Potential Fluctuations PL Modeling Program Manual

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1 Introduction

This program provides the experimentalist with a powerful tool to efficiently analyse photoluminescence (PL) measurements with regards to possible potential fluctuations. The versatility of the program allows for its broad use over different PL spectra, including the possibility to correct for interference, if needed. The program was developed in *Python*. The band gap fluctuations (BGF),[1, 2] electrostatic fluctuations (EF),[3] unified potential fluctuations (UPF)[4] and interference function (IF)[5] models were implemented in this environment, after which a user-friendly interface was developed that bundles the models into one program. This section describes the working of the program and the possibilities available to the user for the interpretation of PL measurements.

2 Basic Description of the Program

The starting screen is shown in Figure 1, which has one tab labelled 'Main'. To import data, click on the 'Open data' button, which opens a window for the user to select the file with measurement data. The first column of the file should contain the independent variable of the measurement (wavelength or energy), and the rest of the columns the PL intensity at the corresponding wavelength for different measurements. Select the proper units of the data from the drop-down list under the 'Open data' button. Each PL spectra is opened in a separate tab and labelled according to the column name.

To fit all the opened data according to a specific model for IF and PL, select the desired models from the drop-down list in the 'Fit all data' section. Then, depending on whether the user wants to fit the IF and PL or only the PL parameters, click on the corresponding button in the same section. This action fits the selected models to each of the opened data tabs and shows the fit results in the table under the section 'Fit results' when the fitting routine is completed. Assuming the imported data file consists of two measurements ('PL1' and 'PL2'), the window shown in Figure 2 is obtained after fitting the BGF model with no interference.

The user can save the fit results by clicking on the 'Save fit results' button in the 'Fit results' section (this outputs the displayed table to a `.csv` file) or export the plot data for all measurements by clicking on the 'Export all plot data' button in the same section (this outputs the data, IF model, data corrected with IF and PL model at each wavelength for each measurement, also to a `.csv` file). The independent variable for the exported data will be the one selected from the drop-down list in the 'Fit all data' section. The 'Model error' in the table is also computed based on this variable.

Instead of fitting all the data to the same models, the user may choose to analyse each measurement individually, which can be done by clicking on the corresponding tab. Taking as an example 'PL1', the

