Introduction to *ab-initio* methods for EXAFS data analysis

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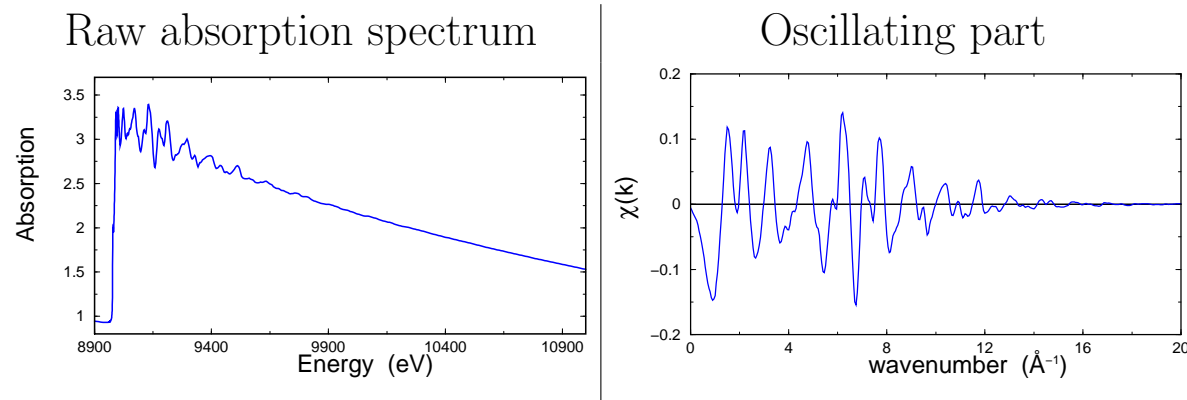dacapito@esrf.fr

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Contents

1 Data analysis methods

In an EXAFS experiment, the absorption coefficient μ is collected:

Raw absorption spectrum

Oscillating part

but only the oscillating part contains the information on the local structure like coordination numbers, bond lengths, bond length distribution [1].

The quantitative analysis method method consists in:

- Extract the Oscillating part (χ function) from the absorption μ.

- Filter the desired signal χ

- Fit the χ to a suitable model

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Consider the basic EXAFS formula:

$$\chi(k) = S_0^2 \frac{N A(k)}{k R^2} e^{\frac{-2R}{\lambda}} sin(2kR + \phi(k) + \phi_c) e^{-2k^2\sigma^2} \tag{1}$$

The **conventional** way of analyzing EXAFS data is to use empirical standards, often in conjunction with Fourier filter techniques.

In this approach, an *unknown* structure (blue parameters) is studied by extracting the **backscattering parameters** from the experimental spectrum of a *known* model compound.

In this lecture, the use of *ab-initio* methods and in particular the University of Washington XAFS package (UWXAFS) in EXAFS analysis based on theoretical standards will be discussed. This method uses theoretical calculations to provide the red parameters and has to be used in a variety of cases, namely:

- no empirical standards are available

  - non-resolved shells (BCC $1 - 2^{nd}$ shell)

  - complex structures

- strong Multiple Scattering effects involved

  - collinear configurations (FCC 4th shell)

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2 X-ray absorption cross section

2.1 General formulation

When measuring the X-ray absorption coefficient we measure the (mainly) dipole mediated transition of an electron from a deep core state $|i\rangle$ to an unoccupied state $|f\rangle$. From the Fermi Golden Rule

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \langle f|\hat{\epsilon} \cdot \mathbf{r}|i\rangle^2 \delta(E_f) \tag{2}$$

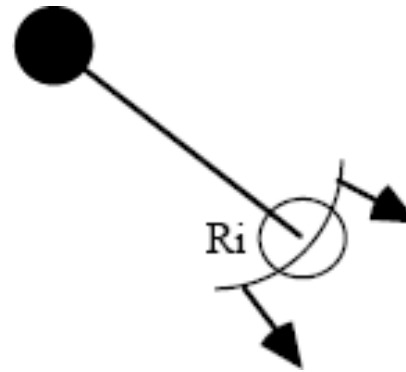There are two ways to solve this equation [2]:

- Find an expression for $|i\rangle$ and $|f\rangle$ and evaluate directly the integral.

- Use the Green function method where only the potential and the initial state are needed

Amplitude of the photoelectron wave: a simple derivation.
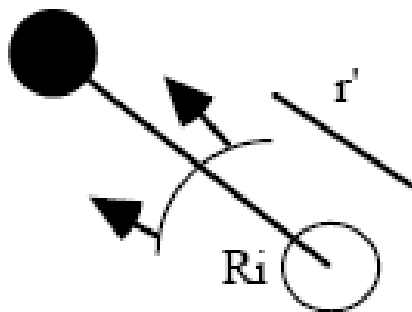

$$e^{i\delta}\frac{e^{ikR}}{kR}cos\Theta \qquad (3)$$
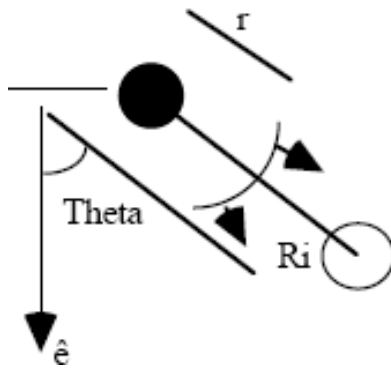
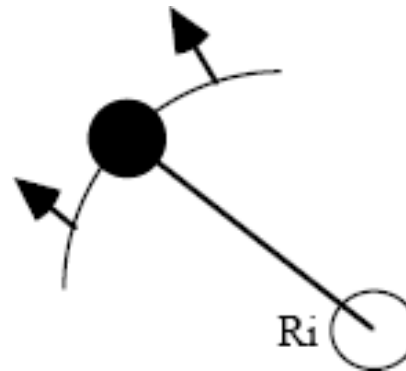$$e^{i\delta}\frac{e^{ikR_i}}{kR_i}cos\Theta \qquad (4)$$

$$e^{i\delta}\frac{e^{ikR_i}}{kR_i}T(k)e^{i\beta}\frac{e^{ikR}}{kR}cos\Theta \qquad (5)$$

$$e^{i\delta}\frac{e^{ikR_i}}{kR_i}T(k)e^{i\beta}\frac{e^{ikR_i}}{kR_i}e^{i\delta}cos\Theta \qquad (6)$$

2.2 The Multiple Scattering approach

In the Green function method the X-ray absorption cross section is written as [3],[4], [5]:

$$\mu(E) \propto -\frac{1}{\pi}\Im\langle i|\hat{\epsilon}^* \cdot rG(r,r`,E)\hat{\epsilon} \cdot r`|i\rangle\Theta(E-E_F) \tag{7}$$

Where:

$$G(r,r`,E) = \frac{1}{E-H+i\eta}$$

(E= photon energy, H = one-particle Hamiltonian)
That can be explicitated as [4]:

$$\mu(E) \propto \mu^{at}\Im\{\frac{1}{sin^2\delta_{L_0}^0}\frac{1}{2^{L_0+1}}\sum_{m_0}[T((1-GT)^{-1})_{L_0,L_0}^{0,0}\}$$

Where:

T= Atomic Scattering matrix

$$T = \begin{pmatrix} t_0 & 0 & \ldots \\ 0 & t_1 & \ldots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Scattering from $i^t h$ atom

G Propagator matrix

$$G = \begin{pmatrix} 0 & G_{0,1} & \ldots \\ G_{1,0} & 0 & \ldots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Propagation from $i^t h$ to $j^t h$ atom

The $(1 - GT)^{-1}$ term can be approximated by a serie expansion

$$T(1 - GT)^{-1} \approx \sum_n [T(GT)^n]$$

Yelding:

$$\mu(E) \propto \mu^{at}\Im\{\frac{1}{sin^2\delta_{L_0}^0}\frac{1}{2^{L_0+1}}\sum_{m_0}\underbrace{\sum_n[T(GT)^n]_{L_0,L_0}^{0,0}}_{MultipleScattering}\}\tag{8}$$

Physical meaning of the various terms:

Note: '0' Indicates the absorber, i and j neighbors.

Math term	Picture	Meaning
$T_0G_{0,i}T_iG_{i,0}T_0$		Single Scattering
$T_0G_{0,i}T_iG_{i,j}T_jG_{j,0}T_0$		Double Scattering
⋮	⋮	⋱

The convergence of the serie in (8) is achieved under strict conditions on the energy range and scattering amplitudes (see [3]). Moreover (8) is not generally reducible to a simple analytical expression. However it has been found [5], [6] that each of the various terms of the expansion of (8) can be written as:

$$\chi_\Gamma(k) = \left(S_0^2 e^{-2\sigma^2 k^2}\right) \Im \left(\frac{f_{eff}}{kR^2} e^{2i(kR+\phi)}\right) \tag{9}$$

Here Γ is the path index and f_{eff} and ϕ are the effective amplitude and phases of the path under analysis. These quantities can be thus calculated separately and then introduced in a fitting procedure.

2.3 Other terms in the EXAFS expression

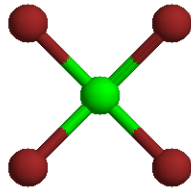$$\chi(k) = S_0^2 \frac{NA(k)}{kR^2} e^{\frac{-2R}{\lambda}} sin(2kR + \phi(k) + \phi_c) e^{-2k^2\sigma^2} \tag{10}$$

- The Debye-Waller Factor σ^2

- The Photoelectron Mean free path λ

- The Many Body amplitude reduction factor S_0^2
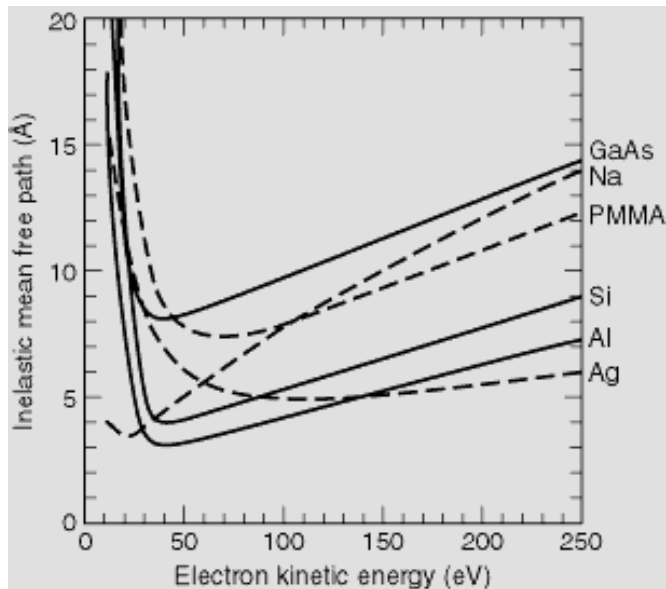
The electron mean free path in solids.

2.4 Generalization of the parameters

When using the Multiple Scattering formalism we must adopt a generalized definition of the variables N, R and σ^2.

In the case of a 3 centers configuration N becomes the number of triangles per absorbing atom in the structure. Clockwise and counterclockwise are counted separately. In this case $N_3 = 8$.
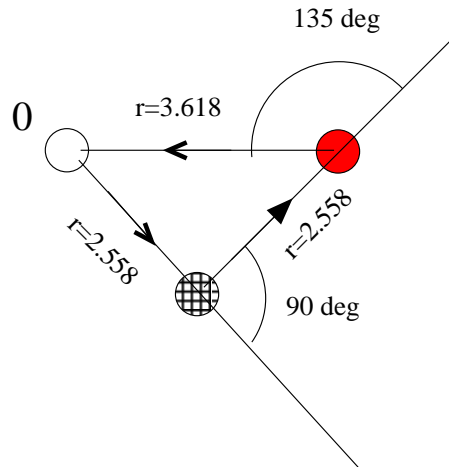
In a MS path the path length R becomes the half length of the roundtrip. In the present case $R = 4.367$ Å
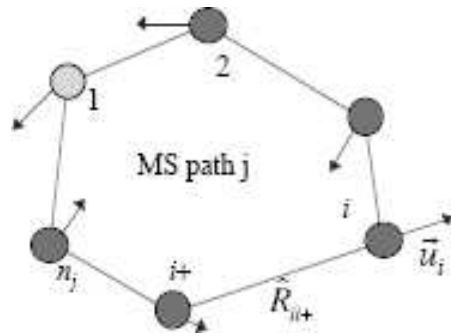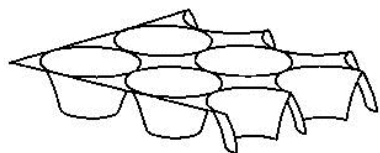
MS path j

In a MS path the Debye-Waller factor is defined as follows:

$$\sigma_j^2 = \frac{1}{4}\langle[\sum_{i=1}^{n_j}(\vec{u_i} - \vec{u_{i+}}) \cdot \hat{R}_{ii+}]^2\rangle \qquad (11)$$

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2.5 Computing theoretical terms

Here we describe the steps in the generation of theoretical paths:

1.

