Time optimal control in spin systems

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In this paper, we study the design of pulse sequences for nuclear magnetic resonance 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 between states. 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. 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 nuclear magnetic resonance (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 system.

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I. INTRODUCTION

Many spectroscopic fields, such as NMR, electron magnetic resonance, and optical spectroscopy rely on a limited set of control variables in order to create desired unitary transformations [5–7]. 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 antiphase [6,10,11] 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 [12] and demonstrate the optimality of some previously known sequences.

During the last decade the questions of controllability of quantum systems have generated considerable interest [13,14]. 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 [15]. 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 a final state, we would like to determine controls that achieve the task in minimum possible time [14,16].

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

$$U(t) = -iH(t)U(t), \quad U(0) = I,$$

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

$$H = H_d + \sum_{j=1}^{m} v_j H_j ,$$

where H_d is the part of Hamiltonian that is internal to the system and we call it the *drift* or *free Hamiltonian* and $\sum_{j=1}^{m} v_j(t) H_j$ 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

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the initial state ρ_0 to a final state ρ_F. Thus, we will be interested in computing the minimum time required to steer the system

$$\dot{U} = -i\left(H_d + \sum_{j=1}^{m} v_j H_j\right)U, \qquad (1)$$

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

In this paper 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.

Keeping the interests of a broad audience in mind, we have organized the paper into two parts. The first part (Secs. II–IV) expresses the main ideas of the paper more intuitively and stresses physical applications. The ideas presented in the first part are then developed from a control theory perspective in the second part (Secs. V–VII) of the paper. The reader can choose to read in any order depending on her or his taste.

II. MAIN IDEAS

In this section we present a summary of main geometric ideas used in the paper. The goal is to develop intuition and motivate the mathematical results. We also give here references to the lemmas and theorems of Secs. V–VII, where the ideas laid down in this section are presented in detail.

Recall that the evolution of the unitary propagator from Eq. (1) is

$$\dot{U} = -i\left(H_d + \sum_{j=1}^{m} v_j H_j\right)U, \quad U(0) = I,$$

where H_d is the internal or drift Hamiltonian and H_j are the control Hamiltonians, which can be externally changed. As described in the introductory section, the central goal of the paper is to find the minimum time it takes to implement a unitary propagator in a quantum system and to find the controls v_j that produce the propagator in the minimum time. In the context of NMR, the controls v_j correspond to the pulse sequences. The key geometric ideas involved in the search for these time optimal pulse sequences are as follows.

A. Control Hamiltonians generate a subgroup

Let G denote the unitary group under consideration. Observe that the control Hamiltonians $\{H_j\}$, generate a subgroup K, given by

$$K = \exp(\{H_j\}_{\mathrm{LA}}),$$

where $\{H_j\}_{LA}$ is the Lie algebra generated by elements $\{-iH_1, -iH_2, \ldots, -iH_m\}$. The subgroup K is the set of unitary propagators that can be produced, if there were no H_d present in the Eq. (1). We assume that the strength of the control Hamiltonians can be made arbitrary large. Please note this is an idealization, which is a good approximation to the case when the strength of external Hamiltonians can be made large compared to the internal couplings represented by H_d.

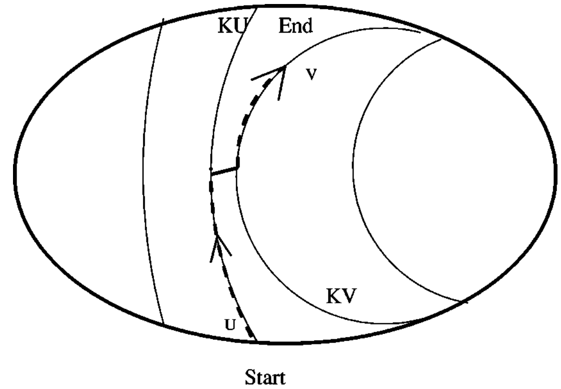

FIG. 1. The panel shows the time optimal path between elements U and V belonging to G. The dashed line depicts the fast portion of the path corresponding to movement within the coset KU and, in traditional NMR language, corresponds to the pulse and the solid line corresponds to the slow portion of the curve connecting different cosets and corresponds to evolution of the couplings.

B. Minimum time to go between cosets

If the strength of the control Hamiltonians can be made very large, then starting from identity propagator, we can generate any unitary propagator belonging to K in almost no time. Similarly, starting from U_1, we can produce any kU_1, $k \in K$, in almost no time. This strongly suggests that if we are trying to find the time optimal controls v_j that drive the evolution (1) from U_1 to U_2 in minimum possible time, we should look for the fastest way to get from the coset KU_1 to KU_2 (the coset KU_1 denotes the set $\{kU_1 | k \in K\}$), because it takes no time to travel inside a coset and once inside the right coset we can reach the desired element in negligible time. This is illustrated in the Fig. 1. Therefore one is motivated to look at the quotient space G/K, where each point represents some coset KU.

C. Controlling the direction of flow in G/K space

The problem of finding the fastest way to get between points in G reduces to finding the fastest way to get between corresponding points (cosets) in G/K space. It is well known that the space G/K has the structure of a differentiable manifold. Let $\mathfrak{g}$ represent the Lie algebra of the generators of G and $\mathfrak{k} = \{H_j\}_{LA}$ represent the Lie algebra of the generators of the subgroup K. We can then decompose $\mathfrak{g} = \mathfrak{p} \oplus \mathfrak{k}$ such that $\mathfrak{p}$ is orthogonal to $\mathfrak{k}$ and represents all possible directions to move in the G/K space. (Observe if we move in G, in directions represented by $\mathfrak{k}$, we always stay inside a coset and therefore do not go anywhere in the space G/K.) The flow in the group G, is governed by the evolution equation (1) and therefore constrains the directions we can choose to move in the G/K space. The directions in G/K, which we can choose to move directly, are represented by the set

$$Ad_K(H_d) = \{Ad_{k_1}(H_d) = k_1^{\dagger} H_d k_1 | k_1 \in K\} \in \mathfrak{p}.$$

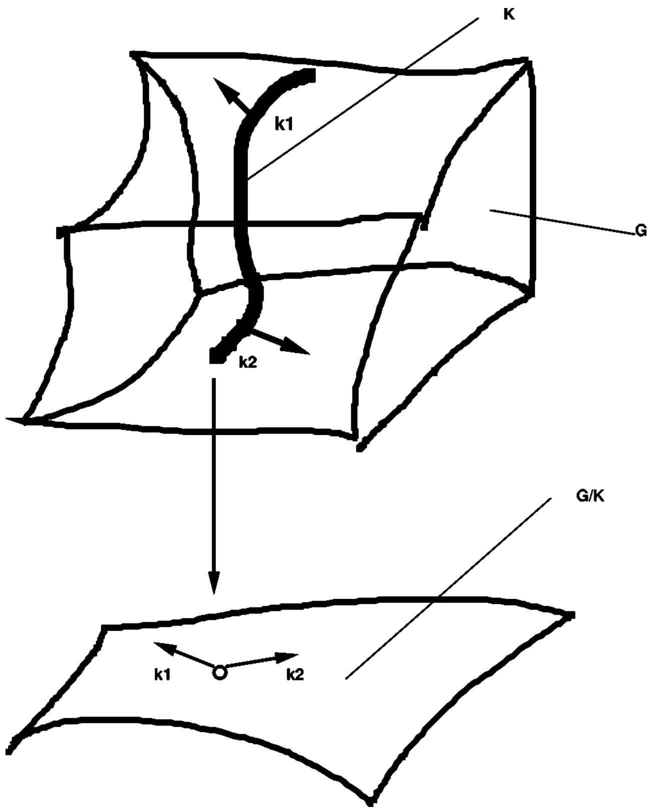

FIG. 2. The panel illustrates how the direction of flow in the G/K space, under the evolution of the drift H_d, depends on where one is in the coset K. The arrows depict the direction of motion under the influence of the drift term.

