Resolution enhancement for infrared spectroscopy data

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Abstract: The analysis and utilization of spectroscopic data represent an emergent technology of increasing importance from both practical and theoretical perspectives. The reasons for this include:

 (i) It is now relatively inexpensive to rapidly collect, for the material being examined, a highly accurate measurement on a (very) fine wavelength grid of its spectroscopic response to a given electromagnetic stimulus.

(ii) Because of the availability of such data, sophisticated algorithms can be applied to recover information of relevance to the application context within which the spectroscopic data have been recorded. They include:

   (a) **Derivative Spectroscopy** (Anderssen and Hegland [2010]; Wiley et al. [2009]). The classical numerical analysis *mantra* about the need to explicitly invoke regularization methodology to stabilize the application of finite difference differentiators related to the fact that the available observational data was sparse and noisy. The sparseness of the data precluded the use of finite difference differentiators with large footprints. For accurate data on a fine grid, the stablization can be invoked explicitly by choosing finite difference differentiators with large footprints. As explained in Anderssen and Hegland [1999], and earlier in Anderssen and de Hoog [1984], large footprint finite difference differentiators implicitly perform averaging with the size of the footprint taking on the role of the regularization parameter.

   (b) **Resolution Enhancement** (Hegland and Anderssen [2005]). In the analysis of measured spectra, the goal is the identification of the positions and heights of the spectral lines which correspond to different molecular aspect of the material being studied. In some situations, as in mass spectroscopy, the associated technology can yield highly accurate positions and heights for the spectral lines. In others, such as near infrared (NIR) and mid infrared (mid-IR) spectroscopy, the technology only recovers a smooth approximation of the lines. When the lines are closely spaced and broadened, overlapping betweem them occurs. The recovery of the positions and heights of the lines then becomes a challenging problem especially when explicit models for the measured shape of the peaks approximating the lines are unknown. Numerous methods have been proposed for resolving the fine scale structure in the latter situations. They include a variety of non-linear least squares methods. Their disadvantage is that good starting solutions for the subsequent numerical iterations are required. The alternative approach of resolution enhancement aims to undo the broadening occuring as a result of the measurement process in order to yield an informative reconstruction of the actual positions and heights of the lines.

Here, we investigate the recovery of molecular information from mid-IR data using the peak sharpening (narrowing) methodology of Hegland and Anderssen [2005], and compare it with the traditional resolution enhancement techniques of derivative spectroscopy Anderssen and Hegland [2010].

Keywords: derivative spectroscopy, resolution enhancement, peak sharpening, NIR, mid-IR

1 BACKGROUND

Because the measured spectroscopic response of a material records the proportional presence of specific molecular features of its molecular components, the information contained in such data can be exploited in multiple ways. For example, NIR spectroscopy, from a practical perspective, is used to assess the sugar levels in fruit before they are picked; to perform *in-situ* biomedical monitoring; to monitor pharmaceutical processes; to allow, in plant breeding trials, a huge number of plants to be rapidly screened for the presence-absence of specific molecules; to measure the quality of recently harvested wheat with respect to the criteria that determines the price to be paid to farmers. The effectiveness, reliability, acceptability and legality of such activities rests heavily on the quality of the science and mathematics involved in their implementation.

An illustrative example of such utility is the recent use of NIR spectroscopy to gain insights about the protein composition and morphology of barley mutants. In Wiley et al. [2009], it was shown how derivative spectroscopy can be used to inhance the information extracted from their NIR spectra. The importance of the differentiation is its potential to increase spectral resolution, in the form of peak sharpening, and that this represents an opportunity for improving the recovery of molecular information from NIR spectra.

In spectroscopy, the importance of peak identification is that the frequency (wavelength) of the location of the peak is the link, via quantum vibrational theory, to the known types of molecular moieties that vibrate at that frequency in response to the type of electromagnetic stimulus being activated. Such information, in conjunction with the known molecular components forming the material being studied, allows the proportional presence of individual molecular components to be assessed and compared.

NIR spectroscopy is only one of a number of electromagnetic spectroscopic measurement platforms. Other include Raman and mid-IR. Their relative importance relates to the fact that each records indirectly a different aspect of the molecular composition of the material being examined. This fact has been exploited in various ways. On the one hand, the nature of the required information about the material determines the choice of spectroscopy – NIR for the rapid (qualitatively quantative) assessment of molecular side-chain structure; Raman for the assessment of molecular back-bone structure; mid-IR for a more accurate quantitative assessment of molecular side-chain structure. On the other hand, joint inversion becomes a possibility as explained in Anderssen et al. [2005], where NIR and Raman measurements were used jointly to enhance the accuracy of calibration-and-prediction for the molecular properties of wheat. The rationale behind the choice of NIR and Raman relates to the fact that an NIR stimulus excites vibrations mainly in the side chains on organic molecules, whereas a Raman stimulus excites vibrations in the backbones of organic molecules.

