Journal of Mathematical Chemistry 22 (1997) 1–10

On the class of attainable multidimensional NMR spectra

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Received 6 May 1997

It is shown that a large class of two-dimensional NMR spectra is characterized by a matrix algebra and an invariant subspace. Both the matrix algebra and the invariant subspace are determined by the system matrices of the bilinear system which describes the NMR experiments.

1. Introduction

In an earlier paper ([4]) the following system theoretic setup was introduced to describe (multidimensional) NMR experiments. (For a general introduction to NMR experimentation see, e.g., [1,2].) The basic relationship between *inputs* u_1 and u_2 to the system, i.e., the excitation signals or, in particular, the radiofrequency pulses, and the measured *output* y, i.e., the measured induced magnetization, is given described by a bilinear system,

$$\begin{aligned}\dot{x}(t) &= Ax(t) + u_1(t)N_1x(t) + u_2(t)N_2x(t) + b_1u_1(t) + b_2u_2(t), \quad x(t_0) = x_0,\\ y(t) &= cx(t),\end{aligned}$$

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.

A key step in analyzing NMR experiments is the analysis of the effects of a typical input, i.e., a pulse. In [4] it was shown that, for example, in the case of a weakly coupled two spin system, the effects of a radiofrequency input can be described after a suitable state-space transformation by a bilinear system with constant input. More precisely, an NMR system is usually such that if the inputs are given by

$$u_1(t) = B_1\cos\bigl(\omega_p(t - t_0 + \Delta t)\bigr), \qquad u_2(t) = B_1\sin\bigl(\omega_p(t - t_0 + \Delta t)\bigr), \quad t \geqslant t_0,$$

the input–output relationship can be described by a bilinear system of the form

$$\begin{aligned}\dot{x}_r(t) &= A_r(\omega_p)x_r(t) + N_r(\omega_p, \Delta t)x_r(t) + b_r(\omega_p, \Delta t)u_r, \quad x_r(t_0) = x_0,\\ y(t) &= \mathrm{e}^{\mathrm{i}(t-t_0)\omega_p}cx_r(t),\end{aligned}$$

with $u_r = B_1$. The important fact is that the input $B_1 = u_r$ is constant. If $A_p(\omega_p, \Delta t, B_1) := A_r(\omega_p, \Delta t) + u_r N_r(\omega_p, \Delta t)$ is invertible, this equation can be solved with the solution given by

$$x_r(t) = \mathrm{e}^{(t-t_0)A_p(\omega_p,\Delta t,B_1)} x_0 + \left(\mathrm{e}^{(t-t_0)A_p(\omega_p,\Delta t,B_1)} - I\right) A_p(\omega_p, \Delta t, B_1)^{-1} b_r(\omega_p, \Delta t) B_1, \quad t \geqslant t_0.$$

For the remainder of the paper we will assume that $A_p(\omega, \Delta t, B_1)$ is invertible whenever we write $(A_p(\omega, \Delta t, B_1))^{-1}$. If a system is in state x_0 at time t_0 just before a pulse is applied, the pulse will move the system to the state

$$x_1 = P_1 x_0 + z_1$$

at time $T > t_0$, where

$$P_1 := P_1(T, t_0, \omega_{p,1}, \Delta_1 t, B_1) := \mathrm{e}^{(T-t_0)A_p(\omega_{p,1},\Delta_1 t,B_1)},$$
$$z_1 := \left(\mathrm{e}^{(T-t_0)A_p(\omega_{p,1},\Delta_1 t,B_1)} - I\right) A_p(\omega_{p,1}, \Delta_1 t, B_1)^{-1} b_r(\omega_{p,1}, \Delta_1 t) B_1.$$

