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A double Lorentzian line shape for asymmetric photoelectron peaks

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Content

Abstract

In this Internal Report it is introduced the double-Lorentzian asymmetric line shape. This is employed for fitting photoelectric spectra, such as in X-ray (XPS) or Ultraviolet (UPS) Photoelectron Spectroscopy. In contrast with the standard Doniach-Sunjic (DS) line shape, the double Lorentzian method is integrable. It has advantages over other empirical line shapes since its parameters can be compared with those from Voigt functions. It also provides better fits than the standard DS function.

I. Introduction

I.1. Asymmetric core levels

As described by Briggs and Riviere in Reference 1, the line shape of some X-Ray Photoelectron Spectroscopy (XPS) metallic peaks show an extended tail in the low kinetic energy side of the spectrum. This is exemplified with the Fe 2*p* spectrum shown in Figure 1.

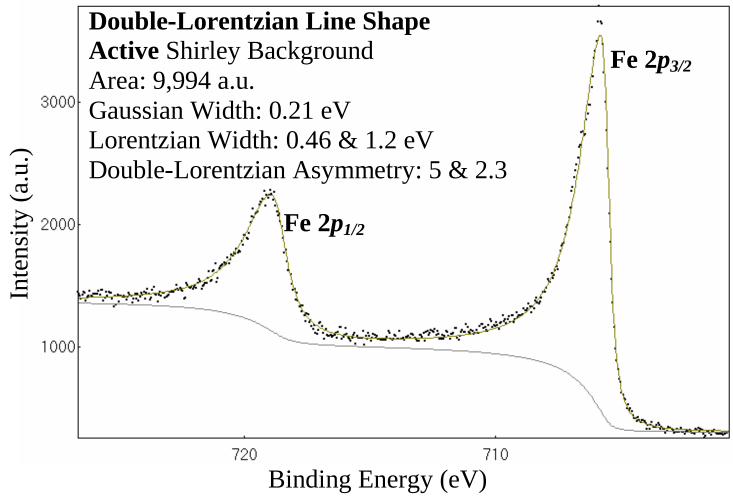

Figure 1. Clean Fe 2*p* XPS spectrum showing strong asymmetry. The analysis shows that the asymmetry is not the same for the two branches. The fit was done employed is the double-Lorentzian line shape, described in Section II, and the *active* background method, described in Reference 2.

The extended tail can be explained in terms of the interaction of the photoelectron with the valence band electrons. Other metals, such as Au and Ag, do not show this asymmetry because the density of valence band electrons near the Fermi edge is small.[1]

I.2. The Doniach-Sunjic line shape

In their 1970 paper,[3] Doniach and Sunjic proposed a photoelectron peak line shape based on a "combination of the Kondo effect and a transient and singular re-adjustment of the ground state of the entire Fermi gas to the presence of the effective potential of the hole." By dealing with these effects employing Many-Body theory, they deduced the following analytical form for metallic peaks

Equation 1

$$I(E) \sim \frac{\cos\left[\frac{\pi\alpha}{2} + (1-\alpha)\arctan\frac{E-E_0}{\gamma}\right]}{\left[(E-E_0)^2+\gamma^2\right]^{\frac{1-\alpha}{2}}},$$

where $I(E)$ is the photoelectric signal at energy E, E_0 is the peak "center", γ is the lifetime Lorentzian width, and α is the "asymmetry factor". Although it is explicitly claimed that this form is integrable,[3] it is not. Figure 2 shows the integral of Equation 1 as a function of integration limits; it grows indefinitely.

