

XAFS Data Processing: Getting to $\chi(k)$

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Steps for reducing measured data to $\mu(E)$ and then to $\chi(k)$:

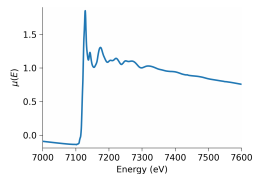
- 1 convert measured intensities to $\mu(E)$.
- 2 subtract a smooth pre-edge function, removing instrumental background and absorption from other edges.
- 3 normalize $\mu(E)$ to go from 0 to 1.
Analyze normalized $\mu(E)$ as XANES.
- 4 remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS $\chi(E)$.

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

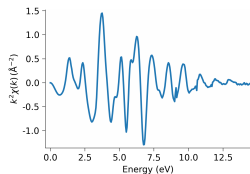
- 5 identify the threshold energy E_0 , and convert from E to k space: $k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$
- 6 weight the XAFS $\chi(k)$ and Fourier transform from k to R space.

After we get the EXAFS $\chi(k)$, we can model this with FEFF calculations.

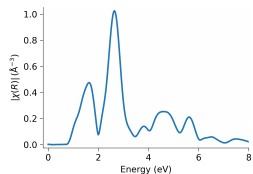
XAS VIEWER (part of Larch) provides a GUI for processing beamline data to $\chi(k)$.



Collected Spectra $\mu(E)$



Isolated $\chi(k)$, k -weighted



$\chi(R)$, Fourier Transform of $\chi(k)$

Data Processing features:

- Data Visualization
- Read in beamline data, merge data sets.
- Pre-edge subtraction, Find E_0 , Normalize Spectra
- Background subtraction to $\chi(k)$.
- Fourier Transforms $\chi(k) \rightarrow \chi(R)$.
- Save/Read "Projects".

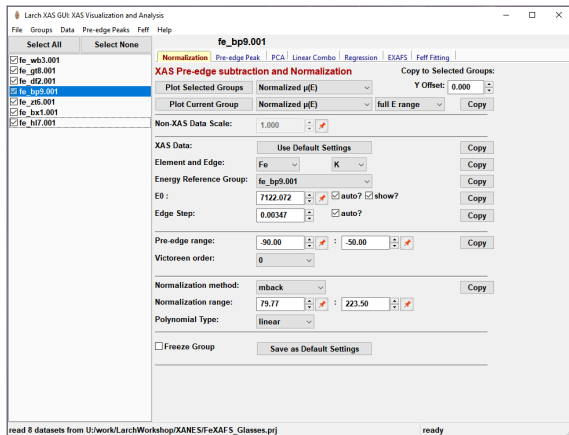
XANES Analysis features:

- Pre-edge peak fitting.
- Linear combination fits.
- Principal Component Analysis

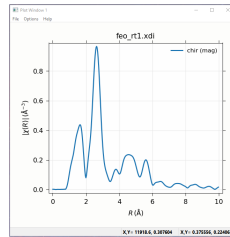
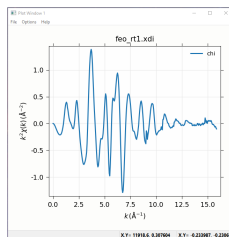
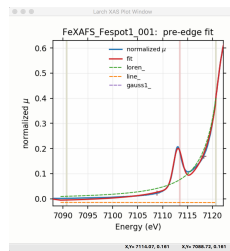
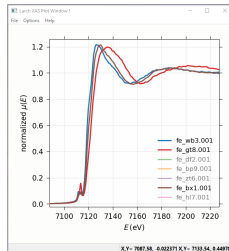
Data Corrections:

- Deglitching.
- Energy Alignment.
- Over-absorption Corrections.
- Smooth, Rebin, Deconvolutions.

XAS VIEWER screenshots



Panels for Normalization, Pre-edge Peak Fitting, PCA, Linear Combination Fitting, EXAFS (Background Subtraction+Fourier Transform), and Feff Fitting.

