

# Basics of EXAFS data analysis

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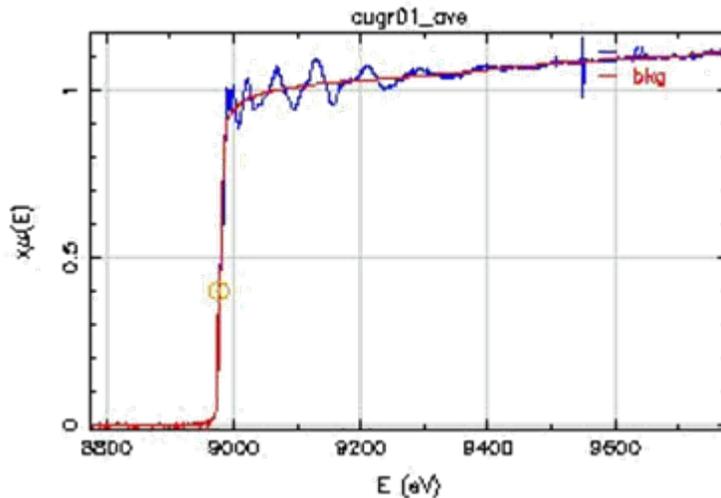
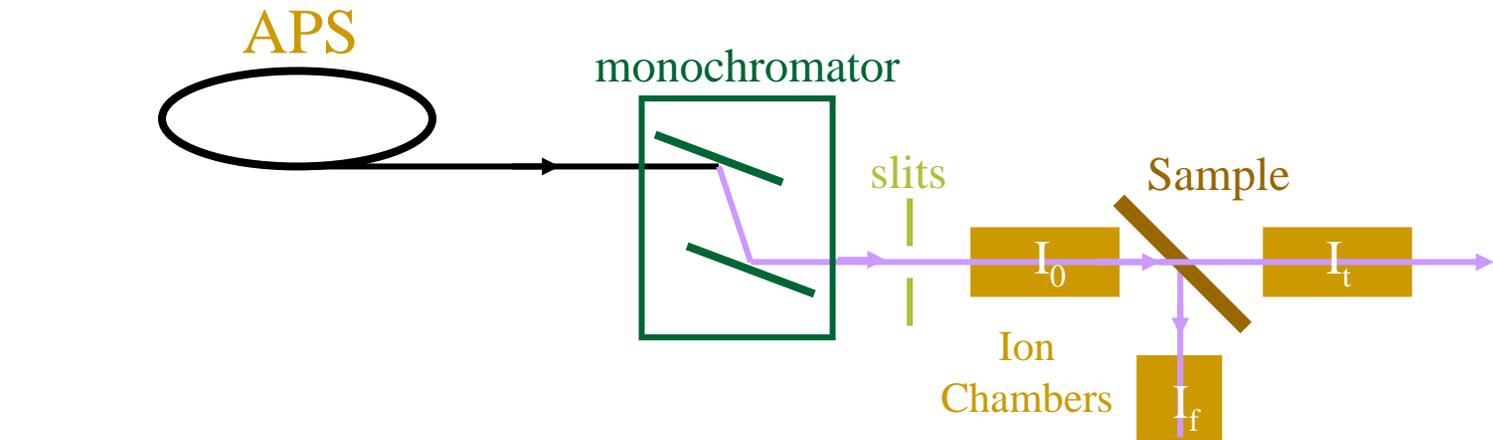
Shelly Kelly

Argonne National Laboratory, Argonne, IL

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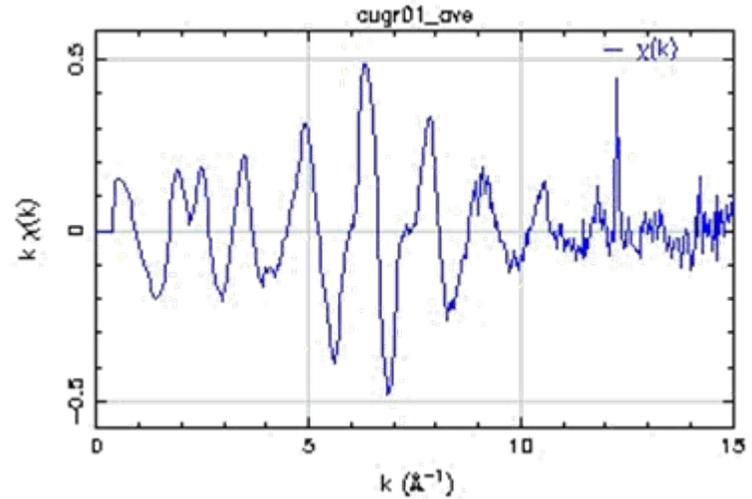
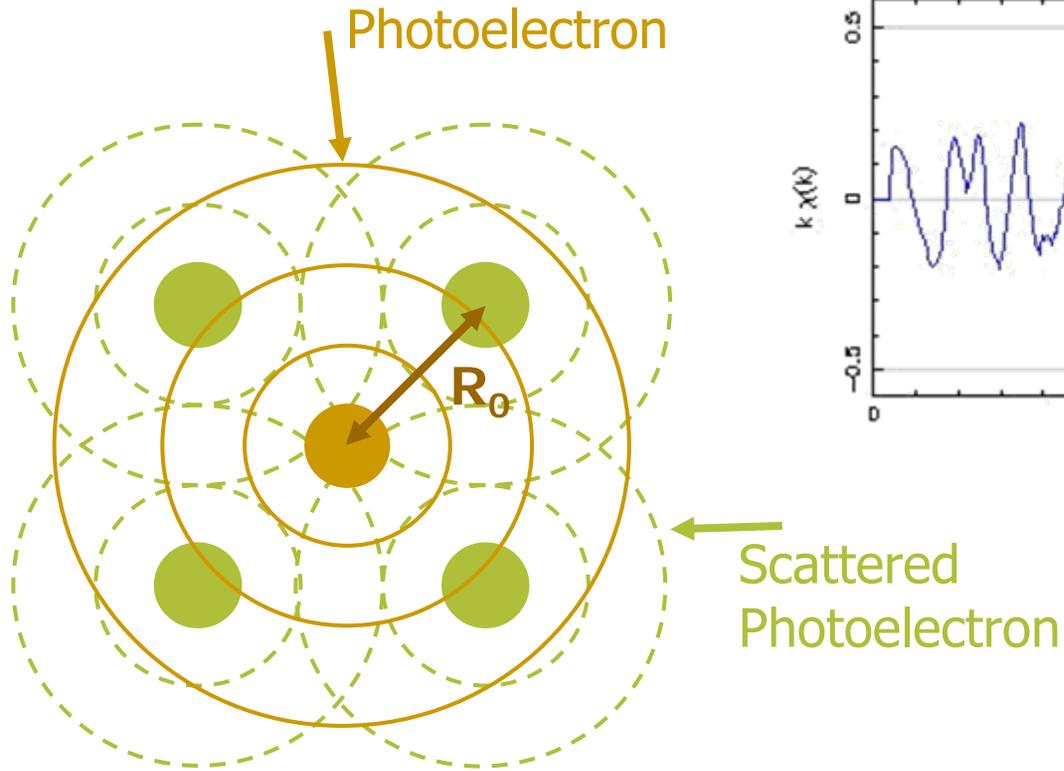


# X-ray-Absorption Fine Structure

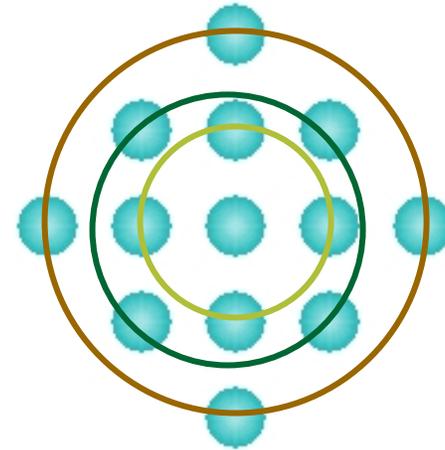
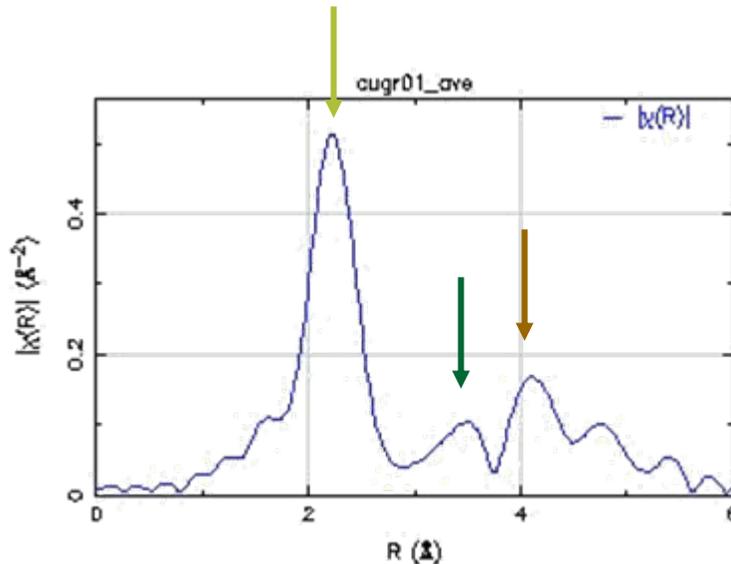


