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High-resolution exponential analysis via regularized numerical inversion of Laplace transforms

V.V. Kryzhniy

Kuban State Technological University, Krasnodar, Russia

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Abstract

The paper describes a new, robust method for the exponential analysis problem solving. In discrete case the regularizing operators of the inverse Laplace transformation are used for transformation of experimental data into a form that is more suitable for determination of decay rates and amplitudes. In the case of a continuous distribution a spectral function is obtained by regularized inverse Laplace transformation of the transient. The proposed method has advantages over known methods and is tolerant to the baseline offset. The results of numerical testing show that the proposed method can be used in high-resolution analysis for determination of spectral functions, decay rates and amplitudes from experimentally measured transients.

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1. Introduction

The problem of exponential analysis arises in semiconductor physics, nuclear physics, nuclear magnetic resonance, chemistry and electrochemistry, biophysics and many other fields [10]. The problem is aimed at determining a continuous spectral function $f(\lambda)$ (continuous case) from experimentally measured decaying function of time $F(t)$:

$$F(t) = B + \int_0^\infty \mathrm{e}^{-\lambda t} f(\lambda)\,\mathrm{d}\lambda, \tag{1}$$

where B is a constant (the baseline offset).

E-mail address: kryzhniy@yahoo.com (V.V. Kryzhniy).

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In the case where the spectral function $f(\lambda)$ can be represented as a sum of delta functions (discrete case), Eq. (1) reduces to the following:

$$F(t) = B + \sum_{i=1}^{N} A_i \exp(-\lambda_i t). \tag{2}$$

In this last case the problem of exponential analysis is in determining the total number of decays N, their rates λ_i and amplitudes A_i. It is important to note that there is a fundamental resolution limit for exponential analysis, determined by signal-to-noise ratio (SNR) in the input data [2].

It has been known for a long time that the problem of exponential analysis may, in principle, be solved with the help of inverse Laplace transformation [8]. Indeed, formally applying inverse Laplace transformation [1] to Eqs. (1) and (2) we will have:

$$\mathscr{L}^{-1}[F(t)] = B\delta(0) + f(\lambda), \tag{3}$$

$$\mathscr{L}^{-1}[F(t)] = B\delta(0) + \sum_{i=1}^{N} A_i \delta(\lambda - \lambda_i), \tag{4}$$

where $\delta(\lambda - \lambda_i)$ is a delta function.

However, despite this theoretical possibility of solving the problem of exponential analysis with the help of inverse Laplace transformation, in practice the most widely used methods exploit other approaches [10], for example, Prony's method [16]. The reason for this is the function $F(t)$ being obtained from experiment contains noise and known only for real $t > 0$, whereas the inverse Laplace transformation is given in the form of Bromwich contour integral. Therefore, only a method for inverting of real-valued Laplace transforms can be applied to this problem solving.

The problem of inverting of real-valued Laplace transforms is well known to be ill-posed [20], and one should use regularization in order to obtain a stable solution. Implementation of a non-regularizing Gavel–Stehfest algorithm [18] with double precision of input data allows to resolve two exponentials if $\lambda_2/\lambda_1 \simeq 1.5$ [17]. This resolution is far away from the resolution limit of exponential analysis [2] when data uncertainty is limited only by rounding errors of double precision arithmetic.

Tikhonov regularization method [20] is used to solve the problem of exponential analysis in the discrete case and is implemented in several computer programs (see review [10] for further references). However, in the continuous case, implementation of Tikhonov theory for inverting real-valued Laplace transforms turned out to be unsuccessful due to some numerical difficulties [21].

A number of other known methods for inverting of real-valued Laplace transforms (see for example [4–7,9]) apply regularization to a second-order problem obtained by discretization or expansion of a Laplace transform or its original function into a series. The method's validity is usually confirmed by testing on a set of somewhat simple Laplace transforms. To the best of author's knowledge, no implementation of the above cited methods to the problem of exponential analysis is described in literature.

A robust method for inversion of real-valued Laplace transforms has been proposed and generalized by the author in [13–15]. The analytical background of the method allows us to determine limitations of inversion of real-valued Laplace transforms and to provide theoretical error analysis. The testing results clearly show substantial advantages of the proposed method over known methods in stability and accuracy [15].

[1] In this paper denotations that are standard for exponential analysis (not for Laplace transformation) are used: Laplace transform and its inverse transform are denoted as $F(t)$ and $f(\lambda)$, respectively.

This paper deals with application of built regularizing operators of the inverse Laplace transformation to the problem of exponential analysis. Theoretical background and selection of parameters of regularizing operators are given in the next section. Then, the results of numerical testing are provided. Finally, features and limitations of the exponential analysis are briefly discussed.

2. Outline of the method

Let $F(t), f(\lambda)$ denote a Laplace transform pair. As shown in [15] a regularized inverse Laplace transform $f_{\mathrm{R}}(\lambda)$ can be calculated from the following integral of convolution type:

$$f_{\mathrm{R}}(\lambda) = \int_0^\infty F(u)\Pi(R, \lambda u)\,\mathrm{d}u, \tag{5}$$

where R is a conjugate parameter of regularization.

The regularized solution $f_{\mathrm{R}}(\lambda)$ tends to the exact one $f(\lambda)$ as $R \to \infty$. The kernel of regularized inverse Laplace transformation $\Pi(R,x)$ is not unique. Multiple kernels can be constructed by selecting an arbitrary continuous function $\varphi(p), \varphi(1) \neq 0$ in the following definition [15]:

$$\Pi(R,x) = \frac{1}{\pi\varphi(1)}\mathscr{L}^{-1}\left[\frac{\sin(R\ln p)}{p-1}\varphi(p)\right],$$

where $\mathscr{L}^{-1}$ is operator of inverse Laplace transformation, p is complex variable.

