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DERIVATIVE SPECTROSCOPY–AN ENHANCED ROLE FOR NUMERICAL DIFFERENTIATION

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ABSTRACT. In many areas of science, through the use of modern computer-controlled instrumentation, highly accurate indirect measurements of the phenomenon/process of interest are being generated on a (very) fine spatial and/or temporal grid. Consequently, this is creating new opportunities for the enhanced recovery of information about the underling phenomenon/process being studied. In particular, an enhanced role for numerical differentiation is emerging in the application of *derivative spectroscopy*, which has its origins in the analysis of various forms of spectroscopic data. For example, through its use, information about the molecular components in plant material, such as barley seeds, is being recovered by comparing the fourth derivatives of their measured near infra-red (NIR) spectroscopic responses. As well as practical matters that arise with the utilization of derivative spectroscopy in the recovery of information, there are theoretical questions that require investigation about the choice of the numerical differentiator, the interpretation of the fourth derivative and an assessment of how high a level of differentiation that given data will support. Such matters have already been investigated in considerable detail except for the question of estimating the maximum level of differentiation that given data can support before the onset of instability. This is the focus of the current paper, which highlights how published results can be reinterpreted to answer this question. In particular, it will be shown that, if circumstances are such that, for a particular numerical differentiator, an accurate approximation to the first derivative of the available observational data can be guaranteed, then it is highly likely that it can be utilized to generate good approximations to second, third and fourth derivatives. Interestingly, this runs contrary to the historical view that, as the order k of the differentiation of observational data increases, the onset of instability increases rapidly.

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1. Introduction. Though it is a technology that dates from the invention of micro-processors in the 1960s, computer-controlled instrumentation, because of the impact of computer micro-chip technology, is playing an increasingly importance role in enhancing the performance of various classes of instruments and devices. Traditionally, the control was external with a computer system designed to interface to a particular instrument in order to improve its operation in a variety of different ways (speed, automation, accuracy) [**6, 7, 19, 24, 25, 32**]. Through the utilization of micro-chip technology, the computer has become an essential internal part of the hardware of the instrument and is programmed to control and enhance its operation.

Examples of the latter class include various types of modern spectrometers [**6, 32**], automated capillary electrophoresis [**24**], automated monitoring of dangerous substances [**19**] and automated remote controlled vehicles [**25**]. In such instruments, the internal computer-control has been programmed to perform a large number of repeated scans of the signal being measured, usually on a very fine temporal and/or spatial grid, and to then average them to become the output signal for subsequent display, analysis and interpretation. Consequently, the averaging ensures that the resulting output is a highly accurate realization of the signal being measured. Having been recorded on a very fine grid, a plot of the output appears, visually, to be a plot of some well-behaved smooth analytic function (e.g., Figures 3, 4 and 5 in Wiley et al. [**34**]).

In many situations, such outputs will correspond to indirect measurements of some underlying phenomenon/process, for which a corresponding information recovery must be performed. Consequently, in solving the associated inverse problem, the availability of such highly accurate indirect measurements has created new opportunities and challenges for the recovery of the relevant information. For example, the need to pre-smooth the data, parametrically or non-parametrically, is often no longer necessary. In a way, this has already been performed by the averaging of a large number of sweeps.

In addition, the availability of such accurate output has created an enhanced opportunity for the numerical differentiation of observational data in the form of *derivative spectroscopy*.

For example, by comparing the fourth derivatives of their measured near infra-red (NIR) spectroscopic responses [**5, 18**], information is

being recovered about the molecular components in plant material, such as barley seeds [**34**], the content of pharmaceutical mixtures [**10**] and the whey protein content in milk [**26**]. As well as the practical matters that arise with the utilization of derivative spectroscopy in the recovery of information, there are theoretical questions that require investigation about the choice of the numerical differentiator, the interpretation of the fourth derivative and an assessment of how high a level of differentiation that a given highly accurate data set will support. Estimating the maximum level of differentiation is the focus of the current paper.

The paper has been organized in the following manner. Section 2 gives background information about derivative spectroscopy and, for motivation, briefly discusses its use in solving an inverse problem associated with the recovery of molecular information from NIR spectroscopy measurements. Section 3 examines, using appropriate numerical estimates including interpolatory inequalities, the problem of estimating the maximum level of differentiation that can be performed on given data before the onset of instability is likely to occur.