- Attenuation of x-rays
$$I_t = I_0 e^{-\mu(E) \cdot x}$$
- Absorption coefficient
$$\mu(E) \propto I_f / I_0$$

# X-ray-Absorption Fine Structure



# Fourier Transform of $\chi(k)$

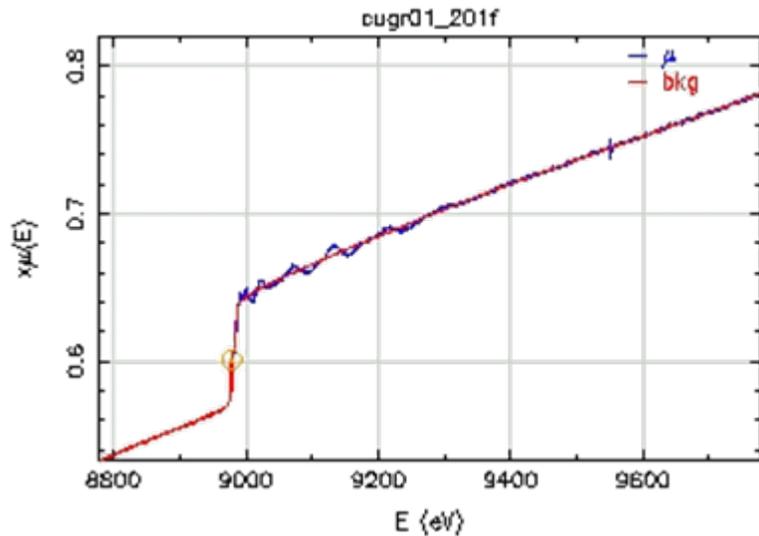


- **Similar to an atomic radial distribution function**
  - Distance
  - Number
  - Type
  - Structural disorder

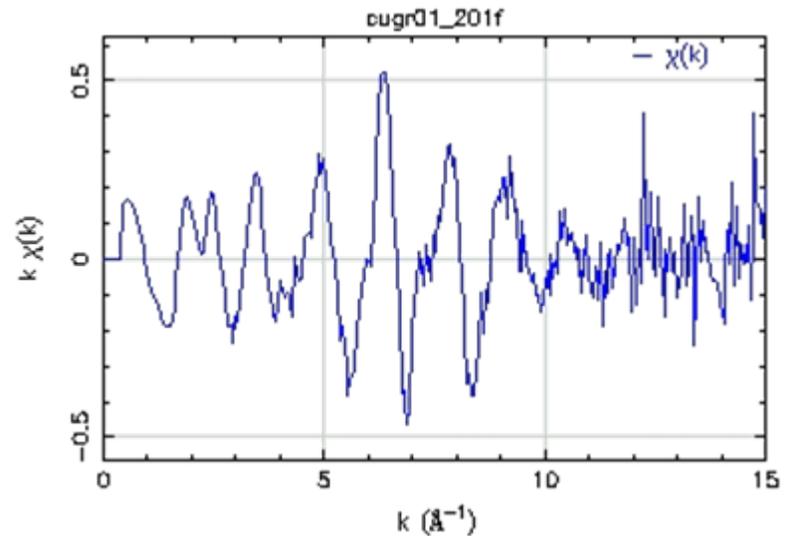
# Outline

- **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

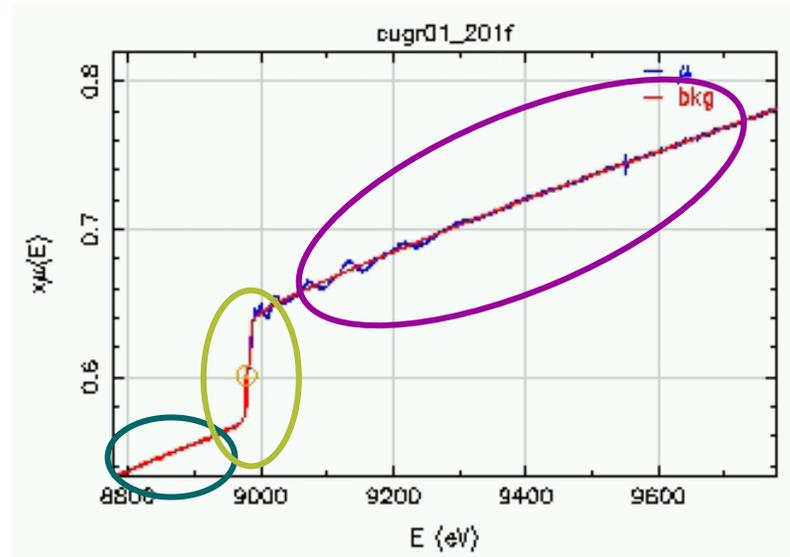
Bkg: Absorption coefficient without contribution from neighboring atoms (Calculated)

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

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

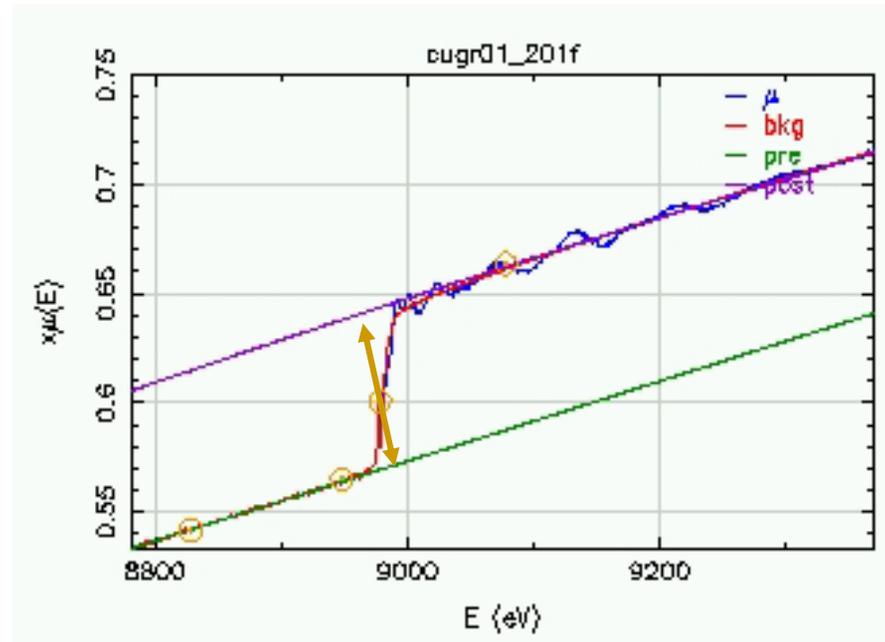
Evaluated at the Edge step ( $E_0$ )

# 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

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### 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

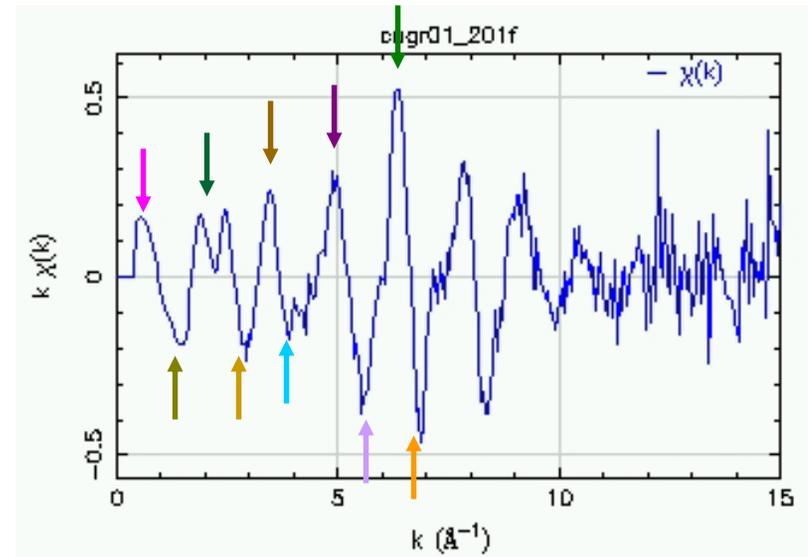
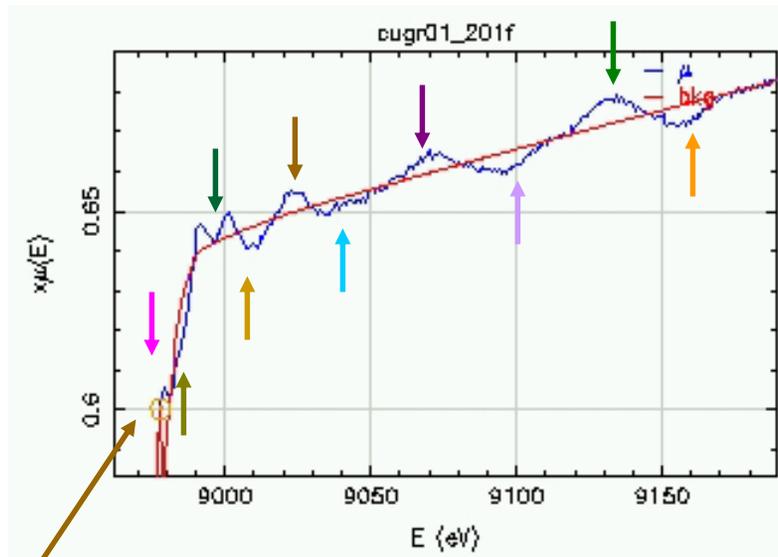
### Plotting options