To see why this is the case, observe that the control Hamiltonians do not generate any motion in G/K space as they only produce motion inside a coset. Therefore all the motion in G/K space is generated by the drift Hamiltonian H_d. Notice that the elements of G belonging to a coset go to different cosets under the evolution of the coupling Hamiltonian H_d. Let k_1 and k_2 belong to K, the coset containing identity. Under the drift Hamiltonian H_d, these propagators after time δt, will evolve to $\exp(-iH_d\delta t)k_1$ and $\exp(-iH_d\delta t)k_2$, respectively. Note

$$\exp(-iH_d\delta t)k_1 = k_1[k_1^\dagger \exp(-iH_d\delta t)k_1]$$

and thus is an element of the coset represented by

$$k_1^\dagger \exp(-iH_d\delta t)k_1 = \exp(-ik_1^\dagger H_d k_1 \delta t).$$

Similarly $\exp(-iH_d\delta t)k_2$ belongs to the coset represented by $\exp(-ik_2^\dagger H_d k_2 \delta t)$. Thus in G/K, we can choose to move in directions given by $k_1^\dagger H_d k_1$ or $k_2^\dagger H_d k_2$, depending on whether we were sitting at k_1 or k_2 initially. This is illustrated in Fig. 2. But now note, we can choose to be at any point in K because we can move in K much faster than evolution under H_d. So we generate all directions $Ad_K(H_d)$ in G/K by choosing to be at the right $k\in K$, which we can do by use of our control Hamiltonians (we can move in K so fast that the system hardly evolves under H_d in that time). This set $Ad_K(H_d)$ is called the *adjoint orbit* of H_d under the action of the subgroup K.

D. Equivalence theorem and adjoint control system

The control Hamiltonians $\{H_j\}$, steer the direction of flow in the G/K space by helping us to be at the right place in a coset. The possible choice of directions is then represented by the set $Ad_K(H_d)$. This form of direction control has been defined as an adjoint control system [Eq. (14)]. Observe that the rate at which we move in the G/K space is always constant because all elements of $Ad_K(H_d)$ have the same norm $\|H_d\| = \|k^\dagger H_d k\|$ (k is unitary so $kk^\dagger$ is identity). All we get to change is the direction of flow in G/K space under H_d. Therefore the problem of finding the fastest way to get between two points in the space G/K reduces to finding the shortest path between those two points under the constraint that the tangent direction of the path must always belong to the set $Ad_K(H_d)$. This is essentially the content of the *equivalence theorem* (theorem 7).

E. Cartan decomposition and Riemannian symmetric spaces

The set of accessible directions $Ad_K(H_d)$, in the general case is not the whole $\mathfrak{p}$, the set of all possible directions in G/K. Therefore we may not be able to move directly in all the directions in G/K space, but motion in all directions in G/K space may be achieved by a back and forth motion in directions we can directly access. This is the usual idea of generating new directions of motion by using noncommuting generators [$\exp(\epsilon A)\exp(\epsilon B)\exp(-\epsilon A)\exp(-\epsilon B) \sim \exp(-\epsilon^2[A,B])$]. The class of coset spaces G/K, which will be of most interest to us in this paper, are the Riemannian symmetric spaces (e.g., $SU(4)/SU(2)\otimes SU(2)$). We will see that the geometric structure of this space plays an important role in finding the time optimal control for a pair of coupled two level quantum systems. If the decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$, $\mathfrak{p}=\mathfrak{k}^\perp$ satisfies the commutation relations

$$[\mathfrak{k},\mathfrak{k}]\subset\mathfrak{k},$$

$$[\mathfrak{p},\mathfrak{k}]=\mathfrak{p},$$

$$[\mathfrak{p},\mathfrak{p}]\subset\mathfrak{k}.$$

We call it a Cartan decomposition of $\mathfrak{g}$. In this case the coset space G/K is identified with $\exp(\mathfrak{p})$ and is called a globally Riemannian symmetric space.

F. Time optimal tori theorem

The key point to note is that if G/K is a Riemannian symmetric space, then we do not generate any new direction in the space G/K by a back and forth motion as $[\mathfrak{p},\mathfrak{p}]\subset\mathfrak{k}$. Thus if the tangent vectors to a path in G/K do not commute, there is a component of the net motion that lies inside a coset, but clearly this cannot be time optimal because we could have produced this motion in the coset much faster by using our control Hamiltonians. This suggests that the time optimal path in the G/K space is the one whose tangent directions always commute. Let $\mathfrak{h}\subset\mathfrak{p}$ denote a subspace of maximally commuting directions or generators (it is not possible to add additional directions and still have everything commute) in G/K space. We call such a subspace the *Cartan subalgebra* of G/K and the dimension of $\mathfrak{h}$ is called the rank of G/K. The interesting fact is that any element $P\in G/K$ has an element of the form $P=k_1^{\dagger}\exp(Y)k_1$, $k_1\in K$, and $Y\in\mathfrak{h}$. This implies that any element of $U_F\in G$ can be written as $k_2\exp(Y)k_1$. This can also be expressed as

$$G=K\exp(\mathfrak{h})K. \tag{2}$$

Now given $U_F=k_2\exp(Y)k_1$, we can produce k_1 and k_2 in negligible time by control Hamiltonians. Therefore the fastest way to reach U_F or the coset P from identity reduces to finding the quickest way to generate the propagator $\exp(Y)$. To do this we need to select from all the paths whose tangent directions commute and that connect identity to $\exp(Y)$, the one that is the shortest. This is achieved by choosing among all possible ways of expressing Y as

$$Y=\sum_{i=1}^{p}\alpha_i Ad_{k_i}(H_d),\quad \alpha_i>0, \tag{3}$$

such that $Ad_{k_i}(H_d)$ commute, the one that has the smallest value of $\Sigma_{i=1}^{p}\alpha_i$ and then flow along directions $Ad_{k_i}(H_d)$ for α_i units of time, which produces the propagator

$$\Pi_{i=1}^{n}\exp[\alpha_i Ad_{k_i}(H_d)]=\exp\left[\sum_{i=1}^{n}\alpha_i Ad_{k_i}(H_d)\right]=\exp(Y).$$

This is essentially the content of time optimal tori theorem (Theorem 10).

If G/K is of rank one, then any $Y\in\mathfrak{p}$ can be written as $Y=\alpha Ad_k(H_d)$, $\alpha>0$ for some $k\in K$. Therefore the fastest way to reach the coset represented by $\exp(Y)$ is to just flow along direction $Ad_k(H_d)$ for α units of time. We give here a classification of qualitative nature of time optimal control sequences in NMR and other coherent quantum control experiments based on the geometry of the coset spaces G/K.

1. Riemannian symmetric case

The coset space G/K in this case is a Riemannian symmetric space. This is a characteristic of one and two spin systems.

(i) Pulse-drift-pulse sequence (characteristic of single-spin systems) In this case, the rank of the symmetric space G/K is one (e.g., $SU(2)/U(1)$). Roughly speaking, the time optimal control v_j take the form of a sequence of hard pulses followed by evolution under drift and then some hard pulses again. See theorem 1.

(ii) 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 (e.g., $SU(4)/SU(2)\otimes SU(2)$). The optimal controls v_j take the form of ''impulse drift impulse'' pattern. The total time for the sequence 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 space and $[\mathfrak{p},\mathfrak{p}]\not\subset\mathfrak{k}$. This is a characteristic of more than two-spin systems. In this case many directions in G/K space can only be generated by back and forth motion in the directions given by $Ad_K(H_d)$. The best and the most relevant example for our purpose is

$$\frac{SU(2^n)}{SU(2)^{\otimes n}},$$

when $n>2$. This is the problem of building or producing an arbitrary unitary transformation on n qubits in the context of quantum computing when we can selectively excite each of the qubit fast and the drift corresponds to the interactions among the qubits.

