Basics of EXAFS data analysis

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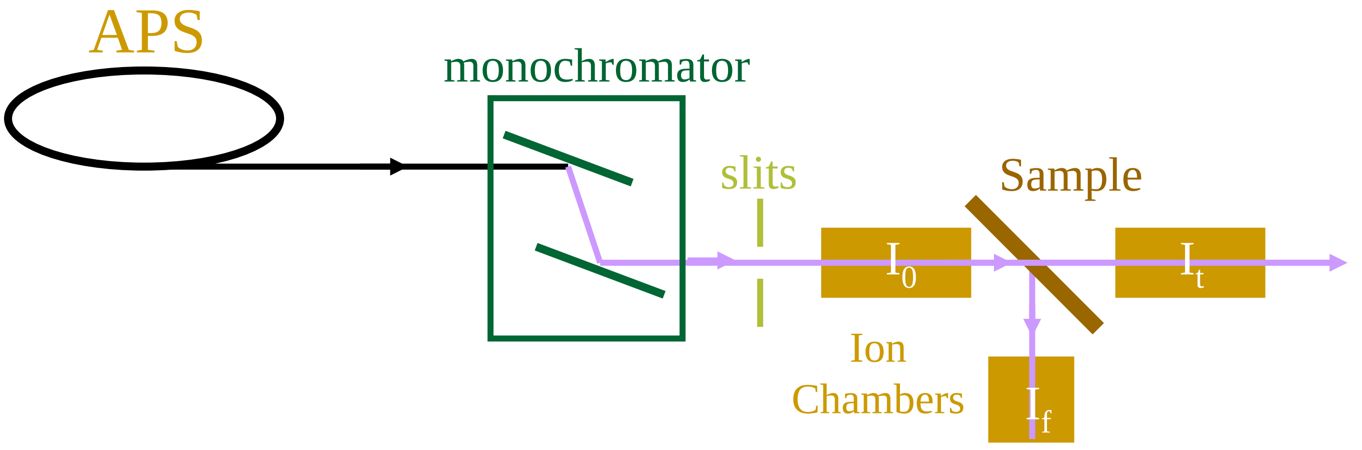
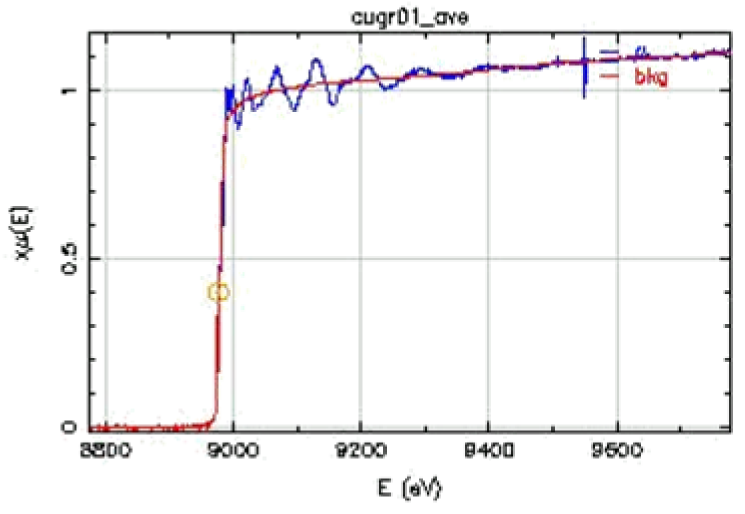
X-ray-Absorption Fine Structure





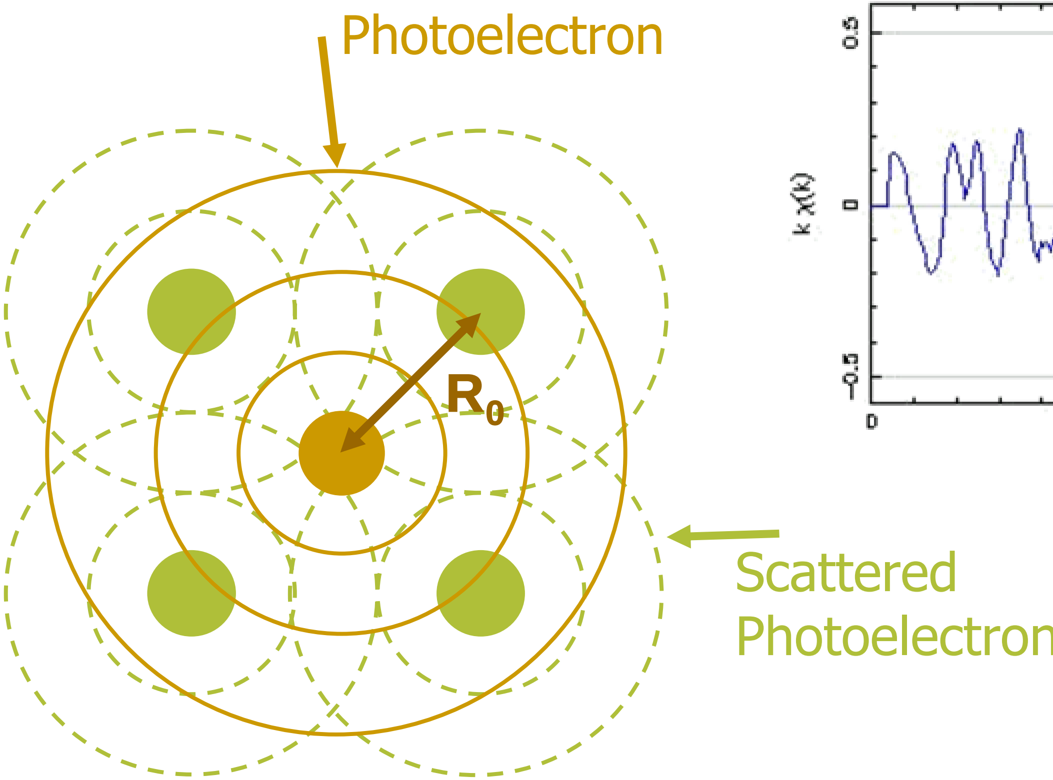
- Attenuation of x-rays

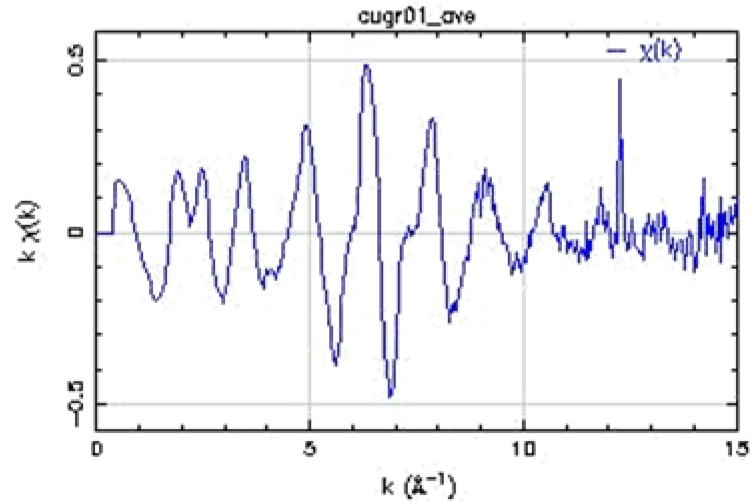
  $I_t = I_0 e^{-\mu(E) \cdot x}$

- Absorption coefficient

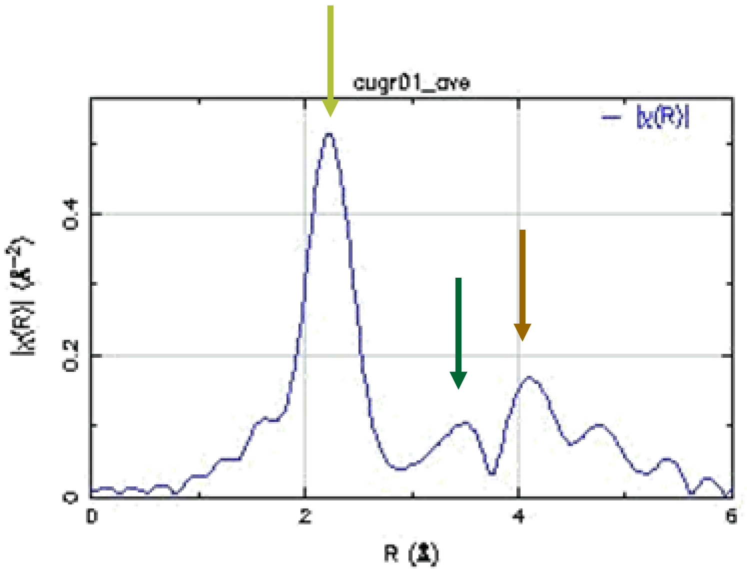
  $\mu(E) \propto I_f / I_0$

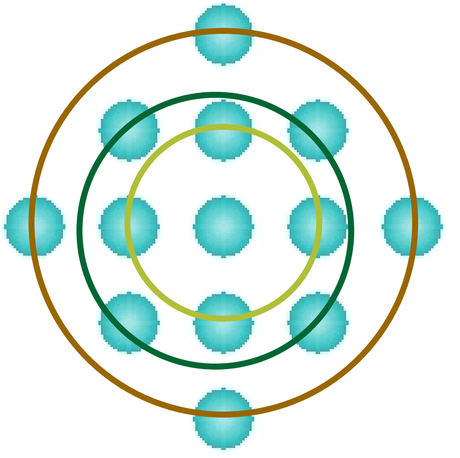
X-ray-Absorption Fine Structure





Fourier Transform of $\chi(k)$



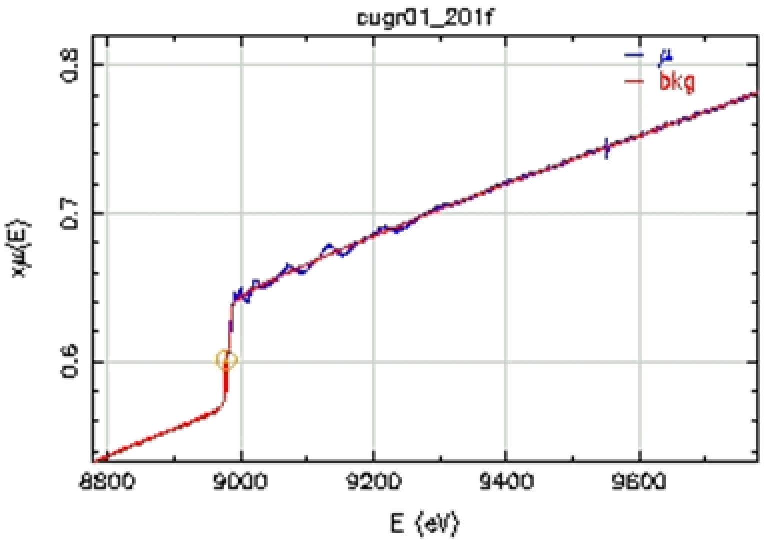


- **Similar to an atomic radial distribution function**
  - Distance
  - Number
  - Type
  - Structural disorder

