A Practical Introduction to Multiple Scattering Theory

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What I hope you take away from this talk

- A broad outline of multiple scattering theory with enough background to talk with a theorist
- An understanding of how multiple scattering theory is used to interpret **XANES** spectra
- An understanding of how multiple scattering theory is used to analyze **EXAFS** spectra
- Some ideas about how to incorporate multiple scattering theory in your research

This talk is about FEFF

There are many approaches to spectroscopy theory out there, including multiplets, band structure, and finite difference methods.

This talk is about FEFF

FEFF is a real-space, multiple scattering code.

- A conceptual summary and simple physical interpretation of what "real-space multiple scattering" means.
- How RSMS is used to make XANES calculations.
- How RSMS is used in fitting EXAFS data.

A simple picture of X-ray absorption

An atom absorbs an x-ray of energy E, destroying a core electron with energy E_0 and emitting a photo-electron with kinetic energy $(E - E_0)$. The core state is eventually filled, ejecting a fluorescent x-ray or an Auger electron.
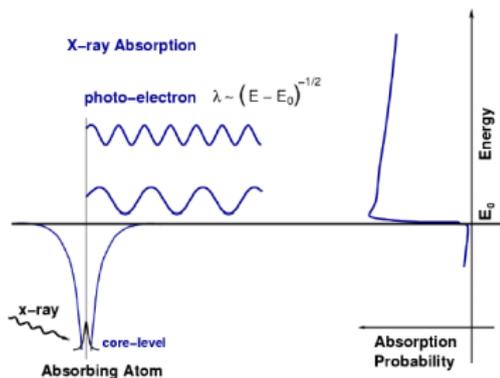
An empty final state is required.

No available state, no absorption!

Once the x-ray energy is large enough to promote a core electron to the continuum, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

X-ray absorption in condensed matter

The ejected photo-electron can scatter from neighboring atoms. R has some relationship to λ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.
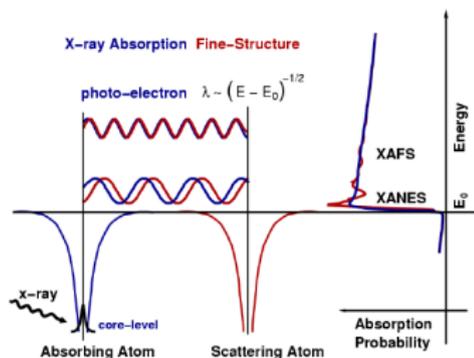
The scattering of the photo-electron wave function interferes with itself.

$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

This interference *at the absorbing atom* will vary with energy, causing the oscillations in $\mu(E)$.

Computing X-ray Absorption from First Principles

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 $|f\rangle$:

Fermi's Golden Rule

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

Broadly speaking, there are two ways to solve this equation:

1. Accurately represent $|i\rangle$[4] and $|f\rangle$[5], 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[6] or propagator formalism:
   $\mu(E) \propto -\frac{1}{\pi} \, \text{Im} \, \langle i | \hat{\epsilon}^* \cdot \mathbf{r} \, \mathbb{G}(r, r'; E) \hat{\epsilon} \cdot \mathbf{r}' | i \rangle \Theta(E - E_F)$.

1. A photon interacts with an electron

2. Typically a *1s*, *2s*, or *2p* electron

3. A bound or continuum state **not** already containing an electron

4. Easy, basic Q.M.

5. Hard work, lots of computation

6. $\mathbb{G}$ is called a Green's function.

Real Space Multiple Scattering

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 photoelectron 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

Expanding the Green's function

$$\mathbb{G} = \left(1 - G^0 t\right)^{-1} G^0 \qquad \text{(XANES)}$$
$$= G^0 + G^0 t G^0 + G^0 t G^0 t G^0 + G^0 t G^0 t G^0 t G^0 + ... \qquad \text{(EXAFS)}$$

Scattering Paths

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

single scattering path (2 legs)
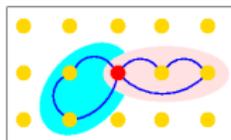
double scattering path (3 legs)

triple scattering path (4 legs)
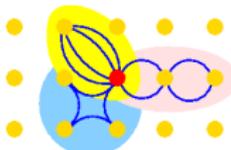
The clever thing about FEFF is that each term is further expanded as a sum of all paths of that order.

$G^0 t G^0$ is expanded as a sum of single scattering paths

$G^0 t G^0 t G^0$ is a sum of all double scattering paths

and so on.

Iron metal: 1st path, 1 shell
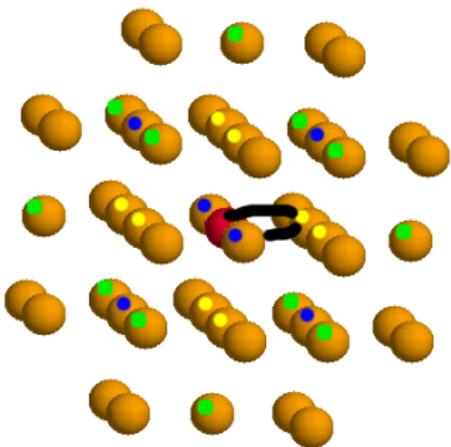
'feff0001.dat'

XANES

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.
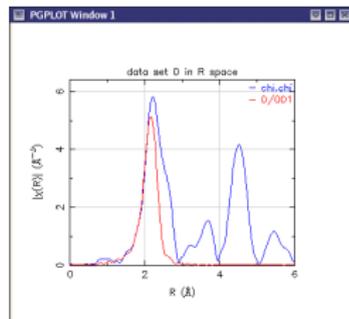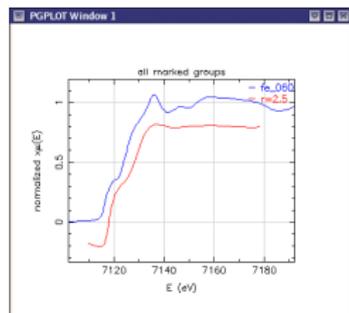
Iron metal: 2nd path, 2 shells
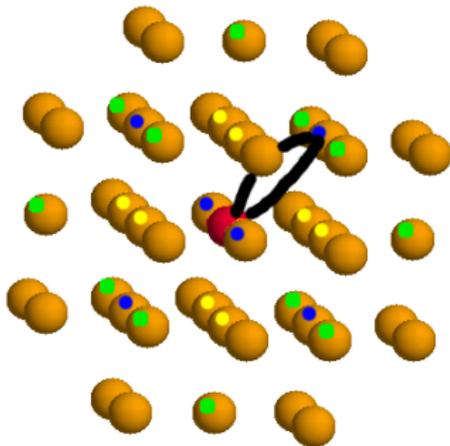
'feff0002.dat'