2. Derivative spectroscopy. In their discussions of and comments about the history of *derivative spectroscopy*, Fell and Smith [**13**] give Lord Rutherford the credit for its original conceptualization for suggesting "*the first derivative for more sensitive mass spectrometric detection of gas excitation potentials*" [**11**]. Fell and Smith went on to comment that, as discussed in [**21, 22**], the concept of second and third derivative detection was patented in 1953 by two industrial chemists who "*first demonstrated the usefulness of higher derivatives in analytic spectroscopy*". Fell and Smith also noted that it was the advent of the "*low noise operational amplifiers*" which initiated the use of high-quality electronic differentiators which led to the early applications of derivatives to the analysis of spectroscopic data. It is now computer-controlled instrumentation that has replaced the "low noise operational amplifiers" as the source for the continuing popularity of derivative spectroscopy.

In conjunction with this scientific activity, various papers were published about the background mathematical methodology [**7, 14**]. In subsequent years, an interesting list of novel applications have emerged which illustrate how derivative spectroscopy has become a key tool for

the recovery of molecular information [**23, 24**]. It is now used to estimate the amount of vitamin C in medication [**31**]. In NIR spectroscopy, in order to have a common basis for comparison, the first and second derivatives of the measured spectrum are routinely utilized to remove the effects attributed to sample particle size and scatter [**29**].

The utility of derivative spectroscopy has been illustrated in two independent ways. In earlier literature [**28**], the effect of successively differentiating the Gauss probability distribution was the popular example. More recently, in order to highlight the spectral enhancement of small amplitude high frequency components in the measured spectrum, the successive differentiation of functions like $y(x) = \sin(x) + A\sin(\omega x)$, with $A \ll 1$ and $\omega > 1$, have become popular [**34**]. Such a model generalizes naturally to the situation where the perturbation in the measured spectrum can be given as a Fourier series.

From a theoretical perspective, the issues that have been discussed in some detail include the optimization of the choice of the numerical differentiation procedure to be applied to the data, the interpretation of the fourth derivatives (relative to the original curve) and error estimates. The popularity of the fourth derivative relates to it being back in phase with the original data, and has been utilized in a wide variety of practical situations [**10, 23, 26, 34**]. The justification includes the facts that the fourth derivative of a Gaussian has a peak back at the same position as the original Gaussian (but modified by the presence of side lobes), that considerable enhancement of the higher frequency structure in the data has occurred and that it has been successful in resolving practical issues in earlier endeavors. However, the level of differentiation that given data can support before the onset of stability has not been specifically addressed. As discussed below, there is an extensive literature on the error analysis for computing higher order numerical derivatives. However, the question of the maximum level that can be performed is not specifically addressed. In fact, it is often tacitly implied that, as the order k of the differentiation of observational data increases, the onset of instability increases rapidly. As the discussion below will highlight, this is not usually the situation.

In practical situations, where derivative spectroscopy has played a key role in resolving or clarifying the issues under investigation, this has been achieved because the information coming from the derivatives of the data can be matched with related quantitative/scientific interpre-

tations which give meaning to the structure exposed by the derivatives. For example, in the differentiation of NIR spectra, the wavelengths, at which peaks occur in the derivatives, actually correspond to the wavelengths at which various molecular side chains vibrate [**29**]. The linking of this vibrational spectroscopic information with the known material components in the sample being studied allows conclusions to be drawn about the proportional presence of various components in the sample. Using just such a strategy allowed Wiley et al. [**34**] to draw conclusions about the protein composition of different classes of barley mutants.

3. Estimating the maximum level of differentiation. There are various ways in which the performance of the numerical differentiation of observational data can be characterized. They include classical numerical analysis [**15, 16, 33**], spectral and Fourier [**1, 9, 30**], regularization [**4**] and interpolatory inequalities [**20**]. As well as deriving error estimates, the emphasis is often the comparison of one numerical procedure with another.

As the discussion below highlights, in most papers, the analysis reduces to determining an upper bound on the error [**4, 15, 16, 20, 30, 33**], and assuming the worst case situation (that such a bound identifies) is representative of the general situation for the onset of instability. Consequently, though useful when they identify, as a function of the level of differentiation being performed, the tradeoff between the error in the data and some property that characterizes the regularity of the methodology being examined, upper bounds are sub-optimal in estimating the maximum level of differentiation that can be performed in a given situation. The resulting numerical derivative might be much more realistic than the upper bound implies. A corresponding situation holds for lower bounds ([**33**, Theorem 3.1]). Even though they identify the best possible outcome, the actual derivative might be quite inferior.