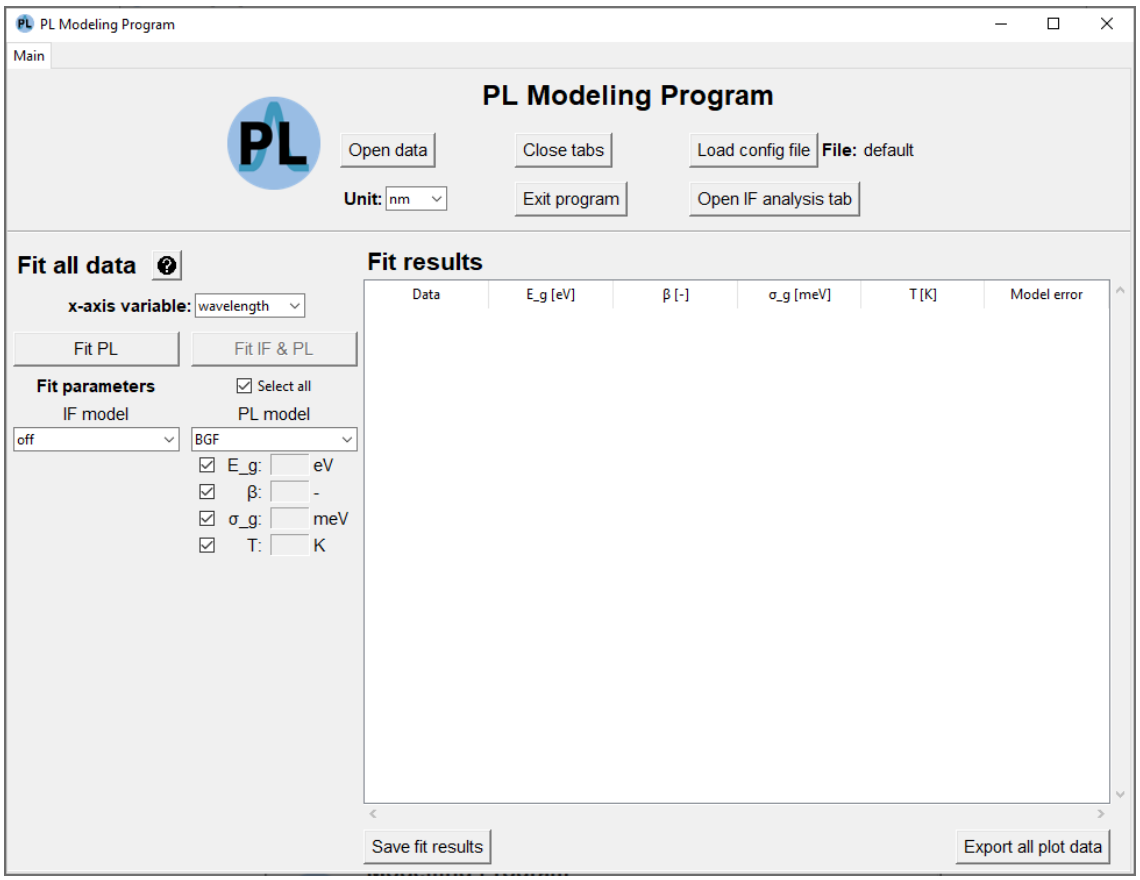

Figure 1: Starting screen of the PL modeling program.

screen in Figure 3 is shown. The plots are located on the left side. The top plot shows the normalised raw data and the current IF model, whereas the bottom depicts the data corrected for interference with the IF and the current PL model. A toolbar at the bottom left allows the user to pan and zoom the plots, configure the layout and save the figure to a file. On the right side, the different models, fit possibilities and other options are shown. The 'Interference Correction' section allows the user to change the model parameters of the currently selected model (the 'PL1' measurement does not need to be corrected for interference; the IF model is only shown for demonstration purposes). This can be done by sliding the blue rectangle, entering the value in the box followed by the 'Enter' key or by clicking on the up and down arrows (placing the cursor in the box and navigating with the 'Up' and 'Down' keys has the same effect). The same is true for the model parameters in the section 'PL Modeling'. The plots are updated dynamically as the parameters are modified.

In the 'Fit' section, the buttons for fitting the IF and PL or only the PL model have the same functionality as in the 'Main' tab, the difference is that here it only applies to the data of the current tab. When the 'Fit' option of the model parameters is selected, the corresponding parameter is taken as a variable in the fitting procedure. Otherwise, the parameter will be kept constant at the current value. This allows the user to input known data of the sample. The 'Select all' check button ensures all parameters are included in the fitting routine. Once the fitting is completed, the parameter values of the currently selected models are set to the optimal values and the plots are updated.

Finally, the 'Options' section has some extra possibilities. The buttons 'Save model values' and 'Export plot data' have the same functionalities as the 'Main' tab, exporting only the data of the current tab. To conclude, the x-axis variable can be changed between 'wavelength' and 'energy' by

