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Curve fitting of photoemission spectra with physically realistic subspectra

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A curve-fitting routine, based on nonlinear iterative least-squares optimization, for photoemission spectra is described in which theoretical or empirical relations between spectral parameters can easily be included. The advantage of the method is that the calculated fits are automatically acceptable from the viewpoint of physics, provided that the correct conditions have been formulated. The procedure is illustrated with a photoemission spectrum of xenon adsorbed on a heterogeneous surface.

I. INTRODUCTION

Curve fitting of photoemission spectra is often carried out by assigning a Lorentzian, Gaussian, or more complicated function to each peak in a spectrum, after which the position, width, and intensity of each peak are varied in an optimization routine until the sum of the functions represents a mathematically acceptable fit to the experimental spectrum, i.e., the sum of squared differences between the fit and the spectrum is a minimum. For relatively simple, one-component spectra consisting of well-separated peaks this procedure is often satisfactory.

When spectra are more complicated, however, such as those of xenon adsorbed on heterogeneous surfaces,¹ the contributions from different three-peak subspectra overlap. In such cases curve fitting with single, unconstrained peaks seldom yields realistic results, because a mathematically acceptable fit is not necessarily acceptable from the viewpoint of physics. For example, peaks may come out too broad or too narrow, or with unrealistic intensities. Occasionally, peaks may even have a negative intensity. In such cases several runs of the fit routine are necessary, in which in each subsequent run more parameters must be fixed.

These problems are mainly caused by the fact that theoretical line shapes are never in 100% agreement with experimentally measured peaks. In such cases the mathematical criterium for a good fit is insufficient to guarantee physically realistic results.

The purpose of this paper is to describe briefly a curve-fitting routine for photoemission spectra in which theoretical and/or empirical constraints are easily included by restricting selected parameters to vary only within a range of values which the operator finds acceptable. The method, which has successfully been applied in the fitting of Mössbauer spectra,² will be illustrated here on a photoemission spectrum of xenon adsorbed on a heterogeneous surface.

II. THEORY

First we will give a mathematical description of the photoemission spectrum in terms of binding energies, intensities, splittings, etc., for photoemission spectra of adsorbed xenon (PAX spectra). The formalism given here is applicable to the usual x-ray photoelectron spectroscopy (XPS)

spectra as well. In this section we will assume that the peaks are Lorentzians and that the background to the spectra has been removed.

Figure 1 shows a Lorentzian with its three characteristic parameters: position E (expressed in eV), peak width W (eV), defined as full width at half-maximum, and peak height I (in arbitrary units). A typical PAX spectrum is shown in Fig. 2. It consists of three Lorentzians, corresponding to the $5p_{1/2}$ (peak 1), $5p_{3/2} - m_j = \pm \frac{1}{2}$ (peak 2), and $5p_{3/2} - m_j = \pm \frac{3}{2}$ (peak 3) electrons of xenon adsorbed on a surface.¹ The splitting of the $5p_{3/2}$ peak is observed in cases where the local Xe coverage is high; it is due to the two-dimensional band structure in the adsorbed layer of Xe. Mathematically, the PAX spectrum of Fig. 2 is described as the sum of three Lorentzians, each with position, width, and intensity.

Two approaches can be taken for curve fitting.

(i) *Fitting with single peaks:* The nine parameters of the three single Lorentzians per xenon adsorption state are varied independently in a nonlinear least-squares program. All peaks are independent entities, relations between the peaks are not included. This method of curve fitting has the disadvantages already mentioned in the introduction that it may give unrealistic results, such as negative intensities of certain peaks, unrealistic widths, etc.

(ii) *Fitting with subspectra:* The three Lorentzians per xenon adsorption state are combined in a subspectrum S ; constraints are introduced such that each variation of the parameters by an optimization program will always yield a realistic PAX spectrum. In order to achieve this, each subspectrum S is written in terms of the position, width, and

FIG. 1. Lorentzian peak with position at energy E , linewidth W (full width at half-maximum), peak height I , and intensity defined as the area under the Lorentzian $A = \frac{1}{2}\pi IW$.

FIG. 2. Typical photoemission spectrum of adsorbed xenon (PAX spectrum), consisting of three Lorentzians along with some of the parameters used in the fitting routine. See Table I for a complete list of definitions.

height of the main peak, labeled 1 in Fig. 2, and furthermore of splittings, linewidth, and intensity ratios for the $5p_{3/2}$ peaks. The complete set of parameters x needed to describe the PAX spectrum of a Xe adsorption state is defined in Table I, along with typical values encountered in practice. Some of the parameters are indicated in Fig. 2 as well.

Expressions (1) and (2) in Table II give the mathematical formula for the PAX spectrum $S_v(x)$, where the index v numbers the N energy channels. When n different Xe adsorption states are present, the spectrum S_v^{fit} is the sum of n subspectra $S_v^j(x^j)$, characterized by n sets of parameters x^j ($j = 1, \dots, n$); see expression (3) in Table II.

This spectrum S_v^{fit} is fitted to the measured spectrum S_v^{exp} , by varying the parameters x^j in a nonlinear least-squares optimization routine. The criterium for a good fit is that the sum of squared differences $(S_v^{fit} - S_v^{exp})^2$ is a minimum.

In order to ensure that the subspectra remain realistic during the minimization, the parameters are restricted to vary within certain ranges only. We have used two methods to constrain the value of a parameter.

(1) When the expected value of a parameter x_i is p and only small deviations from p are acceptable, the expression $(x_i - p)^2$ should be a minimum. One can combine this condition with the requirement for a good fit by using a Lagrangean multiplier:

$$\sum_{v=1}^N (S_v^{fit} - S_v^{exp})^2 + \lambda (x_i - p)^2 \text{ is a minimum.}$$

The multiplier λ determines the weight of the second condition with respect to the first. One can include as many terms of this kind as desired. Although this way of constraining parameters works well, it has the disadvantage that the appropriate values of the multipliers λ must be chosen.

