Time Optimal Control in Spin Systems

Navin Khaneja,* Roger Brockett,† Steffen J. Glaser‡

June 28, 2000

Abstract

In this paper, we study the design of pulse sequences for NMR spectroscopy as a problem of time optimal control of the unitary propagator. Radio frequency pulses are used in coherent spectroscopy to implement a unitary transfer of state. Pulse sequences that accomplish a desired transfer should be as short as possible in order to minimize the effects of relaxation and to optimize the sensitivity of the experiments. Here, we give an analytical characterization of such time optimal pulse sequences applicable to coherence transfer experiments in multiple-spin systems. We have adopted a general mathematical formulation, and present many of our results in this setting, mindful of the fact that new structures in optimal pulse design are constantly arising. Moreover, the general proofs are no more difficult than the specific problems of current interest. From a general control theory perspective, the problems we want to study have the following character. Suppose we are given a controllable right invariant system on a compact Lie group, what is the minimum time required to steer the system from some initial point to a specified final point? In NMR spectroscopy and quantum computing, this translates to, what is the minimum time required to produce a unitary propagator? We also give an analytical characterization of maximum achievable transfer in a given time for the two-spin systems.

1 Introduction

Many areas of spectroscopic fields, such as nuclear magnetic resonance (NMR), electron magnetic resonance and optical spectroscopy rely on a limited set of control variables in order to create desired unitary transformations [5, 6, 7]. In NMR, unitary transformations are used to manipulate an ensemble of nuclear spins, e.g. to transfer coherence between coupled spins in multidimensional NMR-experiments [5] or to implement quantum-logic gates in NMR quantum computers [8]. However, the design of a sequence of radio-frequency pulses that generate a desired unitary operator is not trivial [9]. Such a pulse sequence should be as short as possible in order to minimize the effects of relaxation or decoherence that are always present. So far, no general approach was known to determine the minimum time for the implementation of a desired unitary transformation [6]. Here we give an analytical characterization of such time optimal pulse sequences related to coherence transfer experiments in multiple spin systems. We determine, for example, the best possible in-phase and
anti-phase [6, 10] coherence transfer achievable in a given time. We show that the optimal in-phase transfer sequences improve the transfer efficiency relative to the isotropic mixing sequences [11] and demonstrate the optimality of some previously known sequences.

During the last decade the questions of controllability of quantum systems have generated considerable interest [16, 17]. In particular, coherence or polarization transfer in pulsed coherent spectroscopy has received lot of attention [6, 9]. Algorithms for determining bounds quantifying the maximum possible efficiency of transfer between non-Hermitian operators have been determined [6]. There is utmost need for design strategies for pulse sequences that can achieve these bounds. From a control theory perspective, this is a constructive controllability problem [14]. At the same time it is desirable that the pulse sequences be as short as possible so as to minimize the relaxation effects. This naturally leads us to the problem of time optimal control, i.e. given that there exist controls that steer the system from a given initial to final state, we would like to determine controls that achieve the task in minimum possible time [17, 15].

In non-relativistic quantum mechanics, the time evolution of a quantum system is defined through the time-dependent Schrödinger equation

\[ \dot{U}(t) = -iH(t)U(t), \quad U(0) = I, \]

where \( H(t) \) and \( U(t) \) are the Hamiltonian and the unitary displacement operators, respectively. In this paper, we will only be concerned with finite-dimensional quantum systems. In this case, we can choose a basis and think of \( H(t) \) as a Hermitian matrix. We can split the Hamiltonian

\[ H = H_d + \sum_{i=1}^{m} v_i(t)H_i, \]

where \( H_d \) is the part of Hamiltonian that is internal to the system and we call it the drift or free Hamiltonian and \( \sum_{i=1}^{m} v_i(t)H_i \) is the part of Hamiltonian that can be externally changed. It is called the control or rf Hamiltonian. The equation for \( U(t) \) dictates the evolution of the density matrix according to

\[ \rho(t) = U(t)\rho(0)U^\dagger(t). \]

The problem we are ultimately interested in is to find the minimum time required to transfer the density matrix from the initial state \( \rho_0 \) to a final state \( \rho_F \). Thus, we will be interested in computing the minimum time required to steer the system

\[ \dot{U} = -i(H_d + \sum_{i=1}^{m} v_iH_i) \quad U, \]

from identity, \( U(0) = I \), to a final propagator \( U_F \).

In the following section we establish a framework for studying such problems. For reasons suggested before our approach is more general than the current application requires, but this added generality does not complicate the development.

## 2 Preliminaries

We will assume that the reader is familiar with the basic facts about Lie groups and homogeneous spaces [1]. Throughout this paper, \( G \) will denote a compact semi-simple Lie group and \( e \) its identity
Theorem 1

If \( h \) is a subalgebra of \( g \), then \( \text{ad}_K(h) = \text{ad}_K(h') \).

1. There exists an element \( \xi \in h \) whose centralizer in \( m \) is just \( h \).
2. There is an element \( k \in K \) such that \( \text{ad}_k(h) = h' \).
3. \( m = \bigcup_{k \in K} \text{ad}_k(h) \).

Thus the maximal abelian subalgebras of \( m \) are all \( \text{ad}_K \) conjugate and in particular they have the same dimension. The dimension will be called the rank of the symmetric space \( G/K \) and the maximal abelian subalgebras of \( m \) are called the Cartan subalgebras of the pair \( (g, \mathfrak{t}) \). We will see in what follows that the structure of the time optimal control depends on the rank in an important way. We state a useful corollary of the above theorem [3].

Corollary 1 Let \( G/K \) be a Riemannian symmetric space. Let \( h \) be a Cartan subalgebra of the pair \( (g, \mathfrak{t}) \) and define \( A = \exp(h) \subset G \). Then \( G = KAK \).
**Proof:** \( G = KP \), where \( P = \exp(m) = \exp(\bigcup_{k \in K} \text{ad}_k(h)) = \bigcup_{k \in K} \text{ad}_k(\exp(h)) = \bigcup_{k \in K} \text{ad}_k(A) \subset KAK \). Now \( G = KKA \). Q.E.D.

Note the space \( G/K \) is a union of maximal abelian subgroups \( \text{ad}_k(A) \), called maximal tori.

**Assumption 1** Let \( U \in G \) and let the control system
\[
\dot{U} = [X_d + \sum_{i=1}^{m} v_i X_i] U, \quad U(0) = e
\]
be given. Please note we are working with the matrix representation of the group. We use \( \{X_d, X_1, \ldots, X_m\}_{LA} \) to denote the Lie algebra generated by \( \{X_d, X_1, \ldots, X_m\} \). We will assume that \( \{X_d, X_1, \ldots, X_m\}_{LA} = \mathfrak{g} \), and since \( G \) is compact, it follows that the system (2) is controllable [4]. Let \( t = \{X_i\}_{LA} \) and \( K = \exp\{X_i\}_{LA} \) be the closed compact group generated by \( \{X_i\} \). Given the direct sum decomposition \( \mathfrak{g} = \mathfrak{m} + \mathfrak{t} \) where \( \mathfrak{m} = \mathfrak{t}^\perp \) with respect to the bi-invariant metric \( <,>_G \), let \( X_d \in \mathfrak{m} \). We will assume that \( \text{ad}_k(\mathfrak{m}) \subset \mathfrak{m} \), in which case one says the homogeneous space \( G/K \) is reductive. All our examples will fall into this category.

