Lorentzian Asymmetric Lineshape

Version 2.3.14 of CasaXPS introduces a variation on a theme based on a numerical convolution of a Lorentzian with a Gaussian to produce a lineshape which is a superset of the Voigt functions in the sense that asymmetric Voigt like lineshapes are possible as well as the traditional Voigt profiles.

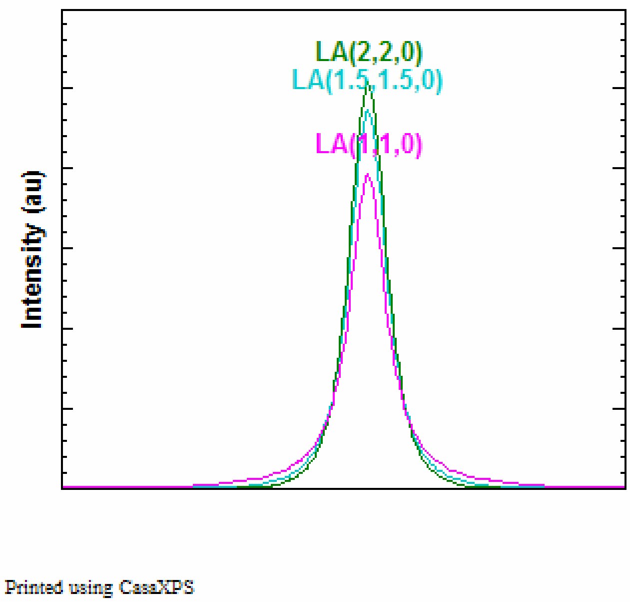

Figure 1: Symmetrical lineshapes generated form the LA definition in CasaXPS.

The Lorentzian lineshape with FWHM F and position (in kinetic energy) E is given by

$$L(x) = \frac{1}{1 + 4\left(\frac{x - E}{F}\right)^2}$$

The underlying lineshape depicted in Figure 1 is obtained from

$$LA(\alpha, \beta) = \begin{cases} [L(x)]^{\alpha} & x \le E \\ [L(x)]^{\beta} & x > E \end{cases}$$

where α and β are set equal and plotted for values of 1, 1.5 and 2. The consequence of increasing the parameters α and β is a reduction in the spread of the tail for the Lorentzian curve resulting in steeper edges to the lineshape. The use of these two parameters enables the spread of the Lorentzian tail to be different either side of the peak maximum and therefore an asymmetric profile is made possible. Figure 2 shows three possible lineshapes corresponding to $\beta = 2$ and $\alpha = 1, 1.5$ and 2.

The implementation of the asymmetric Lorentzian lineshape in CasaXPS includes a parameter specifying the width of Gaussian used to convolute the Lorentzian curve, namely LA(α, β, *m*), where *m* is an integer between 0 and 499 defining the width of the

Gaussian. By way of example, consider the silicon doublet fitted using two LA lineshapes in Figure 3. The asymmetry in the lineshapes is achieved by using a smaller α than β parameters, coupled with a relatively small modification to the overall lineshape via a convolution with a Gaussian of width characteristic of m = 50.

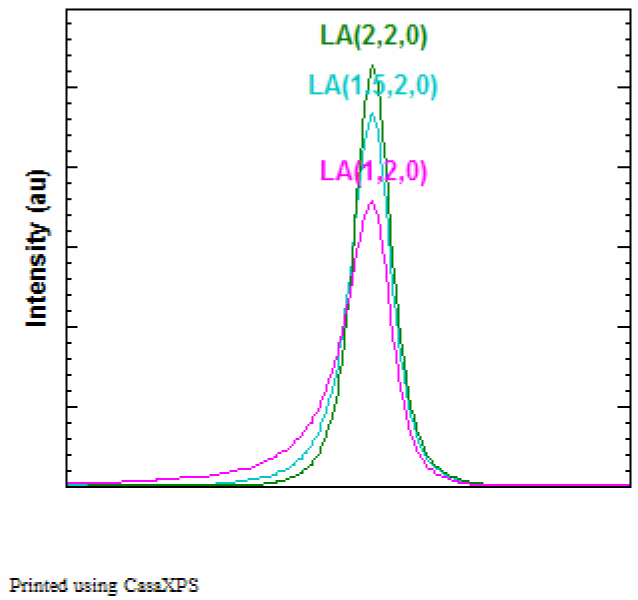

Figure 2: Asymmetric possibilities for the LA lineshape.