Compute atomic potentials and phase shifts

Use neutral, free, atomic spheres to construct a muffin tin potential. The embedded atoms are spherical and the interstitial region is flat.

Find all scattering geometries in a cluster

2. Use a heap to construct successively higher orders of MS paths. In this way *all* possible scattering geometries are found in a cluster up to a specified order.

3.
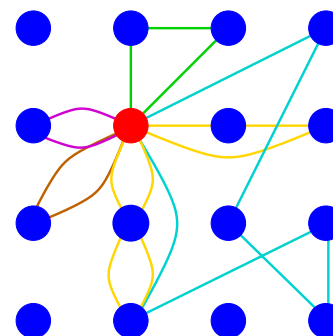
Compute the contribution from each path

Using the list of enumerated paths and the atomic potentials, compute the curved-wave, effective scattering amplitudes and phase shifts for all paths. Polarization is considered *a priori* for all paths.
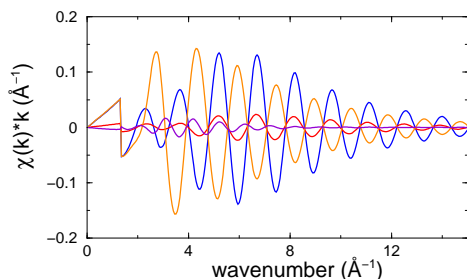
3 Overview of the UWXAFS package

The package UXWAFS [7] contains all the programs necesary to the generation of the theoretical paths, signal extraction and fit. Here you find a flowchart of the package:

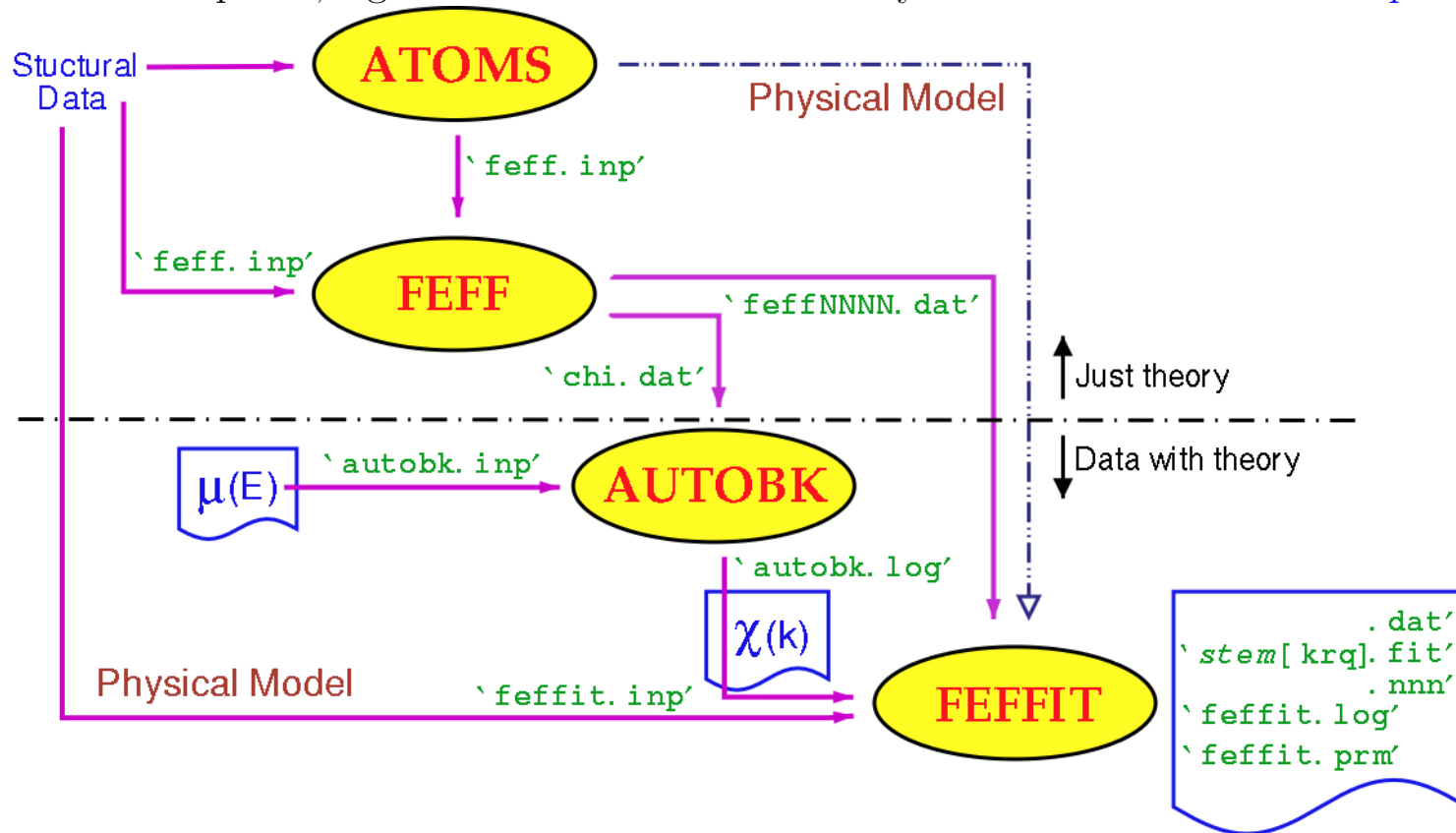The UWXAFS package is made-up of 4 main programs

(TK)ATOMS Atoms takes the crystallographic data of the compound of interest and generates a suitable file for the program Feff. The file contains the atomic coordinates in the crystal up to a certain distance from the absorber and some control cards for Feff

FEFF Starting from the atomic coordinates Feff calculates the amplitude and phases of scattering paths up to a given order and 'intensity'.

AUTOBK (ATHENA) Used to extract EXAFS $\chi(k)$ part from the absorption spectrum

FEFFIT (ARTEMIS) Fits the EXAFS spectrum with a theoretical model based on the paths calculated by Feff.

Making a comparison with another package (*GNXAS*) we can here resume sinoptically the operations of the various programs:

| UWXAFS	GNXAS	Operation
TKATOMS	CRYMOL, GNPEAK	Atomic coordinates generation
FEFF	GNPEAK, GNXAS	Path search and signal calculation
ATHENA	No analogous	EXAFS signal extraction
ARTEMIS	FITHEO	Signal fitting

Here we will provide a brief introduction to the use of the package. For a complete description and program manuals refer to the project home page [7] on the Web.

4 ATHENA

The ATHENA code is used to subtract the atomic background from the raw absorption spectrum and yields the oscillating χ EXAFS function. Here we show a typical screenshot from ATHENA: the page contains all the necessary fields to adjust the subtraction routine to the current data. It is based in the AUTOBK routine that shapes the atomic absorption spline function by minimizing the Fourier Transform amplitude of the subtracted data under a given R_{bkg} value. R_{bkg} is typically taken about 1.0 Å.

The main window of the ATHENA program
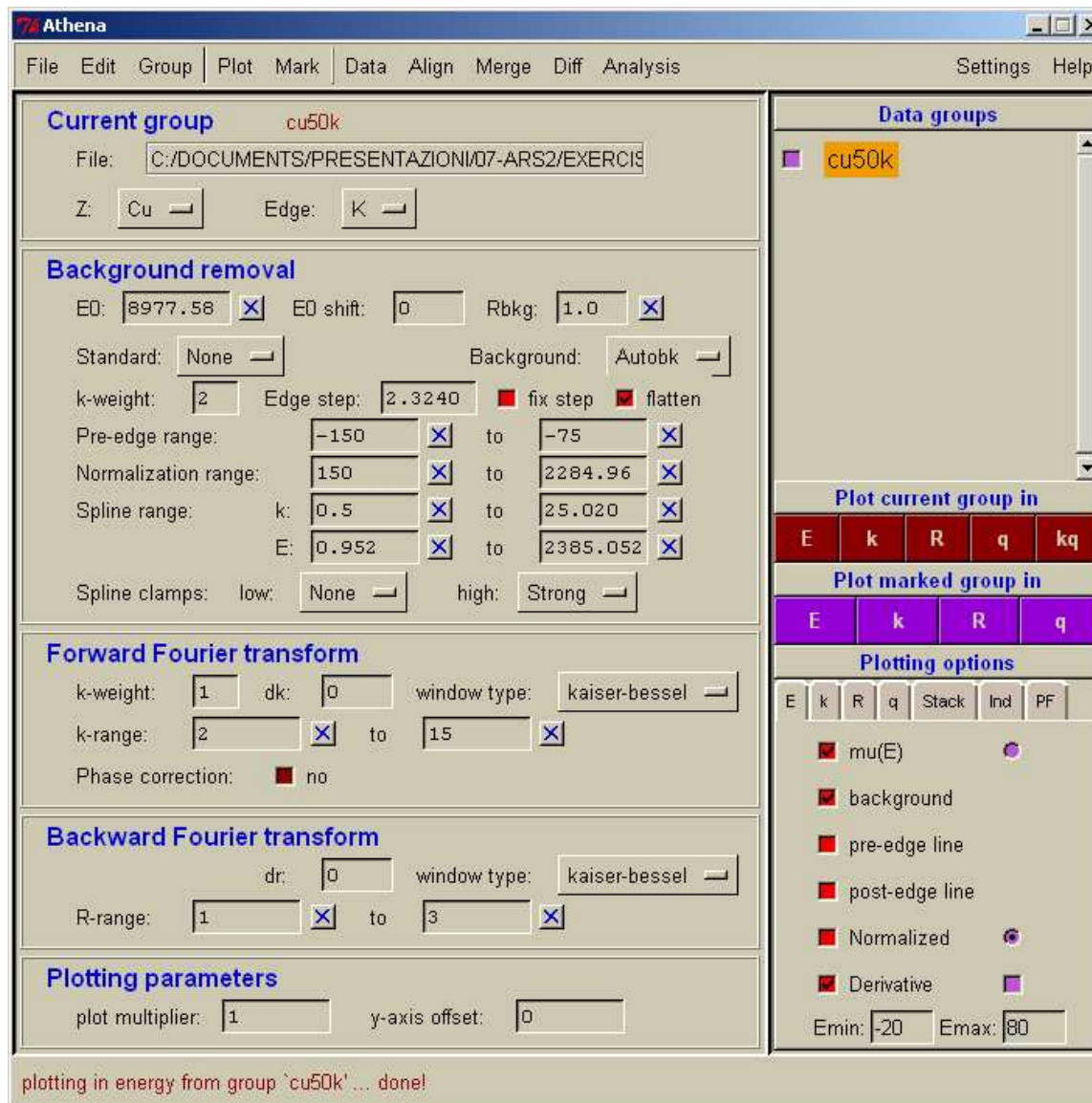
4.1   Operations carried out by ATHENA

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- Pre-edge subtraction

    – Pre edge Range x to y

- Edge Position determination

    – E0

- Atomic background subtraction

    – Rbkg

    – k-weight

    – Spline Range k x to y

    – Spline Range E x to y

- Edge step determination

    – Normalization Range x to y

4.2   Pre-edge subtraction

ATHENA carries out a linear approximation to the pre-edge region between the Pre-edge region limits.
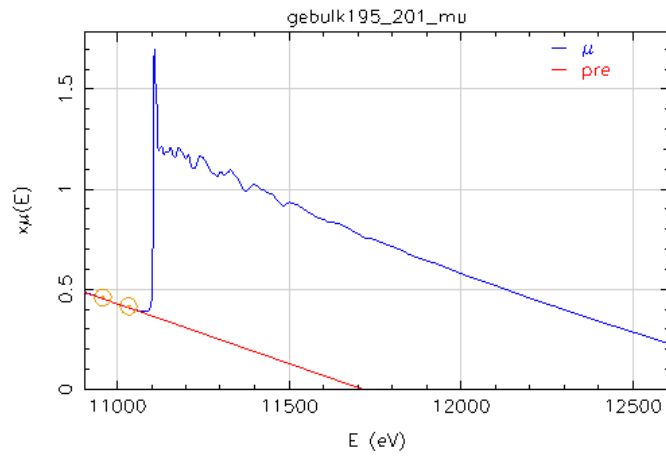
A G O O D pre-edge subraction
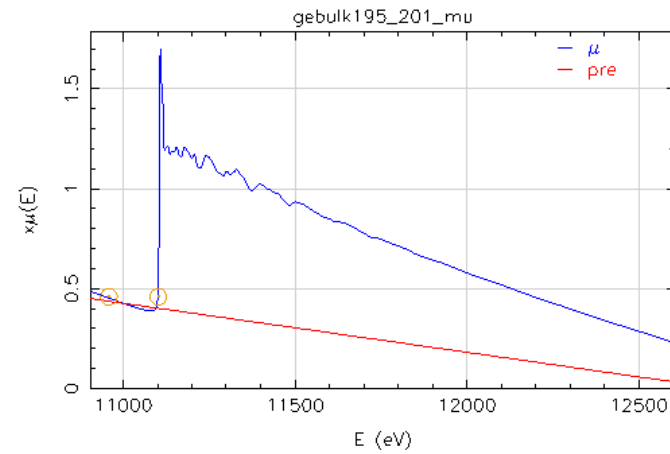
A B A D one.