In this paper we will confine ourselves to the Riemannian symmetric case. The nonsymmetric case will be treated in detail in a forthcoming paper. This concludes the section on overview of basic geometric ideas in the design of time optimal pulse sequences. We will now elucidate these ideas using examples from NMR. We first quickly review here the product operator formalism used in NMR.

III. PRODUCT OPERATOR BASIS

The Lie group G of most interest to us is $SU(2^n)$, the special unitary group describing the evolution of n interacting spin $\frac{1}{2}$ particles. [Please note that we focus on $SU(2^n)$ instead of $U(2^n)$ because a global phase is not of interest to us.] The 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 product of Pauli spin matrices [17] (product operator basis). We choose to work in these bases because of their widespread use in the NMR literature and our desire to look at the implementations of NMR quantum computers. Recall the Pauli spin matrices I_x, I_y, and I_z defined by

$$I_x=\frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},$$

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

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

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

$$[I_x,I_y]=iI_z;\quad [I_y,I_z]=iI_x;\quad [I_z,I_x]=iI_y; \tag{4}$$

$$I_x^2=I_y^2=I_z^2=\frac{1}{4}1, \tag{5}$$

where

$$1=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}.$$

Notation 1: The orthogonal basis $\{iB_s\}$, for $\mathfrak{su}(2^n)$ take the form

$$B_s=2^{q-1}\prod_{k=1}^{n}(I_{k\alpha})^{a_{ks}}. \tag{6}$$

where $\alpha=x$, y, or z and

$$I_{k\alpha}=1\otimes\ldots\otimes I_{\alpha}\otimes 1, \tag{7}$$

where I_α, the Pauli matrix, appears in the above expression only at the kth position, and $\mathbf{1}$ the two-dimensional identity matrix, appears everywhere except at the kth position. a_{ks} is 1 in q of the indices and 0 in the remaining. Note that $q\geqslant 1$ as $q=0$ corresponds to the identity matrix and is not a part of the algebra.

Example 1: As an example for $n=2$ the basis for $\mathfrak{su}(4)$ takes the form

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

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

IV. ONE- AND TWO-SPIN EXAMPLES: BUILDING FAST QUANTUM GATES

To elaborate on the ideas developed in Sec. 2, let us start with the example of controlling a spin 1/2 nuclei in a magnetic field by rf pulses that can produce a rapid x rotation on the spin.

Theorem 1: Let $U\in G=SU(2)$, and let I_x and I_z represent the Pauli spin matrices given in Eq. (4). The unitary evolution of the single-spin system is given by

$$\dot{U}=-i[I_z+vI_x]U, \quad U(0)=I,$$

where the control $v\in\mathbb{R}$. Given any $U_F\in SU(2)$, there exists a unique $\beta\in[0,2\pi]$ such that $U_F=\exp(-i\alpha I_x)\exp(-i\beta I_z)\exp(-i\gamma I_x)$, where α, $\gamma\in\mathbb{R}$, and the minimum time for producing U_F is β.

Proof: First note that the Lie algebra $\mathfrak{g}=\mathfrak{su}(2)$ has a Cartan decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{h}$, where $\mathfrak{p}=\text{span}\{iI_y,iI_z\}$, $\mathfrak{k}=\text{span}\{iI_x\}$, and $G/K=SU(2)/U(1)$ has rank 1. Therefore from Eq. (2), any $U_F\in SU(2)$ has a decomposition $U_F=\exp(-i\alpha I_x)\exp(-i\theta I_z)\exp(-i\gamma I_x)$. [This is well known as Euler angle decomposition of $SU(2)$]. Note $\exp(-i\alpha I_x)$ and $\exp(-i\gamma I_x)$ are generated in no time. All the time is spent in producing $\exp(-i\theta I_z)$ under the drift Hamiltonian I_z. Because $\exp(-itI_z)$ is periodic with period 4π, the smallest value of $|\beta|$ such that $\exp(-i\theta I_z)=\exp(-i\beta I_z)$ is θ mod$[-2\pi,2\pi]$. Because the Hamiltonian $-I_z$ can also be produced, we can restrict β to the interval $[0, 2\pi]$.

Remark 1: We now generalize to the case of two coupled nuclear spins. We will apply our general results on time optimal control to the specific case of a heteronuclear two-spin system with a scalar J coupling [6]. It should be emphasized here that the methods developed in this paper are general enough to give time optimal control laws for producing a unitary propagator in any pair of coupled two level quantum system. Therefore these methods will find immediate applications in building 2 qubit gates in various implementations of quantum computing. Also we want to emphasize that although we look at a specific form of coupling between the spins, our results are general enough to give time optimal pulses for any kind of coupling. These time optimal pulses for other kinds of couplings like isotropic and dipolar couplings will be given with experimental details in future publications.

Example 2: Suppose we have two heteronuclear spins coupled by a scalar J coupling [6]. Furthermore assume we can individually excite each spin (perform one qubit operations in context of quantum computing). The goal now is to produce any arbitrary unitary transformation $U\in SU(4)$, from this specified coupling and single-spin operations. This structure appears often in the NMR situation. The unitary propagator U, describing the evolution of the system in a suitable rotating frame, is described by

$$\dot{U}=-i\left(H_d+\sum_{j=1}^{4}v_jH_j\right)U, \quad U(0)=I, \tag{8}$$

where

$$H_d=2\pi J I_{12}I_{22},$$

$$H_1=2\pi I_x,$$

$$H_2=2\pi I_y,$$

$$H_3=2\pi S_x,$$

$$H_4=2\pi S_y,$$

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 Sec. III. 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 the spins. Observe that the subgroup K generated by $\{H_j\}$ is $SU(2)\otimes SU(2)$. Therefore the unitary transformations belonging to $SU(2)\otimes SU(2)$ can be produced very fast by hard pulses that excite each of the spins individually.

The Lie algebra $\mathfrak{g}=\mathfrak{su}(4)$, has the direct sum decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$, where

$$\mathfrak{k}=\text{span}\quad i\{I_x,I_y,I_z,S_x,S_y,S_z\},$$

$$\mathfrak{p}=\text{span}\quad i\{I_xS_x,I_xS_y,I_xS_z,\ I_yS_x,I_yS_y,$$
$$I_yS_z,\ I_zS_x,I_zS_y,I_zS_z\}.$$

Please note that span in above equations denotes all linear combinations with real coefficients. Using the well-known commutation relations

$$[A\otimes B,C\otimes D]=[A,C]\otimes(B.D)+(C.A)\otimes[B,D],$$

and Eqs. (4) and (5), it is easily verified

$$[\mathfrak{k},\mathfrak{k}]\subset\mathfrak{k},[\mathfrak{p},\mathfrak{k}]=\mathfrak{p},[\mathfrak{p},\mathfrak{p}]\subset\mathfrak{k}.$$

Therefore the decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$ is a Cartan decomposition of $\mathfrak{su}(4)$. As the subalgebra $\mathfrak{k}=\mathfrak{su}(2)\oplus\mathfrak{su}(2)$ generates the group $K=SU(2)\otimes SU(2)$, the coset space

$$\frac{SU(4)}{SU(2)\otimes SU(2)}$$

is a Riemannian symmetric space. Note that the Abelian subalgebra $\mathfrak{h}$ generated by

$$i\{I_xS_x,I_yS_y,I_zS_z\}$$

is contained in $\mathfrak{p}$ and is maximal Abelian and hence a Cartan subalgebra of the symmetric space $SU(4)/SU(2)\otimes SU(2)$. Therefore using Eq. (2) (see theorem 6) any $U_F\in SU(4)$ can be decomposed as

$$U_F=K_1\exp[-i(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)]K_2,$$

where $K_1,K_2\in SU(2)\otimes SU(2)$.

