eXPFit Peak Fitting Utility for MS-Excel

eXPFit is a peak fitting utility/template running under Microsoft Excel. It has been specifically set-up for the analysis of X-ray photoelectron spectroscopy (XPS) data, but it could be used to fit other types of spectroscopic data.

This software is suitable for those people who commonly use Excel for manipulating data and assumes a certain familiarity with Excel.

Within these constraints it provides great flexibility, but *if you want a completely robust, user-proof or computationally-efficient peak fitting routine then look elsewhere; this software makes no pretence of meeting any of these requirements* !

Features

- Backgrounds : linear and/or Shirley
- Maximum of 10 peaks/spectrum
- Up to 1001 data points per spectrum
- Locking of peak parameters
- Linking of peak parameters to those of other peaks
- Each peak may be optimised with regard to the following parameters :
    - peak location/binding energy
    - FWHM (symmetric or asymmetric)
    - Gaussian/Lorentzian mix (symmetric or asymmetric)

Conditions of Use

This software utility is supplied free-of-charge for personal use by individuals at home, or for anyone working in an academic (college, university etc.) environment. However, please note the Disclaimer regarding its use. The software must be registered and the requisite licensing payment made to the author (see below) before use in any other commercial or other non-academic research environment.

Hardware & Software Requirements

The Visual Basic code is not particularly efficient but runs quickly enough on modern PCs. The workbook was originally prepared and tested using the version of Excel distributed in Office 97, but it has been tested and shown to work with all subsequent releases of Office up to and including Office 2007, provided that the installation instructions given in the documentation below are followed.

Installation

1. Copy the supplied Excel file to the directory of your choice.
2. Start-up Microsoft Excel.
3. Check if the Solver Add-In is installed in Excel – in Office 2003 you should be able to see Solver under the Tools menu; in Office 2007 you should see Solver in the *Analysis* section on the *Data* tab (if it is not installed, then you must do so by following the instructions in the Excel on-line Help).

4. Open the supplied Excel file (you will receive a warning that the workbook contains macros - you will have to enable this content)
5. Start the Solver (from the Tools menu, or from the Data tab) and then immediately click on the "Close" button to shut it down (this is to resolve some library referencing problems).
6. Re-save the Excel file.

Using the Program

This workbook is designed to be operated exclusively from the "Ft" worksheet, and any alterations that you make to other sheets of the workbook may affect the way that it operates. You may wish to run Excel in the Full Screen mode (select this option from the View menu/tab) if you are using a small display.

Changing the Settings

The *Settings* button enables you to alter the spectral (binding energy) range over which the fitting program operates - this is assumed to be the appropriate range for the data which you are attempting to fit but no check is made to confirm this. You are required to supply the *Initial Binding Energy*, the *Step Size* (between individual points) and the *Final Binding Energy* - units are assumed to be eV although this is immaterial for operation of the program. The step size may be entered as a positive value even if the final binding energy is lower than the initial energy. Note that some of the peak parameters are automatically reset when new settings are supplied. (Warning - this operation can take a long time on some old versions of Excel).

Importing Data to be Fitted

If you use the *Import New Data* button facility, then the data to be fitted is assumed to be present in another open Excel workbook. It is further assumed that the worksheet contains a number of similar spectra in columns (e.g. a series of O 1s spectra), where each column contains a single spectrum represented by the signal intensity (in integral counts) with a single header row containing some form of spectral identification (e.g. the original filename); the basic structure is illustrated below.

	A	B	C	D
1	BE / eV	Spectrum 1	Spectrum 2	Spectrum 3
2	536.0	21345	22300	22356
3	535.9	21222	22356	22343
4	535.8	21192	22978	22401

If you wish to fit the spectra only over a more limited range of binding energies, then you will need to delete the appropriate rows from this worksheet. It is recommended that you only have one datafile open at any one time in addition to the main workbook; furthermore, if this contains multiple sheets it will be easier if you make the required sheet the active worksheet before switching to the main workbook.

When you click on the *Import New Data* button the display will switch to the first other open workbook (i.e. hopefully the required datafile, although you can use the *Window* menu, or Windows task-bar, to switch to another file). To select a spectrum (a column of data) you should select the entire column by clicking on the column identifier header tab (the grey cell at the top containing an alphabetic character). To transfer this data you should then press the *Enter* key, or click on the *OK* button of the dialog box. The new data is placed in the second column (column B) of the "Data" worksheet.

If you do not wish to use the *Import New Data* facility, then it is also possible to transfer new spectral data onto the "Data" worksheet manually, using successive copy and paste operations.