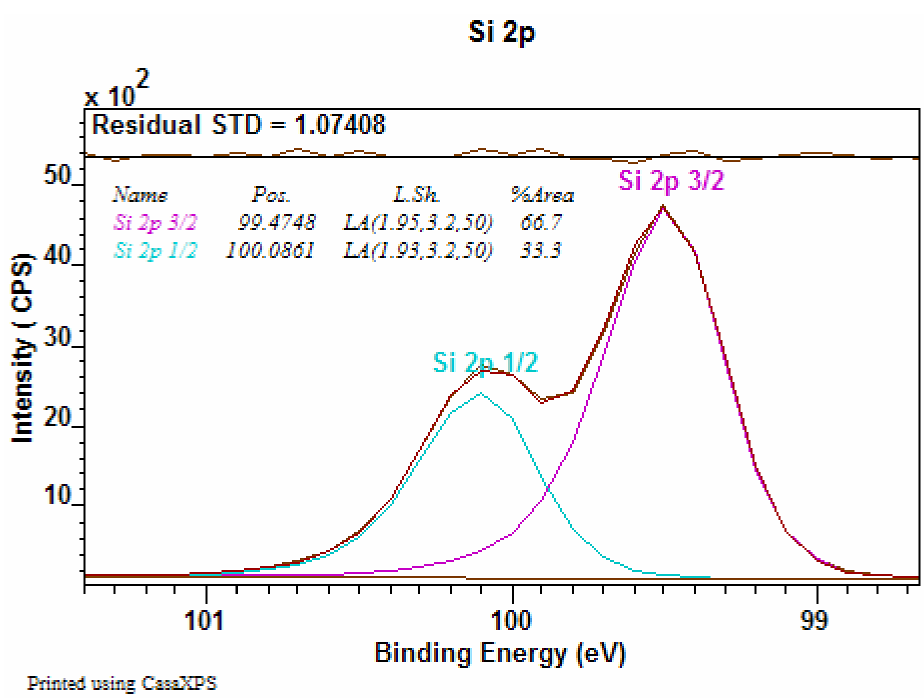

Figure 3: Elemental Silicon doublet pair fitted using asymmetric Lorentzian lineshapes. Data supplied from a JEOL XPS at University of Wageningen, NL.

Lorentzian Asymmetric Lineshape with Tail Damping

Version 2.3.15

An extension to the LA lineshape is to introduce a further parameter, the purpose of which is to limit the range of the asymmetric tail. The problem with asymmetric peaks is matching a lineshape to the data shape after a background is removed, while still maintaining a functional form for the lineshape suitable for measuring the intensity of the transition. Any peak fitted to the data may have intensity in the tails extending beyond the integration limits defined by the background, or even the data itself, thus, unlike integration regions, the peak area measured using a lineshape is not limited to the measured data. When measuring intensities for transitions using both regions and components, it is important that these intensities are comparable. For asymmetric lineshapes, the challenge is to both model the data and allow the measurement of peak areas, therefore the new lineshape, LF(α, β, w, m), uses the same functional form as the LA lineshape, but introduces a damping parameter w to force the tail to reduce towards the limits of the integration limits.