For any of these situations, a variety of resolution enhancement techniques are available. They include the traditional ones base on derivative spectroscopy (Anderssen and Hegland [2010]), and the peak sharpening (narrowing) techniques of Hegland and Anderssen [2005]. The goal of this paper is a simulation study of the numerical performance of these two protocols when applied to mid-IR data.

2 NIR AND mid-IR SPECTRA

The motivation for comparing resolution enhancement techniques on mid-IR data relates directly to the fundamental difference in the vibrational characteristics of NIR and mid-IR spectra.

Though NIR instruments record at higher energy levels (because radiation levels from black body emitters are higher at shorter wavelengths than longer wavelengths), and have high sensitive photo-conductive detectors and low manufacturing costs, their major technological weakness is that the wavelengths, at which they record the NIR quantum response, correspond to the overtones of the fundamental vibrations the wavelengths of which are located at mid-IR frequencies. As a result of this frequency difference, the peaks which form an NIR spectra are broader than the corresponding peaks which form the mid-IR spectra of the same material. Consequently, the resultant recovery of information from NIR spectra and their utilisation in calibration-and-prediction procedures tends to be less quantitative from a decision-making perspective.

Though mid-IR instruments record at lower energy levels, are more expensive to manufacture and must cope with the strong absorption of mid-IR by materials, they have some clear advantages. They include

the fact that because organic functional groups have characteristic and well delineated absorption bands at mid-IR wavelengths and mid-IR spectra of mixtures are additive, molecular identification is more quantitative and associated calibration-and-prediction more reliable.

Consequently, mid-IR spectra, because they represent a combination of individual and overlapping reasonably narrow spectral peaks, represent appropriate data on which to compare resolution enhancement techniques.

3   RESOLUTION ENHANCEMENT

When a spectrum is known to contain overlapping peaks at the wavelengths of interest, the need for resolution enhancement arises naturally. Such situations occur regularly in all branches of spectroscopy. In mass spectroscopy, the degree of the overlapping is inversely proportional to the sophistication (and hence the cost) of the instrument. Because this is not an option for other classes of spectroscopic data, resolution enhancement algorithm design is an important aspect of modern computational mathematics.

Here, the focus is on derivative spectroscopic and peak sharpening (narrowing) techniques.

3.1   Derivative Spectroscopy

From the early days of NIR spectra analysis and interpretation, numerical differentiation was one of the techniques applied to remove the linear scatter effect which polluted each individual spectra, resulting from the stochastic nature of the particle packing of a sample (Osborne et al. [1993]). However, initially, the peak sharpening resolution enhancement resulting from the differentiation was not fully exploited. Independently and moreorless simultaneously, as explained in Anderssen and Hegland [2010], the role of numerical differentiation as a peak sharpening and location protocol was utilized in the analysis of analytic chemistry data. It was within that context that the differentiation of data was referred to as *"derivative spectroscoy"*, in order to highlight its resolution enhancement potential. The essence of the situation is easily explained. The differentiation of data enhances higher frequency components in a signal more strongly than lower frequency components. In this way, hidden small amplitude high frequency structure in the original data can be uncovered. This is easily illustrated algebraically using a signal of the form

$$y(t) = \sin(t) + \epsilon \sin(\omega t), \qquad \epsilon << 1, \qquad \omega >> 1,$$

for which the second and fourth derivatives take the form

$$\frac{d^2 y}{dt^2} = -\sin(t) - \epsilon \omega^2 \sin(\omega t), \qquad \frac{d^4 y}{dt^4} = \sin(t) + \epsilon \omega^4 \sin(\omega t).$$

3.2   Peak sharpening (narrowing)

In the modelling of spectra, it is usually assumed that the effect of the measurement process can be modelled as a broading of the actual spectral response $R(t)$ of the given material to the applied electromagnetic stimulus. The unknown broading is often defined as a known peak function $B_\gamma(t)$ (e.g. Gaussian) with γ being a proportional characterization of the unknown degree of the broadening. A measured spectrum $S(t)$ is then modelled as the convolution of the chosen broadening function $B_\gamma(t)$ and the actual spectral response $R(t)$:

$$B_\gamma * R\,(t) = S(t). \tag{1}$$

In NIR spectroscopy, the independent variable t corresponds to wavelength or frequency, depending on the perspective of the application.

The essence of the peak sharpening ansatz is the assumption that the convolution equation (1) can be decomposed to take the form

$$B_\alpha * R^\#\,(t) = S(t), \quad R^\#(t) = B_\beta * R\,(t), \quad B_\alpha * B_\beta = B_\gamma. \tag{2}$$

This yields a solution $R^\#(t)$ which has sharper peaks than the original measured spectra $S(t)$ and, hopefully, will have resolved the location and structure of some of the broader peaks forming overlapping

structure in $S(t)$. In terms of the error analysis discussed in Hegland [2010], the relationship $R^{\#}(t) = B_{\beta} * R(t)$ corresponds to the source condition.