E k R q Help

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

Rmin: 0 Rmax: 6

# 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 numerator)  
 Edge Energy  $E_0$  (points to the numerator)  
 Plank's constant  $\hbar$  (points to the denominator)

# 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

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**

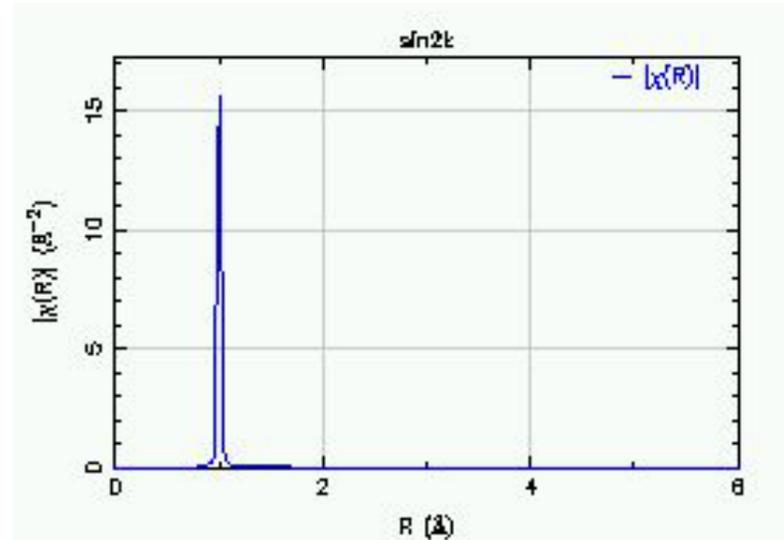
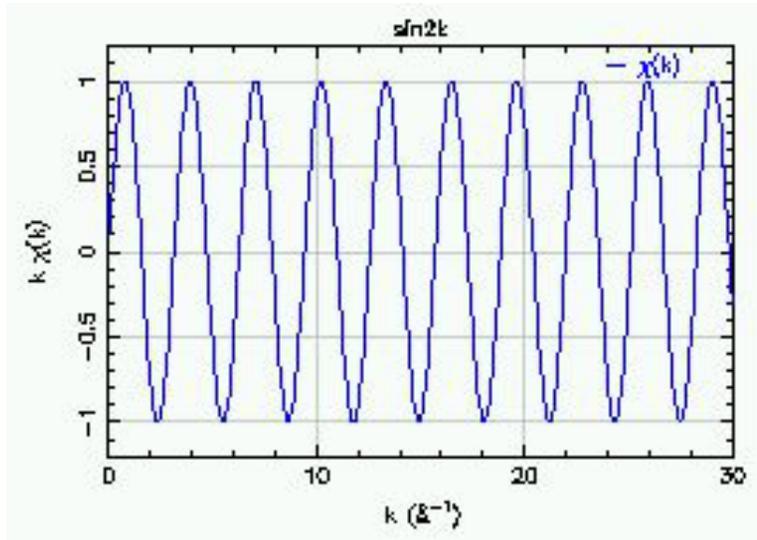
E k R q Help

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

Rmin: 0 Rmax: 6

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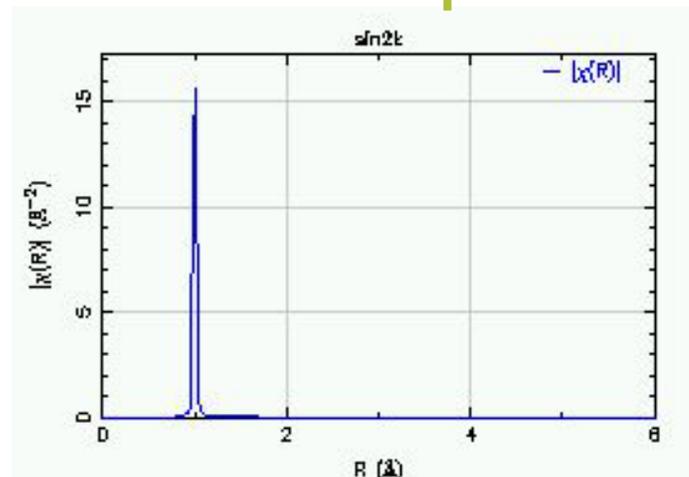
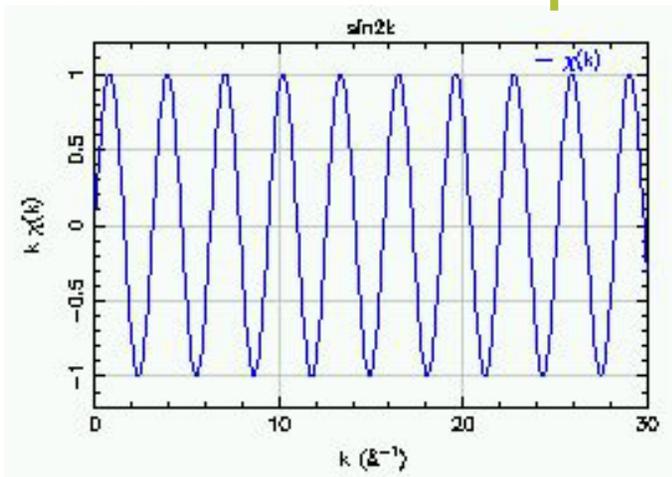
# Fourier Transform is a frequency filter



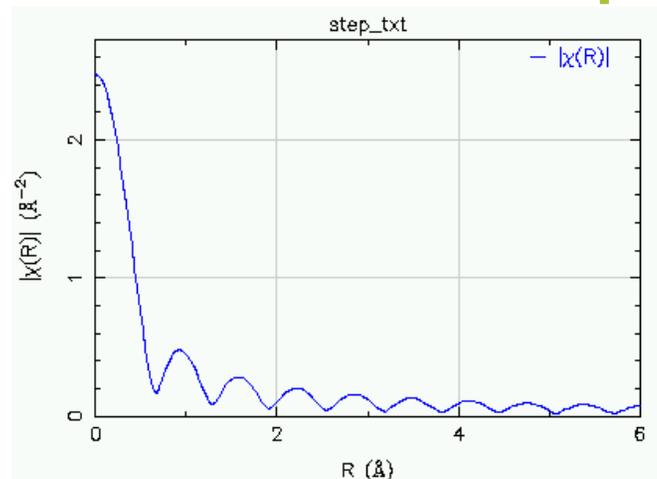
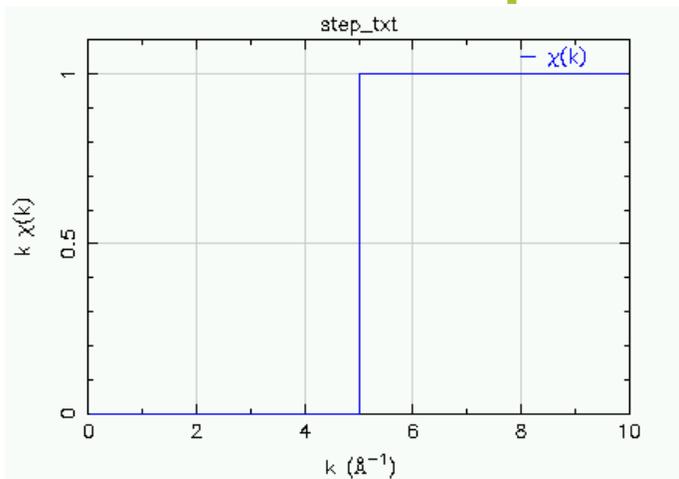
- FT of  $\sin(2Rk)$  is a peak at  $R=1$
- FT of infinite sine wave is a delta function
- Signal that is de-localized in  $k$ -space is localized in  $R$ -space
- FT is a frequency filter

