

# Basics of EXAFS data analysis

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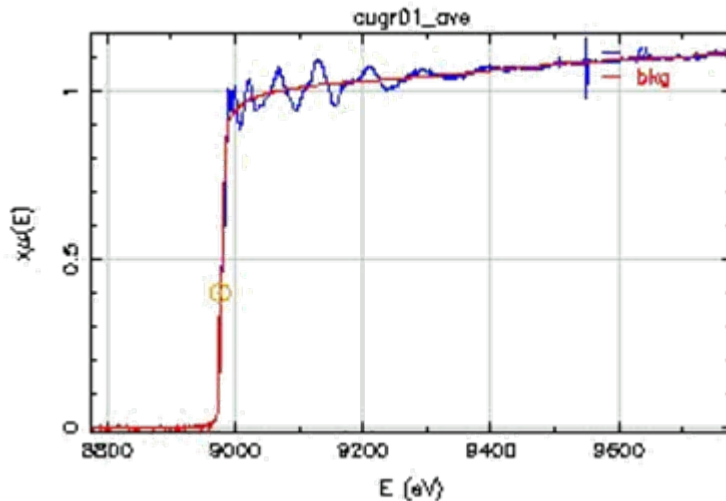
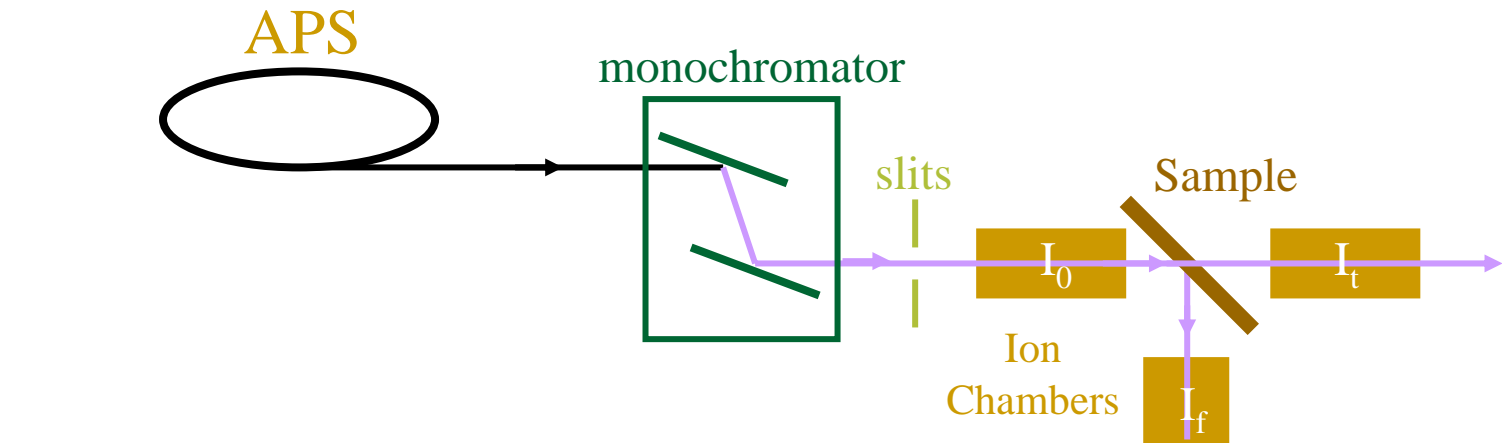
Shelly Kelly

Argonne National Laboratory, Argonne, IL

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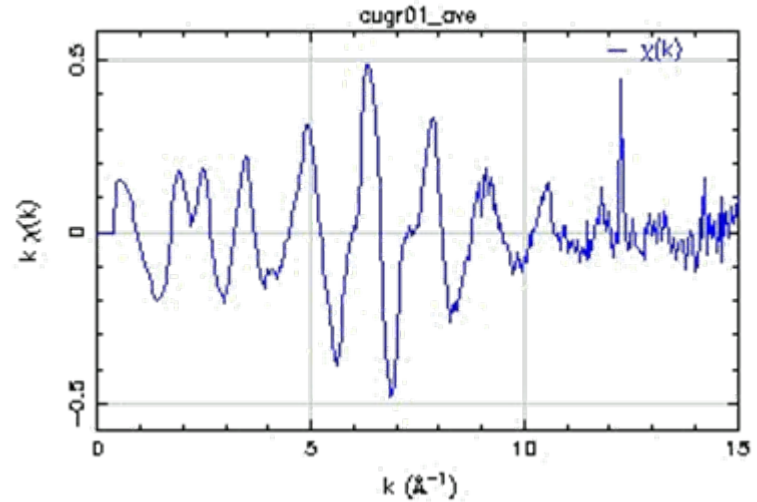
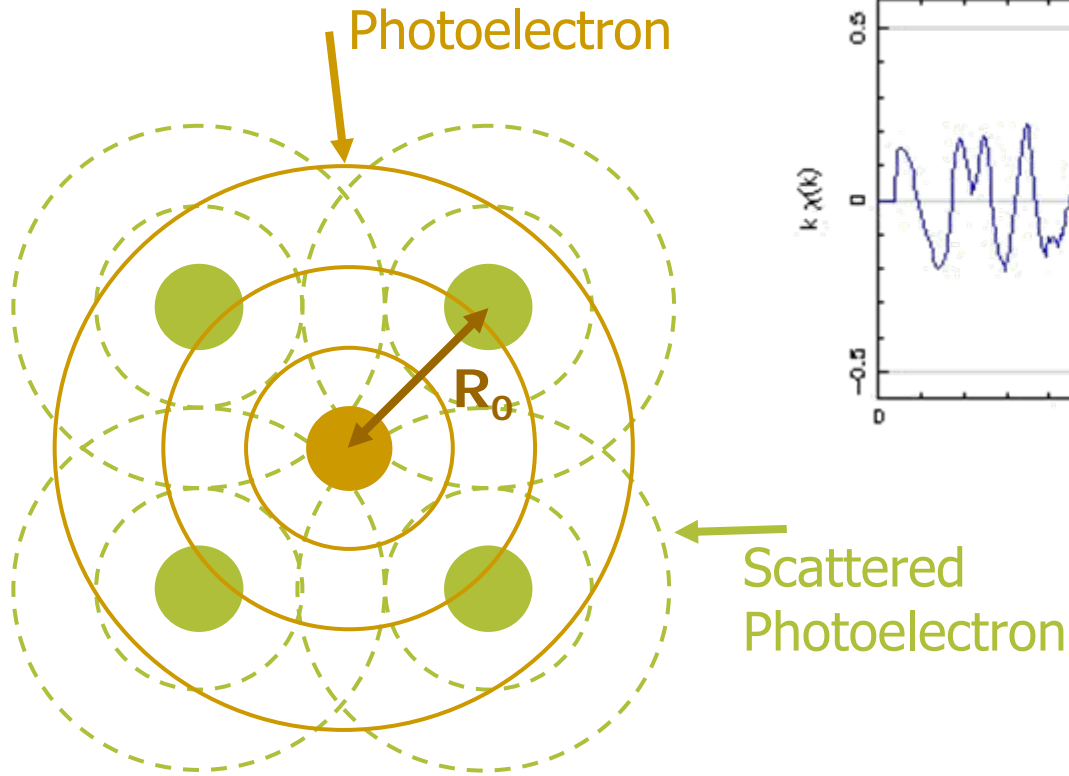


# X-ray-Absorption Fine Structure

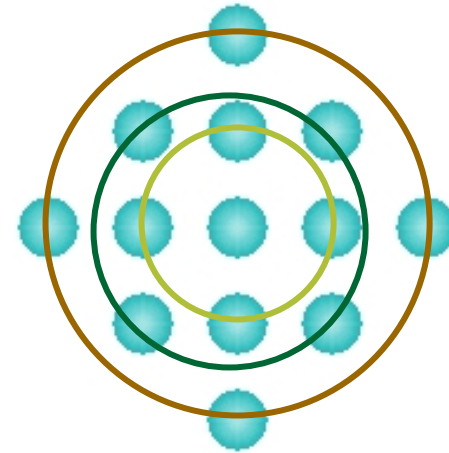
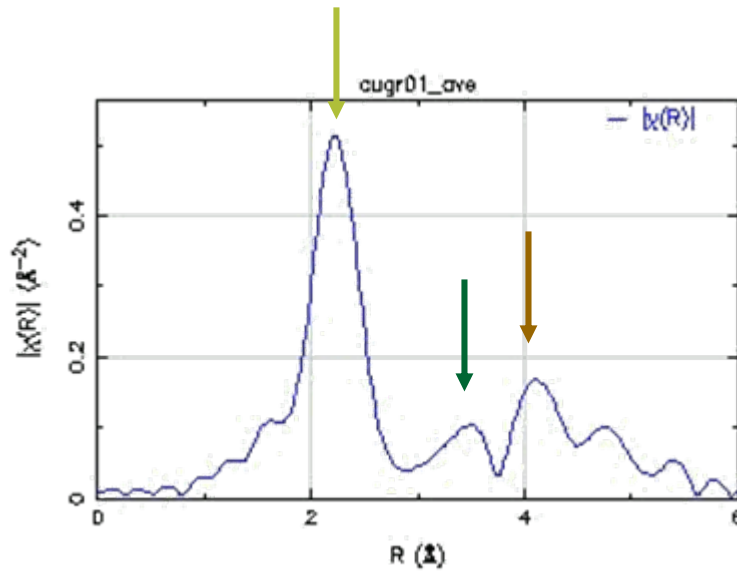


