Basics of EXAFS Processing

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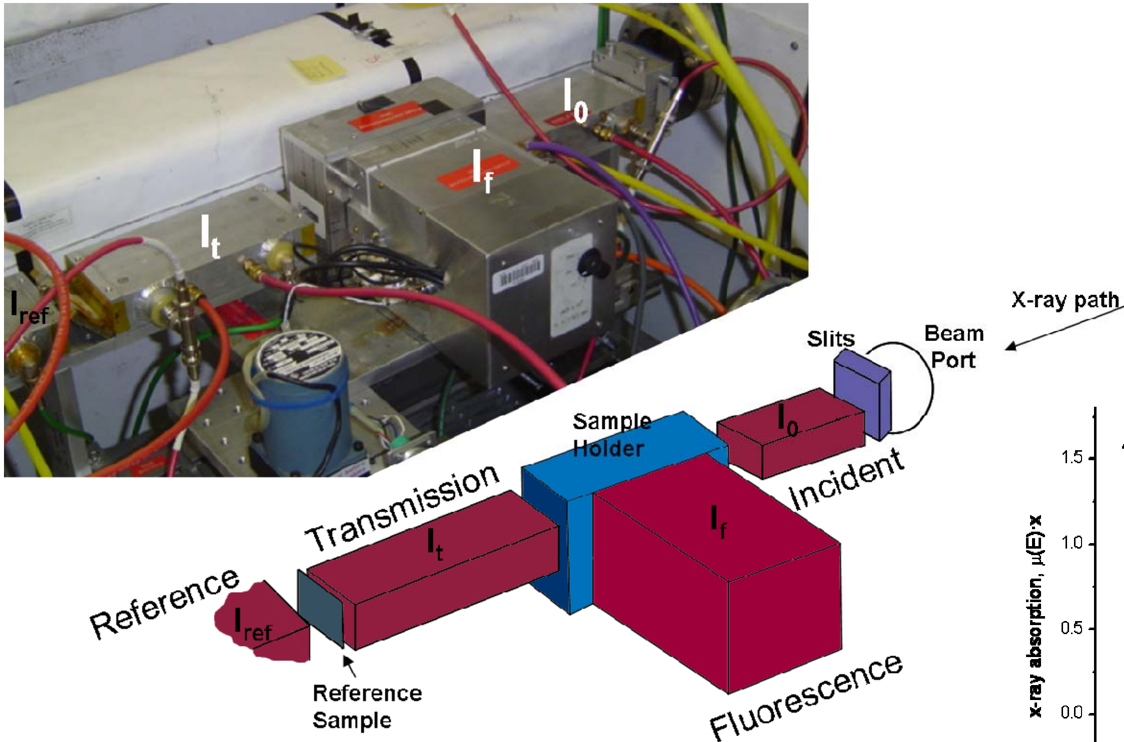
Honeywell

X-ray-Absorption Fine Structure

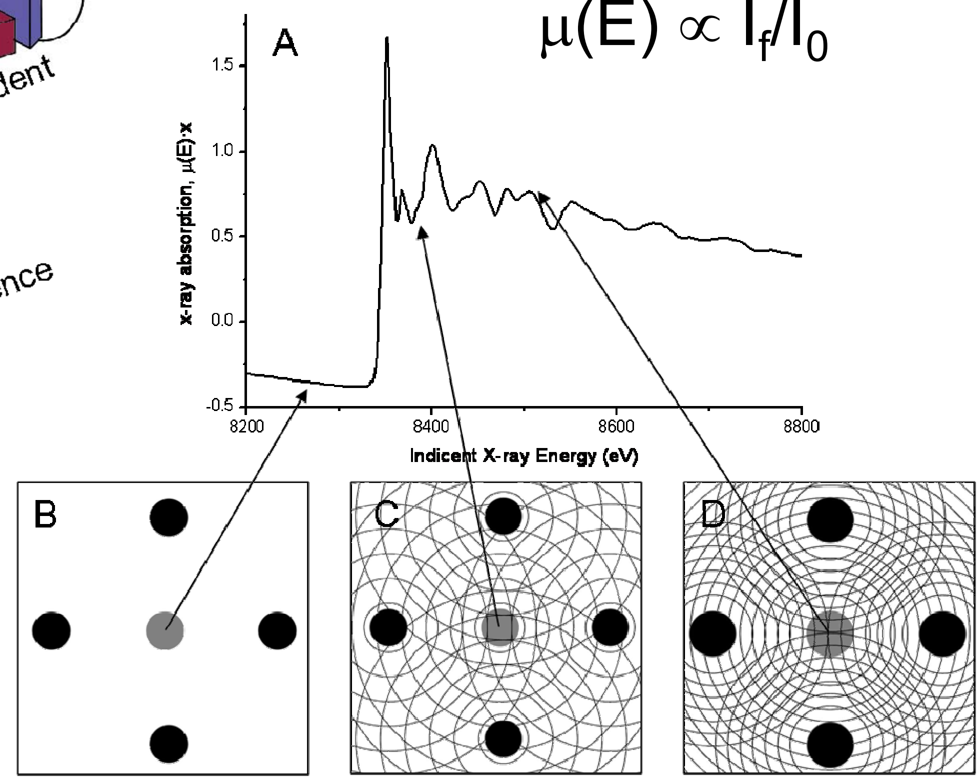


- Attenuation of x-rays

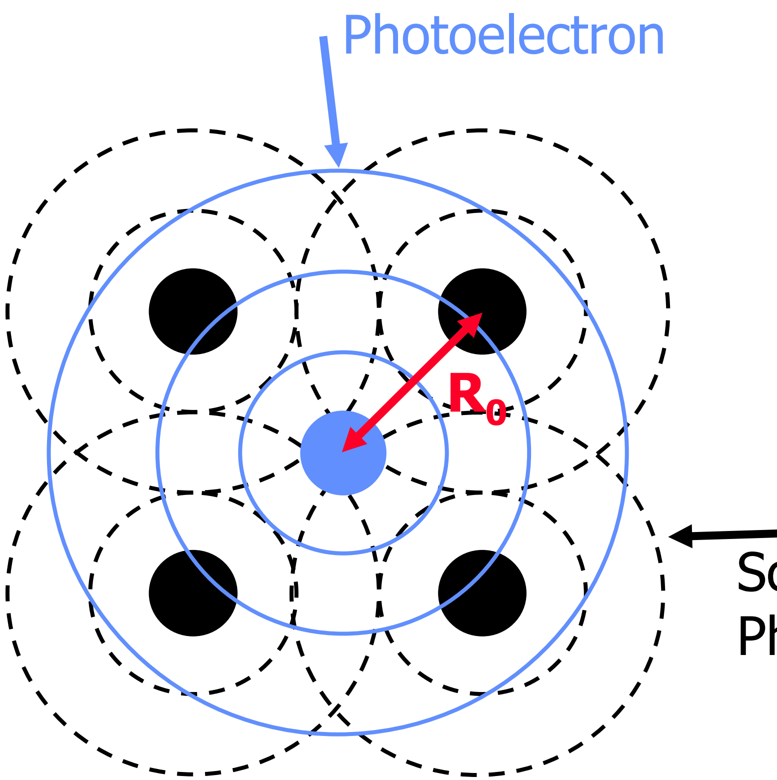
$$I_t = I_0 e^{-\mu(E)\cdot x}$$

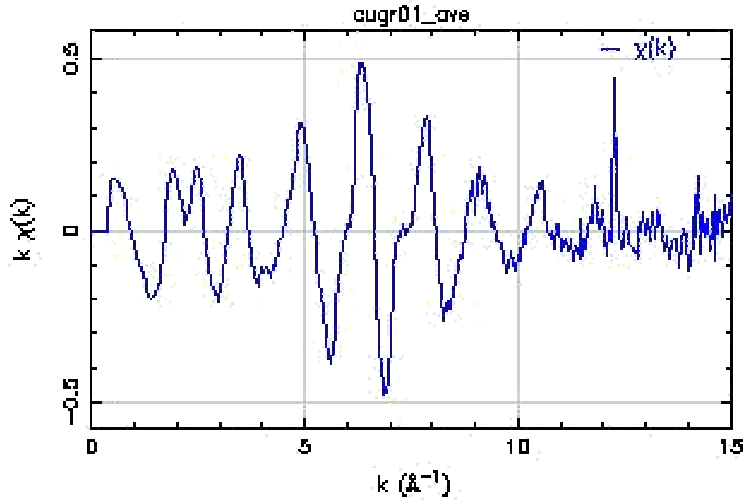
- Absorption coefficient

$$\mu(E) \propto I_f / I_0$$

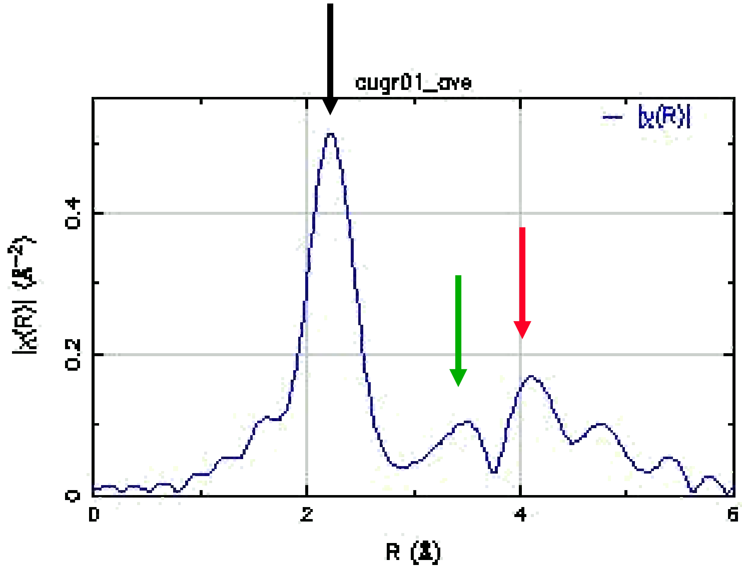


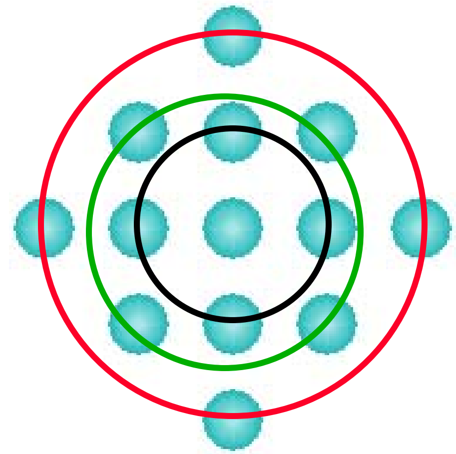
X-ray-Absorption Fine Structure





Fourier Transform of $\chi(k)$





- Similar to an atomic radial distribution function
  - Distance
  - Number
  - Type
  - Structural disorder
- Fourier transform is not a radial distribution function
  - See http://www.xafs.org/Common_Mistakes