Note that this representation also includes the case in which no pulse has been applied. In this case $z_1 = 0$ and $P_1 = \mathrm{e}^{(T-t_0)A_r}$. Hence the effects of a sequence of k pulses on an initial state is given by

$$x_k = P_k\left(P_{k-1}\left(\cdots\left(P_2(P_1 x_0 + z_1) + z_2\right)\cdots\right) + z_{k-1}\right) + z_k$$
$$= P_k P_{k-1} \cdots P_1 x_0 + P_k P_{k-1} \cdots P_2 z_1 + P_k P_{k-1} \cdots P_3 z_2 + \cdots + P_k z_{k-1} + z_k.$$

Therefore we can write

$$x_k := T_1 x_0 + e_1,$$

where

$$T_1 := P_k P_{k-1} \cdots P_1$$

and

$$e_1 := P_k P_{k-1} \cdots P_1 x_0 + P_k P_{k-1} \cdots P_2 z_1 + P_k P_{k-1} \cdots P_3 z_2 + \cdots + P_k z_{k-1} + z_k.$$

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) represents any possible pulses in the middle of the evolution period, and (T_3, e_3) describes the pulses during the mixing period. Note that any pulse within a block of pulses during which no input signal is applied is also considered to be a pulse, i.e., a pulse with zero level input. Hence ([4]) the free induction decay of such a system is given by

$$s(t_1, t_2) = c\mathrm{e}^{t_2 A} T_3 \mathrm{e}^{(t_1/2)A} T_2 \mathrm{e}^{(t_1/2)A} T_1 x_0 + c\mathrm{e}^{t_2 A} T_3 \mathrm{e}^{(t_1/2)A} T_2 \mathrm{e}^{(t_1/2)A} e_1$$
$$+ c\mathrm{e}^{t_2 A} T_3 \mathrm{e}^{(t_1/2)A} e_2 + c\mathrm{e}^{t_2 A} e_3, \quad t_1, t_2 \geqslant 0.$$

As usual, in the above expression 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 then given by

$$G(\omega_1,\omega_2)=c(2\pi\mathrm{i}\omega_1 I-A)^{-1}\left[T_3P(\omega_1)(T_1x_0+e_1)+T_3\left(2\pi\mathrm{i}\omega_1 I-\tfrac{1}{2}A\right)^{-1}e_2+\delta_0(\omega_1)e_3\right],$$

where

$$P(\omega_1):=\int_0^\infty \mathrm{e}^{(t_1/2)A}T_2\mathrm{e}^{(t_1/2)A}\mathrm{e}^{-2\pi\mathrm{i}\omega_1 t_1}\,\mathrm{d}t_1,\quad \omega_1\in\Re,$$

and $\delta_0(\omega_1)$ stands for the delta function with mass concentrated at 0.

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., $x_0=0$. Then the spectrum is given by

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

The term $\delta_0(\omega_1)e_3$ arises from the term $c\mathrm{e}^{t_2A}$ in the time domain data. Note that since it is independent of t_1, it is a constant in the t_1 time direction. In the analysis of experimental data this term would be removed before applying the Fourier transform. We can therefore assume that the spectrum is given by

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

Thus far, we have not taken into consideration techniques such as phase-cycling (see, e.g., [1,2]). Phase-cycling can be seen to be a special case of adding together free induction decays corresponding to different experiments. We will therefore study experiments which are obtained by adding free induction decays together with the same evolution period t_2 and for which only one of the blocks of pulses is changed. Using such *addition schemes* we therefore obtain spectra of the form

$$G(\omega_1,\omega_2)=c(2\pi\mathrm{i}\omega_1 I-A)^{-1}\left(\sum_{j=1}^{k_3}\lambda_jT_{3,j}\right)(2\pi\mathrm{i}\omega_2 I-A)^{-1}\left(\sum_{l=1}^{k_1}\mu_l e_{1,l}\right),$$
$$\omega_1,\omega_2\in\Re.$$

Here $T_{3,1},T_{3,2},\dots,T_{3,k_3}$ determine k_3 different pulse blocks in the mixing period, and $\lambda_1,\lambda_2,\dots,\lambda_{k_3}$ are complex constants. The k_1 vectors $e_{1,1},e_{1,2},\dots,e_{1,k_1}$ are determined by the k_1 different preparation pulse blocks, and $\mu_1,\dots,\mu_{k_1}$ are complex constants.

