

XAFS

Experimental & data Analysis

1. XAFS data analysis software
2. From XAS to XAFS: how to deal with the data
- 3. Training: EXAFS data refinement**
4. Training: Linear combination analysis of XANES

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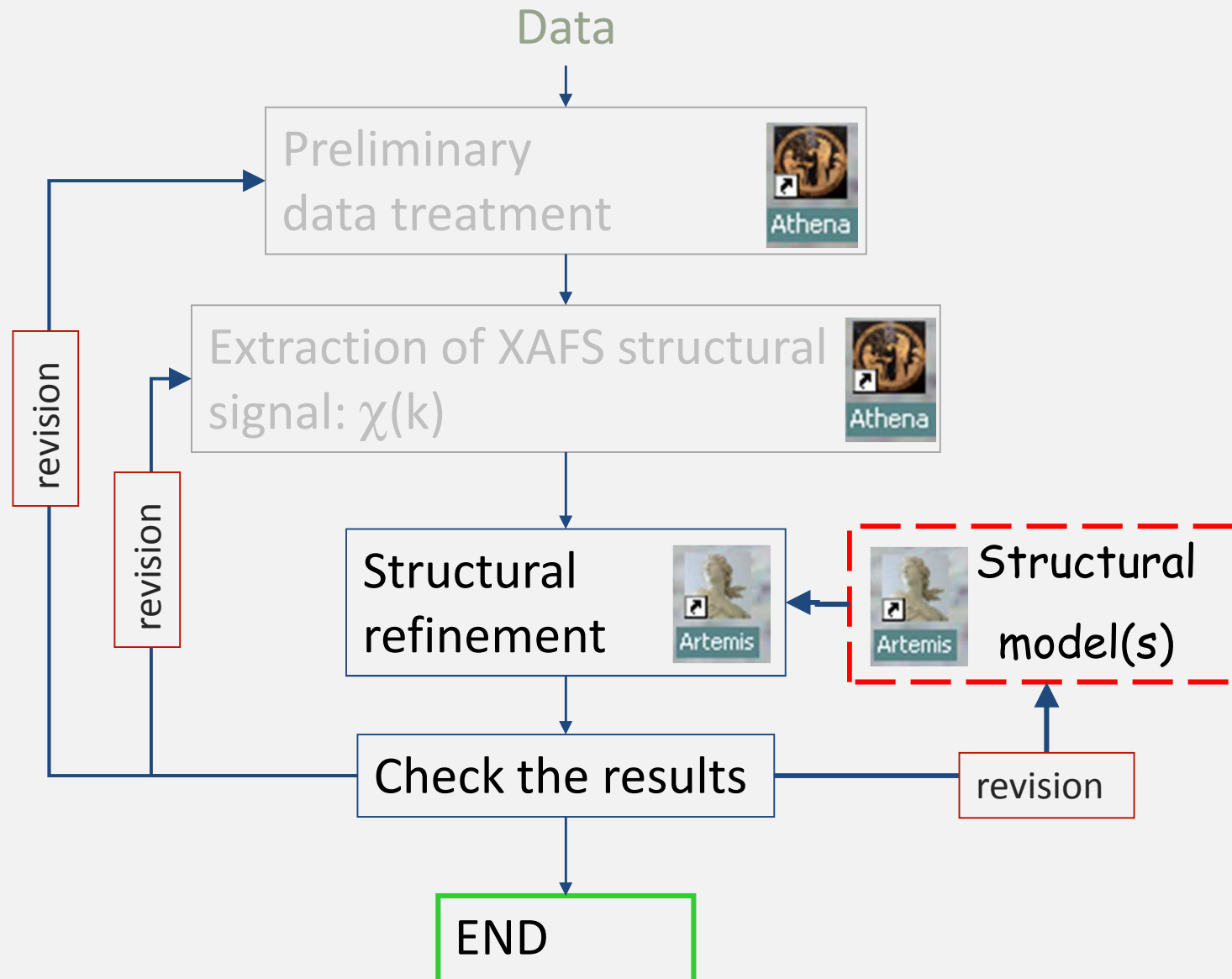
carlo.meneghini@uniroma3.it



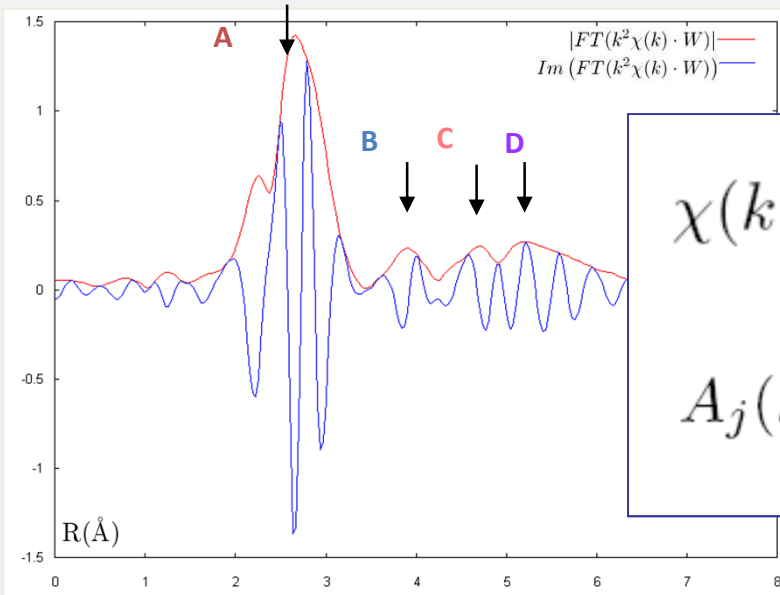
XIV School on Synchrotron Radiation:
Fundamentals, Methods and Applications
Muggia, Italy / 18-29 September 2017



