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Resolving overlapped spectra with curve fitting

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Abstract

A novel method of curve fitting based on Gaussian function, which is used to resolve the overlapped peaks, is presented in this paper. The resolution of several kinds of overlapped peaks with noise simulated by computer has been performed and discussed in details. This method has been used for resolving of the UV–vis overlapped spectrum. The results indicate that the proposed algorithm can been used to resolve overlapped spectra effectively and satisfactorily.

Keywords: Overlapped peaks; Curve fitting; Gaussian function

1. Introduction

One of the important tasks of spectral analysts is to resolve the overlapped peaks, which has also been a difficult and challenging problem for spectral analysts. Besides preventing the overlap by chemical and instrumental methods, the mathematical means has to be an important tool to resolve the overlapped peaks. As for the algebraic methods, the most conventional approach is based on curve fitting, the principle of which is to represent peaks by certain analytical functions with some undetermined parameters and optimize these parameters to approximate the actual curve, and the individual peak area can be calculated with optimized parameters after the precision of approximation is satisfied. Nevertheless, the achievement of a good representative fitting requires the knowledge of the number of component bands, their positions, shapes and widths. The most important values for input to curve fitting route are the number of bands and their positions. Up to present, there are many methods employed for doing this. Maddams and coworkers [1,2] applied the second or fourth derivative in determining the number and the position of overlapped peaks. Fourier self-deconvolution (FSD) is an alternative method for an estimation of parameters in curve fitting [3,4]. Apart from these methods, natural computation [5,6] also was applied to peak detection. Wavelet transform is a novel signal processing technique developed from the Fourier transform and has been widely used to resolving and quantifying the overlapped peaks effectively [7–9]. Now using wavelet technique to resolve the overlapped signal is an active field. However, just as below-mentioned reasons, all these methods cannot to located and identified accurately in the case of severe overlapping.

In the present, the theoretical basis of curve fitting based on the Gaussian model is introduced. Then the procedure based on the minimum interval of separable peak–peak and the plot of the error of curve fitting for extracting the peak positions of overlapping peaks have been given. Lastly, the simulated spectral data set and experimental UV–vis spectrum are used to validate the performance of the proposed method in the resolving of overlapped spectra.

2. Theory

2.1. The model

Generally, the individual peak can be described by a Gaussian distribution function, which contains three parameters

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indicating the peak height, width and position, and is usually expressed as follows:

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

where $\propto$ and $\sigma_\propto$ are the peak position and the standard deviation (width), and $A_\propto$ is the peak height. The fitting curve can be represented as

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

In practical computation, since the signal to be analyzed is often discrete sampling data, the discrete form of Eq. (1) is necessarily used, which will become as

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

Thus, the fitting curve can be expressed as:

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

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

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

where $f^*(j)$ and $f(j)$ are the original dataset and the fitted dataset, respectively, and j is the number of data points.

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

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

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

In order to improve the stability of iterative process, we introduce an inertia factor α into the adjustment formula as follows:

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

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

where $\Delta A_i(t)$ and $\Delta A_i(t+1)$ are the adjustment of A_i at the time t and $t+1$, respectively, P_A and α_A are the adjust step and the inertia factor of A_i, respectively.

The generality of the proposed approach in this work is that this approach can be also applicable to the signal that can be described by Gaussian or Lorentzian function, because Gaussian or Lorentzian signal also has similar properties.

2.2. The nonuniqueness of curve fitting

For any original signal $f^*(j)$ ($j = 1, 2, \ldots, N$) whereas we can find or not, it always can 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

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

This shows that any signal may be fitted by some different Gaussian peaks under allowable error. In other word, curve fitting is nonunique. One of the main drawbacks involved is that as the bands become more overlapped, or the number of overlapped bands increases, the problem becomes progressively more ill-conditioned.

3. Algorithms

Firstly, we define two terms of the following. The minimum interval of real peak–peak (MIR) R is the minimum value in all intervals of adjacent peaks, and can be expressed as $R = \min(\lambda_{i+1} - \lambda_i)_{i=1,2,\ldots,n-1}$ The minimum interval of separable peak–peak (MIS) r is the lower limit interval of real peak–peak which the program can separate. The proposed method comprises two main aspects: extracting the peak position and determining peak height and peak width.

3.1. Estimating iterative time T_{max}

For estimating iterative time, the key steps of the procedure consist of the following:

Step 1: Initially, taking A_i,σ_i ($i = 1, 2, \ldots, N$) are in (0,1) randomly, $p = 0.1$, $\alpha = 0.3$, $\Delta A_i(1) = 0$, $\Delta\sigma_i(1) = 0$ ($i = 1, 2, \ldots, N$) and $t = 1$. Specifying the allowable error of curve fitting $E_{\max}$;
Step 2: E is computed according to Eqs. (4) and (5);
Step 3: If $E \leq E_{\max}$, jump to the Step 6;
Step 4: The derivative of A_i, σ_i($i = 1, 2, \ldots, N$) are computed according to Eqs. (6) and (7);
Step 5: $\Delta A_i(t+1)$ and $\Delta\sigma_i(t+1)$ ($i = 1, 2, \ldots, N$) are computed according to Eqs. (8) and (9), let $t = t+1$, return Step 2;
Step 6: $T_{\max} \geq t \times 3$, end. The above-mentioned algorithms are the continue curve fitting to original spectrum, namely suppose that the independent peak may exist in all places. In this case, the peak widths are all very narrow. Though the curve fitting is quickly, and the error can reach very small,