The shape of spectral lines: widths and equivalent widths of the Voigt profile

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Abstract

In this work, we present a new lineshape computing method. The lineshape, commonly known as the Voigt profile, is a convolution of the Gaussian and Lorentzian profiles. Moreover, we present a simple approach to describe the width of the Voigt profile as a function of the relative contributions of Gaussian and Lorentzian broadening. A novel expression of the equivalent width of Lorentz shapes can be calculated from numerical approximation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Voigt profile; Voigt function; Integrated absorption; Equivalent width

1. Introduction

In many fields of physics, one encounters the lineshape which results both from the Doppler effect and from the effects of pressure broadening. Because of combined contributions from these mechanisms, the lineshape is well given by a Voigt profile which is a convolution of the Gaussian and Lorentzian profiles [1].

When the broadening of a spectral line is due to contributions from a Gaussian shape and from an independent Lorentz shape, the resulting reduced absorption coefficient may be expressed by [2]

$$K(x, y) = \frac{k_y}{k_0} = \frac{y}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{y^2 + (x-t)^2} dt,$$

(1)

usually called the Voigt function and the Voigt profile is then given by

$$P(x, y) = \frac{1}{\alpha_0} \left( \frac{\ln 2}{\pi} \right) \frac{1}{2} K(x, y),$$

(2)

which is a probability distribution normalized to unity on the wave number scale $$\nu - \nu_0$$, where $$\nu$$ is
the wave number at which $k_\nu$ is to be evaluated and $\nu_0$ is the wave number at the line center. We design in Eqs. (1) and (2) the dimensional constant of the reduced absorption coefficient, the ratio of Lorentz to Doppler widths, the wave number scale in units of Doppler width, the integrated line strength the Lorentz half-width and the Doppler half-width by:

$$k_0 = \frac{S}{\alpha_D} \left( \frac{\ln 2}{\pi} \right)^{1/2}, \quad y = \frac{\alpha_L}{\alpha_D} \left( \ln 2 \right)^{1/2},$$

$$x = \frac{\nu - \nu_0}{\alpha_D} \left( \ln 2 \right)^{1/2},$$

$$S = \int_{-\infty}^{+\infty} k_s \, d\nu, \quad \alpha_L \text{ and } \alpha_D \text{ respectively.}$$

The purpose of this paper is to give a new method of computing the equivalent widths of the Voigt profile and a rational expression to describe the width of the lineshape. Our first main interest herein is to evaluate the width and its Voigt profile with a maximum accuracy.

2. Numerical evaluation of the Voigt function

From Eq. (1), we evaluate the important quantity $k_\nu$ as

$$k_\nu = k(\nu) = \Re \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{y^2 + (x - t)^2} \, dt,$$

(3)

with $\Re = S/(\alpha_D \pi)(\ln 2/\pi)^{1/2}$. The integral in Eq. (3) can be related to the error function of a complex variable through [3]

$$k(\nu) = \Re \pi \text{Re}(W(z)),$$

(4)

where $W(z) = \exp(-z^2)\text{erfc}(-iz) = \exp(-z^2)2/\pi i e^{-t^2} dt$, with erfc is the complementary error function, $z = x + iy$ ($x$ is real and $y > 0$) and Re is the real part.

Then, using the relation: $\text{erfc}(z) = 1 - \text{erf}(z)$ and the infinite series approximation for complex error function

$$\text{erf}(-iz) = \text{erf}(y - i x),$$

$$= \text{erf}(y) + \frac{\exp(-y^2)}{2\pi y} \left[ \left( 1 - \cos 2xy \right) - i \sin 2xy \right]$$

$$+ \frac{2}{\pi} \exp(-y^2) \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{1}{4}n^2\right)}{n^2 + 4y^2} \left[ f_n(y, -x) + ig_n(y, -x) \right] + O(x^3),$$

(5)

with

$$f_n(y, -x) = 2y - 2y \cos(ny) \sin(2xy)$$

$$- n \sinh(ny) \sin(2xy),$$

$$g_n(y, -x) = -2y \cosh(ny) \sin(2xy)$$

$$+ n \sinh(ny) \cos(2xy),$$

and $|e(x, y)| \approx 10^{-16}|\text{erf}(z)|$, and the rational approximation (for $0 \leq y < \infty$): $\text{erf}(y) = 1 - (k_1 t + k_2 t^2 + k_3 t^3 + k_4 t^4) \exp(-y^2) + e(y)$, with $t = 1/(1 + py)$ and $|e(y)| \leq 1.5 \times 10^{-7}$, we obtain:

$$k(\nu) = \Re \pi \text{Re}(W(z))$$

$$= \Re \pi \text{Re} \left[ \exp(-z^2 - y^2) \left( k_1 + k_2 t^2 + k_3 t^3 \right) + k_4 t^4, \right]$$

$$+ \frac{1}{2\pi y} \left[ \left( 1 - \cos 2xy \right) - \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{1}{4}n^2\right)}{n^2 + 4y^2} \right.$$

$$\left. \times \left[ f_n(y, -x) + ig_n(y, -x) \right] \right].$$

(6)