Data Refinement



The EXAFS standard formula



$$\chi(k) = \frac{1}{k} \sum_j A_j(k, r_j) \sin(2kr_j + \psi_j(k))$$

$$A_j(k, r_j) = S_o^2 \frac{N_j}{r_j^2} |f_j(k, r)| e^{-2k^2 \sigma_j^2} e^{-2r_j/\lambda}$$

$$k = \sqrt{\frac{2m}{\hbar}} (E - (E_o + \Delta E))$$

parameters

$f_j(r, k)$ = photo-electron scattering amplitude

$\psi_j(r, k)$ = photo-electron scattering phase

λ = photo-electron mean free path

S_o^2 = many body losses

ΔE = energy shift

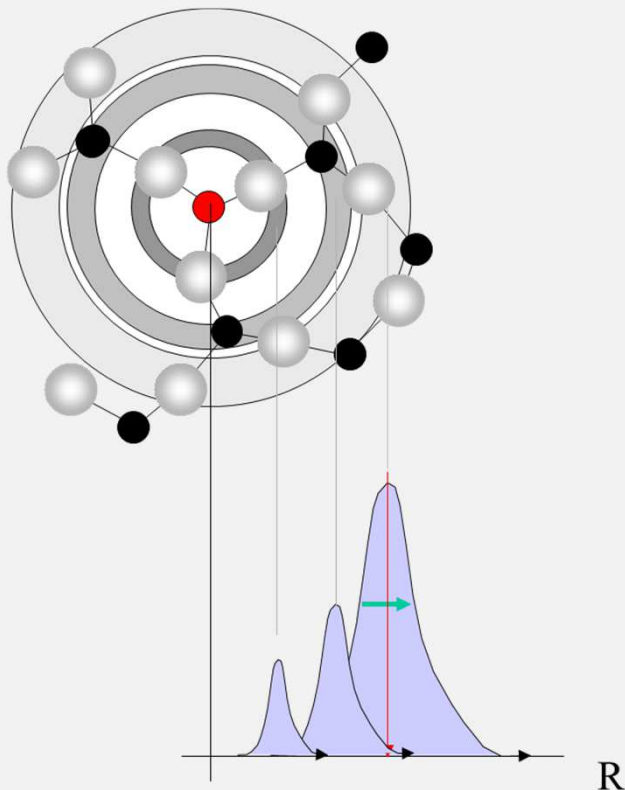
Structure

N_j = multiplicity (coordination number)

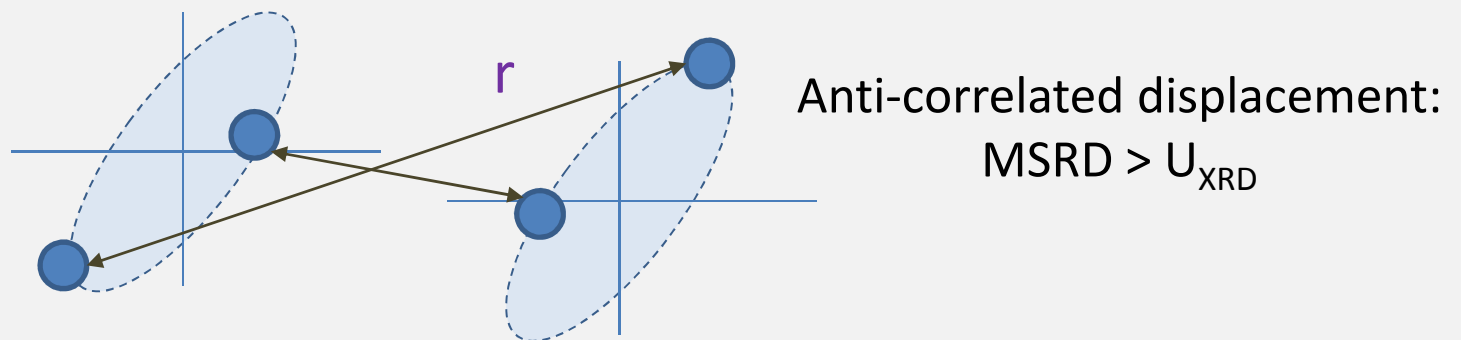
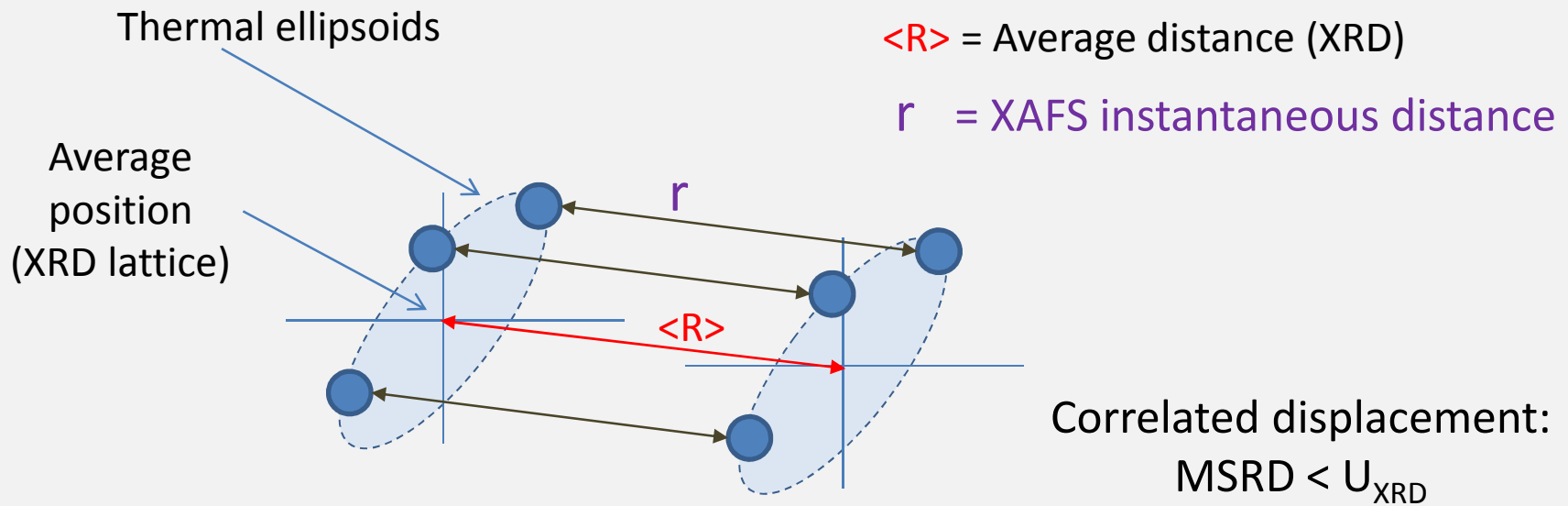
r_j = half path length (coordination distance)

σ_j^2 = variance of the path length distribution

(Mean Square Relative Displacement: MSRD)