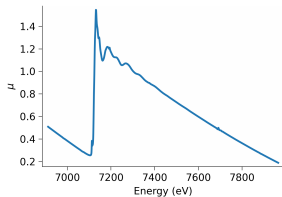


Data Reduction: Converting Raw Data to $\mu(E)$

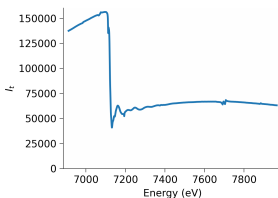
Step 1: Starting with measured intensities, we construct $\mu(E)$:

Transmission XAFS: $I_t = I_0 e^{-\mu(E)t}$

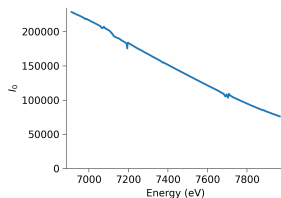
$$\mu(E)t = -\ln(I_t/I_0)$$



$$\mu = -\ln(I_t/I_0)$$



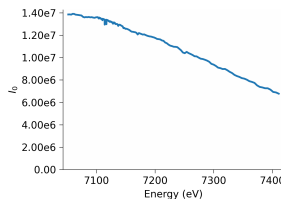
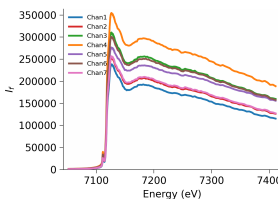
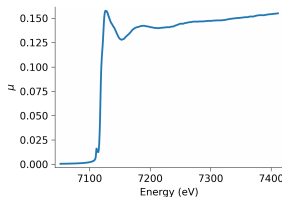
$$I_t$$



$$I_0$$

Transmission measurements are needed for high concentration elements, above ($\sim 5\text{wt}\%$).

Fluorescence XAFS: $\mu(E) \propto I_f/I_0$



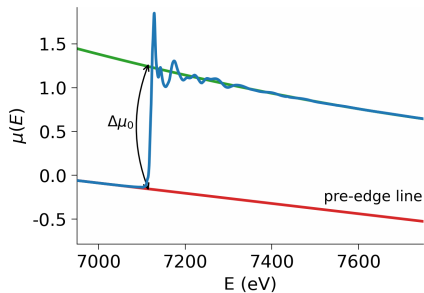
Real Data is typically measured in several scans. These scans can be *merged* together to give better statistics.

Important issues when processing data

- The monochromator energy calibration may drift with time.
 - ▶ scans can be aligned so that E_0 is constant for all scans.
 - ▶ a *Reference Channel* – often a metal foil – can be measured *during the scan* and used for energy alignment.
 - ▶ if the drift is bad enough (every scan, etc), consult the beamline scientist.
- At certain energies, I_0 jumps – a *glitch* – that may not normalize out of $\mu(E)$. These points should be removed.
- *over-absorption* for concentrated samples measured in fluorescence.

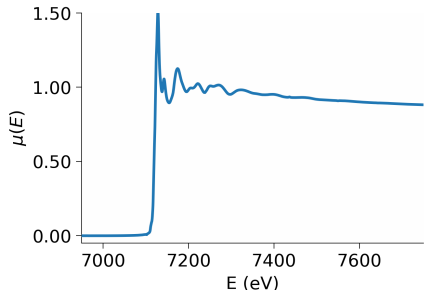
XAS VIEWER can help with these. So can ATHENA and SIXPACK.

Data Reduction: Pre-Edge Subtraction, Normalization



Pre-Edge Subtraction

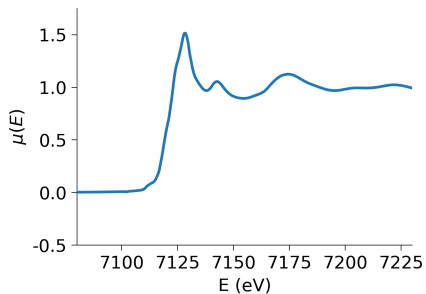
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other absorption edges (say, the Fe L_{III} edge).