# Fourier Transform of a function that is:

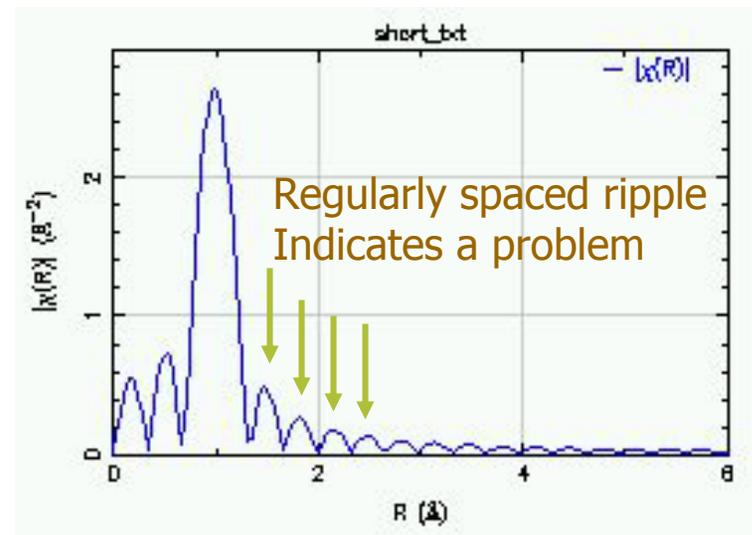
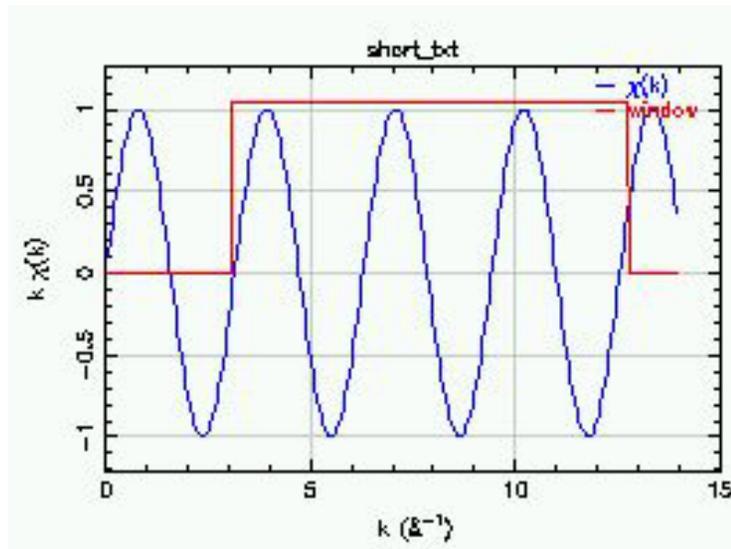
De-localized in  $k$ -space  $\Rightarrow$  localized in  $R$ -space



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

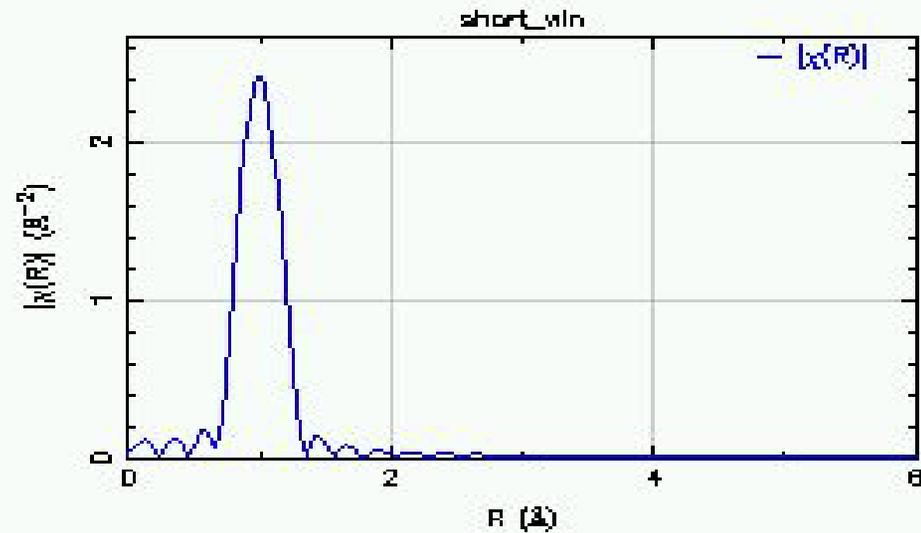
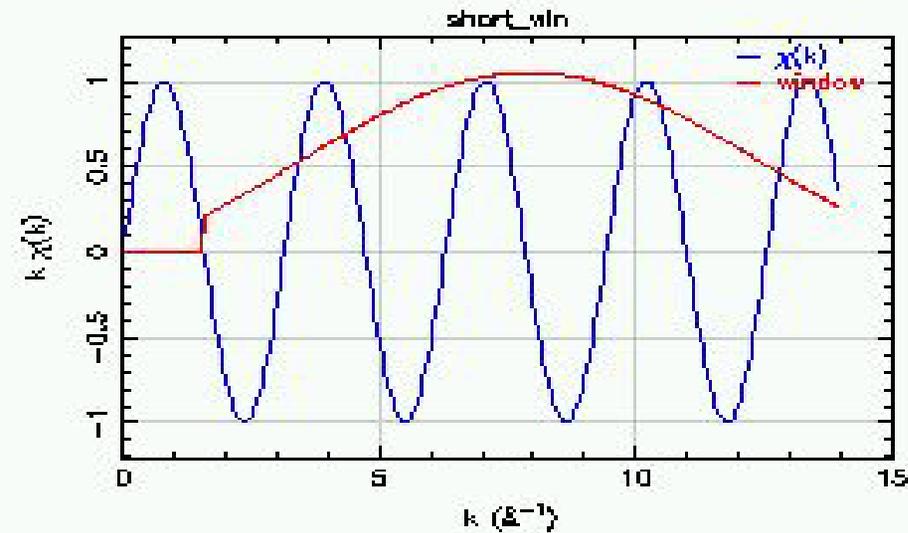


# Fourier Transform is a frequency filter



- 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



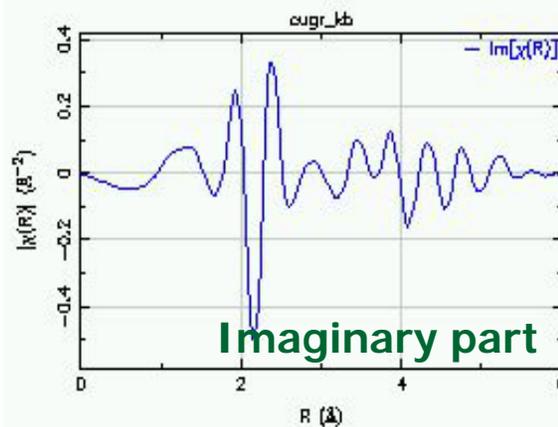
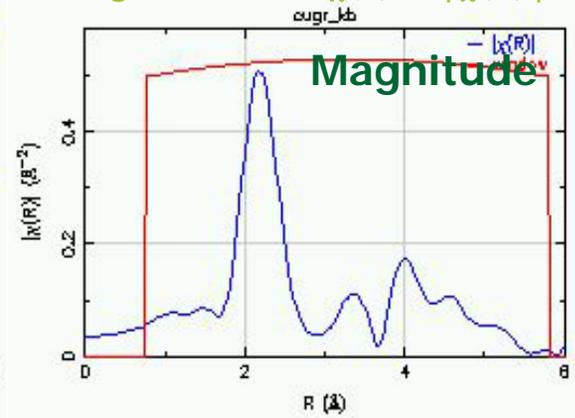
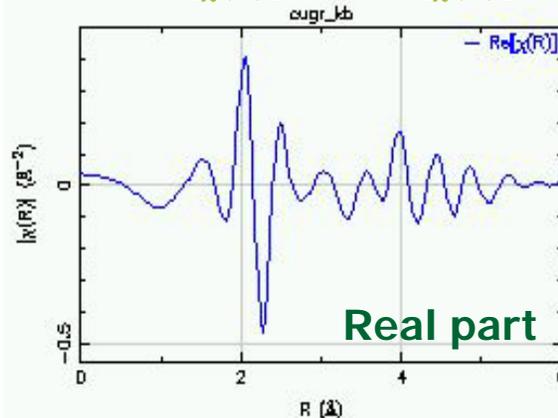
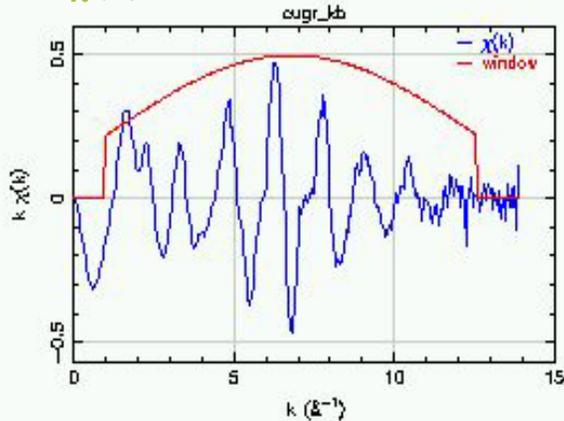
- Multiplying the discrete sine wave by a window that gradually increases the amplitude of the data smoothes the FT of the data.