**Notation:** Let \( \mathcal{C} \) denote the class of all locally bounded measurable functions defined on the interval \([0, \infty)\) and taking value in \( \mathbb{R}^n \). \( \mathcal{C}[0, T] \) denotes their restriction on the interval \([0, T]\). We will assume throughout that in equation (2), \( v = (v_1, v_2, \ldots, v_m) \in \mathcal{C} \). Given \( v \in \mathcal{C} \), we use \( U(t) \) to denote the solution of equation (2) such that \( U(0) = e \). If, for some time \( t \geq 0 \), \( U(t) = U' \), we say that the control \( v \) steers \( U \) into \( U' \) in \( t \) units of time and \( U' \) is attainable or reachable from \( U \) at time \( t \).

**Definition 1 (Reachable Set):** The set of all \( U' \in G \) attainable from \( U_0 \) at time \( t \) will be denoted by \( R(U_0, t) \). Also we use the following notation
\[
R(U_0, T) = \bigcup_{0 \leq t \leq T} R(U_0, t) \\
R(U_0) = \bigcup_{0 \leq t \leq \infty} R(U_0, t).
\]
We will refer to \( R(U_0) \), as the reachable set of \( U_0 \).

**Remark 1** From the right invariance of control systems it follows that \( R(U_0, T) = R(e, T)U_0 \), \( R(U_0, T) = R(e, T)U_0 \), and \( R(U_0) = R(e)U_0 \). Note that \( R(U_0, T) \) need not be a closed set, we use \( \overline{R(U_0, t)} \) to denote its closure.

**Definition 2 (Infimizing Time):** Given \( U_F \in G \), we will define
\[
t^\ast(U_F) = \inf \{ t \geq 0 | U_F \in \overline{R(e, t)} \} \\
t^\ast(KU_F) = \inf \{ t \geq 0 | kU_F \in \overline{R(e, t)}, k \in K \}
\]
and \( t^\ast(U) \) is called the infimizing time.

From a mathematical point of view, we may identify two goals in this paper: (1) to characterize \( \overline{R(e, t)} \) and hence compute \( t^\ast(U_F) \), the infimizing time for \( U_F \in G \), and (2) to characterize the infimizing control sequence \( v^\ast \) in (2), which in the limit \( n \to \infty \), achieves the transfer time \( t^\ast(U_F) \) of steering the system (2) from identity \( e \) to \( U_F \). From the physics point of view, these results will help to establish the minimum time required and the optimal controls (the rf pulse sequence in NMR experiments) to achieve desired transfers in a spectroscopy experiment.
Figure 1: The panel shows the time optimal path between elements $U$ and $V$ belonging to $G$. The dashed line depicts the fast portion of the path corresponding to movement within the coset $KU$ and, in traditional NMR language, corresponds to the pulse and the solid line corresponds to the slow portion of the curve connecting different cosets and corresponds to evolution of the couplings.

3 Time Optimal Control

The key observation is the following. In the control system (2), if $U_F \in K$ then $t^*(U_F) = 0$. To see this, note that by letting $v$ in (2) be large, we can move on the subgroup $K$ as fast as we wish. In the limit as $v$ approaches infinity, we can come arbitrarily close to any point in $K$ in arbitrarily small time with almost no effect from the term $X_d$. By same reasoning for any $U \in G$, $t^*(U) = t^*(kU)$ for $k \in K$. Thus, finding $t^*(U_F)$ reduces to finding the minimum time to steer the system (2) between the cosets $Ke$ and $KU_F$.

This is illustrated in the Figure 1, where the cosets $KU$ and $KV$ are depicted and the infimizing time path between elements $U$ and $V$ belonging to $G$ is shown. The dashed part of the curve illustrates the fast motion within the coset. The solid part of the curve corresponds to the drift part of the flow (also known as the evolution of couplings in NMR literature). The minimum time problem then corresponds to finding shortest path between these cosets or, in other words, the shortest path in the space $G/K$.

With this intuitive picture in mind, we now state some lemmas.

Lemma 1 Let $U \in G$ and $X : \mathbb{R} \to \mathfrak{g}$ be a locally bounded measurable function of time. If $X_n(t)$ converges to $X(t)$ in the sense that

$$\lim_{n \to \infty} \int_0^T \|X(t) - X_n(t)\| dt = 0,$$

then the solution of the differential equation $\dot{U} = X_n(t)U$ at time $T$ converges to the solution of $\dot{U} = X(t)U$ at time $T$.

The proof of the above result is a direct consequence of the uniform convergence of the Peano-Baker series. We use this to show
Lemma 2 For the control system in equation (2), \( t^*(U_F) = t^*(KU_F) \).

**Proof:** We first show that if \( k \in K \), then \( t^*(k) = 0 \). Because \( \exp\{X_1, \ldots, X_m\}_{LA} = K \), given any \( T > 0 \) there exists \( \bar{v} \in C(T) \), such that the solution of

\[
\dot{U} = \sum_{i=1}^{m} \bar{v}_i(t)X_i|U, \ U(0) = e
\]

takes on the value \( k \) at time \( T \). Now consider the family of control systems

\[
\dot{U} = [X_d + \alpha \sum_{i=1}^{m} \bar{v}_i(\tau)X_i]|U, \ U(0) = e.
\]

Rescaling time as \( \tau = \alpha t \), we obtain

\[
\frac{dU}{d\tau} = \left[ \frac{X_d}{\alpha} + \sum_{i=1}^{m} \bar{v}_i(\tau)X_i \right]|U, \ U(0) = e.
\]

Observe that, by Lemma 1, as \( \alpha \to \infty \), \( U(\tau)_{\tau=T} = k \) or \( \lim_{\alpha \to \infty} U(t)_{t=\frac{T}{\alpha}} = k \). Therefore \( k \in R(e, T) \), for all \( T > 0 \), implying \( t^*(k) = 0 \).