In this paper we analyze the class of spectra that can be obtained by applying different pulse sequences and addition schemes. It is clear that such an analysis of the mixing period necessitates a careful study of all the possible combinations $\sum_{j=1}^{k_3}\lambda_jT_{3,j}$. This is the topic of section 2. In section 3 we will examine the term $\sum_{l=1}^{k_1}\mu_le_{1,l}$, which characterizes the preparation period of the experiment.

We will only study 2-D experiments in this paper. However, the extension of the methods presented here to higher dimensional experiments is obvious.

2. The mixing period and matrix algebras

In this section we are going to study the set $\mathcal{T}$ given by all possible matrix expressions of the form $\sum_{j=1}^{k_3} \lambda_j T_{3,j}$. As pointed out in section 1 the mixing period of a two-dimensional NMR experiment is characterized by such an expression. We aim to derive representations of this vector space which are more amenable to computations and analysis than this general description. In fact, we are going to show that this set is a matrix algebra and we are going to determine generators of it.

It follows from the discussion in section 1 that each matrix T_3 has a representation of the form

$$T_3 = \prod_{j=1}^{k} \mathrm{e}^{(t_j - t_{j-1})(A_r(\omega_{p,j}) + B_{1,j} N_r(\omega_{p,j}, \Delta_j t))},$$

for $0 < t_0 < t_1 < \cdots < t_k$. Note that this representation immediately implies that the matrix product of two elements in $\mathcal{T}$ is again in $\mathcal{T}$, i.e., that $\mathcal{T}$ forms an algebra. (See, e.g., [3] for the definition of an algebra.)

We now show that for each $\omega \geqslant 0$, $B_1 \geqslant 0$, $\Delta t \geqslant 0$, $A_r(\omega_p) + B_1 N_r(\omega, \Delta t) \in \mathcal{T}$. To see this first note that $\mathcal{T}$ is closed since it is a finite dimensional vector space. As $\mathrm{e}^{t(A_r(\omega_p) + B_1 N_r(\omega, \Delta t))} \in \mathcal{T}$ for each $t \geqslant 0$ we also have that the derivative $(A_r(\omega_p) + B_1 N_r(\omega, \Delta t))\mathrm{e}^{t(A_r(\omega_p) + B_1 N_r(\omega, \Delta t))} \in \mathcal{T}$ for $t \geqslant 0$. Therefore the derivative evaluated at 0, i.e., $(A_r(\omega_p) + B_1 N_r(\omega, \Delta t))$ is also in $\mathcal{T}$. Since $(A_r(\omega_p) + B_1 N_r(\omega, \Delta t)) \in \mathcal{T}$ for all $B_1 \geqslant 0$ we also have that $A_r(\omega_p) \in \mathcal{T}$. Since $\mathcal{T}$ is a vector space this also implies that $N_r(\omega_p, \Delta t) \in \mathcal{T}$.

We now show the following theorem.

Theorem 1. (1) $\mathcal{T}$ is a matrix algebra (over the complex field) which is generated by the matrices $A_r(\omega_p)$, $N_r(\omega_p, \Delta t)$, $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, i.e., each element in $\mathcal{T}$ can be obtained by forming linear combinations of arbitrary products of these matrices.

(2) If $A_r(\omega_p) = A_r^1 + \omega_p A_r^2$ and if $N_r(\omega_p, \Delta t) = \mathrm{e}^{\mathrm{i}\omega_p \Delta t} N_r^1 + \mathrm{e}^{-\mathrm{i}\omega_p \Delta t} N_r^2$, then $\mathcal{T}$ is generated by A_r^1, A_r^2, N_r^1 and N_r^2. Here A_r^1, A_r^2, N_r^1 and N_r^2 are assumed to be constant matrices independent of ω_p and Δt.