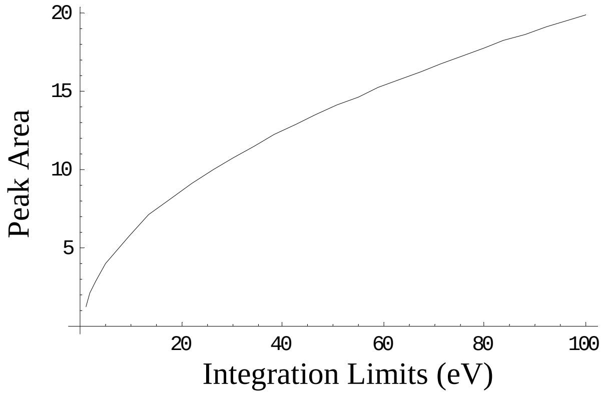

Figure 2. Area of the Doniach-Sunjic line shape (with α = 0.5 and γ = 1 eV) as a function of integration limits. This non-converging behavior is maintained regardless of the values for α and γ.

This is a huge problem that makes this shape unusable for quantitative analysis. The non-integrability is inherited from the photoelectron-valence band cross section that they derived[3]

Equation 2 $$\frac{d\sigma}{dE} \sim \frac{1}{\left(E - E_0\right)^{1-\alpha}},$$

which is not integrable for any value of α between 0 and 1, which are, in turn, the possible values for this parameter (Equation 1 results from the convolution of this cross section and a Lorentzian curve).

Although the non-integrability of the Doniach-Sunjic line shape is a well known problem,[4] there has not been another proposed shape with solid theoretical foundations. To quantify areas of asymmetric peaks, the user has to employ closed asymmetric forms that fit the data. In this Report it is proposed an empirical shape with some important advantages.

II. The double-Lorentzian line shape

The double-Lorentzian line shape is very similar to a Voigt function except that the Lorentzian width is different between the two sides of the peak. The fit shown in Figure 1 was in fact done with line shapes of the double-Lorentzian type. Figure 3a shows a fit to a C 1s XPS spectrum employing the parameters shown in Figure 3b. The software employed is AAnalyzer®.[5]

