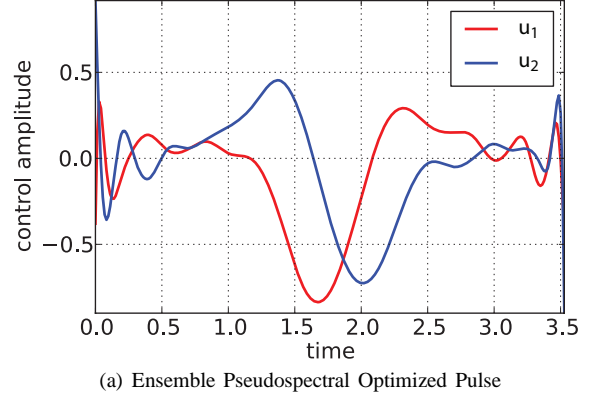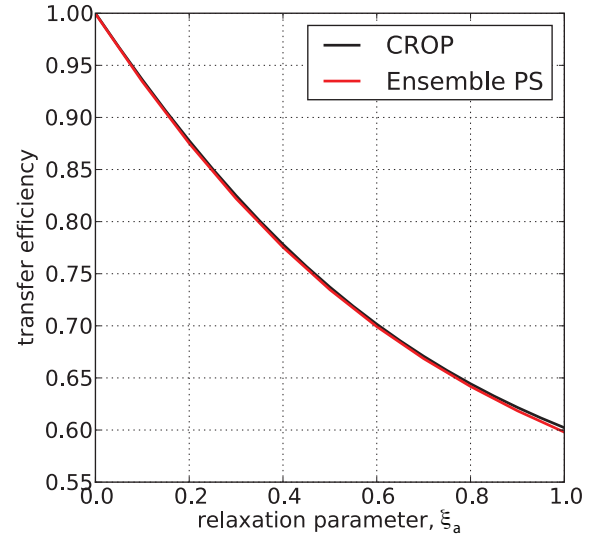
(a) Ensemble Pseudospectral Optimized Pulse
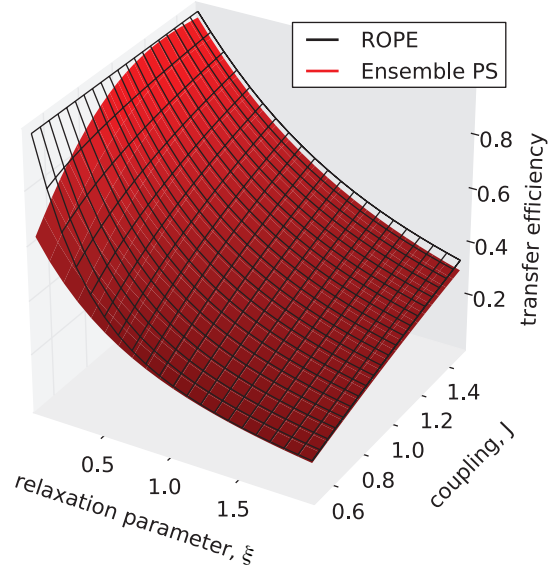
(b) Transfer Efficiency over the Ensemble

Fig. 2. The ensemble optimal control pulse shown in (a) effectively compensates for all variations of ξ on the interval $[0,2]$ and J on the interval $[0.5, 1.5]$ with comparable efficiency (b) to each ROPE pulse [3] for a specific ξ and J. This optimal ensemble pulse was developed by maximizing average transfer efficiency and minimizing energy with $N = 24$, $N_\xi = 8$, and $N_J = 4$ and free terminal time.

compensates for the variation in $\xi \in [0,2]$ and $J \in [0.5, 1.5]$ while achieving a transfer efficiency (Fig. 2b) that compares favorably with each ROPE pulse, which again is optimized for a single choice of ξ and J. As with the prior optimization, the cost function was selected to have both minimum energy and maximum transfer components, however, now the maximum transfer contribution is written as a double summation, taking an average of the transfer efficiency over all choices of ξ and J. It is insightful to note that by employing the minimum energy cost function component in addition to the maximum transfer efficiency cost function, the pseudospectral method is able to select *the* solution with minimum energy from the many that achieve the maximum efficiency - not easily implemented with current methods. The inherent smoothness of the polynomial curves makes these pulses easier to implement and, therefore, more likely for the simulation to match the experimental outcome.

(a) Ensemble Pseudospectral Optimized Pulse

(b) Transfer Efficiency over the Ensemble

Fig. 3. The ensemble optimal control pulse (a) effectively compensates for all variations of ξ_a ($\xi_c = 0.75\xi_a$) on the interval $[0, 1]$ with only minor losses in the transfer efficiency (b) when compared to each analytic CROP pulse designed for a single value of ξ_a [4]. This optimal ensemble pulse was developed with $N = 28$ and $N_{\xi_a} = 6$.

