

User's Guide

QUEELS - XPS

**Quantitative Analysis of Electron Energy Loss in
XPS Spectra**

Version 2.1

by

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**Software for Quantitative
Calculation of Inelastic Electron
Energy Loss Processes in XPS**

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The software builds on the results published in:

AC Simonsen, F Yubero, and S Tougaard Phys. Rev. B56, p. 1612
(1997)

Examples of its practical use can be found in:

S Tougaard, F Yubero Surf Interf Anal. 36, 824 (2004)

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Surface and core hole effects in X-ray photoelectron spectroscopy
Surf Sci 604 (2010) 1193-1196

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Core hole and surface excitation correction parameter for XPS peak intensities
Surface Science 605 (2011) 1556-1562

Contents

1. Introduction	6
1.1 The QUEELS-XPS software package.....	7
1.2 Outline of this manual.....	8
2. Theoretical background.	8
2.1 Photoelectron spectra	8
2.2 Dielectric response model of XPS energy loss processes.....	9
2.2.1 Effects of the core hole and of the surface	11
3. Experimental verification of the validity of the dielectric response XPS model	14
4. Brief description of the input and output of the QUEELS-XPS software	19
4.1 Introduction	19
4.2 Input.....	19
4.3 Output.....	20
5. Examples of applications	22
6. Practical brief overview	23
7. Install QUEELS-XPS	24
7.1 Running QUEELS-XPS.....	24
8. Features and practical application of the QUEELS-XPS software package.....	24
8.1 Tutorial example. Calculation of the loss structure of photoelectrons emitted from a thick silicon sample.	25
8.1.1 Input the dielectric function parameters to describe the	

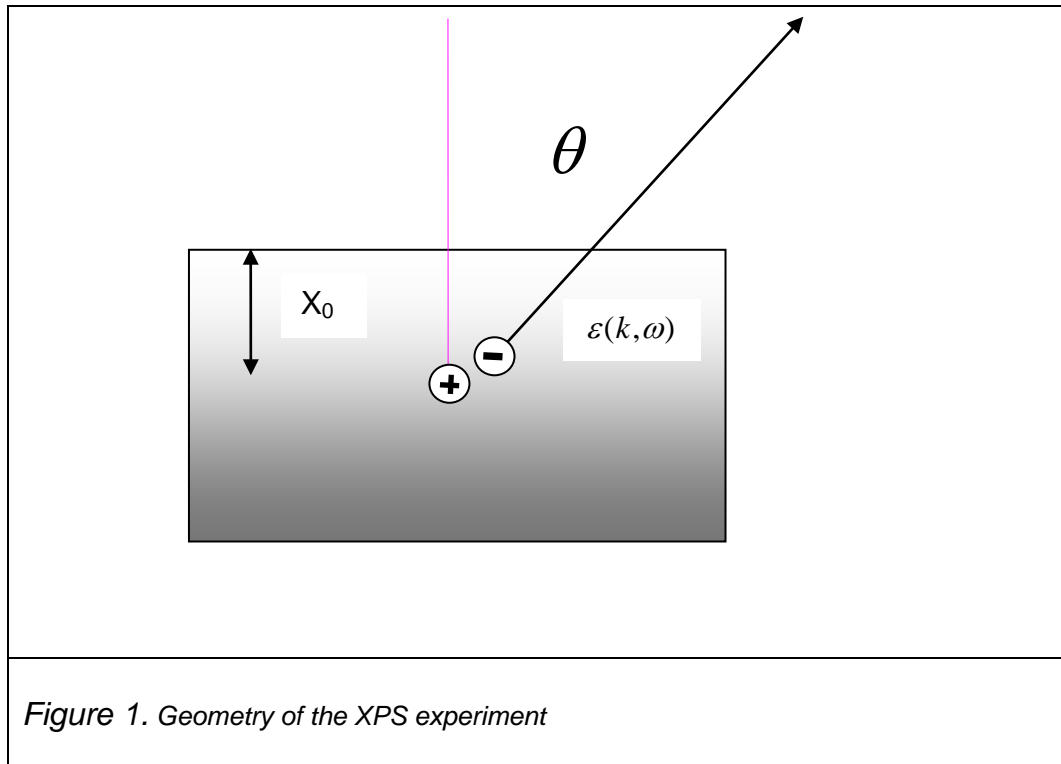
medium.....	25
8.1.2 Calculation of inelastic scattering cross sections for photoelectrons with QUEELS-XPS	27
8.1.3 Convolution with the primary spectrum $F(E)$ for direct comparison to experimental XPS.....	31
9. File Formats and File Management.....	32
9.1 File Formats.....	33
10. References.....	35

1. Introduction

The physical processes that take place when a charged particle moves nearby a solid surface involve complex interactions with the electrons in the solid. [4,5,9,10,6,7,8,8]. Models to describe this are important for quantitative understanding of surface analysis techniques based on the interpretation of electron spectra such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), transmission electron energy loss spectroscopy (TEELS) and reflection electron energy loss spectroscopy (REELS). These are influenced by the inelastic scattering processes that take place when an electron moves in the region near a solid surface. The actual energy losses depend on the particular experimental situation. Thus, an electron is attracted by its image charge when it is moving in the vacuum. It will therefore lose energy even after it has left the surface and similarly, an electron that moves in vacuum towards the solid surface may gain energy[6]. Likewise, the scattering properties for an electron moving close to the surface are different from those of an electron moving in the bulk of the solid. In XPS and Auger experiments the electric field of the static hole will also affect the scattering probabilities of the electron in the first few Å as it moves away from the point of excitation. These effects will also cause the “effective” inelastic mean free path to depend on the position of the electron with respect to the surface and with respect to the point of excitation [6,7,8].

We have been involved [6,7,8,9,10,11] in the development of semi-classical models based on a dielectric response description of the interaction between the moving electron and the electrons in the solids as well as the core hole in photo- and Auger- electron spectroscopy. The resulting expressions are rather complex and this has been a main hindrance for widespread practical use of the results. With the purpose of making the calculations available to the general community, we decided in 2001 to start development of user friendly and practical software packages. In 2005 we released the software package QUEELS- $\epsilon(k,\omega)$ -REELS [11] which describe the energy loss processes in a REELS experiment. From a straight forward analysis of a reflected electron energy loss spectrum (REELS) this software allows to determine the dielectric properties of a material. Since the theory is valid for energies down to a couple of hundred eV where the inelastic electron mean free path (IMFP) is on the order of 1 nm, the method can be used to determine the dielectric and optical properties of nanometer thin films. The present manual and software package QUEELS-XPS is the second in this series of such packages.

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1.1 The QUEELS-XPS software package

The present software provides a tool to calculate the energy loss processes in photoelectron spectra which are caused by the transport of the electron in the presence of the static core hole and the surface.

The situation in photoelectron spectroscopy is shown in fig.1 where the incoming photons excite core electrons in atoms in the surface region of the material.

After it has been excited, the photo-electron moves towards the surface while the core hole is left at the point of excitation. The photo-electron will interact with the field set up by the static core hole as well with the electrons of the solid. The presence of the surface complicates the

interaction processes because it influences the boundary conditions for the electric field. After the electron has left the surface, there is still a considerable interaction with the electrons in the solid while the electron travels in the vacuum just above the surface. The time varying fields give rise to excitations of the electrons and the energy for this is taken from the photoelectron which therefore loses energy. The result is a redistribution of the energy in the photoelectron spectrum. It is these effects that are calculated by the QUEELS-XPS software package.

1.2 Outline of this manual

In *Chapter 2*, we outline the theoretical background. It is mainly a summary of our previous papers []. The reader can find additional information in these references. A thorough reading and understanding of this chapter is not needed for practical use of the software.

In *Chapter 3* we summarize some experimental investigations on the validity of the model.

In *Chapter 4* we summarize the input and output of the calculations provided by the QUEELS-XPS software package.

In *Chapter 5*, we give a few practical examples.

Chapter 6 gives a quick overview of the practical steps involved in the calculation of model spectra.

Chapter 7 describes the installation and running of the software.

Chapter 8 illustrates the practical application of the software by a worked through tutorial example.

Chapter 9 describes the file formats.

