On the role of reachability and observability in NMR experimentation

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It is shown that the system theoretic concepts of reachability and observability are relevant to the analysis of NMR experiments. Moreover, the sets of reachable states are examined and Lie theoretic criteria are given for the reachability of the system. The question is investigated how the set of reachable states depends on the class of input functions that are allowed. Both one-dimensional and multi-dimensional NMR experiments are considered.

1. Introduction

In the paper [9] the following system theoretic setup was introduced to describe one- and multi-dimensional NMR experiments (for a general introduction to NMR experimentation see, e.g., [1]). The basic relationship between *inputs* u to the system, i.e., the excitation signals or in particular the radio frequency pulses and the measured *output* y, i.e., the measured induced magnetization, is described by a bilinear system

$$\begin{aligned} \dot{x}(t) &= Ax(t) + u_1(t)N_1x(t) + u_2(t)N_2x(t) + b_1u_1(t) + b_2u_2(t), \\ y(t) &= cx(t), \end{aligned} \tag{R}$$

$x(t_0) = x_0$, where x is a *state vector*, A, N_1, N_2 are square matrices, b_1 and b_2 are column vectors and c is a row vector. The state space X is an n-dimensional Euclidean space, i.e., $X = \mathbb{C}^n$, for some $n \geqslant 1$. In the description of the system (R) we also assume that A has all its eigenvalues in the open left half-plane to ensure the stability of the system, i.e., the fact the NMR system relaxes to the equilibrium state $x = 0$. Moreover, we assume that N_1 and N_2 are skew-hermitian.

It is to be expected that assuming no relaxation is present significantly simplifies the analysis. In this special case it is often more convenient to work with the equivalent bilinear system [9]

$$\begin{aligned} \dot{z}(t) &= Az(t) + u_1(t)N_1z(t) + u_2(t)N_2z(t), \\ y(t) &= cz(t), \end{aligned} \tag{NR}$$

where $z(t) = x(t) + v_{\text{eq}}$, with v_{eq} the vector representation of the equilibrium density matrix. The assumption that relaxation can be neglected translates to the assumption that A is skew-hermitian. As in the description of the system (R), we also assume that N_1 and N_2 are skew-hermitian.

These bilinear systems (R) and (NR) were derived from the master equation which in the case of (R) includes a general relaxation super operator. In most of the standard approaches to NMR which use super operator formulations, relaxation is ignored, especially during the application of inputs. In our approach, however, a relaxation term is always included in the bilinear system (NR). In addition, note that in contrast to other approaches of describing NMR experimentation no assumptions such as the hard pulse approximation are made concerning the class of input functions that are considered. The classes of input functions that will be considered are discussed later.

One of the purposes of this paper is to illustrate that basic notions of systems and control theory such as the reachable states of the system (R) or (NR) are of fundamental importance in the description of NMR experiments. For the system (R), given an initial state $x_0 = 0$ at time t_0, a state x_1 is called reachable (from x_0) if there exists an input $u(t)$, $t \geqslant t_0$, such $u(t_1) = x_1$ for some $t_1 \geqslant t_0$. Note that what we call reachability here is often also referred to as controllability. For a one-dimensional pulse experiment it is shown in section 2 that the reachable states from 0 of the bilinear system (R) completely characterize all possible spectra. To characterize all possible spectra of a two-dimensional experiment of a particular system an associated bilinear system has to be introduced whose state space is the space of square matrices. All two-dimensional spectra are then determined by the set of reachable states of the bilinear system (R) and the associated system.

It should be pointed out that in an earlier paper [10] a similar characterization problem was considered. The set up in that paper was, however, different in that we also incorporated into the treatment what we called addition schemes that include phase cycling. The inclusion of these addition schemes had as a result that quite different mathematical techniques could be used to those being discussed here. In this paper we will mainly use techniques from differential geometry to analyze the problems at hand.

We then consider the problem of deciding whether or not all states in the state space or particular subsets such as a sphere of appropriate radius can be reached. Explicit criteria are given that make use of Lie theoretic methods that were developed in nonlinear systems and control theory [5,6].

We also address the question of how a chosen class of input functions determines the set of reachable states. Generally speaking, it is clear that the set of states that can be reached will depend on the set of inputs that can be applied to the system. Here we will examine this question for three classes of inputs. One of the classes is the set of piecewise constant inputs, another class is that of all admissible inputs, which includes piecewise constant ones. An input is called admissible if existence and uniqueness are guaranteed for the corresponding initial value problem. A third class contains infinitely often differentiable input functions. We examine the relationship between the sets of states that are reachable given the different classes of inputs. Moreover, we are going to give sufficient criteria when these various sets of reachable states coincide.

