WAXS_toolbox Documentation

WAXS_toolbox is a software suite dedicated to the Pair Distribution Function analysis of nanoparticles. WAXS_toolbox is developped in Python and depends on 2 libraries : ase and diffpy-cmi. The suite allows the following tasks :

- **Creation of basic structural models**, either using a cif file to build spherical, ellipsoidal or cylindrical particles of known crystalline structures, or building nanoclusters such as icosahedra, decahedra or octahedra based on ASE python library.

- **Simulate** both scattering **S(q)** (based on Debye equation) **and PDF (G(r))** from a structural model

- **Refine an experimental PDF** with a structural model.

I. Installation and dependencies

I.1 Create python environment with relevant packages

WAXS_toolbox was developped in Python. As WAXS_toolbox depends on diffpy-cmi package, the requirements for using WAXS_toolbox are the same as those found for diffpy-cmi installation. The creation of a Python 3.7 environment is therefore strongly encouraged. We remind here the following steps :

- if not already installed, download and install anaconda on your system

Create environment and install package dependencies

- open anaconda prompt (Windows) or console (Linux)

- create an environment for Python 3.7, typing the following command (here the name is py37 but you can change it)

```
>conda create --name=py37 python=3.7
```

- activate the environment

```
>conda activate py37
```

- **install required packages** :The following package list is mandatory to fully exploit WAXS_toolobox : numpy, diffpy-cmi [1], ase [2], matplotlib, scipy. Note that the numerical calculations of scattering factors in the simulation tab involves the use of xraylarch library, which is only compatible with python>3.8. This library should therefore be installed in the base environment (and note in your Python 3.7 environment).

```
>conda install ase

>conda config --add channels diffpy

>conda install diffpy-cmi

>conda install numpy

>conda install matplotlib
```

>conda install scipy

>conda install webbrowser

>conda install xraydb

>conda install functools

>conda install requests

>conda install io

>conda install bs4

>conda install urllib

The last seven packages are used to compute X-ray form factor of a given element at a given energy and on a specified q range by consulting the NIST database avaliable on the web. This calculations will be detailed in a further section. In the case when no web connection is available, the X-ray form factor is calculated as being equal to f0.

Additionally, a structure viewer such as jmol should be installed on your cumputer to benefit from a full experience of WAXS_toolbox capabilities.

I.2 WAXS_toolbox installation and Run

WAXS_toolbox is distributed under the form of a zip file. To install WAXS_TOOLBOX , simply unzip the file in the directory of your choice, herefater named ***mypath***.

To run WAXS_toolobox, perform the folloing steps :

- open anaconda prompt

- activate the environment

>conda activate py37 (or other name if you specified another name)

- browse to ***mypath***.

>cd ***mypath***

- call WAXS_toolbox

>python WAXS_toolbox.py

II.Drop-down menus description

II.1 Menu « Menu »

The WAXS_Toolbox « **Menu » (top left of the window)** gives you access to useful functions, such as :

- **Set Working/Output Directory** : this function allows you to select the default directory that will be accessed by WAXS_Toolbox

- **View structure with jmol**: this function allows you to view a structure file with jmol program. This option will work only if you have jmol installed on your computer.

- **plot 1D data file(s) :** This function allows the inspection of several 1D data file(s). All files should be located in the same directory.

- **convert xyz to pdb**: as indicated, this function converts a .xyz file to a .pdb file. Although not necessary for internal use, pdb file format is often required by third party software.

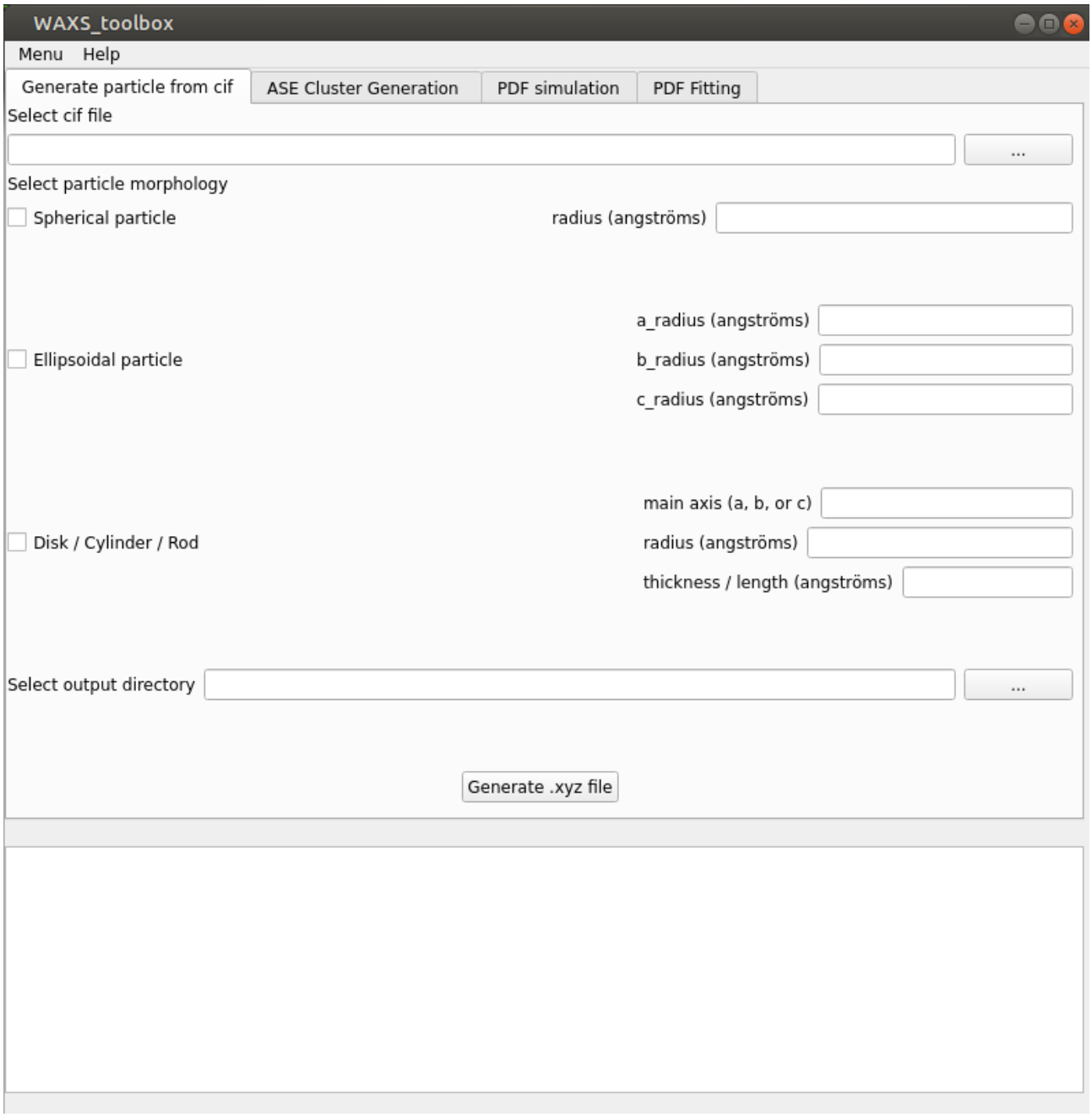


Figure 1 : View of WAXS_toolbox window

II.2 Menu « Help »

The Help Menu provides you a useful link to ase library documentation. For a sake of completeness, the main useful informations will be reported in this documentation.

III. Creation of structural models

III.1 Using a cif file

WAXS_toolbox allows the creation of particles of basic shapes using a cif file.

Three shapes are implemented :

- perfectly spherical particle of given radius

- ellipsoidal particles of given (a, b, c) radii

- disk/cylinder/rods of given main axis (a, b or c), radius, and thickness

Note that all numerical values are expressed in angströms.

