
A Practical Introduction to Multiple Scattering Theory

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

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Abstract

In recent years, the ability to interpret and analyze X-Ray Absorption Spectroscopy data has progressed dramatically thanks, in large part, to the rapid development of *ab initio* theories of the absorption spectrum. One such theory, the FEFF program, has proven especially successful and is in wide use throughout the world. In this talk, I will present an outline of the real-space, multiple-scattering theory used by FEFF and explain how FEFF is applied to both the near-edge and extended portions of the absorption spectrum. This talk is intended to be both practical and accessible. It is a talk by a synchrotron experimentalist intended for synchrotron experimentalists.

Bruce Ravel

ravel@phys.washington.edu

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

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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

We will be talking about

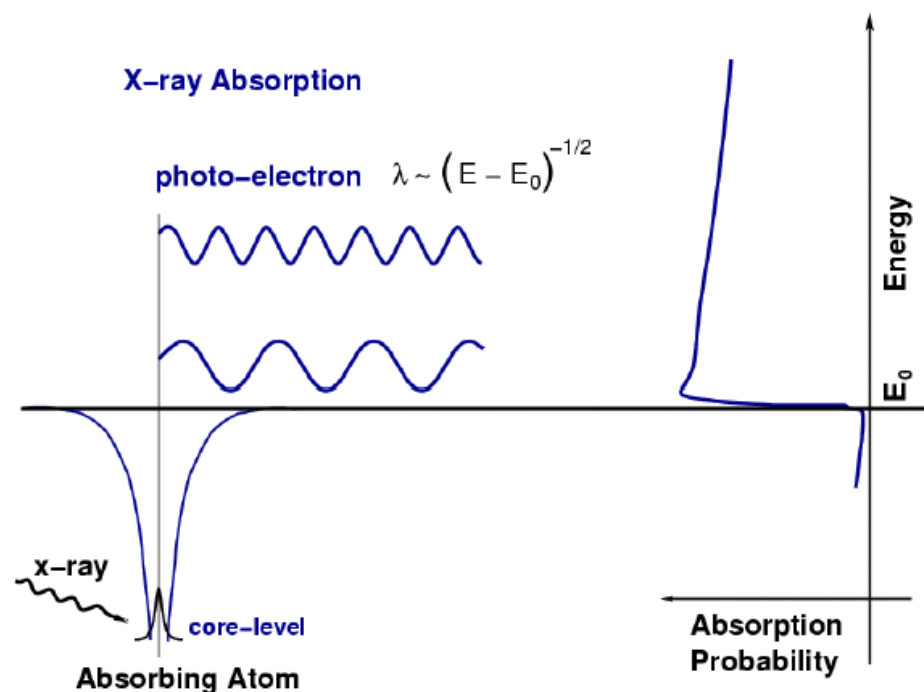
FEFF

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.

X-ray absorption by a free atom

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



An empty final state is required.

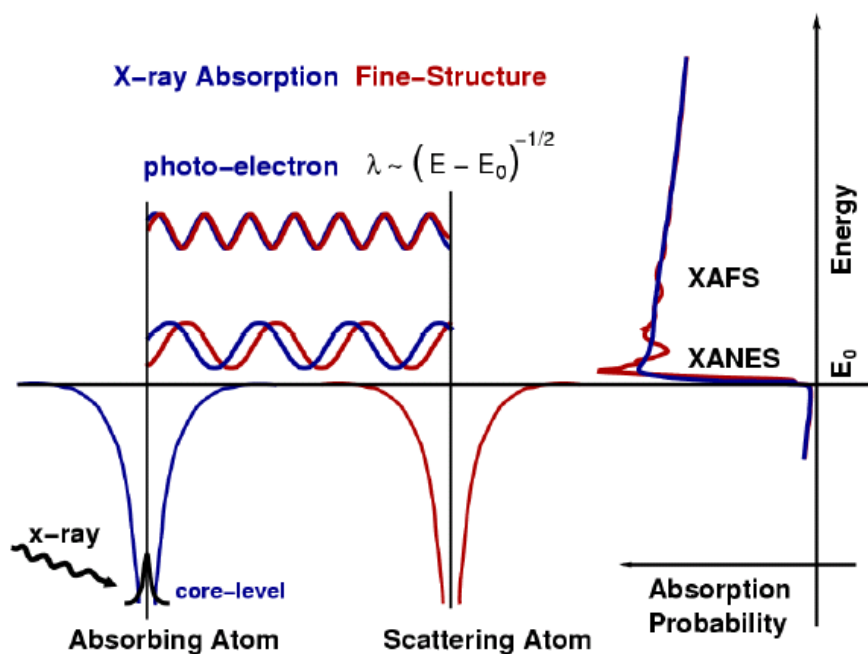
No available state,
no absorption!

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 with photo-electron scattering

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 $\mu(E)$.

