
Introduction to EXAFS Analysis Using Theoretical Standards

Part 1: Presentation

Bruce Ravel
The Naval Research Laboratory

Version 0.02

February 7, 2001

Abstract

This document contains the presentation materials for a seminar entitled *Introduction to EXAFS Analysis Using Theoretical Standards*. 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/>

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Overview of Multiple Scattering Theory

Introduction to the EXAFS measurement. A heuristic picture of multiple scattering. Fermi's Golden Rule. Multiple scattering paths.

Fundamentals of Analysis with Theoretical Standards

EXAFS as a sum of paths. The EXAFS equation. Computing the terms in the EXAFS equation. Choosing important paths Copper metal as an example.

Applications of Multiple Scattering Theory

Several interesting problems which are difficult or impossible to solve without using theory.

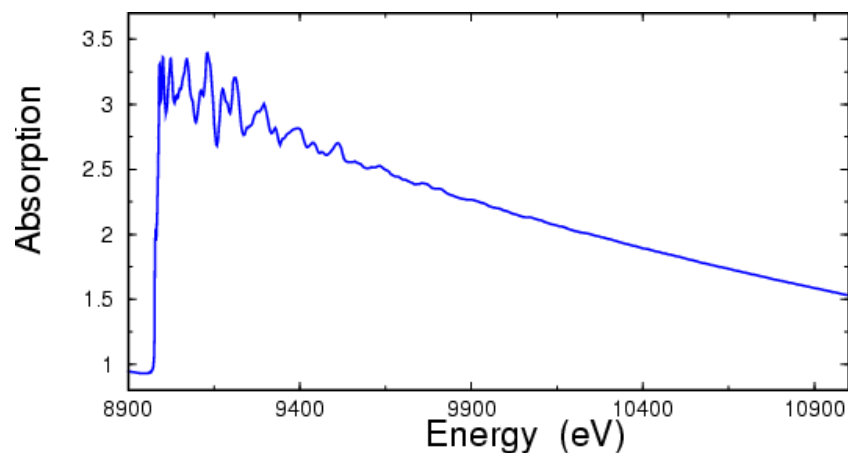
Conclusion

Summary, acknowledgments, and URLs.

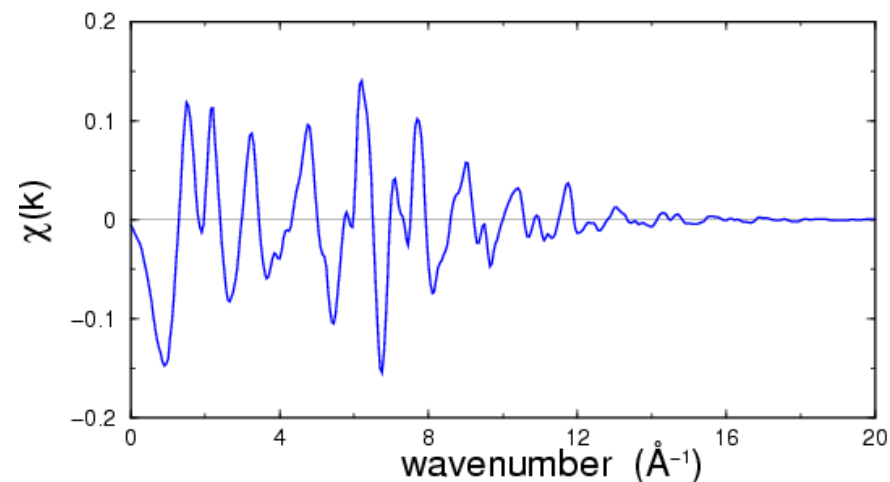
EXAFS Data

In an EXAFS experiment, one measures an **absorption spectrum**.

It looks something like this:



We first extract the wiggly part:



And then we analyze these data to obtain local structural information such as **coordination numbers**, **bond lengths**, and **thermal RMS deviations in bond length**.

How can we best extract information from these data?

