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Mathematical Analysis of Asymmetrical Spectral Lines

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Abstract: *Mathematical analysis of seven non-integral theoretical and phenomenological forms of asymmetrical lines was performed by their decomposition into the product of symmetrical and asymmetrical parts. The decomposition errors were evaluated. For the purpose of comparison, the x coordinate of each profile was normalized to the uniform scale. The dependences of the maximum peak positions, the maximum intensities, the widths of the lines, and their symmetrical parts on the asymmetry parameter were obtained. The ratio of the absolute values of the first-order derivative extremes of the line profile and the ratio of the satellite amplitudes of the second-order derivative were proposed as new measures of line asymmetry. The new concept of the integral angular function of the asymmetrical part was introduced. The scaled difference between the left- and the right-hand (relative to the peak maximum) components of this function was found to be the most sensitive indicator of line asymmetry. The obtained equations may be useful for modeling asymmetrical lines in spectroscopic studies.*

Keywords: *spectroscopy; asymmetrical lines; line form parameters; normalization; approximation*

I. Introduction

The form of the spectral components (lines and bands) and their parameters, such as location, intensity, width and statistical moments, constitute the main source of spectrochemical information [1]. It was shown theoretically [1] that the observed form of the isolated symmetrical components in an optical spectrum (in the absence of background) is accounted for by the impact of physical (Heisenberg's uncertainty principle, Doppler and collision-induced broadening) and instrumental factors. However, in practice, the assumption of the line symmetry is often violated for such reasons as: intermolecular interactions in complex systems (IR- [2] and fluorescence spectra [3] of large molecules in condensed phase), the impact of fluorescence on Raman spectra [1], mixing of reflection and absorption bands of IR components [4], the sample heterogeneities and instrumental factors (inhomogeneities of the static magnetic field arising from imperfect shimming in NMR-spectroscopy [5, 6], the intrinsic properties of the radiation source in astronomy [7], heterogeneity of the photoionization absorption in optically thick laser-induced plasma [8], and intermolecular interactions induced by strong vibrational excitation in laser spectroscopy of gases [9].

The study of asymmetrical lines is of great importance in ESR spectroscopy [10]. The relationship between the form of the central part of spectral profiles and their wings, on the one hand, and physicochemical processes in gases and liquids, on the other hand, was studied both theoretically and experimentally [11-13]. The determination of the cis:trans ratio in some biologically active compounds [14] is an interesting example of the practical application of the ESR-spectrum line asymmetry.

Theoretical expressions for asymmetrical profiles are often quite complicated and, therefore, cannot be applied in practice [15]. For this reason, asymmetrical peaks are commonly described by empirical functions. For example, a phenomenological model of the asymmetrical shape of X-ray photoelectron peaks was developed and studied thoroughly [16]. A large number of mathematical functions of asymmetrical spectroscopic and chromatographic peaks was described in review [17] and research article [18]. However, no general approach to the mathematical analysis of asymmetrical line profiles has been introduced yet. This approach would allow establishing the main patterns of the physical-chemical processes by searching common properties of their spectral line models. *The choice of the appropriate mathematical model is particularly important for decomposition of complex spectral contours. The evaluation of the measurement errors in detecting the positions of overlapping peaks prior to deconvolution also relies on the proper selection of the line model. Such selection of the "best" model out of numerous model functions is very difficult and is usually performed empirically. Such selection requires the concept of the model proximity to the experimental spectral contour (e.g., the minimum least squared error). In this connection, the method of comparing and choosing the parameters of different models based on a unified mathematical description would be very helpful. The goal of the present study was developing such method using some simple models of asymmetrical lines used in spectroscopy. The models did not include integral equations [17]. The apparent line asymmetry is sometimes caused by uncorrected background in the spectra and by unresolved structure of spectral lines and bands. These issues require special consideration and lie out of the scope of the present study.*

For simplicity, we use the short term "line" instead of the long term "line and band". The standard algebraic notations are used throughout the article. All calculations were performed and the plots were built using the MATLAB program.

II. Theory

In general, the form of an asymmetrical spectral line can be modeled by function

$$hS(v, v_m, \mathbf{p}), \quad (1)$$

where h is the maximal line amplitude (line height), v is abscissa of the spectrum (e.g., the wavelength), v_m is the x -coordinate of the line maximum, $\mathbf{p}$ is the vector of the line-form parameters which define the full line width at half-maximum (FWHM, w ,) and the line asymmetry.

The mathematical analysis of the non-standardized Function 1 aimed at comparing different line profiles, proves to be too complicated. To simplify the analysis, (1) is transformed to the new dimensionless variable:

$$x = \beta v_i / w, \quad (2)$$

where β is a line shape parameter and $i = -m, -m+1, \dots, 0, \dots, m-1, m$. Transformation (2) is valid for all line models described by Function 1 that include dimensionless asymmetry coefficients. However, asymmetry coefficients which have dimension are also sometimes included for the sake of better fitting the theoretical line profile to the experimental one. For example, the Parabolic-Variance Modified Gaussian model [18] contains coefficient, whose unit measure is $1/v$. These coefficients are physically unreasonable and, therefore, the corresponding models are not considered here.

Without loss of generality, we can assume that $h = 1$. So,

$$hS(v, v_m, \mathbf{p}) \rightarrow F(x, \tau, \mathbf{p}_{tr}), \quad (3)$$

where τ is the line asymmetry parameter and $\mathbf{p}_{tr}$ is the vector of additional line-form parameters. These parameters appear when F is described as a combination of elementary components (e.g., a product of Gaussian and Lorentzian lines). For symmetrical lines, the maximum of F is located at $x_m = 0$. In the general case, x_m and w may depend on the line asymmetry coefficient. This fact must be taken into account when using Eq. 3. For study of its properties, function F is decomposed into the product of its symmetrical and asymmetrical parts:

$$F(x) = F^{sym}(x)F^{asym}(x) \quad (4)$$

While the symmetrical part is always an even function of x , the asymmetrical part is not necessary an odd function. Decomposition (4) is generally just an approximation.

Since the dependence of the line form on the line asymmetry parameter is specific for each model, a special criterion of constant asymmetry is required for the purpose of comparing different models of line form under the same conditions.