We now prove the general assertion. Let \( t^*(U_F) = T \), we show that if \( U_1 = kU_F \) for \( k \in K \), then \( t^*(U_1) = T \). Because \( t^*(U_F) = T \), for any \( T_1 > T \), \( U_F \in R(e, T_1) \), therefore there exists a family of control laws \( v^r[0, T_1] \) such that the corresponding solutions \( U^r(t) \) to the equation (2) satisfy \( U^r(T_1) \to U_F \). From the first part of the proof, for any \( T_2 > T_1 \) there exists a control sequence \( v^p[T_1, T_2] \) such that the solutions \( U^p(t) \) to the family of control systems

\[
\dot{U} = [X_d + \sum_{i=1}^{m} v_i^p X_i]|U, \ U(T_1) = U_F
\]

satisfies \( U^p(t^p) \to U_1 \), for \( t^p < T_2 \) and \( t^p \to T_1 \). Using the continuity of the solution of the differential equation to its initial condition and Lemma 1, we conclude that there exists a family of control laws \( v^n[0, T_2] \) such that the corresponding solutions \( U^n(t) \) to the family of control systems

\[
\dot{U} = [X_d + \sum_{i=1}^{m} v_i^n X_i]|U, \ U(0) = e
\]

satisfy \( U^n(t^n) \to U_1 \), for \( t^n < T_2 \). Therefore, \( U_1 \in R(e, T_2) \). Since \( T_2 > T_1 \) is arbitrary \( t^*(U_1) \leq T_1 \). Because \( T_1 > T \) is also arbitrary, we infer that \( t^*(U_1) \leq T \). This shows that \( t^*(U_1) \leq t^*(U_F) \). Now reverse the roles of \( U_F \) and \( U_1 \) to get the opposite inequality. This proves the claim. **Q.E.D.**

**Remark 2** The above observation will help us make a bridge between the problem of computing \( t^*(U_F) \) and the problem of computing minimum length paths for a related problem which we now explain.

**Definition 3 (Adjoint Control System):** Let \( P \in G \). Associated with the control system (2) is the right invariant control system

\[
\dot{P} = XP,
\]

where now the control \( X \) no longer belongs to the vector space but is restricted to an adjoint orbit i.e., \( X \in Ad_K(X_d) = \{ k^{-1}X_d k | k \in K \} \). We call such a control system an adjoint control system.
For the control system (3), we say that $KU_F \in B(U_0, t')$ if there exists a control $X[0, t']$ which steers $P(0) = U_0$ to $P(t') \in KU_F$ in $t'$ units of time. We use the notation

$$B(U_0, T) = \bigcup_{0 \leq t \leq T} B(U_0, t).$$

From Lemma 1, we see that $B(U_0, T)$ is closed.

We use

$$L^*(KU_F) = \inf \{ t \geq 0 \mid KU_F \in B(e, t) \}$$

to denote the minimum time required to steer the system (3) from identity $e$ to the coset $KU_F$. We call it the minimum coset time.

**Theorem 2 (Equivalence theorem):** The infimizing time $t^*(U_F)$ for steering the system

$$\dot{U} = [X_d + \sum_{i=1}^m v_i X_i]U$$

from $U(0) = e$ to $U_F$ is the same as the minimum coset time $L^*(KU_F)$, for steering the adjoint system

$$\dot{P} = XP, \ X \in Ad_K(X_d)$$

from $P(0) = e$ to $KU_F$.

**Proof:** Let $Q \in K$ satisfy the differential equation

$$\dot{Q} = \sum_{i=1}^m v_i X_i Q, \ Q(0) = e. \quad (4)$$

Let $P \in G$ evolve according to the equation

$$\dot{P} = (Q^{-1}X_d Q) P, \ P(0) = e. \quad (5)$$

Then observe that

$$\frac{d(QP)}{dt} = [X_d + \sum_{i=1}^m v_i X_i](QP), \ Q(0)P(0) = e,$$

which is the same evolution equation as that of $U$, and since $U(0) = Q(0)P(0) = e$, by the uniqueness theorem for the differential equations, $U(t) = Q(t)P(t)$. Therefore, given a solution $\dot{U}(t)$ of equation (2) with the initial condition $\dot{U}(0)$, there exist unique curves $\dot{P}(t)$ and $\dot{Q}(t)$, defined through equations (4) and (5), satisfying $\dot{U}(t) = \dot{Q}(t)\dot{P}(t)$. Observe that if $\dot{U}(T) = U_F$ then it follows that $\dot{P}(T) \in KU_F$. If $U_F \in K(e, T)$, then there exists a sequence of control laws $v^r[0, T]$ such that the corresponding solutions $U^r(t)$ of (2) satisfy $U^r(T) \rightarrow U_F$. Therefore, the solutions $P^r(t)$ of the associated control system (4) satisfy $\lim_{r \rightarrow \infty} P^r(T) \in KU_F$. Because $B(e, T)$ is closed, it follows that $KU_F \in B(e, T)$, which implies that $L^*(KU_F) \leq t^*(U_F)$.

To prove the equality observe that if $KU_F \in B(e, T)$, then there exists a control $X[0, T]$ such that the corresponding solution $\dot{P}(t)$ to (3) satisfies $\dot{P}(T) \in KU_F$. Because $X(t) \in Ad_K(X_d)$, we can express $\dot{X}(t)$ as $\dot{Q}(t)^{-1}X_d\dot{Q}(t)$. It is well known [13] that we can find a family $v^r(t)$ of control laws such that the corresponding solution $Q^r(t)$ of

$$\dot{Q}^r = \sum_{i=1}^m v^r_i X_i Q^r, \ Q^r(0) = e$$

7
satisfy \( \lim_{r \to \infty} \int_0^T \| \dot{Q}(t) - Q^r(t) \| dt = 0 \). Hence, \( \lim_{r \to \infty} \int_0^T \| \vec{X}(t) - (Q^r(t))^{-1} X_d Q^r(t) \| dt = 0 \). Using Lemma 1, we claim that the solutions to family of differential equations

\[
\dot{P}^r = [(Q^r)^{-1}(t)X_d Q^r(t)]P^r, \quad P^r(0) = e
\]
satisfies \( \lim_{r \to \infty} P^r(T) \in KU_F \). Therefore, \( t^*(KU_F) \leq T \). Since the choice of \( T \) was arbitrary, it follows \( t^*(KU_F) \leq L^*(KU_F) \). Because \( t^*(KU_F) = t^*(U_F) \), it follows that \( t^*(U_F) \leq L^*(KU_F) \). Hence the proof. Q.E.D

Remark 3 The control system (2) evolves on the group \( G \) and induces a control system on the coset space \( G/K \) through the projection map \( \pi \). The adjoint control system (3) is a representation of this induced control system. Observe that since \( \| X \| = 1 \) in (3), we can also define \( L^*(KU_F) \) as the infimizing value of \( \int_0^1 \langle \dot{P}, \dot{P} \rangle \frac{1}{2} dt \) for steering the system

\[
\dot{P} = \gamma XP, \quad \gamma > 0
\]

from \( P(0) = e \) to \( P(1) \in KU_F \).

We will now compute \( t^*(U_F) \) using the properties of the set \( Ad_K(X_d) \). Based on the qualitative nature of time optimal trajectories of the system (2), we make the following classification.

1. **Riemannian Symmetric Case** In addition to Assumption 1, if we have the restriction \([m, m] \subset \mathfrak{k}\), then we are in the Riemannian symmetric case as described in the section 2. We can further classify this case based on the rank of the symmetric space \( G/K \).

   - **Pulse-drift-pulse sequence** (characteristic of single-spin systems) In this case, the rank of the symmetric space \( G/K \) is one. Roughly speaking the trajectories of the infimizing control sequence \( v^r \) (which in the limit \( r \to \infty \), achieves the transfer time \( t^*(U_F) \)) converge to an impulse (which resembles an impulse of appropriate shape), followed by evolution under drift (for time \( t^*(U_F) \)) and a final impulse.