Normalization

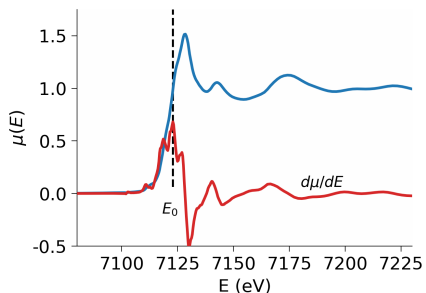
We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple curve the above $\mu(E)$ to the edge.

$$\mu_{\text{norm}}(E) = \mu(E) / \Delta\mu_0(E_0)$$



XANES

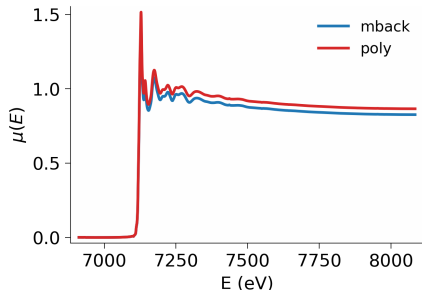
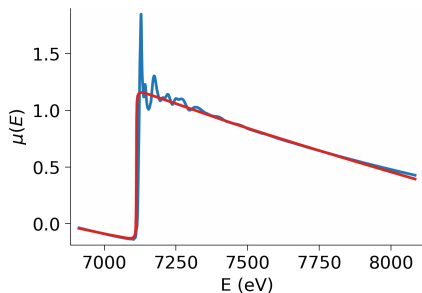
The XANES part of $\mu(E)$ shows a fairly rich spectral structure. We'll use $\mu_{\text{norm}}(E)$ for XANES analysis.



Derivative

We can select E_0 roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we'll keep in mind that we may need to refine this value later on.

Data Reduction: Normalization with tabulated $\mu(E)$



Using tabulated $\mu(E)$

Tabulated values (Chanter, et al) can also be used to normalize the data.

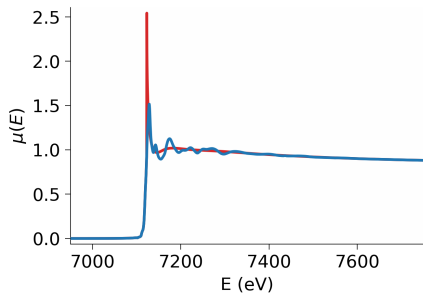
This can improve consistency, as the same functional form is used for all spectra of an element and edge.

Polynomial vs tabulated values

The difference is typically at the margin, but consistency is good!

This is based on the MBACK procedure of T.C. Weng, et al.

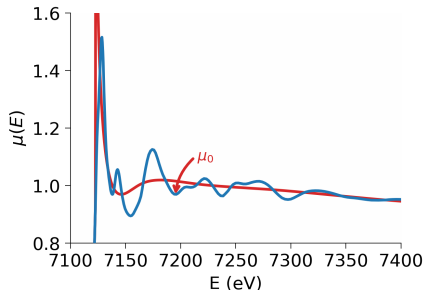
Data Reduction: Post-Edge Background Subtraction



Post-Edge Background

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

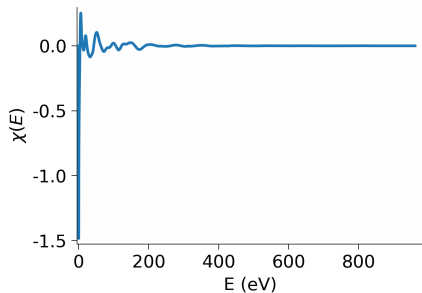
We don't have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).



We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.

This can be dangerous – a flexible enough spline could match $\mu(E)$ and remove all the EXAFS! We want a spline that will match the *low frequency* components of $\mu(E)$.

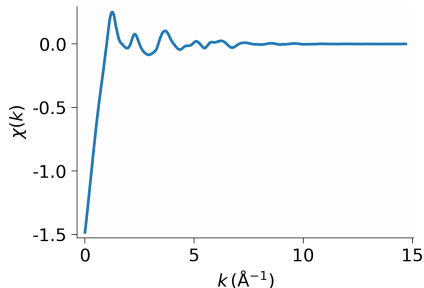
Data Reduction: $\chi(E)$ to $\chi(k)$



$\chi(E)$

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

where $\Delta\mu_0(E_0)$ is the Edge Step found earlier.