In the theory of probability and in statistics, it is common to use *skewness* as a measure of the asymmetry of the probability distribution:

$$\gamma_{as} = \mu_3 / \mu_2^{3/2}, \quad (5)$$

where μ_k is the k -central moment of distribution. It is known that the values of γ_{as} strongly depend on the range of integration when the central moments are calculated. This is an essential drawback because, in practice, the range of integration is limited by the finite wings of the observed line profiles. Therefore, instead of the skewness, we suggest using the ratios of:

the first-order derivative extremes (Fig. 1b):

$$\gamma_{d1} = F'_{max} / |F'_{min}| \quad (6)$$

and the amplitudes of the left and the right satellites in the second-order derivative (Fig. 1c):

$$\gamma_{d2} = F''_{sL} / F''_{sR} \quad (7)$$

Coefficient γ_{d2} is indicative of the line asymmetry at larger distances from the line centre than γ_{d1} . The evaluation of the symmetry measure using higher-order derivatives becomes too difficult because of the strong impact of noise. Differentiation of the line profiles is performed using the polynomial procedure [21].

III. Results and Discussion

The mathematical details of the study are presented in Appendix. Decomposition of seven model functions into the product of their symmetrical and asymmetrical parts, the positions of the line maxima, as well as the widths of the symmetrical and the asymmetrical parts are shown in Table 1.

Table 1

PMG [18]	$F_{G1}(x) = \exp(-x^2/(1-t)^2) = \exp\left(-x^2 \frac{1+t^2}{(1-t^2)^2}\right) \exp\left(-x^2 \frac{2t}{(1-t^2)^2}\right)$, where $t = \tau x$.
	$x_m = 0$, $w_{G1} = w_G / (1 - \tau^2 \ln 2) \cong w_G (1 + 0.82\tau^2)$, $w_{G1}^{sym} \cong w_G / \sqrt{(1 + 3\tau^2 \ln 2)} \approx w_G (1 - 0.70\tau^2)$, where $w_G = 2\sqrt{\ln 2}$
Stancik-G[2]	$F_{G2}(x) = \exp(-x^2[(1 + \exp(t))/2]^2) \cong \exp[-x^2(1 + 0.9300t^2)] \exp[-x^2(0.9807t + 0.5034t^3)]$
	$x_m = 0$, $w_{G2} \cong w_G / (1 - (0.25 \ln 2)\tau^2) \cong w_G (1 + 0.18\tau^2)$ $w_{G2}^{sym} \cong w_G \sqrt{(1 + 0.93\tau^2 \ln 2) / (1 + 1.86\tau^2 \ln 2)} \approx w_G (1 - 0.26\tau^2)$

Dobosh[8]	$F_{L1}(x) = \frac{\exp(\tau(1 - \arctan(x)))}{(1+x^2)} \cong \frac{\exp(\tau)}{1+x^2} \left\{ \begin{array}{l} \exp(-\tau x P(x)) \\ \exp(-\tau(\text{sign}(x)\pi/2 - (1/x)P(1/x))) \end{array} \right\}, x \leq 1, x > 1,$ $\text{where } P(x) = \frac{1+0.65591x^2+0.04055x^4}{1+0.98917x^2+0.17082x^4}.$
	$x_m = \tau/2, \quad w_{L1} \cong w_L(1 + 1.164\tau^2), \quad w_{L1}^{sym} = w_L, \quad \text{where } w_L = 2$
Stancik-L[2]	$F_{L2}(x) = \frac{1}{1 + [x(1 + \exp(t))/2]^2} = \left(\frac{1}{1+x^2} \right) \left(\frac{1+x^2}{1 + [x(1 + \exp(\tau x))/2]^2} \right) \approx \frac{\exp(-0.22t^2)}{1+x^2} \exp(-t)$
	$x_m = 0, w_{L2} \cong w_L/(1 - 0.25\tau^2) \cong w_L(1 + 0.26\tau^2), \quad w_{L2}^{sym} \cong w_L/\sqrt{1 + 0.44\tau^2} \cong w_L(1 - 0.20\tau^2)$
Log-normal[19]	$F_{LN}(x) = \begin{cases} \exp\left(-\frac{1}{\tau_{LN}} \ln^2(1-x)\right) \cong \exp\left[-\frac{1}{\tau_{LN}}\left(x^2 + \frac{11}{12}x^4\right)\right] \exp\left[-\frac{1}{\tau_{LN}}\left(x^3 + \frac{1}{2}x^5\right)\right], & x < 1 \\ 0, & x \geq 1 \end{cases}$
	$x_m = 0, \quad \begin{array}{l} w_{LN} = (1 - 1/\rho_{max})(\rho + 1/\rho), W_{LN}^{left} = const \\ w_{LN} = \rho_{max} - 1/\rho_{max} = const \\ w_{LN} = (1 - 1/\rho_{max})(\rho + 1), W_{LN}^{right} = const \end{array}, \quad \rho = \exp(\sqrt{(\ln 2)\tau_{LN}})$ $w_{LN}^{sym} \cong 4 \ln \rho (1 - (11/18) \ln \rho^2) w_{LN} / (\rho - 1/\rho) \cong k_2 \rho^2 + k_1 \rho + k_0,$ $\text{where } k_2 = -1.0618, k_1 = 2.0612, k_0 = 0.0636.$
Losev [16]	$F_{LV}(x) = \frac{2}{\exp(-(1 - \tau_{LV})x) + \exp((1 + \tau_{LV})x))} = \frac{2}{\exp(-x) + \exp(x)} \exp(-\tau_{LV}x)$
	$x_m = \frac{1}{2} \ln \frac{1 - \tau_{LV}}{1 + \tau_{LV}}, w_{LV} \cong w_{LV}^{sym} (0.98\tau_{LV}^2 - 0.094\tau_{LV} + 1.006), \quad w_{LV}^{sym} = 2 \operatorname{arccosh}(2) = 2.6339$
BWF[20]	$F_{BWF}(x) = \frac{(1 - \tau_{BWF}x)^2}{(1+x^2)} \cong \frac{\exp(-t^2)}{(1+x^2)} \exp(-2t - (2/3)t^3)$
	$x_m = -\tau_{BWF}, \quad w_{BWF} = 2\sqrt{1 + 2\tau_{BWF}^2}/(1 - 2\tau_{BWF}^2) \cong w_L(1 - 0.125\tau_{BWF} + 4\tau_{BWF}^2), \quad w_{BWF}^{sym} \cong w_L$