   - **Chained Pulse-drift-pulse sequence** (characteristic of two-spin system) In this case, the rank of the symmetric space \( G/K \) is more than one. The trajectories corresponding to an infimizing control sequence \( v^r \) in (3) converge to a chain of "impulse drift impulse" pattern. The infimizing time \( t^*(U_F) \) is the time spent when the system just evolves under drift.

2. **Chatter sequence** In this case, \( G/K \) is no more a Riemannian symmetric case, i.e. \([m, m] \not\subset \mathfrak{k}\).

   This is a characteristic of more than two-spin systems.

In this paper we will confine ourselves to the Riemannian symmetric case. The non-symmetric case will be treated in detail in a forthcoming paper.

**Pulse-drift-pulse sequence**

We begin with the first case where the rank of the symmetric space \( G/K \) is one. It follows from Theorem 1 that \( m = \bigcup_{\alpha \geq 0} ad_K(\alpha X_d) \). In this case, computing \( t^*(U_F) \) reduces to finding the geodesic distance on the homogeneous space \( G/K \). Given the bi-invariant metric \( <, >_G \) on \( G \), there is a corresponding left invariant metric \( <, >_n \), on the homogeneous space \( G/K \) arising from the restriction of \( <, >_G \) to \( m \). Let \( L_n(\gamma) \) represent the length of a curve \( \gamma \in G/K \) under the standard
is the Riemannian distance between $o$ and $Ad^Q U e$ geodesics under the metric steering the system spin matrices. Given the unitary evolution of the single-spin system (sequence) for the system (2), which steers the system form Remark 4 Roughly speaking, the time optimal trajectory (obtained as a limit of the infimizing Q.E.D the proof.

where the control $v \in \mathbb{R}$. Let $U_x = \exp(-i I_x t)$ represent the one-parameter subgroup generated by $I_x$. Given $U_F \in SU(2)$, there exists a unique $\beta \in [0, 2\pi]$ such that $U_F = U_1 \exp[-i\beta I_x]U_2$, where $U_1, U_2 \in U_x$. The infimizing time $t^*(U_F) = \beta$.

Proof: First note that the Lie algebra $\mathfrak{g} = su(2)$ has the decomposition $\mathfrak{m} = \{iI_y, iI_z\}$, $\mathfrak{t} = \{iI_x\}$, and $Ad_{U_F}(I_z) = \mathfrak{m}$. Observe from corollary 1 that any $U_F \in SU(2)$ has a representation $U_F = Q_1 \exp[-i\alpha I_z]Q_2$, where $Q_1, Q_2 \in U_x$. Because $\exp[-it I_x]$ is periodic with period $4\pi$, the $\beta$ with the
smallest absolute value for which \( U_F = U_1 \exp[-i\beta I_2]U_2 \) holds, belongs to the interval \([-2\pi, 2\pi]\). Because \(-I_2 \in Ad_{U_1}(I_2)\), we can restrict \( \beta \) to the interval \([0, 2\pi]\). The proof then follows directly from the Theorem 3. \( \text{Q.E.D.} \)

**Corollary 3** Let \( \Theta \in G = SO(3) \), and let \( \Omega_x = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \Omega_z = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \) represent the generators of rotation around \( x- \) and \( z- \)axis. Consider the control system

\[
\dot{\Theta} = [\Omega_z + v\Omega_x]\Theta,
\]

where the control \( v \in \mathbb{R} \). Let \( \Theta_x = \exp(\Omega_x t) \) represent the one-parameter subgroup generated by \( \Omega_x \). Given \( \Theta_F \in SO(3) \), there exists a unique \( \beta \in [0, \pi] \) such that \( \Theta_F = Q_1 \exp[\beta \Omega_x]Q_2 \), where \( Q_1, Q_2 \in \Theta_x \). The infimizing time \( t^*(\Theta_F) = \beta \).

**Proof:** First note that the Lie algebra \( g = so(3) \) has the decomposition \( m = \{\Omega_y, \Omega_z\}, \mathfrak{f} = \{\Omega_x\} \), and \( Ad_{\Theta_x}(\Omega_z) = m \). Observe that any \( \Theta_f \in SO(3) \) has a representation \( \Theta_f = Q_1 \exp[\alpha \Omega_x]Q_2 \), where \( Q_1, Q_2 \in \Theta_x \). Because \( \exp[t\Omega_z] \) is periodic with period \( 2\pi \), the proof is on the same lines as Corollary 2. \( \text{Q.E.D.} \)

We now generalize the example to the case where \( G = SO(n) \), the group of \( n \times n \) orthogonal matrices. The Lie algebra is \( g = so(n) \), the set of \( n \times n \) skew-symmetric matrices. The bi-invariant metric on \( G \) is \( \langle \Omega, \Omega \rangle = tr(\Omega^T \Omega) \). Consider the following decomposition of \( g \). Let \( m \) consists of skew-symmetric matrices which are zero except the first row and column and \( \mathfrak{f} \) consists of skew symmetric matrices which are zero in the first row and column. Observe that \( \mathfrak{f} \) generates the subgroup \( SO(n-1) \). Then we have

**Corollary 4** Let \( \Theta \in G = SO(n) \) and let the control system

\[
\dot{\Theta} = [\Omega_d + \sum_{i=1}^{m} v_i \Omega_i] \Theta, \ \Theta(0) = I
\]

be given, where \( \Omega_d \in \mathfrak{m}, v_i \in \mathbb{R}, \Omega_i \in \mathfrak{f} \) and \( \Omega_d \in \mathfrak{m} \), such that \( \exp[t\Omega_d] \) has period \( 2\pi \). Suppose that \( K = \exp[\{\Omega_i\}]_{LA} = SO(n-1) \). Given \( \Theta_f \in SO(n) \), there exists a unique \( \beta \in [0, \pi] \) such that \( \Theta_f = \Theta_1 \exp[\beta \Omega_x]\Theta_2 \), where \( \Theta_1, \Theta_2 \in \Theta_x \). The infimizing time \( t^*(\Theta_f) = \beta \).

**Proof:** Observe that \( Ad_K(\Omega_d) = \mathfrak{m} \) and hence the proof is on the same lines as Corollary 2. \( \text{Q.E.D.} \)

**Chained Pulse-drift-pulse sequence**

Let us now consider the second case in our classification scheme. We now analyze the case when the rank of the Riemannian symmetric space \( G/K \) is greater than one.

**Definition:**(Schur Horn Polytope) Given the decomposition \( g = m + \mathfrak{f} \), let \( \mathfrak{h} \subset m \) represent the maximal abelian subalgebra containing \( X_d \). We use the notation \( \Delta_{X_d} = \mathfrak{h} \cap Ad_K(X_d) \) to denote the maximal commuting set contained in the adjoint orbit of \( X_d \). We define the convex hull \( \{\sum_{i=1}^{n} \beta_i X_i | \beta_i \geq 0, \sum \beta_i = 1, X_i \in \Delta_{X_d}\} \) as the Schur Horn polytope of \( X_d \). We define the positive cone \( \text{Sp}(\Delta_{X_d}) = \{\sum_{i=1}^{n} \beta_i X_i | \beta_i \geq 0, X_i \in \Delta_{X_d}\} \), as the Schur Horn cone of \( X_d \).