- Attenuation of x-rays
$$I_t = I_0 e^{-\mu(E) \cdot x}$$
- Absorption coefficient
$$\mu(E) \propto I_f / I_0$$

# X-ray-Absorption Fine Structure



# Fourier Transform of $\chi(k)$

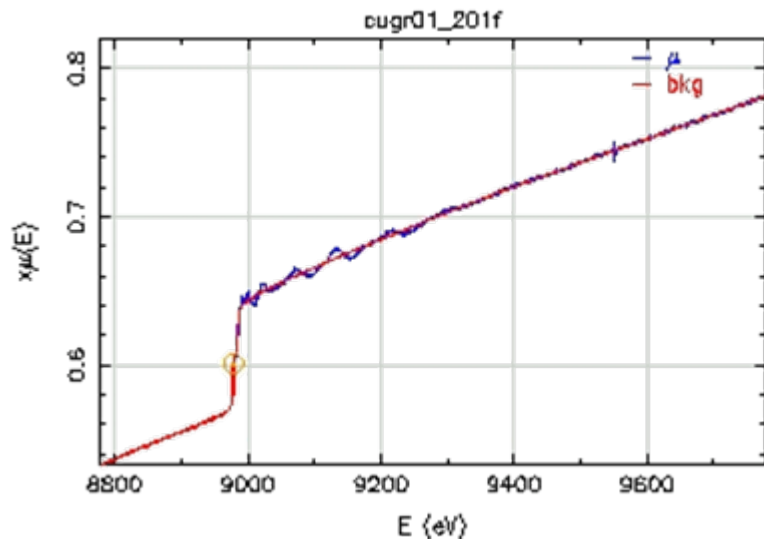


- **Similar to an atomic radial distribution function**
  - Distance
  - Number
  - Type
  - Structural disorder

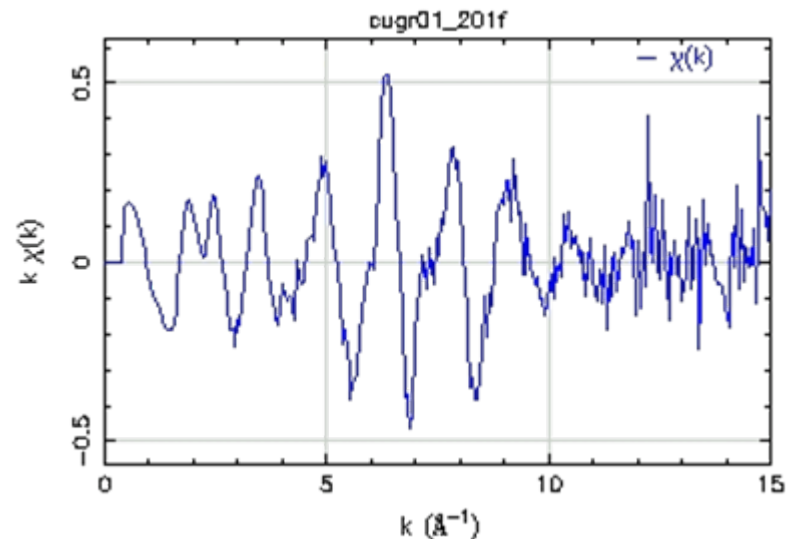
# Outline

- **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
- **IFEFFIT method for constructing the background function**
  - FT and background (bkg) function
  - Wavelength of bkg
  - Fitting the bkg
- **EXAFS Equation**

# Definition of EXAFS



⇒



Normalized oscillatory part of absorption coefficient

Measured Absorption coefficient

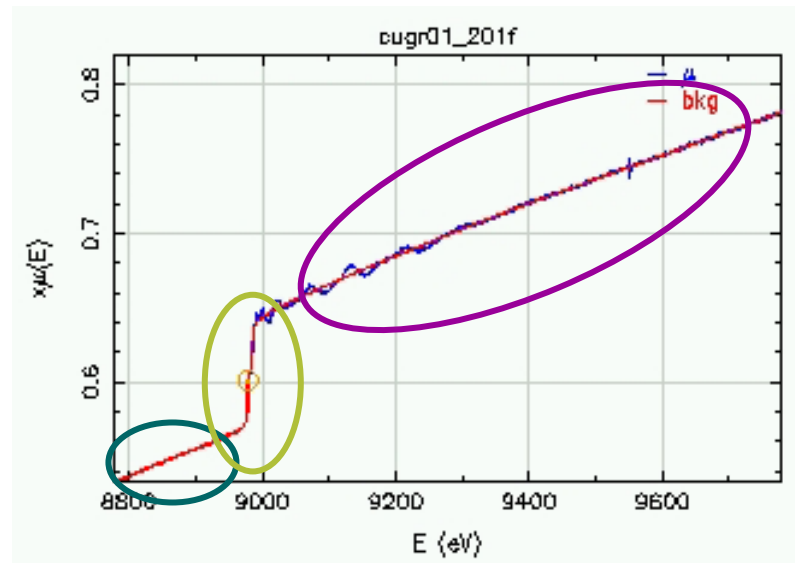
Bkg: Absorption coefficient without contribution from neighboring atoms (Calculated)

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

$$\sim \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}$$

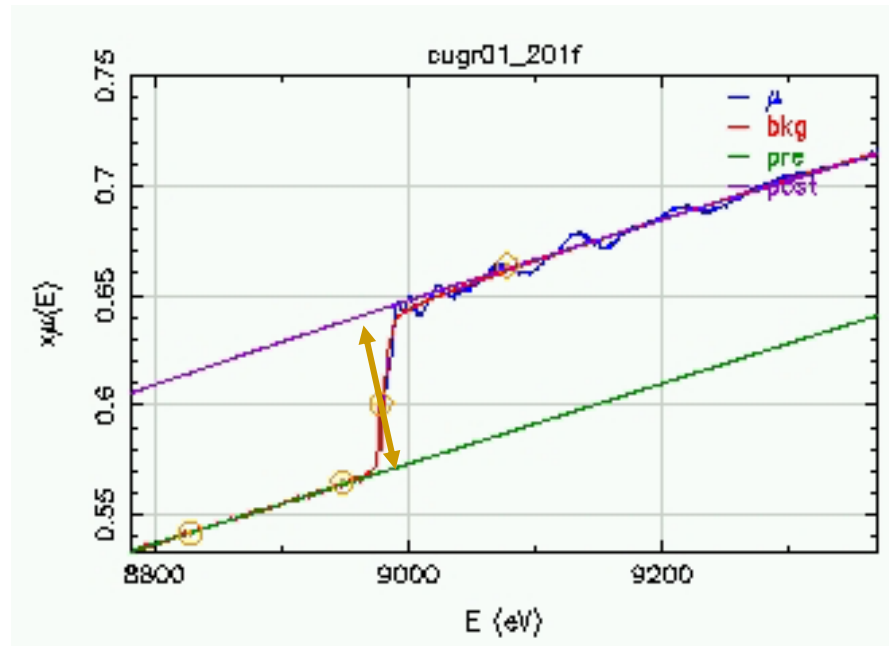
Evaluated at the Edge step ( $E_0$ )

# 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



- **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

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

dr: 0.5 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

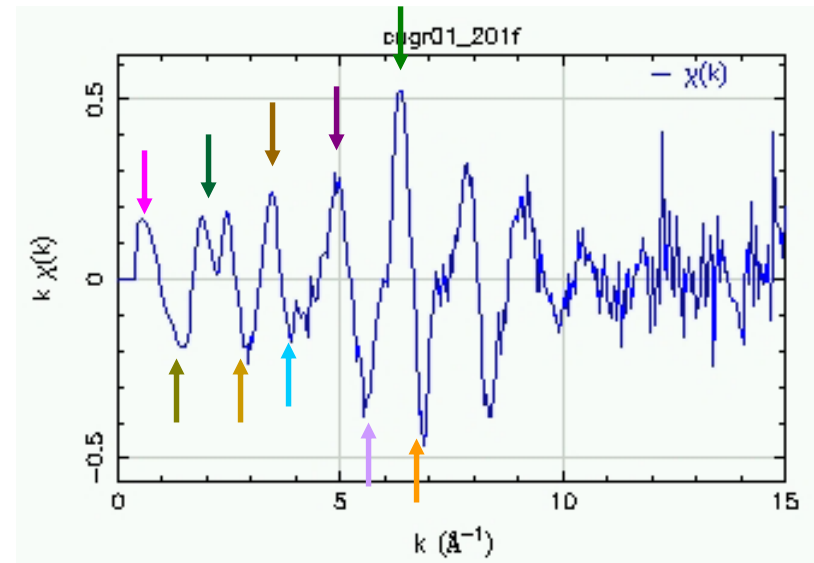
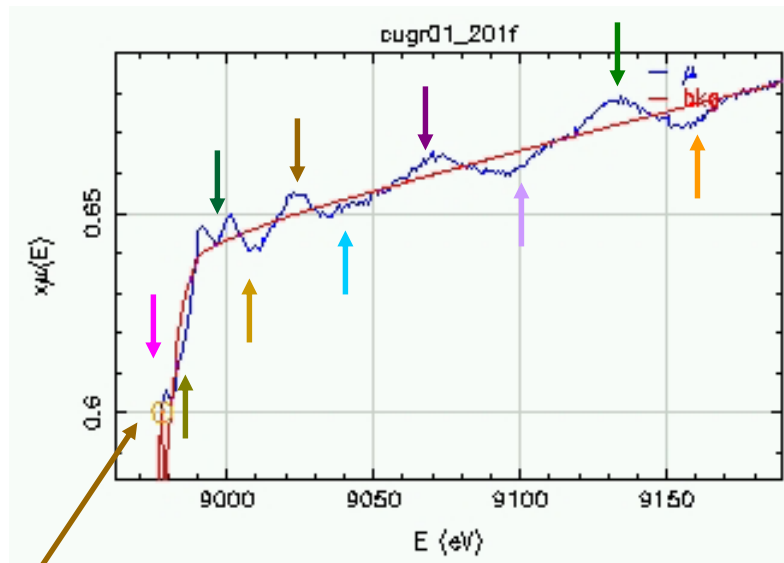
E k R q Help

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

Rmin: 0 Rmax: 6

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# Energy to wave number



$E_0$  Must be somewhere on the edge

$$k^2 = \frac{2 m_e (E - E_0)}{\hbar^2} \sim \frac{\Delta E}{3.81}$$

Mass of the electron  $m_e$  points to the coefficient 2 in the numerator.  
Edge Energy  $E_0$  points to the  $E_0$  term in the numerator.  
 $\hbar$  points to the denominator  $\hbar^2$ .  
Plank's constant  $\hbar$  points to the denominator  $\hbar^2$ .