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



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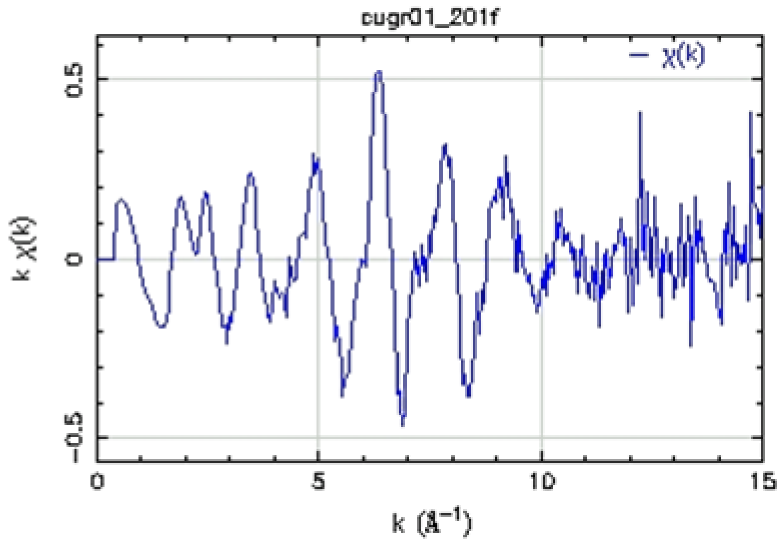


Normalized oscillatory part of absorption coefficient

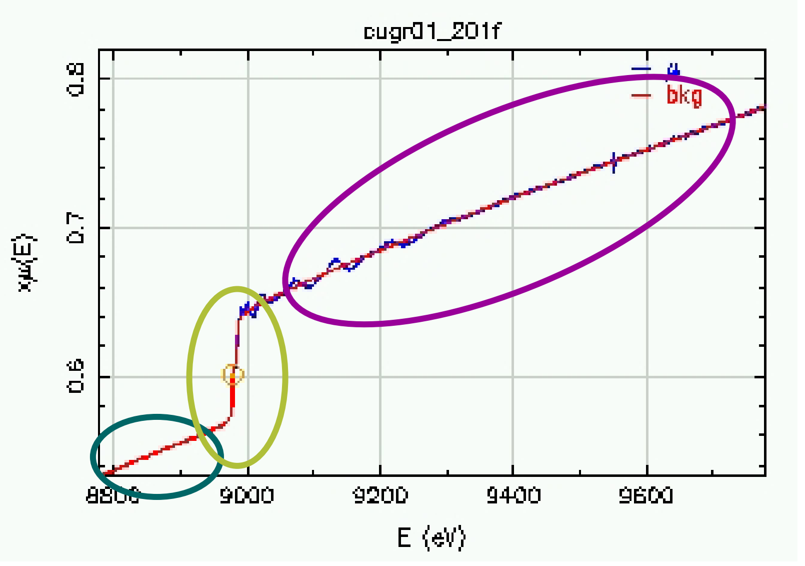
Measured Absorption coefficient

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

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

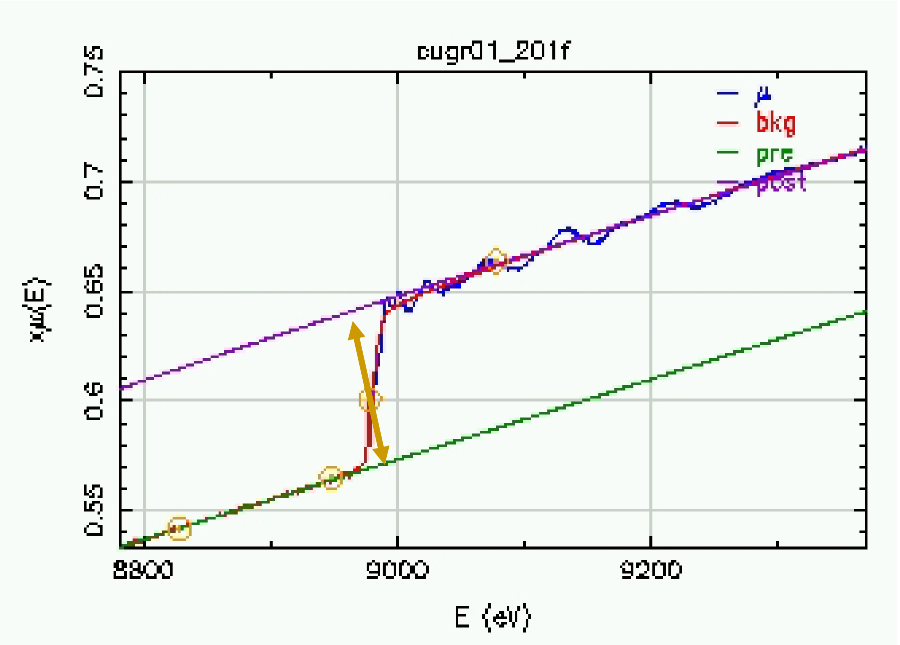
Evaluated at the Edge step (E_0)

Absorption coefficient



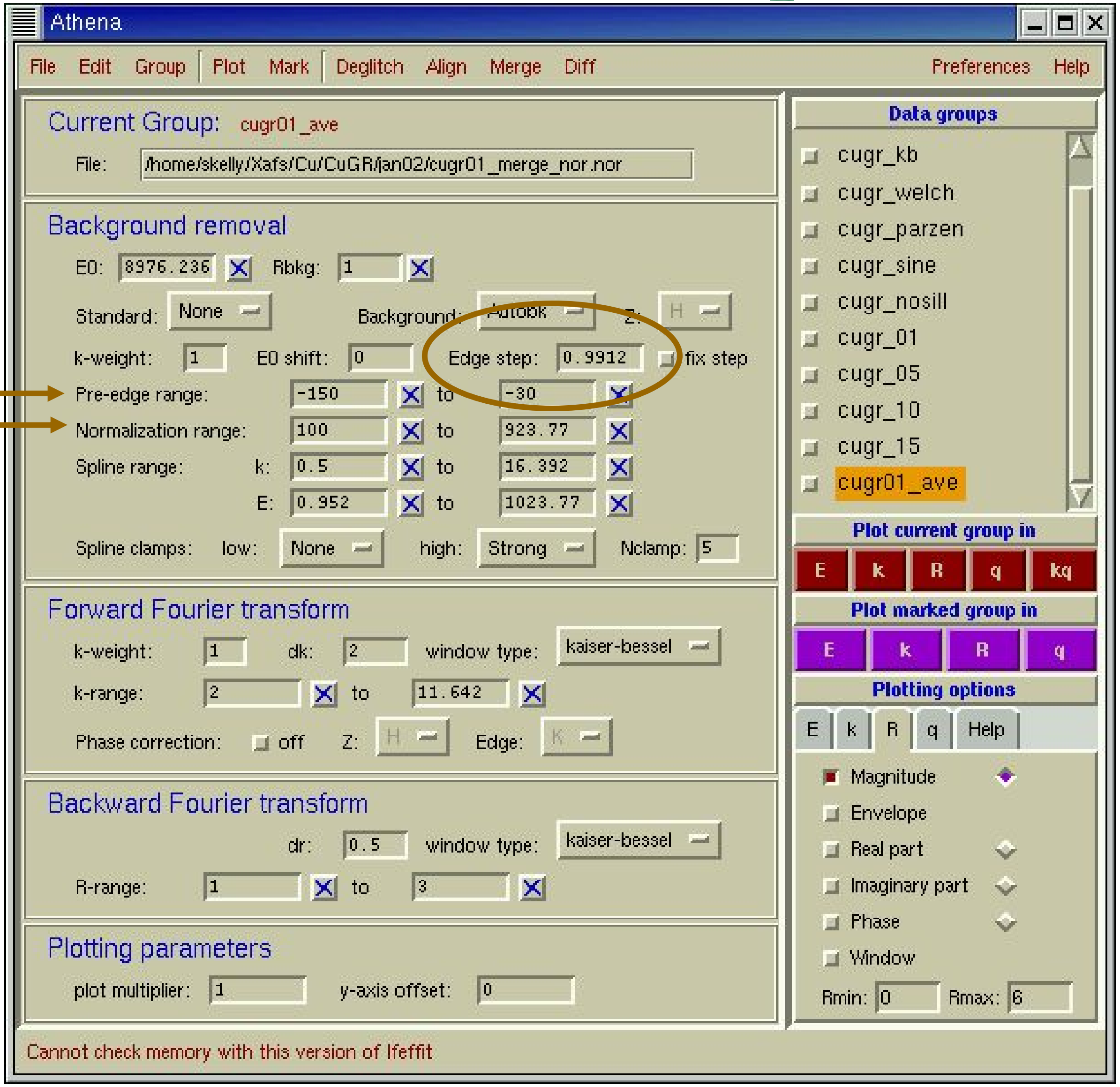
- **Pre-edge region** **300 to 50 eV before the edge**
- **Edge region** **the rise in the absorption coefficient**
- **Post-edge region** **50 to 1000 eV after the edge**

Edge step

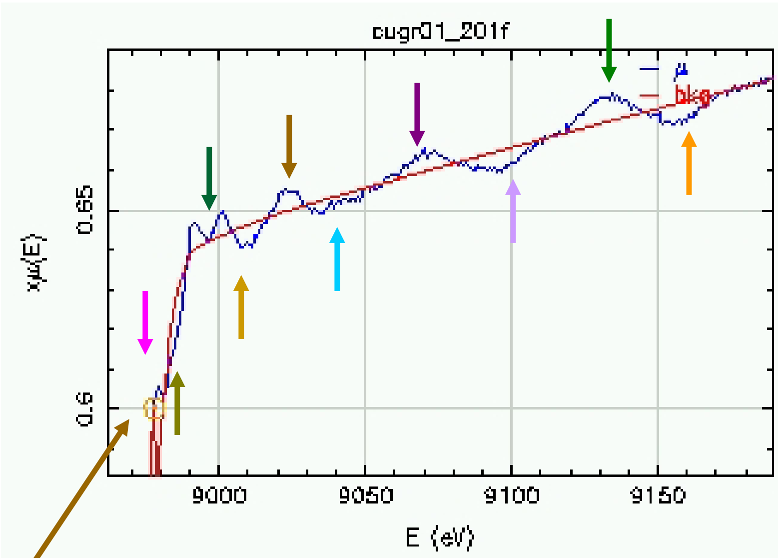


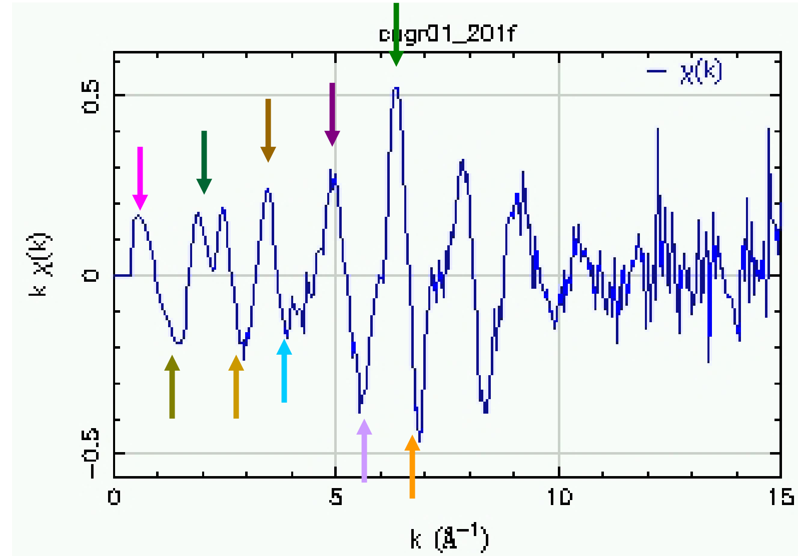
- **Pre-edge line** 200 to 50 eV before the edge
- **Post-edge line** 100 to 1000 eV after the edge
- **Edge step** the change in the absorption coefficient at the edge
  - Evaluated by taking the difference of the pre-edge and post-edge lines at E_0

