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Tougaard, Sven Mosbæk

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Comparison between surface excitation parameter obtained from QUEELS and SESINIPAC†

N. Pauly,a* M. Novák,a A. Dubusa and S. Tougaardb

Surface excitations significantly influence the measured peak intensities in elastic peak electron spectroscopy. They are characterised by the surface excitation parameter (SEP) defined as the change in excitation probability of an electron caused by the presence of the surface in comparison with an electron moving in an infinite medium. It is thus important to have a large database of SEP values or to have the possibility to determine it with a user-friendly software. Recently, Novák developed the programme Software for Electron Solid Inelastic Interaction Parameter Calculations (SESINIPAC) within the model of Tung, Chen, Kwei and Chou, which allows to determine inelastic mean free path, differential inelastic mean free path, SEP and differential SEP for various energy loss function models and dispersion relations with as only input the energy loss function of the material. Using SESINIPAC, we calculate SEP for 27 different types of materials (metals, semiconductors and insulators) and for various angles and energies. We compare these results with those obtained previously with the software Quantitative Analysis of Electron Energy Losses at Surfaces (QUEELS), which uses the Yubero-Tougaard model. We show that the dependence on angle of emission and energy is quite similar for the two models. However, the absolute values calculated with SESINIPAC are generally larger than those calculated with QUEELS, and the mean relative difference is 20% for metals and semiconductors but exceeds 50% for insulators. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: surface excitation parameter, SEP; dielectric function; dispersion relation

Introduction

Quantification in surface-sensitive electron spectroscopies such as X-ray photoelectron spectroscopy, Auger electron spectroscopy, elastic peak electron spectroscopy or reflection electron energy loss spectroscopy (REELS) requires a precise knowledge of all inelastic interactions undergone by an electron travelling within a solid. These inelastic interactions can be divided into two categories: bulk excitations calculated for a solid considered as infinite[11] and surface excitations occurring while the electron is moving in the vacuum and in a shallow region in the medium.[2–4]

Thus, the availability of a user-friendly software that allows to calculate quantities characterising both excitations is of high importance. One package named Quantitative Analysis of Electron Energy Losses at Surfaces (QUEELS),[5,6] which implements the semiclassical model developed by Yubero and Tougaard[2] (denoted YT model in the following), allows to perform these calculations. Another software that calculates directly the surface excitation parameter (SEP), among several parameters, has recently been developed by Novák and named Software for Electron Solid Inelastic Interaction Parameter Calculations (SESINIPAC).[7] SESINIPAC calculates the inelastic mean free path (IMFP), the SEP as well as their corresponding energy-differential distributions (DMFP and DSEP) for electrons in solids from dielectric response theories developed by Lindhard,[8] Ritchie[9] and Tung et al.[10] (denoted as TCKC model in the following) for bulk and surface excitations, respectively. The available dielectric models in SESINIPAC are the extended Drude (ED),[10] the Drude–Lindhard (DL) model[11] and the Mermin (ME)[12,13] model (with full dispersion relation given by the Fermi energy[14] or with a quadratic dispersion approximation[15] for ED and DL models, whereas the dispersion relation is included in the ME model).

In the study of Pauly and Tougaard,[16] we calculated SEP values for 27 materials (including metals, oxides, polymers and semiconductors) for electron energies between 300 and 3400 eV, and for angles between 0° and 70° to the surface normal from a procedure described in details by Pauly and Tougaard[17] using the software QUEELS. In the present work, we compare SEP results obtained by Pauly and Tougaard[18] and values obtained with SESINIPAC using the same input parameters. In the following section, we briefly describe the models used in QUEELS and SESINIPAC for SEP calculation.

Theoretical models

QUEELS

QUEELS is developed from the YT model and allows to perform calculations of electron energy losses in a REELS geometry[15] according to the surface reflection model,[18,19] which describes the interactions of REELS electrons with a semi-infinite medium in terms of the dielectric properties of the bulk material.