Outline

- Definition of EXAFS
  - **Edge Step**
  - **Energy to wave number**
- Fourier Transform (FT) of χ**(k)**
  - **FT is a frequency filter**
  - **Different parts of a FT and backward FT**
  - **FT windows and sills**
  - **Determining Kmin and Kmax of FT**
- IFEFFIT method for constructing the background function
  - **FT and background (bkg) function**
  - **Wavelength of bkg**
- EXAFS Equation

Definition of EXAFS

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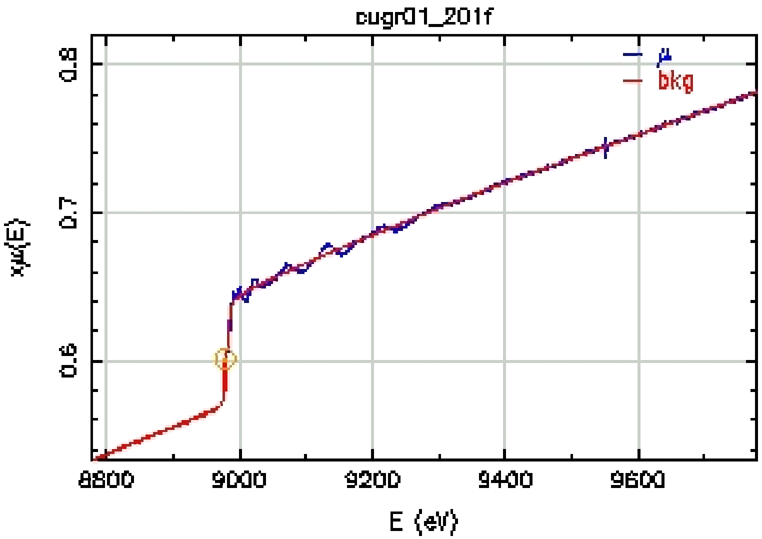

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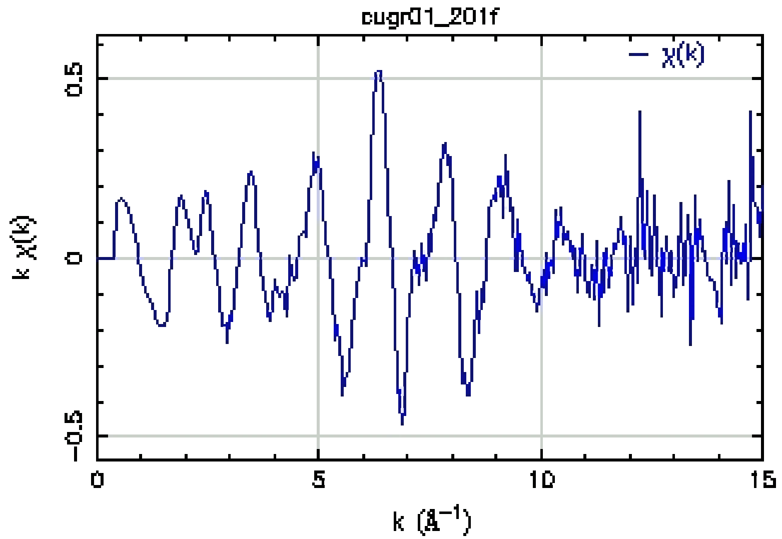


Normalized oscillatory part of absorption coefficient

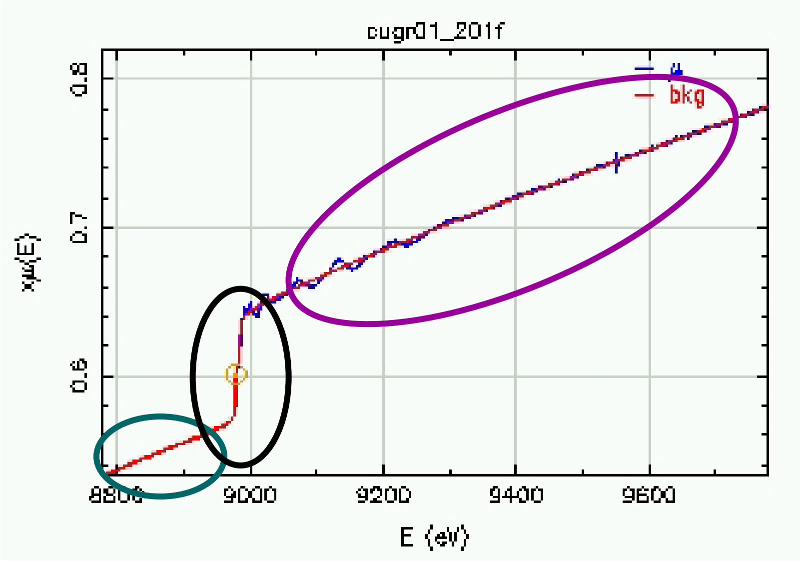
Measured Absorption coefficient

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

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

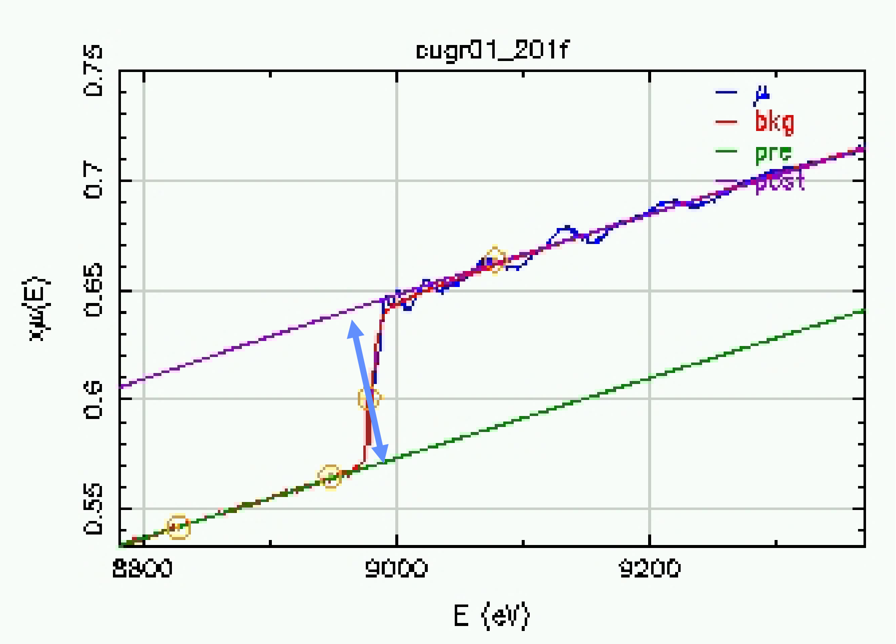
Evaluated at the Edge step (E_0)