Proof. (1) As was argued above $\mathcal{T}$ is an algebra. It follows from the remarks preceding the statement of the theorem that the algebra $\mathcal{T}'$ generated by $A_r(\omega_p)$, $N_r(\omega_p, \Delta t)$, $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, is a subalgebra of $\mathcal{T}$.

To show the other inclusion, i.e., that $\mathcal{T} \subseteq \mathcal{T}'$ recall that by the Cayley–Hamilton theorem each matrix exponential can be written as the linear combination of a finite number of powers of the matrix. This implies that each element in $\mathcal{T}$ can be generated by the matrices $A_r(\omega_p)$, $N_r(\omega_p, \Delta t)$, $\omega_p \geqslant 0$, $\Delta t \geqslant 0$.

(2) If $A_r(\omega_p) = A_r^1 + \omega_p A_r^2$, $\omega_p \geqslant 0$, then clearly A_r^1 and A_r^2 are in $\mathcal{T}$. If $N_r(\omega_p, \Delta t) = \mathrm{e}^{\mathrm{i}\omega_p \Delta t} N_r^1 + \mathrm{e}^{-\mathrm{i}\omega_p \Delta t} N_r^2$, then

$$N_r(\omega_p, \Delta t) = \cos(\omega_p \Delta t)\big(N_r^1 + N_r^2\big) + \mathrm{i}\sin(\omega_p \Delta t)\big(N_r^1 - N_r^2\big), \quad \omega_p \geqslant 0.$$

From this it follows immediately that $N_r^1 + N_r^2$ and $N_r^1 - N_r^2$ are in $\mathcal{T}$. Hence, N_r^1 and N_r^2 are also in $\mathcal{T}$.

Given A_r^1, A_r^2, N_r^1 and N_r^2, the generating matrices of (1) can be obtained in the obvious way. Hence, A_r^1, A_r^2, N_r^1 and N_r^2 indeed generated $\mathcal{T}$. □

The special situation which is treated in part (2) of the theorem is encountered in NMR, for example, for the case of two weakly coupled spins (see [4]). In this case it is also straightforward to obtain spanning vectors for the vector space $\mathcal{T}$, which is useful for computational purposes.

Corollary 1. With the assumption and notation of part (2) of the theorem let

$$M_0 := \left[A_r^1 \ A_r^2 \ N_r^1 \ N_r^2\right]$$

and recursively define M_k by setting

$$M_k := \left[A_r^1 M_{k-1} \ A_r^2 M_{k-1} \ N_r^1 M_{k-1} \ N_r^2 M_{k-1}\right], \quad k = 1, 2, \ldots.$$

Then the block entries of M_k, $k = 1, 2, \ldots,$ span $\mathcal{T}$.

As discussed in section 1 the spectrum of a 2-D experiment is given by

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

where we have set $b := e_1$. If we assume that A is diagonal with eigenvalues $a_1, a_2, \ldots, a_n$, then the spectrum can be written as

$$G(\omega_1, \omega_2) = \sum_{j=1}^{n} \sum_{l=1}^{n} \frac{c_j}{2\pi \mathrm{i}\omega_1 - a_j} t_{jl} \frac{b_l}{2\pi \mathrm{i}\omega_2 - a_l},$$

where $c := c(c_1, c_2, \ldots, c_n)$, $b := (b_1, b_2, \ldots, b_n)^{\mathrm{T}}$, $T_3 := (t_{ij})_{1 \leqslant i,j \leqslant n}$.

Redundancies occur in this description of the spectrum if A has eigenvalues with multiplicities. Assume that $a_1^r, a_2^r, \ldots, a_k^r$ are the eigenvalues of A with all possible multiplicities removed. To remove the redundancies in the description of the spectrum, we construct the $k \times n$ matrix Q, whose entries are either zeros or ones. The first row of Q is constructed as follows. In the first entry enter 1 corresponding to the eigenvalue a_1. Then enter a zero in the second entry if $a_2 \neq a_1$, otherwise enter 1. Similarly, in the jth entry enter 0 if $a_k \neq a_1$ and 1 if $a_k = a_1$. The rth row, $1 < r \leqslant k$, of Q is constructed as follows: Consider the first eigenvalue a_l in the list $a_1, a_2, \ldots, a + l, \ldots, a_n$ which is not equal to any of the eigenvalues $a_1^r, a_2^r, \ldots, a_{k-1}^r$ and enter 1 at the corresponding entry of the row, i.e., its lth entry. Enter 0 in the first $l-1$ entries of this row. Then enter a zero in the $(l+s)$th entry of the row if $a_{l+s} \neq a_l$ and 1 otherwise, for $s = 1, \ldots, n-k$.

