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PEAK PARAMETERS DETERMINATION USING FRACTIONAL DERIVATIVE SPECTROMETRY

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Abstract. In this paper we propose a simple mathematical tool in terms of fractional derivative spectrometry (DS) to determine the overlapping bands spectral parameters. It is possible due to several positive effects of DS connected with the behavior of its zero-crossing and maximal amplitude. For acquiring a stable and unbiased FD estimate we utilize the statistical regularization method. Along with the well-known distributions such as Lorentzian, Gaussian and their linear combinations the Tsallis distribution is used as a model to correctly indentify overlapped bands.

The derivative spectrometry (DS) method is a simple and attractive instrument in analytical spectroscopy that provides a score of positive effects such as separating overlapping peaks, background noise suppression. It is possible due to the considerable increase in contrast to the derivative spectrum compared to original one. Even small changes of monotonicity in the initial spectrum are clearly recorded by its derivatives. Traditionally, DS has been successfully applied to the determination of a number of completely unresolved peaks and their positions (Salakhov and Kharintsev, 2001).

However, the application of integer-order derivatives is not always sufficient, since shapes of n-th and $(n+1)$-th differentiation curves are not close to each other in a qualitative sense and, therefore, some information on the data under study can be lost. On the other hand, as the differentiation order increases a high-frequency color noise amplifies strongly, so that the signal-to-noise ratio decreases sharply. This circumstance does not allow to utilize higher order derivatives for studying spectra. In order to weaken these restrictions and to make DS more flexible for processing and interpretation of the data it is necessary to generalize the DS method for non-integer (fractional) orders, that will be refered to as *fractional* derivative spectrometry (FDS). A fractional derivative (FD) provides information “gain” allowing one to follow the smooth variation in the analyzed data (Schmitt, 1998; Salakhov and Kharintsev, 2001). This redundancy can be rather useful when studying the behavior of non-simple points, for example, zero-crossing, extremum value, etc.

This paper demonstrates some effects of FD to be used to extract such spectral parameters as half-width, amplitude, shape, etc. and for further assigning overlapping peaks. Here we will not concern the determination of a number of individual components and their positions that have been the subject of intensive study (Salakhov and Kharintsev, 2001).

Traditionally, we will use the finite-difference expression known as Grunwald and Letnikov formulation of FD (Oldham and Spanier, 1974; Miller and Ross, 1993)

$$D_c^{\nu}\left[f(x)\right] \equiv \frac{d^{\nu} f(x)}{d(x-c)^{\nu}} = \lim_{N\to\infty} \Delta x_N^{-\nu} \sum_{k=0}^{N-1} c_k^{\nu}\ f\left(x - k\Delta x_N\right), \tag{1}$$

$$c_k^{\nu} = \frac{\Gamma(k-\nu)}{\Gamma(-\nu)\,\Gamma(k+1)},$$

where ν is a fractional exponent ($-\infty < \nu < \infty$), N is a number of samples, $\Delta x_N = (x-c)/N$, x variation range: $c \le x < \infty$.

In order to demonstrate the effects of FD let us consider the ordinary Gaussian peak centered at $\bar{x}$ with a half-width of σ and amplitude of A: $G(x) = A\exp\left[-(x-\bar{x})^2/2\sigma^2\right]$. Figure 1 shows variation of the Gaussian contour during its differentiation at different ν values as an example of applying the FD operator to spectral curves. The dynamics of a zero-crossing point is indicated with circles in Fig. 1. The peak parameters were $\bar{x}=0$, $A=1$ and $\sigma=0.1$. A number of samples was equal to 200.

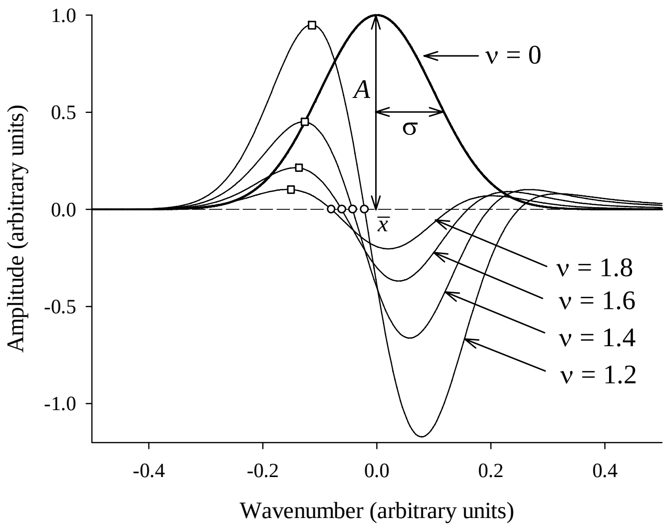

Fig. 1: Fractional derivatives of a Gaussian peak at various ν.