XANES

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.
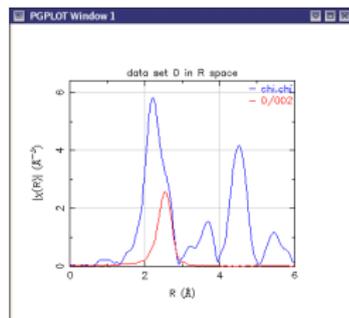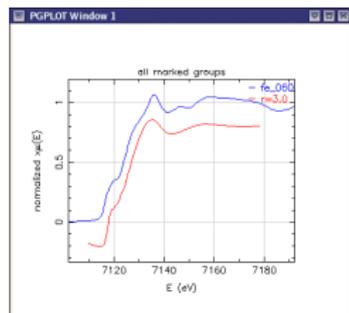
Iron metal: 3rd path, 1 shell
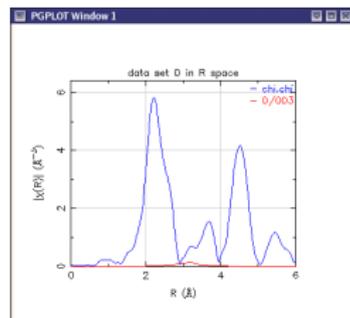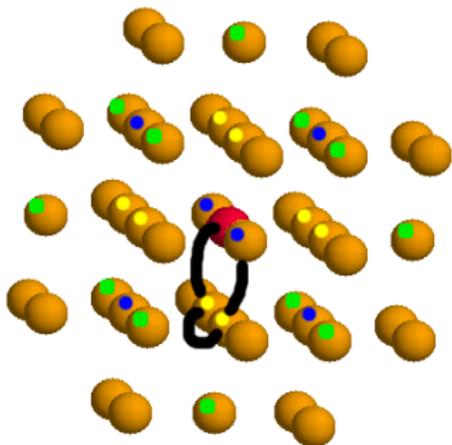
'feff0003.dat'
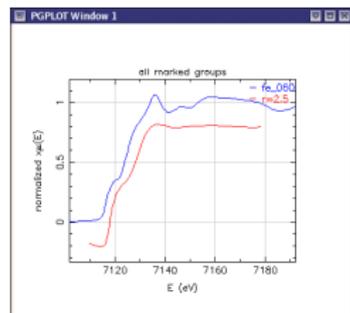
XANES

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.

Iron metal: 4th path, 2 shells
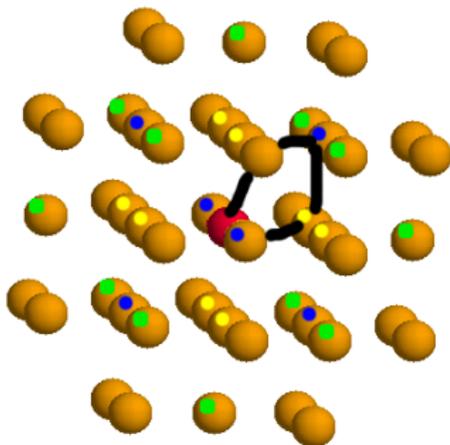
'feff0004.dat'

XANES

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.
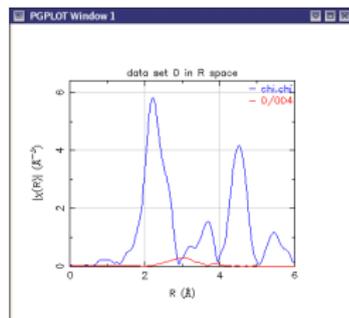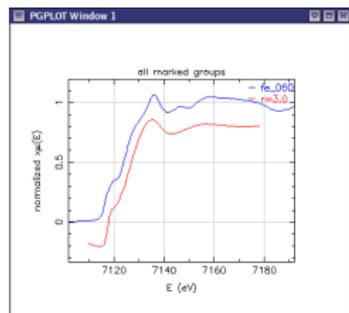
Iron metal: 5th path, 3 shells
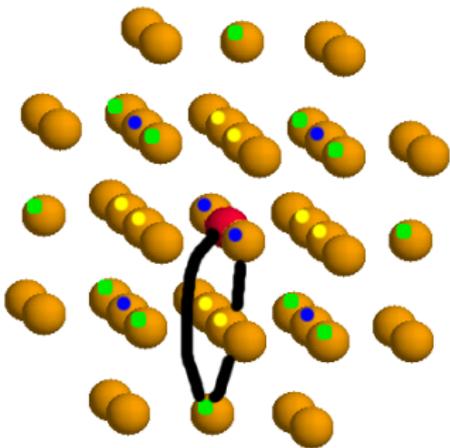
'feff0005.dat'

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.
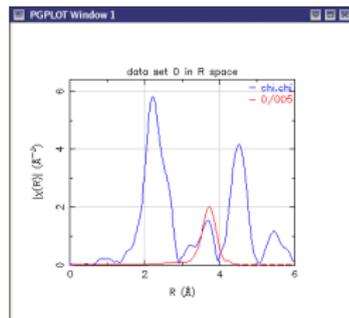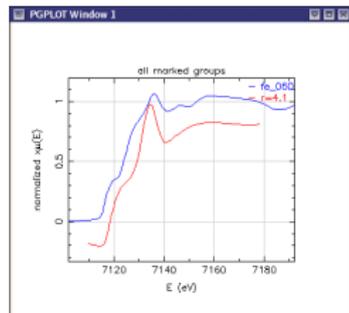
XANES

Iron metal: 8th path, 4 shells
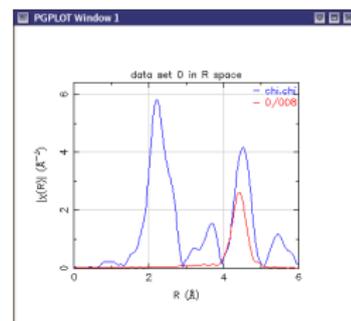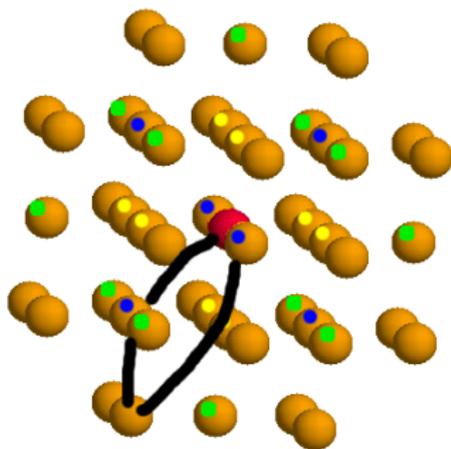
'feff0008.dat'
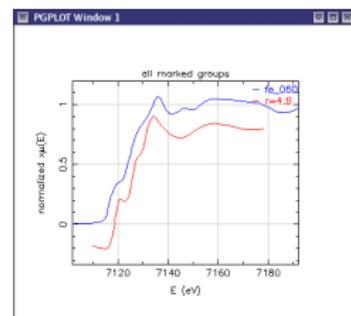
XANES

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.