Empirical and Theoretical Fitting Standards

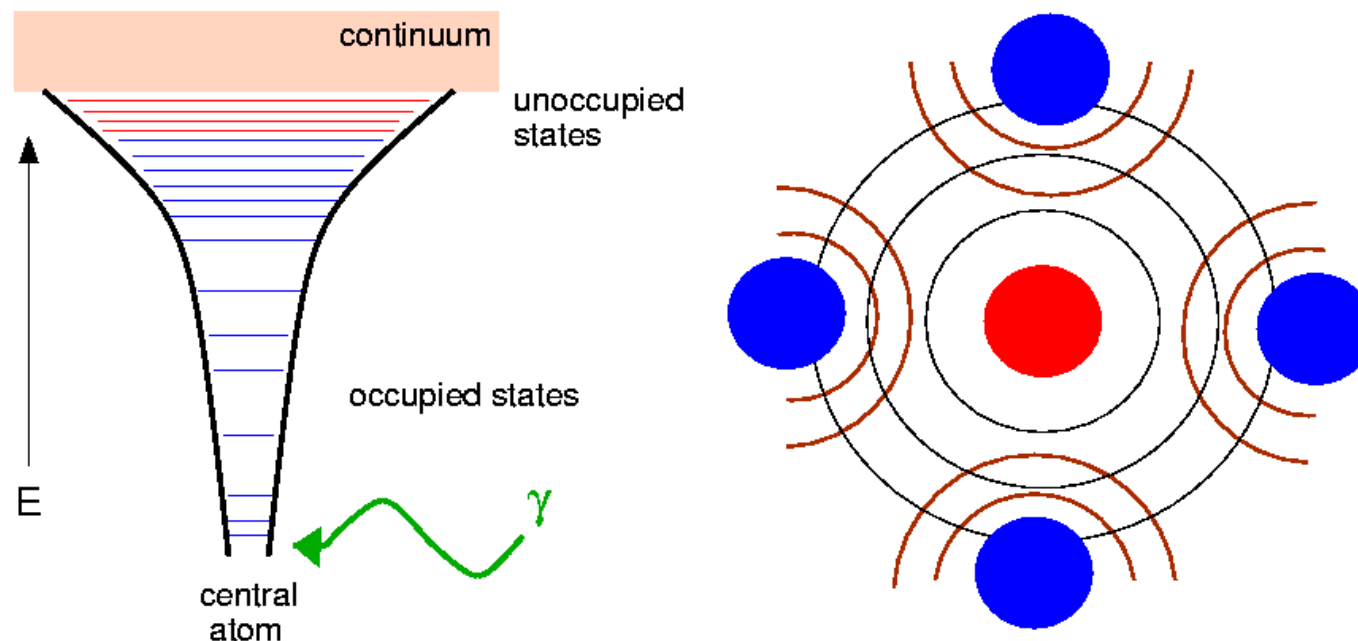
The “traditional” way of analyzing EXAFS data is to use empirical standards, often in conjunction with Fourier filter techniques.

In this approach, an *unknown* structure is understood by comparison with a *known* standard.

In this lecture, I will discuss the use of **theoretical standards** in EXAFS analysis and (I hope) convince you that theoretical standards are more powerful and flexible than empirical standards.

Heuristic Picture of EXAFS

In an EXAFS measurement, a deep core electron is excited into a state above the Fermi energy.



The photoelectron propagates as a spherical wave and scatters off the surrounding atoms. This cartoon is overly simplistic, but serves to motivate **multiple scattering theory**.

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 $|f\rangle$:

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

There are two ways to solve this equation:

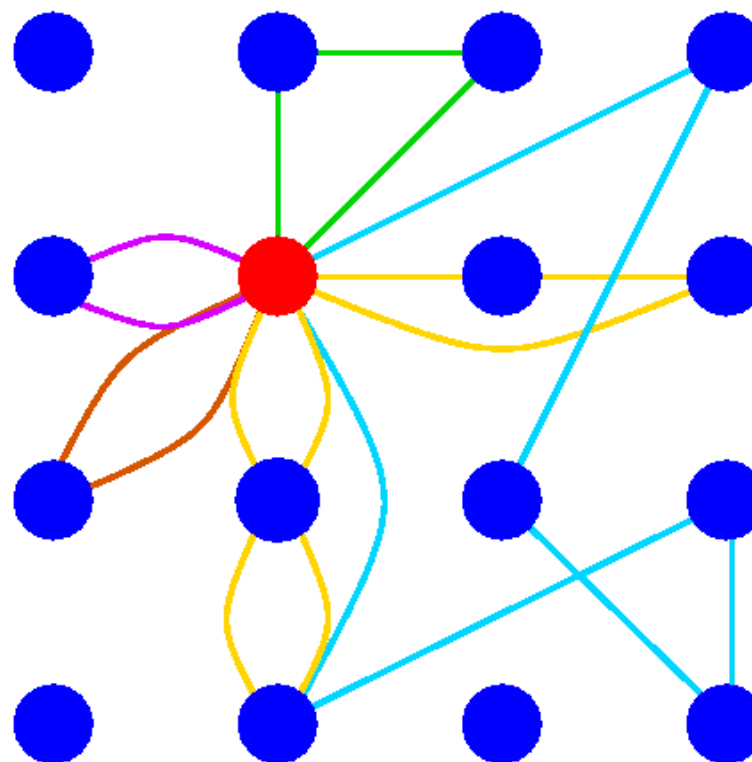
1. Accurately represent $|i\rangle$ and $|f\rangle$, then evaluate the integral directly. This is the approach taken, for example, by molecular orbital theory.
2. Use **multiple scattering theory**:

$$\mu(E) \propto -\frac{1}{\pi} \text{Im} \langle i | \hat{\epsilon}^* \cdot \mathbf{r} \mathbb{G}(\mathbf{r}, \mathbf{r}'; E) \hat{\epsilon} \cdot \mathbf{r}' | i \rangle \Theta(E - E_F).$$

Photoelectron Scattering in a Lattice

Consider a simple lattice of atoms. Choose one atom (the **red** one) as the central atom. 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.

