KherveFitting
Help Guide

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Copyright

Authors

Dr. Gwilherm Kerherve & William SKinner, Department of Materials, Imperial College London, g.kerherve@imperial.ac.uk

Overview

KherveFitting, see Fig. 2, 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, Panda for manipulating Excel files.

Opening Files

KherveFitting can open Excel files (.xlsx) and import/convert VAMAS files (.vms), AVG 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.

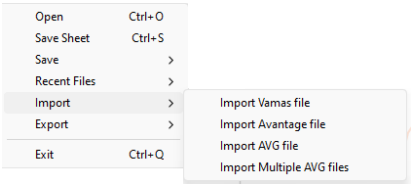


Figure 1: Import File Menu.

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 Excel (.xlsx) or VAMAS (.vms) 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 Donwards 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

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

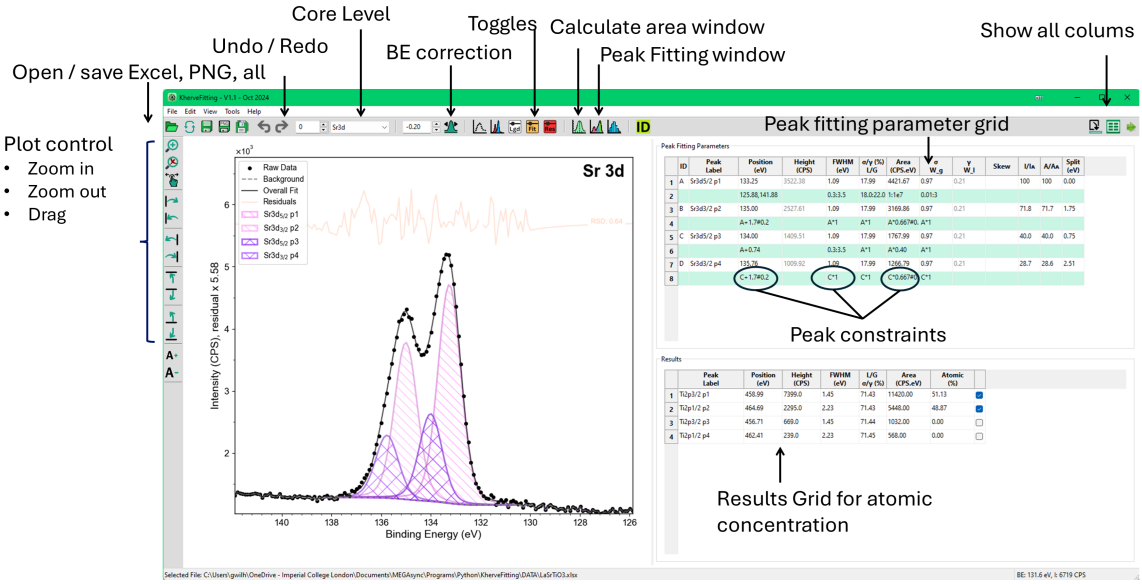


Figure 2: KherveFitting Main View

- 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 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 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

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 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: This is 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 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 pa-

rameters (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	☑
2	Sr3d3/2 p2	134.24	68128.83	0.98	27.99	80734.01	0.00	☐
3	Ti2p3/2 Ti Lattice	458.0	88040.5	1.03	36.29	114752.96	19.06	☑
4	Ti2p1/2 p2	463.74	25273.35	1.97	36.18	63027.98	0.00	☐
5	O1s O-Lattice	529.11	133453.7	1.12	17.96	172524.97	42.35	☑
6	O1s O-Surface	530.98	26126.81	2.42	17.95	72969.95	17.91	☑

Figure 3: Results grid after fitting the Sr 3d of $SrTiO_3$ 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.

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. 4. 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.

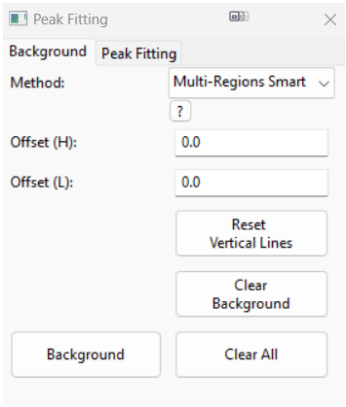


Figure 4: The Background tab.

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 5.