# Fourier Transform parts

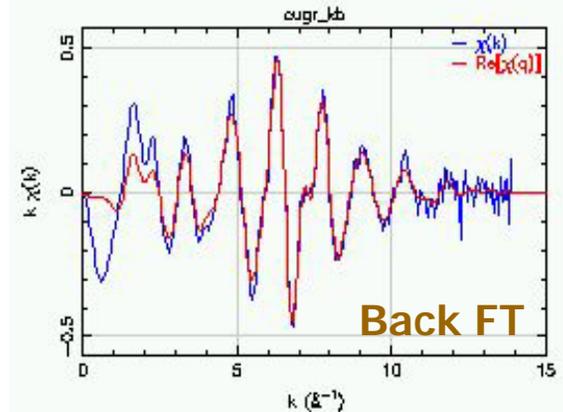
Real and imaginary parts of FT  $\chi(k)$   
 =  $\text{Re}[\chi(R)]$  and  $\text{Im}[\chi(R)]$

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

$\chi(k)$  data and FT window

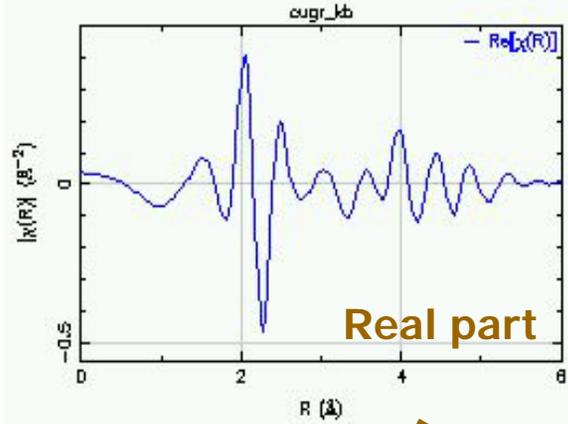


back FT of  $\chi(R) = \chi(q)$

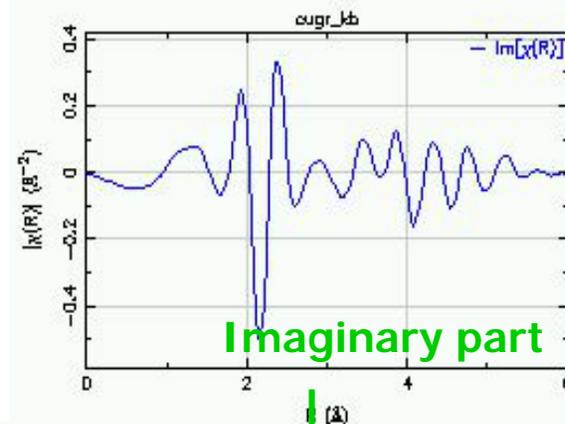


# Understanding the different parts of FT

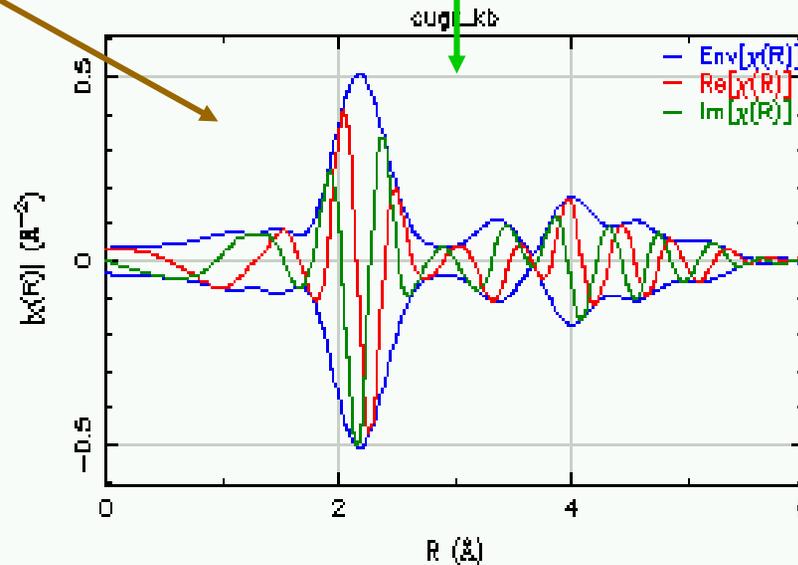
Real part of FT  $\chi(k) = \text{Re} [\chi(R)]$



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 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**
  - 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**

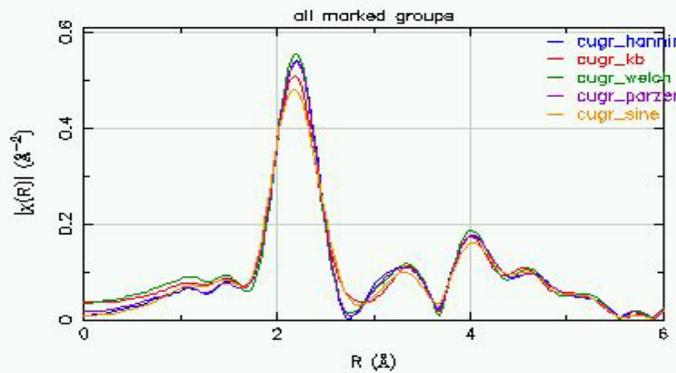
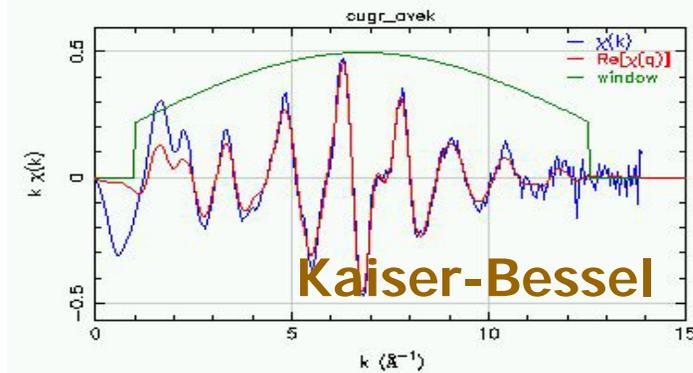
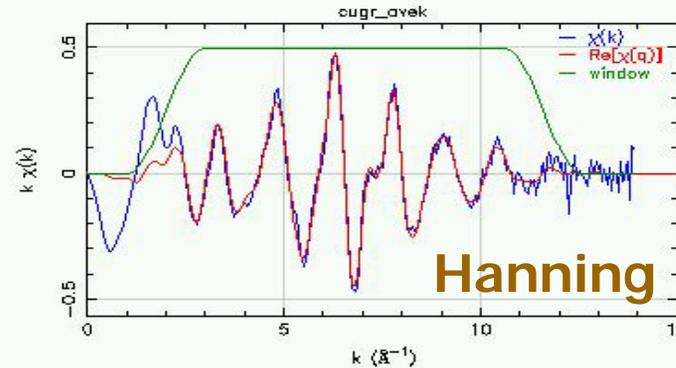
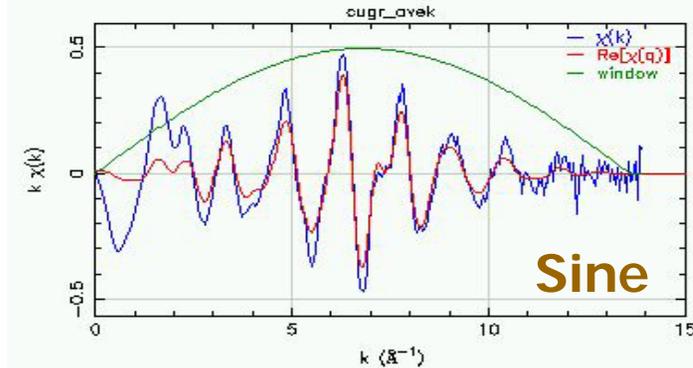
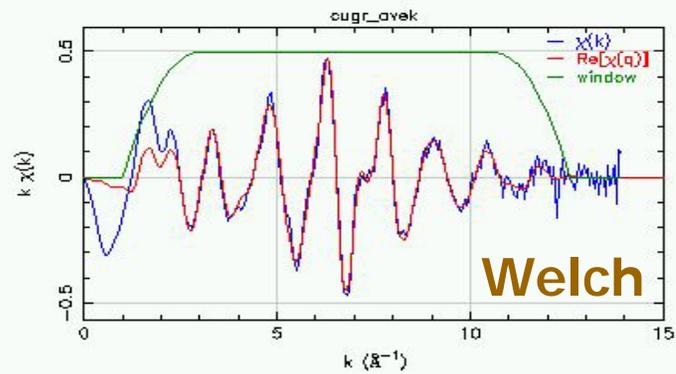
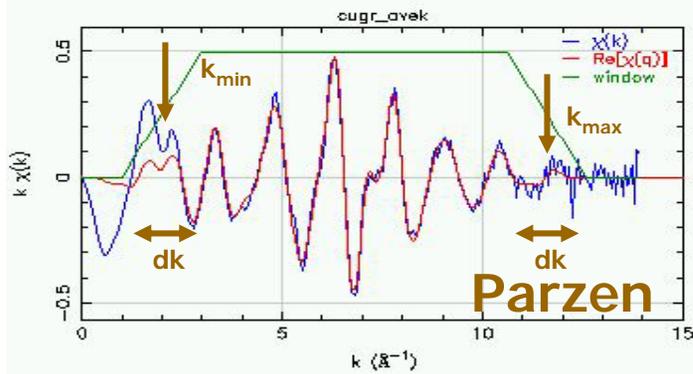
**Plot marked group in**