Now let

$$Qb := b^1 := \begin{pmatrix} b_1^1 \\ b_2^1 \\ \vdots \\ b_k^1 \end{pmatrix},$$

$$cQ^* := c^1 := \begin{pmatrix} c_1^1 & c_2^1 & \dots & c_k^1 \end{pmatrix},$$
$$QT_3Q^* := T_3^1 := \left(t_{jk}^1\right)_{1 \leqslant j,l \leqslant k}.$$

With this notation we then have a 'reduced' representation of the spectrum given by

$$G(\omega_1, \omega_2) = \sum_{j=1}^{k} \sum_{l=1}^{k} \frac{c_j^1}{2\pi \mathrm{i}\omega_1 - a_j^r} t_{jl}^1 \frac{b_l^1}{2\pi \mathrm{i}\omega_2 - a_l^r}.$$

Further redundancies can occur in the description of the spectrum if b^1 or c^1 have zero entries. If c_j^1, the jth entry of c^1, is zero then the pole $1/(2\pi \mathrm{i}\omega_1 - a_j^r)$ will not appear in the spectrum. Similarly, if the lth entry of b^1 is zero, then the pole $1/(2\pi \mathrm{i}\omega_2 - a_l^r)$ will not appear in the spectrum. Moreover, if c_j^1 is zero then the jth row of T_3^1 is irrelevant for the appearance of the spectrum and similarly, if b_l^1 is zero then the lth column of T_3^1 is irrelevant for the appearance of the spectrum. To study this effect on the algebra $\mathcal{T}$ let $\mathcal{C}$ be the 'projection matrix' that is obtained from the $k \times k$ identity matrix by deleting the jth row if the $c_j^1 = 0$, for some $j \in \{1, \dots, k\}$. Analogously, define $\mathcal{B}$ to be the projection matrix that is obtained from the $k \times k$ identity matrix by deleting the lth column if $b_l^1 = 0$, for some $l \in \{1, 2, \dots, k\}$. Let now

$$T_3^r := \left(t_{jl}^r\right)_{\substack{1 \leqslant j \leqslant n_b \\ 1 \leqslant l \leqslant n_c}} := \mathcal{C} T_3^1 \mathcal{B},$$
$$b^r := \begin{pmatrix} b_1^r \\ b_2^r \\ \vdots \\ b_{n_b}^r \end{pmatrix} := \mathcal{B}^* b^1,$$
$$c^r := \begin{pmatrix} c_1^r & c_2^r & \dots & c_{n_c}^r \end{pmatrix} := c^1 \mathcal{C}^*.$$

Then

$$G(\omega_1, \omega_2) = \sum_{j=1}^{n_c} \sum_{l=1}^{n_b} \frac{c_j^r}{2\pi \mathrm{i}\omega_1 - a_j^r} t_{jl}^r \frac{b_l^r}{2\pi \mathrm{i}\omega_2 - a_l^r}.$$

Note that in general $n_b \neq n_c$, i.e., T_3^r is not necessarily a square matrix.

In the 'reduced' representation of the spectrum which was just discussed, the set of all T_3^r matrices is given by

$$\mathcal{T} := \mathcal{C} Q \mathcal{T} Q^* \mathcal{B} = \left\{ \mathcal{C} A T_3 Q^* B \mid T_3 \in \mathcal{T} \right\}.$$

While in general $\mathcal{T}_r$ is not a matrix algebra it is in an obvious way a subspace of the vector space of $n_c \times n_b$ matrices with complex entries.