4.3 Edge position determination

ATHENA calculates the derivative of the absorption coefficient $\frac{\delta\mu}{\delta E}$ and sets the edge position on the First maximum. The resuls is written in the Eo field.
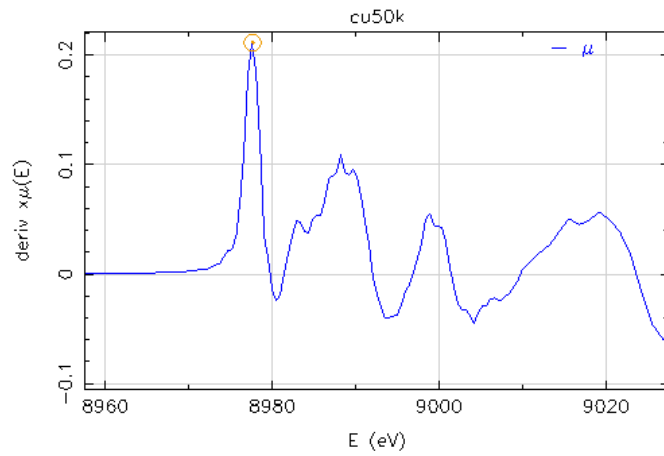
A G O O D Edge determination
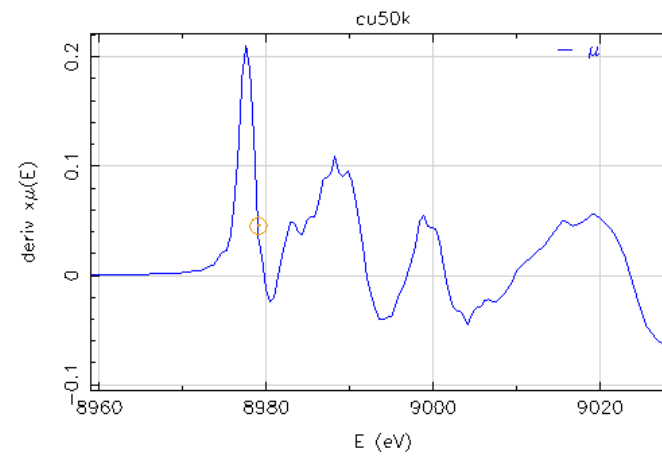
A B A D one.

4.4 Atomic background subtraction

ATHENA approximates the atomic background via a spline function. This function minimizes the residual in R space for frequencies below Rbkg.
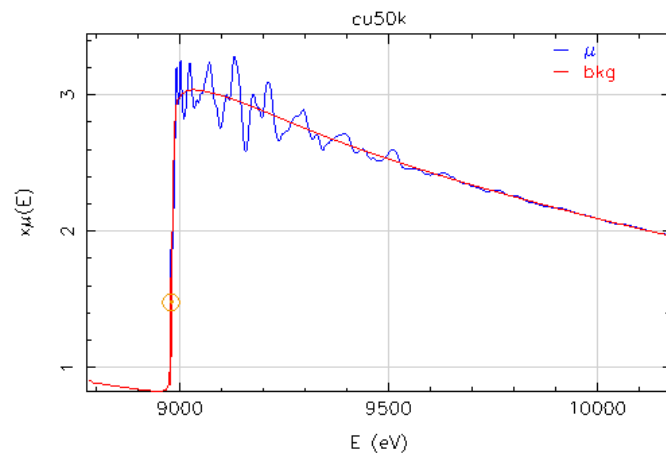
A **G O O D** Edge determination
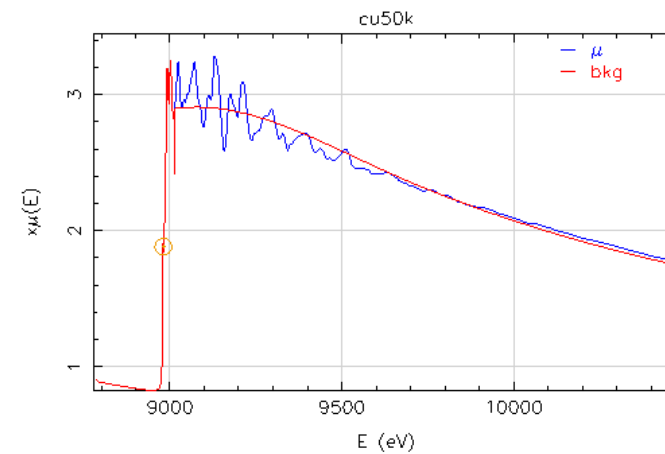
A **B A D** one.

4.5 Edge step determination

ATHENA approximates the post-edge region by a quadratic function. It is used to extrapolate the value of the absorption coefficient to E0. The limits of the function are defined in the Normalization Range fields.
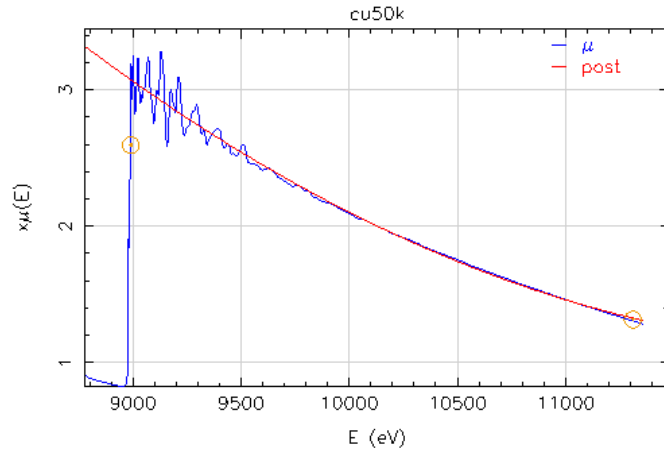
A G O O D Edge determination
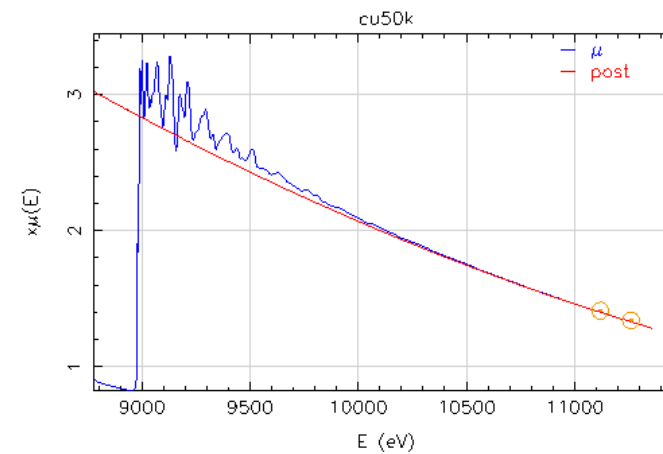
A B A D one.

The result of a good spectrum extraction is shown below:
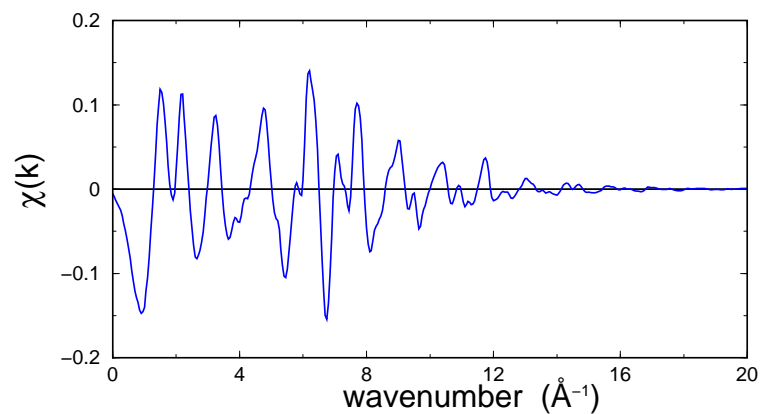
The $\chi(k)$ function oscillates symmetrically around the zero line.
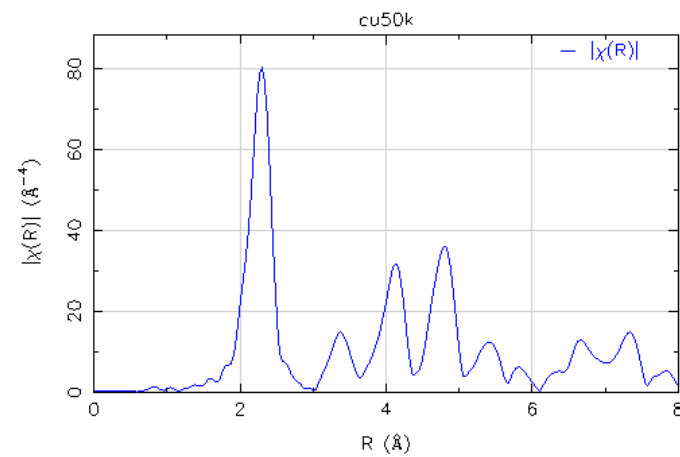
There are no peaks in the Fourier Transform at low (< 1 Å) R values.

5 TKATOMS

In order to generate the correct EXAFS signals it is mandatory to start from a system with electron densities, bond distances and angles as much similar as possible to the sample in analysis.

For (strained, doped, ...) crystals the starting model will be the (undistorted, undoped, ...) crystal, for amorphous samples it is preferable to use a crystalline compound with similar composition.

The instructions for the program are loaded in the program interface page: see here an example for metallic Cu.

It is made up of a series of fields where the details of the crystal (Space group, cell dimension and angles, crystallographic sites) are inserted. These parameters can be found from different sources like:

- R.N.G. Wychoff's *Crystal Structures* [8]. A quite popular book on crystal structures.

- The ICSD database [9] This is a powerful and complete database with more than 76,500 entries in its complete form (needs registration).

- The American Mineralogist database (free access).

