
Introduction to EXAFS Experiments and Theory

Bruce Ravel

Version 0.02

May 2, 2000

Abstract

This document contains the presentation materials for a seminar entitled *Introduction to EXAFS Experiment and Theory*. This file is suitable for presentation directly from a computer or for printing onto transparency sheets.

Bruce Ravel

ravel@phys.washington.edu

<http://feff.phys.washington.edu/~ravel/>

This document is copyright © 2000 Bruce Ravel.

This document is distributed under the GNU Free Document License.

Permission is granted to make and distribute verbatim copies of this manual provided the copyright notice and this permission notice are preserved on all copies.

Permission is granted to copy and distribute modified versions of this manual under the conditions for verbatim copying, provided that the entire resulting derived work is distributed under the terms of a permission notice identical to this one.

Permission is granted to copy and distribute translations of this manual into another language, under the above conditions for modified versions, except that this permission notice may be stated in a translation approved by the author.

Acknowledgements

A lot of people have contributed in some manner to the development of this document and the supporting materials. I would like to thank the following people:

- Wim Bras, Bert Weckhuysen, and Patrick Van Esch for inviting me to give this lecture for the first time.
- Matt Newville, Dani Haskel, Shelly Kelly, Anatoly Frenkel, and Yanjun Zhang for joining me for hours of fun at the beamline in graduate school.
- Ed Stern and John Rehr, for teaching me so much so well

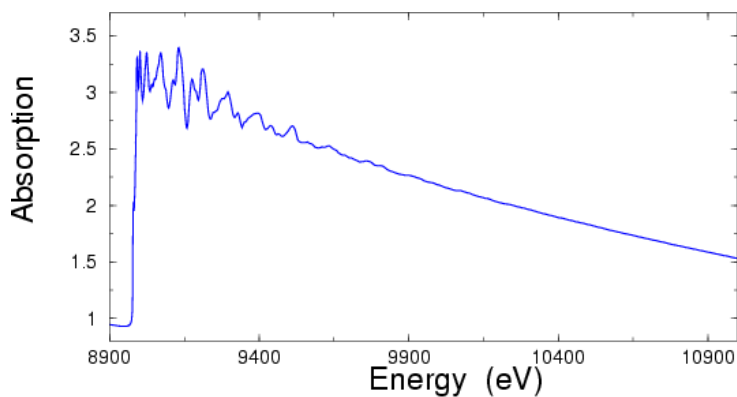
Table of Contents

Introduction to the EXAFS experiment	1
EXAFS Data	1
The physical process in EXAFS	2
A heuristic picture of EXAFS	3
Acronyms	4
What EXAFS can tell us	5
Local structure	5
What makes EXAFS a unique measurement?	6
The EXAFS Experiment	7
EXAFS experiment schematic	7
Beamline optics	8
Sample environment	9
Detectors	10
Sample Preparation	11
Sample preparation fundamentals	11
Transmission sample preparation	12
Fluorescence sample preparation	13
Which geometry should you use?	14
Sample Environments and Extrinsic Parameters	15
Some interesting sample environments	15
Why extrinsic parameters are important	16
Other EXAFS and EXAFS-Like Experiments	17
Other things that can be done with EXAFS	17
Introduction to Scattering Theory	18

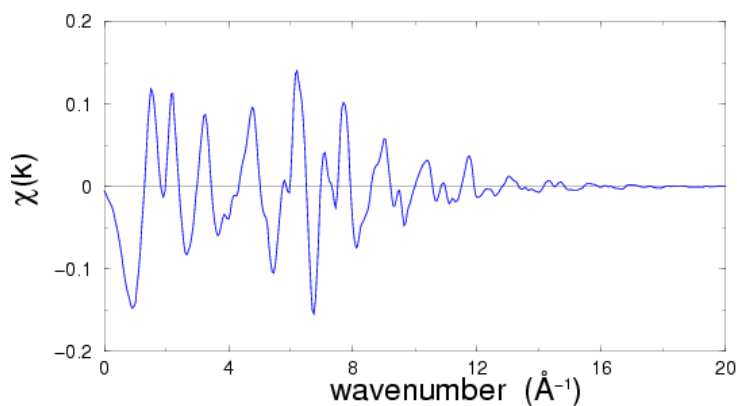
Fermi's Golden Rule	18
Multiple Scattering in a Lattice	19
Several Types of Multiple Scattering	20
Important Paths	21
Sum of Paths	22
The EXAFS Equation	23
A Fit to the Copper Data	24
Magnitude of the Fourier Transform	25
Paths at the Fourth Shell Distance	26
Real Part of the Fourier Transform	27
Conclusion	28
Conclusion	28
Contacting Me	29