# 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  Rokg: 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

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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**

- 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**

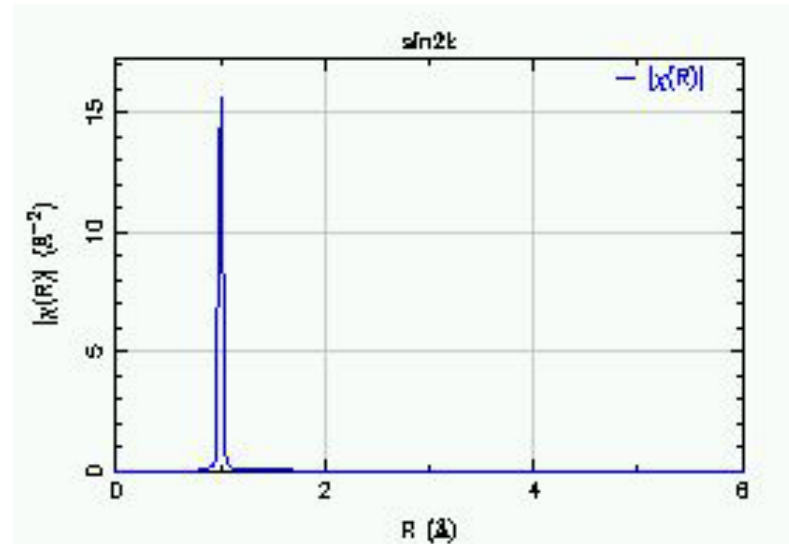
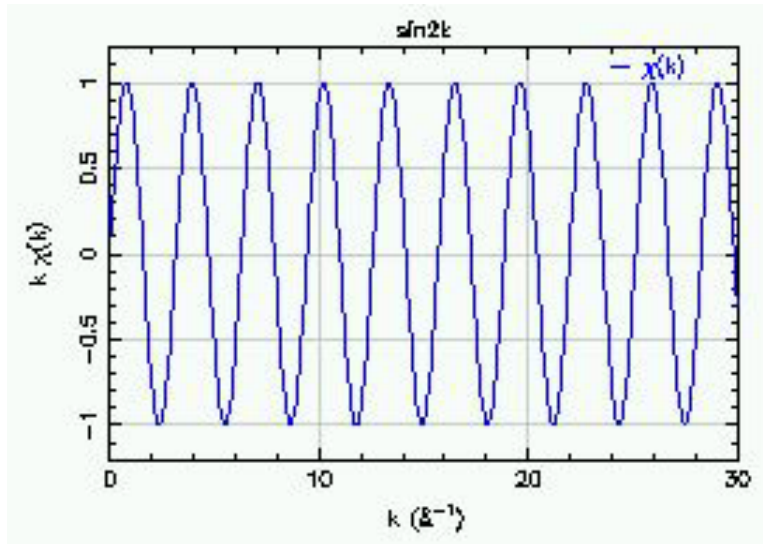
E k R q Help

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

Rmin: 0 Rmax: 6

Cannot check memory with this version of lfeffit

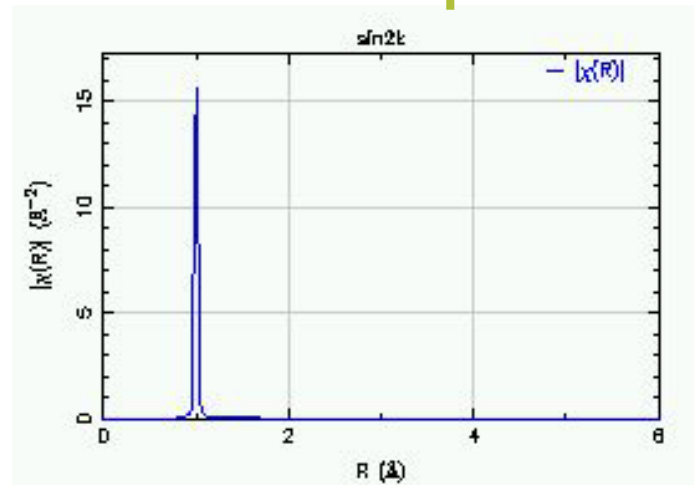
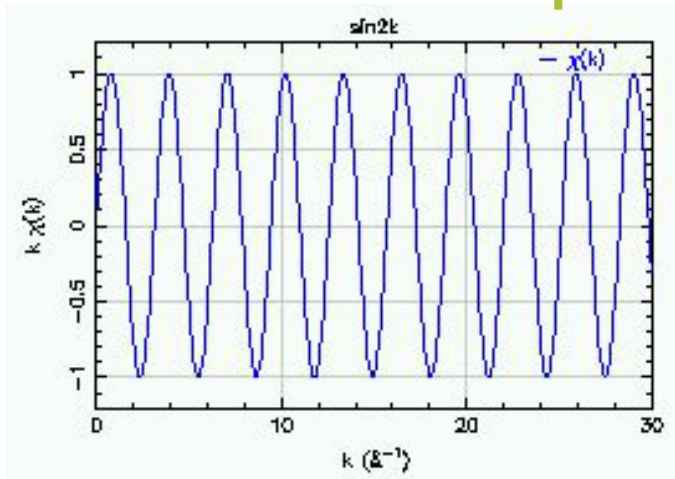
# Fourier Transform is a frequency filter



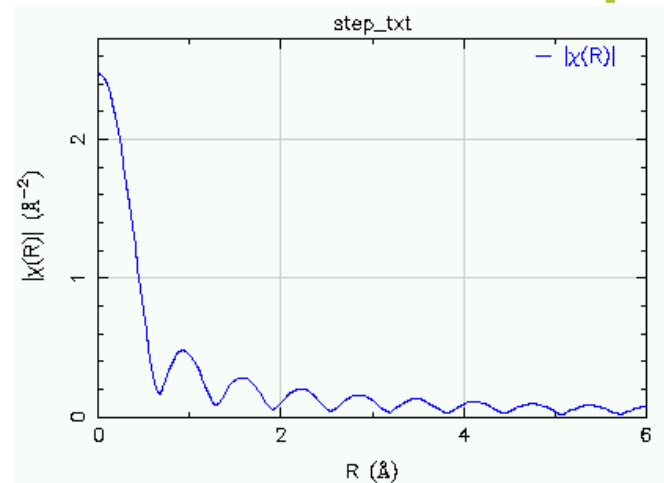
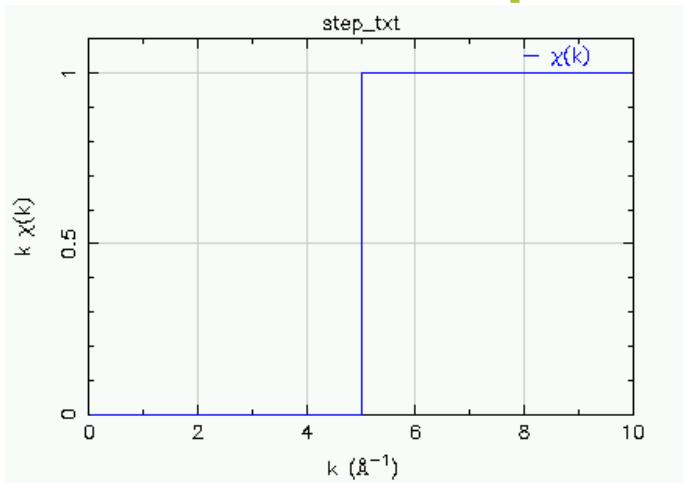
- FT of  $\text{Sin}(2Rk)$  is a peak at  $R=1$
- FT of infinite sine wave is a delta function
- Signal that is de-localized in  $k$ -space is localized in  $R$ -space
- FT is a frequency filter

