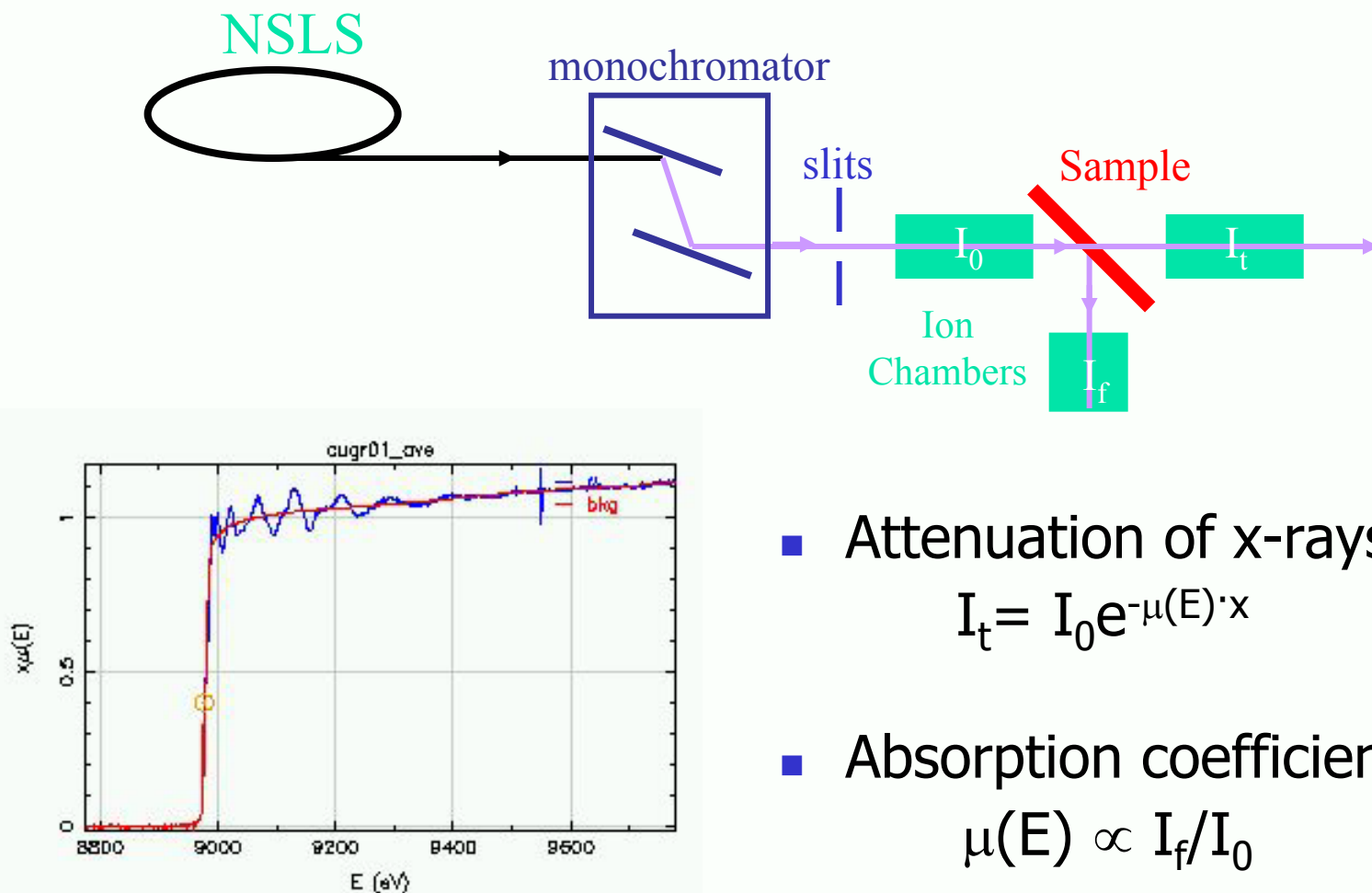# Basics of EXAFS data analysis

Shelly Kelly
Argonne National Laboratory, Argonne, IL
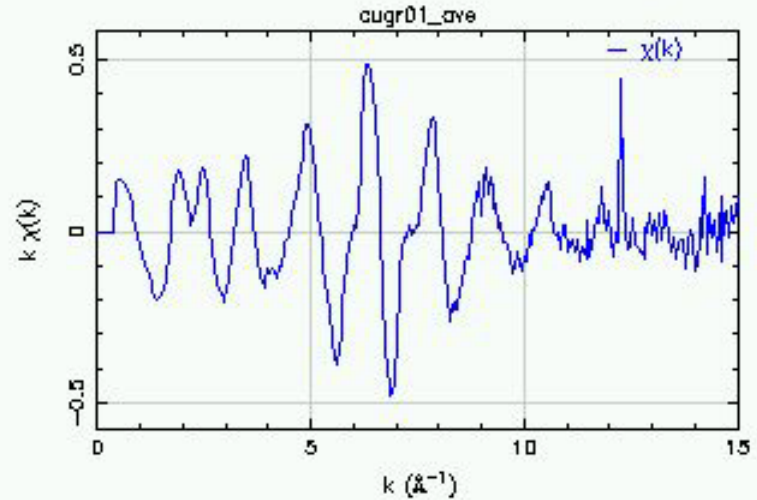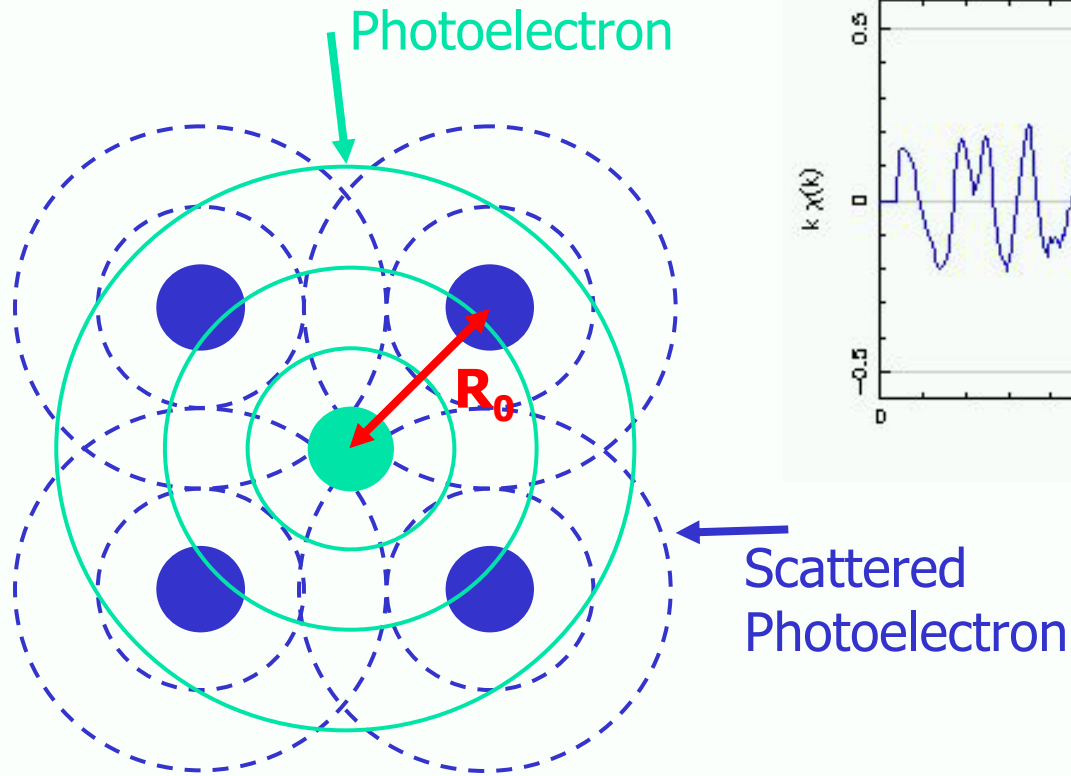
X-ray-Absorption Fine Structure