**Plotting options**

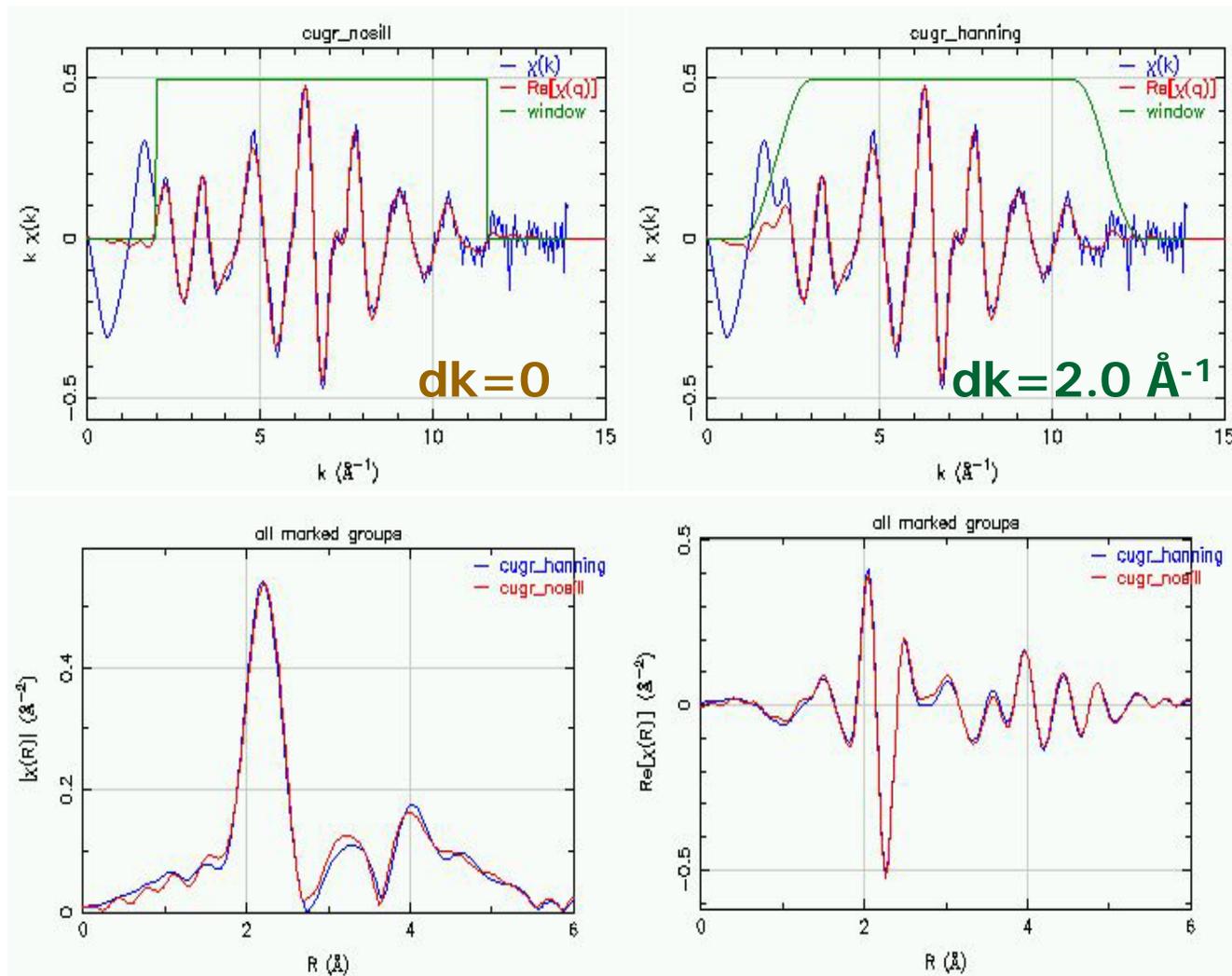
- Magnitude
- Envelope
- Real part
- Imaginary part
- Phase
- Window
- Rmin: `0` Rmax: `6`

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# Fourier Transform Windows



# Fourier Transform window sill



- A small sill can distort FT

# Fourier transform parameters in Athena

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

dk: 0.5 window type: kaiser-bessel

R-range: 1  to 5

### 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

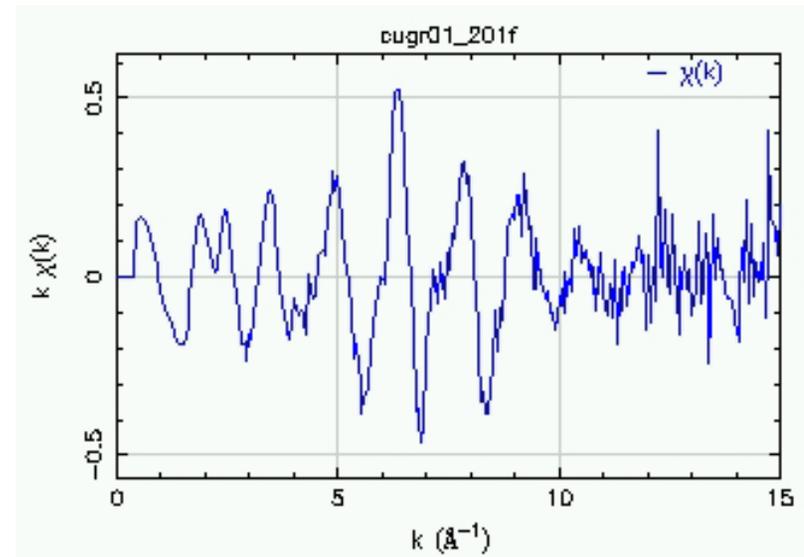
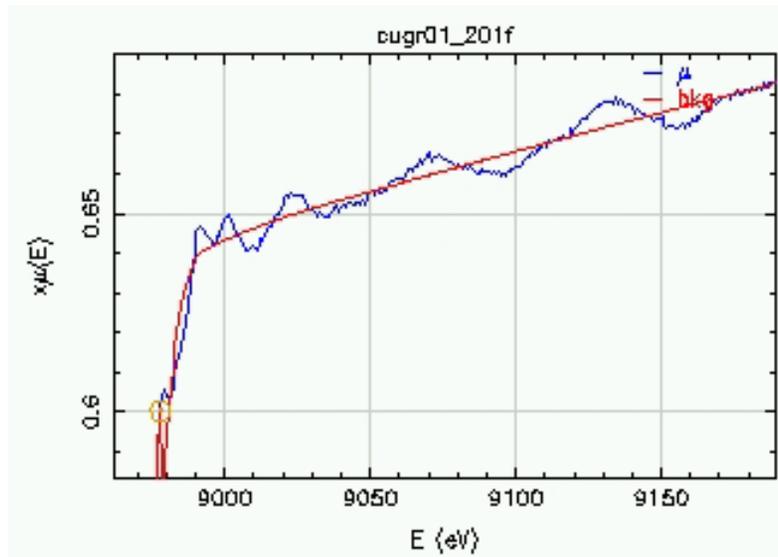
E k R q Help

