Control of a coupled two-spin system without hard pulses

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Constructive techniques for preparing a specific unitary generator from a coupled two-spin system, via bounded amplitude radio frequency selective single spin pulses, are presented. The frequency of any pulse in the sequence is one of the two Larmor frequencies, while the phase takes one of two values. The fact that the amplitude is bounded implies that the Larmor frequency separation between the two spins need not be large to maintain selectivity. In addition, the contribution of the J coupling term to single spin evolution is not neglected, but instead plays a crucial role. The procedure is based on a certain decomposition of SU(4) available in the literature. A method for determining the parameters entering this factorization, in terms of the entries of the target unitary generator, is also provided.

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I. INTRODUCTION

The inverse problem of producing pulse sequences that will prepare any desired unitary generator has attracted considerable interest in various ''quantum'' communities [1–16]. One impetus for this question stems from problems in quantum computation and cryptography, where several implementation issues are explicitly cast in the form of preparing desired states and unitary generators [17,18,19,11,8,20–22,23]. In these applications accurate preparation of the desired generator is a key requirement. Any form of avoidable inaccuracy is undesirable since it might call for increased use of error correction schemes or may not be amenable to extant error correction techniques [24]. In principle, every quantum objective amounts to preparing prescribed states and generators. For instance, it is shown in Refs. [25–27] that all one-dimensional (1D) and 2D nuclear magnetic resonance (NMR) spectra can be explicitly parametrized by such unitary generators. In such applications also minimizing approximations is useful.

In this paper, the problem of producing an explicit protocol for a radio frequency pulse—delay sequence that will prepare exactly a specific unitary generator, when applied to a pair of coupled spin $\frac{1}{2}$ particles, is studied. The usage of the word ''exactly'' is, of course, within the model supposed by this work. Briefly, we suppose selective excitation and the weak coupling limit in keeping with the universal practice in liquid NMR quantum information processing [11,12,5] but, in contrast to the usual practice, *do not neglect* the contribution of J coupling to single spin evolutions. Thus, one key contribution of this paper is the exact treatment of the J coupling while *simultaneously* ensuring the limits believed to be sufficient for the selectivity requirement (viz., effective radio frequency amplitude much lower than Larmor separation). This, in turn, is effected via a new factorization of single spin exponentials (see Appendix A), which could also be implemented in the laboratory in techniques different from the one suggested here.

A coupled system of two spins is probably the most widely examined system in nuclear magnetic resonance, since it is the lowest dimensional system that exhibits essential phenomena present in all systems. The Hamiltonian chosen is the standard Hamiltonian, dominating much of liquid NMR, which describes a pair of spin $\frac{1}{2}$ particles coupled by J coupling and being interrogated selectively by a sequence of radio frequency fields [28–34,12],

$$H = H_{B_0} + H_J + H_{\mathrm{RF}}, \tag{1.1}$$

where H_{B_0} describes the interaction with the static magnetic field, H_J models the J coupling interaction between the two particle, and H_{RF} provides the interaction with the radio frequency field. Further details concerning this Hamiltonian are in Sec. III.

The starting point of this approach is the following ''Euler'' angle type factorization of any 4×4 special unitary matrix:

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$$S=\prod_{k=1}^{Q}\exp(-it_kM_k). \tag{1.2}$$

In this factorization the M_k are each one of the operators $I_{1z}I_{2z}, I_{ij}$, $i=1,2$; $j=x,y$ (see Sec. II and the Appendixes for more on this factorization). The steps involved then are the following.

Step R1. The application of a sequence of radio frequency fields whose frequencies and phases are chosen so as to render the dynamics in a suitable rotating frame to have a constant times $I_{1z}I_{2z}$ as the free Hamiltonian, while the interaction Hamiltonian transforms into a constant times one of the I_{ij}, $i=1,2$, $j=x,y$. The constant in these Hamiltonians depends on the duration and amplitude of the pulses.

Step R2. The determination of the amplitudes and durations of the pulses explicitly, assuming the t_k in Eq. (1.2) are known, so that the target S is prepared exactly within our model. It is also shown how to constructively incorporate any prespecified amplitude bound. This means that selective single spin excitation is possible even if the Larmor frequency separation is quite low. In the process certain matrix exponentials for two spin systems are explicitly computed, which may be of interest in its own right. Indeed, these calculations facilitate a factorization (see Appendix A), which represent the innovation enabling the exact treatment of the J coupling term in single spin evolutions.

Step R3. The specification of an algorithmic procedure for finding the t_k from the entries of the target S.

The idea of using factorizations of unitary matrices to prepare unitary generators is not new. For instance, Ref. [3] studies the constructive and exact generation of unitary generators in two level systems in this way. In Ref. [5] a similar decomposition is used to prepare unitary generators for coupled spin systems. Inherent in Ref. [5] were, however, approximations due to the use of hard pulses. Such pulses only prepare the unitary generator approximately (with the error introduced not being of the phase error type) but also require a very wide separation of frequencies. In addition, a crucial step, viz., the determination of the parameters t_k, was not provided. Since t_k provide essential information about the pulse sequence in their approach also, such an algorithm is vital. In this paper we provide a complete solution to this problem without resorting to such approximations and also provide an algorithm to find t_k.

This paper is organized as follows. In the following section some notation is provided. Section III derives the rotating frame and shows how to determine frequencies and phases of the pulses in the sequence to obtain the desired target. Section IV provides an algorithm that yields the amplitude and duration of the requisite pulse sequence. Section V discusses an example. Some conclusions are offered in Sec. VI. Finally, two appendixes are included. The first proves a proposition on which the algorithm in Sec. IV is based. The second shows how to find t_k of Eq. (1.2).

II. NOTATION AND TERMINOLOGY

The Pauli matrices will be denoted by

$$\sigma_x=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},$$

$$\sigma_y=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},$$

and

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

The following notation will be used throughout: $I_{1k}=\sigma_k\otimes I_2$; $I_{2k}=I_2\otimes\sigma_k$, $k=x,y,z$.

Note. The customary factor of $\frac{1}{2}$, in the definition of the Pauli matrices, has been omitted to minimize the book keeping in Appendix B. It does not affect any of the results below.

Phraseology. To prevent circumlocution, the following convention is employed. (i) Hard pulse will mean any scheme that neglects J coupling during a selective rf pulse. (ii) Soft pulse will be reserved for the pulse scheme proposed by us. (iii) Throughout, unless explicit mention is made to the contrary, ''NMR'' will refer only to liquid NMR.