NSLS

monochromator

slits

Sample

I_0

I_t
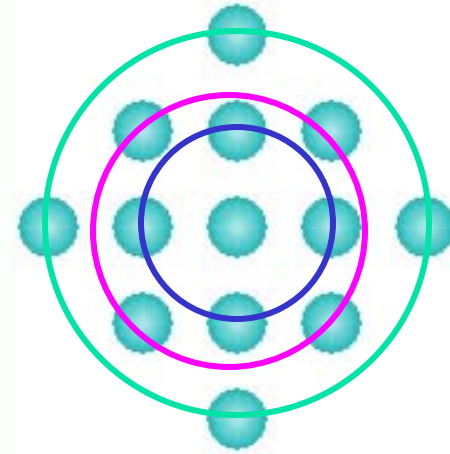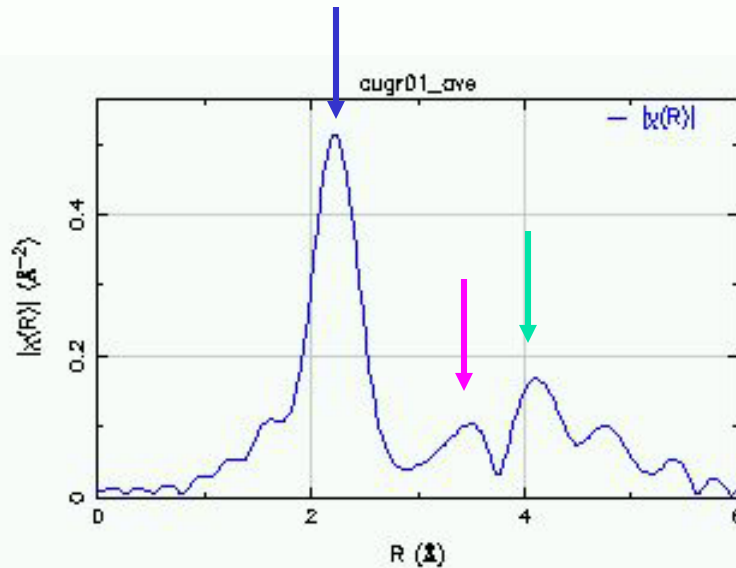
Ion Chambers

I_f

cugr01_ave

$\chi\mu(E)$

E (eV)

- Attenuation of x-rays
  $$I_t = I_0 e^{-\mu(E)\cdot x}$$

- Absorption coefficient
  $$\mu(E) \propto I_f/I_0$$

X-ray-Absorption Fine Structure

Photoelectron

R_0

Scattered
Photoelectron

cugr01_ave

$k \chi(k)$

k (Å^{-1})

Fourier Transform of $\chi(k)$

- **Similar to an atomic radial distribution function**
  - Distance
  - Number
  - Type
  - Structural disorder

Outline

- Overview of Athena interface
- Definition of EXAFS
  - Edge Step
  - Energy to wave number
- Fourier Transform (FT) of $\chi(k)$
  - FT is a frequency filter
  - Different parts of a FT and backward FT
  - FT windows and sills
- AUTOBK method for constructing the background function
  - FT and background (bkg) function
  - Wavelength of bkg
  - Fitting the bkg
- EXAFS Equation

Athena Overview

List of files
That you have
Opened into
Athena.
Each file is a
group. Each
Group contains
Data and
parameters.

Current group
Listed here

Background
Parameters
For the
Current
Group

The parameters for
the highlighted
group are shown on
the right.

Orange buttons plot
the highlighted data

Fourier
Transform
Parameters
For the current
group

Purple buttons will
plot several marked
data sets together

Backward
Fourier
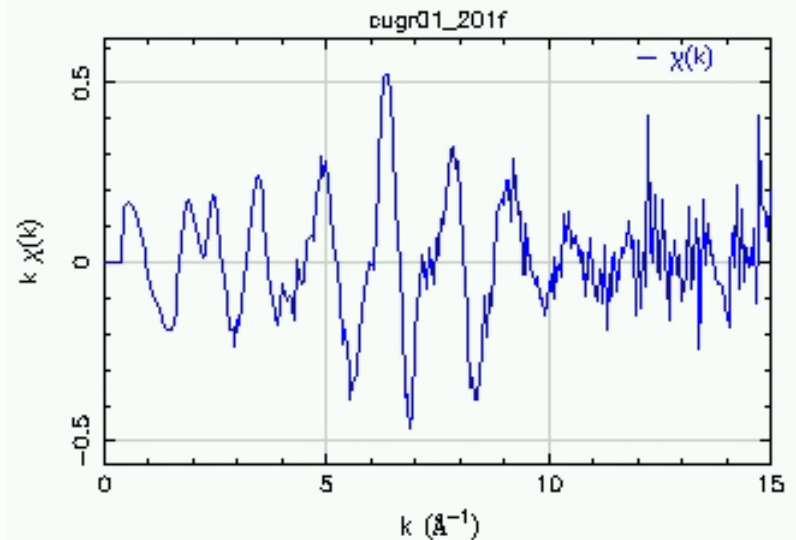Transform
Parameters
For the current
group

Plotting options

Definition of EXAFS

=>
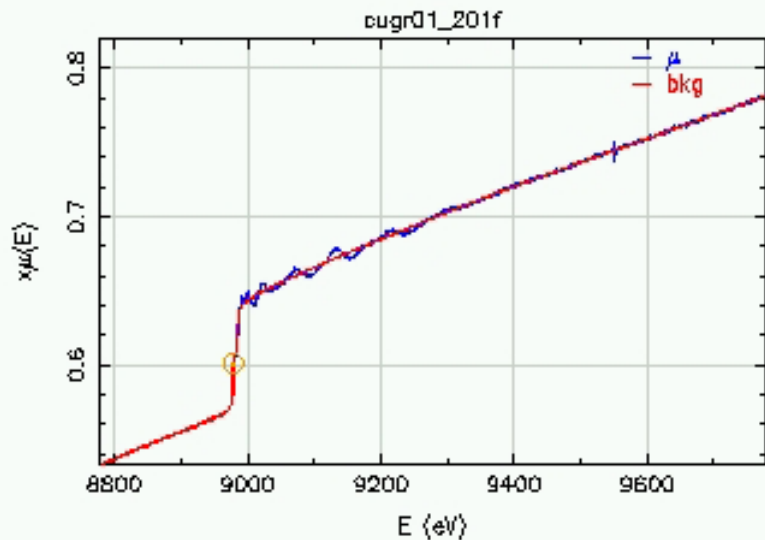
Normalized oscillatory part of absorption coefficient
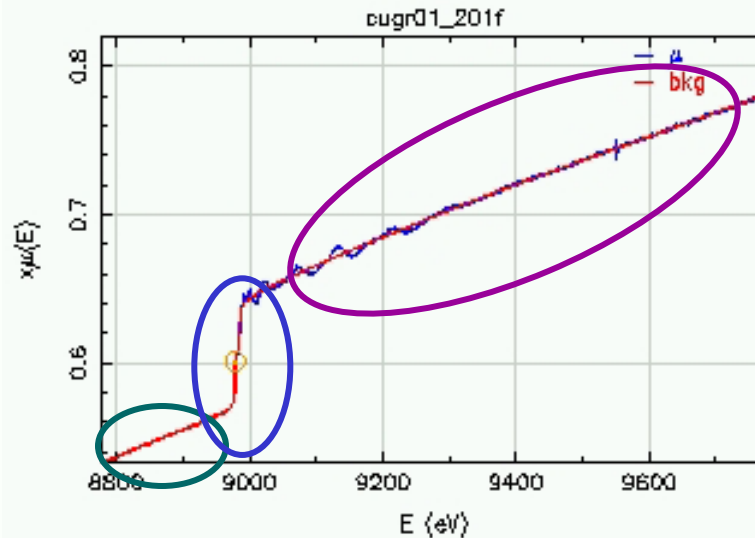
Measured Absorption coefficient

Bkg: Absorption coefficient without contribution from neighboring atoms (Calculated)

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)} \sim \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}$$
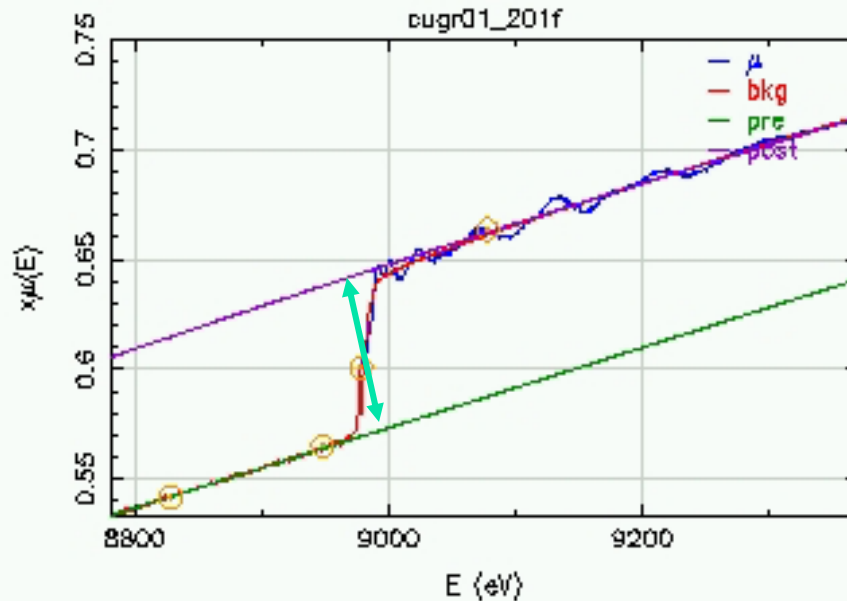
Evaluated at the Edge step (E_0)

