



Identification of Peak Positions Using Second-Order Derivative Spectra and Tikhonov Deconvolution Method: A Comparison Study

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Abstract: The dependences of the relative peak shifts of the second-order derivatives of spectral doublets and of the deconvoluted doublets on the separation of the doublet components were evaluated numerically. Doublets were composed of symmetrical Gaussian and Lorentzian lines with widely ranging relative intensities and widths. It was shown that the deconvolution method is preferable over derivative spectroscopy for precise identification of badly resolved peaks.

Keywords: Spectral peak positions; Tikhonov deconvolution method; second-order derivative spectra.

I. Introduction

Spectrometry is one of the most widespread theoretical and experimental physical methods [1]. However, overlapping spectral components (lines and bands) often complicate the practical implementation of spectrochemical analysis. This drawback is explained by the non-zero width of the instrumental function of the spectral instruments and by internal and external interactions which occur in atoms and molecules in the samples under study. Resolution of the overlapping spectral components can be partly improved by a spectrum processing named deconvolution. The nuts and bolts of deconvolution were discussed in the critical review [2]. In our opinion deconvolution should be understood as a resolution enhancement (line sharpening by eliminating of the instrumental disturbances) and as artificial improvement of spectral resolution (pseudo deconvolution). It was shown [2] that a deconvolution algorithm must be chosen according to the problem under study. In the case of the measurement of the spectral peak positions the required resolution enhancement must ensure acceptable peak shifts from their precise values. In the case of intensity measurements, the overlapping of spectral lines must be negligible. However, in both cases the high resolved power of the deconvolution algorithm may produce wrong side lobes which give erroneous results. Only a compromise between resolution enhancement and intensity of the side lobes is possible.

Deconvolution and the second-order derivative spectroscopy [3] are the main competing methods for identification of badly resolved spectral peaks. Both methods may give errors in determination of peak positions. However, only the shifts of the peak maxima from their precise values in spectra and in the second-order derivatives of spectra have been evaluated [4, 5]. The comparison between deconvoluted spectra and their second- and forth-order derivatives was performed only qualitatively using some examples [6]. The purpose of the present study is to compare the peak shifts in spectra which were processed by applying the Tikhonov deconvolution method and the second-order differentiation.

Standard mathematical notations are used throughout the paper. Bold upper-case letters denote matrices. Upper-case and lower-case italicized letters denote scalars. All calculations were performed and the plots were built using the MATLAB program.

II. Theory

A. Models

Consider a doublet with the maxima located at $-x_0$ and x_0 , respectively:

$$D(x) = F(x + x_0) + RF((x - x_0)/r), \quad (1)$$

where $F(x)$ is the doublet line; $x = \beta i/w$; β is the line shape parameter; $i = -m, -m + 1, \dots, 0, \dots, m - 1, m$; w is the full line width at half maximum; $x_0 = \beta\delta/2$; $\delta = \Delta/w$ and $\Delta = 2i_0$ are the relative and the absolute separation of the doublet components, respectively; i_0 is the line maximum position in the i^{th} scale; R and r are the relative intensity and the relative width of the second doublet line, respectively.

We studied symmetrical Gaussian and Lorentzian functions [1]:

$$F_G(x) = \exp(-x^2), \quad (2)$$

$$F_L(x) = 1/(1 + x^2), \quad (3)$$

where $\beta_G = 2\sqrt{\ln 2}$ and $\beta_L = 2$.

B. Relative shift

The relative shift of the line position is usually measured relative to the line width. However, in practice, the widths can be evaluated very approximately because the lines are overlapping [7]. Therefore, we chose to

calculate the shifts with respect to the separation of the doublet components, which estimation can be readily obtained visually. In this case, the relative shift of the resolved doublet peak for the i^{th} component has the form:

$$\xi_i = (x_{mi} - (-1)^i x_0) / 2 x_0, \quad (4)$$

where $i = 1, 2$ and x_{mi} is the measured point of i^{th} -peak maximum.

It must be pointed out that the shifts of non-ideal derivative peaks depend also on the accuracy of the numerical differentiation [3]. Smoothing a noisy spectrum causes broadening of the derivative spectra, which results in decreased resolution and the shifts different from those obtained for ideal derivatives. However, these effects are significant for the doublet separation close to the resolution limit where the shifts are very large [5]. Using such poorly-resolved derivatives for precise peak identification leads to erroneous results.