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* Correspondence to: Nicolas Pauly, Service de Métrologie Nucléaire (CP 165/84), Université Libre de Bruxelles, 50 av. F. D. Roosevelt, B-1050 Brussels, Belgium. E-mail: nipauly@ulb.ac.be
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Departments of Physics and Chemistry, University of Southern Denmark, DK-5230 Odense M, Denmark
According to this model, the effective inelastic electron scattering cross-sectional $K_{sc}(E, k_0, x_0, \theta_e, \theta_r)$ is determined. $K_{sc}(E, k_0, x_0, \theta_e, \theta_r)$ is defined as the average probability that an electron of energy $E$ elastically backscattered at a depth $x_0$ loses an energy $\hbar\omega$ per unit energy loss and per unit path length travelled in the solid (with an angle $\theta_e$ measured with respect to the surface normal at the entrance and $\theta_r$ at the exit). In REELS experiments, electrons that have reached a wide range of depths contribute to the final spectrum. It is thus necessary to calculate a weighted average of $K_{sc}$ over all path lengths. This results in the differential inelastic electron scattering cross-sectional spectrum $K_{sc}(E, k_0, \theta_e, \theta_r)$ characteristic of REELS for an electron following a V-type trajectory inside the solid.

Once $K_{sc}$ is known, the SEP can be determined. Indeed, the SEP is defined as the change in excitation probability, for an electron, caused by the presence of the surface in comparison with the situation where the electron travels the same distance in an infinite medium. Thus, the surface contribution $K_s$ to the inelastic cross section is

$$K_s = \int (K_{sc} - K_{wi})d\omega$$

(1)

where $K_{sc}(E, k_0)$ is the inelastic electron scattering cross section (per unit energy loss and per unit path length travelled in the solid) for electrons moving in an infinite medium. Then, we obtain from $K_s$, the probability of surface excitation for an electron crossing the surface twice

$$P_1(E, \theta_e, \theta_r) + P_2(E, \theta_e, \theta_r) = \frac{K_s(E, k_0^s, \theta_e, \theta_r)}{\int K_{sc}(E, k_0, \theta_e, \theta_r)d\omega}$$

(2)

From this and considering in our calculations, a constant incident angle $\theta_i = 45^\circ$ as well as an equal contribution to the SEP from incoming and outgoing electrons, the single-surface-crossing SEP, $P_s(E, \theta)$ is finally given by

$$P_s(E, \theta) = \frac{K_s(E, 45^\circ, \theta)}{\int K_{sc}(E, k_0, 45^\circ, \theta)d\omega} - P_s(E, 45^\circ)$$

(3)

**SESINIPAC**

SESINIPAC uses the TCKC model and allows to perform IMFP, DIMFP, SEP and DSEP calculations within three dielectric models: ED, DL and ME. We only give here the basic ingredients needed for the determination of the SEP, which is the object of this work. The TCKC model, which is derived from earlier calculations of Ritchie and Reather for a sample thickness large enough to consider a saturated surface excitation probability,

$$P_s(E, \theta) = \frac{1}{\pi E \cos \theta} \int_{k_s}^{k_t} \text{Im} \left\{ \frac{(i(k, \omega) - 1)^2}{i(k, \omega)(i(k, \omega) + 1)} \right\} \left| k_t \right|^2 dk$$

(4)

with

$$k_s = \left[ k^2 - \left( \frac{\hbar^2 k^2}{2E} \right)^2 \right]^{1/2} \cos \theta$$

(5)

In Eqs (4) and (5), $i(k, \omega)$ is the dielectric function of the medium, $k_t$ is the parallel component of momentum transfer along the surface plane and $k_s = \sqrt{2E - \sqrt{2(E - \hbar\omega)}}$ comes from the energy and momentum conservation laws.