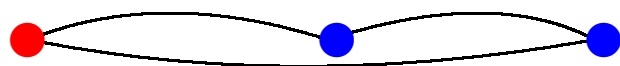


Types of Scattering Paths



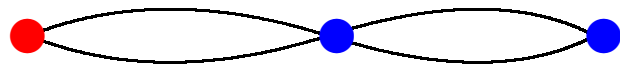
Single scattering path

These paths are very similar in concept to a *scattering shell* and are roughly equivalent to empirical standards.



Double scattering path

Paths with a single bounce off an intermediate atom.



Triple scattering path

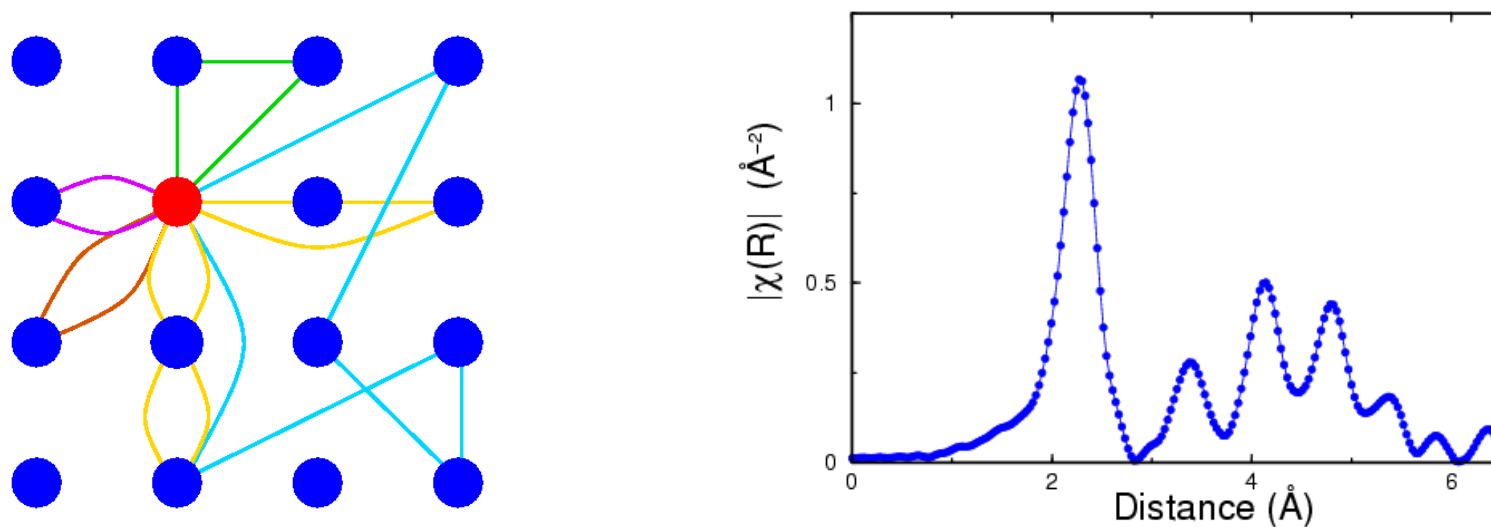
Paths with two bounces off one or two intermediate atoms.

Multiple scattering paths are most important when the **scattering** angle is close to 0° or 180° , i.e. **focused** scattering events.

Only the paths which contribute significantly need be considered.

The Fourier Transform

The Fourier transform of $\chi(k)$ is somewhat related to the radial distribution function of atoms around the absorber.

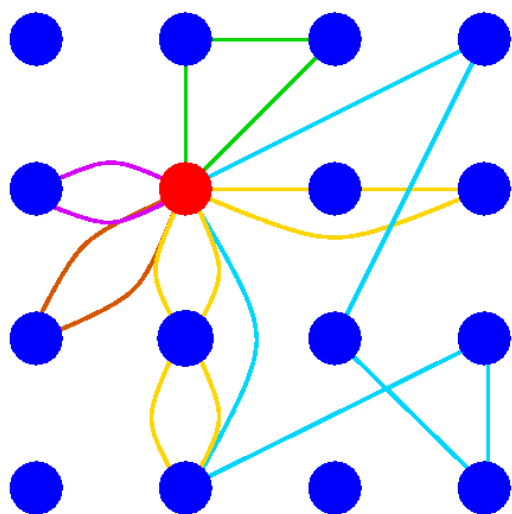


In fact, the figure of merit is not radial distance, but **path length**.