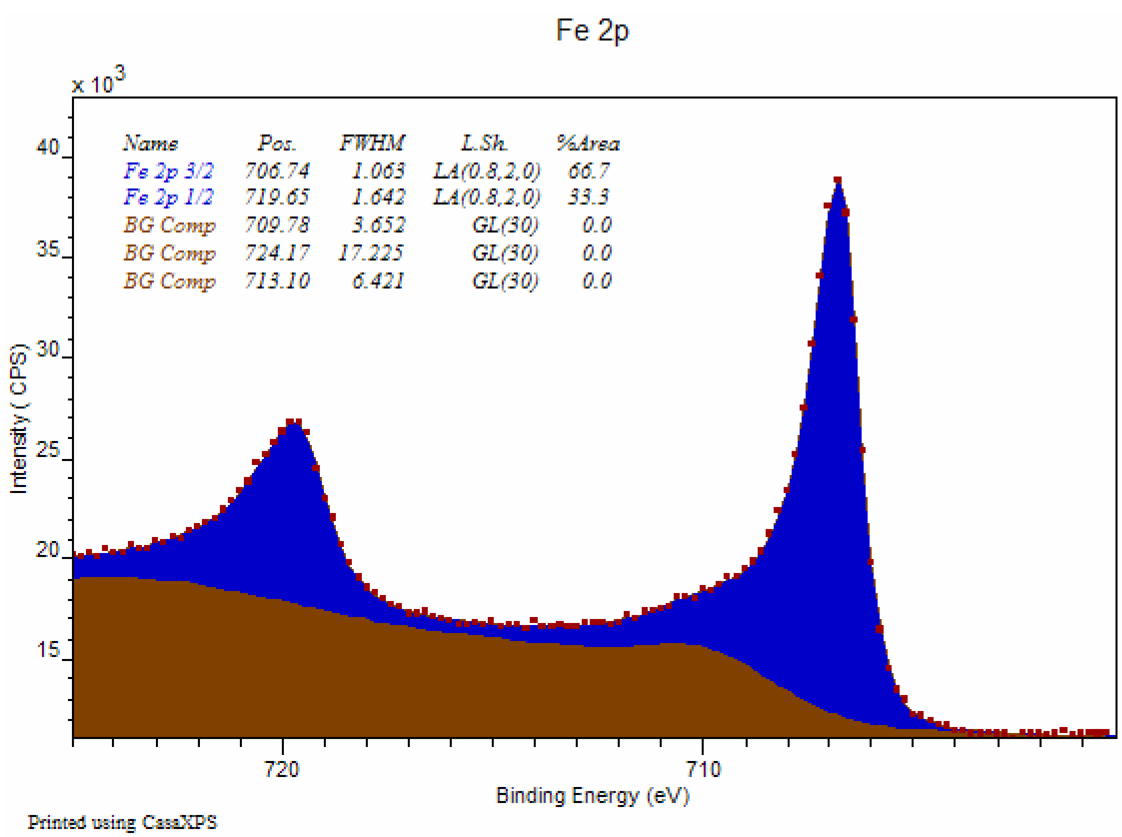

Figure 4: Fe 2p Doublet fitted using LA lineshapes with parameters such that the tail extends beyond the integration limits. Note the α parameter is 0.8 which creates a "super" Lorentzian tail.

The data in Figure 4 illustrates the problem with extended asymmetric tail functions. The fit has been achieved by defining the shape of the asymmetric lineshape and fixing the relative intensities of the two peaks from the Fe 2p doublet to 2:1. A constant background is subtracted from the data on top of which three additional GL peaks, representing the background shapes, are allowed to adjust as the asymmetric peaks are fitted. While aesthetically pleasing, from a quantitative perspective the intensity measured by the asymmetric peaks clearly extends beyond the data limits, therefore it would not be possible to simply integrate the data to obtain the same Fe 2p intensity as obtained from the lineshapes. Further, the flexibility in the background would make the model unstable and without any strong physical reason for accepting the background shape, any quantitative results would be doubtful.