We compute the infimizing time for the system (2), in the following Theorem (4), which is a generalization of the rank one case.
Remark 5: Recall from corollary (1) that, if $A = \exp(\mathfrak{h})$, where $\mathfrak{h}$ is the maximal abelian subalgebra contained in $\mathfrak{m}$, then $G = KAK$. Therefore given any $U_F \in G$, we can express $U_F = Q_1 \exp(Z)Q_2 = Q_1 Q_2 \exp(Ad_{Q_2}(Z))$, where $Q_1$, $Q_2 \in K$ and $Z \in \mathfrak{h}$. Suppose $Z$ belongs to the Schur horn cone of $X_d$, i.e. $Z = \sum_{i=1}^{n} \beta_i X_i$, $\beta_i \geq 0, X_i \in \Delta_{X_d}$. By choosing $X(t)$ to be $Ad_{Q_2}(X_i)$ for $\beta_i$ units of time we can steer the adjoint control system $\dot{P} = X(t)P$ from the identity to the coset $KU_F = K \exp(Ad_{Q_2}(Z))$. The claim of the following theorem is that this is indeed the fastest way to reach the coset $KU_F$. In other words the quickest way to get to the coset $KU_F$ is to flow on the maximal torus, $Ad_{Q_2}(A)$, $Q_2 \in K$, containing the cosets $KU_F$.

We will show that the trajectories of the adjoint control system $\dot{P} = \gamma XP$ satisfying $P(0) = e$, $P(1) \in KU_F$, which render the cost function $\int_0^1 < \dot{P}, \dot{P} > \frac{1}{2} dt$ stationary are confined to the maximal tori as explained above. We will not go into the details of proving that there exist no abnormal minimizers of this cost function. A more complete proof of the following theorem will be presented elsewhere.

Theorem 4 (Stationary Maximal Tori Theorem): Let $G$ be a compact matrix Lie group and $K$ be a closed subgroup with $\mathfrak{g}$ and $\mathfrak{k}$ their Lie algebras, respectively. Let the direct sum decomposition $\mathfrak{g} = \mathfrak{m} + \mathfrak{k}$, such that $\mathfrak{m} = \mathfrak{k}^\perp$, be given. Consider the right invariant control system

$$\dot{U} = [X_d + \sum_{i=1}^{m} v_i X_i]U, \quad U \in G, \quad U(0) = e,$$

where $v_i \in \mathbb{R}$, $X_d \in \mathfrak{m}$, $\{X_i\}_{LA} = \mathfrak{k}$. Suppose $G/K$ is a Riemannian symmetric space, then any $U_F = Q_1 \exp(Y)Q_2$, where $Q_1$, $Q_2 \in K$, and $Y \in Sp(\Delta_{X_d})$ belongs to the closure of the reachable set. The infimizing time $t^*(U_F)$ is the smallest value of $\alpha > 0$, such that we can solve

$$U_F = Q_1 \exp(\alpha Z)Q_2,$$

where $Q_1$, $Q_2 \in K$ and $Z$ belongs to the Schur horn polytope of $X_d$.

Proof: To compute $L^*(KU_F)$, we first characterize the trajectories of the adjoint control system $\dot{P} = \gamma XP$ satisfying $P(0) = e$, $P(1) \in KU_F$, which render the cost function $\int_0^1 < \dot{P}, \dot{P} > \frac{1}{2} dt$ stationary. For this, we derive the first-order necessary conditions for $P(t)$ to be a stationary trajectory. We incorporate the constraints by using Lagrange multiplier $\lambda$. Following [19], we represent the linear functional on $\dot{P}$ as $\phi_\lambda(\dot{P}) = \text{tr}(\dot{P} \lambda) = \gamma \text{tr}(XP\lambda)$. Since the control $X$ belongs to an adjoint orbit we restrict $P\lambda$ to an adjoint orbit $Ad_K(\xi)$, $\xi \in \mathfrak{m}$. In particular, we choose $\xi$ to a be regular element, i.e the centralizer of $\xi$ is a maximal abelian algebra contained in $\mathfrak{m}$. The modified cost then takes the form

$$h(P, \lambda, X, \gamma) = \gamma \text{tr}(\lambda XP) + \frac{1}{2} \gamma^2 \text{tr}(X^T(t)X(t)).$$

As $\|X\| = 1$, we have

$$h(P, \lambda, X, \gamma) = \gamma \text{tr}(\lambda XP) + \frac{1}{2} \gamma^2.$$

The first order conditions of stationarity are [18], $\dot{\lambda} = -\frac{\partial h}{\partial P}, \frac{\partial h}{\partial \lambda} = 0$ and $\frac{\partial h}{\partial X} = 0$, which imply

$$\dot{\lambda}(t) = -\gamma \lambda(t)X(t)$$

$$\gamma = -\text{tr}(\lambda XP)$$

$$\text{tr}(dX P\lambda) = 0.$$

Observe that $X = Q^{-1}X_dQ$, where $Q \in K$, and therefore $dX = [dA, X]$, where $dA \in \mathfrak{k}$, implying

$$\text{tr}(dA[X, P\lambda]) = 0.$$
Since $A \in \mathfrak{k}$ is arbitrary this implies that

$$[X, P\lambda] \in \mathfrak{m}. \quad (6)$$

Let $M = P\lambda$. The evolution equation for $M$ satisfies

$$\dot{M} = \gamma^2 [X, M]. \quad (7)$$

Since $X \in \mathfrak{m}$ and $M \in \mathfrak{m}$, the condition $[\mathfrak{m}, \mathfrak{m}] \in \mathfrak{k}$ implies that if (6) holds then $[X, M] = 0$. From (7), it follows that $\dot{M} = 0$. Therefore, extremal $X(t)$ satisfies $[X(t), M(0)] = 0$. From (7), it follows that $\dot{M} = 0$. Therefore, extremal $X(t)$ satisfies $[X(t), M(0)] = 0$. Hence the proof. \quad Q.E.D

**Remark 6** The theorem characterizes $B(e, t)$, the reachable set for the adjoint system. This is given by

$$KB(e, t) = K \exp(\alpha Z)K, \ 0 \leq \alpha \leq t$$

where $Z$ belongs to the Schur Horn polytope of $X_d$.