III. DETERMINATION OF THE FREQUENCIES AND PHASES

Consider a pair of coupled spins in the weak coupling limit [28,29,31–33,11]. Thus, the J coupling constant satisfies $|\omega_1-\omega_2|\gg 2\pi J$, where ω_1 and ω_2 are the Larmor frequencies of the two particles. It is not assumed that the gyromagnetic ratios of the two spins, γ_1 and γ_2 are different. Since, typically, the two particles experience different shielding effects, $\omega_1\neq\omega_2$ even if $\gamma_1=\gamma_2$. This system is probed by a radio frequency field sequence, tuned to one of the two Larmor frequencies. It is assumed that selective excitation is possible, i.e., off-resonant effects can be neglected. This means that the effective amplitude of the fields, i.e., amplitude times the respective gyromagnetic ratio, has to be much smaller than the Larmor separation of the two particles [28,29,31,32,11,12]. This possibility is universally supposed in liquid NMR quantum information processing [11,12,5]. Since, it will be shown that any bound on the amplitude can be accommodated, the selectivity assumption poses no further restrictions on the frequency separation itself.

Suppose that the radio frequency field is tuned to excite the first particle, and as usual, is linearly polarized along the x axis. Thus, the field is $2c\cos(\omega_1 t+\phi)$, where $2c$ and ϕ are the amplitude and phase of the field. Then the Hamiltonian describing the system is a sum of three terms, $H=H_J+H_{B_0}+H_{\mathrm{RF}}$, where

$$H_J=\frac{J\pi}{2}I_{1z}I_{2z},\quad H_{B_0}=\tfrac{1}{2}(\omega_1 I_{1z}+\omega_2 I_{2z}),$$

$$H_{\mathrm{RF}}=\frac{c\gamma_1}{2}[I_{1x}\cos(\omega_1 t+\phi)+I_{1y}\sin(\omega_1 t+\phi)].$$

This is precisely the familiar Hamiltonian describing a pair of J coupled, spin $\frac{1}{2}$ particles being interrogated selectively by a radio frequency field [28,29,31–33,11,12]. Note that

some of the constants in the Hamiltonian appear different from the standard expression. This is due to the absence of $\frac{1}{2}$ in our Pauli matrices.

Functional form of H_J. The weak coupling limit, used in liquid NMR quantum information processing works [11,12,5], ensures this form of H_J. In this regime, the interaction between the two spins in liquid state is to great precision given by H_J, with the scalar terms in the x,y directions neglected [28,29,31,11,12]. Since J is at most in kHz (for instance, the highest value of J to be found in Ref. [33] occurs for a phosphorus-platinum single bond and is equal to 4.64 kHz), while with current static magnetic fields the Larmor separation runs from tens to hundreds of megahertz and thus $2\pi J \ll |\omega_1 - \omega_2|$, this assumption is quite valid. Situations that are not susceptible to this include, of course, equivalent spins and coherence transfer experiments in isotropic mixing. It should be pointed out that for weak coupling an extra requirement, viz., radio frequency amplitude much lower than static field, is needed too. This work ensures this.

Functional form of H_{RF}. Our truncated expression for H_{RF} is identical to the one in Refs. [11,12,5]. Besides the selective excitation assumption (i.e., off-resonant effects negligible), it supposes the usual fact that the field may be split into two components, one of which (the counter-rotating term) can be neglected if the amplitude of the field is much smaller than the static magnetic field [28,29,31,32]. Since the approach will allow any amplitude bound, this is a valid approximation. Effects such as the Bloch-Sieget shift will be negligible in our approach. If it is possible to apply two independent radio frequency fields in the x and y directions then the expression for H_{RF} is exact (within the selectivity assumption, of course) if the field in the x direction is $c\cos(\omega_1 t+\phi)$ and it is $c\sin(\omega_1 t+\phi)$ in the y direction.

If the second particle is being interrogated the only difference in the Hamiltonian would be the replacement of I_{1j}, $j=x,y$ by I_{2j}, $j=x,y$ and ω_1 by ω_2.

Passing to a rotating frame, $U(t)=e^{tF}V(t)$ with

$$F=\frac{i}{2}(\omega_1 I_{1z}+\omega_2 I_{2z})$$

yields, for the first particle, the following dynamics:

$$\dot{U}=-\frac{i}{2}(J\pi I_{1z}I_{2z})U-\frac{ic\gamma_1}{2}(\Delta\otimes I_2)U, \tag{3.1}$$

with

$$\Delta=\begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix}.$$

By choosing the phase $\phi=0$, Δ is σ_x and if we set $\phi=\pi/2$, Δ is σ_y. A similar calculation reveals that the *same rotating frame* can be used to address the other spin to obtain

$$\dot{U}=-\frac{i}{2}(J\pi I_{1z}I_{2z})U-\frac{ic\gamma_2}{2}(I_2\otimes\Delta)U. \tag{3.2}$$

This implies that by choosing the frequency of the field to be resonant with one of the spins and by choosing the phase appropriately, passing to a rotating frame, yields the following system controlled by constant inputs:

$$\dot{U}=-\frac{i}{2}AU-\frac{i}{2}dBU, \quad U\in \mathrm{SU}(4), \tag{3.3}$$

with $A=J\sigma_z\otimes\sigma_z$ and B one of the matrices I_{1x}, I_{2x}, I_{1y}, I_{2y} where $I_{1j}=\sigma_j\otimes I_2$, $j=x,y$ and $I_{2j}=I_2\otimes\sigma_j$, $j=x,y$. The constant d is related to the amplitude of the field and other constants of the system. This is useful because the decomposition, Eq. (1.2), consists precisely of the exponentials of one of $I_{1z}I_{2z}, I_{ij}$, $i=1,2$, $j=x,y$.

IV. DETERMINING THE AMPLITUDES AND DURATIONS

Recall Eq. (1.2), $S=\Pi_{k=1}^{Q}e^{-it_kM_k}$. Suppose for the moment that the constants t_k are known. Note that t_k, whatever they are, may be supposed to be in $[0, 2\pi)$, though this is not necessary. To generate factors for which M_k is $I_{1z}I_{2z}$, free evolution for time $2t_k/J\pi$ suffices. Preparing the remaining factors is equivalent to factorizing the exponentials, $e^{-iLJ_{ij}}$, $i=1,2$, $j=x,y$ for any $L\in[0,2\pi)$ in the form

$$e^{-iLI_{ij}}=\prod_{k=1}^{R} e^{(-ia_kI_{1z}I_{2z}-ib_kI_{ij})}, \quad i=1,2,\ j=x,y \tag{4.1}$$

satisfying (i) condition O1, $a_k>0$ and (ii) condition O2, $|b_k/a_k|\leqslant C$, $k=1,\ldots,R$. Up to constants, a_k is the duration of the kth pulse and b_k/a_k its amplitude. This explains the conditions O1 and O2. Obtaining such a factorization is addressed by Proposition 1 in Appendix A. The proof of this Proposition leads to the following algorithm.