Recently Lie theoretic methods have been introduced to give precise answers to the question as to when a quantum control system is reachable [12]. In quantum computation such methods are also of relevance. For example, Lyod [8] discusses how generically any two gates are universal for quantum computation. In [11] it is shown that the notion of universality is the same as that of the reachability of an associated quantum control system. To the best of our knowledge the work in this paper is the first time that Lie theoretic methods have been systematically examined for their use in NMR spectroscopy.

We do not address here the problem of how to devise an input that will drive the current state of the NMR system to a desired new one. This so-called path planning problem requires completely different methods. One approach to the path planning problem is given in a series of publications (e.g., [2,13]). There unitary transformations are designed that are meant to move the system from a first state to a second state. The question that is, however, left unanswered is whether this transformation can indeed be realized by propagators, i.e., whether or not the second state is reachable (see [2] for a discussion of this topic). It might also be worthwhile noting that the approach taken there does not allow for the incorporation of relaxation.

In the final section we will show how the system theoretic notion of observability is an important concept in the description of NMR experiments.

2. Reachability and NMR experiments

As a means of introduction to this section we will first consider the case of one-dimensional experiments. It was shown in [9] that the free induction decay (FID) of a typical one-dimensional NMR pulse experiment is given by

$$s(t) = c\mathrm{e}^{(t-t_m)A}x_0, \quad t \geqslant t_m,$$

where x_0 is the state of the system at time t_m, the time when the measurements start. The obtained spectrum (ignoring sampling effects, etc.), i.e., the Fourier transform of the FID is then given by

$$G(\omega) := c(2\pi\mathrm{i}\omega I - A)^{-1}x_0, \quad \omega \in \mathbb{R}.$$

It is therefore clear that the only influence that an experimenter has on the outcome of the experiment is through the vector x_0. It should be emphasized that here we do not take into consideration phase cycling, etc.

We are therefore interested in the set of all states that the system can attain. But this is what is known as the reachability or controllability problem in linear and nonlinear system theory (see, e.g., [6]). Before proceeding we need to review the definition of reachability. In order to do this we need to be concerned with the class of input functions. In this paper three classes of input functions will be considered: (i) Admissible inputs: these inputs satisfy the conditions of Caratheodory's theorem for existence and uniqueness of solutions to the corresponding initial value problem. Let us denote this class by the symbol U_{ad}; (ii) Piecewise constant inputs: these are inputs which are concatenations of constant inputs. These will be denoted by U_{pc}; (iii) Smooth inputs: these are inputs which are C^{∞}, i.e., infinitely often continuously differentiable functions of time. These will be denoted by U_{∞}. Note that the latter two classes are contained in the first class and that the second is dense (see [3] for details of the topology) in the first. In section 3 consequences of the choice of the class of input functions will be further discussed.

Our definition of reachability will be based on the largest class of inputs for which a solution for the system can be obtained. A state x_2 of the system is said to be *reachable* from the state x_1 if there exists an admissible input u, i.e., $u \in U_{\mathrm{ad}}$ with

$$u(t) = \begin{pmatrix} u_1(t) \\ u_2(t) \end{pmatrix}, \quad t_1 \leqslant t \leqslant t_2,$$

such that if the system is in state x_1 at time t_1, the input u will drive the system to state x_2 for some time t_2. The set of all states which are reachable from the state x_1 by an admissibile input is denoted by $\mathcal{R}^{\mathrm{ad}}(x_1)$. Similarly, we denote by $\mathcal{R}^{\mathrm{pc}}(x_1)$ ($\mathcal{R}^{\infty}(x_1)$) the set of states that are reachable from x_1 by piecewise constant (smooth) inputs. We will often drop the superscript and write $\mathcal{R}(x_1)$ for $\mathcal{R}^{\mathrm{ad}}(x_1)$. In the study of NMR systems it is usually assumed (although not always satisfied in practice) that the system is in equilibrium, i.e., in state 0, when the experiment is started. We are therefore particularly interested in $\mathcal{R}(0)$. It should also be pointed out that the notions of reachable state and reachability are often also referred to as controllable state and controllability.

