
Multiple Scattering Theory and Third Generation Synchrotron Science

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Version 0.1
February 17, 2006

Abstract

In the 80's and 90's a powerful multiple scattering formalism was developed and applied to the profusion of XAS data coming from the many bending magnet spectroscopy lines around the world. The new century has seen the maturation of the third generation light source characterized by high flux and high brilliance. These beam qualities have enabled the development of a variety of powerful new techniques that push the applicability of spectroscopy far beyond the bounds of what was conceivable in the early days. Whether your experiment involves novel instrumentation (such as focusing optics or time-domain spectroscopy) or novel techniques (such as RIXS or DAFS), or you use a bending magnet for bulk XAS, your measurement requires the interpretation of an XAS spectrum. The methods developed 20 years ago remain directly relevant today.

In this talk, I present a broad overview of how multiple scattering theory is applied to the interpretation of the near-edge and the extended portion of the XAS spectrum. I then present a real-world environmental science problem that demonstrates the sophisticated application of multiple scattering theory and analysis.

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Table of Contents

Introduction	1
What I'll cover in this talk	1
Synchrotron Science Across the Generations	2
The physical formalism of XAS	3
The XAS formalism, continued	4
Types of scattering paths	5
Examining the feff calculation	6
The first path in iron metal	6
The second path in iron metal	7
The third path in iron metal	8
The fourth path in iron metal	9
The fifth path in iron metal	10
The eighth path in iron metal	11
The fifth shell in iron metal	12
Uranium Adsorbed on Biomass	13
Uranium Contaminated Ground Water	13
A Cartoon View of Biogeochemistry	14
Uranium on <i>B. Subtilis</i>	15
Physical Model for Uranium Adsorbtion	16
Constraints and Restraints	17
Setting This Up in ARTEMIS	18
Results	19
Concluding Remarks	20
Abstraction of Parameters	20
Abstract Concepts in Modeling	21
Obtaining FEFF, IFEFFIT, ATHENA, and ARTEMIS	22

What I'll cover in this talk

- An explanation of why techniques developed for spectroscopy at second generation light sources remains very relevant today
- An overview of how multiple scattering theory is used to interpret **XANES** spectra
- An overview of how multiple scattering theory is used to analyze **EXAFS** spectra
- An example of how multiple scattering theory is used to gain insight into a real-world, environmental science problem

We will be talking about

FEFF

There are other MS codes, including EXCURV, GNXAS, and others.
There are other XAS codes using techniques such as multiplets, band structure, and finite difference solutions to Schrödinger's equation.

Synchrotron Science Across the Generations

Nowadays

1. Focussing
 - micron-scale with KB mirrors
 - nano-scale with zone plates
2. Time domain
 - Very quick scans
 - Pump-probe + time structure of the beam
 - Dispersive optics
3. Environmentally and biologically relevant concentrations
4. Resonant Inelastic X-ray Scattering (RIXS)
5. Diffraction Anomalous Fine Structure (DAFS)

as well as...

1. bulk XAS at a bending magnet

In the old days

1. bulk XAS at a bending magnet

The formalism (both theoretic and analytical) developed in the old days is still relevant.

At the end of the day, all these techniques produce an XAS spectrum!

The physical formalism of XAS

In XAS we measure the *dipole mediated*^[1] transition of an electron in a *deep core*^[2] state $|i\rangle$ into an *unoccupied*^[3] state $|f\rangle$:

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

There are two common ways of solving this^[4] equation:

1. Accurately represent $|i\rangle$ ^[5] and $|f\rangle$ ^[6], then evaluate the integral directly. This is the approach taken, for example, by molecular orbital theory.
2. Use multiple scattering theory, AKA a Green's function^[7] or propagator formalism:

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

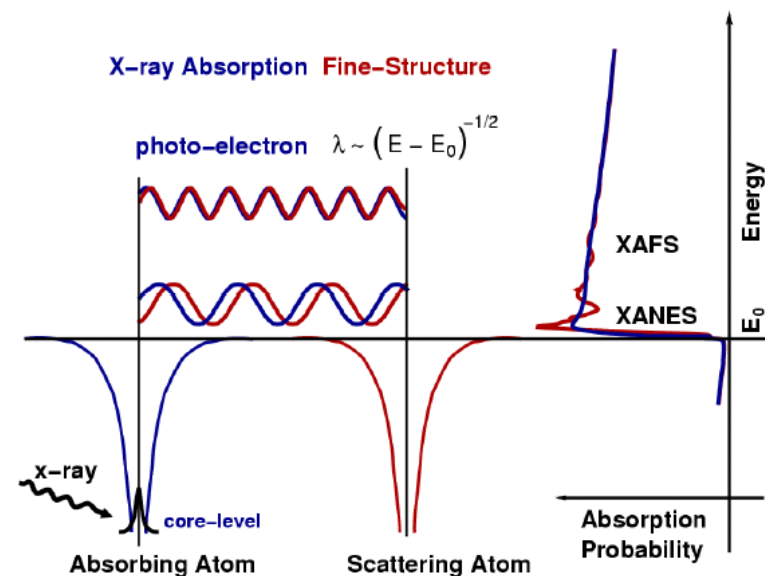


Figure courtesy Matt Newville

1. A photon interacting with an electron is a dipole interaction.
2. Typically a $1s$, $2s$, or $2p$ electron.
3. A bound or continuum state **not** already containing an electron.
4. This is an example of *Fermi's Golden Rule*.
5. Easily computed using basic quantum mechanics.
6. Hard work, lots of computation!
7. \mathbb{G} is called a Green's function.

The XAS formalism, continued

In multiple scattering theory, all the hard work is in computing the Green's function.

- \mathbb{G} the function that describes all possible ways for a photo-electron to interact with the surrounding atoms
- G^0 the function that describes how an electron propagates between two points in space
- t the function that describes how a photo-electron scatters from a neighboring atom

$$\mathbb{G} = (1 - G^0 t)^{-1} G^0 \quad (1)$$

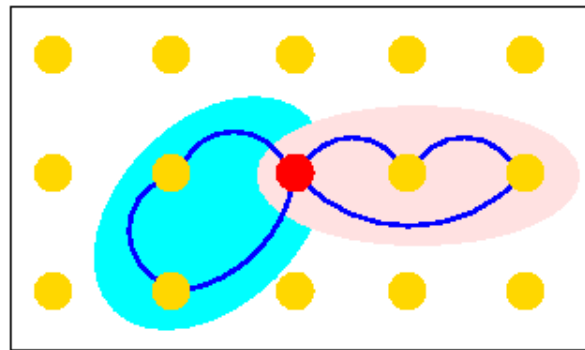
$$= G^0 + G^0 t G^0 + G^0 t G^0 t G^0 + G^0 t G^0 t G^0 t G^0 + \dots \quad (2)$$

spectrum	use	how	limitations
XANES	Eqn. 1	brute force matrix algebra	limited energy and cluster size
EXAFS	Eqn. 2	further expand each order of scattering	bookkeeping, no XANES