Now let us see how this decomposition makes obvious the choice of pulse sequences for producing this propagator. Note that for $K_y^-=\exp(-i\,\pi/2\,I_y)\exp(-i\,\pi/2\,S_y)$ and $K_y^+=\exp(i\,\pi/2\,I_y)\exp(-i\,\pi/2\,S_y)$, we have

$$K_y^{\pm}\exp(-iI_zS_z)(K_y^{\pm})^{-1}=\exp(\pm iI_xS_x).$$

Similarly for $K_x^{\pm}=\exp(\pm i\pi/2\,I_x)\exp(-i\pi/2\,S_x)$ we have

$$(K_x^{\pm})^{-1}\exp(-iI_zS_z)K_x^{\pm}=\exp(\pm iI_yS_y).$$

This makes transparent, that we can generate any Hamiltonian from the set

$$\{\pm I_zS_z,\pm I_yS_y,\pm I_xS_x\},$$

and therefore any Hamiltonian of the form

$$\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z,\quad \alpha_i\in\mathbb{R}$$

and hence every element of the Cartan subalgebra $\mathfrak{h}$. The unitary propagators $K_x^{\pm}$, $K_y^{\pm}$, K_1, and K_2 can be produced by selective hard pulses, and takes almost no time. We now claim that synthesizing U_F, using the decomposition given above, is indeed the fastest way to generate U_F.

Theorem 2: For the heteronuclear spin system, described by Eq. (8), let $\mathfrak{k}=\{H_j\}_{LA}$. The minimum time required to produce a unitary propagator $U_F\in SU(4)$ is the smallest value of $\Sigma_{i=1}^3|\alpha_i|$, such that we can solve

$$U_F=Q_1\exp[-i2\pi J(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)]Q_2,$$

where $\alpha_i\in\mathbb{R}$, Q_1, and Q_2 belong to $\exp(\mathfrak{k})=SU(2)\otimes SU(2)$.

Proof: As is shown in the example above the decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$, where $\mathfrak{p}=\mathrm{span}\,i\{I_\alpha S_\beta\}$, $\mathfrak{k}=\mathrm{span}\,i\{I_\alpha,S_\beta\}$, and $(\alpha,\beta)\in(x,y,z)$ is a Cartan decomposition of $\mathfrak{g}$ such that

$$\mathfrak{h}=\mathrm{span}\quad i\{I_zS_z,I_xS_x,I_yS_y\},$$

is a Cartan subalgebra. Therefore any unitary propagator $U\in SU(4)$ has the decomposition $U=Q_1\exp[-i2\pi J(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)]Q_2$, where $Q_1,Q_2\in SU(2)\otimes SU(2)$. Observe Q_1 and Q_2 take almost no time to produce. Therefore we need to compute the minimum time required to produce the propagator $A=\exp[-i2\pi J(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)]$. The maximally commuting set of Hamiltonians that can generate the above propagator is $\{\pm I_zS_z,\pm I_xS_x,\pm I_yS_y\}$. Since we can produce all of these Hamiltonians [they belong to the set $Ad_K(H_d)$], we can produce the above propagator A in $\Sigma_{i=1}^3|\alpha_i|$, units of time. Therefore, the minimum time for producing U_F is the smallest value of $\Sigma_{i=1}^3|\alpha_i|$, such that we can solve

$$U_F=Q_1\exp[-i2\pi J(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)]Q_2.$$

Remark 2: From the nature of time optimal control sequences, it is clear that the set of unitary propagators that can be produced in a given time T take the form

$$Q_1\exp[-i2\pi J(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)]Q_2,$$

$$|\alpha_1|+|\alpha_2|+|\alpha_3|=T, \quad (9)$$

where $Q_1,Q_2\in SU(2)\otimes SU(2)$. This set is the reachable set of the control system (8), for time T.

Now we address the question of maximum possible achievable transfer by a pulse sequence in some given time T. For this purpose we define the transfer efficiency.

Definition 1 (Transfer Efficiency): Given the evolution of the density matrix $\rho(t)=U(t)\rho(0)U^\dagger(t)$, where

$$\dot{U}=-i\left(H_d+\sum_{j=1}^m v_jH_j\right)U,\quad U(0)=I,$$

define the transfer efficiency $\eta(t)$ from $\rho(0)$, to some given target operator F as

$$\eta(t)=\|\mathrm{Tr}[F^\dagger U(t)\rho(0)U^\dagger(t)]\|.$$

Remark 3: 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., $\mathrm{Tr}(F^\dagger F)=1$].

We will now look at the in-phase and antiphase transfers in the two-spin system, whose evolution is given by Eq. (8). We give here expressions for maximum transfer efficiencies. We first state some lemmas, which will be required in computing transfer efficiencies. For proofs see the Appendix.

Lemma 1: Let

$$p=\begin{bmatrix}1\\-i\\0\end{bmatrix}$$

and let Σ be a real diagonal matrix

$$\Sigma=\begin{bmatrix}a_1&0&0\\0&a_2&0\\0&0&a_3\end{bmatrix}.$$

If $|a_i|\geqslant|a_j|\geqslant|a_k|\geqslant 0$, where $\{i,j,k\}\in\{1,2,3\}$ and let U, $V\in O(3)$, then the maximum value of $\|p^\dagger U\Sigma Vp\|$ is $|a_i|+|a_j|$.

Lemma 2: Consider the function $f(\alpha_1,\alpha_2,\alpha_3)=\sin(J\pi\alpha_1)\sin(J\pi\alpha_3)+\sin(J\pi\alpha_2)\sin(J\pi\alpha_3)$. If $\alpha_1,\alpha_2,\alpha_3\geqslant 0$ and $\alpha_1+\alpha_2+\alpha_3=T$, where $T\leqslant 3/2J$, 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 $\tan(J\pi a)=2\tan(J\pi b)$.

Theorem 3 (Maximum in-phase transfer): Consider the evolution for the heteronuclear IS spin system as defined by Eq. (8). Let $\rho(0)=S_x-iS_y/\sqrt{2}$ and $F=I_x-iI_y/\sqrt{2}$. For $t\leqslant 3/2J$, 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 $t\geqslant 3/2J$ the maximum achievable transfer is one.

Proof: Let

$$\Lambda(\alpha_1,\alpha_2,\alpha_3)=\exp[-i2\pi J(\alpha_1I_xS_x+\alpha_2I_yS_y+\alpha_3I_zS_z)].$$

From now on we will simply write $\Lambda(\alpha_1,\alpha_2,\alpha_3)$ as Λ. From Theorem 2, any unitary propagator U_F belonging to the set

$$\mathbf{R}(e,t)=\left\{Q_1\Lambda Q_2|Q_1,Q_2\in K,\alpha_i>0,\sum_{i=1}^{3}\alpha_i\leqslant t\right\},$$

can be produced by appropriate pulse sequence in Eq. (8). Therefore we will maximize

$$\eta(t)=\|\mathrm{Tr}[F^\dagger U(t)\rho(0)U^\dagger(t)]\|,$$

for $U(t)\in\mathbf{R}(e,t)$. 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

$$\eta(t)=\|\mathrm{Tr}[Q_1^\dagger F^\dagger Q_1\Lambda Q_2\rho(0)Q_2^\dagger\Lambda^\dagger]\|,$$