We can describe the set of all possible one-dimensional NMR spectra (within our framework and without phase cycling) by

$$\left\{c(2\pi\mathrm{i}\omega I - A)^{-1}x \mid x \in \mathcal{R}(0)\right\}.$$

In the above discussion we considered admissible input functions or excitation signals. In practice, excitation signals are in many situations radio frequency pulses. With a suitable coordinate transformation they can often be translated to constant inputs (see, e.g., [1,9]). This is, however, not central to our current study. We are interested in constant or piecewise constant inputs since they are of importance from a theoretical point of view since the bilinear system of equations has an analytical solution in the case of constant/piecewise constant inputs. In many situations there is no loss of generality in restricting the inputs to piecewise constant ones for the purposes of calculating the reachable sets. A precise statement appears in the next section.

If a constant input

$$\begin{pmatrix} u_1(t) \\ u_2(t) \end{pmatrix} = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

is applied to the bilinear system for $t_0 \geqslant t \geqslant t_0 + \Delta t$, it was shown in [9] that the solution to the bilinear system is given by

$$x(t) = \mathrm{e}^{\Delta t A_p} x(t_0) + \left(\mathrm{e}^{\Delta t A_p} - I\right) A_p^{-1} b_p$$

for $t_0 \geqslant t \geqslant t_0 + \Delta t$, where $A_p := A + u_1 N_1 + u_2 N_2$ and $b_p := b_1 u_1 + b_2 u_2$. Here, as in the remainder of the paper, we assume that A_p is invertible whenever we write A_p^{-1}.

If a system is in state $x(t_0)$ at time t_0 when the "pulse" input is started, the pulse will move the system to the state

$$x(t_0 + \Delta t) = P x(t_0) + z$$

at time $t_0 + \Delta t$, where $P = \mathrm{e}^{\Delta t A_p}$ and $z = (\mathrm{e}^{\Delta t A_p} - I) A_p^{-1} b_p$. Note that this representation also includes the case in which no pulse has been applied. In this case, $z = 0$ and $P = \mathrm{e}^{\Delta t A}$. This solution is more complicated than the "usual" unitary evolution since relaxation is specifically included here.

This "affine" structure implies that the effect of a sequence of k pulses is to move an initial state $x(t_0)$ to the state

$$T x(t_0) + e_1,$$

where $T = P_k P_{k-1} \cdots P_1$ and

$$e_1 = P_k P_{k-1} \cdots P_2 z_1 + P_k P_{k-1} \cdots P_3 z_2 + \cdots + P_k z_{k-1} + z_k,$$

with $P_j = \mathrm{e}^{\Delta_j t A_p}$ and $z_j = (\mathrm{e}^{\Delta_j t A_p} - I) A_p^{-1} b_p,\ j = 1, \ldots, k$.

The three blocks of pulses that often characterize a two-dimensional experiment are therefore determined by three matrices $T_1,\ T_2$ and T_3 and three vectors $e_1,\ e_2$ and e_3. Here the notation is such that the pair (T_1, e_1) describes the preparation block of pulses, (T_2, e_2) stands for any possible pulses in the middle of the evolution period and (T_3, e_3) describes the pulses during the mixing period. In this paper we will only consider the case where $T_2 = I$ and $e_2 = 0$, i.e., the case when no pulses are applied in the center of the evolution period. Moreover, we shall assume that before each scan the system is in equilibrium, i.e., $x_0 = 0$. Note that any pulse within a block of pulses during which no input signal is applied is formally also considered to be a pulse with zero level input. Hence [9] the free induction decay of such a system is given by

$$s(t_1, t_2) = c\mathrm{e}^{t_2 A} T_3 \mathrm{e}^{t_1 A} e_1 + c\mathrm{e}^{t_2 A} e_3, \quad t_1, t_2 \geqslant 0.$$

In the above expression as usual t_1 stands for the measured time and t_2 for the length of the evolution period. The spectrum of a two-dimensional experiment is given by

$$G(\omega_1, \omega_2) = c(2\pi \mathrm{i} \omega_1 I - A)^{-1} T_3 (2\pi \mathrm{i} \omega_2 I - A)^{-1} e_1 + \delta_0(\omega_1) e_3,$$