For instance, a Co particle of hexagonal crystalline structure having a rod shape along c axis, a diameter of 1.5nm and a length of 10nm can be generated by filling the form as in the figure below :

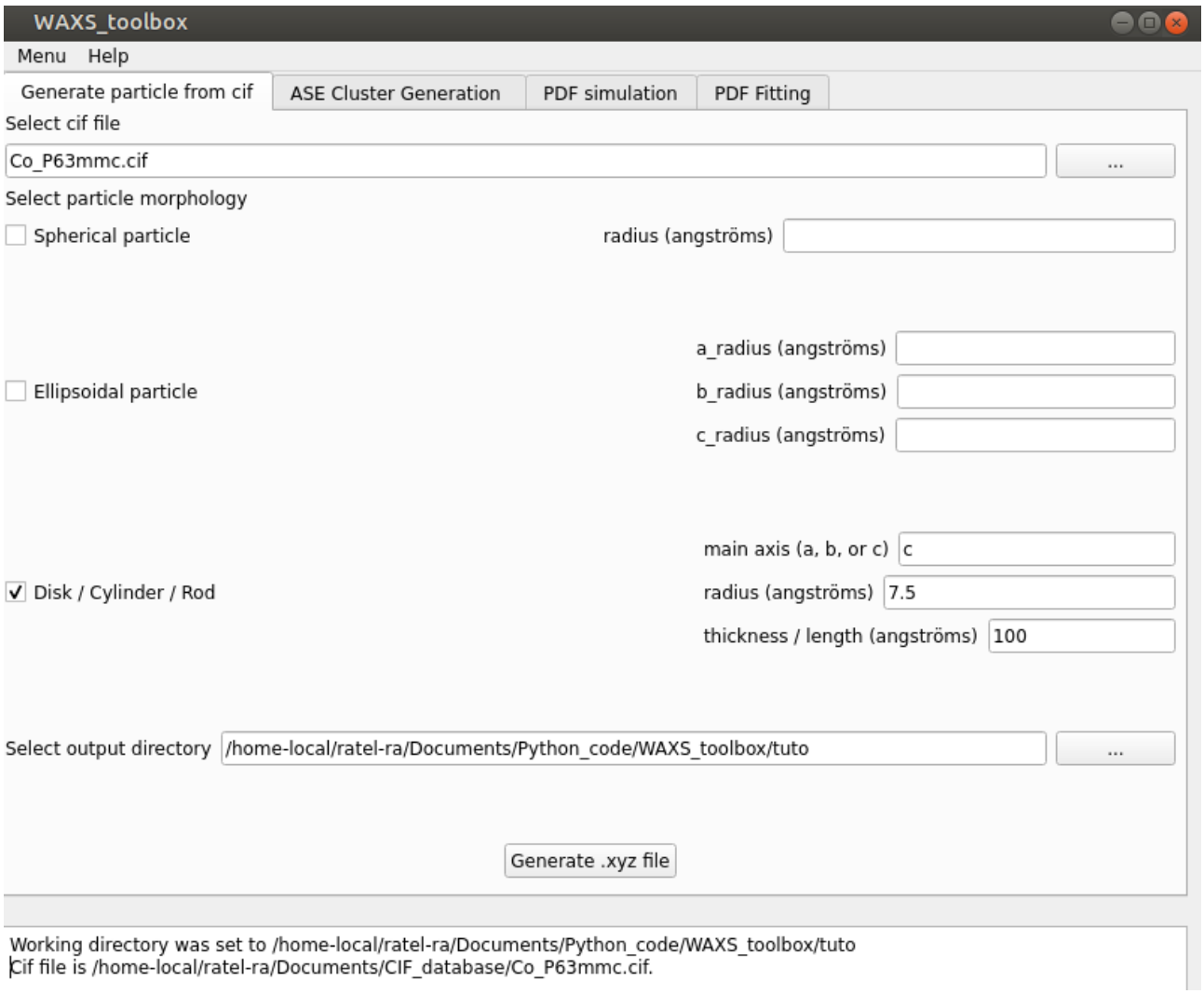


Figure 2 : Example of model structure generation using a cif file

Clicking on the button « Generate .xyz file » automatically stores the structure file in the selected output directory.

Note that all tabs in WAXS_toolbox show an « Output directory » field. To have them automatically filled, use Menu/select Working/Output directory

III.2 Cluster models using ASE library

The ASE library gives the possibility to generate three types of morphologies of particles :

- icosahedral particles

Parameters:
- **symbol** (*str or int*) – The chemical symbol (or atomic number) of the element.
- **noshells** (*int*) – The number of shells (>= 1).
- **latticeconstant** (*float, optional*) – The lattice constant. If not given, then it is extracted from $ase.data$.

- decahedral particles

-

Parameters:
- **symbol** (*Chemical symbol (or atomic number) of the element.*) –
- **p** (*Number of atoms on the (100) facets perpendicular to the five*) –
- **axis.** (*fold*) –
- **q** (*Number of atoms on the (100) facets parallel to the five fold*) –
- **facets.** (*axis. q = 1 corresponds to no visible (100)*) –
- **r** (*Depth of the Marks re-entrence at the pentagon corners. r = 0*) –
- **re-entrence.** (*corresponds to no*) –
- **(optional)** (*latticeconstant*) –

octahedral particles

Type	Condition
Regular octahedron	cutoff = 0
Truncated octahedron	cutoff > 0
Regular truncated octahedron	length = 3 * cutoff + 1
Cuboctahedron	length = 2 * cutoff + 1

Parameters:
- **symbol** (*str or list*) – The chemical symbol or atomic number of the element(s).
- **length** (*int*) – Number of atoms on the square edges of the complete octahedron.
- **cutoff** (*int, default 0*) – Number of layers cut at each vertex.
- **latticeconstant** (*float, optional*) – The lattice constant. If not given, then it is extracted from $ase.data$.

To use ASE functions, select **ASE Cluster Generation** tab in WAXS_toolbox. The tab contains field to specify :

- atom type

- lattice parameters

- 3 sub-tabs to choose the particle morphology and provide corresponding parameters. For further information, do not hesitate to consult the ASE documentation.

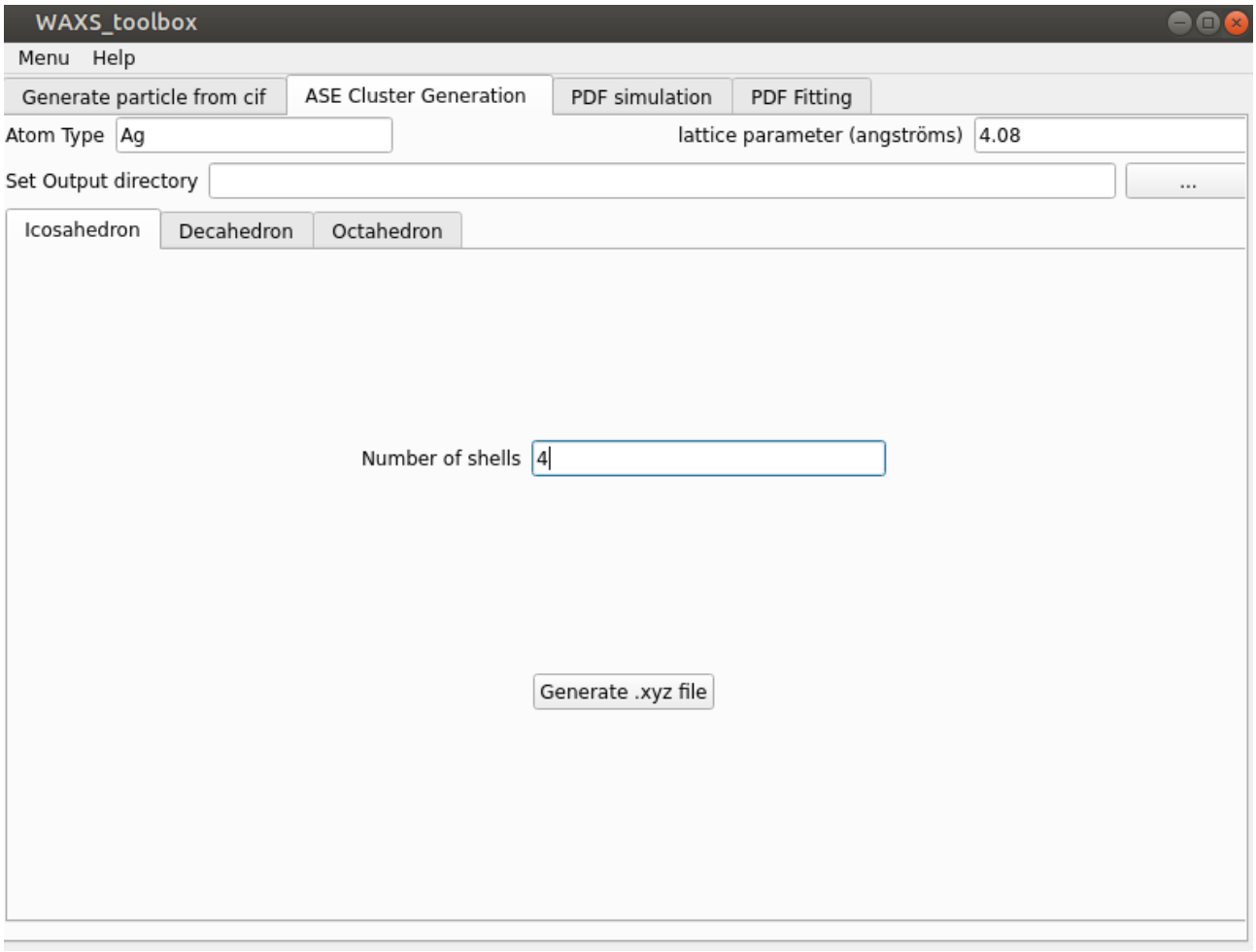


Figure 3 : ASE Cluster generation tab

The structure is finally generated by clicking on « Generate .xyz » button. The resulting structure can be viewed using jmol.