Note. (i) The following algorithm supposes that $J>0$. Geminal and vicinal couplings often have negative J. For such situations condition O1 must be modified to $a_k<0$. It is possible to modify the proof of Proposition 1 to ensure this. The details are omitted in the interest of brevity. (ii) In the algorithm below whenever the amplitude turns out to be negative, one must add π to the corresponding phase to ensure its positivity. (iii) The algorithm is written in a form that addresses the preparation of each factor of S in Eq. (1.2). When S itself is prepared, many free evolution terms coalesce to either disappear or become free evolution terms with shorter durations (keep in mind the periodicity of $I_{1z}I_{2z}$ and $e^{-i\pi I_{1z}I_{2z}}=-I_4$). (iv) From this point on, c is taken to be the amplitude. If the the rotating wave approximation is used in arriving at H_{RF} then the amplitude should be twice that reported.

Algorithm I

Step 1. Determine, using Appendix B, the parameters t_k in the factorization of S in Eq. (1.2).

Step 2. If for some k, $M_k=I_{1z}I_{2z}$ switch off the field and let the system evolve for $2t_k/J\pi$.

Step 3. If $M_k=I_{1x}$, first determine if $\cos(t_k)$ is (i) positive, (ii) negative, or (iii) zero. If $\cos(t_k)>0$, apply the following pulse sequence. First, switch off the field for $1/2J$ units of

time. Next, apply a pulse with frequency ω_1, phase 0, duration $\cos(t_k)/J$, and amplitude given by $(-2J\pi/\gamma_1)\tan(t_k)$. Finally, switch off the field for $13/2J$ units of time.

If $\cos(t_k)<0$, apply the following sequence. First, let the system evolve freely for $3/2J$ units of time. Next, tune the frequency to ω_1, set the phase 0, amplitude $(2J\pi/\gamma_1)\tan(t_k)$, and duration $-\cos(t_k)/J$. Follow this with free evolution for $9/2J$ units.

If $\cos(t_k)=0$ and $\sin(t_k)=1$, use the following sequence. First, let the system evolve freely for $1/2J$ units. Next, apply a field with frequency ω_1, phase 0, amplitude $2J\pi/\gamma_1$, and duration $1/\sqrt{2}J$ units. Next, apply another pulse with the same frequency, phase, and duration, but with amplitude $-1/\sqrt{2}J$. Finally, let the system evolve freely for $7/2J$ units.

If $\cos(t_k)=0$, but $\sin(t_k)=-1$, proceed as in the preceding case except that the second and third pulses are interchanged.

Step 4. If $M_k=I_{1y}$, determine if $\cos(t_k)$ is (i) positive, (ii) negative, or (iii) zero. If $\cos(t_k)>0$, first switch off the field for $7/2J$ units. Next, apply a field with frequency ω_1, phase $3\pi/2$, duration $\cos(t_k)/J$, and amplitude $(2J\pi/\gamma_1)\tan(t_k)$. Finally, let the system evolve freely for $7/2J$ units of time.

If $\cos(t_k)<0$, first let the system evolve freely for $9/2J$ units of time. Next, switch on the field with the same frequency and phase as in the preceding step, but with duration $-\cos(t_k)/J$ units, with amplitude $(2J\pi/\gamma_1)\tan(t_k)$. If $\cos(t_k)=0$, proceed as in the $\cos(t_k)=0$ subcases in step 3, except that the first free evolution is executed for $7/2J$ units, while the last requires $1/2J$ units.

Step 5. If M_k is I_{2x} (I_{2y}), follow step 3 (step 4), except that the frequency should now be ω_2.

Step 6. If an amplitude bound D is given, first find t_k for the factors for which $M_k\neq I_{1z}I_{2z}$. For such factors, translate the bound D into a bound $|\tan(t_k)|\leqslant C$. If t_k does not satisfy this bound, then factor $\exp(-it_kM_k)$ as $\Pi_{l=1}^{r}\exp(-it_k^lM_k)$ with each t_k^l satisfying this bound. Then generate every factor $\exp(-it_k^lM_k)$ using step 3 (or step 4 or 5, depending on what M_k is).

Motivation for pulse sequence. The principal difference between our pulse sequence and that in Ref. [5] is that the former prepares one spin generator, i.e., exponentials of the I_{ij}, $i=1,2$, $j=x,y$ accurately by actively using the J coupling term, whereas the second views the Hamiltonians, I_{ij}, as just the control coupling in the rotating frame, and thus proposes approximate generation of its exponential via hard pulses, thereby ignoring the difficulty posed by these terms not commuting with the J coupling term. The J coupling term, in control theoretic parlance, is the drift. Its presence is known to be a challenge for the problem of explicit and exact preparation of states [35]. In this work, the I_{ij} are viewed as an iterated commutator of the J coupling term with the corresponding I_{ij}. In this commutator the J coupling term occurs twice. This inspired us to look for a pulse sequence in which there are two free evolution term sandwiching a control pulse, thereby enabling the exact preparation of S. Note that factors for which $M_k=I_{1z}I_{2z}$ terms require free evolution in either technique. Factors with no such M_k's are tensor products and cannot create additional entanglement.

Omitting certain terms. If the objective is to control the expectation value of an observable and the initial state contains no coherences, then S and SD for any diagonal matrix D will yield the same performance. Since $e^{-iLI_{1z}I_{2z}}$ is diagonal for any real L one may, for such an objective, omit the first free evolution in generating the last factor, $e^{-it_QM_Q}$ in the decomposition equation (1.2) of S.

Frequency spread. If a pulse is applied for too short a time, then selectivity is compromised by virtue of the uncertainty principle (this is a potential difficulty, though less potent in comparison to the problems caused by high amplitudes, in the hard pulse regime). In the setting of this paper, selectivity issues associated to short durations can arise only if $J/\cos(t_k)$ is comparable to the Larmor separation. Here t_k is the corresponding coefficient of such M_k, in Eq. (1.2), which necessitate control pulses. Step 6 of the algorithm can be used to fix this problem too. Since such a circumstance is likely only when t_k is close to either $\pi/2$ or $3\pi/2$, one should simply factor $e^{-it_kM_k}$ into factors with smaller coefficients.