The following conclusions can be drawn from the data presented in Table 1:

1. For the Polynomially Modified Gaussian (PMG) ($F_{G1}(x)$ [18]) and Losev ($F_{LV}(x)$) models, the maximum peak position is shifted from zero value, the shift being dependent on the asymmetry parameter. The physical explanation of this phenomenon was given earlier [11].
2. Asymmetry causes line broadening. The dependence of the line width (FWHM) on the asymmetry parameter is well approximated by the 2nd- or the 3rd-order polynomial. The width of the symmetrical part (w^{sym}) is constant or decreases very slowly with the increase of the asymmetry parameter.
3. From the decomposition of the model functions into the product of their symmetrical and asymmetrical parts, it follows that

$$F^{sym}(-x) = F^{sym}(x) \quad (8)$$

$$F^{asym}(-x) = 1/F^{asym}(x) \quad (9)$$

Then

$$F^{asym}(x) = \sqrt{F(x)/F(-x)} \quad (10)$$

$$F^{sym}(x) = \sqrt{F(x)F(-x)} \quad (11)$$

The validity of Eqs. 10 and 11 was checked for precise decomposition of $F_{G1}(x)$ and $F_{LV}(x)$ functions. In the rest cases only numerical solution is possible.

4. Due to the exponential character of the asymmetrical part,

$$\lim_{x \rightarrow \infty} F^{asym}(-x) = \infty \quad (12)$$

$$\lim_{x \rightarrow 0} F^{asym}(x) = 0. \quad (13)$$

Because of this, the comparison of the impacts of the left and the right sides of the asymmetrical part on the line wings is very complicated. For mathematical convenience, $F^{asym}(x)$ is transformed to the following angular function (see Fig. 2):

$$\varphi(x) = \arctan(F(x)/F^{sym}(x)) = \arctan(F^{asym}(x)). \quad (14)$$

Then

$$\varphi(0) = \pi/4 \quad (15)$$

$$\lim_{x \rightarrow \infty} \varphi(x) = \pi/2 \quad (16)$$

$$\lim_{x \rightarrow 0} \varphi(x) = 0 \quad (17)$$

Function $\varphi(x)$, which reflects the impact of the asymmetrical part on the ordinate of the asymmetrical line

$$F(x) = F^{sym}(x) \tan \varphi(x) \quad (18)$$

can be formally considered as “the phase angle of asymmetry” at given point x .

Using Eq. 9, the phase shift between the line wings can be expressed as:

$$\Delta\varphi(x) = \arctan(F^{asym}(-x)) - \arctan(F^{asym}(x)) = \pi/2 - 2\arctan(F^{asym}(x)) \quad (19)$$

In the region of the line wings, function $\Delta\varphi(x)$ becomes very close to its limit value of $\pi/2$ (Eq. 16), which makes it difficult to use. To overcome this difficulty, instead of Eq. 19, we used the integral expression:

$$I_\varphi(x_m) = (1/\pi x_m) \int_0^{x_m} \Delta\varphi(x) dx = 0.5 - (2/\pi x_m) \int_0^{x_m} \arctan(F^{asym}(x)) dx \quad (20)$$

For comparison of different models the dependences $I_\varphi(\tau, x_m = \text{const})$ must be normalized to the constant value of one of the asymmetry coefficients (Eqs. 6 and 7).

5. The dependences of γ_{d1} (6) and γ_{d2} (7) on the line asymmetry parameter for all models are shown in Fig. 3, plots a, b respectively. These plots can be normalized to the similar form by scaling of the asymmetry parameter:

$$\tau_{scale} = K(\tau)\tau, \quad (21)$$

where $K(\tau) = a_2\tau^2 + a_1\tau + a_0$. For the function $F_{G1}(x)$ $K = 0.5$. In the rest cases the coefficients of $K(\tau)$ were obtained by the polynomial approximation of the array of $K(\tau_i)$ values (Fig. 4) which were calculated from equation:

$$\gamma_d\{K(\tau_i)\tau_i\} = \gamma_d^{G2}(\tau_i) \quad (22)$$

where τ_i were taken from the interval $[0.05, 0.5]$.

The results of scaling are represented in Fig. 3c. Scaling of the log-normal model to γ_d^{G2} is impossible since the maxima of the satellites of the derivative spectra do not appear in the limited region of x .

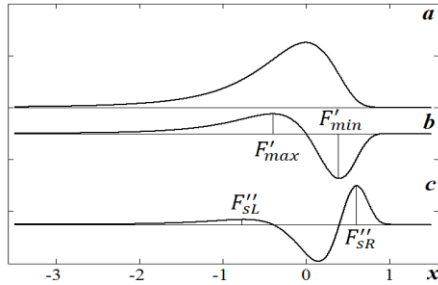


Figure 1. The asymmetrical line (a) and its first- (b) and second-order (c) derivatives.

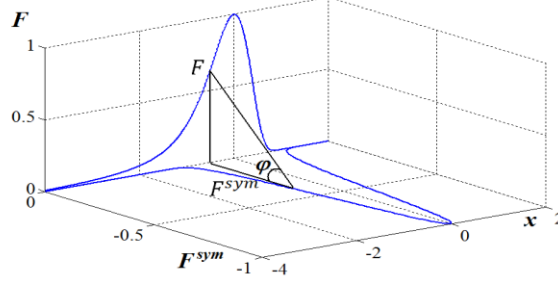


Figure 2. Definition of phase angle φ (Eq. 14).

6. $I_\varphi(\tau, x_m = \text{const})$ dependences and the dependences of the line forms on the line asymmetry parameter were normalized according to Eq. 21 (see Figs. 5 and 6, respectively). $K(\tau)$ polynomials were calculated using Eq. 22 and asymmetry ratios γ_{d1} (Eq. 6) and γ_{d2} (Eq. 7).