# Fourier Transform of a function that is:

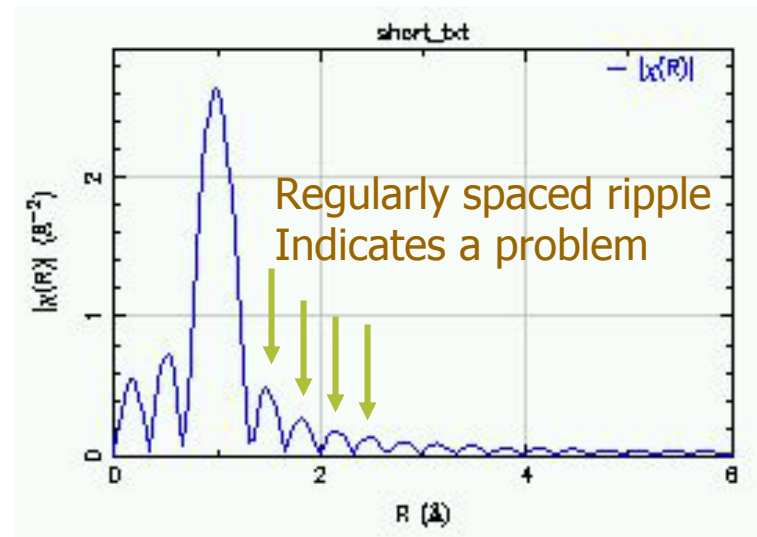
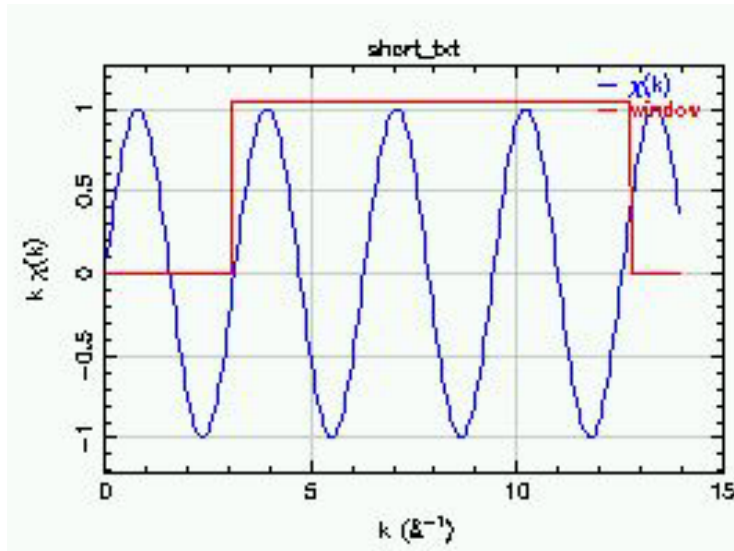
De-localized in  $k$ -space  $\Rightarrow$  localized in  $R$ -space



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

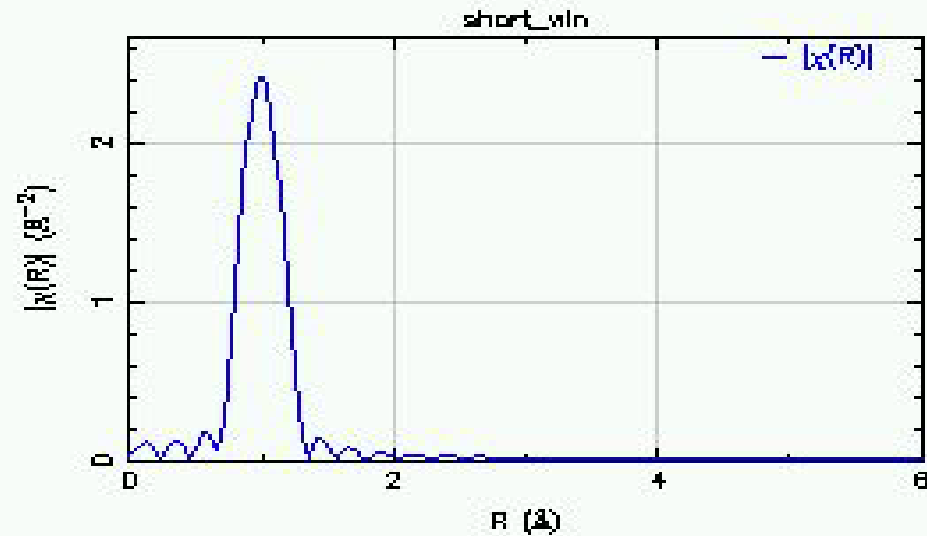
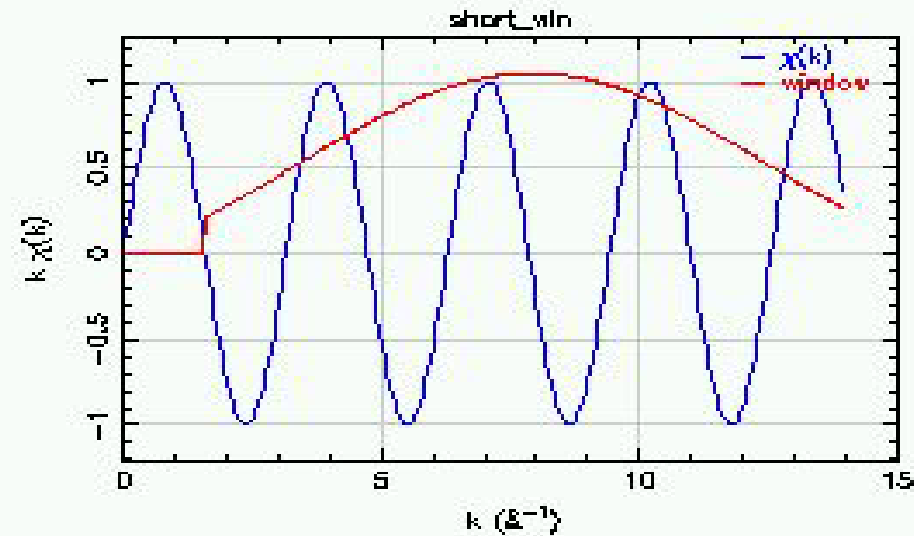


# Fourier Transform is a frequency filter



- 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



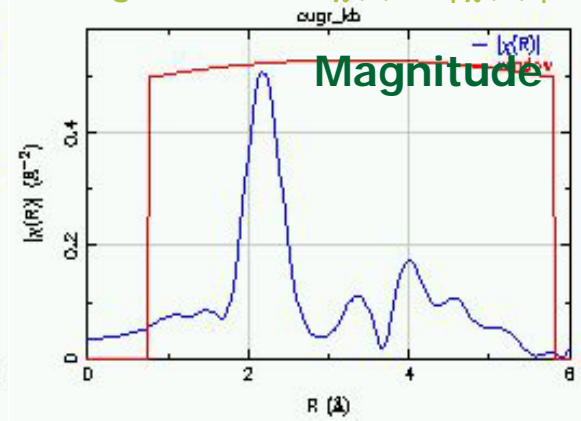
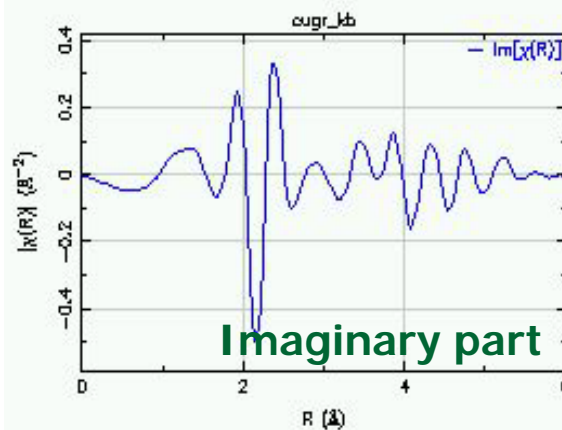
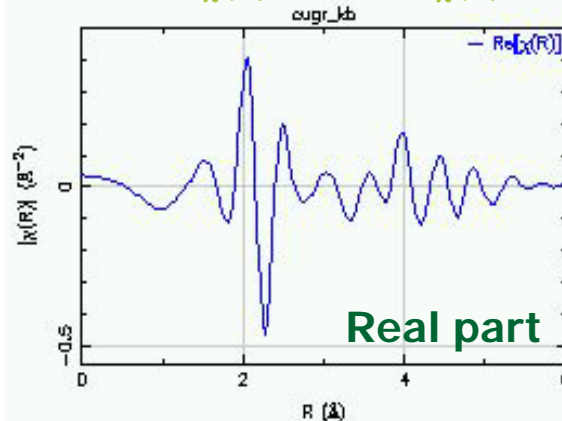
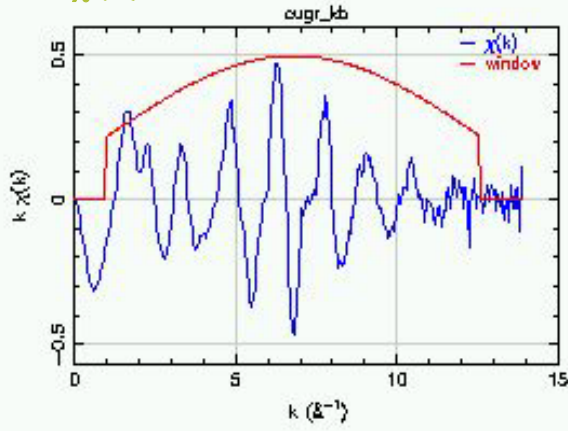
- Multiplying the discrete sine wave by a window that gradually increases the amplitude of the data smoothes the FT of the data.