V. EXAMPLE AND DISCUSSION

To illustrate the pulse sequence, consider a two spin system with $J=200$ Hz, $\gamma_1=267.516\times10^6$ rad T^{-1} s^{-1} and $\gamma_2=67.2640\times10^6$ rad T^{-1} s^{-1}. We take $\omega_1=500$ MHz and $\omega_2=125.7215$ MHz. This corresponds to a static field of approximately 12 T. Such a system could, for instance, arise in a H^1-C^{13} (single) bond. The J for such a bond is reported to be in the 110 to 270 Hz range in Ref. [33]. The remaining data are also from Ref. [33], except that our Larmor frequencies are bigger in keeping with current static fields. However, in the discussion below we will indicate the effect of using lower strength magnetic fields. Since the principal difference between the approach here and the hard pulse approach occurs in the preparation of single spin evolutions, the target chosen is $S=\exp[i(\pi/4)I_{1y}]$.

Pulse sequence. If the effect of the rotating frame is unimportant (see below) then the following sequence prepares S. First, let the system evolve freely for 0.75×10^{-2} s. Next, apply a field of frequency 500 MHz, phase $\pi/2$, amplitude 4.697×10^{-6} T for 3.536×10^{-3} s. Finally, switch off the field for 0.75×10^{-2} s. The total duration is 18.536 ms. This sequence uses the factorization of $e^{-iLI_{1y}}$ introduced in this paper, *together* with the observation that for $L=-\pi/4$, the two delay terms sandwiching the pulse term each contain a $e^{-i\pi I_{1z}I_{2z}}=-I_4$ factor in them. The two $-I_4$'s can be dispensed to yield a shorter duration than that suggested for general L (cf., the comment just prior to the algorithm in the preceding section).

Undoing the rotating frame. If S has been prepared in T_S units of time in the rotating frame then the actual unitary generator prepared is $V(T_S)=e^{-T_SF}S$. Since $e^{-T_SF}=\mathrm{diag}(e^{i(T_S/2)(-\omega_1-\omega_2)}, e^{i(T_S/2)}(-\omega_1+\omega_2), e^{i(T_S/2)(-\omega_2+\omega_1)}, e^{i(T_S/2)(\omega_1+\omega_2)})$, this introduces phase errors in each entry of S. Since S and $e^{-T_SF}S$ are not similar matrices, they do not represent the same linear transformation acting on the two qubits. Depending on the application, this difference may be undesirable. This problem is present in the hard pulse method too. For targets that are not tensor prod-

ucts of SU(2) matrices there will be at least one exponential of $I_{1z}I_{2z}$ in the decomposition equation (1.2). Since these are generated by free evolution in either technique, T_S cannot be made negligibly small. Indeed, even for single spin evolutions in the hard pulse approach the additional error introduced by the $e^{-T_S F}$ factor is not negligible. For instance, in this example the hard pulse technique would need a time in the nanosecond or shorter regime for the error to be negligible (since ω_i are in the 10^8 Hz regime). However, this will require amplitudes that will make the implicit approximations invalid. For brevity, it is left to the reader to verify that the putative remedy of following the pulse sequence that prepared $e^{-T_S F}S$ (via calculations in the rotating frame) by a delay (in the laboratory frame) to prepare $e^{T_S F}$ is fraught with problems and will in general not work even approximately. In other words, except for special targets one cannot neglect the J coupling's contribution to the delay and even when it can (e.g., via direct neglection of H_J or decoupling methods—which themselves use implicit approximations), the method introduces no further errors only if $\omega_1+\omega_2$ is rotationally related to $\omega_1-\omega_2$.

To rectify this problem we propose the preparation of the target $e^{T_0 F}S$ for a parameter $T_0>0$ such that the total time taken to prepare $e^{T_0 F}S$ in the rotating frame is T_0 itself (i.e., using the algorithm of Sec. IV for $e^{T_0 F}S$ instead of S). This will lead to the preparation of S in T_0 units of time in the laboratory frame. T_0 is found by solving a transcendental equation. This equation can be shown to be solvable. We will illustrate this procedure for the example being considered. The equation to be solved is

$$T_0=\frac{1}{J}\left[5+\frac{5\sqrt{2}}{2}+\cos\left(\frac{T_0\omega_1}{2}\right)+\cos\left(\frac{T_0\omega_2}{2}\right)\right], \quad (5.1)$$

with the above values for J, ω_i, $i=1,2$. This equation was obtained by concatenating free evolution terms in $e^{T_0 F}$ and S. If such concatenation is not used a different equation results, which can be also used for the same purpose (which, however, will require more time).

The solution to this equation was found by implementing line search with Newton-Raphson iteration on Matlab [36]. An accuracy of order 10^{-11} was used as a convergence criterion so that the phase errors in the target produced should be of order 10^{-3} in the exponent, since the ω_i are in the 10^8 regime (which is indeed the case, see below). The corresponding solution turns out to be $T_0=0.043\,101\,501\,284\,331$. The value of the right-hand side of Eq. (5.1) with this T_0 turns out to be $T_R=0.043\,101\,501\,282\,614\,7$ s. This difference between the two values is 3.662×10^{-11}, which is in the regime expected. *This accuracy, can of course, be increased to any desired limit.*

Due to the transcendental nature of Eq. (5.1), there is of course some residual error in the prepared target. Specifically, the pulse sequence given by the algorithm of Sec. IV (not shown for brevity) yields the unitary generator S_P in the laboratory frame:

$$S_P=\begin{pmatrix} 0.7071+i0.0081 & 0 & 0.7071+i0.0081 & 0 \\ 0 & 0.7071+i0.0048 & 0 & 0.7071+i0.0048 \\ -0.7071+i0.0048 & 0 & 0.7071-i0.0048 & 0 \\ 0 & -0.7071+i0.0081 & 0 & 0.7071-i0.0081 \end{pmatrix} \simeq S=\exp\left(i\frac{\pi}{4}I_{1y}\right).$$

Figure 1 shows the entries of S and S_P (note the scales on the x and y axes are different). S_P coincides with S, except for phase factors stemming from the difference between T_0 and T_R [the right-hand side of Eq. (5.1)]. This error is much smaller than what would be the situation if the effect of the rotating frame was not rectified. Further, this error can be made as small as desired by improving the accuracy to the solution for Eq. (5.1).