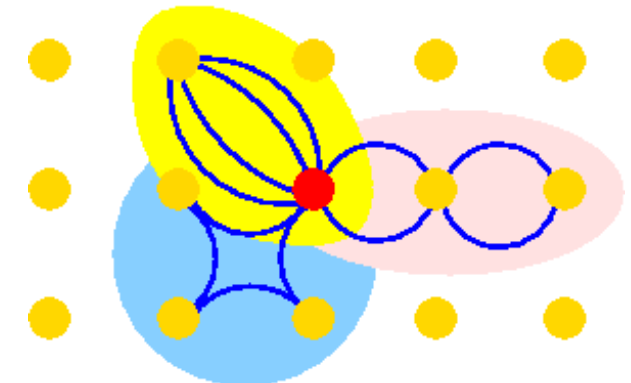
Types of scattering paths



single scattering path
two legs



Triangular and collinear
double scattering paths
three legs



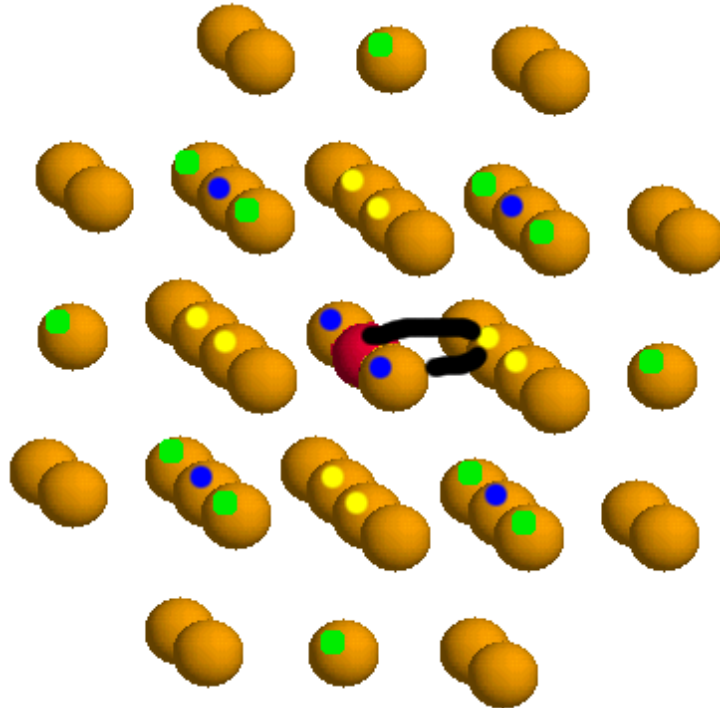
Collinear and other
triple scattering paths
four legs

..... and so on

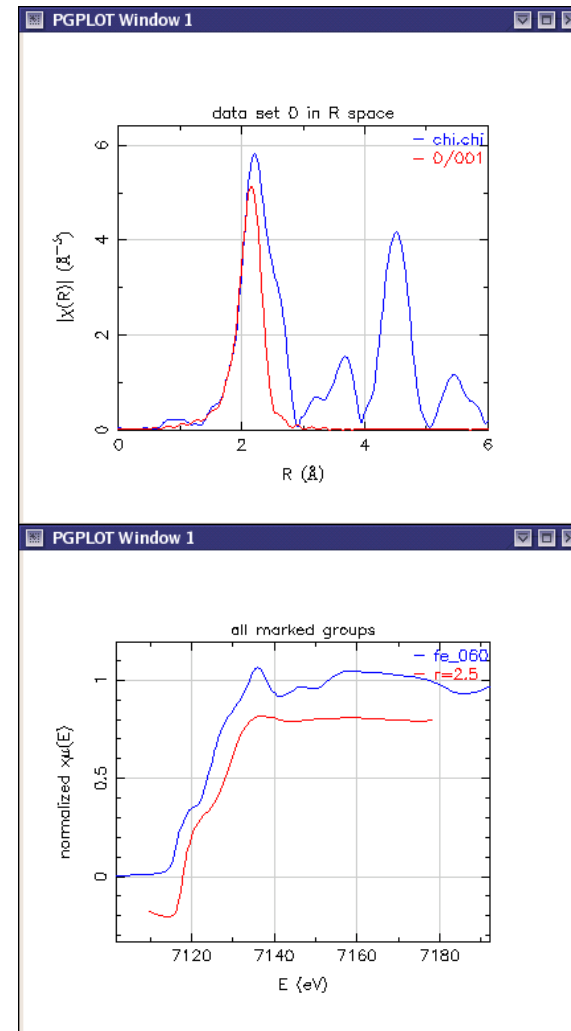
Solving $\mathbb{G} = (1 - \mathbb{G}^0 \mathbb{t})^{-1} \mathbb{G}^0$ considers these and ALL other paths within some cluster of atoms.

The clever thing about FEFF is that each term is further expanded as a sum of all paths of that order. $\mathbb{G}^0 \mathbb{t} \mathbb{G}^0$ is expanded as a sum of single scattering paths, $\mathbb{G}^0 \mathbb{t} \mathbb{G}^0 \mathbb{t} \mathbb{G}^0$ is a sum of all double scattering paths, and so on.

The first path in iron metal



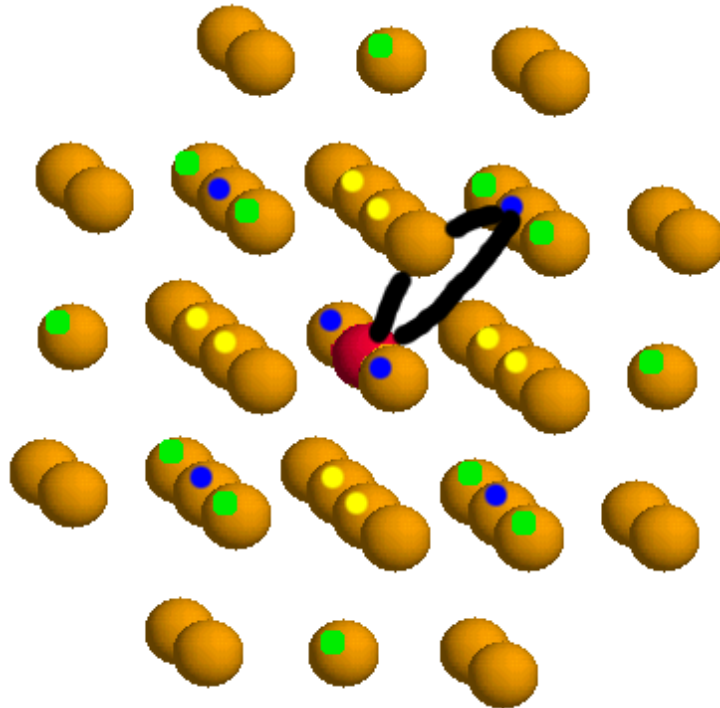
1. The first path is much, but not all, of the first peak in $|\tilde{\chi}(R)|$. Degeneracy = 8.
2. The first shell XANES calculation shows little of the structure.



