

KhervFitting

Help Guide

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tion. When using KherveFitting in academic or research contexts, appropriate citation would be appreciated to acknowledge the software's contribution.

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Overview

KerveFitting, see Fig. 18, is an open-source software developed in Python, using wxPython for the graphical user interface, Matplotlib for data visualization, NumPy and lmfit for numerical computations and curve fitting algorithms, and Panda for manipulating Excel files.

It is aimed at users who wants to analyse a single sample with multiple core levels. KerveFitting is designed to be elegant and simple to use.

Note

KerveFitting is currently under heavy improvements and so some of the Figures shown here does not correspond to the current version and are from a previous version. After version 2.0, the software should have found its permanent look and feel

Getting Started

1. Instrument Settings

Before starting the analysis, ensure that you select the correct sensitivity factor for the instrument used to measure the data. This can be found in *Edit → Preferences → Instrument Settings*, highlighted in red in Fig. 1. The following configurations are required for some instruments:

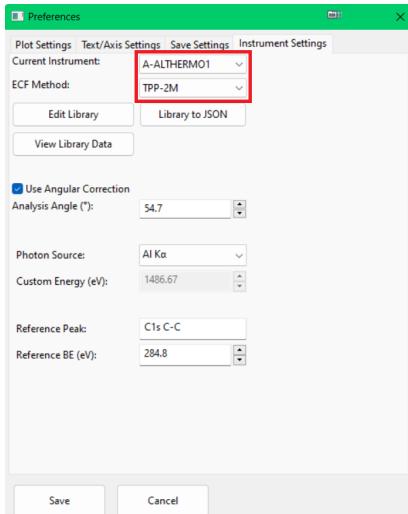


Figure 1: Instrument settings tab in the Preferences window.

- **General settings:** C-Al1486 and TPP-2M
- **Thermo Kalpha and Nexsa:** A-ALTHERMO1 and TPP-2M
- **Kratos (new instrument):** C-KRATOSF1S - Al1486 and TPP-2M
- **Kratos (older instrument):** C-KRATOSC1S - Al1486 and TPP-2M

Depending on your instrument, the angle from the X-ray source to the analyzer can also be adjusted, with the default value being the magic angle (54.7°). The Doublet Splitting (DS) values are stored in C-Al1486 and used for all instruments.

2. Open Files

Drag the XPS file (.xlsx, .vms, .kal, .spe) into the plot area. If the file is not in KherveFitting format, the program will create an Excel file in the correct format. Transmission data will also be exported, and raw data will be corrected, as shown in Fig. 2.

As an example, drag the file named "STO.xlsx" located in *KherveFitting → Data*. Using the middle mouse button, scroll to the Sr3d core level. This file shows XPS data obtained on a SrTiO₃ thin film on a XPS Thermo Kalpha. Make sure you have selected the RSF A-ALTERMO01 from the preference window.

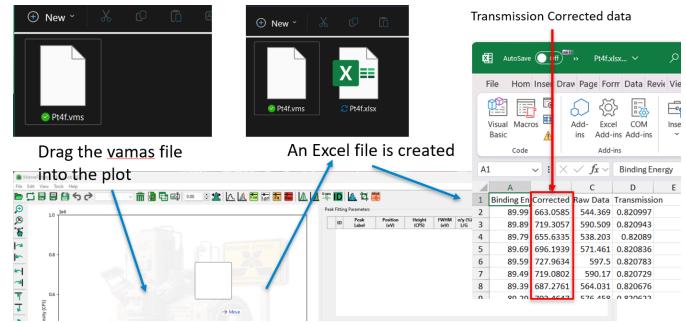


Figure 2: Opening a file: Example of a Vamas file.

3. Plot and Core Level Control

To familiarize yourself with KherveFitting, it is important to learn the different shortcuts. Scroll down the mouse button to switch between different core levels. Alternatively, use **Ctrl+Left** or **Ctrl+Right**. Pressing the **Ctrl** key allows you to change plot properties. Below is a list of the most useful shortcuts:

1. **Ctrl+Left or Ctrl+Right:** Move left or right along the X-axis.
2. **Ctrl+Up or Ctrl+Down:** Zoom in or out along the Y-axis.
3. **Ctrl+"+" or Ctrl+"-":** Zoom in or out along the X-axis.
4. **Ctrl+Shift+Left:** Zoom in and out along the X-axis while keeping the Low BE minimum constant.

Alternatively, you can zoom in and out using the right-click menu or the zoom toolbar.

4. Prepare for Peak Fitting



Press the peak fit icon to open the peak fitting window. The fitting window (see Fig. 3) consists of two tabs: *Background* and *Peak Fitting*. Select the *Background* tab to create a background. The default method, *Multi-Regions Smart*, is suitable for most fitting applications.

To create peaks, select the *Fitting* tab. The default fitting method is *least squares*, which is appropriate for most models. The default fitting model is the product of Gaussian and Lorentzian GL(Area), a simple model useful for users new to XPS. However, the recommended fitting model is *Voigt (Area, L/G, σ)*, as it is the most physically meaningful. The *LA (Area, σ/γ, γ)* model lacks physical meaning but is familiar to users experienced with CasaXPS.

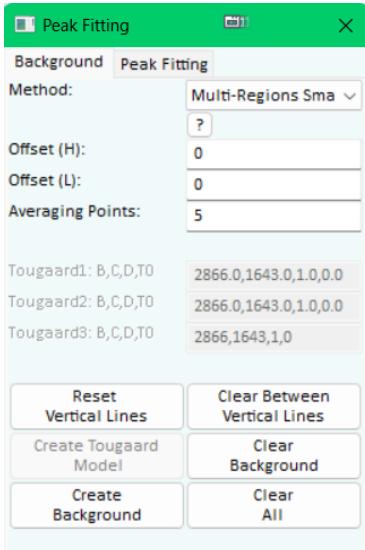


Figure 3: Peak fitting screen (KherveFitting v1.4).

5. Create a Background

To create a background, click on the left side (high BE) and right side (low BE) of the plot, ideally in a flat region about 1-2 eV away from the peaks. Press the *Create Background* button. When using *Multi-Regions Smart*, it will generate a Shirley background between the two vertical lines, see Fig. 4.

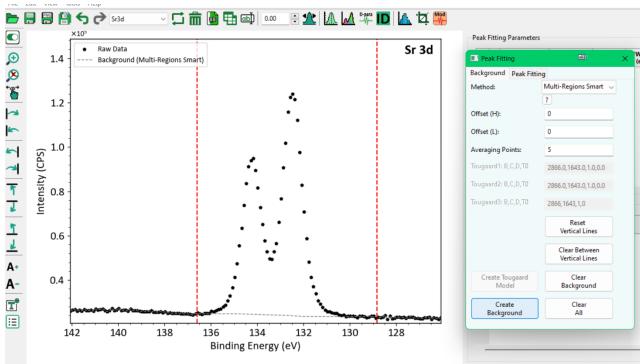


Figure 4: Create a Shirley background.

6. Create a Peak Model

Press the peak fitting tab of the peak fitting window. The fitting model is set by default to the GL model. In this case, the Sr3d core level is composed of two peaks (doublet) of width (FWHM) around 1 eV split by about 1.7 eV. Press the *Add 2 Peaks* button 5. This will create 2 peaks namely A and B where peak B is linked to peak A with the following characteristics:

- Position of $A + 1.7 \# 0.2$:** Peak B will be spaced 1.7 eV away from peak A with a possible variation of ± 0.2 eV.

- FWHM of $A \times 1$:** The width or FWHM of peak B is fixed to the one of peak A. No variation is given here.
- Area of $A \times 0.667 \# 0.05$:** The area of peak B is constrained to the one of peak $A \times 0.667$ or $/1.5$ with a possible variation of ± 0.05 . In a d shell, the number of electrons in the $5/2$ shell is 6 and the number of electrons in the $3/2$ shell is 4 so the ratio is therefore 0.667.

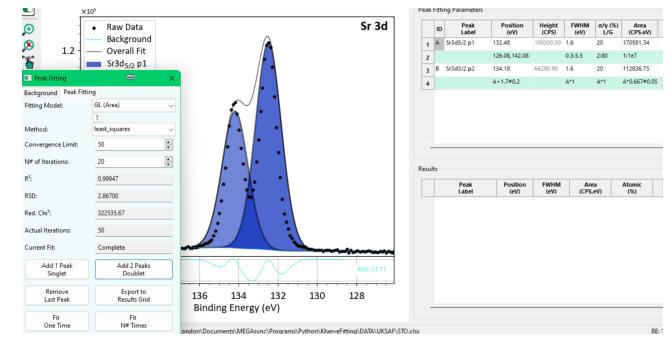


Figure 5: Add two GL peaks.

7. Fit the Peak Model

Press the *Fit N# times* button and wait for the 20 iterations to complete, see Fig. 6. Once the fit complete, The Residual standard deviation (RSD) is around 2.8-3.4 which is acceptable for a GL model. The results show that the peaks have a FWHM of around 1.0 eV and a L/G ratio of about 62%.

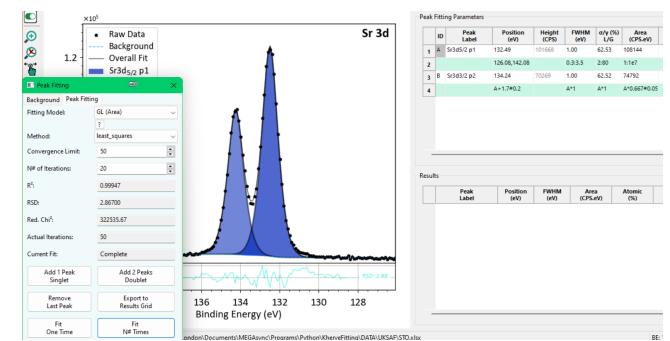


Figure 6: Fit two GL peaks.