$\omega_1, \omega_2 \in \mathbb{R}$. The term $\delta_0(\omega_1)e_3$ arises from the term $c\mathrm{e}^{t_2 A}$ in the time domain data. Note that since it is independent of t_1, it in fact shows up as a constant in the t_1 time direction. In any practical situation this term would be removed before Fourier transforming the data, since it is common practice to remove a constant level in a signal before the Fourier transform is carried out. We can therefore assume that the spectrum is given by

$$G(\omega_1, \omega_2) = c(2\pi\mathrm{i}\omega_1 I - A)^{-1} T_3 (2\pi\mathrm{i}\omega_2 I - A)^{-1} e_1,$$

$\omega_1, \omega_2 \in \mathbb{R}$. As pointed out above, the matrix T_3 which determines the pattern of cross peaks in the spectrum is given by $T_3 = P_k \cdots P_1$ for some $k \geqslant 1$, where

$$P_j = \mathrm{e}^{(t_j - t_{j-1})(A + u_1^j N_1 + u_2^j N_2)}$$

for $0 < t_0 < t_1 < \cdots < t_k$, and $u_1^j, u_2^j \in \mathbb{R},\ j = 1, \ldots, k$. It is important to note that T_3 and e_1 are independent of each other. We denote by $\mathcal{RT}$ the set of all matrices T_3 as defined above.

A key observation for our derivation is that $\mathcal{RT}$ can be seen to be the set of reachable states from the identity matrix of the system

$$\dot{U} = AU + u_1 N_1 U + u_2 N_2 U, \qquad \text{(MR)}$$

driven by piecewise constant inputs. The state space here is the space of square matrices $\mathbb{C}^{n \times n}$, i.e., $U(t) \in \mathbb{C}^{n \times n}$ for $t \geqslant t_0$. The matrices A, N_1 and N_2 are defined as in the case of the system (R), i.e., A is a square matrix whose only constraint is the stability assumption that all its eigenvalues are in the open left half-plane. The matrices N_1 and N_2 are assumed to be skew-hermitian.

We will also investigate the situation in which we assume that relaxation is negligible. In this case we consider the system

$$\dot{U} = AU + u_1 N_1 U + u_2 N_2 U, \qquad \text{(NMR)}$$

in which again the matrices N_1 and N_2 are assumed to be skew-hermitian as in the system (MR). But in this case we now assume that the A matrix is skew-hermitian. In the next section we will analyze the systems (MR) and (NMR) in order to investigate the set $\mathcal{RT}$ of matrices T_3 which determine the cross-peak patterns of two-dimensional spectra.

3. Properties of the set of reachable states

In this section we are going to consider properties of the set of reachable states of the systems that were introduced in the previous sections. In fact, we will use results from the theory of nonlinear systems (see, e.g., [6]) to deduce the characterizations that are of importance to us.

In order to fix the terminology, we will first review some basic facts concerning nonlinear systems. This is then followed by a detailed discussion of the specific systems that are of importance here. The main feature of the states reachable from a given point x is that they belong to the orbit of the family of vector fields generated by the nonlinear system which passes through the point x. To describe what is meant by an orbit, we consider a general nonlinear system of the form

$$\dot{x} = f(x) + \sum_{i=1}^{m} u_i g_i(x),$$

where the state x is an element of a differentiable manifold M and f and g_i are smooth vector fields on M. Now consider the Lie algebra generated by f and the g_i. Call this Lie algebra L. Consider the subspace, at each point $z \in M$, of the tangent space at z given by $\Delta(z) = \{V(z);\ V \in L\}$. Then the collection of tangent spaces $\Delta(z),\ z \in M$, forms an involutive distribution. If f and g_i are real-analytic (which is certainly the case for the applications considered in this paper), then through each point x there passes a unique connected (immersed) submanifold $O(x)$ which integrates this involutive distribution, i.e., for every $y \in O(x)$, the tangent space at y is $\Delta(y)$. This submanifold $O(x)$ is called either the maximal integral manifold through x or the slice through x or the orbit of the nonlinear system through x. We shall adopt this last terminology.

Before going on to an analysis of the sets of reachable states for the systems that are considered in this paper we will quote results that explain the role of the different classes of inputs on the set of reachable states. Since piecewise constant controls are attractive from many standpoints (especially for the application at hand) and these are dense in U_{ad}, a reasonable question is whether every state that is reachable from x via an admissible control is also reachable from x via a piecewise constant or smooth control. It turns out that this is nearly so (see [3,4,6]). Of course, if it took T units of time to reach a state y from x via a certain admissible control, it is not necessary that it also only takes exactly T units of time to reach y from x via a piecewise constant or smooth control.