Absorption coefficient

- **Pre-edge region** 300 to 50 eV before the edge
- **Edge region** the rise in the absorption coefficient
- **Post-edge region** 50 to 1000 eV after the edge

Edge step: $\Delta\mu(E_0)$

- **Pre-edge line** 200 to 50 eV before the edge

- **Post-edge line** 100 to 1000 eV after the edge

- **Edge step** the change in the absorption coefficient at the edge

  - **Evaluated by taking the difference of the pre-edge and post-edge lines at E_0**

Athena normalization parameters

Energy to wave number

E_0 Must be somewhere on the edge

Mass of the electron

Threshold Energy

$$k^2 = \frac{2\,m_e\,(E - E_0)}{\hbar^2}$$

Planck's constant

$\Delta E(eV) \sim 3.81\,k^2$

Athena: Edge energy E0

Properties of a Fourier Transform
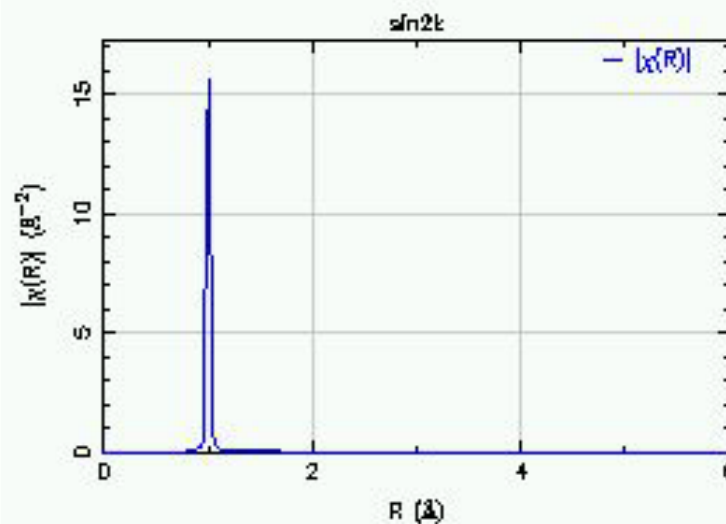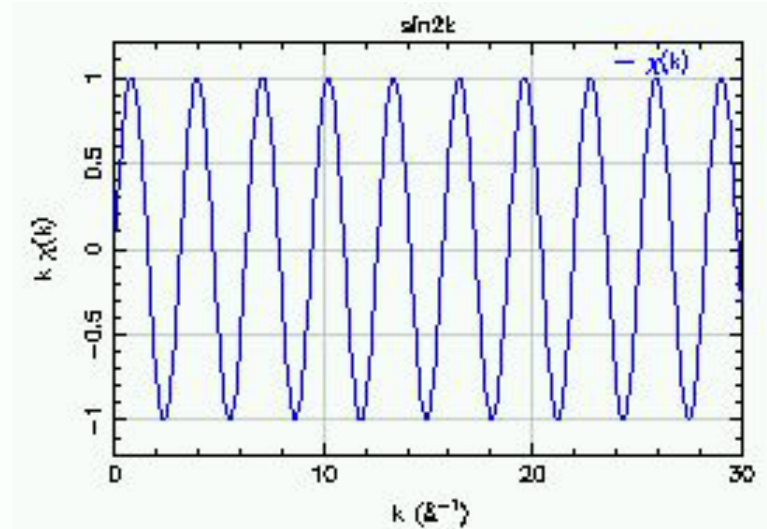
- FT of infinite sine wave is a delta function
- FT of Sin(2k) is a peak at R=1
- FT is a frequency filter
- Signal that is de-localized in k-space is localized in R-space

Fourier Transform of a function that is:

De-localized in k-space ⇒ localized in R-space
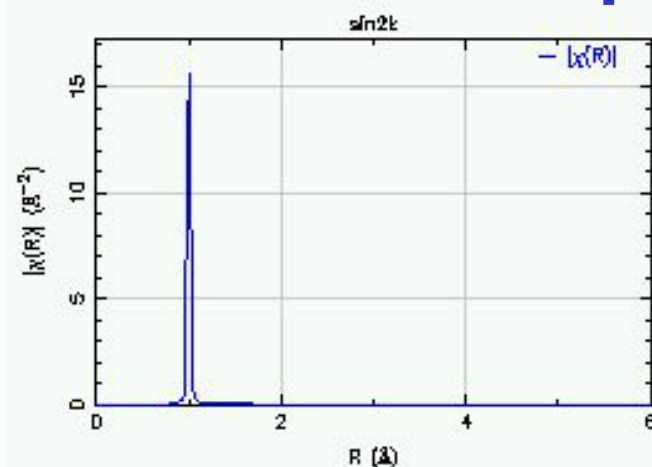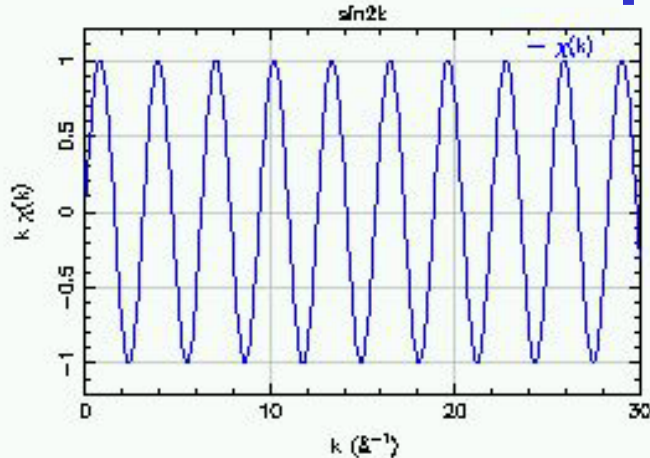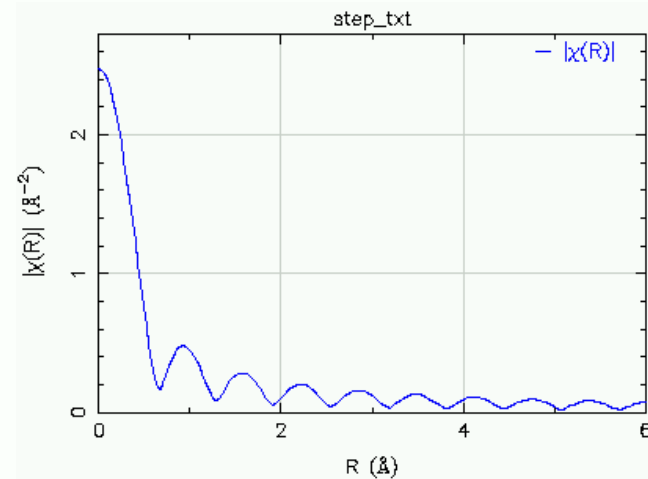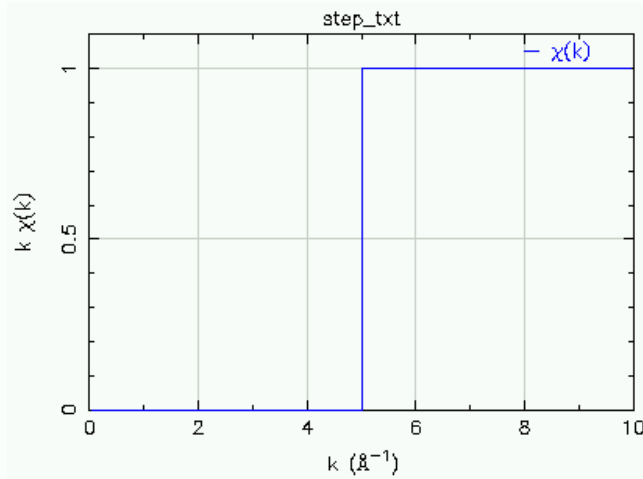