Discussion. The cumulative time is roughly of the order of 43 ms (just 18.5 ms if the error due to the rotating frame is ignored). Further, the amplitudes (even without using step 6 of the algorithm) are at most of the order of 10^{-4} T (at most 10^{-6} T if the effect of the rotating frame is ignored), which renders all the approximations used in arriving at the system model valid. This cumulative time is substantially shorter than even the T_2 relaxation times (T_1 relaxation times are typically longer) of many spin systems. Since, at least for quantum information processing, the chemical system is at the designer's disposal, this suggests that the greater time our technique takes is compensated for by its greater accuracy, without running into problems with relaxation (this suggestion is system and target dependent and should be used on a case by case basis).

Of course, depending on the system and the target there will be situations where hard pulses should be used. In this connection, it is worth noting that targets not in $SU(2)\otimes SU(2)$ even the hard pulse approach will consume a finite amount of time, which is in the J^{-1} regime, i.e., not orders of magnitude shorter than the times consumed by our technique. The maximum possible accuracy in the hard pulse method, due to neglecting the J coupling term's contribution, even if the rotating frame's effect is ignored, is limited by two factors. First, the amplitude cannot be made infinitely large, which directly limits the minimum time taken. Less prominently, the minimum time is also limited by the time-energy uncertainty principle, which precludes selectivity if the pulse is too short. In our technique, there is no error if the rotating frame is ignored. Even if it cannot be ignored, the

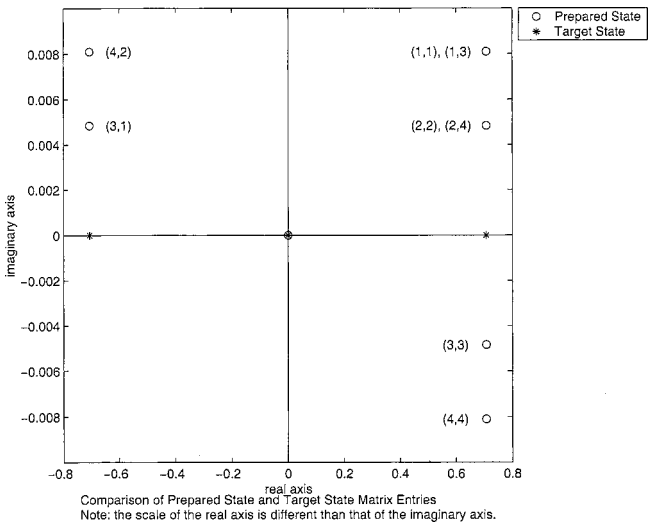

FIG. 1. The 16 entries of S and S_P, where S_P is the target prepared by the pulse sequence, which rectifies the deviation due to the rotating frame. As mentioned in the text, Eq. (5.7) is a transcendental equation that can be solved to desired accuracy and that determines the T_0 needed to nullify the effects of the rotation frame. For example, a tolerance of 10^{-11} was chosen as the convergence criterion for solving Eq. (5.7). With this criterion the difference between S and S_P should be phase factors with 10^{-3} in the exponent. The figure shows that many of the entries of S and S_P overlap. For instance, the eight zeroes of S are represented by the star at the origin. The corresponding eight entries of S_P are also zero, which is depicted by the circle at the origin. The rest of the figure should be self-explanatory. Note that the scales on the x and y axes are quite different, and thus the predicted near equality of S_P with S is reflected by the figure.

only error is due to the transcendental nature of Eq. (5.1), and thus can be rendered, in principle, nil (though there are limitations in the laboratory due to inherent lack of resolution, beyond a certain limit, in timing devices).

Low Larmor separation. While the example chosen is heteronuclear, it is obvious that the technique here extends to systems that have very low separation of Larmor frequencies, in particular homonuclear systems. Consider, for instance, the toy system of a homonuclear pair with $\omega_1 = 500\,\mathrm{MHz}$, gyromagnetic ratio equal to $267.516 \times 10^8\ \mathrm{rad\,T^{-1}\,s^{-1}}$, $J = 200\,\mathrm{Hz}$, but with Larmor separation only 0.013 MHz. Then the pulse sequence, described earlier, would still prepare the target S (ignoring the rotating frame) without recourse to step 6 of the algorithm. If one uses the rule of thumb that $X \gg Y$ stands for Y being no more than one-tenth of X, then the weak coupling limit is still operative. Selective excitation requires that the effective amplitude of the radio frequency field be at most 1300 Hz. This corresponds to an amplitude bound of 5×10^{-6} T (which is indeed the case with the pulse sequence proposed). This amplitude bound is also that which would apply for the hard pulse regime. Since in this technique the total time taken is determined by the maximum amplitude, it follows that the time taken would be roughly $\frac{\pi}{52} \times 10^{-2}$ s. However, now the J coupling term is no longer negligible and thus, in effect, the hard pulse technique would be inapplicable in such a situation.

Static magnetic fields. High static fields have their pros and cons. For instance, higher static fields lead to higher S/N ratio, but also enhance chemical shift anisotropy induced relaxation. They also require expensive instrumentation. Therefore, it is worth noting that our technique typically does not require high static magnetic fields (though the choice of high versus low should be made on a case by case basis, keeping in mind the pros and cons). Indeed, as long as the static field ensures that the coupling between the two particles may be modeled by H_J, much of the technique goes through. This is because the radio frequency strengths yielded by the technique, even without recourse to step 6 of the algorithm of Sec. (IV), would typically still be lower than the modified Larmor separation. Further, if the rotating frame's effect is ignored, the cumulative times do not depend on the Larmor frequencies (and thus, on the static field). If the correction to the rotating frame is taken into account, then the cumulative time does not change much [this is because, the only fashion in which the Larmor frequencies affect the time consumed is via factors of the form $|\cos(\omega_i T_0)/J|$—this follows from an analysis of the algorithm].

The above discussion suggests that except for the combination of a system with adequate Larmor separation, with low J values, low relaxation times and a tensor product target, the technique proposed here is a viable alternative to methods that ignore the effect of the J coupling term. Since, at least for quantum information processing purposes, the specific chemical system chosen can be quite arbitrary, the results here suggest one promising technique to generate targets very precisely. While the algorithm in Sec. IV provides one pulse sequence to generate targets S, it is emphasized that the key enabling factor is the factorization of single spin evolutions provided by Appendix A. This factorization could possibly be implemented by different pulse sequences and thus provides new means to generate single spin evolutions. Of course, ingenious NMR techniques themselves use tacit approximations. In this context, the value of our work is that the factorization in Appendix A is exact (independent of modeling assumptions) and thus the additional error, stemming from neglecting J coupling in single spin exponentials, is not present.