The identity of modified Gaussian functions $F_{G1}(x, \tau/2)$ and $F_{G2}(x, \tau)$ is illustrated by comparing plots a and b in Fig. 5. The graphs of all functions (except for F_{G1} and F_{G2}) are especially clearly distinguished in the wing regions when ratio γ_{d2} is used for normalization (compare plots b1-e1 and b2-e2 in Fig. 6). This result is accounted for by the fact that ratio γ_{d2} reflects the line asymmetry at larger distances from its centre than γ_{d1} . Plots $I_\varphi(\tau)$ were found to be most sensitive to the changes of the line forms (Fig. 5). In the future, we intend to use function $I_\varphi(\tau)$ for the analysis of asymmetrical lines.

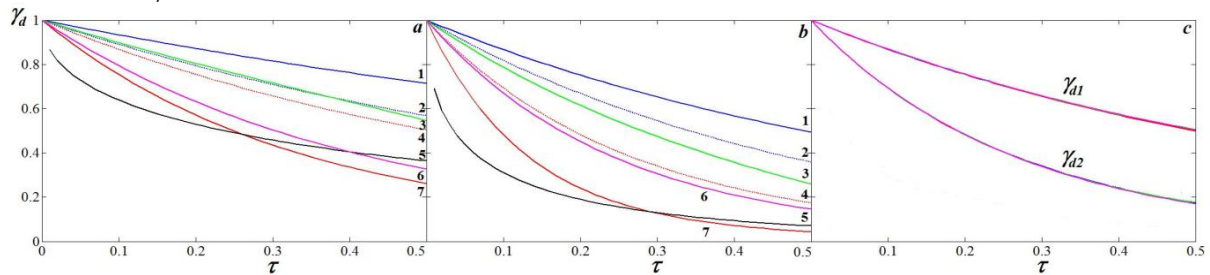


Figure 3. Non-normalized (a - γ_{d1} , b - γ_{d2}) and normalized (c) dependences of the asymmetry parameters on the asymmetry coefficient. Plots 1-7 correspond to $F_{L1}, F_{L2}, F_{LV}, F_{G2}, F_{LN}, F_{BWF}$ and F_{G1} .

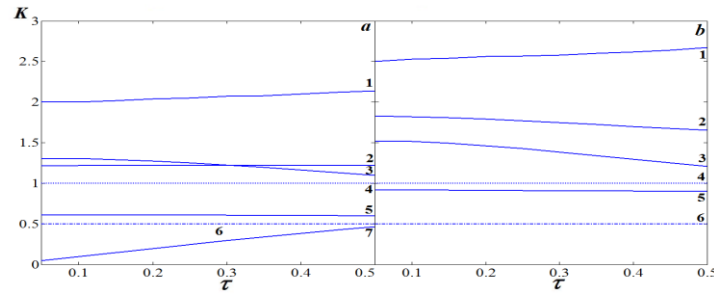


Figure 4. $K(\tau)$ dependences normalized to γ_{d1}^{G2} (a) and to γ_{d2}^{G2} (b). Plots 1-7 correspond to $F_{L1}, F_{L2}, F_{LV}, F_{G2}, F_{BWF}, F_{G1}$, and F_{LN} functions.

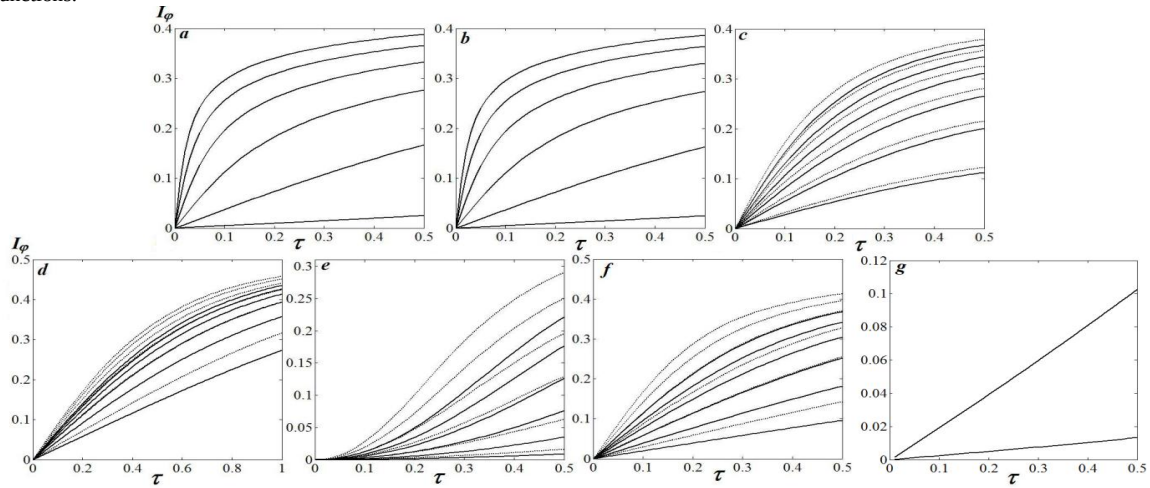


Figure 5. $I_\varphi(\tau, x_m = \text{const})$ dependences normalized to γ_{d1}^{G2} (continuous lines) and to γ_{d2}^{G2} (dotted lines) for $F_{G1}, F_{G2}, F_{LV}, F_{L1}, F_{L2}, F_{BWF}$, and F_{LN} functions (plots a-g, respectively). x_m values are equal to 0.5, 1, 1.5, 2, 2.5, and 3 (curves from bottom to top, respectively). For F_{LN} , only the values of $x_m = 0.5$ and 1 are appropriate.

