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A simple quasi-analytical method for the deconvolution of Voigtian profiles

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ABSTRACT

In electron spin resonance spectroscopy, spectral lineshapes are often assumed to be Voigtian. A number of researchers have suggested ways to approximate the Voigtian profile. Herein, we have devised a new quasi-analytical method to deconvolve it. In particular, we have derived an equation that relates the Lorentzian-to-Gaussian linewidth ratio directly to the product of the linewidth and the maximum value of a normalized Voigtian profile. Our calculations show that the Lorentzian and Gaussian linewidths obtained by the quasi-analytical deconvolution of computer-generated Voigtian absorption spectra are accurate within an error range of 1% in the absence of noise. Also, simulations with noise-added spectra reveal that, in the presence of white noise, our method is valid to a certain extent that depends on several factors such as the number of data points and the spectral sweep width. The new deconvolution method is valuable in that it estimates the Lorentzian and Gaussian linewidth in a rapid manner. The method may be also useful in other fields of science, such as optical spectroscopy, especially if some a priori knowledge about the lineshape is given.

1. Introduction

Electron spin resonance (ESR) spectroscopy is one of the most common methods used for the detection of chemical species with unpaired electron(s). In general, the lineshape of an experimental ESR spectrum obtained at room temperature is fit by a Voigtian profile, the convolution of a Lorentzian profile and a Gaussian profile, representing homogenous and inhomogeneous broadening, respectively [1]. If the lineshape is almost exclusively Lorentzian or Gaussian, the use of the apparent peak-to-peak linewidth, W_{p-p}, of the first derivative spectrum is common, as W_{p-p} is convertible to the full-width at half-maximum (FWHM) or half-width at half-maximum (HWHM) of the absorption spectrum by multiplication with a known constant. However, if both Lorentzian and Gaussian component of the spectrum are significant, the mere measurement of the peak-to-peak linewidth is inadequate to describe the lineshape, and the exact values of the Lorenzian and Gaussian linewidth cannot be directly measured from the experimental ESR spectrum.

Thus, it is desirable that the two components in the Voigtian profile be separately considered. The best approach would be to deconvolve the Voigtian line into the Lorentzian and Gaussian component. Unfortunately, the deconvolution is often arduous because a Voigtian profile cannot be expressed in a closed form [2]. To reduce the computation time, some researchers have approximated a Voigtian line as a simpler expression such as a finite sum of elementary functions [3–9]. In particular, Halpern et al. [9] have combined the approximation strategy with the Levenberg–Marquardt optimization algorithm [10] to fit inhomogeneously broadened ESR spectra with a dispersive component due to the microwave phase shift. Alternatively, Smirnov and Belford [11] have used a fast Fourier-transform algorithm to extract information about individual lineshapes from Voigtian lines containing a dispersive component.

Also, Bales [12,13] has introduced an interesting apporoach where the linewidth and the intensity of a first derivative ESR spectrum are analyzed to deconvolve a Voigtian profile. Furthermore, in other fields, efforts have been recently made to develop a clearer way of deconvolution [14–16].

Herein, we introduce a new approach to the deconvolution of Voigtian profiles. We calculate the Lorentzian and Gaussian HWHM linewidths of computer-generated Voigtian profiles by employing a quasi-analytical method that exploits the empirical approximation of the Voigtian profile developed by Olivero and Longbothum [17]. The key feature of our method lies in the calculation of the Lorentzian-to-Gaussian linewidth ratio using an analytical expression that

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contains the product of the linewidth and the maximum intensity, both of which can be measured from a normalized absorption spectrum.

2. Theory

2.1. ESR spectral lineshape

It is known that experimentally obtained ESR spectra are not always satisfactorily described by the Lorentzian function and/or the Gaussian function. The ESR lineshape is dependent upon temperature, spin exchange, the modulation amplitude and modulation frequency, and the type of the paramagnetic species [18–21]. Other lineshape functions, such as the Lévy distribution and the Tsallis distribution, have been suggested as alternatives [22,23]. Nevertheless, in a number of cases, ESR spectra obtained at room temperature are considered to contain both Lorentzian and Gaussian component due to homogeneous and inhomogeneous broadening, respectively. The linewidth of the Lorentzian component is inversely proportional to the spin–spin relaxation time, T_2, which is the reciprocal of the spin–spin relaxation rate, R_2, [24–27]. On the other hand, the linewidth of the Gaussian component is determined by several factors including magnetic field inhomogeneity and unresolved isotropic hyperfine lines [28].