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

Rmin: 0 Rmax: 6

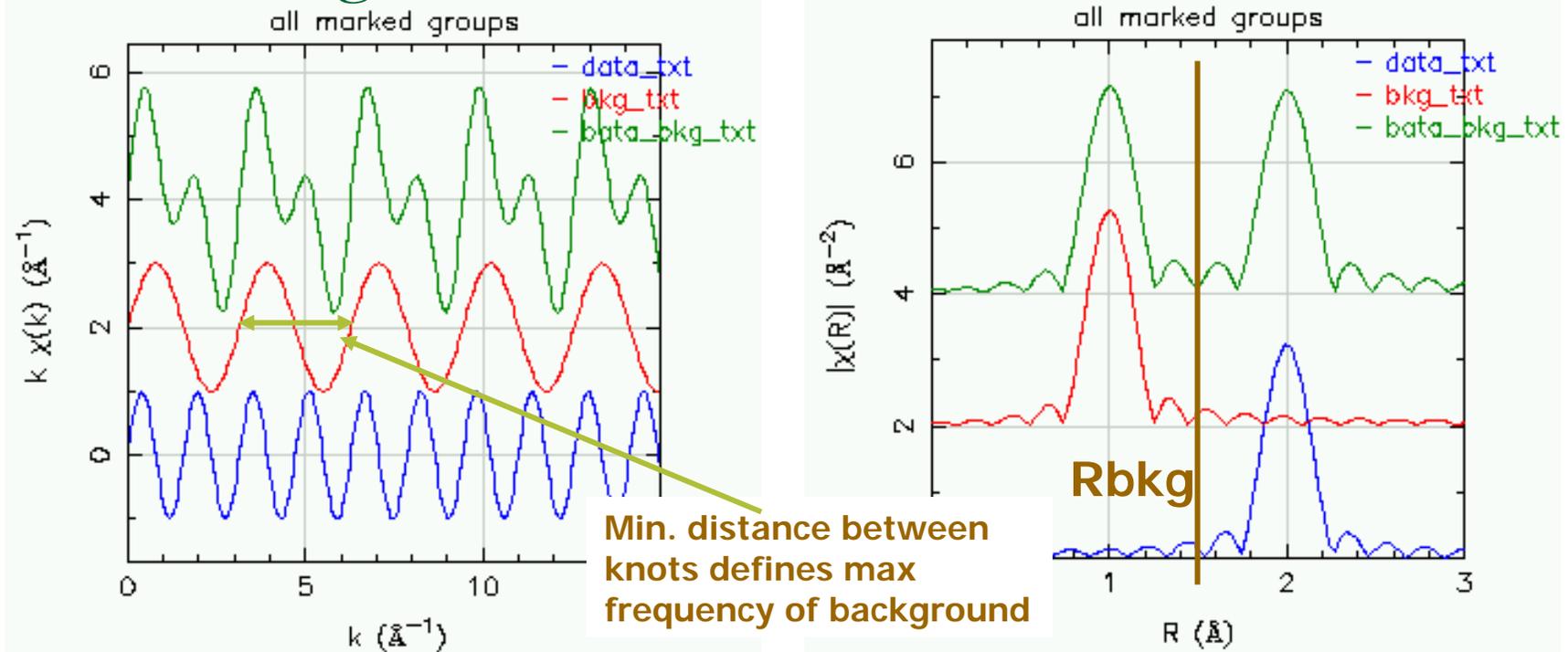
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# Background function overview



- 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



Min. distance between knots defines max frequency of background

- 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`

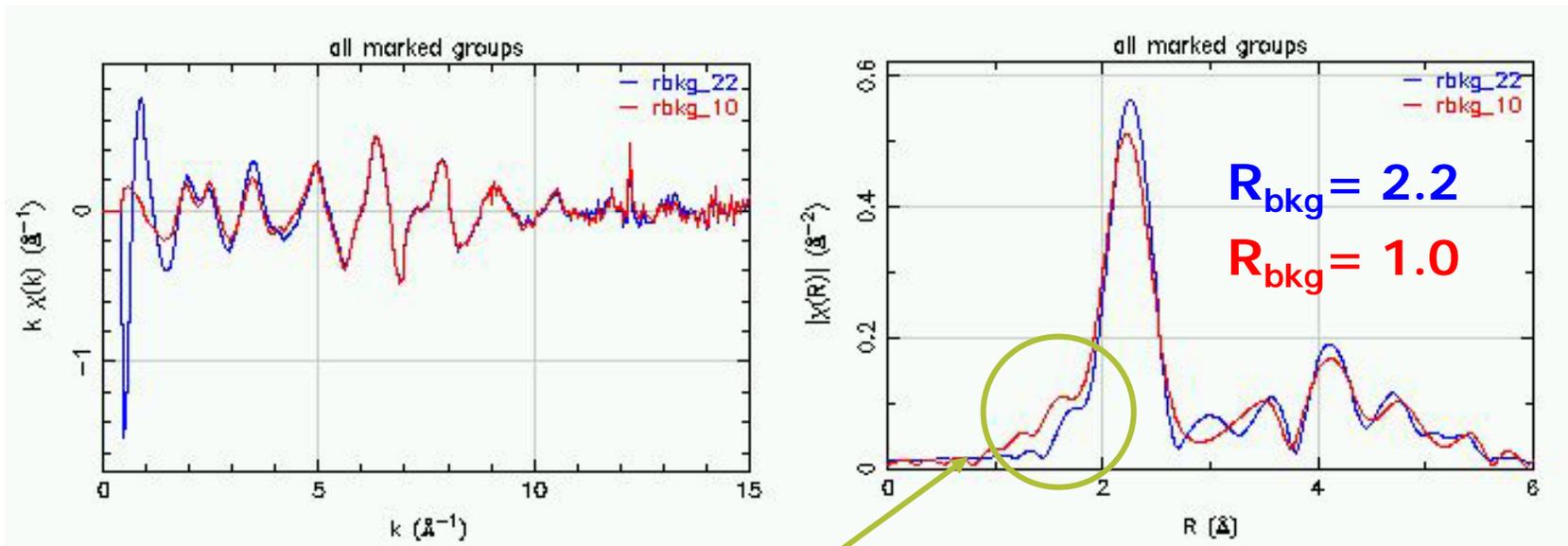
**Plotting options:**

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

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

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

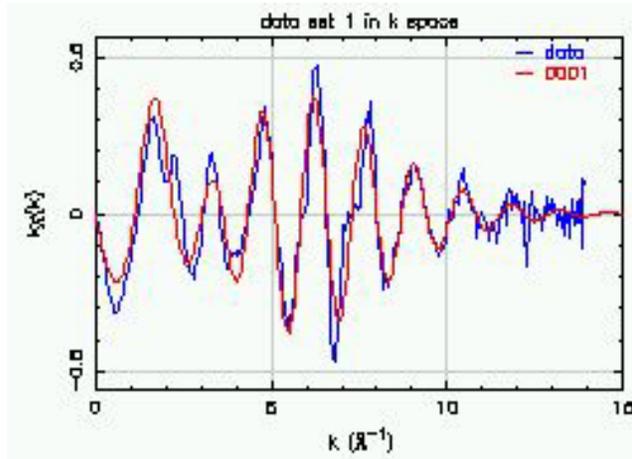


A Hint that R<sub>bkg</sub> may be too large.  
Data should be smooth, not pinched!

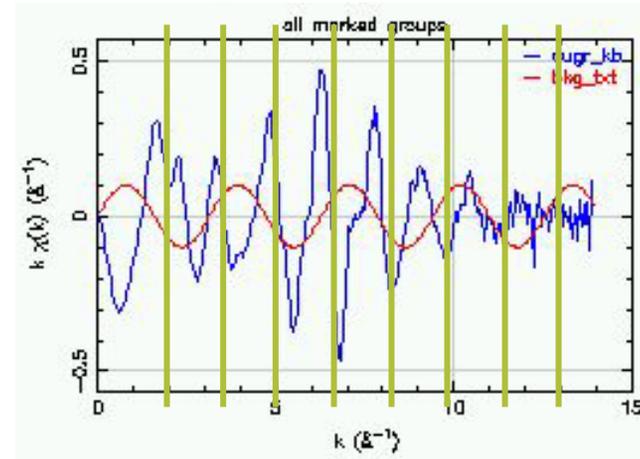
- An example where background distorts the first shell peak.
- $R_{bkg}$  should be about half the R value for the first peak.