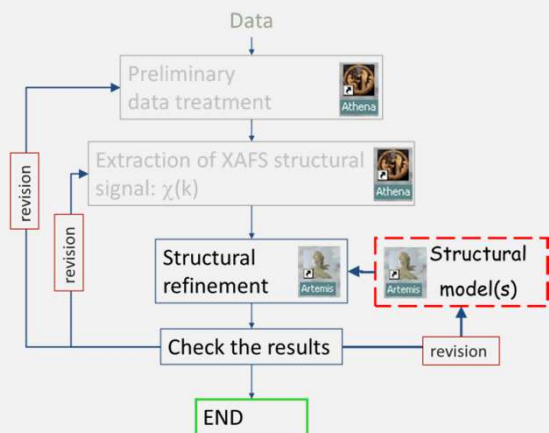


MSRD and σ^2



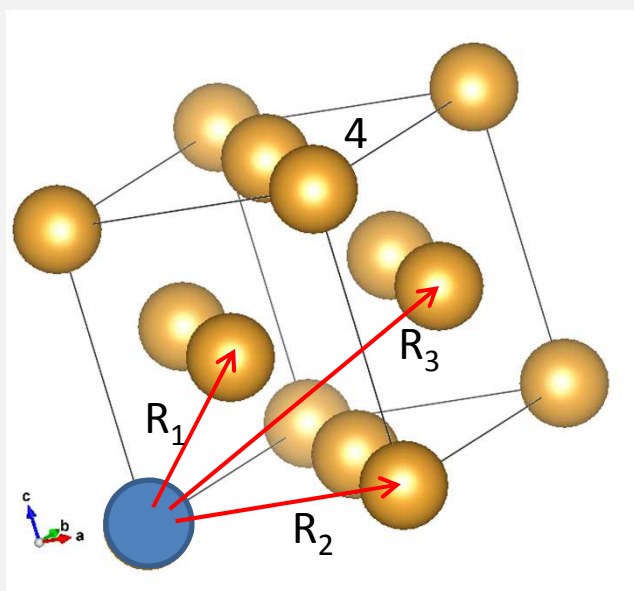


Structural model & Data refinement



We will analyze Cu EXAFS firstly

1. search Cu metal structure (cif)
2. visualize with Vesta
3. draw a local structure model
4. draw a local cluster with Atoms

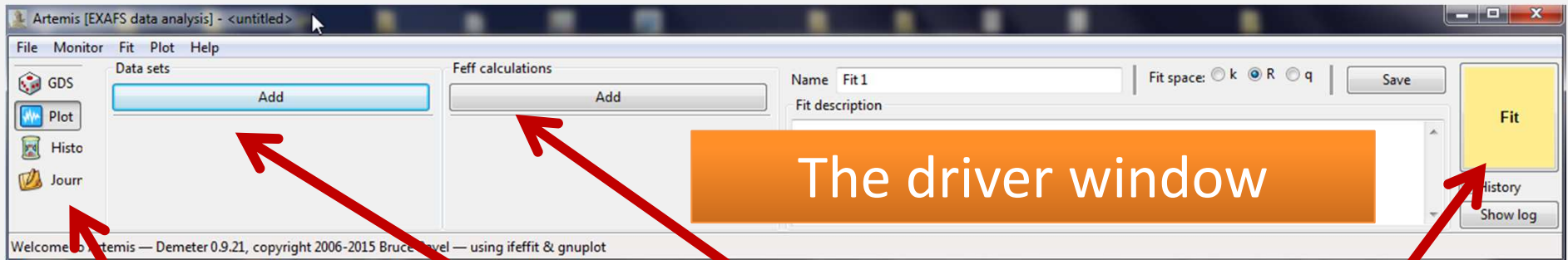


icsd_43493_Copper.cif

Cu metal
 SPG: fcc, f m 3 m (# 220)
 a = 3.61 Å
 Cu 0.0 0.0 0.0

Sh	R	N	R _{Cu} (Å)
I:	$a/\sqrt{2}$	12	2.553
II:	a	6	3.610
III:	$a\sqrt{3}/2$	24	4.421
IV:	$a\sqrt{2}$	12	5.105
V:	$a\sqrt{5}/2$	24	5.708
....			

Start Arthememis better on la larger monitor!



3
select
refinement
pram., plot,
etc...