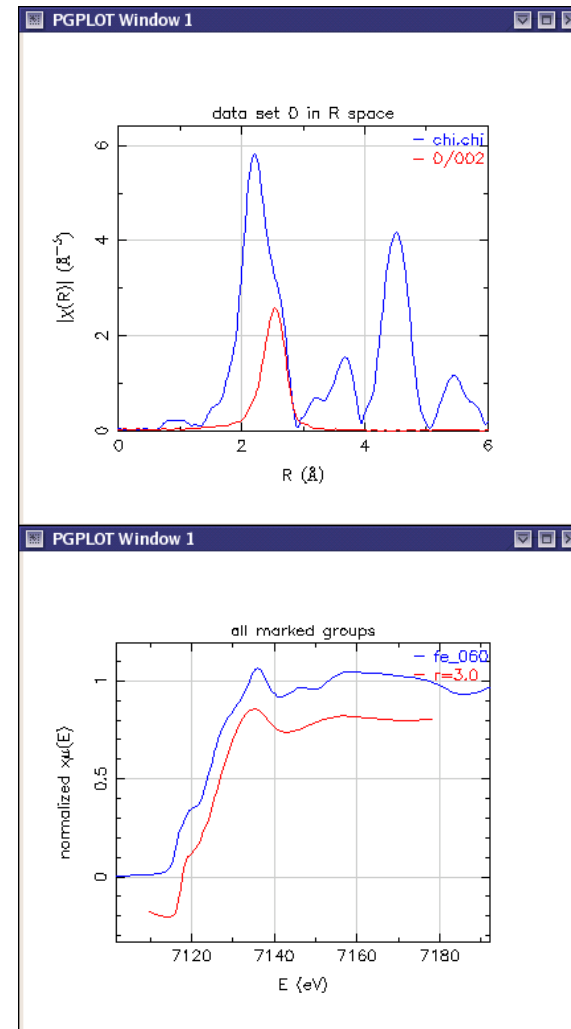
f
e
f
f
0
0
0
1

X
A
N
E
S

The second path in iron metal



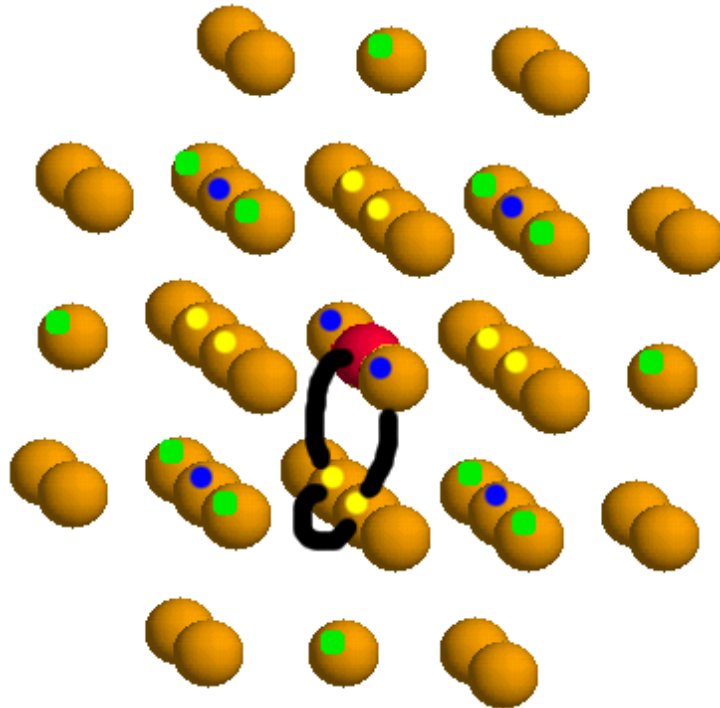
1. The second path overlaps the first in $|\tilde{\chi}(R)|$. Degeneracy = 6.
2. The XANES calculation begins to show the structure of the spectrum.