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

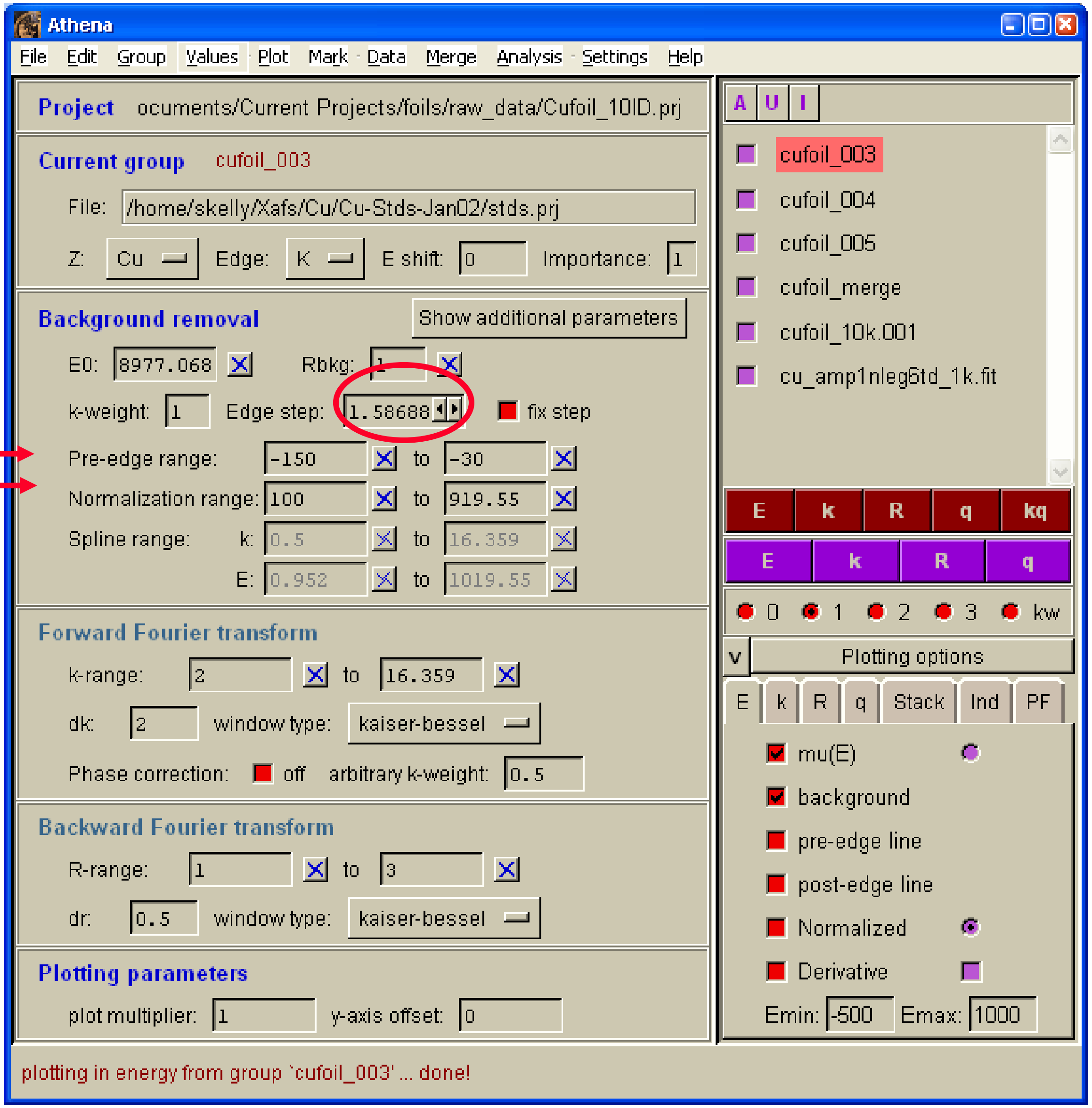
Edge step



- 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

File Number

Athena normalization parameters



Energy to wave number

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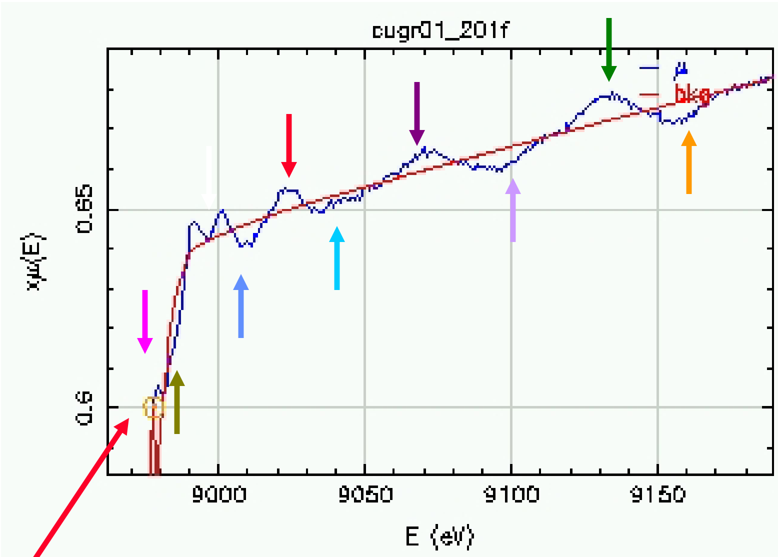
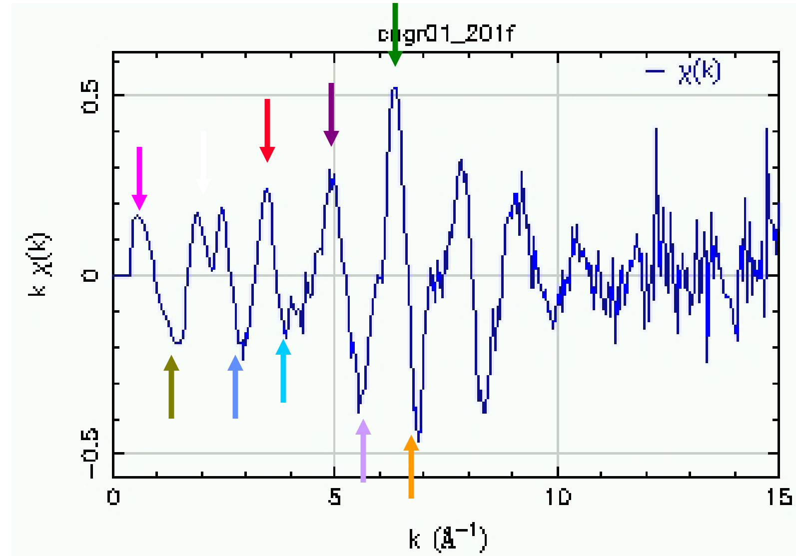




E_0 Must be somewhere on the edge

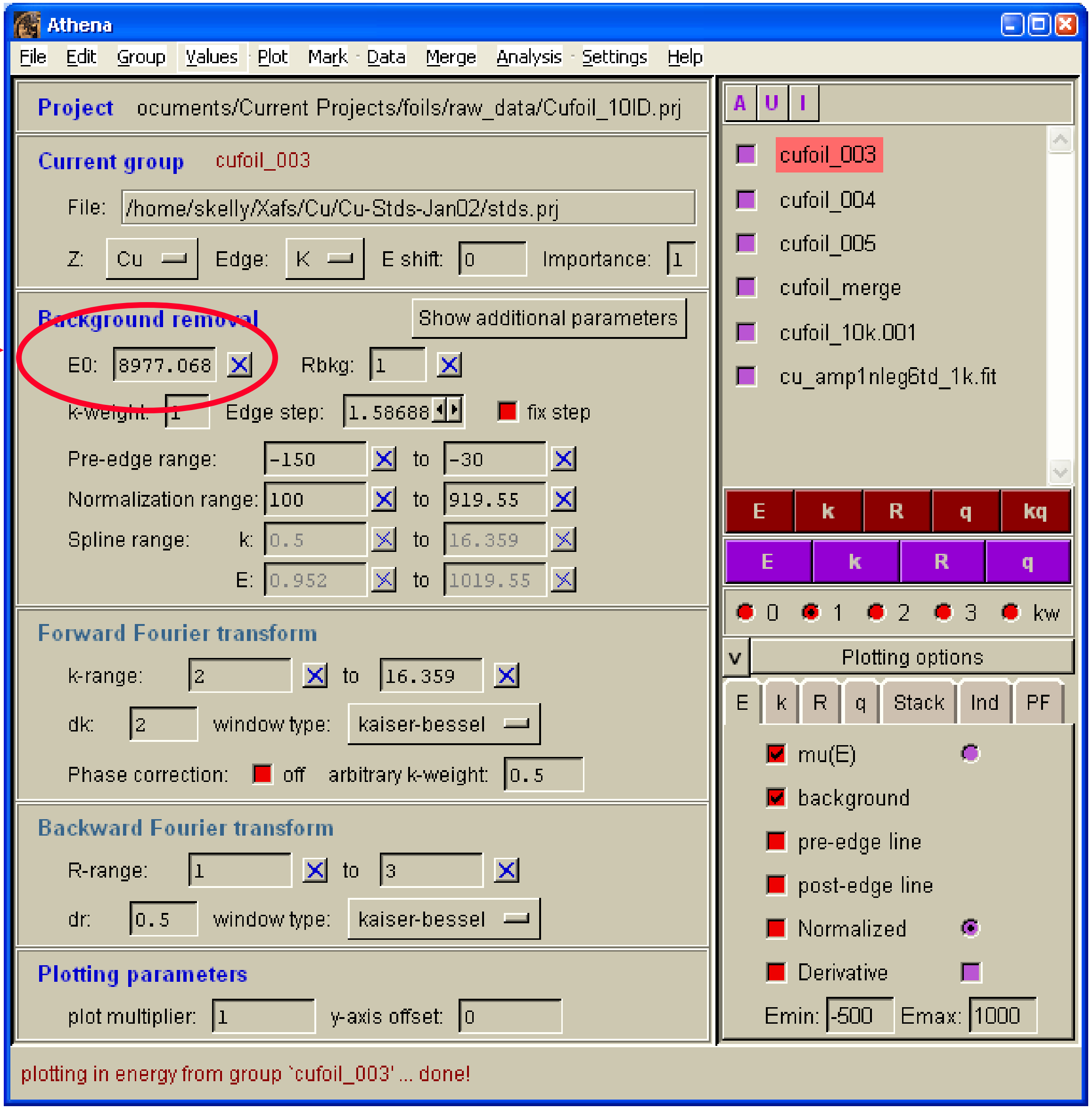
Mass of the electron

Edge Energy

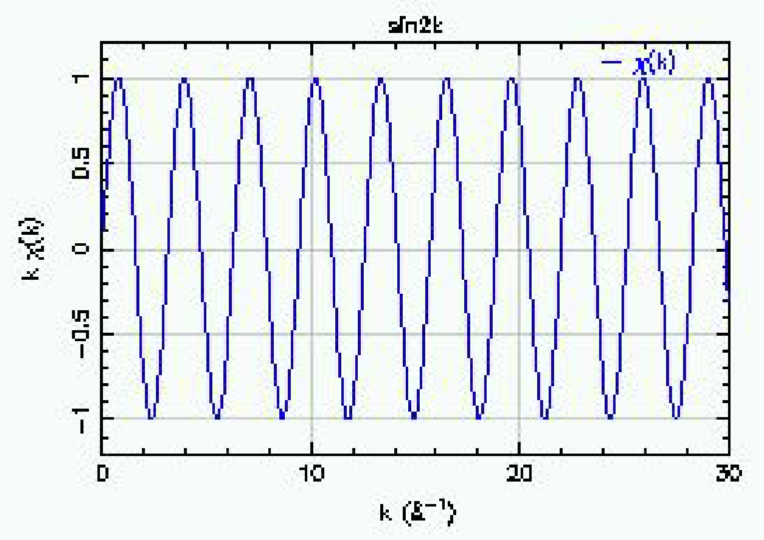
$$k^2 = \frac{2\, m_e\, (E - E_0)}{\hbar} \sim \frac{\Delta E}{3.81}$$

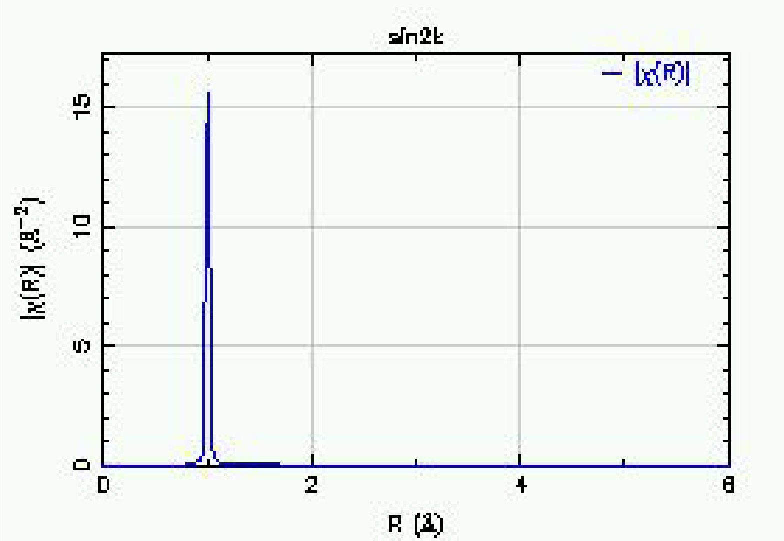
Plank's constant

Athena edge energy E0



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:

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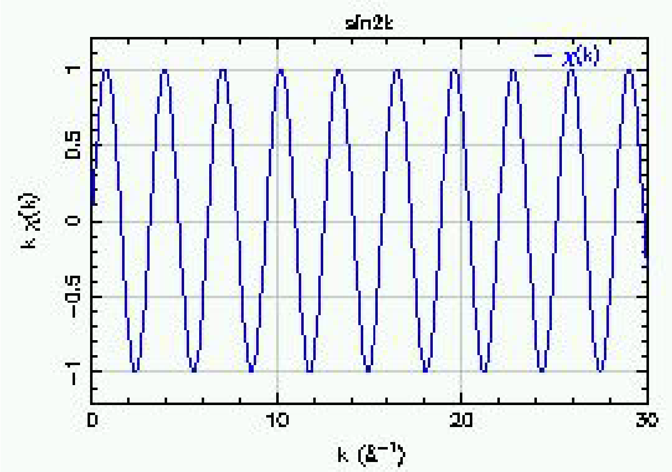
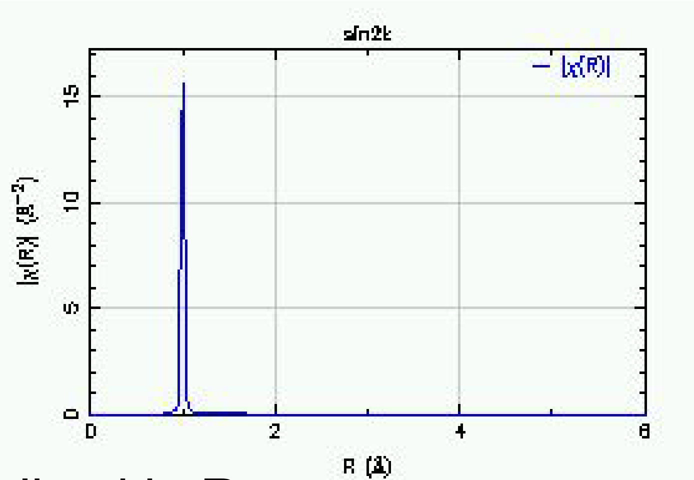
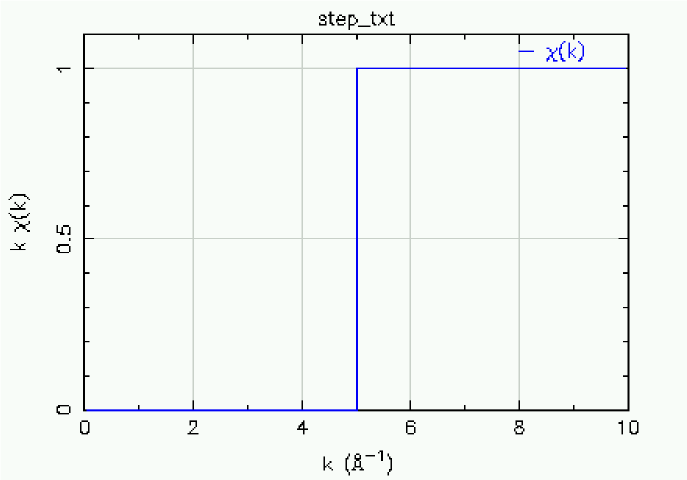
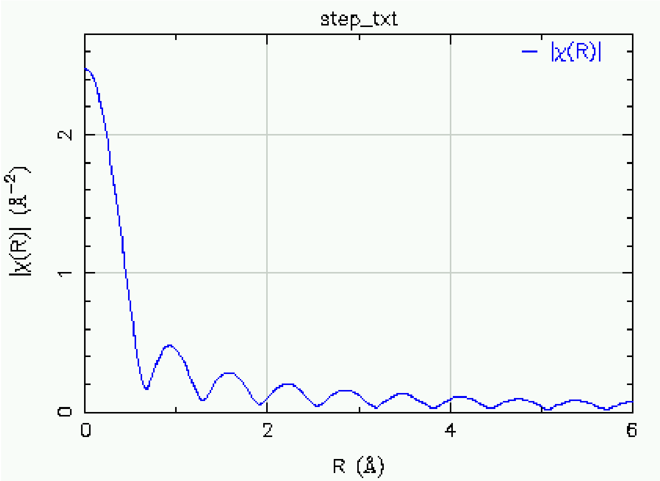
De-localized in k-space ⇒ localized in R-space