2. Theoretical background.

2.1 Photoelectron spectra

In the simplest interpretation of XPS, a one-electron wave function is used in the “sudden approximation” and the effects of the surface are neglected. However for a fundamental understanding of the photoelectron intensity and energy spectrum, it is essential to consider a model that includes many-electron and surface effects. The energy loss structure originates from both the static core-hole created during the photoexcitation of the core electron and by the excitations that take place during transport of the photoelectron out of the solid. The corresponding energy loss processes are usually called “intrinsic” and

“extrinsic” excitations. Intrinsic (also called shake-up) excitations can sometimes be seen as distinct peaks on the low kinetic energy side of the main photoelectron peak. Several models have been proposed in the past for evaluation of XPS spectral line shapes [Error! Reference source not found.,8,12,13,14,15,16,17,18,19,20,21]. Most models have been based on a quantum-mechanical description of the perturbation induced by the photo-excitation process of the electron states of the solid. A review on this subject was recently reported [20]. This first-principles approach has been extremely valuable to enlighten the fundamental mechanisms behind the photo-excitation process. But the complexity of this approach makes it impractical for calculations of the energy loss processes in XPS for solids other than the free-electron jellium-type solids (see example in the upper panel of Fig.4 below). It is, however, very rare that electronic excitations in solids can be quantitatively described within this model and, in general, it is insufficient. This approach is therefore of little practical use. A method which makes calculations practically manageable for general materials was proposed in [8] and it is precisely this model that the present QUEELS-XPS software builds on. In this semiclassical model, the interaction of the medium with the core hole and the effect of the surface, as well as the excitations that take place during transport of the electron, are described by the complex dielectric function of the medium. A clear advantage of this dielectric response description over the quantum-mechanical models is that extensions beyond materials that can be described by the nearly free-electron model are straightforward because the only input in the calculations is the dielectric function. This is of paramount importance for practical applications because, as mentioned above, very few materials are well described within the free-electron model. The dielectric function may be taken from the literature [5] or it may be determined from analysis of an experimental REELS spectrum using the QUEELS- $\epsilon(k,\omega)$ -REELS software package [11].

2.2 Dielectric response model of XPS energy loss processes

The basic mechanism in the dielectric response description is that the static core hole as well as the moving photo-electron induces a potential in the medium. The photo electron is in turn affected by this potential and this leads to energy loss processes in which energy $\hbar\omega$ and momentum $\hbar k$ are transferred to the valence electrons of the solid. The variation in time and space of the induced potential is conveniently described by the complex dielectric function $\epsilon(k,\omega)$ of the medium. For an electron travelling in an infinite medium we define by $K(E_0, T)$ the differential inelastic electron scattering cross section, i.e. $K(E_0, T)dRdT$ is the probability that an electron of energy E_0 will lose energy in the interval $T, T+dT$ after having travelled a path length dR in

the solid. This is given by [1,2]

$$K(E_0, \hbar\omega) = \frac{1}{\pi a_0 E_0} \int_{k_-}^{k_+} \frac{dk}{k} \text{Im}\{1/\epsilon(\mathbf{k}, \hbar\omega)\} \quad (2)$$

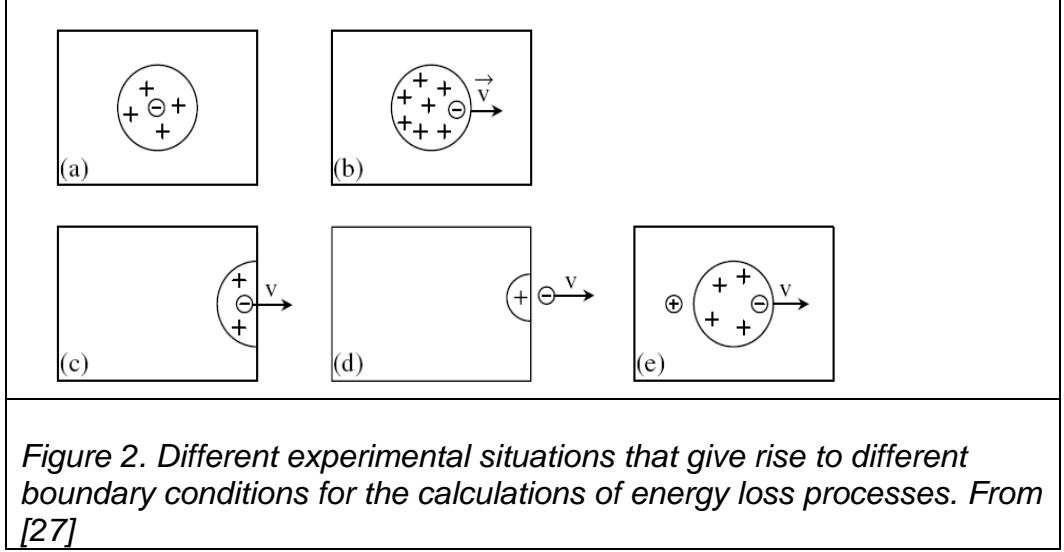
where $\hbar\omega = T$, E_0 is the initial energy of the electron, a_0 is the Bohr radius, and k is the wave vector transferred from the electron. $k_{\pm} = (2m/\hbar^2)^{1/2} [E_0^{1/2} \pm (E_0 - \hbar\omega)^{1/2}]$ are the limits on the k vector imposed by energy and momentum conservation in the inelastic scattering process.

The complex dielectric function of the medium is conveniently described by an expansion in terms of oscillators [22]

$$\text{Im}\left\{\frac{1}{\epsilon(\mathbf{k}, \hbar\omega)}\right\} = \theta(\hbar\omega - E_g) \sum_{i=1}^n \frac{A_i \gamma_i \hbar\omega}{\left(\left(\hbar\omega_{0i} + \alpha_i \frac{\hbar^2 k^2}{2m}\right)^2 - \hbar\omega^2\right)^2 + (\gamma_i \hbar\omega)^2} \quad (3)$$

where A_i , γ_i and $\hbar\omega_{0i}$ is the strength, width and energy position of the i 'th oscillator. The dispersion for each oscillator is α_i . For a free electron like material as Al, $\alpha_i = 1$, while $\alpha_i \sim 0$ for core electrons and for wide gap insulators like SiO_2 [23,24] because of the typical weak k -dispersion for the corresponding electron energy bands. The step function $\theta(\hbar\omega - E_g)$ is included to simulate the effect of a possible energy gap E_g because no energy loss processes are possible for $\hbar\omega < E_g$. Eq.(4) describes the energy loss processes of an electron moving in an infinite medium.

Fig.2 shows schematic representations of different situations in which an electron interacts with the surrounding valence electrons in the medium nearby a surface [22,25,27]. Thus, Figure 2a shows a static situation where the charge of an electron at rest is screened by the surrounding ion cores in the solid and an electric field is set up. Fig. 2b shows the situation where the electron is moving in the solid. The screening charge lags behind the moving electron and this gives rise to a time varying electric field and the electrons of the solid may interact with this field and be excited to states at higher energy. The excitation energy is taken from the moving electron which, in turn, loses energy. Fig. 2c shows the situation where the electron is approaching the surface. Here the spatial extension of the electric field is modified by the presence of the surface. After the electron has left the surface it will still induce charge redistributions in the solid and the electron will interact with this field and may thus still lose energy while it moves outside the solid in the vacuum as in Fig. 2d. Fig. 2e shows the situation where there is a static core-hole left behind at the point of excitation corresponding to a photon excited core electron. The photoelectron will interact with the electric field from this static positive charge in the first few angstroms as it moves away which, in turn, will change the probability distribution for energy loss.



2.2.1 Effects of the core hole and of the surface

In the semiclassical model [8,22] based on a dielectric description of the electron energy losses of a photon excited core electron, it is assumed that an electron-hole pair (both considered as point charges) is created at a given depth inside a semi-infinite medium, characterized by a dielectric function $\varepsilon(\mathbf{k}, \omega)$. The calculation applies the “specular reflection model” which allows one to solve the electrodynamic problem with the proper boundary conditions for the electric potential and field at the surface-vacuum interface. The geometry of the situation is defined in the inset in Fig.3. The core-hole is assumed to be static with infinite lifetime, i.e. it remains at a fixed location forever after being created at time $t=0$. The photoelectron escapes from the semiinfinite medium with a velocity \mathbf{v} in a rectilinear trajectory. Within this model, one defines an effective inelastic scattering cross section $K_{\text{eff}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ in terms of the induced potential. $K_{\text{eff}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ is defined as the average probability that a photoelectron excited at depth x_0 with energy E_0 shall loose energy $\hbar\omega$ per unit energy loss and per unit path length while traveling in the specified geometry. The energy loss includes processes that take place after the electron has left the surface but the average is taken over the path length traveled inside the solid, i.e. $x = x_0/\cos\theta$, where θ is the angle to the surface normal. Neglecting angular electron deflection one gets [8]