Both the models used on QUEELS (YT) and SESINIPAC (TCKC) are based on a semiclassical dielectric description. The major difference is that in SESINIPAC all electrons are assumed to yield the same surface excitation contribution regardless if it is backscattered at, for example, 1 Å, 5 Å or 20 Å depth (surface excitation are assumed to occur right at the surface). In contrast, the surface contribution in QUEELS varies with the depth. One would therefore expect the YT model to be more accurate. It is however interesting to find the conditions under which the TCKC model used in SESINIPAC is approximately valid because it is much simpler.

**Dielectric model**

Previous SEP results obtained within the YT model implemented in QUEELS have been calculated from an evaluation of the energy loss function (ELF) $\text{Im}[-1/(\epsilon(k, \omega))]$ expanded in DL type oscillators:

$$\text{Im} \left\{ \frac{1}{i(k, \omega)} \right\} = \sum_{n=1}^{N} \frac{A_n \hbar \gamma_n}{\hbar \omega - E_n - i \hbar \gamma_n}$$

(6)

with

$$\hbar \omega_{0k} = \hbar \omega_0 + \frac{\hbar^2 k^2}{2m}$$

(7)

Here, $A_n$, $\hbar \gamma_n$ and $\hbar \omega_{0k}$ are the oscillator strength, width and energy of the $n$th oscillator, respectively; $\gamma$ describes the dispersion; and $E_n$ is the energy band gap for semiconductors and insulators. These parameters for materials considered here can be found in the study of Pauly and Tougaard and references therein.

To allow for a suitable comparison between SEP results obtained from QUEELS and SESINIPAC, we have also chosen for SESINIPAC the DL model, although the ME model seems to be a more accurate model for the ELF. However, the choice of model dielectric function has very little influence on the calculated SEP. Thus, for Cu, we have checked with SESINIPAC the influence of the dielectric model (ED, DL and ME) on the SEP results for various angles ($0^\circ < \theta < 60^\circ$) and energies (300 eV $< E < 5000$ eV), and we have found a maximum deviation of 8% (the deviation is largest for $E = 300$ eV and is negligible for $E > 1000$ eV). The reason is that the three models differ significantly only for high momentum transfer $k$, and as shown in Eqn (4), SEP in the TCKC model is a function of $1/k^3$, implying a small effect for large $k$ values. We can thus conclude that the choice of the dielectric model is insignificant for SEP calculations.

**Results and discussion**

Figure 1 shows energy distributions of the SEP $P_s(E, \theta)$ for Fe obtained from SESINIPAC and QUEELS and for angles $\theta = 30^\circ$ and $\theta = 45^\circ$. Figs 2 and 3 show SEP angular distribution calculated with SESINIPAC and QUEELS for Cu and SiO$_2$, respectively, and for $E = 300$, 1000 and 3400 eV. From these results, it is clear that the general behavior of SEP calculated within the two models is very similar and moreover, absolute values obtained for Fe and Cu are also in good agreement (at least for $\theta < 45^\circ$ and $E < 1000$ eV; for larger energies especially discrepancies increase) and agree well (despite a small overestimation) with other results published in the literature.
However, for SiO$_2$, the differences between SEP obtained from the two models are significant (~70% for all energies and angles).

To understand this large disparity between materials, we have made a comparison of both models for 27 materials (we have chosen elements for which we had previously calculated SEP values with QUEELS as presented by Pauly and Tougaard\cite{17}). More precisely, to simplify the comparison, we have fitted the SEP results in an expression derived by Werner\cite{20} from Oswald’s calculations\cite{25} with one dimensionless material dependent parameter, $a$:

$$P_s(E, \theta) = \frac{1}{0.173a\sqrt{E\cos\theta} + 1}$$

with $E$ in eV and the factor 0.173 in eV$^{-1/2}$. We have then made a comparison between a values obtained from both models for each material, and we denote by $a_Q$ or $a_S$ the values obtained from a fit to SEP results achieved with QUEELS or SESINPAC, respectively.

Results for $a_Q$ and $a_S$ are displayed in Table 1 for the 27 materials. We also show the absolute value of the relative difference $\Delta$ between $a_Q$ and $a_S$ as well as the energy band gap $E_G$ of the material. From these results, a few observations are possible.