Calculation errors of x_{mi} depend on the spectral sampling interval (h). E. g., for $h = 0.002$ and $x_0 = 0.4$ the maximum uncertainty of ξ_i is equal to 0.25%. This error decreases if h decreases. However, it is impractical to further decrease the h -value since the number of the spectral points will be very large. Therefore, for improving precision of the peak position determination, a spectral curve in the vicinity of the peak maximum was approximated by the 3rd-order polynomial. The first derivative of this polynomial is equal to zero in the point x_{mi} .

C. Assessment of doublet resolution

It was found that peak shifts in spectra and in the second-order derivative spectra depend in a complex way on the relative separation of the doublet components [5]. The separation of the doublet lines is minimal at the resolution limit. Resolution increases with increasing separation, however peak shifts do not necessarily decrease.

There are many different methods of evaluation of resolution in spectra [8]. In this study resolution was evaluated on the basis of the relative depth of the dip in the center of a symmetrical doublet (Fig.1a):

$$I_d = \Delta D / D_{max}, \quad (5)$$

where $\Delta D = D_{max} - D_{min}$.

From a statistical point of view ΔD must be roughly three- to fivefold higher than the standard deviations of the doublet noise. For asymmetrical doublet I_d is calculated relative to the intensity of the weakest peak (Fig. 1b). In this case the dip is shifted from the doublet center, and I_d increases if $R < 1$. Unfortunately, Eq. 5 is not applicable to the second-order derivatives of asymmetrical doublets due to the impact of the strong satellite of the main doublet peak (Fig. 1c).

Evaluation of the resolution limit of deconvoluted doublets (DDs) is not a straightforward task since the resolution enhancement depends on the acceptable intensity of the side lobes in deconvoluted spectrum [2]. The intensity of the side lobes was evaluated on the basis of the standard deviation of the DD wings [2] which was not exceed five standard deviations of the doublet noise.

D. Tikhonov-regularized deconvolution

It can be suppose that the measured spectrum is a convolution of a true spectrum with the kernel function

$K(x - x')$ [2]:

$$F_{ms}(x) = \int_{-\infty}^{\infty} K(x - x') F_{tr}(x') dx', \quad (6)$$

where x is the abscissa of a spectrum (e. g., wavelength). The properties of Eq. 6 have been discussed in [2].

Using Tikhonov regularization method [9] Eq. 6 can be approximated by the following matrix equation using numerical integration:

$$(K^T K + \alpha I) F_{tr} = K^T F_{ms}, \quad (7)$$

where K is the kernel matrix, T is the transpose symbol, α is the regularization parameter, and I is the identity matrix. Each row of matrix K includes the discretized kernel function which is successively shifted from the low to the high integration limit in Eq. 6.

The kernel functions are

$$K_G(x - x') = F_G((x - x')/r_K), \quad (8)$$

$$K_L(x - x') = F_L((x - x')/r_K) \quad (9)$$

for Gaussian and Lorentzian doublets, respectively. Parameter r_K controls resolution enhancement [2].

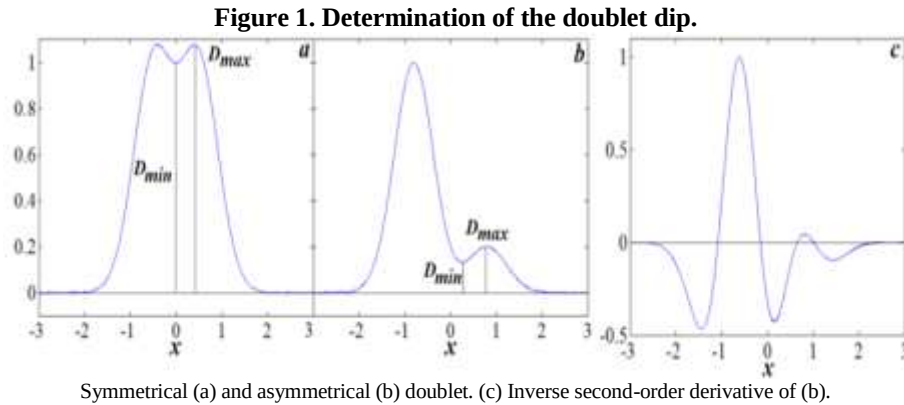
The need for regularization arises from the fact that matrix $K^T K$ is ill-conditioned (condition number is too large) which results in great sensitivity of the solution of Eq. 7 (for $\alpha = 0$) to small perturbations of F_{ms} . The true spectrum is estimated by

$$\hat{F}_{tr} = (K^T K + \alpha I)^{-1} K^T F_{ms} \quad (10)$$

The quasi optimal values of the regularization parameter and the parameter r_K were chosen as a compromise between the maximum resolution enhancement and the acceptable level of side lobes.