Localized in k-space ⇒ de-localized in R-space

Fourier Transform is a frequency filter

Regularly spaced ripple
Indicates a problem
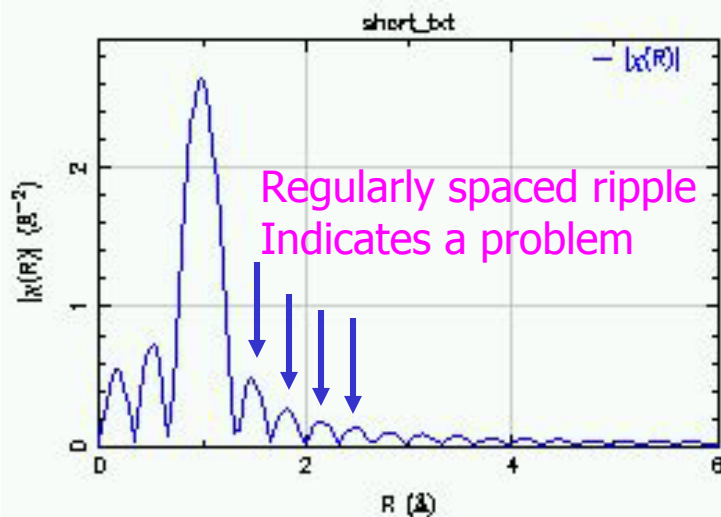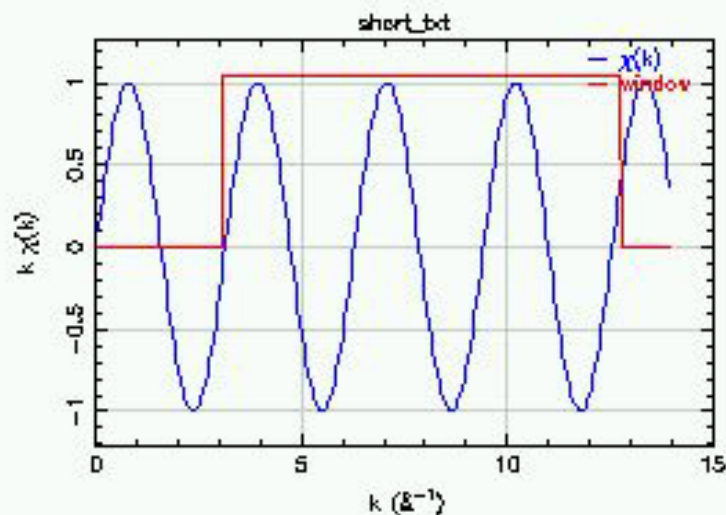
- The signal of a discrete sine wave is the sum of an infinite sine wave and a step function.

- FT of a discrete sine wave is a distorted peak.

- EXAFS data is a sum of discrete sine waves.

- Solution for finite data set is to multiply the data with a window.

Fourier Transform
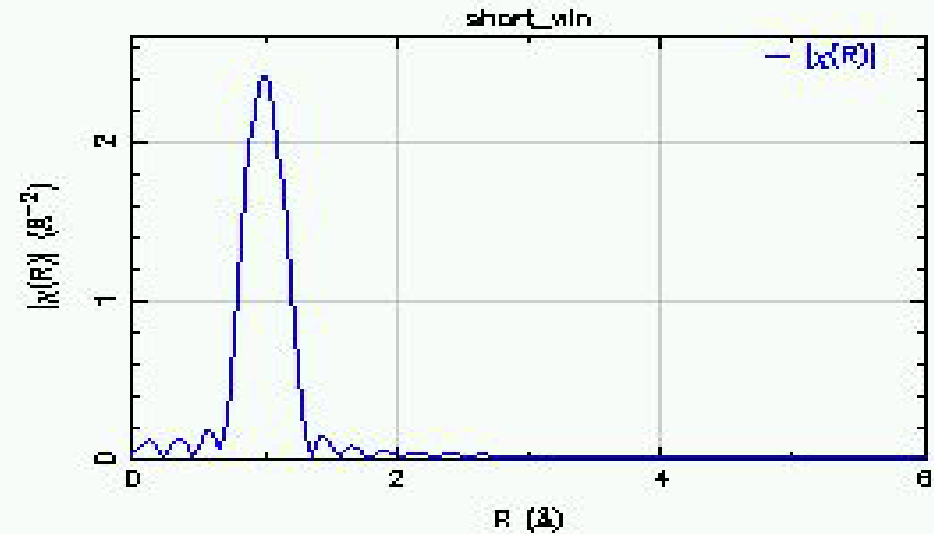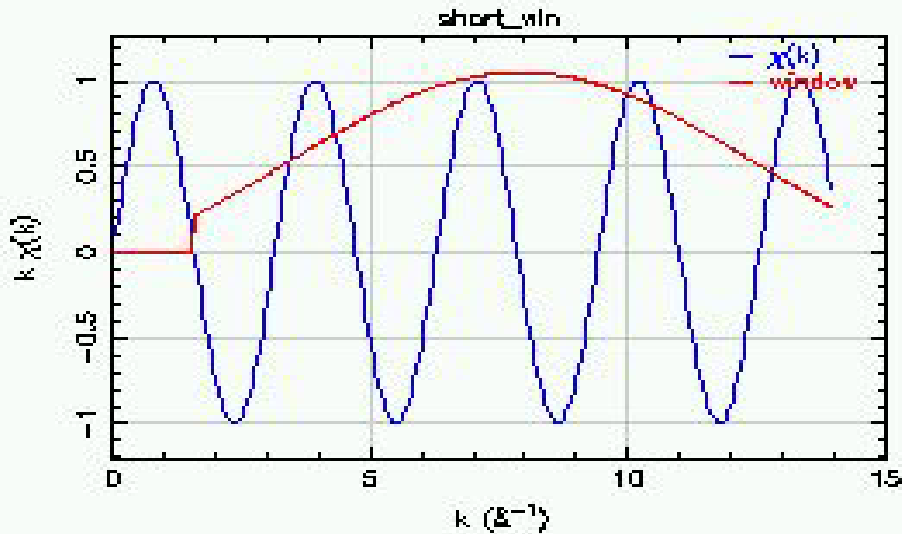
- Multiplying the discrete sine wave by a window that gradually increases the amplitude of the data smoothes the FT of the data.

Fourier Transform parts

Real and imaginary parts of FT $\chi(k)$ = Re [$\chi(R)$] and Im [$\chi(R)$]
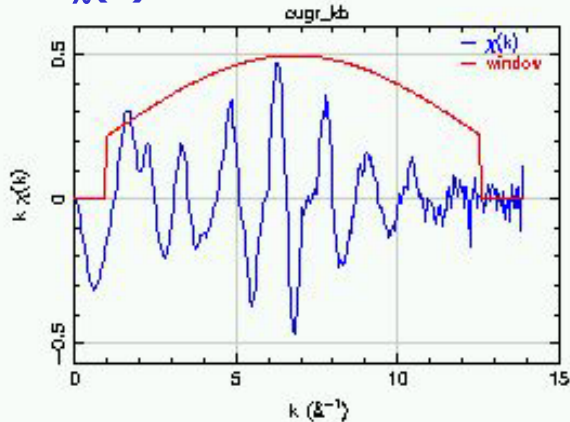
magnitude of FT $\chi(k)$ = |$\chi(R)$|

$\chi(k)$ data and FT window

Real part

Imaginary part
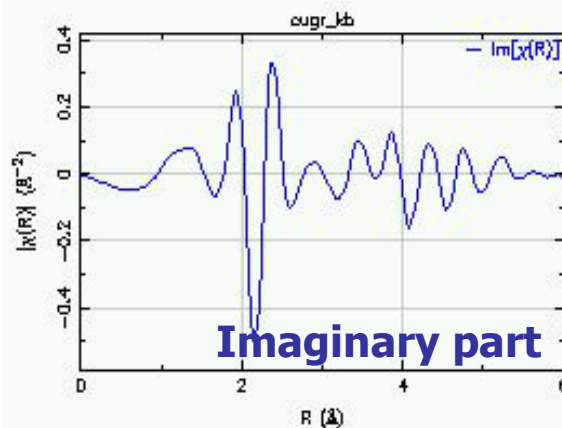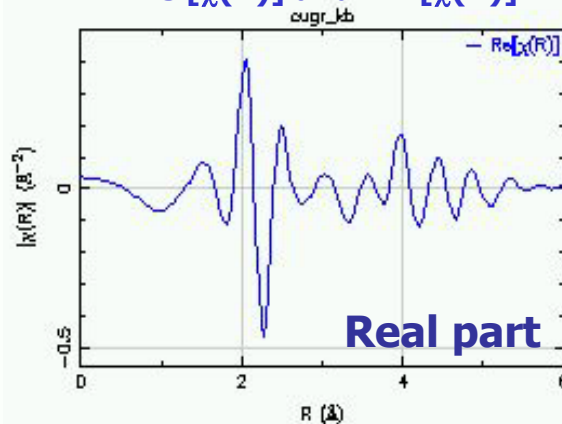
Magnitude
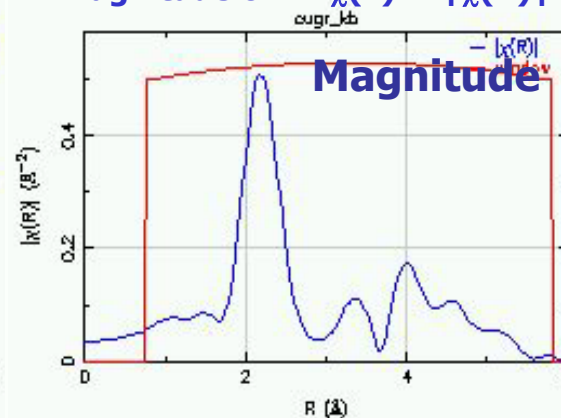
back FT of $\chi(R)$ = $\chi(q)$

