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The Shirley-equivalent electron inelastic scattering cross-section function ☆

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Abstract

The inelastic scattering phenomenon of electrons in solids as seen by procedures using the Shirley-type empirical background is discussed. In close analogy with the Tougaard-type background correction procedure, the inelastic scattering cross-section function resulting in Shirley-equivalent background is derived. The main value of such a function—in addition to providing evidence that the Shirley method is based on a reasonable cross-section function—is in explaining the different energy dependence of both popular methods, especially near to photopeaks. The functional form of the scattering cross-section function is given, with some intuitively determined parameters. Evaluation methods based on the derived cross-section function have been implemented and tested. The cross-section based background calculation method nicely reproduces the results of the classic method and it can be used in generating peak tails, too.

Keywords: X-ray photoelectron spectroscopy; Electron–solid scattering and transmission – inelastic; Electron–solid interactions, scattering, diffraction

1. Introduction

For practical evaluation of an X-ray photoelectron spectrum (XPS), Shirley introduced [1] the first empirical method that successfully solved the task of deriving the inelastic background for a peak measured in a relatively narrow energy region and for the case of a relatively small amount of inelastic scattering. Much later, Tougaard introduced [2] his background calculation method after assuming that the photoelectrons had a particular inelastic energy loss cross-section. Thanks to its simplicity, the Shirley method remained important (although not any more dominant) even after the introduction of the Tougaard background correction method, despite the fact that *no detailed physical interpretation was given for the empirical procedure*. Until now, *the type of inelastic collision cross-section implicitly assumed with use of the Shirley background correction method* is not known. The present paper discusses the principles of the Shirley and Tougaard background evaluation methods in close analogy with each other, provides a derivation of the inelastic cross-section for the Shirley method.

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2. Roots of the derived cross-section function

The present approach is based on three ideas: the original method proposed by Shirley, use of the inelastic energy-loss cross-section function as introduced by Tougaard, and analysis of the contributions due to inelastic scattering for the primary photoelectron distribution rather than for the measured spectrum.

2.1. Shirley's heuristic procedure

Shirley proposed [1] his method *for "narrow" peaks, with a relatively small difference in the intensity levels* of the background-like regions on either side of the main photoelectron peak of interest. The precise algorithmic description introduced by Proctor and Sherwood [3] should, in principle, be the starting point of the today's implementations. The explanation [4] "*...the Shirley method... is thus proportional to the integrated photoelectron intensity to higher kinetic energy*" leads to an equation [5] for the Shirley background intensity $S_S(E)$, belonging to the photopeak $P(E)$, as a function of the electron energy E

$$S_S(E) = k \cdot \int_E^{+\infty} P(E')\,\mathrm{d}E', \tag{1}$$

where k is an arbitrary constant. In practical evaluation, the measured spectrum $j(E)$ rather than the primary spectrum $P(E)$ is available, so Eq. (1) is computed in such a way that the primary distribution $P(E)$ is approximated as the difference of the measured intensity and some approximation to the background $S_{S,i}(E)$

$$S_{S,i}(E) = k \cdot \int_E^{+\infty} (j(E') - S_{S,i-1}(E'))\,\mathrm{d}E'. \tag{2}$$

As initial approximation, a constant background $S_{S,0}$ is assumed. The procedure suggested by Sherwood [4] iterates Eq. (2) until the background converges.

2.2. Tougaard's cross-section function

The great invention by Tougaard [2] was that he assumed the existence of a function that described the probability of losing some energy due to an inelastic collision in function of the lost energy. A fortunate fact is that such functions can be both theoretically derived and experimentally determined. The practical difficulty with applying these cross-sections for spectrum evaluation is that the inelastically scattered electrons measured in the spectrum comprise electrons suffered quite different number of collisions. With Tougaard's analytical ingenuity, a proper method could be derived that accounts for infinite number of collisions in one single step. The Tougaard's approach uses the measured spectrum $j(E)$ as a starting point, and in his formalism the background $S_T(E)$ due to inelastically scattered electrons can be generated in one single convolution step

$$S_T(E) = \int_E^{+\infty} K(E' - E)(j(E') - S_{T,0}(E'))\,\mathrm{d}E', \tag{3}$$

where the $S_{T,0}(E')$ is the contribution from electrons originating from peaks at higher kinetic energies and is usually approximated by fitting a straight line to the slope on the hight energy side of the peak [6]. As a result, practical background determination methods and energy loss cross-section functions of analytic form could be derived [7].

