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Resolution of overlapping spectra by curve-fitting

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Abstract

In this paper we present a novel method of curve-fitting based on Gaussian function, which is used to resolve the overlapping peaks. Correctly choosing the minimum separable peak–peak interval (MSI) is crucial for this type of problem. We propose a method that chooses appropriate MSI by analyzing the curve-fitting error changes with the MSI. The resolution of several kinds of overlapping peaks with computer-simulated noise has been performed and discussed in details. This method has been used for resolving of the UV–vis overlapping spectrum. The results are satisfactory and clearly show the effectiveness of the proposed method.

Keywords: Overlapping peaks; Curve-fitting; Resolving overlapping spectra; Gaussian function

1. Introduction

Resolving overlapping peaks is an important yet difficult and challenging problem for analytical chemists. Besides preventing the overlap by chemical and instrumental methods, the mathematical mean has become an important tool to analyze the overlapping spectra. As for the algebraic methods, the most conventional approach is based on curve-fitting. The principle of curve-fitting is to represent peaks by certain analytical functions with some undetermined parameters and optimize these parameters to approximate the actual curve. Nevertheless, the achievement of a good representative fit requires the knowledge of the number of component bands, their positions, shapes and widths. Fleissner et al. [1] and Maddams and Mead [2] applied the second or fourth derivative in determining the number and the position of overlapping peaks. Fourier self-deconvolution (FSD) is an alternative method to estimate the parameters in curve-fitting [3,4]. Natural computation [5,6] was also applied to peak detection. Applying the wavelet technique to resolve overlapping signals is now an active field [7–9]. However, for severe overlapping cases the non-uniqueness problem becomes dominating. This has not been sufficiently addressed by the existing methods, therefore accurately locating and identifying the Gaussian peaks in such circumstances is still a difficult task.

In this paper, we introduce the theory of curve-fitting based on the Gaussian model to resolve overlapping spectra firstly. We then propose an algorithm based on both the minimum separable peak–peak interval and the curve-fitting error. Lastly, we use both simulated spectral data and experimental UV–vis spectra to verify the performance of the proposed method.

2. Theory

2.1. Mathematical model

Generally, the individual peak can be described by the Gaussian distribution function, which contains three parameters indicating the peak height, width and position, expressed as following:

$$g_{\mu,\sigma_\mu}(\lambda) = \frac{k_\mu}{\sqrt{2\pi}\sigma_\mu} \mathrm{e}^{-(\lambda-\mu)^2/2\sigma_\mu^2} = A_\mu \, \mathrm{e}^{-(\lambda-\mu)^2/2\sigma_\mu^2} \quad (1)$$

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where μ and σ_μ are the peak position and the standard deviation (width), and A_μ is the peak height. The fitting curve can be represented as:

$$f(\lambda) = \int_a^b g_{\mu,\sigma_\mu}(\lambda)\,\mathrm{d}\mu = \int_a^b A_\mu\,\mathrm{e}^{-(\lambda-\mu)^2/2\sigma_\mu^2}\,\mathrm{d}\mu \tag{2}$$

In practical computation, since the signal to be analyzed is often discrete sampling data, the discrete form of Eq. (1) is used:

$$g_{i,\sigma_i}(j) = \frac{k_i}{\sqrt{2\pi}\sigma_i}\mathrm{e}^{-(j-i)^2/2\sigma_i^2} = A_i\,\mathrm{e}^{-(j-i)^2/2\sigma_i^2} \tag{3}$$

The fitting curve can be expressed as:

$$f(j) = \sum_{i=1}^{N} g_{i,\sigma_i}(j) = \sum_{i=1}^{N} A_i\,\mathrm{e}^{-(j-i)^2/2\sigma_i^2},$$
$$(i, j = 1, 2, \ldots, N) \tag{4}$$

For the route of curve-fitting, the goodness of fit criterion is defined as:

$$E = \frac{1}{2}\sum_{j=1}^{N}[f(j) - f^*(j)]^2 \tag{5}$$

where $f^*(j)$ and $f(j)$ are the original dataset and the fitting dataset, respectively. The parameters A_i and σ_i ($i = 1,2,\ldots, N$) are determined by minimizing the mean-square error E. The initialization of A_i, σ_i ($i = 1, 2,\ldots, N$) can affect algorithm convergence. If they are stationed in a flat region of the error surface the convergence can be extremely slow. Typically, A_i and σ_i ($i = 1, 2,\ldots, N$) are initialized with non-negative random numbers near zero. In this paper, the initial A_i, σ_i ($i = 1, 2,\ldots, N$) are randomly chosen within (0, 1). We also refer to the initial A_i, σ_i ($i = 1, 2,\ldots, N$) as the initial conditions.