Theorem 1. Consider the systems (R), (NR), (MR) and (MNR).

1. Assume that x is in the interior (relative to the topology of $O(x)$) of the reachable set $\mathcal{R}^{\mathrm{ad}}(x)$ due to admissible inputs. Then
   (a) $\mathcal{R}^{\mathrm{ad}}(x)$ is open in $O(x)$;
   (b) every state which is in $\mathcal{R}^{\mathrm{ad}}(x)$ is also reachable from x via a piecewise constant input, i.e.,
   $$\mathcal{R}^{\mathrm{ad}}(x) = \mathcal{R}^{\mathrm{pc}}(x).$$
2. Let y be reachable by piecewise constant inputs from x and assume that y is in the interior of the set of reachable states from x, i.e., assume that $y \in \mathrm{int}(\mathcal{R}^{\mathrm{pc}}(x))$, then y can also be reached from x by smooth inputs, i.e., $y \in \mathcal{R}^{\infty}(x)$.

Proof. Note that the systems (R), (NR), (MR) and (NMR) are real-analytic.

(1) See corollary 4.4 in [3].

(2) See [4] and [6]. □

In our effort to obtain properties of the state of reachable states we are first going to consider the most general system description, i.e., the bilinear system (R) which describes the NMR dynamics including relaxation. The first main fact about reachable sets is part 2 of the following theorem (see, e.g., [6]) which shows that the set of reachable states from a point x is not merely a subset of the orbit through x but a "large" subset, since $\mathcal{R}(x)$ contains a non-empty open subset of the orbit.

Theorem 2. Consider the system (R). Let $x \in \mathbb{C}^n$, then:

1. $\mathcal{R}^{\mathrm{ad}}(x)$ (and, hence, $\mathcal{R}^{\mathrm{pc}}(x)$ and $\mathcal{R}^{\infty}(x)$) is contained in the immersed submanifold $O(x)$ of $\mathbb{C}^n$. Here $O(x)$ is the orbit of the system through x.
2. There exists a non-empty open subset $\mathcal{A}$ of $O(x)$ (in the topology of $O(x)$) which is contained in $\mathcal{R}^{\mathrm{pc}}(x)$, i.e., $\mathcal{A} \subseteq \mathcal{R}^{\mathrm{pc}}(x) \subseteq \mathcal{R}^{\mathrm{ad}}(x)$.
3. $\mathcal{R}^{\mathrm{pc}}(x) = \mathcal{R}^{\mathrm{ad}}(x) = \mathcal{R}^{\infty}(x) = \mathbb{C}^n$ if $\dim(\Delta(x)) = 2n$, where Δ is the involutive distribution generated by Az, $N_1 z$ and $N_2 z$ for $z \in \mathbb{C}^n$.

Proof. (1), (2) See [6].

(3) By assumption A is invertible. Therefore $\mathcal{R}^{\mathrm{ad}}(x) = \mathbb{C}^n$ by theorem 11 in [6, p. 184]. Hence $\mathcal{R}^{\mathrm{ad}}(x)$ is open and, hence, theorem 1 implies the equality of the reachable sets with different input spaces. □

From physical considerations it is unlikely that the conditions of part 3 of the theorem are satisfied in a typical situation, since one would expect the set of reachable states to be bounded. It is not known (to us) whether the appropriate statement is still true in the event that the distribution has lower dimension, i.e., whether the reachable set through x_0 equals the orbit through x_0.

Significantly more can be said for the system (NR), i.e., the bilinear system which describes the NMR dynamics assuming no relaxation is present.

Theorem 3. Consider the system (NR). Let $x \in \mathbb{C}^n$, $x \neq 0$. Then:

1. $O(x) = \mathcal{R}(x) = \mathcal{R}^{\mathrm{ad}}(x) = \mathcal{R}^{\mathrm{pc}}(x) = \mathcal{R}^{\infty}(x)$, i.e., the set of states reachable from x equals the orbit $O(x)$ of the system (NR) through x. In particular, $\mathcal{R}(x)$ has the structure of an immersed submanifold of $\mathbb{C}^n$.
2. Let $S_{\|x\|}$ be the sphere in $\mathbb{C}^n$ of radius $\|x\|$. Let Δ be the involutive distribution generated by Az, $N_1 z$ and $N_2 z$, $z \in \mathbb{C}^n$. If $\dim\Delta(x) = n-1$, then $\mathcal{R}(x) = O(x) = S_{\|x\|}$.