In case where $\varphi(p) = p^a/(p+1)$, the kernel $\Pi(R,x)$ is given by formula [14]

$$\Pi(R,x) = \frac{-2}{\pi^2} \times \mathrm{I}m\left[\sin\pi(a+\mathrm{i}R)\Gamma(a-1+\mathrm{i}R)x^{1-a-\mathrm{i}R}{}_1F_2\left(1;\frac{2-a-\mathrm{i}R}{2},\frac{3-a-\mathrm{i}R}{2};\frac{x^2}{4}\right)\right], \tag{6}$$

where $a < 2$ is a real parameter,

$${}_1F_2\left(1;\frac{2-a-\mathrm{i}R}{2},\frac{3-a-\mathrm{i}R}{2};\frac{x^2}{4}\right)$$

is generalized hypergeometric function, and $\Gamma(a-1+\mathrm{i}R)$ is gamma function.

It is also shown in [14] that regularized inverse Laplace transform $f_{\mathrm{R}}(\lambda)$ is connected to the exact one $f(\lambda)$ as

$$f_{\mathrm{R}}(\lambda) = \frac{2}{\pi}\int_0^\infty f(\lambda u)u^a\frac{\sin(R\ln u)}{u^2-1}\,\mathrm{d}u, \tag{7}$$

and $f_{\mathrm{R}}(\lambda) \to f(\lambda)$ as $R \to \infty$ if the last integral converges. Also Laplace transforms $F(t)$ and $F_{\mathrm{R}}(t) = \mathscr{L}[f_{\mathrm{R}}(\lambda]$ are connected as follows:

$$F_{\mathrm{R}}(t) = \frac{2}{\pi}\int_0^\infty F(tu)\frac{u^{1-a}}{u^2-1}\sin(R\ln u)\,\mathrm{d}u. \tag{8}$$

Eqs. (5) and (6) define a regularizing operator for inverting a given Laplace transform whenever there is a valid value of parameter a for which integral (5) converges [14]. Using formulae given above, we can find a continuous spectral function by calculating integral (5). The accuracy of obtained solution depends on accuracy of input data. It tends to be higher for monotonic functions [13,14].

To analyze problem in the discrete case, consider the following Laplace transform pair:

$$\mathscr{L}[\delta(\lambda-\lambda_0)] = \exp(-\lambda_0 t). \tag{9}$$

For $F(t) = \exp(-\lambda_0 t),\ \lambda_0 > 0$ integral (8) converges for any $a < 2$. Substituting $\exp(-\lambda_0 t)$ into Eq. (8), we can find the regularized Laplace transform of $\exp(-\lambda_0 t)$

$$\mathscr{L}[\delta_R(\lambda - \lambda_0)] = \frac{2}{\pi}\int_0^\infty e^{-\lambda_0 t u}\frac{u^{1-a}}{u^2-1}\sin(R\ln u)\,du. \tag{10}$$

It is apparent from (10) that

$$\mathscr{L}[\delta_R(\lambda - \lambda_0)] = \frac{2}{\pi}\mathscr{L}\left[\frac{\lambda^{1-a}\sin(R\ln\lambda)}{\lambda^2-1};\lambda_0 t\right]. \tag{11}$$

Then, in accordance with properties of Laplace transformation we have

$$\delta_R(\lambda - \lambda_0) = \frac{1}{\pi\lambda_0}\frac{\sin R\ln\frac{\lambda}{\lambda_0}}{\sinh\ln\frac{\lambda}{\lambda_0}}\left(\frac{\lambda}{\lambda_0}\right)^{-a}. \tag{12}$$

Fig. 1 shows the function $\delta_R(\lambda - 1)$ obtained by calculating integral (5) for $F(t) = \exp(-t)$, $R = 3$, and $a = 0$. Graph in Fig. 1 coincides with theoretical function defined by Eq. (12). It is worth mentioning that for $a = 0$ (the value is used in calculations throughout this paper) the function $\delta_R(\lambda - \lambda_0)$ is symmetric in semilogarithmic coordinates, and its main maximum is at $\lambda = \lambda_0$. In simple cases this feature allows us to distinguish monoexponential and multiexponential cases by analyzing graph's symmetry.

Zeroes of $\delta_R(\lambda - \lambda_0)$ depend only on values of R and λ_0. The value of λ_0 can be calculated using simple formulae that involve zeroes' abscissas $(\lambda_{left}, \lambda_{right})$ that surround the main maximum: $\lambda_0 = \lambda_{left}\exp(\pi/R)$

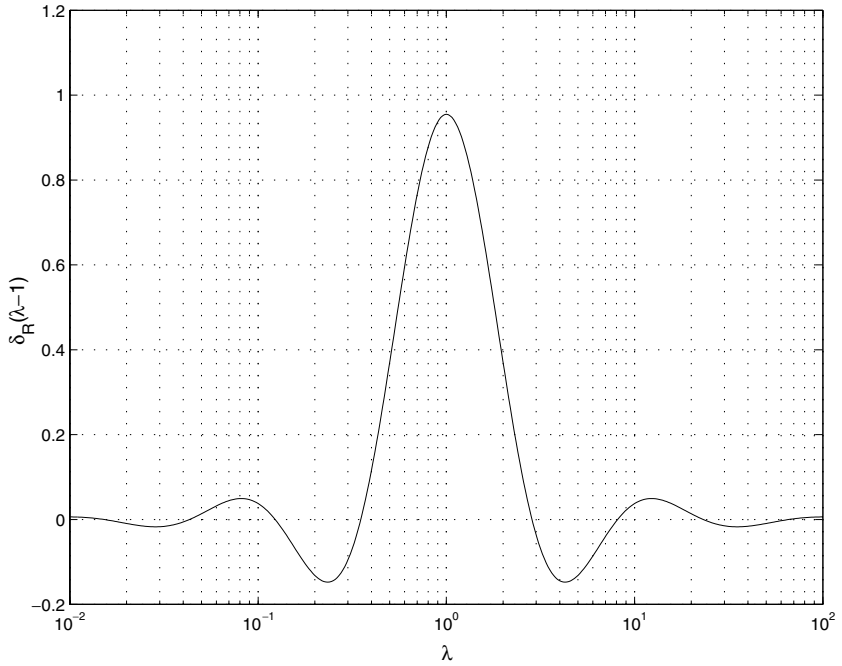

Fig. 1. Function $\delta_R(\lambda - 1)$ obtained from Laplace transform $F(t) = \exp(-t)$.

and $\lambda_0 = \lambda_{\text{right}} \exp(-\pi/R)$. Theoretically in monoexponential case the obtained values of λ_0 are the same. In multiexponential case the calculated values are different, which allow us to conclude that more than one exponential decay is present.