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





Fourier Transform is a frequency filter

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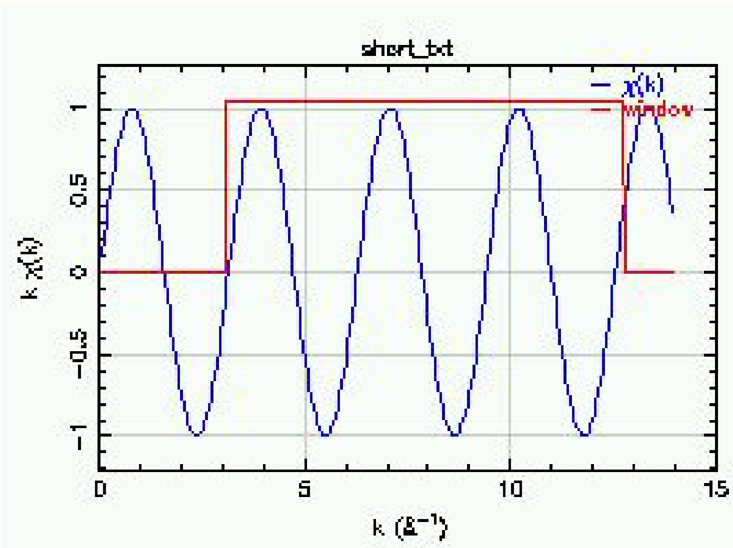
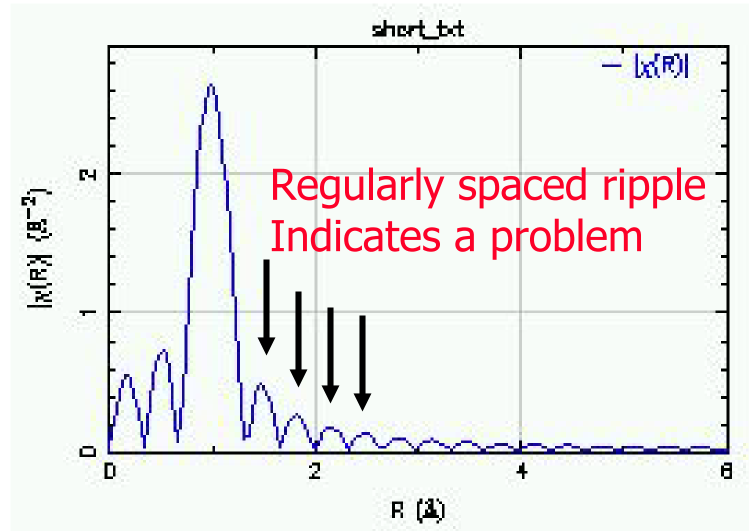
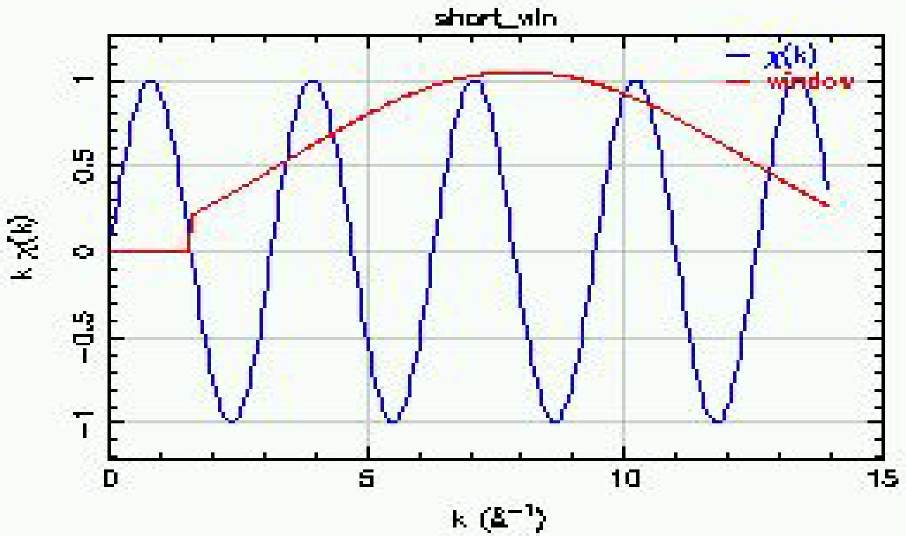
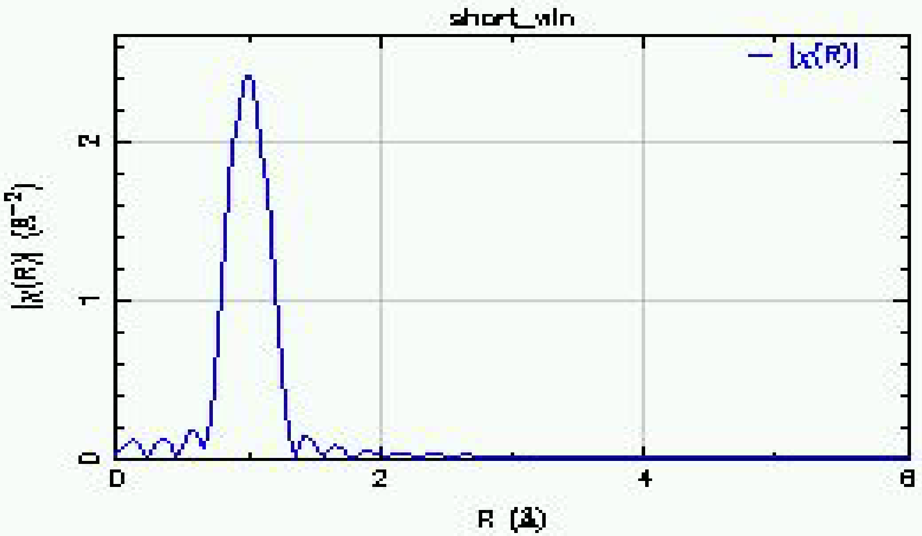




- The signal of a discrete sine wave is the sum of an infinite sine wave and a step function.
- FT of a discrete sine wave is a distorted peak.
- EXAFS data is a sum of discrete sine waves.
- Solution for finite data set is to multiply the data with a window.