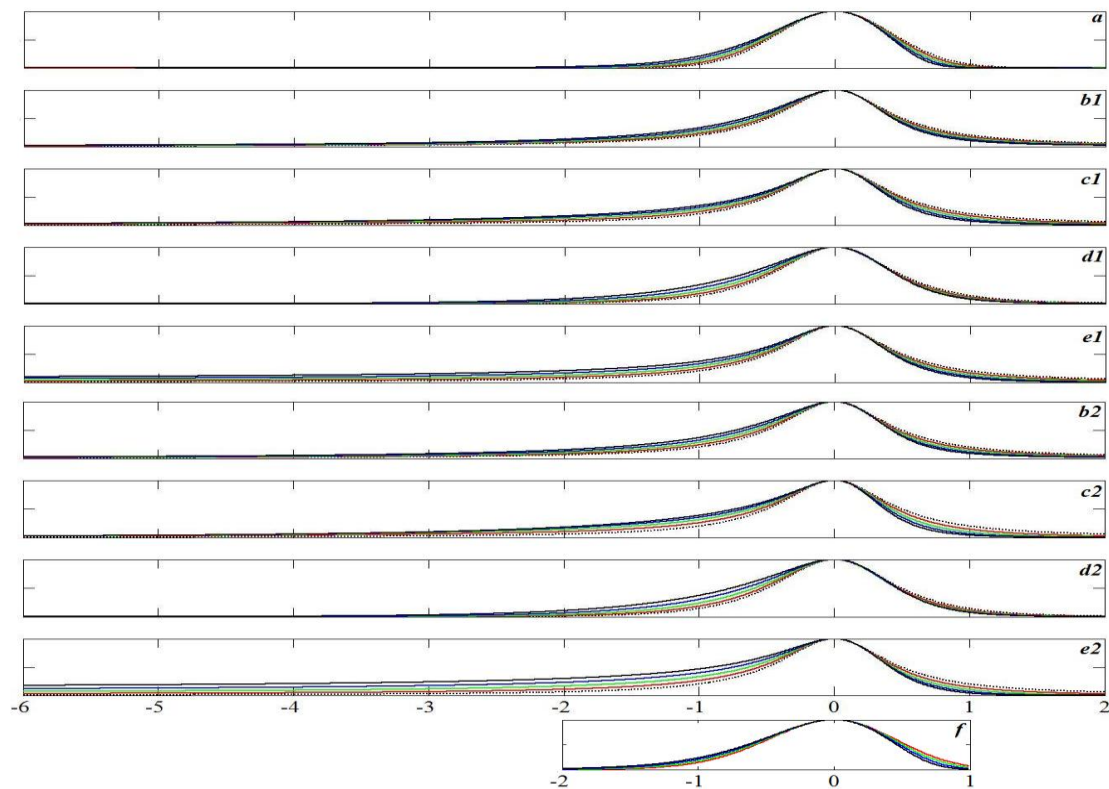


Figure 6. (a) Normalized F_{G1} and F_{G2} line forms. Pairs of F_{L1}, F_{L2}, F_{LV} and F_{BWF} line forms (curves b1-b2, c1-c2, d1-d2, and e1-e2, respectively) are normalized to γ_{d1}^{G2} and γ_{d2}^{G2} . (f) F_{LN} line form normalized to γ_{d1}^{G2} . $\tau = 0$ (dotted lines), 0.1 (red), 0.2 (green), 0.3 (blue), and 0.4 (black).

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Appendix

Decomposition of the line models into symmetrical and asymmetrical parts

In what follows, the sign of the asymmetry parameter was chosen to provide the "left-hand" asymmetry of all line models. The FWHM-values of line profiles are expressed in dimensionless units of the x -axis.

1. Gaussian function with a constant FWHM (PMG model [18]).

Taking a Taylor expansion of the exponential function, we have:

$$F_{G1}(x) = \exp(-x^2/(1-\tau x)^2) = \exp(-x^2 \sum_{i=1}^{\infty} i t^{i-1}), \quad (A1)$$

where $t = \tau x$. Eq. A1 can be expressed as the product of the symmetrical and asymmetrical parts over x :

$$F_{G1}(x) = F_{G1}^{sym}(x) * F_{G1}^{asym}(x), \quad (A2)$$

where $F_{G1}^{sym}(x) = \exp(-x^2 \sum_{i=1}^{\infty} (2i-1)t^{2(i-1)}) = \exp(-x^2 \frac{1+t^2}{(1-t^2)^2})$,

$F_{G1}^{asym}(x) = \exp(-x^2 2t \sum_{i=1}^{\infty} i t^{2(i-1)}) = \exp(-x^2 \frac{2t}{(1-t^2)^2})$. The summing was performed using formulas [22].

It is easily to show that $x_m = 0$ is the point where $F_{G1}(x)$ reaches the maximum value.

The FWHM of the $F_{G1}(x)$

$$w_{G1} = 2\sqrt{\ln 2}/(1 - \tau^2 \ln 2) \cong 2\sqrt{\ln 2}(1 + 0.82\tau^2) \quad (A3)$$

is the solution of

$$w_{G2} = x_{left} + x_{right}$$

$$\begin{aligned} (x_{left})^2 / (1 + \tau x_{left})^2 &= \ln 2 \\ (x_{right})^2 / (1 - \tau x_{right})^2 &= \ln 2 \end{aligned} \quad (A4)$$

It was found that the absolute error of the approximation (A3) to the correct value is $|\Delta| \leq 0.0128$ for $\tau \leq 0.5$. The relative error is less than 0.54%.

The FWHM of the $F_{G1}^{sym}(x)$

$$w_{G1}^{sym} \cong 2\sqrt{\ln 2} / \sqrt{(1 + 3\tau^2 \ln 2)} \approx 2\sqrt{\ln 2} (1 - 0.70\tau^2) \quad (A5)$$

is the solution of

$$\left(\frac{w_{G1}^{sym}}{2}\right)^2 \frac{1 + \left(\tau \frac{w_{G1}^{sym}}{2}\right)^2}{\left(1 - \left(\tau \frac{w_{G1}^{sym}}{2}\right)^2\right)^2} = \ln 2 \quad (A6)$$

It was found that the absolute errors of the first and the second approximations (A5) to the correct value are $|\Delta_1| \leq 0.0225$ and $|\Delta_2| \leq 0.0239$, respectively, $\tau \leq 0.5$. The relative error is less than 1.5%.

2. Gaussian function with a variable FWHM

According to the model [2] the line width depends on the abscissa of a spectrum:

$$w = 2w_0 / (1 + \exp(ai)), \quad (A7)$$

where w_0 is the width at $i = 0$, a is the asymmetry parameter of this model. Substituting Eq. A7 in Eq. 2 leads to

$$x_{new} = \beta i / w = x(1 + \exp(\tau x)) / 2, \quad (A8)$$

where $x = \beta i / w_0$, $\tau = aw_0 / \beta$. If $a = k / w_0$, where k is a constant, then $\tau = k / \beta$ does not depend on the line width. Then Gaussian function with a variable FWHM can be expressed in the form

$$F_{G2}(x) = \exp(-x^2[(1 + \exp(\tau x)) / 2]^2) \quad (A9)$$

It is easily to show that $x_m = 0$ is the point where $F_{G2}(x)$ reaches the maximum value.