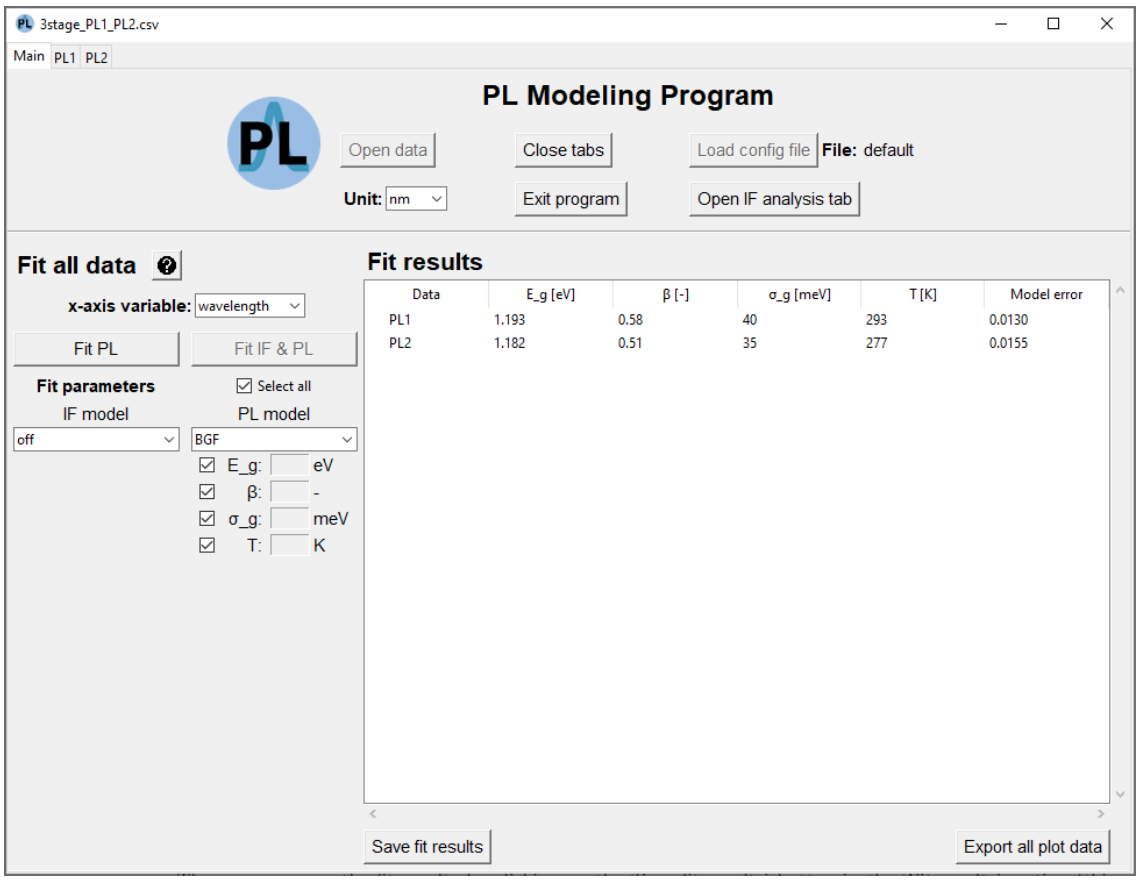

Figure 2: Result after fitting all the measurements with the BGF model.

clicking on the corresponding button.

The program can be closed by simply clicking on the 'Exit program' button on the 'Main' tab or by closing the window.

3 Detailed Description

The basic description of the program is introduced in Section 2. Here, more details are provided on the features of the program and advanced functionalities available to the user.

3.1 Data Import

The 'Open data' button allows to load data with a `.csv` extension. It is assumed that the first column contains the wavelength or energy data, and the remaining columns PL intensities for a set of measurements. The columns are separated by a comma and the first row holds the column names. Wavelength values must be in units of nm or $\mu\mathrm{m}$ and energy values in eV, and the decimal separator must be the point. Any other formats are not allowed. If necessary, a file can be converted to `.csv` for its use in the program. After a file is correctly imported, the window title is updated to the file name.