In the case of double-exponential decays, a transient and its regularized inverse Laplace transform will be $F(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$, $f_{\text{R}}(\lambda) = A_1 \delta_{\text{R}}(\lambda - \lambda_1) + A_2 \delta_{\text{R}}(\lambda - \lambda_2)$, respectively. Then, we can determine decay rates λ_i and amplitudes A_i by nonlinear least squares fitting of $f_{\text{R}}(\lambda)$ with a sum of functions $\delta_{\text{R}}(\lambda - \lambda_i)$ using the values λ_i calculated from graph's zeroes as an initial approximation.

If $y^{(k)}$ denote the values of the regularized inverse Laplace transform of the transient that were calculated N times at the points $\lambda^{(k)}$, then the parameters in question can be found by minimizing the following function:

$$g(\lambda_1, \lambda_2) = \sum_{k=1}^{N} \left[y^{(k)} - A_1(\lambda_1, \lambda_2) \delta_{\text{R}}(\lambda^{(k)} - \lambda_1) - A_2(\lambda_1, \lambda_2) \delta_{\text{R}}(\lambda^{(k)} - \lambda_2) \right]^2, \tag{13}$$

where amplitudes A_1, A_2 are obtained by least-squares method for any fixed values λ_1, λ_2.

Note, that analytical background of the proposed method [13–15], unlike all other methods for regularized inversion of real-valued Laplace transforms [4–7,9], is crucial for definition of minimization problem (13). In examples below decay rates and amplitudes are obtained by minimizing $g(\lambda_1, \lambda_2)$ with the help of Matlab's function Fminunc.

3. Numerical implementation

For performing calculations using above given formulae we need to find an appropriate value of parameter R. Although the use of optimal value of parameter R results in better accuracy, it is not critical for the method being considered.

In the discrete case, variation in R mainly results in change of functions $\delta_{\text{R}}(\lambda - \lambda_i)$. In the continuous case, the optimal value of parameter R is close to a linear function of a number n of correct digits in input data [15], and it lies, approximately, in the interval $n/2 < R_{\text{opt}} < n$. All calculations given in the next section were performed with $R = 10$ in the case of noise-free transients (double precision of input data), and $R \approx n$ in the case of noisy transients.

In order to obtain a regularized inverse Laplace transform of the transient one needs to compute integral (5). Adaptive quadrature procedures tend to be very effective in practice [12]. An adaptive quadrature algorithm that takes into consideration function's $\Pi(R, x)$ features [14] has been developed for computing integral (5). The effective use of the adaptive quadrature assumes that integrand is smooth and can be obtained at any $t > 0$. On the contrary, only noisy values of $F(t)$ for predefined set of points for $t < T$ (T is the data acquisition time) are known from experiment.

This problem can be resolved by finding a curve that fits experimental data. Since a transient $F(t) \to \text{const.}$ as $t \to \infty$, the same should be true for approximation function. Such an approximation can be found using different approaches. For examples given in this paper, a transient has been transformed into a more suitable form using substitutions $x = \exp(-bt)$ (discrete case) and $x = b/(t + b)$ (continuous case). In both cases the parameter b has been selected so that function $F(x)$ becomes slightly concave. Fig. 2 shows a transient $F(t)$ and function $F(x)$ that is more suitable for approximation.

Then, least-square approximation to the function's $F(x)$ noisy data by a spline with a few degrees of freedom can be found. This step was performed with the help of Matlab's spline toolbox by selecting knots at $[0, 0.2, 0.4, 0.6, 0.8, 1]$. After approximation function $F_{\text{appr}}(t)$ is found, we can calculate integral (5) using $\tilde{F}(t) = F_{\text{appr}}(t) - F_{\text{appr}}(\infty)$. Obviously that function $\tilde{F}(t)$ is not affected by baseline offset presence.

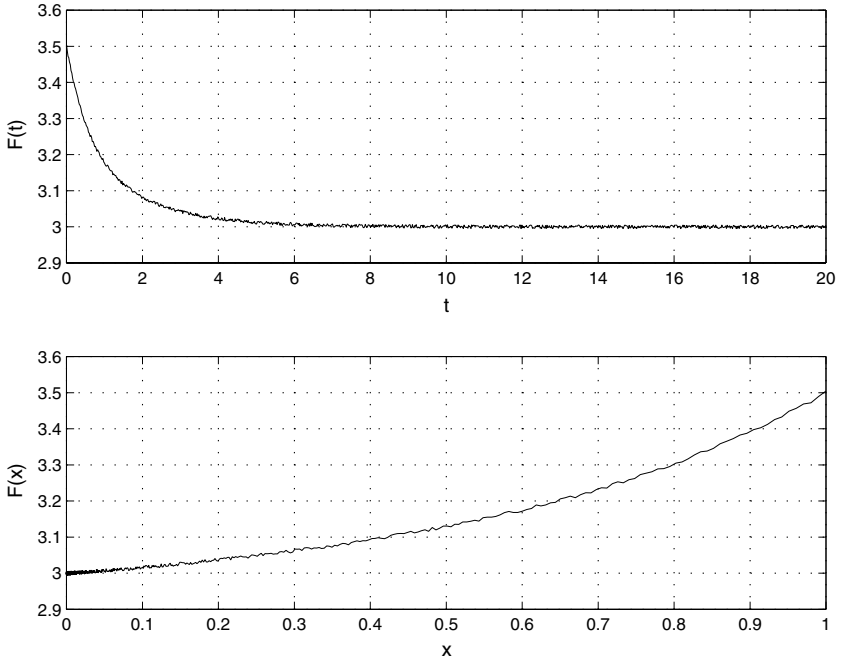

Fig. 2. Noisy transient $F(t) = 0.25\exp(-0.6t) + 0.25\exp(-1.8t) + 3$ and function $F(x)$ obtained with the help of substitution $x = \exp(-t/2)$.