# Fourier Transform parts

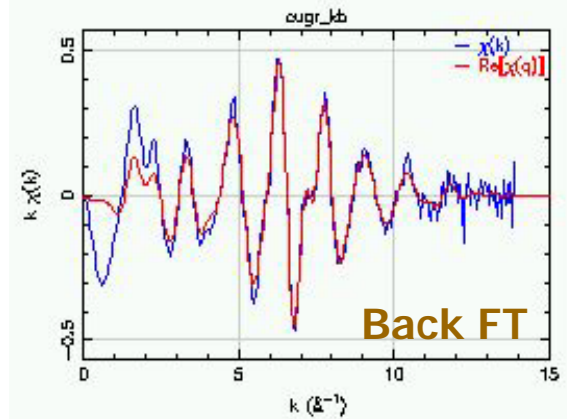
Real and imaginary parts of FT  $\chi(k)$   
 =  $\text{Re}[\chi(R)]$  and  $\text{Im}[\chi(R)]$

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

$\chi(k)$  data and FT window



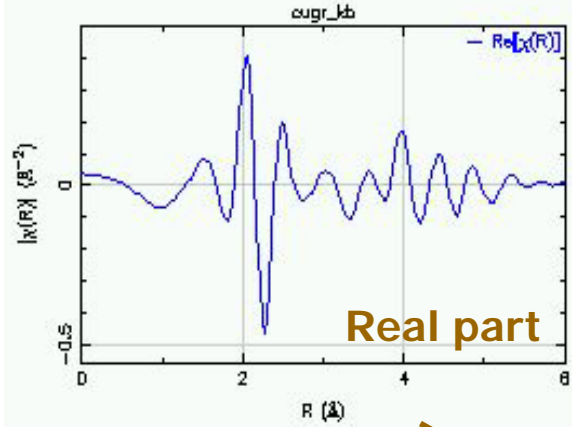
back FT of  $\chi(R) = \chi(q)$



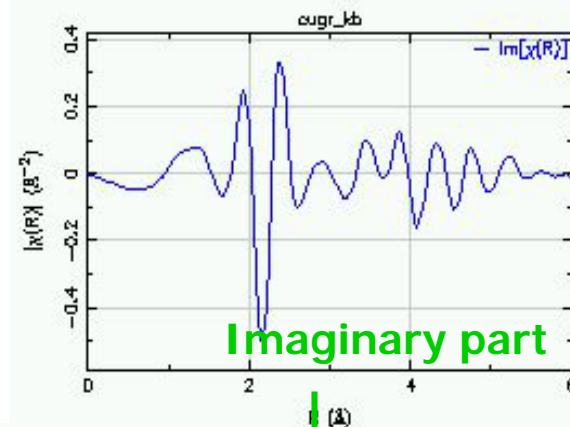


# Understanding the different parts of FT

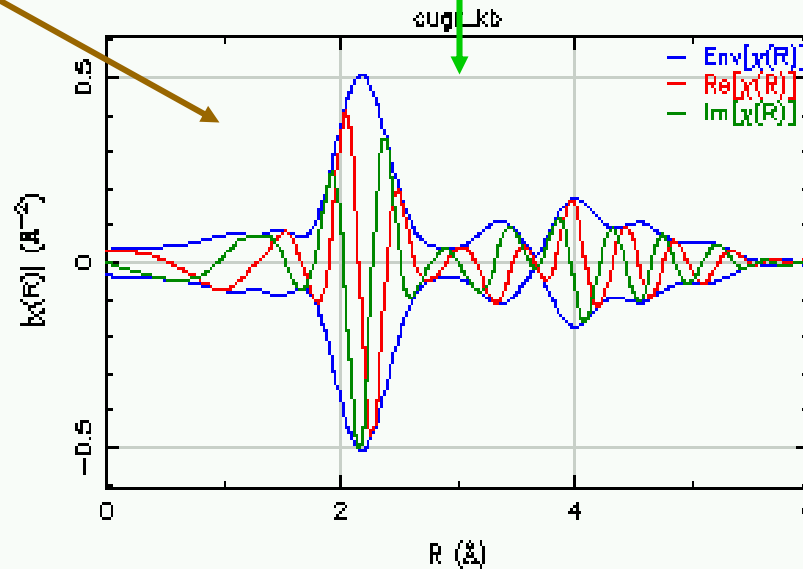
Real part of FT  $\chi(k) = \text{Re} [\chi(R)]$



Imaginary part of FT  $\chi(k) = \text{Im} [\chi(R)]$



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



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

# Athena plotting in R-space

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

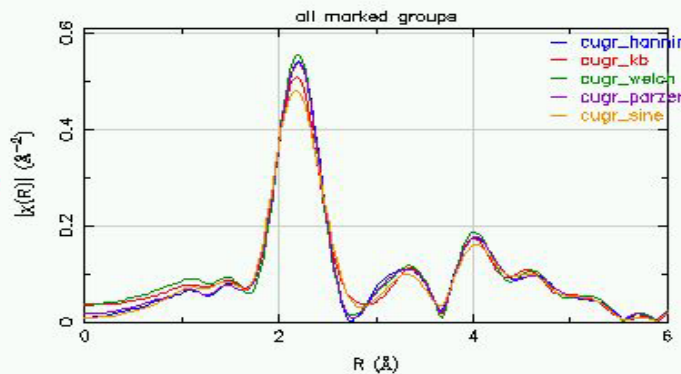
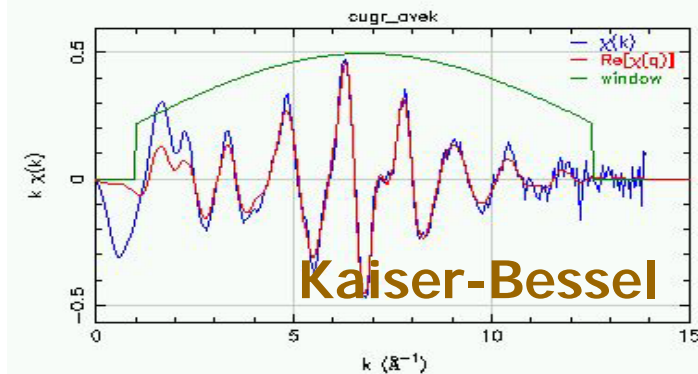
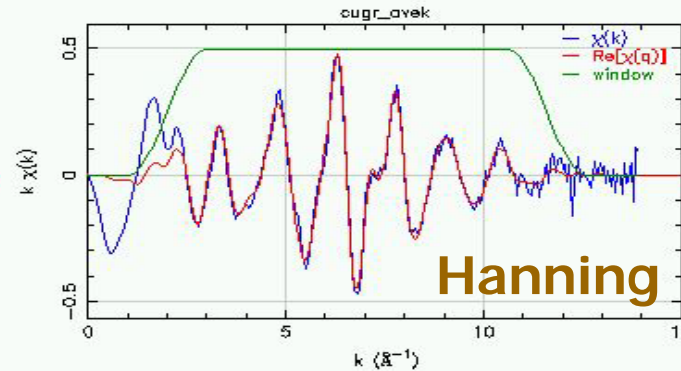
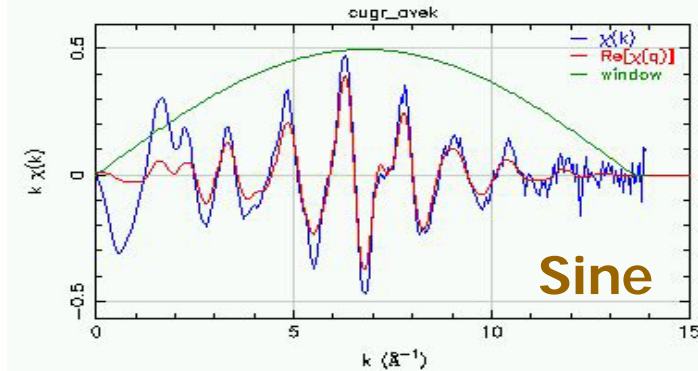
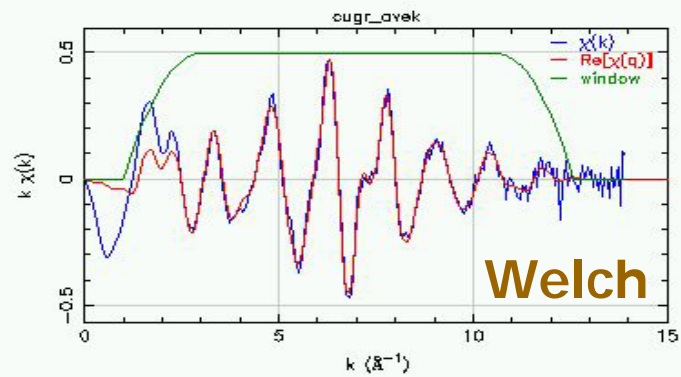
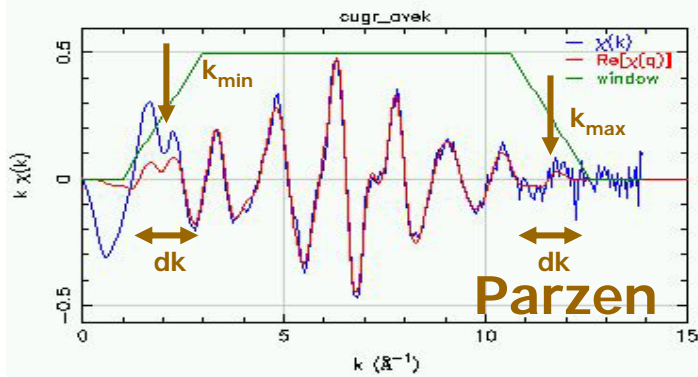
- Current Group:** `cugr01_ave`  
File: `/home/skelly/Xafs/Cu/CuGR/jan02/cugr01_merge_nor.nor`
- Background removal**
  - E0: `8976.236` Rbkg: `1`
  - Standard: `None` Background: `Autobk` Z: `H`
  - k-weight: `1` E0 shift: `0` Edge step: `0.9912`  fix step
  - Pre-edge range: `-150` to `-30`
  - Normalization 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**
  - dr: `0.5` window type: `kaiser-bessel`
  - R-range: `1` to `3`
- Plotting parameters**
  - plot multiplier: `1` y-axis offset: `0`

