

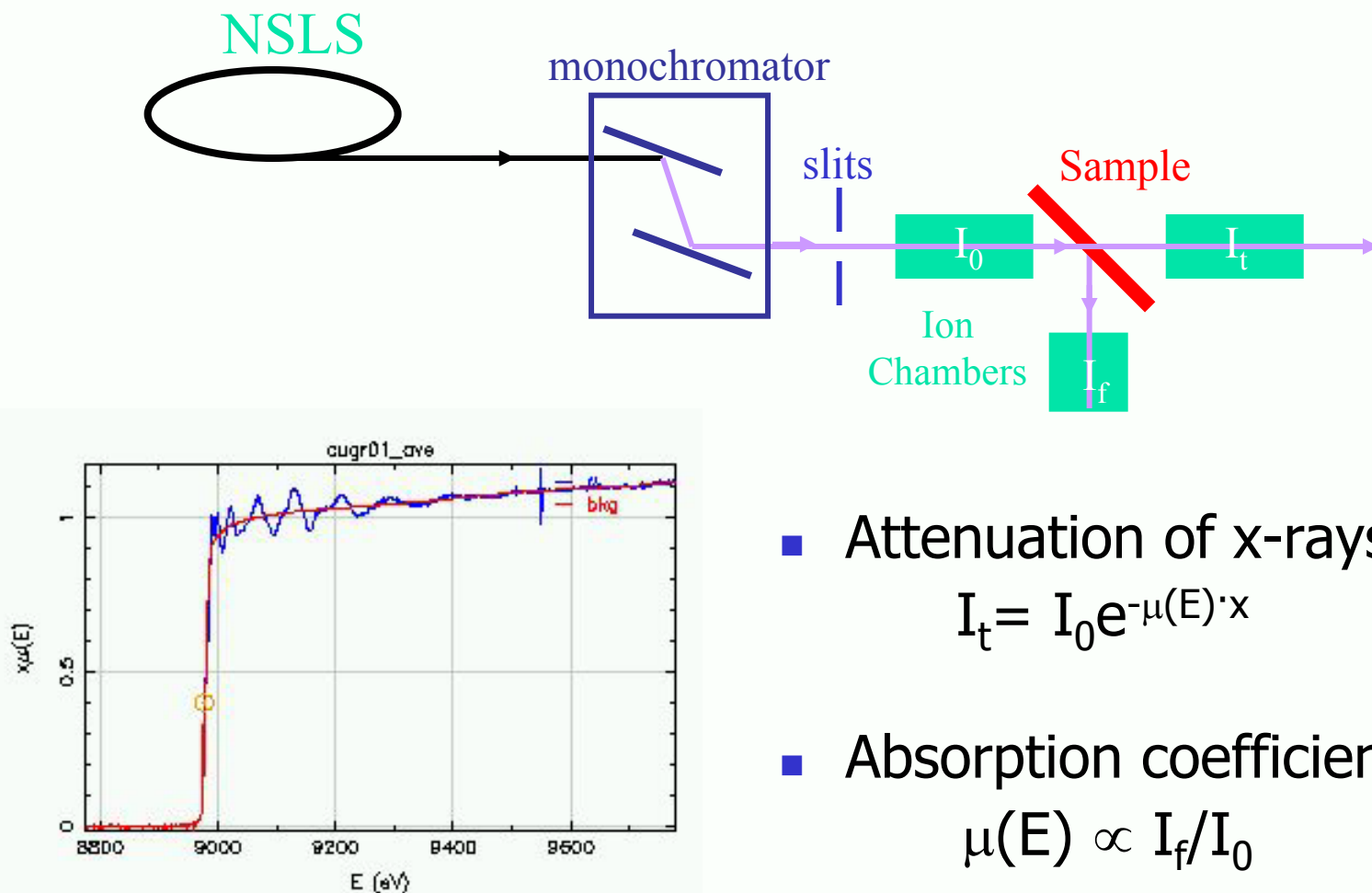
# Basics of EXAFS data analysis

Shelly Kelly

Argonne National Laboratory, Argonne, IL

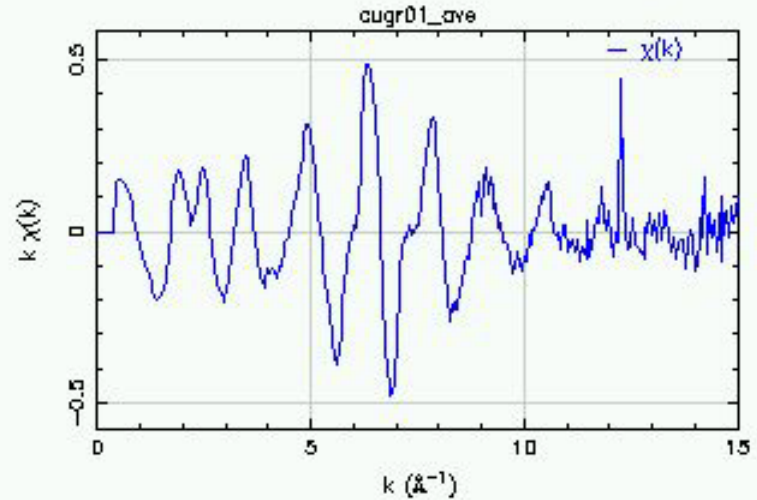
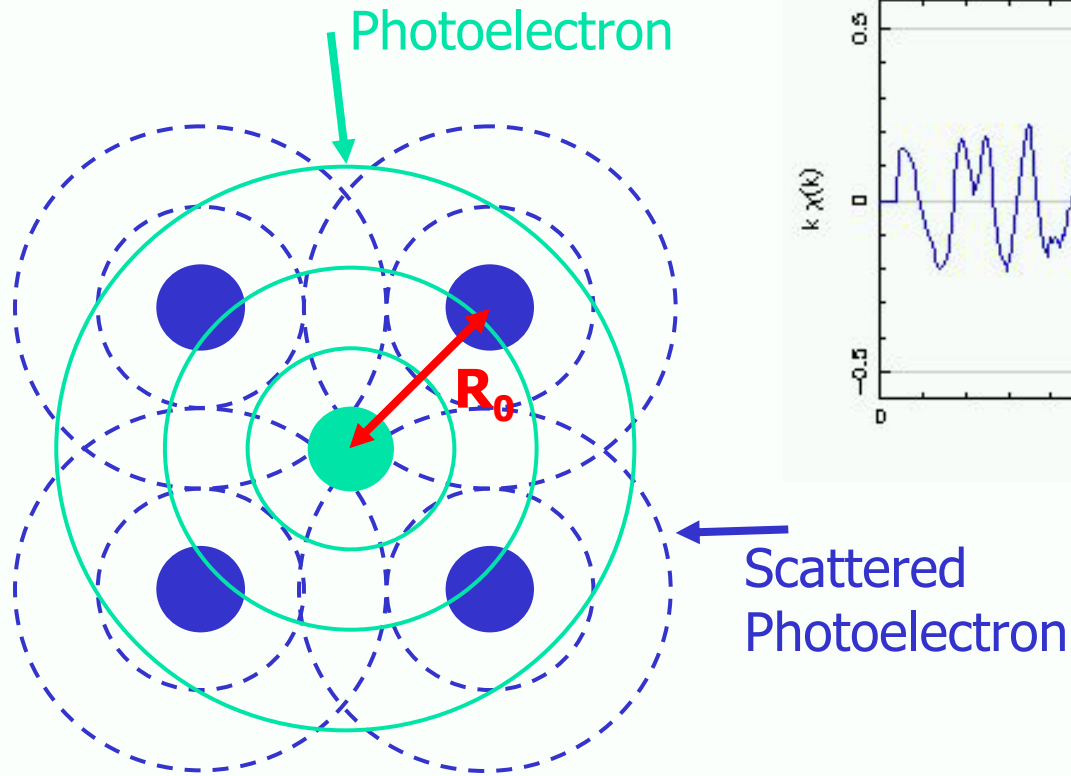


# X-ray-Absorption Fine Structure

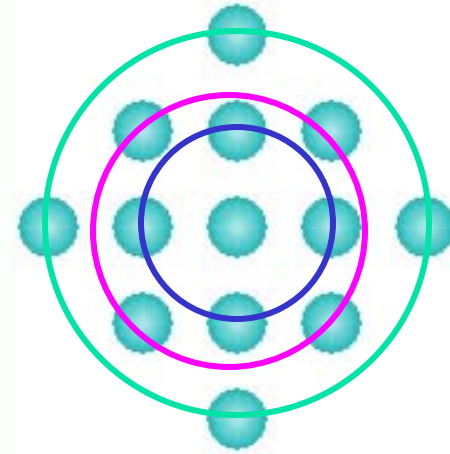
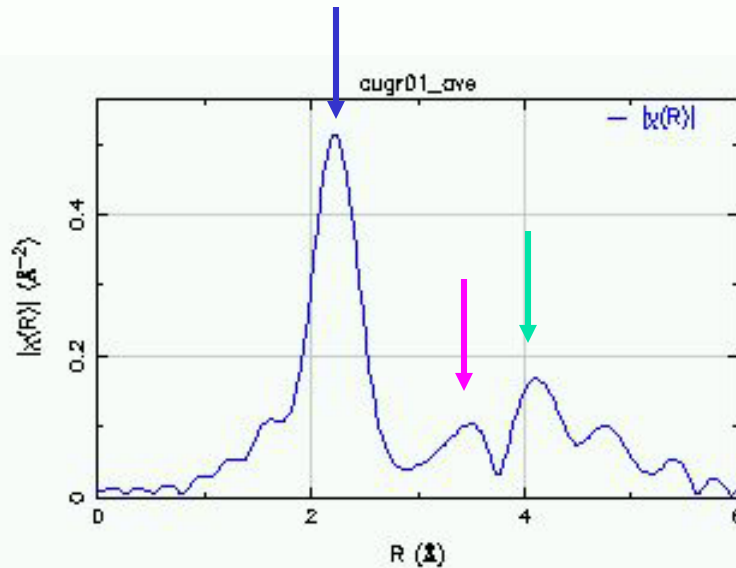


- Attenuation of x-rays
$$I_t = I_0 e^{-\mu(E) \cdot x}$$
- Absorption coefficient
$$\mu(E) \propto I_f / I_0$$

# X-ray-Absorption Fine Structure



# 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

Current group Listed here

Background Parameters For the Current Group

Fourier Transform Parameters For the current group

Backward Fourier Transform Parameters For the current group

The screenshot shows the Athena software interface with several panels:

