## Applications of Bilinear Control Theory in Nonlinear Spectroscopy

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Here, I wish to motivate bilinear system identification techniques for  $3^{\rm rd}$  order spectroscopy.

The von Neumann equation describes time evolution of a density matrix  $\rho = \sum_{i} p_i |\psi_i\rangle \langle \psi_i|$  where  $\{|\psi_i\rangle\}$  spans the Hilbert space:

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [H(t), \rho(t)]$$

Integrating:

$$\rho(t) = \rho(0) + \frac{-i}{\hbar} \int_0^t dt_1[H(t_1), \rho(t_1)]$$

One can solve by repeatedly inserting the above equation into itself:

$$\rho(t) = \rho(0) + \frac{-i}{\hbar} \int_0^t dt_1[H(t_1), \rho(0)] + \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2[H(t_1), [H(t_2), \rho(t_2)]]$$

And so on:

$$\rho(t) = \rho(0) + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n [H(t_1), [H(t_2), \dots [H(t_n), \rho(t_n)] \dots]]$$

This series is traditionally defined as

$$\rho(t) = \sum_{n=0}^{\infty} \rho_n(t) = \rho(0) + \sum_{n=1}^{\infty} \rho_n(t)$$

where  $\rho_0(t) = \rho(0)$  and  $\rho_n(t) = \int_0^t dt_1 \dots \int_0^{t_{n-1}} dt_n[H(t_1), \dots [H(t_n), \rho(t_n)] \dots]$ . Re-inspecting the above equation, I find a recursive relationship for the n<sup>th</sup> order perturbation using linearity of the commutator:

$$\rho_n(t) = \frac{-i}{\hbar} \int_0^t d\tau [H(\tau), \rho_{n-1}(\tau)]$$

By differentiating both sides, I derive an equation of motion for the  $n^{\rm th}$  order perturbation:

$$\frac{\partial \rho_n(t)}{\partial t} = \frac{-i}{\hbar} [H(t), \rho_{n-1}(t)]$$

In nonlinear spectroscopy, polarization is related to the perturbation of the density matrix as follows (see Mukamel):

$$P_n(t) = \langle \mu \rho_n(t) \rangle$$

I wish to use a general form to relate the polarization measurement  $P_3(t)$  with n<sup>th</sup> order perturbations of the density matrix. In superoperator form (where the elements of  $n \times n$  density matrices concatenate to create  $1 \times n^2$  vectors), let us define **x** as a concatenation of  $\rho_n, 0 \le n \le 3$ :

$$\mathbf{x}(t) = \begin{pmatrix} \rho_0(t) \\ \rho_1(t) \\ \rho_2(t) \\ \rho_3(t) \end{pmatrix}$$

The third-order polarization measurement  $P_3(t)$  is therefore

$$P_3(t) = \begin{pmatrix} 0\\0\\0\\F \end{pmatrix} \cdot \mathbf{x}(t)$$

such that applying F (in operator form) behaves as follows:  $F \cdot = \langle \mu \cdot \rangle$ . The  $1 \times 4n^2$  vector  $\mathbf{x}(t)$  is governed by the time evolution equation

$$\frac{\partial \mathbf{x}(t)}{\partial t} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ M(t) & 0 & 0 & 0 \\ 0 & M(t) & 0 & 0 \\ 0 & 0 & M(t) & 0 \end{pmatrix} \mathbf{x}(t)$$
  
where  $\mathbf{x}(0) = \begin{pmatrix} \rho(0) \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$  and applying  $M(t)$  (in operator form) behaves

as

follows:  $M(t) \cdot = \frac{-i}{\hbar} [H(t), \cdot].$ 

This is a general form to describe polarization measurement  $P_3(t)$  and perturbations of the density matrix.

Next, I investigate rudimentary linear control theory.

Standard state-space representation of a linear system has this form:

$$\dot{\mathbf{x}}(t) = A(t)\mathbf{x}(t) + B(t)\mathbf{u}(t)$$

$$\mathbf{y}(t) = C(t)\mathbf{x}(t) + D(t)\mathbf{u}(t)$$

If the system is LTI (linear and time-invariant), then matrices A, B, C, Dwill be time-independent. Our hope is to formulate the nonlinear spectroscopy problem in a form suitable for control theory analysis.

