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 λ_j) over time t:
  - resulting data is matrix:

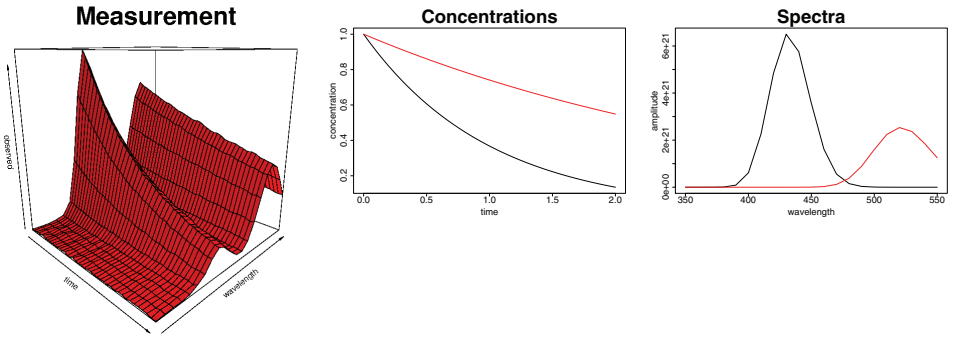
$$\Psi = \begin{array}{c|cccc} & \lambda_1 & \lambda_2 & \dots & \lambda_n \\ t_1 & \psi(t_1,\lambda_1) & \psi(t_1,\lambda_2) & \dots & \psi(t_1,\lambda_n) \\ t_2 & \psi(t_2,\lambda_1) & \psi(t_2,\lambda_2) & \dots & \psi(t_2,\lambda_n) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ t_m & \psi(t_m,\lambda_1) & \psi(t_m,\lambda_2) & \dots & \psi(t_m,\lambda_n) \end{array}$$

- analysis of Ψ provides insight into dynamics of underlying system

[An underlying bilinear model]

Time-resolved spectra Ψ:

$$\Psi = CE^T$$



- C: concentrations in time
- E: spectra
- column c_i of C represents the concentration profile, column e_i of E represents the spectrum of *ith* spectrally distinct component of Ψ

[An inverse problem]

goal: recover C and E from measured Ψ

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

parametric model-based approach:

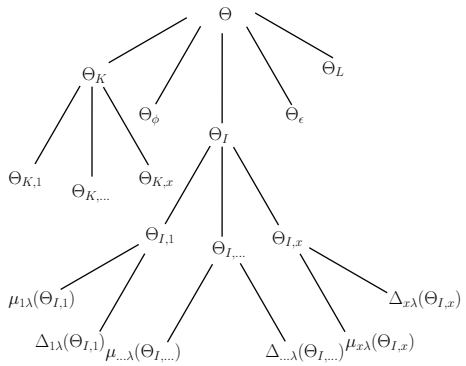
- fit a parametric model to C and solve for the entries of E as conditionally linear: estimation problem becomes

$$Minimize \parallel (I - C(\Theta)C^{+}(\Theta))\Psi \parallel_2$$

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

[R for model representation]

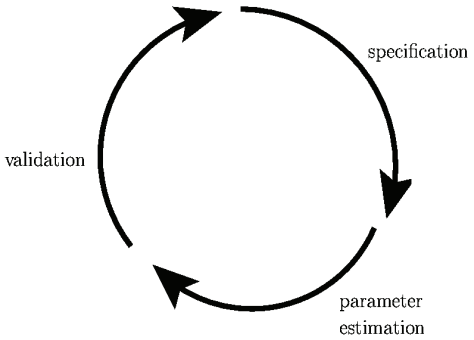
R facilitates representation of models $C(\Theta)$:



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

[R for model specification, parameter estimation, validation]

optimal model discovery iterative process:



R-based problem-solving environment (PSE) facilitates efficient iteration:

- S4 classes for model specification
- nls and numericDeriv functions for fast parameter estimation
- integrated statistical functions for analysis of fit
- flexible graphics for display of results

[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 multiexperiment 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