- Current Group:** `cugr01_ave`. File: `/home/skelly/Xafs/Cu/CuGR/jan02/cugr01_merge_nor.nor`
- Background removal:**
  - EO: `8976.236` Rbkgt: `1`
  - Standard: `None` Background: `Autobk` Z: `H`
  - k-weight: `1` EO shift: `0` Edge step: `0.9912`  fix step
  - Pre-edge range: `-150` to `-30`
  - Normalization range: `100` to `923.77`
  - Spline range: k: `0.5` to `16.392`; E: `0.952` to `1023.77`
  - Spline clamps: low: `None` high: `Strong` Nclamp: `5`
- Forward Fourier transform:**
  - k-weight: `1` dk: `2` window type: `kaiser-bessel`
  - k-range: `2` to `11.642`
  - Phase correction:  off Z: `H` Edge: `K`
- Backward Fourier transform:**
  - dr: `0.5` window type: `kaiser-bessel`
  - R-range: `1` to `3`
- Plotting parameters:**
  - plot multiplier: `1` y-axis offset: `0`

At the bottom, a message reads: "Cannot check memory with this version of lfeffit"

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

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

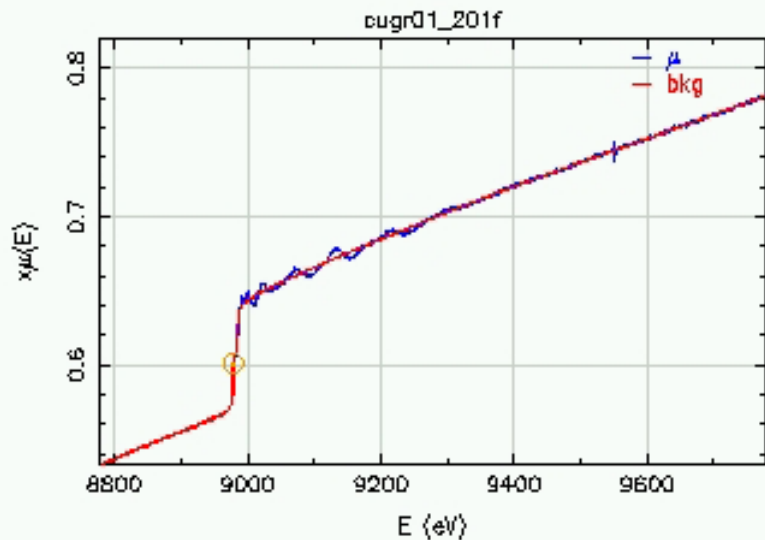
Orange buttons plot the highlighted data

Purple buttons will plot several marked data sets together

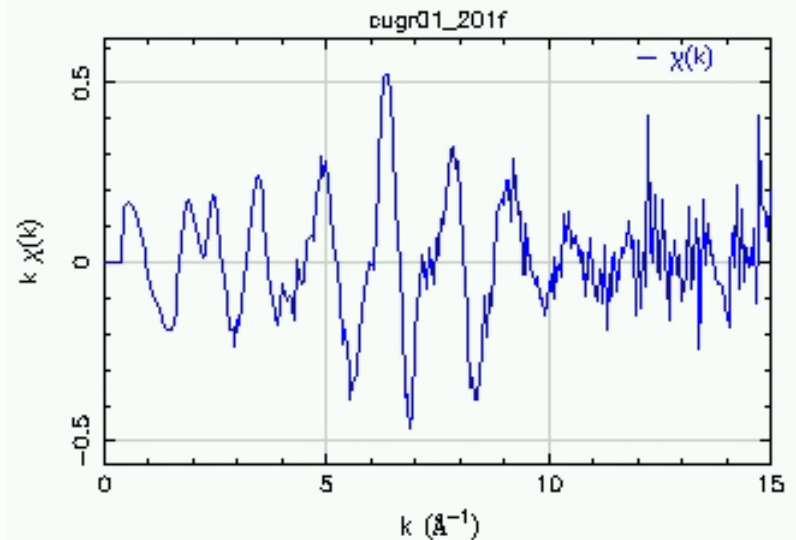
Plotting options



# Definition of EXAFS



=>



Normalized oscillatory part of absorption coefficient

Measured Absorption coefficient

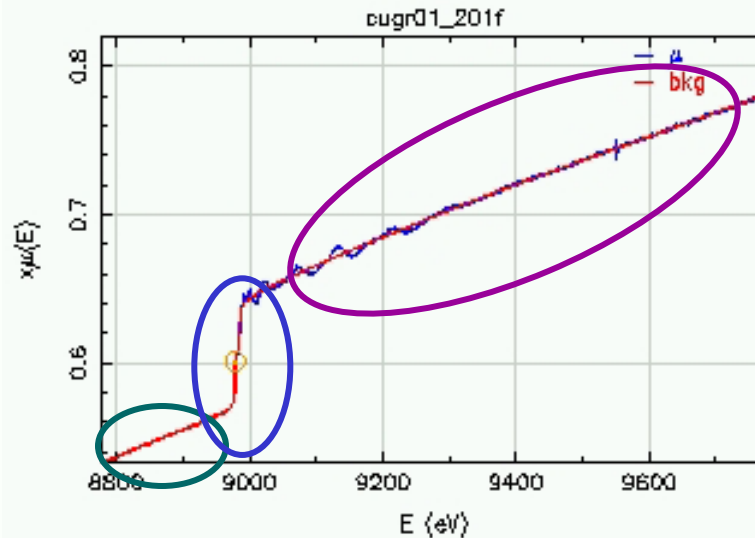
Bkg: Absorption coefficient without contribution from neighboring atoms (Calculated)

$$\chi(\mathbf{E}) = \frac{\mu(\mathbf{E}) - \mu_0(\mathbf{E})}{\Delta\mu(\mathbf{E})}$$

$$\sim \frac{\mu(\mathbf{E}) - \mu_0(\mathbf{E})}{\Delta\mu(\mathbf{E}_0)}$$

Evaluated at the Edge step ( $E_0$ )

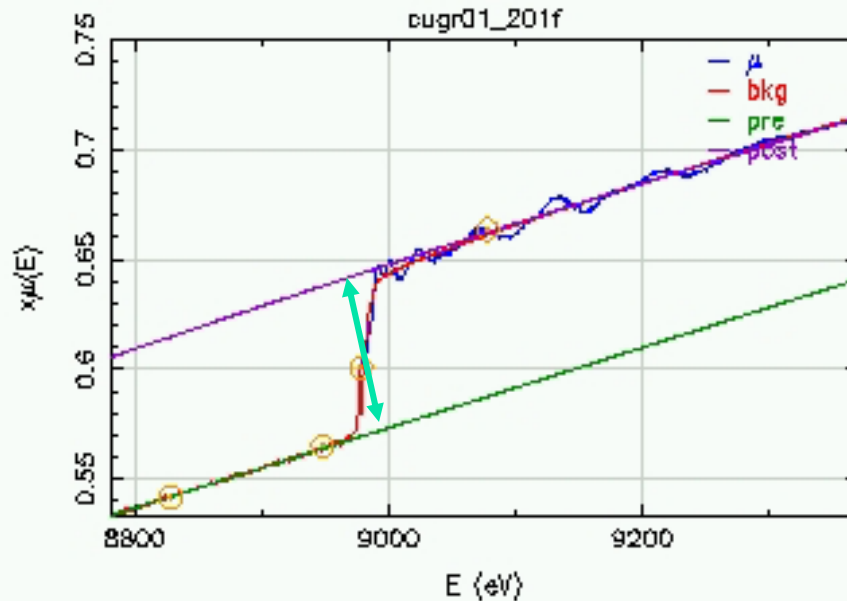
# Absorption coefficient



- **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

**Current Group:** cugr  
File: /home/skelly/Xafs/Cu/CuGR/jan02/athena.prj

**Background removal**  
E0: 8976.236 Rbkg: 0.1  
Standard: None Background: Autobk Z: H  
k-weight: 1 E0 shift: 0 Edge step: 0.9845 fix step  
Pre-edge range: -150 to 30  
Normalization range: 100 to 923.77  
Spline range: k: 0.5 to 16.392 E: 0.952 to 1023.77  
Spline clamps: low: None high: Strong

**Forward Fourier transform**  
k-weight: 1 dk: 2 window type: kaiser-bessel  
k-range: 2 to 11.732  
Phase correction: off Z: H Edge: K

**Backward Fourier transform**  
dr: 0.5 window type: kaiser-bessel  
R-range: 1 to 3

**Plotting parameters**  
plot multiplier: 1 y-axis offset: 0

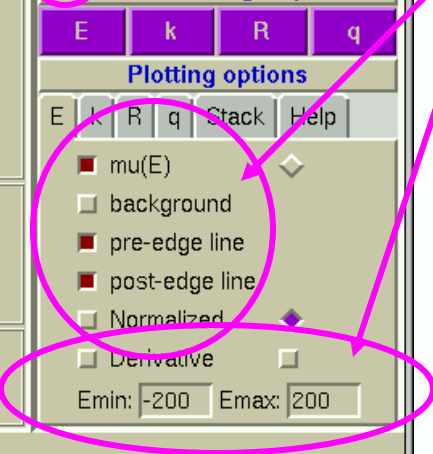
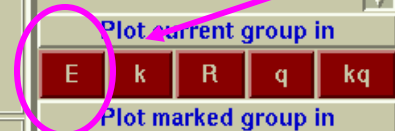
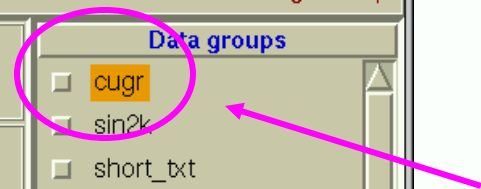
**Data groups**  
 cugr  
 sin2k  
 short\_txt  
 short\_win  
 step\_txt  
 cugr\_hanning  
 cugr\_kb  
 cugr\_welch

**Plot current group in**  
E k R q kq

**Plot marked group in**  
E k R q

**Plotting options**  
E k R q Stack Help  
 mu(E)  
 background  
 pre-edge line  
 post-edge line  
 Normalized  
 Derivative  
Emin: -200 Emax: 200