III. Computer modeling

It is obvious that peak shifts of a noise-free DD are negligible to those shifts in the second-order derivative of the initial doublet (SOD) due to the high resolution enhancement [2]. Therefore, the comparison of peak shifts must



be performed using noisy doublets. However, their signal-to-noise ratio should be high enough, so that the derivatives obtained numerically are very close to the ideal derivatives [3]. In this case the resolution enhancement of these deconvoluted doublets is also high enough [2]. Random normal noise with a mean of zero and a standard deviation of 0.001 was added to the doublet (1). The noise was smoothed using the multiple-pass three point moving average filter. The SODs were obtained using polynomial differentiation. Each statistically independent numerical experiment was repeated 100 times. The mean values and the standard deviations of the measured parameters were calculated. The errors were evaluated at the confidence interval 95%.

IV. Results and discussion

If a separation of the components of a symmetrical doublet increases, then the relative intensity of the central dip (I_d) (Eq. 5) also increases, and the relative peak shift (ξ) decreases for a given processing method (Table 1). However, the shifts in the SODs are larger than in DDs although the I_d values are similar (compare bold italic values in Table 1). There are no clear relationships between I_d and ξ values for asymmetrical doublets which were deconvoluted by the Tikhonov method (Tables 2 and 3). However, the large scattering of I_d around their mean values in repeated measurements is indicative of the effect of noise on I_d values.

The relative shifts were evaluated for the minimal x_0 values that ensure a clear visible resolution of the SODs and DDs (Tables 2 and 3). The values which exceed 10% are bold underlined numbers and were colored by blue and by red for DDs and SODs, respectively. Dependences $\xi(x_0)$ for DDs are given in Figs 2-6. The starting points on the x -axes (x_0^{start}) of some plots $\xi(x_0)$ are less than those that are in the Tables 2 and 3. For these x_0^{start} values the SODs are not resolved.

The following conclusions can be drawn from obtained results:

1. Peak shifts in DDs and SODs often have opposite directions (signs).
2. Number of unacceptable relative shifts (more than 10%) is equal to 11 and 31 for Gaussian DDs and SODs, respectively (Table 2). Corresponding values for Lorentzians are 9 and 25 (Table 3). So, the peak position identification of badly resolved lines using DDs is preferable to that of SODs.
3. The dependences $\xi(x_0)$ for DDs increase very quickly near resolution limit, and the shifts may be very large (Figs. 2-6) as was found in [4].
4. The relationships between dependences $\xi(x_0)$ and DDs parameters (Figs. 2-6) are similar to those that have been established in [4]. For example, if $r > 1$, then the more intensive wide second (right) line causes the larger shifts of the first (left) line; however, its own shifts will be smaller. This effect is significantly enhanced by broader second line. If $r < 1$, then the more intensive wide first line causes the larger shifts of the second line; however, its own shifts will be smaller. This effect is significantly enhanced by broader first line.
5. The peak shifts of the weak wide lines of Gaussian DDs are less than 1% (indicated by bold italic numbers in Table 2). These lines overlap with the side lobes which vary in repeated measurements. That is why, the shifts are strongly scattered around their mean values.

Table 1. Relative intensities of the central dip and the relative peak shifts in symmetrical doublets deconvoluted by the Tikhonov method and by the second-order differentiation.