Only the paths contributing significantly in the R -range of the analysis need be considered.

Sum of Paths

In the **multiple scattering path expansion** the contributions from each path are summed.



Every possible path Γ in the cluster must be enumerated and its contribution computed.

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

We need **rules of thumb** for choosing the most important paths.

- **Filter by amplitude**
- **Filter by path length**

The EXAFS Equation

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

$$R_{\Gamma} = R_{0,\Gamma} + \Delta R_{\Gamma} \quad k = \sqrt{2m_e(E - E_0)/\hbar^2}$$

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

Multiple scattering theory is used to generate the **brown terms**

$R_{0,\Gamma}$ nominal path length
 F_{Γ} effective scattering amplitude
 Φ_{Γ} effective scattering phase shift
 λ mean free path

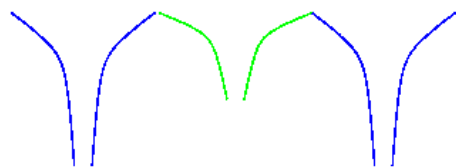
Structural and electronic information is determined from the **blue terms**

ΔR_{Γ} change in half path length
 σ_{Γ} mean squared displacement
 N_{Γ} path multiplicity
 S_0^2 passive electron reduction
 E_0 overall energy shift

Computing the Theory Terms

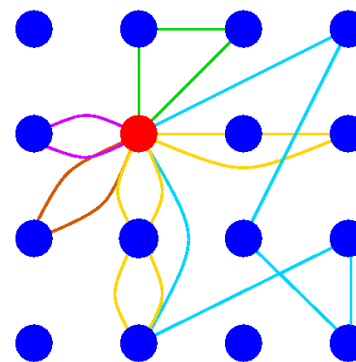
Compute atomic potentials and phase shifts

Use neutral, free, atomic spheres to construct a muffin tin potential. The embedded atoms are spherical and the interstitial region is flat. Self-consistency can be applied to redistributed charge among the spheres.



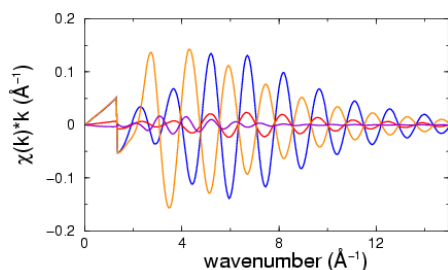
Find all scattering geometries in a cluster

Use a heap to construct successively higher orders of MS paths. In this way *all* possible scattering geometries are found in a cluster up to a specified order. Geometrical and time-reversal degeneracies are found. Polarization may break degeneracies.



Compute the contribution from each path

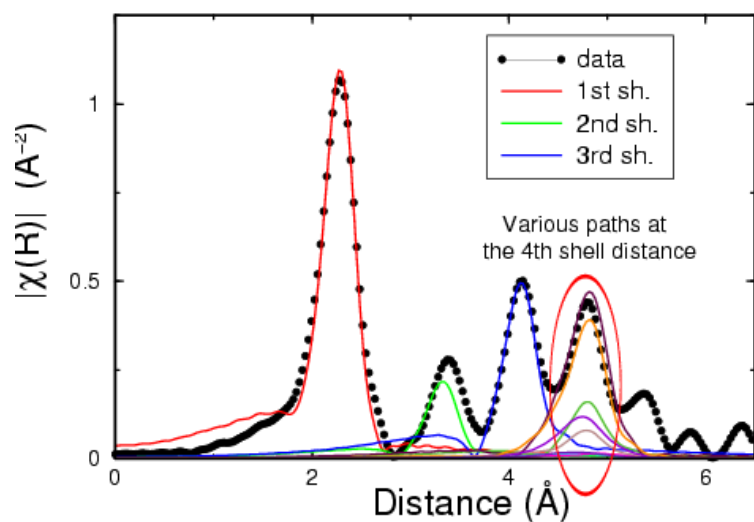
Using the list of enumerated paths and the atomic potentials, compute the curved-wave, effective scattering amplitudes and phase shifts for all paths. Polarization is considered *a priori* for all paths.