Here the coefficients $p$ and $k_i$ in the approximation of the function erf are: $p = 0.3275911$, $k_1 = 0.254829592$, $k_2 = -0.284496736$, $k_3 = 1.421413741$, $k_4 = -1.545152027$ and $k_5 = 1.061405429$ [3].
Table 1
Summary of the literature

<table>
<thead>
<tr>
<th></th>
<th>Region</th>
<th>Method</th>
<th>Method</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young [4]</td>
<td>$y \leq 1.0, x &lt; 10.0$</td>
<td>Runge–Kutta</td>
<td>continued fraction expansion</td>
<td>$y \geq 0, x \geq 10.0$</td>
</tr>
<tr>
<td></td>
<td>$y &gt; 1.0, x &lt; 10.0$</td>
<td></td>
<td></td>
<td>20-point Gauss–Hermite quadrature</td>
</tr>
<tr>
<td></td>
<td>$1.0 &lt; y \leq 2.5, x \leq 4$</td>
<td></td>
<td></td>
<td>y $\geq 2.5, x &lt; 4; y \geq 1.8/(x + 1), x &gt; 4$</td>
</tr>
<tr>
<td></td>
<td>$y &lt; 1.0, x &lt; 4; y &lt; 1.8/(x + 1), x &gt; 4$</td>
<td></td>
<td></td>
<td>Voigt representation of $K$</td>
</tr>
<tr>
<td></td>
<td>$x = 0$; $y = 0$</td>
<td>Dawson’s function using a Chebyshev expansion</td>
<td></td>
<td>$y &lt; 11.0 - 0.6875 x$</td>
</tr>
<tr>
<td></td>
<td>$x \geq 0; y \geq 0$</td>
<td></td>
<td></td>
<td>$y \geq 11.0 - 0.6875 x$</td>
</tr>
<tr>
<td>Gautschi [6]</td>
<td>Region</td>
<td>Stieltjes’ theory of continued fractions</td>
<td></td>
<td>4-point Gauss–Hermite quadrature</td>
</tr>
<tr>
<td></td>
<td>$x \geq 0; y \geq 0$</td>
<td></td>
<td></td>
<td>2-point Gauss–Hermite quadrature</td>
</tr>
</tbody>
</table>
3. Computational methods

Many computational methods and computer routines are now widely employed for evaluate the expression of $k(\nu)$. Young [4], Armstrong [2] and Drayson [5] give some routines by selecting three different methods for use in three regions identified in Table 1. In this latter, we present also the characteristic routine given by Gautschi [6] for computing the complex error function that is used frequently in the atomic and molecular physics community. Note that this routine is more than five times slower than the routine described by Drayson [5].

It was determined that the Voigt profile computing with a modified routine from Young took about 75% of the total execution time in a test calculation of transmittance [7]. Our goal is to give a formula which we can implement in a program as a simple routine. For that, two simple methods were selected for use in two regions identified in Fig. 1 by using Eq. (6).

In the two regions for Drayson [5], we use this equation for evaluating the Voigt profile. A Gauss–Hermite quadrature is satisfactory for large $x$ and $y$. In region II-a, 4-point quadrature is required, and for region II-b, we select as Drayson a 2-point quadrature.

The results obtained were compared with the values given by Armstrong and Drayson. Complete agreement was obtained by taking $1 \leq n \leq 50$ in Eq. (6).

The numerical values and functional behavior demonstrated by the function $K(x, y)$ computed from Eq. (6) are illustrated in Fig. 2(a) and Fig. 2(b). We present in Fig. 2(a), the profile labeled $y = 0$ is the limiting Doppler case.