Of particular interest from an experimental point of view is whether an experiment can be devised such that a particular diagonal- or cross-peak can for example be suppressed or made to appear without unduly influencing other parts of the spectrum. Since a peak has the general form $c_j^r t_{jl}^r b_l^r / ((2\pi \mathrm{i}\omega_1 - a_j^r)(2\pi \mathrm{i}\omega_2 - b_l^r))$, this problem is related to the question whether or not experiments can be found that can set the t^r_{jl}-entry of T^r_3 to zero or to another value without changing the other entries of T^r_3. If this is possible, we call this a switchable 2-D pole. We say that 2-D pole is an (a,b)-pole if the pole is given by $v/((2\pi \mathrm{i}\omega_1 - a)(2\pi \mathrm{i}\omega_2 - b))$ for some constant v. It is easily seen that the (a^r_j, b^r_j)-pole is switchable if and only if $E_{jl} \in \mathcal{T}_r$, where E_{jl} is the $n_c \times n_b$ matrix such that all entries are zero with the exception of the (j,l) entry which is 1.

Similarly, we call a collection $(a^r_{n_1}, b^r_{n_1}), \ldots, (a^r_{n_s}, b^r_{n_s})$ of 2-D poles *switchable* if two experiments can found such that in the first experiment all the coefficients of the poles are non-zero and in the second experiment all coefficients are zero, but the coefficients for the other 2-D poles are the same for both experiments.

We have the following result.

Proposition 1. The collection $(a^r_{n_1}, b^r_{m_1}), \ldots, (a^r_{n_s}, b^r_{m_s})$ of 2-D poles is switchable if and only if there exist nonzero coefficients $\lambda_1, \lambda_2, \ldots, \lambda_s$ such that $\sum_{l=1}^{n} \lambda_l E_{n_s,m_s} \in \mathcal{T}_r$.

3. The preparation period and invariant subspaces

It was shown in section 1 that the preparation period of a two-dimensional NMR experiment is determined by the expression $\sum_{l=1}^{k_1} \mu_l e_{1,l}$. It will be the topic of this section to analyze the set $\mathcal{E}$ of all such expressions. In particular, we are going to show that the set of all such expressions is an invariant subspace of $\mathcal{C}^n$. It was shown in section 1 that each $e_{1,l}$ is given by

$$e_{1,l} := P_{k,l}P_{k-1,l} \cdots P_{2,l}z_{1,l} + P_{k,l}P_{k-1,l} \cdots P_{3,l}z_{2,l} + \cdots + P_{k,l}z_{k-1,l} + z_{k,l},$$

where

$$z_{j,l} := \left(\mathrm{e}^{(t_{j,l} - t_{j,l-1})A_p(\omega_{p,j,l}, \Delta_{j,l}t, B_{j,l})} - I\right) A_p(\omega_{p,j,l}, \Delta_{j,l}t, B_{j,l})^{-1} b_r(\omega_{p,j,l}, \Delta_{j,l}t) B_{j,l}$$

and

$$P_{j,l} := P_{j,l}(t_{j,l}, t_{j,l-1}, \omega_{p,j,l}, \Delta_{j,l}t, B_{j,l}) := \mathrm{e}^{(t_{j,l} - t_{j,l-1})A_p(\omega_{p,j,l}, \Delta_{j,l}t, B_{j,l})},$$

$j = 1, \ldots, k,\ l = 1, 2, \ldots, k_1$. Here we have assumed as will be done throughout the remainder of this paper that $x_0 = 0$.

We have the following theorem.

Theorem 2. (1) We have

$$\mathcal{E} = \operatorname{span}\left\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\right\},$$

where span(V) denotes the linear span of the set of vectors V and $\mathcal{T}$ is defined as in section 2.

(2) $\mathcal{E}$ is the smallest linear subspace of $\mathcal{C}^n$ that contains $b_r(\omega_p, \Delta t)$ for $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, and is invariant under $A_r(\omega_p)$ and $N_r(\omega_p, \Delta t)$ for all $\omega_p \geqslant 0$, $\Delta t \geqslant 0$.

