Restoration of valence density of states from XPS spectra

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Abstract. The technique is presented of restoring the electronic density of states of the valence band from data of X-ray photoelectron spectroscopy. The originality of the technique consists in using a stochastic procedure to solve an integral equation relating the density of states and X-ray photoelectron spectra. The results are presented for bulk metals of gold, silver, and copper. The method can be applied to materials with unknown crystal structure, such as ensembles of nanoclusters.

1. Introduction

Low-dimensional structures, being at intermediate position between single atoms and bulk materials, possess unique physical properties, which separate them in the special area of condensed matter physics. Studying the properties of such structures, and nanoscale systems in particular, attracts now an increased interest both from a fundamental point of view, and in connection with numerous applications. The practical use of low-dimensional structures is based mainly on the features of their electronic properties due to strong electron correlations. The necessity of the accounting for electron correlations leads to considerable complexity of the theoretical description of such systems. For this reason, the development of methods which combine both experimental and numerical techniques for the study of the electronic properties of nanoscale structures is an urgent task.

X-ray photoelectron spectroscopy (XPS) allows studying the evolution of the electronic properties of low-dimensional structures depending on their size. This fact makes the XPS technique sensitive to the surface density of electronic states, and gives the opportunity to study physical and chemical properties of low-dimensional samples. The advantage of this technique is also the possibility of direct measurement of the density of electronic states (DOS) of the valence band. The smaller is the instrumentation broadening, which is determined mainly by nonmonochromaticity of the X-ray source and by the operation mode of the energy analyser, the more precise is the determination of DOS. Modern X-ray photoelectron spectrometers equipped with a monochromator have the value of the broadening ranged from 0.4 to 0.6 eV. This broadening leads to smearing of DOS and usually prevents direct study of spectra; therefore, a more sophisticated approach is needed to restore narrow features of DOS.

The purpose of the paper is to propose the technique of restoring the electronic density of states of X-ray photoelectron spectra with the use of the numerical stochastic procedure, which accurately accounts for the instrumentation broadening. XPS spectra from the regions of valence states and core levels allow calculation of the broadening function of the spectrometer; for this purpose, the core level line is used. Further, the stochastic procedure is applied to restore DOS by solving an integral equation. This
technique was used to calculate DOS of bulk gold, silver, and copper. To confirm the accuracy, the obtained DOS were compared with DOS calculated from density functional theory (DFT).

2. Method
The XPS signal can be described by the following convolution [1]:

\[ I(\varepsilon) = S(\varepsilon) \ast I_\tau(\varepsilon) \ast I_\alpha(\varepsilon) \ast I_\sigma(\varepsilon), \]  

(1)

where energy \( \varepsilon \) is measured with respect to the Fermi level,

\[ S(\varepsilon) \sim \delta(\varepsilon - \varepsilon_0) \]  

(2)

is the spectrum of a level with the binding energy \( \varepsilon_0 \), free of any broadening factors;

\[ I_\tau(\varepsilon) \sim \frac{\gamma}{\sqrt{\varepsilon^2 + \gamma^2}} \]  

(3)

describes the broadening of the line caused by the finite lifetime \( \tau \) of a hole on the level; \( \gamma \sim \hbar/\tau \) is the natural broadening;

\[ I_\alpha(\varepsilon) \sim \theta(\varepsilon) e^{\alpha - 1} \]  

(4)

defines the broadening of the line due to many-electron effects; \( 0 \leq \alpha < 1 \) is Anderson parameter of singularity [2];

\[ I_\sigma(\varepsilon) \sim e^{-\varepsilon^2/2\sigma^2} \]  

(5)

has the form of a Gaussian and corresponds to the instrumentation broadening.