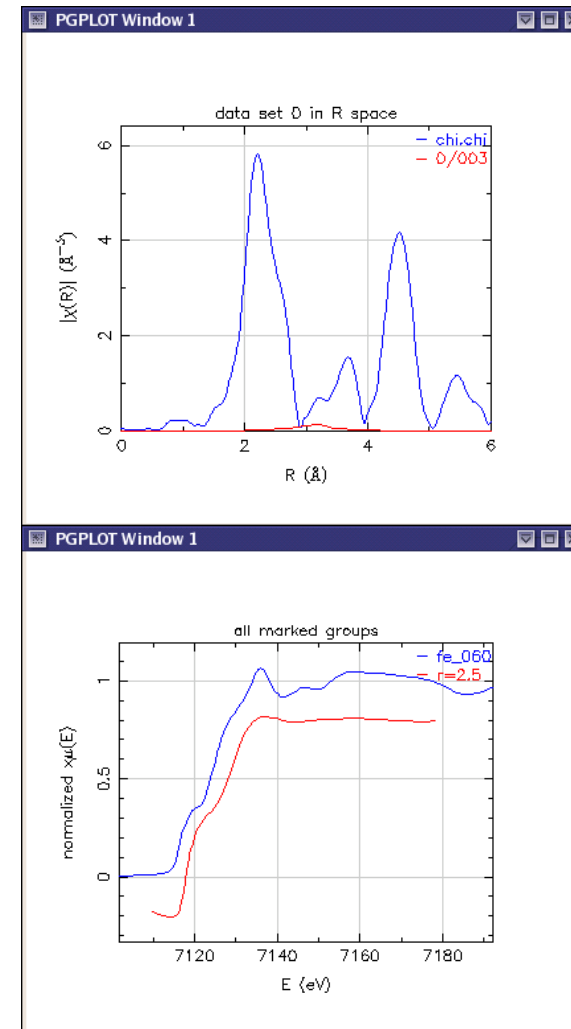
f
e
f
f
0
0
0
2

X
A
N
E
S

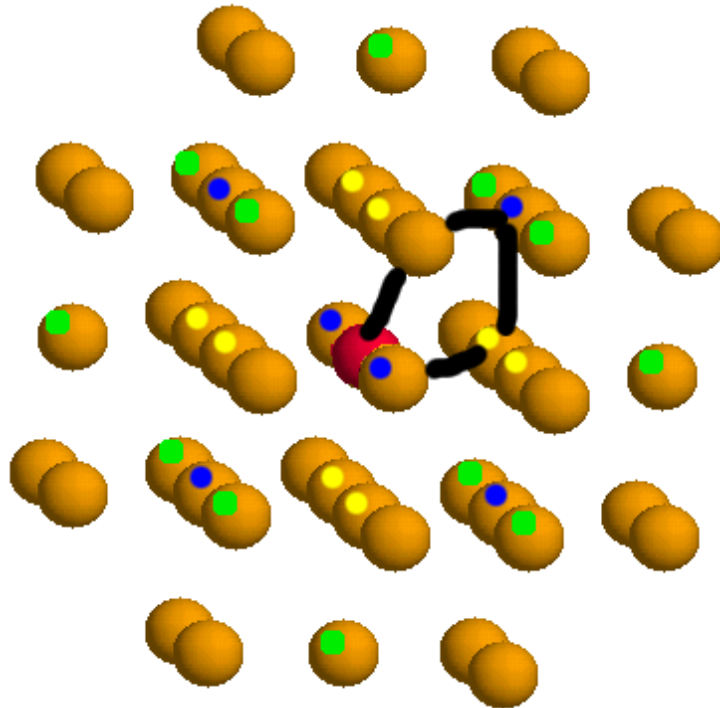
The third path in iron metal



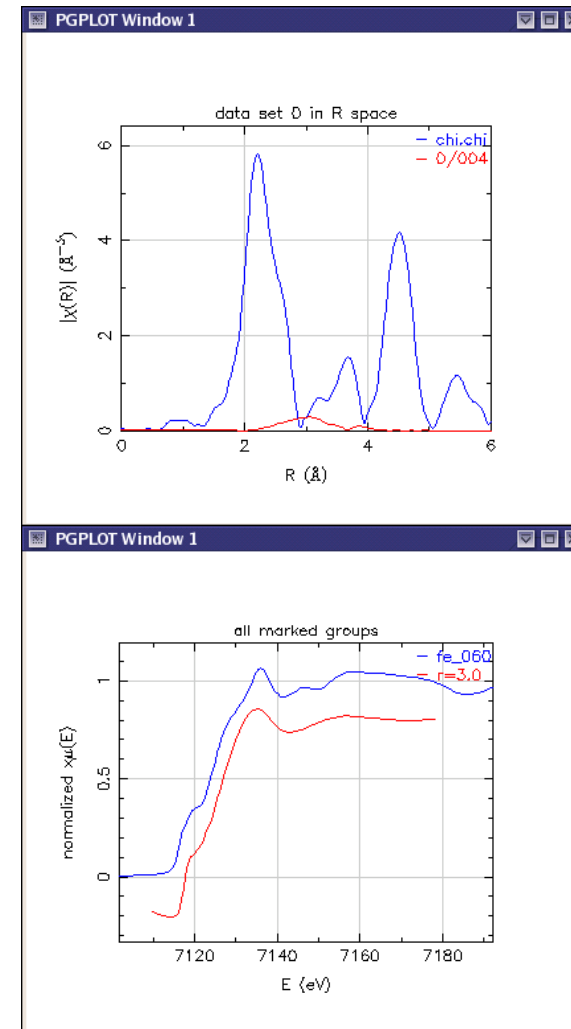
1. This path contributes little to $|\tilde{\chi}(R)|$. Degeneracy = 24.
2. The contribution from this path and all higher order paths scattering among these atoms is in the first shell XANES calculation.

f
e
f
f
0
0
0
3X
A
N
E
S

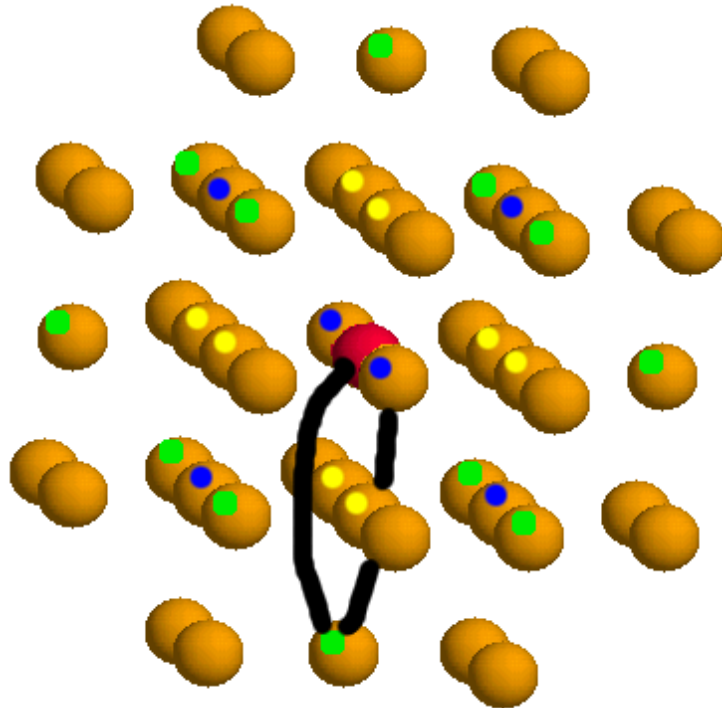
The fourth path in iron metal



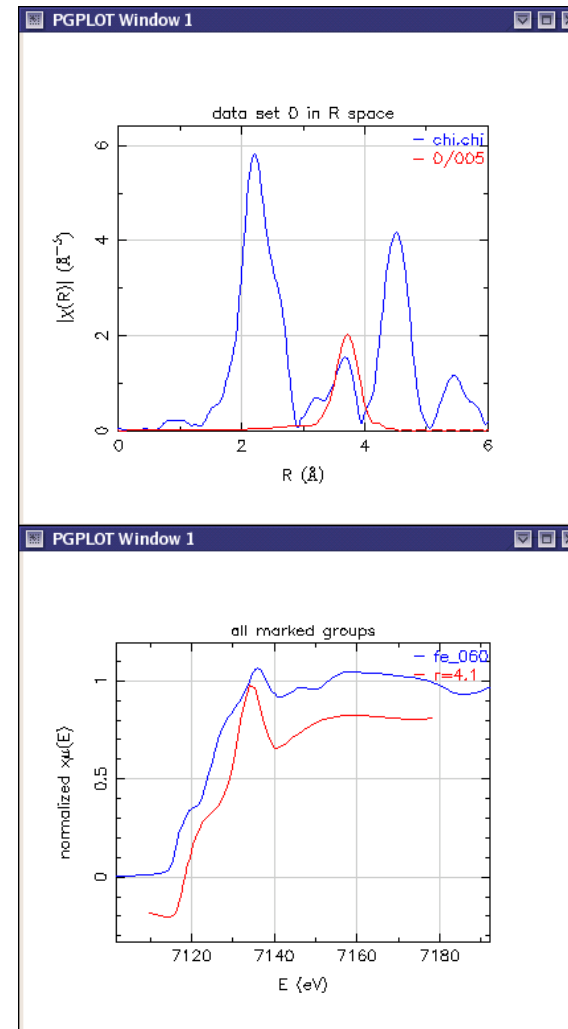
1. This path contributes little to $|\tilde{\chi}(R)|$. Degeneracy = 48.
2. The contribution from this path and all higher order paths scattering among these the first two shells is in the second shell XANES calculation.

