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Analytical Expression for the Convolution of a Fano Line Profile with a Gaussian

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ABSTRACT: Asymmetric Fano line profiles are frequently encountered, e. g., in photoionization spectra of atoms and ions. For the fitting of spectral line profiles to experimental spectra the line profiles have to be convoluted with the experimental window function. The latter is often taken to be a Gaussian. It is shown that the convolution can be represented by a rather simple analytic expression involving the complex error function.

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I. INTRODUCTION

Asymmetric line profiles are frequently encountered, e.g., in atomic photoionization due to a quantum mechanical interference between resonant and nonresonant ionization pathways. According to the quantum mechanical analysis of Fano [1] the photoionization cross section as a function of photon energy E in the vicinity of the resonance energy E_{res} can be represented as

$$\sigma(\epsilon) = \sigma_0 + \sigma_1 \frac{(q+\epsilon)^2}{1-\epsilon^2} \tag{1}$$

where σ_0 and σ_1 are slowly varying functions,

$$\epsilon = \frac{E - E_{res}}{\Delta_L / 2} \tag{2}$$

is a reduced energy, Δ_L is the natural (Lorentzian) line width, and q is the asymmetry parameter. The latter can be calculated theoretically from the transition matrix elements of the interfering resonant and nonresonant ionization channels.

As an example Fig. 1 shows the photoionization cross section of Be-like B^+ ions in the photon energy range 26.5–31.2 eV which was measured at a synchrotron radiation source [2]. The resonances are associated with dipole allowed double photoexcitation of the $1s^2\,2s\ {}^1S$ ground state to $1s^2\,2p\ ns\ {}^1P$ and $1s^2\,2p\ nd\ {}^1P$ states and subsequent autoionization. The principal quantum number n depends on the photon energy. For $n \to \infty$ both Rydberg series converge towards the series limit at about 31.15 eV.

Clearly the individual resonance line shapes are strongly asymmetric. For the extraction of the resonance parameters σ_1, E_{res}, Δ_L and q from the experimental data the resonance lines can be fitted by a Fano profile. In such fits the experimental photon energy distribution (window function) has to be taken into account. In many cases the experimental window function can be represented as a Gaussian where the Gaussian full width at half maximum (FWHM) corresponds to the experimental energy spread. Thus, for a fit to the experimental data the Fano profile has to be convoluted with a Gaussian.

The situation is similar to emission spectroscopy of hot gases where Doppler broadening results in Voigt line profiles, i.e., the convolution of a Lorentzian with a Gaussian. It is well known (see, e.g., [3–6]) that the Voigt profile can be calculated eficiently from the complex error function [7] (also known as the Faddeeva function).

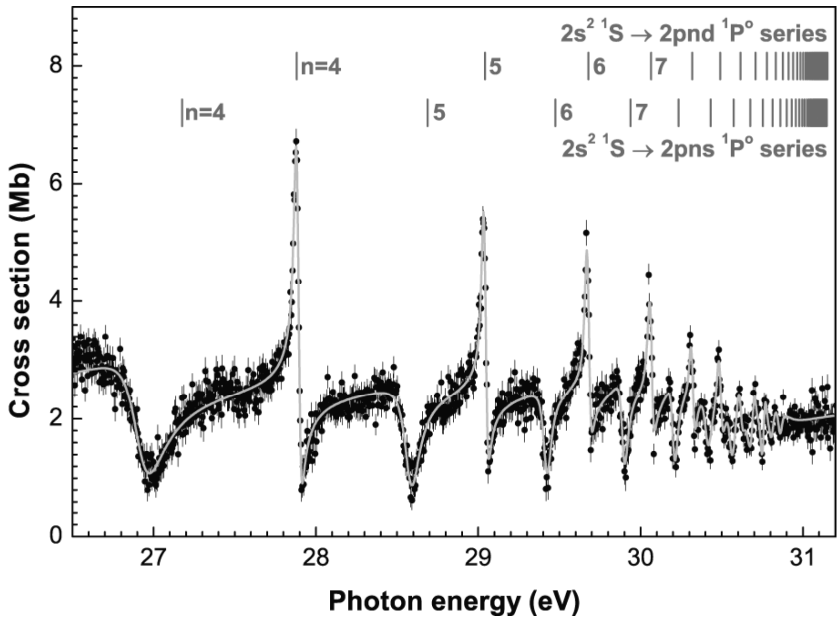

Figure 1: Rydberg series of resonances in the photoionization cross section of Be-like $B^+(1s^2\,2s^2\ ^1S)$ ions [2]. The full line is a fit of Fano profiles convoluted with a Gaussian to the experimental data points. The $2p\ ns\ ^1P$ and $2p\ nd\ ^1P$ series have different asymmetry parameters (cf. Eq. 1) of ~ –0.4 and ~ –2, respectively

It is much less known that also the convolution of a Fano profile with a Gaussian can be represented by the complex error function. A corresponding rather simple formula has already been given in the appendix of a previous publication [8]. The formula allows for a fast and accurate evaluation of the convolution in peak fitting routines. Here its derivation is presented.