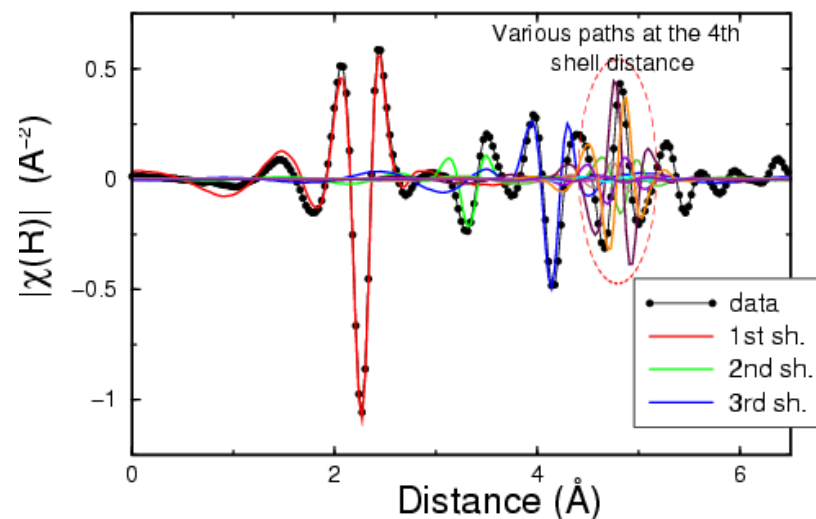
Copper Metal Data and Paths

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

This is the magnitude of the Fourier transform.



This is the real part of the complex transform.



Note that the Fourier transform is related to the **path length distribution function** and involves the detailed balance of many path contributions.

Why Use Theoretical Standards?

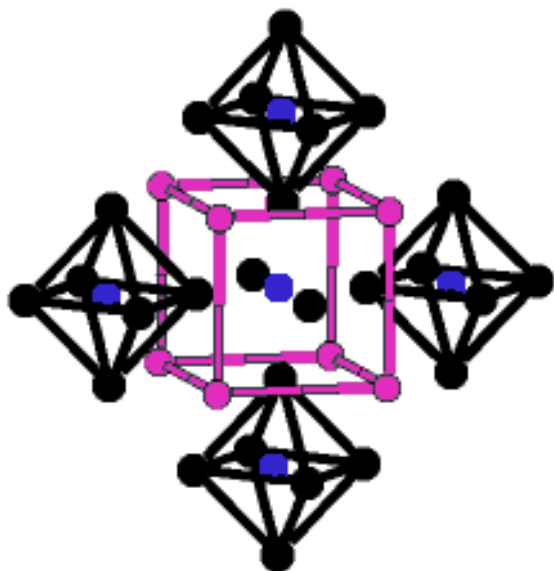
There are many categories of analysis problems for which empirical standards and Fourier filter techniques are inadequate. With theoretical standards, many such problems become tractable.

In this part of the talk I will outline several such examples.

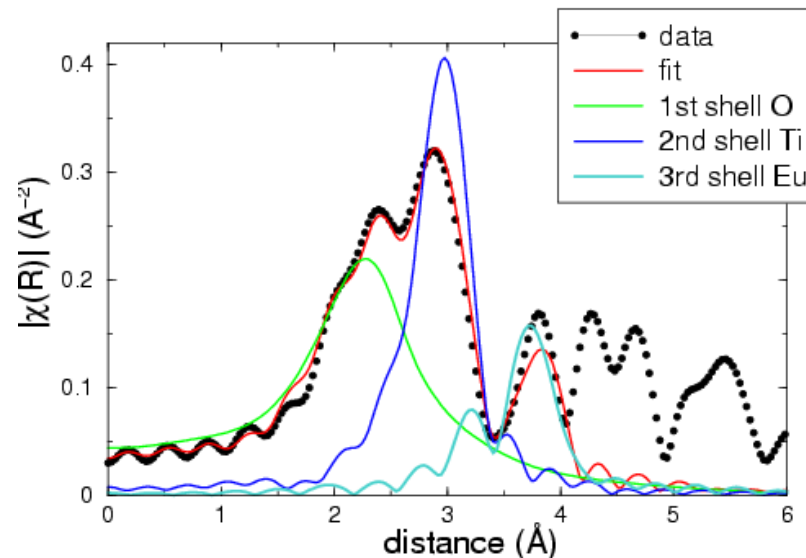
- **Overlapping shells**
- **Molecules with essential MS**
- **Three-body correlations**
- **Polarized measurements**
- **Mixed shells**
- **Exotic materials**

Overlapping Shells: EuTiO_3

EuTiO_3 is a simple cubic perovskite.
It looks like this:



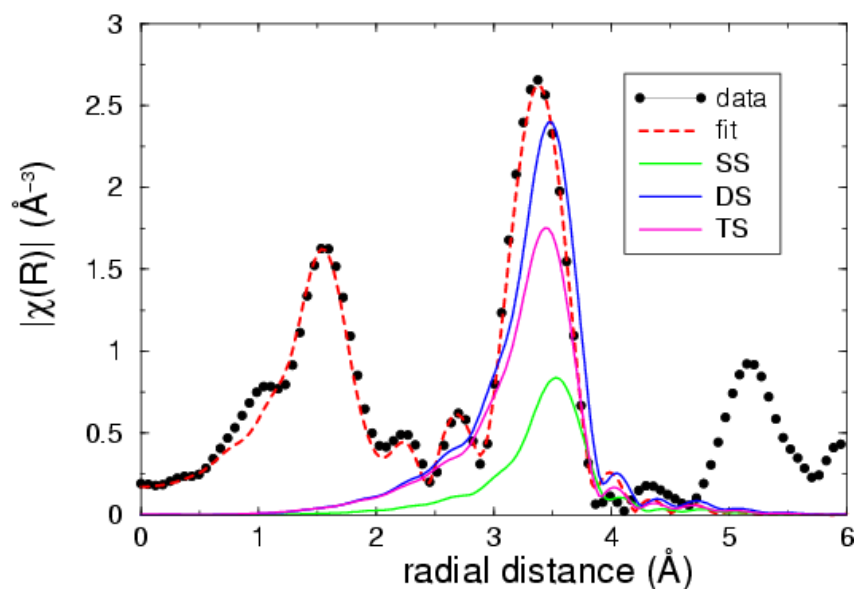
The Fourier transform of the Eu L_{III} data shows that single scattering contributions overlap.



Fourier filter techniques are clearly inappropriate in this case and empirical standards may be suspect at the larger distances.

Three Body Correlations: EuTiO_3

In well-ordered materials it is quite common to find significant contributions from multiple scattering paths at modest distances. Here again is EuTiO_3 , this time the Ti K edge.

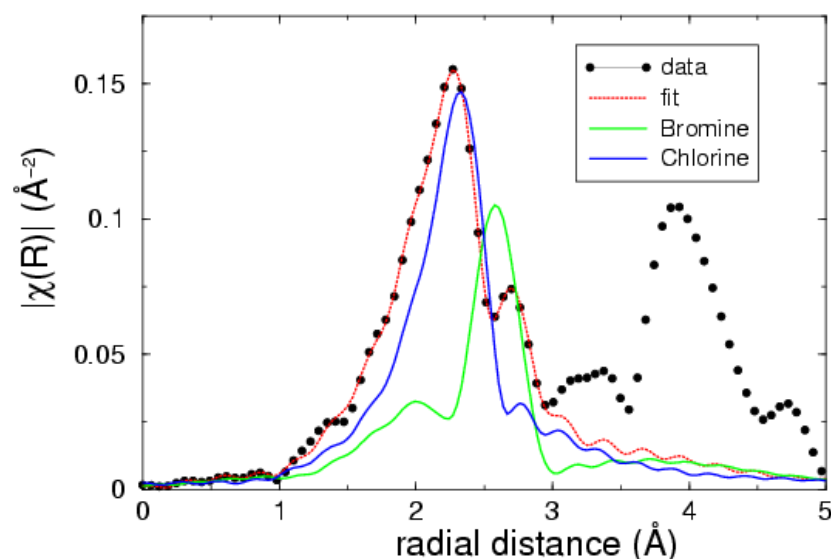


color	path	data
red		Complete fit
green	$\text{Ti}_c\text{-Ti-Ti}_c$	Single scattering
blue	$\text{Ti}_c\text{-O-Ti-Ti}_c$	Once focused DS
pink	$\text{Ti}_c\text{-O-Ti-O-Ti}_c$	Twice focused TS

The peak at the distance of the 3rd shell is composed of 6 paths, the three largest of which are shown. Note that the two MS paths are *larger* than the SS path.

Mixed Shells: $\text{AgBr}_{1-x}\text{Cl}_x$

Using theoretical standards offers significant freedom for considering arbitrarily complex structural models.



This is the Ag K edge with $x \approx 0.5$.