Iron metal: 10th path + MS, 5 shells
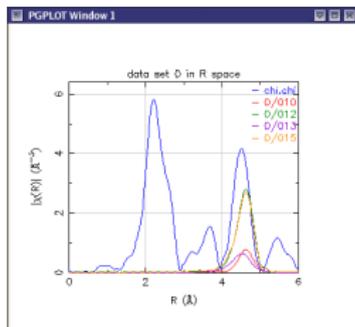
Magnitude
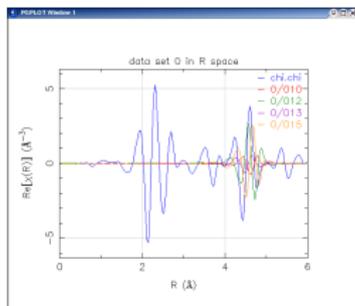
Real part

There are several MS geometries with the same path length as the 5th shell SS path. Some are *bigger* than the SS path!

Convergence of the XANES calculations
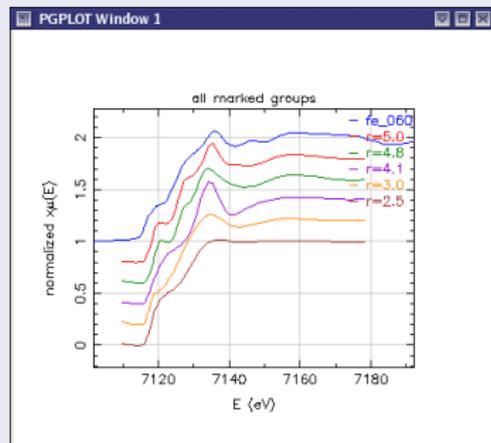
Test convergence in cluster size

Below the plasmon resonance ($\sim 40\,\mathrm{eV}$), the photoelectron's mean free path is quite large and it probes a large cluster of atoms.

The big question

How many atoms must be included in the cluster for a good FEFF calculation?

The general answer

Who knows?

$PbTiO_3$ has $c > a$ and the O and Ti atoms are displaced from sites of centrosymmetry.
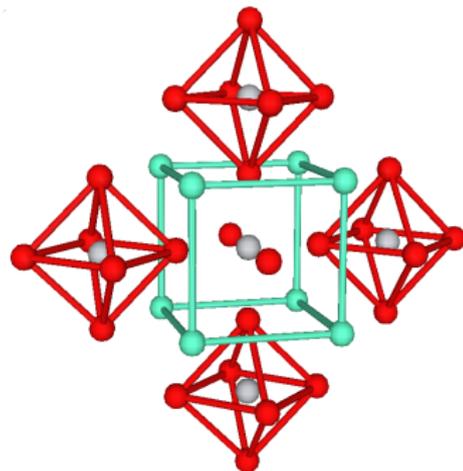
$PbTiO_3$: a tetragonally distorted perovskite
$\bullet = $ Pb $\bullet = $ Ti $\bullet = $ O

First coordination shell of PbTiO$_3$
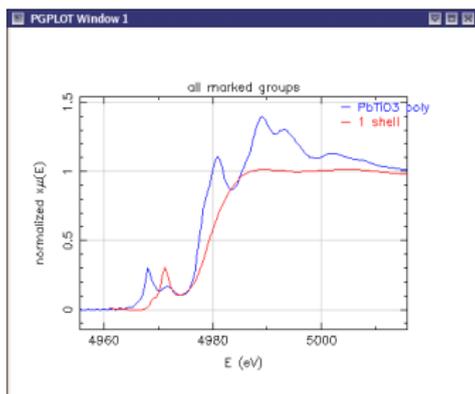
1. **O:** **R=2.40Å, 7 atoms**
2. Pb: R=3.60Å, 15 atoms
3. Ti: R=4.20Å, 21 atoms
4. O: R=5.00Å, 45 atoms
5. Ti: R=5.71Å, 57 atoms
6. O: R=6.30Å, 86 atoms

Comment

We see some indication of the structure just above the Fermi energy, but not much else. Note that the memory requirement of the calculation goes as the square of the matrix size and the time goes as its cube!

Second coordination shell of PbTiO$_3$
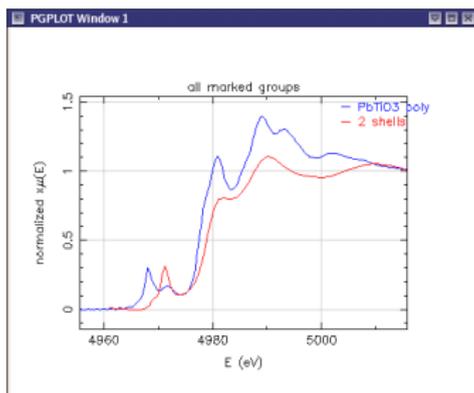
1. O: R=2.40Å, 7 atoms
2. Pb: R=3.60Å, 15 atoms
3. Ti: R=4.20Å, 21 atoms
4. O: R=5.00Å, 45 atoms
5. Ti: R=5.71Å, 57 atoms
6. O: R=6.30Å, 86 atoms

Comment

The XANES structure begins to take shape, but all the features are broad.

Third coordination shell of PbTiO$_3$
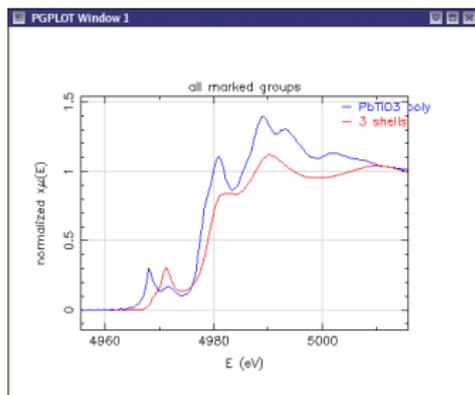
1. O: R=2.40Å, 7 atoms
2. Pb: R=3.60Å, 15 atoms
3. Ti: R=4.20Å, 21 atoms
4. O: R=5.00Å, 45 atoms
5. Ti: R=5.71Å, 57 atoms
6. O: R=6.30Å, 86 atoms

Comment

Very little changes by adding the 3$^{\rm rd}$ shell Ti atoms!