Doublet		Gaussian				Lorentzian			
x_0		0.37	0.38	0.39	0.40	0.28	0.29	0.30	0.31
DD	$I_d, \%$	6.3±0.6	8.7±0.7	11.3±0.7	13.9±0.7	8.8±0.2	12.1±0.2	15.6±0.2	19.3±0.2
	$ \xi , \%$	11.2	9.1	7.4	6.1	8.4	6.2	4.6	3.4
SOD	$I_d, \%$	1.7±0.3	6.4±0.2	13.0±0.3	21.1±0.3	0.5±0.2	3.6±0.1	8.3±0.2	14.3±0.2
	$ \xi , \%$	22.8	14.7	8.7	4.4	30.0	20.8	13.8	8.6

6. Obtained results show that, in general case, deconvolution and the second-order differentiation are useful preprocessing steps for resolution enhancement, suppression of spectral artefacts [3,10] and for finding approximate values of spectral line parameters of unresolved contours. In subsequent processing of data the information needed for spectrochemical analysis is obtained by using chemometric tools.

Table 2. Relative peak shifts (%) of Gaussian doublets deconvoluted by the Tikhonov method and by the second-order differentiation.

r	1/3		0.5		1		2		3	
R	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
0.2	0.1	-8.7	0	-7.2	0.1	-2.0±0.3	0.7	-0.6±0.3	0.6	-0.5±0.7
	-0.3	5.8	-0.8	6.5	-1.6	25.6	0	15.7	0	15.0±0.2
	$x_0=0.52, I_d=4.7±0.1$		$x_0=0.53, I_d=2.9±0.2$		$x_0=0.55, I_d=13±4$		$x_0=0.80, I_d=6.5±0.7$		$x_0=0.90, I_d=7.6±0.8$	
1/3	-0.1	-11.1	-0.10	-11.1	0.3	-4.1±0.2	1.3	-1.3±0.4	0.9	-0.2±0.5
	-2.3	1.6	-3.8	2.2	-2.3	21.3	0.2	23.1	0.1	16.3
	$x_0=0.44, I_d=3.8±0.1$		$x_0=0.45, I_d=1.8±0.1$		$x_0=0.49, I_d=7±2$		$x_0=0.70, I_d=5±2$		$x_0=0.85, I_d=6.2±0.4$	
0.5	2.8	-20.6	2.0	-22.4	1.2	-7.2±0.2	2.1	-0.7±0.3	1.6	-0.9±0.6
	-21.3	-16.4	-14.3	-11.8	-1.9	8.4	0.3	20.6	0.3	24.7
	$x_0=0.24, I_d=1.6$		$x_0=0.32, I_d=1.2±0.1$		$x_0=0.44, I_d=4±2$		$x_0=0.69, I_d=6.2±0.7$		$x_0=0.75, I_d=3.2±0.7$	
1	2.7	-7.9	6.8	8.9	11.2±0.1	11.3±0.1	5.9	-4.0±0.4	5.1	-2.1±0.2
	-35.9	-5.2	-28.1	-5.0	22.8	-22.8	2.0	29.6	0.8	24.8
	$x_0=0.27, I_d=3.0$		$x_0=0.31, I_d=0.8±0.1$		$x_0=0.37, I_d=6.3±0.6$		$x_0=0.57, I_d=1.5±0.7$		$x_0=0.71, I_d=1.4±0.2$	
2	5.2	-3.1	4.6	-3.0	7.3±0.1	-1.3	15.5	-4.7	11.8	-3.4
	-38.4	-1.3	-33.5	-1.3	-11.7	1.4	6.1	25.1	1.9	27.0
	$x_0=0.30, I_d=4.3$		$x_0=0.35, I_d=1.9±0.1$		$x_0=0.44, I_d=4.5±0.7$		$x_0=0.52, I_d=1.3±0.3$		$x_0=0.65, I_d=1.3±0.1$	
3	7.2	-1.8	4.1	-1.6	4.2	-0.3	15.3	0	20.1	-5.8
	-37.9	-0.4	-34.6	-0.5	-22.9	1.8	1.2	6.1	3.3	30.2
	$x_0=0.32, I_d=5.3$		$x_0=0.37, I_d=2.2±0.1$		$x_0=0.49, I_d=9.2±0.6$		$x_0=0.71, I_d=0.8±0.3$		$x_0=0.60, I_d=0.8±0.1$	
5	0.5	-1.1	1.1	-0.8	2.1	-0.1	9.8	0	16.9	-2.9±0.2
	-31.5	0.3	-32.8	-0.1	-27.3	1.2	-2.9	0.5	6.8	40.4
	$x_0=0.36, I_d=2.7$		$x_0=0.40, I_d=3.5±0.1$		$x_0=0.55, I_d=6.7±0.7$		$x_0=0.91, I_d=1.0±0.4$		$x_0=0.50, I_d=2.1±0.2$	