First, $a_Q$ is generally (in 93% of the cases) larger than $a_S$, and thus SEP calculated from QUEELS is mostly smaller than SEP obtained with SESINPAC. This is principally because in the TCKC model, SEP is calculated with the assumption that all the electrons cross the full shallow region inside the material in which surface excitations occur, that is, a saturated value of surface excitation is reached for all electron trajectories, while in the YT model a more realistic situation is used where the electron may be backscattered before it has completely crossed this shallow region. This difference in behaviour implies that a smaller number of surface excitations happen in the YT model.

![Figure 1](image1.png)

**Figure 1.** Energy distribution of $P_s(E, \theta)$ for Fe obtained from SESINPAC (solid lines) and QUEELS (dashed lines) calculated for angles $\theta = 30^\circ$ (□) and $\theta = 45^\circ$ (○).

![Figure 2](image2.png)

**Figure 2.** Angular distribution of $P_s(E, \theta)$ for Cu obtained from SESINPAC (solid lines) and QUEELS (dashed lines) calculated for $E = 300$ eV (□), $E = 1000$ eV (○) and $E = 3400$ eV (△).

![Figure 3](image3.png)

**Figure 3.** Angular distribution of $P_s(E, \theta)$ for SiO$_2$ obtained from SESINPAC (solid lines) and QUEELS (dashed lines) calculated for $E = 300$ eV (□), $E = 1000$ eV (○) and $E = 3400$ eV (△).

Table 1. Values of $a$ determined from the YT model with QUEELS ($a_Q$) and from the TCKC model with SESINPAC ($a_S$); the absolute relative difference in % ($|\Delta|$) between both results is also displayed. Materials are tabulated as a function of their energy band gap $E_G$.

| medium | $a_Q$ | $a_S$ | $|\Delta|$ (%) | $E_G$ (eV) |
|------|------|------|-------------|---------|
| Cu   | 1.03 | 1.23 | 17.70       | 0.0     |
| Au   | 1.05 | 1.09 | 3.74        | 0.0     |
| Ni   | 1.05 | 1.17 | 10.81       | 0.0     |
| Ag   | 1.03 | 0.99 | 3.96        | 0.0     |
| Ti   | 1.05 | 1.78 | 51.59       | 0.0     |
| Fe   | 1.04 | 1.87 | 57.04       | 0.0     |
| Pd   | 1.03 | 1.40 | 30.45       | 0.0     |
| InSb | 1.01 | 1.30 | 25.11       | 0.17    |
| InAs | 1.02 | 0.92 | 10.31       | 0.36    |
| Ge   | 1.06 | 1.14 | 7.27        | 0.67    |
| GaSb | 1.05 | 1.21 | 14.16       | 0.75    |
| Si   | 1.06 | 1.08 | 1.87        | 1.11    |
| InP  | 1.13 | 1.25 | 10.08       | 1.27    |
| PA   | 1.17 | 2.07 | 55.56       | 1.40    |
| GaAs | 1.08 | 1.13 | 4.52        | 1.43    |
| SiC  | 1.11 | 1.60 | 36.16       | 2.20    |
| GaP  | 1.13 | 1.35 | 17.74       | 2.27    |
| ZnSe | 1.33 | 1.78 | 28.94       | 2.58    |
| TiO$_2$ | 1.13 | 2.14 | 61.77       | 3.00    |
| GaN  | 1.16 | 1.80 | 43.24       | 3.21    |
| ZnS  | 1.28 | 1.99 | 43.43       | 3.60    |
| PS   | 1.35 | 3.09 | 78.38       | 4.36    |
| PMMA | 1.41 | 3.22 | 78.19       | 4.40    |
| ZrO$_2$ | 1.21 | 2.29 | 61.71       | 4.50    |
| Al$_2$O$_3$ | 1.47 | 2.77 | 61.32       | 7.10    |
| PE   | 1.81 | 3.61 | 66.42       | 8.80    |
| SiO$_2$ | 1.88 | 3.66 | 64.26       | 9.30    |
Second, the values of $a_Q$ and $a_s$ increase (implying a smaller SEP) when the energy band gap $E_G$ of the material increases. We had previously shown in the study of Pauly and Tougaard$^{[26]}$ that SEP results obtained with QUEELS for insulators are noticeably smaller than those previously found for metals. This was mainly attributed to the energy band gap because surface excitations predominantly occur at small energies and the presence of the gap thus excludes these excitations. However, the effect of an increase of $E_G$ is clearly larger for $a_Q$ than for $a_s$. A good indicator of this behaviour is the mean deviation $|\Delta|$. Indeed $|\Delta|$ is approximately 35.0% when all 27 materials are considered. However, from Table 1, when we separately examine on the one hand metals and semiconductors, on the other hand insulators (we consider an energy band gap limit between semiconductors and insulators of 2 eV$^{[27]}$), we obtain $|\Delta|=20.3\%$ for metals and semiconductors (note however that for a few of them, as Ti and Fe, $|\Delta|$ is larger) and $|\Delta|=53.5\%$ for insulators. The reason for this is that, in the YT model, a quite large fraction of the electrons that are backscattered before having completely crossed the shallow region in which surface excitations occur have an effective energy loss spectrum $K_{el}$ which is peaked at very small energies (see Fig. 2 in Ref.$^{[21]}$). Therefore, an increase of the energy band gap which will exclude small energy excitations strongly reduces the energy loss probability. In the TCKC model, on the contrary, all electrons are assumed to cross the full surface excitations region and the reduction of the SEP is thus smaller for increasing energy band gap.