1
add EXAFS
 $\chi(k)$ or
athena project

2
add a
Structure
.cif or Feff file

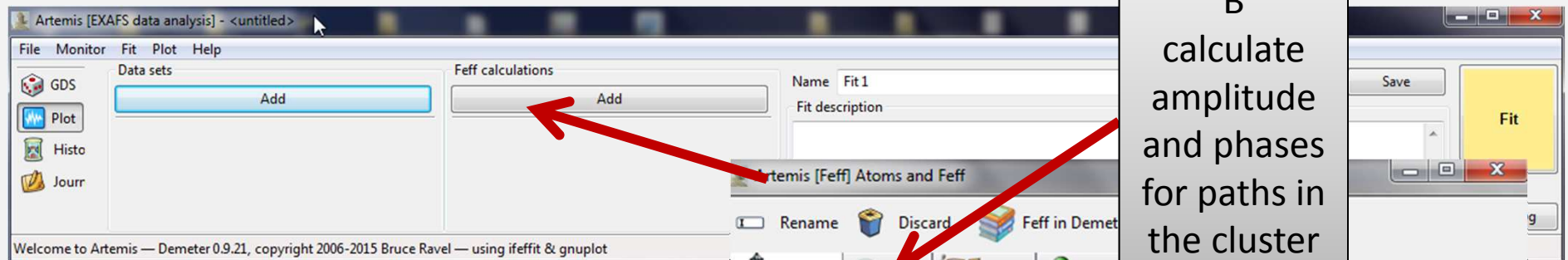
4
Start fit

1: add $\chi(k)$ or Athena project

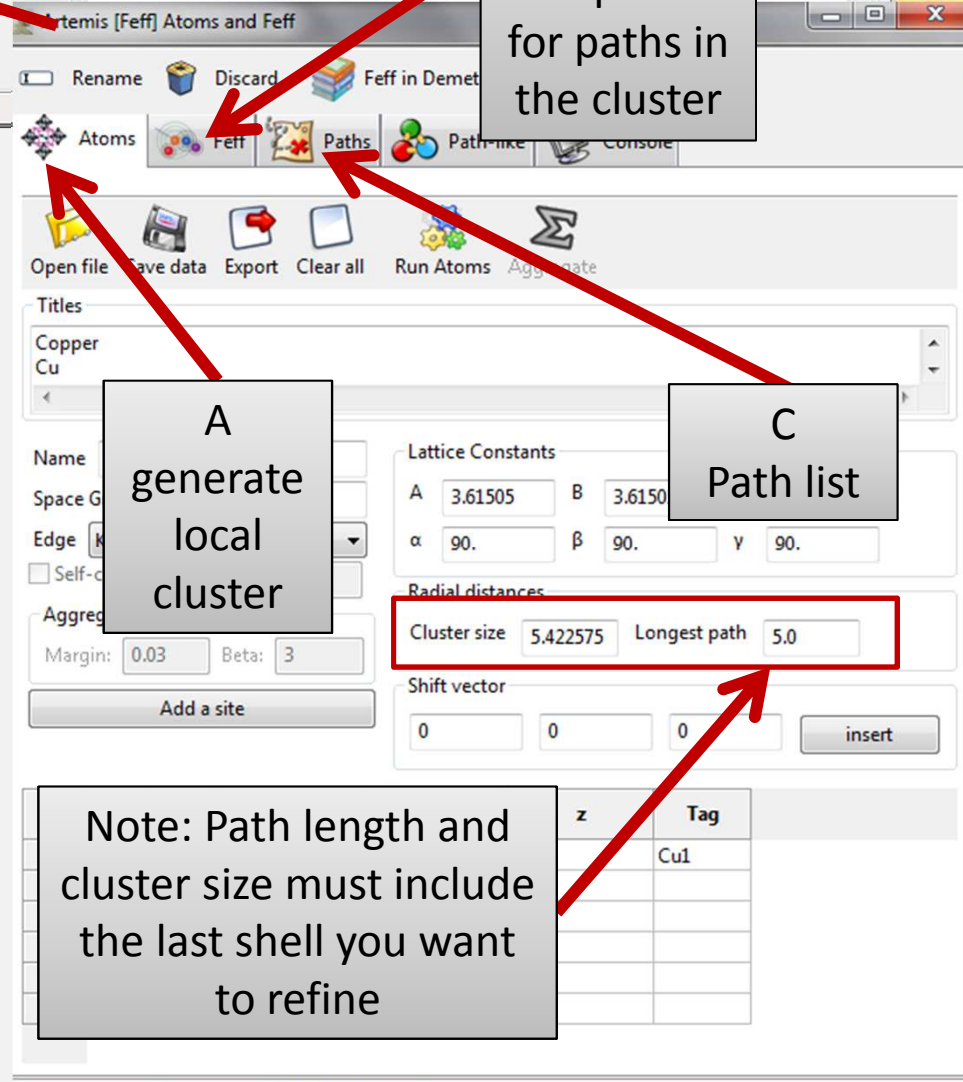
The screenshot shows the Artemis software interface. In the top-left panel, the 'Data sets' section has an 'Add' button highlighted with a red arrow. The main window displays the configuration for the data set 'cu_foil_10k.dat'. The 'Data source' is 'o_Malu_2015\data\ok_Cu_Foil\EXAFS_extraction\athena_Cu10k.prj, 1'. The 'Plot this data set as' section has buttons for 'k123', 'R123', 'Rmr', 'Rk', and 'kq'. The 'Fourier transform parameters' section includes fields for 'kmin' (3.000), 'kmax' (23.019), 'dk' (1), 'rmin' (1), 'rmax' (3), and 'dr' (0.0). The 'Fitting k weights' section has checkboxes for '1', '2', '3', and 'other' (0.5). The 'Other parameters' section has checkboxes for 'Include in fit', 'Plot after fit', 'Fit background', and 'Plot with phase correction', along with a field for $\epsilon(k)$ (0). A 'Path list' panel on the right contains a list of paths and instructions: 'Drag paths from list and drop add paths to'. Below the main window, a plot titled 'cu_foil_10k.dat in k space' shows $k^2 \cdot \chi(k)$ (\AA^{-2}) versus Wavenumber (\AA^{-1}). The plot shows a blue line for the data and a red line for the fit window. A status bar at the bottom indicates 'Transferred data set "cu_foil_10k.dat" to the plotting list.'



2: add model structure (cif or simple pair)



- I. Run Atoms
- II. check paths
- III. Run Feff
- IV. look at the path list



Feff input file

```

1 29 Cu

ATOMS
* x y z ipot tag distance
* this list contains 55 atoms
0.00000 0.00000 0.00000 0 Cu1 0.00000
1.80753 1.80753 0.00000 1 Cu1.1 2.55623
-1.80753 1.80753 0.00000 1 Cu1.1 2.55623
1.80753 -1.80753 0.00000 1 Cu1.1 2.55623
-1.80753 -1.80753 0.00000 1 Cu1.1 2.55623
1.80753 0.00000 1.80753 1 Cu1.1 2.55623
-1.80753 0.00000 1.80753 1 Cu1.1 2.55623
0.00000 1.80753 1.80753 1 Cu1.1 2.55623
0.00000 -1.80753 1.80753 1 Cu1.1 2.55623
1.80753 0.00000 -1.80753 1 Cu1.1 2.55623
-1.80753 0.00000 -1.80753 1 Cu1.1 2.55623
0.00000 1.80753 -1.80753 1 Cu1.1 2.55623
0.00000 -1.80753 -1.80753 1 Cu1.1 2.55623
3.61505 0.00000 0.00000 1 Cu1.2 3.61505
-3.61505 0.00000 0.00000 1 Cu1.2 3.61505
0.00000 3.61505 0.00000 1 Cu1.2 3.61505
    
```


2: add model structure (cif or simple pair)

Artemis [EXAFS data analysis] - <untitled>

File Monitor Fit Plot Help

Data sets Add

Feff calculations

Name Fit1 Fit space: k R q Save

Atoms Feff Paths Path-like Console

Save Plot paths $\chi(k)$ $|x(R)|$ $Re[x(R)]$ $Im[x(R)]$ Rank

Name of this Feff calculation: icso_193_Copper

Description

TITLE Copper
TITL Cu
The central atom is denoted by this token: @

Scattering Paths

Degen	Reff	Scattering path	Rank	Legs	Type
0001	12.000	@ Cu1.1 @	100.00	2	single scattering
0002	6.000	@ Cu1.2 @	22.98	2	single scattering
0003	48.000	@ Cu1.1 Cu1.1 @	10.54	3	acute triangle
0004	48.000	@ Cu1.1 Cu1.2 @	8.56	3	other double scatter
0005	24.000	@ Cu1.1 Cu1.1 @	3.39	3	other double scatter
0006	24.000	@ Cu1.3 @	55.41	2	single scattering
0007	96.000	@ Cu1.1 Cu1.3 @	21.84	3	obtuse triangle
0008	48.000	@ Cu1.1 Cu1.1 @	10.59	3	obtuse triangle
0009	12.000	@ Cu1.4 @	18.94	2	single scattering
0010	24.000	@ Cu1.1 Cu1.4 @	43.63	3	forward scattering
0011	12.000	@ Cu1.1 Cu1.4 Cu1.1 @	32.71	4	double forward sca
0015	12.000	@ Cu1.1 Cu1.1 @	8.45	3	non-forward linear