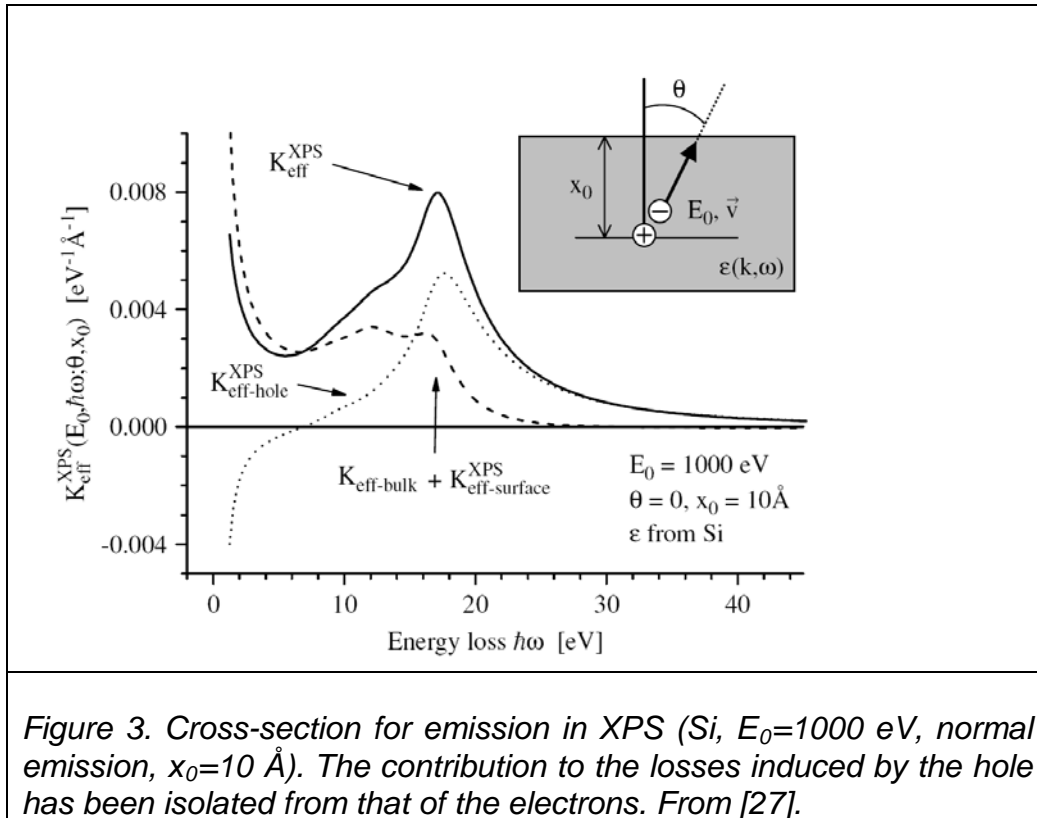
$$K_{\text{eff}}(E_0, \hbar\omega; \varepsilon, \theta, x_0) = \frac{2}{(2\pi)^4 \hbar^2 \omega x} \Re e \left\{ \int dt \int d^3 r \rho_e(\mathbf{r}, t) \int d^3 k \mathbf{k} \cdot \mathbf{v} \Phi_{\text{ind}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0) e^{i(\mathbf{k}\mathbf{r} - \omega t)} \right\} \quad (4)$$

where \mathbf{r} is the position, $\rho_e(\mathbf{r}, t)$ the charge density of the escaping photoelectron, and $\Phi_{\text{ind}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0)$ the Fourier transform of the potential induced by the escaping photoelectron and the static core-hole in the

semiinfinite medium.

The final expression for $\Phi_{\text{ind}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0)$, given in ref [8], has several terms which, from their dependence on the charge of the static hole, can formally be identified as being due to the static core hole (denoted “hole” terms) and the rest which are independent of the hole (denoted “no-hole” terms) so that

$$\Phi_{\text{ind}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0) = \Phi_{\text{ind, no-hole}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0) + \Phi_{\text{ind, hole}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0) \quad (5)$$



With the present software it is possible to calculate and save these components separately. This is a formal division and it is not strictly possible to make this distinction because the different contributions interfere. More details and the precise expressions for the “no-hole” and “hole” contribution to the total induced potential can be found in [8]. The expressions are quite involved and will not be repeated here. It is common to denote those excitations that are due to the potential $\Phi_{\text{ind, hole}}$ as “intrinsic” and those that are due to the potential $\Phi_{\text{ind, no-hole}}$ as “extrinsic”. With this identification, the total cross section is decomposed in the form

$$K_{\text{eff}}(E_0, \hbar\omega; \varepsilon, \theta, x_0) = K_{\text{eff}}^{\text{extr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0) + K_{\text{eff}}^{\text{intr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0) \quad (6)$$

where $K_{\text{eff}}^{\text{intr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ is the sum of the terms that would disappear if the hole were not there and $K_{\text{eff}}^{\text{extr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ is the sum of the remaining terms. These can also be calculated separately with the present software. Note that with this separation in “intrinsic” and “extrinsic” excitations they include the so called “interference” effects that may be attributed to the interference between the fields from the core hole and the moving electron. Since the interference effect diminishes the total energy loss, the intrinsic cross section may be negative (see Fig.3). The total cross section is however always positive.

Fig.3 shows an example of such a calculation [27] of the XPS from photo excitation of a Si core electron to 1000 eV energy in a Si matrix at depth $x_0 = 10 \text{ \AA}$ at normal emission. With the present notation, $K_{\text{eff}}^{\text{extr}} = K_{\text{eff-bulk}} + K_{\text{eff-surf}}^{\text{XPS}}$ and $K_{\text{eff}}^{\text{intr}} = K_{\text{eff-hole}}^{\text{XPS}}$. Note that most of the bulk plasmon losses (seen as the peak at $\sim 16 \text{ eV}$ energy loss) are due to intrinsic excitations. Thus, less than half of the bulk plasmon intensity is caused by the extrinsic processes occurring as the electron is transported from 10 \AA depth and out of the solid while the major part of the bulk plasmon intensity is intrinsic i.e. it is caused by the static core hole. Note that the only input in this calculation (which was done with the present QUEELS-XPS software is the dielectric function for Si.

In an experimental XPS measurement, there will be contributions from photoelectrons excited at a range of depths. It is therefore necessary to account for their relative contributions to the spectrum. This is done by introducing an averaged effective cross section [22,25]

$$K_{\text{eff,av}}(E_0, \hbar\omega; \varepsilon, \theta) = K_{\text{eff,av}}^{\text{extrinsic}}(E_0, \hbar\omega; \varepsilon, \theta) + K_{\text{eff,av}}^{\text{intrinsic}}(E_0, \hbar\omega; \varepsilon, \theta) \quad (7)$$

where the “extrinsic” and “intrinsic” contributions can be estimated as weighted average over the total pathlength x traveled by the electron inside the medium as

$$K_{\text{eff,av}}^{\text{extrinsic/intrinsic}}(E_0, \hbar\omega; \varepsilon, \theta) = \int_0^{\infty} W(E_0; \varepsilon, \theta, x) K_{\text{eff}}^{\text{extrinsic/intrinsic}}(E_0, \hbar\omega; \varepsilon, \theta, x) dx \quad (8)$$

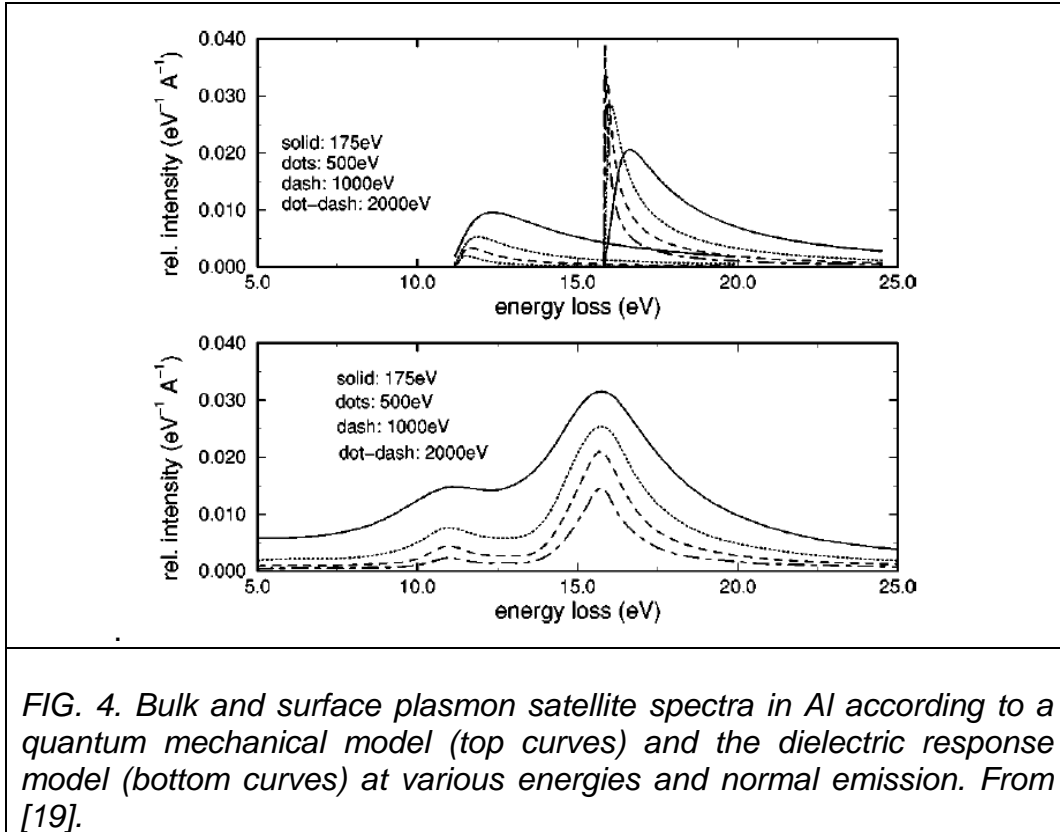
The weight function $W(E_0; \varepsilon, \theta, x)$ takes into account the pathlength distribution of the electrons having suffered only a single inelastic scattering event [25].