Athena normalization parameters



Energy to wave number





E_0 **Must be somewhere on the edge**

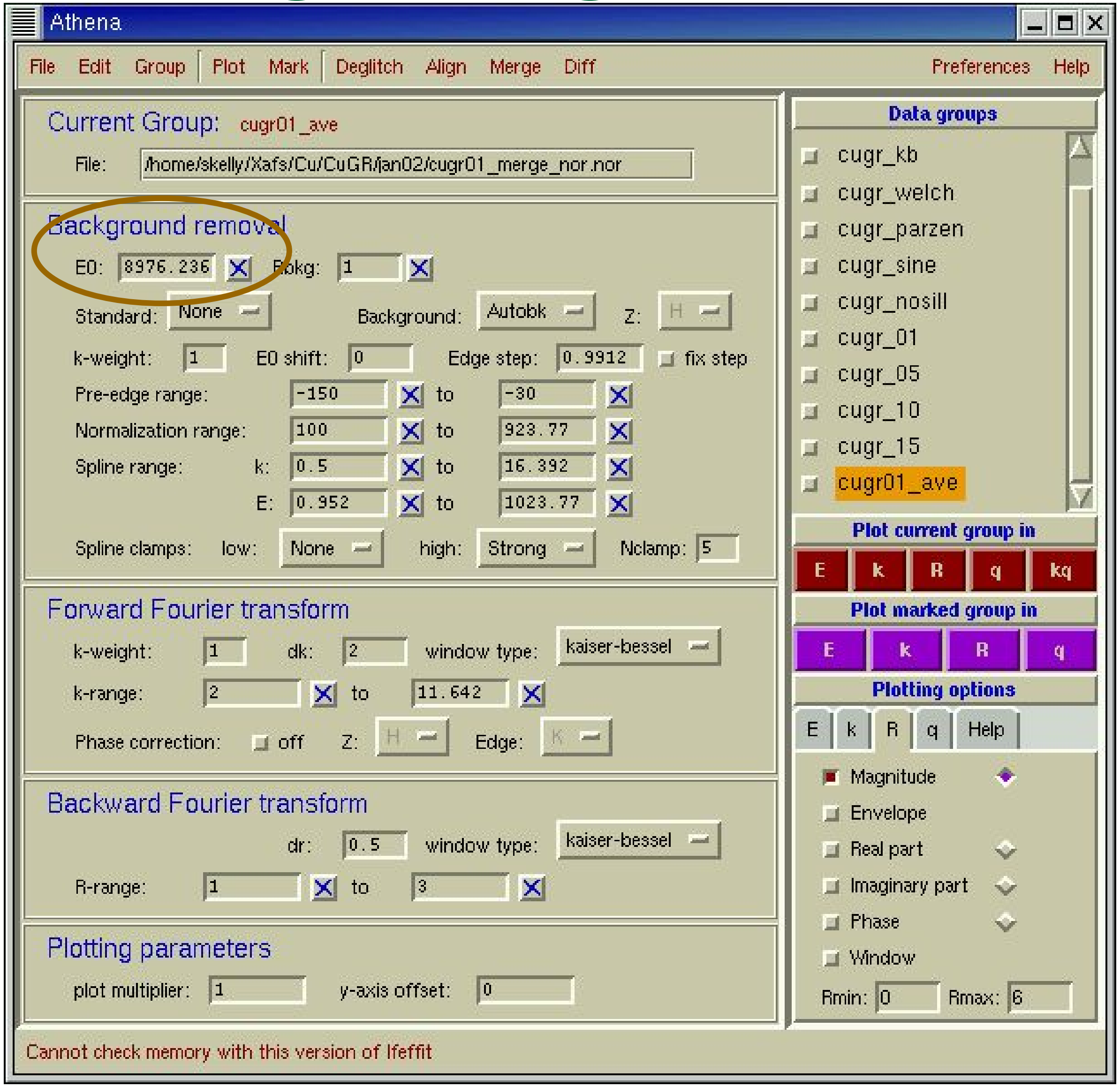
Mass of the electron

Edge Energy

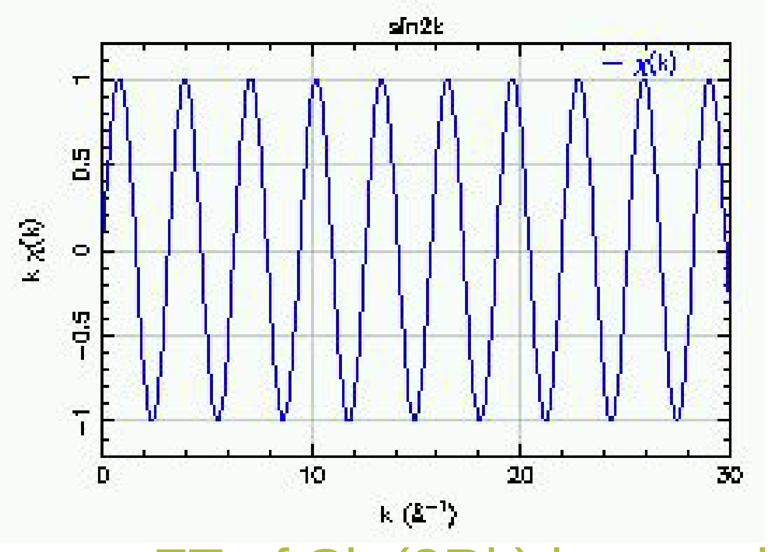
$$k^2 = \frac{2 m_e (E - E_0)}{\hbar} \sim \frac{\Delta E}{3.81}$$

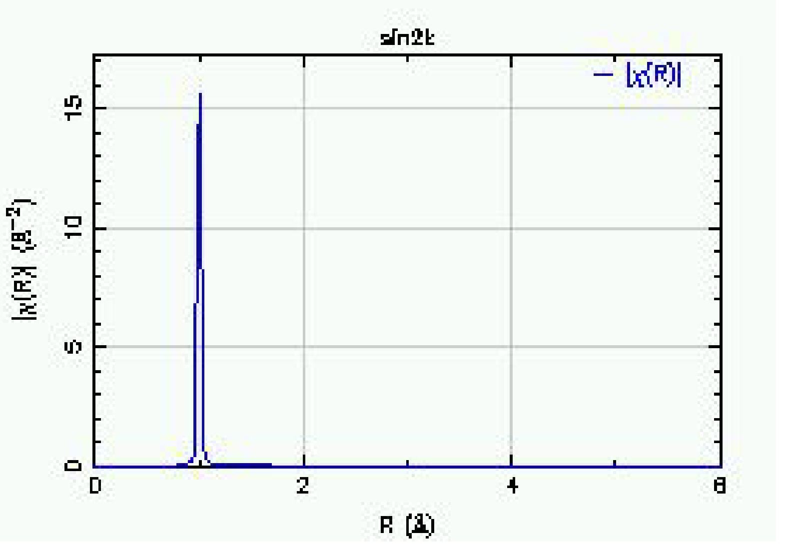
Plank's constant

Athena edge energy E0



Fourier Transform is a frequency filter

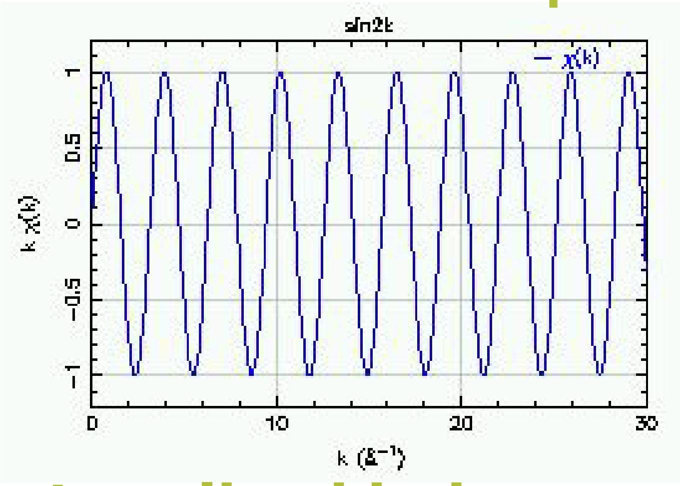


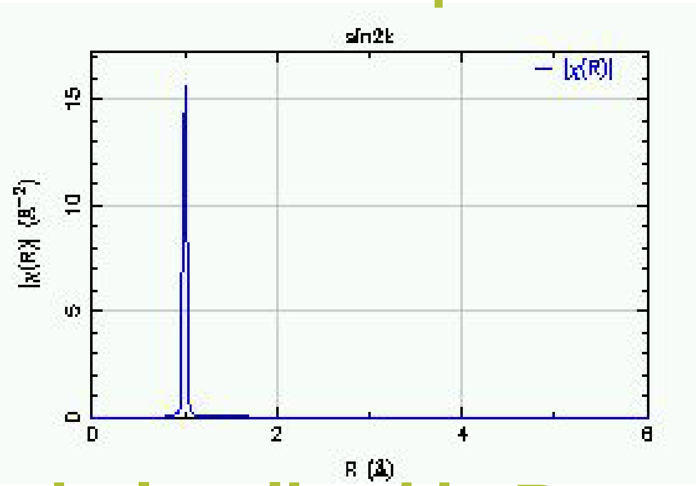


- FT of Sin(2Rk) is a peak at R=1
- FT of infinite sine wave is a delta function
- Signal that is de-localized in k-space is localized in R-space
- FT is a frequency filter

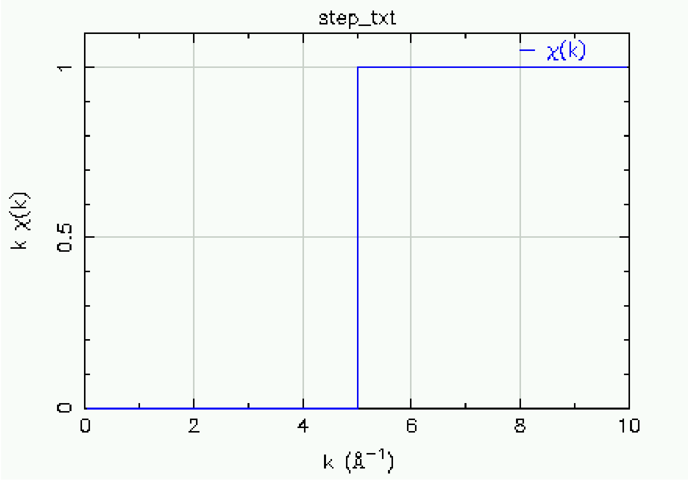
Fourier Transform of a function that is:

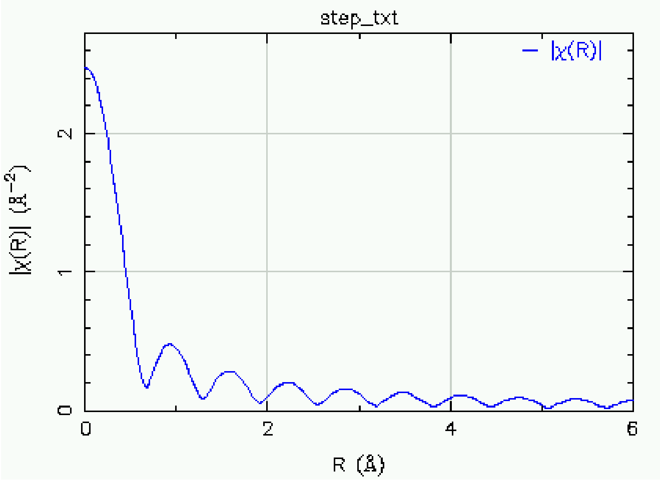
De-localized in k-space ⇒ localized in R-space