Using precise approximation of the exponential function with continued fractions [23] we obtained:

$$1 + \exp(y) = 2 / (1 - y / 2T), \quad (A10)$$

where $T = (1 + 0.1000y^2) / (1 + 0.0166y^2)$. It follows from Eqs. A8 and A10 that

$$x_{new} = x / (1 - \tau x / \varphi(\tau x)), \quad (A11)$$

where $\varphi(\tau x) = (1 + 0.4000\tau^2 x^2) / (1 + 0.0664\tau^2 x^2)$.

Taking Eq. A11, Eq. A9 is transformed to

$$F_{G2}(x) \cong \exp(-x^2 / (1 - \tau x / \varphi(\tau x))^2) \cong \exp(-x^2) \exp(-x^2 S(t)), \quad (A12)$$

where $S(t) = 0.5034t^3 + 0.9300t^2 + 0.9807t$, $t = \tau x$. $S(t)$ was calculated by MATLAB polyfit function in the interval of t (-1, 1). Eq. A12 can be expressed as the product of the symmetrical and asymmetrical parts over x :

$$F_{G2}(x) = F_{G2}^{sym}(x) * F_{G2}^{asym}(x), \quad (A13)$$

where $F_{G2}^{sym}(x) = \exp[-x^2(1 + 0.9300t^2)]$, $F_{G2}^{asym}(x) = \exp[-x^2(0.9807t + 0.5034t^3)]$.

It was found that the absolute error of the approximation (A13) to the correct value is $|\Delta| \leq 0.0074$ for $x = [-3, 3]$, $\tau \leq 0.2$ ($|t| \leq 0.6$).

The FWHM of the $F_{G2}(x)$

$$w_{G2} \cong 2\sqrt{\ln 2} / (1 - (0.25 \ln 2) \tau^2) \cong 2\sqrt{\ln 2} (1 + 0.18 \tau^2) \quad (A14)$$

is the solution of

$$\begin{aligned} w_{G2} &= x_{left} + x_{right} \\ (x_{left})^2 [(1 + \exp(-\tau x_{left}) / 2)]^2 &= \ln 2 \\ (x_{right})^2 [(1 + \exp(\tau x_{right}) / 2)]^2 &= \ln 2, \end{aligned} \quad (A15)$$

taking into account that for $\tau < 1$ $T \approx 1$ (A10).

The relative errors the approximations (A14) are less than 0.044% for $\tau \leq 0.5$.

The FWHM of the $F_{G2}^{sym}(x)$

$$w_{G2}^{sym} \cong 2\sqrt{\ln 2} \sqrt{(1 + 0.93\tau^2 \ln 2) / (1 + 1.86\tau^2 \ln 2)} \approx 2\sqrt{\ln 2} (1 - 0.26\tau^2) \quad (A16)$$

is the solution of

$$\left(\frac{w_{G2}^{sym}}{2}\right)^2 \left(1 + 0.9300 \left(\tau \frac{w_{G2}^{sym}}{2}\right)^2\right) = \ln 2 \quad (A17)$$

It was found that the absolute errors of the first and the second approximations (A16) to the correct value are $|\Delta_1| \leq 0.0017$ and $|\Delta_2| \leq 0.0052$, respectively, for $\tau \leq 0.5$. The relative error is less than 0.32%.

3. *Gaussian-Lorentzian function with a constant FWHM* [8].

$$F_{L1}(x) = \exp(\tau(1 - \arctan(x)))/(1 + x^2) \quad (A18)$$

Using the precise approximation of $\arctan(x)$ with continued fractions [23] we obtained:

$$\arctan(x) = xP(x), \quad (A19)$$

$$\text{where } P(x) = \frac{1+0.65591x^2+0.04055x^4}{1+0.98917x^2+0.17082x^4}.$$

The maximal relative errors of the approximation (A19) are equal to 0.37% for $|x| = 2$. For $|x| > 1$ the more precise approximation is obtained using equation $\arctan(x) = \text{sign}(x)\pi/2 - \arctan(1/x)$:

$$\arctan(x) = \text{sign}(x)\pi/2 - (1/x)P(1/x) \quad (A20)$$

Using Eqs. A19 and A20, Eq. A18 is expressed as the product of the symmetrical and asymmetrical parts:

$$F_{L1}(x) = F_{L1}^{sym}(x) * F_{L1}^{asym}(x), \quad (A21)$$

where $F_{L1}^{sym}(x) = \exp(\tau)/(1 + x^2)$,

$$F_{L1}^{asym}(x) = \begin{cases} \exp(-\tau x P(x)) & , |x| \leq 1 \\ \exp(-\tau(\text{sign}(x)\pi/2 - (1/x)P(1/x))) & , |x| > 1 \end{cases}$$

It was found that the absolute error of the approximation (A21) to the correct value is $|\Delta| \leq 1.4 \times 10^{-5}$ for $\tau \leq 2$.

Since the first-order derivative of Eq. A18:

$$F'_{L1}(x) = \frac{\tau - 2x}{1 + \tau^2 x^2} F_{L1}(x) \quad (A22)$$

reaches zero at the point

$$x_m = \tau/2 \quad (A23)$$

the line maximum is shifted from the zero point.

The FWHM of the $F_{L1}(x)$

$$w_{L1} \cong 2(1 + 1.164\tau^2) \quad (A24)$$

was obtained by solving

$$\exp(\tau(1 - \arctan(x)))/(1 + x^2) = \frac{1}{2} F_{L1}(x_m) = \frac{1}{2} \exp(\tau(1 - \arctan(\tau/2)))/(1 + (\tau/2)^2) \quad (A25)$$

using polynomial approximation. The full width is equal to the sum of two non-equal half-widths on left and right sides relative to the maximum line position which depends on the asymmetry parameter (Eq. A23).

It was found that the absolute error of approximation (A24) to the correct value is $|\Delta| \leq 0.0027$ for $\tau \leq 0.5$. The relative error is less than 0.14%.

The FWHM of the symmetrical part: $w_{L1}^{sym} = 2$, does not depend on the parameter of asymmetry τ .