2.3. Comparing Shirley's and Tougaard's procedures

When scrutinizing these background correction formulas, at least four important differences should be noticed, in addition to their formal similarity.

- The method of Shirley is an empirical method, while the Tougaard method has an established physical model background.
- The Shirley method uses the primary electron distribution, while the Tougaard method uses the measured spectrum as starting point, although makes a simple linear background correction step, i.e. the Shirley method operates on electron spectrum not yet scattered in the solid, while the Tougaard method uses the energy distribution of the already scattered electrons.
- The Tougaard method is based on a cross-section function, while the Shirley method does not involve it. The classic Shirley method does not even

mention if the probability of loosing some energy does depend on the magnitude of the energy loss. The model simply does not contain such an information and does not even mention the idea of the energy loss cross-section function.
- The Shirley method should be iterated in order to deliver the final background contribution, while the Tougaard procedure delivers it as the result of one single convolution step.

2.4. The contribution due to inelastic collisions

The method of taking into account the contribution of primary electron distributions due to inelastic scattering dates back to the first peak tails by Castle et al. [8] and the 7-parameter tailed peak shape by Sherwood [4]. The first analytical form for a per-peak contribution satisfying the Shirley conditions was given by Végh [5]. Later, a numerical procedure was derived [9] for generating peak tails based on the inelastic cross-section introduced by Tougaard.

In case of taking the primary electron distribution as starting point [9] rather than the measured spectrum [2], one faces the practical computational difficulty that in principle an infinite number of convolutions with the inelastic cross-section should be calculated. This disadvantage can be abandoned in the Tougaard approach.

A primary photoelectron spectrum (say a single photopeak) $P(E)$ suffers inelastic collisions inside the solid and the electron contribution $S_1(E)$ due to electrons suffered exactly one collision is described by the convolution (*) of the primary distribution with the inelastic cross-section $K(E)$

$$S_1(E) = P(E) * K(E). \tag{4}$$

The scattered electron can be subject of collision(s) again and in general, the distribution of electrons scattered n times is described as

$$S_n(E) = S_{n-1}(E) * K(E) = P(E) * K(E)^n, \tag{5}$$

where $K(E)^n$ stands for the n-times self-convolution of $K(E)$. The total contribution due to scattered electrons is given then by

$$S(E) = \sum_{n=1}^{\infty} S_n(E). \tag{6}$$

Although in finite energy regions met in practical spectrum evaluation this requirement can be reduced to calculating the first few members of the series [10], it still significantly increases both the complexity and the execution time of the calculation. Efficient algorithms to calculate the multiply scattered spectrum were derived for specific depth profiles in [11].

3. The Shirley cross-section function

In order to derive the Shirley-equivalent cross-section function, we have some physical conditions the sought function needs to meet, a mathematical condition that defines it and some experiences that help to determine the parameters of the function.

3.1. Physical conditions

A cross-section function describes the probability of losing a certain amount of energy, so it must be non-negative and finite all over its range of interpretation. The electrons cannot gain energy due to inelastic collisions, so at negative loss energies its value must be exactly zero. One can expect that very large energy losses have insignificant probability, i.e. the value of the function must disappear as the lost energy approaches infinity, in the same way as the Tougaard-type and the experimental cross-sections do. Conversely, at low loss energies the value of the trial cross-section function must be much higher than that of the Tougaard type functions, in order to explain the greatly different behavior of the two background correction procedures near to photopeaks. The integral of the cross-section function over the interval $[0,\infty]$ means the total probability of loosing energy via inelastic collision, so it must converge. The integral of both types of cross-section must be comparable. Exact equivalence cannot be expected, because in the practical evaluation the cross-sections are integrated over a finite rather than an infinite energy range. The background correction procedure uses the integral over a finite energy range as a measure of the inelastic background and so the integrals of these two total cross-sections over a limited energy

range need to be nearly equal, rather than the integral over the energy interval $[0,\infty]$.

