A new background for extrinsic electron scattering

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Abstract
In this Internal Report it is introduced a background for extrinsic scattering for fitting photoelectric spectra, such as in X-ray (XPS) or Ultraviolet (UPS) Photoelectron Spectroscopy. In contrast with the standard extrinsic background, the proposed background requires only one fitting parameter and account for the finite width of the source photoelectron spectrum. It is usable in the near-peak regime. It also provides better fits than the standard extrinsic background function.

I. Introduction: Intrinsic versus Extrinsic Background

There seems to be confusion in the literature differentiating between intrinsic and extrinsic background in core-level X-ray (XPS) or Ultraviolet (UPS) Photoelectron Spectroscopy. The intrinsic background is caused by the inelastic scattering of the photoelectron as it leaves its hosting atom. In contrast, the extrinsic background is generated by the inelastic scattering, mainly with plasmons, of any electron traveling through the solid. The latter requires accounting for the possibility of multiple scattering events, resulting in a multiple convolution of the cross section. It is usually very well reproduced through the theoretical framework established by Tougaard et al. in 1982. On the other hand, the intrinsic background is empirically very well reproduced through the Shirley method. Since the intrinsic scattering occurs at the most once, the scattering cross section behind the Shirley background can be modeled very simply as a constant. However, some authors portray the Shirley background as a special case of the extrinsic background by allowing the scattering to occur many times and finding a cross section function that could reproduce the Shirley shape. This leads to an unphysical dependence of the cross section on energy loss.
It is possible that this confusion has led to an extended practice of using either the Shirley or the Tougaard background while fitting XPS data, overlooking that both processes yield non-negligible contributions to most XPS spectra. Another issue preventing simultaneously accounting for both intrinsic and extrinsic background in data fitting is that the background is usually removed before peak fitting, and not dynamically obtained during the optimization-process. In another document (AnActiveTreatmentOfTheBackground.pdf) it is described the importance of employing algorithms that treat the background in a dynamic way while fitting photoemission (XPS, UPS) spectra.4

The intrinsic and the extrinsic scattering take place at different times and are independent events. The total background has contributions from both extrinsic and intrinsic scattering. As described in Figure 1, the intrinsic background has a stepwise shape and is very important in the near-peak region. The extrinsic background sits on top of the intrinsic background and becomes more important farther up in binding energy (left side). The initial slope and the plasmon losses are very well modeled through the Tougaard theory of extrinsic background.

![Figure 1](image.png)

**Figure 1.** Background of the Si 2p XPS peak. It has different relative contributions depending on the energy region.

### II. The Proposed Background

To fit a core-level XPS spectrum it is important to properly account for the near-peak intrinsic scattering, reflected mainly in the step in the background at the peak position, and for the extrinsic background, reflected mainly by the change of the slope of the background between the two sides of the peak (see Figure 1). As mentioned before, the stepwise shape is very well reproduced by the Shirley background; it requires only one parameter. The Tougaard background, on the other hand, requires two or even three parameters to reproduce the whole extrinsic background.5

The background introduced in this Report is a method for reproducing the extrinsic background only in the near-peak regime. With an approach very similar to that employed by Shirley, it is
proposed that the change on the slope of the extrinsic background at energy $E$ is proportional to the signal at higher kinetic energies:

\[
\frac{dB_{\text{ex}}(E)}{dE} = -k_{\text{ex}} \int_{E}^{E_{\text{right}}} dE' \left[ I(E') - I_{\text{right}} \right],
\]

where $B_{\text{ex}}(E)$ is the near-peak extrinsic background, $E$ is the kinetic energy, $k_{\text{ex}}$ is the scattering factor quantifying the strength of the background, $I(E)$ is the photoelectric signal, and $(E_{\text{right}}, I_{\text{right}})$ is a point in the flat background region on the high kinetic energy side of the peak.

Figure 2 shows a fit of a Si $2p$ spectrum of a silicon substrate with a layer of silicon carbide employing a) only the Shirley background and b) a combination of the Shirley background with the proposed background. One important difference between the two fits, which is blind to the eye, is that the ratio between the intensities of the carbide and substrate peaks is 7% smaller for the fit employing only the Shirley background. This directly affects the assessment of the silicon carbide layer thickness. Another important difference is that the peak associated to silicon oxide is negligible when the extrinsic background is not employed. The presence of oxidized silicon is an indication of pinholes, which is of importance for the data storage industry. The last difference is that the background is not reproduced as well in the 108-106.5 eV region.
Figure 2. Si 2p XPS spectrum for a silicon substrate with a layer of silicon carbide. The Shirley background employed is the dynamical version described in Reference 7. One fit was made a) without and b) with the proposed background.

The software (AAnalyzer®) and the parameters employed for the fit shown in Figure 2b are displayed in Figure 3.
Figure 3. Snap shots of the software employed for the fit shown in Figure 2. The boxes corresponding to the baseline, Shirley, and the proposed backgrounds are selected. The scattering factor for the Shirley background, as defined in Reference 7, is 0.019 eV\(^{-1}\). The scattering factor for the proposed background, as defined in Equation 1, is 0.0015 eV\(^{-2}\).
III. The Relationship between the Tougaard and the Proposed Background

As shown by Tougaard et al. in Reference 1, in the near-peak regimen the electron flux $J$ emitted at energy $E$ around the solid angle $\Omega$ is given by their Equation 44:

\[
J(E, \Omega) = C \cos \theta \lambda \left[ \delta(E - E_A) + A \lambda (E - E_A) + \ldots \right],
\]

which is valid when the photoelectric peak is replaced by a delta function $C \delta(E - E_A)$, as mentioned in their Equation 42. $\theta$ is the take-off angle, $\lambda$ is the electron inelastic mean free path, and $A$ is defined in terms of the near-peak electron loss cross section, $A(E_A - E)$ for $E_A > E$ and 0 otherwise (defined in their Equation 14). The photoelectric signal is then

\[
I(E, \Omega) = \int_{-\infty}^{\infty} dE_A J(E, \Omega) I_0(E_A, \Omega) \cos \theta \lambda \left[ I_0(E, \Omega) + A \lambda \int_{E}^{\infty} dE_A I_0(E_A, \Omega)(E_A - E) \right],
\]

where $I_0(E, \Omega)$ is the photoelectric signal without scattering. The first term inside the bracket multiplied by $\cos \theta \lambda$ is just the primary experimental peak signal $I_{PE}(E, \Omega)$. The near-peak extrinsic background signal $B_{NP}$ is then

\[
B_{NP}(E, \Omega) = \cos \theta \lambda^2 A \int_{E}^{\infty} dE_A I_0(E_A, \Omega)(E_A - E) = \lambda A \int_{E}^{\infty} dE_A I_P(E_A, \Omega)(E_A - E),
\]

and its derivative is given by

\[
\frac{dB_{NP}(E, \Omega)}{dE} = -\lambda A \int_{E}^{\infty} dE_A I_P(E_A, \Omega),
\]

which is identical to Equation 1 if the Shirley background signal is ignored. This is, in fact, a missing part in the Tougaard theory since the intrinsically scattered electrons also participate in the extrinsic generation of background.

IV. Conclusions

The proposed background can reproduce the extrinsic background in the near-peak regime. In that region, it has many advantages over the Tougaard background:

- Its functional form is the same regardless of the core level.
- It only employs one fitting parameter.
- It account for the finiteness of the peak width in the generation of the background signal.
- Last, but not least, it provides very good fits.

Its functional can be theoretically derived if a linear energy loss cross section is assumed.
References

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