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

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

Let P_I denote the projection on the subspace $\mathfrak{i}$. A simple computation yields that

$$P_I(\Lambda S_x\Lambda^\dagger)=\sin(J\pi\alpha_2)\sin(J\pi\alpha_3)I_x,$$

$$P_I(\Lambda S_y\Lambda^\dagger)=\sin(J\pi\alpha_1)\sin(J\pi\alpha_3)I_y,$$

$$P_I(\Lambda S_z\Lambda^\dagger)=\sin(J\pi\alpha_2)\sin(J\pi\alpha_1)I_z.$$

We denote the target operator $F=1/\sqrt{2}(I_x-iI_y)$ as a column vector $1/\sqrt{2}[1-i0]^T$ in $\mathfrak{i}$. The action $\rho(0)\rightarrow P_I[\Lambda Q_2\pi(0)Q_2^\dagger\Lambda^\dagger]$ 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

$$\eta(t)=\|\mathrm{Tr}[Q_1^\dagger F^\dagger Q_1\Lambda Q_2\rho(0)Q_2^\dagger\Lambda^\dagger]\|$$

as $\eta(t)=\|p^\dagger U\Sigma Vp\|$, where U and V are real orthogonal matrices. Using the result of Lemma 1, we get that for $|\sin(J\pi\alpha_1)|\geqslant|\sin(J\pi\alpha_2)|\geqslant|\sin(J\pi\alpha_3)|$, 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 α_1, α_2, and α_3. From the property of the sine function, it can be seen that we maximize the above expression if $|\alpha_i|\leqslant 1/2J$. In that case it suffices to maximize

$$\frac{\sin(J\pi\alpha_1)\sin(J\pi\alpha_2)+\sin(J\pi\alpha_1)\sin(J\pi\alpha_3)}{2}$$

for $0\leqslant\alpha_1,\alpha_2,\alpha_3\leqslant 1/2J$. Now from Lemma 2, we get the above result.

Now we prove the last part of the theorem. Note for $t=3/2J$, the maximum achievable transfer is one. Because $\rho(0)$ and F are normalized, this is the maximum possible transfer between these operators. If $t>3/2J$, say $t=T+3/2J$, we can always arrange matters so that $U(T)=e$ [by creating a propagator $U(T/2)=\exp[-i2\pi J(T/2I_z S_z)]$ and

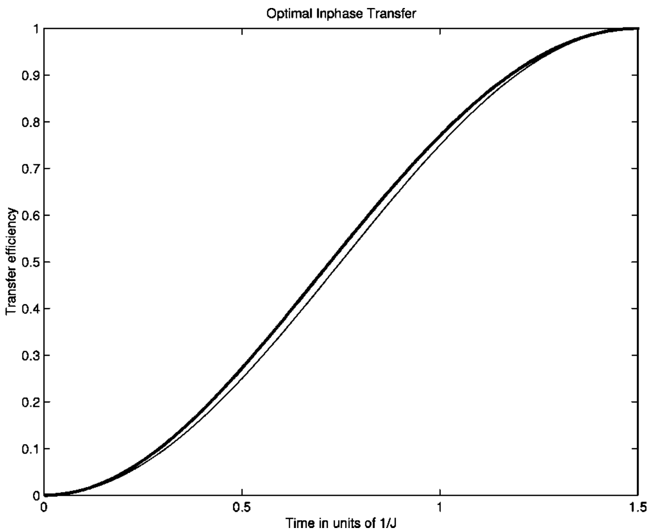

FIG. 3. The panel shows the comparison between the best achievable transfer (bold curve) and the transfer achieved using the isotropic mixing Hamiltonian for the in-phase transfer in 2 spin case. On x axis is plotted time in units of $1/J$.

then creating its inverse $\exp[i2\pi J(T/2 I_z S_z)]$ from $T/2$ to T]. In the remaining $3/2J$ units of time, we can produce the optimal propagator.

The optimal transfer curve is plotted in comparison with the transfer achieved using the isotropic mixing Hamiltonian in the Fig. 3.

Implementation Details: The optimal propagator for the in-phase transfer $S^- \to I^-$ can be implemented in practice simply by modifying the delays of the well-known pulse sequence elements that are commonly used for such coherence transfer (ICOS-CT) experiments (in-phase coherence order selective coherence transfer) [11]. Many different implementations of ICOS-CT experiments have been introduced,which create isotropic mixing conditions in heteronuclear two-spin systems based on pulse-interrupted delays. For a given heteronuclear J coupling term these sequences create effective coupling terms $2\pi J I_x S_x$, $2\pi J I_y S_y$, and $2\pi J I_z S_z$ that are active for durations τ_x, τ_y, and τ_z, respectively [11]. The resulting average Hamiltonian [5] is given by $\mathcal{H} = 2\pi J(\alpha_1 I_x S_x + \alpha_2 I_y S_y + \alpha_3 I_z S_z)$ with $\alpha_1 = \tau_x/\tau$, $\alpha_2 = \tau_y/\tau$, and $\alpha_3 = \tau_z/\tau$ for $\tau = \tau_x + \tau_y + \tau_z$. Whereas an isotropic average Hamiltonian results for $\tau_x = \tau_y = \tau_z = \tau/3$ [11], the desired average Hamiltonian that achieves the optimal transfer amplitude, which is up to a factor $f = 1.12$ larger than the transfer amplitude of isotropic mixing experiments (see Theorem 3) is created simply by modifying τ_x, τ_y, and τ_z such that $\tan(J\pi\tau_z) = 2\tan(J\pi\tau_\perp)$ with $\tau_\perp = \tau_x = \tau_y$. If several ICOS-CT transfer steps occur sequentially in a given experiment (e.g., from ^{13}C to ^1H via ^{15}N), the overall gain factor f_{tot} is the product of the individual gain factors f and may be quite substantial. For example, if a transfer step with a gain factor of only $f = 1.06$ [corresponding to the case $\tau = 3/(4J)$, see Fig. 3] occurs twice in a given NMR experiment, $f_{\text{tot}} = 1.12$ and the required number of accumulations (which for a desired signal-to-noise ratio is proportional to $1/f_{\text{tot}}^2$) and hence the overall measurement time (which can be several days) can be reduced by 20% at no extra cost.

Theorem 4 (Maximum anti-phase transfer): Consider the evolution for the heteronuclear IS spin system as defined by Eq. (8). Let $\rho(0) = \sqrt{2} I_z S^- = \sqrt{2} I_z (S_x - i S_y)$ and $F = I^- = I_x - i I_y/\sqrt{2}$. Then, for $t \leq 1/J$, the maximum achievable transfer $\eta^*(t)$ is

$$\|\mathrm{Tr}[F^\dagger U(t)\rho(0)U^\dagger(t)]\| = \sin(J\pi t/2).$$

For $t \geq 1/J$, the maximum achievable transfer is one.

The proof is exactly on same lines as Theorem 3. The theorem proves that the transfer efficiency achieved using the known mixing sequence [10] is optimal. We now develop all the ideas presented in Sec. II from a mathematical control theory viewpoint.

V. PRELIMINARIES

We will assume that the reader has some familiarity with the basic facts about Lie groups and homogeneous spaces [2].

Throughout this part of the paper, G will denote a compact semisimple Lie group and e its identity element (we use I to denote the identity matrix when working with the matrix representation of the group). As is well known there is a naturally defined bi-invariant metric on G, given by the Killing form. We denote this bi-invariant metric by $\langle , \rangle_G$. Let K be a compact closed subgroup of G. Let $\mathfrak{g}$ and $\mathfrak{k}$ represent the Lie algebra of G and K, respectively. Consider the direct sum decomposition $\mathfrak{g} = \mathfrak{p} \oplus \mathfrak{k}$ such that $\mathfrak{p} = \mathfrak{k}^\perp$ with respect to the metric.