3.2. Mathematical form

We have two independent derivations of the Shirley-type inelastic background. Once the empirical procedure results in Eq. (1) and through summing up the contributions due to inelastically scattered electrons we get Eq. (6). Because both of these expressions represent the same physical object, they must be equal and the sought $K(E)$ function must satisfy the condition:

$$k\int_E^{+\infty} P(E')\,\mathrm{d}E' = \sum_{n=1}^{\infty} P(E) * K(E)^n. \tag{7}$$

This equation provides a possibility for finding the "Shirley-equivalent inelastic energy loss cross-section" function $K(E)$. Omitting the arbitrary constant k and Fourier transforming Eq. (7), the right side transforms into a geometrical series that can be immediately summed up. After transforming the result back one gets the final result that the form of the kernel is

$$K(x) = \delta(x)\frac{1+ix}{1+x^2}. \tag{8}$$

We are obviously interested in the real part of the function and because of the arbitrary constant k in Eq. (1), some physical assumptions are also needed to derive the exact function form. For comparison with the Tougaard's two-parameter "universal" cross-section function

$$K_{\mathrm{T}}(T) = \frac{B_{\mathrm{T}}\cdot T}{(C_{\mathrm{T}}+T^2)^2}, \tag{9}$$

the "Shirley-equivalent" cross-section function derived by the author is sought in form

$$K_{\mathrm{S}}(T) = \frac{B_{\mathrm{S}}}{C_{\mathrm{S}}+T^2}, \tag{10}$$

where T is the lost energy. Here and below, the coefficients B and C are used in connection with both the Shirley-equivalent scattering function and the Tougaard scattering function. In order to avoid confusion, the coefficients are subscripted with the first letter of the corresponding method. Note that because of the dissimilarity of the function forms, B_{T} and B_{S} have different units.

It has been shown [9,12] that the integral of the cross-section function has a physical meaning: it gives the intensity of the first loss spectrum. In case of the Tougaard "universal" cross-section function its integral A is expressed as

$$A = \frac{B_{\mathrm{T}}}{2\cdot C_{\mathrm{T}}}. \tag{11}$$

Replacing B_{T} and C_{T} with the well-known values [7] or the ones found in the elaborate experimental work by Seah [12] (or the ones adjusted to the spectrum in question), one can calculate the value of A. As it has been pointed out above, this number shall be equal to the integral of the sought function. This latter can be expressed as

$$A = \frac{B_{\mathrm{S}}}{\sqrt{C_{\mathrm{S}}}}\cdot\frac{\pi}{2}, \tag{12}$$

i.e. one can derive only the ratio of the coefficients from the area of the function.

Fortunately, there exists some further analogy between the shape of the Tougaard function and that of the present one. The B_{S} coefficient is the "scattering intensity" and C_{S} describes the "distribution width" of the function. The Tougaard function drops to half of its reached maximum height at ca. 25–30 eV higher after reaching its maximum. If one requires a similar feature for the present trial function, one finds that C_{S} should be about 600–900 eV^2 and correspondingly B_{S} about 15–20 eV. These assumptions only serve as a rough guide in guessing the magnitude, the correct values of the coefficients need to be derived from experimental spectra, a work in progress.

3.3. Performance

Using the function form and the estimated coefficients, one can re-formulate the Shirley background correction method (see Eq. (1)) again in complete analogy with the Tougaard method (see Eq. (3)) as

$$S_{\mathrm{S}}(E) = \int_E^{+\infty} K_{\mathrm{S}}(E'-E)\ \left(j(E') - S_{\mathrm{S},0}(E')\right)\mathrm{d}E', \tag{13}$$

where $K_S(E)$ is the cross-section function given by Eq. (10). In the followings Eq. (13) is called the "cross-section based" and Eq. (1) the "classic" Shirley background correction method. One can test the features of the trial cross-section function through comparing them directly or comparing the resulting backgrounds.

In Fig. 1 the trial cross-section function is shown together with Tougaard's "universal" cross-section. The present cross-section has its maximum at zero loss energy and gives much more emphasize to the very low energy inelastic energy losses as it could be expected on the basis of theoretical assumptions or experimental results. The line "ShirleyCS" is calculated with parameters $C_S = 2500$, $B_S = 27.8$, which assumes exact agreement of the integral with that of the Tougaard's function. When using the trial cross-section function for evaluating a measured Ag 3d spectrum (see Fig. 2) the coefficients shall be adjusted to another values ($B_S = 36$, $C_S = 900$), which results in using the cross-section marked by "Shirley" in Fig. 1.

In Fig. 2 the backgrounds fitted to a measured Ag 3d spectrum by the different Shirley methods are compared. The classic Shirley method with no iteration [1] does not provide a satisfactory background, because the difference in the background levels is too big here. After iterating that initial background as described in [3], the method produces a perfect Shirley background. The cross-section based Shirley background (generated in the same way as one produces a Tougaard background) is nearly identical with the classic background, if the parameter B_S is adjusted properly. Note that the parameters of the backgrounds shown in Fig. 2 are slightly changed from their "best" values in order to make the individual curves visible.