Proof. (1) Since A, N_1 and N_2 are skew-hermitian this result follows from the discussion on the controllability of nonlinear systems on Lie groups in [6] which guarantees that the set of reachable states from x equals the orbit through x. The equality of the various sets of reachable states then follow from theorem 1.

(2) The assumptions on the system matrices imply that $O(x)$ in part 1 is a subset of $S_{\|x\|}$. The additional assumption on the dimension of $\Delta(x)$ implies that $O(x)$ equals $S_{\|x\|}$. □

Here, as in other parts of this paper, we also formulate the results for initial states which are not constrained to have unit length. This is of course no restriction and may be useful since in some parts of the NMR literature it is not assumed that the density matrix is normalised.

We now address the problem of characterizing the set $\mathcal{RT}$ of the matrices T_3 which determine the cross peak patterns in a two-dimensional experiment. As pointed out in section 2, this problem is related to the problem of the characterization of the set of reachable states of the system (MR).

Theorem 4. Consider the system (MR). Then:

1. $\mathcal{RT} = \mathcal{R}^{\text{pc}}(I)$, where $\mathcal{R}^{\text{pc}}(I)$ is the set of reachable states with piecewise constant inputs of the system (MR) from the identity matrix I.
2. $\mathcal{R}^{\text{ad}}(I)$ and, hence, $\mathcal{RT} = \mathcal{R}^{\text{pc}}(I)$ is contained in the immersed submanifold $O(I)$ of $\mathbb{C}^{n\times n}$. Here $O(I)$ is the orbit of the system (MR) through the identity matrix I.
3. The interior int($\mathcal{RT}$) of $\mathcal{RT}$ is non-empty. If $I \in$ int($\mathcal{RT}$), then
$$\mathcal{RT} = \mathcal{R}^{\text{ad}}(I) = \mathcal{R}^{\text{pc}}(I) = \mathcal{R}^{\infty}(I).$$
4. There exists an open subset $\mathcal{A}$ of $O(I)$ (open in the orbit topology of $O(I)$) which is contained in $\mathcal{RT}$.

Proof. (1) See section 2.

(2)–(4) These statements and proofs are analogous to those in theorems 2 and 1. □

As before, if it is assumed that relaxation can be neglected, stronger results can be obtained also in the characterization of the set $\mathcal{RT}$. Denote by $U(n)$ the subset of $\mathbb{C}^{n\times n}$ of $n \times n$ unitary matrices. It is easily verified that if the initial condition of this system is a unitary matrix then the state of the system will evolve in $U(n)$. The analysis of the system (MNR) is very similar to the analysis that was carried out in [12].

Theorem 5. Consider the system (MNR). Then:

1.
$$\mathcal{RT} = \mathcal{R}^{\text{ad}}(I) = \mathcal{R}^{\text{pc}}(I) = \mathcal{R}^{\infty}(I) = O(I).$$

In particular, $\mathcal{RT}$ has the structure of an immersed submanifold of $U(n)$.

2. Suppose that the unique connected Lie group G having the Lie algebra L generated by the matrices A, N_1 and N_2 is compact; then

$$\mathcal{RT} = \mathcal{R}(I) = O(I) = G.$$

In particular, if the dimension of L is n^2, then

$$\mathcal{RT} = \mathcal{R}(I) = O(I) = G = U(n).$$

Proof. (1) Since A, N_1 and N_2 are skew-hermitian, this follows from the discussion on the controllability of nonlinear systems on Lie groups in [6] in conjunction with theorem 1.

(2) The first part is the content of a theorem in [7]. The second part follows from the fact that the dimension of the vector space of $n \times n$ (complex) skew-hermitian matrices is n^2. Hence, dimensional arguments imply that the Lie algebra generated by the matrices A, N_1 and N_2 equals the Lie algebra of $n \times n$ skew-hermitian matrices. Therefore G has to be $U(n)$. □

Recall that it is possible to check whether the Lie group G is compact by checking whether the Killing form of the Lie algebra L is negative definite. Alternatively, if one knew in advance that G is closed, then G would be automatically compact.

Corollary 1. Consider system (NR) and the corresponding system (MNR). Let $x \in \mathbb{C}^n$, $x \neq 0$. Let G be as in the theorem. If $\mathcal{RT} = G$ and G acts transitively on $S_{\|x\|}$, in particular, if $G = U(n)$, then the set of reachable states $\mathcal{R}(x)$ of the system (NR) from x is $S_{\|x\|}$.

