PHYSICS 904 Experiment Protocol #3

Numerical Analysis of X-ray Photoelectron Spectroscopy

1 References

- Briggs and Seah: Chap. 3,4; Appendix 3
- P.A. Jansson, Ed., Deconvolution with applications in spectroscopy, Academic Press (1984)

2 Goals

High resolution XPS spectrum. Data analysis for XPS spectra: background subtraction using the Shirley method; and deconvolution using Van Cittert method to extract the "true" line shape from the measured (convoluted) spectrum. Data transfer and conversion among different computer systems. Computer programming skills for scientific calculations.

3 Protocol

1. Sample preparation

   Si(100) or Si(111) wafer (single crystal) cut to 5x9 mm. Standard UHV organic wash cycle. Mount the sample on the special heating stub.
   - Take a survey and a Si 2p scan using 50 eV pass energy, check the XPS Handbook for ranges.
   - Outgas the sample and the stub at 600~650°C by resistive heating. While keeping the pressure low than 10^{-9}torr, quickly bring the sample up to 1100°C to remove the native oxide layer and surface contamination.

2. High resolution Si 2p spectrum
   - Repeat the scans in step 1. Check surface contamination and Si oxides.
   - Use monochromatic Al K_α to obtain a high resolution Si 2p detailed scan. Choose appropriate pass energy (the Si 2p split is about 0.6 eV).

3. Data transfer and conversion

   Use KERMIT to transfer your *.DAT file (in binary mode) to a PC or CSD4. A PC program is available for converting the VG file to ASCII format, you can also write your own conversion program (not required).

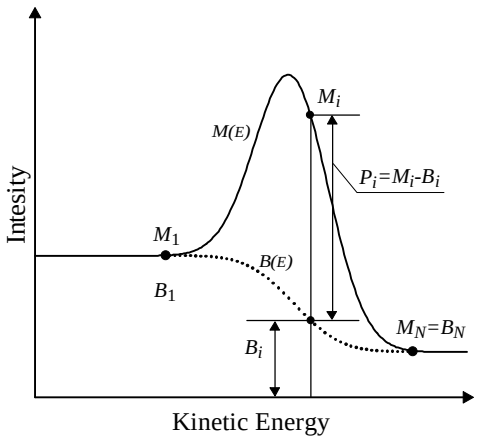

Fig. 1: Definitions for calculation.

4. Background subtraction

Write a short program to perform the tasks. You may use any language available, including Mathematica.

- Shirley background subtraction:

The Shirley background $B(E)$ is defined as, with E=kinetic energy,

$$B(E) = A\int_E^\infty P(E')dE' = A\int_E^\infty (M(E') - B(E'))dE',$$

where P is the peak intensity, M is the measured intensity, and A is a constant describe the secondary electron yield. The value of A can be calculated using iterative method, while the values of $B(E)$ are also obtained during the iteration.

Given a measured XPS spectrum M_i, with i=1 at the lowest kinetic energy, and i=N at the highest, the background value at the starting points are

$$B_N = B_{N-1} = M_N,$$

and the first guess of A is

$$A^{(0)} = 1.$$

The first trial, $B_i^{(0)}$, are then calculated one by one, from high kinetic energy to lower ones using the first guess $A^{(0)}$,

$$B_{N-2}^{(0)} = B_N + A^{(0)} \sum_{j=N-1}^{N} (M_j - B_j^{(0)}),$$

.

$$B_i^{(0)} = B_N + A^{(0)} \sum_{j=i+1}^{N} (M_j - B_j^{(0)}),$$

.

$$B_1^{(0)} = B_N + A^{(0)} \sum_{j=2}^{N} (M_j - B_j^{(0)}).$$

The next iteration starts with a corrected $A^{(1)}$,

$$A^{(1)} = A^{(0)}(1 + \frac{M_1 - B_1^{(0)}}{M_1}).$$

The calculation ends either at a predetermined number of iterations or

$$\left| B_i^{(k+1)} - B_i^{(k)} \right| < Tolerance$$

5. Deconvolution

Write a short program to deconvolve the data, *after background removal*.

- Deconvolution by iterative methods:

The measured spectrum $M(E)$ can be considered as a convolution of the true spectrum, $N(E)$ and the instrument function, $I(E)$,

$$M(E) = N \otimes I = I \otimes N = \int_{-\infty}^{\infty} I(E - E')N(E')dE',$$

where a reasonable approximation to the instrument function is a Gaussian, *viz*

$$I(x) = \frac{1}{s\sqrt{2p}} \exp(-\frac{x^2}{2s^2}).$$

When the measured spectrum is given by a set of discrete values M_i, the iterative method can be expressed as

$$N_i^{(k+1)} = N_i^{(k)} \frac{M(E)}{N^{(k)} \otimes I},$$

with the first guess $N_i^{(0)} = M_i$. The convolution, $N \otimes I$, is performed numerically, of course.

Again, the calculation ends on the number of iterations or when $N_i^{(k)}$ converges. This algorithm converges faster than a slightly different one given in Ref.2 (page 72), called the van Cittert method. The van Cittert method is given by

$$N_i^{(k+1)} = N_i^{(k)} + \left(M(E) - N^{(k)} \otimes I \right).$$

The van Cittert method, which uses an additive correction, rather than a ratio, converges more slowly than the ratio method. *You will probably need to try both methods to find one that works with your data.*

Don't forget to put enough comments in your source code.

6. Summary of tasks

You are expected to produce two computer programs, one which will remove a background and another which will deconvolve an XPS spectrum. To demonstrate that your programs work correctly, you must first show that they work on test data. This means that you must create a test spectrum which looks like Fig. 1, consisting of a peak (a Gaussian) on top of a background (can use a step function or arctangent function), and then recover the Gaussian using your background subtraction program. Next, you need to create a test spectrum consisting of a convolution of two Gaussians, and recover one of them by deconvolution. Finally, you operate on the actual data.

The report should contain the commented code, and graphical demonstrations of your results.