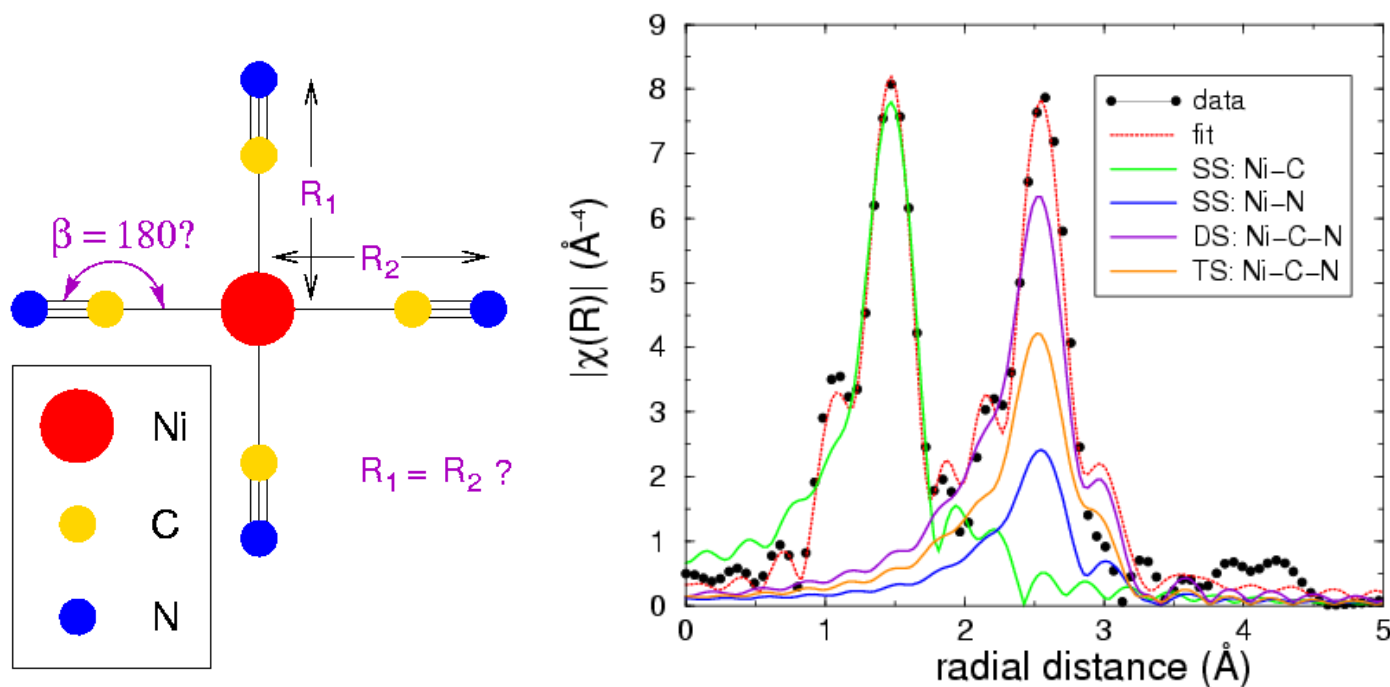
As the mixed first shell is fairly well isolated, this fit could probably be reproduced with empirical standards. But analysis of higher shells would be intractable.

Mixed salts, like mixed III-V semiconductors, have buckled local structures to accommodate the different rigid bond lengths. This sort of extraordinarily complex local structure can (with work) be modeled well beyond the first shell using theory.

A similar problem: Phys. Rev. **B60**, #21 (1999) pp. 14632–14642

Molecules and Multiple Scattering: $[\text{Ni}(\text{CN})_4]^{2-}$

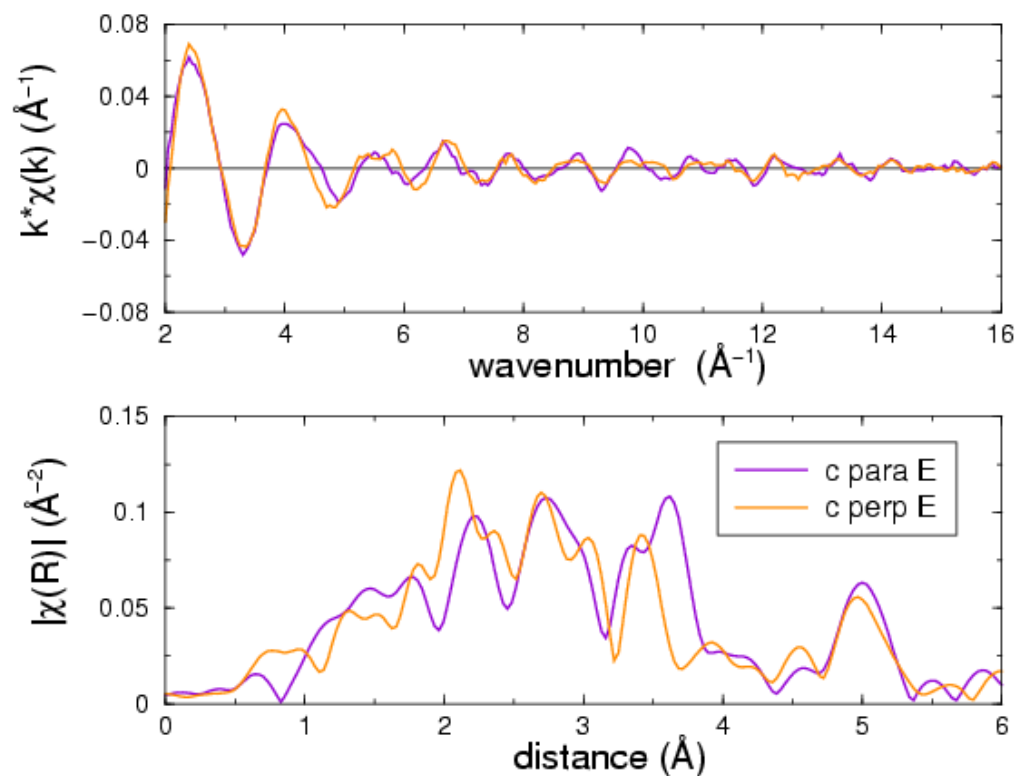
$[\text{Ni}(\text{CN})_4]^{2-}$ is a square planar molecule soluble in water. It has high symmetry, so the MS contributions in the *second* shell are large.