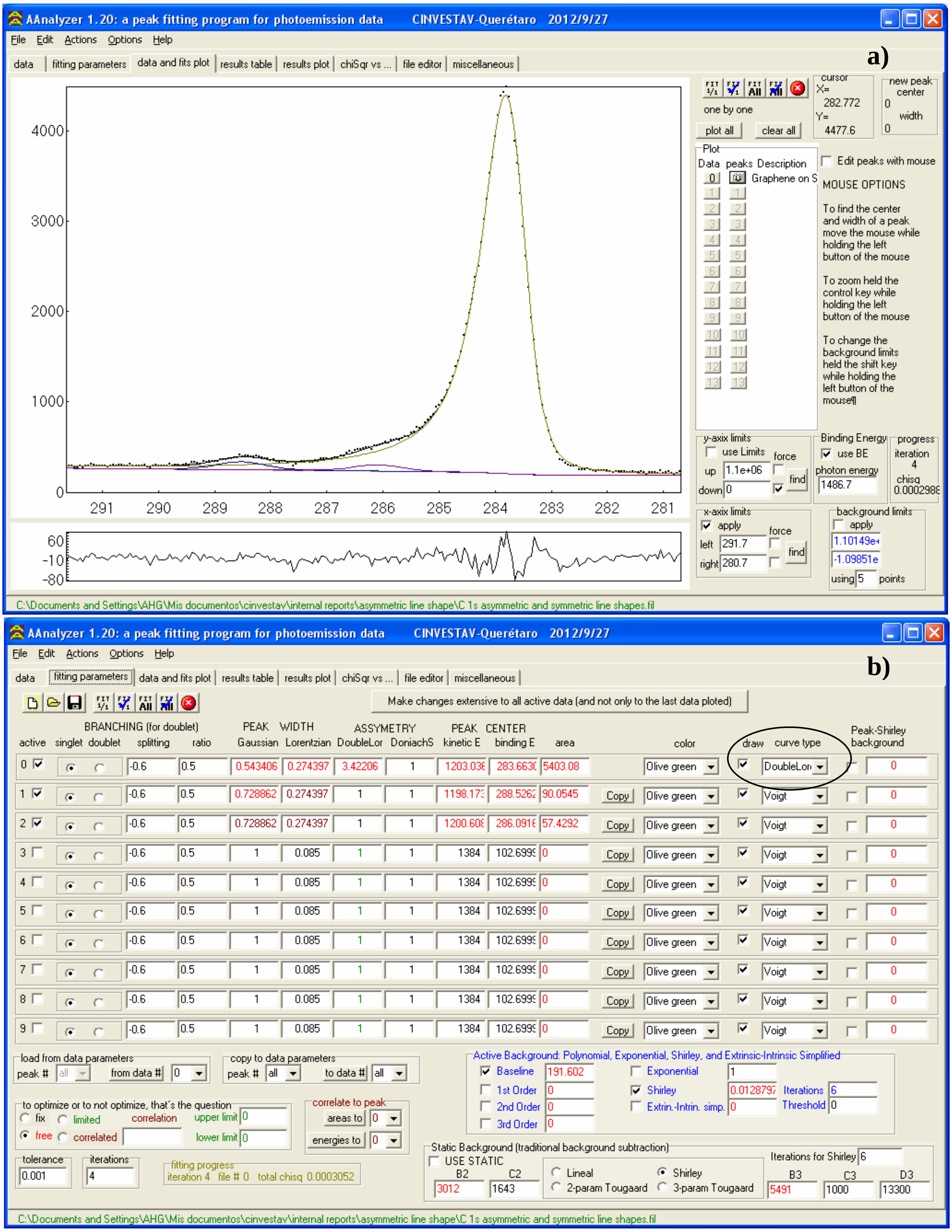

Figure 3. a) Fit of a C 1*s* spectrum. b) Parameters employed for the fit. Note that "DoubleLorentzian" curve type was chosen for the first (and largest) peak. The line shape of the other two peaks area Voigt-type. The active background method was employed.[2]

The largest peak (283.6 eV) corresponds to graphene and shows a strong asymmetry. The Lorentzian width of 0.27 eV (indicated in the box below "Lorentzian" in Figure 3b) corresponds to the high kinetic energy side of the peak (right side). The asymmetry of 3.45 indicates that the Lorentzian width on the left is 3.42 times 0.27 eV, that is, 0.93 eV. That shape is convoluted with a Gaussian curve of 0.54 eV FWHM. The other two carbon chemical species, one at 288.5 eV and the other at 286 eV, are symmetric and share the same Lorentzian width of the right side of the largest peak (0.27 eV). The area of the larger peak, 5403 a.u., is indicated in the first box under "area". The areas of the other two peaks, 90 and 57 a.u., are comparable to each other.

III. Comparing the Doniach-Sunjic with the double-Lorentzian line shape

Figure 4 shows the fit to the same data of Figure 3a but employing the Doniach-Sunjic line shape. The fit in Figure 4a was done employing the active background (Shirley + Baseline), i.e., allowing the background intensity to vary to obtain a better fit.[2] The fit is not as close as in Figure 3a (which was done employing the double-Lorentzian line shape) and it misses the peak at ~ 286 eV. The fit in Figure 4b was done employing the traditional (static) Shirley background, i.e., the background was subtracted prior to data fitting. In this other case the fit is even worse and misses both the peak at ~ 286 eV and at 288.5 eV.