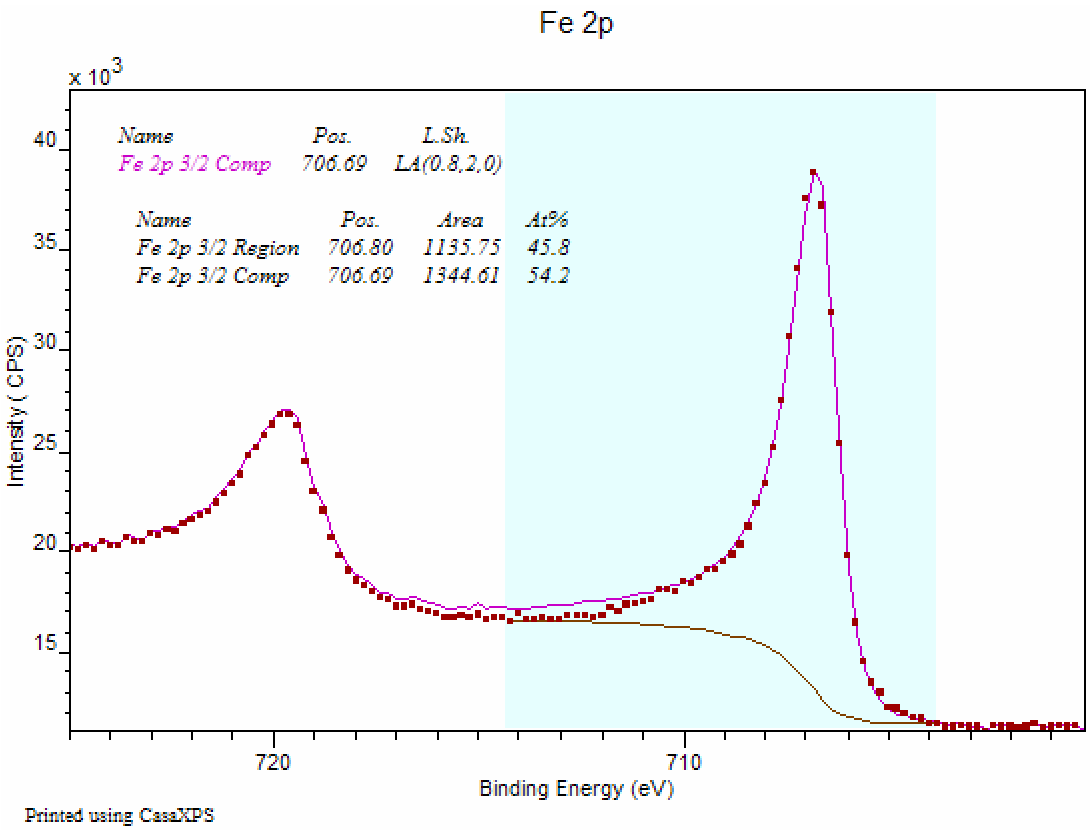

Figure 5: Shirley background applied over the Fe 2p 3/2 peak. The data are fitted using the same LA lineshape in Figure 4.

The most common means of measuring the Fe 2p intensity is to define a Shirley background before fitting any peaks. The lineshape used to fit the data in Figure 4 is incompatible with the integration region in Figure 5, where the lineshape, when fitted to the data minus a Shirley background, is seen to include a tail extending far beyond the region limits. The quantification table over the data in Figure 5 is a comparison of the intensity measured by the region to the intensity measured using the asymmetric lineshape. These results should be compared to the quantification table in Figure 6, where the damped asymmetric lineshape prevents the tail from extending beyond the integration limits resulting in almost identical peak areas when calculated using either the region or the component. The essential shape of the asymmetric peak is retained within the bounds of the peak, but the damping parameter suppresses the extended tail seen in Figure 5.