Please note that the L/G ratio changes with the width of the peak. A sharper peak will tend to be more Lorentzian while a wider peak would tend to be more Gaussian. It is not advisable to keep the peak shape to 30%

8. Move the Peak Model

Use Tab or Q to select the peak A. When a peak is selected, the label is on top of the peak. drag peak A by pressing the left mouse button and with the mouse on top of the cross, see Fig. 7. Note that the peak B moves with peak A as it is constrained to A with position and area. Dragging

peak B moves only peak B. You can also drag the peaks by pressing the Alt key + Left or Right or Down or Up

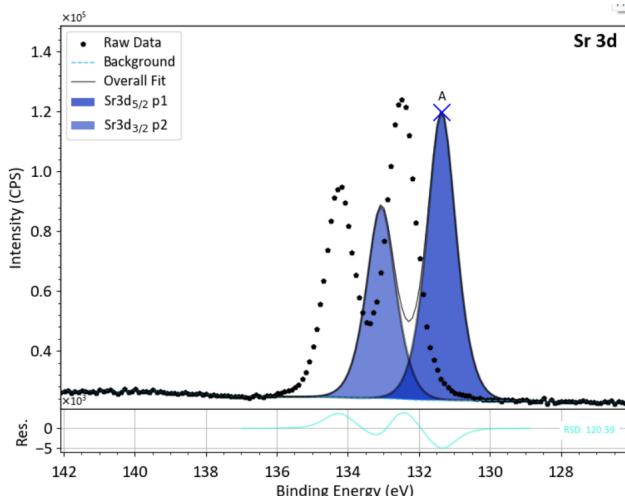


Figure 7: Drag the doublet.

9. Other Models

Press the Remove Last Peak button twice to remove the two GL peaks. Select The LA (Area, σ/γ , γ) model and press the Add 2 Peaks button where two LA peaks are created. Press the Fit N# times button. Note that the RSD is around 1.8-2.4 which is lower than for the GL model. In contrast to the GL model, the LA model is a full Lorentzian model that is powered on the right side by γ and on the left side by σ . The bigger the power, the more gaussian is the model. Fig. 8 shows the peak fitting grid obtained after fitting the Sr3d. The value for σ and γ gives the shape of the peak and are optimised during the fit. A value of σ/γ of 50% ($\sigma = \gamma$) represents a fully symmetric peak (default value). A value of σ/γ of less than 50% is an asymmetric peak. Fit the Pt4f file if you wish to fit assymetric LA.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
1	Sr3d5/2 p1	132.49	100737	0.96	50.00	111374	3.13	3.13
2		126.08,142.08		0.3:3.5	Fixed	1:1e7		0.01:10
3	Sr3d3/2 p2	134.24	69317	0.96	50.00	76884	3.13	3.13
4		A+1.7#0.2		A*1	A*1	A*0.667#0.05	A*1	

Figure 8: Peak fitting grig for the LA model.

Press the Remove Last Peak button twice to remove the two LA peaks. Select The Voigt (Area, L/G , σ) model and press the Add 2 Peaks button where two Voigt peaks are created. Press the Fit N# times button. Note that the RSD is around 2.9-3.1 which is lower than for the GL model. In contrast to other models, the FWHM of the model cannot be changed or constrained. Instead, the user can control and constrain the Gaussian width part of the peak as well as its L/G ratio. The Lorentzian width is then calculated from the L/G ratio. This allows the user

to constraint the L/G ratio to other peak. It has to be noted that:

- A peak with a FWHM of 1.0 to 1.5 eV leads to a L/G ratio around 20%.
- A peak of width above 1.5 eV leads to a L/G ratio between 10-20%.
- A peak of width below 1.0 eV leads to a quick increase of the L/G ratio from 20% to 50-60%.

Fig. 9 shows the peak fitting grid obtained after fitting the Sr3d. The value for W_g and W_l are the width of the Gaussian and Lorentzian, respectively. The column with grey values are for indication only and cannot be changed while the one in black can be changed.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
1	A Sr3d5/2 p1	132.49	99246	0.98	25.28	116321	0.82	0.28
2		126.08,142.08			2:80	1:1e7	0.01:3	
3	B Sr3d3/2 p2	134.24	67847	0.99	26.37	80466	0.82	0.29
4		A+1.7#0.2			A*1	A*0.667#0.05 A*1		

Figure 9: Peak fitting grig for the Voigt model.

Repeat the same fitting process using the Voigt model on Ti2p, see Fig. 11. Note that when adding a doublet for Ti2p or V2p, KherveFitting does not constrain the FWHM of peak B with peak A, as for an oxide the width of Ti2p_{1/2} is wider than that of Ti2p_{3/2} due to the koester krongen effect.

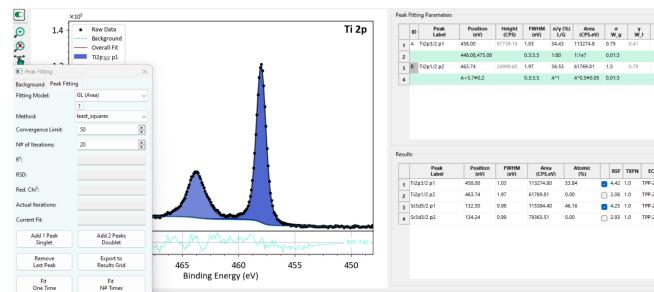


Figure 10: Fit of Ti2p using the Voigt model.

10. Export to Results Grid



The comparison between different core level in term of atomic concentration can be done in the Results grid. Note that the correct RSF library and method needs to be selected prior to this process. To export to the Results grid, Press the Export icon in the toolbar. Export Ti2p and Sr3d data into the Results grid. Tick the Ti2p_{3/2} and the Sr3d_{5/2} and see Fig. 11 for the example.

	Peak Label	Position (eV)	FWHM (eV)	Area (CPS-eV)	Atomic (%)	RSF	TXFN	ECF	Instr.	Norm. Area
1	Ti2p3/2 p1	458.00	1.03	113274.80	53.84	4.42	1.0	TPP-2M	A-ALTHERMO1	404.75
2	Ti2p1/2 p2	463.74	1.97	61769.81	0.00	2.06	1.0	TPP-2M	A-ALTHERMO1	476.14
3	Sr3d5/2 p1	132.50	0.98	115384.40	46.16	4.25	1.0	TPP-2M	A-ALTHERMO1	346.85
4	Sr3d3/2 p2	134.24	0.99	79363.51	0.00	2.93	1.0	TPP-2M	A-ALTHERMO1	346.62

Figure 11: Results grid showing the atomic concentration of Ti2p_{3/2} against Sr3d_{5/2}

Note that the results grid is still under development and sometimes the tick does not refresh. A simple solution is to click on the plot and the correct tick state is shown.

11. Load a Peak Table



Peaks table can be saved as a .json file to be re-used. Scroll down to C1s and press the Load Peaks Parameter icon on the right of the horizontal toolbar. Select the C1s_C-C_4peaks_Voigt_GK_2412.json peak table, see Fig. 13. Note that 4 peaks have been created in the peak fitting grid.

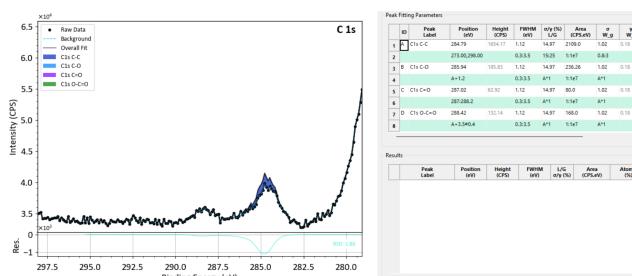


Figure 12: Loading of the C1s peak table using the Voigt model.

The background needs to be created next. Go onto the background Tab and place the vertical lines 1-2 eV away from the peaks. Press on Create Background and a Shirley background is created. Next go back to the Peak Fitting tab and press Fit N# times. C1s should be fitted with a RSD of about 1 eV.

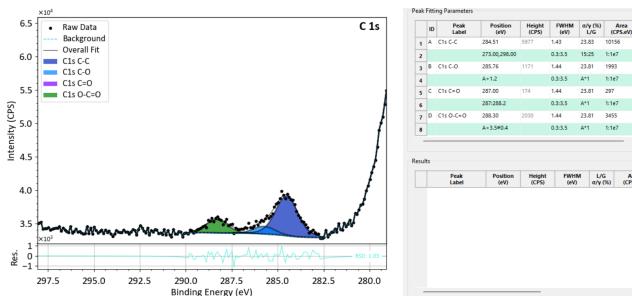


Figure 13: Final result of the fitted C1s core level.

Repeat the same process for the O1s core level but this time using the O1s_O-Lat_3peaks_Voigt_GK_2412.json. Set the background between 527.3 eV and 535 eV. Note that the O-surf peak is almost insignificant and can be removed from the peak table.

12. Binding Energy Correction



KherveFitting looks by default for a peak called C1s_C-C and calculate the difference between the current peak position and 284.8 eV. Note that this can be changed in the Preferences window under Instrument Settings. Press the green peak as shown above and take note of the new corrected value of around 0.29 eV. Now all the peaks in the Peak Fitting grid and in the Results grid have shifted by +0.29 eV. The binding energy correction can be reversed by writing 0.00 in the Numeric control shown above and by clicking on the plot.

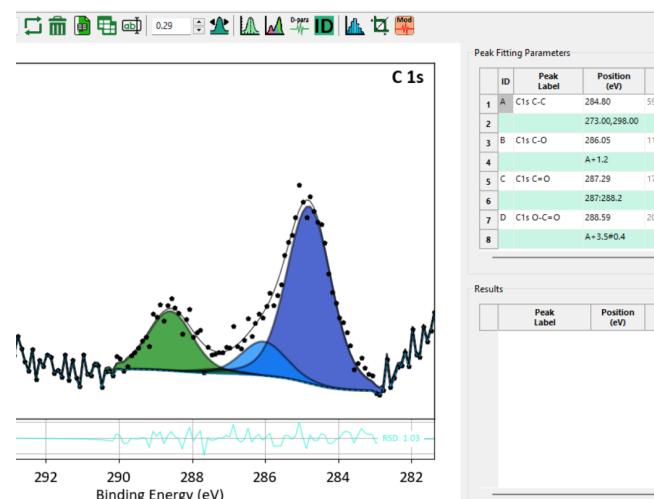


Figure 14: C1s core level corrected to C-C at 284.8 eV.

13. Background Offset

KherveFitting allows to offset the background by mouse control. Scroll down to O1s core level. Zoom down (Ctrl+Down) to the background level. You should get to a plot similar to Fig. 15

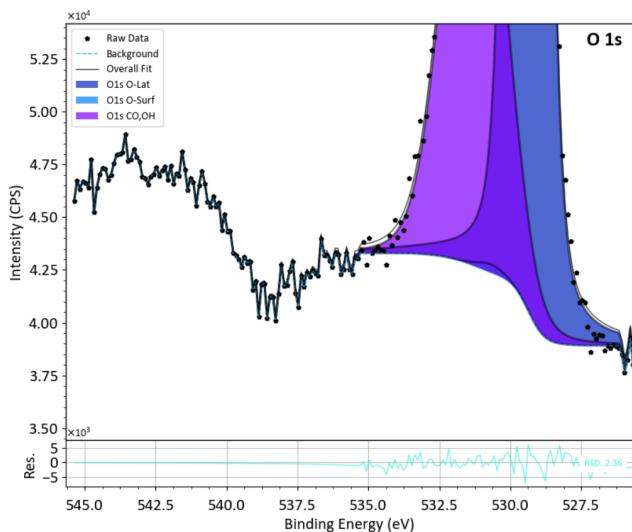


Figure 15: O1s core level zoomed down to background level.