Fourth coordination shell of $PbTiO_3$
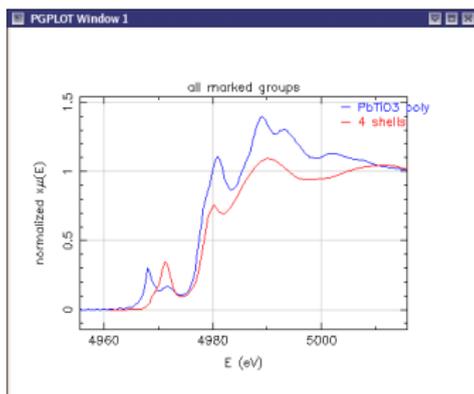
1. O: R=2.40Å, 7 atoms
2. Pb: R=3.60Å, 15 atoms
3. Ti: R=4.20Å, 21 atoms
4. O: R=5.00Å, 45 atoms
5. Ti: R=5.71Å, 57 atoms
6. O: R=6.30Å, 86 atoms

Comment

Adding an oxygen shell causes the features to become much more distinct. Low Z elements have strong scattering at low k. High Z elements have strong scattering at high k.

Fifth coordination shell of PbTiO$_3$
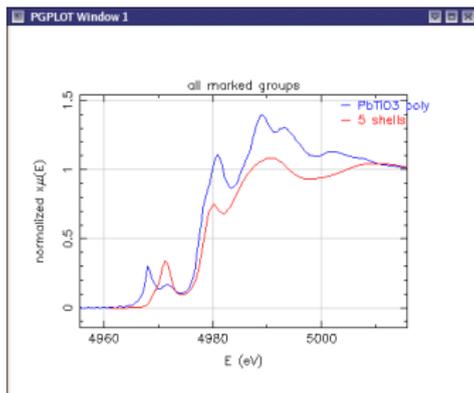
1. O: R=2.40Å, 7 atoms
2. Pb: R=3.60Å, 15 atoms
3. Ti: R=4.20Å, 21 atoms
4. O: R=5.00Å, 45 atoms
5. Ti: R=5.71Å, 57 atoms
6. O: R=6.30Å, 86 atoms

Comment

Again, adding a metal shell does little for the spectrum.

Sixth coordination shell of $PbTiO_3$
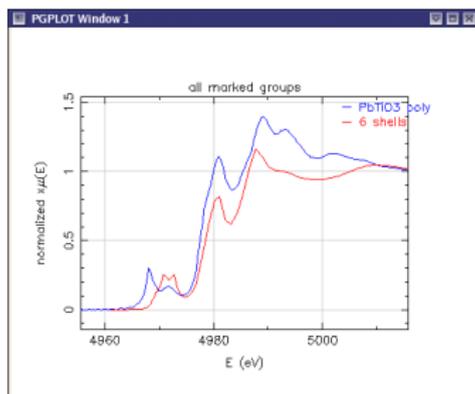
1. O: R=2.40Å, 7 atoms
2. Pb: R=3.60Å, 15 atoms
3. Ti: R=4.20Å, 21 atoms
4. O: R=5.00Å, 45 atoms
5. Ti: R=5.71Å, 57 atoms
6. O: R=6.30Å, 86 atoms

Comment

Once again, adding an oxygen shell causes the features to become much more distinct. Low Z elements have a strong effect on the XANES. Is the calculation converged? Probably not. Large clusters are required!

Scattering amplitude as a function of Z

$PbTiO_3$ has three very different elements:

Low Z Large at low k, tails off quickly

Transition metal Large at intermediate k, tails off slowly

Heavy metal Always there, but with a Ramsauer-Townsend minimum
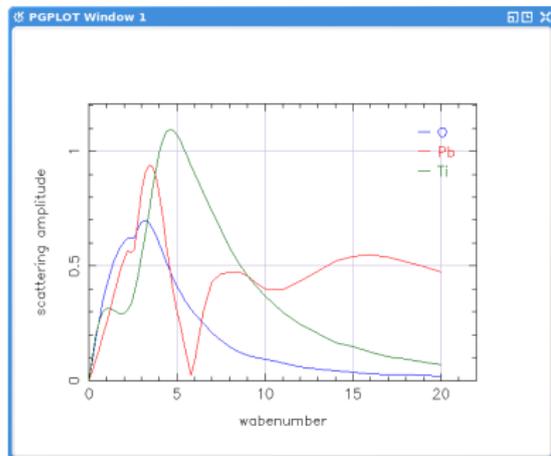
XANES and EXAFS

We can understand both the behavior of the XANES calculations and what we observe in EXAFS data.

Linear dichroism in PbTiO$_3$

$\overline{ab}$ plane
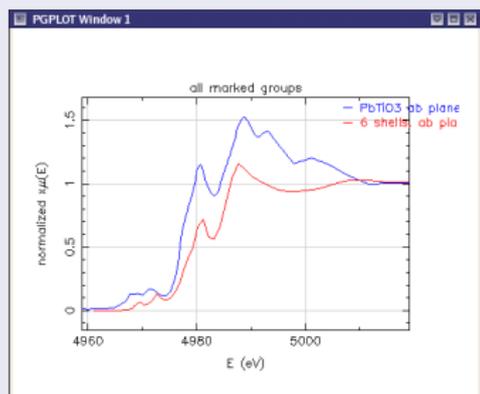
$\hat{c}$ axis
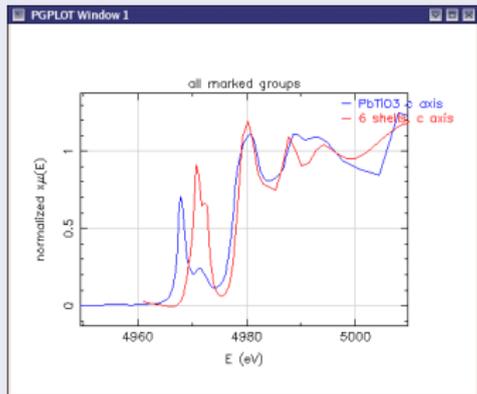
Polarization can be included directly in the XANES calculation and shows the correct behavior compared to the data.

Making useful XANES calculations

The challenge to using FEFF8 *well* is that you need to provide a list of atomic coordinates. But if you already know where the atoms are, you probably don't need to calculate the XANES.

In this section, we will briefly discuss how to handle

- Vacancies and substitutions
- Structural distortions

We will also discuss

- FEFF's concept of computing self consistent potentials
- Fitting XANES spectra as implemented in MXAN and FITIT.

Vacancies and substitutions

- In FEFF, a point in space is occupied by one or zero atoms and may not be partially vacant or fractionally occupied.
- These effects cannot be computed by a single FEFF calculation.
- The most successful strategy is to make multiple calculations, randomly introducing substitutions or vacancies.
- Sum these calculations progressively until the average is converged.
- Convergence will probably happen within 10 or 20 calculations.