4. *Lorentzian function with a variable FWHM* [2].

Using Eq. A8 we obtained:

$$F_{L2}(x) = \frac{1}{1 + [x(1 + \exp(\tau x))/2]^2} \quad (A26)$$

The polynomial approximation of the exponential function gives

$$F_{L2}(x) = \frac{1}{1 + \left[\frac{x}{1 - \tau x / \varphi(\tau x)} \right]^2} \quad (A27)$$

where $\varphi(\tau x)$ is defined in Eq. A11.

Eq A27 can be represented as the product of the symmetrical and asymmetrical parts over x :

$$F_{L2}(x) = \frac{1}{1 + x^2} \frac{1 + x^2}{1 + \left[\frac{x}{1 - \tau x / \varphi(\tau x)} \right]^2} \approx F_{L2}^{sym}(x) * F_{L2}^{asym}(x), \quad (A28)$$

where $F_{L2}^{sym}(x) = \frac{\exp(-0.22t^2)}{1 + x^2}$, $F_{L2}^{asym}(x) = \exp(-t)$, $t = \tau x$.

It was found that the absolute error of the approximation (A28) to the correct value is $|\Delta| \leq 0.0139$ for $\tau \leq 0.3$ and $x = [-5, 5]$.

Zeroing the first-order derivative it is easily to show that the Eq. A28 reaches its maximum value at the point $x = 0$.

The dependence FWHM of the $F_{L2}(x)$ on the parameter of asymmetry was obtained from the solution the equations

$$w_{L2} = x_{left} + x_{right}$$

$$\begin{aligned} (x_{left})^2 [(1 + \exp(-\tau x_{left})/2)]^2 &= 1 \\ (x_{right})^2 [(1 + \exp(\tau x_{right})/2)]^2 &= 1 \end{aligned} \quad (A29)$$

Since $T \approx 1$ for $\tau < 1$ (A10) then

$$w_{L2} \cong 2/(1 - 0.25\tau^2) \cong 2(1 + 0.26\tau^2) \quad (A30)$$

It was found that the absolute error of the first approximation (A30) to the correct value is $|\Delta| \leq 0.017$ for $\tau \leq 0.5$. The relative error is less than 0.85%. The relative error of the second approximation is less than 0.17%. The FWHM of the $F_{L2}^{sym}(x)$

$$w_{L2}^{sym} \cong 2/\sqrt{1 + 0.44\tau^2} \cong 2(1 - 0.20\tau^2) \quad (A31)$$

is the solution of

$$\frac{\exp\left(-0.22\left(\frac{w_{L2}^{sym}}{2}\right)^2\right)}{1 + \left(\frac{w_{L2}^{sym}}{2}\right)^2} \cong \frac{1 - 0.22\left(\tau\frac{w_{L2}^{sym}}{2}\right)^2 + 0.0242\left(\tau\frac{w_{L2}^{sym}}{2}\right)^4}{1 + \left(\frac{w_{L2}^{sym}}{2}\right)^2} = 1/2 \quad (A32)$$

It was found that the absolute error of the first approximation (A31) to the correct value is $|\Delta| \leq 0.0023$ for $\tau \leq 0.5$. The relative error is less than 0.12%. The relative error of the second approximation is less than 0.15%.

5. The log-normal function

The log-normal function [19]:

$$F_{LN}(t) = \begin{cases} \exp\left(-\frac{1}{\tau_{LN}} \ln^2 t\right) & v < a \\ 0 & v \geq a \end{cases} \quad (A33)$$

where $t = \frac{a-v}{a-v_m}$, v is the wavenumber value, $\tau_{LN} = \ln^2 \rho / \ln 2$, v_m is the maximum peak position, ρ is the asymmetry parameter and a is the wavenumber which controls the line limits of the abscissa scale.

Setting $v_m = 0$ and $x = v/a$ in Eq. A33, we have

$$F_{LN}(x) = \begin{cases} \exp\left(-\frac{1}{\tau_{LN}} \ln^2(1-x)\right) & |x| < 1 \\ 0 & |x| \geq 1 \end{cases} \quad (A34)$$

The dependences of the widths of the left (w_{LN}^{left}) and of the right half (w_{LN}^{right}) of the line, and of the all line (w_{LN}) on the asymmetry parameter

$$\begin{cases} w_{LN}^{left} = \rho - 1 \\ w_{LN}^{right} = 1 - 1/\rho \end{cases}, \quad x < 0 \quad (A35)$$

$$w_{LN} = w_{LN}^{left} + w_{LN}^{right} = \rho - 1/\rho \quad (A36)$$

were obtained by solving the following equation:

$$(1/\tau_{LN}) \ln^2(1 - w_{LN}^{left(right)}) = \ln 2 \quad (A37)$$

If $\rho \rightarrow 1$ then the form of the function $F_{LN}(x)$ is close to a fully symmetric with respect to the maximum point. However, $w_{LN} \rightarrow 0$. To eliminate this drawback the x variable of Eq.(A34) is scaled:

$$x_{scaled} = K_\rho x, \quad (A38)$$

where K_ρ can be chosen in three different ways according to Eqs. A35 and A36, that is

$$K_\rho = \begin{cases} (1-\rho)/(1-\rho_{max}) \\ (\rho-1/\rho)/(\rho_{max}-1/\rho_{max}) \\ (1-1/\rho)/(1-1/\rho_{max}) \end{cases}, \quad \begin{aligned} w_{LN} &= (1-\rho_{max})(\rho+1/\rho), w_{LN}^{left} = const \\ w_{LN} &= \rho_{max}-1/\rho_{max} = const \\ w_{LN} &= (1-1/\rho_{max})(\rho+1), w_{LN}^{right} = const \end{aligned}$$

where ρ_{max} is the maximal ρ -value.