Definition 2 (Cartan decomposition of $\mathfrak{g}$): Let $\mathfrak{g}$ be a real semi-simple Lie algebra and let the decomposition $\mathfrak{g} = \mathfrak{p} \oplus \mathfrak{k}$, $\mathfrak{p} = \mathfrak{k}^\perp$ satisfy the commutation relations

$$[\mathfrak{k}, \mathfrak{k}] \subset \mathfrak{k}, \tag{10}$$

$$[\mathfrak{p}, \mathfrak{k}] = \mathfrak{p}, \tag{11}$$

$$[\mathfrak{p}, \mathfrak{p}] \subset \mathfrak{k}. \tag{12}$$

We will refer to this decomposition as a Cartan decomposition of $\mathfrak{g}$. The pair $(\mathfrak{g}, \mathfrak{k})$ will be called an orthogonal symmetric Lie algebra pair [18,2].

It is well known that the (right) coset space $G/K = \{KU : U \in G\}$ (homogeneous space) admits the structure of a differentiable manifold [1]. Let $\pi: G \to G/K$ denote the natural projection map. Define $o \in G/K$ by $o = \pi(e)$. The tangent space plane $T_o(G/K)$ can be identified with the vector subspace $\mathfrak{p}$. Given the bi-invariant metric $\langle , \rangle_G$ on G, there is a corresponding left invariant metric $\langle , \rangle_n$, on the homogeneous space G/K arising from the restriction of $\langle , \rangle_G$ to $\mathfrak{p}$ [1].

The Lie group G acts on its Lie algebra $\mathfrak{g}$ by conjugation $Ad_G : \mathfrak{g} \to \mathfrak{g}$ (called the adjoint action) [2,3]. This is defined as follows. Given $U \in G$, $X \in \mathfrak{g}$, then

$$Ad_U(X) = \left. \frac{dU^{-1}\exp(tX)U}{dt} \right|_{t=0}.$$

To fix ideas if $G=SU(n)$ and $U\in G$, $A\in\mathfrak{su}(n)$, then $Ad_U(A)=U^{\dagger}AU$. We use the notation

$$Ad_K(X)=\bigcup_{k\in K}Ad_k(X).$$

Definition 3 (Cartan subalgebra): Consider the semi-simple Lie algebra $\mathfrak{g}$ and its Cartan decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$. If $\mathfrak{h}$ is a subalgebra of $\mathfrak{g}$ contained in $\mathfrak{p}$, then $\mathfrak{h}$ is Abelian because $[\mathfrak{p},\mathfrak{p}]\in\mathfrak{k}$. A maximal Abelian subalgebra contained in $\mathfrak{p}$ is called a Cartan subalgebra of the pair $(\mathfrak{g},\mathfrak{k})$ [2,3].

Theorem 5: [2] If $\mathfrak{h}$ and $\mathfrak{h}'$ are two maximal Abelian subalgebras contained in $\mathfrak{p}$, then

(1) There is an element $k\in K$ such that $Ad_k(\mathfrak{h})=\mathfrak{h}'$.

(2) $\mathfrak{p}=\cup_{k\in K}Ad_k(\mathfrak{h})$.

Remark 4: If $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$ is a Cartan decomposition then the homogeneous space $G/K=\exp(\mathfrak{p})$, and is called a *globally Riemannian symmetric space* [3]. From the above stated theorem 5, the maximal Abelian subalgebras of $\mathfrak{p}$ are all Ad_K conjugate and in particular they have the same dimension. The dimension is called the *rank* of the globally Riemannian symmetric space G/K.

Theorem 6: [2] Given the semi-simple Lie algebra $\mathfrak{g}$ and its Cartan decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$, let $\mathfrak{h}$ be a Cartan subalgebra of the pair $(\mathfrak{g},\mathfrak{k})$ and define $A=\exp(\mathfrak{h})\subset G$. Then $G=KAK$. The space G/K is a union of maximal Abelian subgroups $Ad_k(A)$, called *maximal tori*.

Definition (Weyl Orbit): Let $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$, be a Cartan decomposition and let $\mathfrak{h}\subset\mathfrak{p}$ be a cartan subalgebra of the pair $(\mathfrak{g},\mathfrak{k})$ containing X_d. We use the notation $W(X_d)=\mathfrak{h}\cap Ad_K(X_d)$ to denote the Weyl orbit of X_d. We use $\mathfrak{c}(X_d)=\{\sum_{i=1}^{n}\beta_iX_i|\beta_i\geqslant 0,\Sigma\beta_i=1,X_i\in W(X_d)\}$, to denote the convex hull of the Weyl orbit of X_d, with vertices given by the elements of the Weyl orbit of X_d.

Assumption 1: Let $U\in G$ and let the control system

$$\dot{U}=\left[X_d+\sum_{i=1}^{m}v_iX_i\right]U,\quad U(0)=I \tag{13}$$

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 (13) is controllable [4]. Let $\mathfrak{k}=\{X_i\}_{LA}$ and $K=\exp\{X_i\}_{LA}$ be the closed compact group generated by $\{X_i\}$. Given the direct sum decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$, where $\mathfrak{p}=\mathfrak{k}^{\perp}$ with respect to the bi-invariant metric $\langle,\rangle_G$, let $X_d\in\mathfrak{p}$. We will assume that $Ad_K(\mathfrak{p})\subset\mathfrak{p}$, 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 $\mathbb{R}^m$. $\mathcal{C}[0,T]$ denotes their restriction on the interval $[0,T]$. We will assume throughout that in Eq. (13), $v=(v_1,v_2,\ldots,v_m)\in\mathcal{C}$. Given $v\in\mathcal{C}$, we use $U(t)$ to denote the solution of Eq. (13) such that $U(0)=e$. If, for some time $t\geqslant 0$, $U(t)=U'$, 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 4 (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

$$\mathbf{R}(U_0,T)=\bigcup_{0\leqslant t\leqslant T}R(U_0,t),$$

$$\mathbf{R}(U_0)=\bigcup_{0\leqslant t\leqslant\infty}R(U_0,t).$$

We will refer to $\mathbf{R}(U_0)$, as the reachable set of U_0.

Remark 5: From the right invariance of control systems it follows that $R(U_0,T)=R(e,T)U_0$, $\mathbf{R}(U_0,T)=\mathbf{R}(e,T)U_0$, and $\mathbf{R}(U_0)=\mathbf{R}(e)U_0$. Note that $\mathbf{R}(U_0,T)$ need not be a closed set, we use $\overline{\mathbf{R}(U_0,t)}$ to denote its closure.

Definition 5 (Infimizing Time): Given $U_F\in G$, we will define

$$t^*(U_F)=\inf\{t\geqslant 0|U_F\in\overline{\mathbf{R}(e,t)}\},$$

$$t^*(KU_F)=\inf\{t\geqslant 0|kU_F\in\overline{\mathbf{R}(e,t)},k\in K\}$$

and $t^*(U)$ is called the *infimizing time*.

From a mathematical point of view, we may identify two goals in this paper: (1) to characterize $\overline{\mathbf{R}(e,t)}$ and hence compute $t^*(U_F)$, the infimizing time for $U_F\in G$, and (2) to characterize the infimizing control sequence v^n in Eq. (13), which in the limit $n\rightarrow\infty$, achieves the transfer time $t^*(U_F)$ of steering the system (13) from identity e to U_F. From the physics point of view, these results establish the minimum time required and the optimal controls (the rf pulse sequence in NMR experiments) to achieve desired transfers in a spectroscopy experiment.

VI. TIME OPTIMAL CONTROL

The key observation as described in Sec. II is the following. In the control system (13), if $U_F\in K$ then $t^*(U_F)=0$. To see this, note that by letting v in Eq. (13) 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 the 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 (13) between the cosets Ke and KU_F. This is illustrated in the Fig. 1.

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

Lemma 3: Let $U\in G$ and $X:\mathbb{R}\rightarrow\mathfrak{g}$ be a locally bounded measurable function of time. If $X_n(t)$ converges to $X(t)$ in the sense that

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

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 4: For the control system in Eq. (13), $t^*(U_F)=t^*(KU_F)$.