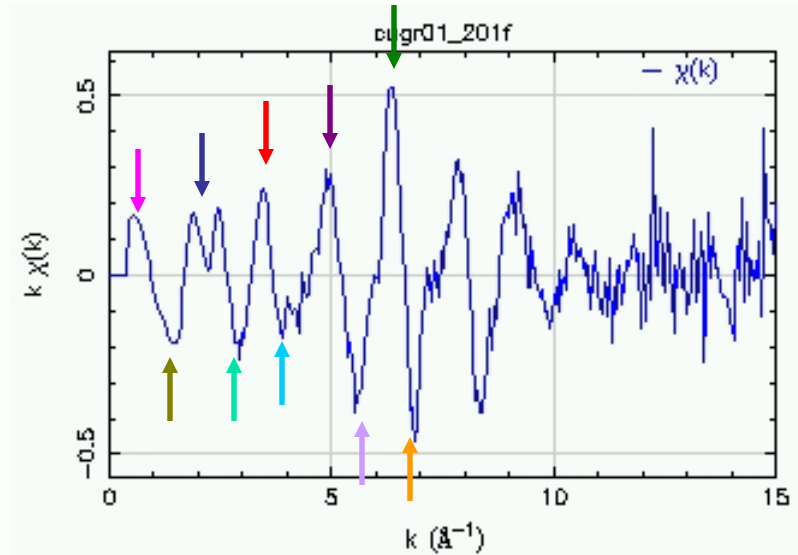
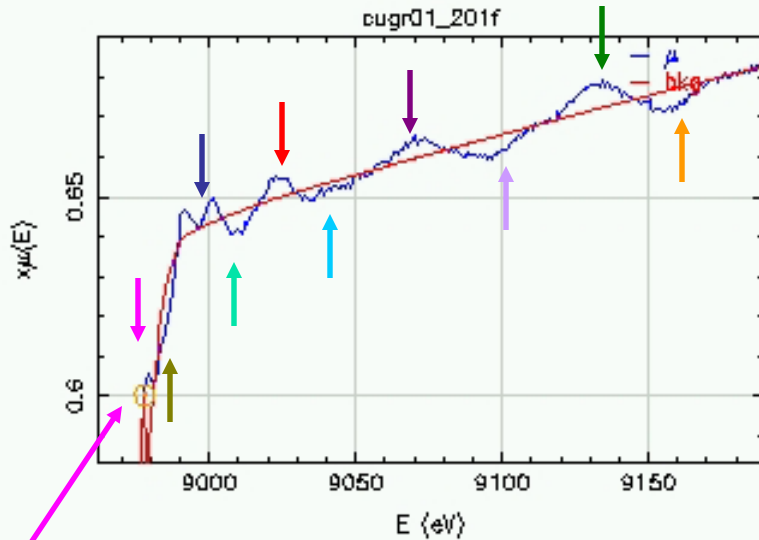
plotting in energy from group `cugr' ... done!



To reproduce  
The plot of the  
Previous slide:  
Highlight the  
Group you  
want to plot.  
Push the  
Orange E button  
And set the  
Plotting options  
As shown.



# Energy to wave number



$E_0$  Must be somewhere on the edge

Mass of the electron

Threshold Energy

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

$\hbar^2$  ← Planck's constant

$$\Delta E(\text{eV}) \sim 3.81 k^2$$

# Athena: Edge energy E0

Athena

File Edit Group Plot Mark Deglitch Align Merge Diff Preferences Help

Current Group: **cugr01\_ave**

File: /home/skelly/Xafs/Cu/CuGR/jan02/cugr01\_merge\_nor.nor

**Background removal**

E0: 8976.236 X k: 1 X

Standard: None Background: Autobk Z: H

k-weight: 1 EO shift: 0 Edge step: 0.9912  fix step

Pre-edge range: -150 X to -30 X

Normalization range: 100 X to 923.77 X

Spline range: k: 0.5 X to 16.392 X

E: 0.952 X to 1023.77 X

Spline clamps: low: None high: Strong Nclamp: 5

**Forward Fourier transform**

k-weight: 1 dk: 2 window type: kaiser-bessel

k-range: 2 X to 11.642 X

Phase correction:  off Z: H Edge: K

**Backward Fourier transform**

dr: 0.5 window type: kaiser-bessel

R-range: 1 X to 3 X

**Plotting parameters**

plot multiplier: 1 y-axis offset: 0

**Data groups**

- cugr\_kb
- cugr\_welch
- cugr\_parzen
- cugr\_sine
- cugr\_nosill
- cugr\_01
- cugr\_05
- cugr\_10
- cugr\_15
- cugr01\_ave**

**Plot current group in**

E k R q kq

**Plot marked group in**

E k R q

**Plotting options**

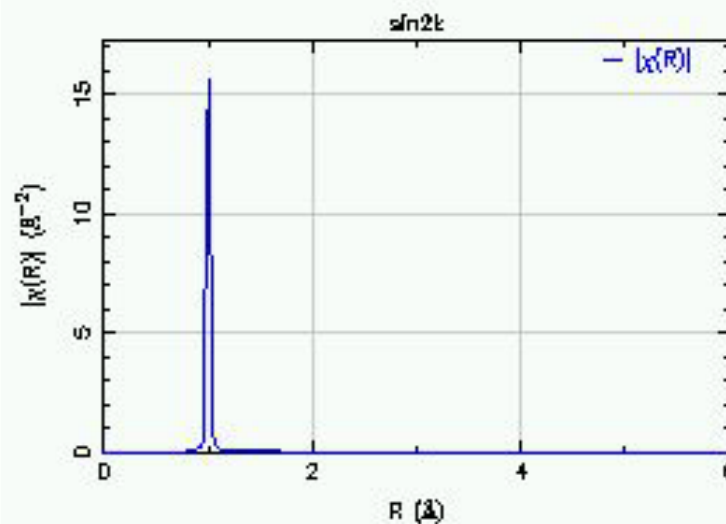
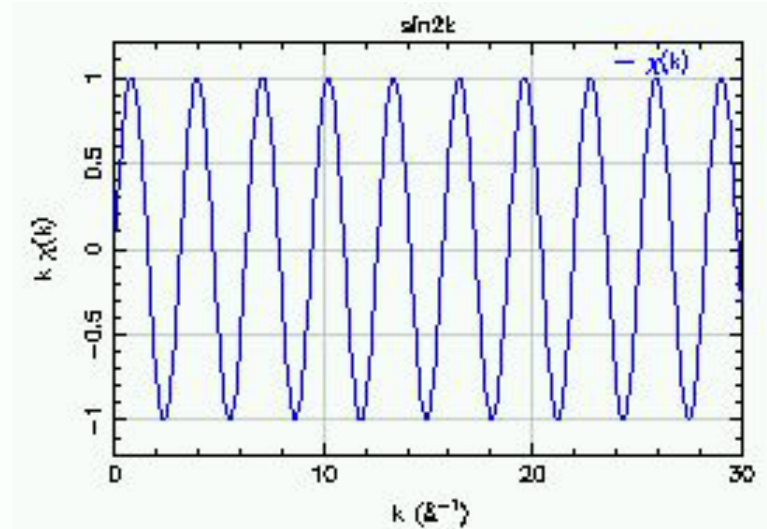
E k R q Help

- Magnitude
- Envelope
- Real part
- Imaginary part
- Phase
- Window

Rmin: 0 Rmax: 6

Cannot check memory with this version of Iffitit

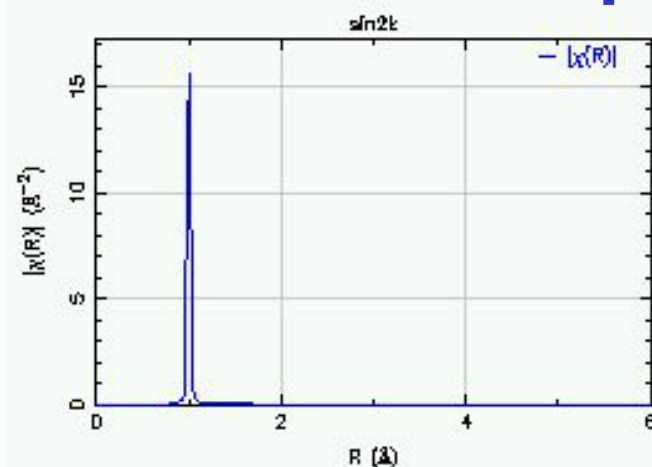
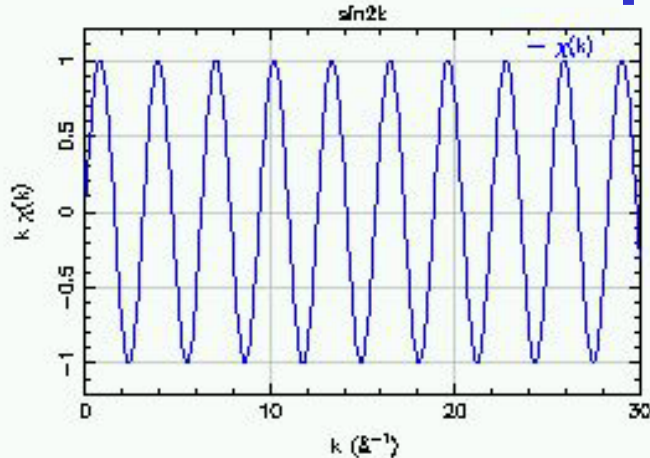
# Properties of a Fourier Transform



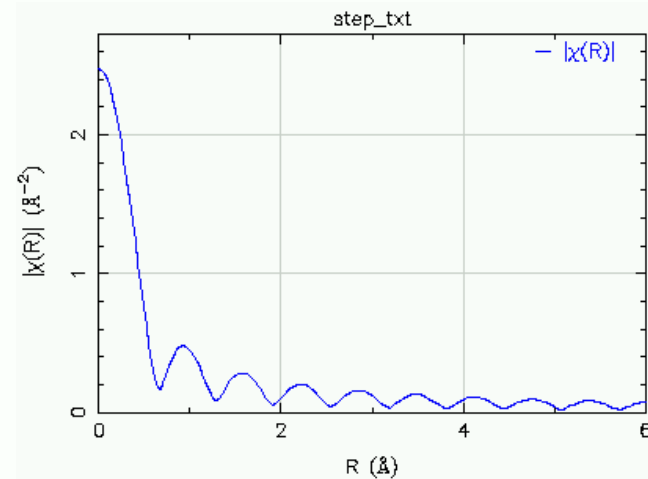
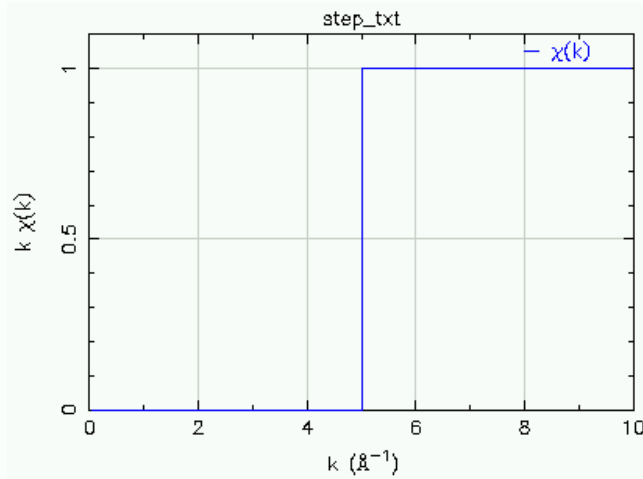
- FT of infinite sine wave is a delta function
- FT of  $\sin(2k)$  is a peak at  $R=1$
- FT is a frequency filter
- Signal that is de-localized in  $k$ -space is localized in  $R$ -space