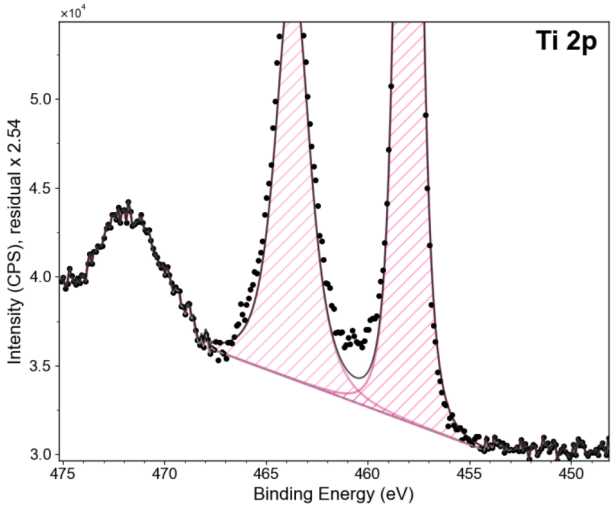


Figure 5: Ti 2p core level fitted with a Linear background

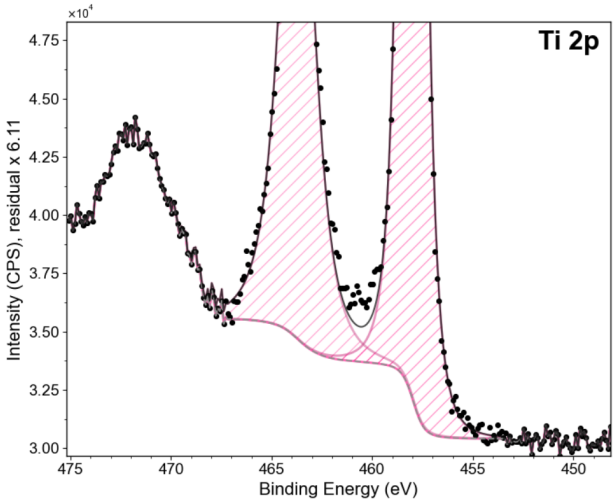


Figure 6: Ti 2p core level fitted with a Shirley background

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:

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

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 KherveFitting is set to 100 by default and for all the other methods. Fig. 6 shows the 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 oversubtraction 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.

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)
- 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:

- R^2: Coefficient of determination (0-1), measures goodness of fit
- RSD: Relative standard deviation, indicates data scatter and goodness of fit
- Red. Chi^2: Reduced chi-square statistic for fit quality
- Actual Iterations: Number of iterations performed
- Current Fit: Displays progress during multiple fits

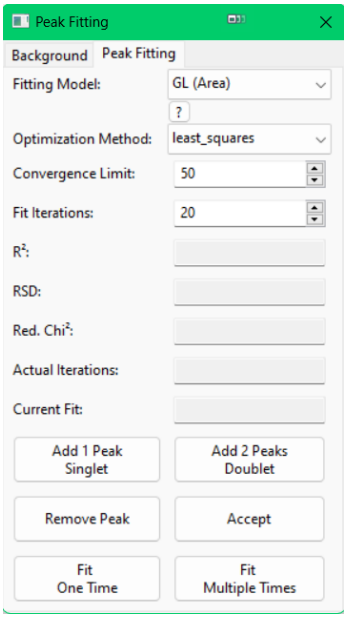


Figure 7: The Peak Model tab.

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:

- "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:

$$G(E;E_c,F,H,lg) = H \times \exp\left[-4 \cdot \ln 2 \times (1-lg) \cdot \left(\frac{E-E_c}{F}\right)^2\right] \quad (3)$$

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:

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

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:

$$V(E; A, E_c, \sigma, \gamma) = \frac{A \cdot \mathrm{Re}[w(z)]}{\sigma \cdot \sqrt{2 \cdot \pi}} \quad (5)$$

where

$$z = \frac{E - E_c + i\gamma}{\sigma\sqrt{2}} \quad (6)$$

and

$$w(z) = e^{-z^2}\,\mathrm{erf}(-iz) \quad (7)$$

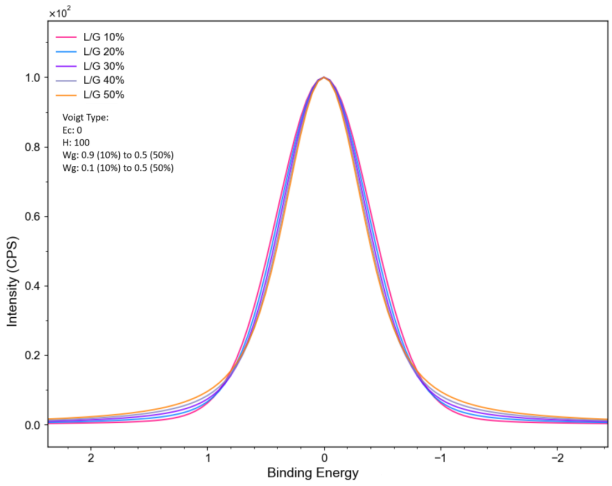


Figure 8: Plot of Voigt models of Height (H) of 100 and of decreasing Gaussian (0.9 to 0.5) width and increasing Lorentzian width (0.1a.i to 0.5a.u.)