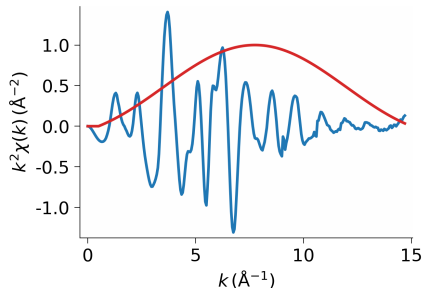
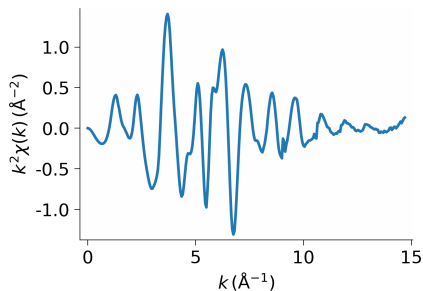


$\chi(k)$

Convert scale from Energy, E , to wavenumber k :

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

Data Reduction: $\chi(k)$, k -weighting



$\chi(k)$

The raw EXAFS $\chi(k)$ decays quickly with k .

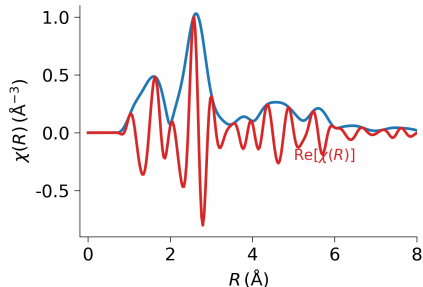
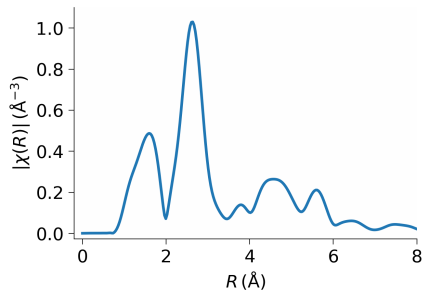
We emphasize the higher- k portion of the spectra by multiplying by k^2 or k^3 .

k -weighted $\chi(k)$: $k^2\chi(k)$

$\chi(k)$ is composed of sine waves, so we'll Fourier Transform from k to R -space.

To avoid "ringing", we'll multiply by a *window function*.

EXAFS Fourier Transform: $\chi(R)$



$\chi(R)$

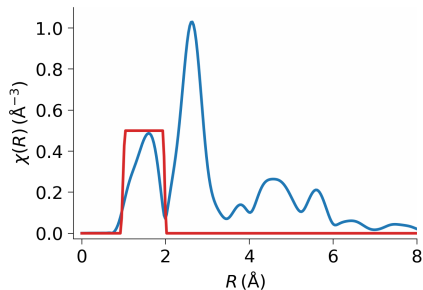
Peaks in $\chi(R)$ often correspond to “coordination shells”. The Fe-O distance in FeO is 2.14\AA – the first peak is at 1.6\AA .

This distance shift is due to the *phase-shift*: $\sin[2kR + \delta(k)]$.

$\chi(R)$ is complex:

Usually only the amplitude is shown, but there are oscillations in $\chi(R)$.

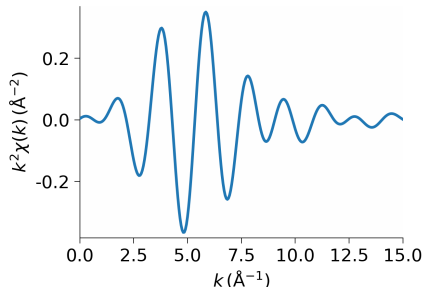
Both real and imaginary parts are used in modeling.



$\chi(R)$

often has well-separated peaks for different “shells”.