Now let B_{α}^{-1} denote the (formal) convolutional inverse of B_{α} such that

$$B_{\alpha}^{-1} * B_{\alpha}(t) = \delta(t)$$

where $\delta(t)$ denotes the Dirac delta function. The solution of equation (2) to recover $R^{\#}(t)$ reduces to evaluating the right hand side of

$$R^{\#}(t) = B_{\alpha}^{-1} * S(t). \tag{3}$$

This can be performed algorithmically in the following manner (cf. Hegland and Anderssen [2005]). We assume that the following scaling relationship holds:

$$B_{\alpha}(t) = B(\alpha t)$$

for the function $B(t) = B_1(t)$. The convolutional inverse B^{-1} of B shall furthermore be approximated by derivatives such that

$$B^{-1} * S(t) \approx \sum_{j=0}^{J} \beta_j (-1)^j \frac{d^{2j}}{dt^{2j}} S(t).$$

By the scaling relationship, one obtains

$$B_{\alpha}^{-1} * S(t) \approx \sum_{j=0}^{J} \beta_j (-\alpha)^j \frac{d^{2j}}{dt^{2j}} S(t) \tag{4}$$

and the Fourier transform is

$$\mathcal{F}[B_{\alpha}^{-1} * S](\omega) \approx \sum_{j=0}^{J} \beta_j \alpha^j \omega^{2j} \mathcal{F}[S](\omega).$$

Formally, one has

$$\mathcal{F}[B^{-1}](\omega) \approx \sum_{j=0}^{J} \beta_j \omega^{2j}$$

and thus a possible choice of the β_j are the Taylor coefficients of $\mathcal{F}[B^{-1}](\omega)$ at $\omega = 0$. This is the approximation used for the Eddington correction, here a more accurate approximation is used.

In a particular application, such as discussed below for the application of peak sharpening to mid-IR data, an optimal-like choice for α is found by examining a range of possibilities. The actual peak sharpening algorithm used in the current simulation study has three parameters: S the length of the footprint of the differentiator; ND the value of J in equation (4); γ the value of α in equation (4) is the extent of the broadining.

4 SIMULATION STUDIES USING MID-IR DATA

The mid-IR spectra analysed in this simulation study are the mid-IR spectra recorded for the same wheat samples that were used by Anderssen et al. [2005] in their joint inversion study with both NIR and Raman spectra.

Figure 1 is a plot, for a wheat sample with a protein content of 9.85%, of the mid-IR data (top-left), the peak-sharpening solution (top-right), the second derivative (bottom-left) and the fourth derivative (bottom-right).

Figure 2 is a plot, for a wheat sample with a protein content of 10.4%, of the mid-IR data (top-left), the peak-sharpening solution (top-right), the second derivative (bottom-left) and the fourth derivative (bottom-right).
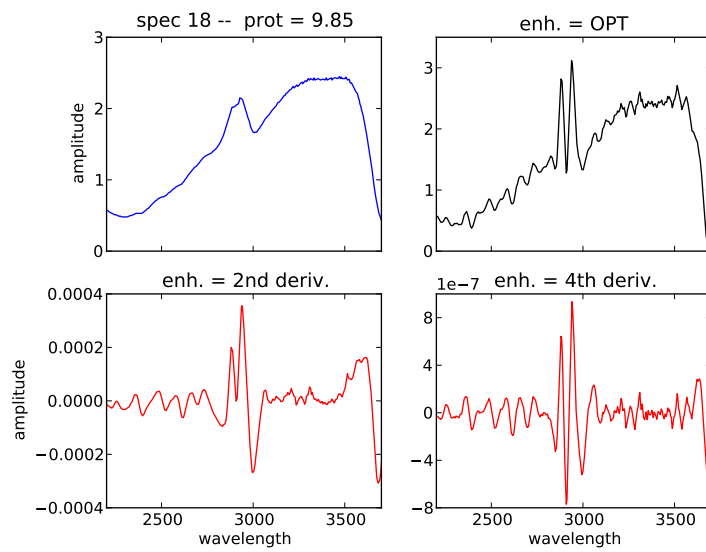
Figure 1: A plot the mid-IR data, its peak-sharpening solution, its second derivative and its fourth derivative.
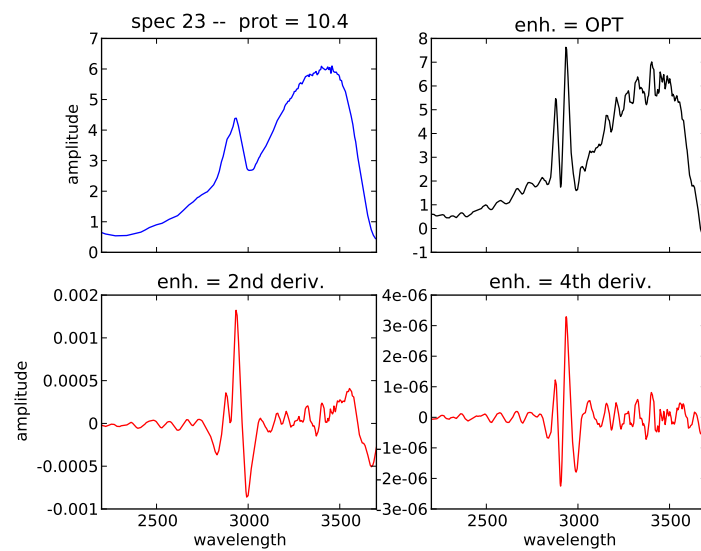