f
e
f
f
0
0
0
4X
A
N
E
S

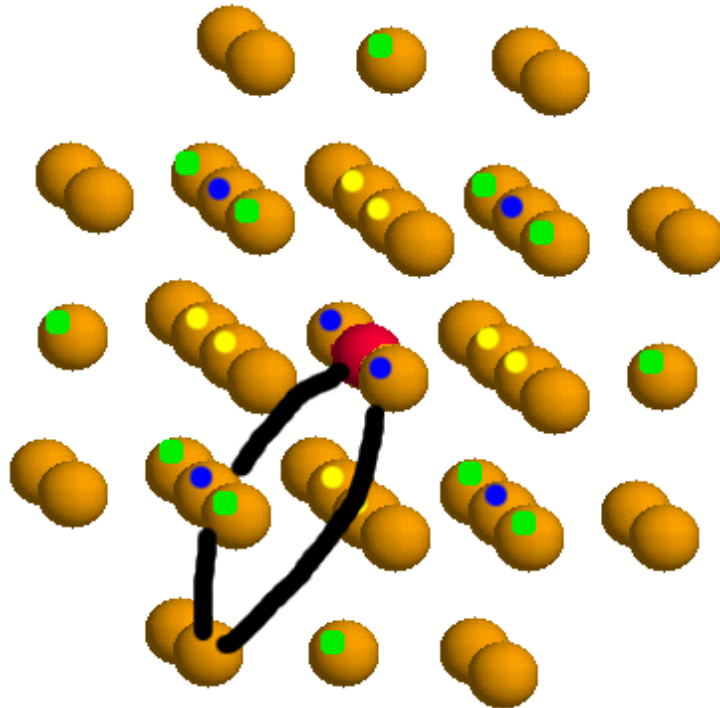
The fifth path in iron metal



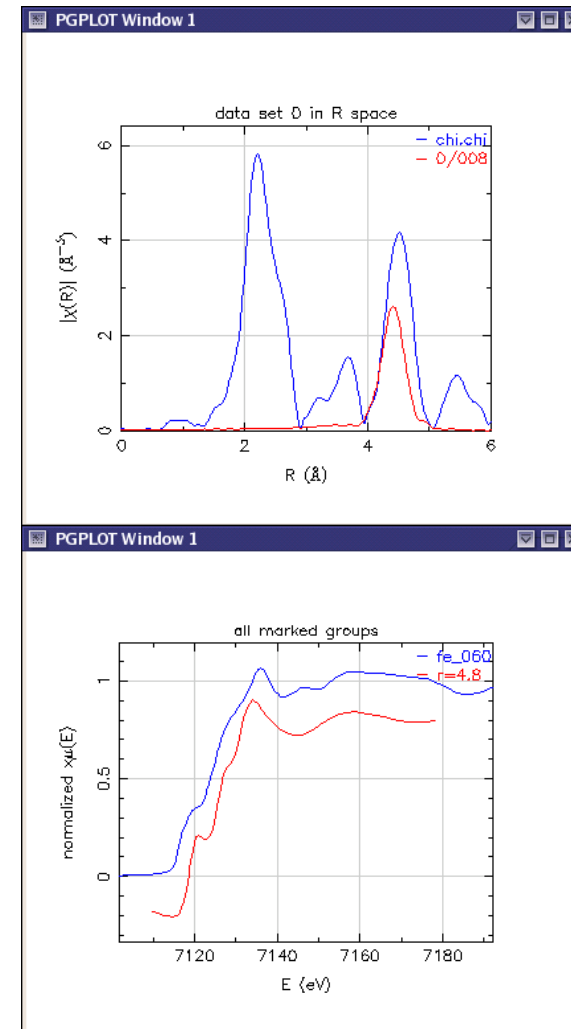
1. This 3rd shell SS path contributes most of the spectral weight to the second peak of $|\tilde{\chi}(R)|$. Degeneracy = 12.
2. The first peak after the edge in the XANES is sharpened considerably by the addition of this shell.

f
e
f
f
0
0
0
5X
A
N
E
S

The eighth path in iron metal



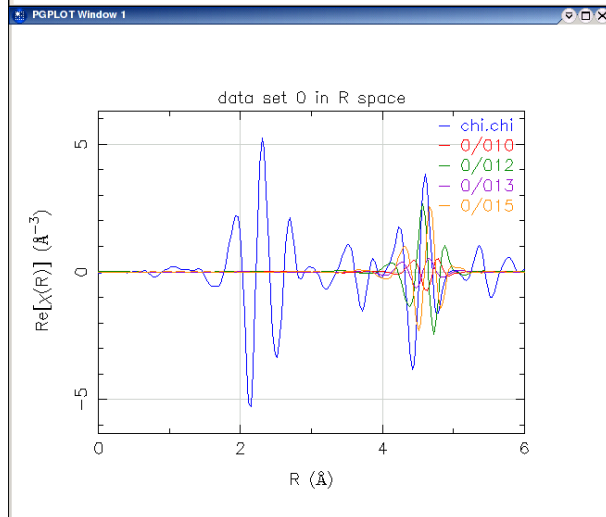
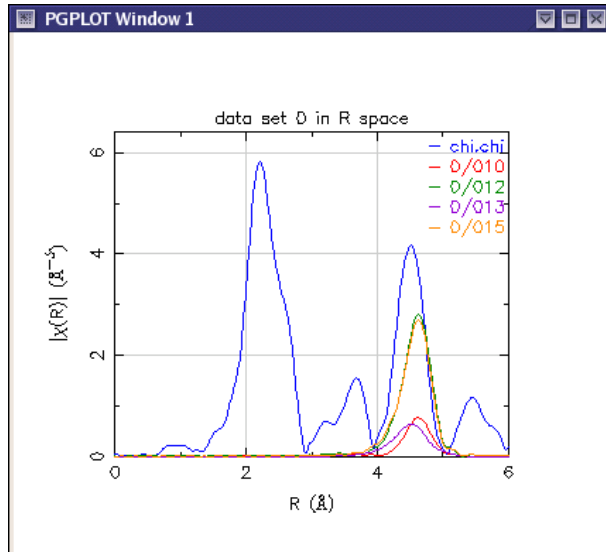
1. The 4th shell SS path contributes to the third peak in $|\tilde{\chi}(R)|$. Degeneracy = 24.
2. Including this shell in the XANES calculation broadens the peak above the edge somewhat. It also introduces the second shoulder..

f
e
f
f
0
0
0
8X
A
N
E
S

The fifth shell in iron metal

5
t
h
s
h
e
l
l

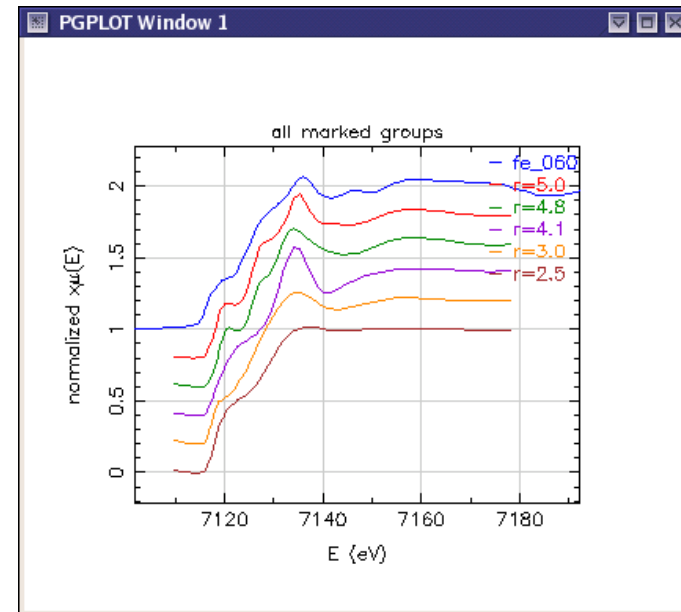
R
e
a
l
P
a
r
t



There are several collinear multiple scattering paths involving the 5th shell atom.

Note that the collinear MS paths are bigger than the SS path!

Below is the shell progression of the XANES calculations. The one including the 5th shell looks a lot like the data.