For comparison to photoemission experiments, the elastic peak must be included. If $F(E)$ is the primary excitation spectrum, the model spectrum $J(E)$ from a homogeneous sample corresponding to a primary spectrum plus one inelastic scattering event is given by

$$J(E) \propto F(E) + \lambda \int_E^{\infty} F(E') K_{\text{eff,av}}(E_0, E'-E) dE' \quad (9)$$

where $E'-E=\hbar\omega$. In order to be selfconsistent with the calculated $K_{\text{eff,av}}$, λ is usually taken as the inverse of the area of $K_{\text{eff,av}}$. Thus, $J(E)$ represents the model XPS spectrum corresponding to a zero-loss peak $F(E)$ together with the single inelastic scattering contribution. In practice, $F(E)$ can be taken as a mixed gaussian-lorentzian curve with a width given by the lifetime broadening of the excitation [25].

In [19], the XPS dielectric response model was compared to a quantum mechanical calculation and Fig. 4 shows the comparison for Al and the dependence of the satellite spectra as a function of photon energy for normal emission. The surface contribution decreases relative to the bulk one, and the bulk peak becomes sharper with increasing energy. The trends roughly agree. The quantum mechanical model does however neglect electron-electron excitations as well as the plasmon broadening effect and the quantum mechanical model does not allow for a quantitative comparison [19].



3. Experimental verification of the validity of the dielectric response XPS model

In this section we will summarise some examples of spectra that has been calculated with the QUEELS-XPS software package. In a later

chapter we will go through the steps of a couple of these examples so the user can do the calculations and verify the results.

The validity of the dielectric model behind QUEELS-XPS for the simulation of XPS spectral lineshapes has been investigated by comparison to experiments [8,25,27,28,29,0]]. For example in [25] it was shown that the theory accounts well for the peakshape observed in experiments for angular dependence of Al2s and Al2p emission. The comparison is shown in Fig. 5 where the bulk and surface plasmons (at ~15 and 10 eV respectively) are clearly seen to depend strongly on the geometry, with the surface plasmon being more prominent for glancing emission angles.

The model calculations reproduces the absolute intensities as well as shapes of both bulk and surface excitations for the whole series of experimental spectra taken at exit angles from 10 to 80 degrees. The only fitting parameter in this model is the width of the elastic peak since the parameters that define the dielectric function were taken from independent experiments. The calculation scheme can easily be applied to other materials and experimental conditions. The only input in the calculations is the dielectric function which for a given solid may be taken from compilations [**Error! Reference source not found.**] or it may be determined experimentally from a fairly simple analysis of REELS spectra using a dielectric response model as implemented in the QUEELS- $\epsilon(k,\omega)$ -REELS software package which was developed for this purpose. [7,11]

In [25], the excitations were split in extrinsic and intrinsic contributions to the measured spectra. As was discussed above, these contributions are related to the electronic excitations due to the moving electron or to the core-hole, respectively. Fig. 6 shows that both extrinsic and intrinsic surface losses are enhanced with respect to the corresponding bulk losses at glancing emission angles. However, the change with angle of emission in the absolute contribution of extrinsic and intrinsic losses to $K_{\text{eff,av}}$ is different. For the “surface” losses (identified as the region around the peak at ~ 10 eV), the “extrinsic” contribution to $K_{\text{eff,av}}$ accounts for more than 95 % of the intensity for all studied angles of emission. Note that as described above the slightly negative intrinsic cross sections in Fig. 6 is due to the “interference” effect [25].

For the bulk losses (identified as the peak at ~ 15 eV and the accompanying tail) the relative intensity of “intrinsic” to “extrinsic” excitation varies with the emission angle. Thus $\sim 62\%$ of the total area of the bulk plasmon is due to intrinsic losses at normal emission, while it is $\sim 35\%$ at 80° [25]. The shape of the intrinsic losses is clearly different from the extrinsic. The intrinsic losses are more step-like in shape being very asymmetric with excitations that extend to much larger energy losses than the extrinsic losses (see Fig. 6). This shows that the characteristic asymmetric shape of the bulk plasmon peak which is observed in experiments is caused by the intrinsic contribution to the bulk plasmon while the extrinsic bulk plasmon has only a small asymmetry towards higher energy loss. The spectra taken at glancing angles have less intrinsic losses than those at normal emission. This is

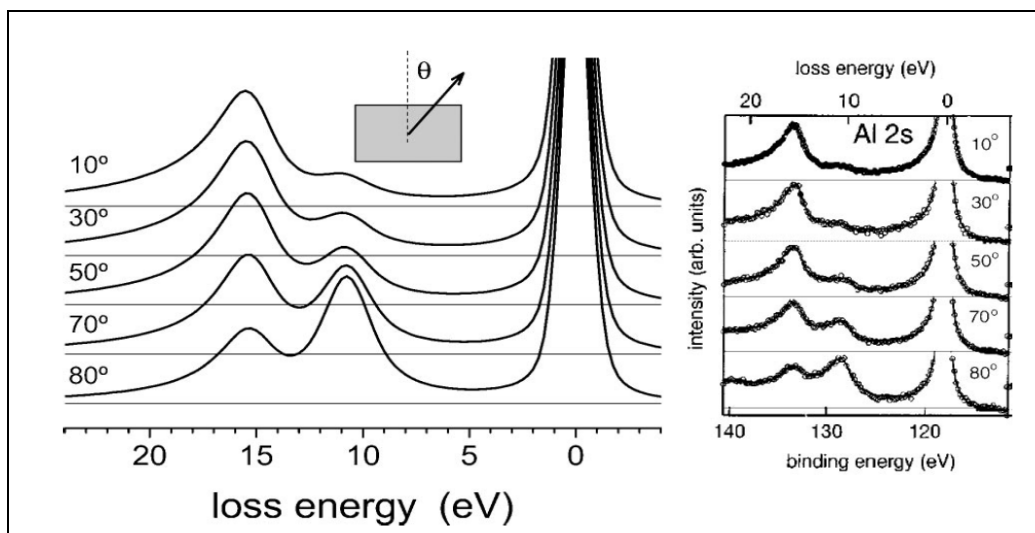


FIG. 5. Left: model photoemission spectra calculated according to Eq.(9) for photoelectrons traveling in Al with 1130 eV kinetic energy for several emission angles. Right: experimental results for Al 2s photoemission in Al sample from [Error! Reference source not found.] for the same experimental conditions used in the model calculations. From [Error! Reference source not found.].

easily understood since, for glancing angles the photoelectron loses more energy (to extrinsic excitations) while it moves in the vacuum above the surface where it interacts for a longer time with the electrons in the solid compared to an electron being emitted normal to the surface. Therefore the relative contribution of intrinsic excitations decreases with increasing emission angle. This is also likely to be the explanation why the surface excitations are almost purely extrinsic for all angles of emission because the extrinsic excitations that take place as the electron travels in the vacuum occur mostly at the surface plasmon energy.[25]

Fig.6 shows that the extrinsic/intrinsic contributions to the energy loss structure vary considerably with energy, geometry and depth and it is not strictly possible to separate the excitations due to the hole, the moving electron, and the effect of the surface. However, as it turns out, for energies > 100 eV, this is in fact a useful and valid model to describe the *changes* in peak intensity and energy loss structure caused by variations in the depth distribution of excited electrons. It is these *changes* that are most important for practical quantitative XPS. For a discussion of this see ref. [22].

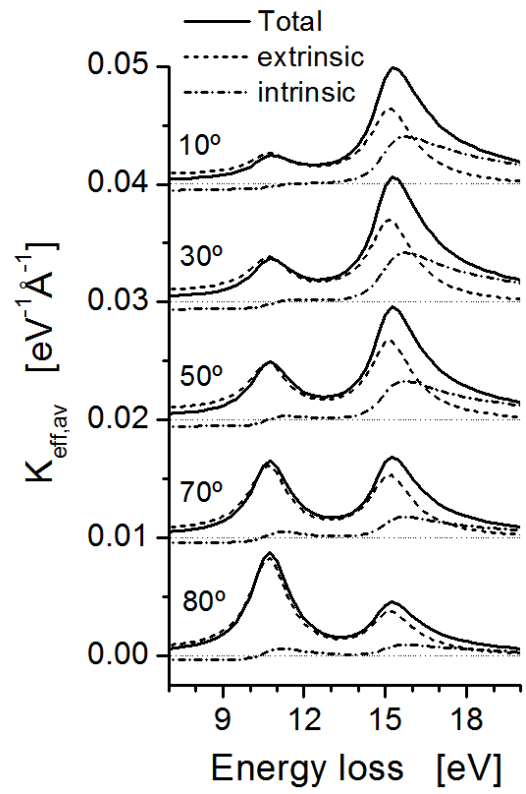


FIG. 6. Effective average cross sections $K_{\text{eff,av}}$ corresponding to the model calculations in Fig. 5. The extrinsic and intrinsic contributions to the spectra are indicated as dashed and dashed-dot lines, respectively. From [Error! Reference source not found.].