Shirley-type Background Subtraction (optional)

The *Shirley Bkgrd* button will subtract a Shirley-type background using an iterative procedure. This is done using a homewritten algorithm and you may wish to check the results against those from other programs. The original data is transferred to the "Shirley" worksheet, whilst the spectrum stored on the "Data" worksheet and displayed on the "Ft" worksheet becomes that obtained after the background subtraction has been performed. All subsequent peak fitting is carried out on this modified data.

Peak Fitting

Peak fitting is accomplished using the Solver Add-In provided with Excel, with the parameters entered on the "Ft" worksheet being the starting values for the fit. As with all fitting program, it is less likely to fail if these initial parameters (including the linear background parameters) give a reasonable fit to the data. You should enter the peak parameters in a continuous fashion from the left starting with Peak 1
(Warning - if the intensity of any peak is initially set to zero then both it and any peaks to the right will be ignored in any subsequent fitting).

The meaning of the basic peak parameters should be self-evident - these being the peak location, height, full-width-half-maximum (FWHM) and the fractional Gaussian character of the Gaussian-Lorentzian peak function (0 = 100% Lorentzian, 1 = 100% Gaussian). However, to permit asymmetry the left and right sides of each peak are assigned separate FWHM and Gaussian-Lorentzian character values. Peak parameters may be set to numerical values or have their values defined by Excel formulae (thus linking them to other parameters).

Examples of possible entries are illustrated below :

Cell	Parameter (all refer to Peak 2)	Units	Sample Value	Constraints	Sample Formula	Meaning of Formula
C2	Binding Energy	eV	530.25	> 0	=B2+2.1	Peak fixed at 2.1 eV to higher BE of Peak 1
C3	Peak Height		44700	≥ 0	=B3*2/3	Peak height constrained to 67% of that of Peak 1
C4	Left FWHM	eV	1.560	> 0	=B4	Left peak width fixed to be equal to that of Peak 1
C5	Right FWHM	eV	1.760	> 0	=C3	Right peak width fixed to be equal to left peak width
C6	Left Gaussian %		0.700	≥ 0 , ≤ 1	=B6	Left peak profile fixed to be equal to that of Peak 1
C7	Right Gaussian %		0.700	≥ 0 , ≤ 1	=C6	Right peak profile fixed to be equal to left peak profile

Note :

1. to make a peak completely symmetric you simply need to set the parameters (FWHM and fractional Gaussian character) for the right-hand side of the peak to be equal to those of the left-hand side using Excel formulae.
2. two further parameters are available; these are the left-hand background and right-hand background values which together define a linear background contributing to the fit to the data.
3. it is not possible to constrain the integrated areas of peaks (these are not parameters)

The procedure for starting the peak-fitting process is outlined below:

(i) Press the *Solve Setup* button.
The cells containing parameters which may be automatically adjusted during fitting will be highlighted in yellow; note that this will not include any peak parameters which are defined by formulae and whose values are therefore linked to those of other cells.

(ii) You will now need to manually start the *Solver* , using the entry on the *Data* tab (Office 2007), or under the *Tools* menu (earlier versions).

When the Solver Parameters dialog box appears you should ensure that the cells whose values may be automatically varied are correct. You can check this by clicking in the "By Changing Cells" edit box and the cells will be briefly highlighted on the main worksheet. If you wish to change these it is generally best to delete all the existing entries and then use the mouse to select the cells to be varied. Hold down the Ctrl key whilst using the mouse to make additional selections.

(iii) Press the *Solve* button on the Solver Parameters dialog box.

Note :

1. You can halt the fitting process at any time by pressing the Esc key.
2. It is possible to add constraints on the parameters within Solver, although this is not usually necessary or particularly recommended. Nevertheless, if you do not, you must check that the fitted-results are reasonable; in particular you are advised to check that the Gaussian-Lorentzian mix of each peak is within the permitted bounds (0–1).
3. If you wish to pause and view the results after each iteration then this may be done using the *Options* button on the Solver Parameters dialog box.

Troubleshooting

If the macros fail to run, giving various obscure error messages, then it is usually due to the incorrect libraries being referenced.

Manually loading the Solver, whilst the spreadsheet is open, and then re-saving the Excel file often solves this problem (this is the basis for the installation procedure described above).

You can also check the References associated with the macros using the procedures outlined in the online Help of Excel.

Disclaimer

If you use this program then you do so at your own risk ! The author takes no responsibility for the accuracy of any results produced by the program or for any actions you may base on them.

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