It is noted that a different, more complex formula has been published earlier without its derivation [9]. It seems, that this formula has not received much attention since even in more recent work the convolution of a Fano profile with a Gaussian has only been treated approximately or by numerical integration (see, e.g., [10, 11]).

The present paper is organized as follows. In section II the calculation of the Voigt profile from the complex error function is reviewed. In section III some relevant properties of the complex error functions are elucidated. An expression for the convolution of the Fano profile with a Gaussian in terms of the complex error function is derived in section IV. A conclusive summary is given in section V.

II. THE VOIGT PROFILE

The convolution of a Lorentzian line profile

$$L(E) = A\frac{2}{\pi}\frac{\Delta_L}{4(E-E_{res})^2+\Delta_L^2} \tag{3}$$

with a Gaussian

$$G(E) = \frac{2}{\Delta_G}\sqrt{\frac{ln 2}{\pi}}\exp\left[-\frac{4(ln 2)E^2}{\Delta_G^2}\right], \tag{4}$$

yields the Voigt profile

$$V(E) = \int_{-\infty}^{\infty} L(E')G(E'-E)dE' \ = A\frac{4\sqrt{ln 2}}{\pi^{3/2}\Delta_G}\int_{-\infty}^{\infty}\frac{\Delta_L}{4(E'-E_{res})^2+\Delta_L^2}\ \exp-\left[\frac{4(ln 2)(E-E')^2}{\Delta_G^2}\right]dE'. \tag{5}$$

The profiles in Eqs. 3 and 4 are normalized such that

$$\int L(E)dE = A \text{ and } \int G(E)dE = 1. \tag{6}$$

The widths Δ_L and Δ_G are the Lorentzian and Gaussian FWHM, respectively. With the definitions

$$t = \frac{2\sqrt{ln\,2}(E' - E)}{\Delta_G}, \tag{7}$$

$$x = \frac{2\sqrt{ln\,2}(E_{res} - E)}{\Delta_G}, \tag{8}$$

$$y = \frac{\Delta_L \sqrt{ln\,2}}{\Delta_G}, \tag{9}$$

Eq. 6 transforms into

$$V(E) = A\frac{2\sqrt{ln\,2}}{\Delta_G\sqrt{\pi}}\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{ye^{-t^2}}{(t-x)^2 + y^2}dt = A\frac{2\sqrt{ln\,2}}{\Delta_G\sqrt{\pi}}\Re\, w(z) \tag{10}$$

where $w(z)$ denotes the complex error function and $z = x + iy$.

III. SOME PROPERTIES OF THE COMPLEX ERROR FUNCTION

The complex error function is defined for $\Im z = y > 0$ as [7, 12]

$$w(z) = \frac{i}{\pi}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{z-t}dt. \tag{11}$$

Its real and imaginary parts are

$$\Re[w(z)] = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{ye^{-t^2}}{(t-x)^2 + y^2}dt \tag{12}$$

and

$$\Im[w(z)] = \frac{-1}{\pi}\int_{-\infty}^{\infty}\frac{(t-x)e^{-t^2}}{(t-x)^2 + y^2}dt. \tag{13}$$

For later use we now calculate the integral

$$I_2(x,y) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{t^2e^{-t^2}}{(t-x)^2 + y^2}dt. \tag{14}$$

To this end we define

$$w_\eta(z) = \frac{i}{\pi}\int_{-\infty}^{\infty}\frac{e^{-\eta t^2}}{z-t}dt. \tag{15}$$

With this definition

$$I_2(x,y) = \frac{-1}{y}\Re\left[\frac{dw_\eta(z)}{d\eta}\right]_{\eta=1}. \tag{16}$$

For the calculation of the derivative on the right-hand side of this equation we exploit the identity $w_\eta(z) = w(\sqrt{\eta}z)$ which follows from the substitution $(\sqrt{\eta}t) \rightarrow t$ in Eq. 15. This yields

$$\frac{dw_\eta(z)}{d\eta} = \frac{dw(\sqrt{\eta}z)}{d\eta} = \frac{d(\sqrt{\eta}z)}{d\eta}\frac{dw(\sqrt{\eta}z)}{d(\sqrt{\eta}z)} = \frac{z}{2\sqrt{\eta}}\left(-2(\sqrt{\eta z})w(\sqrt{\eta}z) + \frac{2i}{\sqrt{\pi}}\right) \tag{17}$$

where in the last step we have used the identity [7, 12]

$$\frac{dw(z)}{dz} = -2zw(z) + \frac{2i}{\sqrt{\pi}}. \tag{18}$$

Combining Eqs. 16 and 17 yields

$$I_2(x,y) = \frac{1}{y}\Re\left[z^2 w(z) - i\frac{z}{\sqrt{\pi}}\right] = \left(\frac{x^2}{y} - y\right)\Re(w) - 2x\,\Im(w) + \frac{1}{\sqrt{\pi}}. \tag{19}$$