4. Brief description of the input and output of the QUEELS-XPS software

4.1 Introduction

The theory builds on the model where a response of the electrons in the solid to the moving electron is described by the complex dielectric function $\varepsilon(k, \omega)$ of the solid. This model was proposed to describe REELS spectra in 1992 [6] for normal incidence and emission angles and in 1996 [7] it was extended to include general incidence and emission angles in REELS experiments. In 1997 [8] the model for photoemission was presented and it is the expressions in that paper which is calculated by the QUEELS-XPS software. It takes the interference effects between the different excitations into account as well as excitations due to the static core hole and at the surface and excitations that take place when the electron moves in the vacuum after it has left the surface of the sample before it enters the electron spectrometer.

Fig.1 shows the geometry of the XPS experiment which is modelled by the QUEELS-XPS software. The software calculates the effective inelastic scattering cross section for photo-electrons that are excited at different depths [7]. From this set of calculated effective cross sections, the average is calculated by a weighted average over the depths. Finally, this is convoluted with the primary excitation peak to give the emitted XPS-spectrum.

4.2 Input

The only inputs in the calculations are the energy loss function (ELF) of the material considered, the angle of emission θ (i.e., the geometry of the process) and the kinetic energy E_0 of the emitted photoelectron.

The ELF is obtained from the dielectric function of the material $\varepsilon(k, \omega)$ as the imaginary part of the inverse of $\varepsilon(k, \omega)$. It is parameterised by an expansion proposed by Ritchie et al [**Error! Reference source not found.**]

$$\text{Im}\left\{-\frac{1}{\varepsilon(k, \omega)}\right\} = \sum_i \frac{A_i \gamma_i \hbar \omega}{\left\{\left(\hbar \omega_{0i} + \alpha_i \frac{\hbar^2 k^2}{2m}\right)^2 - \hbar^2 \omega^2\right\}^2 + (\hbar \gamma_i \hbar \omega)^2} \cdot \theta(\hbar \omega - E_g)$$

where $\hbar \omega_i, \hbar \gamma_i,$ and α_i are parameters that describe the energy, damping and dispersion of the individual oscillators that are used to describe the response in time and space of the electrons of the solid. The step function $\theta(\hbar \omega - E_g)$ is included to describe the effect of a band gap in semiconductors and insulators. For metals one expects that the dispersion $\alpha_i \sim 1$ for oscillators with $\hbar \omega_i < 20-30$ eV while $\alpha_i \sim 0$ for oscillators with $\hbar \omega_i > 30-60$ eV. For semiconductors it is expected that $\alpha_i \sim 0$ for all oscillators when the bandgap is large ($> 3-9$ eV) while $\alpha_i \sim 0.2-0.6$ for all oscillators when the band gap is smaller ($< 1-3$ eV).

The program also includes a facility to ensure that the dielectric function fulfils the optical sum rule **[Error! Reference source not found.]**

$$\frac{2}{\pi} \int_0^{\infty} \text{Im}\left\{-\frac{1}{\varepsilon(k, \omega)}\right\} \frac{d\omega}{\omega} = 1 - \frac{1}{n^2}$$

where n is the refractive index of the material in the optical limit $\hbar \omega \rightarrow 0$. This is discussed further in a following section.

4.3 Output

The effective inelastic scattering cross section $K_{\text{eff}}(E_0, \hbar \omega; \varepsilon, \theta, x_0)$ is defined as the average probability that a photoelectron excited at depth x_0 with energy E_0 shall lose energy $\hbar \omega$ per unit energy loss and per unit path length while travelling in the specified geometry. The energy loss includes processes that take place after the electron has left the surface but the average is taken over the path length travelled inside the solid, i.e. $x = x_0 / \cos \theta$, where θ is the angle to the surface normal. The software calculates $K_{\text{eff}}(E_0, \hbar \omega; \varepsilon, \theta, x_0)$ for a large range of depths x_0 by eq.(4) above:

$$K_{\text{eff}}(E_0, \hbar \omega; \varepsilon, \theta, x_0) = \frac{2}{(2\pi)^4 \hbar^2 \omega x} \Re e \left\{ \int dt \int d^3 r \rho_e(\mathbf{r}, t) i \int d^3 k \mathbf{k} \cdot \mathbf{v} \Phi_{\text{ind}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right\}$$

where \mathbf{r} is the position, $\rho_e(\mathbf{r}, t)$ the charge density of the escaping photoelectron, and $\Phi_{\text{ind}}(\mathbf{k}, \omega; \varepsilon, \theta, x_0)$ the Fourier transform of the potential induced by the escaping photoelectron and the static core-hole in the semiinfinite medium.

The software also calculates the separate “intrinsic”

$K_{\text{eff}}^{\text{intr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ and “extrinsic” $K_{\text{eff}}^{\text{extr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ contributions to the energy loss (see eq(6) above)

$$K_{\text{eff}}(E_0, \hbar\omega; \varepsilon, \theta, x_0) = K_{\text{eff}}^{\text{extr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0) + K_{\text{eff}}^{\text{intr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$$

Note that with this separation in “intrinsic” and “extrinsic” excitations they include the so called “interference” effects that may be attributed to the interference between the fields from the core hole and the moving electron. Since the interference effect diminishes the total energy loss, the intrinsic cross section may be negative (see Fig.3). The total cross section is however always positive. In the software, $K_{\text{eff}}^{\text{intr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$, $K_{\text{eff}}^{\text{extr}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ and $K_{\text{eff}}(E_0, \hbar\omega; \varepsilon, \theta, x_0)$ are stored in three files with the cross sections for all energy loss and all calculated depths x_0 .

In an experimental XPS measurement, there will be contributions from photoelectrons excited at a range of depths. It is therefore necessary to account for their relative contributions to the spectrum. This is done by calculating an averaged effective cross section [**Error! Reference source not found.**]

$$K_{\text{eff,av}}(E_0, \hbar\omega; \varepsilon, \theta) = K_{\text{eff,av}}^{\text{extrinsic}}(E_0, \hbar\omega; \varepsilon, \theta) + K_{\text{eff,av}}^{\text{intrinsic}}(E_0, \hbar\omega; \varepsilon, \theta) \quad (7)$$

where the “extrinsic” and “intrinsic” contributions are estimated as weighted average over the total pathlength x traveled by the electron inside the medium as

$$K_{\text{eff,av}}^{\text{extrinsic/intrinsic}}(E_0, \hbar\omega; \varepsilon, \theta) = \int_0^{\infty} W(E_0; \varepsilon, \theta, x) K_{\text{eff}}^{\text{extrinsic/intrinsic}}(E_0, \hbar\omega; \varepsilon, \theta, x) dx \quad (8)$$

where $x = x_0/\cos\theta$ is the total pathlength traveled by the electron inside the medium and $W(E_0; \varepsilon, \theta, x) = xe^{-x/\lambda_{\text{eff}}}$ is the pathlength distribution function for the considered electrons. λ_{eff} is an “effective” inelastic mean free path which is also calculated for each trajectory by the software. λ_{eff} depends on both x_0 and the angle of emission. In the program λ_{eff} can be either taken as a fixed value given by the available electron inelastic mean free paths from the literature or the software can calculate a self consistent value determined as the inverse of the area of the effective cross section calculated by the software for each photo electron trajectory. It is in general recommended to use the self-consistent values.

For comparison to photoemission experiments, the elastic peak and the inelastic multiple scattering contributions must be included.

If $F(E)$ is the primary excitation spectrum, the model spectrum $J_1(E)$ from a homogeneous sample corresponding to a primary spectrum plus one inelastic scattering event is given by

$$J_1(E) \propto F(E) + \lambda \int_E^{\infty} F(E') K_{\text{eff,av}}(E_0, E'-E) dE' \quad (9)$$

where $E'-E=\hbar\omega$. In order to be selfconsistent with the calculated $K_{\text{eff,av}}$, λ is usually taken as the inverse of the area of $K_{\text{eff,av}}$. Thus, $J(E)$ represents the model XPS spectrum corresponding to a zero-loss peak $F(E)$ together with the single inelastic scattering contribution. In practice, $F(E)$ can be taken as a mixed gaussian-lorentzian curve with a width given by the lifetime broadening of the excitation [**Error! Reference source not found.**].