EXAFS Data

In an EXAFS experiment, one measures an absorption spectrum. It looks something like this copper metal data:



To analyze these data, we need to somehow extract the wiggly part:

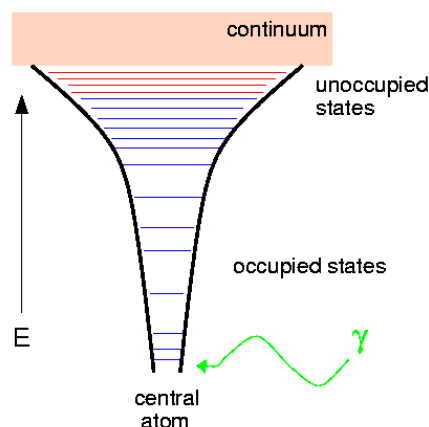


So, how do we measure these data and begin to understand their content?

Welcome to Introduction to EXAFS Experiment and Theory!

The physical process in EXAFS

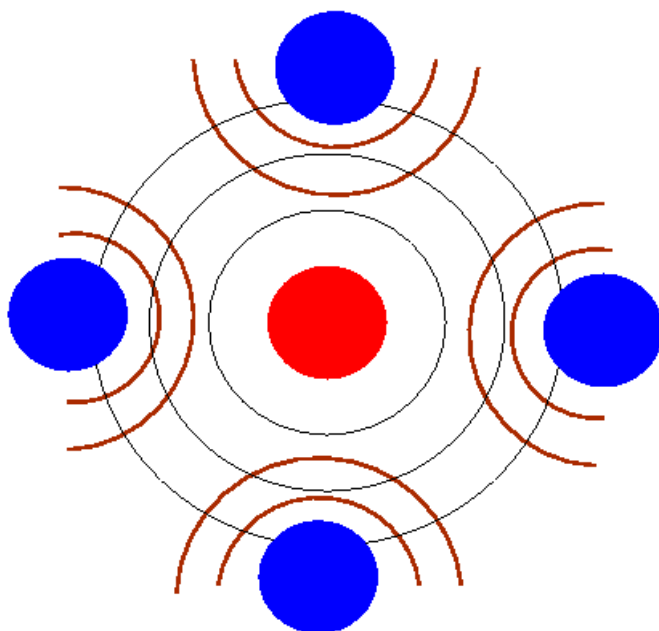
- Excite deep core electrons into high-lying unoccupied or continuum states.



- Using an **energy-tunable source of photons**, a sample is illuminated as the energy of the incident photon beam is ramped in energy.
- Above the binding energy of a deep-core electron of some element, photons are absorbed due to deep-core excitation. EXAFS is a measure of the **energy dependence** of the absorption spectrum.
- The data are characterized by a **step function** centered at the binding energy, broadened by measurement resolution and the lifetime of the core-hole, and monotonically decreasing with increasing energy. On top of this, is an oscillatory **“fine structure”**, which is the interesting part of the measurement.

A heuristic picture of EXAFS

One way of thinking about the EXAFS process is to consider the excited photoelectron as an outwardly propagating spherical wave which scatters from the surrounding atoms.



The **interference** between the outgoing wave and the backscattered waves is the source of the oscillatory structure in EXAFS.

This picture is much too simplistic, but is a good starting point for the rest of this lecture.

Acronyms

XAS X-ray Absorption Spectroscopy

This is a general purpose term used to describe any experiment involving absorbed photons. It includes all of the acronyms below.

XANES X-ray Absorption Near Edge Structure

This is the portion of the X-ray absorption spectrum that extends from below the Fermi energy to about 20 volts above the Fermi energy. It is said to contain a wealth of structural and electronic information about the measured material.

NEXAFS Near-Edge X-ray Absorption Fine Structure

This is a synonym for XANES. There is no difference between the two. I prefer XANES to NEXAFS.

EXAFS Extended X-ray Absorption Fine Structure

This is the portion of the absorption spectrum which starts about 20 volts above the Fermi energy. Typically the EXAFS is analyzed by removing a background function with AUTOBK or a similar program. The resulting oscillatory function is the Fourier transformed.

XAFS X-ray Absorption Fine Structure

This is sometimes used a synonym for EXAFS, but is more appropriately used to mean the entire absorption spectrum. That is, XAFS = XANES+EXAFS, thus XAFS is more a synonym for XAS than for EXAFS.

SEXAFS Surface Extended X-ray Absorption Fine Structure

This is EXAFS performed at a glancing angle so that only the region near the surface of the sample is probed. Also known as Glancing Angle XAFS (GIXAFS).