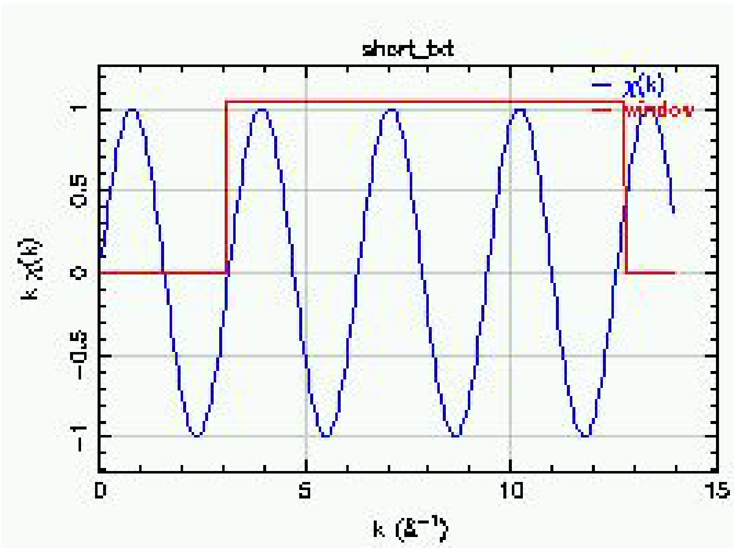


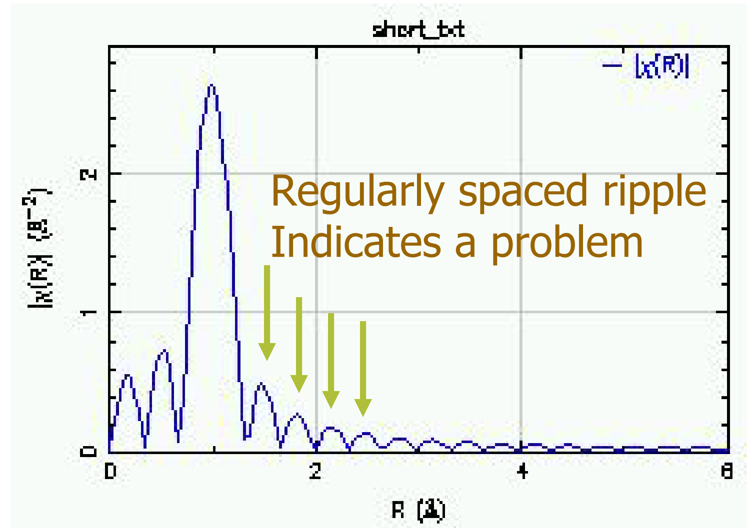
Localized in k-space ⇒ de-localized in R-space





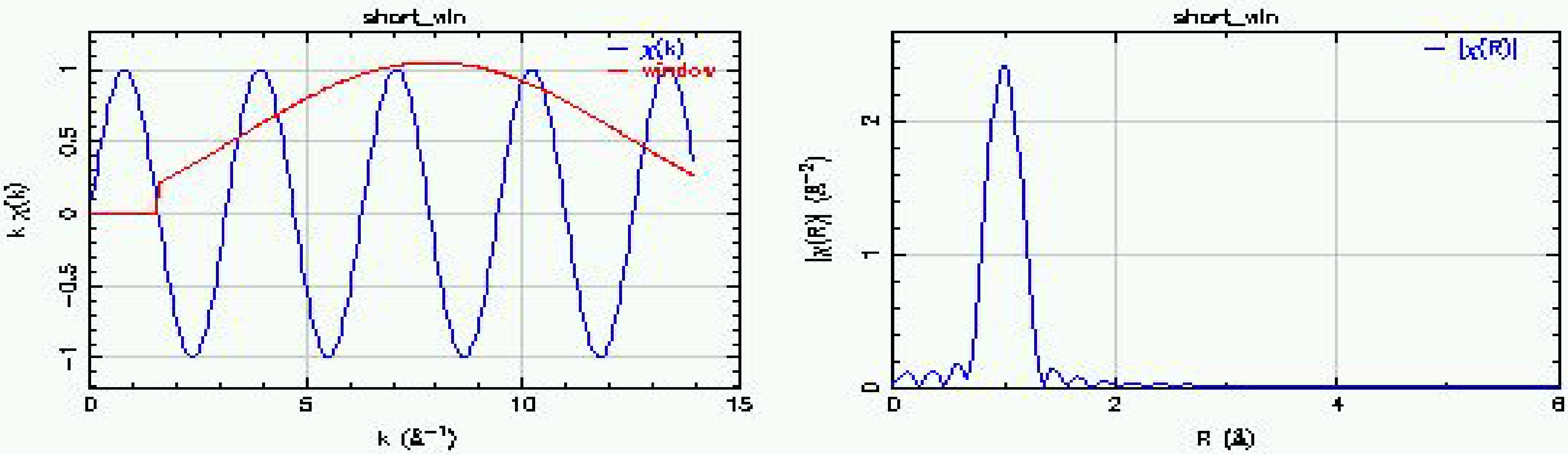
Fourier Transform is a frequency filter





- 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.

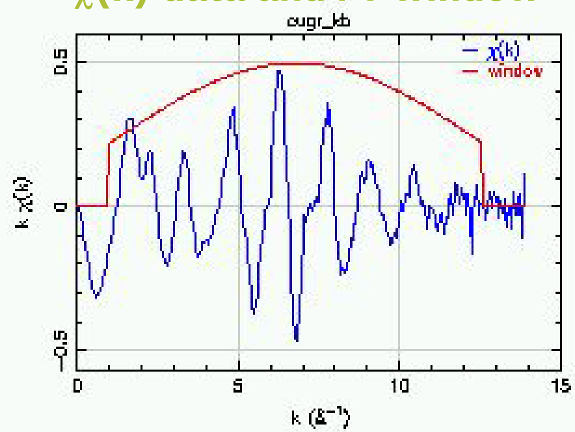
Fourier Transform



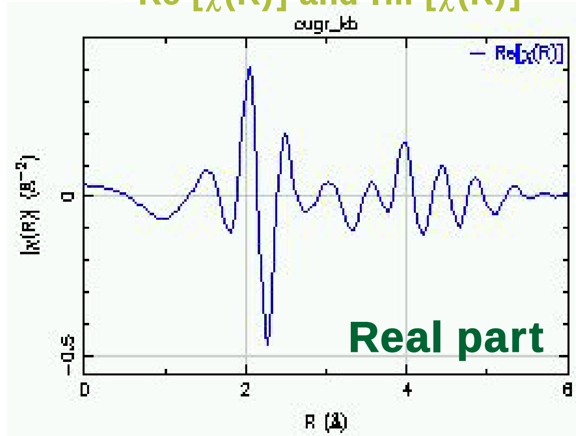
- Multiplying the discrete sine wave by a window that gradually increases the amplitude of the data smoothes the FT of the data.

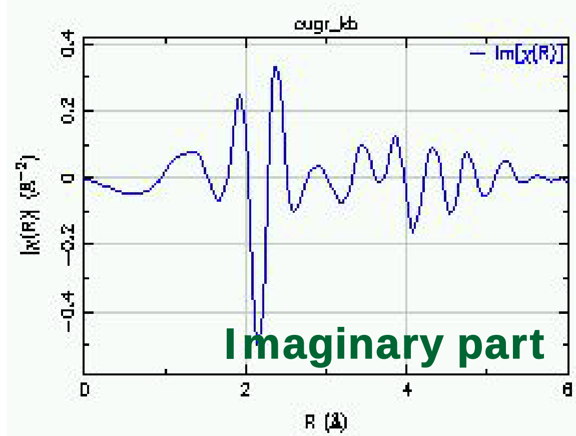
Fourier Transform parts

$\chi(k)$ data and FT window

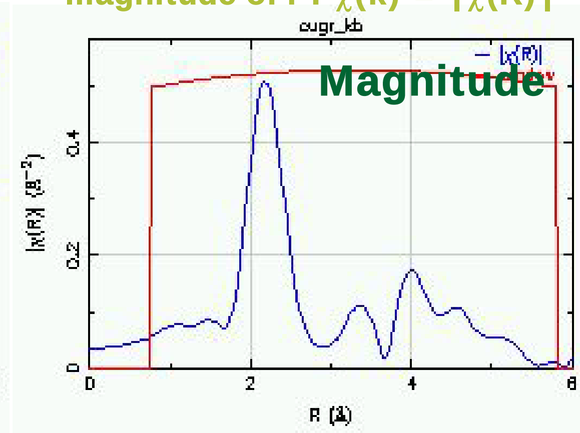


Real and imaginary parts of FT $\chi(k)$ = Re $[\chi(R)]$ and Im $[\chi(R)]$

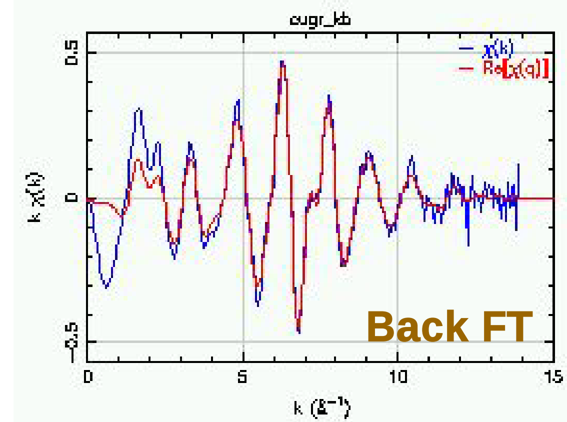




magnitude of FT $\chi(k)$ = $|\chi(R)|$

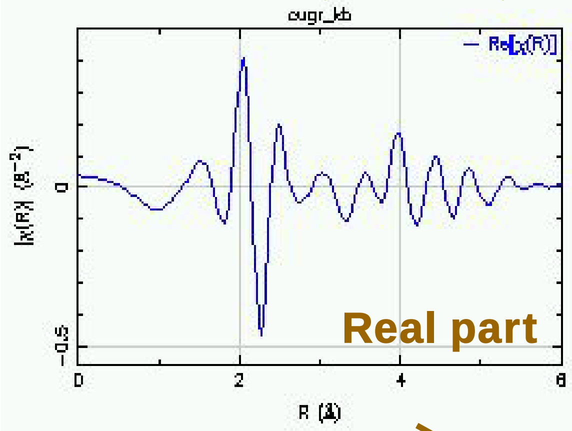


back FT of $\chi(R)$ = $\chi(q)$

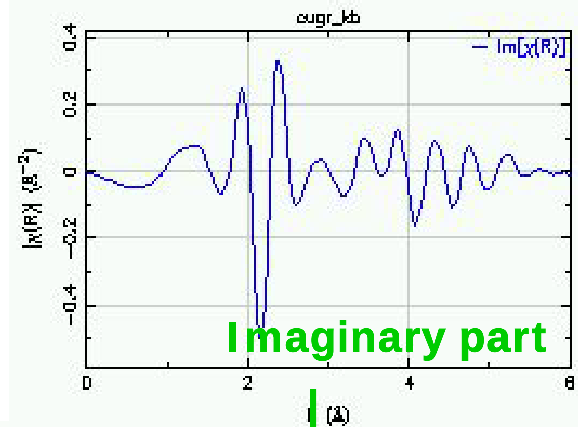


Understanding the different parts of FT

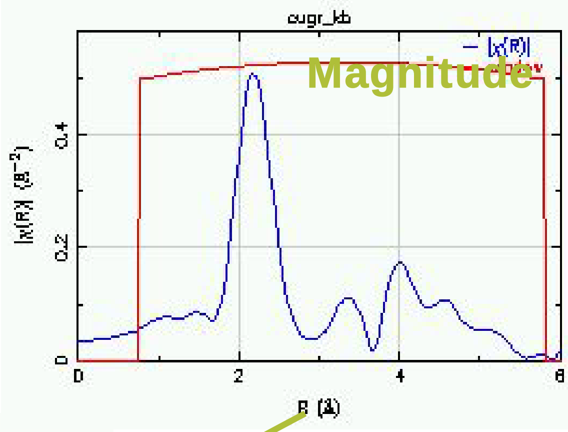
Real part of FT $\chi(k)$ = Re [$\chi(R)$]