The values of noisy transient were simulated by: $F_{\exp}(t_i) = F(t_i) + \theta\varepsilon_i$, where $-1 \leqslant \varepsilon_i \leqslant 1$ are uniformly distributed random numbers. Value of parameter θ has been selected in accordance with SNR: $\theta = (F(0) - B)/\mathrm{SNR}$.

4. Double-exponential analysis

4.1. Noise-free transient

First, consider numerical examples by simulating double-exponential decays with double precision of input data and equal amplitudes:

$$F(t) = \exp(-t) + \exp(-\lambda_2 t). \tag{14}$$

Graphs of the regularized inverse Laplace transforms of the transient (14) for $\lambda_2/\lambda_1 = 1.6$ and $\lambda_2/\lambda_1 = 1.3$ are given in Fig. 3. As seen from the graphs, in the case where $\lambda_2/\lambda_1 = 1.6$ the regularized inverse Laplace transform has two central maxima, and graph becomes more symmetrical for $\lambda_2/\lambda_1 = 1.3$. In both cases, dissymmetry of graphs clearly indicates the presence of more than one exponential decay.

When $\lambda_2/\lambda_1 = 1.6$, we can find decay rates initial approximation by determining abscissas of the main maxima from the graph: $\lambda_1^0 \approx 1, \lambda_2^0 \approx 1.73$. Then, finding the minimum of function (13), we will get final results: $\lambda_1 \simeq 0.99999998$, $A_1 \simeq 1.0000037$, $\lambda_2 \simeq 1.59999998$, $A_2 \simeq 1.0000025$. The errors in determining transient's parameters are of order 10^{-8} for decay rates, and of order 10^{-6} for decay amplitudes.

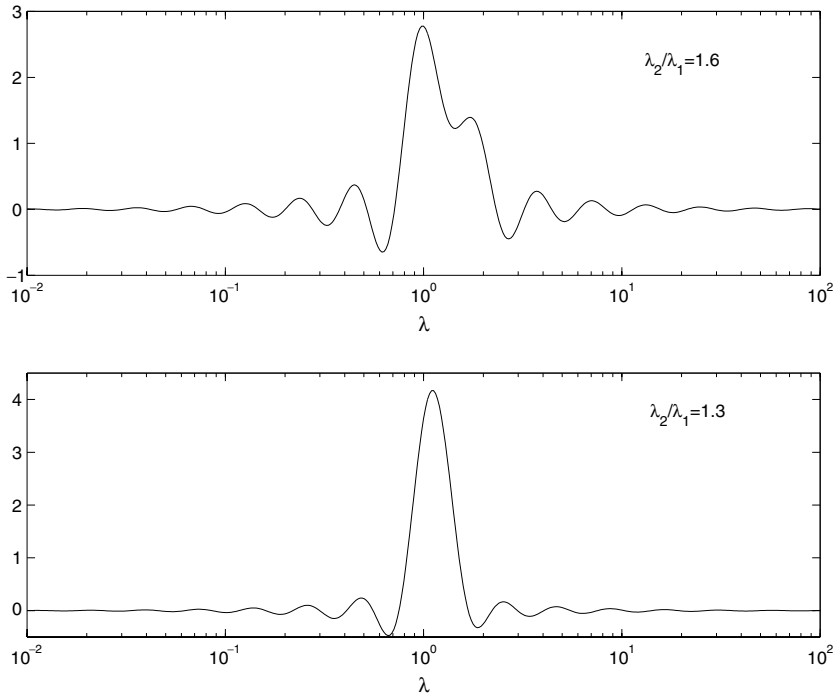

Fig. 3. Regularized inverse Laplace transform of $F(t) = \exp(-t) + \exp(-\lambda_2 t)$, $\lambda_2 = 1.6$ and $\lambda_2 = 1.3$, $R = 10$.

When $\lambda_2/\lambda_1 = 1.3$, initial approximation of the decay rates can be obtained by analyzing function's zeroes ($\lambda_{\text{left}}, \lambda_{\text{right}}$) that surround the main maximum. Let us assume that one of them is close to a corresponding zero of $\delta_R(\lambda - \lambda_1)$, and another one is close to a zero of $\delta_R(\lambda - \lambda_2)$. With this assumption the initial approximation of the decay rates becomes: $\lambda_1^0 \approx 1.02$, $\lambda_2^0 \approx 1.1$. Then, the search for the minimum of function (13) gives: $\lambda_1 \simeq 1.0000016$, $A_1 \simeq 1.0000118$, $\lambda_2 \simeq 1.30000289$, $A_2 \simeq 0.9999923$.

In case where $\lambda_2/\lambda_1 \leqslant 1.3$ the graph of regularized inverse Laplace transform becomes more symmetric (see Fig. 4). However, two exponential decays still can be resolved. When $\lambda_2/\lambda_1 = 1.1$ we have the following initial approximation: $\lambda_1^0 \approx 1.038$, $\lambda_2^0 \approx 1.059$, and final result: $\lambda_1 \simeq 1.000006$, $A_1 \simeq 1.000137$, $\lambda_2 \simeq 1.1000082$, $A_2 \simeq 0.999865$.

As it can be seen, the obtained results are better than the ones that are known from literature. Indeed, from review [10] it appears that two exponential decays can be resolved from noise-free transient if $\lambda_2/\lambda_1 \geqslant 1.5$.