Up to now, only a few papers have been related to the study of surface excitations for insulators (see Ref.$^{[26]}$ and references therein) but theoretical results of Kwei et al.$^{[28]}$ and Kwei, Li and Tung$^{[24]}$ as well as experimental results of Jung et al.$^{[29]}$ show that SEP for SiO$_2$ is largely smaller than SEP obtained for metals. Indeed, considering an average value for incoming and outgoing electrons $P_f(300,0)=0.050$ and $P_i(1000,0)=0.031$ were obtained by Kwei et al.$^{[24,28]}$. These results should be compared with values of $P_f(300,0)=0.084$ and $P_i(300,0)=0.048$ calculated within QUEELS and $P_f(300,0)=0.179$ and $P_i(300,0)=0.102$ obtained with SESINPAC (see Fig. 3). It seems that the results of QUEELS are in better agreement with previously published data than those obtained with SESINPAC.

### Conclusion

In this work, we have presented SEP results obtained for 27 materials within two models, respectively, developed on the one hand by Yubero and Tougaard$^{[21,25]}$ and on the other hand by Tung et al.$^{[10]}$ and implemented in the software QUEELS$^{[3]}$ and SESINPAC.$^{[7]}$ The main difference between the two models is that in SESINPAC, all electrons are assumed to cross the entire surface excitation region while the trajectories in QUEELS are more realistic because they may pass any path of this region. Although SESINPAC is expected to be less accurate it is much simpler and it is therefore important to find its range of validity. For both models, calculations were done within the dielectric response theory for which the only input is the ELF expanded in Drude–Lindhard type oscillators with a quadratic dispersion approximation. We have shown that the mean deviation between SEP calculated within both models is only 20.3% when metals and semiconductors are considered but reaches 53.5% for insulators. Moreover we pointed out that values obtained with QUEELS are in better agreement with other theoretical and experimental results presented in the literature than those calculated with SESINPAC. As a conclusion, we can recommend the use of SESINPAC for SEP calculations for most metals and semiconductors due to its simplicity and its relatively good agreement with QUEELS results but we warn the user against the overestimated SEP values given by SESINPAC for insulators and more generally for materials with a large energy band gap.

### References