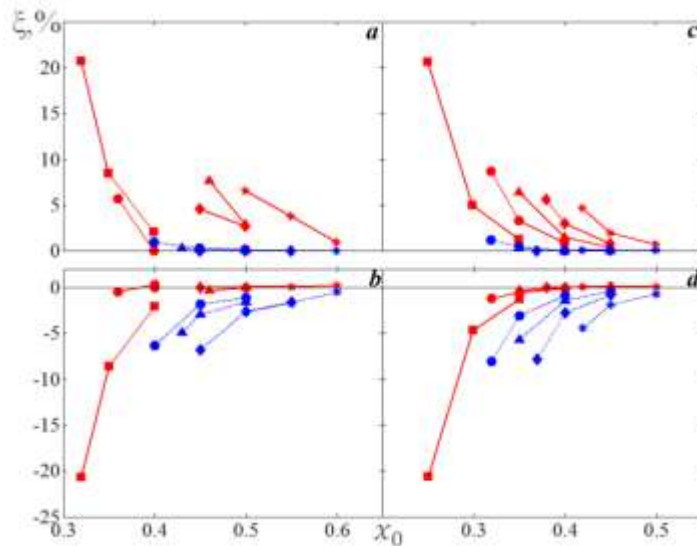
The shifts in DDs and in SODs are given in the first and in the second rows, respectively. The negligible errors are not shown.

Table 3. Relative peak shifts (%) of Lorentzian doublets deconvoluted by the Tikhonov method and by the second-order differentiation.

r	1/3		0.5		1		2		3	
R	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
0.2	0	-8.3	0	-10.2	-1.1	-8.2	0.2	-2.7±0.2	-0.1	-3.0±0.7
	-0.2	2.3	-0.7	4.9	-0.3	16.8	0.1	43.3±0.2	-0.1	41.9±0.3
	$x_0=0.57, I_d=3.8±0.1$		$x_0=0.48, I_d=1.8±0.1$		$x_0=0.37, I_d=1.1±0.4$		$x_0=0.51, I_d=5±1$		$x_0=0.65, I_d=8±1$	
1/3	0	-11.3	0.1	-10.1	-1.0	-4.7	0.6	-2.4±0.2	0.2	-4.1±0.4
	1.0	2.1	-2.0	2.9	-0.2	3.4	0.3	33.4	0	49.7±0.2
	$x_0=0.47, I_d=2.1$		$x_0=0.42, I_d=3.4±0.1$		$x_0=0.36, I_d=7.4±0.4$		$x_0=0.48, I_d=4.9±0.8$		$x_0=0.55, I_d=3±1$	
0.5	0.3	-17.4	1.0	-14.7	-0.5	-4.6	1.2	-2.9±0.1	0.4	-2.6±0.3
	-4.1	0.5	-4.9	-0.8	0.7	-6.6	0.6	28.3	0.1	38.2±0.1
	$x_0=0.38, I_d=0.60$		$x_0=0.35, I_d=2.3$		$x_0=0.34, I_d=9.7±0.3$		$x_0=0.45, I_d=3.8±0.6$		$x_0=0.55, I_d=2.8±0.6$	
1	9.7	-11.3	6.1	-7.2	8.4	-8.3	2.9	-4.5	1.5	-3.3±0.2
	-13.3	-2.0	-10.7	-1.5	29.9	-30.0	2.5	18.1	0.9	32.2±0.1
	$x_0=0.31, I_d=1.3$		$x_0=0.32, I_d=3.1$		$x_0=0.28, I_d=8.8±0.2$		$x_0=0.40, I_d=2.2±0.3$		$x_0=0.47, I_d=1.4±0.4$	
2	6.3	-2.8	6.0	-2.0	4.0	-0.8	9.0	-4.8	4.0	-3.6±0.1
	-17.3	0	-17.8	0	6.5	-0.7	8.5	3.7	2.6	28.0
	$x_0=0.35, I_d=1.1$		$x_0=0.35, I_d=1.3$		$x_0=0.34, I_d=9.4±0.2$		$x_0=0.36, I_d=2.5±0.1$		$x_0=0.43, I_d=1.3±0.2$	
3	5.1	-2.0	4.9	-0.8	4.5	-0.3	17.3	-4.8	6.8	-3.6±0.1
	-18.9	0.1	-21.1	0.2	-4.3	0.2	18.3	-5.0	4.8	21.0
	$x_0=0.37, I_d=1.1$		$x_0=0.37, I_d=1.4$		$x_0=0.36, I_d=7.0±0.2$		$x_0=0.34, I_d=3.8±0.1$		$x_0=0.41, I_d=1.5±0.1$	
5	2.7	-0.9	2.8	-0.6	5.8	0.2	14.1	-0.1	13.9	-5.5
	-19.4	0.1	-23.4	0.2	-17.5	1.4	5.4	2.2	10.7	10.9
	$x_0=0.40, I_d=2.4$		$x_0=0.40, I_d=3.0$		$x_0=0.38, I_d=3.8±0.1$		$x_0=0.48, I_d=0.8±0.1$		$x_0=0.37, I_d=0.9±0.1$	