**Right Panel:**

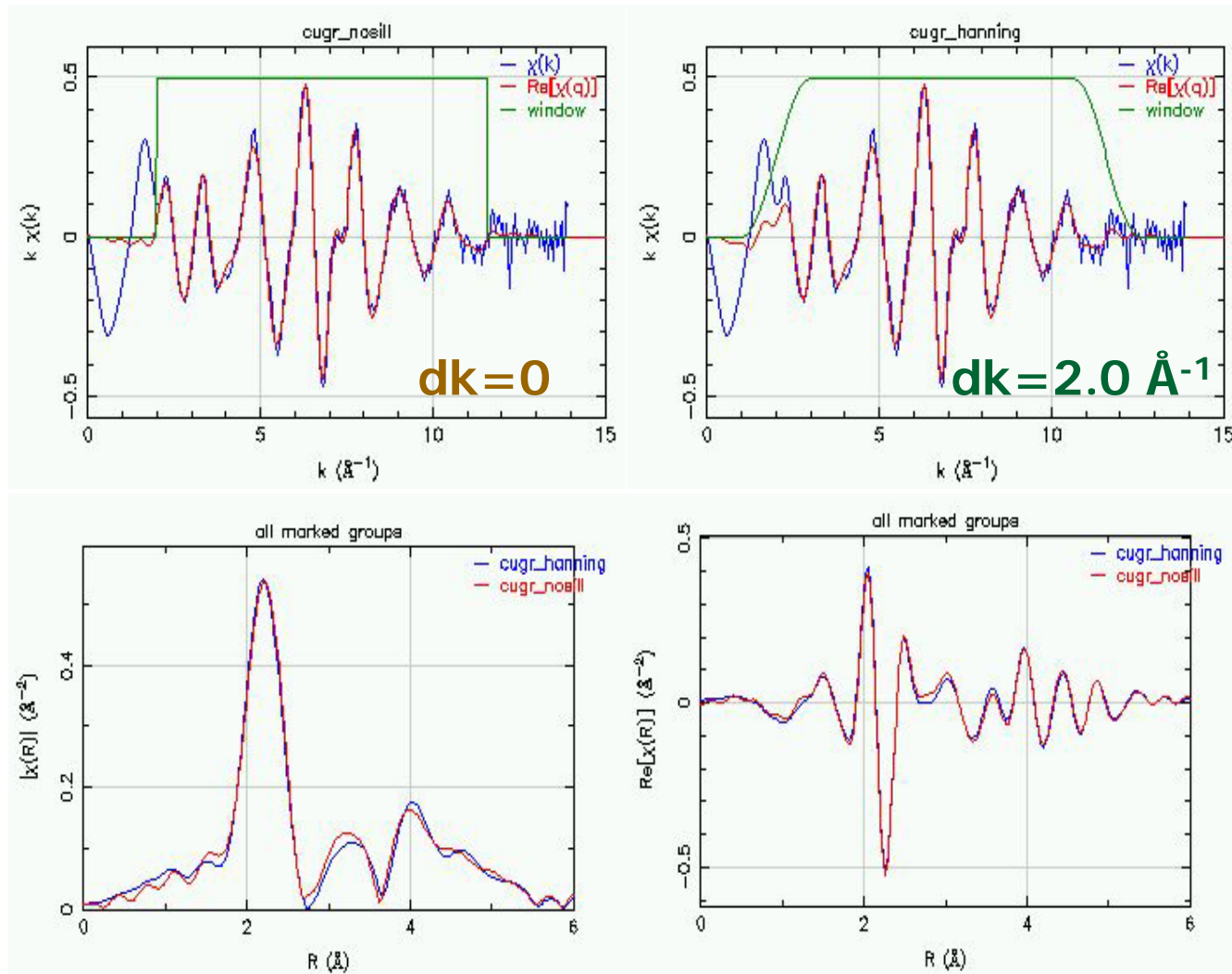
- Data groups:** A list of groups including `cugr_kb`, `cugr_welch`, `cugr_parzen`, `cugr_sine`, `cugr_nosill`, `cugr_01`, `cugr_05`, `cugr_10`, `cugr_15`, and `cugr01_ave` (highlighted).
- Plot current group in:** Buttons for `E`, `k`, `R`, `q`, and `kq`. The `R` button is circled in orange.
- Plot marked group in:** Buttons for `E`, `k`, `R`, and `q`.
- Plotting options:** Buttons for `E`, `k`, `R`, `q`, and `Help`. The `R` button is circled in orange.
  - Magnitude
  - Envelope
  - Real part
  - Imaginary part
  - Phase
  - Window
  - Rmin: `0` Rmax: `6`

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# Fourier Transform Windows



# Fourier Transform window sill



- A small sill can distort FT

# Fourier transform parameters in Athena

The screenshot displays the Athena software interface with the following sections and parameters:

- 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** (circled in orange)
  - k-weight: `1` dk: `2` window type: `kaiser-bessel`
  - k-range: `2` to `11.642` (circled in orange)
  - Phase correction:  off Z: `H` Edge: `K`
- Backward Fourier transform** (circled in orange)
  - dk: `0.5` window type: `kaiser-bessel`
  - R-range: `1` to `5`
- Plotting parameters**
  - plot multiplier: `1` y-axis offset: `0`

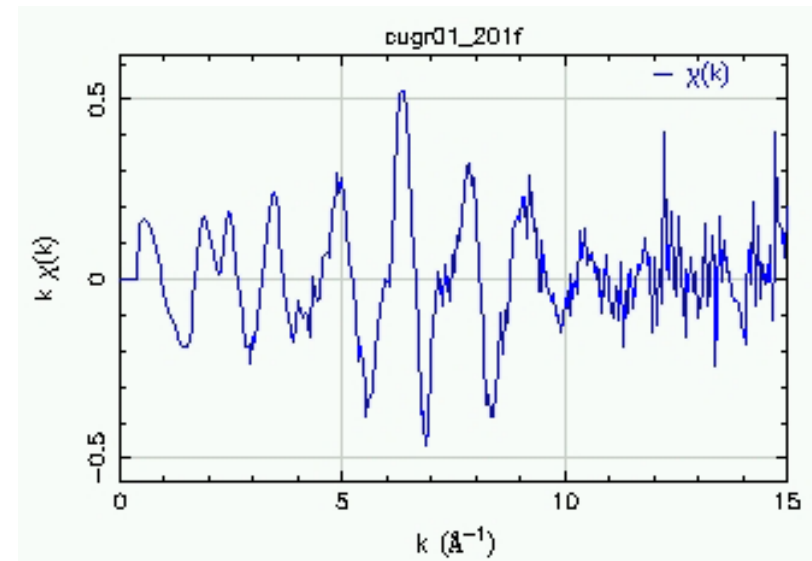
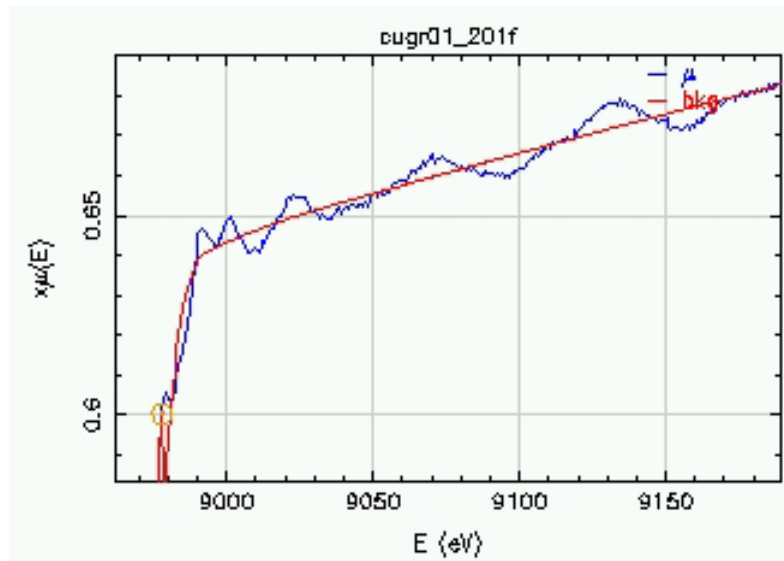
On the right side, there are three panels:

- Data groups:** A list of groups including `cugr_kb`, `cugr_welch`, `cugr_parzen`, `cugr_sine`, `cugr_nosill`, `cugr_01`, `cugr_05`, `cugr_10`, `cugr_15`, and `cugr01_ave` (highlighted).
- Plot current group in:** Buttons for `E`, `k`, `R`, `q`, and `kq`.
- Plot marked group in:** Buttons for `E`, `k`, `R`, and `q`.
- Plotting options:** Checkboxes for `Magnitude` (checked), `Envelope`, `Real part`, `Imaginary part`, `Phase`, and `Window`. Below are `Rmin: 0` and `Rmax: 6`.