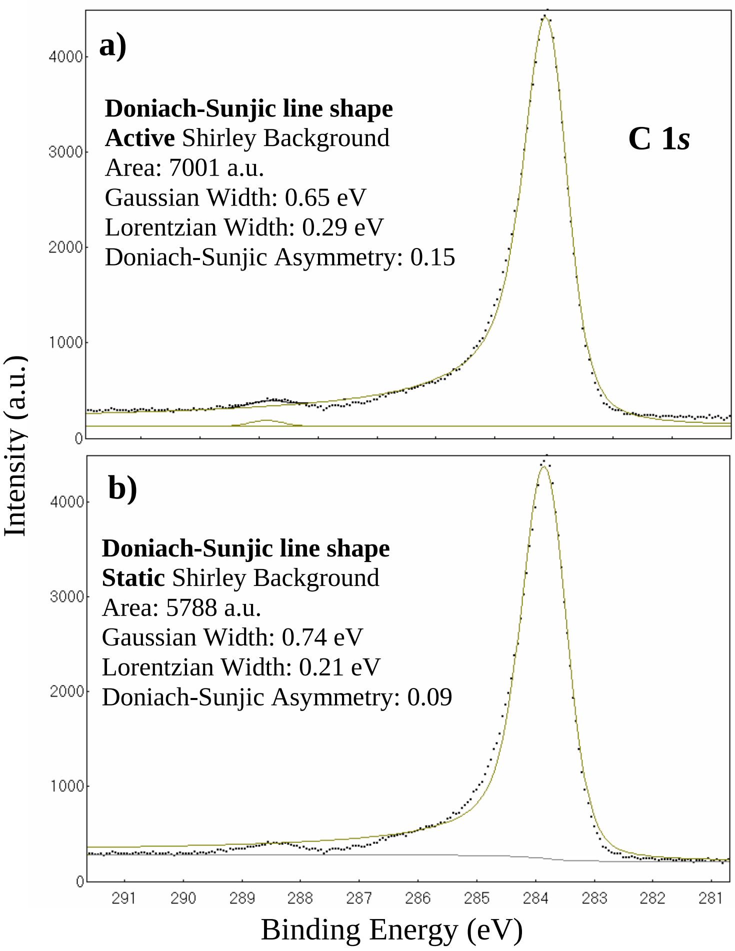

Figure 4. Fit of the same C 1*s* spectrum of Figure 3a but employing the Doniach-Sunjic line shape with the a) active and b) static background methods. In (a) the fit is not as close to the experimental data as in Figure 3a (where the double-Lorentzian line shape was employed) and it misses the peak at 286 eV. In addition, the area of the peak is much larger because of its tail at the high binding energy side. In (b) the fit is even poorer and it misses the two small peaks at 286 and 288.5 eV. The reason of the weakness of the fit is that the Doniach-Sunjic asymmetry-parameter took a smaller than in (a) value during the optimization process to make the tail on the left of the peak as small as possible, compromising the fit in the peak region. When the background is allowed to vary during the optimization process, as it was done in (a), the Doniach-Sunjic asymmetry parameter is optimized to reproduce the data in the peak region. This problem is not present when the double-Lorentzian line shape is employed since, as shown in Figure 3a, the fit is great in all the regions of the spectrum.

Although the fit with the Doniach-Sunjic line shape is not too bad when the active background is employed (compare Figure 4a with Figure 4b), the overestimation of the area is larger in the active background (7001 vs. 5403 a.u.) than in the static background case (5788 vs. 5403 a.u.). This is because the Doniach-Sunjic asymmetry parameter, α, is allowed to take a larger value to improve the fit when the active background method is employed. Larger values of α implies larger peak areas. It should be pointed out that the area of the Doniach-Sunjic peaks strongly depends on the integration range, as shown in Figure 2.

When the Doniach-Sunjic line shape is employed, the problem with the area is stronger for peaks with larger asymmetries, such as the Fe 2*p* spectrum in Figure 1. Figure 5 shows the fit to the same spectrum but employing the Doniach-Sunjic line shape (the fit in Figure 1 was done with the double-Lorentzian line shape). The problems with the fit go in the same direction as for the graphene C 1*s* spectrum: the fit is worse when the static Shirley background is employed (Figure 5b), but the assessment of the area is not as inaccurate.