This shell can be isolated by a Filtered Back-Fourier Transform, using the window shown for the first shell of FeO.



$\chi(q)$ (“Q-space”)

This results in the filtered $\chi(k)$ for the selected shell.

Many analysis programs use such filtering to remove shells at higher R .

Don't do it – it's too hard.

Now that we've seen the basic procedures, a bit more detail on these topics is needed:

Background Subtraction Details on getting from $\mu(E)$ to $\chi(k)$

Fourier Transforms Details on getting from $\chi(k)$ to $\chi(R)$

EXAFS Analysis Modeling to fit experimental $\chi(k)$.

Background Subtraction: $\mu_0(E)$

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

We don't know $\mu_0(E)$, so use a *spline*: a smooth, adjustable function.

This could be dangerous – a flexible enough spline would remove all the XAFS.

The AUTOBK method in LARCH chooses a background spline for $\mu_0(E)$ to

minimize the low- R components of χ

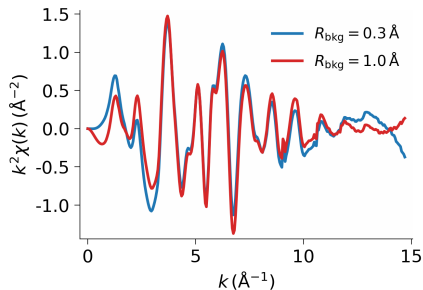
- 1 Spline parameters for $\mu_0(E)$ are guessed.
- 2 $\chi(k)$ is Fourier Transformed to $\chi(R)$.
- 3 Spline parameters optimized so that $\chi(R)$ below R_{bkg} is minimized.
- 4 Note that $\chi(R)$ above R_{bkg} is completely ignored!

Most important parameters:

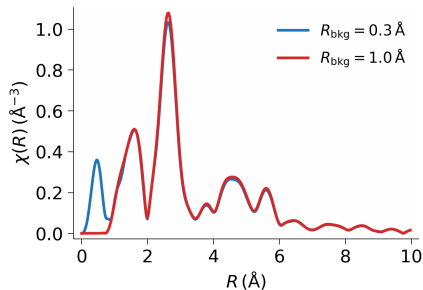
- 1 R_{bkg} : R below which $\chi(R)$ is reduced.
- 2 k -weight: used for Fourier transform: use 1, or 2.
- 3 E_0 : May need to adjust for initial guess (max of $d\mu/dE$).

Background Subtraction in XAS VIEWER

Effect of R_{bkg} on XAFS $\chi(k)$ and $\chi(R)$:



$\chi(k)$ for FeO with $R_{\text{bkg}} = 0.1 \text{ \AA}$
(stiff spline) and $R_{\text{bkg}} = 1.0 \text{ \AA}$.



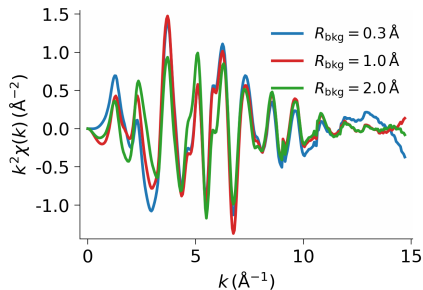
$\chi(R)$ for FeO with $R_{\text{bkg}} = 0.1 \text{ \AA}$
(stiff spline) and $R_{\text{bkg}} = 1.0 \text{ \AA}$.

Rules of thumb:

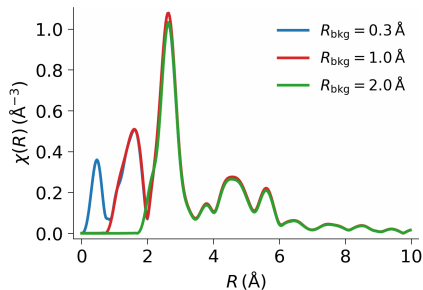
Use $R_{\text{bkg}} = 1.0 \text{ \AA}$ or half the near-neighbor distance.

Don't spend too much time on background subtraction.

Don't make R_{bkg} too big!