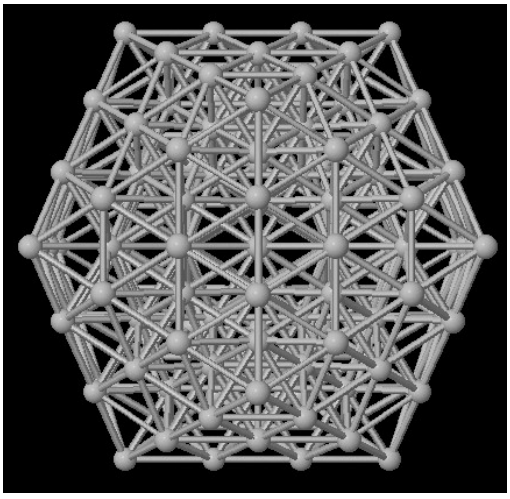


Figure 4 : Icosahedral structure generated with ASE library

IV. I(q) and G(r) simulations

I(q) and pair distribution functions (G(r)) can be simulated using the « PDF simulation » tab.

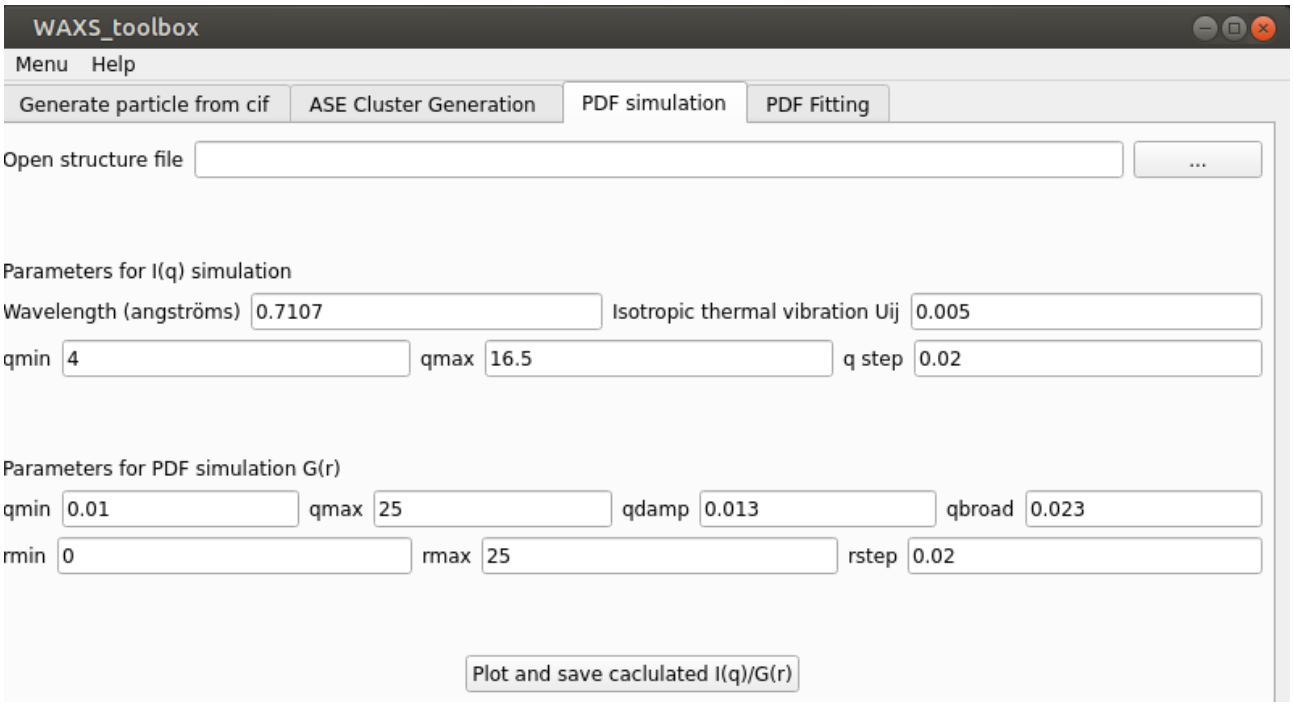


Figure 5 : View of the simulation tab

IV.1 Scattered intensity calculation I(q)

The scattered intensity calculation is based on Debye equation.

$$I(q)=\sum_i \sum_j f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}} * DW$$

where:

- Q is the scattering vector

- $r_{ij}=|r_i-r_j|$ is the distance between atoms i and j

- f_i is the atomic scattering factor. The detailed calculation of the scattering factor can be found on https://github.com/nicoratel/atomic_scattering_factor/blob/main/complex_form_factor.ipynb

- DW is the Debye Waller coefficient to account for thermal vibration, here represented by isotropic atomic displacement parameters U_{ij}.

It requires the provision of an xyz file by the user (it is therefore not applicable to cif files).

IV.2 PDF calculation

The computation of the PDF is based on diffpy-cmi DebyePDFCalculator class.

The user is invited to provide a structure file (cif or xyz), together with a set of parameters describing the experimental conditions (qmin, qmax and qstep), the intrument resolution (qbroad and qdamp parameters), and the real space computation range (rmin, rmax and rstep). Defautls values are provided.

V. PDF refinement

An experimental PDF can be refined with the theoretical PDF computed from a structural model using the « PDF fitting » tab.