# Fourier Transform of a function that is:

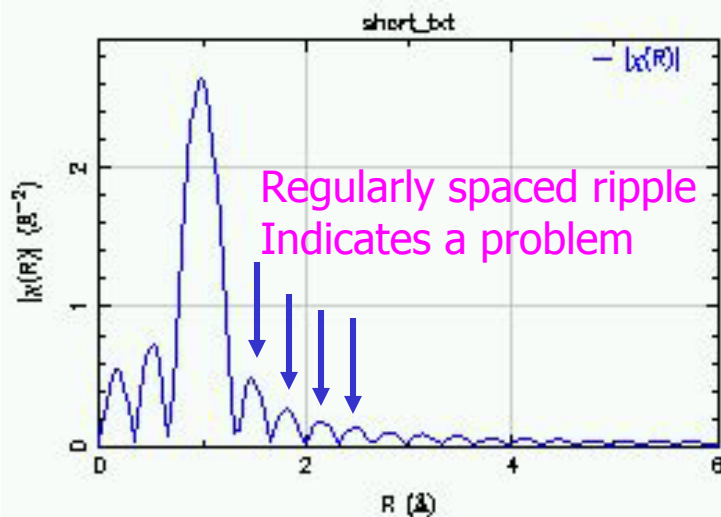
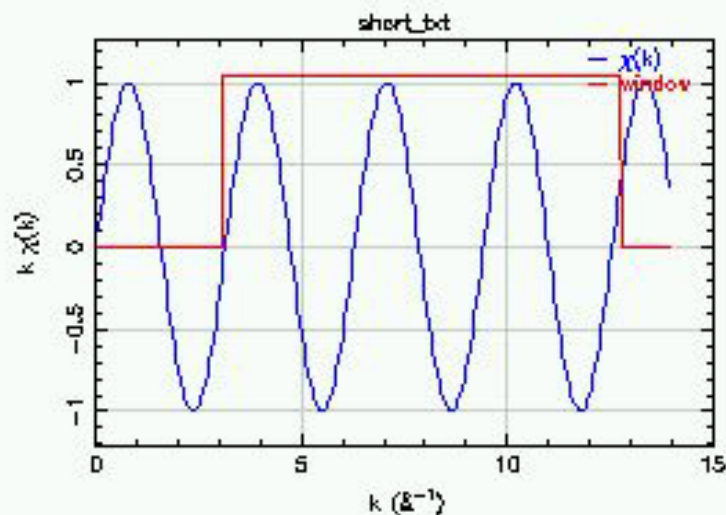
**De-localized in k-space  $\Rightarrow$  localized in R-space**



**Localized in k-space  $\Rightarrow$  de-localized in R-space**

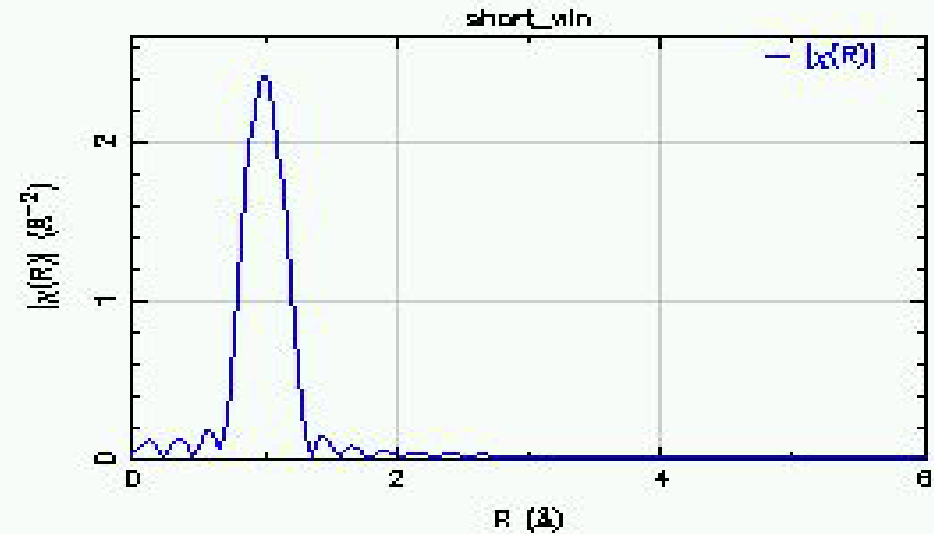
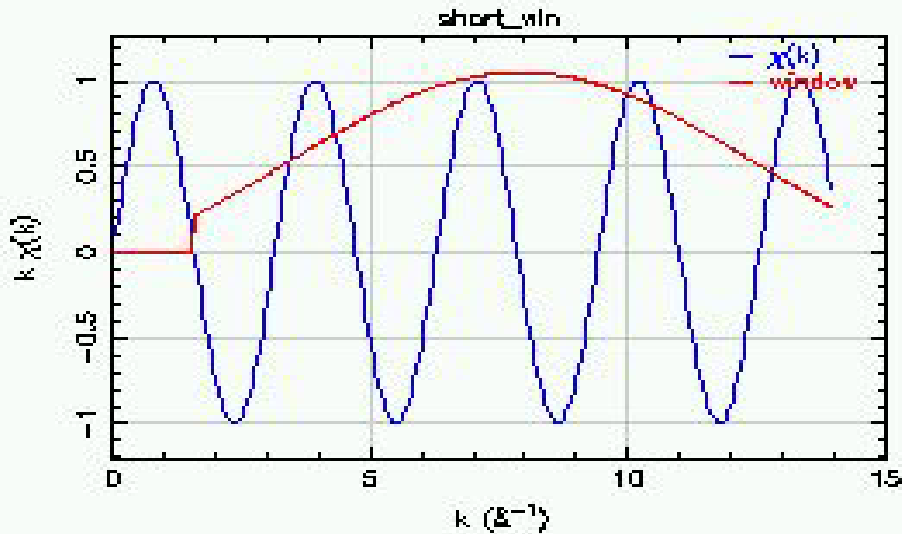


# Fourier Transform is a frequency filter



- 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

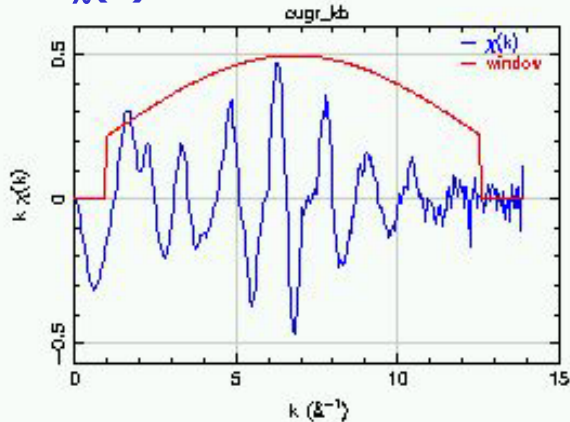


- Multiplying the discrete sine wave by a **window** that gradually increases the amplitude of the data smoothes the FT of the data.

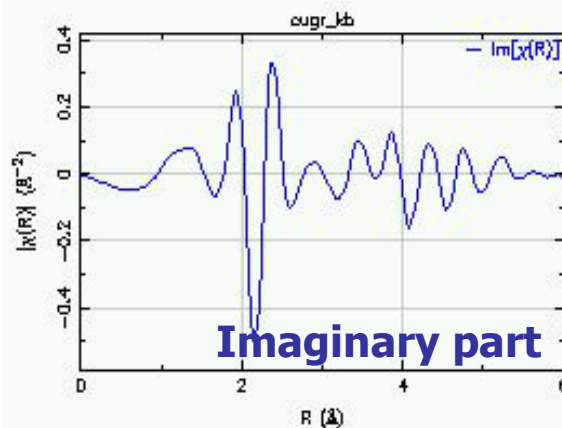
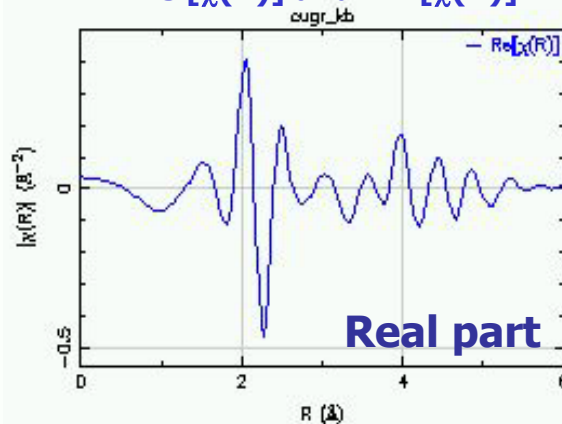


# Fourier Transform parts

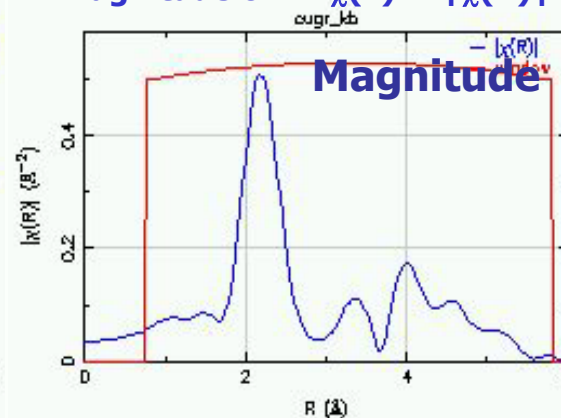
$\chi(k)$  data and FT window



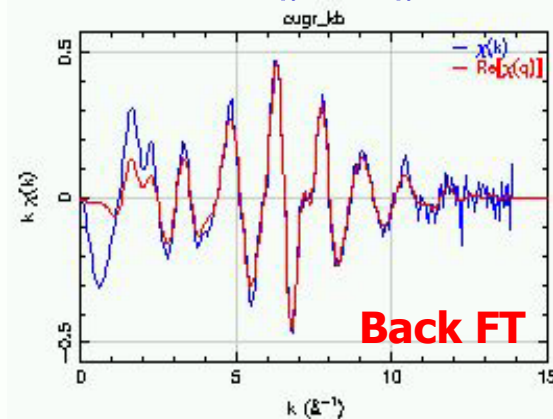
Real and imaginary parts of FT  $\chi(k)$   
=  $\text{Re}[\chi(R)]$  and  $\text{Im}[\chi(R)]$