It is interesting to find a resolution limit of the considered approach. If $\lambda_1 = 1$, $\lambda_2 = 1.05$, the initial approximation is: $\lambda_1^0 \approx 1.016$, $\lambda_2^0 \approx 1.032$. The final results are still satisfactory: $\lambda_1 \simeq 0.99987$, $A_1 \simeq 0.99458$, $\lambda_2 \simeq 1.04985$, $A_2 \simeq 1.0054$.

In the case where $\lambda_1 = 1$, $\lambda_2 = 1.02$ we have the following initial approximation: $\lambda_1^0 \approx 1.0022$, $\lambda_2^0 \approx 1.0236$; and final results are: $\lambda_1 \simeq 1.00247$, $A_1 \simeq 1.2817$, $\lambda_2 \simeq 1.02345$, $A_2 \simeq 0.7183$. In this last case the relative error in determination of decay amplitudes, approximately is 30%.

Thus, the ratio $\lambda_2/\lambda_1 = 1.02$ can be approximately taken as the resolution limit of the presented method in the case of double precision of input data. It is interesting to mention that obtained resolution limit is less than 1.15, which referred to in [2] as theoretical resolution limit in case of double precision of input data and infinite domain.

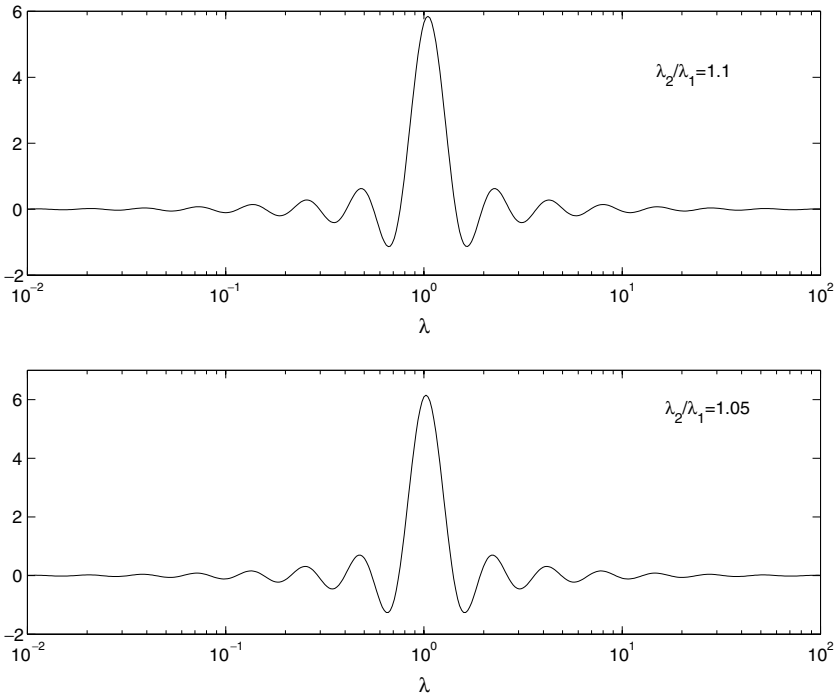

Fig. 4. Regularized inverse Laplace transform of $F(t) = \exp(-t) + \exp(-\lambda_2 t)$, $\lambda_2 = 1.1$ and $\lambda_2 = 1.05$, $R = 10$.

4.2. Noisy transient

Consider the following simulation of experimental data:

$$F(t) = \frac{1}{4}\exp(-0.6t) + \frac{1}{4}\exp(-\lambda_2 t) + B + \theta\varepsilon_i, \tag{15}$$

where $-1 \leqslant \varepsilon_i \leqslant 1$ are uniformly distributed random numbers.

As first example consider the case where $B = 3$, $\theta = 0.005$, $\lambda_2 = 1.8$, that is $\lambda_2/\lambda_1 = 3$ and $\mathrm{SNR} = (F(0) - B)/\theta = 100$. This case has been reported as a resolution reached with the help of Tikhonov regularization method [19] and some other methods without presence of the baseline offset. The presence of the baseline offset usually results in a higher sensitivity to noise and lower resolution [10]. For the baseline insensitive correlation method, two exponential components can be resolved if $\lambda_2/\lambda_1 = 3.4$ and $\mathrm{SNR} > 900$ [11].

Let us simulate noisy values $F(t_i)$, $1 \leqslant i \leqslant N$ in $N = 1000$ points equidistantly placed on an interval $0 \leqslant t \leqslant 20$ and find least-square approximation to the noisy data. Using statistical reasoning we may assume that the approximating function represents the transient with error $\varepsilon \approx 0.001$. Therefore, we can calculate regularized inverse Laplace transform using values $R \approx 3$. The results are given in the left-hand side of Table 1. As can be seen from Table 1, the obtained values for decay rates and amplitudes are stable and quite satisfactory.

The right-hand side of Table 1 shows results obtained for the same transient, in case where the noise level is 3 times greater ($\theta = 0.015$, $\mathrm{SNR} \approx 30$) and the number of simulated data points within the same time

Table 1
Parameter restoration of the transient $F(t) = \frac{1}{4}\exp(-0.6t) + \frac{1}{4}\exp(-1.8t) + 3$

$\lambda_2/\lambda_1 = 3$, SNR = 100, $N = 1000$					$\lambda_2/\lambda_1 = 3$, SNR = 30, $N = 10{,}000$				
R	λ_1	A_1	λ_2	A_2	R	λ_1	A_1	λ_2	A_2
2.0	0.5857	0.2393	1.7497	0.2599	2.5	0.5999	0.2431	1.7213	0.2515
2.5	0.5906	0.2434	1.7809	0.2573	3.0	0.6036	0.2475	1.7349	0.2437
3.0	0.5972	0.2488	1.8325	0.2559	3.5	0.6135	0.2523	1.7585	0.2345
3.5	0.6054	0.2549	1.9107	0.2586	4.0	0.6265	0.2576	1.8038	0.2215