VI. CONCLUSIONS

In this paper, a technique for the preparation of arbitrary two-spin evolutions via a tailored pulse-delay sequence of selective radio frequency fields was introduced. The procedure is fully constructive and depends on a certain factorization of any arbitrary matrix in SU(4). Methods to evaluate the real parameters in this factorization were also provided, and thus this work is of significance to hard pulse techniques to control two-spin systems too. Constructive incorporation of any desired amplitude bounds is a feature of this work, which, in addition to being favorable for instrumentation issues, renders the usual approximations in arriving at the models valid. The most significant innovation is the generation of single spin evolutions exactly through the use of the J coupling, in contrast to hard pulse methods that ignore this

coupling for single spin evolutions and thus generate such evolutions only approximately.

There are several interesting questions that stem from this construction. The first is to use the techniques proposed here in conjunction with the learning procedure [37], to overcome uncertainties in the system's Hamiltonian, inaccuracies in implementing the pulse-delay sequence, etc. Such a study is of relevance regardless of which technique one uses to control spin systems, since such uncertainties are a reality in the laboratory. A different alternative is to examine feedback techniques such as those proposed in Ref. [38]. To correct small deviations from the target. Second, it may be interesting to explore other pulse sequences that will implement the factorization of single spin evolutions in Appendix A, which played a big role in our pulse sequence. The relevance of Appendix A, for whichever method one uses for preparing targets, is that it is exact, independent of modeling assumptions. Extensions to other Hamiltonians in spin systems is obviously of interest. Solid state NMR is a promising candidate for the kind of scaling required for quantum computation. Solid state spins have exceedingly long coherence lifetimes. For instance, Ref. [8] quotes figures of 10^4 s for some nuclear spins, while estimates as high as 10^{10} s have been reported in ideal situations (of course, spin-spin relaxation times are much lower). In principle, it should be possible to produce bounded amplitude pulse sequences to generate any unitary generator. This follows from the abstract controllability studies of quantum systems [39–44,27,45]. Factorizations analogous to Eq. (1.2) should also exist. The real hurdle is carrying out of the analog of the calculation in Appendix B. To appreciate this the reader should notice the prodigious effort involved for even two-spin systems in Appendix B.

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APPENDIX A: VERIFYING O1 AND O2 CONSTRUCTIVELY

The algorithm of Sec. IV is based on the following proposition.

Proposition 1. $\exp(-iLI_{1x})$, $L \in R$, can be factored explicitly as $\Pi_{k=1}^{3} \exp(-ia_k I_{1z}I_{2z} - ib_k I_{1x})$ with $a_k > 0, k=1,\ldots,3$ and $b_1 = 0 = b_3$ if $\cos(L) \neq 0$. If $\cos(L)=0$, four factors are required, with $b_1 = 0 = b_4$. This decomposition can be refined constructively to satisfy $|b_k/a_k| \leqslant D$, for any bound D. Similar statements hold for the exponentials of I_{2x}, I_{1y}, and I_{2y} with appropriately different a_k's and b_k.

Proof. Only the proof for I_{1x} will be given (the others being similar). The first key step is the following:

$$\exp(-iLI_{1x}) = \exp\left(-i\frac{7\pi}{4} I_{1z}I_{2z}\right) \exp(-iL\sigma_y \otimes \sigma_z) \times \exp\left(-i\frac{\pi}{4} I_{1z}I_{2z}\right). \tag{A1}$$

This factorization is possible since each matrix exponential involved is explicitly found. The motivation for it comes from the commutator structures of the free Hamiltonian and the coupling Hamiltonian in the rotating frame. Thus, for the preparation of $\exp(-iLI_{1x})$ free evolution may be used for the first and third factors in this equation. So it remains to prepare the middle factor. Now the matrix $(-ia_k I_{1z}I_{2z} - ib_k I_{1x})$ is, when squared, also $-I_4$ up to a positive constant. This facilitates the expression (which was also inspired by the commutator structure referred to before)

$$\exp(-iL\sigma_y \otimes \sigma_z) = \prod_{k=1}^{2} \exp(-ia_k I_{1z}I_{2z} - ib_k I_{1x}), \tag{A2}$$

where the a_k, b_k are determined by L as follows

The case $\cos L > 0$. Denote by $\lambda_i = \sqrt{a_i^2 + b_i^2}$, $i=1,2$. Choose $\lambda_1 = (3\pi/2)$; $\lambda_2 = (\pi/2)$. Then Eq. (A2) holds if one picks $a_1 = 3\pi/2, b_1 = 0, b_2 = -(\pi/2)\sin L, a_2 = (\pi/2)\cos L$.

The case $\cos L < 0$. Now pick $\lambda_1 = \pi/2 = \lambda_2$. Then Eq. (A2) holds if one sets $a_1 = -(\pi/2)\cos L$, $b_1 = -(\pi/2)\sin L$, $a_2 = \pi/2$, $b_2 = 0$.

The case $\cos L = 0$. Once again let $\lambda_1 = \pi/2 = \lambda_2$. If $\sin L = 1$, pick $a_1 = \lambda_1/\sqrt{2}, b_1 = -\lambda_1/\sqrt{2}, a_2 = \lambda_2/\sqrt{2}, b_2 = \lambda_2/\sqrt{2}$, if $\sin L = -1$, then pick $a_1 = \lambda_1/\sqrt{2}, b_1 = \lambda_1/\sqrt{2}$, $a_2 = \lambda_2/\sqrt{2}$, $b_2 = -\lambda_2/\sqrt{2}$.

Concatenating these pulses with the delay terms in Eq. (A1) gives the stated number of factors for condition O1. To meet condition O2, one needs to consider only the terms that are not delay terms in the factorization for condition O1, since only such terms have amplitudes which are not nil. If $\cos L \neq 0$, the $|b_k/a_k|$ of a nondelay term is precisely $|\tan L|$. So to meet condition O2, L has to be such that $\tan L \leqslant D$. This amounts to saying that L has to be within a prescribed deviation from 0. If L does not already meet this, factor $\exp(-iLI_{1x})$ as $\Pi_{k=1}^{r} \exp(-iL_k I_{1x})$ with each L_k being within the given deviation—this can clearly be always done. If $\cos L = 0$, first factor $\exp(-iLI_{1x})$ as $\exp[-i(L/2)I_{1x}]^2$ and proceed as in the $\cos L \neq 0$ cases.