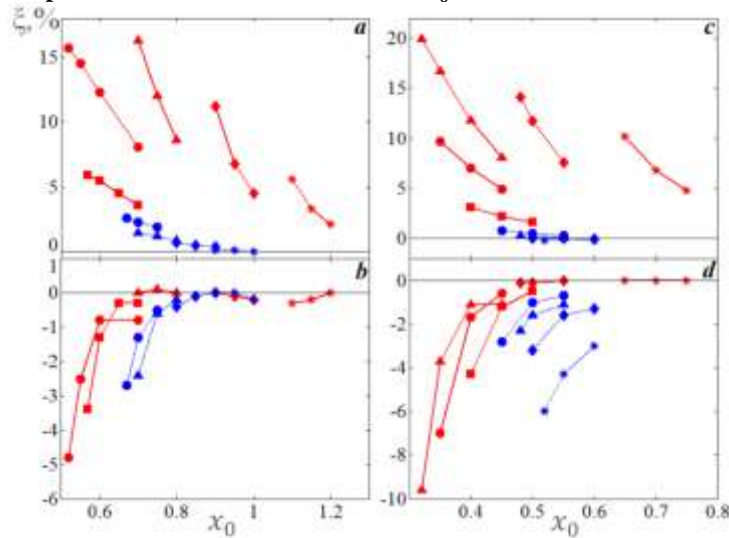
The shifts in DDs and in SODs are given in the first and in the second rows, respectively. The negligible errors are not shown.

Figure 2. Dependences of the relative shift on x_0 for deconvoluted doublets. $r = 1$.



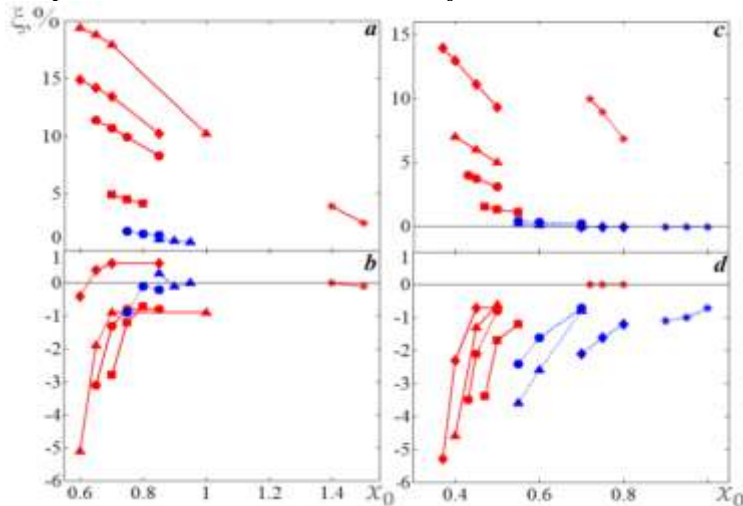
Gaussian (a, b) and Lorentzian (c, d) doublets. Left and right components are shown in the top and in the bottom panels, respectively. $R=1(\blacksquare)$, $2(\bullet)$, $3(\blacktriangle)$, $5(\blacklozenge)$, $10(*)$, $0.5(\bullet)$, $1/3(\blacktriangle)$, $0.2(\blacklozenge)$, and $0.1(*)$.

Figure 3. Dependences of the relative shift on x_0 for deconvoluted doublets. $r = 2$.