2.2. Definition of Lorentzian, Gaussian, and Voigtian linewidth and their relationship with one another

When a pure absorption spectrum obtained in a Fourier-transform (FT)-ESR experiment is fit with a function, the FWHM or HWHM is normally employed as the linewidth parameter. In continuous wave (CW)-ESR spectroscopy, where the first derivative of an absorption spectrum is experimentally obtained, a common definition of the spectral linewidth is the peak-to-peak linewidth $W_{\mathrm{p-p}}$, the distance between the two magnetic fields, at one of which the intensity is a maximum whilst at the other it reaches a minimum. If the lineshape is Lorentzian, FWHM in the corresponding absorption spectrum is equal to $\sqrt{3}W_{\mathrm{p-p}}$. For a pure Gaussian line profile, FWHM corresponds to $\sqrt{2\ln 2}W_{\mathrm{p-p}}$. Also, it is obvious that the ratio of FWHM or HWHM to $W_{\mathrm{p-p}}$ for a Voigtian profile increases as the Lorentzian component becomes more significant. Therefore, a change in $W_{\mathrm{p-p}}$ does not necessarily mean a proportional change in FWHM or HWHM. Hereafter, the linewidth is represented by the HWHM for the sake of simplicity and uniformity, if not otherwise stated.

As a Voigtian profile is the convolution of a Lorentzian profile with a Gaussian profile, the linewidth of the Voigtian profile is related to its component Lorentzian and Gaussian linewidth. It is known that the HWHM of a Voigtian profile is approximated, within an error of less than 0.02%, to be [17]

$$\Gamma_{\mathrm{V}} \approx \alpha\Gamma_{\mathrm{L}} + \sqrt{\beta\Gamma_{\mathrm{L}}^2 + \Gamma_{\mathrm{G}}^2}, \tag{1}$$

where Γ_{V}, Γ_{L}, and Γ_{G} are the HWHM of a Voigtian profile and its component Lorentzian and Gaussian profile, respectively, and α and β are 0.5346 and 0.2166, respectively. In CW-ESR, the Voigtian linewidth Γ_{V} may be obtained from the integral of the first derivative spectrum, and Γ_{L} and Γ_{G} are related to each other by Eq. (1).

Given that Γ_{V} is known, the ratio of Γ_{L} to Γ_{G} or its reciprocal is often used to describe the lineshape of a Voigtian profile. Then, one can surmise that, conversely, the ratio $\Gamma_{\mathrm{L}}/\Gamma_{\mathrm{G}}$ of a given Voigtian profile may be estimated by the analysis of the lineshape. We have found that, in order to obtain an equation for the ratio $\Gamma_{\mathrm{L}}/\Gamma_{\mathrm{G}}$, one can consider the maximum value of the Voigtian profile. As the y-axis of an ESR spectrum is essentially in arbitrary units, the normalized Lorentzian, Gaussian, and Voigtian profile, whose integral over all real numbers is unity, can be used for the sake of simplicity without losing generality.

2.3. Deconvolution of the Voigtian profile using the maximum value of the normalized function

If an absorption spectrum as a function of magnetic field is a pure Lorentzian, which can be thought of as a special case of the Voigtian profile, the normalized version is given by

$$f_{\mathrm{L}}(B_\delta;\Gamma_{\mathrm{L}}) = \frac{\Gamma_{\mathrm{L}}}{\pi(\Gamma_{\mathrm{L}}^2 + B_\delta^2)}, \tag{2}$$

where B_δ is the magnetic field offset. The maximum, which occurs at the zero magnetic field offset, is given by

$$f_{\mathrm{L,max}} = \frac{1}{\pi\Gamma_{\mathrm{L}}}. \tag{3}$$

For a pure Gaussian profile, on the other hand, the normalized function and the maximum value are given by