Local structure

EXAFS is a local structural probe. This means that with EXAFS you can measure

- Local structure with elemental sensitivity
- The radial distribution of atoms around the selected central site, including bond lengths, coordination numbers, and thermal disorder
- Certain information about the electronic structure of the central site

This is valuable information, but how does EXAFS differ from other structural probes, such as diffraction and vibrational spectroscopy?

What makes EXAFS a unique measurement?

EXAFS provides information that may be complimentary or simply unavailable to other measurement techniques.

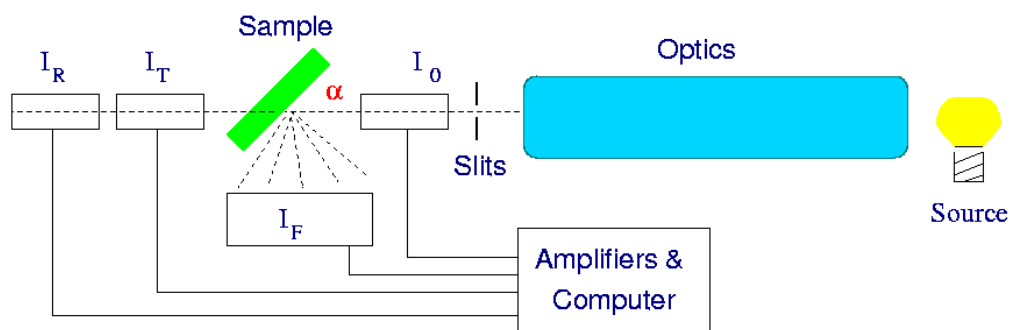
- The theory of EXAFS and analysis of its data do not depend on crystallinity. EXAFS data is analyzed in analogous manner for crystals, proteins, quasicrystals, amorphous solids, liquids, and any other class of material.
- EXAFS is sensitive to correlations on the Ångstrom length scale (but only on the Ångstrom length scale).
- EXAFS is a very fast measurement — the core-hole lifetime is around 10^{-15} seconds.

When structure is correlated on short lengths scales and fast time scales, EXAFS provides complimentary information to diffraction and vibrational spectroscopy.

When materials are not crystalline, EXAFS provides structural data unavailable to other techniques.

EXAFS experiment schematic

Here is a schematic of the basic EXAFS experiment.



There are five parts to the set-up

1. The source (bending magnet or insertion device)
2. The optics (mirrors and monochromators)
3. The sample and sample holder
4. The detectors
5. The amplifiers and computers

The EXAFS signal is

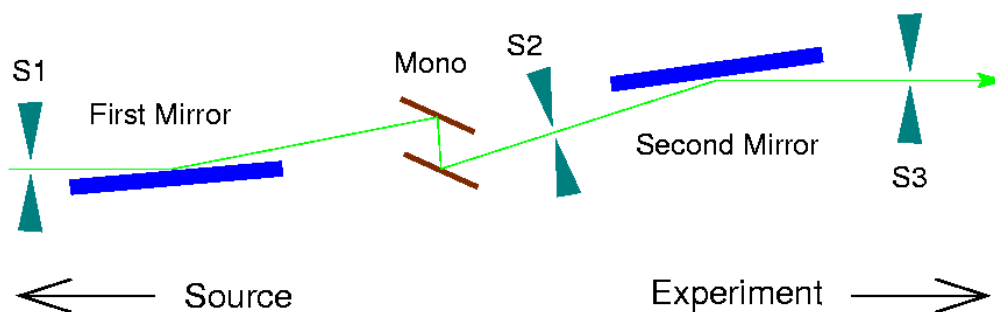
$$\mu(E) = \ln \left(\frac{I_0}{I_T} \right)$$

or

$$\mu(E) = \frac{I_F}{I_0}$$

Beamline optics

The beamline optics filter the white beam coming from the source and deliver useful, narrow-band radiation to the experimental hutch. Here is a schematic of the optics at BM02 at the ESRF:



Mirrors can be used to redirect the beam, reject harmonics, and focus the beam. They work usually by total external reflection (or other means).

Monochromators use Bragg's law for energy selection and tuning. Crystals may be bent to focus the beam. In a multi-crystal setup, one or more crystal can be detuned to provide more harmonic rejection.

Slits are used to limit the spacial extent of the beam incident on the various parts of the optics and on the sample.

Sample environment

The simple layout of the typical EXAFS beamline is appropriate for a technique that can be applied to a wide variety of physical systems.