For valence electrons, the lifetime \( \tau \) is negligibly small, and (1) takes the form

\[ I_{\text{val}}(\varepsilon) = \rho_{\text{val}}(\varepsilon) \ast I_\alpha(\varepsilon) \ast I_\sigma(\varepsilon), \]  

(6)

where \( \rho_{\text{val}}(\varepsilon) \) is the density of valence states. Therefore, for XPS spectra of the core line and valence band, we have the following system:

\[
\begin{cases}
I_{\text{core}}(\varepsilon) = \int_{-\infty}^{+\infty} H(\varepsilon - \varepsilon') I_\tau(\varepsilon') \, d\varepsilon' \\
I_{\text{val}}(\varepsilon) = \int_{-\infty}^{+\infty} H(\varepsilon - \varepsilon') \rho_{\text{val}}(\varepsilon') \, d\varepsilon'.
\end{cases}
\]  

(7)

Here \( H(\varepsilon) = I_\alpha(\varepsilon) \ast I_\sigma(\varepsilon) \) is the broadening function, which takes into account technical characteristics of a spectrometer and many-electron processes. It follows from (7), that, if the parameters \( \gamma, \alpha, \sigma \) are someway known, one can restore the density of states in the valence band \( \rho_{\text{val}}(\varepsilon) \) from the second equation. This equation belongs to the class of Fredholm integral equations of the first kind, and its solution is the ill-posed problem.

One of the very effective approaches which numerically address ill-posed problems of such kind is the "algorithm of random rectangles", proposed in [3]. The solution \( \rho_{\text{val}}(\varepsilon) \) is approximated with a piecewise constant function.
\[ \rho_{\text{val}}(\epsilon) \leftarrow \tilde{\rho}_{\text{val}}(\epsilon) = \sum \chi_{c,w,h}(\epsilon), \]  

which is the sum of rectangles determined by the centre position \( c \), the width \( w \) and the height \( h \) (Fig. 1). The algorithm is based on minimizing the deviation between the input spectrum \( I_{\text{val}}(\epsilon) \) and the approximated one \( \tilde{I}_{\text{val}}(\epsilon) = \int_{-\infty}^{+\infty} H(\epsilon - \epsilon') \tilde{\rho}_{\text{val}}(\epsilon') d\epsilon' \) by generating stochastic configurations of various numbers of rectangles \( \chi_{c,w,h} \) with the use of Monte Carlo and gradient descent schemes.

**Figure 1.** Approximation of the solution \( \rho_{\text{val}}(\epsilon) \) (green) with the sum of random rectangles (red).

### 3. Results

The XPS spectra of gold, silver, and copper were taken from Research Data Australia [4]. The broadening function \( H(\epsilon) \) was restored by fitting the XPS spectra of the core levels by the least square method in accordance with (1). For example, for gold the spectrum is the doublet \( \text{Au}4f_{7/2,5/2} \) formed by the spin-orbit splitting. Its approximation gives the following values: \( \gamma = 0.23 \text{ eV} \); \( \alpha = 0.04 \text{ eV} \); \( \sigma = 0.23 \text{ eV} \) (Fig. 2); the corresponding broadening function \( H(\epsilon) \) is shown in Fig. 3. The same procedure was applied for calculation of the broadening functions of bulk silver and copper.

**Figure 2.** XPS spectrum of \( \text{Au}4f_{7/2,5/2} \) doublet (black line) and its approximation (red dots).
Figure 3. The restored broadening function $H(\epsilon)$ for bulk gold.

The obtained broadening functions $H(\epsilon)$ were used for the calculation of DOS in accordance with the system of integral equations (7). Figure 4 shows the calculated DOS in comparison with DOS obtained by DFT method, which was taken from Computational Electronic Structure Database (CompES-X) of National Institute for Materials Science, Japan [5]. It can be seen that the main features of DOS were correctly reproduced except sharp $\delta$-function peaks in DOS of bulk gold, which are apparently caused by approximations used in DFT technique.

Figure 4. The XPS spectra of the valence band from the database [5] for bulk gold (a), silver (b), and copper (c), the restored DOS, and DOS calculated by DFT method.
4. Conclusions
In this work, we proposed the technique of restoring the electronic density of states from experimental XPS spectra. The method accurately takes into account the instrumentation broadening, and allows obtaining acceptable results even for low-quality XPS spectra. This technique may be applied to materials, which are complicated enough for DFT calculation, such as large low-symmetry systems, or to objects with unknown crystal structure, such as ensembles of nanoclusters.

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