

Chemometrics in Spectroscopy

Derivatives in Spectroscopy

Update

Marking their 100th column contribution to *Spectroscopy*, the authors revisit their series on the analysis of derivatives to correct errors in equations that appeared in previous columns.

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We published previously a set of columns dealing with the analysis of derivatives of spectra (1–4). It seems that, unfortunately, those columns contained some errors. One of the errors was caught early and we were able to get the correction into the subsequent column (2). Some of the others were not detected until some time had passed and various people had the opportunity, time, and inclination to check our work. Some of the errors were relatively minor (typographical errors in tables, for example), but some were substantive (and substantial). However, to get a complete set of corrections in one place, we here list all the errors found (and the corrections). Equation numbering follows that of the original columns.

First, in going from equation 3 to equation 4 (1), when we factored the constants from the derivative we should have taken out $1/\sigma^2$, whereas we factored out $1/\sigma$. Therefore several equations starting with equation 4 on are off by a factor of σ . The correct equations are:

$$\frac{dY}{dX} = \frac{1}{\sigma(2\pi)^{1/2}} e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \left[-\frac{1}{2\sigma^2} \frac{d}{dX}(X-\mu)^2 \right] \quad [4]$$

$$\frac{dY}{dX} = \frac{1}{\sigma(2\pi)^{1/2}} e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \left[-\frac{1}{2\sigma^2} 2(X-\mu) \right] \quad [5]$$

$$\frac{dY}{dX} = \frac{-(X-\mu)}{\sigma^3(2\pi)^{1/2}} e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \quad [6a]$$

$$\frac{dY}{dX} = \frac{-(X-\mu)}{\sigma^2} e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \quad [6b]$$

Similarly, the correct equations for the second derivative of the Normal distribution are:

$$\frac{d^2Y}{dX^2} = \frac{-(X-\mu)}{\sigma^3(2\pi)^{1/2}} e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \frac{d}{dX} \left[-\frac{1}{2} \left(\frac{X-\mu}{\sigma} \right)^2 \right] + e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \frac{d}{dX} \left[\frac{-(X-\mu)}{\sigma^3(2\pi)^{1/2}} \right] \quad [7]$$

$$\frac{d^2Y}{dX^2} = \frac{-(X-\mu)}{\sigma^3(2\pi)^{1/2}} e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \left[-\frac{1}{2\sigma^2} 2(X-\mu) \right] + \left[\frac{-1}{\sigma^3(2\pi)^{1/2}} \right] e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \quad [8]$$

$$\frac{d^2Y}{dX^2} = \left[\frac{(X-\mu)^2}{\sigma^5(2\pi)^{1/2}} - \frac{1}{\sigma^3(2\pi)^{1/2}} \right] e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \quad [9a]$$

$$\frac{d^2Y}{dX^2} = \left[\frac{(X-\mu)^2}{\sigma^4} - \frac{1}{\sigma^2} \right] e^{-\frac{1}{2}\left(\frac{X-\mu}{\sigma}\right)^2} \quad [9b]$$

Next, going from equation 10 to equation 11 for the Lorentzian distribution (in the same column) there were a couple of errors, including a missed sign change and not correctly bringing σ^2 inside the brackets containing an expression that was itself squared. Again, all the subsequent equations derived from equation 11 were themselves then also in error. The corrected derivation follows. This time, we present the derivation in much smaller and more detailed steps than was done initially. In doing this, we give intermediate equations letters, so that the equations labeled with pure numbers correspond to the original equation with the same number and can be compared with it:

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{-1}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \frac{d}{dX} \left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right] \quad [10]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{-1}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \left[0 + \frac{d}{dX} \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right] \quad [10a]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{-1}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \left[2 \left(\frac{2(\mu-X)}{\sigma} \right) \frac{d}{dX} \left(\frac{2(\mu-X)}{\sigma} \right) \right] \quad [10b]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{-1}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \left[\frac{4(\mu-X)}{\sigma} \times \frac{2}{\sigma} \frac{d}{dX}(\mu-X) \right] \quad [10c]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{-1}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \left[\frac{8(\mu-X)}{\sigma^2} \times (0-1) \right] \quad [10d]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{-1}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \left[\frac{-8(\mu-X)}{\sigma^2} \right] \quad [10e]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8(\mu-X)}{\left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right]^2} \times \sigma^2 \quad [10f]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8(\mu-X)}{\left\{ \sigma \left[1 + \left(\frac{2(\mu-X)}{\sigma} \right)^2 \right] \right\}^2} \quad [10g] \text{ This step is where the error crept in previously -- you can't be too careful!}$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8(\mu-X)}{\left[\sigma + \sigma \left(\frac{2(\mu-X)}{\sigma}\right)^2\right]^2} \quad [10h] \qquad \frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8(\mu-X)}{\left[\sigma + \frac{4(\mu-X)^2}{\sigma}\right]^2} \quad [10j] \qquad \frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8\sigma^2(\mu-X)}{\left[\sigma^2 + 4(\mu-X)^2\right]^2} \quad [11]$$