Back FT
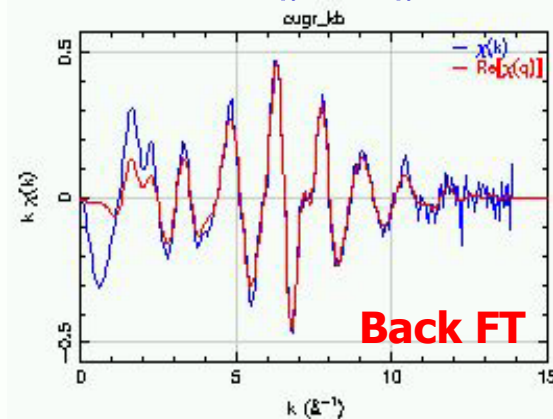
Fourier Filter of EXAFS data
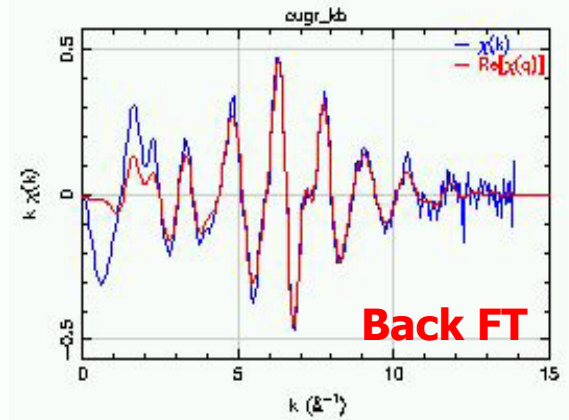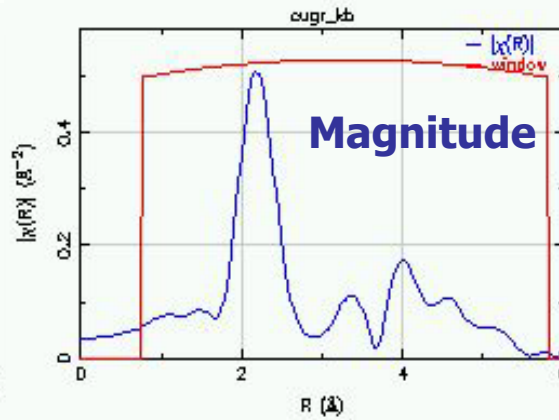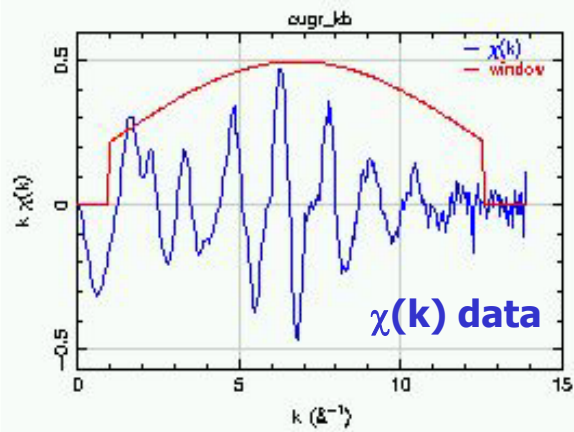
Understanding the different parts of FT
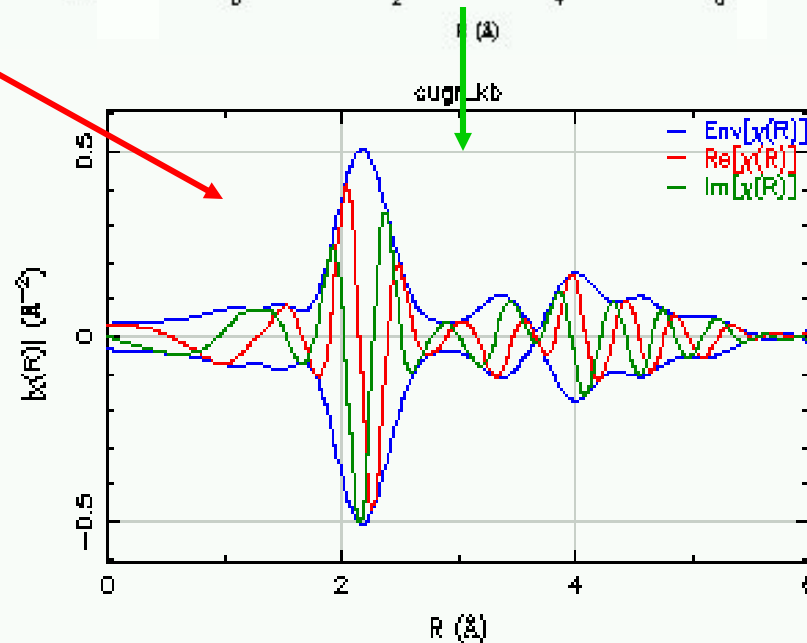
- **|χ(R)| is not unique. Information has been lost.**