APPENDIX B: DETERMINING THE "t_k" IN EQ. (1.2)

Both the hard pulse and soft pulse methods require that the t_k in Eq. (1.2) be known. To that end, note first that Eq. (1.2) stems from a Cartan decomposition of SU(4) in terms of $\mathrm{SU}(2) \otimes \mathrm{SU}(2)$. Expanding the $\mathrm{SU}(2) \otimes \mathrm{SU}(2)$ factors in this decomposition in their (x,y) Euler angles leads to the following factorization of any $S \in \mathrm{SU}(4)$:

$$S = e^{iD_1 I_{1x}} e^{iE_1 I_{1y}} e^{iF_1 I_{1x}} e^{iD_2 I_{2x}} e^{iE_2 I_{2y}} e^{iF_2 I_{2x}} e^{-i(\pi/4) I_{1y}} e^{-i(\pi/4) I_{2y}} e^{-i\theta_1 I_{1z} I_{2z}} e^{-i(7\pi/4) I_{1y}} e^{-i(7\pi/4) I_{2y}} e^{-i(7\pi/4) I_{1x}} e^{-i(7\pi/4) I_{2x}}$$
$$\times e^{-i\theta_2 I_{1z} I_{2z}} e^{-i(\pi/4) I_{1x}} e^{-i(\pi/4) I_{2x}} e^{-i\theta_3 I_{1z} I_{2z}} e^{iD_3 I_{1x}} e^{iE_3 I_{1y}} e^{iF_3 I_{1x}} e^{iD_2 I_{2x}} e^{iE_2 I_{2y}} e^{iF_2 I_{2x}}. \quad \text{(B1)}$$

This is in the form of Eq. (1.2) itself. However, the determination of the t_k from this directly is quite futile and may itself call for a functional quantum computer. The difficulty is that the 16 equations obtained by equating the entries of both sides lack any discernible structure.

To overcome this we will first factorize the given S in a Givens type decomposition, $S=\Pi_{i=1}^{6} S_i$ with each $S_i, i=1,\ldots,6$ determined by a single SU(2) matrix. Specifically, S_6 is a tensor product, viz., $S_6 = e^{i(\pi/4)\sigma_y} \otimes S(\alpha_6,\zeta_6,\mu_6)$, where $S(\alpha_6,\zeta_6,\mu_6)$ is the unique SU(2) matrix (written in Cayley-Klein coordinates—see Ref. [3] for notation) that takes the vector (d_1,d_2) to the vector $(\|(d_1,d_2)\|,0)$, with d_1,d_2 the first two entries of the fourth column of $S^{\dagger}$ (the inverse of S). *The matrix* $S(\alpha_6,\zeta_6,\mu_6)$ *can be explicitly determined*. The remaining $S_i, i=1,\ldots,5$ are, up to permutation, block matrices with blocks equal to I_2 and an *explicitly determined* SU(2) *matrix*, $S(\alpha_i,\zeta_i,\mu_i)$. The next step then is to determine the t_k for each of the $S_i, i=1,\ldots,6$, which is simpler than determining the t_k for S itself.

To execute this the remaining S_i will be described first. The unique SU(2) matrix, $S(\alpha_i,\zeta_i,\mu_i)$ in each $S_i, i=1,\ldots,5$ can be determined *explicitly* from S, almost verbatim, in the fashion described in Ref. [28]. Therefore, we will only describe the structure of the S_i with these SU(2) matrices left floating:

$$S_5 = \begin{pmatrix} I_2 & 0 \\ 0 & S(\alpha_5,\zeta_5,\mu_5) \end{pmatrix},$$

$$S_k = \begin{pmatrix} S(\alpha_k,\zeta_k,\mu_k) & 0 \\ 0 & I_2 \end{pmatrix} \quad \text{for } k=1,3,$$

$$S_4 = \begin{pmatrix} \cos\alpha_4 e^{i\zeta_4} & 0 & 0 & \sin\alpha_4 e^{i\mu_4} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \sin\alpha_4 e^{i(\pi-\mu_4)} & 0 & 0 & \cos\alpha_4 e^{-i\zeta_4} \end{pmatrix},$$

$$S_2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\alpha_2 e^{i\zeta_2} & \sin\alpha_2 & 0 \\ 0 & \sin\alpha_2 e^{i(\pi-\mu_2)} & \cos\alpha_2 e^{-i\zeta_2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Determining the t_k *for the* S_i. For brevity we will determine certain parameters related to the t_k instead of the t_k themselves. Specifically, the Cartan decomposition mentioned before shows that every $T \in \mathrm{SU}(4)$ can be factorized in the form

$$T = K_1 \otimes K_2 e^{-i(\pi/4) I_{1y}} e^{-i(\pi/4) I_{2y}} e^{-i\theta_1 I_{1z} I_{2z}} e^{-i(7\pi/4) I_{1y}} e^{-i(7\pi/4) I_{2y}} e^{-i(7\pi/4) I_{1x}} e^{-i(7\pi/4) I_{2x}} e^{-i\theta_2 I_{1z} I_{2z}} e^{-i(\pi/4) I_{1x}}$$
$$\times e^{-i(\pi/4) I_{2x}} e^{-i\theta_3 I_{1z} I_{2z}} K_3 \otimes K_4, \quad \text{(B2)}$$

with the $K_l, l=1,\ldots,4 \in \mathrm{SU}(2)$ and $\theta_k, k=1,\ldots,3 \in R$. Expanding the K_l in their (x,y) Euler angles (which is explicitly doable) leads to Eq. (B1). So we will specify the K_l and the following three parameters related to the θ_k:

$$P = \frac{\theta_1 - \theta_2}{4}, \quad Q = \frac{\theta_3}{4}, \quad R = \frac{\theta_1 + \theta_2}{4}.$$

S_6. There is nothing to do since S_6 is itself a tensor product.

S_1, S_3, S_5. These matrices have a similar structure and hence we will show the calculations for S_5 and the modifications needed for S_1 and S_3.

Pick $K_1 = I_2$ and choose $K_2 = S(\alpha,\zeta,\mu)$ with these parameters to be determined. Choose $P=R=0$, Q to be determined. Then $S_5 = V K_3 \otimes K_4$ with

$$V = \begin{pmatrix} S(\alpha,\zeta-Q,\mu+Q) & 0 \\ 0 & S(\alpha,\zeta+Q,\mu-Q) \end{pmatrix}.$$

Now pick $K_3 = I_2, K_4 = S(\alpha,\zeta-Q,\mu+Q)^{-1}$. This then yields the following underdetermined system for the unknowns (Q,α,ζ,μ) in terms of the knowns (α_5,ζ_5,μ_5):

$$\sqrt{\cos^2 Q + \cos^2\alpha \sin^2 Q} = \cos\alpha_5; -\cos 2\alpha \tan 2Q = \tan\zeta_5; -\cot(\mu+\zeta) = \tan\mu_5.$$

Note that the first two involve only two unknowns and so standard numerical procedures can be used for them. The one parameter degree of freedom comes from the third equation.