Feff calculation

Demeter 0.9.21 © Bruce Ravel 2008-2015

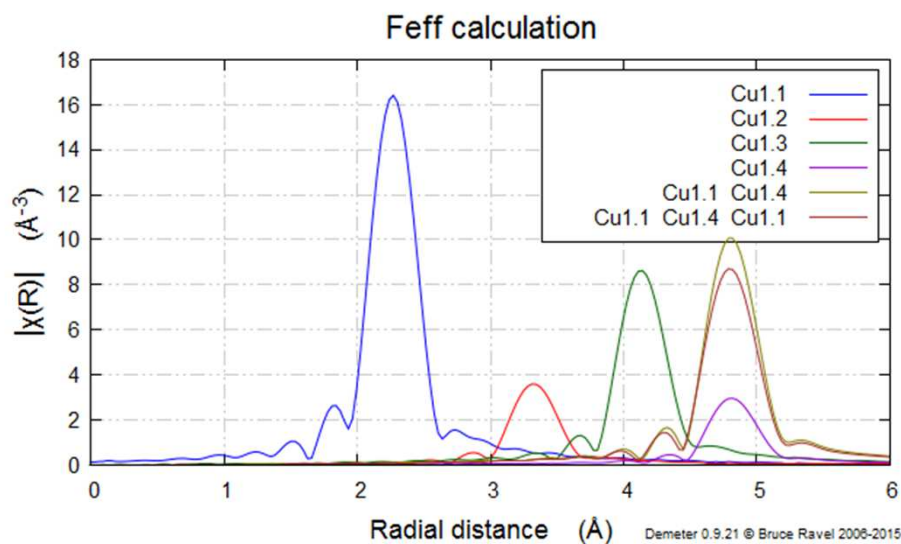
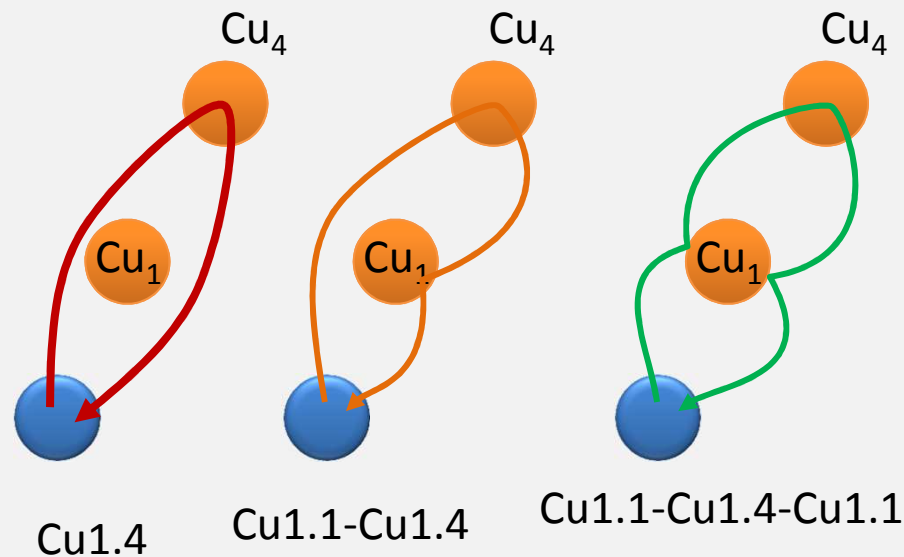
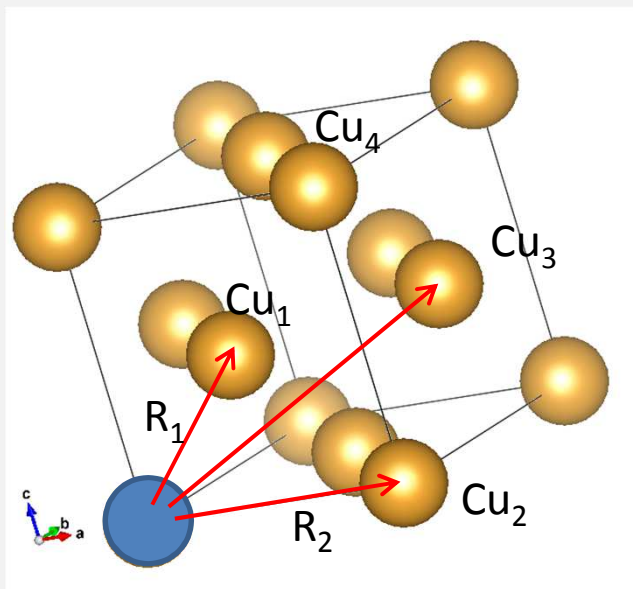
Scattering Paths

Rank	Legs	Type
100.00	2	single scattering
22.98	2	single scattering
10.54	3	acute triangle
8.56	3	other double scatter
3.39	3	other double scatter
55.41	2	single scattering
21.84	3	obtuse triangle
10.59	3	obtuse triangle
18.94	2	single scattering
43.63	3	forward scattering
32.71	4	double forward sca
8.45	3	non-forward linear

Recognize path relevance looking at the Rank &/or at the plots

WARNING This may crashes!

2: Check paths by relevance



Scattering Paths

	Degen	Reff	Scattering path	Rank	Legs	Type
0001	12.000	2.5562	@ Cu1.1 @	100.00	2	single scattering
0002	6.000	3.6151	@ Cu1.2 @	22.98	2	single scattering
0003	48.000	3.8344	@ Cu1.1 Cu1.1 @	10.54	3	acute triangle
0004	48.000	4.3638	@ Cu1.1 Cu1.2 @	8.56	3	other double scatter
0005	24.000	4.3638	@ Cu1.1 Cu1.1 @	3.39	3	other double scatter
0006	24.000	4.4275	@ Cu1.3 @	55.41	2	single scattering
0007	96.000	4.7700	@ Cu1.1 Cu1.3 @	21.84	3	obtuse triangle
0008	48.000	4.7700	@ Cu1.1 Cu1.1 @	10.59	3	obtuse triangle
0009	12.000	5.1125	@ Cu1.4 @	18.94	2	single scattering
0010	24.000	5.1124	@ Cu1.1 Cu1.4 @	43.63	3	forward scattering
0011	12.000	5.1125	@ Cu1.1 Cu1.4 Cu1.1 @	32.71	4	double forward sca
0015	12.000	5.1125	@ Cu1.1 Cu1.1 @	8.45	3	non-forward linear