Clearly, what is required is either some nesting between lower and upper bounds or some tradeoff functional which balances accuracy and instability as a function of the level of differentiation k. An example of the former, which holds for Lagrangian differentiation, is given in Wang and Feng [**33**] and is discussed below. Possible choices for the latter are also examined.

3.1. Standard numerical analysis arguments. In the sequel, f will denote the function (signal) for which an estimate of its k-derivative, $k \geq 1$, is required, while

$$f_\eta = f + \eta, \qquad \|f - f_\eta\| < \varepsilon,$$

denotes the observed form of f that is actually differentiated. Here, the interest is primarily on the dependence of $\|f^{(k)} - f_\eta^{(k)}\|$ on ε for various choices of k, where $f^{(k)} = d^k f/dx^k$, $k = 1, 2, \ldots$. Though quite different methodologies have been proposed for the numerical differentiation of observational data (e.g., [**15, 16, 30, 33**]), the error estimates derived to characterize their numerical performance all take a similar form.

For example, in [**12, 15, 16, 17**], it is shown how optimal convergence rates can be achieved by linking the step-length h, for evenly spaced data, to be a function of ε; namely, $h \sim \varepsilon^{1/p}$, with $p \geq k$. In [**30**], where Fourier truncated kth order differentiators are examined, estimates of the following form are derived,

$$\|f^{(k)} - f_\eta^{(k)}\| \leq E^{k/p} \varepsilon^{(p-k)/p}, \tag{1}$$

where p defines the order of the Sobolev norm $\|f\|_p$ for which the bound $\|f\|_p < E$ holds. A direct argument is used in [**30**] to derive (1). This bound is identical to that which would be derived using interpolatory inequalities [**12**]. In [**12**], the counterpart of having h as a function of ε is a condition that defines the low pass filtering to be performed on the Fourier representation of f_η. In [**33**], where Lagrangian differentiation is analyzed, estimates of the following form are derived

$$\begin{gathered} \|f^{(k)} - f_h^{(k)}\| \leq C_k \varepsilon^{(p-k)/p}, \\ p = n + 1, \quad h = 1/n, \quad h \asymp \varepsilon^{1/p}, \end{gathered} \tag{2}$$

where, here, f_h denotes the chosen form of the Lagrange interpolation formula.

The estimate (1) can be used to explore when high values of k are possible. It is natural to assume that $\varepsilon \ll 1$ because, as explained above, the data to be differentiated, because of the averaging of a large number of replicates on a fine grid, will be quite accurate and dense.

If, in addition, $E < 1$, then accurate estimates for $f^{(k)}$ for large k will be ensured. If $E > 1$, there are two possibilities. If E is close to 1, then k/p can be reasonably large before $\|f^{(k)} - f_h^{(k)}\|$ becomes too large. In this situation, intermediate derivatives are feasible before the onset of instability surfaces. If, however, $E \gg 1$, then numerical differentiation will become infeasible for small values of k. Similar arguments apply for the error estimates for other numerical differentiation procedures. The situation is put on a more rigorous footing in subsection 3.3.

It is clear how the error in the estimation of the kth derivative, for increasing k, depends on the trade-off between an increasing value for $E^{k/p}$ and a decreasing value of $\varepsilon^{1-k/p}$. At least qualitatively, such results are informative. For example, if conditions are such that $E < 1$, $\varepsilon < 1$, $k < p$ and the chosen numerical differentiator generates an accurate approximation to the first derivative, then it will generate accurate approximations to the second, third, fourth and even higher derivatives. In fact, it is possible to write down a condition that guarantees that $\|f^{(k)} - f_h^{(k)}\|$ remains at a constant level δ for changing values of k; namely, as k increases, p is adjusted to guarantee that

$$\frac{k}{p} \sim \frac{(\ln E + \ln \varepsilon)}{(\ln \delta + \ln \varepsilon)}.$$

This represents a qualitative version of the types of conditions that are contained in a variety of papers [**3, 4**] which couple the increasing level of differentiation to be performed with the need for the length of the footprint of the differentiator to be increased.

In fact, the failure of the classical numerical analysis technology to obtain more explicit relationship is a direct consequence of the weak way in which data errors are characterized; namely, $\|f - f_h\| \leq \varepsilon$. In order to determine more definitive results of the type already mentioned, it is necessary, as detailed in subsection 3.3, to be more descriptive about the statistics of the discrete errors in measured (observational) data.