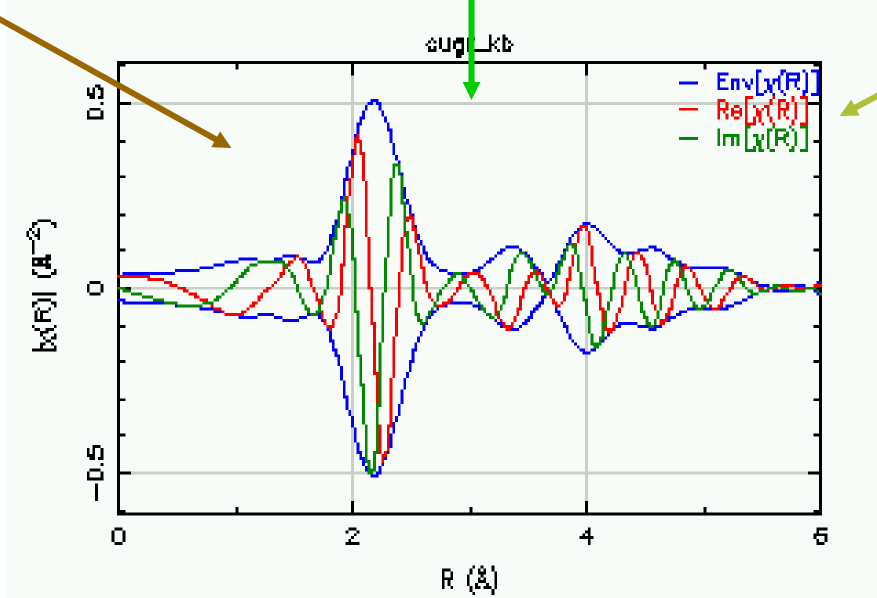


Imaginary part of FT $\chi(k)$ = Im [$\chi(R)$]



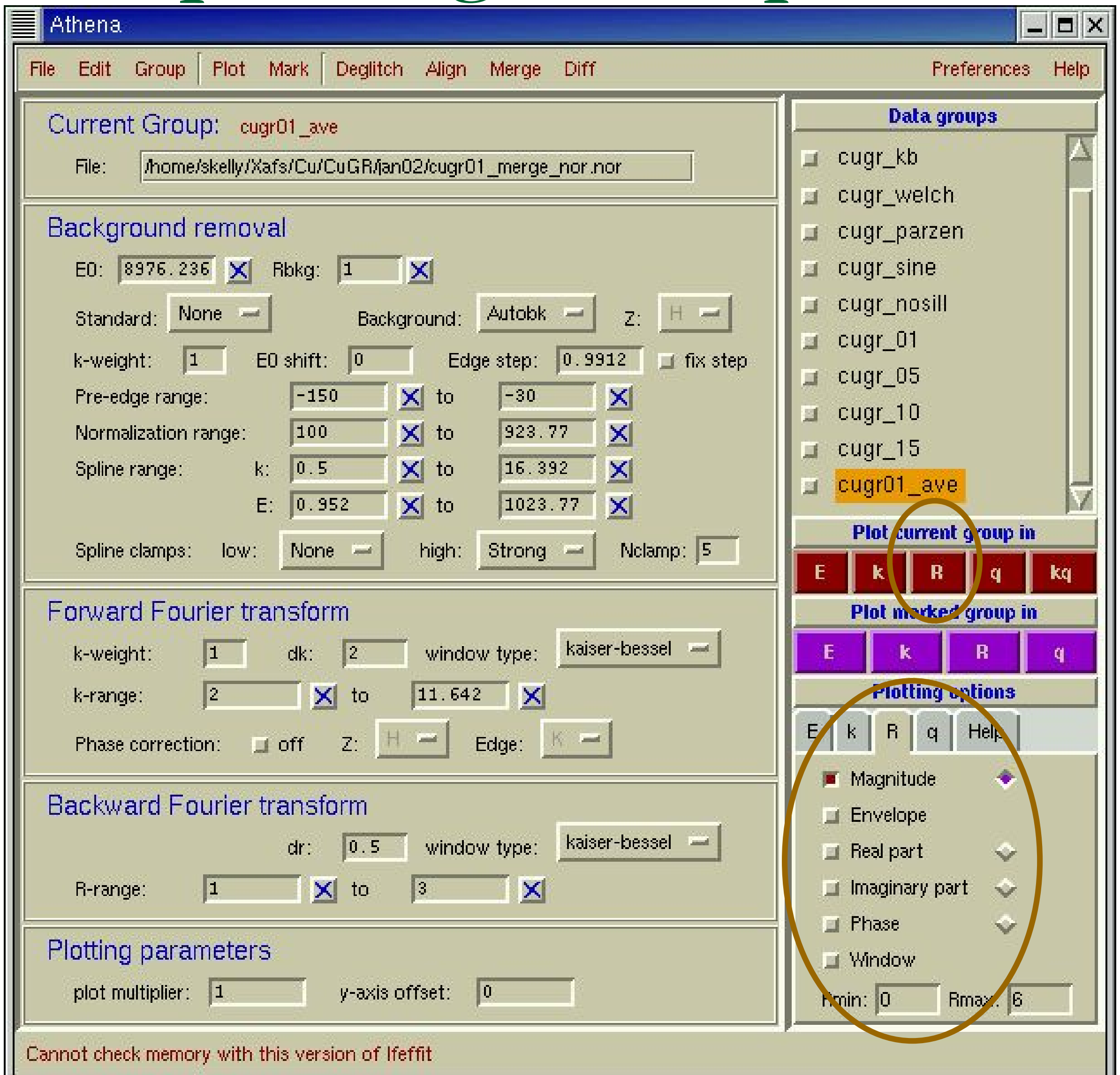
magnitude of FT $\chi(k)$ = |$\chi(R)$|



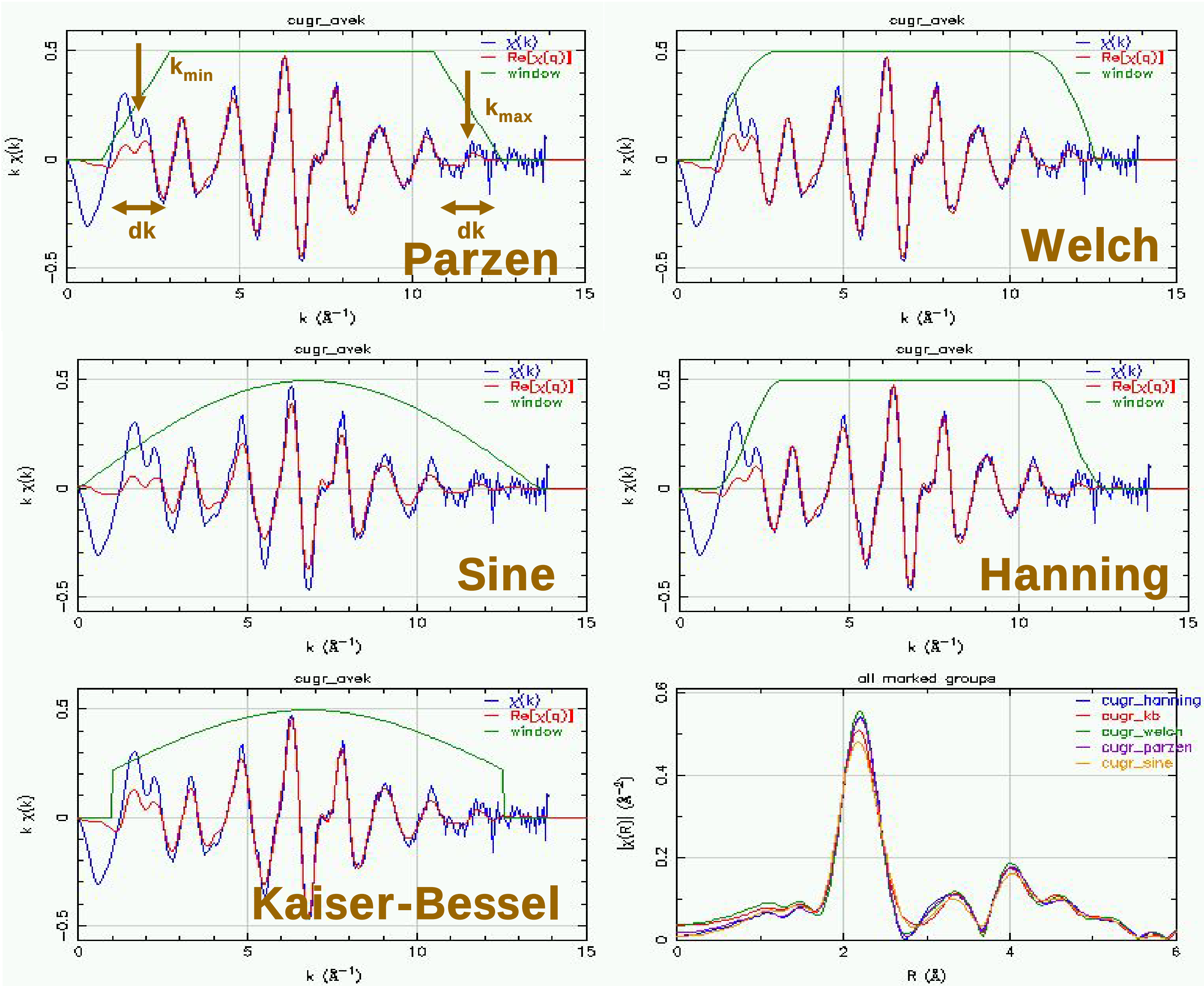


- |$\chi(R)$| is not unique. Information has been lost.