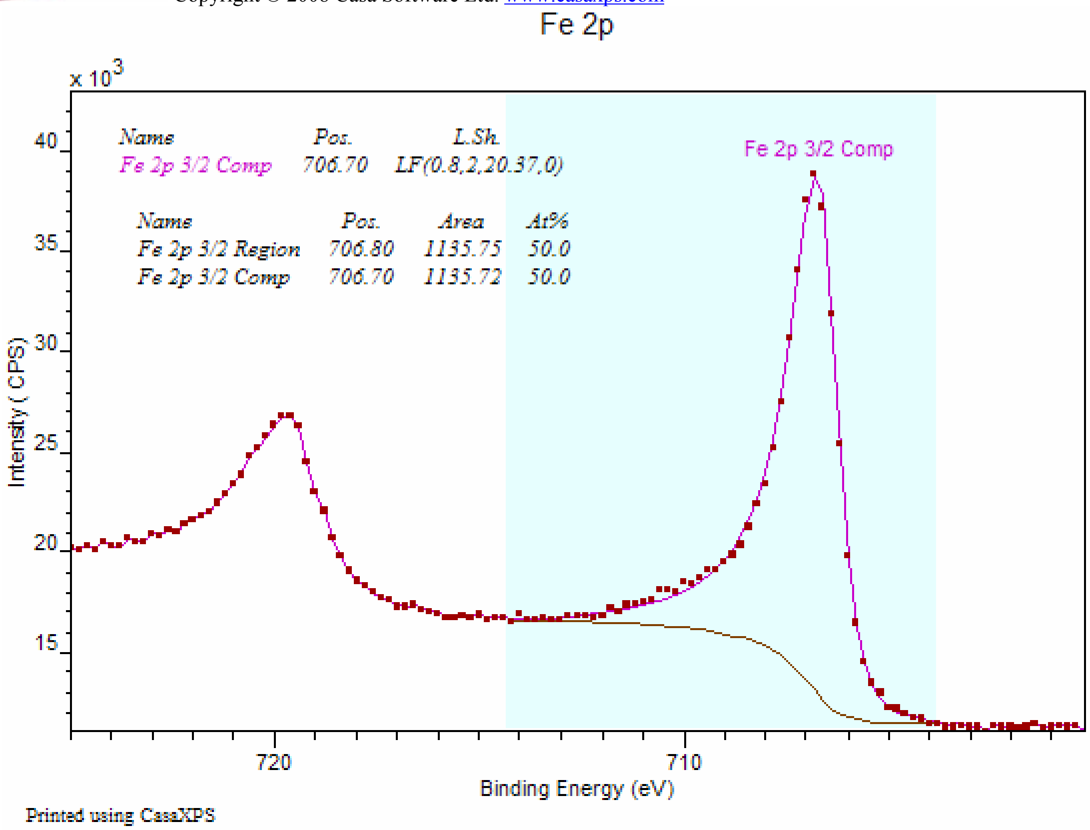

Figure 6: Shirley background applied over the Fe 2p 3/2 peak. The data are fitted using the same LA parameters used in the lineshape in Figure 5, but applied through the LF damped tail lineshape. Note how the extended tail seen in Figure 5 is no longer evident.

The LF lineshape is a tool for creating peak models where asymmetry is important, but where standard background types such as Shirley or Linear approximations force the background to meet the data at some point. As always, it should be emphasized that these background approximations are almost certainly incorrect and therefore the spirit of the LF lineshape is to offer a tool for working in the context of this limitations. It is also worth noting that the asymptotic form of the LA and LF lineshapes is equivalent to the asymptotic form of the theoretical Doniach-Sunjic asymmetric lineshape. These new lineshapes are therefore practical solutions to the infinite nature of the DS lineshape.

LF(α, β, w, m): Identical to the LA lineshape with the exception that the specified values of α and β are force to increase to a constant value via a smooth function determined by the width parameter w. Figure 7 shows a family of lineshapes for various values of the w parameter.

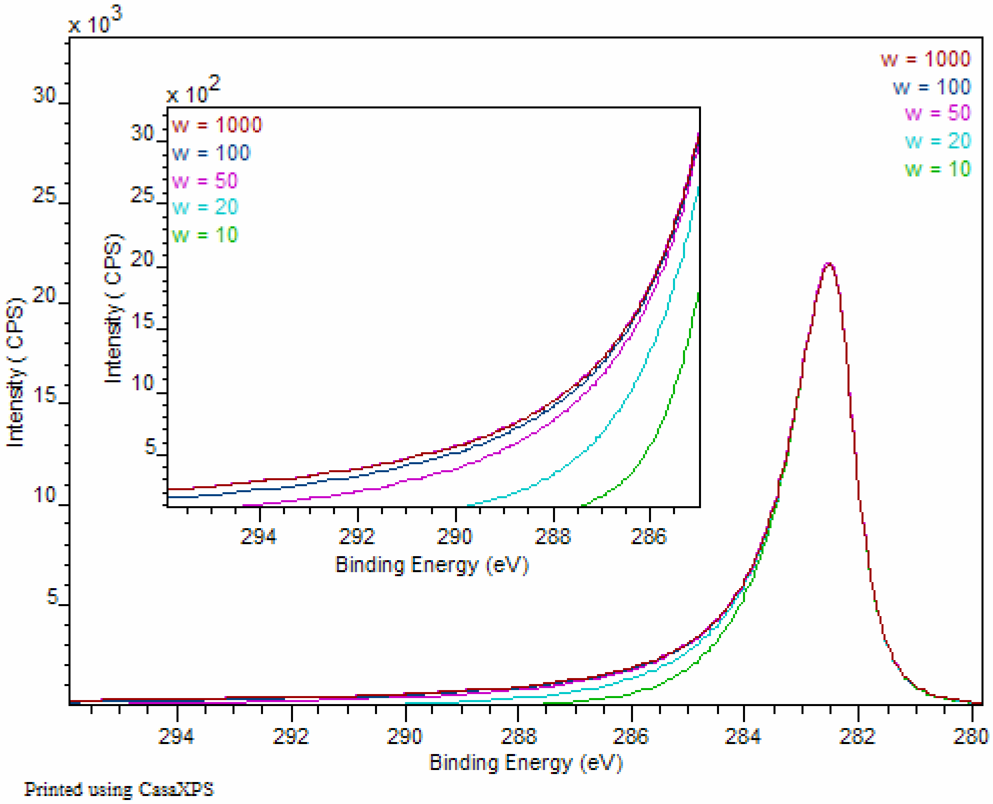

Figure 7: LF(0.8,2,*w*,*0*) lineshape for various values of *w*.