Although the theory used in this software in principle does not apply for multiple inelastic scattering, it is worth including multiple scattering by means of successive self-convolution of the cross section obtained previously, for comparison purposes with experiments.

$$J(E) \propto F(E) + \lambda \int_E^{\infty} F(E') K_{\text{eff,av}}(E_0, E'-E) dE' + \text{multiple scattering} \quad (10)$$

These are the outputs provided by the software. In the next section we will go through two practical examples.

5. Examples of applications

See references

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Surface and core hole effects in X-ray photoelectron spectroscopy

Surf Sci 604 (2010) 1193-1196

N. Pauly and S. Tougaard

Core hole and surface excitation correction parameter for XPS peak intensities

Surface Science 605 (2011) 1556-1562

6. Practical brief overview

Calculation of a photoelectron spectrum involves the following steps:

1. The oscillators in the ELF is set up. This is done with the first menu in the QUEELS-XPS software called: "*SET ELF oscillators*".
2. Calculations are done of energy spectra for photo-electrons excited at several depths within the surface. These depths are automatically selected by the program (they cover the relevant depths determined from the effective inelastic mean free path). This is done with the second menu in the QUEELS-XPS software package called: "*Calculate Set of Cross Sections*".
3. From the file created in step 2, a weighted averaged cross section is calculated. This is done with the third menu in the QUEELS-XPS software package called: "*Calculate averaged Cross Section $K_{eff,av}$ for XPS*".
4. To compare the calculated cross section to an experimental XPS, it must be convoluted with the primary excited (i.e., before electron transport starts) photo excitation spectrum. If this is unknown, the program "Compare to experiment" allows to convolute with a Gauss-Lorentz peak shape.

Note: The program assumes that the American standard for numbers is used (where the decimal place is marked by a ".") and will not run properly if setting is different. To change settings, select *Start* on the Windows menu bar and then select *Settings, Control Panel, Regional Settings, English(United States)* . Alternatively, you may change the number settings for your current Regional settings to the American standard.

7. Install QUEELS-XPS

To install, click the *Setup.exe* program and follow the instructions on the screen. In general it is recommended to respond with a Yes and OK to all questions.

7.1 Running QUEELS-XPS

Start the program by clicking the QUEELS-XPS icon in the QUEELS program menu and get the main menu of the program as in Figure 7

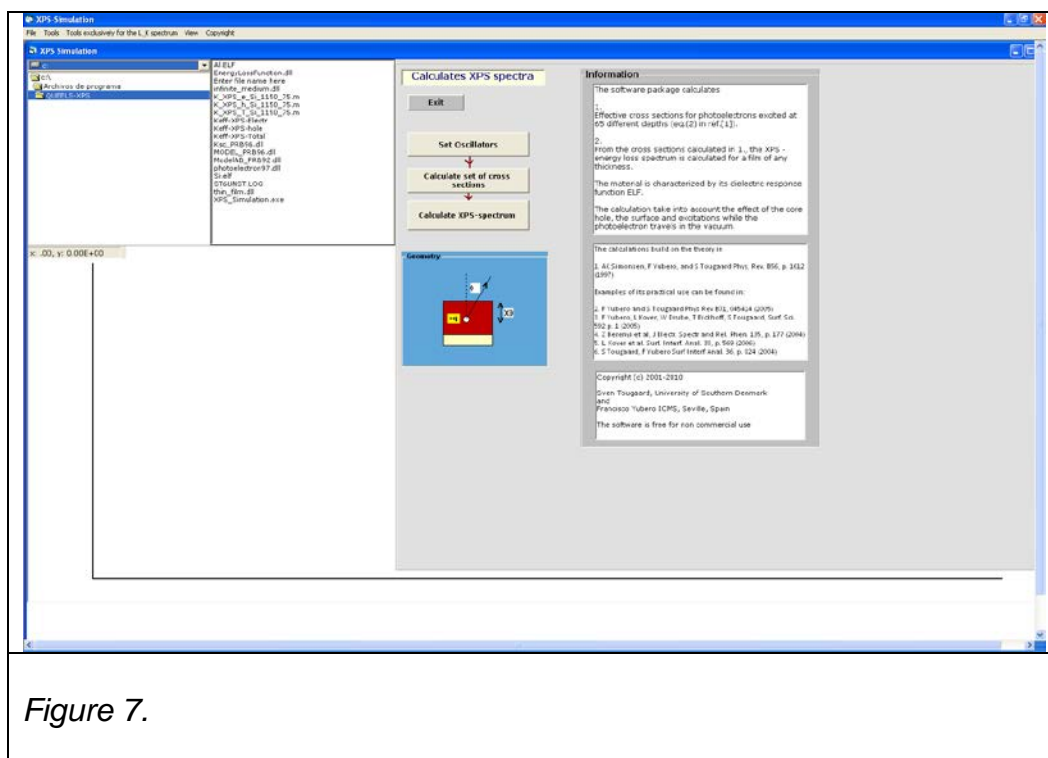


Figure 7.

The functionality will be described in the next chapter.

8. Features and practical application of the QUEELS-XPS software package.

In this chapter we describe the features of the program package. This is done by taking a practical example and we shall go through the procedure step by step.

8.1 Tutorial example. Calculation of the loss structure of photoelectrons emitted from a thick silicon sample.

In this example we will go through the steps needed to calculate some of the simulated spectra corresponding to the photoelectron emission from Si. These results were published in the paper by Yubero et al. Surf. Sci. 592 (2005) 1.

8.1.1 Input the dielectric function parameters to describe the medium.

The dielectric response of the material to be studied (i.e., definition of the parameters describing the ELF of the material where photoemission, i.e., sudden creation of the electron-hole pair and the electron transport, take place) is introduced with the data supplied in the *Set ELF oscillators* section of the program

From the main menu of the QUEELS-XPS program:

- Click *Set ELF oscillators* (see Fig. 8)

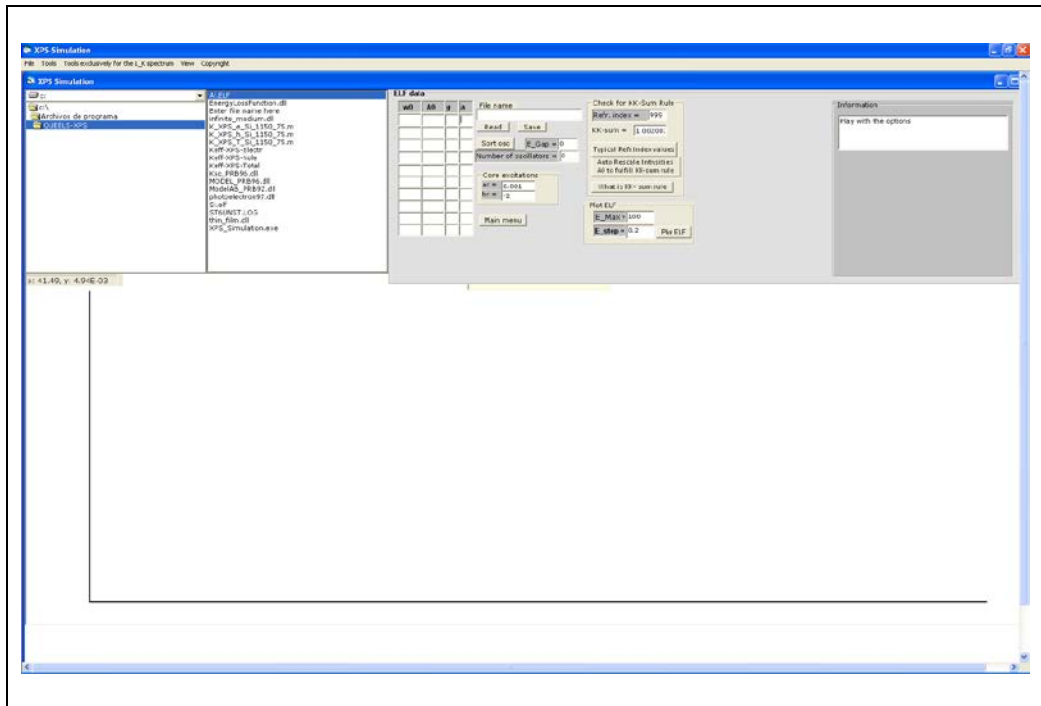


Figure 8

Now input values for the ELF oscillators for Si (see following table). They are taken from ref.[1].

- Type in the values in Table 1;

Table 1

$\hbar\omega_i$ (eV)	A_i (relative strength of peaks)	γ_i (eV)(half width of peaks)	
10.0	6	5.0	0.5
14.0	30	5.0	0.5
16.8	210	3.8	0.5

- Type also the following values characteristic of Si:
 $a_c = 1.2$, $b_c = -3.7$ (accounts for small corrections due to the truncation of the evaluation of the cross sections)
 $E_g = 1.1$, (energy gap in eV)
 $n = 3.6$ (refractive index in the optical limit)

After introducing the parameters describing the dielectric response of the matrix where the photoemission process and electron transport take place,

- Type a filename (in this case *Si.elf*) where the parameters introduced are going to be stored, and
- Click save . Notice that this file is added to file-list. (see Fig.9). You can edit this file by clicking twice on the filename that appears in the file list.