Using Taylor series of the logarithm function of Eq. A34 for $x < 1$, we have

$$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \dots \quad (A39)$$

Eq. A34 can be expressed as the product of the symmetrical and asymmetrical parts over x :

$$F_{LN}(x) = F_{LN}^{sym}(x) * F_{LN}^{asym}(x), \quad (A40)$$

where $F_{LN}^{sym}(x) \approx \exp\left[-\frac{1}{\tau_{LN}}\left(x^2 + \frac{11}{12}x^4\right)\right]$, $F_{LN}^{asym}(x) \approx \exp\left[-\frac{1}{\tau_{LN}}\left(x^3 + \frac{1}{2}x^5\right)\right]$. It was found that the absolute error of the approximation (A40) to the correct value is $|\Delta| \leq 0.0072$ for $\rho \leq 1.3$ ($\tau_{LN} \cong 0.1$) and $x = [-0.99, 0.99]$.

Eq. A40 reaches its maximum value at the point $x = 0$.

The dependence of the FWHM of the $F_{LN}^{sym}(x)$ on the asymmetry parameter was obtained by solving the following equation:

$$\frac{1}{\tau_{LN}} \left((w_{LN}^{sym}/2)^2 + \frac{11}{12} (w_{LN}^{sym}/2)^4 \right) = \ln 2 \quad (A41)$$

This dependence normalized to constant w_{LN} (A38) is equal to

$$w_{LN}^{sym} \cong 4 \ln \rho (1 - (11/18) \ln \rho^2) w_{LN} / (\rho - 1/\rho) \cong k_2 \rho^2 + k_1 \rho + k_0, \quad (A42)$$

where $k_2 = -1.0618, k_1 = 2.0612, k_0 = 0.0636$. It was found that the absolute error of the approximation (A42) to the correct value is $|\Delta| \leq 0.0014$ in the interval of the ρ - values $[1.001, 1.30]$.

6. Losev function

According to the phenomenological model [16]:

$$F_{LV}(v) = 2/(\exp(-av) + \exp(bv)) = F_{LV}^{sym}(v) * F_{LV}^{asym}(v), \quad (A43)$$

where two constants a and b control the line shape, $F_{LV}^{sym}(v) = 2/(\exp(-pv) + \exp(pv))$, $F_{LV}^{asym}(v) = \exp(qv)$, $p = (a+b)/2$, $q = (a-b)/2$.

Assuming that $p=1$ and $\tau_{LV} = -q$, Eq. 43 is transformed to the standard form,

$$F_{LV}(x) = \frac{2}{\exp(-(1-\tau_{LV})x) + \exp((1+\tau_{LV})x)} = F_{LV}^{sym}(x) F_{LV}^{asym}(x), \quad (A44)$$

where $F_{LV}^{sym}(x) = 2/(\exp(-x) + \exp(x)) = \text{cosech}(x)$, $F_{LV}^{asym}(x) = \exp(-\tau_{LV}x)$.

Since the first-order derivative of $F_{LV}(x)$:

$$F'_{LV}(x) = 0.5 F_{LV}^2(x) \left[(1 - \tau_{LV}) \exp(-(1 - \tau_{LV})x) - (1 + \tau_{LV}) \exp((1 + \tau_{LV})x) \right] \quad (A45)$$

reaches zero at the point

$$x_m = \frac{1}{2} \ln \frac{1 - \tau_{LV}}{1 + \tau_{LV}} \quad (A46)$$

the line maximum is shifted from the zero point.

The FWHM of the $F_{LV}(x)$

$$w_{LV} \cong w_{LV}^{sym} (0.98 \tau_{LV}^2 - 0.094 \tau_{LV} + 1.006) \quad (A47)$$

is the solution of

$$F_{LV}^{sym}(x) F_{LV}^{asym}(x) = 0.5 F_{LV}^{sym}(x_m) F_{LV}^{asym}(x_m) \quad (A48)$$

The full width is equal to the sum of two non-equal half-widths on left and right sides relative to the maximum line position (x_m) which depends on the asymmetry parameter (Eq. A46).

It was found that the absolute error of approximation (A47) to the correct value is $|\Delta| \leq 0.0158$ for $\tau_{LV} \leq 0.5$. FWHM of the symmetrical component $F_{LV}^{sym}(x)$:

$$w_{LV}^{sym} = 2 \operatorname{arccosh}(2) = 2.6339 \quad (A49)$$

7. The Breit – Wigner-Fano function

The standardized form of the theoretical Breit – Wigner-Fano model [20] is

$$F_{BWF}(x) = (1 - t)^2 / (1 + x^2), \quad (A50)$$

where $t = \tau_{BWF} x$

The FWHM of the $F_{BWF}(x)$

$$w_{BWF} = 2\sqrt{1 + 2\tau_{BWF}^2} / (1 - 2\tau_{BWF}^2) \cong 2(1 - 0.125\tau_{BWF} + 4\tau_{BWF}^2) \quad (A51)$$

is the solution of

$$\begin{aligned} w_{BWF} &= x_{left} + x_{right} \\ (1 + \tau_{BWF} x_{left})^2 / (1 + x_{left}^2) &= 0.5 \\ (1 - \tau_{BWF} x_{right})^2 / (1 + x_{right}^2) &= 0.5 \end{aligned} \quad (A52)$$

The absolute error of the approximation (A51) to the correct value is $|\Delta| \leq 0.014$ for $\tau_{BWF} \leq 0.3$. The relative error does not exceed 0.7%.

The first-order derivative of Eq. A50

$$F'_{BWF}(x) = (t - 1)(\tau_{BWF} + x) / (1 + x^2)^2 \quad (A53)$$

has two roots: $-\tau_{BWF}$ and $1/\tau_{BWF}$. The first root is the maximum line position which is shifted from the zero point.

Assuming that $(1 - t)^2 = \exp(p)$ and taking expansion (A39), we have

$$p = 2 \ln(1 - t) = -2(t - t^2/2 - t^3/3 - \dots) \quad (A54)$$

Eq. A50 can be expressed as the product of the symmetrical and asymmetrical parts over x :

$$F_{BWF}(x) = F_{BWF}^{sym}(x) * F_{BWF}^{asym}(x), \quad (A55)$$

where $F_{BWF}^{sym}(x) \approx \exp(-t^2)/(1 + x^2)$, $F_{BWF}^{asym}(x) \approx \exp[-2t - (2/3)t^3]$. It was found that the absolute error of the approximation (A55) to the correct value is $|\Delta| \leq 0.0068$ for $|t| \leq 0.4$.

It was found numerically that the width of the symmetrical part $w_{BWF}^{sym} \cong 2$ for $\tau_{BWF} \leq 0.1$.