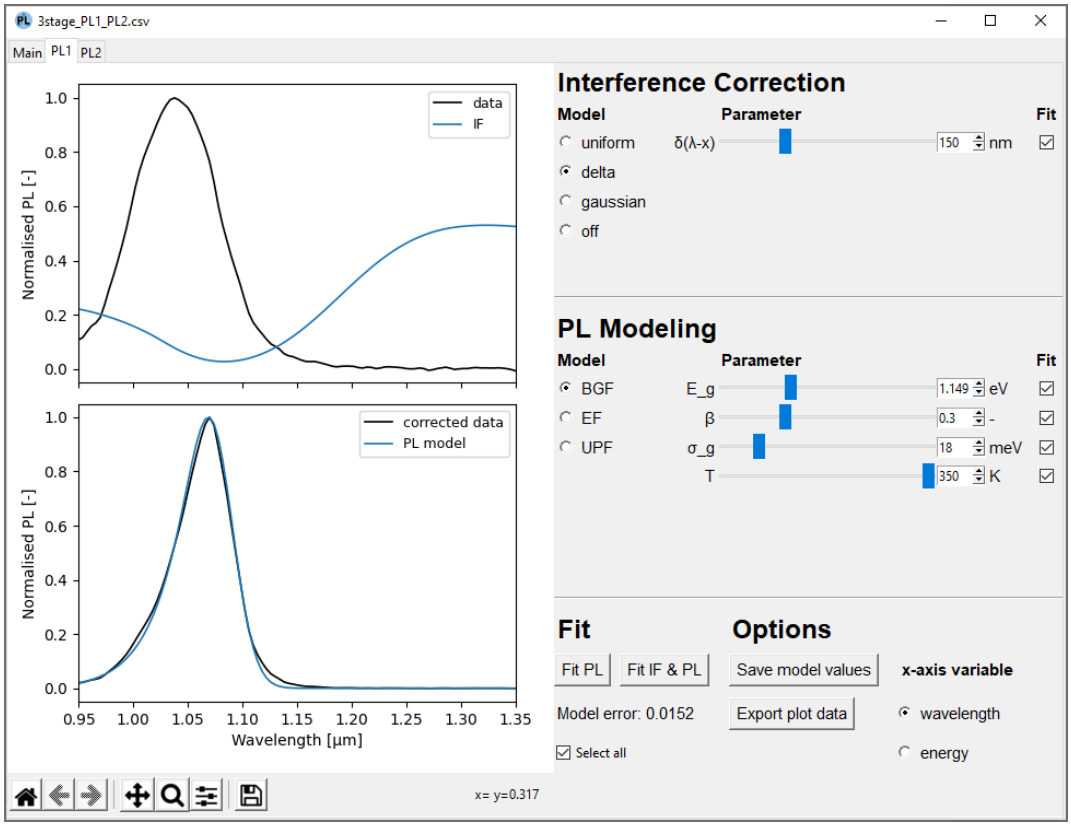

Figure 3: Individual tab for the analysis of the 'PL1' measurement.

3.2 IF Refractive Index Data

From the equations used to compute the interference function, it is clear that the optical data of air, CIGS and Mo need to be known. The program loads a default set of complex refractive indices for these layers. These are shown in Figure 4.

The optical constants are defined in a wavelength range from $0.3\,\mu\mathrm{m}$ to $2\,\mu\mathrm{m}$, which means that the domain of any imported data must be within these values. The user can load a different set of nk data by defining the directory where the optical data is located. In this directory, the nk data must be stored in the filenames `nk_air.csv`, `nk_CIGS.csv` and `nk_Mo.csv`, respectively, for the stack of layers. Each of these files must have the wavelength in nm as first column, and the refractive and absorption index as second and third columns. The column names should be in the first row ('Wavelength', 'n' and 'k'), and the column values are comma-separated. Setting a custom directory to look for these files can be done in the configuration file, which is explained next.

3.3 Configuration File

The models for IF and PL are created with a set of default parameter values and bounds when opening data. The choice of these values allow for a large number of samples to be analysed, but it might be the case that the user requires different parameter bounds or starting values for a set of data. With this in mind, it is possible for the user to change the default parameter settings by means of a configuration file. The default configuration file used is shown next:

```
#####################################################################
```