Uranium Contaminated Ground Water



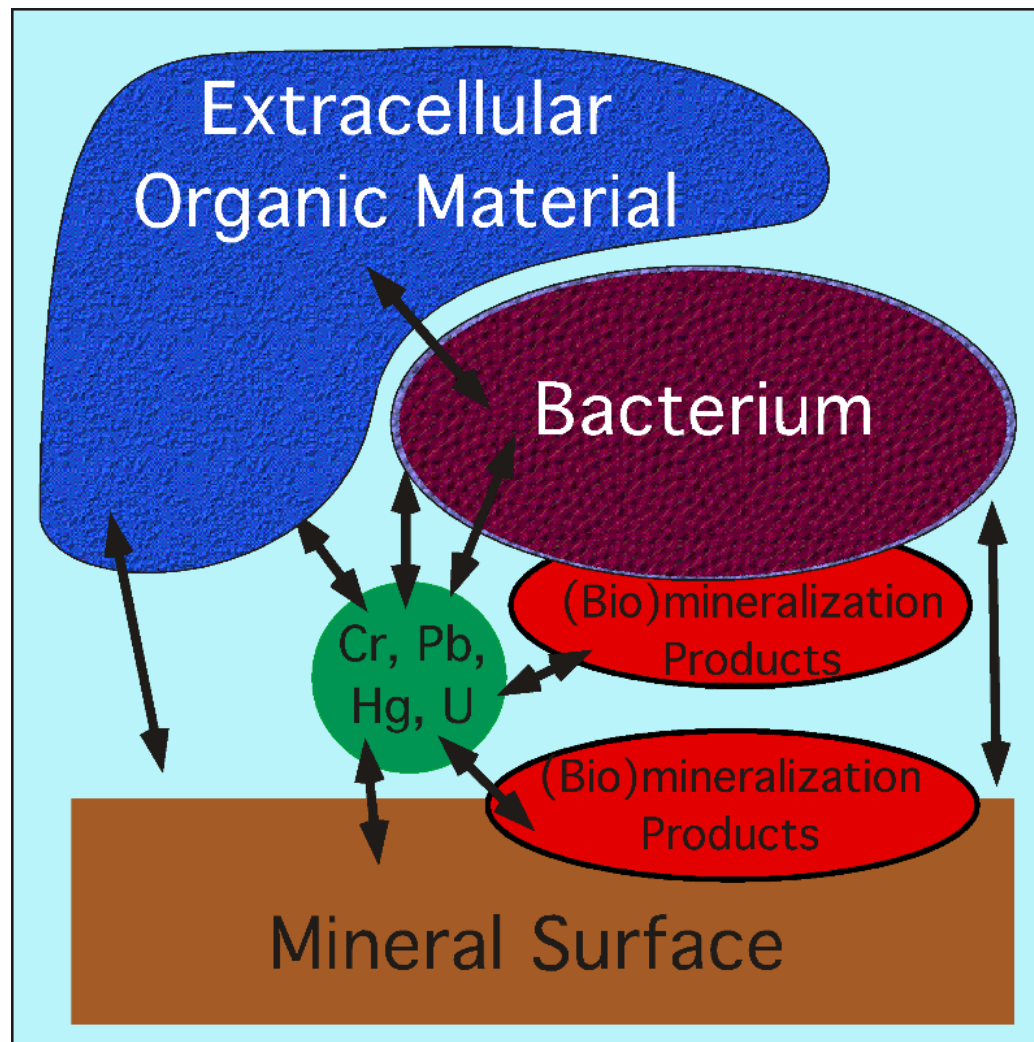
Photo courtesy The Field Research Center, NABIR, and the DOE

A troubling legacy of the production of nuclear materials for energy and warfare purposes is the heavy contamination of waste storage sites at the production facilities.

At Oak Ridge National Laboratory in Tennessee, USA, the Field Research Center is down gradient of capped storage ponds.

These ponds are full of heavy metals (U, Cd, Tc, etc.) and very low pH. The fluid draining from these ponds dissolves the surrounding bedrock, producing a chemically complicated brew.

A Cartoon View of Biogeochemistry



As a contaminant metal travels through a water system, it interacts with:

- The fluid
- Mineral surfaces
- Bacteria
 - Cell wall
 - Cell interior
- Bacterial products
 - Extracellular polymeric materials
 - Mineralization and biomineralization products adhered to mineral surfaces
 - Mineralization and biomineralization products adhered to cell surfaces

Yikes! Very complicated!

As physicists, we like to break complex systems into components.

Uranium on *B. Subtilis*

Motivation

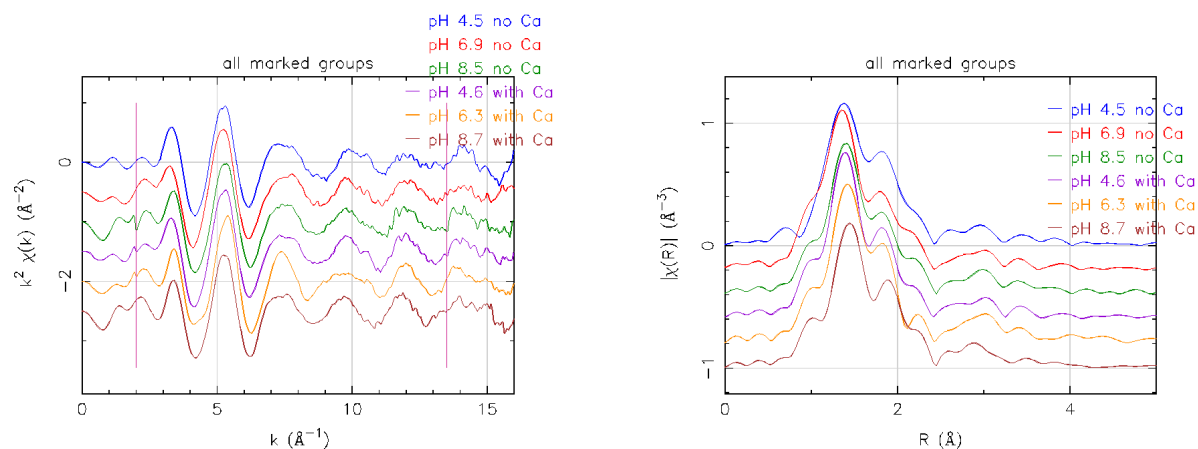
It is well known that bacterial cell walls efficiently adsorb aqueous metal cations. Thus bacterial adsorption reactions can effect metal mobility on near-surface geologic systems.

Culture and adsorption

B. Subtilis is cultured, suspended in 0.01 mol/L NaClO₄, and equilibrated with aqueous U. Surface complexation modelling of U adsorption experiments suggest complexation of U with carboxyl, phosphoryl, and hydroxyl functional groups. These are interpretative rather than direct determination of U complexation.

XAS sample preparation and experiment

The *B. Subtilis* cultures at acidic, circum-neutral, and basic pH values are prepared with and without additional Ca and spun down to a paste. The paste is loaded into a lexan frame suitable for either transmission or fluorescence geometry XAS. The XAS experiments were performed at APS 10ID (MRCAT) using APS undulator A, an LN₂-cooled Si(111) DCM, a Rh-coated harmonic rejection mirror, and simple ion chambers.