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8(\mu-X)}{\left[\sigma + \frac{2(\mu-X)^2}{\sigma}\right]^2} \quad [10i] \qquad \frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{\sigma^2}{\sigma^2} \times \frac{8(\mu-X)}{\left[\sigma + \frac{4(\mu-X)^2}{\sigma}\right]^2} \quad [10k]$$

The error in equation 11 then propagated through to the rest of the equations for the Lorentzian distribution. The correct formulas are as follows:

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{\left[\sigma^2 + 4(\mu-X)^2\right]^2 \times \frac{d}{dX} (8\sigma^2(\mu-X))}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{8\sigma^2(\mu-X) \frac{d}{dX} \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [12]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{\left[\sigma^2 + 4(\mu-X)^2\right]^2 \times 8\sigma^2 \times \frac{d}{dX} (\mu-X)}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{8\sigma^2(\mu-X) \times 2 \left[\sigma^2 + 4(\mu-X)^2\right] \frac{d}{dX} \left[\sigma^2 + 4(\mu-X)^2\right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [12a]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{\left[\sigma^2 + 4(\mu-X)^2\right]^2 \times 8\sigma^2 \times (0-1)}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{8\sigma^2(\mu-X) \times 2 \left[\sigma^2 + 4(\mu-X)^2\right] \frac{d}{dX} \left[\sigma^2 + 4(\mu-X)^2\right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [12b]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{8\sigma^2(\mu-X) \times 2 \left[\sigma^2 + 4(\mu-X)^2\right] \frac{d}{dX} \left[\sigma^2 + 4(\mu-X)^2\right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [13]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{16\sigma^2(\mu-X) \left[\sigma^2 + 4(\mu-X)^2\right] \left[\frac{d}{dX} (\sigma^2) + \frac{d}{dX} \left[4(\mu-X)^2\right] \right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [14]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{16\sigma^2(\mu-X) \left[\sigma^2 + 4(\mu-X)^2\right] \left[0 + (4 \times 2(\mu-X)) \frac{d}{dX} (\mu-X) \right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [14a]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{16\sigma^2(\mu-X) \left[\sigma^2 + 4(\mu-X)^2\right] \left[8(\mu-X) \frac{d}{dX} (\mu-X) \right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [14b]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{16\sigma^2(\mu-X) \left[\sigma^2 + 4(\mu-X)^2\right] \left[8(\mu-X)(0-1) \right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [14c]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{16\sigma^2(\mu-X) \left[\sigma^2 + 4(\mu-X)^2\right] \left[-8(\mu-X) \right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [15] \qquad \frac{d^2Y}{dX^2} = \frac{16}{\pi\sigma} \times \left[\frac{-\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} + \frac{16\sigma^2(\mu-X)^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} \right] \quad [15d]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} - \frac{-128\sigma^2(\mu-X)^2 \left[\sigma^2 + 4(\mu-X)^2\right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [15a] \qquad \frac{d^2Y}{dX^2} = \frac{16}{\pi} \times \left[\frac{-\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2 + 16\sigma^2(\mu-X)^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} \right] \quad [15e]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} + \frac{128\sigma^2(\mu-X)^2 \left[\sigma^2 + 4(\mu-X)^2\right]}{\left[\sigma^2 + 4(\mu-X)^2\right]^4} \right] \quad [15b] \qquad \frac{d^2Y}{dX^2} = \frac{16}{\pi} \times \left[\frac{-\sigma^3 - 4\sigma(\mu-X)^2 + 16\sigma(\mu-X)^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} \right] \quad [15f]$$

$$\frac{d^2Y}{dX^2} = \frac{2}{\pi\sigma} \times \left[\frac{-8\sigma^2 \left[\sigma^2 + 4(\mu-X)^2\right]^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} + \frac{128\sigma^2(\mu-X)^2}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} \right] \quad [15c] \qquad \frac{d^2Y}{dX^2} = \frac{16}{\pi} \times \left[\frac{12\sigma(\mu-X)^2 - \sigma^3}{\left[\sigma^2 + 4(\mu-X)^2\right]^3} \right] \quad [16]$$

This correction also propagates to equation 18 when we set $(X - \mu)$ equal to σ :

$$\frac{dY}{dX} = \frac{2}{\pi\sigma} \times \frac{8\sigma^2(\sigma)}{[\sigma^2 + 4(\sigma)^2]^2} = \frac{2}{\pi} \times \frac{8\sigma^2}{[5\sigma^2]^2} = \frac{16}{25\pi\sigma^2} \quad [18]$$

Third, an error in evaluating the exponential in equation 19 led to the incorrect constant multiplier. The corrected expression is:

$$\frac{d^2Y}{dX_{max}^2} = \left[\frac{(\mu - \mu)^2}{\sigma^3(2\pi)^{3/2}} - \frac{1}{\sigma^3(2\pi)^{3/2}} \right] e^{-\frac{1}{2}\left(\frac{\mu - \mu}{\sigma}\right)^2} = 0 - \frac{e^0}{\sigma^3(2\pi)^{3/2}} = \frac{-1}{\sigma^3(2\pi)^{3/2}} \quad [19]$$

We see, therefore, that the derivative decreases with the third power of σ , the same rate as the derivative of the Normal distribution.