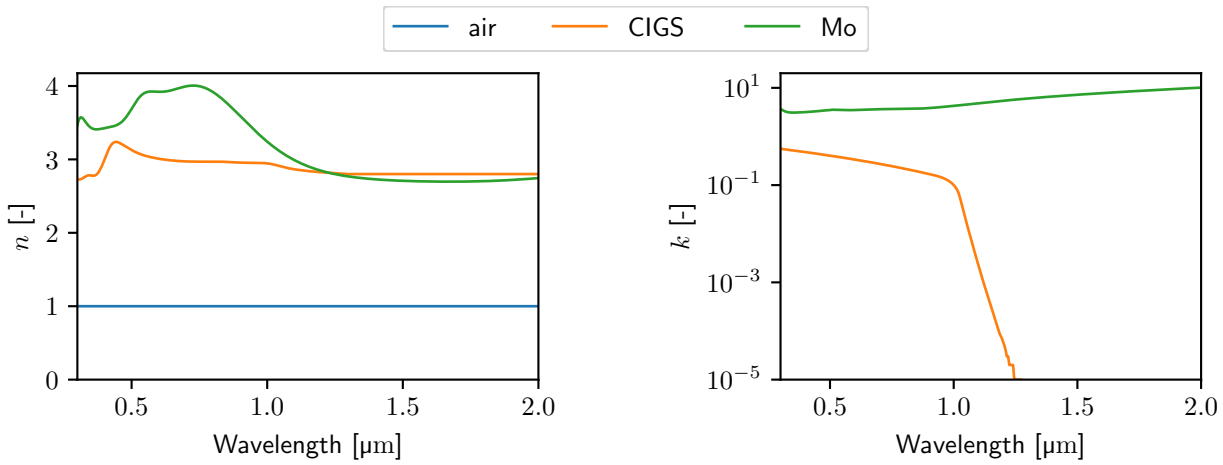

Figure 4: Complex refractive indices of the layers used in the computation of the IF. The absorption index of CIGS beyond $1.28\,\mu\mathrm{m}$ and of air over the whole spectrum is zero.

```
# Interference function model
[IF]
nk_dir = default
# Constants: m, m, m, -
thickness = 500e-9
wave_laser = 532e-9
R_rms = 50e-9
k = 1.0
# Parameters: m, m, m
delta = [0, 150e-9, %(thickness)s]
mu = [0, 150e-9, %(thickness)s]
sigma = [1e-9, 10e-9, %(thickness)s]

# Band gap fluctuations model
[BGF]
# Parameters: eV, -, eV, K
E_g = [1.1, 1.18, 1.25]
beta = [0, 0.5, 1]
sigma_g = [1e-3, 20e-3, 100e-3]
T = [250, 300, 350]

# Electrostatic fluctuations model
[EF]
# Parameters: eV, -, eV, eV, K, -
E_g = [1.1, 1.18, 1.25]
theta = [1, 1.25, 2]
gamma = [1e-3, 10e-3, 100e-3]
delta_mu = [0.1, 0.4, 0.8]
T = [250, 300, 350]
a_0d = [1, 20, 50]
```

```
# Unified potential fluctuations model
[UPF]
# Parameters: eV, -, eV, -, eV, K, -
E_g = [1.1, 1.18, 1.25]
beta = [0, 0.5, 1]
sigma_g = [1e-3, 20e-3, 100e-3]
theta = [1, 1.25, 2]
gamma = [1e-3, 10e-3, 100e-3]
T = [250, 300, 350]
a_0d = [1, 5, 50]
#####################################################################
```

The file is divided into three sections: IF, BGF, EF and UPF. In the case of IF, the user can start by defining the directory where the refractive index data described in Section 3.2 will be looked for. Simply type in the absolute path of the desired directory in the `nk_dir` variable (for example: `C:\Users\eriks\new_nk_dir`). If the value is `default`, the reference optical data is used. Continuing with the IF section, constant values of the model can be edited: absorber layer thickness, excitation laser wavelength of the PL setup, sample rms roughness and a scaling factor k (see [5]). The rest of the parameters in the configuration file correspond to the ones that can be adjusted in the program, and therefore consist of a list of three values: [lower bound, initial value, upper bound].

It is important to keep the same structure when editing the file, including parameter names, spaces, square brackets and commas. The program will show an error when the file format is incorrect or when the parameter values and bounds are inconsistent (it must hold that: lower bound ¡ initial value ¡ upper bound, for each parameter). The units of the constants and parameters are included in the line starting with a number sign '#' before their definition, and are given as a reference to the user; these lines are not relevant for the correct execution of the program. To conclude, the configuration file can only be loaded before importing measurement data with the 'Load config data' button in the 'Main' tab.

3.4 Fixing Parameters in the Main Tab

When fitting all the imported data at once in the 'Main' tab, it is also possible to fix parameters in the fitting routine. By default, all the model parameters are selected for fitting. By clicking on the check box of a parameter, the input field becomes active, allowing the user to input the parameter value in the units displayed next to the box. When the button 'Fit PL' or 'Fit IF & PL' is clicked, the program retrieves the values of the fixed parameters and updates the models of each data tab to indicate the parameters that should be kept constant during the fitting process. The 'Select all' check button at the top of the section ensures all the parameters are fitted. An example is shown in Figure 5, where the mean band gap E_g and temperature T are fixed to $1.18\,\mathrm{eV}$ and $293\,\mathrm{K}$, respectively, for the data imported in Figure 2.

Comparing the fit results to the ones where no parameter were fixed, we see that now both models are forced to a mean band gap of $1.18\,\mathrm{eV}$ and a temperature of $293\,\mathrm{K}$.

3.5 IF Analysis Tab

Clicking on the 'Open IF analysis tab' on the 'Main' tab opens a new tab labelled 'IF analysis'. This can be used to simultaneously correct multiple measurements with the same interference function. An