Gaussian (a, b) and Lorentzian (c, d) doublets. Left and right components are shown in the top and in the bottom panels, respectively. $R=1(\blacksquare)$, $2(\bullet)$, $3(\blacktriangle)$, $5(\blacklozenge)$, $10(*)$, $0.5(\bullet)$, $1/3(\blacktriangle)$, $0.2(\blacklozenge)$, and $0.1(*)$.

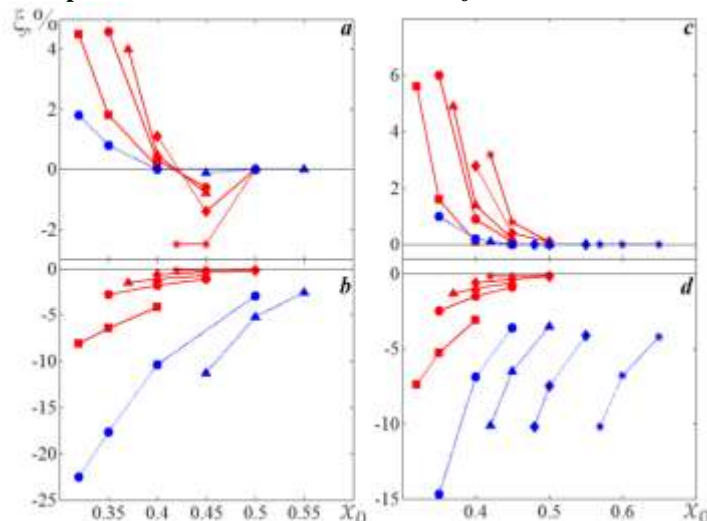
Figure 4. Dependences of the relative shift on x_0 for deconvoluted doublets. $r = 3$.



Gaussian (a, b) and Lorentzian (c, d) doublets. Left and right components are shown in the top and in the bottom panels, respectively.

$R=1(\blacksquare), 2(\bullet), 3(\blacktriangle), 5(\blacklozenge), 10(*)$, $0.5(\bullet)$, $1/3(\blacktriangle)$, $0.2(\blacklozenge)$, and $0.1(*)$.

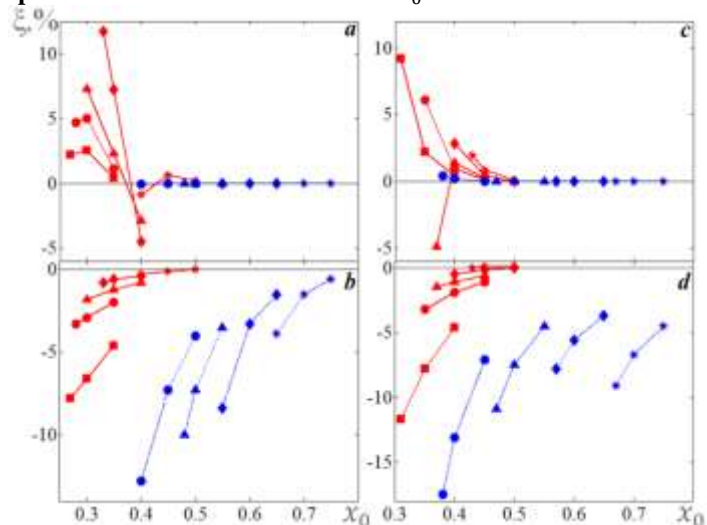
Figure 5. Dependences of the relative shift on x_0 for deconvoluted doublets. $r = 0.5$.



Gaussian (a, b) and Lorentzian (c, d) doublets. Left and right components are shown in the top and in the bottom panels, respectively.

$R=1(\blacksquare), 2(\bullet), 3(\blacktriangle), 5(\blacklozenge), 10(*)$, $0.5(\bullet)$, $1/3(\blacktriangle)$, $0.2(\blacklozenge)$, and $0.1(*)$.

Figure 6. Dependences of the relative shift on x_0 for deconvoluted doublets. $r = 1/3$.



Gaussian (a, b) and Lorentzian (c, d) doublets. Left and right components are shown in the top and in the bottom panels, respectively.

$R=1(\blacksquare), 2(\bullet), 3(\blacktriangle), 5(\blacklozenge), 10(*)$, $0.5(\bullet)$, $1/3(\blacktriangle)$, $0.2(\blacklozenge)$, and $0.1(*)$.

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