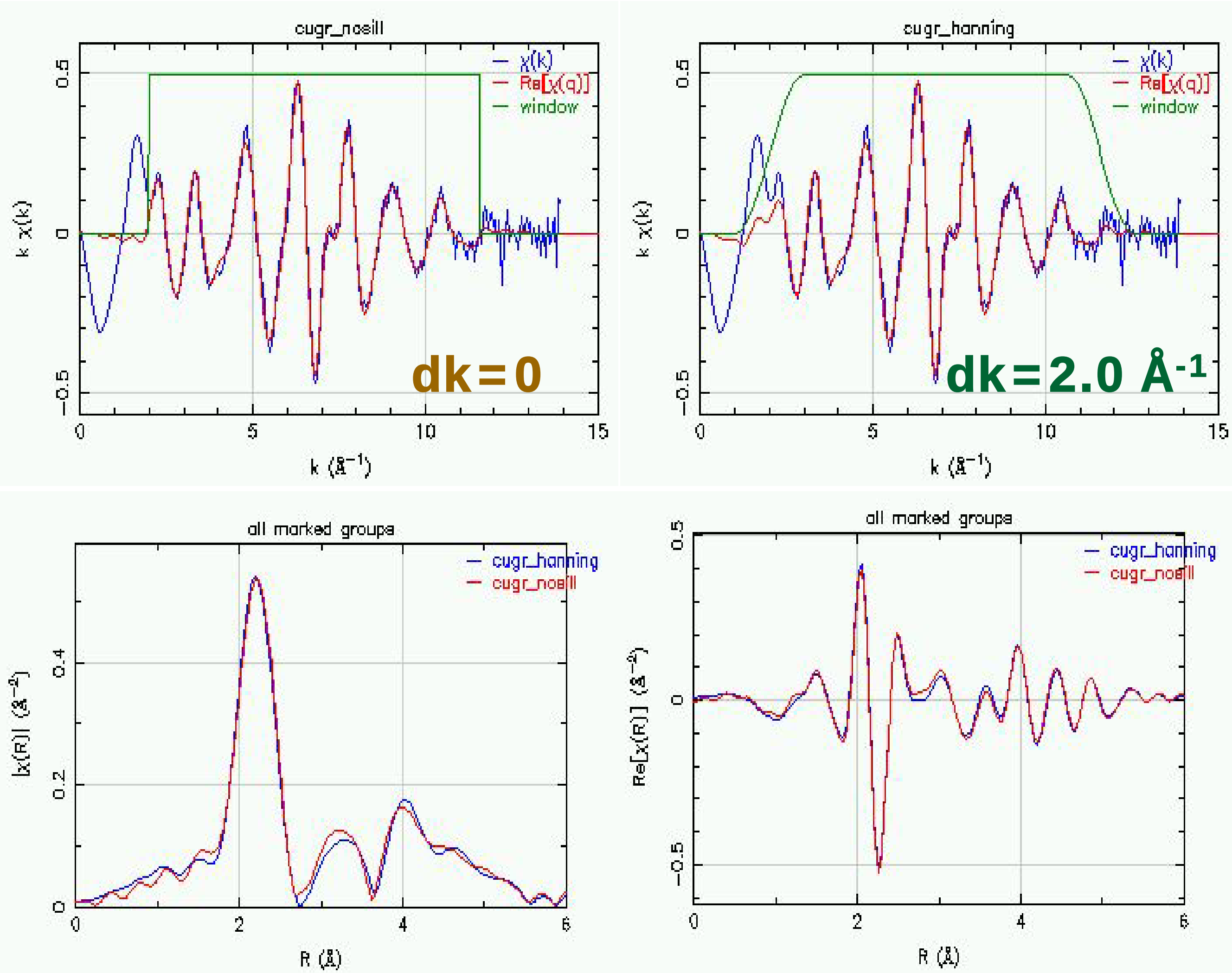
Athena plotting in R-space



Fourier Transform Windows

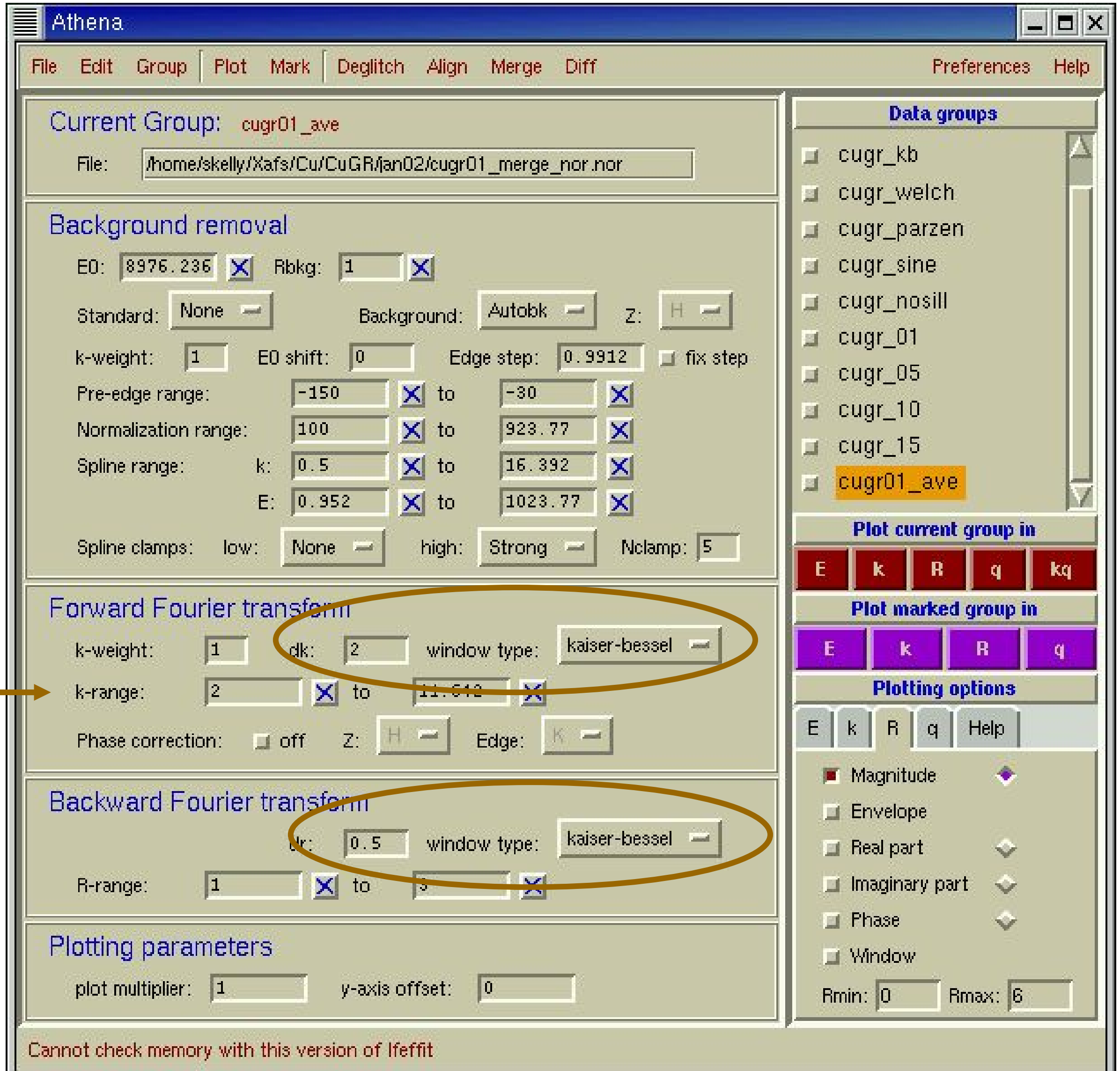


Fourier Transform window sill

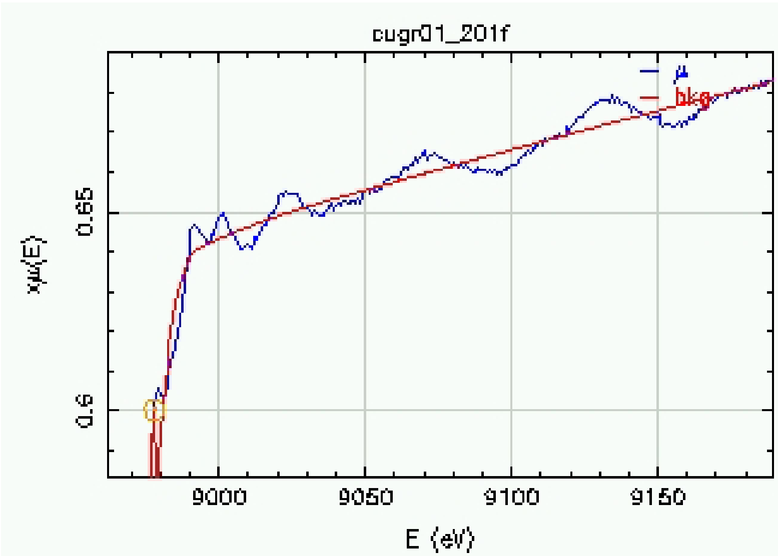


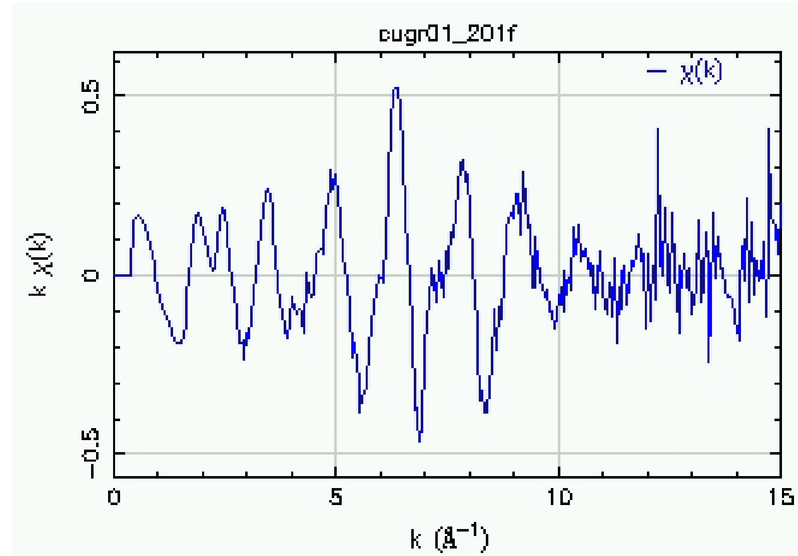
- A small sill can distort FT

Fourier transform parameters in Athena



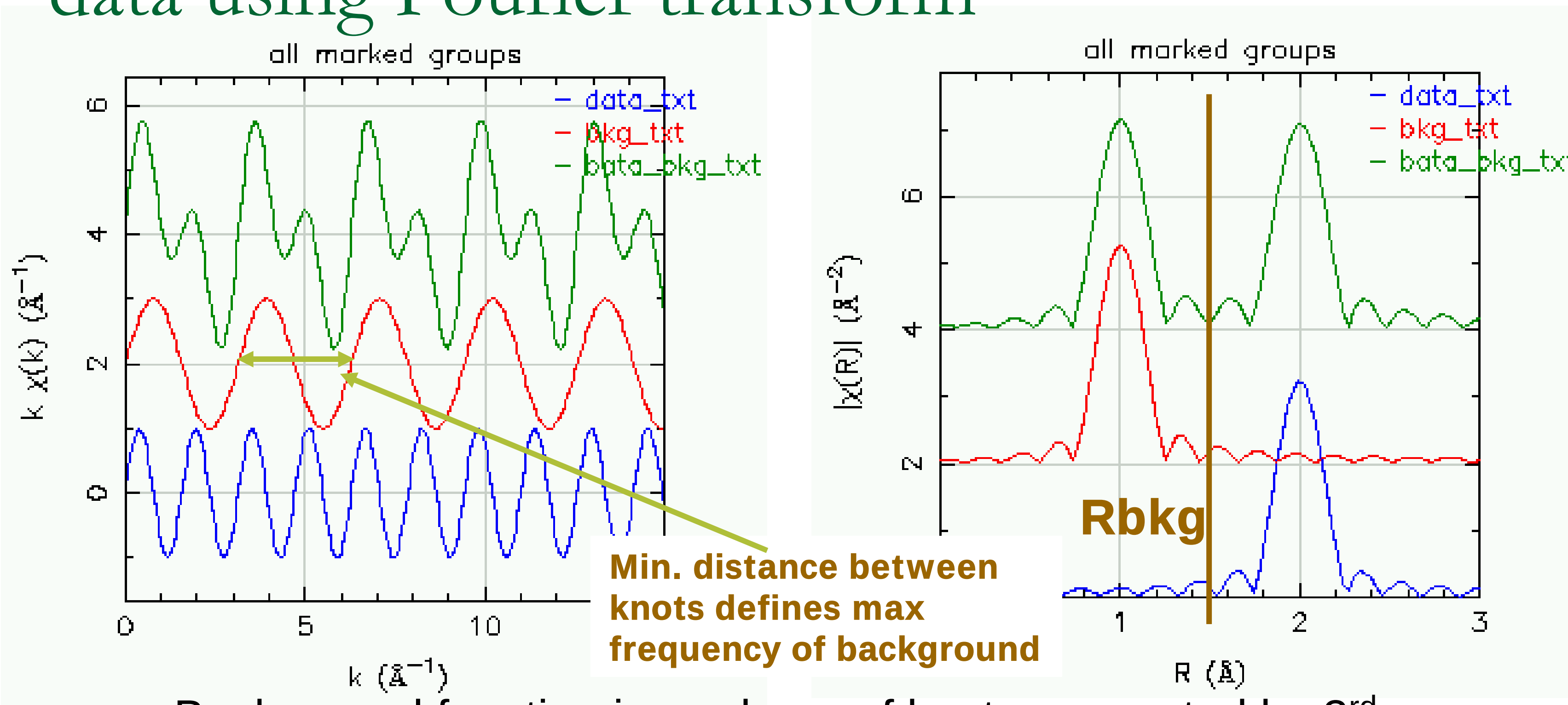
Background function overview





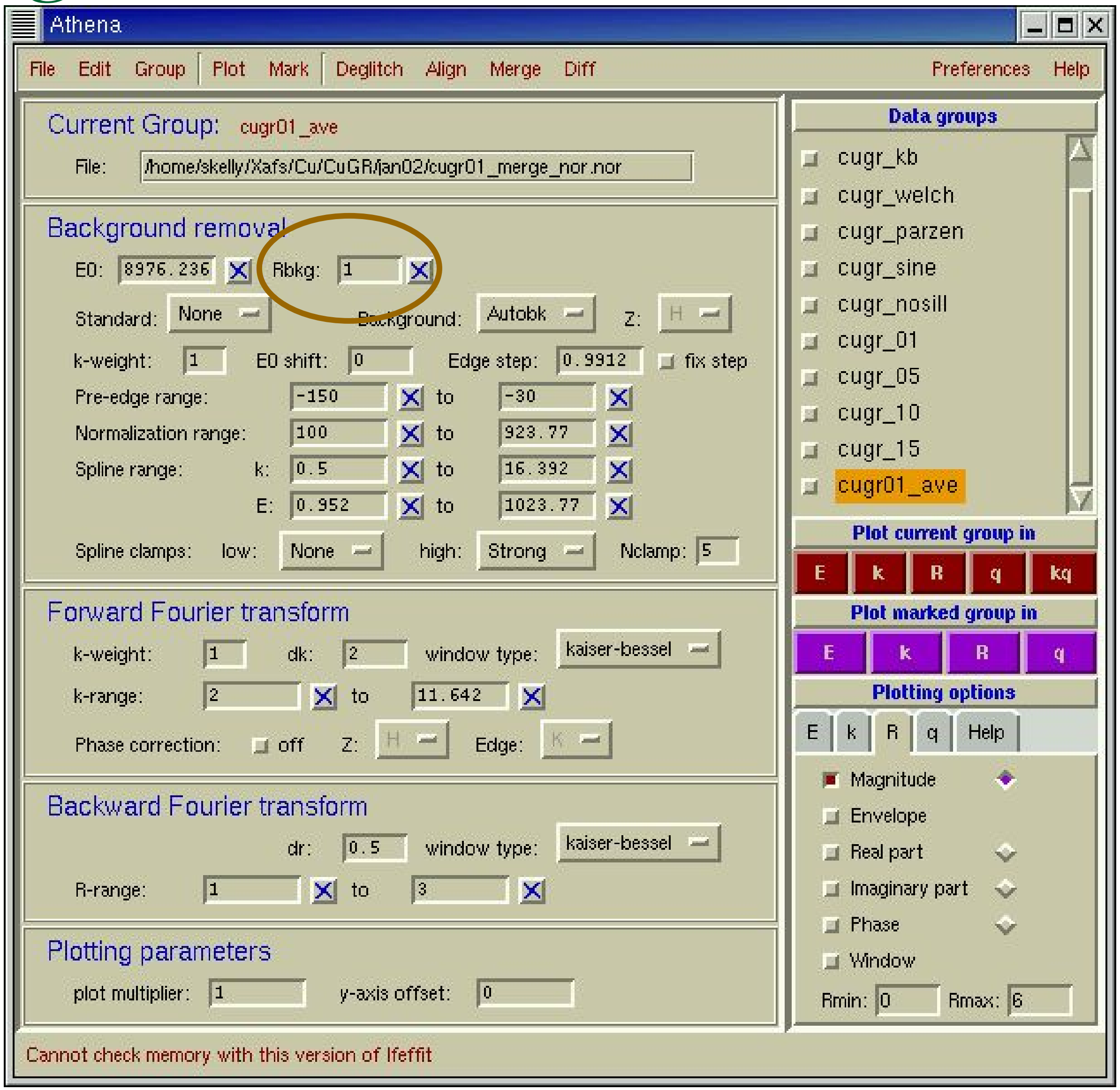
- A good background function removes long frequency oscillations from $\chi(k)$.
- Constrain background so that it cannot contain oscillations that are part of the data.
- Long frequency oscillations in $\chi(k)$ will appear as peaks in FT at low R-values
- FT is a frequency filter – use it to separate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