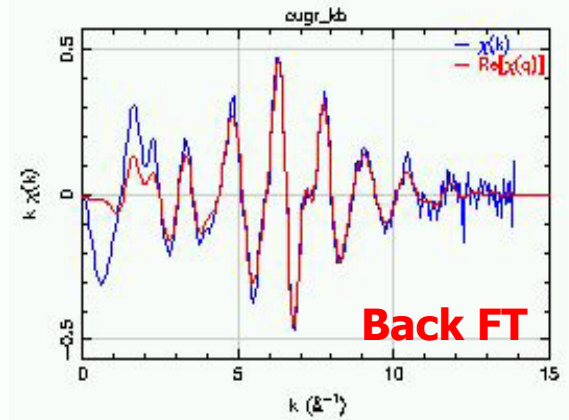
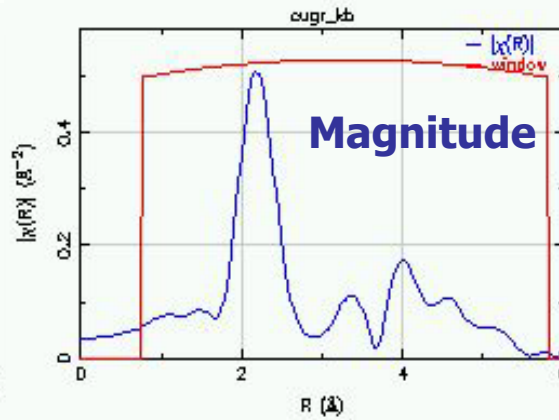
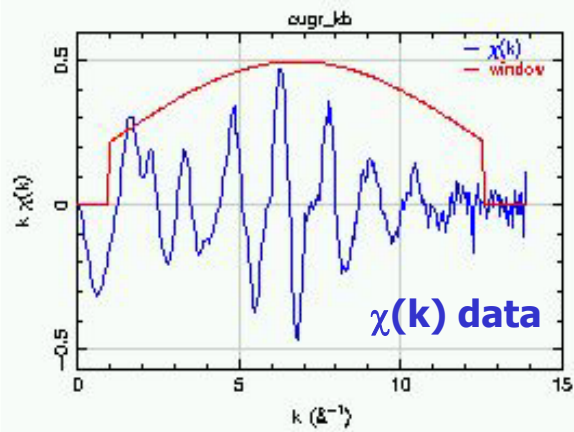
magnitude of FT  $\chi(k) = |\chi(R)|$



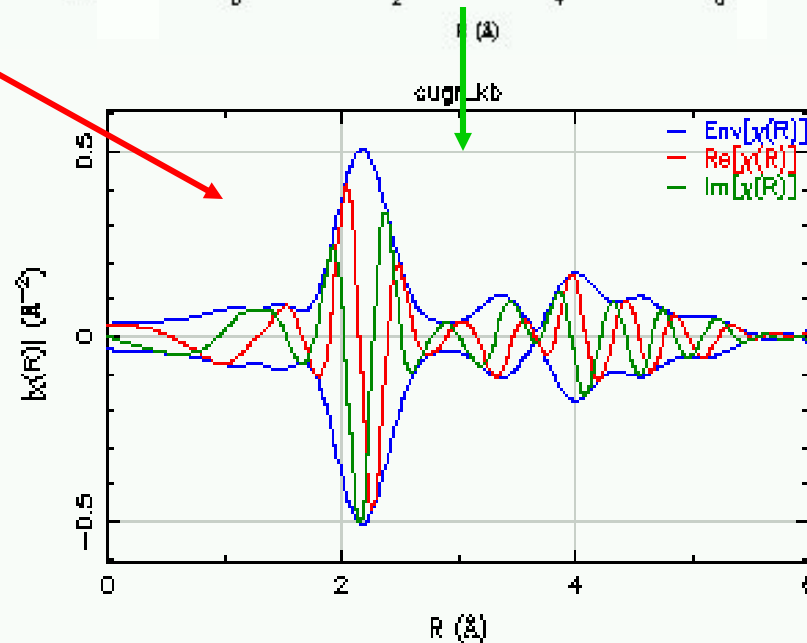
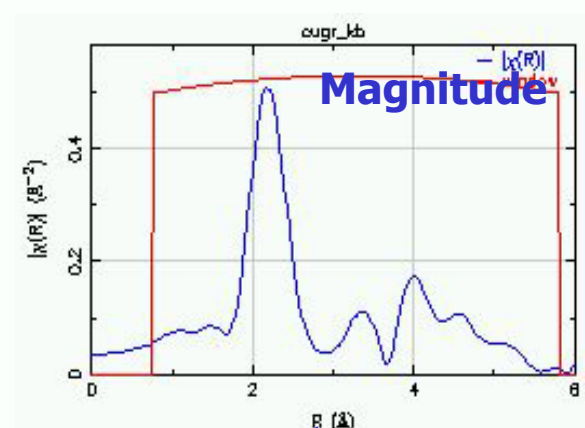
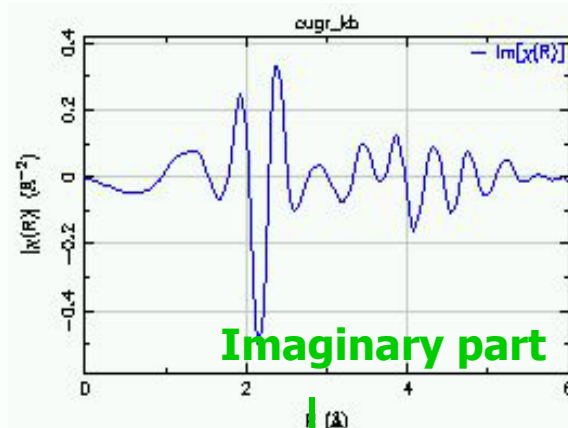
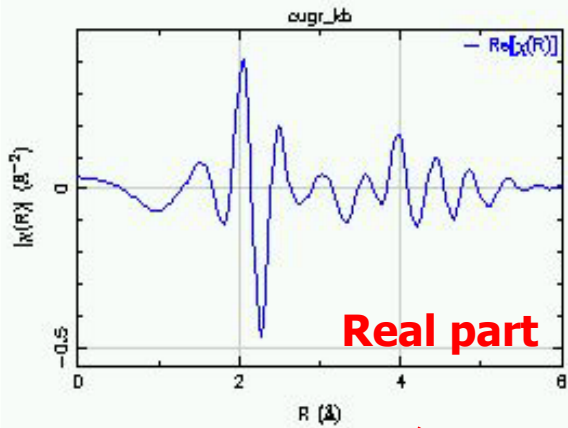
back FT of  $\chi(R) = \chi(q)$



# Fourier Filter of EXAFS data



# Understanding the different parts of FT



- $|\chi(R)|$  is not unique. Information has been lost.

# Athena plotting in R-space

The screenshot shows the Athena software interface with the following settings:

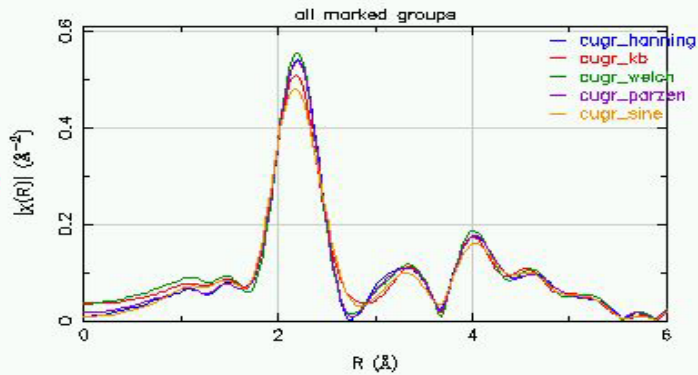
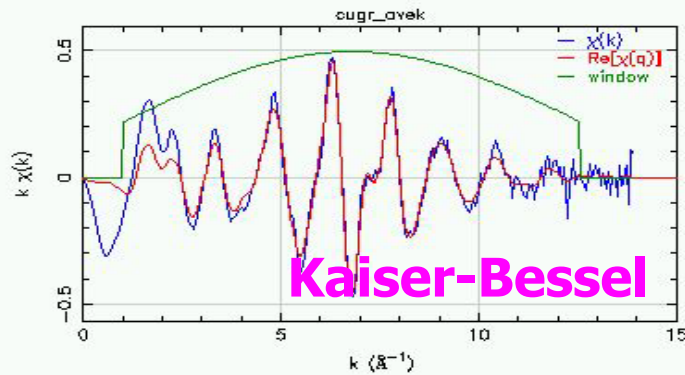
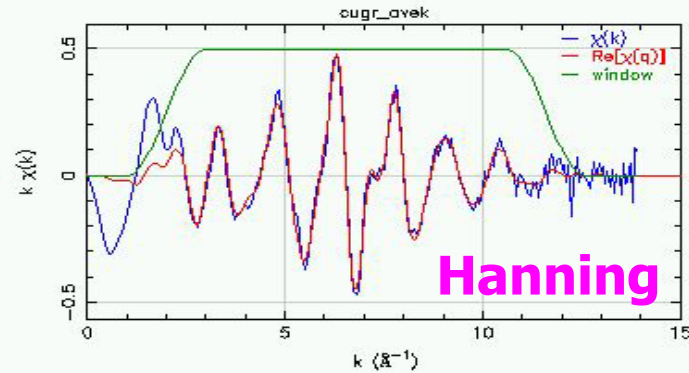
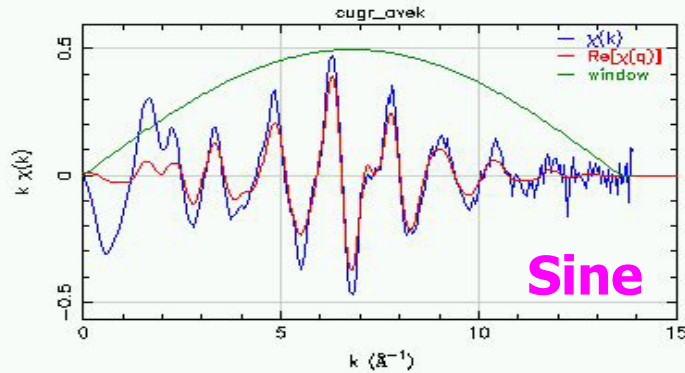
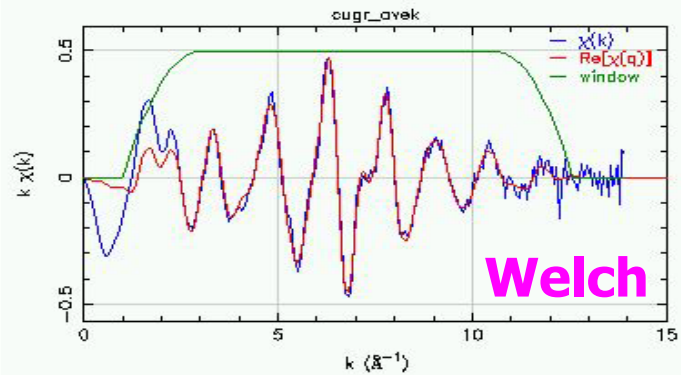
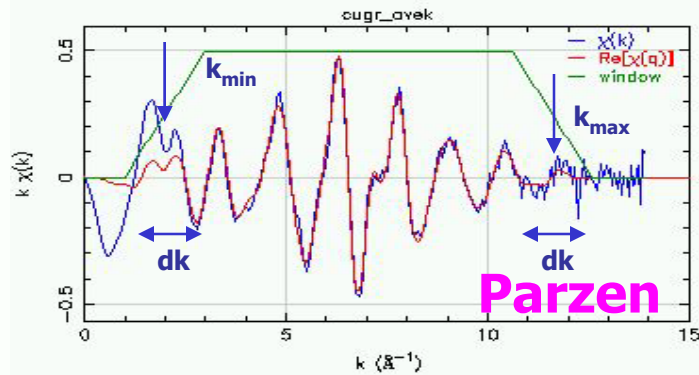
- Current Group:** `cugr01_ave`
- File:** `/home/skelly/Xafs/Cu/CuGR/jan02/cugr01_merge_nor.nor`
- Background removal:**
  - E0: 8976.236, Rbkg: 1
  - Standard: None, Background: Autobk, Z: H
  - k-weight: 1, EO shift: 0, Edge step: 0.9912, fix step:
  - Pre-edge range: -150 to -30
  - Normalization range: 100 to 923.77
  - Spline range: k: 0.5 to 16.392, E: 0.952 to 1023.77
  - Spline clamps: low: None, high: Strong, Nclamp: 5
- Forward Fourier transform:**
  - k-weight: 1, dk: 2, window type: kaiser-bessel
  - k-range: 2 to 11.642
  - Phase correction:  off, Z: H, Edge: K
- Backward Fourier transform:**
  - dr: 0.5, window type: kaiser-bessel
  - R-range: 1 to 3
- Plotting parameters:**
  - plot multiplier: 1, y-axis offset: 0