Go on the Background tab and make sure the Vertical Lines are reset by pressing on Reset Vertical Lines button. Select a range between 527.3 and 537.5 eV, then press Shift and hold the background at high binding energy and shift it down as per Fig. 16

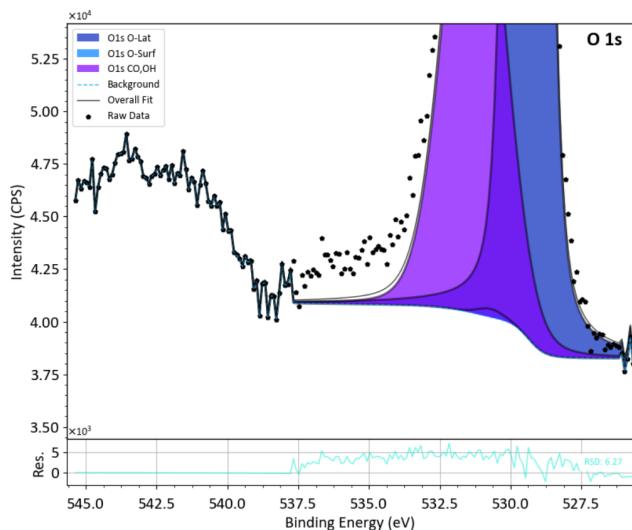


Figure 16: O1s core level zoomed down to background level.

In more details

Opening Files

KherveFitting can open Excel files (.xlsx) and import/convert Avantage Excel (.xlsx), VAMAS (.vms), Kratos (.kal), Thermo (.avg) and Phi (.spe) files and Avantage files into Excel format. For best results:

- Place raw data (X,Y) in Columns A and B, starting at row 0
- Use the row offset control in the horizontal toolbar if needed
- Save each core level in a separate sheet named after the core level. Do not use white spaces, e.g. Si2p, Al2p, C1s, O1s.



Figure 17: Import File Menu.

When reopening a saved fitting, KherveFitting also looks for a JSON file of the same name containing all the required properties.

KherveFitting also supports drag and drop functionality for opening files. Users can simply drag and drop KherveFitting or Avantage Excel (.xlsx), VAMAS (.vms), Kratos (.kal), Thermo (.avg) and Phi (.spe) files directly onto the plot canvas, and the software will automatically open and process the files. This convenient feature allows users to quickly import data without having to navigate through file menus or dialogs. KherveFitting will detect the file type and handle the appropriate opening and conversion process, making the data immediately available for analysis. The drag and drop functionality applies to both single files and multiple files. Users can select one or more Excel or VAMAS files and drop them onto the canvas to have them all loaded and processed by KherveFitting.

Saving Files

KherveFitting offers three saving options:



1. Save corrected binding energy, background, envelope, residuals, and fitted peak data of the active core level to columns Downwards in the corresponding Excel sheet. The picture of the plot is also saved in cell D6. Peak fitting properties for all core levels are saved in a JSON file.

2. Save the figure of the active core level to the corresponding Excel sheet and as a PNG file. The resolution (DPI) is 300 DPI
3. Save all fitted core level data, including figures, to the Excel file. Peak fitting properties for all core levels are saved in a JSON file.

Plot Window

Vertical Toolbar:

The vertical toolbar located on the left side of the plot window provides essential plot manipulation tools:

Zoom Tools

- Zoom In: Click to enable zoom mode, then drag to select area
- Zoom Out: Returns to full view
- Drag: Enables plot panning

Binding Energy Controls

- High BE adjustment
- Low BE adjustment

Intensity Controls

- High intensity adjustment
- Low intensity adjustment

Text Controls

- Increase font sizes
- Decrease font sizes

Toggling Display Elements

Use toggle buttons to show or hide various plot elements:



- Raw data points
- Background line
- Individual fitted peaks
- Overall envelope
- Residuals
- Legend

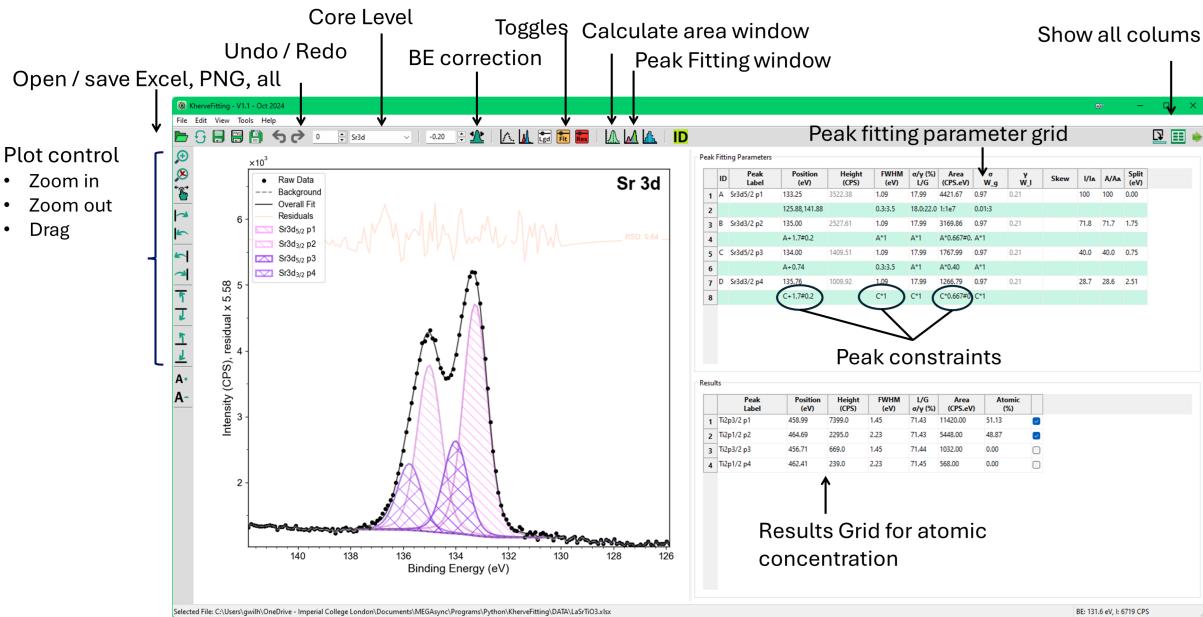


Figure 18: KherveFitting v1.3 Main View. Note that the toggle icons have moved to the left side toolbar

Keyboard Controls for Plot Manipulation

XPS spectra manipulation and peak fitting can be efficiently controlled through keyboard shortcuts:

Peak Navigation and Selection

- Tab/Q: Navigate through peaks (next/previous)
- Alt+Arrow keys: Adjust selected peak
- Alt+Up/Down: Increase/decrease Peak intensity
- Alt+Left/Right: Move peak position to higher/lower BE
- Alt+Shift+Left/Right: Increase/decrease peak FWHM
- Shift+Mouse Left button: Drag to adjust FWHM

Plot Navigation

- Ctrl+[or]: Switch between core levels (previous/next)
- Ctrl+Up/Down: Adjust plot intensity scale
- Ctrl+Left/Right: Shift plot to higher/lower BE
- Ctrl+Plus/Minus: Zoom in/out
- Shift+Left/Right: Adjust high BE range

General Controls

- Ctrl+Z/Y: Undo/Redo (up to 30 events)
- Ctrl+S: Save (grid data only)
- Ctrl+P: Open peak fitting window

- Ctrl+A: Open area calculation window
- Ctrl+K: Display keyboard shortcuts

Plot Preferences

The plot preferences window, see Fig. 19 provides comprehensive control over the visual appearance of XPS spectra through three main tabs. The Plot Settings tab is the primary interface for customizing data visualization. Use the Preferences window to customize the plot appearance, including:

- Colors for raw data, background, fitted peaks, and residuals
- Line styles (solid, dashed, dotted)
- Marker types for data points
- Font sizes and styles
- Axis labels and titles
- Instrument settings with various RSFs and ECF methodologies

Plot Settings Tab

Raw Data Display: Raw XPS data can be displayed either as scattered points or continuous lines. In scatter mode, customize point size (1-50), marker style (circle, square, triangle, diamond, or star), and color. Line mode offers width control (1-10 pixels) and transparency adjustment through the alpha parameter (0-1). These options

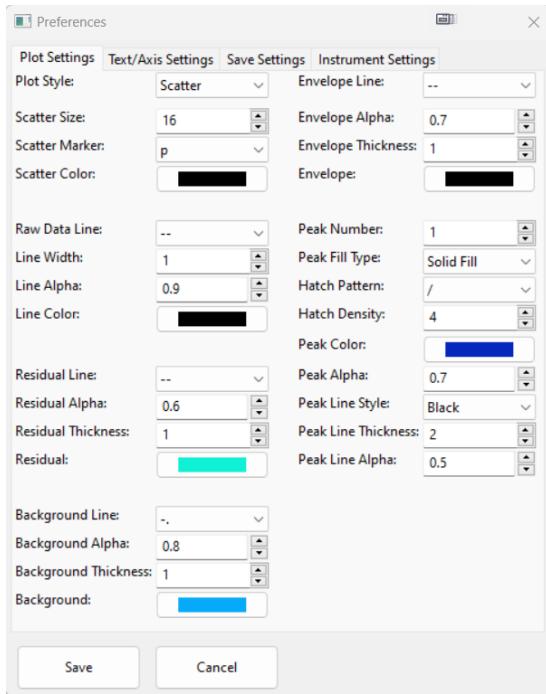


Figure 19: The preference window under the plot settings tab

allow clear visualization of experimental data points while maintaining a clean presentation.

Peak Display: Fitted peaks can be represented with either solid fills or customizable hatch patterns. The hatch density (1-10) controls pattern spacing, while peak transparency is adjusted via the alpha parameter (0-1). Peak outlines can be hidden, colored (black, same as fill, grey, or yellow), with adjustable thickness (1-5 pixels) and transparency. These options enable clear differentiation between multiple peaks while maintaining visual clarity.