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 $|f\rangle$:

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

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:

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

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. This is an example of Fermi's Golden Rule
5. Easy, basic Q.M.
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 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

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

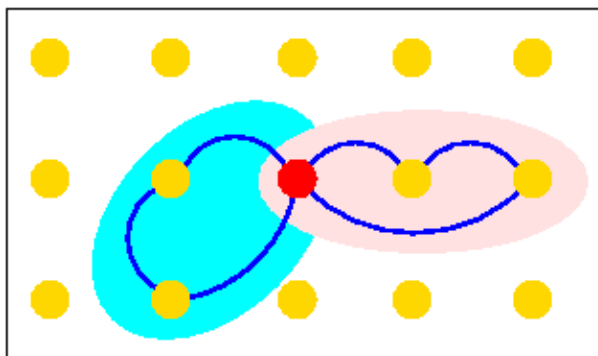
$$= G^0 + G^0 t G^0 + G^0 t G^0 t G^0 + G^0 t G^0 t G^0 t G^0 + \dots \quad (2)$$

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

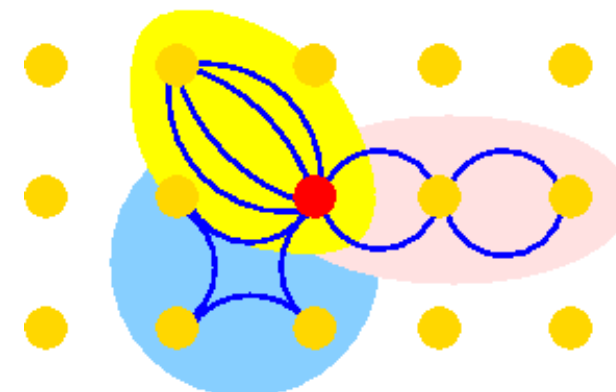
Types of scattering paths



single scattering path
two legs



Triangular and collinear
double scattering paths
three legs



Collinear and other
triple scattering paths
four legs

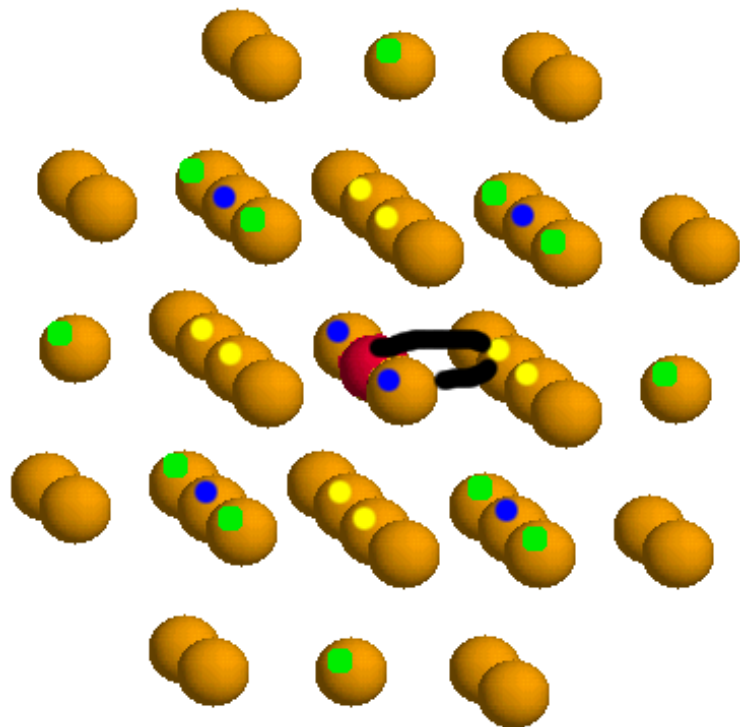
..... and so on

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

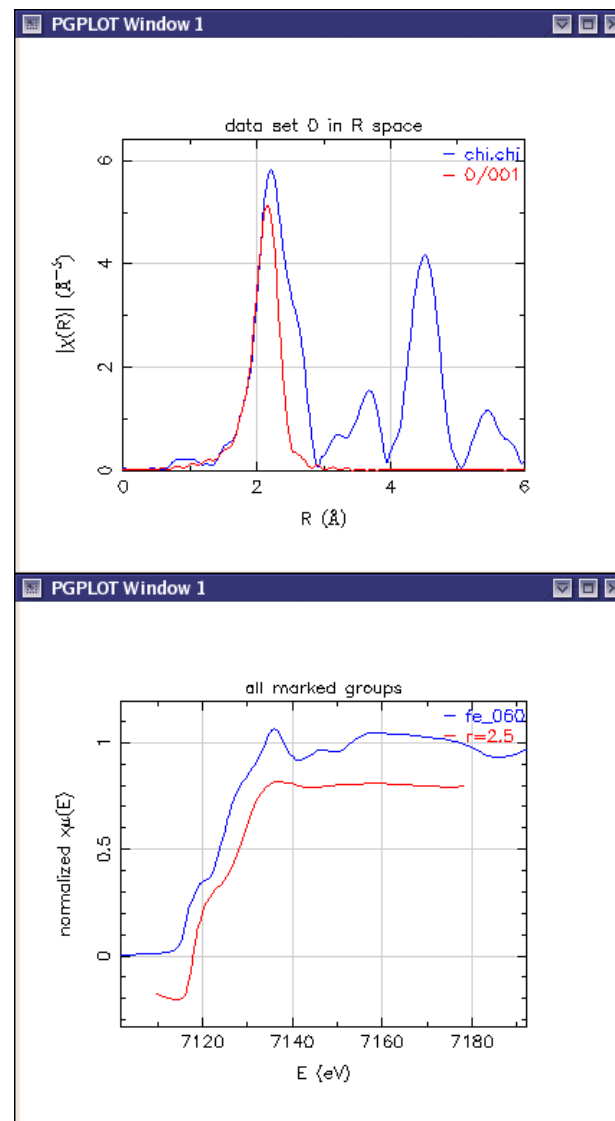
The clever thing about **FEFF** is that each term is further expanded as a sum of all paths of that order.