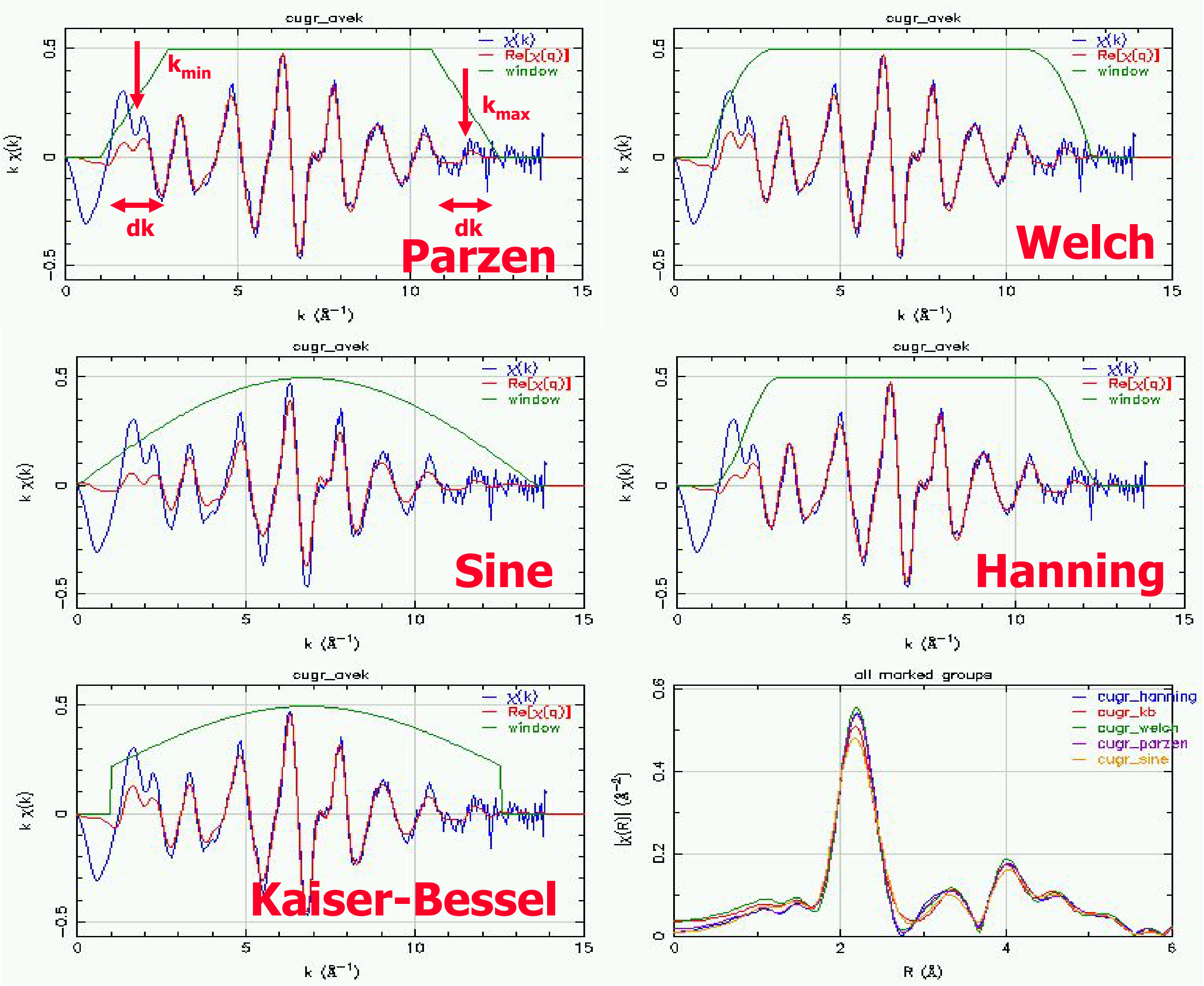
Fourier Transform



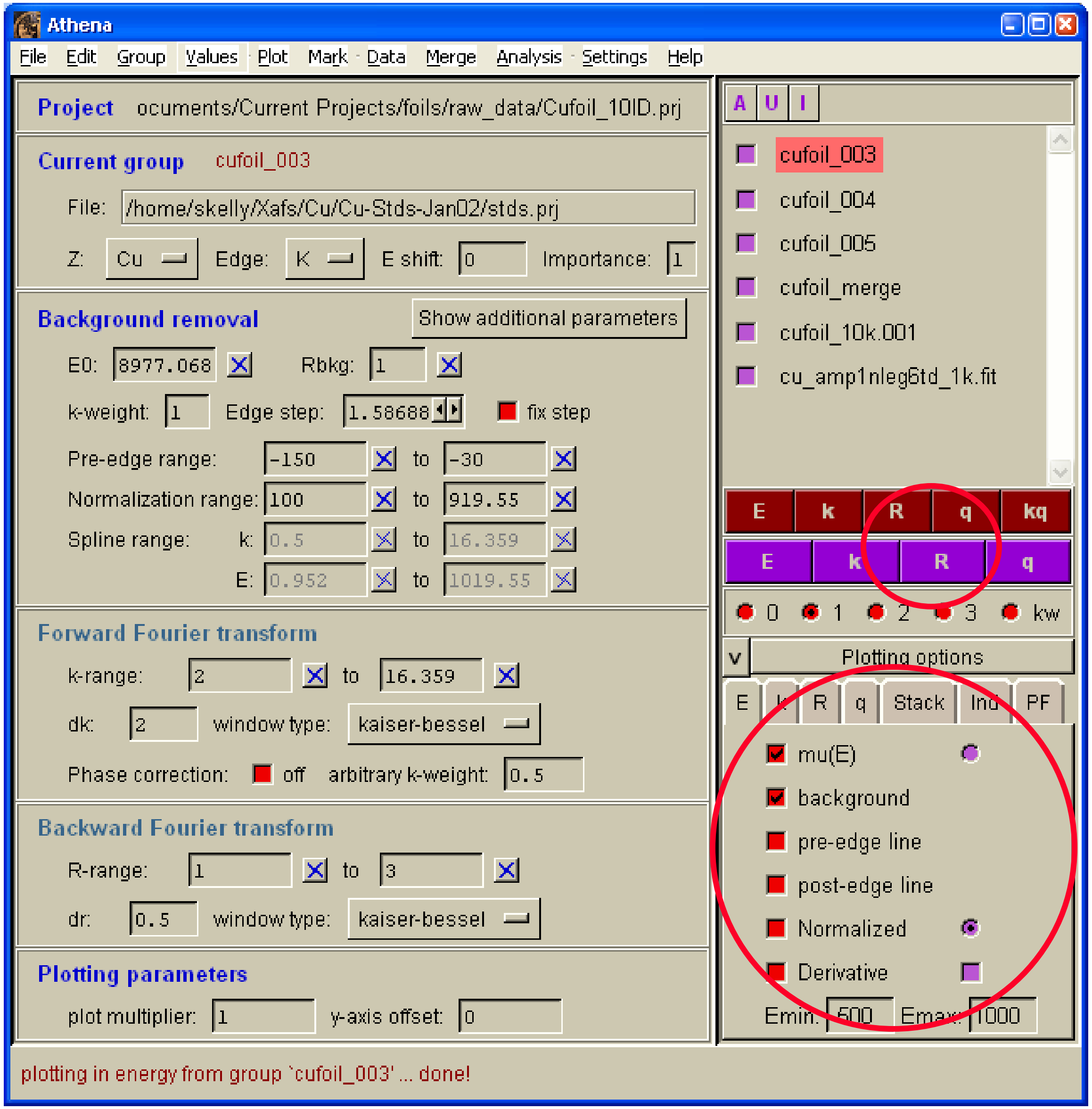


- Multiplying the discrete sine wave by a window that gradually increases the amplitude of the data smoothes the FT of the data.

Fourier Transform Windows



Athena plotting in R-space



Parts of the Fourier transform

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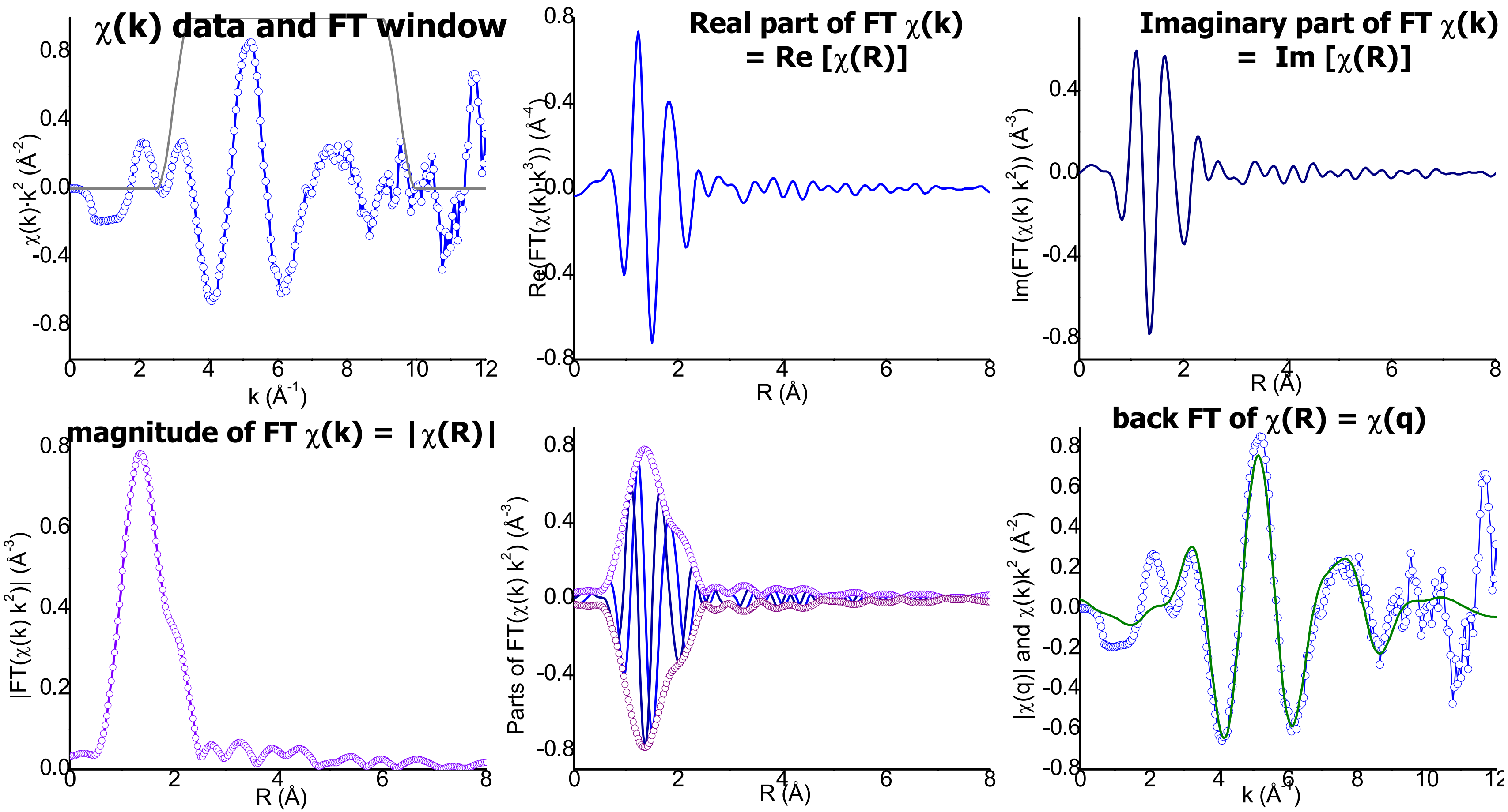
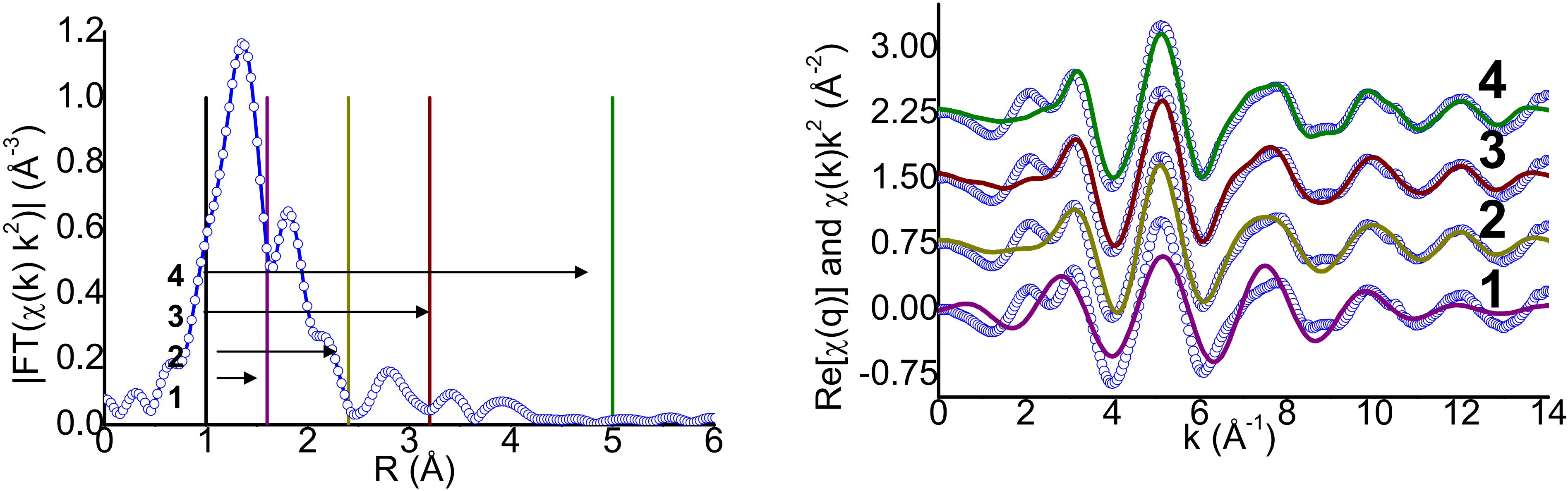