Physical Model for Uranium Adsorption

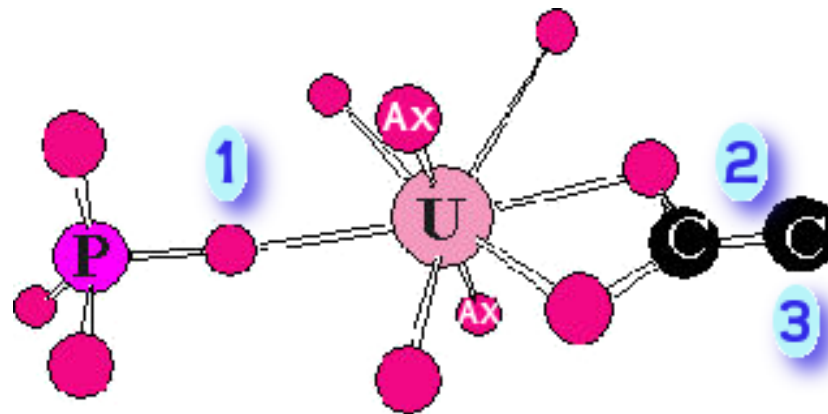


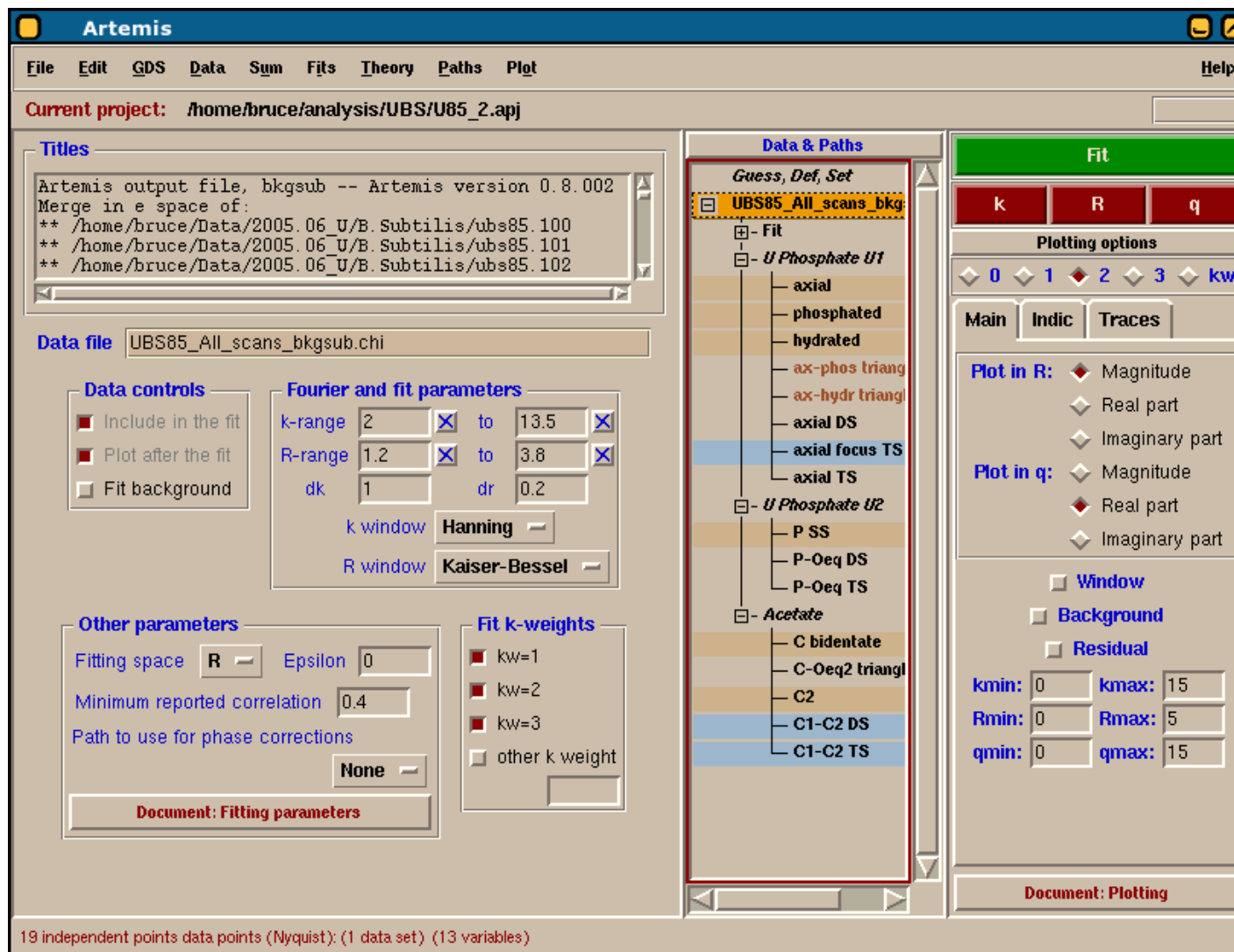
Figure courtesy Shelly Kelly

1. A phosphoryl is bonded with a monodentate oxygen. In the fit, the number of oxygens at $\sim 2.3 \text{ \AA}$ is forced to equal the number of phosphorous atoms.
2. A carboxyl is bonded with bidentate oxygens. In the fit, the number of carbon atoms is restrained to be no more than half the number of oxygens at $\sim 2.47 \text{ \AA}$.
3. The possibility of distinguishing carboxyl from carbonato exists. The distant O scatterer in a carbonato is $\sim 0.15 \text{ \AA}$ shorter than the C in a carboxyl.
 - A hydroxyl or hydration shell is the third option. This would show a distance also around $\sim 2.47 \text{ \AA}$. Any O atoms at that length in excess of twice the number of C are assumed to be hydroxyls/hydration shell O.
 - The multiple scattering paths are strictly determined by the proportionation of phosphoryl and carboxyl ligands. The MS paths involving the axial oxygens are included.