$$f_{\mathrm{G}}(B_\delta;\Gamma_{\mathrm{G}}) = \frac{\sqrt{\ln 2}}{\sqrt{\pi}\Gamma_{\mathrm{G}}}\exp\left[-\ln 2\left(\frac{B_\delta}{\Gamma_{\mathrm{G}}}\right)^2\right], \tag{4}$$

$$f_{\mathrm{G,max}} = \frac{\sqrt{\ln 2}}{\sqrt{\pi}\Gamma_{\mathrm{G}}}, \tag{5}$$

where ln denotes the natural logarithm. It is evident from Eqs. (3) and (5) that the maximum value is inversely proportional to the linewidth and greater in the Gaussian profile than in the Lorentzian profile with the same HWHM. Unsurprisingly, the maximum value of the Voigtian profile is a function of the linewidths of the Lorentzian and Gaussian component.

In general, the normalized Voigtian lineshape is given by

$$f_{\mathrm{V}}(B_\delta;\Gamma_{\mathrm{L}},\Gamma_{\mathrm{G}}) = f_{\mathrm{L}}(B_\delta;\Gamma_{\mathrm{L}}) * f_{\mathrm{G}}(B_\delta;\Gamma_{\mathrm{G}}), \tag{6}$$

where the asterisk sign denotes the mathematical convolution. Using the complex error function, also known as the Faddeeva function, one can rewrite Eq. (6) in a more explicit form, which is [29–31]

$$f_{\mathrm{V}}(B_\delta;\Gamma_{\mathrm{L}},\Gamma_{\mathrm{G}}) = \frac{\sqrt{\ln 2}}{\sqrt{\pi}\Gamma_{\mathrm{G}}}\mathrm{Re}\left\{\exp\left[-\ln 2\left(\frac{B_\delta + i\Gamma_{\mathrm{L}}}{\Gamma_{\mathrm{G}}}\right)^2\right] \times \mathrm{erfc}\left[-i\sqrt{\ln 2}\left(\frac{B_\delta + i\Gamma_{\mathrm{L}}}{\Gamma_{\mathrm{G}}}\right)\right]\right\}, \tag{7}$$

where Re denotes the real part of the complex function, and erfc denotes the complementary error function. The maximum, which also occurs at the zero magnetic field offset, is given by

$$f_{\mathrm{V,max}} = \frac{\sqrt{\ln 2}}{\sqrt{\pi}\Gamma_{\mathrm{G}}}\exp\left[\ln 2\left(\frac{\Gamma_{\mathrm{L}}}{\Gamma_{\mathrm{G}}}\right)^2\right]\mathrm{erfc}\left[\sqrt{\ln 2}\left(\frac{\Gamma_{\mathrm{L}}}{\Gamma_{\mathrm{G}}}\right)\right]. \tag{8}$$

Indeed, Eq. (8) is a generalized form of Eq. (5) as the right hand sides of the two equations are identical if the lineshape is purely Gaussian, that is, $\Gamma_{\mathrm{L}} = 0$. On the other hand, by the asymptotic expansion of the complementary error function, Eq. (8) can be rewritten as

$$f_{\mathrm{V,max}} = \frac{1}{\pi\Gamma_{\mathrm{L}}}\sum_{n=0}^{\infty}(2n-1)!!\left(-\frac{1}{2\ln 2}\right)^n\left(\frac{\Gamma_{\mathrm{G}}}{\Gamma_{\mathrm{L}}}\right)^{2n}, \tag{9}$$

where !! denotes the double factorial. If the lineshape is purely Lorentzian, that is, $\Gamma_{\mathrm{G}} = 0$, the right hand side of Eq. (9) is equal to that of Eq. (3), indicating that Eq. (3) is a special case of Eq. (9).

It is clear from Eqs. (3) and (5) that the product of the linewidth and the maximum value is constant for a specific lineshape: the products are $1/\pi$ and $\sqrt{\ln 2}/\sqrt{\pi}$ for the Lorentzian and Gaussian