You can access this database (http://icsd.ill.fr) and enter the details of your structure, namely the elements name and number:

The database prompts you a list of different structures. You choose that most suited to your investigation and retrieve its the details:

The same holds for the American Mineralogist database (http://rruff.geo.arizona.edu/AMS/amcsd.php). Here's the input page:
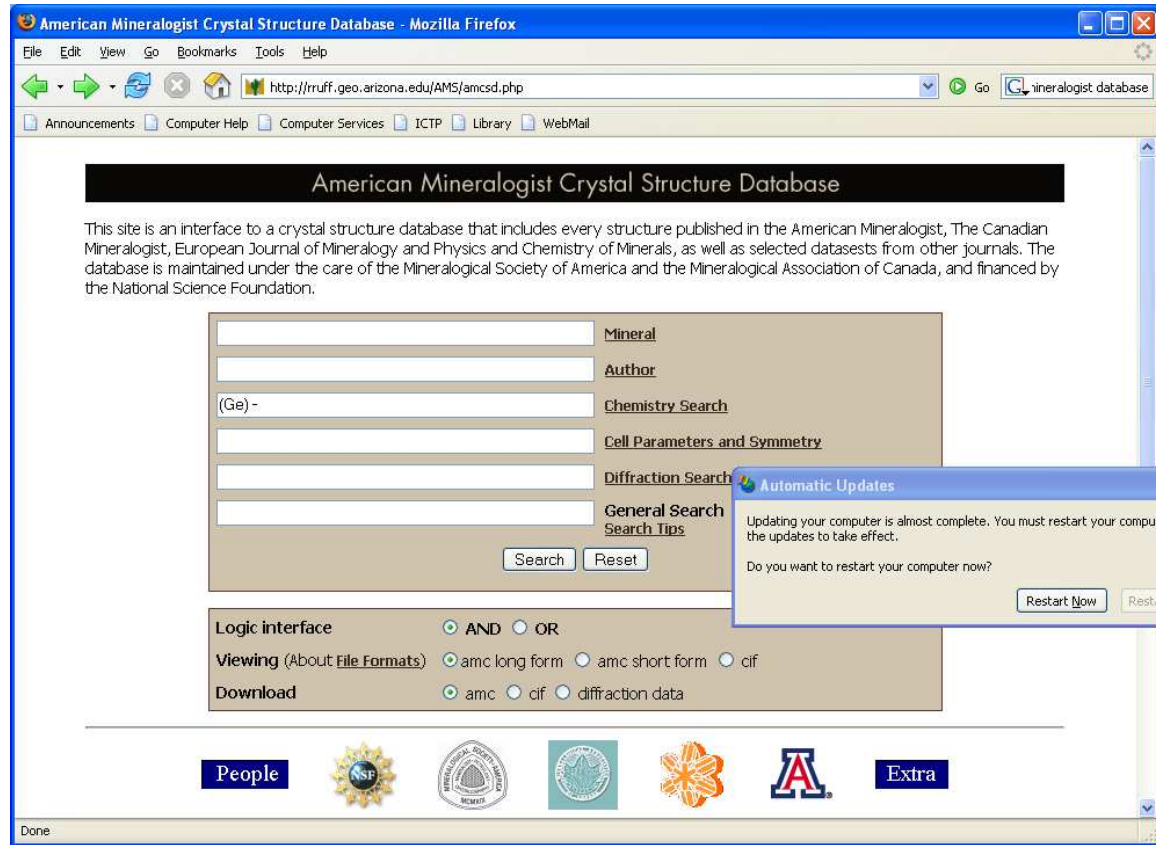
And this is the output:
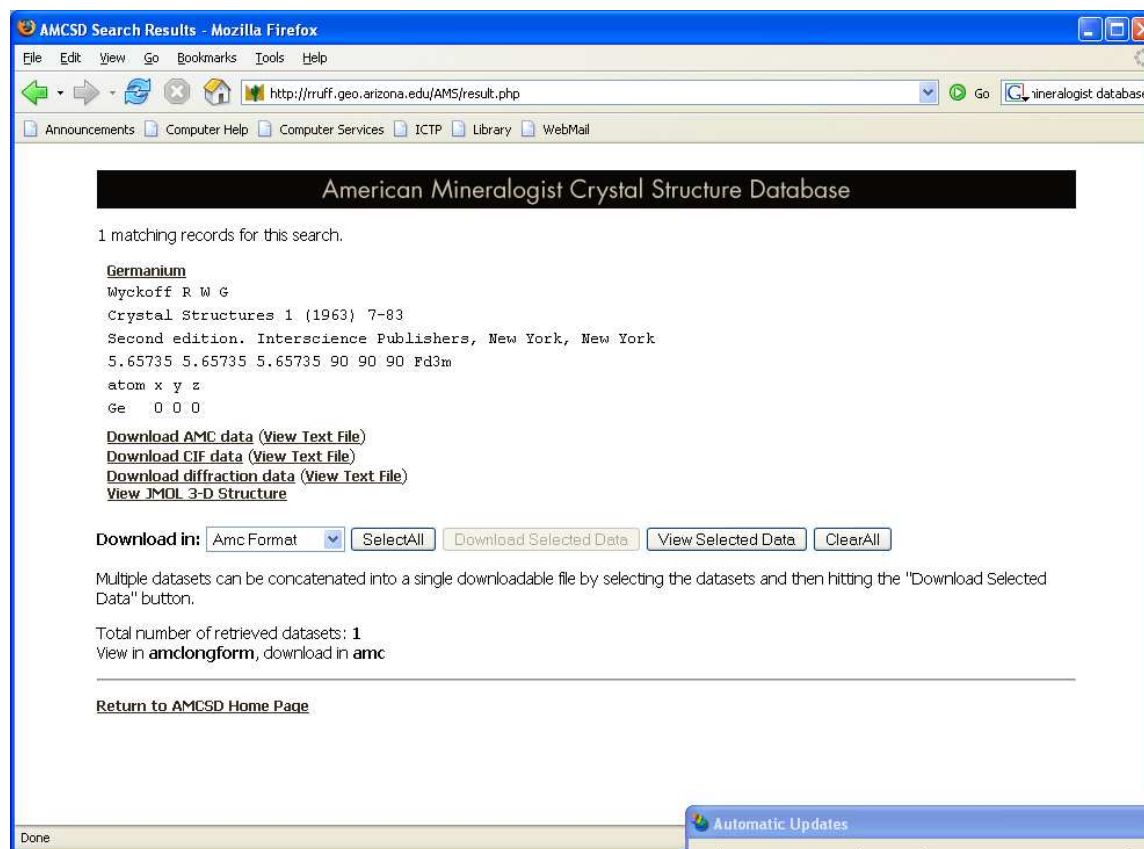
The output of TKATOMS is the $f$eff.inp file that is the input for the following program (feff).

6   FEFF

The Feff program [10], [11] carries out a serie of tasks with the aim of generating the theoretical signals to be used at the fitting stage. The main actions in a run for EXAFS analysis are listed below:

- Calculation of atomic potentials in the Muffin Tin approximation from the given cluster

- Calculation of the phase shifts

- Analysis of the cluster with identification of the multiple scattering paths

- Calculation of the signals.

All these operations are sequentially done by a serie of *modules*.

Here we show an example of input file *feff.inp*:

```
* This feff.inp file generated by ATOMS, version 2.50
* ATOMS written by and copyright (c) Bruce Ravel, 1992-1999

TITLE   Cu crystal fcc
EDGE      K
SO2       1.0


*         pot    xsph  fms   paths genfmt ff2chi
CONTROL  1       1     0     1     1      1
PRINT    1       0     0     0     0      3



*         ixc  [ Vr  Vi ]
EXCHANGE  0       0   0
EXAFS  20
RPATH  11



POTENTIALS
*   ipot   z [ label   l_scmt  l_fms   stoichiometry ]
      0   29    Cu      -1      -1         0
      1   29    Cu      -1      -1         1

ATOMS
   0.00000     0.00000     0.00000    0   Cu1          0.00000
   0.00000    -1.80900     1.80900    1   Cu1          2.55831
   1.80900     0.00000     1.80900    1   Cu1          2.55831

   (follow the positions of the atoms up to the 5th shell)
END
```

6.1 Modules

The calculation proceed as follows: first of all the program is instructed that a K edge spectrum has to be calculated ($EDGE$ card). Then the various modules of the program are marked to be run (1) or not (0) in sequence ($CONTROL$ card) performing the following operations:

pot Calculates the (atomic, muffin tin) scattering potentials.

xsph Calculates the phase shifts.

fms Full multiple scattering calculation of the absorption cross section. Not used in the present example.

paths path identification

genfmt Scattering amplitude calculation.

ff2chi Output of the various theoretical paths on a file.

6.2 Cards

The card *EXCHANGE* defines the energy-dependent potential type to be used, ixc=0 corresponding to the complex Hedin-Lunqvist potential.

There are cards that give to the program some limits for the calculation. Here card *EXAFS* limits the maximum k for the calculation to 20 $\overset{\circ}{A}^{-1}$, the maximum length (half roundtrip) for a path to be considered in the calculation (*RPATH* card) is 11Å and scattering paths up to 4th order ('leg', see next section).
Cards like *SCF, XANES, FMS, LDOS* are created by tkatoms and are needed only for a XANES simulations. In an EXAFS analysis will be commented with a * character.

Then the program is instructed on how associate the various potentials to the different atoms in the cluster through the *POTENTIAL* card. For different chemical species a different potential number is associated (1, 2, . . .) potential 0 is always related to the photoemitter.

Eventually, the *ATOMS* card contains the spatial position and the potential associations are defined for each atom in the cluster.

6.3 Scattering paths in Feff

The scattering order of a path can be defined as the number of lines (legs) you draw between scatterers to describe the process under analysis as shown below:
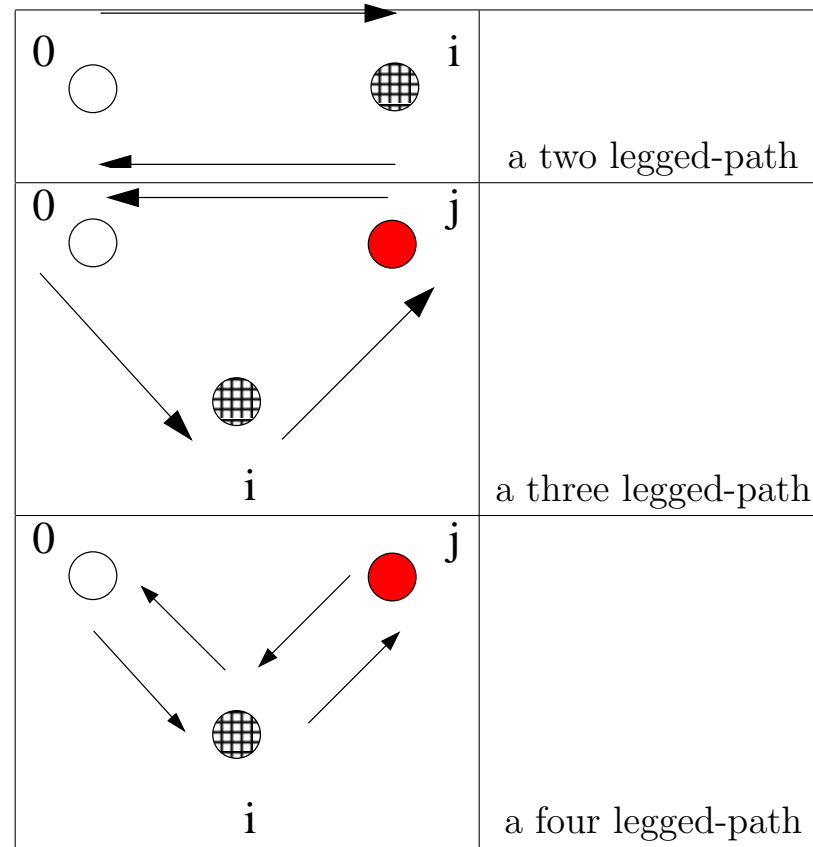
Here '0' denotes the photoabsorber.

If a same 'loop' (same bonds and angles but different involved atoms except the absorber) is found in different atomic arrangements the associated path is said to be 'degenerate' and the degeneration is calculated and accounted for in the path amplitude. Moreover: the same loop can be run in clockwise or counterclockwise direction: this also is accounted for as a 'degeneration' of the path [1]. These degenerations can be removed when calculating the path amplitude accounting for the polarization (see below).

When considering a given atomic arrangement a limited number of different paths have to be considered to correctly account for the its contribution ot the total χ signal. For the three atoms 0, i, j a good choice is to consider:

- 0 - i 2 legged path

- 0 - j 2 legged path

- 0 - i - j - 0 3 legged path

- 0 - i - j - i - 0 4 legged path

The importance of the 3 and 4 legged paths grow dramatically as the $0\hat{i}j$ angle approaches 180 deg (i.e. collinear configuration and 0 deg angle scattering on i). As shown in the following picture (Cu atom, plane wave approx. [12])
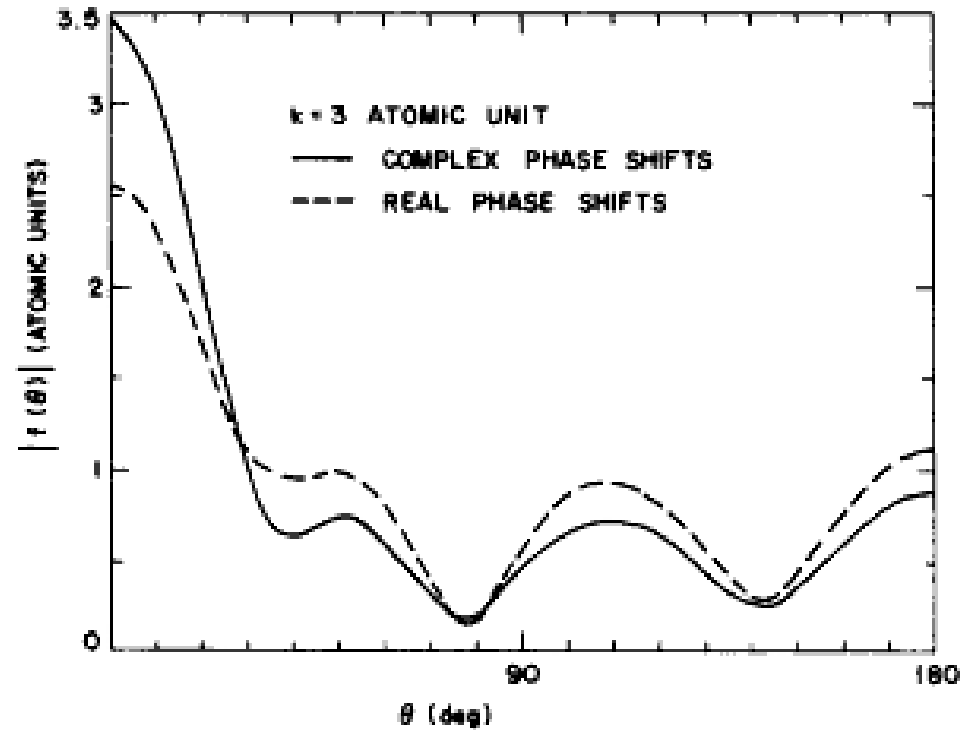
the modulus of the scattering amplitude $|f(\theta)|$ exhibits a marked maximum at 0 deg (forward scattering).