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

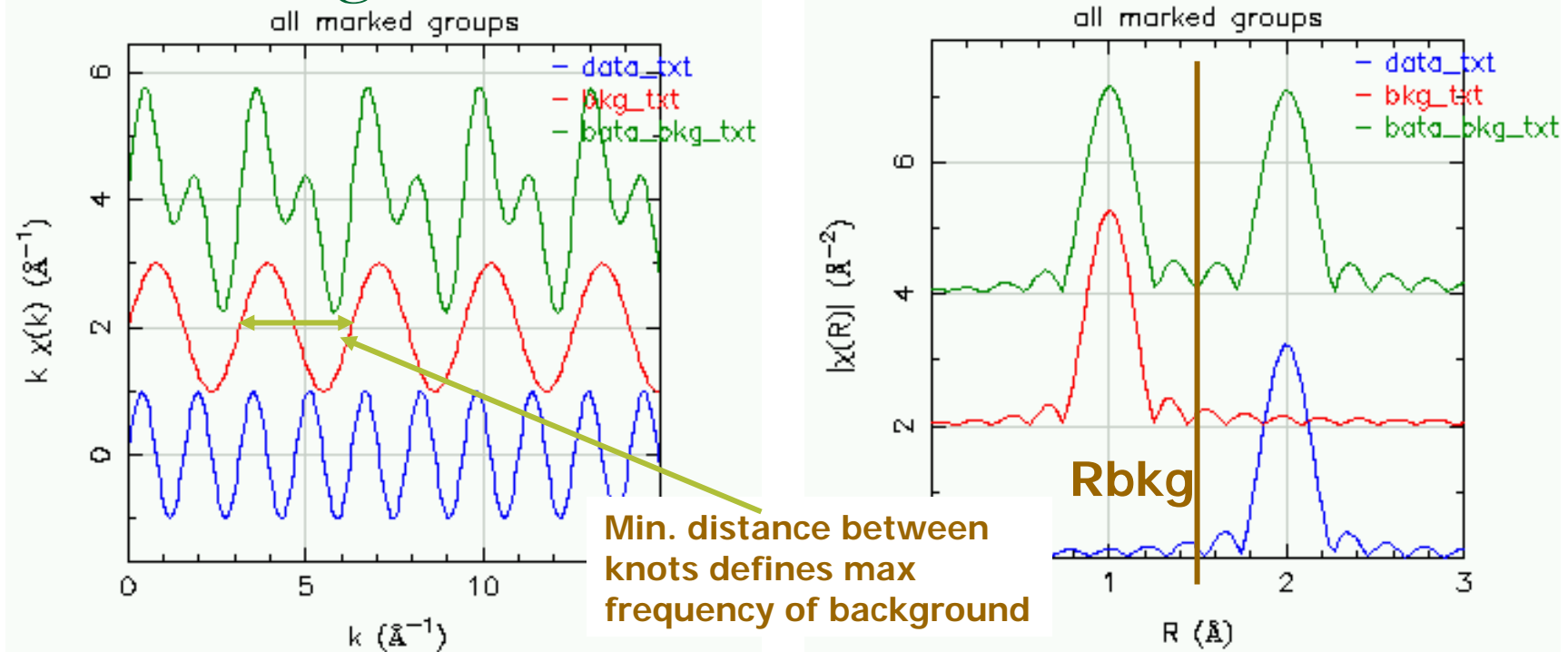


# Background function overview



- 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 up of knots connected by 3<sup>rd</sup> order splines.
- Distance between knots is limited restricting background from containing frequencies that are part of the data.
- The number of knots are calculated from the value for Rbkg and the data range in k-space.

# 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 orange)
  - 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:**

- `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:**

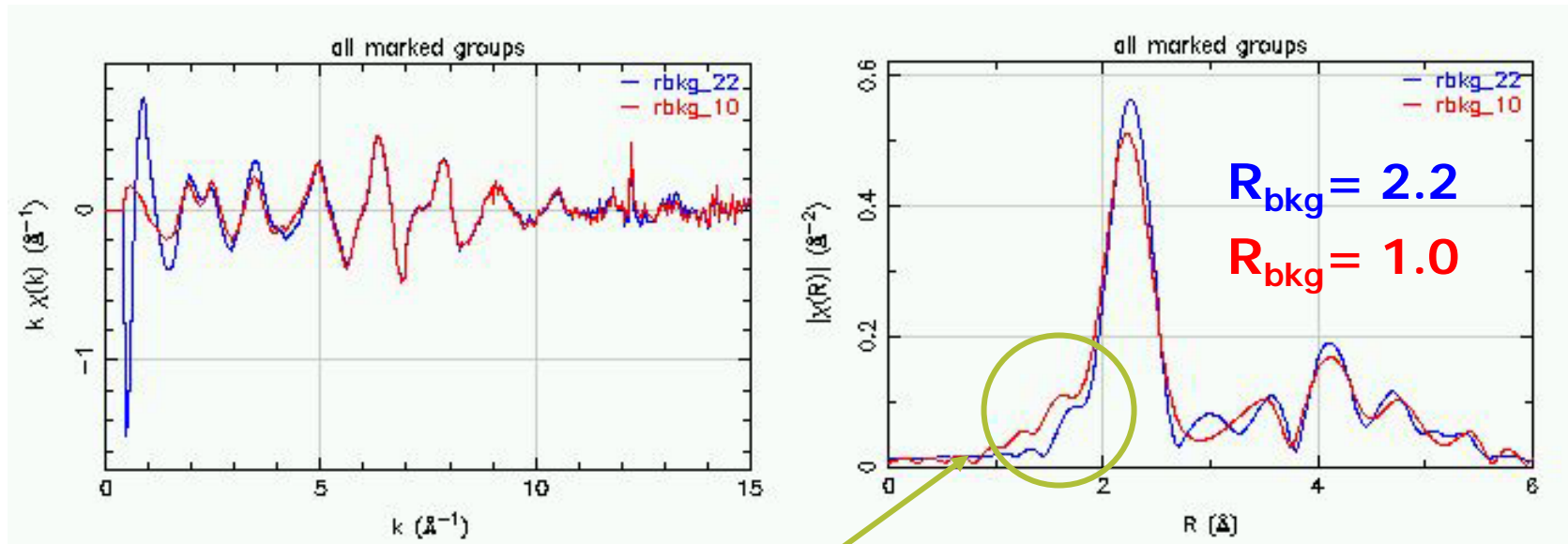
- Magnitude**
- Envelope**
- Real part**
- Imaginary part**
- Phase**
- Window**

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

Cannot check memory with this version of lfeffit



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

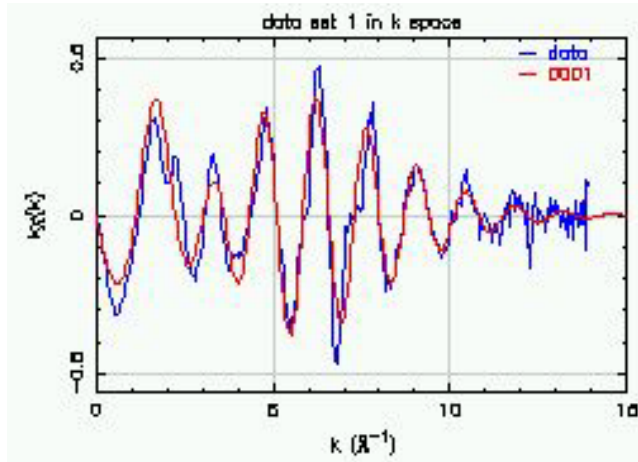


A Hint that R<sub>bkg</sub> may be too large.  
Data should be smooth, not pinched!

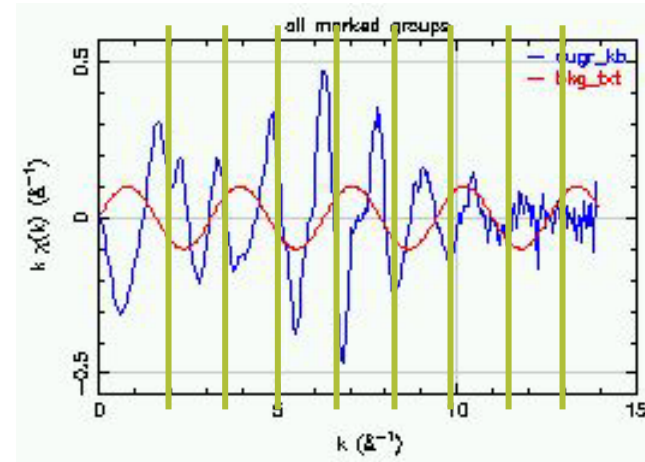
- An example where background distorts the first shell peak.
- $R_{bkg}$  should be about half the R value for the first peak.