$\mathbb{G}^0 \mathbb{t} \mathbb{G}^0$ 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



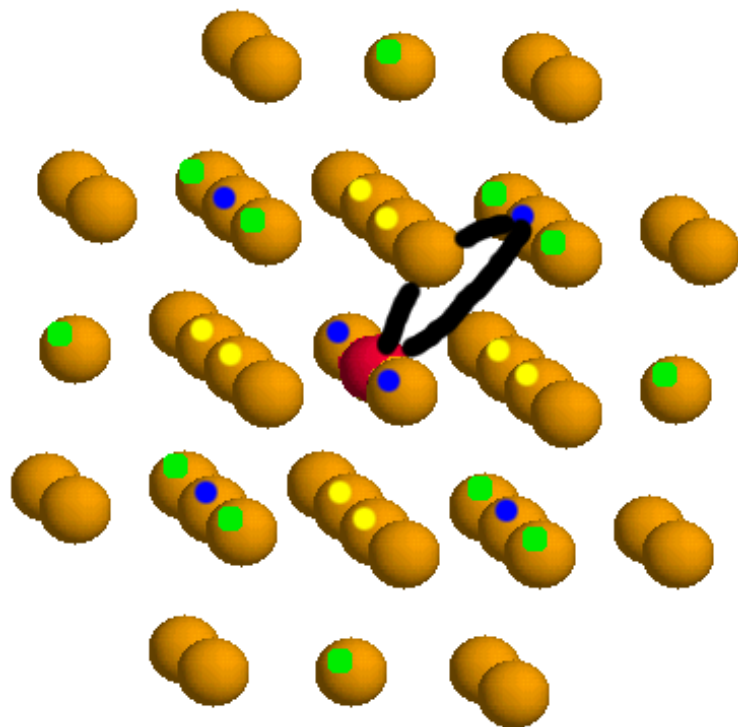
1. The first path is much, but not all, of the first peak in $|\tilde{\chi}(R)|$. Degeneracy = 8.
2. The first shell XANES calculation shows little of the structure.