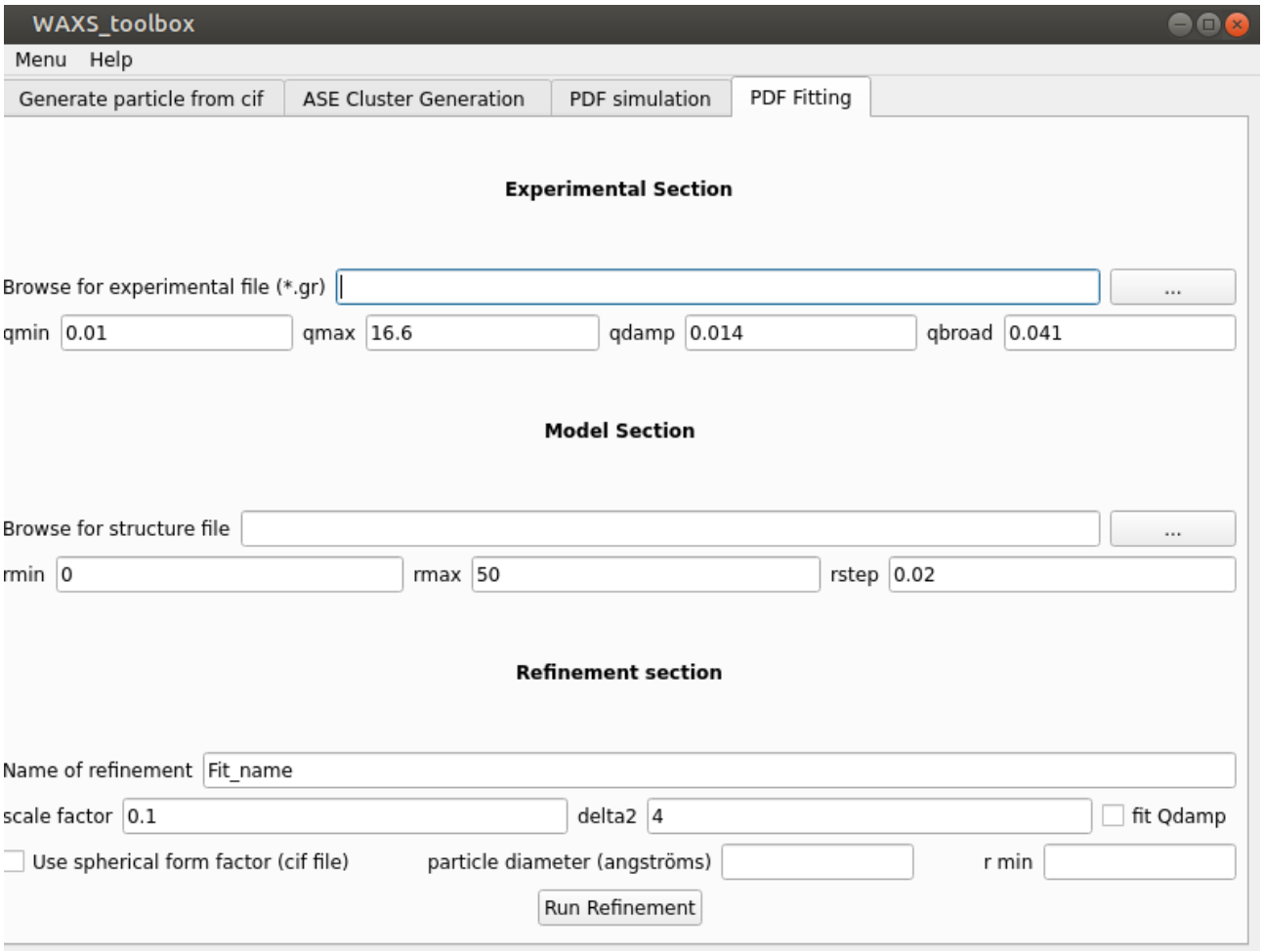


Figure 6: View of the PDF fitting tab

V.1 Experimental section

The experimental pdf file can be provided in this section. It must be accompanied with the following information :

- range in reciprocal space used for pdf extraction from I(q) data, namely qmin and qmax

- intrument resolution parameters qdamp and qbroad

If the pdf was extracted from the scattering data using pdfgetx3 software [3], the qmin and qmax fields will be automatically completed. In other cases, the user is invited to fill those fields, as they can be critical for the refinement.

V.2 Model section

The structure file (.xyz or .cif) can be provided in this section.

The real space range of fitting, described by rmin, rmax and rstep parameters, must be defined in this section.

V.3 Refinement section

In this section, the user can provide a name for the refinement. This name will be used as a file name for the following outputs :

- a res file containing the refinement results, stored in res folder (automatically generated)

- a file containing the calculated pdf, stored in fit folder (automatically generated)

- a pdf file showing a plot for the comparison between experimental and computed pdf, stored in fig folder (automatically generated).

Starting values for scale factor and delta2 parameters sould also be provided (reasonable first guesses are given by default).

When working with cif files, the user has the possibility to apply a characteristic function corresponding to spherical particles. In that case, particle diameter must be provided. Optionally, a lower bound for the partcile diameter can be provided in the rmin field.

For more details, please consult the tuorial section.

By default, the following quantities are refined:

- lattice parameters / zoomscale (zoomscale is a coefficient that allows interatomic distances refinement in finite models, it should be close to 1)

- delta2 parameter, to account for atomic displacement correlations in the small r region

- atomic displacement parameters U_{ij}

Qdamp and Qbraod calibration parameters can be determined through the measurement of a calibration specimen (well crystallized powder). The calibration procedure will be described in section VII.

VI. Tutorials

In the following sections, we will develop two tutorials examples that can illustrate the capabilities of WAXS_toolbox. The first example focuses on Zn3P2 spherical nanoparticles, whose structure can be described by a cif file, while the second example uses icosahedral Au nanoparticles as objects of interest.

Data files corresponding to experimental pair distribution functions can be found in the tutorial directory. This directory should be selected as working directory using Menu/Set Working/Output directory.

VI.1 Cif based refinements : Zn3P2 nanoparticles

The experimental file corresponding to this example is Zn3P2_toluene.gr.

A quick phase search on PDFitc server indicates that the crystal structure of the particles correspond to a teragonal phase of Zn3P2 (structure file COD 1010287.cif)

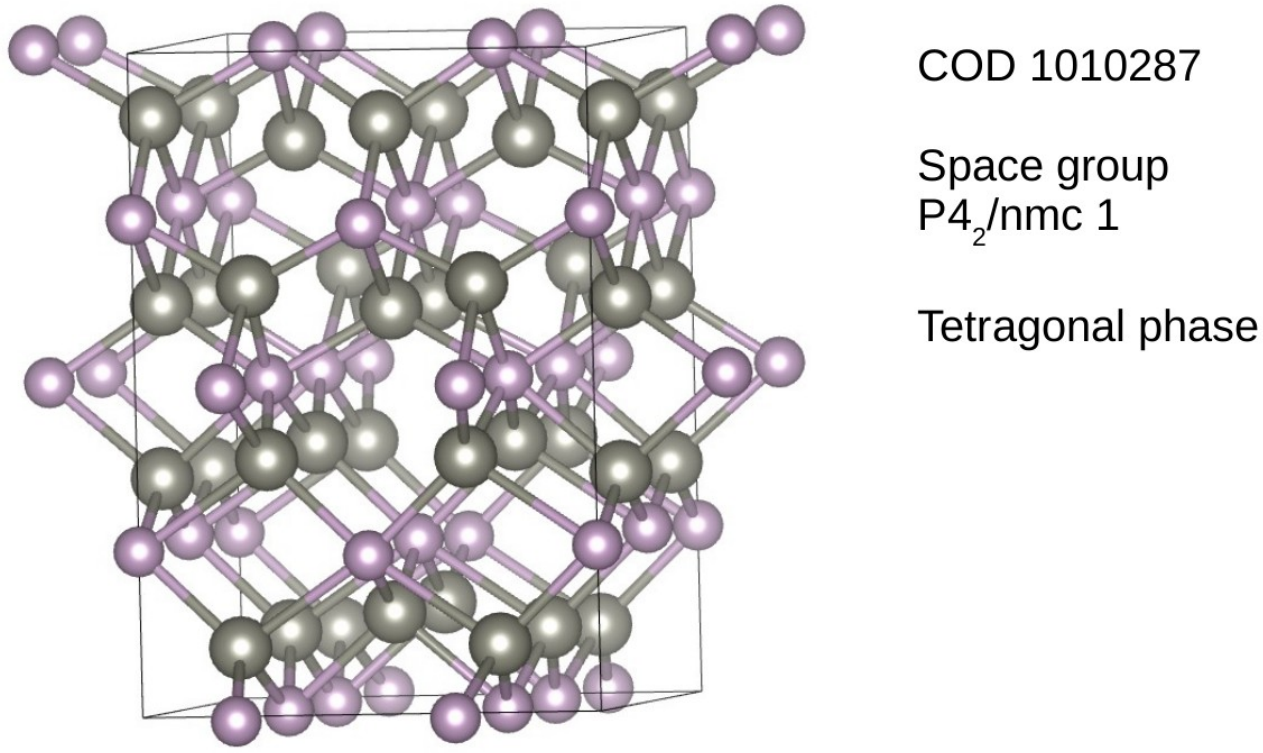
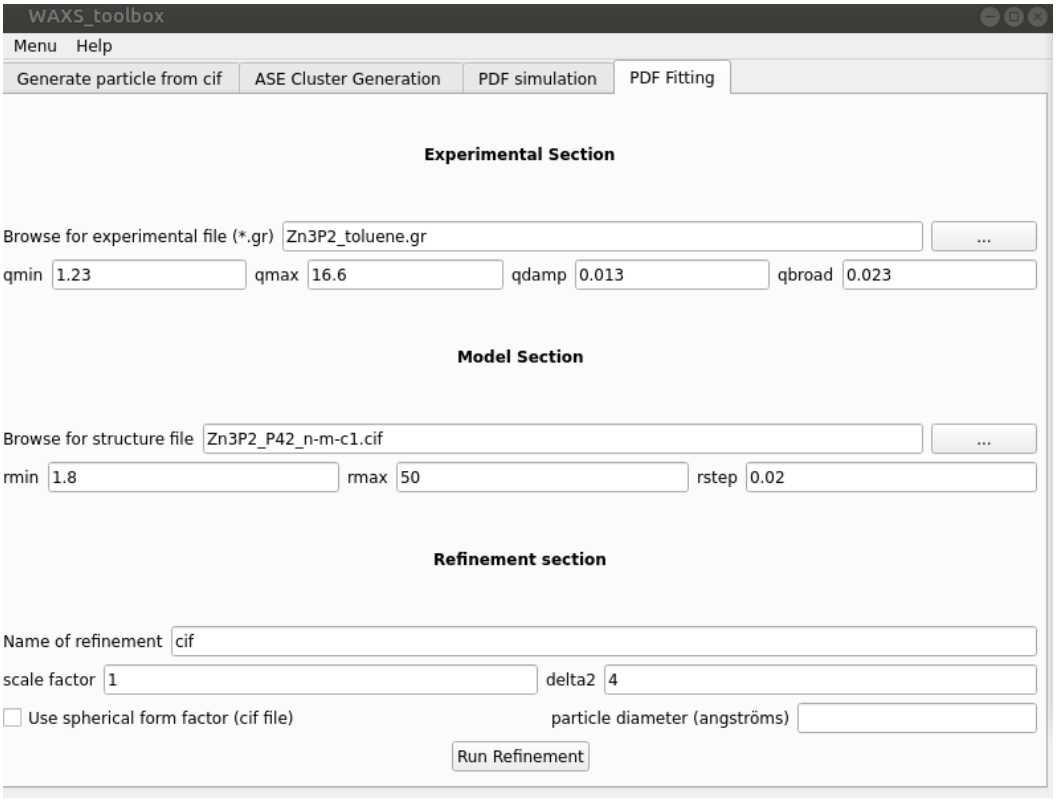
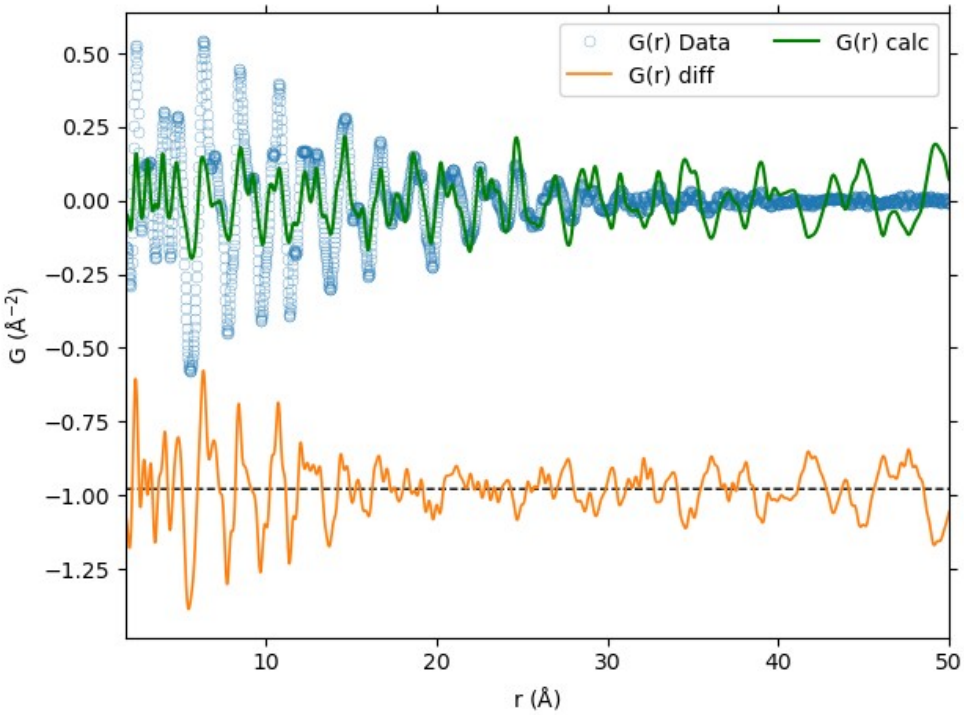