Structural distortion

SF_6 is an octahedral complex with nominal bond length of 1.54 Å. A distortion will mix p and d character in the final state with the peak near 2507 eV in the dDOS contributing spectrum.

- Thermal: $\langle R_{S,F_x} - R_{S,F_{-x}} \rangle \neq 0$
- Jahn-Teller
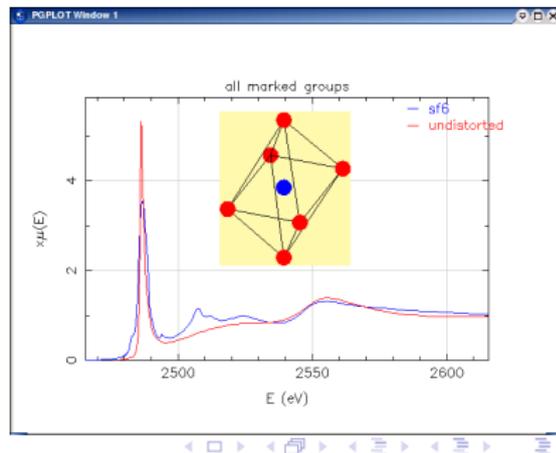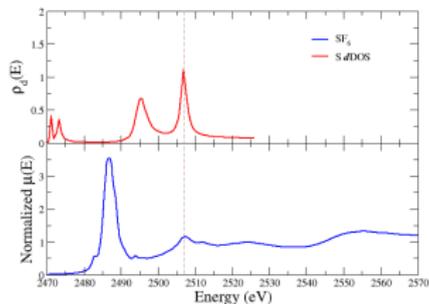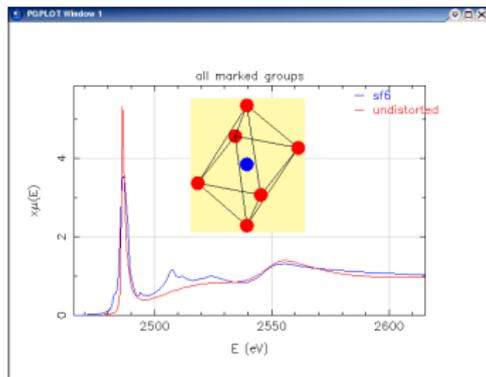
Self consistent potentials

FEFF starts with the potentials of the free atoms, $\rho_0(E)$. It loops through the following calculations until the $\rho(E)$ functions stop changing.

$$\rho_\ell(E) = \rho_{0,\ell}(E)(1 + \chi_\ell(E)) \qquad \ell \in \{0, 1, 2, 3, \cdots\}$$

Self consistency loop

$$\rho_0(E) \longrightarrow F(E), \Phi(E) \longrightarrow \chi(E)$$

$$\uparrow \qquad\qquad\qquad \downarrow$$

$$\text{converged?} \longleftarrow \rho(E)$$
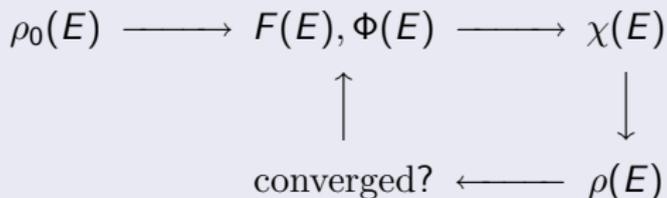
At the end, $\rho(E)$ is integrated in energy. The Fermi energy is where the integral equals the total number of valence electrons among the original free atoms in the cluster. This integral also determines charge transfer.

Fitting XANES spectra: Direct calculation

Compute XANES as a multivariate function of a large parameter space:

Definition (Computed absorption)

$$\mu(E, x_i, \alpha_j, \beta_k)$$

- x_i the positions of all atoms in the cluster
- α_j parameters of the potentials model (muffin tin radii, loss terms, the Fermi energy, etc)
- β_k empirical parameters (broadening, E_0, offset function, etc)

Fitting loop

$$\mu_{\mathrm{init}}(E, x_i, \alpha_j, \beta_k) \longrightarrow \quad \text{compare to data} \quad \longrightarrow \text{adjust } x_i, \alpha_j, \beta_k$$

$$\uparrow \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$\mu_{\mathrm{refined}}(E, x_i, \alpha_j, \beta_k) \longleftarrow \quad \text{converged?}$$
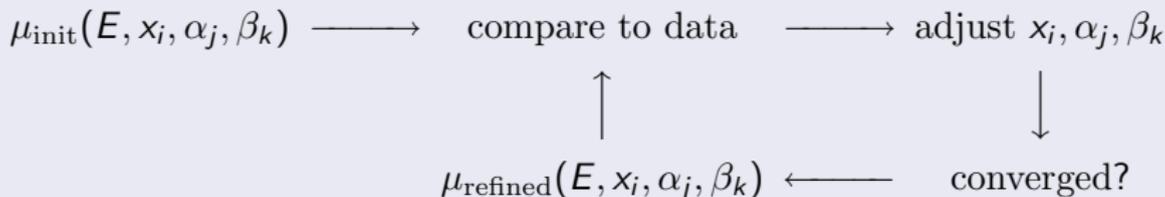
In the FEFF world, this is an open problem. But see, for example, MXAN by M. Benfatto et al. PRB **65** (2002) 174205.

Fitting XANES spectra: multidimensional interpolation approximation

- Another approach to the fitting XANES data is to precompute an adequate grid in the parameters x_i, α_j, and β_k and to place the data within that grid by multidimensional interpolation.
- This approach is quick after the initial computational expense.
- This has been implemented as the program FITIT by Grigory Smolentsev and Alexander V. Soldatov. See http://xafs.org/Software/FitIt