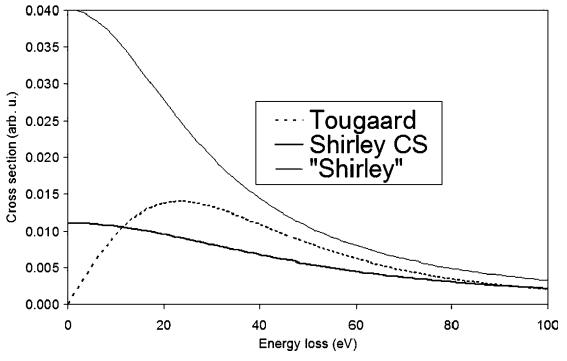

Fig. 1. Comparing the present $1/(1+x^2)$-type cross-sections (the one resulting the same inelastic loss than the Tougard's "universal" function and the one with parameters resulting in a reasonable fit to the background on the left side of the Ag 3d peak shown in Fig. 2) to the Tougaard's "universal" function [7].

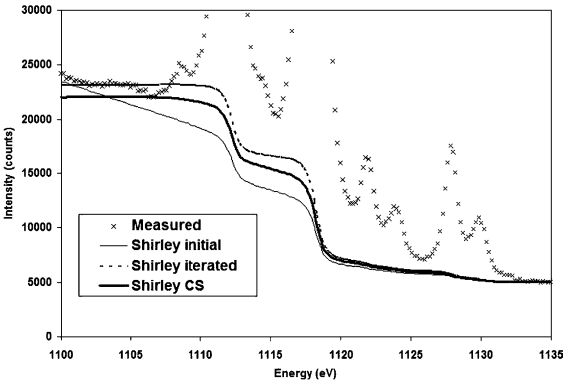

Fig. 2. Different Shirley backgrounds to an Ag 3d spectrum: the non-iterated Shirley method [1], the iterated Sherwood method [3] and the present method.

The present results strongly contradict to the former statements on the shape of this cross-section function like in [13]: "*Shirley's method* is traditionally used but *does not represent the accurate energy loss spectrum* responsible for the peak background to be subtracted: it is assumed that *the probability for one electron of energy E to lose an energy T does not depend on E or on T*". The presented cross-section function proves that *the Shirley phenomenon can be explained* assuming that the inelastic scattering process is governed by an *inelastic cross-section function*. The present paper does not state that the real inelastic energy loss cross-section can be described with the derived function, rather it explains that *such a cross-section function is implicitly assumed when one uses the Shirley background correction procedure*.

3.4. Peak tails

As has been pointed out earlier [5,8,9], attaching the contributions due to inelastically scattered electrons in form of "tails" to the individual photopeaks results in some advantages. One can

derive cross-section based photopeak tail for the present Shirley cross-section in the same way as it was done for the Tougaard cross-section [9]. As Eq. (6) shows, the total contribution due to scattered electrons is given by a sum, i.e. in principle it should be calculated trough convoluting the primary distribution with the inelastic energy loss cross-section function a large number of times and summing up the contributions.

In the linear convolution algorithms, the convolved array does not change during the convolution and the returned result contains the array convolved exactly once. In this special case the features of the inelastic scattering process allow to make modifications [9] on the algorithm due to which the returned result will contain the sum of all contributions up to infinite order, i.e. Eq. (6) can be calculated in one single linear-convolution like step as outlined on the flow chart in Fig. 3. The key points here are the shaded rectangles.

Since the electrons can not gain energy during inelastic collisions (i.e. the cross-section function is exactly zero for negative loss energies), if one calculates the contribution due to the inelastic collision of electrons with energy E_i, it surely will not affect contributions at energies higher than E_i. Because of this, if one starts the calculation at the highest available energy and proceeds towards the lower energy points, the already calculated contributions will not change any more. It is known from the physics of the scattering that the probability of being scattered does not depend on the previous energy losses, i.e. scattered electrons with their new energy are to be accounted immediately when calculating the contributions at energies E_j, $j < i$. Increasing the amount of the electrons at electron energy E_j with the amount of scattered electrons from higher energies accounts for this physical effect and so after repeating the steps until the lowest energy reached, the total contribution due to all inelastic collisions will be produced. The mathematical correctness of this one-step procedure was proved by Graat et al. [14] using Fourier-transform.

In Fig. 4 different peak tails due to inelastic collisions (calculated using the present method and the ones in [5,9]) are added to a peak. As shown, in case of the Shirley-type backgrounds the tail is constant in the low energy side of the spectrum, at reasonable distance from the peak. As expected, in the vicinity of the photopeak the shape of the tail depends strongly on the parameters of the cross-section function.