(2) A more convenient way is to replace x_i in the expression for the spectrum by a function $x_i = f(Z_i)$, ($-\infty < Z_i < \infty$) which has only values in the acceptable range. For example, the intensity x_3 should always be positive. This is ensured by writing the intensity as $x_3 = |Z_3|$. The splitting x_4 between the $5p_{1/2}$ and the $5p_{3/2}$ peaks is always between 1.0 and 1.5 eV and can thus be written as $x_4 = 1.0 + 0.5/(1 + Z_4^2)$. A parameter x_i which must always be larger than 1 is written as $1 + Z_i^2$. With such relations one restricts the parameters to realistic values only. This ensures that when the computer program finds a mathematically acceptable fit, it automatically consists of subspectra which are acceptable from the viewpoint of experimental experience.

As the fit is calculated in an iterative procedure, start values for the calculation of the initial spectrum must be supplied. It is important to provide accurate first guess values for the parameters which determine the peak positions of the peaks. The start values of parameters which determine the intensities on the other hand are less critical. As start parameters for each subspectrum we usually give $(x_1 - x_5)$, and use characteristic values from Table I as default settings for $(x_6 - x_9)$. The program has the option, however, to type in start values for all parameters, and also to select parameters which can be kept constant in the fitting. The latter is a valuable feature when the spectrum contains components for which all parameters are exactly known.

III. APPLICATION

Figure 3 shows an application of the fit routine to a PAX spectrum and one monolayer Xe adsorbed on a sample consisting of Ag and Au evaporated on Ru(001).^{3,4} Visual inspection suggests that the spectrum contains two subspectra with the Xe $5p_{1/2}$ peaks at ~ 6.8 and 7.4 eV. However, spectra of this sample taken at lower Xe coverage⁴ clearly show

TABLE I. Definition of parameters.

Parameter	Definition	Typical value
$x_1 = E_1$	Position in eV	
$x_2 = W_1$	Width in eV	
$x_3 = I_1$	Intensity in kcounts	>0
$x_4 = E_1 - (E_2 + E_3)/2$	Xe $5p_{1/2}$ - $5p_{3/2}$ splitting in eV	1.3 eV
$x_5 = E_2 - E_3$	Xe $5p_{3/2}$ splitting in eV	0.1-0.6 eV
$x_6 = W_2/W_1$	Xe $5p_{3/2}$: $5p_{1/2}$ linewidth ratio (line 2:1)	1.0
$x_7 = W_3/W_2$	Xe $5p_{3/2}$ linewidth ratio (line 3:2)	1.3
$x_8 = A_3/A_2$	Xe $5p_{3/2}$ area ratio (line 3:2)	1.0
$x_9 = (A_3 + A_2)/A_1$	Xe $5p_{3/2}$: $5p_{1/2}$ area ratio (area 3 + 2:1)	1.3

TABLE II. Definition and expressions for curve fitting.

PAX spectrum	$S_v(x) = L(E_v; x_1, x_2, x_3) + L[E_v; x_1 - x_4 + \frac{1}{2}x_5, x_6x_2, x_9x_3/x_6(1+x_8)] + L[E_v; x_1 - x_4 - \frac{1}{2}x_5, x_7x_6x_2, x_8x_9x_3/x_7x_6(1+x_8)],$ $v = 1, \dots, N.$	(1)
Lorentzian of peak i	$L(E_v; E_i, W_i, I_i) = \frac{I_i}{4[(E_v - E_i)^2/W_i^2] + 1}, \quad v = 1, \dots, N.$	(2)
Fit spectrum	$S_v^{fit} = S_v^{fit}(x^1, \dots, x^N) = \sum_{j=1}^N S_j(x^j), \quad v = 1, \dots, N.$	(3)
Fit condition	$\sum_{v=1}^N (S_v^{exp} - S_v^{fit})^2 \text{ is a minimum.}$	(4)

the presence of a third state with the Xe $5p_{1/2}$ peak at 7.20 eV. Because this is the only state populated by Xe at low exposures, the parameters ($x_1 - x_9$) of this component are well known. Therefore, these parameters have been kept constant in the fit of Fig. 3. Only the intensity x_3 of this state was allowed to vary. Hence, the fit routine had 19 fit parameters, of which 7 were unconstrained and 12 constrained as described above. Start values were supplied for the parameters ($x_1 - x_5$) of the two adjustable spectra, all others were default values, equal to the typical values given in Table I. To reach the fit shown in Fig. 3, the routine performed ~ 500 spectrum calculations. The time needed to enter the start

parameters, run the program, and obtain hard copies of print and plot output was < 10 min.

IV. CONCLUDING REMARKS

A curve-fitting routine for photoemission spectra has been described in which an experimental spectrum is fitted with physically realistic subspectra instead of with single peaks. The strength of the procedure is that relationships between spectral parameters which are dictated by physical experience can be automatically enforced. This is especially advantageous when the spectrum consists of a number of overlapping contributions. The procedure has been described for spectra consisting of Lorentzian peaks but it works equally well with other peak forms, such as Gaussian-broadened Lorentzians. For further details on this curve-fitting routine we refer to an internal report,⁵ available from the authors.

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FIG. 3. Fit of an experimental PAX spectrum of a bimetallic Ag-Au surface. The fit, drawn as a full line through the experimental data points, is the sum of the three subspectra which correspond to Xe atoms adsorbed on pure Au sites, on Ag-Au mixed sites, and on pure Ag sites. The percentages give the relative abundance of each kind of site. The lowest trace is the difference between the experimental spectrum and the fit.

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