For S_1, S_3 the procedure is very similar, except that K_4 will be chosen to be the inverse of the bottom block of the matrix which results from multiplying all but the last six factors in Eq. (B2).

S_2, S_4. The procedure for S_2 will be shown and the modifications for S_4 will be given. For S_2, first set $P=Q=0, R=\alpha_2$. Choose $K_l = e^{i\eta_1 \sigma_z}, l=1,2,4$; $K_3 = I_2$ for some real parameters η_l satisfying a system of three equations,

$$\eta_1+\eta_2+\eta_3=0, \quad \eta_1-\eta_2+\eta_3=\zeta_2,$$

$$\eta_1-\eta_2-\eta_3=\mu_2+\frac{\pi}{2}.$$

Since $(\alpha_2, \zeta_2, \mu_2)$ is known beforehand, this completes the determination of the t_k for S_2. For S_4 the only modification needed in this procedure is $R=0, P=\alpha_4$.

[1] C. D. J. Fernandez and B. Mielnik, J. Math. Phys. **35**, 2083 (1994).
[2] V. Ramakrishna *et al.*, Phys. Rev. A **61**, 032106 (2000).
[3] V. Ramakrishna, K. L. Flores, H. Rabitz, and R. J. Ober, Phys. Rev. A **62**, 053409 (2000).
[4] G. Harel and V. Akulin, Phys. Rev. Lett. **82**, 1 (1999).
[5] N. Khaneja and S. J. Glasser, e-print quant-ph/0010100, see also Chem. Phys. **267**, 11 (2001) for a modified version.
[6] C. F. Delgado and B. Mielnik, J. Phys. A **31**, 309 (1998).
[7] C. K. Law and J. Eberly, Phys. Rev. Lett. **76**, 1055 (1996).
[8] D. P. DiVincenzo, Phys. Rev. A **51**, 1015 (1995).
[9] A. Barenco *et al.*, Phys. Rev. A **52**, 3457 (1995).
[10] R. J. Gilmore, *Lie Groups, Lie Algebras and Some of Their Physical Applications* (Wiley-Interscience, New York, 1974).
[11] T. Havel, S. Somaroo, C. Tseng, and D. Cory, e-print quant-ph/9812026.
[12] D. Cory *et al.*, e-print quant-ph/0004104.
[13] W. G. Harter, *Principles of Symmetry, Dynamics and Spectroscopy* (Wiley-Interscience, New York, 1993).
[14] A. D. Greentree, S. G. Schirmer, and A. I. Solomon, e-print quant-ph/0103118.
[15] R. Hermann, *Lie Groups for Physicists* (Benjamin, New York, 1966).
[16] R. T. Sang, G. S. Summy, B. T. V. Varcoe, W. R. MacGilvray, and M. C. Standage, Phys. Rev. A **63**, 023408 (2001).
[17] P. Shor, in *Proceedings of the 25th Annual ACM Symposium on Foundations of Computer Science*, edited by S. Goldwasser, (IEEE Computer Society, Los Alamitos, CA, 1994), p. 124.
[18] P. Olver, *Applications of Lie Groups to Differential Equations*, 2nd ed. (Springer, New York, 1995).
[19] S. Lloyd, Science **261**, 1569 (1993).
[20] P. DiVincenzo, G. Burkard, D. Loss, and E. Sukhorukov, in *Quantum Mesoscopic Phenomena and Mesoscopic Devices in Microelectronics*, Vol. 559 of *NATO Advanced Study Institute, Series B: Physics*, edited by I. Kulik and R. Ellialtioglu (Kluwer Academic, Dordrecht, 2000), also appears on the LANL website as e-print cond-mat/9911245.
[21] D. G. Cory, A. Fahmy, and T. F. Havel, Proc. Natl. Acad. Sci. U.S.A. **94**, 1634 (1997).
[22] N. A. Gershenfeld and I. L. Chuang, Science **275**, 350 (1997).
[23] F. Murnaghan, *The Unitary and Rotation Groups* (Spartan Books, New York, 1960).
[24] See, for instance, D. Gottesman, e-print quant-ph/0004072.
[25] R. J. Ober and E. S. Ward, J. Math. Chem. **20**, 47 (1996).
[26] R. J. Ober and E. S. Ward, J. Math. Chem. **22**, 1 (1997).
[27] R. J. Ober, V. Ramakrishna, and E. S. Ward, J. Math. Chem. **26**, 15 (1999).
[28] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).
[29] J. Cavanagh, W. J. Fairbrother, A. G. Palmer, and N. J. Skelton, *Protein NMR Spectroscopy: Principles and Practice* (Academic, New York, 1986).
[30] D. Sattinger and O. Weaver, *Lie Groups and Algebras With Applications to Physics, Geometry and Mechanics* (Springer, New York, 1986).
[31] R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford University Press, New York, 1987).
[32] C. P. Slichter, *Principles of Magnetic Resonance* (Academic, New York, 1987).
[33] R. S. Macomber, *A Complete Introduction to Modern NMR Spectroscopy* (Wiley-Interscience, New York, 1998).
[34] M. P. Silverman, *Probing the Atom* (Princeton University Press, Princeton, NJ, 1999).
[35] I. Kolmanovsky and N. H. McClamroch, IEEE Control Syst. Mag. **15**, 20 (1995).
[36] C. T. Kelley, *Iterative Methods for Linear and Nonlinear Equations* (SIAM, Philadelphia, 1995).
[37] R. Judson and H. Rabitz, Phys. Rev. Lett. **68**, 1500 (1992).
[38] A. C. Doherty *et al.*, Phys. Rev. A **62**, 012105 (2000).
[39] V. Jurdjevic and H. Sussmann, J. Diff. Eqns. **12**, 313 (1972).
[40] V. Ramakrishna *et al.*, Phys. Rev. A **51**, 960 (1995).
[41] See, for instance, (a) L. Viola, E. Knill, and S. Lloyd, Phys. Rev. Lett. **82**, 2417 (1999); (b) D. Bacon, D. A. Lidar, and K. B. Whaley, Phys. Rev. A **60**, 1944 (1999).
[42] G. Turinici, in *Proceedings of the 39th IEEE Conference on Decision and Control* (IEEE, New York, 2000), p. 1364.
[43] S. G. Schirmer and J. V. Leahy, e-print quant-ph/0010032.
[44] H. Fu, S. G. Schirmer, and A. I. Solomon, J. Phys. A **34**, 1679 (2001).
[45] V. Ramakrishna, e-print quant-ph/0107003.