Our observation  $P_3(t)$  can be interpreted as  $\mathbf{y}(t)$  as shown above. In particular,  $C(t) = C = \begin{pmatrix} 0 & 0 & F \end{pmatrix}$  and  $D(t) = \mathbf{0}$ . Can the time dependence within H(t) be modeled as input  $\mathbf{u}(t)$  to the system? In general,  $H(t) = H_0 + E(t) \cdot \mu$ .

Let us define superoperators  $M_0, M_1$  such that  $M(t) = A_0 + E(t) \cdot M_1$ . By linearity of the commutator, applying  $M_0$  (in operator form) can behave as  $M_0 \cdot = \frac{-i}{\hbar}[H_0, \cdot]$ , and applying  $M_1$  (in operator form) can behave as  $M_1 \cdot = \frac{-i}{\hbar}[\mu, \cdot]$ .

Now, all matrices are time-independent, but there remains coupling between  $\mathbf{x}(t)$  and E(t). In particular, we have the evolution equation:

$$\dot{\mathbf{x}}(t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ M_0 & 0 & 0 & 0 \\ 0 & M_0 & 0 & 0 \\ 0 & 0 & M_0 & 0 \end{pmatrix} \mathbf{x}(t) + \begin{pmatrix} 0 & 0 & 0 & 0 \\ M_1 & 0 & 0 & 0 \\ 0 & M_1 & 0 & 0 \\ 0 & 0 & M_1 & 0 \end{pmatrix} \mathbf{x}(t) E(t)$$

Bilinear system theory may be well-equipped to handle this coupling.

In general,  $3^{rd}$  order spectroscopy experiments employ four-wave mixing: at time  $t = t_0$ , an electric pulse excites a molecule in its ground state. Two more pulses fire at the molecule (at time  $t = t_1, t_2$ ), adjusting the molecular state. A last pulse (at  $t = t_3$ ) is designed such that the molecule is forced back into its ground state, emitting some measured energy. This last pulse is the "measurement".

In a classical controls context, the input  $\mathbf{u}(t)$  models the electric field controls E(t). E(t) is pulse-like at  $t = 0, t_1, t_2$ , and 0 everywhere else. (Since the last pulse constitutes a measurement, there are effectively no inputs after time  $t = t_2$ ).

The system evolution, then, after time  $t = t_2$ , is linear with equations as given below:

$$\dot{\mathbf{x}}(t) = A\mathbf{x}(t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ M_0 & 0 & 0 & 0 \\ 0 & M_0 & 0 & 0 \\ 0 & 0 & M_0 & 0 \end{pmatrix} \mathbf{x}(t)$$
$$\mathbf{y}(t) = C\mathbf{x}(t) = (0 \quad 0 \quad 0 \quad F)\mathbf{x}(t)$$

For convenience, let us define time  $t = t_2 = 0$ . In general, we may not know  $M_0$  nor x(0). We can use classical subspace identification techniques to approximate  $M_0$ . Then, we will use some methods from bilinear control theory to approximate  $M_1$ .

The closed-form solution to this linear system is given below:

$$\mathbf{x}(t) = e^{At}\mathbf{x}(0)$$

Here,  $e^A$  is shorthand for the series expansion of  $e^x$ :

$$e^A = I + A + A^2/2 + A^3/6 + \dots$$

In this formulation, A is nilpotent, so  $e^A$  has a finite number of terms. In particular:

$$e^{At} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ M_0 t & 1 & 0 & 0 \\ M_0^2 t^2 / 2 & M_0 t & 1 & 0 \\ M_0^3 t^3 / 6 & M_0^2 t^2 / 2 & M_0 t & 1 \end{pmatrix}$$

Since  $\mathbf{y}(t) = (0 \quad 0 \quad F)\mathbf{x}(t)$ , we can find a closed-form solution for  $\mathbf{y}(t)$ :

$$\mathbf{y}(t) = F(M_0^3 t^3 / 6 \quad M_0^2 t^2 / 2 \quad M_0 t \quad 1) \mathbf{x}(0)$$

Expanding  $\mathbf{x}(0)$  in terms of its perturbation components, the above equation simplifies:

$$\mathbf{y}(t) = F[M_0^3 t^3 \rho_0(0)/6 + M_0^2 t^2 \rho_1(0)/2 + M_0 t \rho_2(0) + \rho_3(0)]$$

Thus, for a particular E(t), the output polarization maps to a cubic function of time (after the third pulse). System identification techniques to identify  $M_0$ and  $\{\rho_i(0)|1 \le i \le 3\}$  could prove useful. (Here,  $\rho_0$  is a constant, so it should still represent the ground state of the molecule, as it did before E(t) was applied.)