Figure 7 : View of the Zn3P2 tetragonal structure, as described in 1010287.cif taken from COD database

As a preliminary test, simply perform a fit using the cif file and the following parameters :



Once the calculation is performed, the following figure pops up, and text results are displayed in the field at the bottom. The reliability factor of the refinement is around Rw=0.74, which is pretty bad.



Looking at the refinement, we can draw the following conclusions :

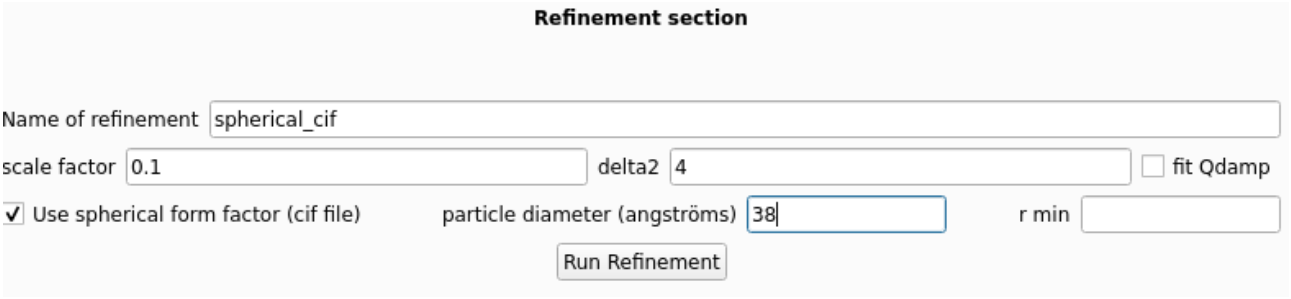
- peak positions are well reproduced, indicating that the structure space group seems to be correct

- peak intensities is poorly reproduced. Calculated peaks are too small in the small r-region, while they appear too large in the large r region. This is due to the fact that we did not take into account

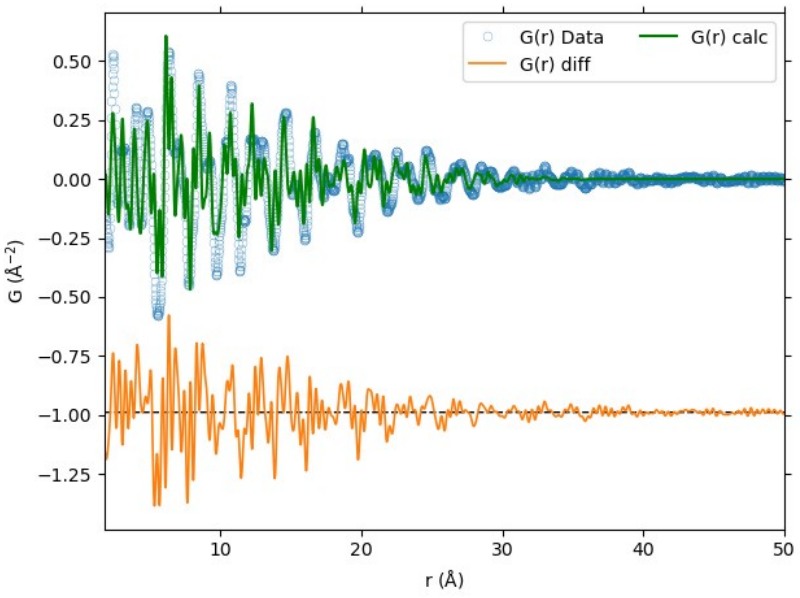
the finite size of the particles in the model. Thus, the algorithm compensates this point trhough the refinement of the scale factor to an average value.

To improve the refinement, we will now account for the spherical shape of the particle. In practice, a contribution, corresponding to an enveloppe function for the PDF, is added to the refinement. This function is the spherical Characteristic function (sphercialCF from diffpy.srfit.pdf.characteristicfunctions module of diffpy-cmi library), which takes as argument the particle diameter.

To implement this in WAXS_toolbox, simply check the « Use spherical form factor » checkBox, and select a starting value for the particle diameter. In our case, the PDF oscillations are strongly attenuated around 0 around r=35Å. We therefore use that value as a starting value for the particle diameter.