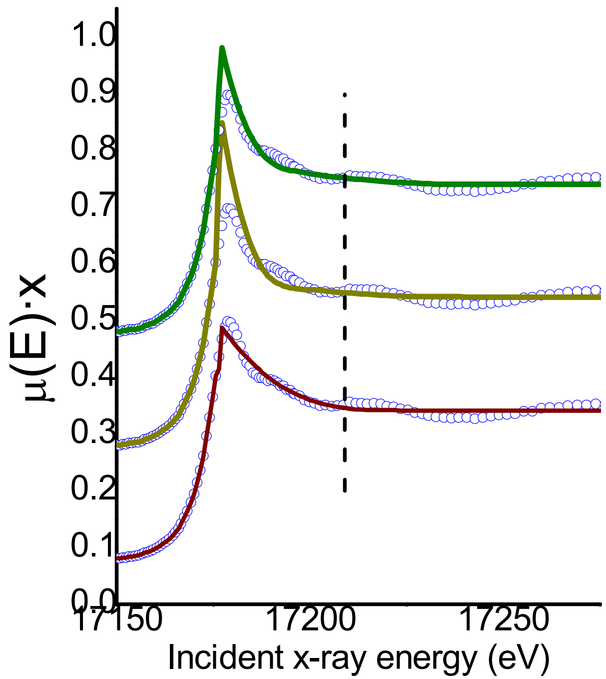
- **The Magnitude of the Fourier transform does not contain as much information as the Real or Imaginary parts of the FT.**

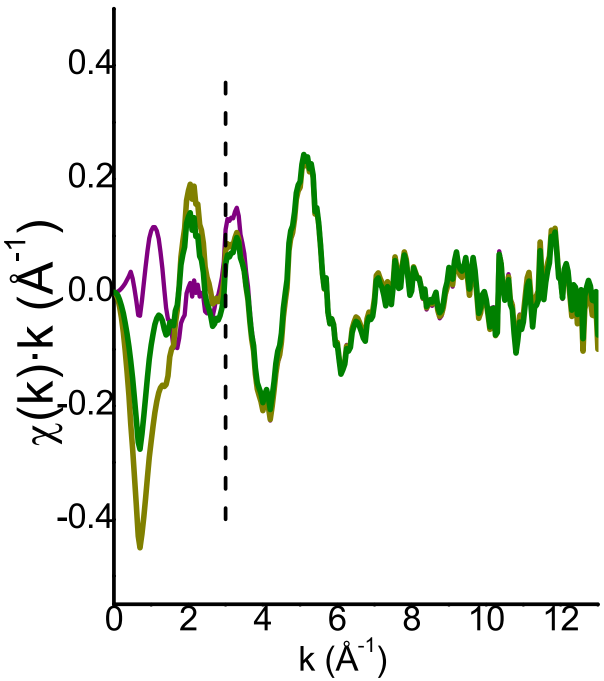
Backward Fourier transform



- Only the wavelengths that are contained in the back Fourier transform R range are present in the Re[chi(q)] spectra
- As a larger R range is included the back FT looks more like the original spectra (blue symbols)

How to Choose Minimum K of FT





- **Choose Kmin in the region where the background doesn't change rapidly.**
  - **Often around 2 to 4 $Å^{-1}$**
  - **Vary E_0 and plot the resulting χ spectra with low k-weight to determine the best value.**

Choosing Maximum K-range

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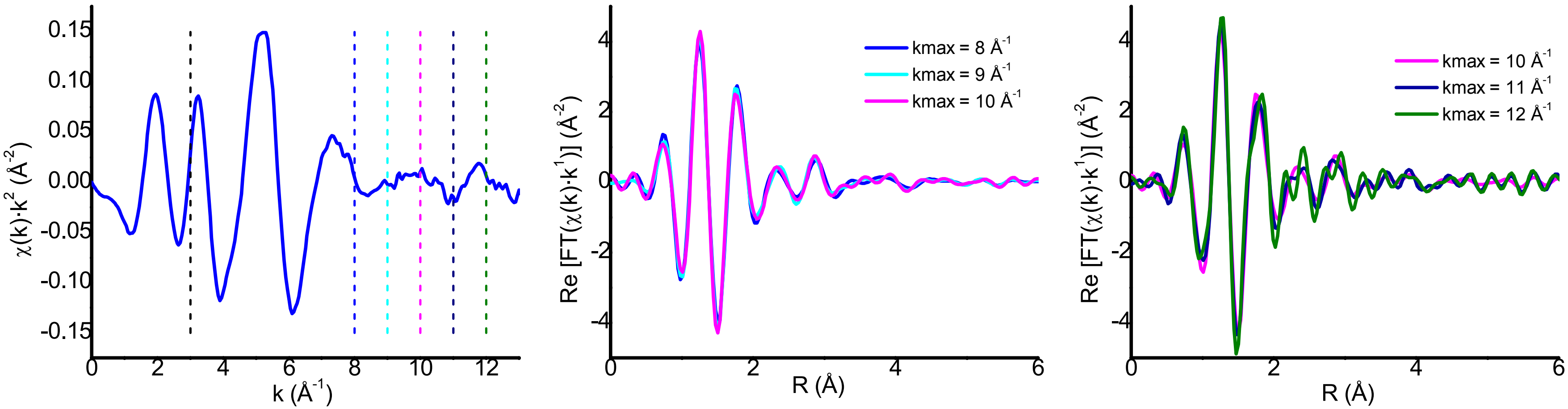
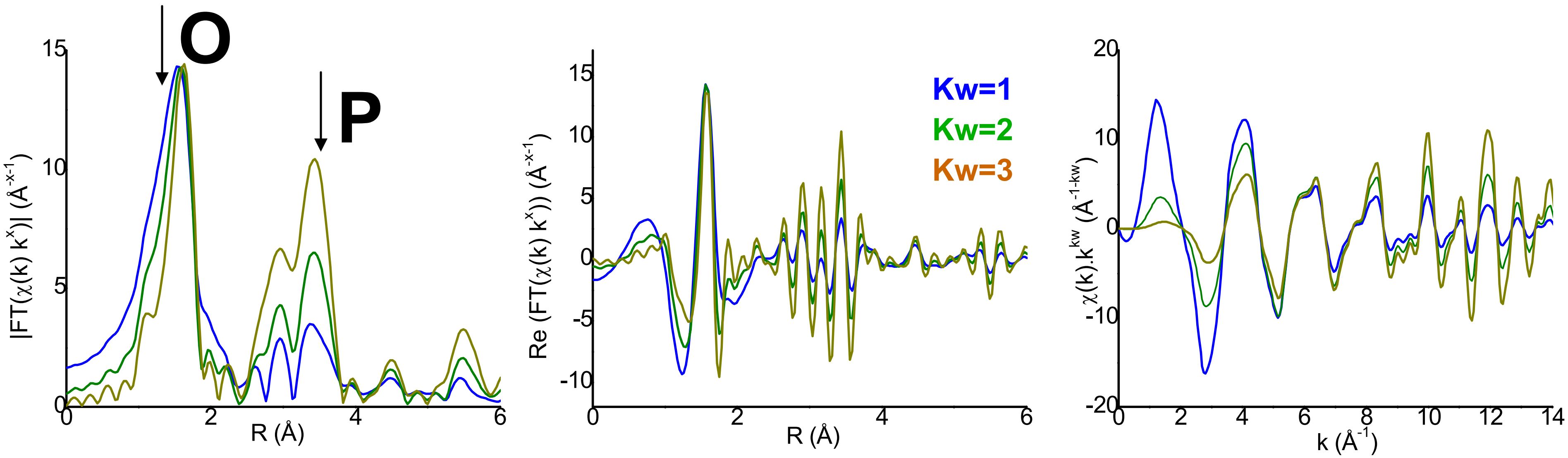


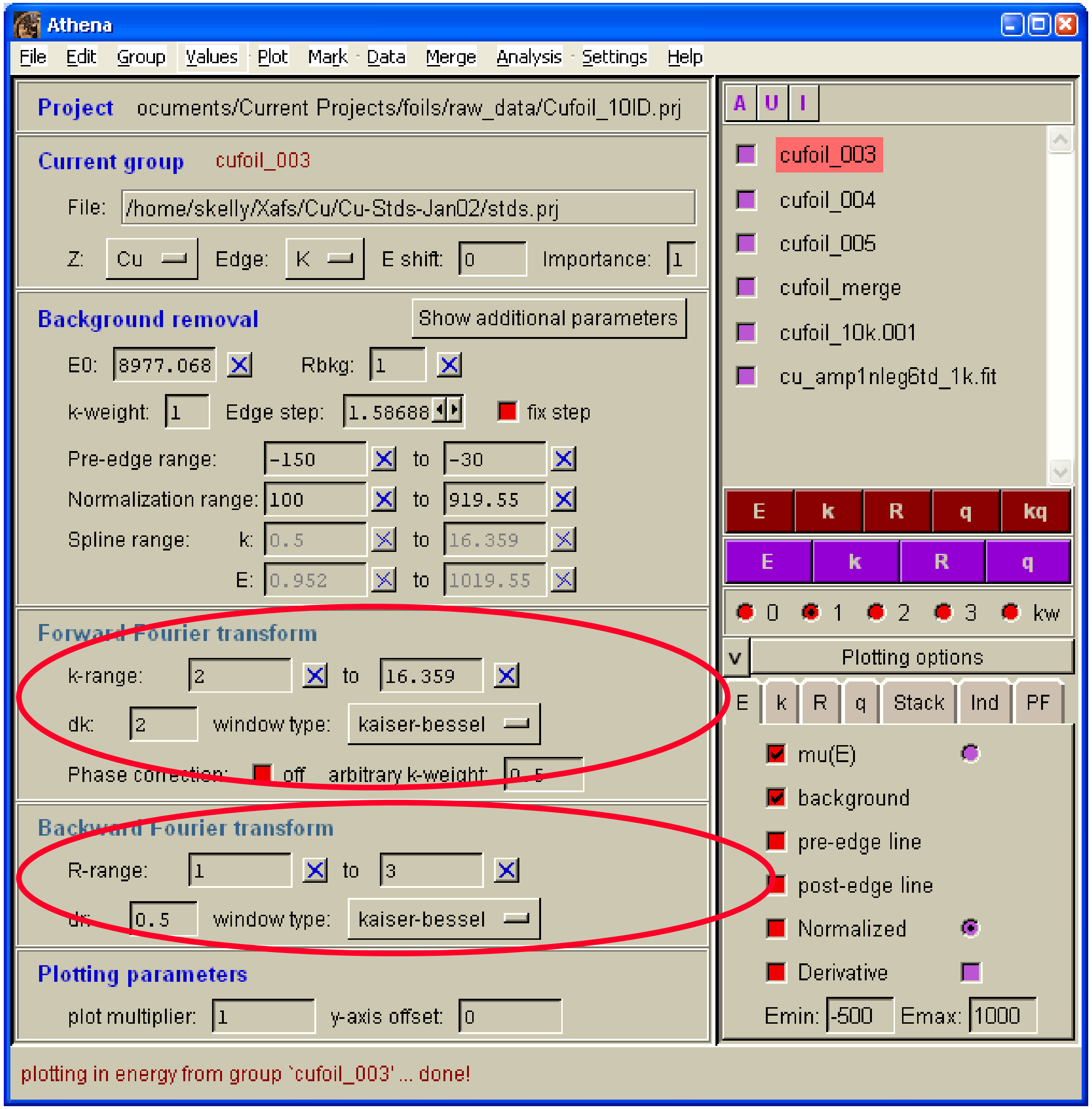
- The FT should be smooth and free of ringing
- To choose Kmax make vary the kmax value and plot the data using the largest k-weight that will be used in modeling
- Look for ringing in the real or imaginary part of FT
- In the example above kmax of 10 or 11 Å^{-1} best