Component Display: Additional spectral components - background, envelope, and residuals - each have customizable line styles and colors. The background can be shown as solid, dashed, or dotted lines with adjustable color and opacity. The envelope (overall fit) and residuals follow similar customization options, allowing for clear visualization of fit quality and individual spectral components.

Text/Axis Settings Tab: This is the Settings for fonts, axis labels, and tick marks

Instrument Settings Tab: These are the XPS instrument-specific parameters.

Peak Fitting Grid

The peak fitting grid displays parameters for each fitted peak across two rows - one for values and one for constraints. The primary visible columns include: Peak ID (A, B, C...), Peak Label, Position (eV), Height (CPS), FWHM (eV), σ/γ ratio or L/G ratio (%), Area (CPS.eV),

σ , γ , Skew. Additional columns, including the fitting model, background parameters, and offset values, are hidden by default but can be displayed using the Toggle Column button in the toolbar. Cell colors indicate editable parameters (white) versus derived values (gray) for different fitting models. The grid automatically updates when peaks are modified through direct plotting manipulation.

Constraints: Constraints can be specified numerically (e.g. "0.3:3.5" or "0.3,3.5") or relative to other peaks from the same peak fitting grid (e.g. "A*0.667" or "A/1.5"). Variance can be inserted to allow the linked peak to move around the set value (e.g. "A*0.667#0.01"). To fix a peak to a known value "fi" or "Fixed" can be inserted. A list of known nomenclature is shown below:

- 'a', 'b', 'c' → 'A*1', 'B*1', 'C*1' (follow peak A, B, or C)
- 'fi' or 'fix' or 'fixe' → 'Fixed'
- '#0.5' → Variance to ± 0.5 eV
- Allowed nomenclature: A*1.5, A/1.5, A+1.5, A-1.5, A*1.5#0.01, #0.1, 'fi'

Results Grid

The results grid provides a summary of all fitted peaks across all core level spectra. Each row represents one peak with columns for: Peak Label, Position (eV), Height (CPS), FWHM (eV), L/G ratio (%), Area (CPS.eV), Atomic (%), selection checkbox, RSF value, fitting model, relative area, model-specific parameters (σ , γ), background type and range, sheetname, and peak constraints. Peak selection via checkboxes enables atomic percentage calculations based on peak areas normalized by RSF values.

	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	L/G σ/γ (%)	Area (CPS.eV)	Atomic (%)	
1	Sr3d5/2 Sr-Lattice	132.49	99538.89	0.98	28.03	118204.12	20.68	<input checked="" type="checkbox"/>
2	Sr3d3/2 p2	134.24	68128.83	0.98	27.99	80734.01	0.00	<input type="checkbox"/>
3	Ti2p3/2 Ti Lattice	458.0	88040.5	1.03	36.29	114752.96	19.06	<input checked="" type="checkbox"/>
4	Ti2p1/2 p2	463.74	25273.35	1.97	36.18	63027.98	0.00	<input type="checkbox"/>
5	O1s O-Lattice	529.11	133453.7	1.12	17.96	172524.97	42.35	<input checked="" type="checkbox"/>
6	O1s O-Surface	530.98	26126.81	2.42	17.95	72969.95	17.91	<input checked="" type="checkbox"/>

Figure 20: Results grid after fitting the Sr 3d of SrTiO₃ crystal. The atomic concentration shows almost a 1 to 1 to 3 ratio between Sr, Ti and O.

New peaks can be added into the Results Grid by pressing the "Export to Results Grid" Icon.



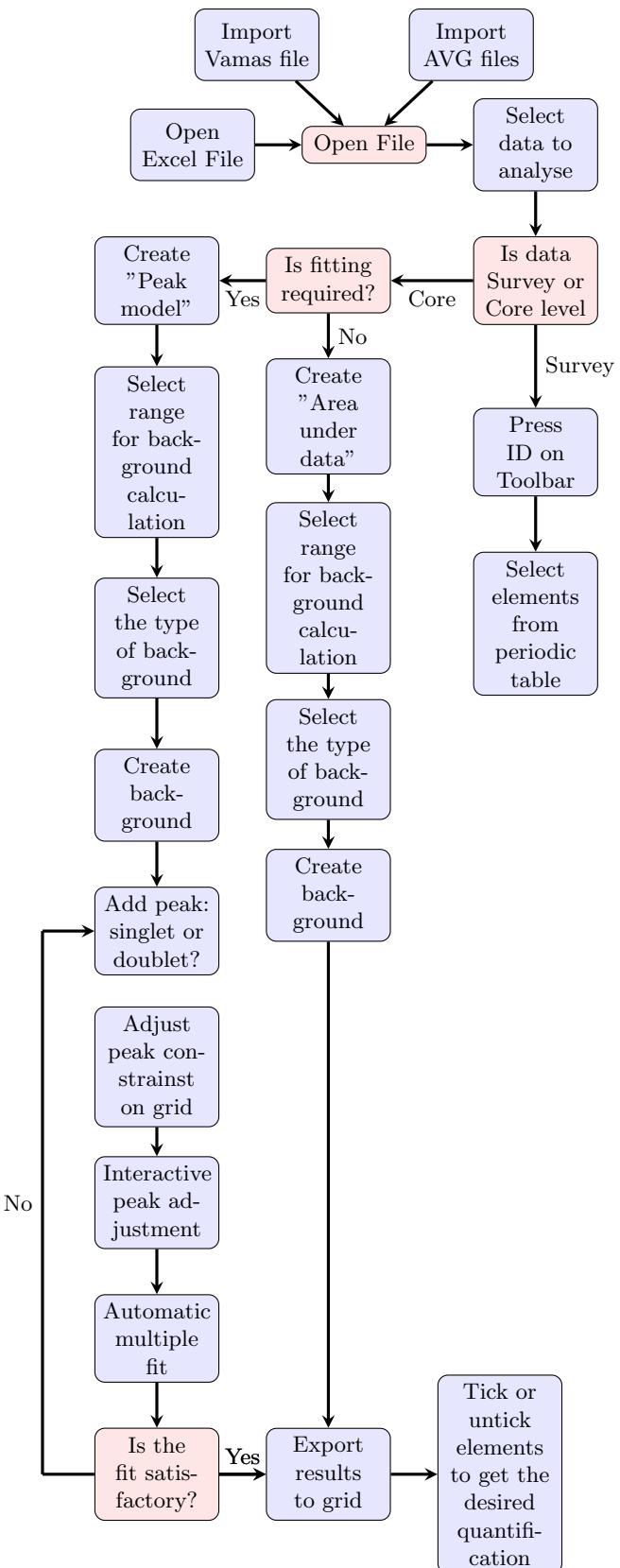


Figure 21: Workflow to analyse XPS data using KherveFitting

Workflow

Create Peak Window

The peak model window is composed of two tabs namely the background tab and the peak fitting tab.

Create Background Model

The background window is shown in Fig. 22. The buttons in the serve the following functions:

- Offset (H):** This input field allows the user to set the offset at the high binding energy end of the background.
- Offset (L):** This input field allows the user to set the offset at the low binding energy end of the background.
- Reset Vertical Lines** This button resets the positions of any vertical lines that have been added to the background.
- Clear Background** This button clears the current background.
- Background** This button applies the current background settings to the document.
- Clear All** This button clears all background settings, including any vertical lines and the background itself.

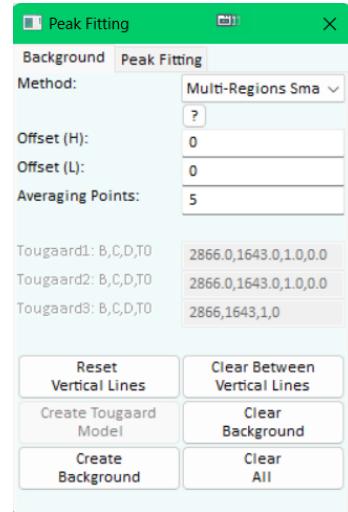


Figure 22: The Background tab.

The "Background" tab provides controls for adjusting the position and shape of the background. There are several method that can be used to creat a background model:

Linear Background: The linear background $B_L(E)$ can be approximated by the following equation:

$$B_L(E) = I_{High} \frac{E_{Low} - E}{E_{Low} - E_{High}} + I_{Low} \frac{E - E_{High}}{E_{Low} - E_{High}} \quad (1)$$

In this approach, E_{High} and E_{Low} denote two distinct energy values, while I_{High} and I_{Low} represent the corresponding intensity values. These parameters are typically selected to ensure the linear background seamlessly integrates with the spectral features at E_{High} and E_{Low} , as illustrated in Figure 23.

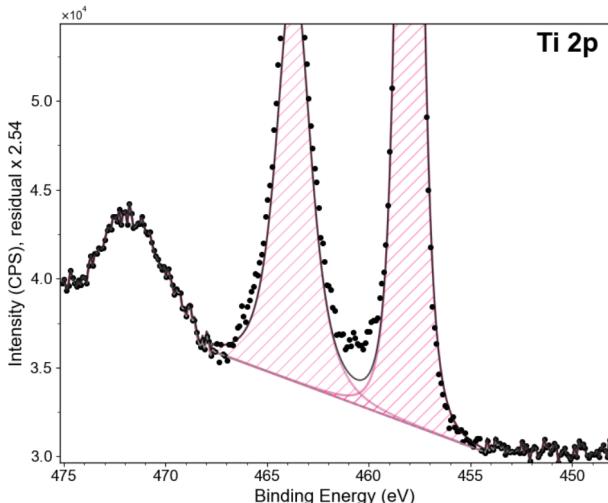


Figure 23: Ti 2p core level fitted with a Linear background

Shirley Background: The Shirley algorithm [2] is an approach that leverages information about the spectrum to construct a background sensitive to changes in the data. The key aspect of the Shirley algorithm is the iterative determination of a background using the areas marked A_{High} and A_{Low} to compute the background intensity $B_S(E)$ at energy E :

$$B_S(E) = I_{Low} + \kappa \frac{A_{Low}(E)}{A_{High}(E) + A_{Low}(E)} \quad (2)$$

Here, κ defines the step in the background and is typically equal to the difference ($I_{High} - I_{Low}$). Notably, the quantities $A_{High}(E)$ and $A_{Low}(E)$ are known provided the background $S(E)$ is already determined. However, since $S(E)$ is initially unknown, the calculation of a Shirley background from spectral data becomes an iterative process. This means that the integrated areas $A_{High}(E)$ and $A_{Low}(E)$ for each point on the background E must first be computed using an approximation to $S(E)$, after which the background $S(E)$ is updated, and the process is repeated until convergence. The number of iteration used by KerveFitting is set to 100 by default and for all the other methods. Fig. 24 shows the Ti 2p core level fitted with a Shirley background.