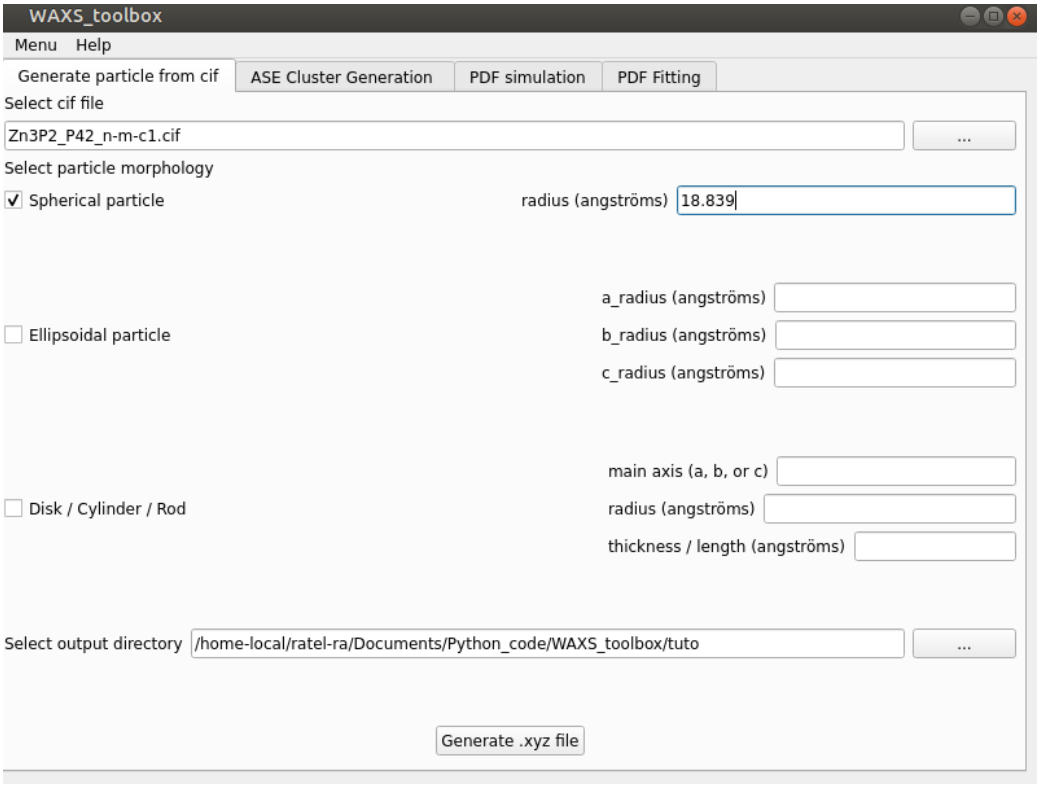
The refinement should produce the following results



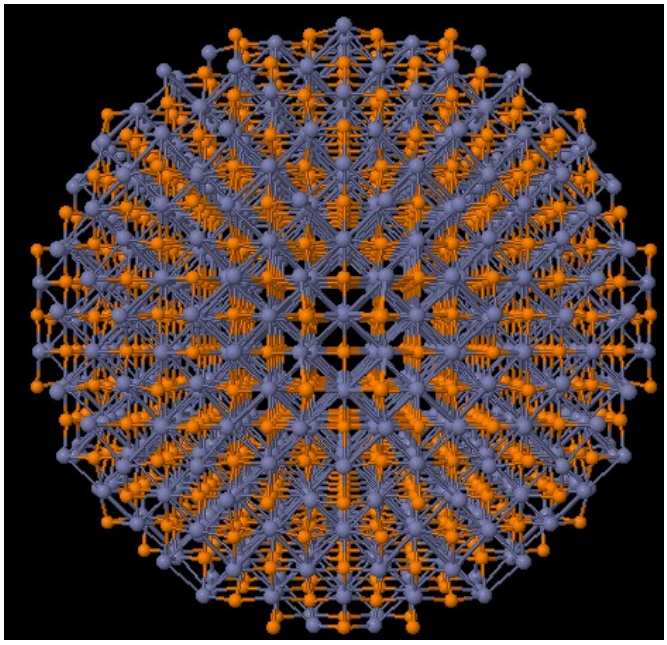
Looking at the refinement results, the refined particle diameter is 37.768Å.

Lets' double check the results and perform a refinement using the model of a spherical particle generated using « Generate particle from cif ».

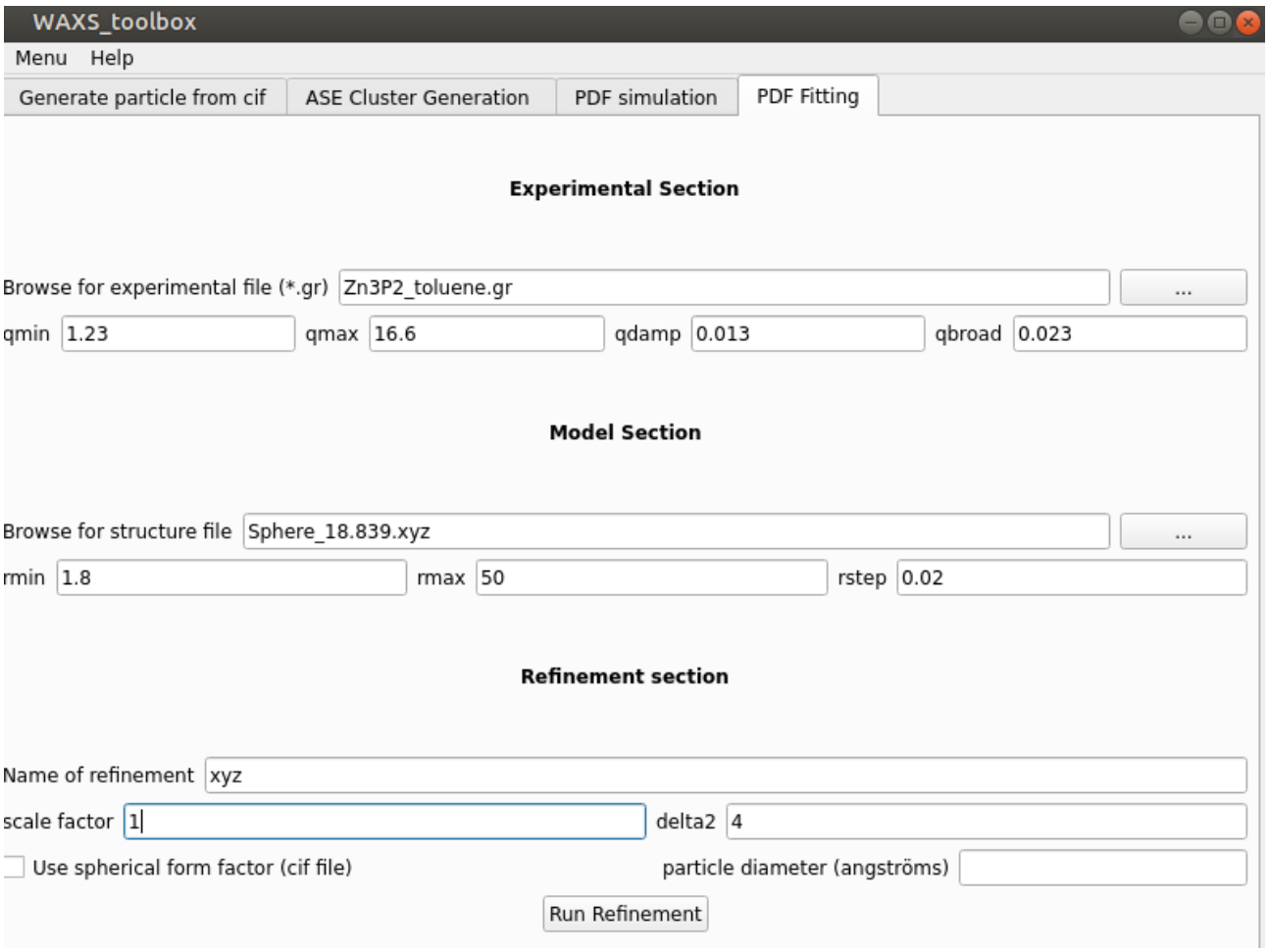
In the present case, the window should look like (beware that radius=diameter/2):