(3) If $A_r(\omega_p) = A_r^1 + \omega_p A_r^2$, if $N_r(\omega_p, \Delta t) = \mathrm{e}^{\mathrm{i}\omega_p \Delta t} N_r^1 + \mathrm{e}^{-\mathrm{i}\omega_p \Delta t} N_r^2$ and if $b_r(\omega_p, \Delta t) = \mathrm{e}^{\mathrm{i}\omega_p \Delta t} b_r^1 + \mathrm{e}^{\mathrm{i}\omega_p \Delta t} b_r^2$, then $\mathcal{E}$ is the smallest subspace of $\mathcal{C}^n$ that contains b_r^1 and b_r^2 and is invariant under A_r^1, A_r^2, N_r^1 and N_r^2. Here A_r^1, A_r^2, N_r^1, N_r^2, b_r^1 and b_r^2 are assumed to be constant matrices independent of ω_p and Δt.

Proof. (1) We begin by showing that $\mathcal{E} \subseteq \operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$. To do this we first show that a vector z as defined above is in $\operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0)\}$. Let $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, $B_1 \geqslant 0$ and set

$$z := \left(\mathrm{e}^{tA_p(\omega_p, \Delta t, B_1)} - I\right) A_p(\omega_p, \Delta t, B_1)^{-1} b_r(\omega_p, \Delta t) B_1.$$

Then

$$\begin{aligned} z &= \left(\mathrm{e}^{tA_p(\omega_p, \Delta t, B_1)} - I\right) A_p(\omega_p, \Delta t, B_1)^{-1} b_r(\omega_p, \Delta t) B_1 \\ &= \left(\sum_{r=0}^{\infty} \frac{1}{r!} \left(tA_p(\omega_p, \Delta t, B_1)\right)^r - I \right) A_p(\omega_p, \Delta t, B_1)^{-1} b_r(\omega_p, \Delta t) B_1 \\ &= \left(\sum_{r=1}^{\infty} \frac{1}{r!} \left(tA_p(\omega_p, \Delta t, B_1)\right)^r \right) b_r(\omega_p, \Delta t) B_1, \end{aligned}$$

which shows that $z \in \operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0)\}$.

We now show that if $y_0 \in \operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$, then for $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, $t > t_0$ and $B_1 \geqslant 0$, we have that

$$Py_0 + z$$

is in $\operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$, where

$$\begin{aligned} P &:= \mathrm{e}^{(t_1 - t_0) A_p(\omega_p, \Delta t, B_1)}, \\ z &:= \left(\mathrm{e}^{(t_1 - t_0) A_p(\omega_p, \Delta t, B_1)} - I\right) A_p(\omega_p, \Delta t, B_1)^{-1} b_r(\omega_p, \Delta t) B_1. \end{aligned}$$

This is the case since $z \in \operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$ by the above argument and since $P \in \mathcal{T}$. Since a general element in $\mathcal{E}$ is the linear combination of elements of the form (see section 1)

$$P_k\left(P_{k-1}\left(\cdots\left(P_2(P_1 x_0 + z_1) + z_2\right)\cdots\right) + z_{k-1}\right) + z_k,$$

the inclusion $\mathcal{E} \subseteq \operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$ follows immediately from what was just shown.

We now need to show that $\operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\} \subseteq \mathcal{E}$. To do this let $v \in \{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$, i.e.,

$$v = P_k P_{k-1} \cdots P_2 b_r(\omega_p, \Delta t),$$

where $\Delta t \geqslant 0$, $\omega_p \geqslant 0$ and

$$P_j = \mathrm{e}^{(t_j - t_{j-1}) A_p(\omega_{p,j}, \Delta_j t, B_j)}$$

with $0 < t_1 < t_2 < \cdots < t_k$ and $\omega_{p,j} \geqslant 0$, $\Delta_j t \geqslant 0$, $B_j \geqslant 0$, $j = 2, 3, \ldots, k$. In order to show that $v \in \mathcal{E}$, we first show that

$$P_k P_{k-1} \cdots P_2 z_1(t) \in \mathcal{E},$$

where

$$z_1(t) := \left(\mathrm{e}^{(t-t_0)A_p(\omega_p, \Delta t, B)} - I\right)\left(A_p(\omega_p, \Delta t, B)\right)^{-1} b_r(\omega_p, \Delta t), \quad 0 < t < t_1,\ B > 0.$$