The sample environment can be as simple as a ring stand. Or it can be

a UHV chamber

a furnace

a cryostat

a high pressure anvil

a liquid cell

a goniometer

a spinner

The sample environment can be whatever is appropriate to your experiment.

Detectors

There are a wide variety of commonly used detection options, including

- Ionization chambers
- Photodiodes
- Photomultipliers
- Energy discriminating detectors (i.e. solid state detectors)
- Wavelength dispersive detectors (i.e. analyzers)

While each has its place, ionization chambers are probably best equipped for the high flux and wide energy range available at modern beamlines.



An ion chamber is just a box filled with gas containing a capacitor. The x-rays ionize the gas, the ions collect at the plates, and this current is amplified and counted.

Sample preparation fundamentals

There are certain constants about sample preparation that have nothing to do with EXAFS, things like

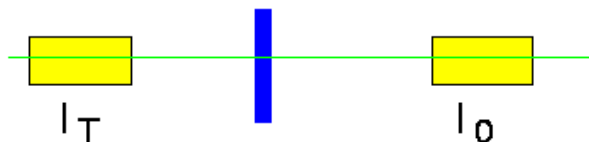
- Use pure, well characterized materials
- Package your sample in a manner appropriate to its environment
- Make it the right size and shape to fit in the sample holder

and so on.

There are some issues that are particular to EXAFS data collection which depend upon your **measurement geometry**.

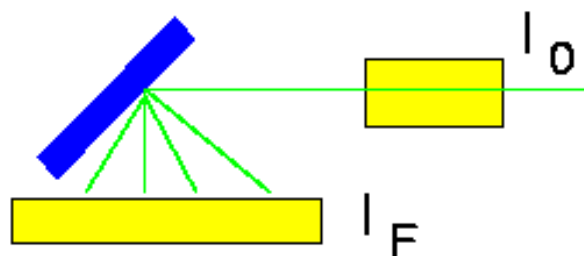
Transmission

In this geometry, $\mu(E)$ is measured as the portion of the signal that is absorbed (i.e. does not pass through) the sample.



Fluorescence

In this geometry, $\mu(E)$ is is the intensity of the secondary process of photon re-radiation after absorption by the sample.



Transmission sample preparation

A sample for [transmission](#) should

1. be about 2 absorption lengths thick
2. have an edge step of around 1
3. be of uniform thickness
4. not have any holes

The often-quoted “ideal” values of total and edge absorption of 2.6 and 1 are based on statistical signal-to-noise arguments. Don’t take those values too seriously — high quality data can be obtained on samples with one or both values far from those numbers.

[Sample uniformity and homogeneity are essential. Don’t compromise.](#)

- Never use powders with particle sizes larger than the absorption length.
- Never use filler materials composed of heavy elements. (Graphite is almost always a good choice.)
- Make sure samples are well dispersed in the filler.
- Pinholes kill data!

Failure to properly prepare transmission samples results in badly distorted data and unreliable values for S_0^2 , σ^2 , and possibly other parameters.

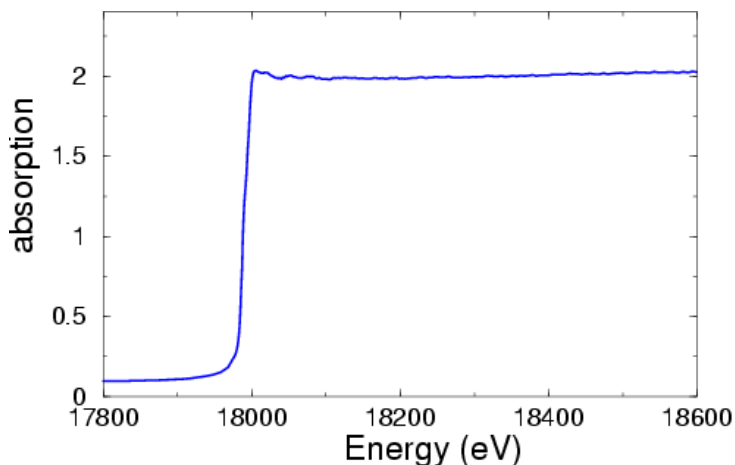
Fluorescence sample preparation

A sample for **fluorescence** should

1. be “dilute and thick” or “dense and thin”
2. be areally homogeneous
3. big enough to subtend the entire beam

By “dilute” and “dense” I refer to the concentration of the absorbing species. A thick, dense sample results in attenuated fine-structure oscillations due to the **self-absorption** effect.

Here is a metallic alloy containing about 70% Zr taken in fluorescence:



With efficient detection and a bright source, high quality data on concentrations in the ppm range can be measured.