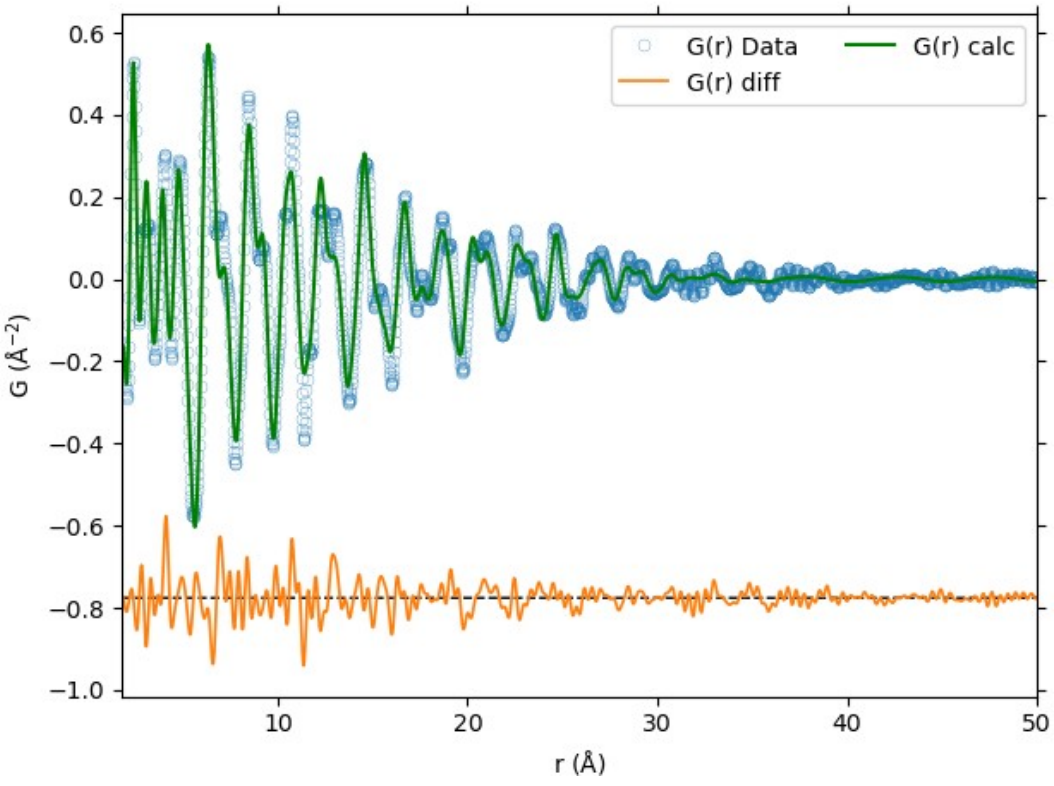
Clicking on Generate .xyz file button will create the structure file for the particle in the specified output directory. This structure file can be visualized using Menu/View structure with Jmol



To check, we restart the refinement using the structure file generated above.



The refinement should converge rapidly and produce the following results (Rw=0,26)



For more details on the results, please check in res folder for the corresponding res file.

VI.2 Tutorial on Au icosahedron

Data file:Au_62mM.gr

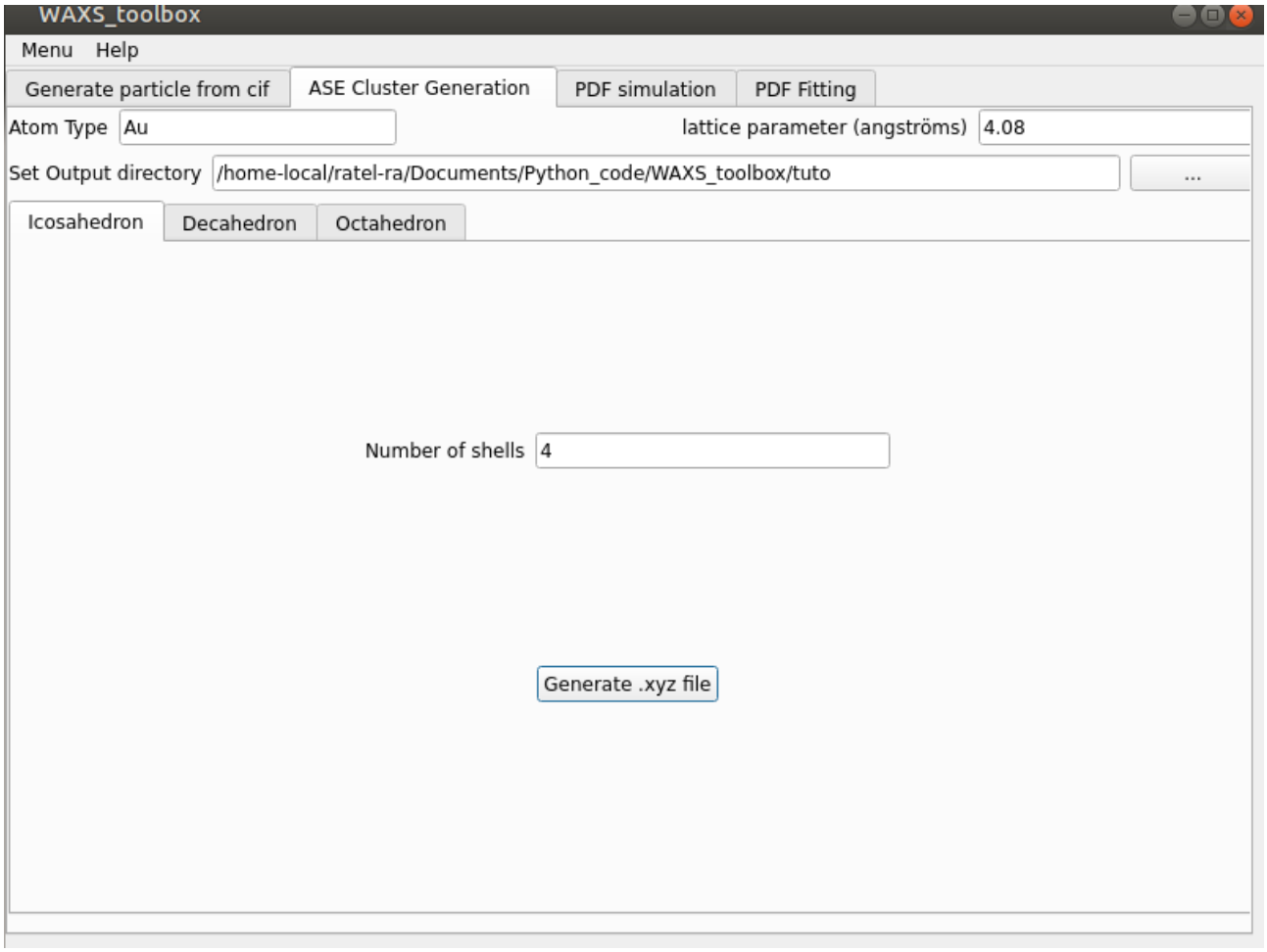
Au icosahedral clusters were synthetized and its pair distribution function were extracted from total scattering data.

Looking at scattering data did not allow the identification of the crystal structure (fcc indexing did not work).

WAXS_toolbox can be used to explore other possibilities, among which icosahedral or decahedral particles in two main steps : 1. structure generation, 2. pdf refinement

VI.2.1 Structure generation

Open the ASE Cluster Generation tab and fill the forms as in the figure below, and click on « Generate xyz file » button.



Once the structure is generated, it can be visualized using Jmol through Menu/View structure with Jmol.