Finally, couple of points need a particular attention when comparing with the GNXAS code:

- The calculated amplitude of a given MS path is valid only for the geometric arrangement considered. The derivatives of amplitude and phase of the path respect to the path length and path angles are not calculated. This has to be considered when analyzing samples with MS paths exhibiting different geometries with respect to the model, especially for the bond angles.

- For what concerns disorder each path is considered to be damped by a Debye-Waller like factor $e^{-\sigma^2 k^2}$ where σ^2 contains bond length and bond angle disorder (thermal or configurational). There is no explicit separation between the two contributions.

6.4 Output Files

Among the files produced by Feff some of them need particular attention. They are all in ASCII format and can be easily listed for checking:

feffXXXX.dat This file contains the major parameters of the associated $XXXX^{th}$ path. It looks like this:

```
Cu crystal fcc                                  Feff  8.00
Abs   Z=29 Rmt= 1.414 Rnm= 1.460 K  shell
Pot 1 Z=29 Rmt= 1.361 Rnm= 1.398
Gam_ch=1.729E+00 H-L exch
Mu=-3.268E+00 kf=1.831E+00 Vint=-1.605E+01 Rs_int= 1.980
Path   1  icalc       2
 -------------------------------------------------------------------
  2  12.000    2.5583    2.6431    -3.26835 nleg, deg, reff, rnrmav(bohr), edge
   x      y      z    pot at#
    0.0000    0.0000    0.0000  0  29 Cu    absorbing atom
    0.0000    1.8090    1.8090  1  29 Cu
   k    real[2*phc]   mag[feff]  phase[feff] red factor   lambda     real[p]@#
  0.000   3.6837E+00  0.0000E+00 -5.0825E+00  9.885E-01  1.6150E+01  1.8324E+00
  0.100   3.6842E+00  4.9963E-02 -5.5819E+00  9.887E-01  1.6173E+01  1.8350E+00
```

where the various columns contain:

- k the photoelectron wavevector

- real[2*phc] the central atom phase * 2

- mag[feff] the path amplitude

- phase[feff] the backscatterer phase

- phase[feff] the central atom reduction factor

- lambda the photoelectrom mean free path

- real[p] the real part of the photoelectrom momentum

This file is directly usable with the *feffit* program or, suitably manipulated, with a generic EXAFS fitting program.

list.dat The 'list.dat' file resumes some basic informations on the calculatios on the various scattering paths. For each (numbered by 'pathindex' that also gives the name to the corresponding feffXXX.dat file) it is indicated:

- the σ^2 factor considered (if any)

- the amplitude ratio respect to the first path

- the degeneracy (that, in case of single scattering path is the number of neighbors)

- the scattering order

- the effective path length (half the loop length, for single scattering coincides with the bond length).

Here we show a typical output for this file:

```
Cu crystal fcc                                                    Feff  8.00
 Abs   Z=29 Rmt= 1.414 Rnm= 1.460 K  shell
 Pot 1 Z=29 Rmt= 1.361 Rnm= 1.398
 Gam_ch=1.729E+00 H-L exch
 Mu=-3.268E+00 kf=1.831E+00 Vint=-1.605E+01 Rs_int= 1.980
 ----------------------------------------------------------------------
  pathindex     sig2   amp ratio    deg    nlegs  r effective
          1   0.00000   100.000   12.000      2   2.5583
          2   0.00000    23.042    6.000      2   3.6180
          3   0.00000    11.967   48.000      3   3.8375
          4   0.00000     9.198   48.000      3   4.3673
          5   0.00000    55.644   24.000      2   4.4311
          6   0.00000    11.632   48.000      3   4.7739
          7   0.00000    24.567   96.000      3   4.7739
          8   0.00000    19.047   12.000      2   5.1166
          9   0.00000     9.492   12.000      3   5.1166
         10   0.00000    43.979   24.000      3   5.1166
         11   0.00000     8.413   12.000      4   5.1166
         12   0.00000     4.189   12.000      4   5.1166
         14   0.00000    31.858   12.000      4   5.1166
```

path00.dat This file contains a more exhaustive description of the paths permitting their identification. Here is a typical output:

```
Cu crystal fcc
Rmax 11.2566,  keep limit  0.000, heap limit  0.000
Plane wave chi amplitude filter   2.50%
---------------------------------------------------------------------
    1    2  12.000  index, nleg, degeneracy, r=  2.5583
    x           y           z      ipot  label      rleg      beta       eta
  0.000000    1.809000    1.809000   1 'Cu     '     2.5583  180.0000    0.0000
  0.000000    0.000000    0.000000   0 'Cu     '     2.5583  180.0000    0.0000
    2    2   6.000  index, nleg, degeneracy, r=  3.6180
    x           y           z      ipot  label      rleg      beta       eta
  0.000000    3.618000    0.000000   1 'Cu     '     3.6180  180.0000    0.0000
  0.000000    0.000000    0.000000   0 'Cu     '     3.6180  180.0000    0.0000
    3    3  48.000  index, nleg, degeneracy, r=  3.8375
    x           y           z      ipot  label      rleg      beta       eta
 -1.809000    1.809000    0.000000   1 'Cu     '     2.5583  120.0000    0.0000
 -1.809000    0.000000   -1.809000   1 'Cu     '     2.5583  120.0000    0.0000
  0.000000    0.000000    0.000000   0 'Cu     '     2.5583  120.0000    0.0000
    4    3  48.000  index, nleg, degeneracy, r=  4.3673
    x           y           z      ipot  label      rleg      beta       eta
  0.000000    3.618000    0.000000   1 'Cu     '     3.6180  135.0000    0.0000
 -1.809000    1.809000    0.000000   1 'Cu     '     2.5583   90.0000    0.0000
  0.000000    0.000000    0.000000   0 'Cu     '     2.5583  135.0000    0.0000
```

For each path it is indicated the number, scattering order, degeneracy and length.

The successive numbers are added to better describe the path but are not considered by genfmt. *rleg* is the leg length, *beta* indicates the photoelectron scattering angle. Namely for path 4 in the previous example if we start from atom with potential '0' (the absorber at 0.0, 0.0, 0.0) going to the first scatterer the photoelectron travels for 2.558 Å then scatters on the neighbor at (-1.809, 1.809, 0.00) with an angle of 90 deg, travels again for 2.558 Å scatters of 135 deg on the neighbor at (0.0, 3.618, 0.0) and travels for 3.618 Å before coming back to the absorber.

The picture below describes path 4 with bond lengths and angles evidenced.
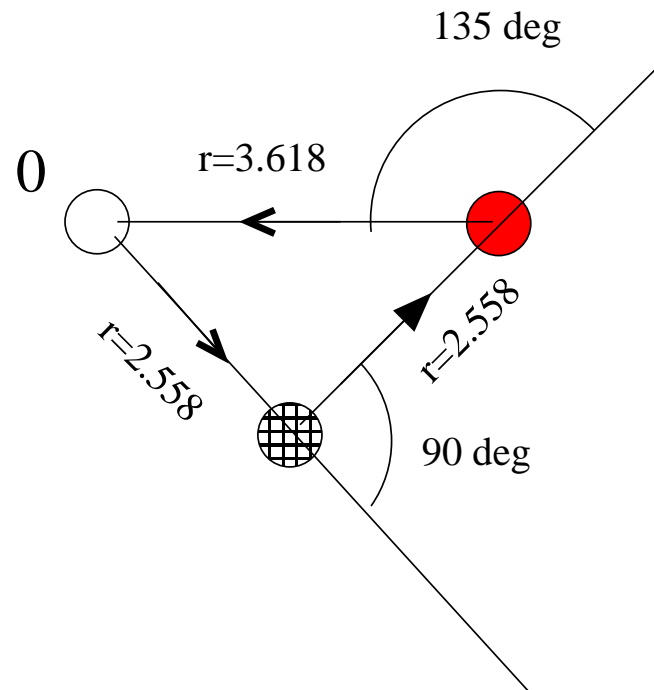
7   ARTEMIS

For data fitting we have the the ARTEMIS code. ARTEMIS takes the experimental $\chi(k)_{exp}$ function and compares it with a theoretical $\chi(k)_{teo}$ function that is build-up using the theoretical EXAFS paths previously calculated with Feff.

Then it creates a difference function Ξ as follows

$$\Xi = \frac{1}{w} \sum_{i=kpoints} (\chi(k^n)_i^{exp} - \chi(k^n)_i^{teo})^2 \tag{12}$$

$\chi(k)_{teo}$ is a function of the structural parameters

$$\chi(k^n)_{teo} = \chi(k^n, N, R, \sigma, \Delta E_0)_{teo} \tag{13}$$

The fitting routine varies these parameter in order to minimize the Ξ function.

7.1   Metallic Cu, I^{st} shell

The picture below presents the input page:
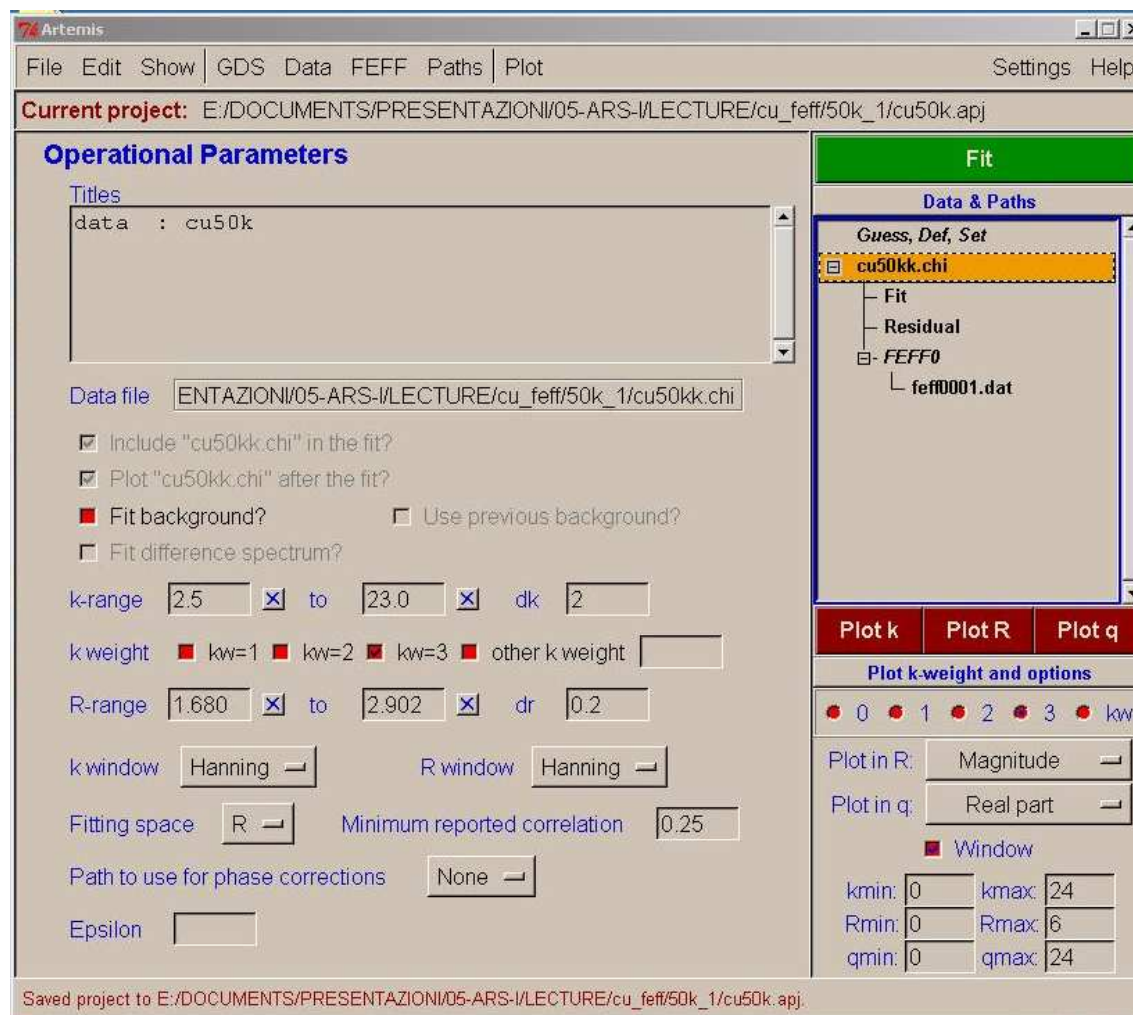
ARTEMIS needs the following inputs:

- an experimental $\chi(k)$ spectrum, extracted (namely) with ATHENA.