4. Integrated absorption of a spectral line with the Voigt profile

The equivalent width of a single line is [8]

$$W(S, m, \alpha_L, \alpha_D) = \int_{-\infty}^{+\infty} \left[1 - \exp(-k(\nu)m)\right] d\nu,$$

(7)
Table 2
Coefficients $c_n$ and $d_n$ used in the development of Rodgers and Williams formulas of $\alpha_0$ [9]

<table>
<thead>
<tr>
<th>$n$</th>
<th>$c_n$</th>
<th>$d_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.99998291698 $\times 10^{-4}$</td>
<td>1.9999989289</td>
</tr>
<tr>
<td>1</td>
<td>$-3.53508187098 \times 10^{-4}$</td>
<td>$5.77491987600 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>$9.60267807976 \times 10^{-5}$</td>
<td>$-5.05367549898 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>$-2.04969011013 \times 10^{-5}$</td>
<td>$8.21896973657 \times 10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>$3.43927368627 \times 10^{-3}$</td>
<td>$-2.52226724530$</td>
</tr>
<tr>
<td>5</td>
<td>$-4.27593051557 \times 10^{-4}$</td>
<td>$6.10070274810$</td>
</tr>
<tr>
<td>6</td>
<td>$3.42209457833 \times 10^{-4}$</td>
<td>$-5.1001627836$</td>
</tr>
<tr>
<td>7</td>
<td>$-1.28380804108 \times 10^{-4}$</td>
<td>$4.65351167650$</td>
</tr>
</tbody>
</table>

where $m$ is the optical density of the medium. In general, the lineshape will be influenced by contributions from both the collision broadening and Doppler effect. For a given $y_0$, one can calculate $k(v)$ as:

$$k(v) = S/\alpha_D \left( \frac{2}{\pi} \right)^{1/2} K(x, y_0) = S/\alpha_D \left( \frac{2}{\pi} \right)^{1/2} K(x).$$

So, in this section, we present a numerical evaluation of the equivalent width per unit Doppler half-width for lines with Voigt contour as

$$\frac{W(X)}{\alpha_D} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left[ 1 - \exp(-\alpha K(x)) \right] dx,$$

(8)

with $\alpha = Sm/\alpha_D (\ln 2/\pi)^{1/2}$.

By using the above computational methods for evaluating $K$ and a numerical integration of the integral in Eq. (8) by 3-point Gauss–Hermite quadrature

$$\frac{W(X)}{\alpha_D} \approx \sum_{i=1}^{n} w_i \exp \left( x_i^2 \right) \left[ 2 - \exp(-\alpha K(x_i)) \right]$$

$$- \exp(-\alpha K(-x_i))],$$

(9)

we can compute the equivalent width per unit Doppler $W(X)/\alpha_D$. The coefficients $w_i$ and $w_i \exp(x_i^2)$ are taken from Ref. [3] and generally for the Gauss–Hermite quadrature, we have:

$$\int_{-\infty}^{\infty} \exp(-x^2) f(x) dx = \sum_{i=1}^{n} w_i f(x_i) + R_n.$$

Essentially the method involves approximating $f(x)$ by a suitable polynomial; difficulty in its use lies in the estimation of the remainder

$$R_n = \frac{n! \sqrt{\pi}}{2^{n} (n!)^{1/2}} f^{(2n)}(\xi) (-\infty < \xi < \infty)$$

in those cases, such as the present, where it is not known to vanish. The result agree with theses of Jansson and Korb [8], but we still have a problem with the asymptotic comportment of $W(X)/\alpha_D$ for large $X$.

We see that the two independent broadening formulas which combine to give the Voigt profile, and to which it must of course, reduce in the proper limits are (with $\delta(x) = \lim_{t \to 0} \frac{1}{\pi} \left( e^{-x^2} + x^2 \right)$):

$$\text{lim}_{b \to b} K(x, y) = \int_{-\infty}^{\infty} \exp(-t^2) \delta(x - t) dt = K(x, 0) = \exp(-x^2),$$

for a pure Doppler, $P(x \to \infty, y \to \infty) = 1/\pi (\alpha_L / (\nu - \nu_0)^2 + \alpha_L^2)$, for a pure Lorentz.