The proof of this corollary is based on an important observation, which gives a second interpretation of the system (MNR). Explaining this point is not only of relevance for an understanding of the proof of the corollary but may also lead to a further clarification of the nature of the set $\mathcal{RT}$ of the matrices T_3 that determine the cross-peak patterns of a two-dimensional NMR spectrum. In fact, the system (MNR) also describes the evolution of the infinitesimal generator corresponding to the system (NR) that describes the dynamics of the NMR system. If the reachable set $\mathcal{R}_{\mathrm{MNR}}(I)$ of the system (MNR) from the identity matrix equals some group G, then the reachable set $\mathcal{R}_{\mathrm{NR}}(x_0)$ of the system (NR) from the state x_0 in the sphere S equals the orbit of the group G through x_0, i.e., $\mathcal{R}_{\mathrm{NR}}(x_0) = \{gx_0 \mid g \in G\}$. Of course, except for some special cases a simple description of the orbit is not possible. Nevertheless, this represents an improvement over the general situation. In the event that the group G turns out to be a group acting transitively on S, then we can assert that for any $x_0 \in S$ the reachable set from x_0 is all of S, i.e., $\mathcal{R}_{\mathrm{NR}}(x_0) = S$. A complete list of the classical matrix Lie groups which act transitively on the sphere is known and of course includes $U(n)$ and $SU(n)$.

4. Observability of NMR systems

Note that in general the pair (A, c) is not observable, i.e., there exist nonzero vectors x such that $c\mathrm{e}^{tA}x = 0$ for $t \geqslant 0$. Lack of observability implies that different states in $\mathcal{R}(0)$ can give rise to the same spectrum. Let ker(O) be the kernel of the observability map, where for $x \in X$, $Ox := (c\mathrm{e}^{tA}x)_{t \geqslant 0}$, i.e., ker($O$) is the subspace of X of all unobservable states. Denote by P_O the orthogonal projection of X onto the orthogonal complement of ker(O) in X. Then for each $x \in X$ and, in particular, for each $x \in \mathcal{R}(0)$,

$$c(2\pi\mathrm{i}\omega I - A)^{-1}x = c(2\pi\mathrm{i}\omega I - A)^{-1}P_O x.$$

In particular, we therefore have that the one-dimensional spectra are parametrized by $P_O\mathcal{R}(0)$.

In the case of two-dimensional systems, the experimenter can influence the resulting spectrum by "choosing" T_3 and e_1. The set of attainable spectra in the setup considered here is therefore given by

$$\left\{c(2\pi\mathrm{i}\omega_1 I - A)^{-1}T_3(2\pi\mathrm{i}\omega_2 I - A)^{-1}e_1 \mid T_3 \in \mathcal{RT}(0),\ e_1 \in \mathcal{R}(0)\right\}.$$

But as in the one-dimensional case we need to consider the possibility that the system pair (A, c) is not observable. As above, let P_O be the orthogonal projection onto the orthogonal complement of the unobservable subspace of (A, c).

Dually, we need to consider the possibility that the pair (A, e_1) is not reachable. In fact, the experimenter may want to design e_1 such that (A_1, e_1) is not reachable in order to suppress parts of the spectrum of A. We need to recall further system theoretic notions. We use definitions that are suitable for our context. A vector x is said to be *orthogonal to the reachable subspace of the pair* (A, e_1) if $x(sI - A)^{-1}e_1 = 0$ for all $s \in \mathbb{C}$. Let P_{U,e_1} be the orthogonal projection of $\mathbb{C}^n$ onto the orthogonal complement of the reachable subspace of (A, e_1) and let $P_{e_1}| = I - P_{U,e_1}$. Then the set of all possible spectra is given by

$$\left\{c(2\pi\mathrm{i}\omega_1 I - A)^{-1}P_O T_3 P_{e_1}(2\pi\mathrm{i}\omega_2 I - A)^{-1}e_1 \mid T_3 \in \mathcal{RT},\ e_1 \in \mathcal{R}(0)\right\}.$$

Hence two-dimensional spectra are parametrized by $P_O T_3 P_{e_1}$ for $T_3 \in \mathcal{RT}$ and $e_1 \in \mathcal{R}(0)$.

We should point out that higher-dimensional spectra can be characterized in an analogous fashion.

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