3.2. The phenomenological (signal-to-noise) characterization. In a discussion of the advantages of derivative spectroscopy, Chadburn [**8**] has given the following relationship (without reference)

$$(S/N)_p \sim \frac{1}{2}(S/N)_0 \left\{ \frac{3\Delta\lambda}{W} \right\}^p \tag{3}$$

where $(S/N)_j$, $j = 1, 2, \ldots, p$, denotes the signal-to-noise ratio after the jth application of a first order differentiator with $(S/N)_0$ denoting the signal-to-noise ratio of the original data, $\Delta\lambda$ the wavelength range of the footprint of the numerical differentiation and W the full bandwidth at half-maximum (FWHM). A related relationship, with a heuristic proof, can be found in O'Haver and Begley [**27**]. The difficulty with such estimates is the choice of the definition and the calculation of the *signal-to-noise ratio*. Depending on the application, it has various meanings, as explained in the Wikipedia entry `http://en.wikipedia.org/wiki/Signal-to-noise_ratio`.

Though phenomenologically correct when $3\Delta\lambda/W \sim 1$, the situation becomes problematic when $3\Delta\lambda/W \gg 1$, because it implies that, as the signal-to-noise ratio increases, the associated over smoothing being performed does not affect the accuracy of the estimate of the derivative recovered. In reality, such a signal-to-noise enhancement can only occur if the footprint of the differentiator is so large that it smooths out fine scale structure in the signal as it performs the differentiation. Nevertheless, it does represent confirming evidence for the comment above that, in many situations, if conditions are appropriate to guarantee an accurate approximation to the first derivative (e.g. $3\Delta\lambda/W \sim 1$), then it is highly likely that it will generate good approximations to second, third, fourth and even higher derivatives.

The mentioned ambiguity, in the interpretation of the relationship (3), is a result of assuming that the "*lumping*" of the discrete measurement errors into a single signal-to-noise ratio term is representative of the instability encapsulate in the performance of numerical differentiation of observational data. As shown in some detail below, by taking explicit account of the effect of numerical differentiation on statistically defined observational error, this "*lumping*" assumption is problematic.

In addition, such formulas assume that the numerical differentiation is implemented as p successive first order differentiations. Consequently, the formula (3) is also sub-optimal because it does not allow for the possible use of a single pth order numerical differentiator.

3.3. The statistically defined error characterization. By defining the actual statistical properties of the errors occurring in the measurements

$$y_i = f(t_i) + \varepsilon_i,\ \varepsilon_i \sim \text{i.i.d zero mean random errors},\ i = 0, 1, 2, \ldots, n,$$

one is able to examine algebraically the action of different operations on the measurements. This approach is therefore different from that discussed in the above subsections where the assumptions about the errors are less specific. As is clear from the results found in Anderssen et al. [**2, 3**], though the technical details can become quite involved, the clear advantage of this approach is that the actual order k (p in their notation) of the differentiation to be performed is built explicitly into the conditions that guarantee convergence and stability.

A related analysis can be found in O'Haver and Begley [**27**]. In their approach, successive smoothing is applied to the kth derivative of the data, after it has been determined. In [**2, 3**], the averaging is performed as an essential part of the construction of the kth order differentiator. It is therefore the analysis of [**2, 3**] that is utilized in the sequel. It represents an extension of the results in O'Haver and Begley [**27**].

Let (using the notation in [**3**] with $D^k f$ equivalenced with $f^{(k)}$):

(a) f be a real-valued function defined on the unit interval $[0,1]$ with sufficient regularity that its k-derivative exists.

(b) $D^k f$ $(= f^{(k)})$ denote the kth derivative of f.

(c) $\mathcal{G}_h$ denote the uniform grid of points

$$t_j = jh, \quad j = 0, 1, 2, \ldots, n, \quad h = 1/n.$$

(d) $\Delta_{h,m}^{(k)}$ denote the family of central-difference operators with grid spacing of mh, $m = 1, 2, \ldots$, which satisfy

$$f_i^{(k)}[m] = \Delta_{h,m}^{(k)} f(ih) = (D^k f)(ih) + O((mh)^2),$$

where $\Delta_{h,m}^{(k)} f(ih)$ only involves the grid values $f(t_{i \pm jm})$ with $j = 0, 1, \ldots, k/2$, when k is even, and $j = 1, 2, \ldots, (k+1)/2$, when k is odd. The traditional formulas for numerical differentiation correspond to the choice of $m = 1$. For $m > 1$, the same number of evaluations of f are involved with the footprint of the kth order differentiator having a length of km.