- the feffxxxx.dat theoretical paths generated by feff

Successively, the details for FT transformation and fit have to be added like:

- *krange* The range in k space for FT

- *kweight* n in the k^n weight for exp. data

- *dk* The 'width' of the window

- *kwindo* The window type (see manual)

- *R-range* The fit range in R space (if used)

- *Fitting space* Can be k, R or q.

The theoretical paths to be used for the fit can be added under the menu FEFF → Add a feff path and a window pops up with the details of the path:
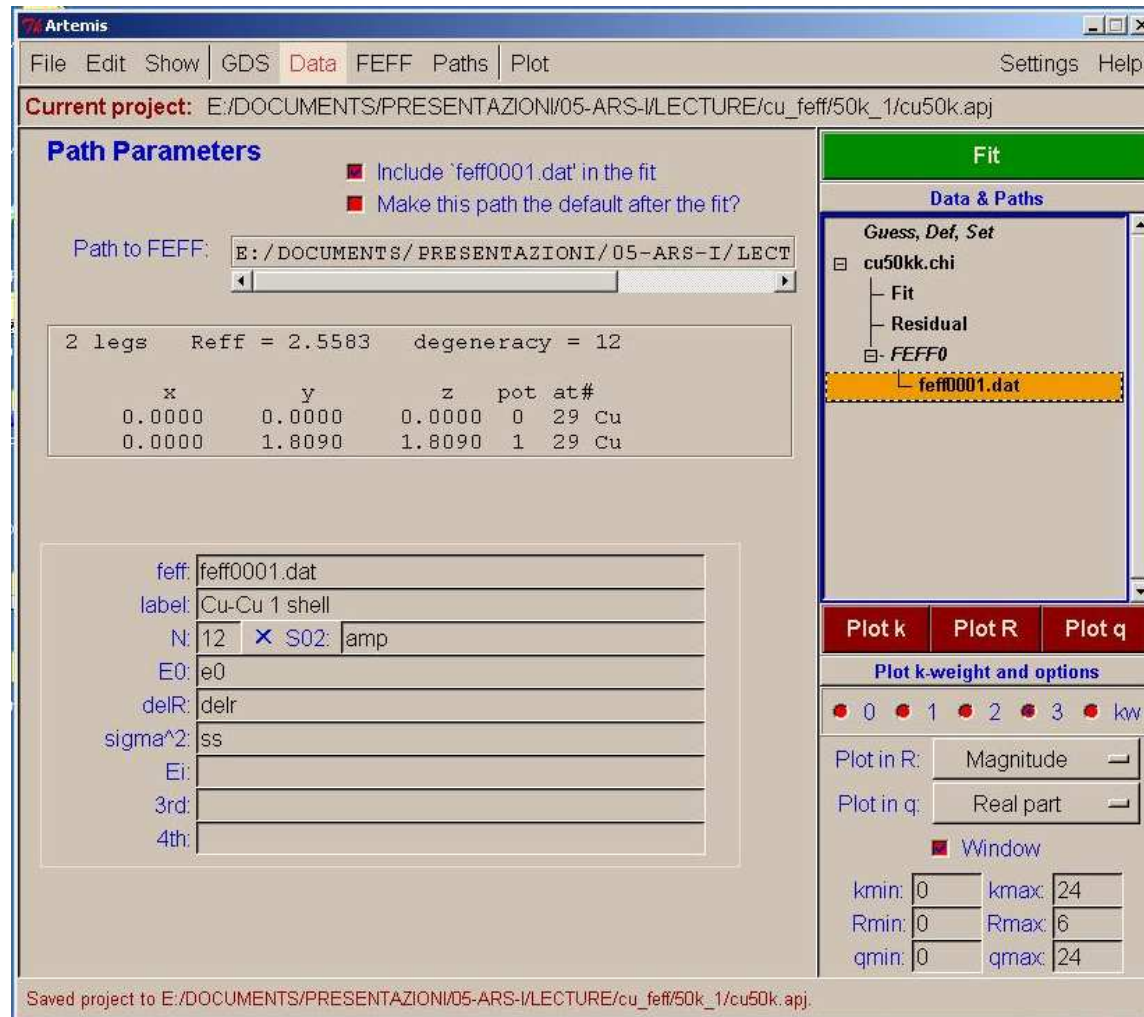
For each path (only one in this case) a name for each variable has to be chosen to be used in the following section. In this case we considered the number of neighbors 12 so we decide to fit:

- the S02 parameter, amp

- the edge shift E0, e0

- the deviation from the theoretical bond length delR , reff*delR

- the Debye-Waller factor ss2, ss.

Finally the *user variables* to be fitted are declared with the guess or set commands with their initial values:
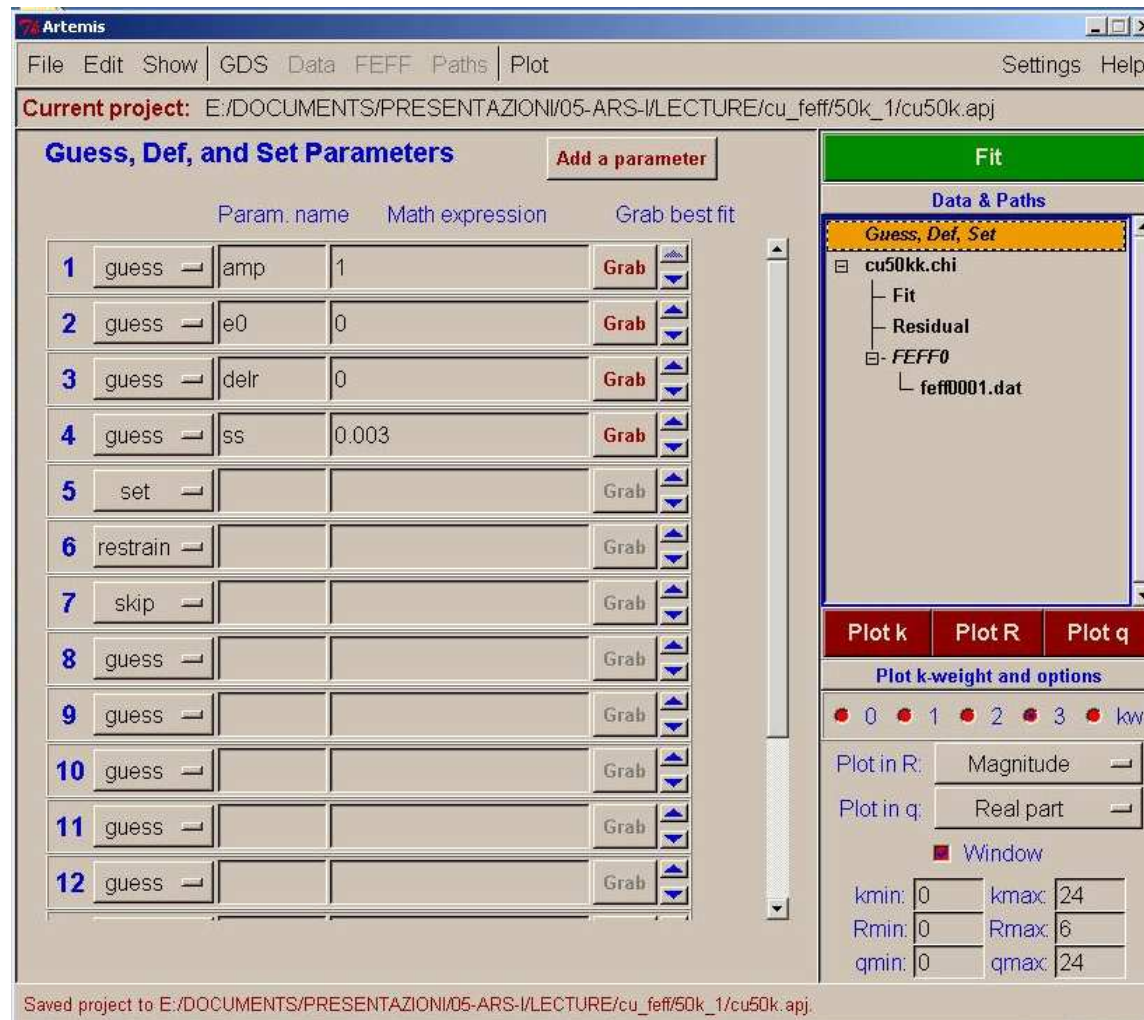
Set can be also used to define relations between the variables that represents one of the major points of the *ARTEMIS* program. This permits to reduce the free parameters by introducing a little physics in the problem.

Eventually clicking the FIT button starts the fit. ARTEMIS uses equation (10) to fit data in a given R range. In this way only paths with a length less than R have to be considered in the fit permitting the analysis on a limited frequency region of the spectrum.

The results of the fits are shown below:
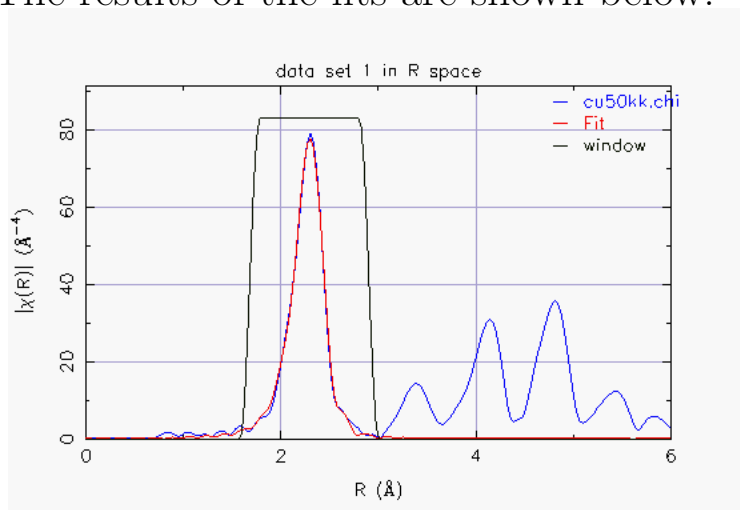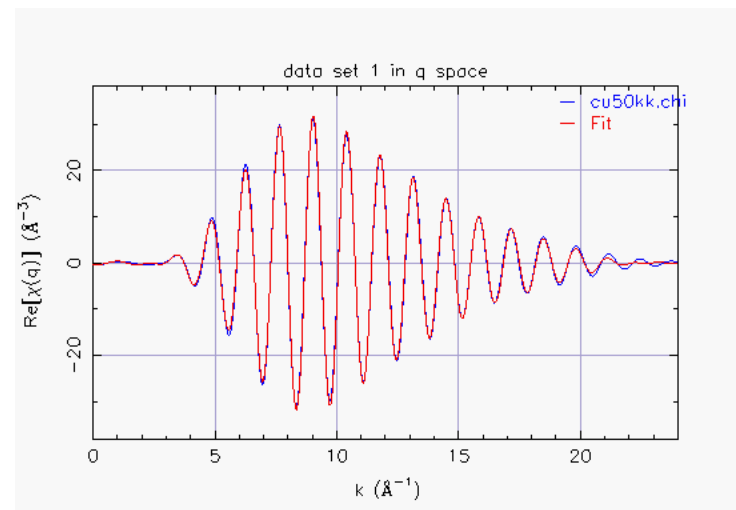
The R space fit.

The q space fit.