Separating the background function from the data using Fourier transform

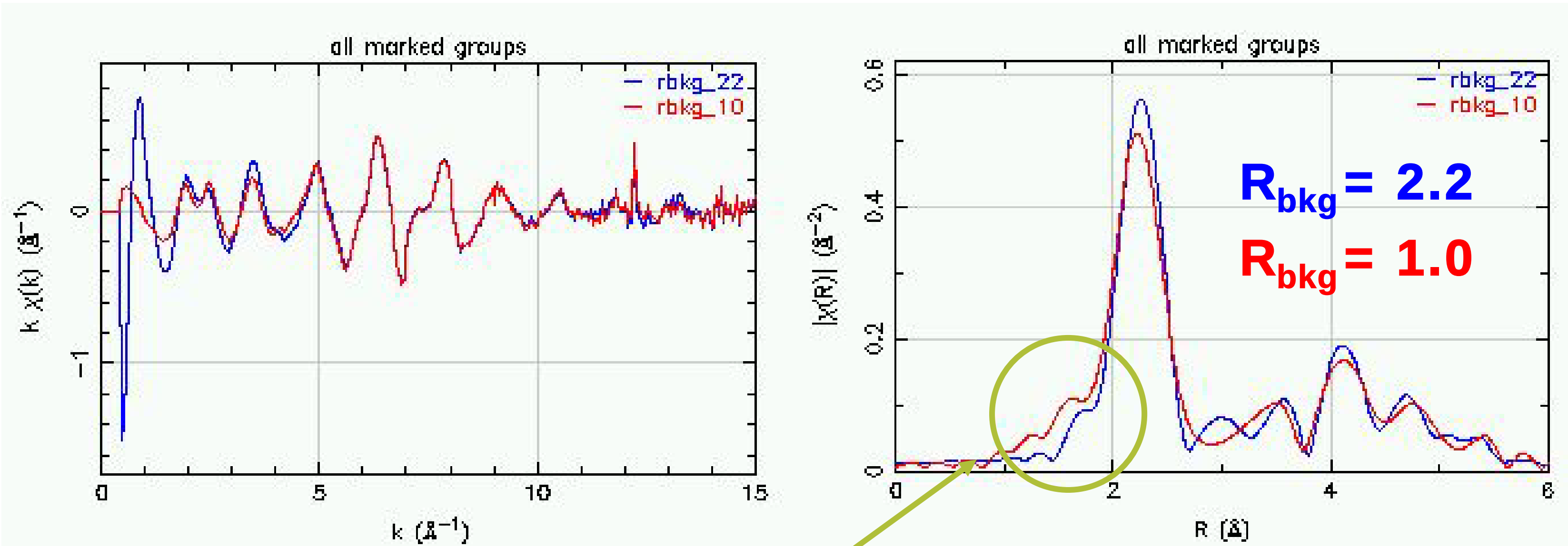


- Background function is made up of knots connected by 3rd order splines.
- Distance between knots is limited restricting background from containing frequencies that are part of the data.
- The number of knots are calculated from the value for Rbkg and the data range in k-space.

Rbkg value in Athena



How to choose Rbkg value

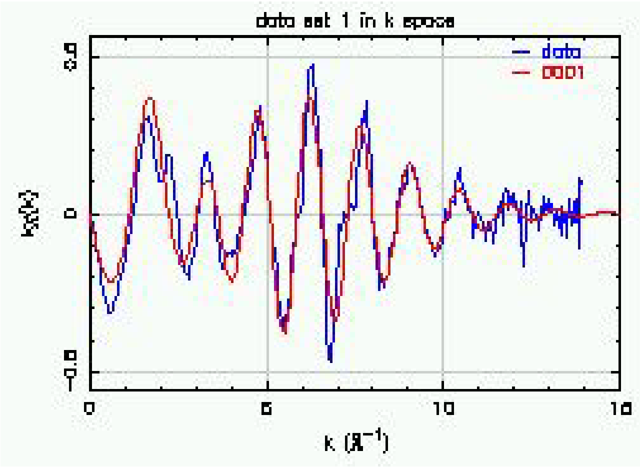


A Hint that Rbkg may be too large.
Data should be smooth, not pinched!

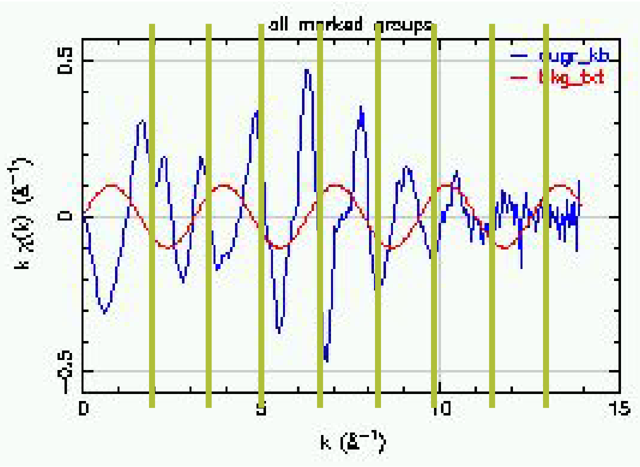
- An example where background distorts the first shell peak.
- R_{bkg} should be about half the R value for the first peak.