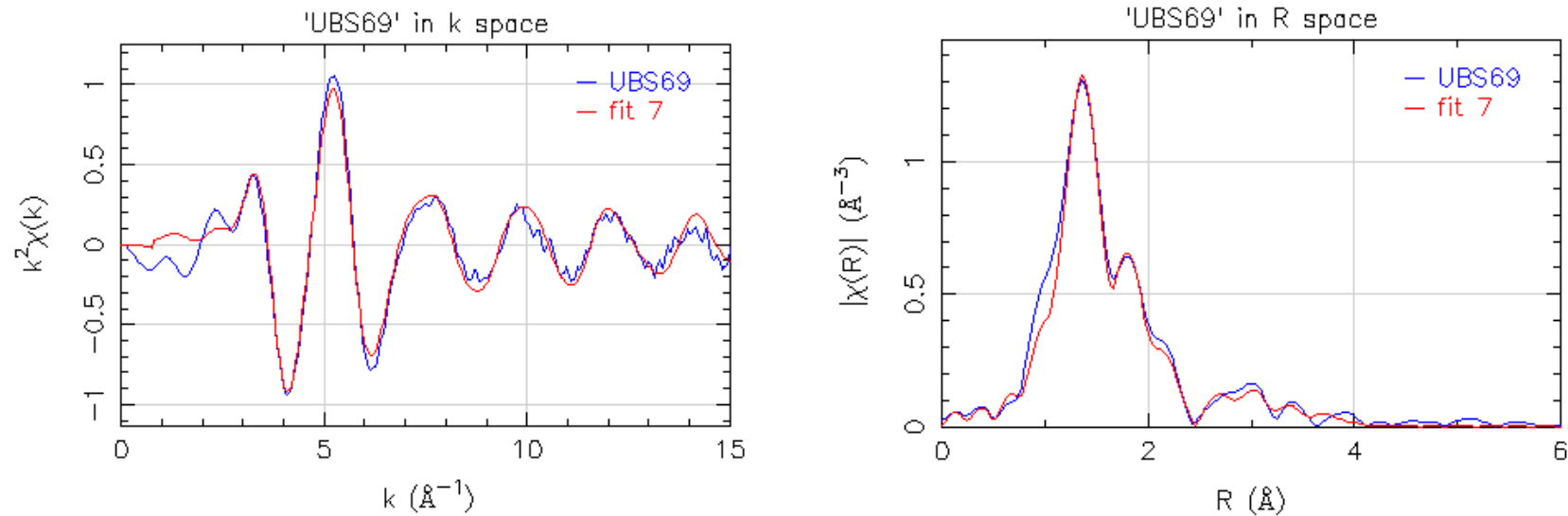
Constraints and Restraints

1. set $s_{O2} = 1$
2. set $N_{ax} = 2$
3. guess $N_{eq}(\text{short})$; constrain $N_{eq}(\text{long}) = 6 - N_{eq}(\text{short})$ *tried different models for the number of equatorial oxygen atoms, included fixed to 5, fixed to 6, restrained to be no more than 6, completely free*
4. Constrain number of phosphorous scatterers to equal the number of short equatorial oxygens $N_p = N_{oeq1}$
5. guess N_c , the number of carbon scatterers with restraint $\text{penalty}(nc, 0, noeq2/2)$. If N_c is less than $N_{eq}(\text{long})$, the remainder are hydroxyls.
6. Use the same guessed σ^2 for both equatorial oxygens.
7. Independent guessed σ^2 's for axial O, P, C.
8. One guessed E_0 parameter (*considered the possibility of an independent E_0 for the axial oxygens*)
9. Independent guessed ΔR parameters for axial O, both equatorial O, P, and C.
10. Included all relevant MS paths without introducing new guessed parameters.
11. k -range: [2 : 13.5], R -range: [1.2 : 3.8], Hanning window, $dk = 1$, fit with weights of 1 and 3, $N_{idp} = 18.6$, $N_{var} = 13$ or less.

Setting This Up in ARTEMIS



Results



We find:

1. All samples without Ca are complexed with 3.5(6) phosphoryl complexes. The low pH, no Ca sample sees 0.5(3) carboxyl and the rest hydroxyl, the other two see 1.25(3) carboxyl. (fit to circum-neutral, no Ca data is shown.)
2. With Ca:
 - low pH: 3.5(6) phosphoryl, 1.3(3) carboxyl
 - circum-neutral: 5.0(6) phosphoryl, 0.5(3) carboxyl
 - high pH: evidence of other species

Abstraction of Parameters

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

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

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

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

The terms in **blue** are **NOT** the variable in the fit.
They are written *in terms of* the abstract variables of the fit.

Abstract Concepts in Modeling

Interesting data analysis requires creativity – there is no **ATOMS** input file for U on *B. Subtilis*!

Here are some rules of thumb:

Rule #1: The **FEFF** calculation only needs to be “close enough” to be relevant.

Rule #2: Use more than one **FEFF** calculation and pick out those parts of the calculation that you need.

Rule #3: Use **IFEFFIT/ARTEMIS** to introduce distortions into your fitting model.

Rule #4: Use **IFEFFIT/ARTEMIS** to handle S_0^2 and other amplitude effects as well as *all* σ^2 parameters. Never run **FEFF** with $S_0^2 \neq 1$ or $\sigma^2 \neq 0$

And here are some suggestions:

Suggestion #1: Use multiple data sets when appropriate. More measurements of something is always better.

Suggestion #2: Use constraints and restraints. You almost always know something about your data *before* starting the analysis. Prior knowledge is good.

Suggestion #3: The EXAFS equation maps very nicely onto a histogram representation of a non-cumulant partial pair distribution.

Obtaining FEFF, IFEFFIT, ATHENA, and ARTEMIS

The **IFEFFIT** package includes **FEFF6**, **ATHENA**, **ARTEMIS**, and other stuff (including Sam Webb's **SIXPACK**).

The package has freely available source code, is freely redistributable, and is free of cost. It runs on all major platforms (including all Windows systems, Linux, Mac OSX, BSD unix, Solaris, and so on).

IFEFFIT web page

<http://cars9.uchicago.edu/ifeffit/>

ATHENA and ARTEMIS

<http://cars9.uchicago.edu/~ravel/software/exafs/>

We have a mailing list which is highly active and high signal-to-noise. We have a knowledge base in the forms of a FAQ, a Wiki, and a depository of instructional materials. We have a variety of web applications, including databases of model compounds and **ATOMS** input file and a web interface to **ATOMS**.

We're a big, friendly community. Come join us!

References

A link to a copy of this PDF file is on my web site:

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

The main reference for **FEFF** is J.J. Rehr and R.C. Albers, *Theoretical approaches to x-ray absorption fine structure*, Review of Modern Physics, **73**:3 (2000) pp. 621–654. This paper has all the details this talk glossed over and much more.

Other references for **FEFF** are

1. J. Mustre de Leon, J.J. Rehr, and S. I. Zabinsky, Phys. Rev. **B44**:9 (1991), pp. 4146–4156
2. S.I. Zabinsky, *et al.*, Phys. Rev. **B52**:4 (1995), pp 2995–3009
3. A.L. Ankudinov, *et al.*, Phys. Rev. **B58**:12 (1998), pp. 7565–7576

General references on multiple scattering theory:

1. J.L. Beeby, Proceedings of the Royal Society, **A302**, (1967), pp. 113–136
2. P. Lloyd and P.V. Smith, Adv. Phys. **21**, (1972), pp. 69–142

Other major multiple scattering codes for XAS

1. GNXAS: A. Filipponi, A. Di-Cicco, and C. R. Natoli, Phys. Rev. **B52**:21 (1995), pp. 15122-15149
2. MXAN: M. Benfatto, *et al* Phys. Rev. **B65** (2002) 174205
3. EXCURVE: S.J. Gurman, N. Binsted and I. Ross, Journal of Physics: **C19** (1986) pp. 1845–1861

URLs for the analysis software in this presentation:

1. **FEFF**: <http://feff.phys.washington.edu/feff/>
2. **IFEFFIT**: <http://cars.uchicago.edu/ifeffit/>; Ref: M. Newville J. Synchrotron Radiat. **8**, (2001) pp. 322-324
3. **ATOMS**, **ATHENA**, **ARTEMIS**: <http://feff.phys.washington.edu/~ravel/software/exafs/>; **ATOMS** Ref: B. Ravel J. Synchrotron Radiat. **8**, (2001) pp. 314-316; **ATHENA** & **ARTEMIS** Ref: B. Ravel and M. Newville J. Synchrotron Radiat. **12**:4, (2005) pp. 537-541.

About this document

The first version of this document was composed for the Workshop on X-Ray Absorption Spectroscopy and Micro-Spectroscopic Techniques, 20-21 February, 2006 at the Swiss Light Source.

You can find a copy of this talk at <http://cars9.uchicago.edu/~ravel/talks/Welcome.html>.

This document was created using a variety of free software tools, including PDF \LaTeX , the Emacs and XEmacs text editors and the really excellent AU \TeX mode, XFIG, RASMOL, and GHEMICAL. All of the screenshots were made using KSnapshot. Some image editing was done with the GIMP. KPDF and the Adobe Acrobat Reader (which is free of cost, but is not really free software) were used to view the document as I was writing it.

All of the screenshots were made while using the data analysis programs **ATHENA**, or **ARTEMIS**. All x-y data plots are screenshots of the PGPLOT window used by **IFEFFIT** to display data. **IFEFFIT** is the work of Matt Newville. **ATHENA**, and **ARTEMIS** both use **IFEFFIT** and were written by me. **FEFF6** was used for all EXAFS examples and **FEFF8** was used for all XANES examples. All versions of **FEFF** are the work of John Rehr and his students and collaborators.

The text and layout of this document is just \LaTeX , pure and good! The source files are available from my web page, as is a PDF file of this document.

Notes