Athena plotting in R-space

Fourier Transform Windows
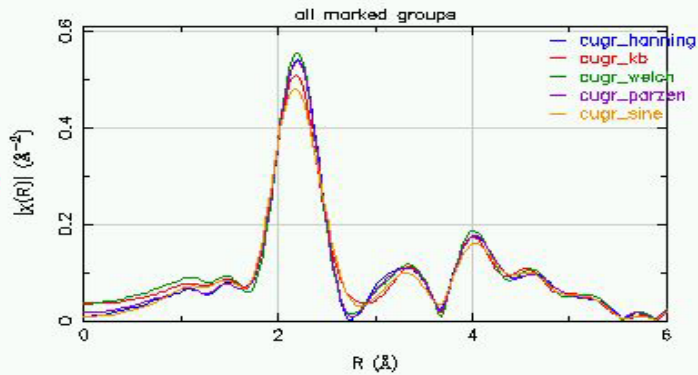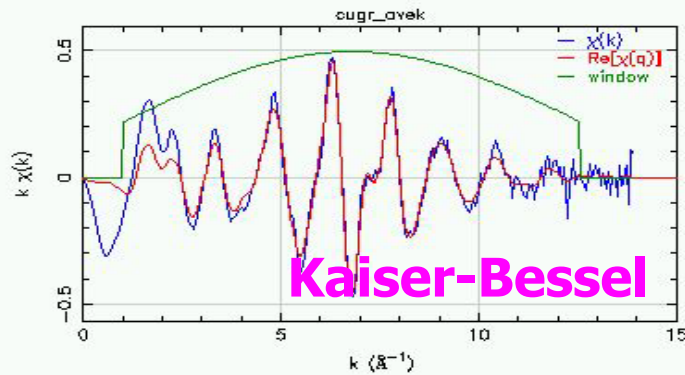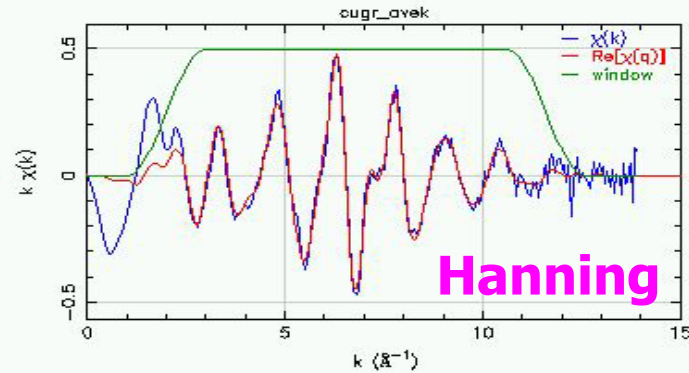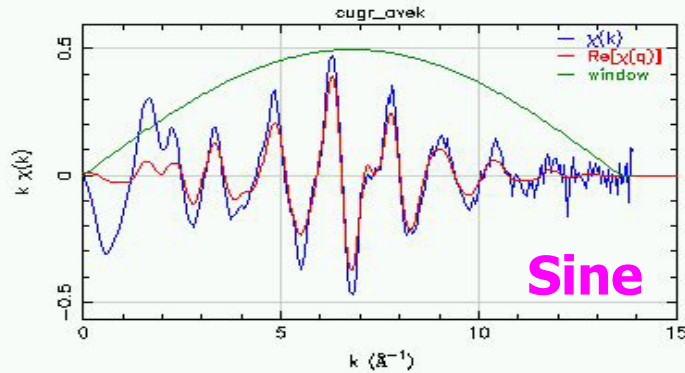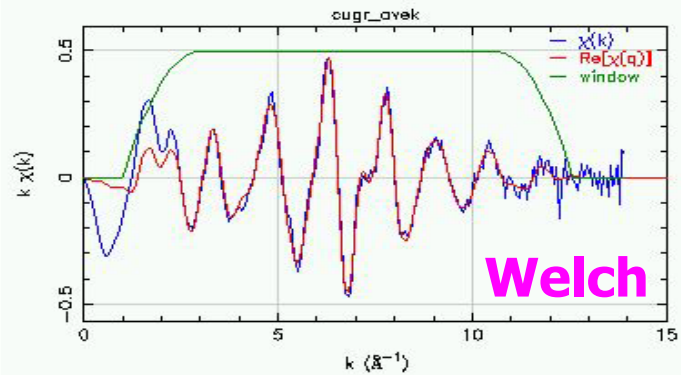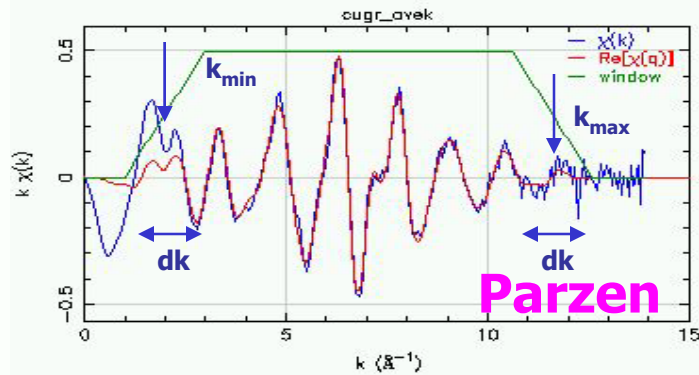
Fourier Transform window sill

dk=0

dk=2.0 Å⁻¹
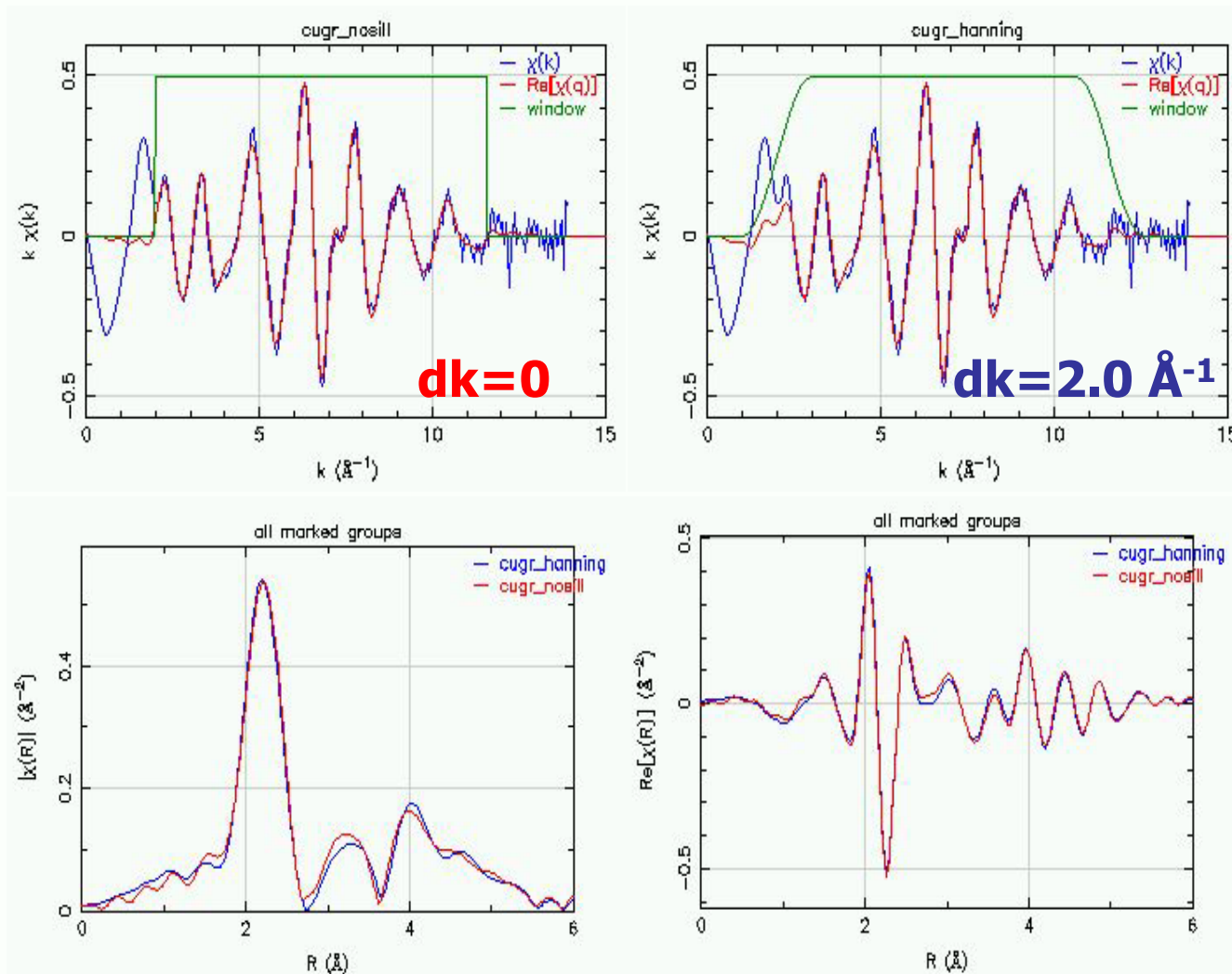
■ A small sill can distort FT

Fourier transform parameters in Athena

Choose k-range end points at points of symmetry, like a node.

k-weight used in FT of data

- $\chi(k)$ data is often weighted by k^w. W is called the k-weight.

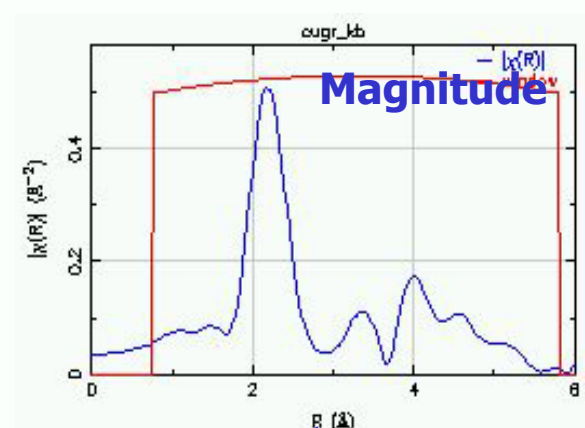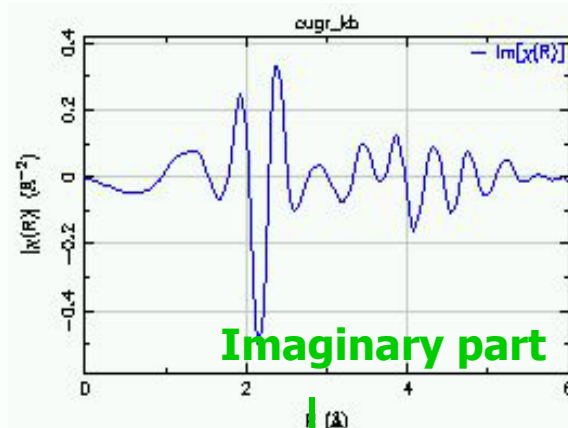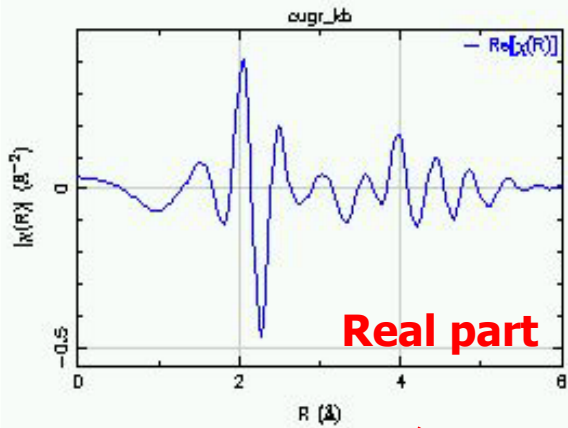- Typical values for k-weight = 1, 2, or 3.