# Frequency of Background function

Data contains this and shorter frequencies

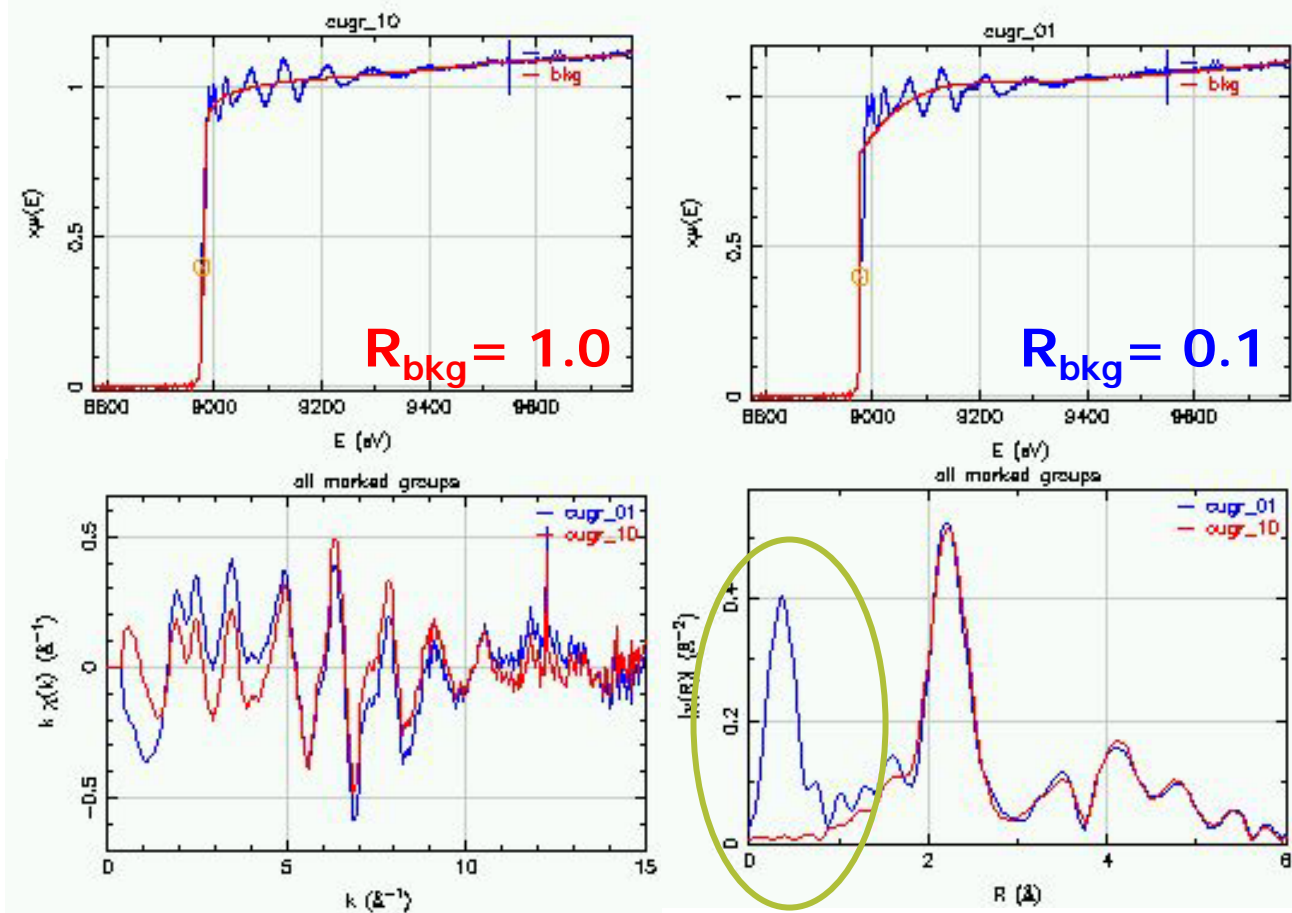


Bkg contains this and longer frequencies



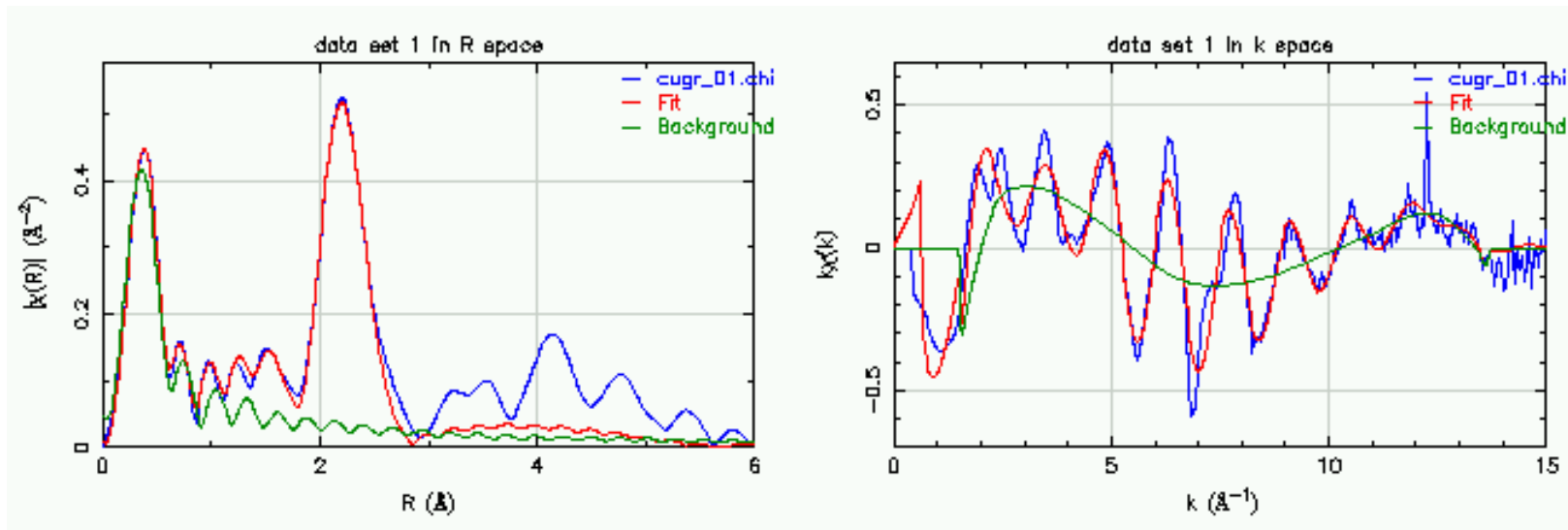
- Constrain background so that it cannot contain frequencies that are part of the data.
  - Use information theory, number of knots =  $2 R_{\text{bkg}} \Delta k / \pi$
  - 8 knots in bkg using  $R_{\text{bkg}}=1.0$  and  $\Delta k = 14.0$
- Background may contain only longer frequencies. Therefore knots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

# 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 knots and the number of knots are constrained by the data range and the value for  $R_{bkg}$ .
- Notice that not all the knots (8) were needed to remove the background. Knots are not constrained.
- Using the FT to frequency filter the data, means that IFEFFIT doesn't need your help to place the knots.

# Artemis, Fitting the background

The screenshot shows the Artemis software interface with the following components:

- Menu Bar:** File, Edit, GDS, Data, Sum, Fits, Theory, Paths, Plot, Settings, Help.
- Current project:** C:/Documents and Settings/skelly/My Documents/XAFS/background\_tutorial/Mo03-final.apj
- Data & Paths Panel:** Lists data files under 'FEFF0', including feff0001.dat through feff0007.dat.
- Fit Panel:** Contains a 'Fit' button, tabs for 'k', 'R', and 'q', and 'Plotting options' for 'Plot in R' and 'Plot in q'.
- Fit Parameters Panel:** Includes 'Fourier and fit parameters' (k-range, R-range, dk, dr, k window, R window) and 'Fit k-weights' (kw=1, kw=2, kw=3, other k weight).
- Other parameters:** Fitting space (R), Epsilon (0), Minimum reported correlation (0.25), Path to use for phase corrections (None).
- Document: Fitting parameters:** A summary of the current fit parameters.
- Document: Plotting:** A summary of the current plotting options.

An arrow points to the 'Fit background' checkbox, which is checked. The 'Fit background' checkbox is highlighted with a yellow circle.

Read project description 'C:\Program Files\lfeffit\horae\stash\artemis.project.1\descriptions\artemis'



# The EXAFS Equation

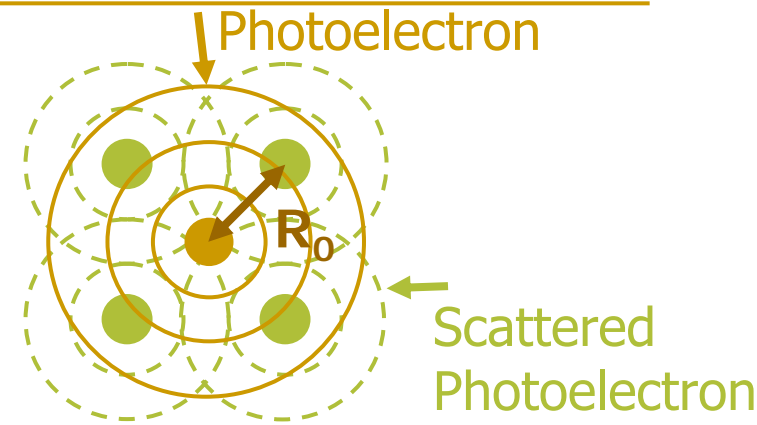
$$\chi(k) = \sum_i \chi_i(k)$$

with

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

$$R_i = R_0 + \Delta R$$

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



Theoretically calculated values

- $F_i(k)$  effective scattering amplitude
- $\varphi_i(k)$  effective scattering phase shift
- $\lambda(k)$  mean free path

Starting values

- $R_0$  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