**Plotting options (circled in blue):**

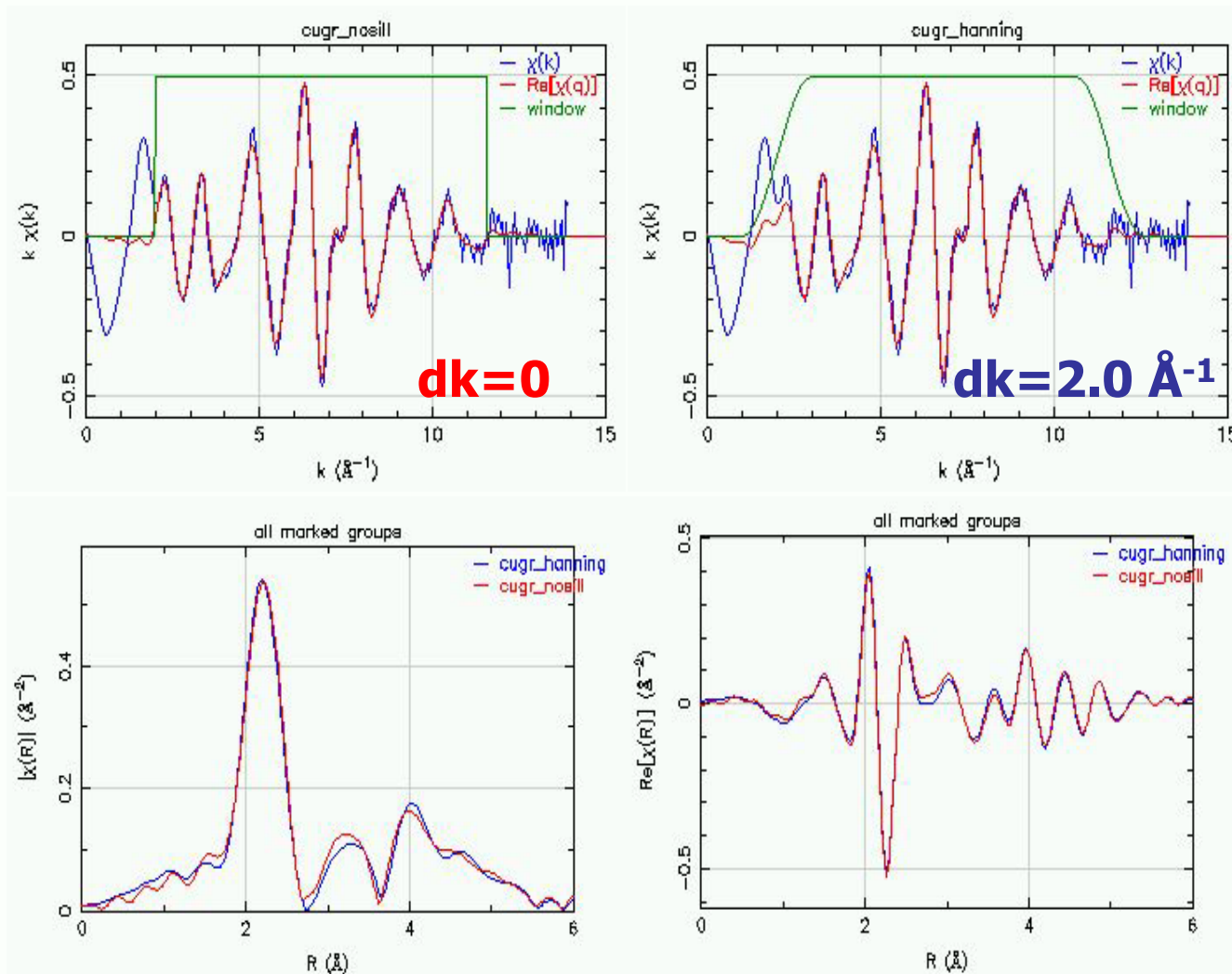
- Plot current group in:** E, k, R, q, kq (R is selected)
- Plot marked group in:** E, k, R, q (R is selected)
- Plotting options:** Magnitude (selected), Envelope, Real part, Imaginary part, Phase, Window
- Rmin: 0, Rmax: 6

Cannot check memory with this version of lfeffit

# Fourier Transform Windows



# Fourier Transform window sill



- A small sill can distort FT

# Fourier transform parameters in Athena

Athena

File Edit Group Plot Mark Deglitch Align Merge Diff Preferences Help

Current Group: **cugr01\_ave**

File: /home/skelly/Xafs/Cu/CuGR/jan02/cugr01\_merge\_nor.nor

### Background removal

E0: 8976.236 Rbkg: 1

Standard: None Background: Autobk z: H

k-weight: 1 E0 shift: 0 Edge step: 0.9912  fix step

Pre-edge range: -150 to -30

Normalization range: 100 to 923.77

Spline range: k: 0.5 to 16.392  
E: 0.952 to 1023.77

Spline clamps: low: None high: Strong Nclamp: 5

### Forward Fourier transform

k-weight: 1 dk: 2 window type: kaiser-bessel

k-range: 2 to 11.642

Phase correction:  off z: H Edge: K

### Backward Fourier transform

k-range: 0.5 to 3 window type: kaiser-bessel

R-range: 1 to 3

### Plotting parameters

plot multiplier: 1 y-axis offset: 0

### Data groups

- cugr\_kb
- cugr\_welch
- cugr\_parzen
- cugr\_sine
- cugr\_nosill
- cugr\_01
- cugr\_05
- cugr\_10
- cugr\_15
- cugr01\_ave**

### Plot current group in

E k R q kq

### Plot marked group in

E k R q

### Plotting options

E k R q Help

- Magnitude
- Envelope
- Real part
- Imaginary part
- Phase
- Window

Rmin: 0 Rmax: 6

Cannot check memory with this version of lfeffit

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

The screenshot shows the Athena software interface with the following sections and settings:

- Current Group:** `cugr01_ave`  
File: `/home/skelly/Xafs/Cu/CuGR/jan02/cugr01_merge_nor.nor`
- Background removal:**  
EO: `8976.236` Rbkg: `1`  
Standard: `None` Background: `Autobk` Z: `H`  
k-weight: `1` EO shift: `0` Edge step: `0.9912`  fix step  
Pre-edge range: `-150` to `-30`  
Normalization range: `100` to `923.77`  
Spline range: k: `0.5` to `16.392`  
E: `0.952` to `1023.77`  
Spline clamps: low: `None` high: `Strong` Nclamp: `5`
- Forward Fourier transform:**  
k-weight: `1` dk: `2` window type: `kaiser-bessel`  
k-range: `2` to `11.642`  
Phase correction:  off Z: `H` Edge: `K`
- Backward Fourier transform:**  
dr: `0.5` window type: `kaiser-bessel`  
R-range: `1` to `3`
- Plotting parameters:**  
plot multiplier: `1` y-axis offset: `0`