A FEFF6 input file

Here is an example of a FEFF6 input file:

```
TITLE Cobalt sulfide  CoS_2

HOLE 1 1.0 *  Co K edge (7709.0 eV)

*        mphase,mpath,mfeff,mchi
CONTROL   1     1      1     1
PRINT     1     0      0     0

RMAX     6.0

POTENTIALS
*    ipot   Z  element
      0    27   Co
      1    27   Co
      2    16   S

             * continued ------>
```

```
ATOMS   * this list contains 71 atoms
*    x         y         z     ipot  tag    distance
   0.00000   0.00000   0.00000  0  Co1      0.00000
   2.14845   0.61305   0.61305  2  S1_1     2.31678
   0.61305  -2.14845   0.61305  2  S1_1     2.31678
  -0.61305   0.61305   2.14845  2  S1_1     2.31678
  -0.61305   2.14845  -0.61305  2  S1_1     2.31678
  -2.14845  -0.61305  -0.61305  2  S1_1     2.31678
   0.61305  -0.61305  -2.14845  2  S1_1     2.31678
  -3.37455   0.61305   0.61305  2  S1_2     3.48415
   0.61305   3.37455   0.61305  2  S1_2     3.48415
   0.61305  -0.61305   3.37455  2  S1_2     3.48415
   3.37455  -0.61305   0.61305  2  S1_2     3.48415
  -0.61305  -3.37455  -0.61305  2  S1_2     3.48415
  -0.61305   0.61305  -3.37455  2  S1_2     3.48415
  -2.14845  -2.14845   2.14845  2  S1_3     3.72122
   2.14845   2.14845  -2.14845  2  S1_3     3.72122
   2.76150   2.76150   0.00000  1  Co1_1    3.90535
  -2.76150   2.76150   0.00000  1  Co1_1    3.90535
   2.76150  -2.76150   0.00000  1  Co1_1    3.90535
  -2.76150  -2.76150   0.00000  1  Co1_1    3.90535
   2.76150   0.00000   2.76150  1  Co1_1    3.90535
  -2.76150   0.00000   2.76150  1  Co1_1    3.90535
   0.00000   2.76150   2.76150  1  Co1_1    3.90535
*
* etc...
*
END
```

A FEFF8 input file

Here is an example of a FEFF8 input file:

```
TITLE Cobalt sulfide  CoS_2
EDGE K
S02  1.0

*    pot   xsph  fms   paths genfmt ff2chi
CONTROL  1     1     1     1     1      1
PRINT    1     0     0     0     0      0

EXCHANGE   0
SCF        4.0
XANES      4.0
FMS        5.09694  0
LDOS       -30   20   0.1
RPATH      0.1
*EXAFS     20

POTENTIALS
*   ipot  Z  element  l_scmt  l_fms  stoi.
     0   27   Co        2       2      0
     1   27   Co        2       2      4
     2   16   S         2       2      8
                            * continued ------>
```

```
ATOMS    * this list contains 71 atoms
*   x          y          z      ipot  tag    distance
  0.00000    0.00000    0.00000   0   Co1     0.00000
  2.14845    0.61305    0.61305   2   S1_1    2.31678
  0.61305   -2.14845    0.61305   2   S1_1    2.31678
 -0.61305    0.61305    2.14845   2   S1_1    2.31678
 -0.61305    2.14845   -0.61305   2   S1_1    2.31678
 -2.14845   -0.61305   -0.61305   2   S1_1    2.31678
  0.61305   -0.61305   -2.14845   2   S1_1    2.31678
 -3.37455    0.61305    0.61305   2   S1_2    3.48415
  0.61305    3.37455    0.61305   2   S1_2    3.48415
  0.61305   -0.61305    3.37455   2   S1_2    3.48415
  3.37455   -0.61305   -0.61305   2   S1_2    3.48415
 -0.61305   -3.37455   -0.61305   2   S1_2    3.48415
 -0.61305    0.61305   -3.37455   2   S1_2    3.48415
 -2.14845   -2.14845    2.14845   2   S1_3    3.72122
  2.14845   -2.14845   -2.14845   2   S1_3    3.72122
  2.76150    2.76150    0.00000   1   Co1_1   3.90535
 -2.76150    2.76150    0.00000   1   Co1_1   3.90535
  2.76150   -2.76150    0.00000   1   Co1_1   3.90535
 -2.76150   -2.76150    0.00000   1   Co1_1   3.90535
  2.76150    0.00000    2.76150   1   Co1_1   3.90535
 -2.76150    0.00000    2.76150   1   Co1_1   3.90535
  0.00000    2.76150    2.76150   1   Co1_1   3.90535
*
* etc...
*
END
```

Using ATOMS to prepare the FEFF input file

ARTEMIS includes a tool called ATOMS that converts crystallographic data into a FEFF input file.
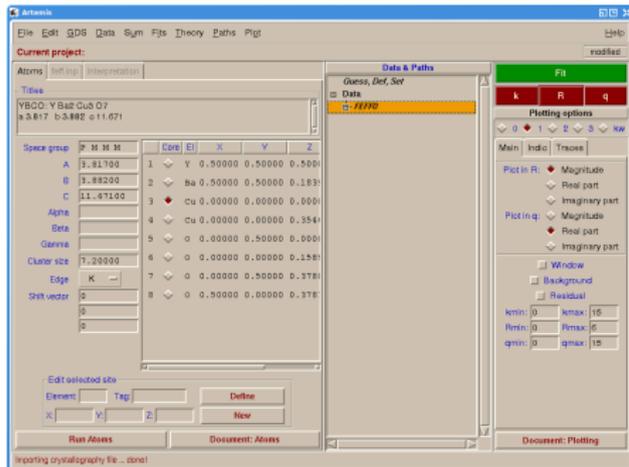
The input data can be a CIF file or this simple format:

```
title YBCO: Y Ba2 Cu3 O7
space P M M M
rmax=5.2   a=3.823   b=3.886 c=11.681
core=cu2
atoms
! At.type   x      y      z         tag
  Y        0.5    0.5    0.5
  Ba       0.5    0.5    0.184
  Cu       0      0      0         cu1
  Cu       0      0      0.356     cu2
  O        0      0.5    0         o1
  O        0      0      0.158     o2
  O        0      0.5    0.379     o3
  O        0.5    0      0.377     o4
```

These data are typically taken from the crystallography literature, the *Inorganic Crystal Structure Database*, or from:
http://cars9.uchicago.edu/~newville/adb/search.html

Preparing the FEFF input file for non-crystalline materials

There are many sources of structural data about molecules, proteins, and other non-crystalline materials. A bit of googling turned up this Protein Data Bank File for cisplatin:
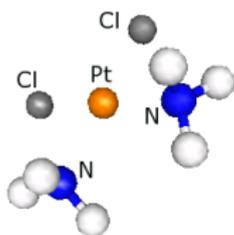

```
ATOM      1  PT1  MOL A   1      -0.142   0.141   7.747  1.00  1.00
ATOM      2  CL2  MOL A   1      -0.135  -2.042   8.092  1.00  1.00
ATOM      3  CL3  MOL A   1       2.064   0.127   7.615  1.00  1.00
ATOM      4  N4   MOL A   1      -0.147   2.166   7.427  1.00  1.00
ATOM      5  N5   MOL A   1      -2.188   0.154   7.870  1.00  1.00
ATOM      6  1H4  MOL A   1       0.793   2.489   7.319  1.00  1.00
ATOM      7  2H4  MOL A   1      -0.570   2.625   8.208  1.00  1.00
ATOM      8  3H4  MOL A   1      -0.668   2.370   6.598  1.00  1.00
ATOM      9  1H5  MOL A   1      -2.464   0.303   8.819  1.00  1.00
ATOM     10  2H5  MOL A   1      -2.546  -0.724   7.552  1.00  1.00
ATOM     11  3H5  MOL A   1      -2.551   0.889   7.298  1.00  1.00
TER
```