Proof: Observe it suffices to show that if $k\in K$, then $t^*(k)=0$. From [4] (Theorem 5.1), for every $T>0$, we have $R(e,T)=K$ and therefore the result follows. **Q.E.D.**

Remark 6: 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 that we now explain.

Definition 6 (Adjoint Control System): Let $P\in G$. Associated with the control system (13) is the right invariant control system

$$\dot{P}=XP, \tag{14}$$

where now the control X no longer belongs to the vector space but is restricted to an adjoint orbit i.e., $X\in \mathrm{Ad}_K(X_d)=\{k^{-1}X_d k|k\in K\}$. We call such a control system an *adjoint control system*.

For the control system (14), we say that $KU_F\in B(U_0,t')$ if there exists a control $X[0,t']$ that steers $P(0)=U_0$ to $P(t')\in KU_F$ in t' units of time. We use the notation

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

From Lemma 3, it follows that $\mathbf{B}(U_0,T)$ is closed. We use

$$L^*(KU_F)=\inf\{t\geqslant 0|KU_F\in \mathbf{B}(e,t)\}$$

to denote the minimum time required to steer the system (14) from identity e to the coset KU_F. We call it the *minimum coset time*.

Theorem 7 (Equivalence theorem): The infimizing time $t^*(U_F)$ for steering the system

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

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

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

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

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

$$\dot{Q}=\left[\sum_{i=1}^{m} v_i X_i\right]Q,\quad Q(0)=e. \tag{15}$$

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

$$\dot{P}=(Q^{-1}X_d Q)P,\quad P(0)=e. \tag{16}$$

Then observe that

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

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 $\hat{U}(t)$ of Eq. (13) with the initial condition $\hat{U}(0)$, there exist unique curves $\hat{P}(t)$ and $\hat{Q}(t)$, defined through Eqs. (15) and (16), satisfying $\hat{U}(t)=\hat{Q}(t)\hat{P}(t)$. Observe that if $\underline{\hat{U}(T)=U_F}$ then it follows that $\hat{P}(T)\in KU_F$. If $U_F\in \mathbf{R}(e,T)$, then there exists a sequence of control laws $v^r[0,T]$ such that the corresponding solutions $U^r(t)$ of Eq. (13) satisfy $U^r(T)\to U_F$. Therefore, the solutions $P^r(t)$ of the associated control system (15) satisfy $\lim_{r\to\infty}P^r(T)\in KU_F$. Because $\mathbf{B}(e,T)$ is closed, it follows that $KU_F\in \mathbf{B}(e,T)$, which implies that $L^*(KU_F)\leqslant t^*(U_F)$.

To prove the equality observe that if $KU_F\in \mathbf{B}(e,T)$, then there exists a control $\overline{X}[0,T]$ such that the corresponding solution $\overline{P}(t)$ to Eq. (14) satisfies $\overline{P}(T)\in KU_F$. Because $\overline{X}(t)\in Ad_K(X_d)$, we can express $\overline{X}(t)$ as $\overline{Q}(t)^{-1}X_d\overline{Q}(t)$. It is well known [21] that we can find a family $v^r(t)$ of control laws such that the corresponding solution $Q^r(t)$ of

$$\dot{Q}^r=\left[\sum_{i=1}^{m} v_i^r X_i\right]Q^r,\quad Q^r(0)=e$$

satisfies $\lim_{r\to\infty}\int_0^T\|\overline{Q}(t)-Q^r(t)\|dt=0$. Hence, $\lim_{r\to\infty}\int_0^T\|\overline{X}(t)-[Q^r(t)]^{-1}X_d Q^r(t)\|dt=0$. Using Lemma 3, 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, $t^*(KU_F)\leqslant T$. Since the choice of T was arbitrary, it follows $t^*(KU_F)\leqslant L^*(KU_F)$. Because $t^*(KU_F)=t^*(U_F)$, it follows that $t^*(U_F)\leqslant L^*(KU_F)$. Hence the proof. **Q.E.D.**

Remark 7: We will now compute $t^*(U_F)$ using the properties of the set $Ad_K(X_d)$. In this paper we will confine to the case when the coset space G/K is a globally Riemannian symmetric space. We consider the following two cases based on the rank of the symmetric space.

A. Rank one case

Remark 8: We begin with case where the rank of the symmetric space G/K is one. As the Cartan subalgebra is one dimensional, it follows from Theorem 5 that $\mathfrak{p}=\{\alpha Ad_K(X_d)|\alpha\in\mathbb{R}\}$. Furthermore, if G/K is rank one, then $(-X_d)\in Ad_K(X_d)$, [2] (Theorem 2.12, Chapter 7). Therefore

$$\mathfrak{p}=\{\alpha Ad_K(X_d)|\alpha\geqslant 0\}.$$

Therefore computing $t^*(U_F)$ reduces to finding the geodesic distance in the homogeneous space G/K.

Theorem 8: Let G be a compact semi-simple Lie group with a bi-invariant metric $\langle , \rangle$, and K be a closed subgroup. Let $\mathfrak{g}$ and $\mathfrak{k}$ denote their Lie algebras such that the decomposition $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$ is a Cartan decomposition and the rank of G/K is one. For the right invariant control system

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

where $v_i\in\mathbb{R}$, $X_d\in\mathfrak{p}$, and $\{X_i\}_{LA}=\mathfrak{k}$, the infimizing time $t^*(U_F)$ is the smallest value of $\alpha>0$ such that we can solve $U_F=Q_1\exp(\alpha X_d)Q_2$ with $Q_1, Q_2\in K$.

Proof: By the equivalence theorem, $t^*(U_F)$ is the same as the minimum time for steering the system

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

from $P(0)=e$ to KU_F. From Ref. [1], the geodesics in G/K under the standard metric $\langle , \rangle_n$ originating from o take the form $\pi[\exp(\tau Y)]$ for $Y\in\mathfrak{p}$. Because G/K is a Riemannian symmetric space of rank one, the set

$$\{\alpha Ad_K(X_d)|\alpha\geqslant 0\}=\mathfrak{p}$$

and generates all the geodesics in G/K space. Hence the result follows.

Remark 9: Roughly speaking, the time optimal trajectory (obtained as a limit of the infimizing sequence) for the system (13), which steers the system from $U(0)=e$ to $U_F=Q_1\exp(\alpha X_d)Q_2$, takes the form $e\rightarrow Q_2\rightarrow\exp(\alpha X_d)Q_2\rightarrow Q_1\exp(\alpha X_d)Q_2$, where the first and last step of this chain takes no time, and all the time is required for the drift process (second step).

B. Rank greater than one case

Let us now consider the case when the rank of the Riemannian symmetric space G/K is greater than one. Please refer to [19] for the role of symmetric spaces in control theroy. We first state a convexity theorem due to Kostant.

Theorem 9 [20] (Kostant's Convexity Theorem): Let $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$ be a Cartan decomposition and $\mathfrak{h}\subset\mathfrak{p}$ a Cartan subalgebra of $(\mathfrak{g},\mathfrak{k})$ containing X_d. Let $\Gamma:\mathfrak{p}\rightarrow\mathfrak{h}$, be the orthogonal projection of $\mathfrak{p}$ onto $\mathfrak{h}$ with respect to the killing metric. Then $\Gamma:Ad_K(X_d)=\mathfrak{c}(X_d)$, where $\mathfrak{c}(X_d)$ is the convex hull of the Weyl orbit of X_d.