$\chi(k)$ for FeO with $R_{\text{bkg}} = 2.0 \text{ \AA}$



$\chi(R)$ for FeO with $R_{\text{bkg}} = 2.0 \text{ \AA}$ Note: we have removed the first shell!!

Having R_{bkg} too big is the most important thing to avoid.

R_{bkg} that's a little bit small and gives a small peak at very low R is not that big of a problem.

Fourier Transforms are an important part of XAFS Analysis:

$$\chi(R) = \text{FT}[\chi(k)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{i2kR} k^w \chi(k) \Omega(k)$$

- $\Omega(k)$ is the Window Function
- w is the k -weighting

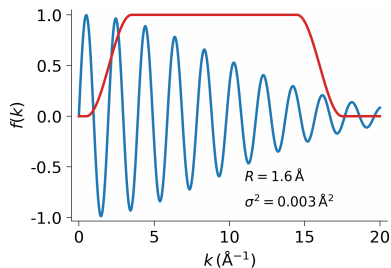
We really use a discrete version and Fast Fourier Transform

$$\chi(R_m) = \frac{i\delta k}{\sqrt{\pi N_{\text{fft}}}} \sum_{n=1}^{N_{\text{fft}}} e^{2\pi i n m / N_{\text{fft}}} k_n^w \chi(k_n) \Omega(k_n)$$

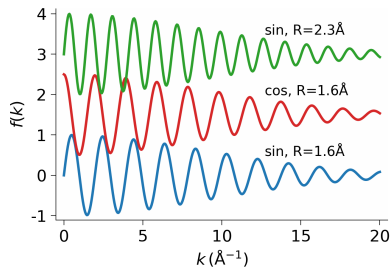
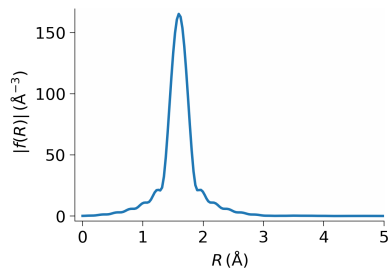
- $\chi(k)$ is put on a uniform k -grid with spacing of $\delta k = 0.05 \text{ \AA}^{-1}$.
- $\chi(k)$ is filled with zeros past the real data range.
- $N_{\text{fft}} = 2048$: $\chi(k)$ can go to 102.4 \AA^{-1} ($\sim 40 \text{ keV}$) past the edge.
- $\chi(R)$ is on a R -grid with spacing $\sim 0.031 \text{ \AA}$, and can go to 31.4 \AA .

Fourier Transforms: Basic Properties

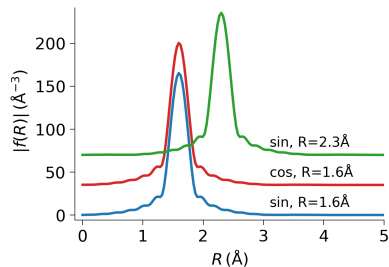
Fourier Transform of a sine wave:



\Rightarrow

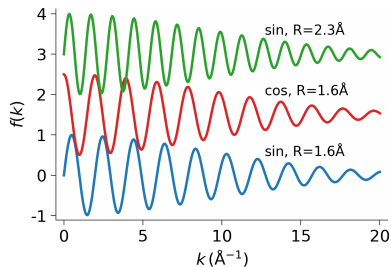


\Rightarrow

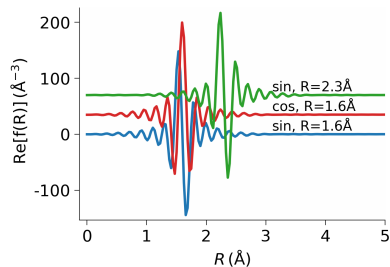


Fourier Transforms: Basic Properties(2)

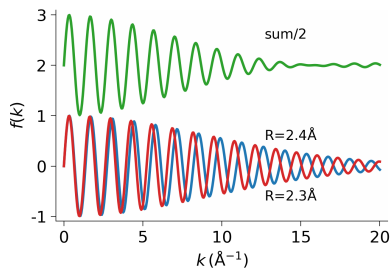
Fourier Transforms are complex:



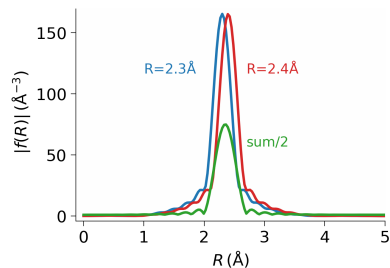
\Rightarrow



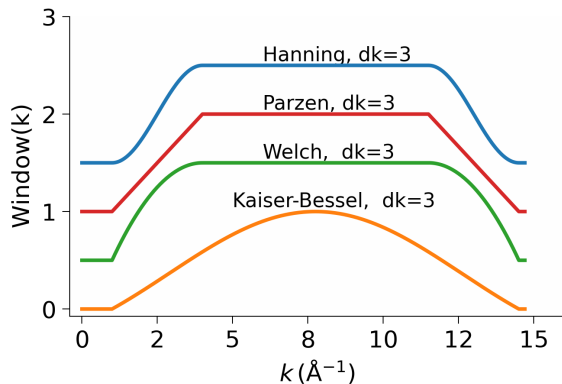
Waves with slightly different frequencies can cancel each other out, causing “beats”



\Rightarrow



Fourier Transform Window Types



Typical Window Functions

A Window Function:

- goes from 0 to 1 and back to 0
- dk gives the width of the Window "sill"

Most important rule:

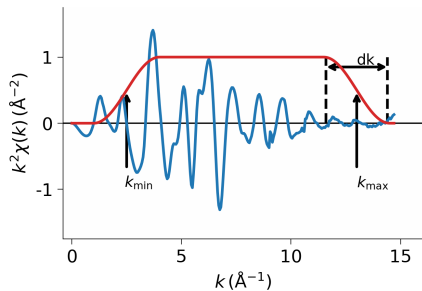
Pick a window type and stick with it.

Kaiser-Bessel and Hanning are the most commonly used, and recommended.

Personal Recommendation:

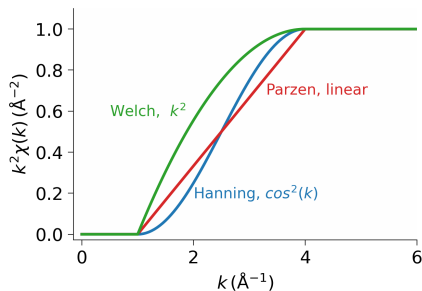
Kaiser-Bessel Window, $dk = 4$.

Fourier Transform Window Types



Fourier Window Function

The meaning of k_{\min} , k_{\max} , and dk .

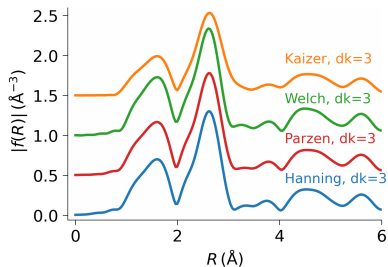
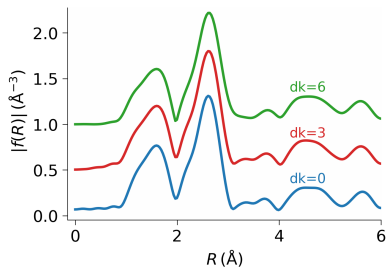
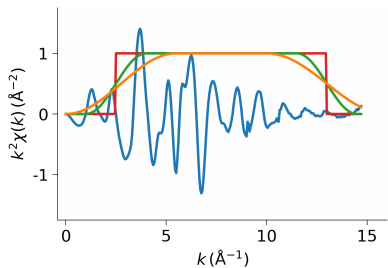


Parzen, Hanning, Welch

Details of the different Window "sills".
all with $k_{\min} = 2 \text{\AA}^{-1}$ and $dk = 3 \text{\AA}^{-1}$.