Table 2
Parameter restoration of the transient $F(t) = \frac{1}{4}\exp(-0.6t) + \frac{1}{4}\exp(-1.2t) + 2$

$\lambda_2/\lambda_1 = 2$, SNR = 100, $N = 1000$					$\lambda_2/\lambda_1 = 2$, SNR = 100, $N = 10000$				
R	λ_1	A_1	λ_2	A_2	R	λ_1	A_1	λ_2	A_2
2.0	0.5326	0.1634	1.0399	0.3314	3.0	0.5892	0.2299	1.1419	0.2651
2.5	0.5307	0.1600	1.0314	0.3336	3.5	0.6009	0.2420	1.1610	0.2515
3.0	0.5330	0.1612	1.0308	0.3316	4.0	0.6208	0.2638	1.2104	0.2295

frame is increased to $N = 10{,}000$. As it could be seen from Table 1 the restored values of decay rates and amplitudes are as accurate as in first example for SNR = 100 and $N = 1000$.

Next, consider the transient (15) with parameters $\lambda_2 = 1.2$, $B = 2$, $\theta = 5 \times 10^{-3}$, that is $\lambda_2/\lambda_1 = 2$ and SNR = 100. The results for $N = 1000$ are shown in the left-hand side of Table 2. As seen from the table, in this case the error of output results increased substantially in comparison with first example. Nevertheless, the ratio is $\lambda_2/\lambda_1 \approx 2$. It is under the resolution limit [2] for given SNR = 100. From this observation one can conclude that parameters are estimated poorly. We can try to improve results with the help of increasing the number of simulated data points by 10 times within the same time frame. The results indicated on the right-hand side of Table 2 show significant improvement of the output.

Thus, the method being considered has advantages over other known methods. The possibility to use approximating function offers opportunity to improve SNR and solve the problem by measuring more data, whereas for other known methods "the increasing number of data points results in an increase of computational time without any improvement in resolution" [10, p.1240].

5. Continuous spectral function

As it was mentioned above a continuous spectral function $f(\lambda)$ can be found with some degree of accuracy by calculating integral (5). In case of continuous spectral function, a transient usually tends to a constant much slower, which results in significant increasing of the time frame in which data is acquired.

Following [3], consider restoration of a gamma distribution, but with baseline offset presence:

$$F(t) = 1.0 + 256/(4+t)^4 + \theta\varepsilon_i, \quad f(\lambda) = 128\lambda^3\exp(-4\lambda)/3. \tag{16}$$

First, let us simulate $N = 20{,}000$ noisy data points within the interval $0 \leqslant t \leqslant 98$ with $\theta = 0.005$. Again, we may assume that approximating function represents $F(t)$ with error of order 10^{-4}. Therefore, we can safely use $R \simeq 4$ while calculating integral (5). The results of calculations are shown in Fig. 5 (dotted line). As it is seen from the graph, the obtained function $f(\lambda)$ is negative for $t > 2.8$, which contradicts with the meaning of spectral function. From this observation we can conclude that spectral function was estimated roughly.

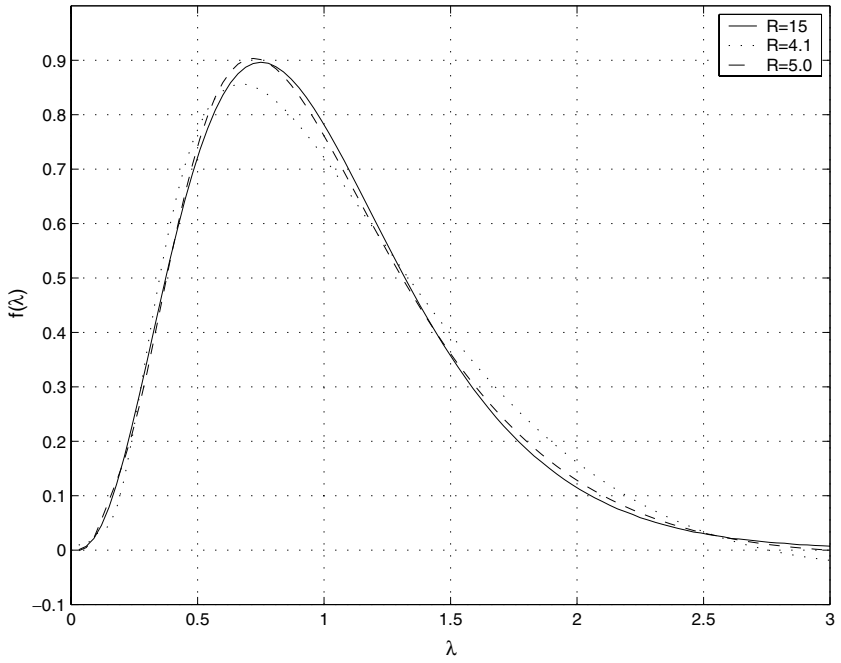

Fig. 5. Restoration of a gamma distribution (16) from double precision input data (full curve), and approximations obtained using $N = 20{,}000$ (dotted curve) and $N = 100{,}000$ (dash curve) data points.

In order to obtain more accurate results let us find approximation using $N = 100{,}000$ data points. The results are shown in Fig. 5 (dash line). In this case the function $f(\lambda)$ is positive, so we may assume that obtained results are satisfactory. Graph in Fig. 5 shows also results obtained for $R = 15$ and double precision of input data.

Thus, with the help of the proposed method it is possible to find a spectral function from noisy data. It is worth mentioning that in the proposed method no assumptions about type of distribution were made, which is an advantage over methods that fit $f(\lambda)$ with predefined set of functions [1].