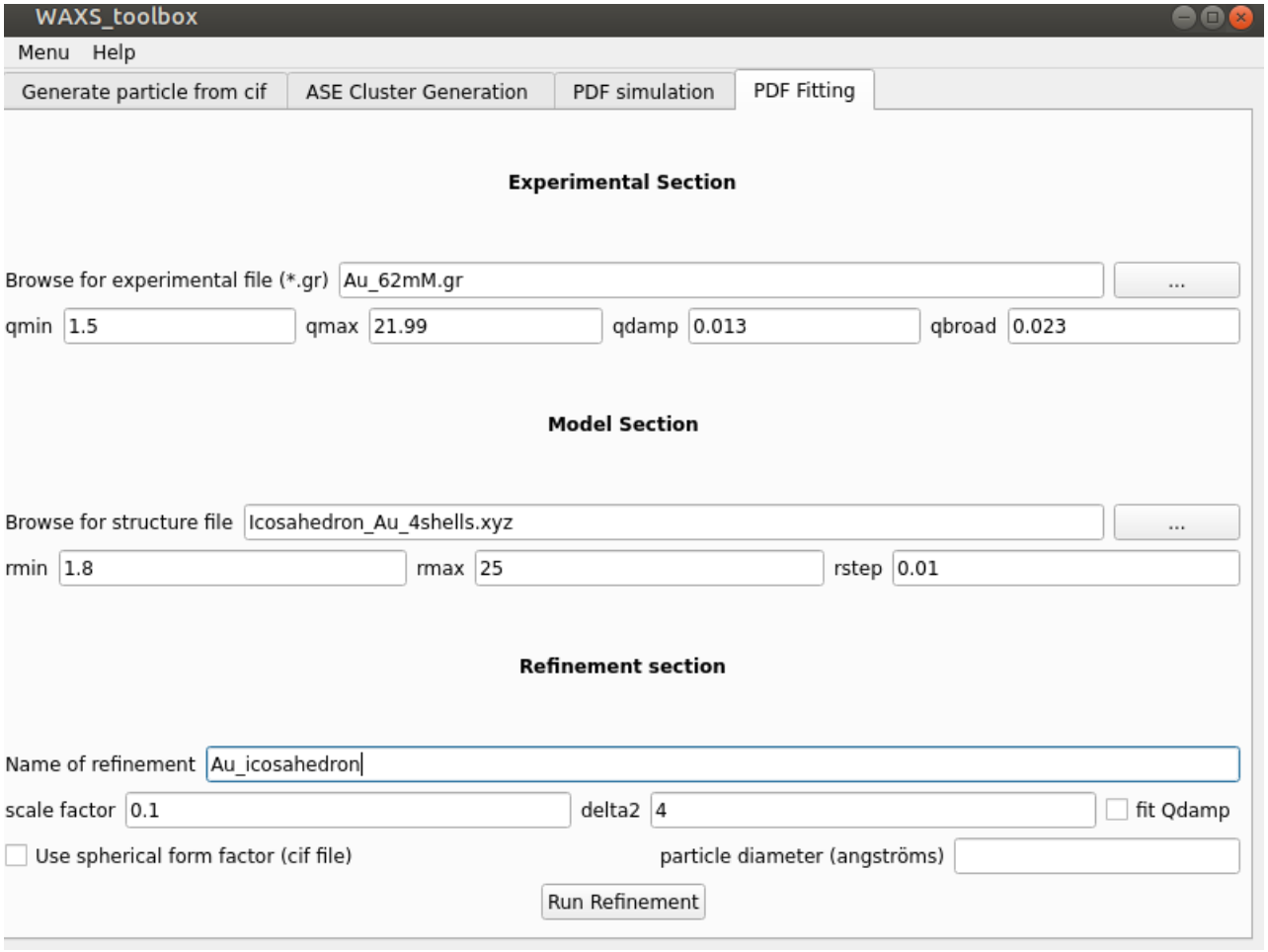
VI.2.2 Structure refinement

Open the PDF fitting tab.

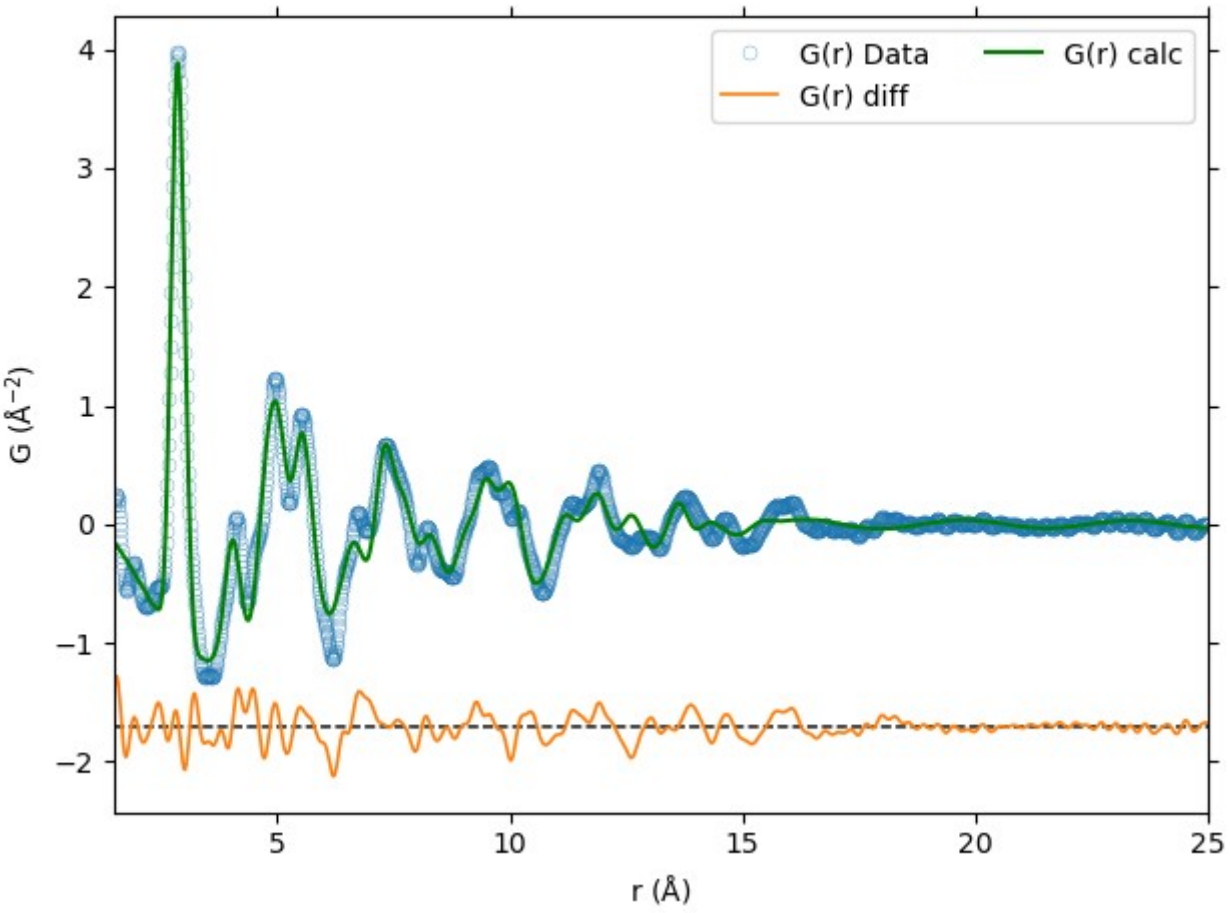
The data file to be used is Au_62mM.gr. A quick inspection of the file in a text editor gives access to the parameters (such as qmin and qmax) that have been used for pdf extraction. Those parameters must be given as an input for the pdf refinement.

Qdamp and Qbraod parameters can be determined through the measurement of a calibration specimen (well crystallized powder). The calibration procedure will be described in a further section.

In the present case, the first peak of the experimental pdf is around 2.88Å and the pdf quickly attenuates after 20Å. We can therefore define the refinement range as being between rmin=1.8Å and rmax=25Å.



When the refinement is completed, the following figure should pop up. The reliability factor of the refinement is around Rwp=0,26.



VII. Calibration procedure

The aim of the calibration is to define Qbroad and Qdamp parameters, which relates to instrument resolution parameters affecting the pair distribution function.

An estimation of these parameters can be obtained through the total scattering measurement of a specimen of known crystalline structures showing large crystallites, such as Si, oxydes, LaB6, … A pair distribution function can be extracted from scattering data, on which PDF attenuation at large r values should be related only to instrumental resolution effects.

In WAXS_toolbox, simply provide the pdf function as input, together with the cif file corresponding to the crystalline structure of the crystal used for the calibration measurement, and check the fitQdamp box in the refinement section of the PDF fitting tab. Simply run the refinement and write down the Qdamp and Q broad results.

References

[1] P. Juhás, C. L. Farrow, X. Yang, K. R. Knox and S. J. L. Billinge, Complex modeling: a strategy and software program for combining multiple information sources to solve ill posed structure and nanostructure inverse problems, *Acta Crystallogr. A* **71**, 562-568 (2015).

[2] Ask Hjorth Larsen, Jens Jørgen Mortensen, Jakob Blomqvist, Ivano E. Castelli, Rune Christensen, Marcin Dułak, Jesper Friis, Michael N. Groves, Bjørk Hammer, Cory Hargus, Eric D. Hermes,Paul C. Jennings, Peter Bjerre Jensen, James Kermode, John R.Kitchin,Esben Leonhard Kolsbjerg, Joseph Kubal, Kristen Kaasbjerg, Steen Lysgaard, Jón Bergmann Maronsson, Tristan Maxson, Thomas Olsen, Lars Pastewka, Andrew Peterson, Carsten Rostgaard, Jakob Schiøtz, Ole Schütt, Mikkel Strange, Kristian S. Thygesen, Tejs Vegge, Lasse Vilhelmsen, Michael Walter, Zhenhua Zeng, Karsten Wedel Jacobsen, The Atomic Simulation Environment—A Python library for working with atoms J. Phys.: Condens. Matter Vol. 29 273002, 2017

[3] Juhas, P., Davis, T., Farrow, C. L. & Billinge, S. J. L. (2013). PDFgetX3: a rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. J. Appl. Cryst. 46, 560-“566.