The results of the fits are written in the file *.log

```
Project title :  Fitting cu50kk.chi
Prepared by   :
Contact       :
Started       :  14:07:30 on 13 April, 2007
This fit at   :  14:18:33 on 13 April, 2007
Environment   :  Artemis 0.6.009 using Windows XP, perl 5.006001, Tk 800.023, and Ifeffit 1.2.5


============================================================


Independent points          =       15.845703125
Number of variables         =        4.000000000
Chi-square                  =       11.856670253
Reduced Chi-square          =        1.000925832
R-factor                    =        0.002451116
Measurement uncertainty (k) =        0.000630000
Measurement uncertainty (R) =        1.471120523
Number of data sets         =        1.000000000


Guess parameters +/- uncertainties:
  amp         =        0.8705065  +/-        0.0257853
  e0          =        5.7637639  +/-        0.4419175
  delr        =       -0.0013737  +/-        0.0005666
  ss          =        0.0035691  +/-        0.0001233
```

Explicit data on the various paths (namely r and σ^2) are shown in the remainder of the *.log file

```
===== Paths used to fit cu50k.chi

FEFF0: feff0001.dat (ifeffit group = feff0_1)
   feff      = C:\DOCUMENTS\PRESENTAZIONI\07-ARS2\EXERCISES\CU\TEO\feff0001.dat
   id        = reff  =  2.5527, degen  = 12.0, path: Cu->Cu->Cu
   r         =      2.549193
   reff      =      2.552700
   degen     =    12.000000
   n*s02     =      0.870506
   e0        =      5.763764
   dr        =     -0.003507
   reff+dr   =    2.549193
   ss2       =      0.003569
```

As a general rule in the first part the results on the 'fitted' variables are resumed together with the statistical analysis of the fit (χ^2 analisys, error analysis, correlations, ...).
Then the fit conditions (weight, boundaries, ...) are shown.
Finally the results on the path variables are resumed. Note a few tricks:

- Take care to the relations you established between path and user variables.

- For the bond length R the actual fitted variable is delR. To know the R value you have to see the value of {reff + delR}

- *ARTEMIS* considers by default the path with its geometrical degeneracy. So in this case we got 12 neighbours (degen) without explicitly telling the program as it went from the calculation. If the number of neighbors is your unknown you have to run the program with the N card $= 1$ and attribute to each path an amplitude $S_0^2 \times$ N where S_0^2 is found from a reference compound and N is the number of neighbors to be fitted.

7.2 Error analysis

A few considerations now on the error analysis made by *ARTEMIS*. The fitting routine works through the minimization of a χ^2-like function. For the correct statement of such a function (in order to perform a statistical analysis on it) it is mandatory to correctly determine the noise Epsilon on the data. When working in Fourier Transformed space it is hard to establish a relation between the noise you can estimate on the spectrum (by the square root of counts or by empirical techniques) and the error that propagates through the fourier filter. An accurate error analysis is necessary to:

- decide whether what we have found is a good fit or not

- attribute error bars to the best-fitting quantities

ARTEMIS has an automatic routine that determines the 'noise' on the data from the residual extracted from the Fourier Transformed data between $R = 15 - 25$ Å. In this way values of the χ^2_ν (χ-square function divided by the number of free parameters ν) well above 1 are obtained even for the best looking fits, preventing a correct statistical analysis. ARTEMIS circumvents this problem by calculating the parameters uncertainties by multiplying the square root of the diagonal elements of the correlation matrix by $\sqrt{\chi^2_\nu}$. This is equivalent to rescale Epsilon to obtain a $\chi^2_\nu = 1$ that is to assume *a priori* the goodness of the fit and attributing to statistical *noise* the misfit.

7.3   Multiple Scattering analysis

Metallic Cu

50 K
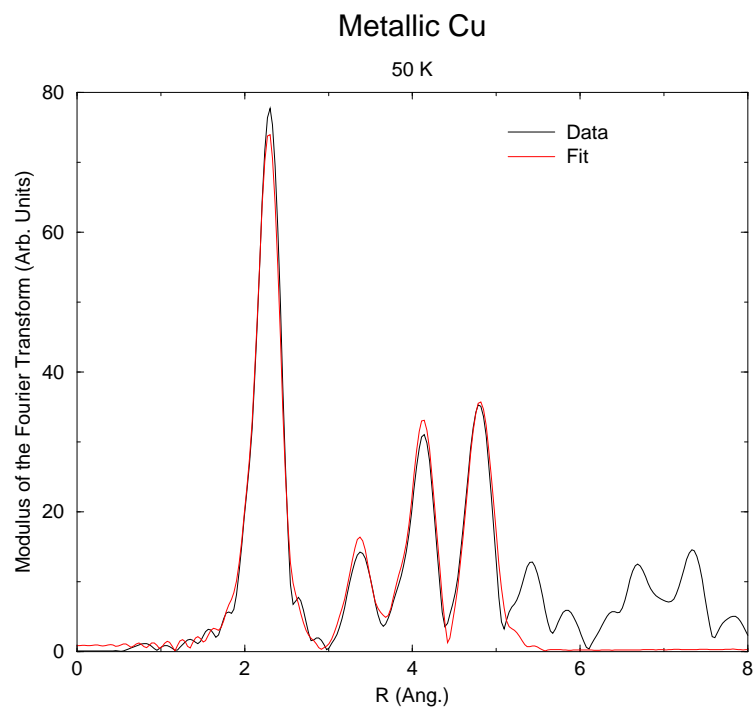
In the Fourier Transform of the metallic Cu foil several coordination shells are well visible above the first.

```
    --------------------------------------------------------
pathindex      sig2    amp ratio       deg    nlegs   r effective
      1      0.00000    100.000     12.000       2     2.5527
      2      0.00000     23.055      6.000       2     3.6100
      3      0.00000     12.006     48.000       3     3.8290
      4      0.00000      9.191     48.000       3     4.3577
      5      0.00000     55.708     24.000       2     4.4213
      6      0.00000     11.690     48.000       3     4.7633
      7      0.00000     24.544     96.000       3     4.7633
      8      0.00000     19.077     12.000       2     5.1053
      9      0.00000      9.524     12.000       3     5.1053
     10      0.00000     44.354     24.000       3     5.1053
     11      0.00000      8.648     12.000       4     5.1053
     12      0.00000      4.228     12.000       4     5.1053
     14      0.00000     32.552     12.000       4     5.1053
```

Also from the *feff* calculation (file list.dat) several higher order paths (3 and 4 legged) result to have a considerable amplitude.

A fit of the higher coordination shells can give a deeper insight in the material structure. Moreover for such task the inclusion of Multiple Scattering (MS) paths is mandatory.

feff has already indicated the stronger paths to be considered. By constructing our model we only have to avoid free parameter proliferation due to the increased number of paths.
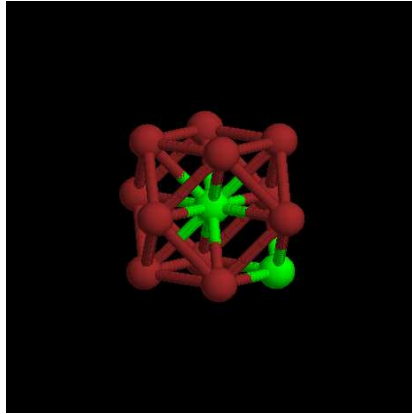
With *ARTEMIS* path parameters can easily linked so minimizing the number of free parameters.

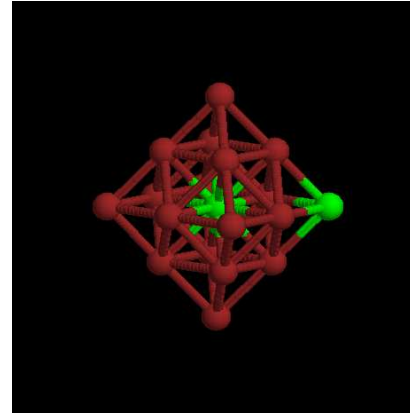Below we show the input page for a 4 shell fit of metallic Cu:
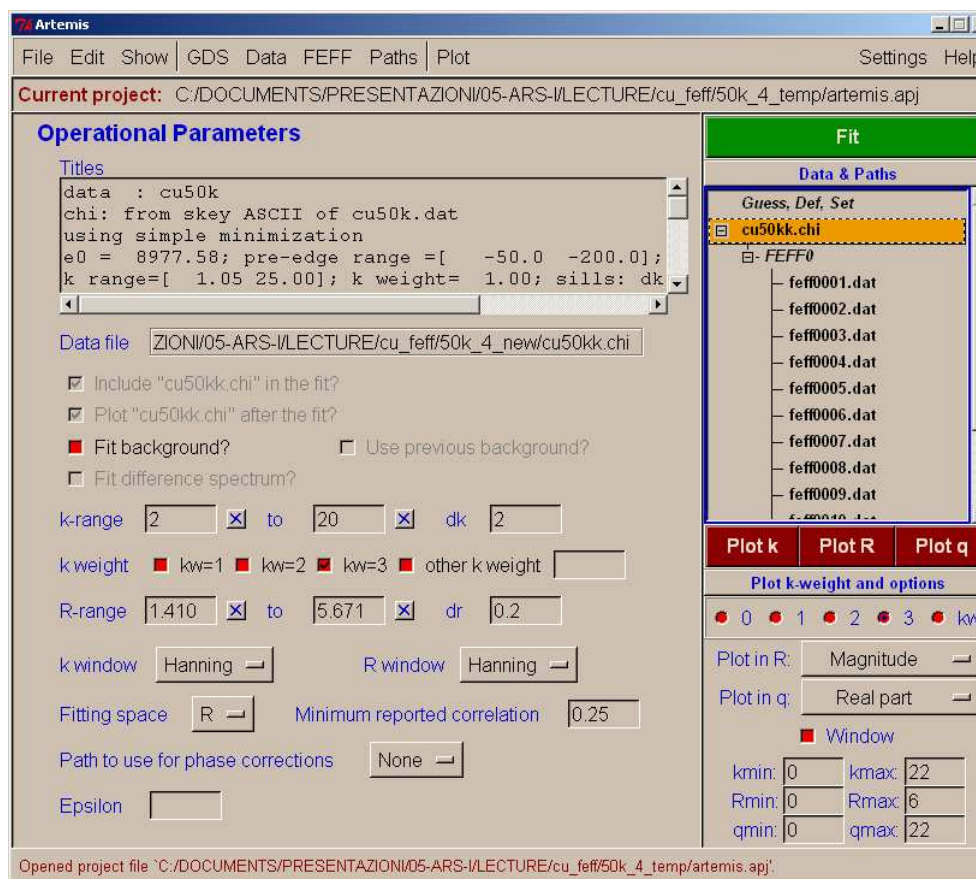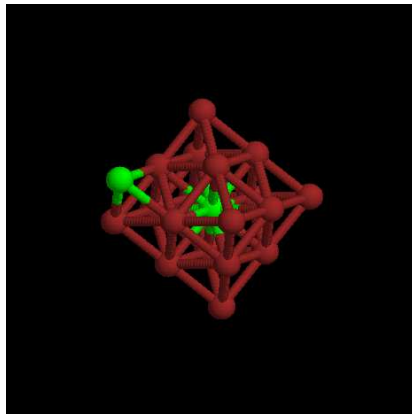
Here the path list includes :

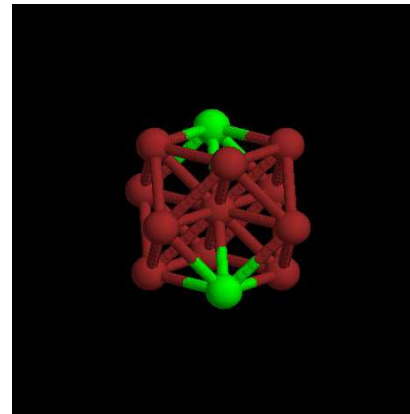Single scattering paths from the first to the fourth shell (paths 1, 2, 5, 8)
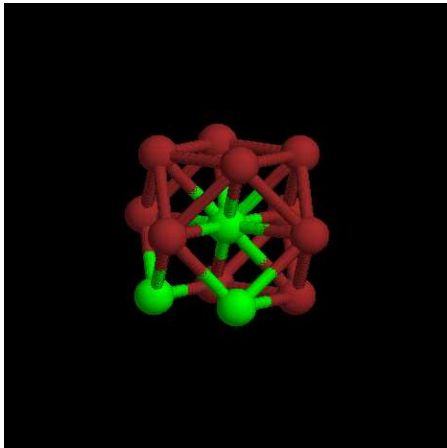

1st Shell (Path 1)

2nd shell (Path 2)

3rd shell (Path 5)

4th shell (Path 8)

Double scattering between absorber and 2 Nearest Neighbors (NN) with the absorber in the vertex of a 60 deg angle (path 3).
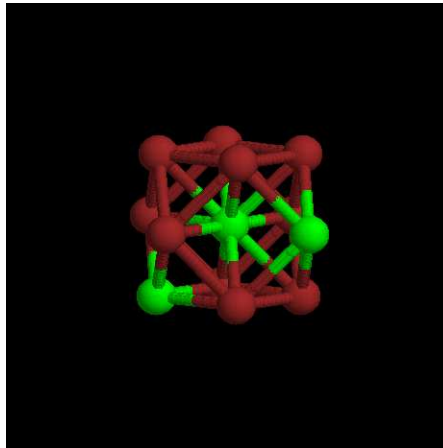
Double scattering between the absorber and 2 NN. The absorber is on the vertex of a 120 deg angle (path 6).
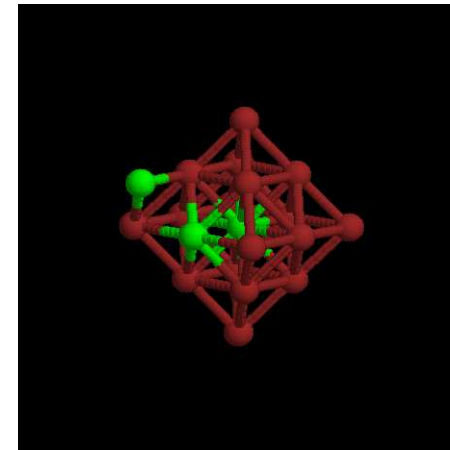
Double scattering between the absorber, a 1 NN and a 3 NN (path 7).