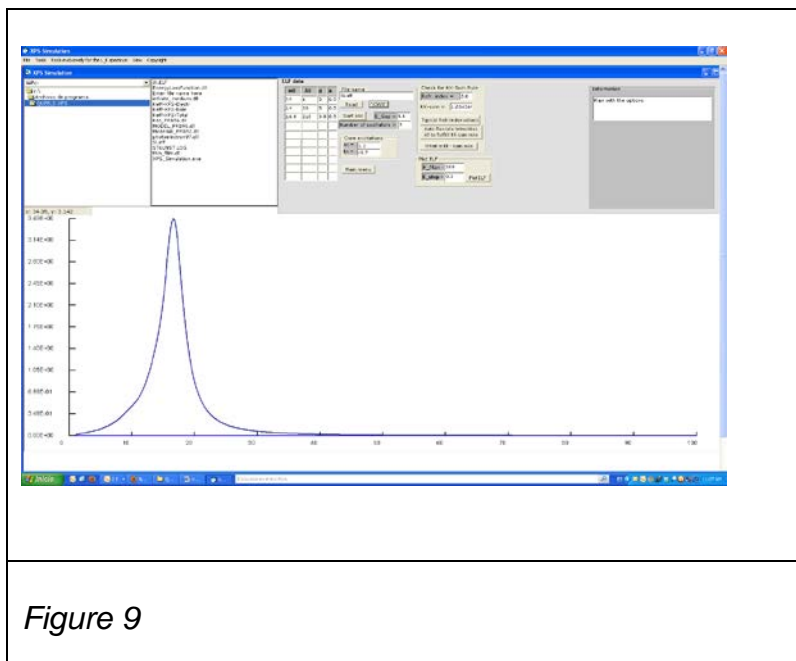


Figure 9

- Click *main menu* to quit this part of the program

8.1.2 Calculation of inelastic scattering cross sections for photoelectrons with QUEELS-XPS

The evaluation of inelastic scattering cross sections of emitted photoelectrons (in presence of a core hole) is done according to eqn.(.) in ref. []. Within this software, this is done in two steps.

First step:

From the main menu of the QUEELS-XPS program

- Click *Calculate Set of Cross Sections*. This part of the program calculates the energy spectra for electrons that are emitted at several (65) depths. The depths are selected automatically by the program with distributed over the relevant path-lengths.
- Select a file (click once on it) with the ELF data in file-list (here: *Si.elf*).
- Click *Read ELF file*.
- Set the parameter values:
 - $E_p = 1150$ (primary kinetic energy in eV)
 - Theta = 75 (angle of emission in degrees);
 - Emax = 100 (maximum energy loss in eV evaluated);
 - Emin= 0.2 (minimum energy loss in eV evaluated)
 - Estep = 0.2 (energy step in eV considered in the calculations)
 - q_hole = 1 (effective charge of the hole; 1 by default)
- Write the name of the files where you wish to save the calculated spectra for the 65 depths in the appropriate textbox. Here we choose the names:
 - K_XPS_T_Si_1150_75.m*,
 - K_XPS_e_Si_1150_75.m*, and
 - K_XPS_h_Si_1150_75.m*
 for the total, electron (extrinsic) and hole (intrinsic) contributions to K_{eff} , respectively.
- Click *Calculate Keff(X0)* to calculate the set of cross sections K_{eff} for the 65 depths. Let the PC run until the program is finished (it takes ~ 1-5 min. depending on the CPU of the PC). The successive cross sections that are calculated according to the parameters introduced previously are shown on the screen. *Note that the program may stop if you run another program simultaneously.*

When the calculations finish, the data are automatically saved to the files *K_XPS_T_Si_1150_75.m*, *K_XPS_e_Si_1150_75.m*, *K_XPS_h_Si_1150_75.m* included in to the file-list. The total calculation time is also shown on the screen. (see Fig.10)

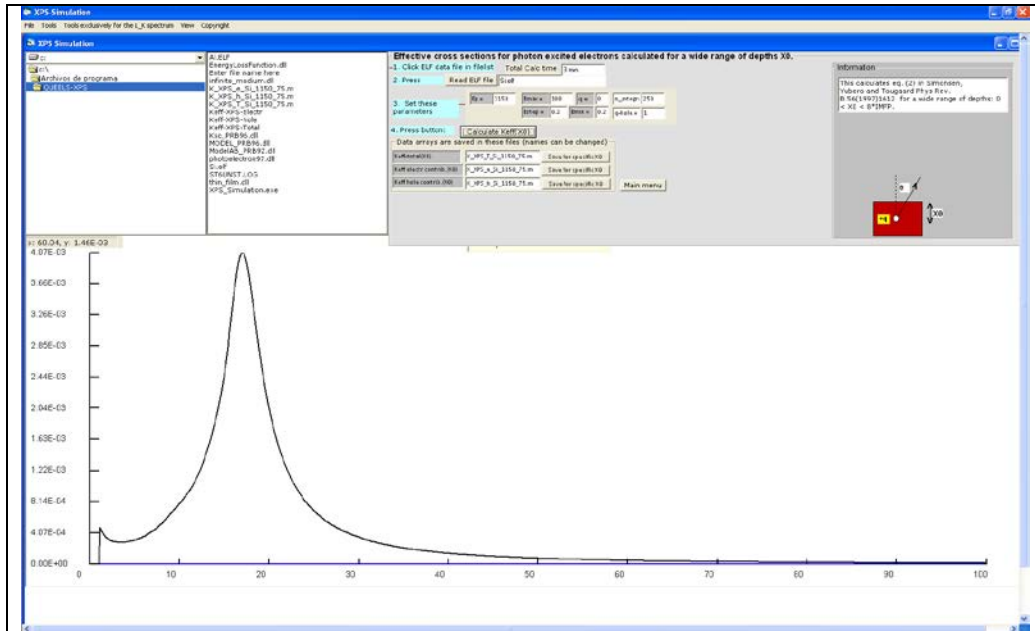


Figure 10

- Click *Save for specific x0*.

A new dialog box appears (see Fig.11). It provides also facilities to show graphs of the calculated cross sections and effective inelastic mean free paths for the various path lengths traveled. These options are included to make it possible to study individual effective cross sections for selected path lengths and it is quite instructive to go through the 65 files and see the gradual development in the shape as the influence of the surface gets increasingly smaller. There is also a facility to save the cross sections for individual paths.

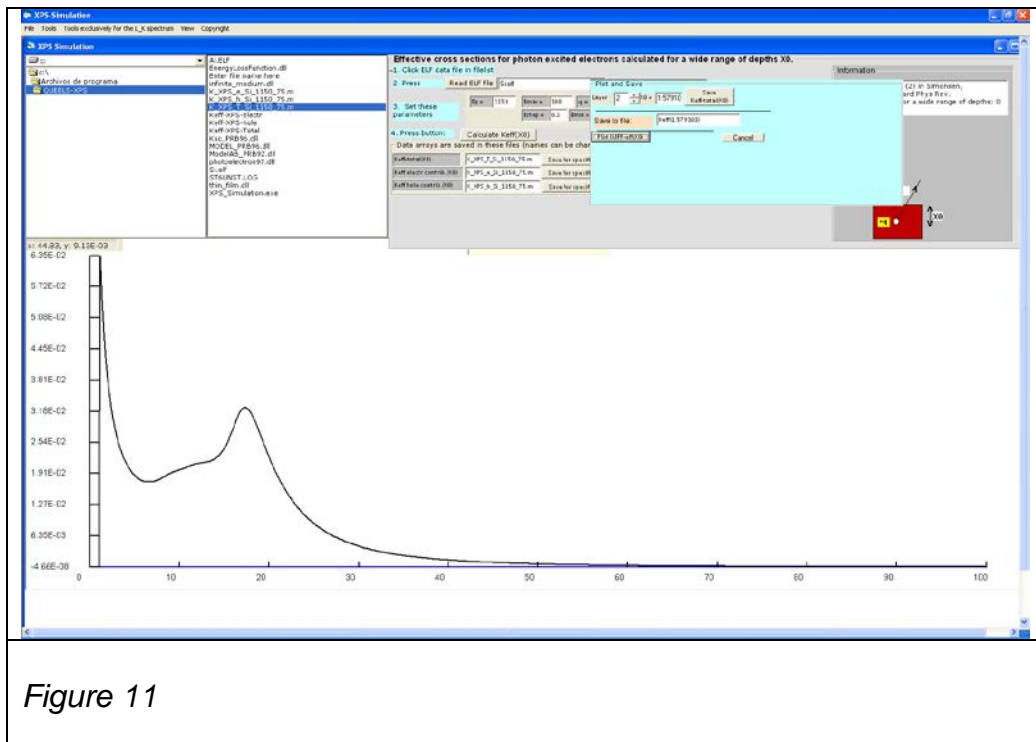


Figure 11

- Click *Cancel*
- Click *Main Menu*

Second step:

Evaluation of a weighted average of the inelastic cross sections of emitted photoelectrons (in presence of a core hole) according to eqn.(.) in ref. [].