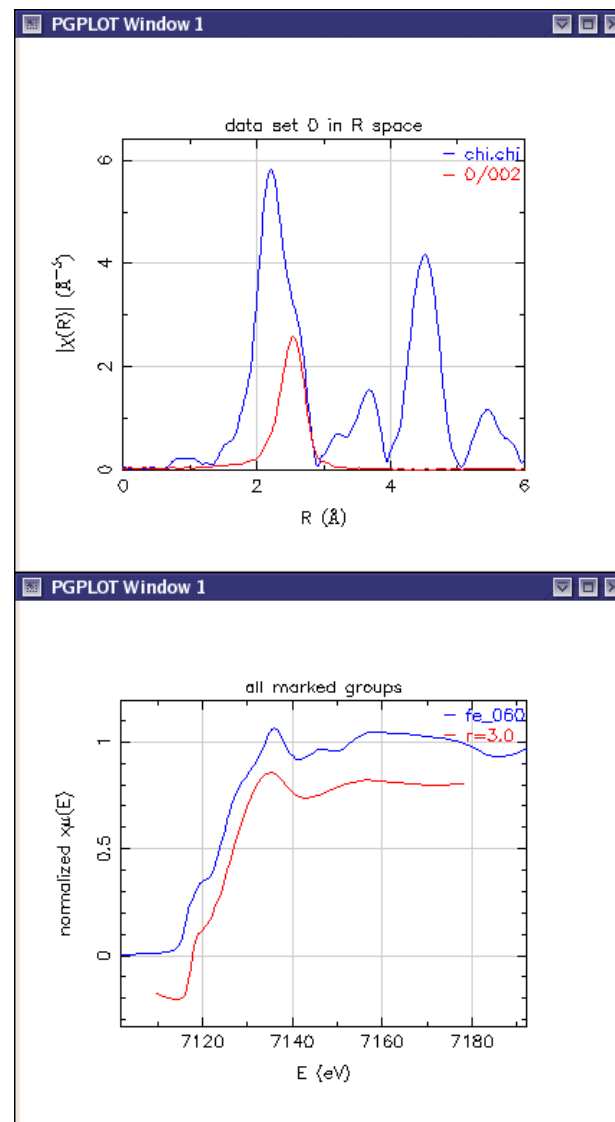
f
e
f
f
0
0
0
1

X
A
N
E
S

The second path in iron metal



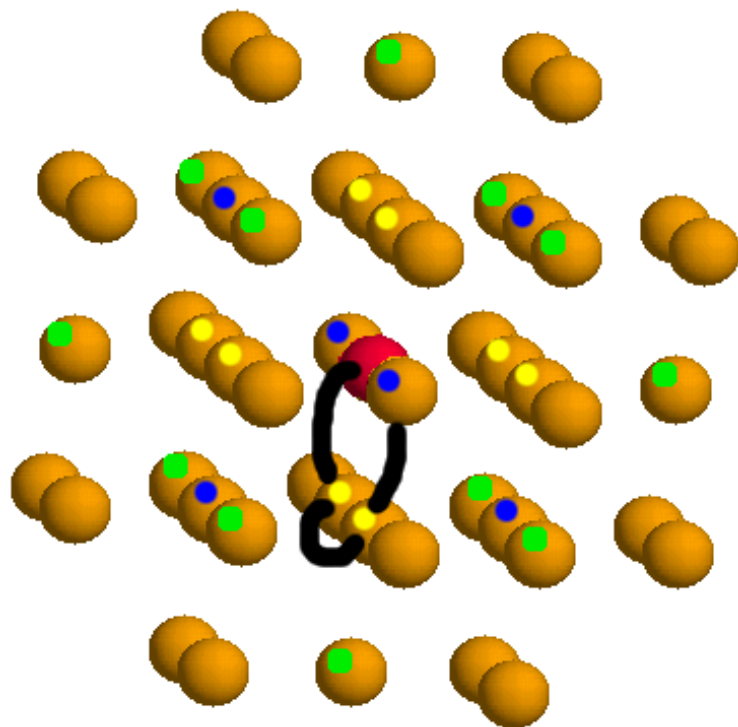
1. The second path overlaps the first in $|\tilde{\chi}(R)|$. Degeneracy = 6.
2. The XANES calculation begins to show the structure of the spectrum.



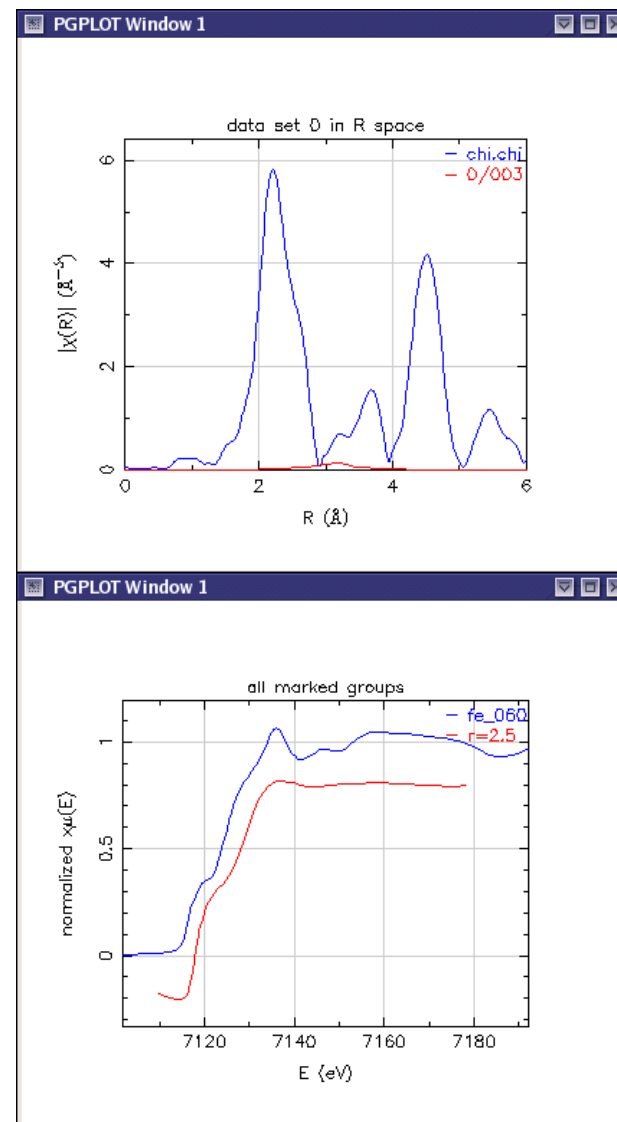
f
e
f
f
0
0
0
2

X
A
N
E
S

The third path in iron metal



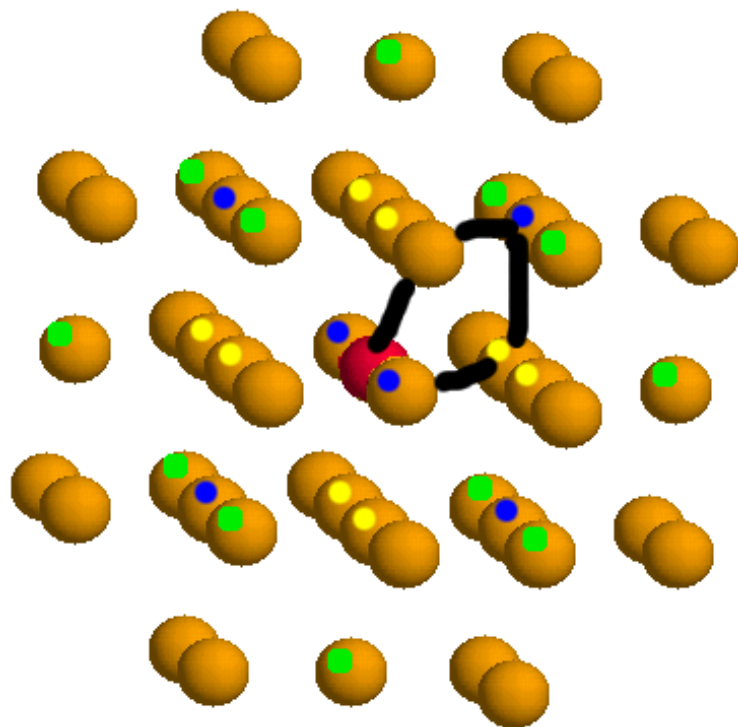
1. This path contributes little to $|\tilde{\chi}(R)|$. Degeneracy = 24.
2. The contribution from this path and all higher order paths scattering among these atoms is in the first shell XANES calculation.