with 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. 8 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, KherveFitting 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. 9. 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
		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+1.7#0.2				A*0.667#0.	A*1	A*1	

Figure 9: Voigt(Area, σ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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. 10 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. 9.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
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 10: Voigt(Area, lg, σ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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.

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

$$GL(E; E_c, F, H, lg) = H \times L(E; E_c, F, 1, lg) \times G(E; E_c, F, 1, lg) \quad (8)$$

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. 11 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.

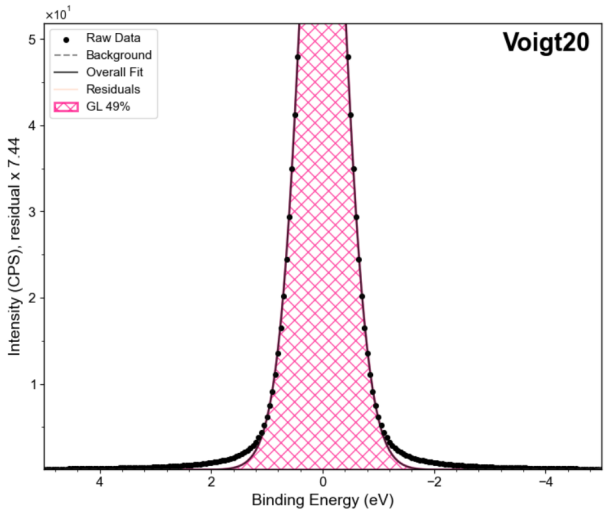


Figure 11: Comparison plot between the Voigt model of area A: 100 , a height H of 95, a lg ratio of 20% with the GL(lg) with a lg ratio of 49%.

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_l
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 12: GL(Area) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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:

$$SGL(E; E_c, F, H, lg) = lg \times H \times L(E; E_c, F, 1, 1) + (1 - lg) \times G(E; E_c, F, 1, 0) \quad (9)$$

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.

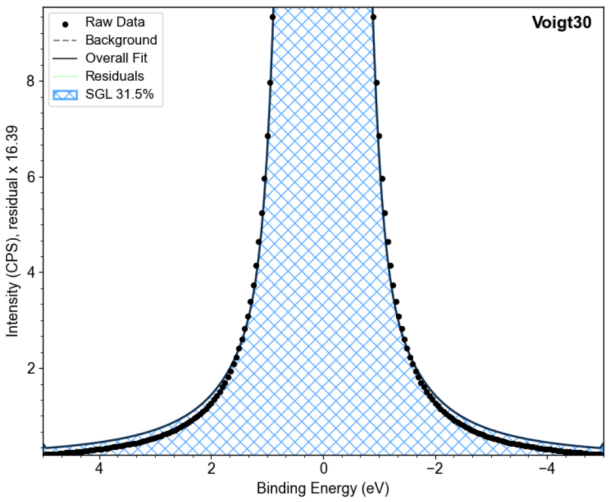


Figure 13: Comparison plot between the Voigt model of area A: 100 , a height H of 93, a lg ratio of 30% with the SGL(lg) with a lg ratio of 31.5%.

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_l
A	Sr3d5/2 p1	132.49	99969	0.98	28.47	104343		
		126.08,142.08	1:1e7	0.3:3.5	20:40			
B	Sr3d3/2 p2	134.24	68565	0.98	28.47	71518		
		A+1.7#0.2	A*0.667#0.05	A*1	A*1			

Figure 14: SGL(Height) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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. :

$$f(E;A,E_c,\sigma,lg) = \frac{(1-lg)\cdot A}{\sigma_g\sqrt{2\pi}}\exp\left[-\frac{(E-E_c)^2}{2\sigma_g^2}\right] + \frac{lg\cdot A}{\pi}\left[\frac{\sigma}{(E-E_c)^2+\sigma^2}\right] \tag{10}$$

where

$$\sigma_g = \frac{\sigma}{\sqrt{2\ln(2)}} \approx \frac{\sigma}{1.17741} \tag{11}$$

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_l
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 15: Pseudo-Voigt(Area) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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:

$$\mathrm{LA}(E;H,E_c,F,\sigma,\gamma,0) = \begin{cases} \frac{H}{\left[1+4\cdot\left(\frac{E-E_c}{F}\right)\right]^{\alpha}} & E \le E_c \\ \frac{H}{\left[1+4\cdot\left(\frac{E-E_c}{F}\right)\right]^{\beta}} & E > E_c \end{cases} \tag{12}$$

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 LA(α, β, 0). Fig. 16 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 fround 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 $\approx$ 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 LA(α, β, 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. 17 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*1.