Note that features of the proposed method can be studied analytically in the case of gamma distribution [13–15]. Let us demonstrate those features considering spectral function with two maxima:

$$\begin{aligned} F(t) &= \exp(-\sqrt{0.5t}) + 256/(4+t)^4, \\ f(\lambda) &= \frac{1}{\sqrt{\pi}(2\lambda)^{3/2}} \exp(-1/8\lambda) + 128\lambda^3 \exp(-4\lambda)/3. \end{aligned} \tag{17}$$

The results of restoration, obtained for $R = 15$, $R = 6$ and $R = 5$, are shown in Fig. 6. As can be seen from Fig. 6, graphs obtained with $R = 5$ and $R = 6$ are practically coincident with each other, and $f(\lambda) > 0$ as it should be. Having this in mind one can conclude that spectral function has been found with acceptable accuracy.

On the other hand, consider another spectral function with two maxima in similar places:

$$\begin{aligned} F(t) &= \frac{0.5}{(1+t/32)^6} + \frac{0.5}{(1+3t/64)^{12}}, \\ f(\lambda) &= \frac{32^6}{5!2}\lambda^5 \exp(-32\lambda) + \frac{(64/3)^{12}}{11!2}\lambda^{11} \exp(-64\lambda/3). \end{aligned} \tag{18}$$

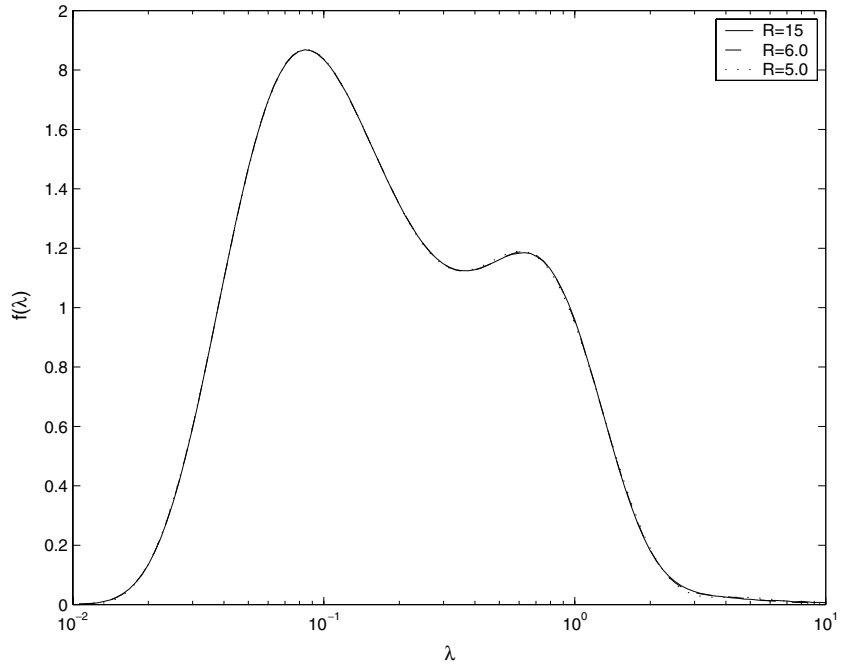

Fig. 6. Restoration of spectral function form the transient (17) for $R = 15$ (full curve), $R = 6$ (dash curve) and $R = 5$ (dotted curve).

The results of restoration are shown in Fig. 7. As seen from Fig. 7, obtained spectral function is negative for some $\lambda > 1$, which indicates that the value of parameter R is lower, than it is necessary for accurate results. Comparing graphs obtained for $R = 6$ and $R = 5$, it is easy to see that functions differ the most in areas of extrema. Observing the trend of graphs' changes, one can assume that spectral function in question has sharper peaks.

The last two examples illustrate features of the proposed method discussed in [13] that are intuitively clear: for the same accuracy of input data the lesser errors are seen for more monotonic and smooth functions. Redrawing graph 7 in coordinates $(\lambda, f(\lambda))$ (see Fig. 8), one can observe that for the same input accuracy the sharper peaks can be more accurately restored for smaller λ values than for larger ones.

6. Conclusion

Summing the discussion above we can state that regularized numerical inversion of real-valued Laplace transforms can be successfully used for exponential analysis problem solving in discrete and continuous cases.

An acceptable value for conjugate regularization parameter R can be found by estimating input data inaccuracy. The results obtained using $R \approx n$ (n is a number of correct digits in input data) are stable and nearly as accurate as possible for given SNR.

The method is tolerant to the baseline offset and allows to resolve two exponential decays with ratio λ_2/λ_1 close to theoretical resolution limit for given SNR.

The application of a spline least-square approximation to the noisy data allows to improve SNR and output results by increasing the number of input data points. An acceptable approximating function can be found with the help of standard tools, although some additional research may be required, especially in the

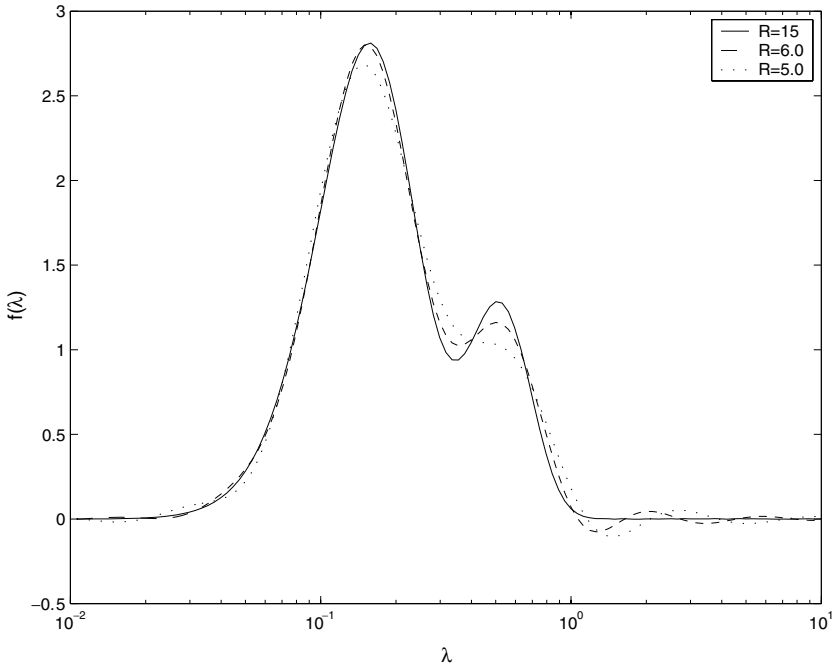

Fig. 7. Restoration of spectral function from the transient (18) for $R = 15.0$ (full curve), $R = 6.0$ (dash curve) and $R = 5.0$ (dotted curve).