- Click *Calculate XPS averaged cross section $K_{eff,av}$* . (see Fig.12)
This part of the program calculates the weighted average of the inelastic scattering cross sections for electrons that are emitted in standard XPS experiments.
- Select *K_XPS_T_Si_1150_75.m* on the file list
- Click *Read $K_{eff}(X_0)$*
- Click *plot and save individual cross sections*. This opens a box-dialog that allows plot and save individual cross sections
- Click *Cancel* to exit the **plot and save** box-dialog
- Click *Calculate XPS averaged cross section $K_{eff,av}$*

A new dialog-box appears (see Fig.12). This is used to calculate a weighted average of the inelastic scattering cross section. You have

several options: chose between selfconsistent or external use of inelastic mean free path, and the option of including the possible effect of elastic scattering.

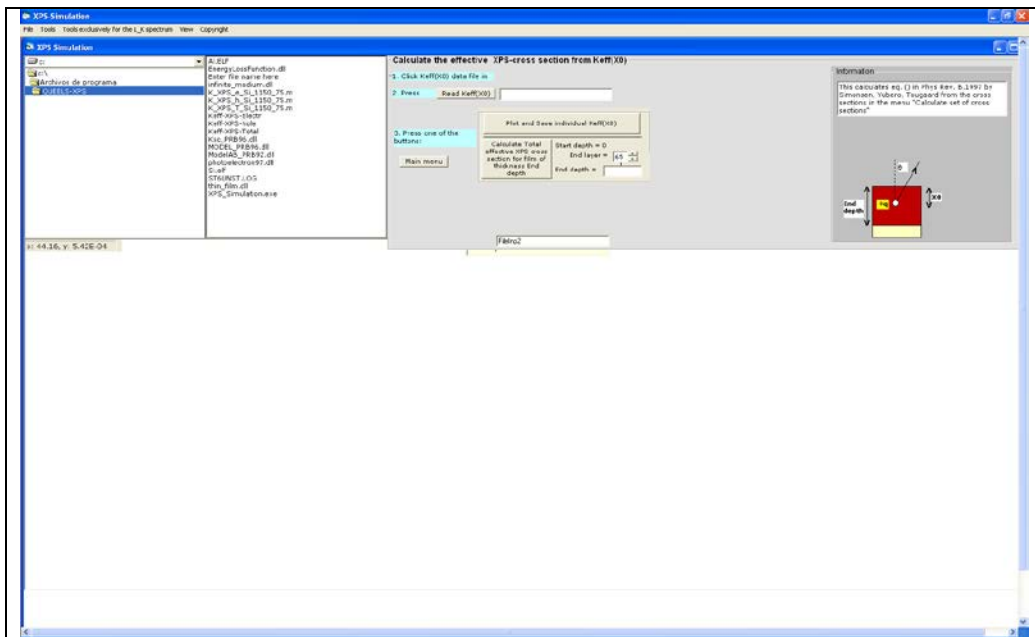


Figure 12

- Click **Save** to enter a box-dialog that allows to save the result with a filename of your choice
- Click **Cancel** to exit the **Save XPS average Keff,av** box-dialog
- Click **Cancel** to exit the **Calculation of XPS average Keff,av** box-dialog

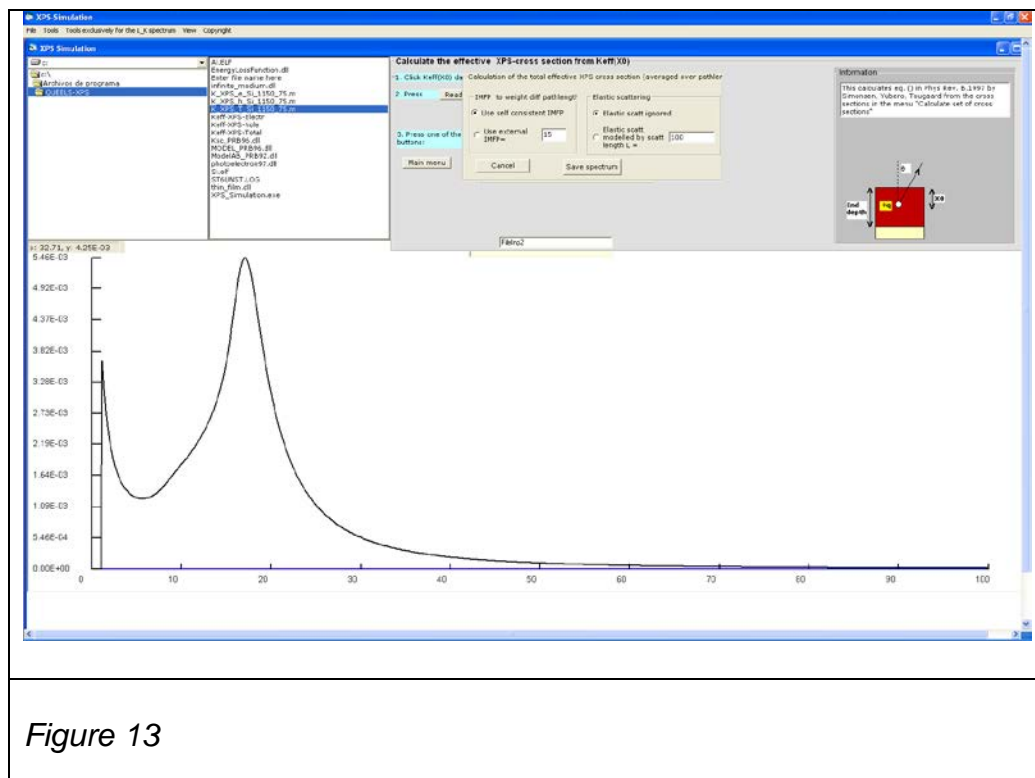


Figure 13

8.1.3 Convolution with the primary spectrum $F(E)$ for direct comparison to experimental XPS

In order to compare with experimental results we have to convoluted the obtained cross section with an primary spectrum $F(E)$ according to the expressions in eqn.(9) and eqn.(10).

You may do this in a spreadsheet or in Origin. Alternatively you may do this with our software “comp_with_experiment.exe” program which has some facilities for this purpose.

Note that the calculations for very low energy loss may be less accurate in part because the model dielectric function given by the shape in eq.(3) imposes a particular behaviour as $\omega \rightarrow 0$. Therefore it is recommended to set a lower limit for the calculated energy loss. This is done in the Calculate set of cross sections menu (see Sec. 8.1.2 and Figure 10). The value of E_{min} is set to e.g. 0.5 or 1 eV.

9. File Formats and File Management

It is helpful to be able to keep track of the experimental data files as well as of the files created by the programs.

The data format of the files is described below. If problems are met in the execution of the programs it may be necessary to check the data format and maybe to make changes to the files to make them consistent with the required data format.

To facilitate these operations, a file management system has been included. It appears in the upper left part of the screen and consists of three boxes, which list the **DiskDrive**, the **Directories** and the **FileNames**.

The **DiskDrive** displays the current drive. Clicking the arrow on the right of the DiskDrive box, the box drops down and displays all valid drives on your system. You can select a new drive from the list which will then appear in the **DiskDrive** box.

The **Directory** box displays the directory structure of the current drive. You may move up and down in the list of directories or use the scroll bar at the right of the box. By double-clicking a directory the box will display the selected directory and its subdirectories. The Filelist list box to the right shows the files in the current directory.

Edit

*The easiest way to **Edit** a file is by simply double-clicking the filename in the **FileList** box.*

This opens the file with the Notebook editor which provides all the well-known facilities for file editing, saving, printing etc. To exit the editor, select Exit from the File menu.

9.1 File Formats.

QUEELS-XPS uses the following data structure:

```
Gold Au4d Sample # 205
@
366.4180 2.5168
366.8359 2.5122
367.2539 2.5266
367.6719 2.5116
368.0898 2.5200
368.5078 2.5124
368.9258 2.5348
369.3438 2.5287
369.7617 2.5142
```

The first several lines are comments while the data read by the programs start after the line following the character @.

The data are in columns where the first column is the kinetic energy of the electrons and the second is intensities.

It is required that the increment in energy in the first column is the same for the whole data set.

Note that your data file must have a line with the character @ otherwise the file will not be read.

Note also: The program assumes that the American standard for numbers is used (where the decimal place is marked by a ".") and will not run properly if setting is different. To change settings, select *Start* on the Windows menu bar and then select *Settings, Control Panel, Regional Settings, English (United States)* . Alternatively, you may change the number settings for your current Regional settings to the American standard.

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QUEELS-XPS