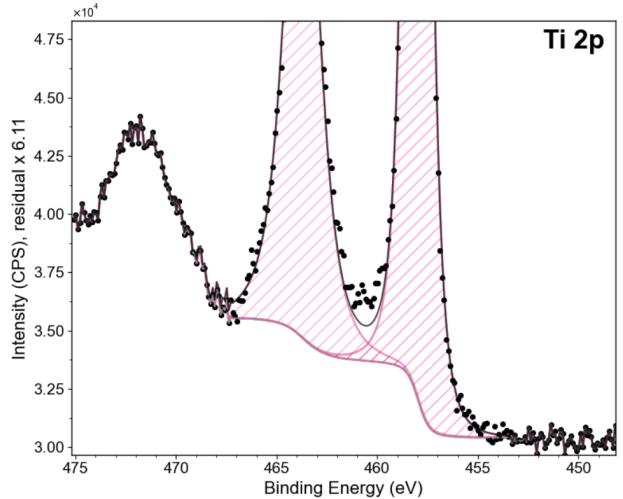


Figure 24: Ti 2p core level fitted with a Shirley background

Smart Background: The "Smart" background is an adaptive background correction method that seeks to automatically determine the appropriate background type for the given XPS spectrum. This approach combines the strengths of both linear and Shirley-type backgrounds to handle a variety of spectral shapes and conditions.

Automatic Background Type Determination: The software will automatically choose between a linear background and a Shirley-type background based on the shape of the spectrum. If the intensity is generally decreasing with increasing binding energy, a linear background is used; if the intensity shows the typical curvature associated with inelastic scattering, a Shirley-type background is employed.

Adaptive Background Calculation: The Smart background is calculated in an adaptive manner, adjusting the background based on changes in the spectrum. This allows the background to better follow and adapt to the underlying spectral features.

Safeguards Against Over-Subtraction: The software ensures that the calculated background does not exceed the raw spectral intensity at any point, preventing over-subtraction of the background and the resulting distortion of peak shapes.

Multiple Regions Smart Background: The "Multiple Regions Smart Background" is an extension of the standard "Smart Background" approach, which allows for more flexibility in handling different regions of the XPS spectrum.

Adaptive Background Across Multiple Regions: Unlike the standard Smart Background, which applies a single adaptive background calculation across the entire spectrum, the Multiple Regions Smart Background divides the spectrum into multiple user-defined regions. This enables the background correction to be tailored to

the specific characteristics of each region.

Defining Background Regions: Users can specify the energy regions of interest by placing vertical lines on the plot. These lines define the boundaries between the different regions, allowing the software to apply an adaptive background calculation independently for each region.

Region-Specific Background Determination: Within each defined region, the Multiple Regions Smart Background algorithm will automatically determine the appropriate background type, whether linear or Shirley-type, based on the shape of the spectrum in that particular energy range.

Seamless Background Integration: The background calculated for each region is then merged together to provide a continuous background that follows the changes in the spectral features across the entire energy range. This ensures a smooth transition between the different background types applied in each region.

Preventing Over-Subtraction: Similar to the standard Smart Background, the Multiple Regions Smart Background implementation includes safeguards to prevent over-subtraction of the background, maintaining the integrity of the underlying peaks.

Tougaard U4 Background: This background was introduced and developed by Svend Tougaard and is a widely used model in X-ray photoelectron spectroscopy (XPS) to describe the inelastic scattering of electrons as they exit a sample. Unlike the simpler Shirley background, which assumes a monotonic buildup of signal due to electron scattering, the Tougaard background incorporates a more physically accurate model by accounting for energy losses that photoelectrons experience due to inelastic scattering processes.

The Tougaard background equation, as previously provided, is:

$$U(E; B, C, D, T_0) = \begin{cases} \frac{B \cdot E}{(C-E)^2 + D \cdot E^2} & \text{if } E \geq T_0, \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

In this equation:

- B : This is a scaling factor that adjusts the overall intensity of the background. It does not carry physical meaning but is necessary for normalizing the background to the measured data.
- C : A parameter closely tied to the position of the maximum energy loss in the scattering tail. This value depends on the material properties and is associated with plasmon excitation energy.
- D : This parameter governs the broadening (width) of the scattering tail. Reflects the spread of inelastic scattering energy losses.

- T_0 : This is the energy threshold below which the Tougaard background is zero, corresponding to regions where no inelastic scattering is expected.

Different Tougaard models are implemented on the basis of the parameters used:

- **U2-Tougaard**: The parameter B is calculated and the user defines C with $C < 0$, while D and t_0 are fixed to 0.
- **U3-Tougaard**: The parameter B is calculated and the user defines C, D , and t_0 .
- **U4-Tougaard**: The user defines all parameters B, C, D , and t_0 .

The KherveFitting tool provides the U4-Tougaard background model, see Fig. 25, allowing users to manually specify the values for B, C, D , and t_0 to achieve precise background subtraction.

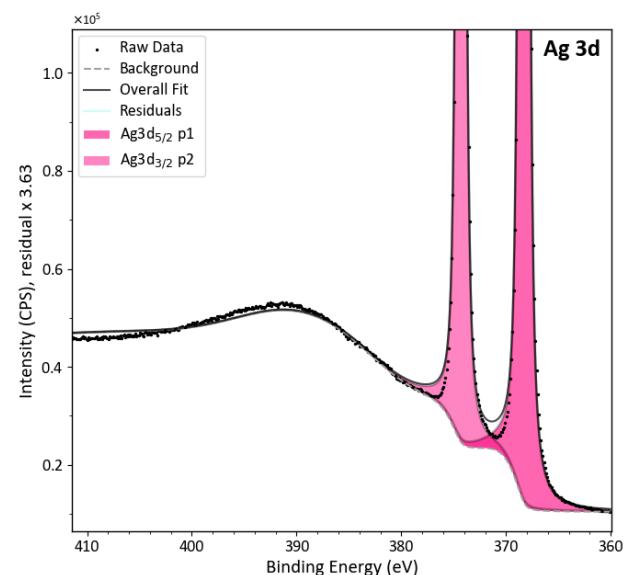


Figure 25: Ag3d core level fitted with a double U4-Tougaard background. The background fit is only shown for representation and does not constitute a good fit.

In addition, a dedicated Tougaard fitting tool is available (Fig. 26), which can assist users in optimizing these parameters for their specific data sets.

Create Peak Models

The peak fitting tab provides a comprehensive interface for controlling the fitting process and peak manipulation. At the top, users can select the peak shape through the **Fitting Model** dropdown menu, which includes various functions:

- Area-based models: GL (Area), SGL (Area), Voigt (Area, σ, γ), Voigt (Area, L/G, σ), Pseudo-Voigt (Area)

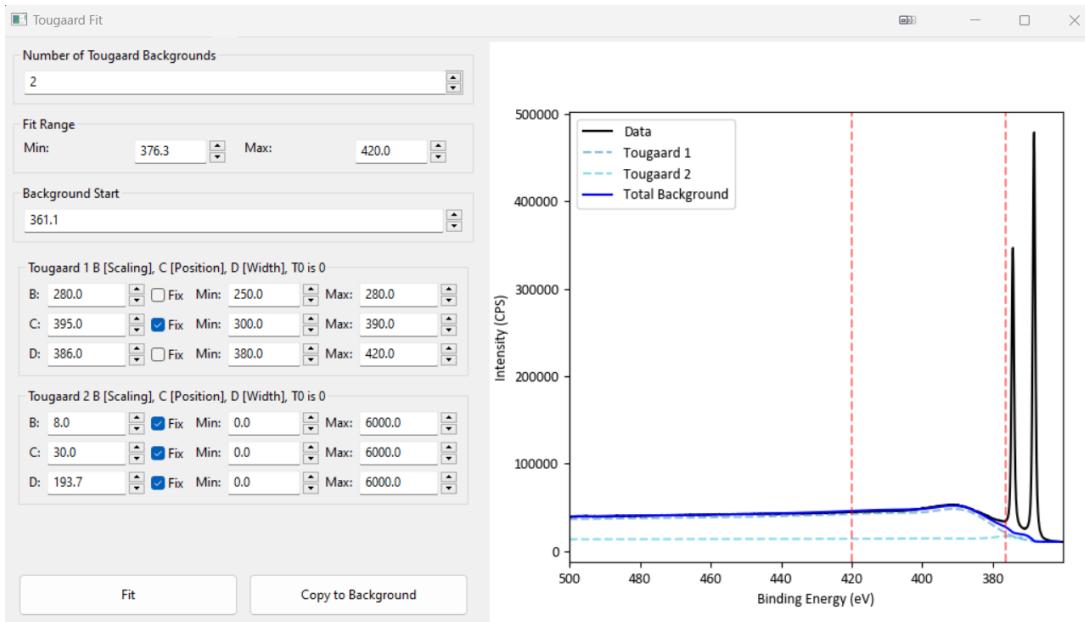


Figure 26: Tools to fit Tougaard background

- Height-based models: GL (Height), SGL (Height)
- Advanced models: Exp.Gauss, LA (Area, σ , γ), LA (Area, σ/γ , γ), LA*G (Area, σ/γ , γ)

The **Optimization Method** dropdown allows selection of different fitting algorithms:

- least squares: Default method, suitable for most cases
- powell: Derivative-free method, useful for complex problems
- nelder: Simplex algorithm for robust optimization
- cobyla: Constrained optimization method
- trust-constr: Trust-region method for constrained problems

Fitting Parameters:

- Convergence Limit: Sets maximum iterations for each fit (default: 50)
- Fit Iterations: Number of consecutive fitting cycles (default: 20)

Fit Quality Indicators:

- Coefficient of determination (R^2) measures goodness of fit (0-1):

$$R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2} \quad (4)$$

where y_i are the observed values, f_i are the predicted values, and \bar{y} is the mean of observed values.

- Relative Standard Deviation (RSD) indicates data scatter and goodness of fit:

$$RSD = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{y_i - f_i}{\sqrt{y_i}} \right)^2} \quad (5)$$

where N is the number of data points, y_i are the observed values, and f_i are the predicted values.

