DECOMPOSITION OF EXPONENTIAL CURVES IN SPECTROMETRY

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Two algorithms for decomposition of exponential dependences are described. One of the algorithms is an iterative generalization of the well-known method of stepwise extraction of exponential components on a semi-logarithmic scale, and the other allows visualization of the set of possible solutions with interactive choice of a satisfactory approximation by user-specified criteria. The algorithms have been implemented on an IBM PC.

1. Introduction

A common problem in experimental spectroscopy requires estimation of the unknown parameters of a solution represented as a sum of exponential terms. This by now classical problem has a long list of applications. In particular, the parameters of "decaying" exponentials are needed in the analysis of exponential spectra in experiments with identification of isomeric levels, determination of transverse NMR relaxation times, estimation of luminescence decay kinetic parameters, modeling of the evolution dynamics of populations of living organisms, analysis of the mechanisms of various chemical reactions, and other problems. The common spectrometric problem of multiplet decomposition with determination of the location and intensity of the peaks is reduced to this problem by application of the two-sided Laplace transform.

We only consider exponential sums whose parameters satisfy the nonnegativity condition:

\[ f(t) = \sum_{j=1}^{m} A_j \exp(-T_j \cdot t), \quad T_j > 0, \quad T_j = T_i \Leftrightarrow i = j, \quad A_j > 0. \]  

(1)

Instead of the true function \( f(t) \) we observe its perturbed values \( \tilde{f}_i \) on some grid \( \{t_i\}, i = 1, ..., n \). The measurement errors \( df_i > 0 \) such that \( |\tilde{f}_i - f_i| \leq df_i \) are also known.

If the number of components \( m \) in (1) is given, then the problem can be stated in the following form: given the values of the exponential sum (with an error!),

1) estimate the exponents and the intensities \( (T, A) \);
2) estimate the approximate errors in the sought parameters \( (dT, dA) \).

The sought parameters are obtained with some admissible final error because the initial exponential spectrum is given with an error and because computer processing introduces an unavoidable numerical error (due to the finite computer word length and the associated rounding errors).

The main difficulties in the solution of this inverse problem are the following:

- the exponential spectrum is always observed with errors (random noise or systematic trend);
- the parameters of the components may have certain specific features that substantially complicate the solution of the problem (close or conversely very different exponents, simultaneous presence of components with very low and very high intensities, etc.);
- the number of exponential terms in the sum is unknown.

Because of these factors, the problem of decomposition of the exponential sum into components is unstable to small perturbations of the initial spectrum. A stable solution of this problem can be constructed only if we have additional prior information about the characteristics of the sought exponentials. For instance, we may have the minimum and/or maximum bounds of the parameters, their relationships, the region of most likely solutions, the admissible difference between the parameters, etc. This useful additional information is used to formulate solution-choosing criteria that substantially restrict the set of allowed solutions.
A fairly broad range of basic mathematical methods are currently available for the solution of this problem. A classification of these methods is given in [1]. The approaches considered in [2] can also be viewed as methods of this category.

In this article we describe two approaches. One approach is a "computer" iterative generalization of the well-known method of stepwise extraction of exponentials on a semi-logarithmic scale. It produces satisfactory approximations for sufficiently widely separated exponentials. The second approach has been specially developed to analyze two exponential components. The latter method allows visualization of the set of possible solutions with interactive choice of a satisfactory approximation by user-specified criteria. Combined with the integro-differential and semi-logarithmic approaches, expert judgments, and the methodology of fuzzy-set theory, and also supported by good computer graphics, this method may develop into a sufficiently powerful and efficient apparatus for solving various problems of decomposition of exponential dependences.

2. Decomposition Algorithms

Generalized logarithmic method (with successive—recursive refinement of parameters)

Recall the classical version of the logarithmic method. The values of some exponential spectrum are given on an arbitrary grid, and the spectrum is normalized so that $f(i) \geq 1$. We assume that the exponents are not too close to one another. This means that ultimately, in the last section of the spectrum, the effect of all components, except that with the exponent of least absolute value (the "long-lived" component), is small. The logarithmic function of the spectrum in the last section is thus approximately described by a linear segment, whose slope determines the "longevity" of the exponential component, and the value at zero ($t = 0$) determines the second parameter (intensity).

As soon as these parameters have been determined, the identified component is subtracted from the general sum. We are thus basically left with random noise in the last section, and this section can be omitted from analysis.

The second step of the algorithm repeats everything from the beginning.

Thus, we identify one component in each step, and the final result produces the sought decomposition.

This method, like most other methods designed to produce an exact solution of problem (1), does not work well if $f(t)$ is perturbed and the exponential sum contains at least two terms with close exponents. For such close components, it is difficult and often actually impossible to identify a section where the effect of one component is substantially greater than the effect of the other.

We present a generalization of the logarithmic method, which is fairly easy to implement on a computer. The main purpose of the generalization is to reduce the error associated with the residual influence of the "high-order" exponentials and error buildup.

Step 1. First execute step 1 in accordance with the classical approach: on a logarithmic scale find the left (B1) and the right (E1) bounds of the section at the end of the spectrum such that the measurements of $\hat{f}_i$ are closely approximately by a straight line. Then find the initial approximations for the parameters of the first exponential from the condition

$$\{T_1, A_1\} = \arg \min_{T \geq 0, A > 0} \sum_{i = B1}^{E1} [\hat{f}_i - A \exp(-T \cdot t_i)]^2 \cdot w_i^2,$$

where $w_i$ are weights (for instance, $w_i = 1/df_i$).

Next subtract the identified component everywhere from the initial spectrum:

$$d_i = \hat{f}_i - A_1 \exp(-T_1 \cdot t_i);$$

Step k. In the k-th section [Bk, Ek] estimate the initial approximations for the parameters of the k-exponential:

$$\{T_k, A_k\} = \arg \min_{T \geq 0, A > 0} \sum_{i = Bk}^{Ek} [d_i^{k-1} - A \exp(-T \cdot t_i)]^2 \cdot w_i^2.$$

Then successively refine all the parameters, starting with the 1st section. To this end, in the p-th section ($p = 1, 2, \ldots, k$) find