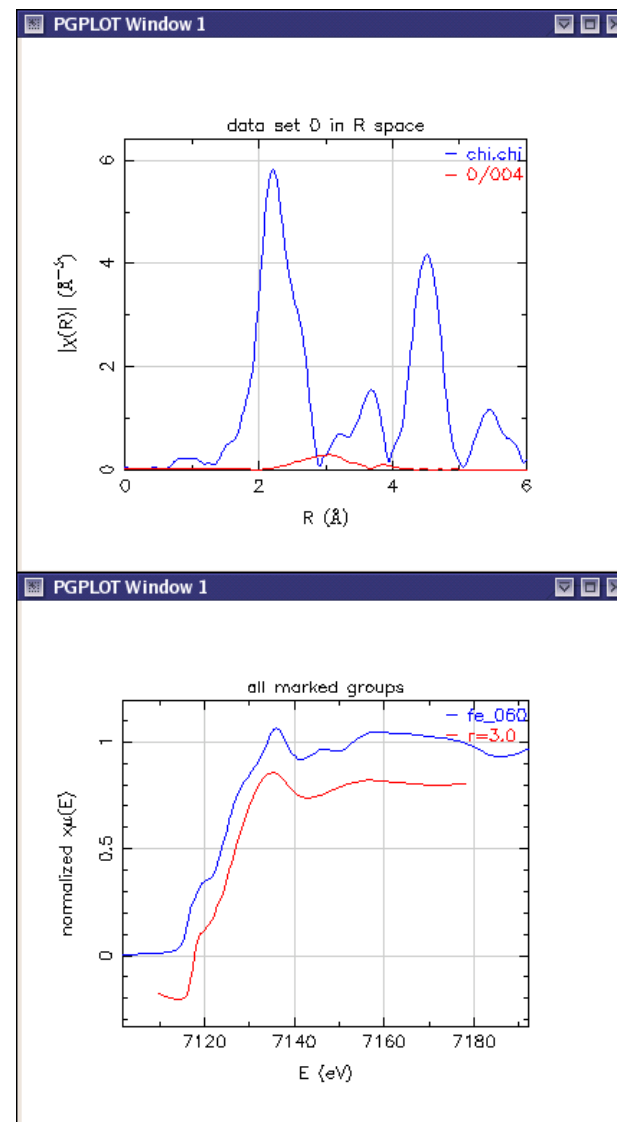
f
e
f
f
0
0
0
3

X
A
N
E
S

The fourth path in iron metal



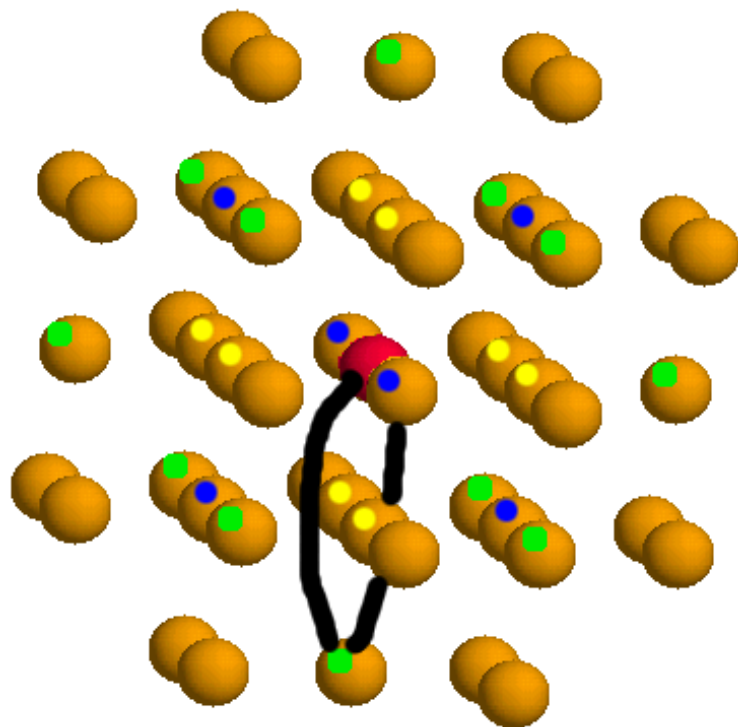
1. This path contributes little to $|\tilde{\chi}(R)|$. Degeneracy = 48.
2. The contribution from this path and all higher order paths scattering among these the first two shells is in the second shell XANES calculation.