Figure 2: A plot of the mid-IR data, its peak-sharpening solution, its second derivative and its fourth derivative.
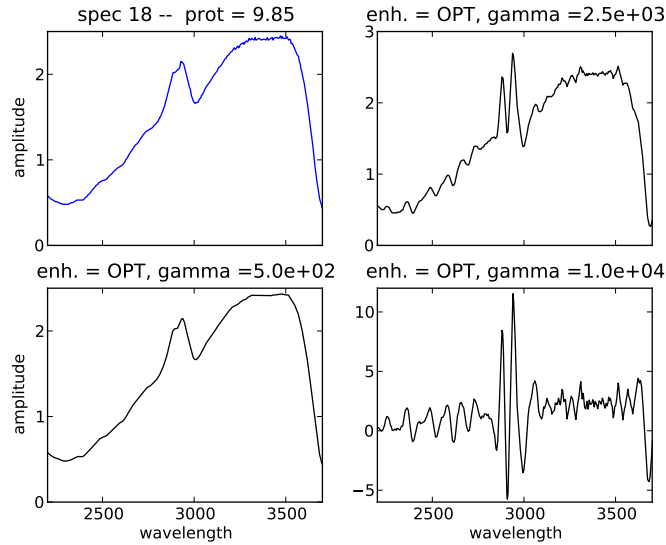
Figure 3: A validation of the role of the broadening parameter γ: A plot of the mid-IR data, its peak-sharpening solution, the reconstruction of the original data, and a reconstruction of the fourth derivative.

As already mentioned, the peak sharpening algorithm has the three parameters: S the length of the footprint of the differentiator; ND the value of J in equation (3); γ the extent of the broadining. Figure 3 is a validation study of the performance of the peak sharpening parameter γ. For the wheat sample with a protein content of 9.85% of Figure 1, Figure 3 is a plot of the the mid-IR data (top-left); the "optimal" peak-sharpening solution (top-right) with $S = 12$, $ND = 2$ and $\gamma = 2.5e + 03$; for $S = 12$, $ND = 2$ and $\gamma = 5.0e + 02$, the peak sharpening algorithm yields a good reconstruction of the mid-IR data (bottom-left); and, for $S = 12$, $ND = 2$ and $\gamma = 1.0e + 04$, the peak sharpening algorithm yields a good reconstruction of the fourth derivative (bottom-right) of the mid-IR data.

On the basis of a comparison of the results in Figures 1-3, one can make the following observations:

(i) In Figures 1 and 2, the peak sharpening reconstruction compares favourably with the second and fourth derivative reconstructions. Whereas the second and fourth derivative reconstructions, respectively, remove the underlying linear and cubic trends in the data, the peak sharpening algorithm removes the polynomial trend in the null space of B_α^{-1} of equation (4).

(ii) A comparison of the second and fourth derivatives in both Figures 1 and 2 confirms that the fourth derivative gives a more accurate location of the peaks and uncovers structure not seen in the second derivative.

(iii) The advantage of the second and fourth derivative reconstruction is the accentuated location of the peaks that they achieve. However, it appears that this is achieved at the expense of obtaining a good estimate of the proportional presence of the associated molecules.

(iv) The advantage of the peak sharpening reconstruction is that it gives a more realsitic estimate for the proportional presence of the molecules contributing to the vaious peaks. However, this is at the expense of obtaining accurate locations for the peaks.

5 CONCLUSIONS AND RECOMMENDATIONS

On the basis of the above results, it is clear that the choice of algorithm for performing the reconstruction should be based on the information required. It is recommended that a fourth derivative reconstruction is

used to locate the position of the peaks, and the peak sharpening reconstruction when the relative heights of the peaks relates to the matter being examined.

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