### 4 Spin Algebra

The Lie Group which we will be most interested in is $SU(2^n)$, the special unitary group describing the evolution of $n$ coupled spins $\frac{1}{2}$. Its Lie algebra $\mathfrak{su}(2^n)$ is a $4^n - 1$ dimensional space of traceless $n \times n$ skew-Hermitian matrices. The orthonormal basis which we will use for this space is expressed as tensor products of Pauli spin matrices [12]

$$I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The matrices $(I_x, I_y, I_z)$ are the generators for rotation in the two dimensional Hilbert space and basis for the Lie algebra of traceless skew-Hermitian matrices $\mathfrak{su}(2)$. They obey the well known commutation relations

$$[I_x I_y] = iI_z; \quad [I_y I_z] = iI_x; \quad [I_z I_x] = iI_y.$$

Then the basis for $\mathfrak{su}(2^n)$ takes the form $\{iB_s\}$ where

$$B_s = 2^{n-1} \prod_{k=1}^{n} (I_{k\alpha})^{a_{ks}}. \quad (8)$$

12
where $I_{\alpha}$ the Pauli matrix appears in the above expression only at the $k^{th}$ position, and $1$ the two dimensional identity matrix, appears everywhere except at the $k^{th}$ position. $a_{k\alpha}$ is 1 for $q$ of the indices and 0 for the remaining. Note that $q \geq 1$ as $q = 0$ corresponds to the identity matrix and is not a part of the algebra. As an example for $n = 2$ the basis for $\mathfrak{su}(4)$ takes the form

$$
q = 1 \quad I_{1x}, I_{1y}, I_{1z}, I_{2x}, I_{2y}, I_{2z} \\
q = 2 \quad 2I_{1x}I_{2x}, 2I_{1y}I_{2y}, 2I_{1z}I_{2z} \\
\quad 2I_{1y}I_{2x}, 2I_{1y}I_{2y}, 2I_{1y}I_{2z} \\
\quad 2I_{1z}I_{2x}, 2I_{1z}I_{2y}, 2I_{1z}I_{2z}.
$$

It is important to note that these operators are only normalized for $n = 2$ as

$$
tr(B_r B_s) = \delta_{rs}2^{n-2}.
$$

To fix ideas, let’s compute one of these operators explicitly for $n = 2$

$$
I_{1z} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}
$$

which takes the form

$$
I_{1z} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}.
$$

We will often refer to the algebra of $\mathfrak{su}(2^n)$ as the spin algebra.

### 5 Optimal Transfer in Two-Spin Systems

In this section, we will apply our general results on the time optimal control for the specific case of a heteronuclear two-spin system. In particular, we consider the following important heteronuclear two-spin system discussed in detail in [6]. By going to a rotating frame, the free evolution part of the Hamiltonian has been reduced to just a scalar coupling evolution. The system then takes the following form.

Let $U \in SU(4)$, which evolves as

$$
\dot{U} = -i(H_d + \sum_{i=1}^{4} u_i H_i)U,  \quad (10)
$$

13
where

\[
H_d = 2\pi J z S_z \\
H_1 = 2\pi I_x \\
H_2 = 2\pi I_y \\
H_3 = 2\pi S_x \\
H_4 = 2\pi S_y,
\]

where \(I_x, I_y\) and \(I_z\) represent operators for the first spin and have the same meaning as \(I_{1x}, I_{1y}\) and \(I_{1z}\), respectively, as explained in previous section 4. Similarly \(S_x, S_y,\) and \(S_z\) represent operators for the second spin and have the same meaning as \(I_{2x}, I_{2y}\) and \(I_{2z}\). The symbol \(J\) represents the strength of the scalar coupling between \(I\) and \(S\). Observe that the subgroup \(K\) generated by \(\{H_i\}_{i=1}^4\) is \(SU(2) \times SU(2)\).

We first compute the infimizing time for steering the system (10).

**Theorem 5** For the heteronuclear spin system, described by the equation (10), the infimizing time \(t^*(U_F)\) is the smallest value of \(\sum_{i=1}^3 \alpha_i, \alpha_i > 0\), such that we can solve

\[
U_F = Q_1 \exp(-i2\pi J(\alpha_1 I_x S_x + \alpha_2 I_y S_y + \alpha_3 I_z S_z))Q_2,
\]

where \(Q_1\) and \(Q_2\) belong to \(K\).

**Proof:** Consider the direct sum decomposition \(g = m + k\), where \(m = \text{span}\{I_{\alpha} S_{\beta}\}, k = \text{span}\{I_{\alpha}, S_{\beta}\}\), and \((\alpha, \beta) \in (x, y, z)\). Then observe \([m, m] \in k, [m, k] \in m,\) and \([k, k] \in k\). Furthermore, observe that \(\Delta_{I_z S_z} = \{\pm I_z S_z, \pm I_z S_y\}\), and also \(\text{Ad}_K(S\sigma(\Delta_{I_z S_z})) = m\). Thus the above example satisfies all the conditions of the theorem 4. Hence the proof. Q.E.D

Now we address the question of maximum possible achievable transfer in some given time \(T\). For this purpose we define the transfer efficiency.

**Definition 4 (Transfer Efficiency):** Given the evolution of the density matrix \(\rho(t) = U(t)\rho(0)U^\dagger(t)\), where

\[
\dot{U} = -i( H_d + \sum_{i=1}^m u_i H_i )U, \quad U(0) = I,
\]

define the transfer efficiency \(\eta(t)\) to some given target operator \(F\) as

\[
\eta(t) = \|\text{tr}(F^\dagger U(t)\rho(0)U^\dagger(t))\|.
\]

**Remark 7** In the formula for the transfer efficiency, we always assume that the starting operator \(\rho(0)\) and the final operator \(F\) are both normalized to have norm one (i.e. \(\text{tr}(F^\dagger F) = 1\)).

We will now look at the in-phase and anti-phase transfers in the two-spin system, whose evolution is given by equation (10). We give here expressions for maximum transfer efficiencies. We first prove some lemmas, which will be required in computing transfer efficiencies.

**Lemma 3** let \(p = \begin{bmatrix} 1 \\ -i \\ 0 \end{bmatrix}\) and let \(\Sigma\) be a real diagonal matrix

\[
\Sigma = \begin{bmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{bmatrix}.
\]
If \(a_i \geq a_j \geq a_k \geq 0\), where \(\{i, j, k\} \in \{1, 2, 3\}\) and let \(U, V \in \text{SO}(3)\), then the maximum value of \(|p^1U \Sigma V p|\) is \(a_i + a_j\).

**Proof:** Let

\[
\Lambda = \begin{bmatrix}
\sqrt{a_1} & 0 & 0 \\
0 & \sqrt{a_2} & 0 \\
0 & 0 & \sqrt{a_3}
\end{bmatrix}.
\]

By definition \(\Sigma = \Lambda^\dagger \Lambda\). Using Cauchy Schwartz inequality \(|p^1U \Sigma V p| \leq |AVp| \|AUp||\). Observe, the maximum value of \(|AVp|\) is \(\sqrt{a_i + a_j}\). Therefore \(|p^1U \Sigma V p| \leq a_i + a_j\). Clearly for appropriate choice of \(U\) and \(V\), this upper bound is achieved (For example, in case \(a_1 \geq a_2 \geq a_3\), the bound is achieved for \(U\) and \(V\) identity). Hence the result follows. Q.E.D.

**Lemma 4** Consider the function \(f(\alpha_1, \alpha_2, \alpha_3) = \sin(J\pi\alpha_1) \sin(J\pi\alpha_2) + \sin(J\pi\alpha_1) \sin(J\pi\alpha_3)\). If \(\alpha_1, \alpha_2, \alpha_3 \geq 0\) and \(\alpha_1 + \alpha_2 + \alpha_3 = T\), where \(T \leq \frac{3\pi}{2}\), then the maximum value of \(f(\alpha_1, \alpha_2, \alpha_3)\) is \(2\sin(J\pi a) \sin(J\pi b)\), where \(a + 2b = t\) and \(\tan(J\pi a) = 2\tan(J\pi b)\).