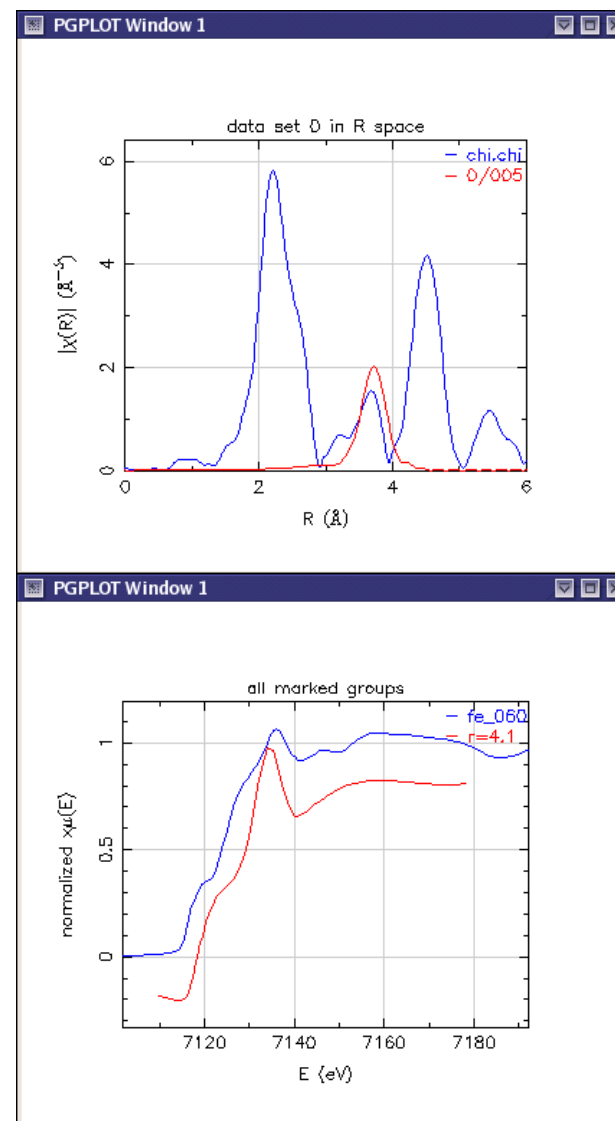
f
e
f
f
0
0
0
4

X
A
N
E
S

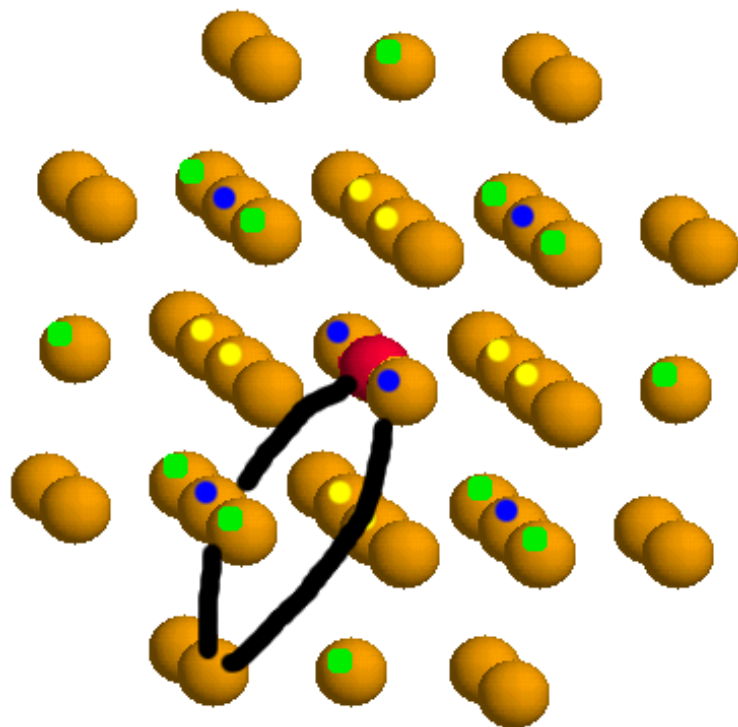
The fifth path in iron metal



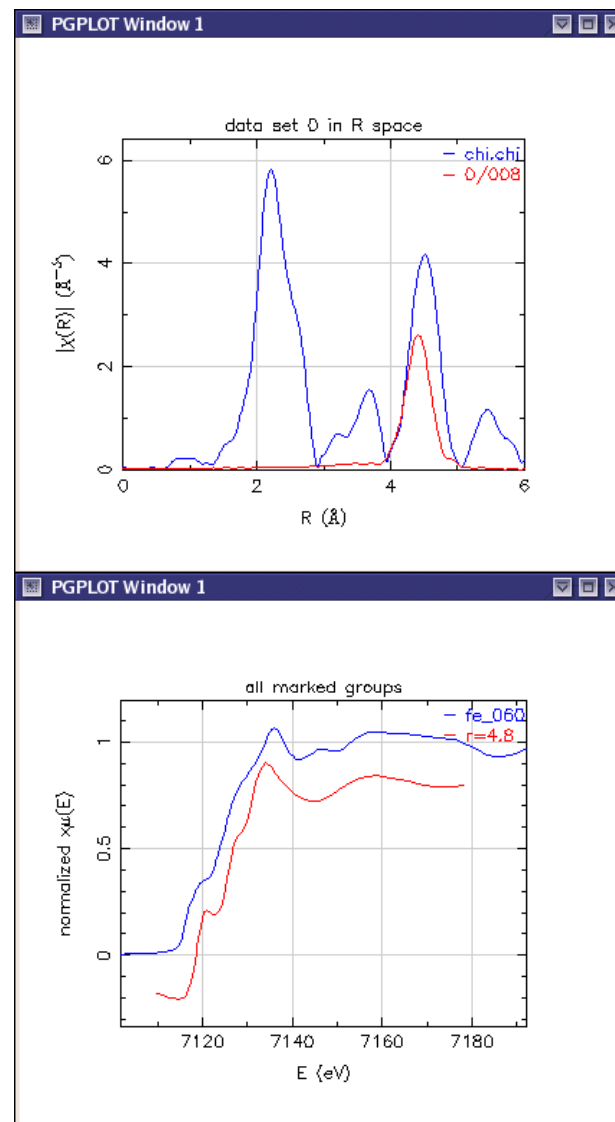
1. This 3rd shell SS path contributes most of the spectral weight to the second peak of $|\tilde{\chi}(R)|$. Degeneracy = 12.
2. The first peak after the edge in the XANES is sharpened considerably by the addition of this shell.