- Reduced chi-square statistic (Red. Chi 2) for fit quality:

$$\chi^2_{red} = \frac{1}{N-p} \sum_{i=1}^N \frac{(y_i - f_i)^2}{\sigma_i^2} \quad (6)$$

where N is the number of data points, p is the number of fitted parameters, y_i are the observed values, f_i are the predicted values, and σ_i are the uncertainties in the measurements.

- Actual Iterations: Number of iterations performed
- Current Fit: Displays progress during multiple fits

Peak Management Controls:

- "Add 1 Peak Singlet": Adds individual peak at maximum residual
- "Add 2 Peaks Doublet": Adds spin-orbit split pair with appropriate intensity ratios and energy splitting based on orbital type (p, d, f)
- "Remove Peak": Deletes currently selected peak
- "Accept": Validates current fit and updates results grid

Fitting Execution:

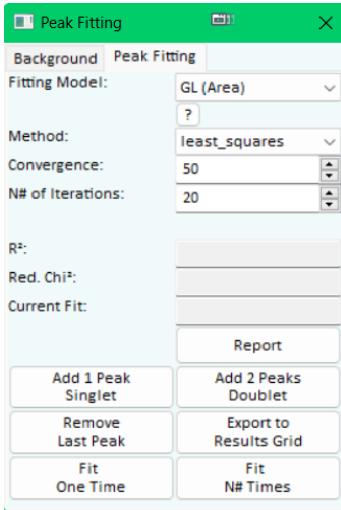


Figure 27: The Peak Model tab.

- "Fit One Time": Performs single optimization cycle
- "Fit Multiple Times": Executes specified number of consecutive fits, useful for escaping local minima

Peak parameters and constraints can be adjusted directly in the peak fitting grid or through interactive manipulation in the plot window. The fitting tab continuously updates quality indicators during optimization to help users assess fit convergence and reliability.

Gaussian G(E): The Gaussian line shape is defined as:

$$G(E; E_c, F, H, lg) = H \times \exp \left[-4 \cdot \ln 2 \times (1 - lg) \cdot \left(\frac{E - E_c}{F} \right)^2 \right] \quad (7)$$

where F is the full width at half maximum of the Gaussian function and E_c is the position (in energy) of the peak, H is the height of the peak and lg is the ratio between Lorentzian and Gaussian. The Gaussian peak has a symmetric, bell-shaped profile.

Lorentzian L(E): The Lorentzian line shape is defined as:

$$L(E; E_c, F, H, lg) = \frac{H}{1 + 4 \cdot lg \cdot \left(\frac{E - E_c}{F} \right)^2} \quad (8)$$

where F is the full width at half maximum of the Lorentzian function and E_c is the position (in energy) of the peak and H is the height of the peak. The Lorentzian peak resembles the classical, bell-shaped Gaussian peak, but it has two important features that distinguish it from a Gaussian: it is a little narrower at its apex and it extends out further on its sides/edges.

Voigt V(E): The Voigt function is a combination of a Gaussian function convolved to a Lorentzian function. The FWHM (F) cannot be directly provided and depends on the width of the Gaussian ($2.355 \cdot \sigma$) and of the Lorentzian ($2 \cdot \gamma$). The function is directly provided by the LMFIT library and is expressed as followed:

$$V(E; A, E_c, \sigma, \gamma) = \frac{A \cdot \text{Re}[w(z)]}{\sigma \cdot \sqrt{2 \cdot \pi}} \quad (9)$$

where

$$z = \frac{E - E_c + i\gamma}{\sigma \sqrt{2}} \quad (10)$$

and

$$w(z) = e^{-z^2} \text{erf}(-iz) \quad (11)$$

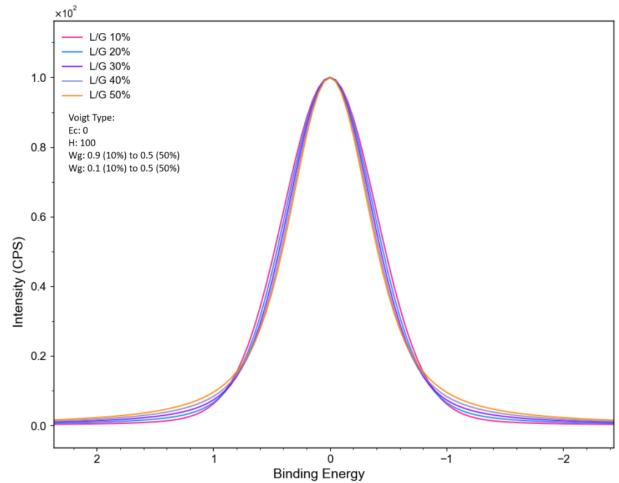


Figure 28: Plot of Voigt models of Height (H) of 100 and of decreasing Gaussian (0.9 to 0.5) width and increasing Lorentzian width (0.1a.i to 0.5a.u.)

with $\text{erf}()$ is the complementary error function, A corresponds to the amplitude/area, E_c to the center, and σ to the Gaussian width. The parameter γ is linked to the Lorentzian width. Fig. 28 shows models of different L/G ratio. It has to be noted that the Voigt model is considered to be the most true model. Therefore all the other model are compared to the Voigt model. From experiment, it was found that a peak with a width between 1.0 to 1.6 eV has a L/G ratio value of 20%; a peak with a width > 1.6 eV has a L/G ratio between 10-20% and a peak with a width < 1.0 eV has a L/G ratio between 20-60%. Because the width peak cannot directly be given, Kherve-Fitting provides two models, namely Voigt(Area, σ , γ) and Voigt(Area, lg , σ).

Voigt(Area, σ , γ): This model allows to change and constraint the position (E_c), Area (A), width of the Gaussian part (W_g or $2.355 \cdot \sigma$) and the width of the Lorentzian part (W_l or $2 \cdot \gamma$). In a doublet or 2 peaks model, the width of the Gaussian and Lorentzian can be varied independently as shown in Fig. 29. Note that for a voigt model, the title of the columns after the "FWHM (eV)" column is named "L/G", "Area (CPS.eV)", "W_g", "W_l".

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_l}	S
A	Sr3d5/2 p1	132.49	99535	0.98	27.89	118110	0.80	0.31	0.6 ^a
		126.08,142.08			1:1e7	0.01:3	0.01:3		
B	Sr3d3/2 p2	134.24	68223	0.98	27.92	80766	0.80	0.31	0.6 ^a
		A+1.7#0.2			A*0.667#0. A*1	A*1			

Figure 29: Voigt(Area, σ , γ) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The Height (H), FWHM (F), lg ratio are not adjustable. The lg ratio is calculated from the value of W_g and W_l .

Voigt(Area, lg , σ): This model allows to change and constraint the position (E_c), Area (A), lg ratio and the width of the Gaussian part (W_g or $2.355 \cdot \sigma$). The width of the Lorentzian part (W_l or $2 \cdot \gamma$) is obtained from the value of the lg ratio. This is particularly useful as one would want to keep the lg ratio the same in peaks model where peaks have different overall calculated FWHM (F). Fig. 30 shows the peak fitting parameter grid for a doublet or 2 peaks model. Like the Voigt(Area, σ , γ), The FWHM (F), peak Height (H) and the width of the Gaussian can be varied/constrained independently as shown in Fig. 29.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_l}	S
A	Sr3d5/2 p1	132.49	99569	0.98	28.21	118386	0.80	0.31	
		126.08,142.08			2:80	1:1e7	0.01:3		
B	Sr3d3/2 p2	134.24	68278	0.98	27.61	80452	0.80	0.31	
		A+1.7#0.2			A*1	A*0.667#0. A*1			

Figure 30: Voigt(Area, lg , σ) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The Height (H), FWHM (F), lg ratio are not adjustable. The width of the Lorentzian or $2 \cdot \gamma$ is calculated from the value of W_g and lg ratio.

SkewVoigt(Area, lg , σ , skew): This model is similar to the Voigt(Area, lg , σ) that is it allows the change and constraint the position (E_c) Area (A), lg ratio and the width of the Gaussian (W_g) and an additional variable named the skew which allows the possibility of creating asymmetric Voigt models. Fig ?? shows the peak fitting parameter grid for a doublet. The values in Grey (like Height and FWHM) are calculated values that cannot be changed nor controlled.

Gaussian-Lorentzian Product GL(E, lg): The Gaussian-Lorentzian product (GL) peak shape is a combination of the Gaussian and Lorentzian functions:

$$GL(E; E_c, F, H, lg) = H \times L(E; E_c, F, 1, lg) \times G(E; E_c, F, 1, lg) \quad (12)$$

where lg is the Lorentzian to Gaussian ratio in %, F is the full width at half maximum of the Lorentzian function and E_c is the position (in energy) of the peak and H is the height of the peak. The GL model is a pseudo-voigt model that mimic the voigt function. Table 2 shows the lg ratio value required to fit a true Voigt peak model of Area 100

and of different lg ratio. This shows that the GL model does not fit well the Voigt peak with a lg ratio above 30%. Fig. 31 shows the poor fit even for a Voigt model with a lg ratio of 20%

Voigt lg (%)	GL lg (%)	Errors
10	30.27	RSD: 0.46, Area: 99.6
20	49.04	RSD: 0.55, Area: 95.3
30	66.14	RSD: 0.59, Area: 89.8
40	80.44	RSD: 0.57, Area: 83.7
50	90.46	RSD: 0.49, Area: 77.0

Table 1: Conversion table between the lg ratio values of the voigt model and GL model. The voigt peak has an area A of 100, a Height H of 95, a width ≈ 1 eV and a varying lg ratio.

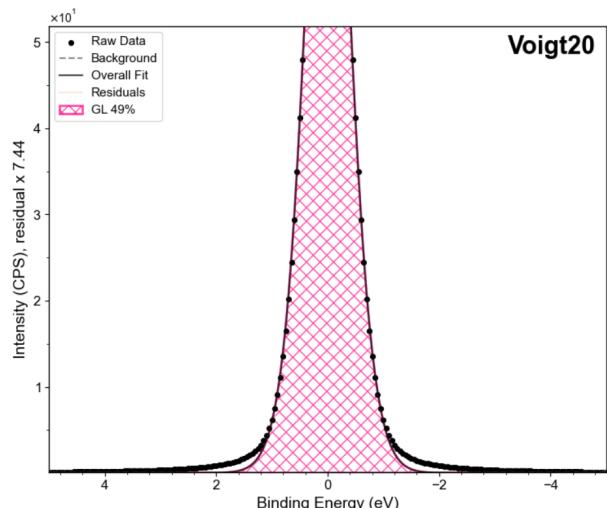


Figure 31: Comparison plot between the Voigt model of area A: 100, a height H of 95, a lg ratio of 20% with the GL(lg) with a lg ratio of 49%.