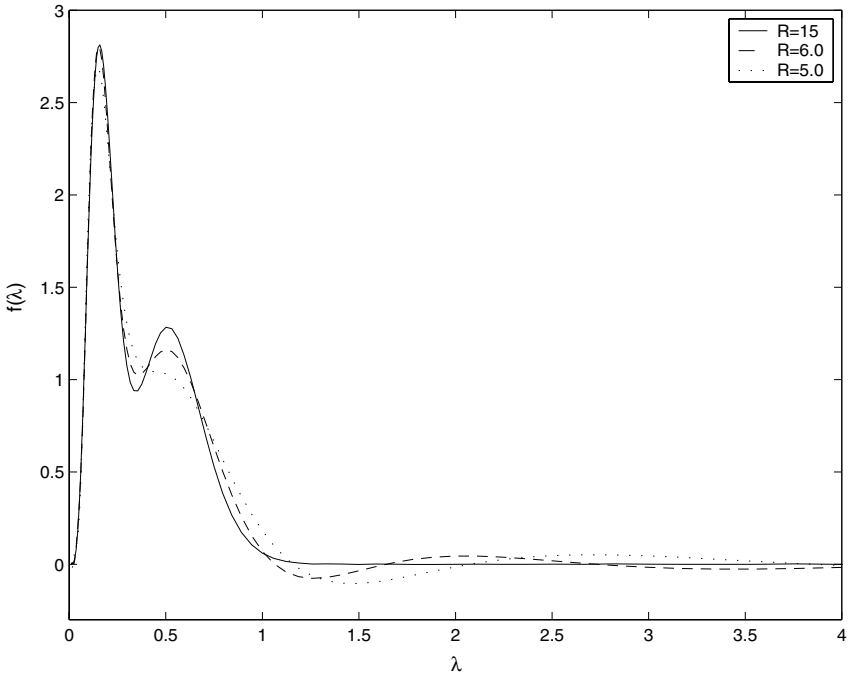

Fig. 8. Graph 7 in coordinates $(\lambda, f(\lambda))$.

continuous case. It is worth to emphasize that usage of more accurate approximation is beneficial for the presented method. Nevertheless, usage of any reasonable approximation does not affect its vital capacity.

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References

[1] P. Barone, A. Ramponi, G. Sebastiani, On numerical inversion of Laplace transforms for nuclear magnetic resonance relaxometry, Inverse Problems 17 (2001) 77.
[2] M. Bertero, P. Boccacci, E.R. Pike, On recovery and resolution of exponential relaxation rates from experimental data I, Proc. R. Soc. A 383 (1982) 15.
[3] M. Bertero, P. Brianzi, E.R. Pike, On recovery and resolution of exponential relaxation rates from experimental data: Laplace transforms inversions in weighted spaces, Inverse Problems 1 (1985) 1.
[4] P. Brianzi, M. Frontini, On regularized inversion of the Laplace transform, Inverse Problems 7 (1991) 355.
[5] D.E. Chauveau, A.C.M. van Rooij, F.H. Ruymgaart, Regularized inversion of noisy Laplace transforms, Adv. Appl. Math. 15 (1994) 186.
[6] L. D'Amore, A. Murli, Regularization of a Fourier series method for the Laplace transform inversion with real data, Inverse Problems 18 (2002) 1185.
[7] C.W. Dong, A regularization method for numerical inversion of the Laplace transform, SIAM J. Numer. Anal. f30 (1993) 759.
[8] G. Doetsch, Handbuch der Laplace-transformation, Birkhäuser, Basel, 1950.
[9] M. Iqbal, On spline regularized inversion of noisy Laplace transforms, J. Comput. Appl. Math. 83 (1997) 39.
[10] A.A. Istratov, O.F. Vyvenko, Exponential analysis in physical phenomena, Rev. Sci. Instrum. 70 (1999) 1233.
[11] A.A. Istratov, The resolution limit of traditional correlation functions for deep level transient spectroscopy, Rev. Sci. Instrum. 68 (1997) 3861.
[12] D. Kahaner, C. Moler, S. Nash, Numerical Methods and Software, Prentice-Hall, Englewood Cliffs, NJ, 1988.
[13] V.V. Kryzhniy, Direct regularization of the inversion of real-valued Laplace transforms, Inverse Problems 19 (2003) 573.
[14] V.V. Kryzhniy, Regularized inversion of integral transformations of Mellin convolution type, Inverse Problems 19 (2003) 1227.
[15] V.V. Kryzhniy, On regularized numerical inversion of Laplace transforms, J. Inverse Ill-posed Problems (to appear).
[16] S.L. Marple Jr., Digital Spectral Analysis with Applications, Prentice-Hall, Englewood Cliffs, NJ, 1987.
[17] D.D. Nolte, E.E. Haller, Optimization of the energy resolution of deep level transient spectroscopy, J. Appl. Phys. 62 (1988) 900.
[18] H. Stehfest, Algorithm 368: Numerical inversion of Laplace transforms, ACM 13 (1970) 47.
[19] V.I. Tarasov, The method for analysis of multicomponent exponential decay curves, Optoelectron. Instrum. Data Process. 2 (1992) 117.
[20] A.N. Tikhonov, V. Yu, Arsenin, Solutions of Ill-posed Problems, Winston and Sons, Washington, DC, 1977.
[21] A.N. Tikhonov, V.B. Glasko, About approximate solution of Fredholm integral equations of the first kind, Zh. Vychisl. Mat. Mat. Fiz. 4 (1964) 564.