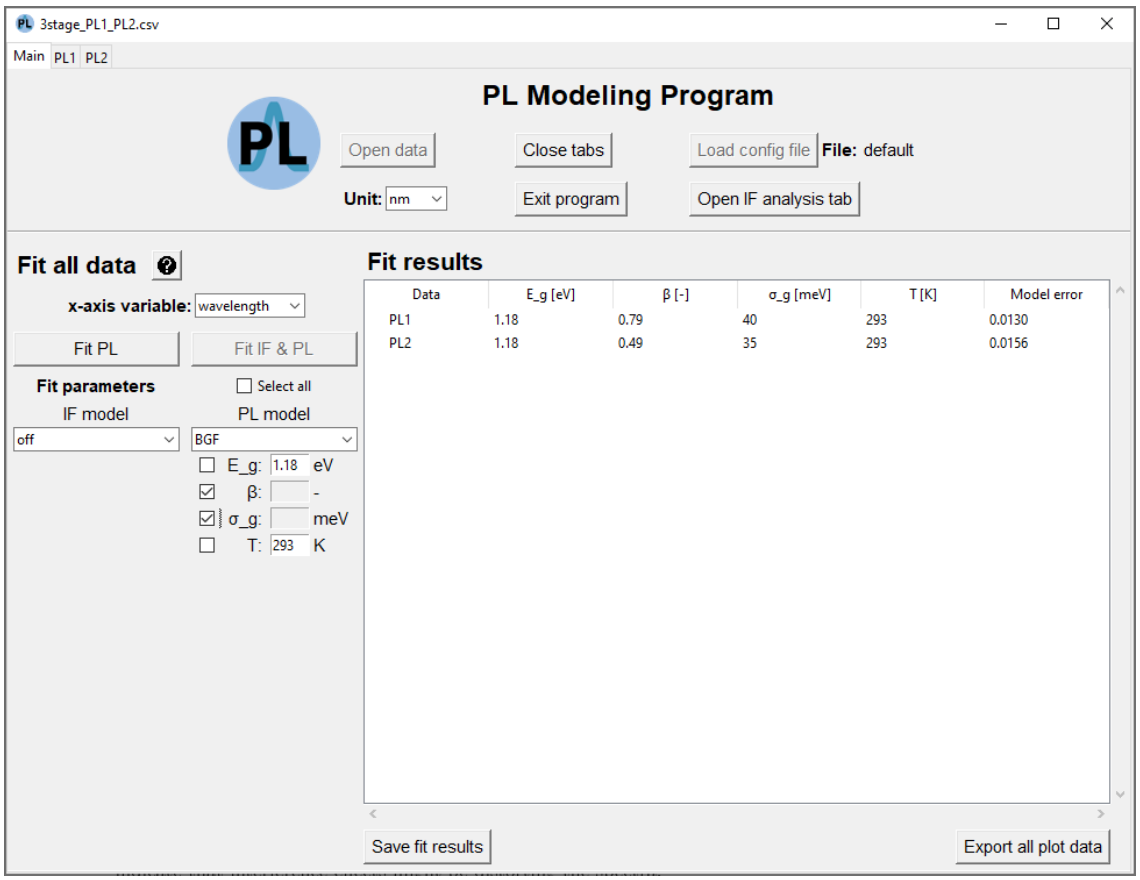

Figure 5: Result after fitting all the data with the BGF model, fixing the value of E_{g}.

image of the 'IF analysis' tab is shown in Figure 6, where two measurements on the same spot of a sample were done at excitation intensities of $0.3\,\mathrm{mW}$ and $30\,\mathrm{mW}$. Large shoulders close to the main emission peak indicate that interference effects might be distorting the spectra.

When the 'Open IF analysis tab' button is clicked, the program collects the PL data of the currently opened tabs. All these are plotted in the same figure of the 'IF analysis' tab, as shown in the top plot in Figure 6. The bottom plot shows all the data with interference correction for the IF model and parameters indicated in the tab's 'Interference Correction' section with a continuous line. It therefore ignores the selected interference function model in the each data's individual tab with the purpose of applying the same correction to all data. Again, the IF model and parameter values can be changed and the plots will be updated accordingly. The dashed lines in the bottom plot show the modeled PL spectra according to the parameter values in each of the data tabs. These will not change unless the data is fitted, as explained next.

In the section 'PL Modeling', the user can select the desired model for the fitting routine, which will be applied to all the imported data. As in the 'Main' tab, parameters can be given a fixed value by unchecking the corresponding check box. Finally, the common IF model parameters can be found by clicking on the 'Fit IF & PL' button. This action will attempt to simultaneously fit all the PL spectra by using the same correction for interference in each dataset. Once the fit is done, the parameter values in each measurement's tab will be updated, both for the IF as for the PL model. This will therefore also update the dashed lines in the bottom plot, as the PL model parameters might have changed. For more details on the individual PL fitting parameters, check the measurement's tab or fit all the data in the 'Main' tab with the optimal IF found.