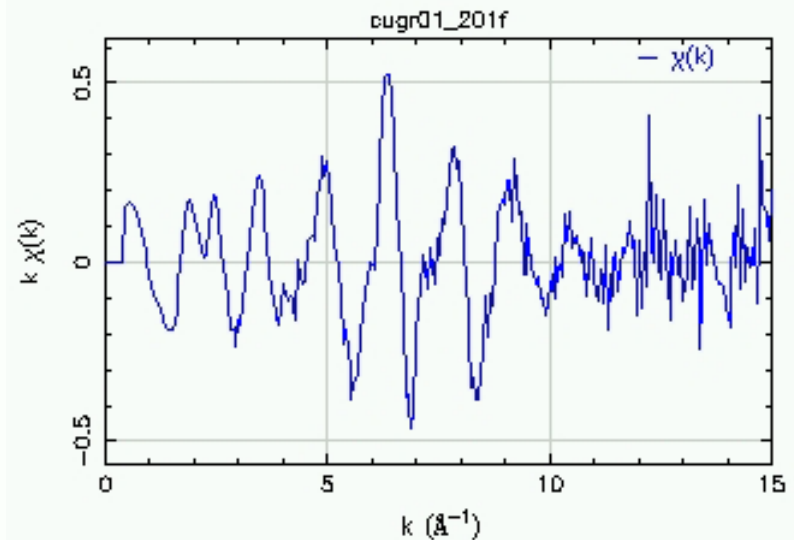
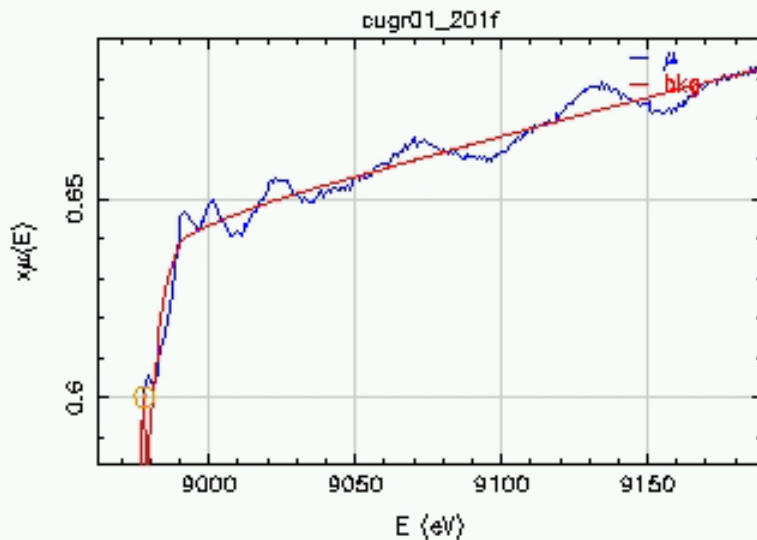
On the right side, the **Data groups** list includes: `cugr_kb`, `cugr_welch`, `cugr_parzen`, `cugr_sine`, `cugr_nosill`, `cugr_01`, `cugr_05`, `cugr_10`, `cugr_15`, and `cugr01_ave` (highlighted). Below this are buttons for **Plot current group in** (E, k, R, q, kq) and **Plot marked group in** (E, k, R, q), with the **R** button highlighted. The **Plotting options** section includes:  Magnitude,  Envelope,  Real part,  Imaginary part,  Phase,  Window, Rmin: `0`, Rmax: `6`.

At the bottom, a message states: "Cannot check memory with this version of lfeffit".

- 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.

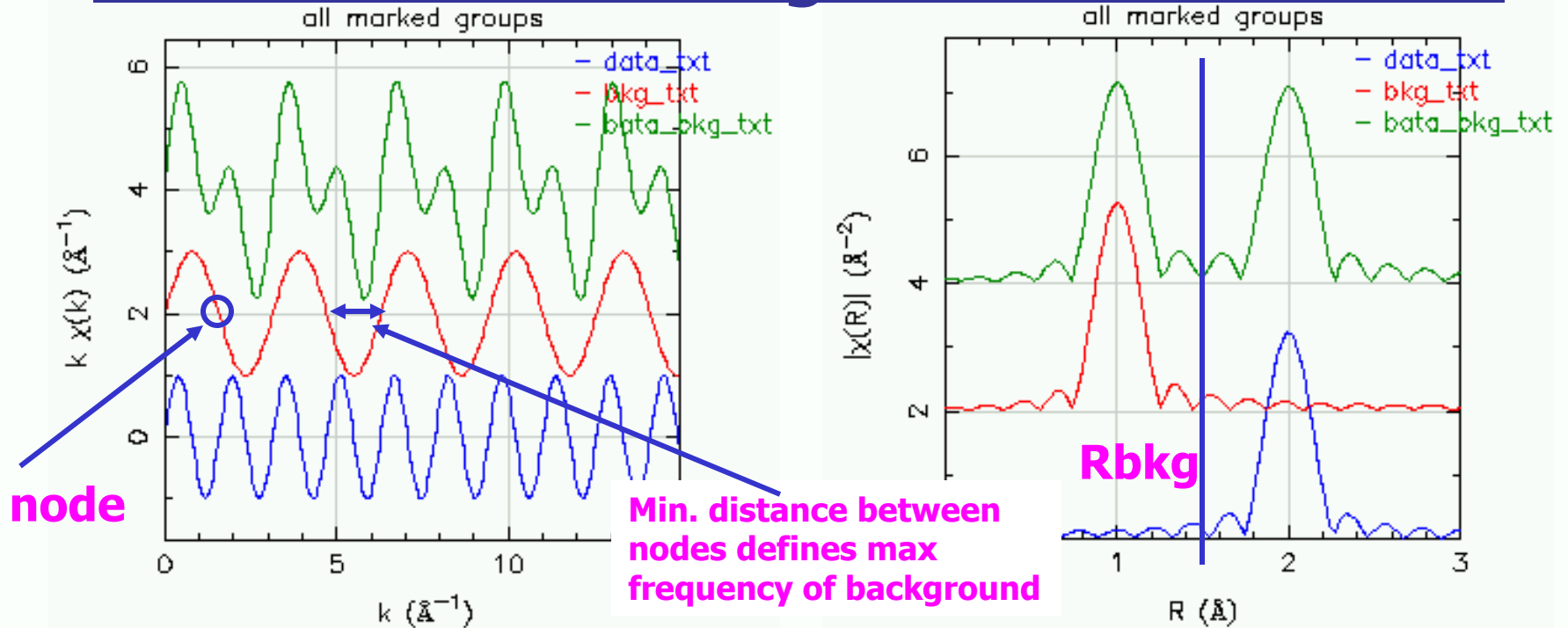


# Background function overview



- 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

The screenshot shows the Athena software interface with the following settings:

- Current Group:** `cugr01_ave`
- File:** `/home/skelly/Xafs/Cu/CuGR/jan02/cugr01_merge_nor.nor`
- Background removal:**
  - E0:** 8976.236
  - Rbkg:** 1 (circled in blue)
  - Standard:** None
  - Background:** Autobk
  - Z:** H
  - k-weight:** 1
  - E0 shift:** 0
  - Edge step:** 0.9912
  - fix step:**
  - Pre-edge range:** -150 to -30
  - Normalization range:** 100 to 923.77
  - Spline range:** k: 0.5 to 16.392; E: 0.952 to 1023.77
  - Spline clamps:** low: None, high: Strong, Nclamp: 5
- Forward Fourier transform:**
  - k-weight:** 1
  - dk:** 2
  - window type:** kaiser-bessel
  - k-range:** 2 to 11.642
  - Phase correction:**  off
  - Z:** H
  - Edge:** K
- Backward Fourier transform:**
  - dr:** 0.5
  - window type:** kaiser-bessel
  - R-range:** 1 to 3
- Plotting parameters:**
  - plot multiplier:** 1
  - y-axis offset:** 0