The GL model allows to constraint the peak position (E_c), the FWHM (F), the L/G ratio (lg), and the height or area depending on whether GL (Height) or GL (Area) has been chosen. The figure below shows the peak fitting table of the 2 GL(Area) peak models that were used to fit the Sr3d doublet of a STO crystal. The constraint rows are colored in green for ease of distinction and the columns/cells that are not editable are left blank. Unlike CasaXPS where it is typically fixed (e.g., GL(30)), the GL models allow for the L/G ratio (lg) to be a variable parameter that can be optimized automatically during fitting. The lg ratio would differ depending on the width of the peak. For broad peaks, the fit typically converges to a more Gaussian-like shape (10-30%), while narrow peaks tend toward more Lorentzian character (40-80%). In the case of Fig. ??, the lg was fixed to 30%. The area of peak B was set to A*0.667 with a variation of +/- 0.05 eV. The variation sign is understood by the software by using the "#" symbol.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_I}
A	Sr3d5/2 p1	132.49	100007	1.05	30.00	112093		
		126.08,142.08		0.3:3.5	Fixed	1:1e7		
B	Sr3d3/2 p2	134.24	69733	1.06	30.00	78690		
		A+1.7#0.2		A*1	A*1	A*0.667#0.05		

Figure 32: GL(Area) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The height, σ and γ are not adjustable.

Gaussian-Lorentzian Sum SGL(E, lg): The Gaussian-Lorentzian sum (SGL) peak shape is a linear combination of the Gaussian and Lorentzian functions:

$$SGL(E; E_c, F, H, lg) = lg \times H \times L(E; E_c, F, 1, 1) + (1 - lg) \times G(E; E_c, F, 1, 0) \quad (13)$$

Voigt lg (%)	GL lg (%)	Errors
10	10.23	RSD: 0.06, Area: 95.92
20	20.29	RSD: 0.13, Area: 91.55
30	31.47	RSD: 0.20, Area: 87.09
40	43.54	RSD: 0.25, Area: 83.0
50	56.44	RSD: 0.27, Area: 78.3

Table 2: Conversion table between the lg ratio values of the voigt model and SGL model. The voigt peak has an area A of 100, a Height H of 95, a width ≈ 1 eV and a varying lg ratio.

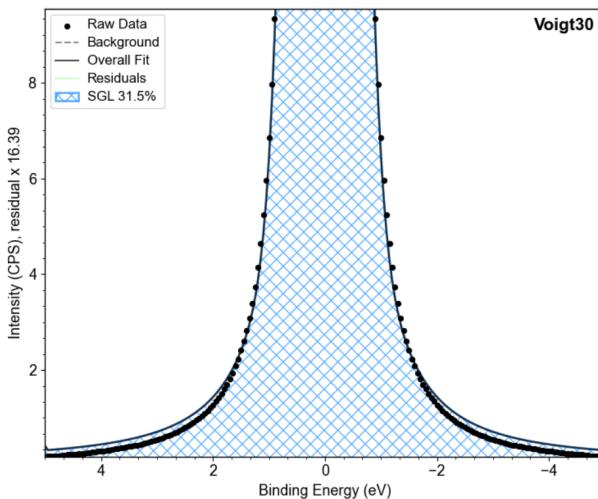


Figure 33: Comparison plot between the Voigt model of area A: 100 , a height H of 93, a lg ratio of 30% with the SGL(lg) with a lg ratio of 31.5%.

Like the GL model, the SGL model allows to constraint the peak position (E_c), the FWHM (F), the L/G ratio (lg), and the height or area depending on whether SGL (Height) or SGL (Area) has been chosen. The constraint rows are colored in green for ease of distinction and the rows that are not editable are left blank. In the case shown below, the lg ratio was let to vary between 20 to 40% and the best fit value was obtained for a lg of 28%.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_I}
A	Sr3d5/2 p1	132.49	99969	0.98	37.00	118473		
		126.08,142.08		0.3:3.5	2:80	1:1e7		
B	Sr3d3/2 p2	134.24	68565	0.98	37.00	81202		
		A+1.7#0.2		A*1	A*1	A*0.667#0.05		

Figure 34: SGL(Height) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The Area, σ and γ are not adjustable.

Pseudo-Voigt by LMFIT: The Pseudo-Voigt peak shape is a linear combination of Gaussian and Lorentzian functions and is similar to the SGL model but is directly given by the LMFIT library. :

$$f(E; A, E_c, \sigma, lg) = \frac{(1 - lg) \cdot A}{\sigma_g \sqrt{2\pi}} \exp \left[-\frac{(E - E_c)^2}{2\sigma_g^2} \right] + \frac{lg \cdot A}{\pi} \left[\frac{\sigma}{(E - E_c)^2 + \sigma^2} \right] \quad (14)$$

where

$$\sigma_g = \frac{\sigma}{\sqrt{2 \ln(2)}} \approx \frac{\sigma}{1.17741} \quad (15)$$

and the parameters are:

- A : Amplitude
- E_c : Peak center
- σ : Sigma (half width at half maximum of the Gaussian component)
- lg : Fraction of Lorentzian component, must be between 0 and 1 in this equation however it is given in % in the peak fitting grid.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_I}
A	Sr3d5/2 p1	132.49	99969	0.98	37.00	118473		
		126.08,142.08		0.3:3.5	2:80	1:1e7		
B	Sr3d3/2 p2	134.24	68565	0.98	37.00	81202		
		A+1.7#0.2		A*1	A*1	A*0.667#0.05		

Figure 35: Pseudo-Voigt(Area) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The height value is given as an indication but not readable.

Asymmetric Lorentzian (LA): The Asymmetric Lorentzian (LA) or split Lorentzian line shape is a Lorentzian line shape raised by the power σ or γ . The LA model is a pure Lorentzian model if both σ or γ are equal to 1. This model is symmetrical if σ is equal to γ . LA(E) is expressed as follow:

$$LA(E; H, E_c, F, \sigma, \gamma, 0) = \begin{cases} \frac{H}{[1+4 \cdot (\frac{E-E_c}{F})]^\gamma} & E \leq E_c \\ \frac{H}{[1+4 \cdot (\frac{E-E_c}{F})]^\sigma} & E > E_c \end{cases} \quad (16)$$

where F is the full width at half maximum, E is the peak position, and α and β are the asymmetry parameters on the lower and higher kinetic energy sides of the peak, respectively. The LA line shape allows for independent control of the asymmetry on the two sides of the peak, providing more flexibility in the peak fitting.

In contrast to CasaXPS, two of these models originate from a pure Lorentzian with no convolution of Gaussian and is comparable to the CasaXPS $\text{LA}(\alpha, \beta, 0)$. Fig. 36 show a comparison of different LA models with the true Voigt and Table 3 gives the required σ and γ values for different lg ratios. It shows that the LA model fails to fit well the voigt model but the results found for the are shows that the fit is better than the GL and SGL model.

lg (%)	σ & γ	Errors
10	9.58	RSD: 0.45, Area: 97.8
20	4.42	RSD: 0.46, Area: 95.8
30	2.74	RSD: 0.42, Area: 94.0
40	1.98	RSD: 0.35, Area: 94.0
50	1.57	RSD: 0.22, Area: 93.0

Table 3: Conversion table between lg ratio values and σ and γ for a voigt peak of area A of 100, a width ≈ 1 eV and a varying lg ratio

KherveFitting provides three different control of the LA model:

LA(Area, σ , γ): This model allows the control of σ and γ independently of each other. This is similar to the LA function in CasaXPS called $\text{LA}(\alpha, \beta, 0)$ with a Gaussian of width of 0 meV.

It differs to it, however as constraints can be implemented to σ and γ allowing it to tune the peak shape automatically. One drawback of tuning σ and γ independently is that the symmetry of the peak is difficult to keep constant if one wants to have calculated automatically using constraint. Fig. 37 shows the peak fitting parameter grid for a doublet or 2 peaks model using this model. The Height (H) and the ratio σ/γ are grey as they can be read but cannot be changed. In this doublet the peak B shows that FWHM (F), σ and γ are in function of peak A by A^* .

LA(Area, σ/γ , γ): This model allows the control of γ and the ratio between σ and γ , namely σ/γ (%). This is particularly useful to control the symmetry and asymmetry of the peak model. Like the LA(Area, σ , γ), this model is similar to the casaXPS $\text{LA}(\alpha, \beta, 0)$, but the constraints imposed by KherveFitting on γ and σ/γ make it much more powerful. In addition to the fact that this model is easy to compute, it makes it a good candidate to replace the Voigt model. Fig. 38 shows the peak fitting parameter grid for the Sr 3d model using this peak shape. Here, the Height (H) and σ are read-only and cannot be changed. The value of σ is calculated from γ and the σ/γ ratio.

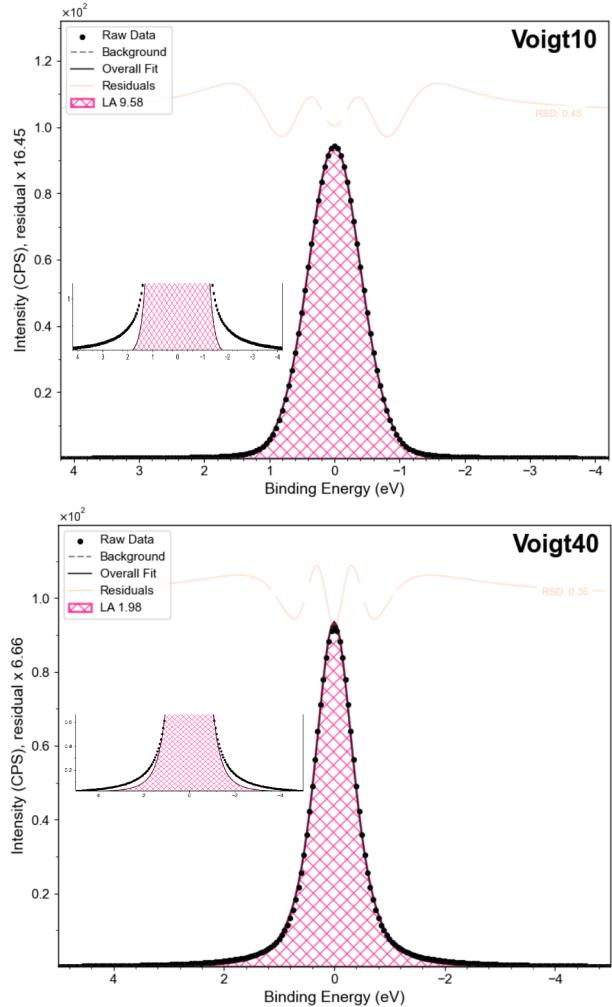


Figure 36: Comparison plot between the Voigt model of area A: 100 with lg of 10% (top figure) and 40% (bottom figure) with the $\text{La}(\sigma, \gamma, 0)$ (No gaussian width). σ and γ values are shown in Table 3. The inset shows a zoom to about $\times 100$.