Next, the matrices in (3) contain several erroneous entries. There are a number of sign errors, and some errors in values, mostly resulting from formatting problems in the manuscript. The corrected matrices for those are shown below. For equation 25, the fourth entry on the fourth line had a formatting problem; the correct value is 1588.

(Equation 26) $(\mathbf{M}^T\mathbf{M})^{-1} =$	0.333333	0	-0.0476190	0
	0	+0.262566	0	-0.0324074
	-0.0476190	0	0.01190476	0
	0	-0.0324074	0	0.00462962

(Equation 27) $(\mathbf{M}^T\mathbf{M})^{-1}\mathbf{M}^T =$

-0.095238	0.14285714	0.28571428	0.333333	0.28571428	0.14285714	-0.0952381
0.087301	-0.2658730	-0.2301587	0	0.23015873	0.2658730	-0.0873015
0.059523	0	-0.0357143	-0.047619	-0.0357143	0	0.05952381
-0.027777	0.0277777	0.0277777	0	-0.0277777	-0.0277777	0.0277777

(Equation 28) $(\mathbf{M}^T\mathbf{M})^{-1}\mathbf{M}^T$ (corrected for scaling) =

-0.095238	0.1428571	0.2857143	0.333333	0.285714	0.142857	-0.095238
0.0873016	-0.265873	-0.230158	0	0.230158	0.265830	-0.087301
0.1190476	0	-0.071428	-0.09523	-0.071428	0	0.1190476
-0.166666	0.166666	0.166666	0	-0.166666	-0.166666	0.166666

The next (and final) item is, perhaps, not so much an error as a question of possible differences in interpretation of the results and meanings of some of the derivative computations presented. One of our respondents pointed out that the magnitudes of the various derivatives, and especially the relative magnitudes of derivatives of different orders, depend upon the units used, particularly the units used to describe the x axis. Now, while in fact we didn't specify any units in our discussion, (see, for example, Figure 1 in [1], where the x axis contains only the label "Wavelength"), given our backgrounds it is true enough that we implicitly had nanometers in mind for our X units. In the case of real spectra, however, if spectra were measured using micrometers as the units for the x axis, the same spectrum would have a calculated value for the first derivative that was 1000 times what would be calculated for a "nm-based" derivative. In that case, the first derivative (for a 10-nm-wide band, which would be a 0.01- μm -wide band) would be 100 times greater than the maximum spectral value, rather than being 1/10 of it, as the value computed using nanometers for the X scale came out to. The second derivative would then be 10^6 times what we calculated and therefore 10,000 times greater than the maximum spectral value, instead of being 1/100 of it, the value we showed.

In principle this all is correct. In practice, however, if we ignore Fourier transform infrared (FT-IR) and specialty technologies such as acousto-optic tunable filter (AOTF) spectroscopy, then the vast majority of instruments in use today for modern near infrared (NIR) spectroscopy (still primarily diffraction grating-based instruments) use nanometers as their wavelength unit, and usually collect data at some small integer number of nanometers. Furthermore, the vast majority of those have a 10-nm bandpass, so that 10 nm is the minimum bandwidth that would be measured. Also, even for instruments with higher resolution, the natural bandwidths of many, or even most, absorbance bands of materials that are measured commonly are greater than 10 nm in the NIR. Given all this, the use of a 10-nm figure to represent a typical NIR absorbance band is realistic, and gives the reader a realistic assessment of what a typical user can expect from the NIR spectra he measures, and their derivatives. The choice of units, of course, does not affect the instrumental characteristic of signal-to-noise, which is what is important, and which we discuss in part IV of the subseries (4).

If we consider FT-IR instrumentation, then the situation is trickier, because the equivalent resolution in nanometers varies across the spectrum. But even keeping the spectrum in its "natural" wavenumber units, we again find that, except for rotational fine structure of gases, the natural bandwidth of many (most) absorbance bands is greater than 10 wavenumbers. So again, using that figure shows the typical user how he can expect his own measured spectra to behave.

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References

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3. H. Mark and J. Workman, *Spectroscopy* **18**(12), 106–111 (2003).
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Authors' Note: We have available a MathCad worksheet (MathSoft Engineering & Education, Inc., Cambridge, MA) that is used for computing the statistical parameters and graphics discussed throughout our recent "Comparison of Goodness of Fit Statistics for Linear Regression" column series. It is recommended that the statistics incorporated into this series of worksheets be used for evaluations of goodness of fit statistics such as the correlation coefficient, the coefficient of determination, the standard error of estimate, and the useful range of calibration standards used in method development. This worksheet can be downloaded from http://www.nearinfrared.com/r2_study01cis1.mcd.

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