# Frequency of Background function

Data contains this and shorter frequencies

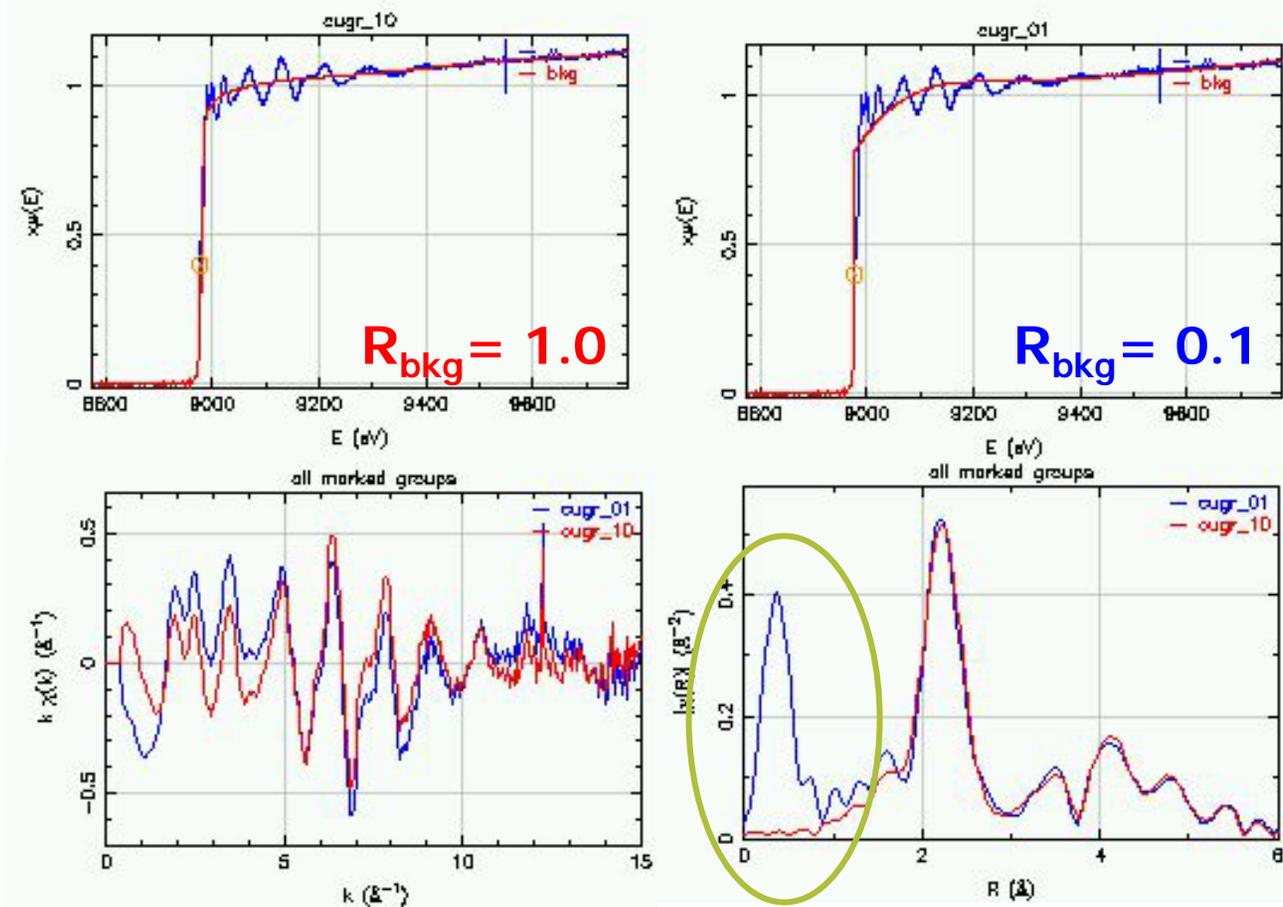


Bkg contains this and longer frequencies



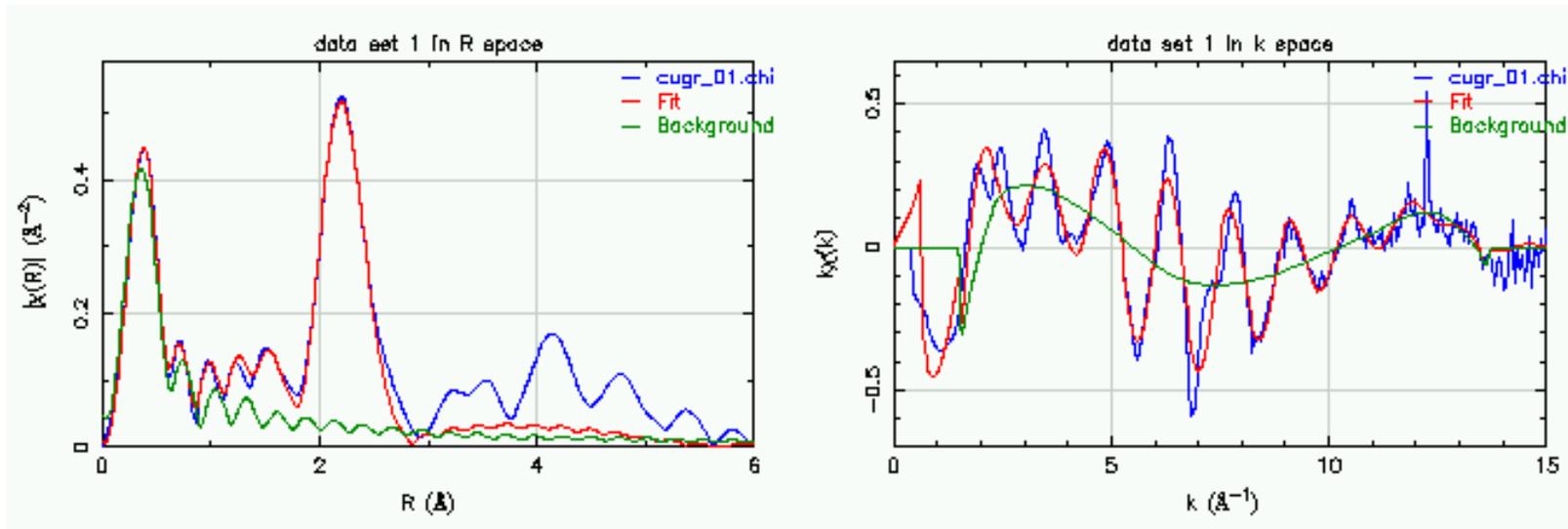
- Constrain background so that it cannot contain frequencies that are part of the data.
  - Use information theory, number of knots =  $2 R_{\text{bkg}} \Delta k / \pi$
  - 8 knots in bkg using  $R_{\text{bkg}}=1.0$  and  $\Delta k = 14.0$
- Background may contain only longer frequencies. Therefore knots 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. The main window title is "Artemis" and the menu bar includes "File", "Edit", "GDS", "Data", "Sum", "Fits", "Theory", "Paths", "Plot", "Settings", and "Help". The current project path is "C:/Documents and Settings/skelly/My Documents/XAFS/background\_tutorial/Mo03-final.apj".

The interface is divided into several panels:

- Titles:** Contains text describing the data file and background parameters: "Athena data file -- Athena version 0.8.034", "Saving moo3-th (group=moo\_co?2) as chi(k)", ". Element=Mo Edge=K", "Background parameters", ". E0=20009.000 Eshift=0.000 Rbkg=1.100".
- Data file:** Set to "moo3-th.chi".
- Fourier and fit parameters:** Includes fields for "k-range" (4.0 to 14), "R-range" (1.1 to 2.5), "dk" (1), "dr" (0.1), "k window" (Hanning), and "R window" (Hanning).
- Other parameters:** Includes "Fitting space" (R), "Epsilon" (0), "Minimum reported correlation" (0.25), and "Path to use for phase corrections" (None).
- Fit k-weights:** Includes checkboxes for "kw=1", "kw=2", "kw=3", and "other k weight".
- Data & Paths:** Lists files under "FEFF0", including "moo3-th.chi" (selected), "feff0001.dat", "feff0002.dat", "feff0003.dat", "feff0004.dat", "feff0005.dat", "feff0006.dat", and "feff0007.dat".
- Fit Panel:** Features a green "Fit" button, tabs for "k", "R", and "q", and "Plotting options" for "Plot in R:" and "Plot in q:". The "Fit background" checkbox is checked and circled in orange.
- Document: Fitting parameters** and **Document: Plotting** are visible at the bottom.

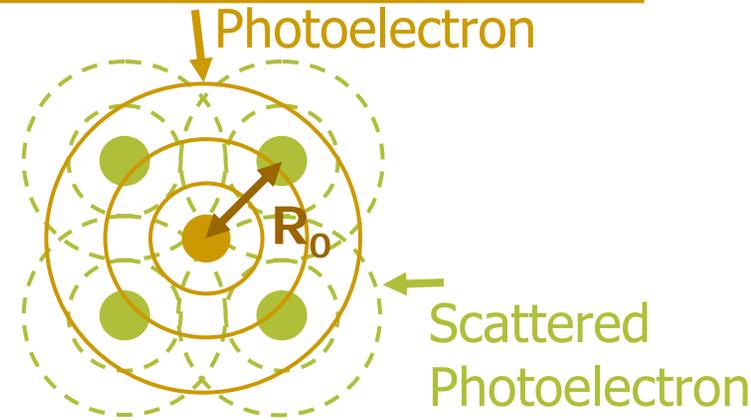
At the bottom of the window, a status bar reads: "Read project description 'C:/Program Files/lfeffit/horae\stash\artemis.project.1\descriptions\artemis'"



# 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