2: drag and drop relevant paths to the data window

The screenshot displays the Artemis software interface for data extraction. The main window is titled "Artemis [Data] cu_foil_10k.dat". The interface includes a menu bar (Data, Path, Marks, Actions, Debug, Help) and a toolbar with icons for Atoms, Feff, Paths, Path-like, and Console. The "Paths" tab is active, showing a list of scattering paths. The "Description" field contains the following text:

```
# TITLE Copper  
# TITLE Cu  
# The central atom is denoted by this token: @  
# Cluster size = 5.50 Å, containing 54 atoms  
# 25 paths were found within 5.500 Å  
# Forward scattering cutoff 20.00
```

The "Scattering Paths" table is shown below:

	Degen	Reff	Scattering path	Rank	Legs	Type
0001	12.000	2.5562	@ Cu1.1 @	100.00	2	single scattering
0002	6.000	3.6151	@ Cu1.2 @	22.98	2	single scattering
0003	48.000	3.8344	@ Cu1.1 Cu1.1 @	10.54	3	acute triangle
0004	48.000	4.3638	@ Cu1.1 Cu1.2 @	8.56	3	other double scatter
0005	24.000	4.3638	@ Cu1.1 Cu1.1 @	3.39	3	other double scatter
0006	24.000	4.4275	@ Cu1.3 @	55.41	2	single scattering
0007	96.000	4.7700	@ Cu1.1 Cu1.3 @	21.84	3	obtuse triangle
0008	48.000	4.7700	@ Cu1.1 Cu1.1 @	10.59	3	obtuse triangle
0009	12.000	5.1125	@ Cu1.4 @	18.94	2	single scattering
0010	24.000	5.1124	@ Cu1.1 Cu1.4 @	43.63	3	forward scattering
0011	12.000	5.1125	@ Cu1.1 Cu1.4 Cu1.1 @	32.71	4	double forward sca
0015	12.000	5.1125	@ Cu1.1 Cu1.1 @	8.45	3	non-forward linear

The "Data" window on the right shows a list of paths with checkboxes. The path "[icsd_434] Cu1.1 Cu1.4 Cu1.1" is selected. The "Parameters" section shows the following values:

- kmax: 23.019
- dk: 1
- rmax: 3
- dr: 0.0

Two blue arrows indicate the drag-and-drop action from the "Scattering Paths" table to the "Data" window.

2: Define parameters

[icsd_434] Cu1.1

- [icsd_434] Cu1.2
- [icsd_434] Cu1.3
- [icsd_434] Cu1.4
- [icsd_434] Cu1.1 Cu1.4
- [icsd_434] Cu1.1 Cu1.4 Cu1.1

[icsd_43493_Copper] Cu1.1

Include path Plot after fit

Use this path for phase corrected plotting.

@ Cu1.1 @

(0001) single scattering, high (100.00)

x	y	z	i:
1.807530	1.807530	0.000000	
0.000000	0.000000	0.000000	

Label: Reff=2.556, nleg=2, degen=12

N: 12

So2

ΔE0: De_0

ΔR: dr_1

ss_1

right click for options

Clear S₀²

- Export this S₀² to every path in THIS Feff calculation
- Export this S₀² to every path in THIS data set
- Export this S₀² to every path in EVERY data set
- Export this S₀² to marked paths in THIS data set

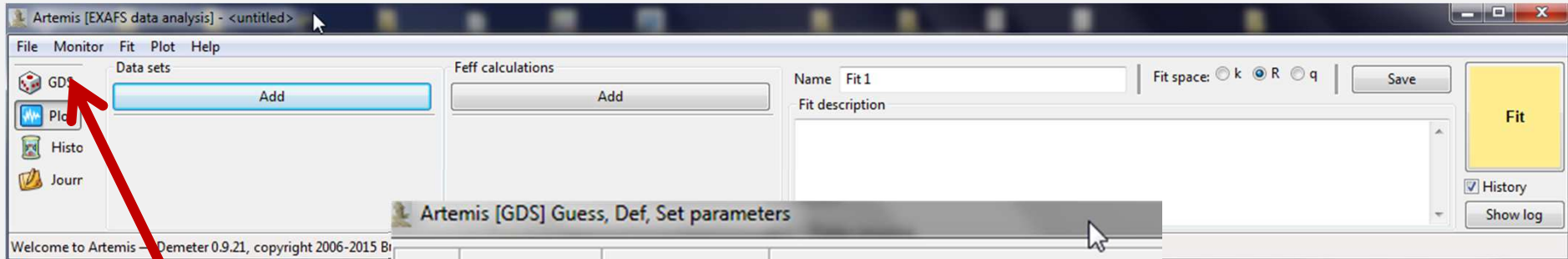
Grab S₀² from previous path

Grab S₀² from next path

Give a name to each parameter to adjust

NOTE:
DE and So2 should be the same for absorbers in the same structure

3: Define parameters



3

select **refinement
param.**, plot, etc...
USE GDS button

Artemis [GDS] Guess, Def, Set parameters

	Type	Name	Math expression
1	guess	So2	0.8
2	guess	De_0	0.0
3	guess	dr_1	0.0
4	guess	ss_1	0.003
5	guess	dr_2	0.0
6	guess	ss_2	0.003
7	guess	dr_3	0.0
8	guess	ss_3	0.003
9	guess	dr_4	0.0
10	guess	ss_4	0.003
11	guess	ss_41	0.003
12	guess	ss_42	0.003

Note:
Initialize to >0
the σ^2 parameters

Note:
Constraint to physical
meaning structural
parameters (es. MS paths)



3: Define parameters

The screenshot displays the Artemis software interface for EXAFS data analysis. The main window shows the 'Data' tab for 'cu_foil_10k.dat'. The 'Fourier transform parameters' section is highlighted with a red box, containing the following values:

kmin	3.000	kmax	23.019	dk	1
rmin	1	rmax	3	dr	0.0

A red arrow points from the 'Data' tab to the 'Actions' menu, which is also highlighted with a red box. The 'Actions' menu contains the following options:

Make VPath from marked	Alt+Shift+v
Transfer marked	Alt+Shift+t
Compute bond valence sum	Alt+Shift+b
Include marked	Alt+Shift+c
Exclude marked	Alt+Shift+x
Discard marked	
Plot marked after fit	Alt+Shift+p
Plot no paths after fit	Alt+Shift+u

A red arrow points from the 'Include marked' option to a note box. Another red arrow points from the 'Fit' button in the top right to a note box. A red arrow also points from the 'Data' tab to the 'Fourier transform parameters' section.