Table 3
Polynomial approximations used to evaluate Ladenburg–Reich function

<table>
<thead>
<tr>
<th>Range</th>
<th>Polynomial approximation</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 \leq x \leq 3.75$</td>
<td>$I_0(x) = 1 + 3.515622997r^4 + 3.089949r^4 + 1.2067492^r^6 + 0.2659732r^8$</td>
<td>$</td>
</tr>
<tr>
<td>$0 \leq x \leq 3.75$</td>
<td>$x^{-1}I_0(x) = 0.5 + 0.8789905942^r^6 + 0.51498869^r^4 + 0.15084934^r^6$</td>
<td>$</td>
</tr>
<tr>
<td>$0 \leq x \leq 3.75$</td>
<td>$x^{-1/2}e^{-1/2}I_0(x) = 0.39894228 + 0.01328592^r^4 + 0.0225319^r^2$</td>
<td>$</td>
</tr>
<tr>
<td>$3.75 \leq x &lt; \infty$</td>
<td>$x^{-1/2}e^{-1/2}I_0(x) = 0.39894228 - 0.03980824^r^2 - 0.00225319^r^2$</td>
<td>$</td>
</tr>
<tr>
<td>$3.75 \leq x &lt; \infty$</td>
<td>$x^{-1/2}e^{-1/2}I_0(x) = 0.39894228 - 0.03980824^r^2 - 0.00225319^r^2$</td>
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<td>$</td>
</tr>
</tbody>
</table>
We have found, if we take the Rodgers and Williams formulas of $\alpha_L$ [9], we do not obtain the Lorentzian comportment of $W(X)$, but for small $X$ the Doppler effect is rightly described by $W_0 = \alpha_L/((\ln 2)^{1/2})D\Sigma_m/\alpha_0((\ln 2/\pi)^{1/2})$, where $D\Sigma_m = \pi^{1/2}\Sigma_{m=0}^\infty c_m z^{-m}$ for $0 \leq z \leq 5$ and $D\Sigma_m = (\ln z)^{1/2}\Sigma_{m=0}^\infty d_m (\ln z)^{-m}$ for $z > 5$. The coefficients $c_m$ and $d_m$ are listed in Table 2. This point suggest us to revise the expression of $\alpha_L$.

5. The equivalent width of a Lorentz line

For lines with Lorentz shape, the equivalent width is given by the well-known Ladenburg–Reich equation namely [10]

$$W_L = 2 \pi \alpha_L L(z) = 2 \pi \alpha_L \exp(-z) [J_0(i z) - i J_1(i z)],$$ (10)

where $z = Sm/(2 \pi \alpha_L)$, and $J_0$ and $J_1$ are the Bessel functions of order 0 and 1, respectively. By using the modified Bessel functions: $I_n(z) = e^{-z/2}(\sqrt{\pi/2})n!J_n(\sqrt{\pi/2}z)$, Eq. (10) becomes: $W_L = 2 \pi \alpha_L \exp(-z) [I_0(z) + i I_1(z)]$, with $z$ real [3].

One can express, with an error of $2.2 \times 10^{-7}$, the Ladenburg–Reich function $L$ as a polynomial approximation: $L(z) = z^{1/2}\Sigma_{n=0}^{13} a_n z^{-n}$ for $0 \leq z \leq 3.75$ and $L(z) = z^{1/2}\Sigma_{n=0}^{13} b_n z^{-n}$ for $z > 3.75$. This relation have obtained directly from the polynomial approximations given in Table 3 by taking $t = x/3.75$ [3]. The coefficients $a_n$ and $b_n$ are listed in Table 4.

Fig. 3 shows the difference between our results computed from Eq. (10) and Rodgers and Williams expansion [9] for the equivalent width of Lorentz shaped spectral line. For small values of $Sm/\alpha_0$, the difference is very large but decrease rapidly for large values.

6. Rational representation of the width of a Voigt profile

It is also very interesting to determine the width of a Voigt profile in the plane $x-y$. Since the maximum value of $K(x,y)$ for a given value of $y$ is at $x = 0$, the half-width $w$ of a line profile for a given value is obtained from the equation: $K(w, y) = K(0, y)/2$. The purpose of this section is to give a rational expression to describe $w$ as a function of the relative importance of Lorentzian and Gaussian contributions. We have used the method described by Minguzzi and Di Lieto [11]. Their integral $V(\delta, y) = \int_{-\infty}^{\infty} (\exp(-z^2/2))/((z - \delta)^2 + y^2)dz$ is equivalent to our $K(x, y)$ by considering: $V(\delta, y) = (\pi/\delta)K(x, y)$.