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..

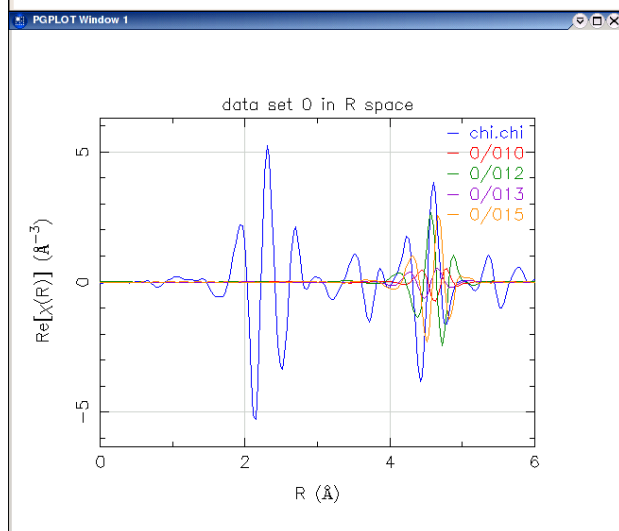
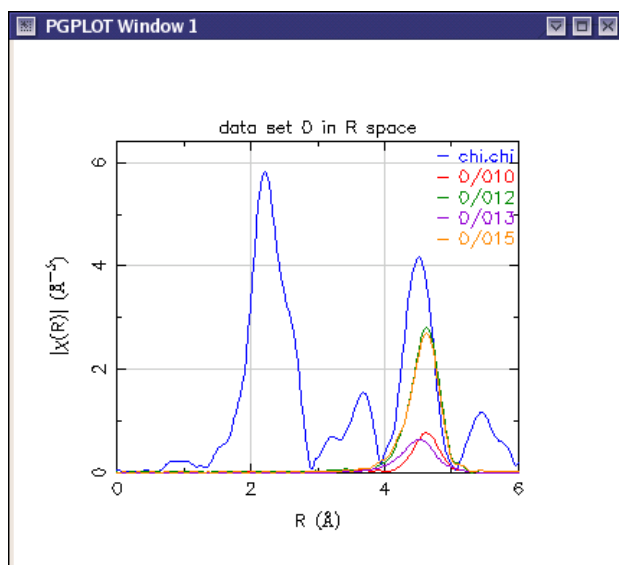


f
e
f
f
0
0
0
8

X
A
N
E
S

The fifth shell in iron metal

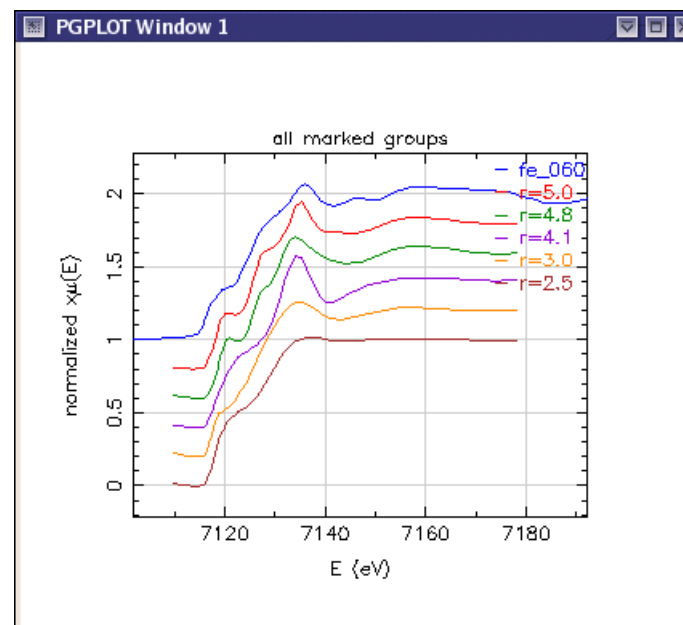
5
t
h
s
h
e
l
l

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.