- Double scattering between the absorber and collinear NN and 4th neighbor, the absorber at an edge of the chain (path 10)

- Triple scattering back and forth touching all the atoms in a configuration similar to path 10 (path 14)

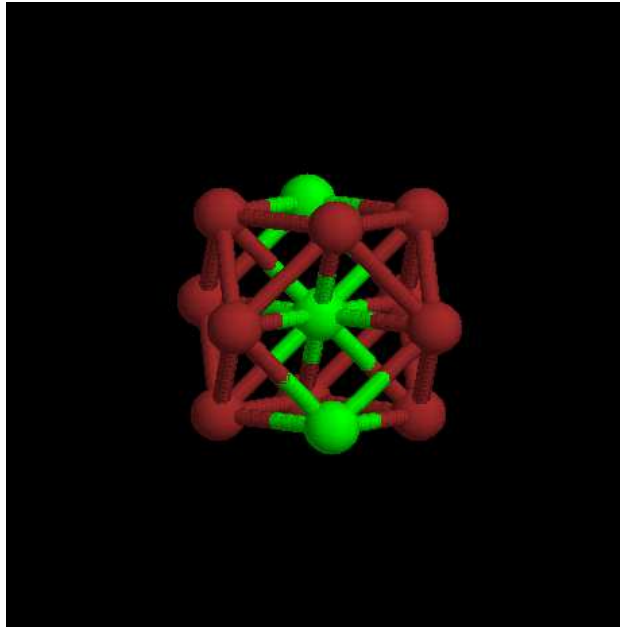The grouping of the parameters can be done as follows:

- a common value of e0 and s02 can be used for all.

- an overall scaling of the path lengths can be done by using the feffit function *reff*. This can be useful when treating global expansion due to doping, temperature, ...It can coupled to the delr variable of all paths with the command:

$$reff * delR$$

  in this way for each path the length R is calculated as a fraction delR of the theoretical length reff. delR is the only fitting parameter for the bond lengths.

- Debye-Waller factors calculated with a correlated Debye model [17, 16] using the special function

$$Debye(meas_{temp}, Debye_{temp})$$

  . The σ^2 of the firs shell is left free.

Following these prescriptions we end up to fit the spectrum of metallic Cu up to the fifth shell with 10 paths and only 5 free (e0, s02, delR, ss, temp) parameters. The results are shown below:
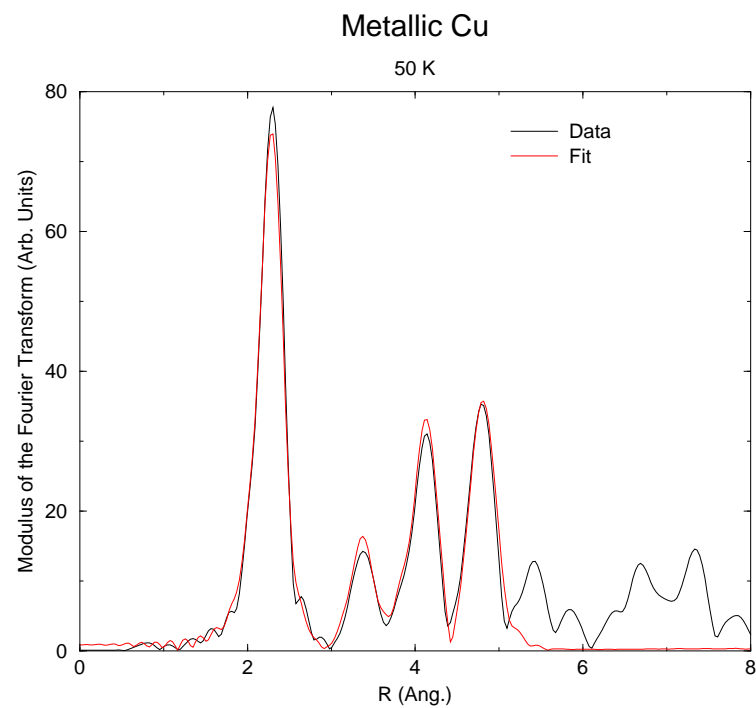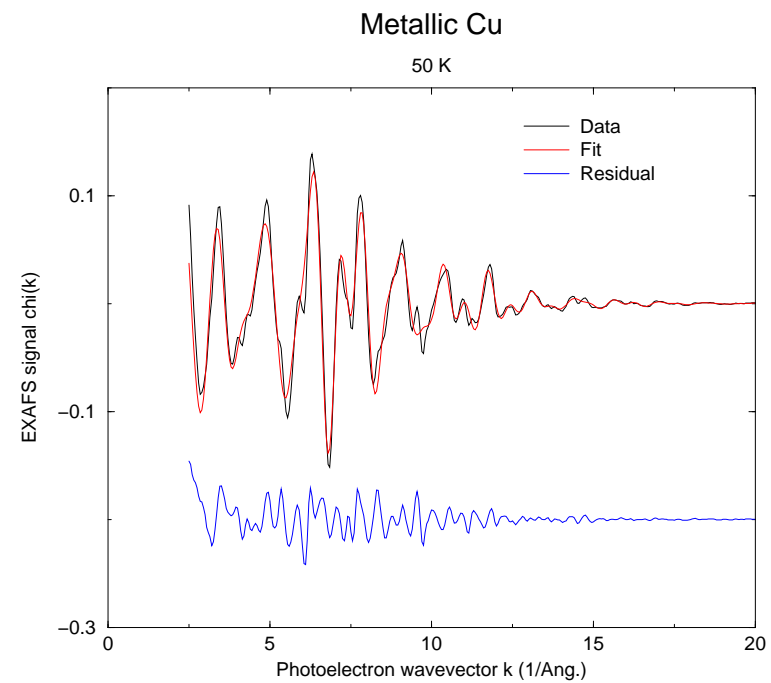
The R space fit.

The k space fit.

Contribution of the various paths to the total spectrum:
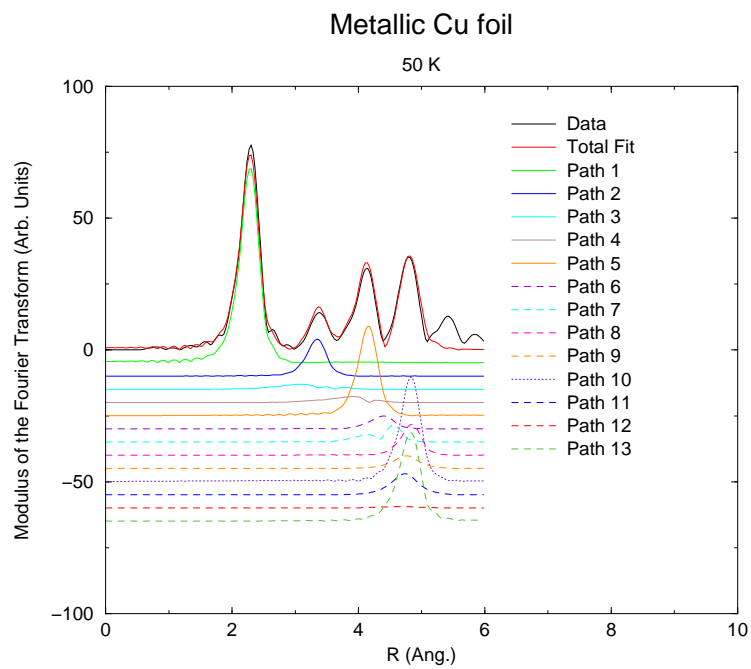
The R space.
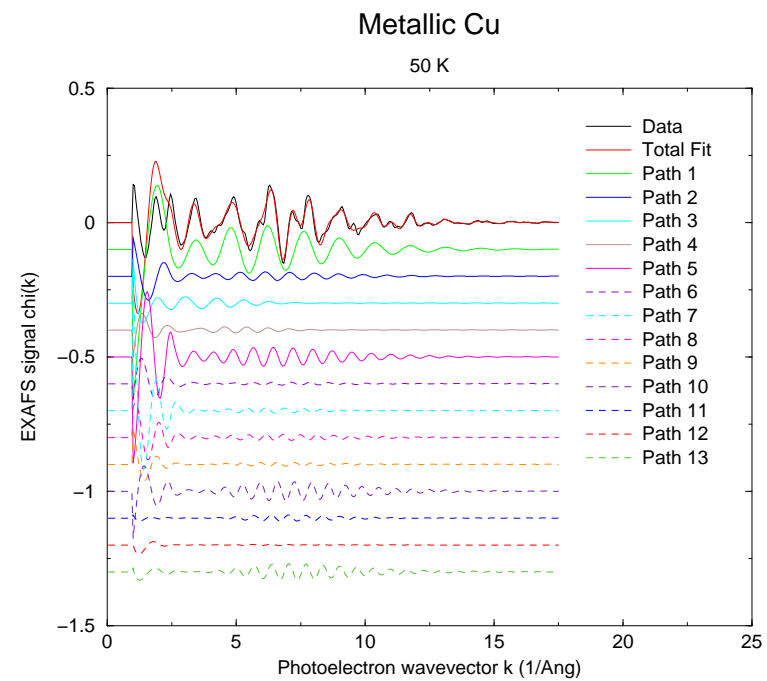
The r space.

The results are shown in the *feffit.log* file:

```
Project title :  Fitting cu50kk.chi
Prepared by   :
Contact       :
Started       :  14:07:30 on 13 April, 2007
This fit at   :  14:25:09 on 13 April, 2007
Environment   :  Artemis 0.6.009 using Windows XP, perl 5.006001, Tk 800.023, and Ifeffit 1.2.5


=============================================================


Independent points          =       46.703125000
Number of variables         =        5.000000000
Chi-square                  =       41.728342234
Reduced Chi-square          =        1.000604685
R-factor                    =        0.012413644
Measurement uncertainty (k) =        0.000909000
Measurement uncertainty (R) =        2.122616754
Number of data sets         =        1.000000000


Guess parameters +/- uncertainties:
  amp         =       0.9166783  +/-       0.0333725
  e0          =       4.6087464  +/-       0.4168785
  delr        =      -0.0018688  +/-       0.0005401
  ss          =       0.0037685  +/-       0.0001616
  temp        =     261.7400839  +/-       8.3454342
```

7.4   Comparison with known physical data

Parameter	EXAFS result	Literature data
a_0 (Å)	3.603 ± 0.002	3.610
T_{Debye} (° C)	262 ± 8	315

7.5   A tetrahedral compound: crystalline Ge

This is left as an ⟨exercise for the students⟩. Here I will only suggest the *atoms.inp* file:

```
\title GE
space DIAMOND a= 5.65735 rmax = 6       core= Ge

out = feff.inp

atom ! Type       x        y        z        tag
   Ge     0.125    0.125    0.125    Ge1
--------------------
```

Then proceed as follows:

- Calculate the cluster

- Calculate the theoretical paths

- Try a first shell fit

- try a multiple shell (and multiple scattering) fit up to the 3rd shell.

8   Conclusion

Here we have briefly introduced the UWXAFS analysis package for EXAFS data. We warmly recommend the students to further train themselves on well known structures (bcc, zincblende, ...) to gain a full control of the various parts of the program before approaching a *real* unknown sample. Due to its introductory form this lecture is far from being exhaustive so we invite the students to refer to the programs manuals (available on the relative web pages). Another introductory course (to which a lot of pages of the present lecture are inspired) can be find in [20]. For further questions, feel free to contact me at the address: dacapito@esrf.fr.

References

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