First shell analysis is clearly insufficient – half the molecule is in the second shell!
We *need* theory for this one.

Polarized Measurements: $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$

Theoretical standards can accurately model the polarization dependence of the synchrotron beam.



This is the La K edge of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$.

The spectra are distinct for the two orientations. This is because $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$ is orthorhombic with $c \gg a$ and $c \gg b$.

All paths, including the MS paths, have polarization intrinsic to the calculation.

Exotic Compounds

Perhaps the most significant drawback to empirical standards is that one must exist for your compound of interest. For many important problems, no suitable empirical standards exist.

Uranium and Plutonium	Rare earth metals	Organometallics
Bonding with these elements involves <i>f</i> electrons. Multiple valence states exists. It may be impossible to find a standard with an electronic structure similar to your sample.	These also have complex bonding and standards may be prohibitively expensive.	Solid state empirical standards may not be chemically transferable to some organic compounds.

Summary

Theoretical standards allow the EXAFS experimentalist to quantitatively analyze problems of significant complexity. With theoretical standards higher shells, multiple scattering contributions, mixed shells, polarization and many other effects can be treated rigorously.

Using the theory is easy and accessible. Many current analysis programs make excellent use of existing theory.

Recently, an excellent review article on modern XAS theory was published.
Rehr and Albers. Rev. Mod. Phys, v. 72, #3, (2000)

Acknowledgments

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

- The EXAFS group at LNLS and the program committee for the Inter-American Workshop on the Use of Synchrotron Radiation, for this invitation
- **Matt Newville**, for writing **FEFFIT** and for other contributions too numerous to count
- **Sofía Díaz-Moreno**, for contributing the $[\text{Ni}(\text{CN})_4]^{2-}$ data
- **Daniel Haskel**, for contributing the polarization dependent data on $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$
- Jean-Louis Hodeau and the program committee of HERCULES 2000, for my first opportunity to give this lecture
- **John Rehr**, **Jose Mustre de Leon**, **Steve Zabinsky**, and **Alex Ankudinov**, for writing **FEFF**

This document was created with free software. I used PDF \LaTeX and the \TeX typesetting system. I edited with XEMACS, along with the AU \TeX , ref \TeX , and bib-cite packages. I created figures using XMGR, XFIG, and RASMOL. I analyzed EXAFS data using **FEFF** 6.01, **FEFFIT** 2.54, and **AUTOBK** 2.63. *The \LaTeX Companion* was an invaluable reference.

Obtaining Theory and Analysis Codes

Sadly, none of the major theory codes are free software both in the sense of *without cost* and of *available source code*. But all are of high quality and well suited to the problems discussed in this talk.

CODE	URL	cost ^a	src ^b	GUI ^c	IA ^d
FEFF	http://feff.phys.washington.edu/feff	yes	yes	no	no
GNXAS	http://gnxas.unicam.it/	no	no	no	yes
EXCURVE	http://www.msi.com/materials/cerius2/exafs.html	LOTS!	no	yes	yes

^a Is a licensing fee required?

^c Are there integrated graphics?

^b Do you get access to the source code?

^d Is there integrated analysis?

A fairly complete list of analysis programs can be found at

<http://www.esrf.fr/computing/scientific/exafs/>

FEFFIT (my favorite analysis program!) can be found at

<http://cars9.uchicago.edu/~newville/feffit/>

Notes from a three day course on EXAFS analysis can be found at

<http://leonardo.phys.washington.edu/~ravel/course/>

Notes