It is often necessary to use filters and/or Soller slits to reduce noise. For low count rates, energy discriminating detectors may improve statistics.

Which geometry should you use?

The simple answer is
“Whichever one is more convenient.”

From a statistical argument involving signal-to-noise calculations, one can show that the size of the edge step matters. If the edge step is larger than about 0.03 (i.e. the absorber is more than about 3% of the total absorption), then it is probably better to do transmission. In any case, transmission experiments are usually easier.

Other experiments may require glancing angle geometry, electron yield detectors, or other exotic experimental setups.

Some interesting sample environments

For many systems, it is of experimental and scientific interest to measure the dependence of the data on some extrinsic parameter. Examples include

- **Temperature** (using a furnace or a cryostat)
- **Pressure** (using diamond or boron nitride anvils)
- **Doping** fraction
- **Orientation** (using the polarization properties of the synchrotron beam)
- **Concentration** in a solution

Sometimes a practical consideration of the beamline or of the sample precludes changing an extrinsic parameter. However...

A well-designed experiment always includes changing an extrinsic parameter.

Why's that?

Why extrinsic parameters are important

Correlated parameters

Many parameters of interest in EXAFS analysis are highly correlated. Examples include energy shifts and bond lengths and amplitudes and Debye–Waller factors.

Invariant parameters

Some parameters should be independent of changes in the extrinsic parameters. For example, within a phase, energy shifts and S_0^2 should not change with temperature or pressure.

By measuring with respect to an extrinsic parameter, you obtain information which allows you to decouple otherwise correlated parameters.

Since many parameters should behave predictably with respect to the extrinsic parameter, you can use this dependence as constraint on what is a reasonable result of the fit.

Other things that can be done with EXAFS

Diffraction Anomalous Fine Structure

DAFS combines the local structure sensitivity of EXAFS with the crystallographic sensitivity of diffraction, allowing direct measurement of spectra which are difficult or impossible to measure with EXAFS. This requires a goniometer.

Dispersive XAFS

DXAFS uses a bent-crystal *polychromator* to project broadband light onto a sample. Using a linear or areal detector, entire XAFS spectra can be collected in a small fraction of a second.

Micro-Fluorescence

Sample surfaces can be mapped with submicron and smaller resolution using a micro-focused beam. This requires special focusing optics, such as Kirkpatrick-Baez mirrors.

High Energy XAFS

Using a silicon 511 or 711 crystals, K edges between 40 and 120 keV can be probed.

Fermi's Golden Rule

In XAS we measure the dipole mediated transition of an electron in a deep core state $|i\rangle$ into an unoccupied state $|f\rangle$:

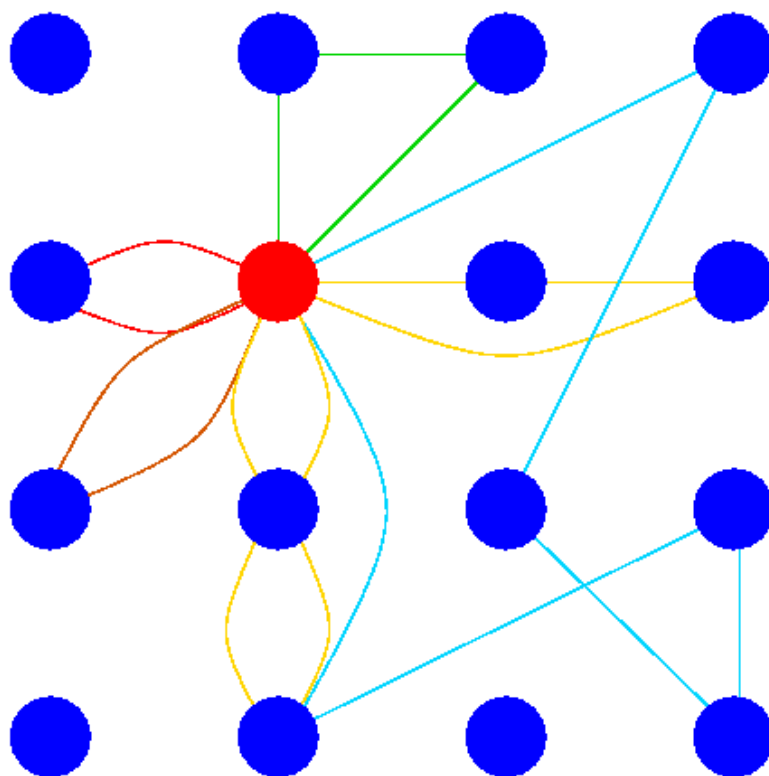
$$\mu(E) \propto \sum_{f}^{E_f > E_F} |\langle f | \hat{\mathbf{e}} \cdot \mathbf{r} | i \rangle|^2 \delta(E_f)$$

There are two ways to solve this equation:

1. Accurately represent $|i\rangle$ and $|f\rangle$, then evaluate the integral directly. This is the approach taken by MO and Band theories.
2. Use [multiple scattering theory](#).