From equation 18 the partial derivatives of $w(z)$ with respect to x and y are easily calculated as

$$\frac{\partial\Re(w)}{\partial x} = \frac{\partial\Im(w)}{\partial y} = -2x\Re(w) + 2y\Im(w), \tag{20}$$

$$\frac{\partial\Im(w)}{\partial x} = -\frac{\partial\Re(w)}{\partial y} = -2y\Re(w) - 2x\Im(w) + \frac{2}{\sqrt{\pi}}. \tag{21}$$

These are of use, e.g., in least-squares fitting routines.

IV. CONVOLUTION OF A FANO PROFILE WITH A GAUSSIAN

For the purpose of peak fitting we define the Fano line profile somewhat difierently as suggested by Eq. 1, i.e.,

$$F(E) = \frac{2A}{q^2\Delta_L\pi}\left[\frac{(q+\epsilon)}{1+\epsilon^2} - 1\right]. \tag{22}$$

The term -1 inside the square brackets ensures that $F(E) \rightarrow 0$ for $E \rightarrow \pm\infty$. For $q \rightarrow \infty$ the Fano profile as defined by Eq. 22 approaches a symmetric Lorentzian (Eq. 3), i. e., $F(E) \rightarrow L(E)$. With the definitions of t, x and y from Eqs. 7, 8, and 9, respectively, the convolution with a Gaussian as defined by Eq. 4 can be expressed as

$$\begin{aligned} C(E) &= \int_{-\infty}^{\infty} F(E')G(E'-E)dE' = A\frac{2}{q^2\Delta_L\pi}\left[\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{[qy+(t-x)]^2 e^{-t^2}}{(t-x)^2+y^2}dt - 1\right] \\ &= A\frac{2}{q^2\Delta_L\sqrt{\pi}}\left[\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{[q^2y^2 + 2qy(t-x) + t^2 - 2x(t-x) - x^2]e^{-t^2}}{(t-x)^2+y^2}dt - \frac{1}{\sqrt{\pi}}\right] \\ &= A\frac{2}{\Delta_L\sqrt{\pi}}\left\{y\Re(w) + \frac{2y}{q}\Im(w) + \frac{1}{q^2}I_2 + \frac{2x}{q^2}\Im(w) - \frac{x^2}{q^2y}\Re(w) - \frac{1}{q^2\sqrt{\pi}}\right\} \end{aligned} \tag{23}$$

$$= A\frac{2y}{\Delta_L\sqrt{\pi}}\left\{\Re(w)+\frac{2}{q}\Im(w)+\frac{1}{q^2}\left(\frac{x^2}{y^2}\Re(w)-\Re(w)-\frac{2x}{y}\Im(w)+\frac{2}{y\sqrt{\pi}}\right)+\frac{2x}{yq^2}\Im(w)-\frac{x^2}{q^2y^2}\Re(w)-\frac{1}{yq^2\sqrt{\pi}}\right\}.$$

In the equations above the definitions of $\Re(w)$ (Eq. 12), $\Im(w)$ (Eq. 13), and I_2 (Eq. 14) as well as Eq. 19 have been used. After gathering all terms one finally arrives at

$$C(E) = A\frac{2\sqrt{ln\,2}}{\Delta_G\sqrt{\pi}}\left\{\left(1-\frac{1}{q^2}\right)\Re[w(z)]-\frac{2}{q}\Im[w(z)]\right\}. \tag{24}$$

It is easily seen that $C(E) \to V(E)$ for $q \to \infty$ as expected.

V. SUMMARY

It has been demonstrated that the convolution of a Fano line profile (Eq. 22) with a Gaussian (Eq. 4) can be evaluated analytically (Eq. 24) by using the complex error function $w(z)$ with $z = x + iy$ and with x and y from Eqs. 8 and 9, respectively. Various fast and accurate algorithms for computing the complex error function have been described in the liteature [3, 4, 6, 13–17]. Their performances have been critically evaluated repeatedly [5, 6, 18, 19]. According to the findings of Zaghloul and Ali [6] their algorithm is the most accurate available to date.

The line profile $C(E)$ has been implemented by the author as a user-supplied fit function for the commercial software Origin [20] and successfully used in various contexts (see, e.g., Fig. 1). The implementation is available from the author upon request.

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