TIMP: A package for parametric modeling of multiway spectroscopic measurements

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February 24, 2006

Multiway spectroscopic measurements Ψ are collections of spectra representing a photophysical system at many different times or other conditions. Simultaneous analysis of such measurements in terms of a parametric model (*global analysis* in the photophysical literature) provides insight into the dynamics of the underlying system.

Measurements Ψ represent a superposition of the contributions of n_{comp} spectrally distinct components. The concentration and spectral property of each component may be represented as column l of matrices C and E, respectively, where C is of dimension $nt \times n_{comp}$, E is of dimension $nl \times n_{comp}$, nt is the number of times or other conditions at which spectra were measured, and nl is the number of (wavelength or wavenumber) points by which spectra are represented. The basic superposition model for such measurements is $\Psi = CE^T$.

Given Ψ, the inverse problem of recovery of the entries of C or E in terms of physically significant parameters (descriptive of, e.g., the decay rate of a component, or the location of the maximum of a spectrum) is often of interest. Adequate parameterizations of either C or E are nonlinear, and are often hierarchical in nature. For example, column l of C may be described as $C_l = exp(-k_l t) \otimes gaus(\mu, \sigma)$, where k_l is a decay rate parameter, t is time, $\otimes$ is convolution and μ and σ are location and width parameters, respectively. Parameters μ and σ may in turn be described as nonlinear functions of e.g., wavelength λ, so that C_l is wavelength-dependent and the model description is hierarchical [1]. Once a model is parameterized for C or E, the entries of the remaining matrix may often be treated as conditionally linear, taking advantage of the separable model form [2]. Intrinsically nonlinear parameter estimates may be derived by nonlinear regression, which has the advantage of returning parameter confidence estimates valuable in model interpretation and validation [3].

R has been used to prototype a problem-solving environment for parametric modeling of multiway spectroscopic measurements. Hierarchical models for multiway spectroscopic measurements find natural description as a hierarchy of S4 classes. S4 methods provide a means to differentiate the treatment of many different model types while maintaining uncomplicated calling code. The *nls* and *numericDeriv* functions provide a fast basis for nonlinear regression. An extended version of the problem-solving environment for public release is being developed as the package "TIMP".

References

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