As $K(x, y) = \Re(\pi Re(W(z)))$, we can calculate the derivatives $dK/dz$ and $d^2K/dz^2$, because the error
function obeys the following differential equation \[ W^{(n+2)}(z) + 2zW^{(n+1)}(z) + 2(n+1)W^{(n)}(z) = 0, \] with \( W^{(0)}(z) = W(z) \) and \( W^{(1)}(z) = \frac{dW(z)}{dz} = -2zW(z) + \frac{2i}{\sqrt{\pi}}. \)

From Eq. (11), one obtains:

\[ W^\sigma(z) = \frac{d^2W(z)}{dz^2} = -2zW^{(1)}(z) - 2W(z) = (4z^2 - 2)W(z) - \frac{4iz}{\sqrt{\pi}}. \]  

So in the first region, one obtains:

\[ \frac{dk}{d\nu} = \frac{ln2}{\alpha_0} \Re \pi \Re \left[-2zW(z)\right], \]

and

\[ \frac{d^2k}{d\nu^2} = \frac{ln2}{\alpha_0} \Re \left[-2W(z) + 4z^2W(z) - \frac{4i}{\sqrt{\pi}z}\right], \]

where \( W(z) \) is given by Eq. (6). On the other hand, Eq. (1) give us \( dK/dx \) and \( d^2K/dx^2 \) as

\[ \frac{dK}{dx} = \frac{2y}{\pi} \int_{-\infty}^{t} \frac{(t-x)\exp(-t^2)}{y^2 + (x-t)^2} \, dt. \]

and

\[ \frac{d^2K}{dx^2} = \frac{2y}{\pi} \int_{-\infty}^{t} \frac{3(x-t)^2 - y^2)\exp(-t^2)}{[y^2 + (x-t)^2]^2} \, dt. \]

Those last expressions are available in the region III and must be evaluated by the Gauss–Hermite quadrature. One can now use Eqs. (14)–(17) to compute \( dK/dx \) and \( d^2K/dx^2 \). For the first case, the width is derived from the distance between the abscissa of the maximum and minimum points. For the second derivative, the width is defined as the distance from the center to the maximum of the curve.

7. Model

We present here a very accurate method for solving the problem of the measurement of the width of absorption lines featuring both Gaussian and Lorentzian effects. This method, which determines the width of the Voigt profile as a function of a given \( y \), can be applied to a large class of experimental situations in spectroscopy or other various fields.

One used the width \( w \) of \( K(x, y) \) as a function of \( y \). We give a rational expression for \( w(y) \) which becomes asymptotic to the line \( x/y = 1 \) for large \( x \) and \( y \). The necessity of this asymptotic behavior arises from the definition of \( \alpha_1 \); when \( \nu - \nu_0 = \alpha_1 \) for a pure Lorentz line, the profile has fallen to one-half its peak value. We propose here the following form as Minguzzi and Di Lieto: \( w^{(i)}(y) = y + \eta^{(i)}(y) \), with \( \lim_{y -> 0} \eta^{(i)}(y) = 0 \) and for \( y = 0 \), the value of \( w \) turns out to be \( w = 0.83 \) [2]. We have determined \( w(0) \) which is in good agreement with the result of Armstrong: \( w(0) = 0.83250 \).

At a fixed \( y \), the Voigt function \( K(x, y) \) is computed at many different values of \( x \), ranging from zero up to the half-width at half-maximum which is conventionally understood for the width of all line-shapes; this computation is repeated for many different values of \( y \) in the interval \( 0 \leq x \leq 100 \) with a step of 0.0001.

<table>
<thead>
<tr>
<th>Case (i)</th>
<th>( p_0^{(i)} )</th>
<th>( p_1^{(i)} )</th>
<th>( p_2^{(i)} )</th>
<th>( p_3^{(i)} )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.83250</td>
<td>0.33049</td>
<td>0.92857</td>
<td>0.45814</td>
<td>( 3 \times 10^{-7} )</td>
</tr>
<tr>
<td>(b)</td>
<td>0.71000</td>
<td>0.16382</td>
<td>0.83314</td>
<td>0.92582</td>
<td>( 2 \times 10^{-5} )</td>
</tr>
<tr>
<td>(c)</td>
<td>1.22000</td>
<td>0.39577</td>
<td>0.69951</td>
<td>0.34358</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
A nonlinear least-squares fitting program was used for compute the best values for the coefficients \( p_i \) of the function \( \eta(y) \) considered as a ration of polynomials:

\[
\eta^{(i)}(y) = \frac{p_1^{(i)} + p_2^{(i)} y}{1 + p_3^{(i)} y + p_4^{(i)} y^2}.
\]  

(18)

The results of the nonlinear least-squares fitting with a \( \chi^2 = 1.1 \times 10^{-7} \) are listed in Table 5.

Fig. 4 describes the comportment of the half-width at half-maximum \( w \) as a function of \( y \) evaluated by the rational expression given by Eq. (18).

In summary, we have studied the shape of spectral lines given by a Voigt profile. We have investigated a numerical evaluation of the Voigt function and of the integrated absorption of a spectral line with this profile. Our work presents also a more general analysis of the widths and equivalent widths of the Voigt profile.

References