- Different fitting parameters have different k-dependencies. Using different k-weights when fitting the model to the data will help break the correlation between these parameters.

- The EXAFS signal from different atoms have different k-dependencies. Comparing the FT of data with different k-weights can help distinguish atoms from different rows on the periodic table.

Using k-weight to distinguish different atom types

- Rescale the FT so that the first shell has the same amplitude with all three k-weights.

- Other shells that do not have the same amplitude are most likely due to different atoms.

- Shells that grow with increasing k-weight may contain atoms with larger atomic number.

- Shells that diminish with increasing k-weight may contain atoms with smaller atomic number.

Athena: Compare k-weight FT

- Use Ctrl-y to copy the data set.
- Choose a different k-weight for each copy.
- Rescale the data using the plot multiplier. So that first shell peak has the same amplitude.
- Mark each data set.
- Plot in R-space.

Background function overview
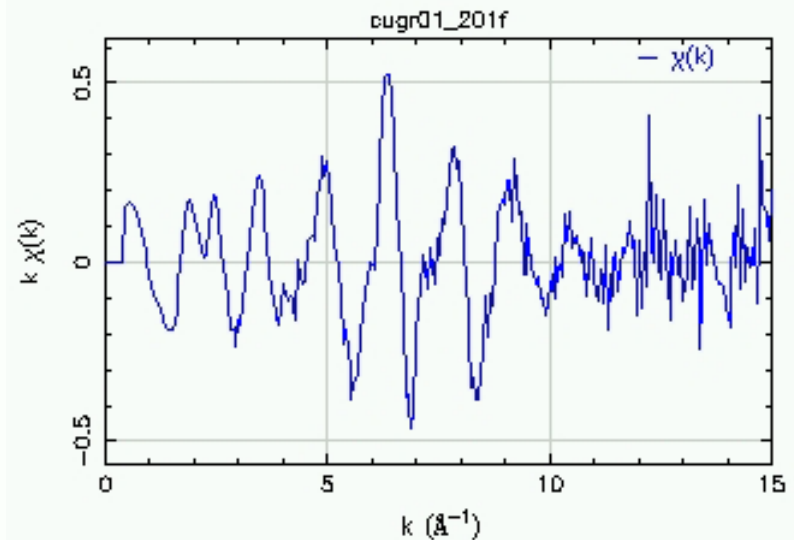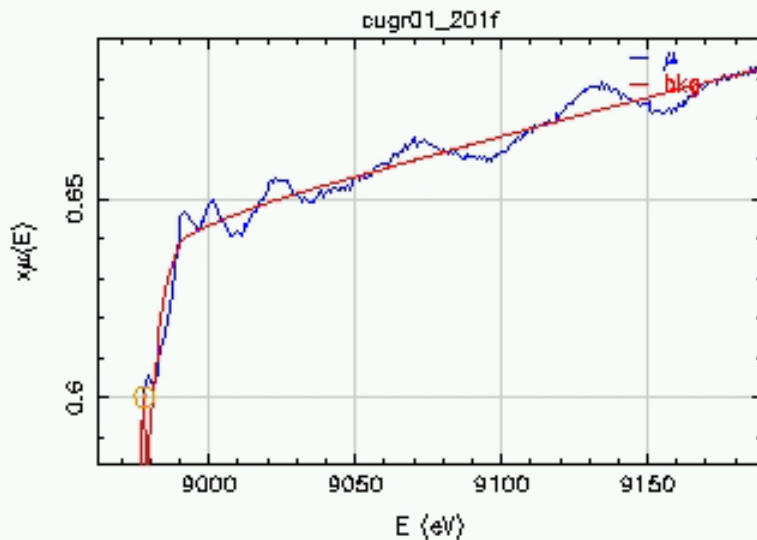
- A good background function removes long frequency oscillations from $\chi(k)$.

- Constrain background so that it cannot contain oscillations that are part of the data.

- Long frequency oscillations in $\chi(k)$ will appear as peaks in FT at low R-values

- FT is a frequency filter – use it to separate the data from the background!

Separating the background function from the data using Fourier transform
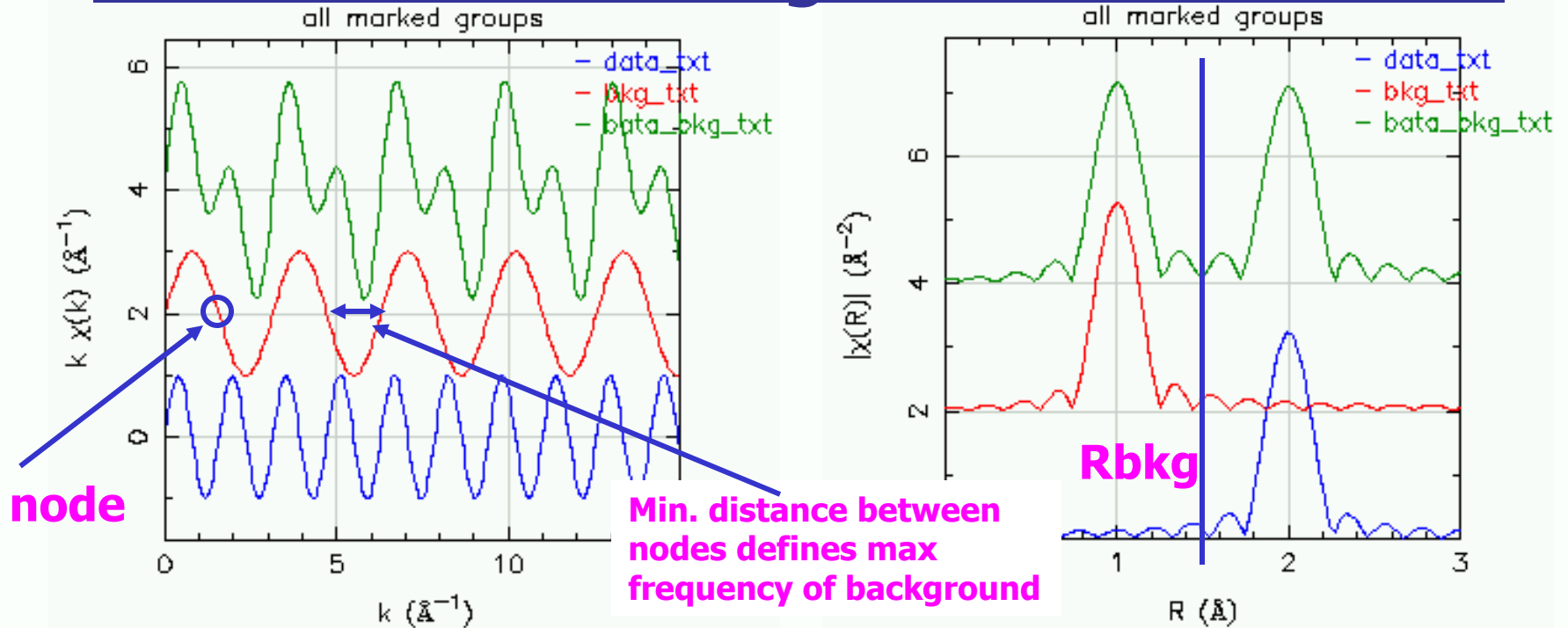
- Background function is made from splines connected by evenly distributed knots.
- Each spline is allowed one node.
- The number of knots are calculated from the value for Rbkg and the data range in k-space.
- Distance between nodes is limited restricting background from containing frequencies that are part of the data.