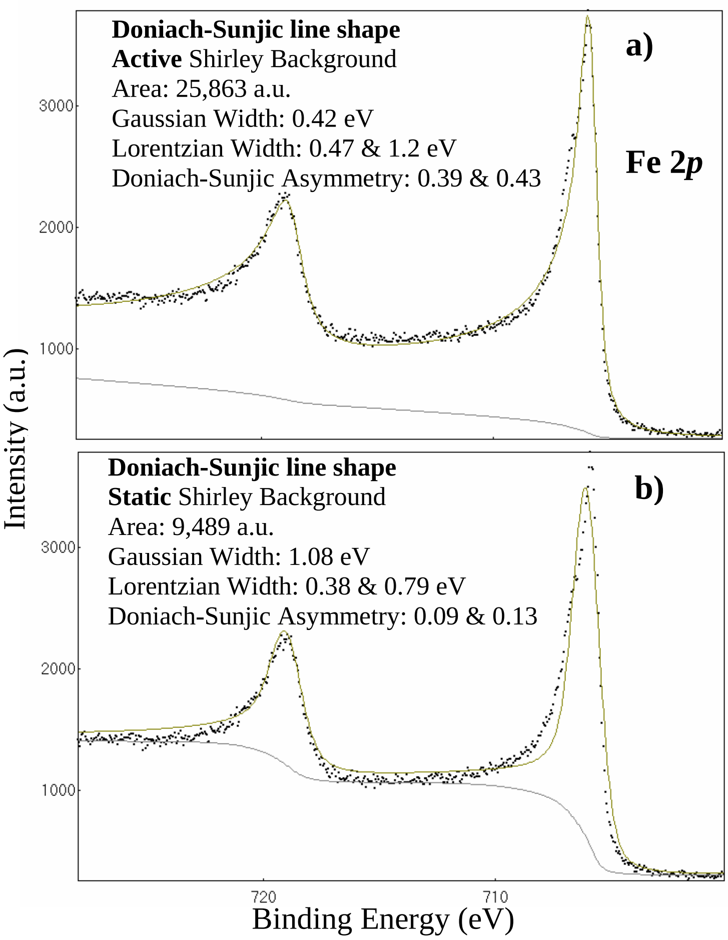

Figure 5. Fit of the same Fe 2*p* spectrum of Figure 1 but employing the Doniach-Sunjic line shape and the a) active and b) static background methods. In (a) the fit is not as close to the experimental data as in Figure 1 (where the double-Lorentzian line shape was employed) and the assessed area of the peak is huge (25,863 vs 9,994 a.u.) because of its tail at the high binding energy side. In (b) the fit is poorer, although the area is not that far off (9,489 vs 9,994 a.u.).

IV. Conclusions

Regarding the fit of asymmetric peaks, the double-Lorentzian line shape has many advantages:

- It is integrable, so it can be used for quantitative studies.
- Its parameters can be compared with simple Voigt functions. As in the example of Figure 3, the right side Lorentzian width of the asymmetric peak is the same as the Lorentzian width of the other two peaks, which have a symmetric Voigt shape.

- Since it is integrable, it has a hope to actually have a theoretical foundation; some work is been done in that direction.
- Last, but not least, it provides very good fits.

References

1 D. Briggs and J.C. Riviere, in: D. Briggs, M.P. Seah (Eds.), Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Wiley, Chichester, 1983 (Chapter 3, p. 132).

2 A. Herrera-Gomez. Internal Report. “An active treatment of the background.” Internal Report. CINVESTAV-Unidad Querétaro. (Created: 3/2011. Last Update: 1/2012). http://www.qro.cinvestav.mx/~aherrera/reportesInternos/activeVsStaticBackground.pdf.

3 S. Doniach and M. Sunjic, J. Phys. C 3, 285 (1970).

4 S. Evans. Surf. Interface Anal. 17, 85 (1991).

5 More information about the software can be found at www.rdataa.com/aanalyzer.