TIMP: A package for parametric modeling of multiway spectroscopic measurements

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The data: time-resolved spectra

- how do (bio)physical systems interact with light?
- can investigate by time-resolved spectroscopy:
  - measure spectra (i.e., intensity of light over wavelengths $\lambda_j$) over time $t$:
    - resulting data is matrix:

  $\Psi = \begin{bmatrix}
  \psi(t_1, \lambda_1) & \psi(t_1, \lambda_2) & \cdots & \psi(t_1, \lambda_n) \\
  \psi(t_2, \lambda_1) & \psi(t_2, \lambda_2) & \cdots & \psi(t_2, \lambda_n) \\
  \vdots & \vdots & \ddots & \vdots \\
  \psi(t_m, \lambda_1) & \psi(t_m, \lambda_2) & \cdots & \psi(t_m, \lambda_n)
  \end{bmatrix}$

- analysis of $\Psi$ provides insight into dynamics of underlying system

An underlying bilinear model

Time-resolved spectra $\Psi$:

$\Psi = CE^T$

- $C$: concentrations in time
- $E$: spectra
- column $c_i$ of $C$ represents the concentration profile, column $e_i$ of $E$ represents the spectrum of $i$th spectrally distinct component of $\Psi$

An inverse problem

goal: recover $C$ and $E$ from measured $\Psi$

- $C$ and $E$ large ($1000 \times 10$)
- this nonlinear estimation problem has thousands of parameters

parametric model-based approach:

- fit a parametric model to $C$ and solve for the entries of $E$ as conditionally linear:
  estimation problem becomes

  \[
  \text{Minimize } \| (I - C(\Theta)C^+(\Theta))\Psi \|_2
  \]

- typical models $C(\Theta)$ have $\Theta$ of $10^1 - 10^2$ parameters
- parameter estimates valuable for physical interpretation; unrealistic estimates falsify model
R facilitates representation of models $C(\Theta)$:

- nonlinear parameter vector $\Theta$ partitioned into groups representing distinct model aspects
- parameters may be functions of other parameters, leading to hierarchy
- S4 class objects organize hierarchical models

**Conclusions**

- a PSE for modeling time-resolved spectra and other multi-way spectroscopic measurements has been implemented in R
  - numerous model types and options for multieperiment modeling, constraints on parameters supported

- R facilitates efficient iterative model specification, parameter estimation and validation

Future work:

- public release of the package
- extension of a GUI prototyped with tcl/tk package
- further development of models