**Data groups:** A list of data groups is shown on the right, with `cugr01_ave` highlighted in orange.

**Plot current group in:** E, k, R, q, kq

**Plot marked group in:** E, k, R, q

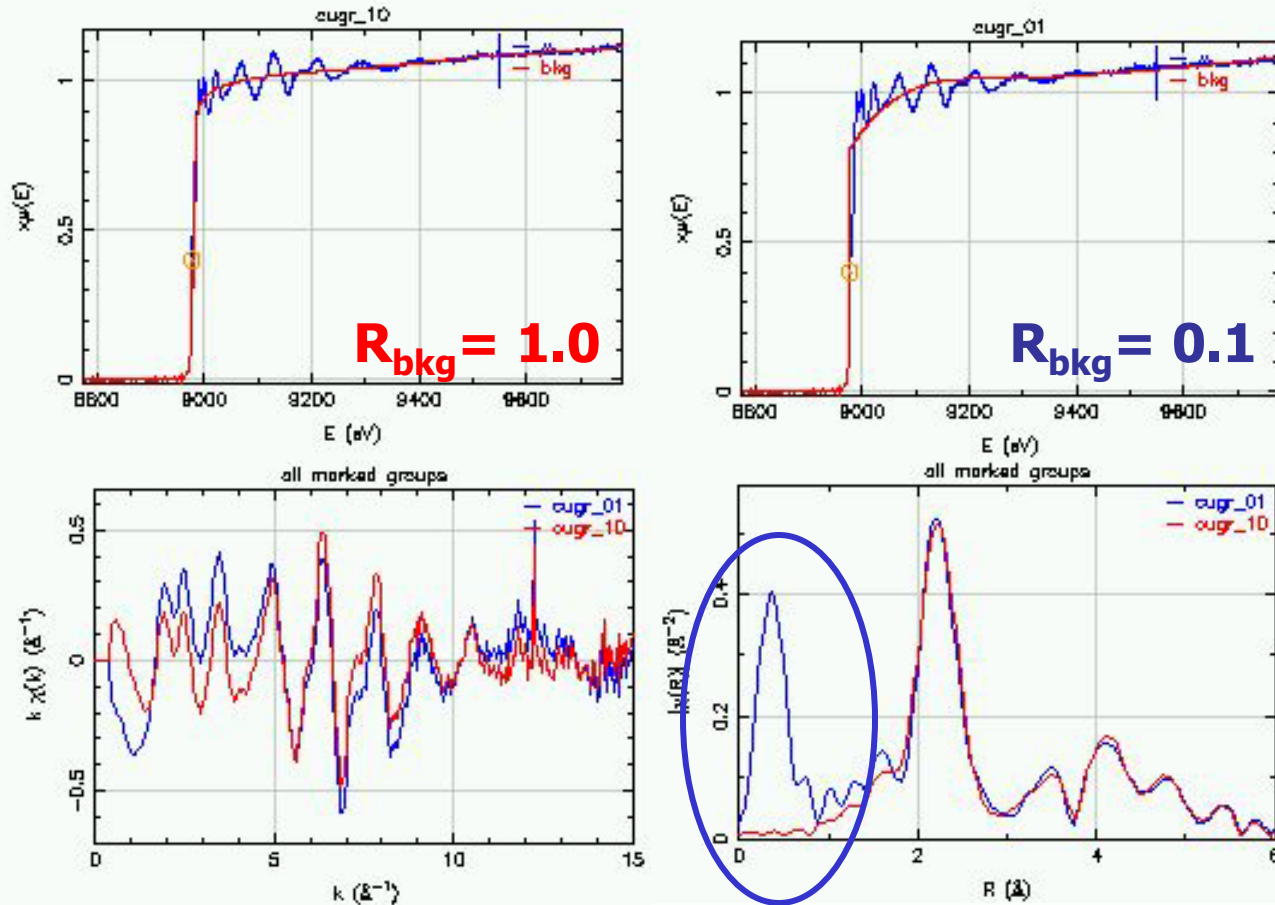
**Plotting options:** E, k, R, q, Help

- Magnitude
- Envelope
- Real part
- Imaginary part
- Phase
- Window

**Rmin:** 0 **Rmax:** 6

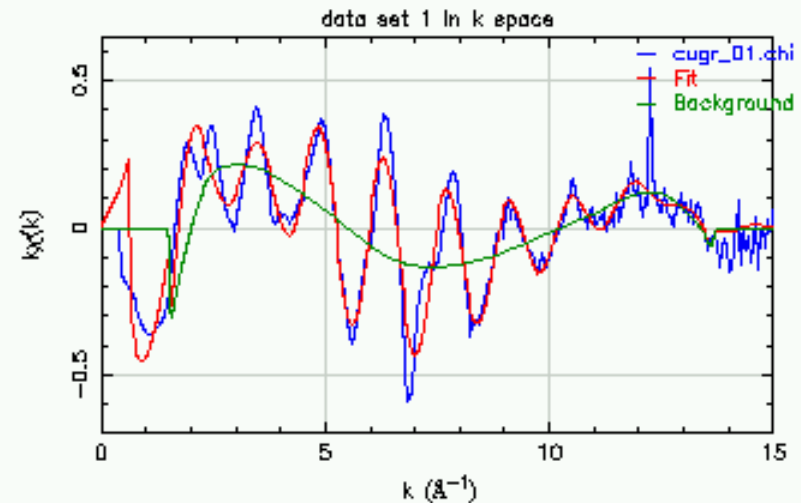
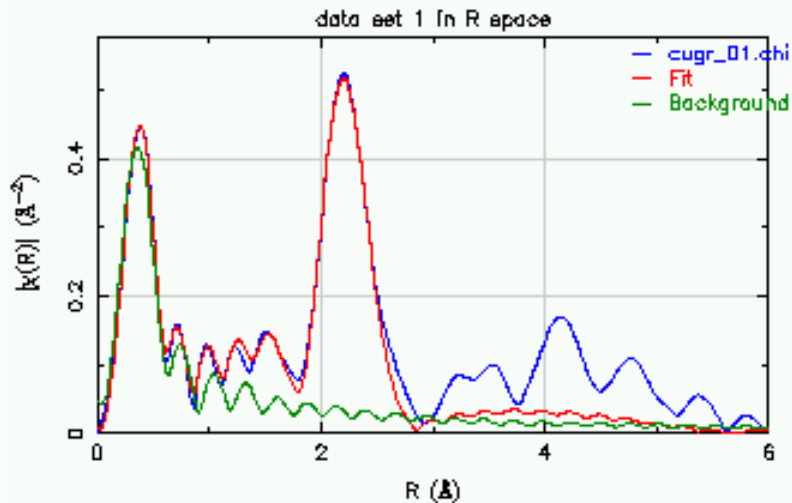
Cannot check memory with this version of Iffitit

# FT and Background function



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

# Fitting background and data using Artemis



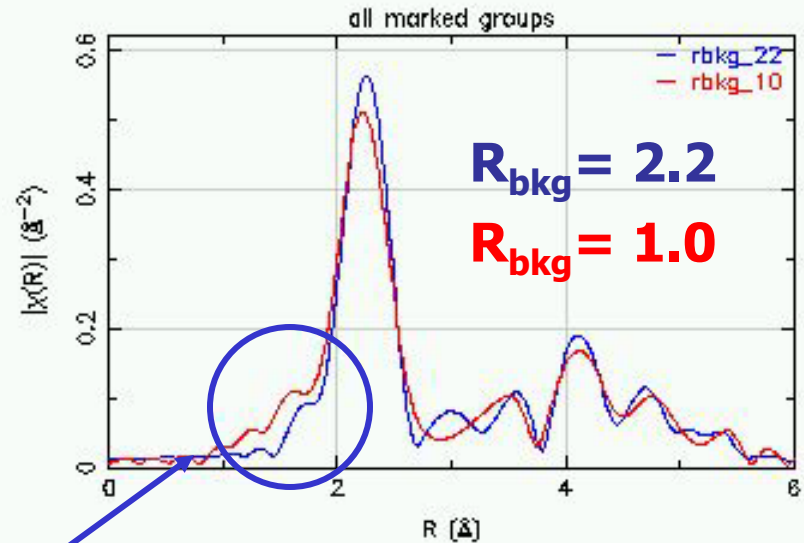
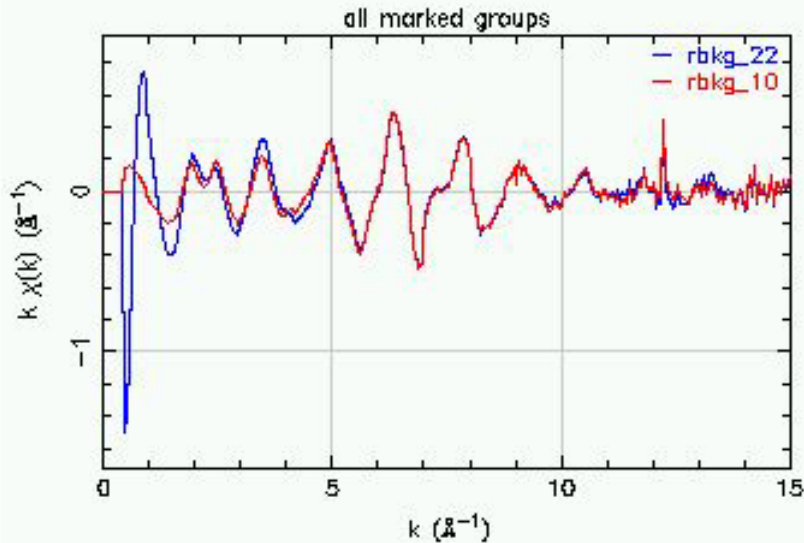
- Minimum distance between nodes and the number of knots are constrained by the data range and the value for Rbkg.
- Notice that not all the nodes (8) were needed to remove the background. Nodes are not constrained.
- Using the FT to frequency filter the data, means that IFEFFIT doesn't need your help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

# Artemis, Fitting the background

The screenshot shows the Artemis software interface. The main window is titled 'Artemis' and has a menu bar with 'File', 'Edit', 'GDS', 'Data', 'FEFF', 'Paths', 'Plot', 'Settings', and 'Help'. The 'Operational Parameters' panel is active, showing various settings for data fitting. A blue arrow points to the 'Fit background?' checkbox, which is circled in blue. Other settings include 'Data file' set to '/home/skelly/Xafs/Cu/CuGR/jan02/cugr\_01.chi', 'k-range' from 1.593 to 13.647, 'R-range' from 1.788 to 2.938, and 'k window' set to 'Kaiser-Bessel'. The 'Fit' panel on the right shows a tree view of the fit components, including 'cugr\_01.chi', 'Fit', 'Background', 'Residual', and 'FEFF0' (with sub-items 'feff0001.dat' and 'feff0002.dat'). The status bar at the bottom indicates 'Plotting in r space ... done!'.



# How to choose R<sub>bkg</sub> value

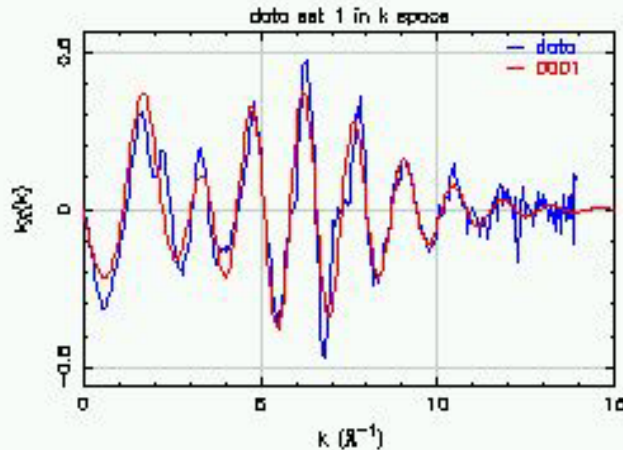


A Hint that  $R_{bkg}$  may be too large.  
Data should be smooth, not pinched!

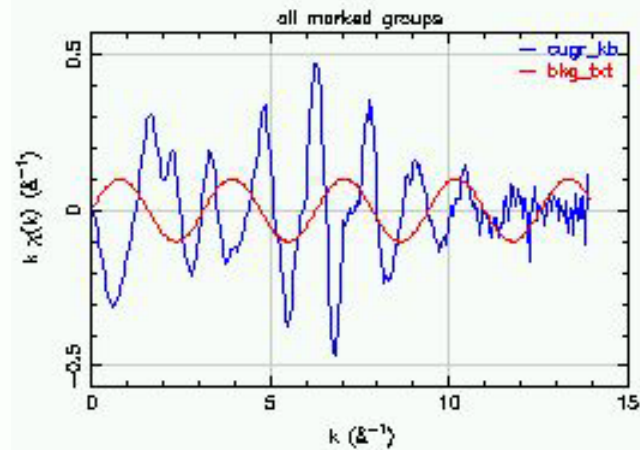
- An example where background distorts the first shell peak.
- $R_{bkg}$  should be about half the  $R$  value for the first peak.

# Frequency of Background function

Data contains this and shorter frequencies



Bkg contains this and longer frequencies

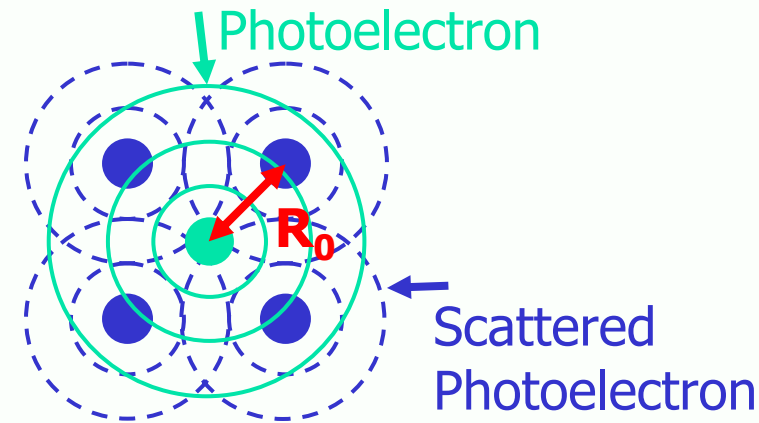


- Constrain background so that it cannot contain frequencies that are part of the data.
  - Use information theory, number of knots =  $2 R_{\text{bkg}} \Delta k / \pi$
  - 8 knots in bkg using  $R_{\text{bkg}}=1.0$  and  $\Delta k = 14.0$
- Background may contain only longer frequencies. Therefore knots are not constrained.

# The EXAFS Equation

$$\chi(k) = \sum_i \chi_i(k)$$

with



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

$$R_i = R_0 + \Delta R$$

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

Theoretically calculated values

- $F_i(k)$  effective scattering amplitude
- $\phi_i(k)$  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
- $\sigma_i^2$  mean squared displacement
- $E_0$  energy shift
- $\Delta R$  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