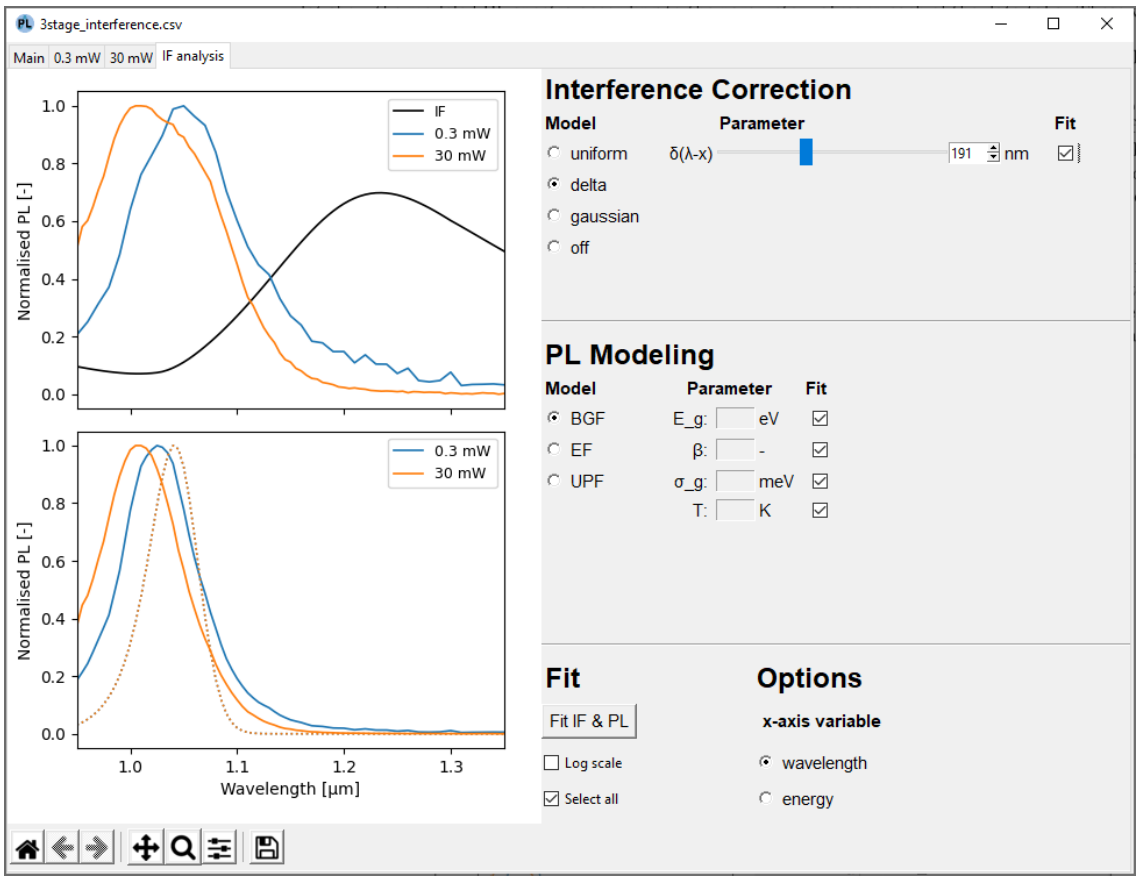

Figure 6: IF analysis tab. The IF fitting is already done.

It is worth noting that there is a large number of parameters involved in this simultaneous fitting routine, which results in a very broad parameter space. This leads to occasional non-ideal fit values. Moreover, the result depends to a large extent on the initial values. For this reason, the fitting routine can give the user an indication about how the optimal IF looks like, but the precise values might not be the optimal ones. Practice has learned that slightly modifying the parameters values found with the fit can improve the correction. The user must therefore always actively judge the fit results. In this regard, plotting the corrected data on a logarithmic scale might help, which can be done by checking 'Log scale' in the 'Fit' section. Finally, this analysis can only be used with the assumption that the interference function is the same for all the imported measurements. This is the case when the measurements were performed at exactly the same spot on the sample, for different excitation powers or temperatures, for instance. The common IF constants such as the roughness, thickness and laser wavelength can be adjusted in the configuration file, as explained in Section 3.3.