Rbkg value in Athena

FT and Background function

R_{bkg} = 1.0

R_{bkg} = 0.1

- An example where long wavelength oscillations appear as (false) peak in the FT

Fitting background and data using Artemis
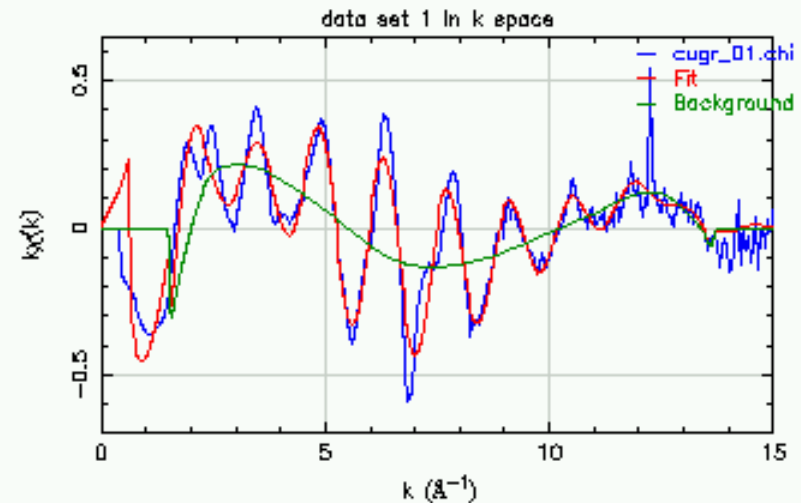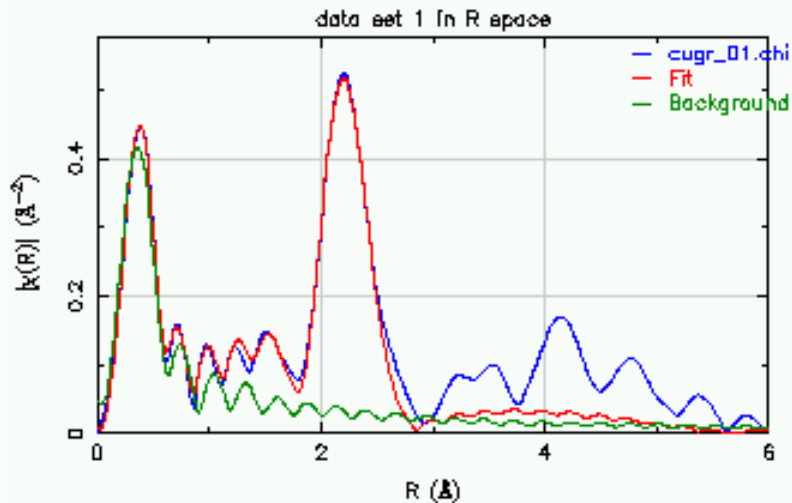
- Minimum distance between nodes and the number of knots are constrained by the data range and the value for Rbkg.
- Notice that not all the nodes (8) were needed to remove the background. Nodes are not constrained.
- Using the FT to frequency filter the data, means that IFEFFIT doesn't need your help to place the nodes.

Artemis, Fitting the background

How to choose Rbkg value

R_{bkg} = 2.2
R_{bkg} = 1.0

A Hint that Rbkg may be too large.
Data should be smooth, not pinched!

- An example where background distorts the first shell peak.
- R_{bkg} should be about half the R value for the first peak.

Frequency of Background function

Data contains this and shorter frequencies
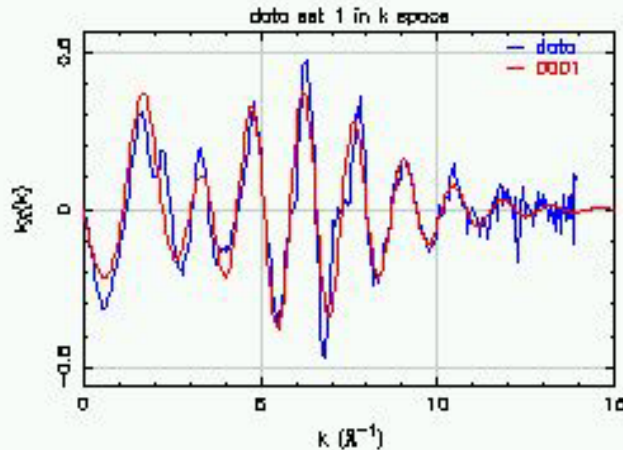
Bkg contains this and longer frequencies
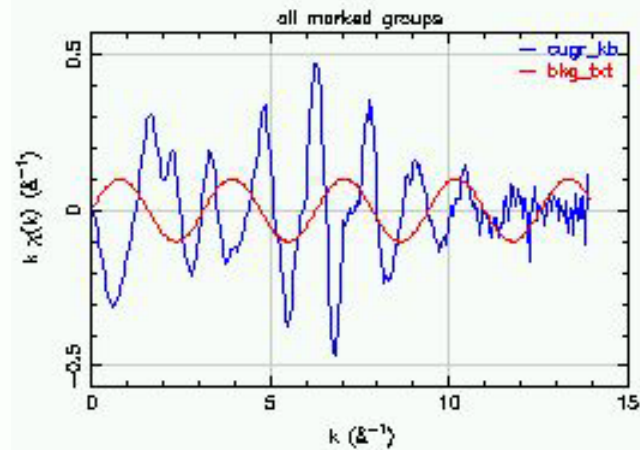
- Constrain background so that it cannot contain frequencies that are part of the data.

    - Use information theory, number of knots = $2 R_{bkg} \Delta k / \pi$

    - 8 knots in bkg using R_{bkg}=1.0 and $\Delta k = 14.0$

- Background may contain only longer frequencies. Therefore knots are not constrained.

The EXAFS Equation

$$\chi(k) = \Sigma_i \; \chi_i(k)$$

with
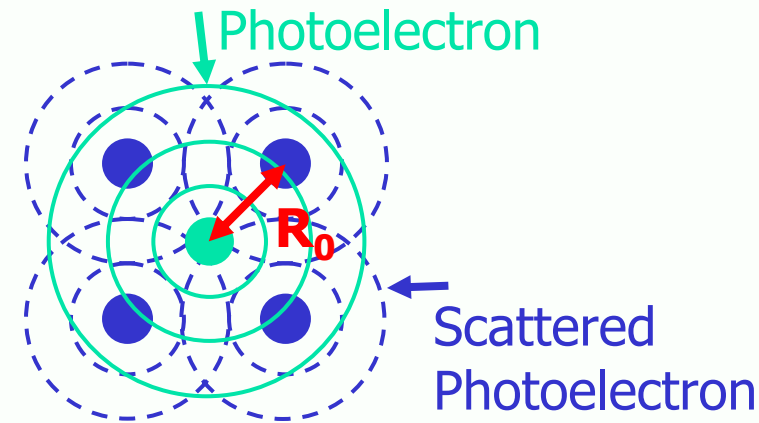
$$\chi_i(k) = \left(\; \frac{(N_i S_0^2) F_i(k)}{k R_i^2} \; \sin(2kR_i + \varphi_i(k)) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \; \right)$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2 \, m_e (E - E_0) / \hbar$$

Photoelectron

R_0

Scattered Photoelectron

Theoretically calculated values
$F_i(k)$ effective scattering amplitude
$\varphi_i(k)$ effective scattering phase shift
$\lambda(k)$ mean free path
R_0 initial path length

Parameters often determined from a fit to data
N_i degeneracy of path
S_0^2 passive electron reduction factor
σ_i^2 mean squared displacement
E_0 energy shift
ΔR change in half-path length

Athena: Summary

- **Background removal parameters**
  - Rbkg, cutoff frequency for background, should be about half the first peak position in R-space
  - Value for E0, defines wave number k, should be somewhere on the edge, will be optimize in fit.
  - Pre-edge range, used to normalize the data and determine the edge step, values are relative to E0 and should be in the pre-edge region (negative) .
  - Normalization range, used to normalize the data and determine the edge step, values are relative to E0 and should be in the post-edge region (positive).
  - Edge step: Value used to scale $\chi(k)$ data and normalize the absorption data.
  - Spline range, in wave number and energy. This is the range that will be used for the background spline. "Bad" data at really high energy should not be included. White lines at low energy should not be included.
- **Fourier Transform parameters**
  - K-weight, used to emphasize different regions of the data. Values of 1,2, or 3 are often used.
  - dk: width of sill used in the FT window. Values of 2 to 0.8 inverse angstroms are often used
  - Window type: type of window function used. Kb is usually fine.
  - K-range: This is the range of data in k-space that will be FT. Pick nodes usually one or two cycles from the ends.
- **Backward Fourier transform**
  - dr: width of the sill used in the FT window. Usually 0.5 inverse angstroms is fine.
  - Window type: type of window used in FT. Kb is usually fine.
  - R-range: The range of frequencies that you want to include in the backward FT.
  - To compare the backward FT to the original $\chi(k)$ data pick the orange kq button