According to Eqs. (4) and (5), we can deduce that:

$$\frac{\partial E}{\partial A_i} = \sum_{j=1}^{N}[f(j) - f^*(j)]\,\mathrm{e}^{-(j-i)^2/2\sigma_i^2} \tag{6}$$

and

$$\frac{\partial E}{\partial \sigma_i} = \sum_{j=1}^{N}[f(j) - f^*(j)]\,\mathrm{e}^{-(j-i)^2/2\sigma_i^2} A_i\frac{(j-i)^2}{\sigma_i^3} \tag{7}$$

In order to improve the stability of the iterative process, an inertia factor α is introduced into the adjustment equations as follows:

$$\Delta A_i(t+1) = -p_A\frac{\partial E}{\partial A_i} + \alpha_A\Delta A_i(t) \tag{8}$$

and

$$\Delta\sigma_i(t+1) = -p_\sigma\frac{\partial E}{\partial \sigma_i} + \alpha_\sigma\Delta\sigma_i(t) \tag{9}$$

where $\Delta A_i(t)$ and $\Delta A_i(t+1)$ are the adjustment of A_i at the time t and $t+1$, p_A and α_A the adjust step and the inertia factor of A_i, $\Delta\sigma_i(t)$ and $\Delta\sigma_i(t+1)$ the adjustment of σ_i at the time t and $t+1$, p_σ and α_σ the adjust step and the inertia factor of σ_i. Selection of p and α can be difficult. The same problem appears in the training for the neural network [10]. The adjust step p determines the size of the adjustment each time. A large adjust step p will accelerate convergence. However, this may cause the search to oscillate on the error surface and never converge, thus increasing the risk of overshooting a near-optimal solution. In contrast, a small adjust step will converge slowly and may also result in falling into some local minima other than a global minimum. The inertia factor α determines the change rate of p to help the search escape local minima and reduce the likelihood of search instability. In this paper, we choose $p = 0.1$–0.6 and $\alpha = 0.03$–0.3. The simulation experiments show such a choice is appropriate.

The proposed approach can be applied to the signals, whose individual peak can be described by the Gaussian or Lorentzian function.

2.2. Non-uniqueness of the curve-fitting

For any original signal $f^*(j)$ ($j = 1, 2,\ldots, N$), it can always be fitted with:

$$f(j) = \sum_{i=1}^{N} g_{i,\sigma}(j) = \sum_{i=1}^{N} f^*(i)\,\mathrm{e}^{-(j-i)^2/2\sigma^2}$$

where $\sigma \to 0$ and $\sigma \neq 0$. Then

$$\mathrm{e}^{-(j-i)^2/2\sigma^2} = \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases}$$

and obviously, $f(j) = f^*(j)$.

This shows that any signal may be fitted by different groups of Gaussian peaks under an acceptable error. In other words, curve-fitting is mathematically non-unique. One of the main drawbacks involved is that as the bands become more overlapped or the number of overlapping bands increases, the problem becomes progressively more ill-conditioned. Even so, it is still possible to carry on curve-fitting effectively with some knowledge that includes the characteristic of material and the resolution ratio of spectra, etc. A part of this knowledge is related to the characteristic absorption band, the real peak–peak interval or peaks intensity ratio of the spectrum, and so on. In the following algorithm, we try to resolve overlapping spectra using the theory mentioned above.

3. Algorithms

First we define two terms: the minimum real peak–peak interval (MRI) R, which is the minimum value in all intervals of adjacent peaks, $R = \min(\lambda_{i+1} - \lambda_i)_{i=1,2,\ldots,N-1}$; and the minimum separable peak–peak interval (MSI) r, which is the minimum interval between the peaks that can be separated by the present procedure. The proposed method includes two