**Proof:** Let

\[
H(\alpha_1, \alpha_2, \alpha_3, \lambda) = \sin(J\pi\alpha_1) \sin(J\pi\alpha_2) + \sin(J\pi\alpha_1) \sin(J\pi\alpha_3) + \lambda(\alpha_1 + \alpha_2 + \alpha_3 - T).
\]

The necessary condition for optimality gives \(\partial H/\partial \alpha_1 = 0\), \(\partial H/\partial \alpha_2 = 0\), \(\partial H/\partial \alpha_3 = 0\), which imply respectively that

\[
\begin{align*}
\pi J(\cos(J\pi\alpha_1) \sin(J\pi\alpha_2) + \cos(J\pi\alpha_1) \sin(J\pi\alpha_3)) + \lambda &= 0 \quad (11) \\
\pi J(\sin(J\pi\alpha_1) \cos(J\pi\alpha_2) + \sin(J\pi\alpha_1) \cos(J\pi\alpha_3)) + \lambda &= 0 \quad (12) \\
\pi J(\sin(J\pi\alpha_1) \cos(J\pi\alpha_3)) + \lambda &= 0 \quad (13)
\end{align*}
\]

From equation (12) and (13), we obtain that either \(\sin(J\pi\alpha_1) = 0\) or \(\cos(J\pi\alpha_2) = \cos(J\pi\alpha_3)\). The first condition does not give a maxima as it makes \(f\) identically zero. The second condition implies

\[
J\pi\alpha_2 = 2m\pi + J\pi\alpha_3. \quad (14)
\]

Since \(\alpha_2, \alpha_3 \geq 0\) and \(\alpha_2 + \alpha_3 \leq T \leq \frac{3\pi}{2}\), condition (14) is only satisfied for \(m = 0\). Therefore, \(\alpha_1 = \alpha_2\). Now substituting this in (11) and using the equations (11) and (12), we get the desired result

Q.E.D.

**Theorem 6 (Maximum in-phase transfer)** Consider the evolution for the heteronuclear IS spin system as defined by Equation (10). Let \(\rho(0) = \frac{S_z - i S_y}{\sqrt{2}}\) and \(F = \frac{I_z - i I_y}{\sqrt{2}}\). For \(t \leq \frac{3\pi}{2J}\), the maximum achievable transfer

\[
\eta^* (t) = \sin(J\pi a) \sin(J\pi b),
\]

where \(a + 2b = t\) and \(\tan(J\pi a) = 2\tan(J\pi b)\). For \(t \geq \frac{3\pi}{2J}\) the maximum achievable transfer is one.

**Proof:** Let

\[
\Lambda(\alpha_1, \alpha_2, \alpha_3) = \exp(-i2\pi J(\alpha_1 I_z S_x + \alpha_2 I_y S_y + \alpha_3 I_z S_z)).
\]

From now on we will simply write \(\Lambda(\alpha_1, \alpha_2, \alpha_3)\) as \(\Lambda\). From Theorem 5, any unitary propagator \(U_F\) belonging to the set

\[
\mathcal{R}(e, t) = \{Q_1 \Lambda Q_2 | Q_1, Q_2 \in K \quad \alpha_i > 0, \sum_{i=1}^{3} \alpha_i \leq t\},
\]

15
can be produced by appropriate pulse sequence in (10). Therefore we will maximize \( \| tr(F^\dagger U(t)\rho(0)U(t)) \| \), for \( U(t) \in \mathbb{R}(e, t) \). Let \( I = \exp\{iI_x, iI_y, iI_z\} \) and \( S = \exp\{iS_x, iS_y, iS_z\} \). By definition, \( K = S \times I \).

In the expression

\[
\eta(t) = \| tr(Q_1^4F^\dagger Q_1\Lambda Q_2\rho(0)Q_2^\dagger\Lambda^\dagger) \|, \]

\( \rho(0) \) commutes with \( I \) and \( F \) commutes with \( S \), therefore it suffices to restrict \( Q_1 \) and \( Q_2 \) to \( I \) and \( S \), respectively.

Let \( s \) denote the subspace spanned by the orthonormal basis \( \{ S_x, S_y, S_z \} \) and \( i \) denote the subspace spanned by the orthonormal basis \( \{ I_x, I_y, I_z \} \). We represent the starting operator \( \rho(0) = \frac{1}{\sqrt{2}}(S_x - iS_y) \) as a column vector \( p = \frac{1}{\sqrt{2}}[1 - i 0]^T \) in \( s \). The action \( \rho(0) \rightarrow Q_2\rho(0)Q_2^\dagger \) can then be represented as \( p \rightarrow Vp \) where \( V \) is an orthogonal matrix.

Let \( P_i \) denote the projection on the subspace \( i \). A simple computation yields that

\[
\begin{align*}
P_i(\Lambda S_z\Lambda^\dagger) &= \sin(J\pi\alpha_2)\sin(J\pi\alpha_3)I_x, \\
P_i(\Lambda S_y\Lambda^\dagger) &= \sin(J\pi\alpha_1)\sin(J\pi\alpha_3)I_y, \\
P_i(\Lambda S_z\Lambda^\dagger) &= \sin(J\pi\alpha_2)\sin(J\pi\alpha_3)I_z. 
\end{align*}
\]

We denote the target operator \( F = \frac{1}{\sqrt{2}}(I_x - iI_y) \) as a column vector \( \frac{1}{\sqrt{2}}[1 - i 0]^T \) in \( i \). The action \( \rho(0) \rightarrow P_i(\Lambda Q_2\rho(0)Q_2^\dagger\Lambda^\dagger) \) can be written as \( p \rightarrow \Sigma Vp \), where

\[
\Sigma = \begin{bmatrix}
\sin(J\pi\alpha_2)\sin(J\pi\alpha_3) & 0 & 0 \\
0 & \sin(J\pi\alpha_1)\sin(J\pi\alpha_3) & 0 \\
0 & 0 & \sin(J\pi\alpha_1)\sin(J\pi\alpha_2)
\end{bmatrix},
\]

Therefore we can rewrite \( \eta(t) = \| tr(Q_1^4F^\dagger Q_1\Lambda Q_2\rho(0)Q_2^\dagger\Lambda^\dagger) \| \) as \( \eta(t) = \| p^\dagger U\Sigma Vp \| \), where \( U \) and \( V \) are real orthogonal matrices. Using the result of Lemma (3), we get that for \( \sin(J\pi\alpha_1) \geq \sin(J\pi\alpha_2) \geq \sin(J\pi\alpha_3) \geq 0 \), the maximum value of \( \eta(t) \) is

\[
\frac{\sin(J\pi\alpha_1)\sin(J\pi\alpha_2) + \sin(J\pi\alpha_1)\sin(J\pi\alpha_3)}{2}.
\]

Now we maximize the above expression with respect to \( \alpha_1, \alpha_2, \alpha_3 \) as worked out in Lemma 4 to get the above result.