Note:
Run fit starting with first shell then add progressively far away contributions

Note:
FT range must include the last shell you want to fit

4: FIT

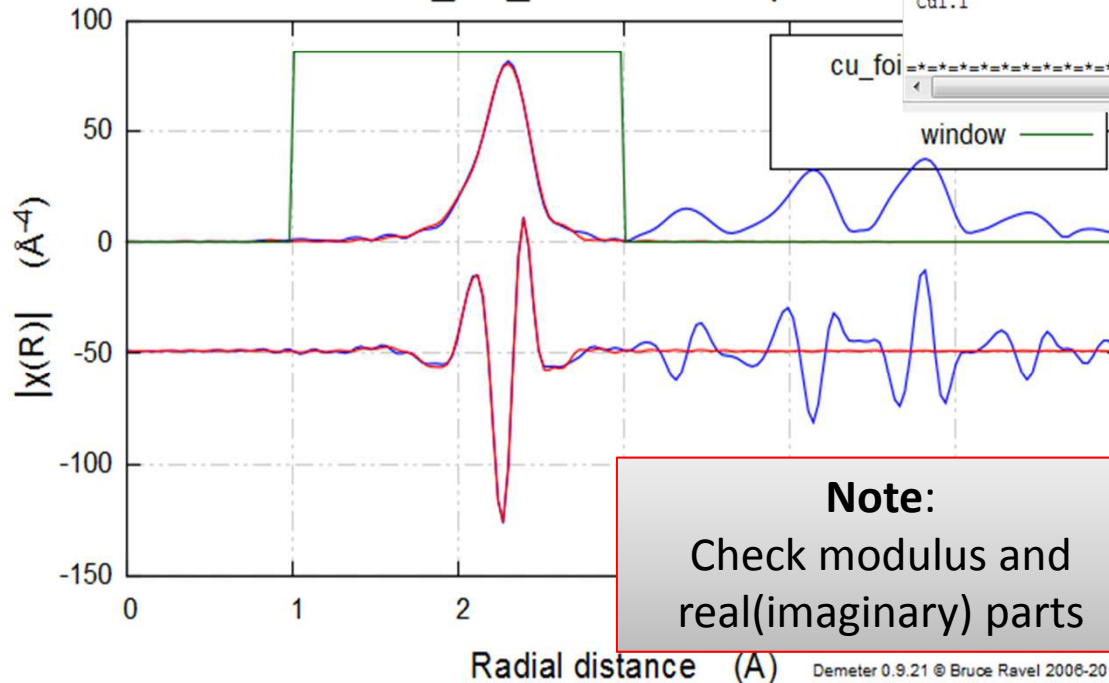


```
Artemis [Log] Fit 1
: Athena project      = C:\Users\carlo\Dropbox\Seminar_Malu_2015\dati\ok_Cu_Foil\EXAFS_est
: name               = cu_foil_10k.dat
: k-range            = 3.000 - 23.019
: dk                 = 1
: k-window           = hanning
: k-weight           = 1,2,3
: R-range            = 1 - 3
: dR                 = 0.0
: R-window           = hanning
: fitting space      = r
: background function = no
: phase correction   = no
: background removal = E0: 8977.58, Rbkg: 1.0, range: [0:25.019], clamps: 0/24, kw: 2
: epsilon_k by k-weight = 1.857e-004
: epsilon_r by k-weight = 4.857e-001
: R-factor by k-weight = 1 -> 0.00421, 2 -> 0.00225, 3 -> 0.00273
```

name	N	S02	sigma^2	e0	delr	Reff	R
Cu1.1	12.000	0.904	0.00345	5.419	-0.00827	2.55620	2.54793

name	ei	third	fourth
Cu1.1	0.00000	0.00000	0.00000

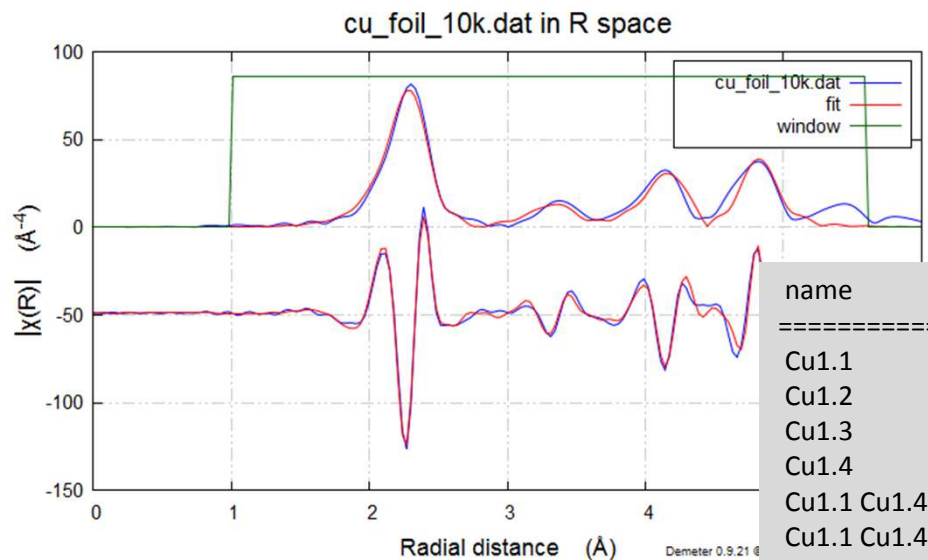
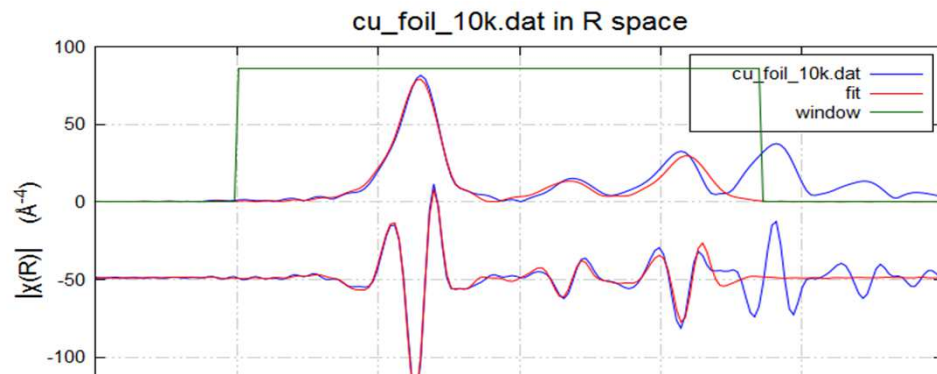
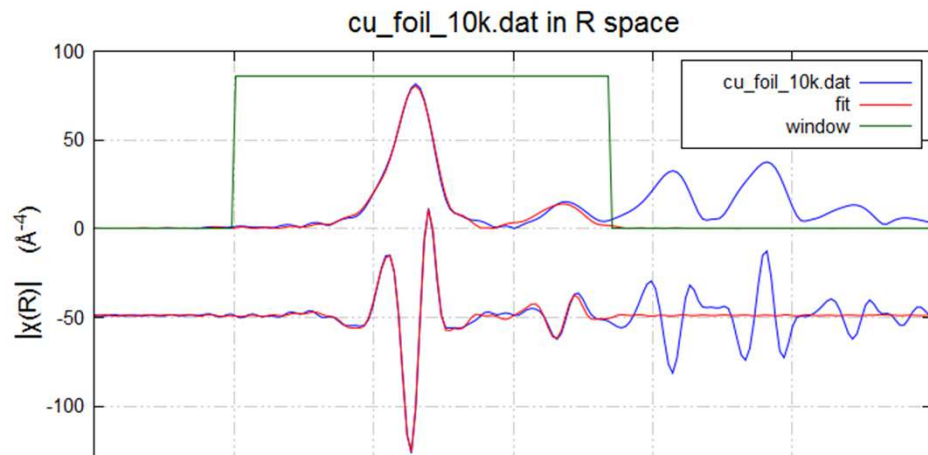
cu_foil_10k.dat in R space