Cut, paste, insert some boilerplate, and voilá!.

```
TITLE cisplatin
HOLE  4  1.0
RMAX  8
POTENTIALS
    0   78   Pt
    1   17   Cl
    2    7   N
    3    1   H

ATOMS
  -0.142   0.141   7.747   0
  -0.135  -2.042   8.092   1
   2.064   0.127   7.615   1
  -0.147   2.166   7.427   2
  -2.188   0.154   7.870   2
   0.793   2.489   7.319   3
  -0.570   2.625   8.208   3
  -0.668   2.370   6.598   3
  -2.464   0.303   8.819   3
  -2.546  -0.724   7.552   3
  -2.551   0.889   7.298   3
```

Note that the absorber need not be at (0,0,0) and

the list need not be in any particular order.

FeS$_2$: Single scattering paths in a crystal

• = Fe
• = S
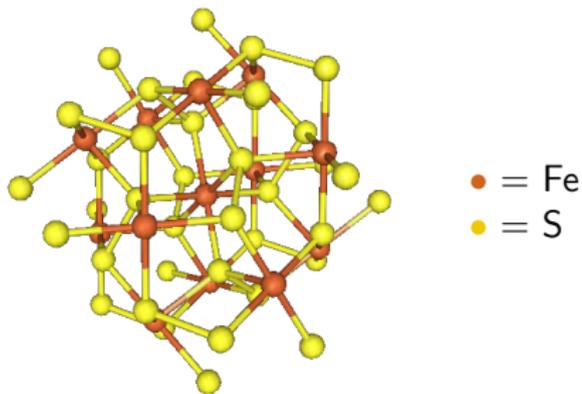
The first sulfur SS path is from the octahedron surrounding the Fe atom. It provides most of the spectral weight under the first peak.[a]

The next two S and one Fe SS paths overlap between 2.5 and 3.5 Å.

---

[a] Data from http://cars9.uchicago.edu/ newville/ModelLib
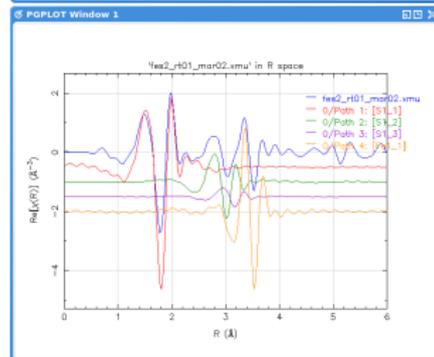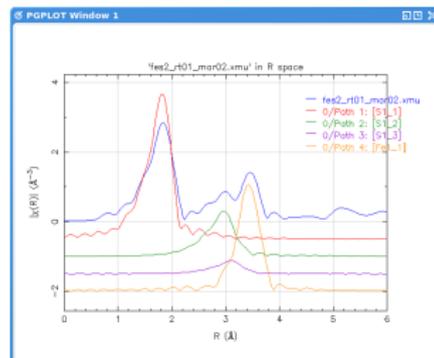
FeS$_2$: Multiple scattering paths in a crystal
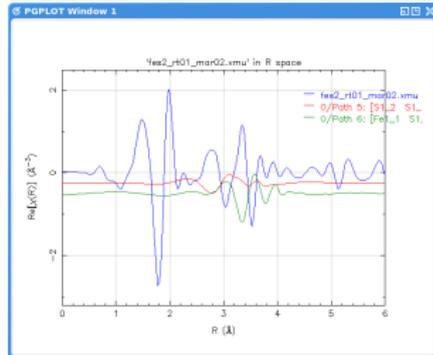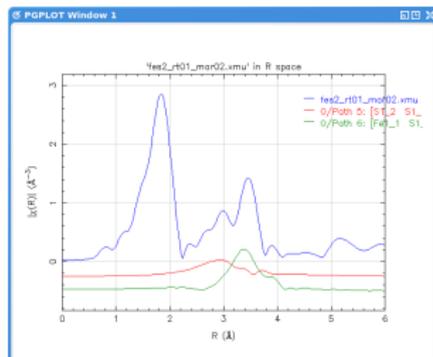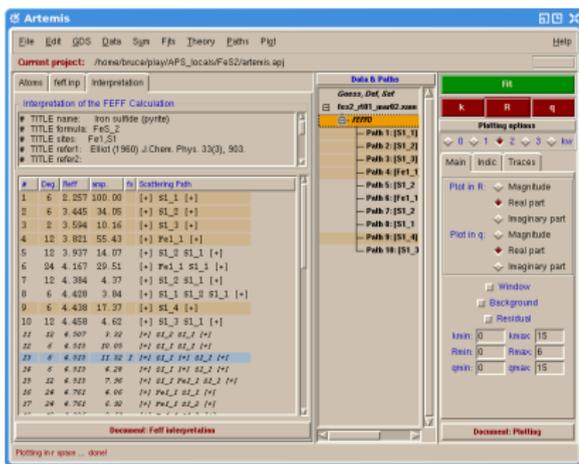
The relationship between the EXAFS spectrum and atomic structure can be quite complicated due to multiple scattering.

A sulfur–sulfur triangle and a sulfur–iron contribute significantly between 2.5 and 3.5 Å.

$[Ni(CN)_4]^{2-}$: Paths in a molecule
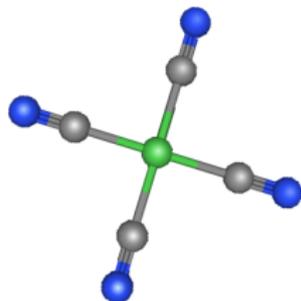
$\bullet$ = Ni $\bullet$ = C $\bullet$ = N

Multiple scattering is **not** just for the materials scientists. $[Ni(CN)_4]^{2-}$ in solution is **not** a crystal.
Without consideration of the MS paths, the huge second peak in these data cannot be fit.