Now we prove the last part of the theorem. Note for \( t = \frac{3}{4} \), the maximum achievable transfer is one. Because \( \rho(0) \) and \( F \) are normalized, this is the maximum possible transfer between these operators. If \( t > \frac{3}{4} \), say \( t = T + \frac{3}{4} \), we can always arrange matters so that \( U(T) = e \) (by creating a propagator \( U(T/2) = \exp(-i2\pi J(\frac{2}{3}I_zS_z)) \) and then creating its inverse \( \exp(i2\pi J(\frac{2}{3}I_zS_z)) \) from \( T/2 \) to \( T \)). In the remaining \( \frac{3}{4} \) units of time, we can produce the optimal propagator.

Q.E.D

The optimal transfer curve is plotted in comparison with the transfer achieved using the isotropic mixing Hamiltonian in the Figure 2. The unitary propagator \( U(t) \) in the isotropic mixing Hamiltonian case takes the form

\[
U(t) = \exp(-i\frac{2\pi Jt}{3}(I_zS_z + I_xS_x + I_yS_y)).
\]

For small mixing times the transfer amplitude achieved by the optimal experiment is up to 12.5% larger than the transfer achieved by isotropic mixing. This is a previously unknown result that will find immediate practical applications in NMR spectroscopy.
Figure 2: The panel shows the comparison between the best achievable transfer (bold curve) and the transfer achieved using the isotropic mixing Hamiltonian for the in-phase transfer in 2 spin case. On X axis is plotted time in units of $1/J$.

**Theorem 7 (Maximum anti-phase transfer)** Consider the evolution for the heteronuclear IS spin system as defined by equation (10). Let $\rho(0) = \sqrt{2} I_z S^- = \sqrt{2} I_z (S_x - i S_y)$ and $F = I_x - i I_y$. Then, for $t \leq 1/J$, the maximum achievable transfer $\eta^*(t)$ is

$$||\text{tr}(F^\dagger U(t)\rho(0)U^\dagger(t))|| = \sin(J\pi t/2).$$

For $t \geq \frac{1}{J}$, the maximum achievable transfer is one.

**Proof:** Let

$$\Lambda = \exp(-i2\pi J(\alpha_1 I_x S_x + \alpha_2 I_y S_y + \alpha_3 I_z S_z)).$$

From theorem 5

$$U(t) \in \{Q_1 \Lambda Q_2 | Q_1, Q_2 \in K, \alpha_i > 0, \sum_{i=1}^{3} \alpha_i \leq t\}.$$ 

Let $S = \exp\{iS_x, iS_y, iS_z\}$ and $I = \exp\{iI_x, iI_y, iI_z\}$. By definition $K = S \times I$. In the expression for

$$\eta = ||\text{tr}(F^\dagger Q_1 \Lambda Q_2 \rho(0)Q_2^\dagger \Lambda Q_1^\dagger)||,$$

let $Q_2 = Q_{2I} \times Q_{2S}$, where $Q_{2I} \in I$ and $Q_{2S} \in S$. Let the optimal $Q_2^* = Q_{2I}^* \times Q_{2S}^*$ be such that

$$Q_{2I}^* \rho(0)Q_{2I}^{*\dagger} = Q_{2I}^* I_z S^- Q_{2I}^{*\dagger} = a_z I_z S^- + a_y I_y S^- + a_x I_x S^-,$$

17
where $a_x^2 + a_y^2 + a_z^2 = 1$. Denote

$$
\eta_z = \| \text{tr}(F^\dagger(Q_1\Lambda Q_2S_2^\dagger)(\sqrt{2}I_z S^-)(Q_2^\dagger S_2^\dagger))\|
$$

$$
\eta_y = \| \text{tr}(F^\dagger(Q_1\Lambda Q_2S_2^\dagger)(\sqrt{2}I_y S^-)(Q_2^\dagger S_2^\dagger))\|
$$

$$
\eta_x = \| \text{tr}(F^\dagger(Q_1\Lambda Q_2S_2^\dagger)(\sqrt{2}I_x S^-)(Q_2^\dagger S_2^\dagger))\|.
$$

Then observe that

$$
\eta(t) \leq a_z\eta_z + a_y\eta_y + a_x\eta_x.
$$

We first compute the maximum of $\eta_z$. Let $P_I$ denote the projection on the subspace generated by $\{I_x, I_y, I_z\}$, then a simple computation yields

$$
P_I(\Lambda I_z S_x \Lambda^\dagger) = \frac{1}{2} \sin(J\pi\alpha_1)I_y
$$

$$
P_I(\Lambda I_z S_y \Lambda^\dagger) = \frac{1}{2} \sin(J\pi\alpha_2)I_x
$$

$$
P_I(\Lambda I_z S_z \Lambda^\dagger) = 0.
$$

Since $\{I_zS_x, I_zS_y, I_zS_z\}$ forms an orthogonal pair, we can rewrite

$$
\| \text{tr}(F^\dagger Q_1\Lambda Q_2S_2^\dagger(\sqrt{2}I_z S^-)(Q_2^\dagger S_2^\dagger))\|
$$

as

$$
\eta(t) = \| p^\dagger U\Sigma Vp \|
$$

where $p = [1 - i 0]^T$,

$$
\Sigma = \begin{bmatrix}
\sin(J\pi\alpha_2)/2 & 0 & 0 \\
0 & 0 & \sin(J\pi\alpha_1)/2 \\
0 & \sin(J\pi\alpha_1)/2 & 0
\end{bmatrix},
$$

and $U$ and $V$ are real orthogonal matrices. From Lemma 3, it follows that the maximum value of $\eta_z$ is

$$
\frac{\sin(J\pi\alpha_2)}{2} + \frac{\sin(J\pi\alpha_1)}{2}.
$$

We can compute the maximum of the above expression under the constraint $\alpha_1 + \alpha_2 = t \leq 1/(J)$. The maximum value of the above expression is obtained for $\alpha_1 = \alpha_2$. The maximum value is $\sin(J\pi t/2)$ for $t \leq 1/J$. Similarly, the maximum value of $\eta_x$ and $\eta_y$ is as above. Since $a_x^2 + a_y^2 + a_z^2 = 1$, we get the desired result.

The final proposition of the theorem has the same proof as in Theorem 5. Q.E.D.

6 Conclusion

In this paper, we presented a mathematical formulation of the problem of finding shortest pulse sequences in coherent spectroscopy. We showed how the problem of computing minimum time to produce a unitary propagator can be reduced to finding shortest length paths on certain coset spaces.
Figure 3: The panel shows the best achievable transfer as a function of time measured in units of $1/J$ for the anti-phase transfer in 2 spin case.

A remarkable feature of time optimal control laws is that they are singular, i.e. the control is zero most of the time, with impulses in-between. We explicitly computed the shortest transfer times and maximum achievable transfer in a given time for the case of heteronuclear two-spin transfers. In a forthcoming paper, we plan to extend these results to higher spin systems.

References


L. E. Kay; *J. Am. Chem. Soc.* **115**, 2055 (1993);  

P. Caravatti, L. Braunschweiler, R. R. Ernst, *Chem. Phys. Lett.* **100**, 305 (1983);  