B. Spin Pair with Cross-Correlated Relaxation

The first example system corresponded to a problem of polarization transfer between two spins in which we neglected a specific type of relaxation due to interference effects called DD-CSA cross-correlated relaxation [4]. In some quantum scenarios this effect cannot be neglected, e.g. for large molecules, and admits a more complicated dynamical model. This coherence transfer problem is described by maximizing $x_6(T)$ subject to the initial state $x(0) = (1, 0, 0, 0, 0, 0)^T$ and the dynamics

$$
\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \\ \dot{x}_4 \\ \dot{x}_5 \\ \dot{x}_6 \end{bmatrix} = \begin{bmatrix} 0 & -u_1 & u_2 & 0 & 0 & 0 \\ u_1 & -\xi_a & -\omega & -J & -\xi_c & 0 \\ -u_2 & \omega & -\xi_a & -\xi_c & J & 0 \\ 0 & J & -\xi_c & -\xi_a & \omega & -u_2 \\ 0 & -\xi_c & -J & -\omega & -\xi_a & u_1 \\ 0 & 0 & 0 & u_2 & -u_1 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{bmatrix},
$$

(18)

where again x_i are expectation values of the original spin components, $\xi_a \in [\xi_{a1}, \xi_{a2}]$ is the relaxation parameter as in the previous system, $\xi_c \in [\xi_{c1}, \xi_{c2}]$ is the relaxation parameter corresponding to newly introduced interference effects, J is the spin-spin coupling constant, ω is the frequency, and $u_1(t)$ and $u_2(t)$ are the applied controls [8]. In this problem we now consider the variation $\xi_a \in [0, 1]$ and we select the case in which $\xi_c = 0.75\xi_a$, $J = 1$, and the frequency does not show variation, i.e. $\omega = 0$ in the rotating frame. The single ξ_a valued system has been studied analytically and the so-called CROP [4] control yields a transfer efficiency again given by (17), but in which ξ now takes the value,

$$\xi = \sqrt{\frac{\xi_a^2 - \xi_c^2}{1 + \xi_c^2}} \, . \tag{19}$$

Keeping the coupling constant and frequency fixed, we used the ensemble pseudospectral method to solve this problem over the interval $\xi_a \in [0, 1]$, $\xi_c = 0.75\xi_a$. Implemented in the same manner as the previous problem, Fig. 3a shows the ensemble optimized pulse for $N = 28$ and $N_{\xi_a} = 6$. This discrete optimal control problem includes $28 \times (6 \text{ states} + 2 \text{ controls}) = 224$ decision variables. In conservative estimate, a gradient method would use 1000 points to discretize the time axis, leading to a minimum of $1000 \times (2 \text{ controls}) = 2000$ decision variables - almost a 10 fold increase over the pseudospectral method. The corresponding ensemble transfer efficiency curve is plotted in Fig. 3b in red along with the optimal single ξ_a value CROP η in black. Again, an excellent agreement is exhibited such that the one ensemble control pulse computed by the pseudospectral method, robust to all values of $\xi_a \in [0, 1]$, is comparable to all of the single ξ_a valued CROP pulses. Although the system definition required more states to characterize the dynamics, the pseudospectral method was quickly and easily adapted to this modified problem definition.

IV. CONCLUSION

As pulse sequence design for quantum systems becomes more complex, such as the consideration of parameter variation, these challenging problems require increasingly more flexible numerical methods to find solutions. We present here a highly adaptable framework based on pseudospectral discretization methods which converts the continuous optimal control problem to a constrained minimization problem on a finite dimensional vector space. This methodology admits a natural extension to consider optimal sampling for ensembles of quantum systems, indexed by variations in parameter values. In our previous work, we illustrated the ability of the pseudospectral method to match the performance of analytic and gradient-based control pulses while at the same time allowing for more diverse cost function options and faster convergence rates [8]. Taking the same two examples from liquid NMR, we demonstrated the ability of the pseudospectral method to extend these results to the ensemble case, where the open quantum systems are characterized by variations in relaxation rates and coupling constants.

Manipulating quantum systems is a rich field for optimal control problems and we are at the beginning of adapting the pseudospectral method to quantum control. Such systems are beset with parameters that show variation due to many environmental interactions. Variation in natural frequency is common amongst almost all spin systems in which interactions with the surrounding molecules causes shifts in the frequency. On a bulk level these individual shifts are observed as Larmor dispersion in which the sample frequency lies in a band $[\omega_0 - B, \omega_0 + B]$, $B > 0$, about a central frequency ω_0. Designing a broadband (robust to variation in ω) pulse for the system in (18) is of particular interest for our future work. While the pseudospectral method empirically exhibits exponential convergence, a formal proof of convergence exists for only a small class of systems. We aim to extend these results to a broader family of systems, which includes those studied for pulse sequence design.

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