(e) $y_i^{(k)}[m]$ denote the values obtained when the chosen central-difference operator is applied to the observational data $\{y_i\}$.

Note. The application of the chosen central-difference formula is limited to the subsets of $\{y_i\}$ values for which a match with the footprint of the differentiator occurs.

The algorithm proposed in [**3**] is based on averaging the values $y_\ell^{(k)}[m]$ on the neighborhood of points $t_\ell = t_{i-r}, \ldots, t_i, \ldots, t_{i+r}$ centered on t_i; namely,

$$\overline{y_i^{(k)}}[m] = \overline{y^{(k)}}[m](t_i) = \sum_{j=-r}^{r} W_j y_{i+j}^{(k)}[m], \qquad \sum_{j=-r}^{r} W_j = 1. \tag{4}$$

In [**3**], the $W_j = 1/(2r+1)$. The essence of the stabilization comes from the fact that, for very small h (i.e. when n is very large), each of the estimates $y_{i+j}^{(k)}[m]$, $j = -r, -(r-1), \ldots, r-1, r$ can be viewed as an independent statistical estimate of the mean $f_i^{(k)}[m]$, which are being averaged. An alternative explanation for the stabilization comes from the fact that $\overline{f_i^{(k)}}[m]$ equals the application of the kth differentiation formula to the following averaged estimate of f_i

$$\overline{y}(t_{i\pm jm}) = \sum_{\ell=r}^{r} W_\ell y(t_{i\pm jm+\ell}), \qquad \sum_{j=-r}^{r} W_j = 1,$$

with $j = 0, 1, \ldots, k/2$, when k is even, and $j = 1, 2, \ldots, (k+1)/2$, when k is odd. In both cases, when the terms are statistically independent with a common mean, the averaging reduces the variance by a factor of $1/(2r+1)$.

In order to avoid statistical dependence (correlation) effects, which arise if multiple use is made of some of the $f(t_i)$, the value of m was chosen to have the form $\theta r + 1$ with $\theta \geq 2$ [**3**]. The choice $\theta = 2$ corresponds to the situation where the differentiator uses all successive points, with no overlap, when they are averaged in blocks of $2r+1$ points.

It is shown in [**3**] that, for $h \to 0$, convergence is guaranteed if the values of r and θ have been chosen to ensure that the following three conditions are satisfied

$$\theta r h \longrightarrow 0, \qquad rh \longrightarrow 0, \qquad r^{1/2}(\theta r h)^k \sim 1. \tag{5}$$

The first two conditions put implicit constraints on the growth of the number of grid points $2r+1$ and the size of the grid point spacing θ as h decreases. The third yields the required constraint on k. Here, it is

assumed that the failure of convergence is the identifier for the onset of instability. If it is assumed that

$$\theta r h = h^s, \quad 0 < s < 1,$$

then the first condition in (5) is automatically satisfied. Moreover, it follows from the third and second conditions that

$$r \sim h^{-2ks}, \quad \text{and} \quad h^{1-2sk} \longrightarrow 0,$$

respectively. Consequently, a necessary condition for this to occur is

$$k < \frac{1}{2s}, \tag{6}$$

which implies that k can be increased by decreasing s without occurring divergence. In turn, since $\theta r = h^{s-1}$, it follows that, for a given h, the product θr must be sufficiently large to guarantee a large value of k. As the size of s directly controls the error of the approximation, the condition (6) describes the trade-off between the order of differentiation and the reconstruction error.

4. Conclusions. As explained above, numerical differentiation is playing an increasingly important role in the recovery of information from highly accurate data generated by computer controlled instrumentation, and that by using appropriate numerical differentiation formulas there is no difficulty in obtaining accurate estimates of higher derivatives. In derivative spectroscopy, it is common to work with the fourth. Interestingly, the above deliberations illustrate how careful one must be when talking about the ill-posed nature of numerical differentiation.

In the analysis above, it is shown that, for accurate data on a very fine grid, if the footprint of the differentiator is such the θr is sufficiently large then accurate estimates of higher derivatives up to the fourth or higher are guaranteed.

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