3.6 Model Error

In order to assess the resemblance of the modeled and experimental PL spectra, the program quantifies the difference between these two and displays it under 'Model error' in the fit section of each data tab. To compute the difference, Equation (1) is used:

$$\text{Model error} := \sqrt{\frac{\sum_i \left(I_{\text{PL,i}} - I_{\text{PL,i}}^{\text{mod}}\right)^2}{N}}, \tag{1}$$

with $I_{\mathrm{PL,i}}$ and $I_{\mathrm{PL,i}}^{\mathrm{mod}}$ the experimental and modeled normalised PL intensity sampled according to the input data, respectively, and N the total number of samples in the measurement. Note that the PL intensities can be displayed in the wavelength or energy domain, which has an impact on the magnitude of the error. The model error is updated dynamically as the parameter values are modified. Moreover, the model error is also displayed in the last column of the table in the 'Main' tab, which quickly gives an indication of the quality of the model when fitting all the imported data.

3.7 Fitting Algorithm

All the fits in the program are done with the `curve_fit` tool in `scipy.optimize`, which is a non-linear least square fitting routine that follows the Levenberg-Marquardt algorithm. It is wrapped around a function that enables the dynamic variation of the number of parameters to be fitted, given the user's choice to fix model parameters. When a fit button is pressed, the currently displayed parameter values are used as initial values for the fit algorithm. The bounds are determined by the configuration file, and can be quickly viewed by checking the slider limits. As if often the case with fitting algorithms, decent initial values are necessary to arrive at the optimal solution. In case the fit fails, the user should manually adjust the parameter values to improve the starting point of the algorithm, or temporarily fix some parameters to gradually reach the optimum.

3.8 Export Data

In each of the data tabs, the 'Export plot data' button allows the user to save the data of the plots currently displayed on the left side of the tab. The user can choose the target directory and filename. The output will be a `.csv` file with the current x-axis values in the first column, and the data, interference function, corrected data and PL model in the subsequent columns. Therefore, the user can choose whether to save the data as a function of wavelength or energy, as is also the case for the 'Export all plot data' button in the 'Main' tab.

3.9 Close Tabs

After the user has completed the data analysis on a set of measurements, the program can be reset by clicking on the 'Close tabs' button in the 'Main' tab. This brings the program back to the start screen shown in Figure 1, closing previously opened data tabs and the 'IF analysis' tab, if open. Now, a new configuration file can be loaded, if necessary, and new data can be imported. Closing the tabs using the mentioned button does not reset the configuration file to the default one. For this to happen, the program needs to be restarted or the default configuration file should be manually loaded.

3.10 General Comments

- Data normalisation: the program automatically normalises the imported data. All the modeling is performed on the normalised data, since this is sufficient for the analysis of potential fluctuations.
- Disabled buttons: in some cases, an action by the user may result in a button becoming disabled. This is done to avoid errors in the program. For instance, no IF can be fit if the model is set to 'off' or 'uniform', since there are no parameters to fit in such cases. Moreover, the configuration file can only be selected before importing data and data cannot be imported twice. The user has to close the tabs in order to import new data.

- Computation time: the computation time of the IF models is minimal. The same holds for the BGF model, given that it is expressed in an analytical form. For the EF model, the convolution operation is computationally expensive, which is why the output of the convolution integral was stored in a look-up table for input values of θ, γ and ΔE. By interpolating the stored values, the result is retrieved in an effective way. This leads to an almost instant fit when using the EF model. With regards to the UPF model, no analytical form is available, and two integrations need to be performed for each set of parameters. This makes fitting with this model considerably slower than the BGF or EF.

- Window not responding: when the program is busy computing a result, the window will be inactive until the computation is completed. If the user clicks on the window, it might be marked as 'Not responding'. This will remain until the calculation is finished. Be patient! The program will eventually conclude the calculation, either resulting in a fit error or an optimum set of parameters. Long fitting times happen mostly when the UPF model is used.

- Model information button: in the 'Fit all data' section of the 'Main' tab, there is a button with a question mark. This provides a pop-up window with details about the models and where to look for more information:

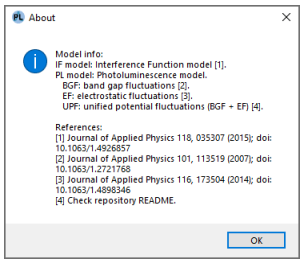

Figure 7: Pop-up window displaying information on the models used in the program.

References

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[2] Julian Mattheis, Uwe Rau, and Jürgen H. Werner. "Light absorption and emission in semiconductors with band gap fluctuations—A study on Cu(In,Ga)Se2 thin films". In: *Journal of Applied Physics* 101.11 (2007), p. 113519. DOI: 10.1063/1.2721768.

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