Multiple Scattering in a Lattice

Consider a simple lattice of atoms. Choose one atom (the red one) as the central atoms. We can represent a scattering event, (i.e. a photoelectron propagating out from the central atom, bouncing off of neighbors, and propagating back to refill the core-hole), with a simple diagram. There are many such diagrams.

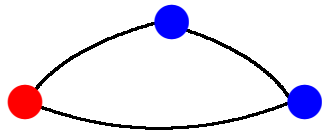


Several Types of Multiple Scattering

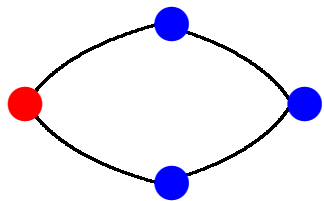
The red circle ● represents the central atom.
The blue circles ● represent the scattering atoms.



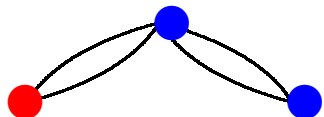
Single scattering path. These paths are very similar in concept to a “scattering shell” and are roughly equivalent to empirical standards.



Double scattering path. These paths are most important when the forward scattering angle is close to 180° .



Quadrilateral triple scattering path. These paths are rarely important if one or more scattering angle is far from 0° or 180° .



Triangular triple scattering path. This sort of path is very important when the scattering angle at the middle atom is nearly 180° .

Important Paths

Single scattering

Single scattering paths are always important.

Collinear multiple scattering

MS paths with all scattering angles equal to 0° or 180° .

Nearly collinear multiple scattering

MS paths with all scattering angles not far from 0° or 180° .

Short triangle path

Sometimes non-collinear MS between near neighbor atoms cannot be neglected.

The function that describes the amplitude and phase shift of the scattering event is **strongly peaked** in the forward and backward directions. At intermediate angles, the amplitude is much smaller.

In fact, the scattering amplitude is so strong in the forward direction that paths which include forward scattering are often called **focused** paths. Focused MS paths can be *larger* than SS paths of the same length!

Sum of Paths

The full $\chi(k)$ spectrum, calculated within a multiple scattering formalism is then a sum of paths.

$$\chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k)$$

where $\chi_{\Gamma}(k)$ is the contribution calculated from a particular scattering path.

Γ may denote a SS path or a MS path of any order.

One convenient thing about the approach taken in FEFF is that SS and MS paths are handled equivalently and transparently.

The EXAFS Equation

A multiple scattering formalism is used to represent $\chi(k)$. Theoretical standards are modified on a path-by-path basis according to this equation:

$$\chi_{\Gamma}(k) = \Im m \left(\frac{(N_{\Gamma} S_0^2) F_{\Gamma}}{k R_{\Gamma}^2} e^{i(2k R_{\Gamma} + \Phi_{\Gamma})} e^{-2\sigma_{\Gamma}^2 k^2} e^{-2R_{\Gamma}/\lambda} \right)$$

$$\text{where } k = \sqrt{2m(E - E_0)/\hbar^2}.$$

Multiple scattering theory is used to generate the **terms in orange**.

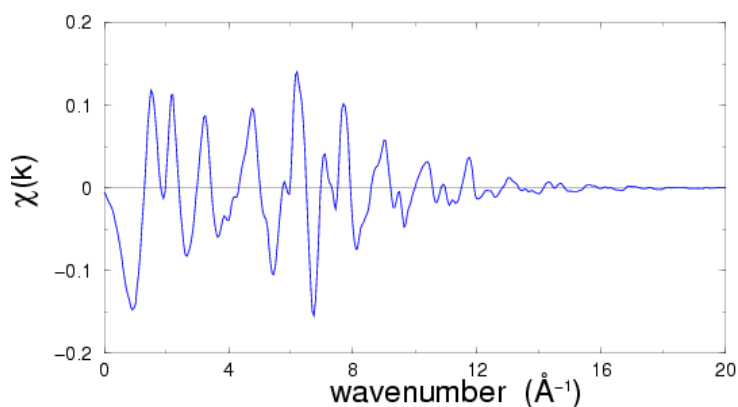
- F_{Γ} the effective scattering amplitude
- Φ_{Γ} the effective phase shift
- λ the mean free path

Structural and electronic information is contained in **the terms in blue**.