`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 LA(α, β, 0), but the constraints imposed by KherveFitting on γ and σ/γ make it

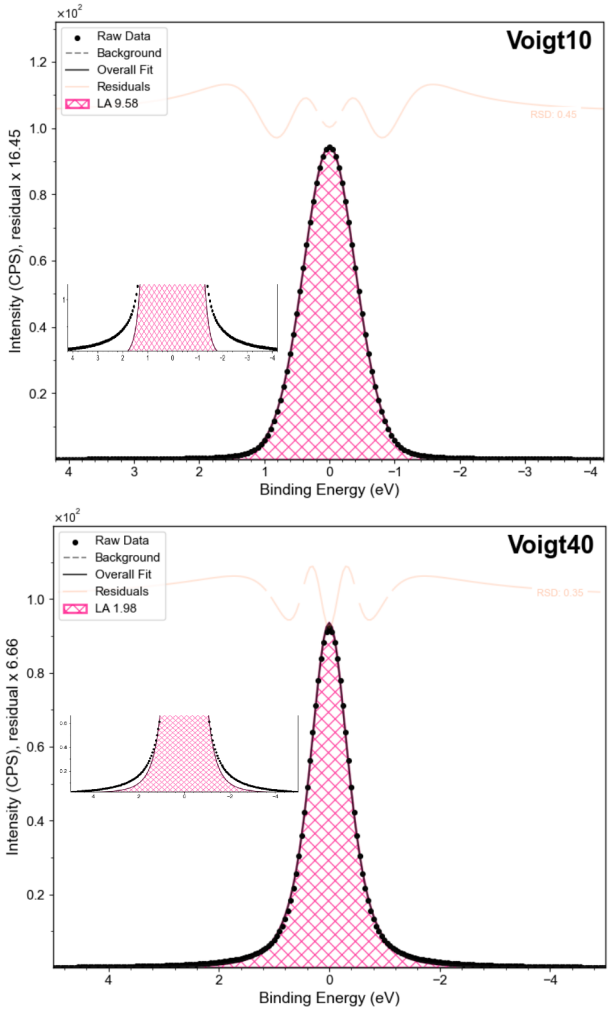


Figure 16: Comparison plot between the Voigt model of area A: 100 with lg of 10% (top figure) and 40% (bottom figure) with the La(σ, γ, 0) (No gaussian width). σ and γ values are shown in Table 3. The inset shows a zoom to about x100.

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. 18 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.

`LAxG(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. 19 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

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l
A	Sr3d5/2 p1	132.49	101227	0.96	50.71	112805	2.86	2.78
		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
		A+1.7#0.2		A*1		A*0.667#0.	A*1	A*1

Figure 17: LA(Area, σ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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_l	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*1	A*0.667#0.		A*1	

Figure 18: LA(Area, σ/γ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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 %.

calculated from γ and the σ/γ ratio.

ID	Peak Label	Position (eV)	Height (CPS)	FWHM (eV)	σ/γ (%) L/G	Area (CPS.eV)	σ W_g	γ W_l	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		0.01:4	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*1	A*0.667#0.		A*1	A*1

Figure 19: LAxG(Area, σ/γ, γ) peak fitting grid after fitting the Sr 3d of $SrTiO_3$ 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.

ExpGauss(Area, σ, γ) Exponentially Modified Gaussian: The Exponentially Modified Gaussian (ExpGaussian) 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 model is defined as:

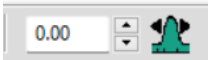
$$\text{ExpGaussian}(E; A, E_c, \sigma, \gamma) = \frac{A\gamma}{2} \exp\left[\gamma\left(E_c + \gamma\sigma^2/2 - E\right)\right] \text{erfc}\left(\frac{E_c + \gamma\sigma^2 - E}{\sigma\sqrt{2}}\right) \quad (13)$$

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.

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.



Additional Features

- Export results to summary table
- Noise analysis tools
- Survey Analysis