Fourier Transform Window and real data

The effect of dk (for Hanning Window) and different Window Function:

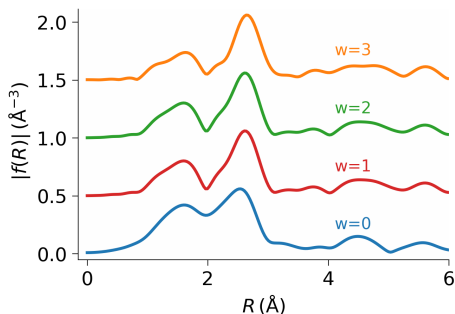


Changing dk and Window functions gives relatively small changes to $\chi(R)$, most noticeable in the “ringing” of small peaks.

Fourier Transform Window and k -weight

$$\chi(R) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{i2kR} k^w \chi(k) \Omega(k)$$

Changing w , the k -weighting has a significant impact:



Fe-Fe scattering dominates with higher w .

low w emphasizes low- k , and low- Z scatterers.

high w emphasizes high- k , and high- Z scatterers.

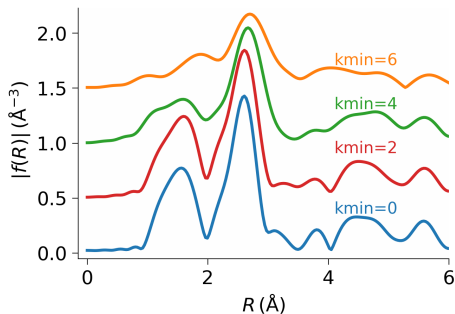
This is important when trying to determine the Z of a scatterer.

Again, $w = 2$ and $w = 3$ are most common, and recommended.

Fourier Transform Window and k_{\min}

k_{\min} and k_{\max} are important too.

- k_{\max} should be the end of useful data.
- With k -weight = 2, 3, it is not too important to avoid “very low k ”.



Conventional wisdom: keep
 $k_{\min} > 2 \text{ \AA}^{-1}$

But: don't make it too big.

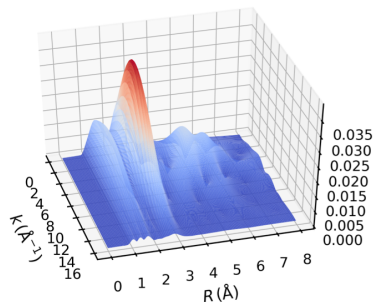
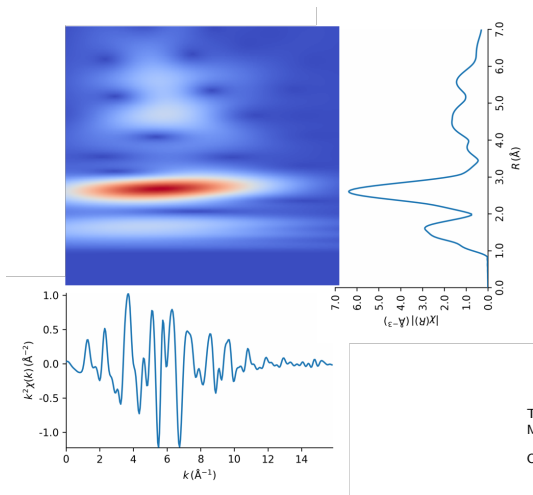
Use Kaiser-Bessel with $dk = 4$, $k_{\min} = 2 \text{ \AA}^{-1}$

Use k -weight=2, or 3.

Don't obsess too much.

Wavelet transforms for EXAFS analysis

The Fourier transform is fundamental to understanding EXAFS. Wavelet transforms extend Fourier transforms, mixing k and R . They have been used by a handful of groups.



Wavelet transform for FeO data.

This is using the “Continuous Cauchy” wavelet transform, as described by Munoz, Argoul, and Farges, *Am Mineralogist*, 2003

Others (Funke *et al*, Penfold, *et al*) have used Morlet wavelets.

XAFS processing to $\chi(k)$ should not be too difficult.

Be consistent.

Don't over-think it.

More information on X-rays and X-ray Absorption Spectroscopy:

<https://xafs.xrayabsorption.org/>

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