Effect of K-weight on FT

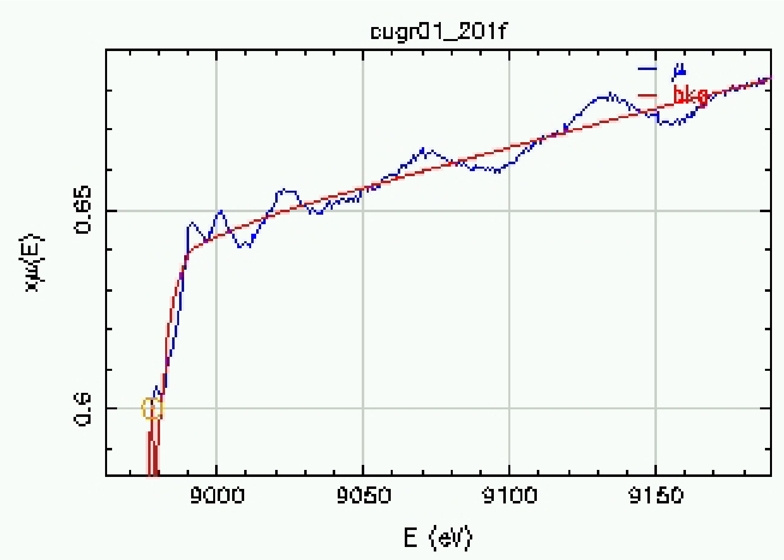


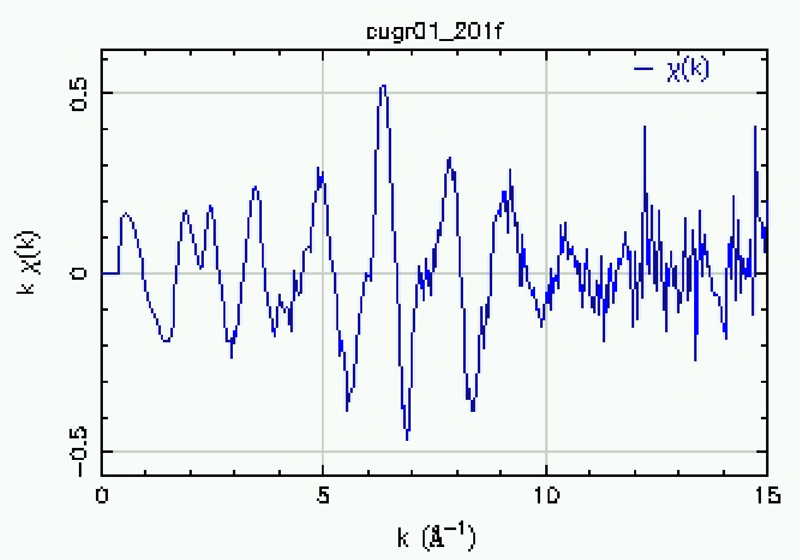
- These spectra have been k-weighted by 1, 2, and 3 and then rescaled so that the first peak in the FT are the same height
- The higher k-weight values give more importance to the data above 6 $Å^{-1}$, this emphasizes the signal due to the P neighbor relative to the O in the first shell

Fourier transform parameters in Athena



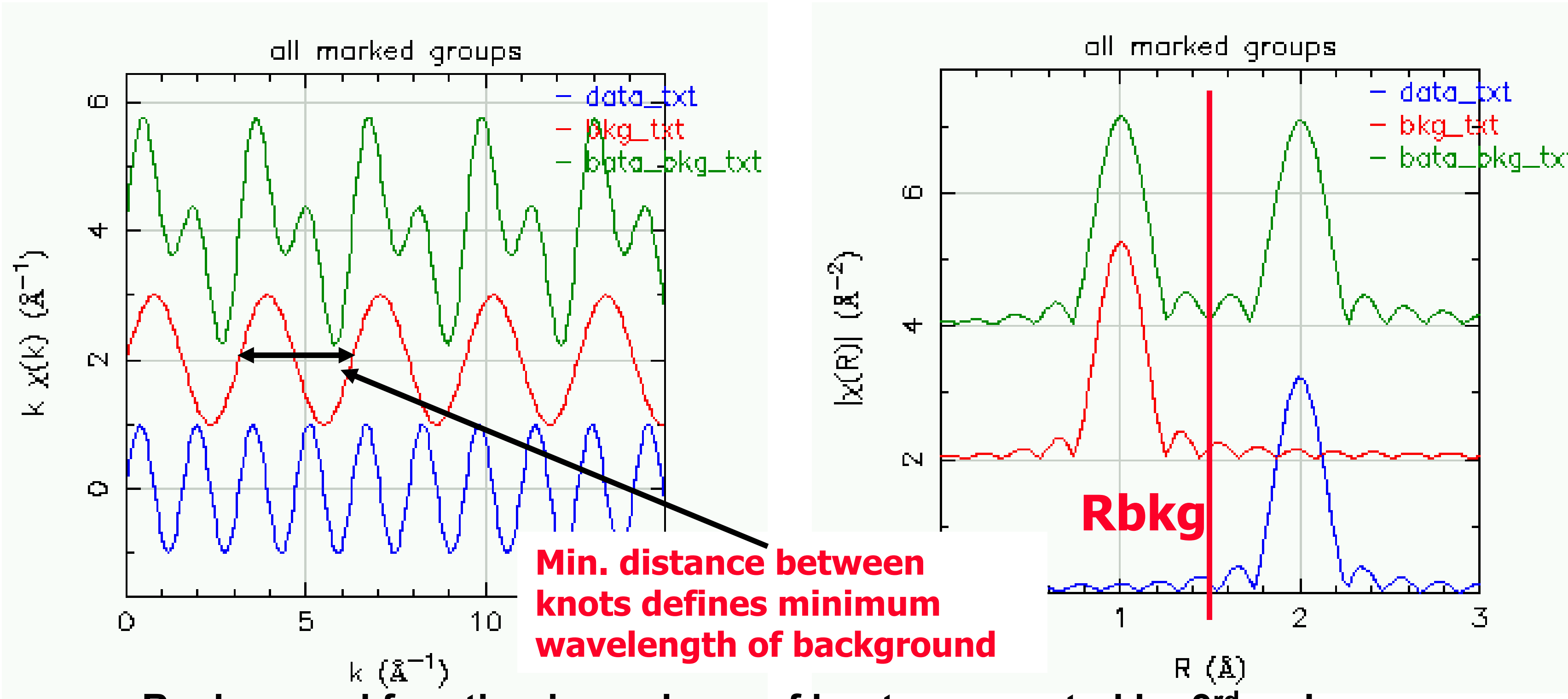
Background function overview





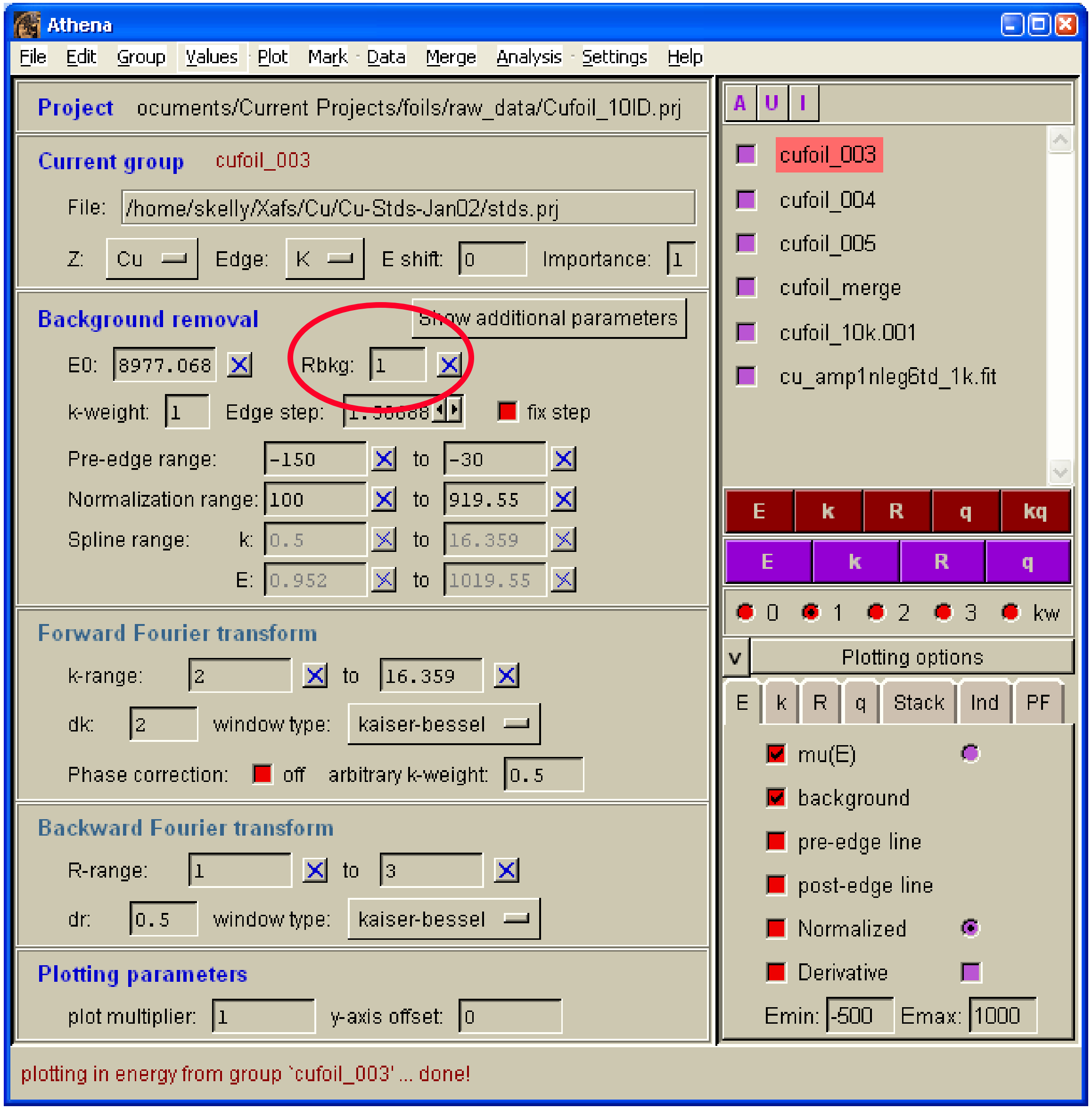
- A good background function removes long wavelength oscillations from $\chi(k)$.
- Constrain background so that it cannot contain oscillations that are part of the data.
- Long wavelength oscillations in $\chi(k)$ will appear as peaks in FT at low R-values
- FT is a frequency filter – use it to separate the data from the background!