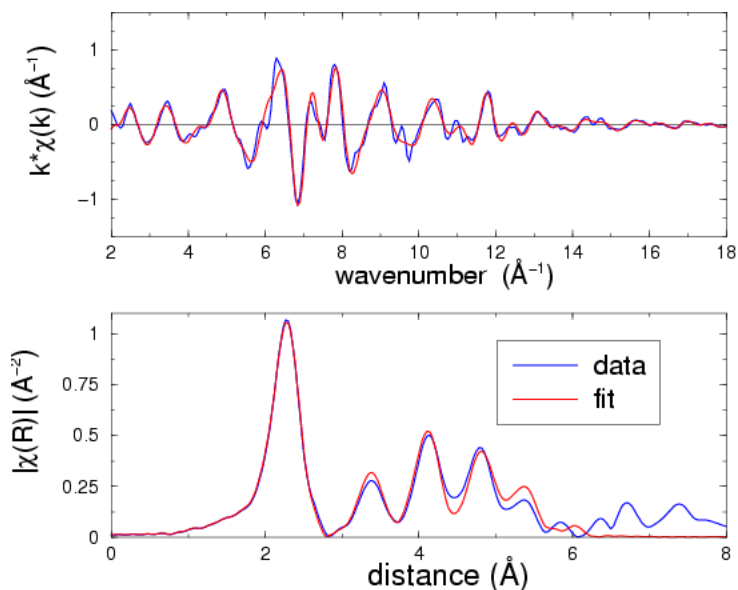
- R_{Γ} the half path length
- σ_{Γ} the mean squared displacement
- N_{Γ} the multiplicity of the path
- E_0 a shift of the overall energy scale
- S_0^2 the passive electron amplitude reduction factor

A Fit to the Copper Data

You remember this data from the beginning of the talk:



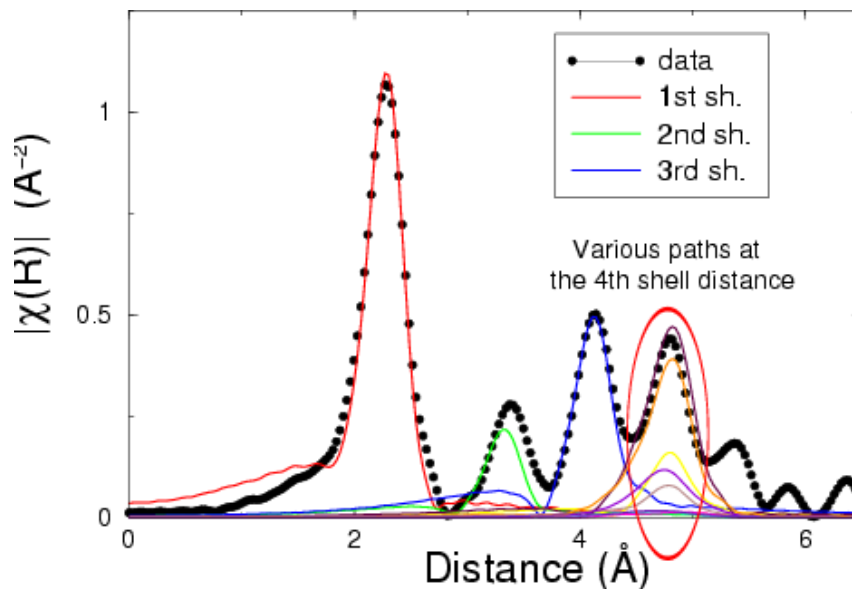
Here is the result of a simple analysis of this data using FEFF's fitting standards, shown in k and R space:



So how is multiple scattering theory used?