Note: always use physical meaning constraints i.e. for Cu foil N_j are that of fcc structure

Note: Check modulus and real(imaginary) parts

4: FIT, extend the analysis to further shells



Fourier transform parameters

kmin kmax dk

rmin rmax dr

Note:
shell 3 and 4 should be included together

name	N	S02	sigma^2	e0	delr	Reff	R
Cu1.1	12.000	0.980	0.00388	4.001	-0.01367	2.55620	2.54253
Cu1.2	6.000	0.980	0.00513	4.001	-0.02943	3.61510	3.58567
Cu1.3	24.000	0.980	0.00514	4.001	0.00381	4.42750	4.43131
Cu1.4	12.000	0.980	0.00092	4.001	0.00862	5.11250	5.12112
Cu1.1 Cu1.4	24.000	0.980	0.00271	4.001	0.00862	5.11250	5.12112
Cu1.1 Cu1.4 Cu1.1	12.000	0.980	0.00322	4.001	0.00862	5.11250	5.12112

4: Check best fit log file

Note:

Keep correlations among the parameters low, maybe add physical meaning constraints.

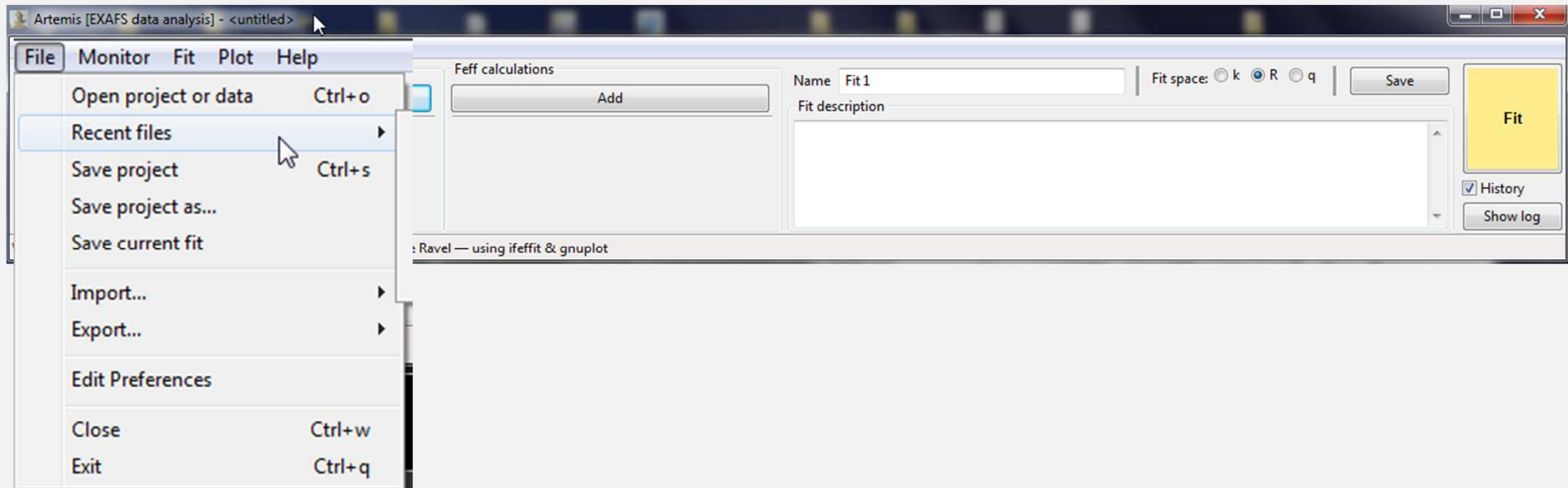
Far away shell parameters are generally less accurate, use them with care

Correlations between variables:

ss_42 & ss_4	--> 0.8812
ss_1 & so2	--> 0.8229
ss_43 & ss_42	--> 0.8137
ss_43 & ss_4	--> 0.8062
dr_1 & de_0	--> 0.7729
ss_43 & dr_4	--> 0.7515
dr_3 & de_0	--> 0.6824
dr_3 & dr_1	--> 0.5290
ss_3 & so2	--> 0.5153
ss_42 & so2	--> 0.4289
ss_3 & ss_1	--> 0.4239

All other correlations below 0.4

5: Always save best fit and output files



6: Check your results and your hypothesis about local atomic structure... if mismatches check hypothesis, extraction, quality of the data...

Your Exercises

CoO-oxide directory contains Co K edge EXAFS spectra measured on CoO powders

1. Extract EXAFS signals and save data
2. Merge data
3. Analyze Co EXAFS signals

Fe-Temperature directory contains Fe EXAFS spectra measured on Fe foils at different temperatures..

1. Extract EXAFS signals
2. Qualitatively compare the data
3. Check the proper edge alignment
4. Analyze Fe EXAFS signals and account for structural changes as a function of temperature