# Applications of Bilinear Control Theory in Nonlinear Spectroscopy 

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

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

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

Integrating:

$$
\rho(t)=\rho(0)+\frac{-i}{\hbar} \int_{0}^{t} d t_{1}\left[H\left(t_{1}\right), \rho\left(t_{1}\right)\right]
$$

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

$$
\rho(t)=\rho(0)+\frac{-i}{\hbar} \int_{0}^{t} d t_{1}\left[H\left(t_{1}\right), \rho(0)\right]+\left(\frac{-i}{\hbar}\right)^{2} \int_{0}^{t} d t_{1} \int_{0}^{t_{1}} d t_{2}\left[H\left(t_{1}\right),\left[H\left(t_{2}\right), \rho\left(t_{2}\right)\right]\right]
$$

And so on:
$\rho(t)=\rho(0)+\sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^{n} \int_{0}^{t} d t_{1} \int_{0}^{t_{1}} d t_{2} \ldots \int_{0}^{t_{n-1}} d t_{n}\left[H\left(t_{1}\right),\left[H\left(t_{2}\right), \ldots\left[H\left(t_{n}\right), \rho\left(t_{n}\right)\right] \ldots\right]\right]$
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 $\rho_{n}(t)=\int_{0}^{t} d t_{1} \ldots \int_{0}^{t_{n-1}} d t_{n}\left[H\left(t_{1}\right), \ldots\left[H\left(t_{n}\right), \rho\left(t_{n}\right)\right] \ldots\right]$.
Re-inspecting the above equation, I find a recursive relationship for the $\mathrm{n}^{\text {th }}$ order perturbation using linearity of the commutator:

$$
\rho_{n}(t)=\frac{-i}{\hbar} \int_{0}^{t} d \tau\left[H(\tau), \rho_{n-1}(\tau)\right]
$$

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

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

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

$$
P_{n}(t)=\left\langle\mu \rho_{n}(t)\right\rangle
$$

I wish to use a general form to relate the polarization measurement $P_{3}(t)$ with $\mathrm{n}^{\text {th }}$ 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 $\mathbf{x}$ as a concatenation of $\rho_{n}, 0 \leq n \leq 3$ :

$$
\mathbf{x}(t)=\left(\begin{array}{c}
\rho_{0}(t) \\
\rho_{1}(t) \\
\rho_{2}(t) \\
\rho_{3}(t)
\end{array}\right)
$$

The third-order polarization measurement $P_{3}(t)$ is therefore

$$
P_{3}(t)=\left(\begin{array}{c}
0 \\
0 \\
0 \\
F
\end{array}\right) \cdot \mathbf{x}(t)
$$

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

$$
\frac{\partial \mathbf{x}(t)}{\partial t}=\left(\begin{array}{cccc}
0 & 0 & 0 & 0 \\
M(t) & 0 & 0 & 0 \\
0 & M(t) & 0 & 0 \\
0 & 0 & M(t) & 0
\end{array}\right) \mathbf{x}(t)
$$

where $\mathbf{x}(0)=\left(\begin{array}{c}\rho(0) \\ 0 \\ 0 \\ 0\end{array}\right)$ 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 $A, B, C, D$ will 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, $C(t)=C=\left(\begin{array}{llll}0 & 0 & 0 & F\end{array}\right)$ 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 $M_{0} \cdot=\frac{-i}{\hbar}\left[H_{0}, \cdot\right]$, 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:

$$
\dot{\mathbf{x}}(t)=\left(\begin{array}{cccc}
0 & 0 & 0 & 0 \\
M_{0} & 0 & 0 & 0 \\
0 & M_{0} & 0 & 0 \\
0 & 0 & M_{0} & 0
\end{array}\right) \mathbf{x}(t)+\left(\begin{array}{cccc}
0 & 0 & 0 & 0 \\
M_{1} & 0 & 0 & 0 \\
0 & M_{1} & 0 & 0 \\
0 & 0 & M_{1} & 0
\end{array}\right) \mathbf{x}(t) E(t)
$$

Bilinear system theory may be well-equipped to handle this coupling.
In general, $3^{\text {rd }}$ 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 $E(t) . \quad E(t)$ 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:

$$
\begin{gathered}
\dot{\mathbf{x}}(t)=A \mathbf{x}(t)=\left(\begin{array}{cccc}
0 & 0 & 0 & 0 \\
M_{0} & 0 & 0 & 0 \\
0 & M_{0} & 0 & 0 \\
0 & 0 & M_{0} & 0
\end{array}\right) \mathbf{x}(t) \\
\mathbf{y}(t)=C \mathbf{x}(t)=\left(\begin{array}{llll}
0 & 0 & 0 & F
\end{array}\right) \mathbf{x}(t)
\end{gathered}
$$

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:

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

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

$$
e^{A}=I+A+A^{2} / 2+A^{3} / 6+\ldots
$$

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

$$
e^{A t}=\left(\begin{array}{cccc}
1 & 0 & 0 & 0 \\
M_{0} t & 1 & 0 & 0 \\
M_{0}^{2} t^{2} / 2 & M_{0} t & 1 & 0 \\
M_{0}^{3} t^{3} / 6 & M_{0}^{2} t^{2} / 2 & M_{0} t & 1
\end{array}\right)
$$

Since $\mathbf{y}(t)=\left(\begin{array}{llll}0 & 0 & 0 & F\end{array}\right) \mathbf{x}(t)$, we can find a closed-form solution for $\mathbf{y}(t)$ :

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

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

$$
\mathbf{y}(t)=F\left[M_{0}^{3} t^{3} \rho_{0}(0) / 6+M_{0}^{2} t^{2} \rho_{1}(0) / 2+M_{0} t \rho_{2}(0)+\rho_{3}(0)\right]
$$

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 $\left\{\rho_{i}(0) \mid 1 \leq i \leq 3\right\}$ 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.)