A. Muñoz-Páez et al. Inorg. Chem. **39** (2000) pp. 3784–3790
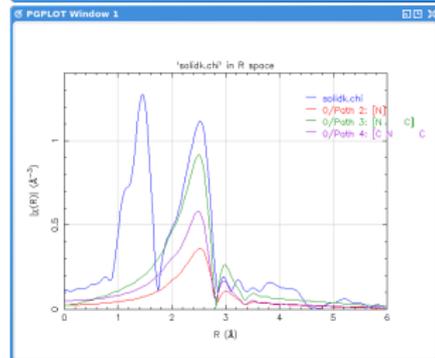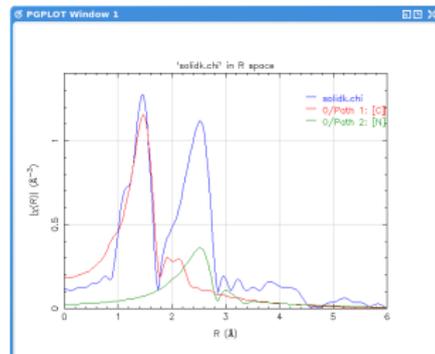
Starting from analogs
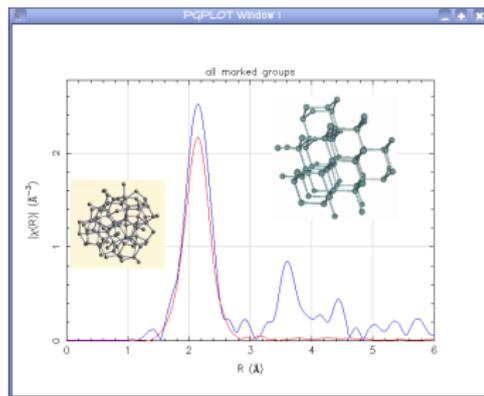

```
title germanium diamond structure
space f d 3 m
rmax=6.0    a=5.658
atoms
! At.type   x      y      z      tag
   Ge      1/8    1/8    1/8
```
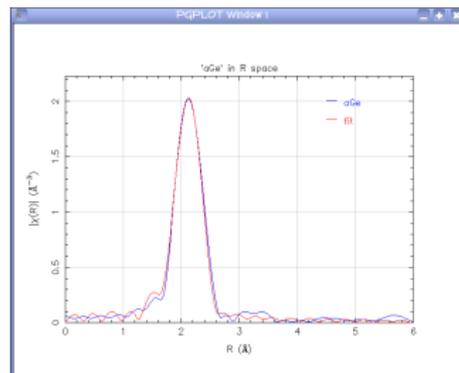

Use the 'feff0001.dat' file from the Ge crystal[a] FEFF calculation

---

[a]Crystalline data is from the NSLS X18 standards database
http://www.nsls.bnl.gov/beamlines/x18b/data.htm
Amorphous data courteously provided by Dale Brewe and Joe Woicik.

	crystal	amorphous
N	4	4.0(8)
R_1 (Å)	2.441(3)	2.451(11)
σ^2 (Å²)	0.00419(55)	0.00528(155)

Close is usually good enough

Solid solution of $AgBr_{0.5}Cl_{0.5}$ at 20 K

The first shell contains both Br and Cl scatterers. We use the known crystal structure for AgBr to compute the Ag–Br path.

```
title rocksalt silver bromide at room temperature
space F M -3 M
rmax=6    a=5.7745
core=Ag
atoms
! At.type    x      y      z        tag
    Ag      0.0    0.0    0.0
    Br      1/2    1/2    1/2
```

We simply replace Br with Cl and run ATOMS and FEFF again.
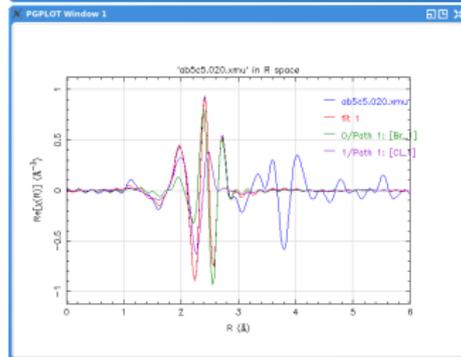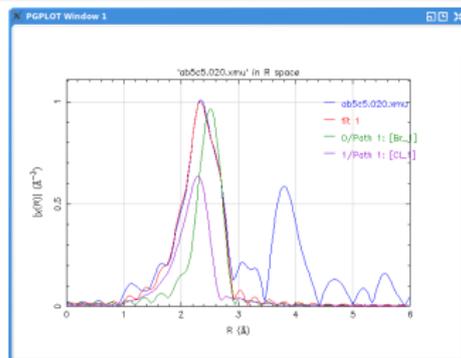
$$\Delta R_{Br} = -0.032(4) \text{Å} \qquad \Delta R_{Cl} = -0.105(12) \text{Å}$$

Pick and choose

The data are uranyl acetate mixed with a *B. Subtilis* culture and brought to equilibrium at $pH \sim 8$.
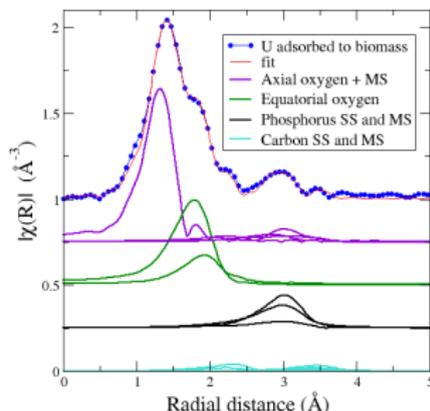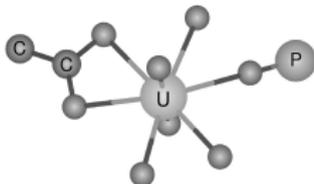
triuranyl diphoshate tetrahydrate This mineral provides paths for axial and equatorial O of the appropriate lengths as well as SS and MS to the monodentate P

Rutherfordine, UO_2CO_3 This mineral provides paths for SS and MS involving the bidentate C

Resources

- Websites
  - http://xafs.org offers tutorials, links to resources, information about upcoming workshops, and much more
  - IFEFFIT homepage: http://cars9.uchicago.edu/iffwiki/About
  - FEFF homepage: http://feff.phys.washington.edu
  - ATHENA and ARTEMIS: http://cars9.uchicago.edu/ ravel/software/
- Journal articles
  - The FEFF reference: Rehr and Albers review article: J.J. Rehr and R.C. Albers, Rev. Mod. Phys. **73**:3 (2000) pp. 621–654
  - Two excellent references on multiple scattering theory: J.L. Beeby, Proc. Royal Soc. **A274** (1964) pp. 309–317 and **A279** (1967) pp. 82–97.
- Other Software
  - XANES calculations using Mulitplets: http://xafs.org/Software/TtMultiplet
  - XANES calculations by finite difference method: http://xafs.org/Software/FDMNES
  - Band structure: The work of Eric Shirley (http://physics.nist.gov/Divisions/Div844/facilities/theorModel/tmopm.html) and Aleksi Soininen, Helsinki University
  - XANES fitting: FITIT (http://xafs.org/Software/FitIt) and MXAN (PRB **65** (2002) 174205).

Notes