Frequency of Background function

Data contains this and shorter frequencies

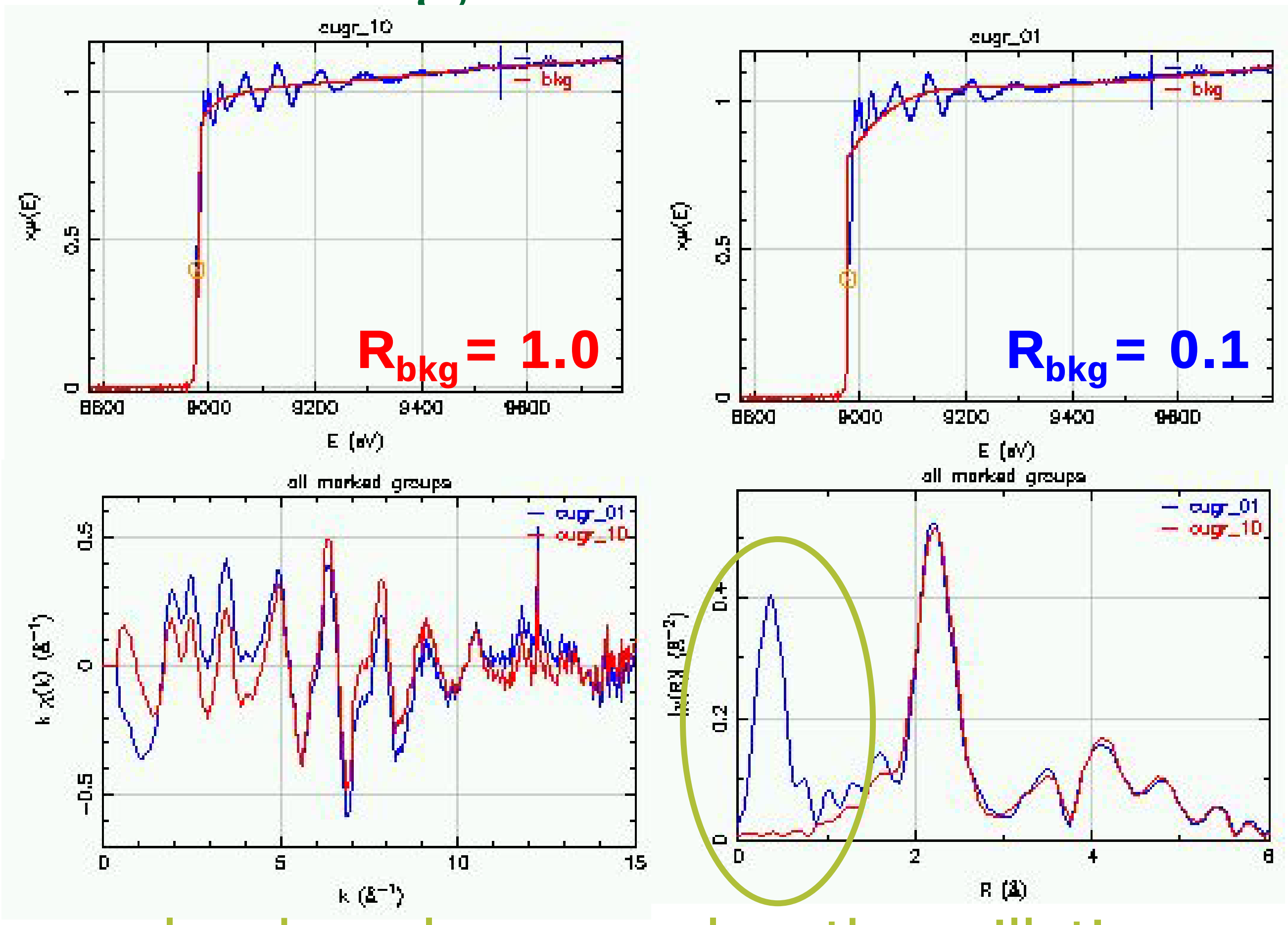


Bkg contains this and longer frequencies



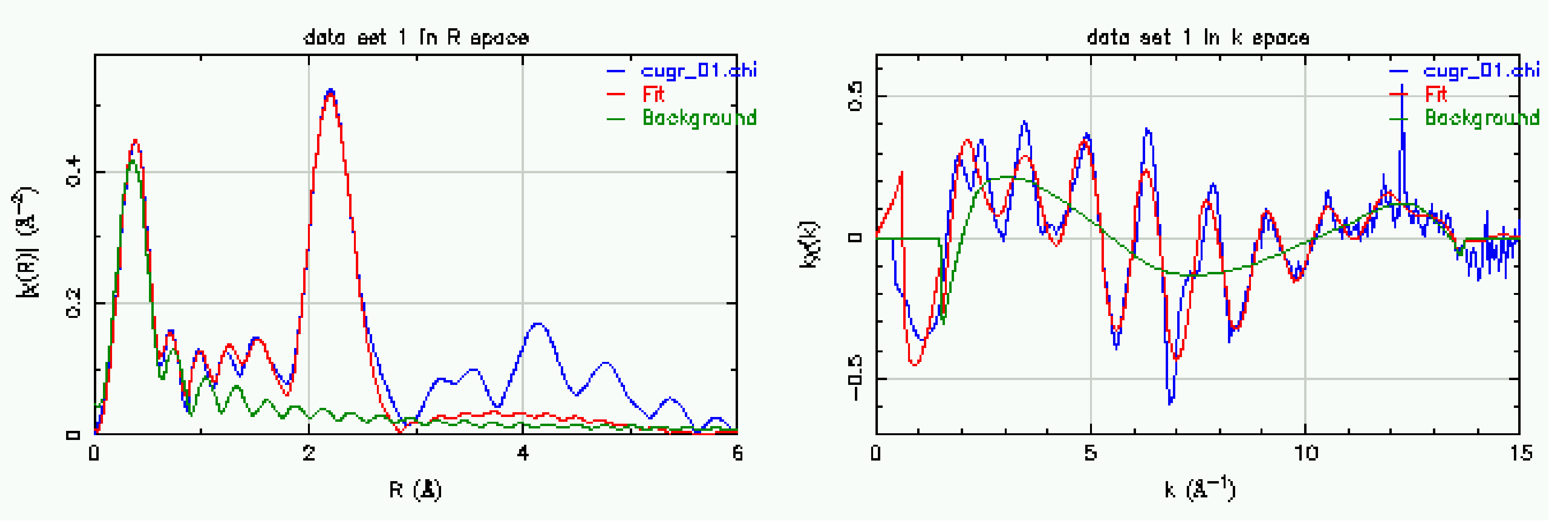
- Constrain background so that it cannot contain frequencies that are part of the data.
  - Use information theory, number of knots = 2 R_{bkg} Δk / π
  - 8 knots in bkg using R_{bkg}=1.0 and Δk = 14.0
- Background may contain only longer frequencies. Therefore knots are not constrained.

FT and Background function



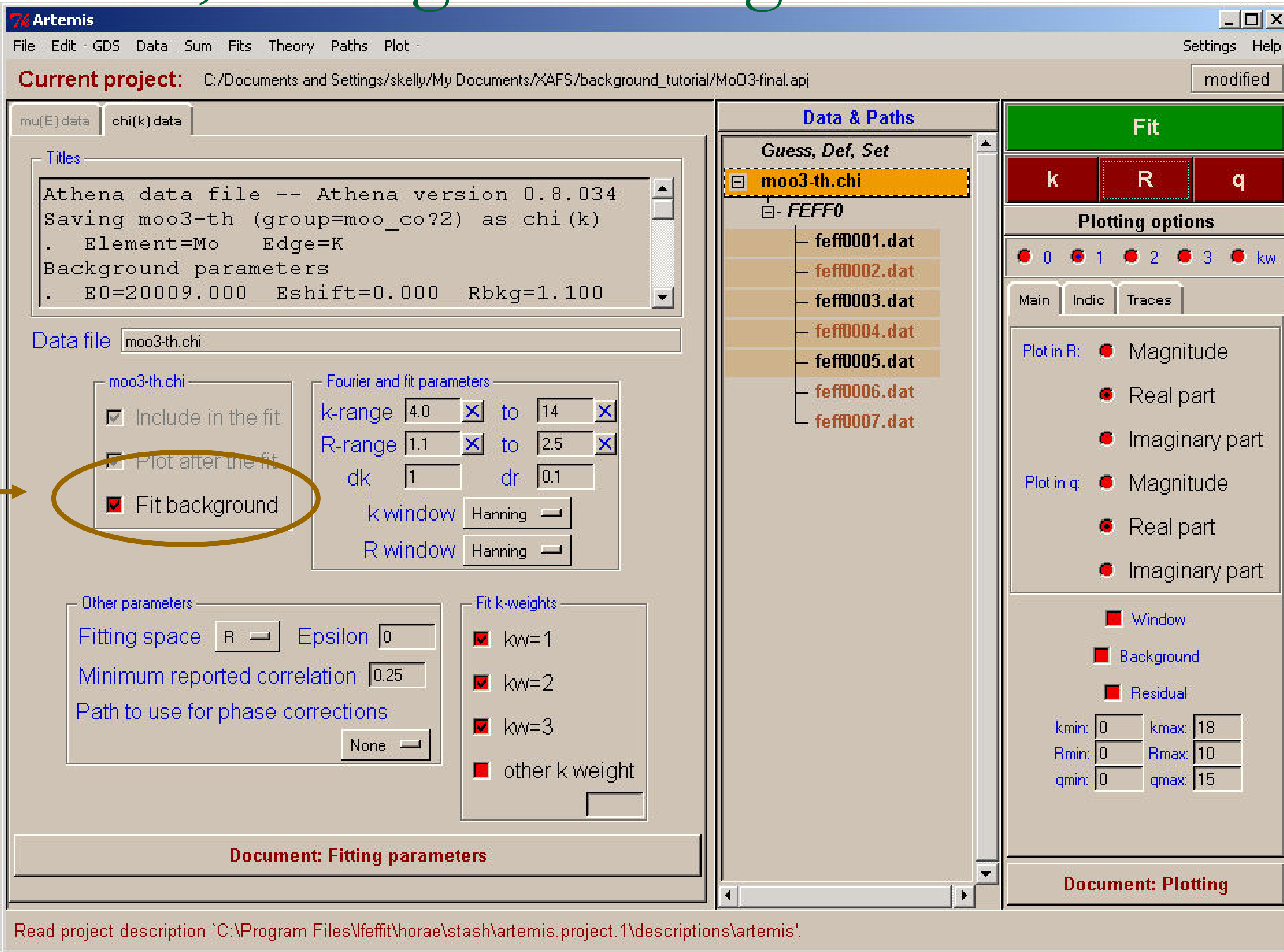
- An example where long wavelength oscillations appear as (false) peak in the FT

Fitting background and data using Artemis

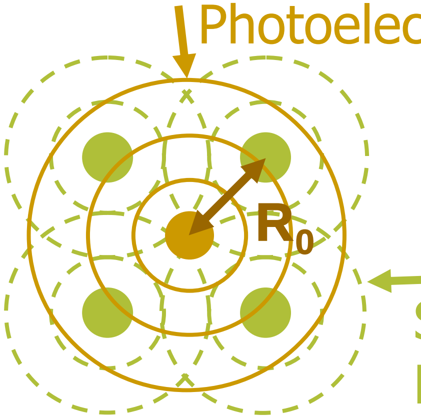


- Minimum distance between knots and the number of knots are constrained by the data range and the value for Rbkg.
- Notice that not all the knots (8) were needed to remove the background. Knots are not constrained.
- Using the FT to frequency filter the data, means that IFEFFIT doesn't need your help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

Artemis, Fitting the background



The 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

N_i degeneracy of path

S_0^2 passive electron reduction factor

σ_i^2 mean squared displacement

E_0 energy shift

ΔR change in half-path length