L_{AxG}(Area, σ/γ , γ): This model is similar to the LA(Area, σ/γ , γ) model but the asymmetric Lorentzian is then convoluted by a Gaussian peak of a width W_g . This model allows for the control of γ , the ratio between σ and γ (σ/γ), and the width of the convoluting Gaussian peak (W_g). The convolution with a Gaussian peak can help to better fit peaks that have a more Gaussian-like shape while still maintaining the asymmetry provided by the LA function. Fig. 39 shows the peak fitting parameter grid for a doublet model using this peak shape. The Height (H) and σ are read-only and cannot be changed, with σ being calculated from γ and the σ/γ ratio.

ExpGauss(Area, σ , γ) Exponentially Modified Gaussian: The Exponentially Modified Gaussian (Exp-Gaussian) model is a convolution of a Gaussian and an exponential decay function. It is commonly used to describe peaks with an asymmetric tail. The ExpGaussian

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_I}	Skew
A	Sr3d5/2 p1	132.49	101227	0.96	50.71	112805	2.86	2.78	0.61
		126.08,142.08		0.3:3.5		1:1e7	0.01:10	0.01:10	
B	Sr3d3/2 p2	134.25	69747	0.96	50.70	78114	2.86	2.78	0.60
		A+1.7#0.2		A*1		A*0.667#0.	A*1	A*1	

Figure 37: LA(Area, σ , γ) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The Height (H), σ/γ ratio are not adjustable where the latter is calculated from the value of σ and γ .

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_I}	Skew
A	Sr3d5/2 p1	132.49	101295	0.96	50.00	113088	2.77	2.77	0.64
		126.08,142.08		0.3:3.5		Fixed	1:1e7	0.01:10	
B	Sr3d3/2 p2	134.25	69508	0.96	50.00	78031	2.77	2.77	0.64
		A+1.7#0.2		A*1		A*0.667#0.	A*1	A*1	

Figure 38: LA(Area, σ/γ , γ) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The Height (H) and σ are not adjustable but with the latter being calculated from the value of γ and σ/γ ratio This ratio is given in %.

model is defined as:

$$\text{ExpGaussian}(E; A, E_c, \sigma, \gamma) = \frac{A\gamma}{2} \exp [\gamma (E_c + \gamma\sigma^2/2 - E)] \operatorname{erfc} \left(\frac{E_c + \gamma\sigma^2 - E}{\sigma\sqrt{2}} \right) \quad (17)$$

where A is the amplitude, μ is the center of the Gaussian component, σ is the standard deviation of the Gaussian component, and γ is the rate of exponential decay. The erfc function is the complementary error function. The ExpGaussian model introduces asymmetry to the peak shape through the exponential decay component. The degree of asymmetry is controlled by the γ parameter. When $\gamma = 0$, the model reduces to a pure Gaussian. As γ increases, the asymmetry becomes more pronounced, with a longer tail on one side of the peak. The ExpGaussian model is particularly useful for fitting peaks in spectroscopic data where the peaks exhibit asymmetry due to various physical processes, such as detector response or sample inhomogeneity. It provides a more accurate representation of the peak shape compared to a symmetric Gaussian or Lorentzian model. Fig. ?? shows a comparison of the ExpGaussian model with different values of γ , illustrating the effect of the exponential decay on the peak shape. The asymmetry becomes more evident as γ increases, with a longer tail on the right side of the peak.

SkewVoigt(Area, σ , γ) Exponentially Modified Gaussian: The Exponentially Modified Ga

Corrected Area

The Corrected Area A_c of a peak of area A_{peak} fitted using the models above can be obtained using the formula:

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ_{W_g}	γ_{W_I}	Skew
A	Sr3d5/2 p1	132.48	100311	0.64	50.00	114796	1.52	1.52	0.61
		126.08,142.08		0.3:3.5		Fixed	1:1e7	0.01:14	0.2:2
B	Sr3d3/2 p2	134.23	68700	0.64	50.00	78520	1.53	1.53	0.60
		A+1.7#0.2		A*1		A*0.667#0.	A*1	A*1	

Figure 39: LAXG(Area, σ/γ , γ) peak fitting grid after fitting the Sr 3d of SrTiO₃ crystal. The Height (H) and σ are not adjustable, with the latter being calculated from the value of γ and σ/γ ratio. The ratio is given in %. The width of the convoluting Gaussian peak is denoted as W_g .

$$A_c = \frac{A_{\text{peak}}}{\text{RSF} \times \text{TXFN} \times \text{ECF} \times \text{ACF}} \quad (18)$$

where:

- RSF: Relative Sensitivity Factor for the element
- TXFN: Transmission Function of the instrument for a specific pass energy PE. This is set to 1.0 for Thermo Kalpha instrument. If the file was imported using Vamas (.vms), or Kratos (.Kal), or Ulvac-Phi (.spe) then KherveFitting read the transmission values and correct the intensity values accordingly. The results is shown on Col B, C, D of the Excel file.
- ACF: Angle Correction Factor, which accounts for the angular distribution of photoelectrons. The factor is given by:

$$\text{ACF} = 1 - \frac{\beta}{4} (3 \cos^2 \theta - 1) \quad (19)$$

where β is the asymmetry parameter for the orbital of interest, and θ is the take-off angle of the photoelectrons relative to the sample surface. For instruments with a magic angle of 54.7°, the correction factor ACF = 1.

- ECF: Energy Compensation Factor

The ECF depends on the selected library and accounts for either:

- The inelastic mean free path (Scofield libraries)
- The transmission function included in the original Wagner sensitivity factors

Three methods are available for ECF calculation:

1. Kinetic Energy Approximation

- Scofield: $\text{ECF} = \text{KE}^{0.6}$
- Wagner: $\text{ECF} = \text{KE}^{1.0}$
- Auger: $\text{ECF} = 1.0$

2. TPP-2M Method for calculating Inelastic Mean Free Path (IMFP), short for Tanuma, Penn, and Powell, who developed this relation (Tanuma et al., 1993),

provides an accurate empirical formula for calculating the inelastic mean free path (IMFP or λ) of electrons in various materials. This method is based on the kinetic energy (E) of electrons and incorporates material properties such as density, molecular weight, and the number of valence electrons. The IMFP (λ) calculation is vital in surface-sensitive techniques like XPS, where understanding the escape depth of electrons is crucial for quantification. The TPP-2M formula for IMFP (λ) is given by:

$$\lambda = \frac{E}{E_{pl}^2} \left[\beta \ln(\gamma \cdot E) - \frac{C}{E} + \frac{D}{E^2} \right], \quad (20)$$

where:

$$E_{pl} = 28.8 \sqrt{\frac{N_v \cdot \rho}{M}} \quad (21)$$

$$\beta = -0.10 + \frac{0.944}{\sqrt{E_{pl}^2 + E_g^2}} + 0.069\rho^{0.1} \quad (22)$$

$$\gamma = 0.191\rho^{-0.5} \quad (23)$$

$$C = 1.97 - 0.91 \left(\frac{N_v \cdot \rho}{M} \right) \quad (24)$$

$$D = 53.4 - 20.8 \left(\frac{N_v \cdot \rho}{M} \right), \quad (25)$$

where E is the electron kinetic energy (eV), ρ is the material density (g/cm^3), M is the molecular weight (g/mol), N_v is the number of valence electrons per atom, E_{pl} is free electron plasmon energy (eV) and E_g is the bandgap energy (eV). The resulting IMFP (λ) is reported in nanometers (nm).

For a general approximation applicable to metals and inorganic compounds, average matrix parameters can be used. Based on reference data, the following average values are assumed:

$$N_v = 4.684 \quad (\text{valence electrons/atom})$$

$$\rho = 6.767 \text{ g}/\text{cm}^3$$

$$M = 137.51 \text{ g/mol}$$

$$E_g = 0 \text{ eV}.$$

Substituting these values into the equations, we get:

$$E_{pl} = 28.8 \sqrt{\frac{4.684 \cdot 6.767}{137.51}} \approx 16.26 \text{ eV},$$

$$U = \frac{N_v \cdot \rho}{M} \approx 0.230.$$

To ensure consistency with software like Avantage, a scaling factor of 26.2 was applied to the calculated IMFP. This allows to match corrected areas with those obtained using $E^{0.6}$.

$$\text{ECF} = \lambda \times 26.2. \quad (26)$$

3. EAL Method for calculating the Inelastic Mean Free Path for Thin Film Sample.

An alternative to

the TPP-2M approach is the approximation using Martin Seah's universal equations for IMFP (λ) and the Effective Attenuation Length (EAL):

$$\lambda = \frac{0.73 + 0.0095E^{0.872}}{Z^{0.3}} \text{ (nm)} \quad (27)$$

$$\text{EAL} = \frac{0.65 + 0.007E^{0.93}}{Z^{0.38}} \text{ (nm)} \quad (28)$$

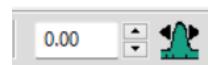
where:

- E : Photoelectron kinetic energy (in eV),
- Z : Average atomic number of the material.

The IMFP (λ) describes the average distance electrons can travel before undergoing inelastic scattering, while the EAL accounts for attenuation effects that reduce the signal's effective sampling depth. For thin-film quantification in XPS, the EAL model is particularly relevant as it adapts the analysis depth based on material and kinetic energy parameters. This ensures accurate quantification of elements in homogenous thin films and avoids overestimation of the signal contribution from deeper layers.

BE Correction

The BE correction button looks for a peak labeled 'C1s C-C' and calculates the difference from 284.8 eV. This correction is applied to all core levels. Fit all data before applying the BE correction.



Identification and quantification of Survey, to be continued...

KherveFitting allows for the measurement of areas over a certain range. This is particularly useful when quantifying from a Survey. Fig. ???. It can also be useful when a core level does not need to be peak fitted but only the areas needs to be obtained e.g. Mn2p, Fe2p.

Additional Features

- Export results to summary table
- Save to Excel and export to a word report
- Noise analysis tools
- Survey identification
- D-parameter analysis