Interested in studying the behavior of the zero-crossing we need to solve the following equation

$$D^{\nu}\left[G(x)\right]\Big|_{x=x_0} = 0. \tag{2}$$

Thus, we obtain the zero-crossing $x_0(\nu)$ as a function of ν:

$$x_0(\nu) = \bar{x} - (\nu - 1)\sigma . \tag{3}$$

From the obtained linear dependence such parameters as a position $\bar{x}$ and a half-width σ can be easily evaluated. This procedure will be referred to as estimator I.

The next step is to study the behavior of a maximal value of FD indicated by square boxes in Fig. 1. The position of this point $x_{\max}$ can be found by solving the equation

$$D^{1+\nu}\left[G(x)\right]\Big|_{x=x_{\max}} = 0 . \tag{4}$$

Table 1. Estimators I* and II** for some types of distributions (see text).

	Gaussian	Lorentzian	Tsallis
	$A\mathrm{e}^{-\frac{(x-\bar{x})^2}{2\sigma^2}}$	$\dfrac{A}{(x-\bar{x})^2+\sigma^2}$	$A\left[1+\dfrac{q-1}{3-q}\cdot\dfrac{(x-\bar{x})^2}{\sigma^2}\right]^{-\frac{1}{q-1}}$
$x_0(\nu)^*$	$\bar{x}-(\nu-1)\sigma$	$\bar{x}-\dfrac{(\nu-1)}{\sqrt{3}}\sigma$	$\bar{x}-(\nu-1)\dfrac{\left(2q+3-q^2\right)^{1/2}}{(1+q)}\sigma$
$H(\nu)^{**}$	$\ln[F(\nu)]-\ln(\nu)$	$\ln[F(\nu)]-(3/2)\ln(\nu+2)$	$\ln[F(\nu)]+\dfrac{q}{q+1}\ln(\nu q-\nu+1)$
a	$-\ln(\sigma)-1$	$-\ln(\sigma)-\ln(2)$	$-\ln(\sigma)-\dfrac{1}{2}\ln(3-q)+\ldots$ $\ldots+\dfrac{3}{2}\ln(1+q)-\ln(2q-1)$
b	$\ln(A)+1/2$	$-2\ln(2)-2\ln(\sigma)+\ln(A)$	$\ln(A)-\dfrac{2-q}{q-1}\ln(1+q)+\ldots$ $\ldots+\dfrac{1}{q-1}\ln(2)-\ln(2q-1)$

After that we derive the maximal amplitude

$$F(\nu) \equiv D^{\nu}\left[G(x_{\max})\right] = A\nu\,\sigma^{-\nu}\,\mathrm{e}^{-(\nu-1/2)} \tag{5}$$

which contains the parameters of A and σ. It is convenient to linearize this relationship. After not complicated manipulations we rewrite Eq. (5) as:

$$H(\nu) = a\nu + b, \tag{6}$$

where we introduced the following denotations: $H(\nu) = \ln\left[F(\nu)\right] - \ln(\nu)$, $a = -\ln(\sigma) - 1$ and $b = \ln(A) + 1/2$. The magnitudes of a and b represent a slope and intercept, respectively. Note that these formulas are valid for the Gaussian peak only. We can interpret the magnitude of $H(\nu)$ as an eigencoordinate of a Gaussian peak. This approach will be referred to as estimator II. In contrast to estimator I, this permits to extract both the amplitude and the half-width.

Finally, we have two estimators based on features of FD that allow to determine, at least, the half-width in an independent way. There is no preference between them while a peak shape is *a priori* known. Otherwise the using of both is required.

By analogy with above stated, we can describe the behavior of nonsimple points for a peak having an arbitrary shape. In table 1 some types of distributions are considered. In particular, outputs of the estimators for the Tsallis (1999) distribution are given. In our case this approach enables to generalize the well-known distributions such as Gaussian and Lorentzian ones by varying a nonextensivity parameter q in the range of $0 < q < 3$. The Tsallis distribution recovers these when $q = 1$ and $q = 2$, respectively.

Tt was difficult before to say about a peak shape without additional research. Conventional nonlinear fitting methods based on the OLS approach are unsuitable to unambiguously assign the overlapped peaks. This implies that a composite band can be decomposed into elementary components of a given shape with the same integral reconstruction error in a large number of ways.

To avoid this uncertainty we suppose to use both the estimators in order to identify a peak shape in such a way that the half-widths obtained by these coincide. This fitness is accomplished by varying the nonextensivity parameter q in the range of $q \in [0,3]$. In the case of lack of coincidence for any q we conclude that the Tsallis model is unsuitable to fit the overlapping peaks.

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