Separating the background function from the data using Fourier transform

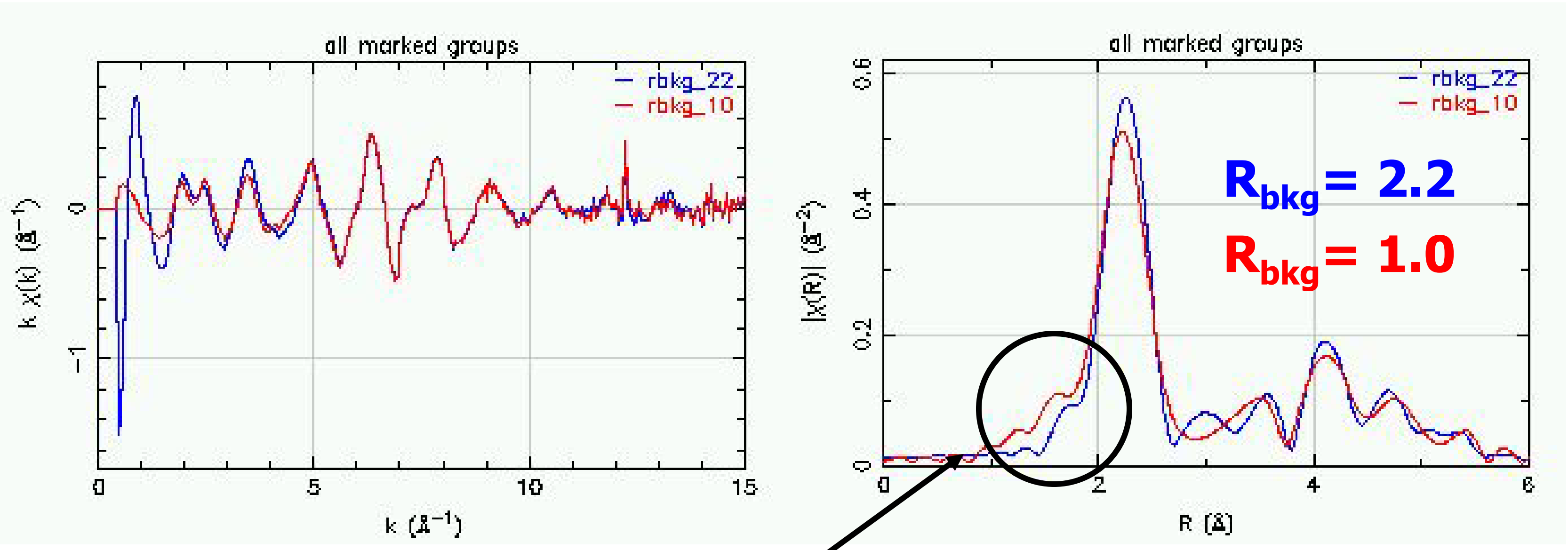


- Background function is made up of knots connected by 3rd order splines.
- Distance between knots is limited restricting background from containing wavelengths that are part of the data.
- The number of knots are calculated from the value for Rbkg and the data range in k-space.

Rbkg value in Athena



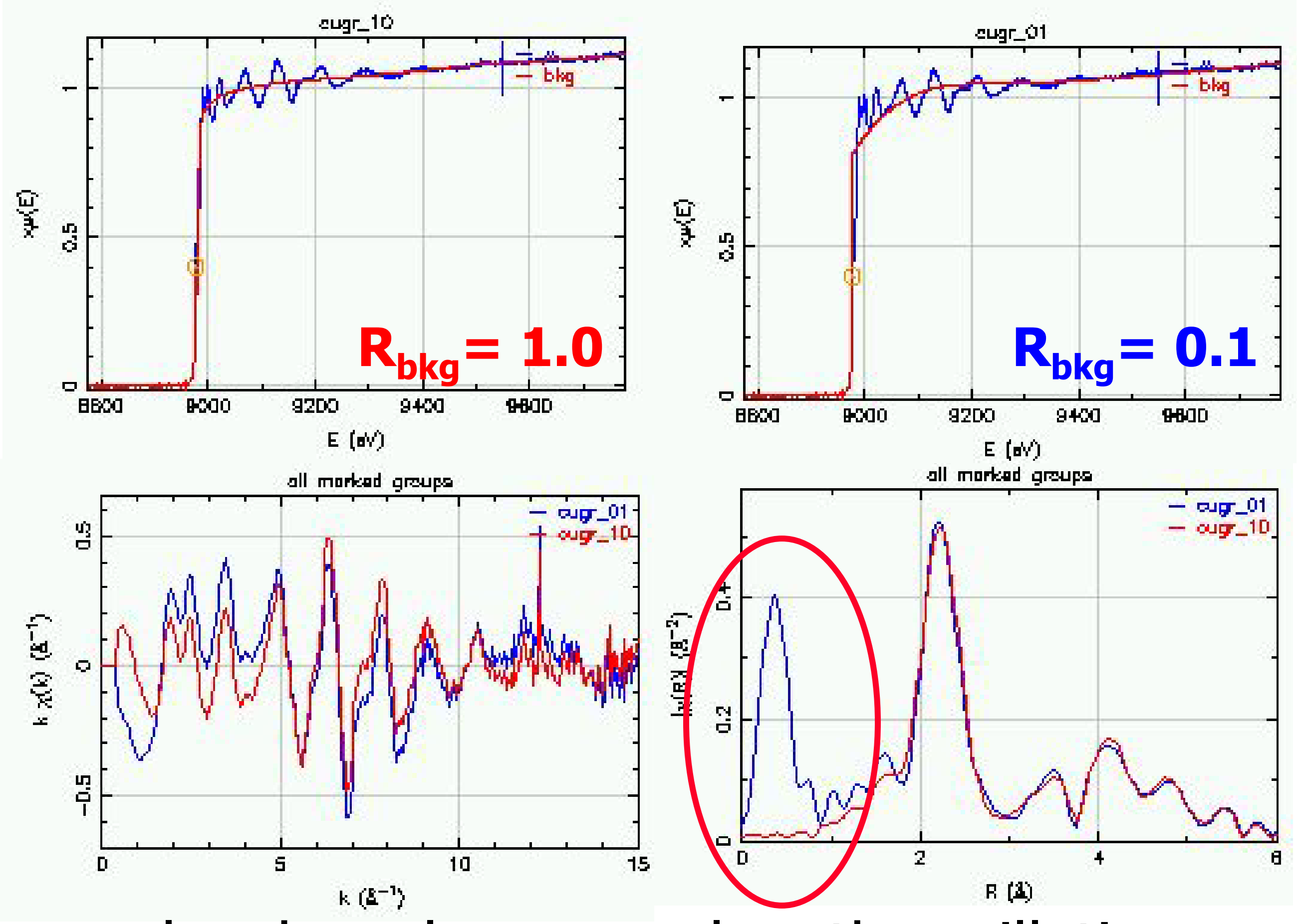
How to choose Rbkg value



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.

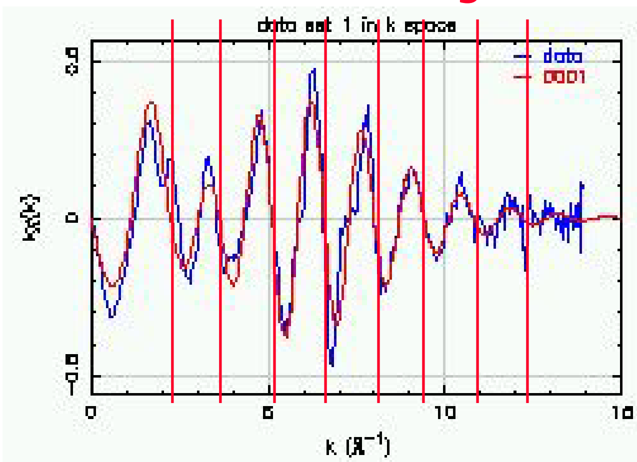
FT and Background function



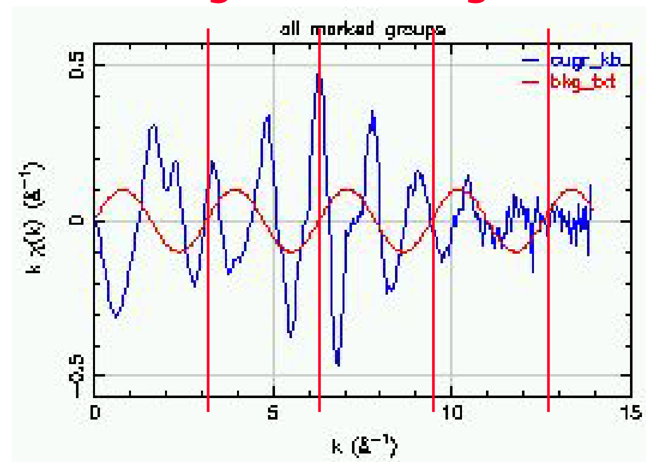
- An example where long wavelength oscillations appear as (false) peak in the FT

Frequency of Background function

Data contains this and shorter wavelengths

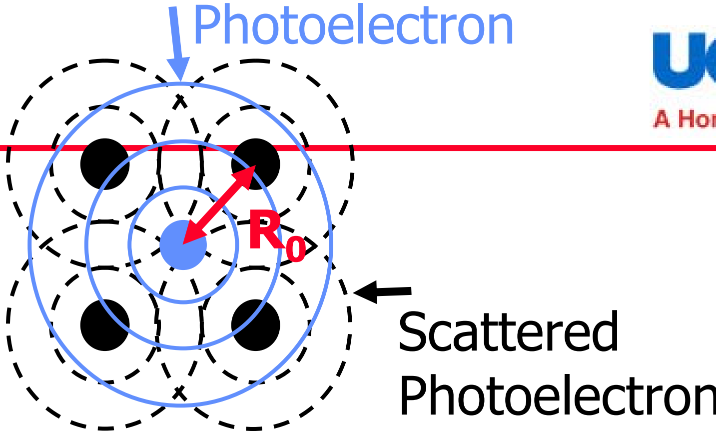


Bkg contains this and longer wavelengths



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

The EXAFS Equation



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

with

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

$$R_i = R_0 + \Delta R$$

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

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

$\mathbf{N_i}$ degeneracy of path

$\mathbf{S_0^2}$ passive electron reduction factor

σ_i^2 mean squared displacement of half-path length

$\mathbf{E_0}$ energy shift

$\Delta\mathbf{R}$ change in half-path length

More Information

- www.xafs.org

- Kelly, S D, Hesterberg, D and Ravel, B. Analysis of soils and minerals using X-ray absorption spectroscopy. In *Methods of soil analysis, Part 5 -Mineralogical methods*; Ulery, A. L., Drees, L. R., Eds.; Soil Science Society of America: Madison, WI, USA, 2008; pp 367.