Theorem 10 (Time Optimal Tori Theorem): Let G be a compact semi-simple Lie group and K be a closed subgroup with $\mathfrak{g}$ and $\mathfrak{k}$ their Lie algebras, respectively. Let $\mathfrak{g}=\mathfrak{p}\oplus\mathfrak{k}$ be a Cartan decomposition. Consider the right invariant control system

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

where $v_i\in\mathbb{R}$, $X_d\in\mathfrak{p}$, $\{X_i\}_{LA}=\mathfrak{k}$. Then any $U_F=Q_1\exp(\alpha Y)Q_2$, where $\alpha>0$, Q_1, $Q_2\in K$, and $Y\in\mathfrak{c}(X_d)$, 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

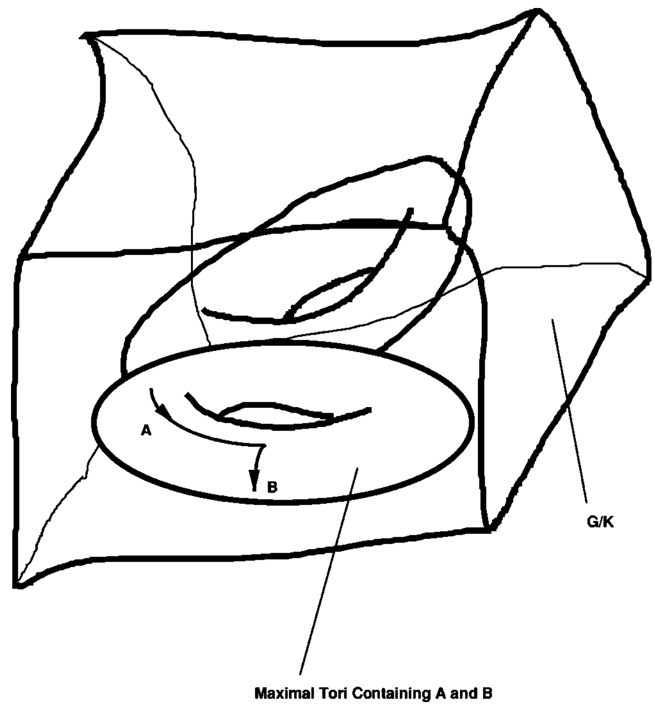

FIG. 4. The panel illustrates the fastest way to get between two pcosets A and B is to flow on a maximal torus containing the cosets

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

where Q_1, $Q_2\in K$, and Y belongs to the convex hull $\mathfrak{c}(X_d)$.

We sketch here the outline of a proof.

Let $\mathfrak{h}$ be a Cartan subalgebra of G/K containing X_d and let $A=\exp(\mathfrak{h})$. It suffices to prove the theorem for $U_F\in A$ as by theorem 6, $G=KAK$. For $U_F\in A$, let T be the smallest value of $\sum_{i=1}^{m}\alpha_i, \alpha_i\geqslant 0$ such that $U_F=\exp(\sum_{i=1}^{m}\alpha_i X_i)$, where $X_i\in W(X_d)$. It is immediate that $t^*(U_F)\leqslant T$ as the adjoint control system $\dot{P}=XP$, can be steered to U_F in T units of time, by letting X be X_i for α_i units of time.

To see that $t^*(U_F)=T$, let $\overline{P(t)}$ be the shortest (or time optimal) trajectory of the adjoint control system $\dot{P}=XP$ that steers $P(0)=e$ to the coset KU_F. Let $a(t)$ be its projection under the map π_A: $G/K\rightarrow A$ such that $\pi_A:k_1\exp(Y)k_1^{\dagger}\rightarrow\exp(Y)$, $Y\in\mathfrak{h}$, $k_1\in K$ [note that the projection is only unique modulo a Weyl group action, to make it unique, fix a Weyl chamber $\mathfrak{b}$ in $\mathfrak{h}$ and consider projection onto $\exp(\mathfrak{b})$]. The projection π_A induces the map $\pi_{A_*}:\dot{\overline{P(t)}}\rightarrow\dot{a}(t)$. The evolution of the curve $a(t)$ has the form $\dot{a}(t)=\Omega a(t)$, where $\Omega=\Gamma[Ad_{\tilde{k}}(X_d)]$, for some $\tilde{k}\in K$ (recall $\Gamma:\mathfrak{p}\rightarrow\mathfrak{h}$ is the orthogonal projection onto $\mathfrak{h}$). Now using Kostant's convexity theorem, we have $\Omega\in\mathfrak{c}(X_d)$. Therefore we can write $\dot{a}(t)=(\sum_{i=1}^{m}\beta_i X_i)a(t)$, where $X_i\in W(X_d)$ and $\sum_{i=1}^{m}\beta_i=1$ for $\beta_i\geqslant 0$. This makes clear that if $T=\sum_{i=1}^{m}\alpha_i$ is the smallest value for which $U_F\in A$ satisfies $U_F=\exp(\sum_{i=1}^{m}\alpha_i X_i)$ for $\alpha_i\geqslant 0$, then the path $a(t)$ will at least take T units of time to reach U_F.

Remark 10: The essence of the above theorem is that the space G/K is a union of maximal tori $Ad_K(A)$, and the fastest way to steer the adjoint control system between two points is to always move on a maximal torus containing these points. This is illustrated in Fig 4. The theorem characterizes $\mathbf{B}(e,t)$, the reachable set for the adjoint system. This is given by

$$K\mathbf{B}(e,t)=K\exp(\alpha Y)K, \quad 0\leqslant\alpha\leqslant t,$$

where Y belongs to the convex hull $\mathbf{c}(X_d)$.

VII. CONCLUSION

In this paper, we presented a mathematical formulation of the problem of finding the 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 the shortest length paths on certain coset spaces. 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.

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APPENDIX

Proof of Lemma 1: It suffices to consider $a_1,a_2,a_3\geqslant 0$ as we can absorb the negative sign using the orthogonal matrices U or V. 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 $\|p^\dagger U\Sigma Vp\|\leqslant\|\Lambda Vp\|\|\Lambda Up\|$. Observe, the maximum value of $\|\Lambda Vp\|$ is $\sqrt{a_i+a_j}$. Therefore $\|p^\dagger U\Sigma Vp\|\leqslant a_i+a_j$. Clearly for the appropriate choice of U and V, this upper bound is achieved (for example, in case $a_1\geqslant a_2\geqslant a_3$, the bound is achieved for U and V identity). Hence the result follows.

Proof of Lemma 2: Let

$$\begin{aligned}H(\alpha_1,\alpha_2,\alpha_3,\lambda)&\\ =\sin(J\pi\alpha_1)\sin(J\pi\alpha_3)&+\sin(J\pi\alpha_2)\sin(J\pi\alpha_3)\\ &+\lambda(\alpha_1+\alpha_2+\alpha_3-T).\end{aligned}$$

The necessary condition for optimality gives $\partial H/\partial\alpha_1=0$, $\partial H/\partial\alpha_2=0$, and $\partial H/\partial\alpha_3=0$, which implies respectively, that

$$\pi J[\cos(J\pi\alpha_1)\sin(J\pi\alpha_3)]+\lambda=0, \tag{17}$$

$$\pi J[\cos(J\pi\alpha_2)\sin(J\pi\alpha_3)]+\lambda=0, \tag{18}$$

$$\pi J[\sin(J\pi\alpha_1)\cos(J\pi\alpha_3)+\sin(J\pi\alpha_2)\cos(J\pi\alpha_3)]+\lambda=0. \tag{19}$$

From Eqs. (17) and (18), we obtain that either $\sin(J\pi\alpha_3)=0$ or $\cos(J\pi\alpha_2)=\cos(J\pi\alpha_1)$. The first condition does not give a maxima as it makes f identically zero. The second condition implies

$$J\pi\alpha_1=2m\pi+J\pi\alpha_2. \tag{20}$$

Since α_1, $\alpha_2\geqslant 0$, and $\alpha_1+\alpha_2\leqslant T\leqslant 3/2J$, condition (20) is only satisfied for $m=0$. Therefore, $\alpha_1=\alpha_2$. Now substituting this in Eq. (19) and using the Eqs. (18) and (19), we get the desired result.

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