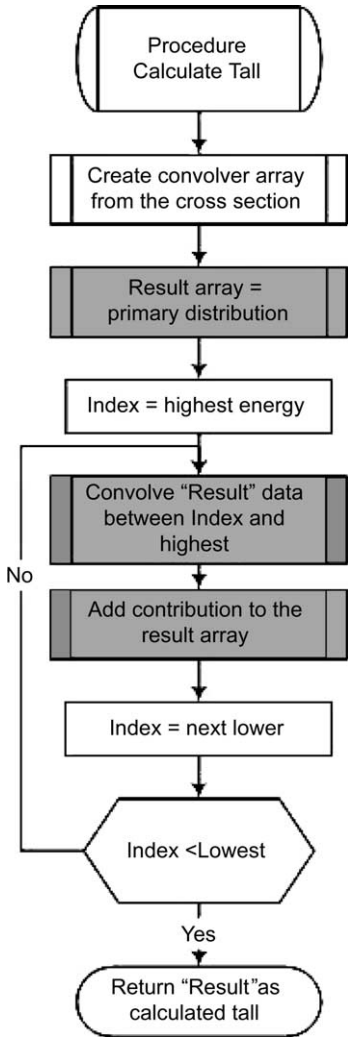

Fig. 3. The one-step linear convolution algorithm for calculating in one-step the tailed peak shape due to inelastic scattering contributions.

4. Summary

Although the Shirley background correction method is one of the most widely used spectrum

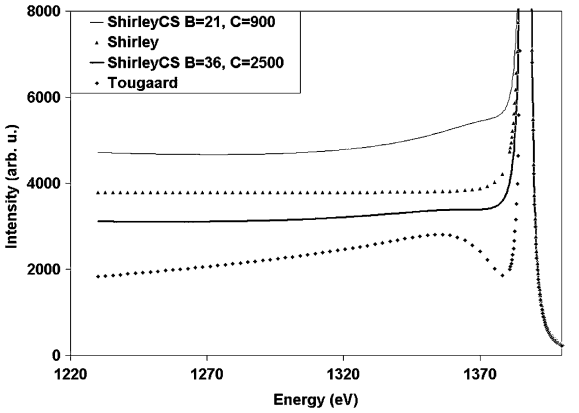

Fig. 4. Comparing tailed peaks generated assuming different loss cross-sections: the "classic" Shirley tail [5], the Tougaard tail [9], and the present method, using two different sets of coefficients, leading to different background shape near to the photopeak.

evaluation methods, its physical details have not been discovered until now and even some misbelieves have been published about it. Introducing the Shirley-equivalent cross-section makes this picture cleaner and opens several research tasks. The present results prove that *the Shirley phenomenon can be explained* assuming that the inelastic scattering process is governed by an inelastic cross-section function and that *such an inelastic energy loss cross-section function is implicitly assumed* when one uses the Shirley background correction procedure.

The analysis of the cross-sections might help in discovering some *systematic errors due to incorrect background determination* when evaluating *the asymmetry of the photopeaks* or *separating intrinsic/extrinsic contributions* to the primary photopeak. As elegantly pointed out by Cohen Simonsen et al. [15] in connection with the Tougaard method, the inelastic contribution of type Eq. (6) comprises only the extrinsic energy loss contributions, the intrinsic energy loss cannot be accounted in this way. The introduced cross-section function puts the Shirley evaluation method in complete analogy with the Tougaard evaluation method. The mathematical techniques are absolutely identical, the only difference is in the functional form of the assumed cross-section. Because of this, *the Shirley method removes only the extrinsic energy loss contributions*, too. Methods like the one published by Salvi and Castle [16] determine the difference due to the different cross-section functions assumed by the two different background correction methods rather than the intrinsic energy loss alone.

The analysis of the functional form of the cross-section function in comparison with that of the Tougaard's function reveals *why the Tougaard and Shirley background correction methods produce so very much different background height in the vicinity of the photopeaks*. The resulting cross-section form allows to verify if *the conditions of using the Shirley background correction procedure apply*. The derived cross-section function can be compared to the experimentally determined ones *for materials where the Shirley method is unexpectedly successful*.

Although the method shall yet be tested on experimental spectra to discover the dependence of values of coefficients B_S and C_S on material features, its application for practical spectrum evaluation seems to be very promising. The procedures mentioned in this paper are implemented and built into the freely available spectrum evaluation program wxEWA [17], so the interested reader can try the procedures on his own measured data.

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