Magnitude of the Fourier Transform

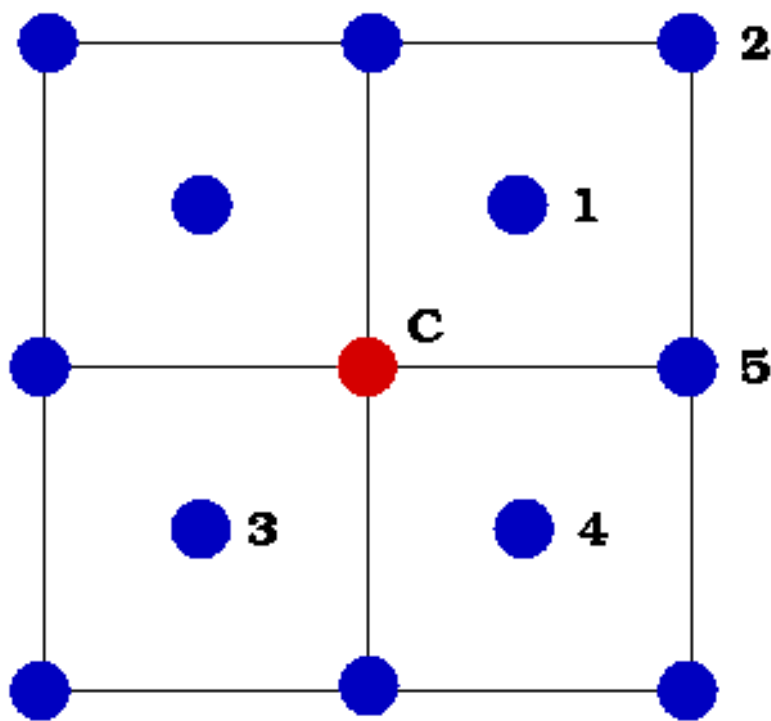
Here is data for copper metal plotted with several of the paths calculated by FEFF. This is the magnitude of the Fourier transform.



Note that there are many paths at the distance of the fourth neighbor.

Paths at the Fourth Shell Distance

There are a variety of paths which contribute at the fourth shell distance. Here is a schematic of the (100) plane in copper metal.



SS: $C \rightarrow 2 \rightarrow C$

TS: $C \rightarrow 1 \rightarrow C \rightarrow 3 \rightarrow C$

DS: $C \rightarrow 1 \rightarrow 2 \rightarrow C$

TS: $C \rightarrow 1 \rightarrow C \rightarrow 1 \rightarrow C$

DS: $C \rightarrow 1 \rightarrow 3 \rightarrow C$

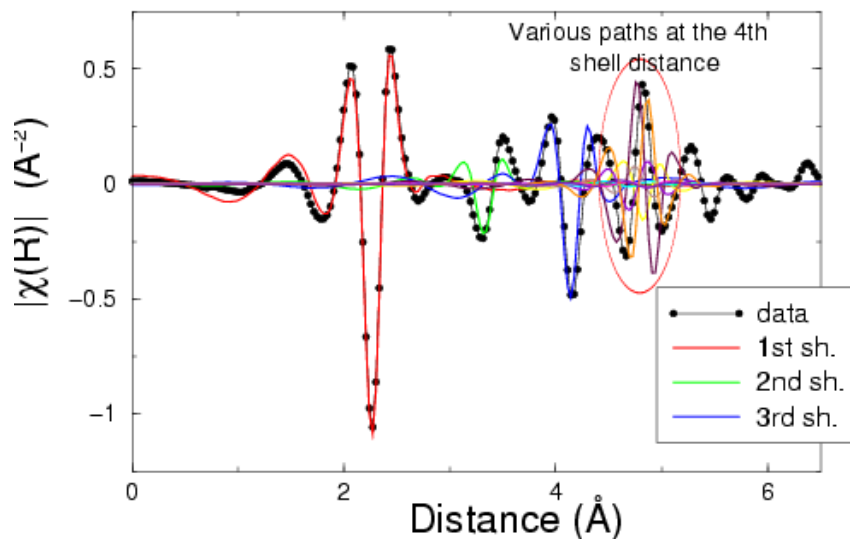
TS: $C \rightarrow 1 \rightarrow C \rightarrow 4 \rightarrow C$

TS: $C \rightarrow 1 \rightarrow 2 \rightarrow 1 \rightarrow C$

TS: $C \rightarrow 1 \rightarrow 5 \rightarrow 1 \rightarrow C$

Real Part of the Fourier Transform

Here are the same data as before, but plotted as the real part of the complex transform.



The various paths at the fourth neighbor distance are slightly out of phase. Correctly accounting for this detailed phase relationship is essential to analyzing EXAFS data.

Conclusion

This lecture has been a whirlwind introduction to EXAFS experiments and theory. Among the many things I have not discussed are

- Computational requirements of a multiple scattering theory
- XANES interpretation or theory
- Relative value of theoretical and empirical fitting standards
- Methods of EXAFS analysis
- Interpretation of EXAFS analysis

The last three points in that list are among the topics of my course “EXAFS Analysis Using **FEFF** and **FEFFIT**”.

Contacting Me

Bruce Ravel

ravel@phys.washington.edu

<http://feff.phys.washington.edu/~ravel/>

This document is on the CD and Web site associated with my course “EXAFS Analysis Using **FEFF** and **FEFFIT**”. I welcome comments and suggestions.