Set

$$z_j := \left(\mathrm{e}^{(t_j - t_{j-1})A_p(\omega_{p,j}, \Delta_j t, B_j)} - I\right)\left(A_p(\omega_{p,j}, \Delta_j t, B_j)\right)^{-1} b_r(\omega_{p,j}, \Delta_j t) B_j,$$

$j = 2, 3, \ldots, k$. By definition of $\mathcal{E}$, $z_j \in \mathcal{E}$ for $j = 1, 2, \ldots, k$, and $P_k z_{k-1} + z_k \in \mathcal{E}$. Since $\mathcal{E}$ is a vector space this implies that $P_k z_{k-1} \in \mathcal{E}$. Similarly, by definition of $\mathcal{E}$, we have that $P_k P_{k-1} z_{k-2} + P_k z_{k-1} + z_k \in \mathcal{E}$. Again using that $\mathcal{E}$ is a vector space, this implies that $P_k P_{k-1} z_{k-2} \in \mathcal{E}$. Proceeding recursively we show that

$$P_k P_{k-1} \cdots P_2 z_1(t) \in \mathcal{E}, \quad 0 < t < t_1.$$

Let $T_3 := P_k P_{k-1} \cdots P_2$ and set $r(t) := T_3 z_1(t)$, $0 < t < t_1$. Since $\mathcal{E}$ is a finite dimensional subspace of $\mathcal{C}^n$, it is closed. Hence,

$$\begin{aligned} v &= P_k P_{k-1} \cdots P_2 b_r(\omega_p, \Delta t) = T_3 A_p(\omega_p, \Delta t, B)\left(A_p(\omega_p, \Delta t, B)\right)^{-1} b_r(\omega_p, \Delta t) \\ &= T_3 \lim_{t \to 0} \frac{z_1(t)}{t} = \lim_{t \to 0} \frac{r(t)}{t} \in \mathcal{E}. \end{aligned}$$

(2) Clearly, $\mathcal{E} = \operatorname{span}\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$ is a linear subspace of $\mathcal{C}^n$ that contains $b_r(\omega_p, \Delta t)$ for $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, and by the characterization of $\mathcal{T}$ in theorem 1 is invariant under $A_r(\omega_p)$ and $N_r(\omega_p, \Delta t)$ for all $\omega_p \geqslant 0$, $\Delta t \geqslant 0$.

Conversely, an invariant subspace of $\mathcal{C}^n$ that contains $b_r(\omega_p, \Delta t)$ for $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, and is invariant under $A_r(\omega_p)$ and $N_r(\omega_p, \Delta t)$ for all $\omega_p \geqslant 0$, $\Delta t \geqslant 0$, contains the elements of $\{\mathcal{T} b_r(\omega_p, \Delta t) \mid \omega_p \geqslant 0,\ \Delta t \geqslant 0\}$.

(3) The statement follows from (2) in conjunction with theorem 1. □

In [4] it was shown that the spectrum of a 1-D NMR experiment is given by

$$G(\omega) = c(2\pi \mathrm{i} I - A)^{-1} e_0, \quad \omega \in \Re,$$

for some vector e_0. The only parameter in this description which can be adjusted in an experiment is e_0. If addition schemes are introduced that are analogous to those introduced in section 1 for 2-D systems, then the set $\mathcal{E}$ describes all possible vectors e_0.

Acknowledgements

This work was supported in part by the National Science Foundation and the National Institutes of Health (grant numbers: AR39169, AI31592).

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