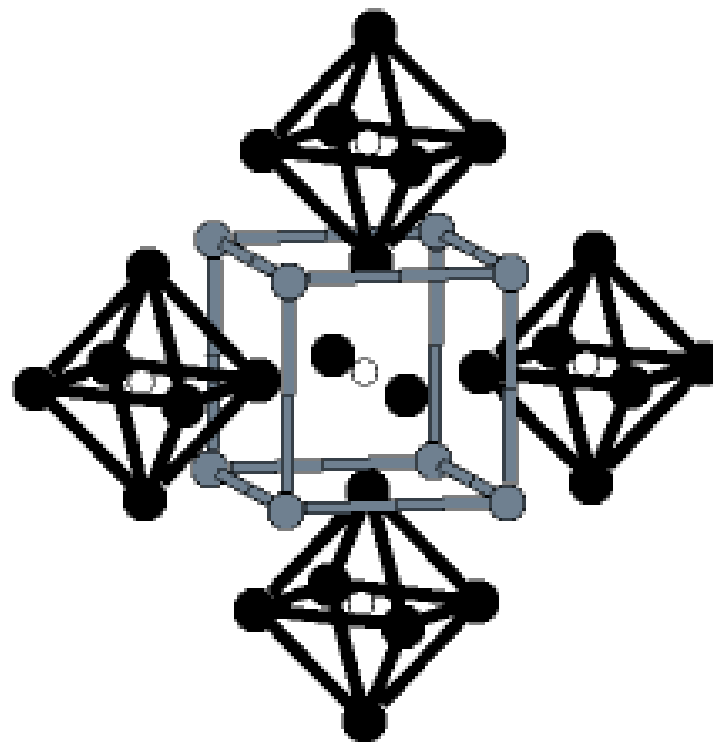


Testing convergence in cluster size

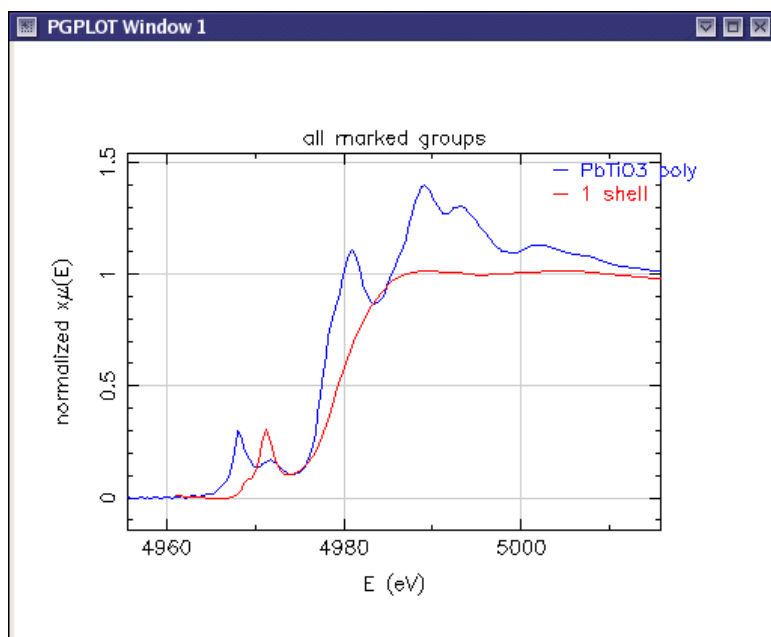
Below the plasmon resonance (~ 40 eV), the photoelectron mean free path is quite large and the photoelectron probes a large cluster of atoms. How many atoms must be included in the cluster for a **FEFF** calculation?

The general answer: *who knows?*

We will examine how the XANES calculation for PbTiO_3 changes as we add shells to the calculation. PbTiO_3 has $c > a$ and the O and Ti atoms are displaced from sites of centrosymmetry.



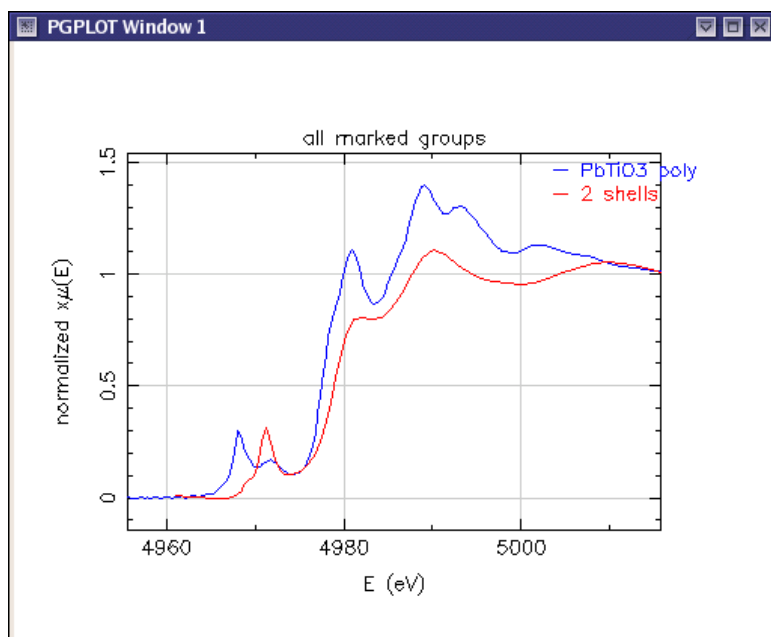
PbTiO_3 : a tetragonally distorted perovskite
 $\circ = \text{Ti}$, $\bullet = \text{O}$, $\bullet = \text{Pb}$

First coordination shell of PbTiO_3 

shell	element	radius (Å)	number	matrix
1	O	2.40	7	33
2	Pb	3.60	15	161
3	Ti	4.20	21	215
4	O	5.00	45	311
5	Ti	5.71	57	419
6	O	6.30	86	535

We see some indication of the structure just above the Fermi energy, but not much else.

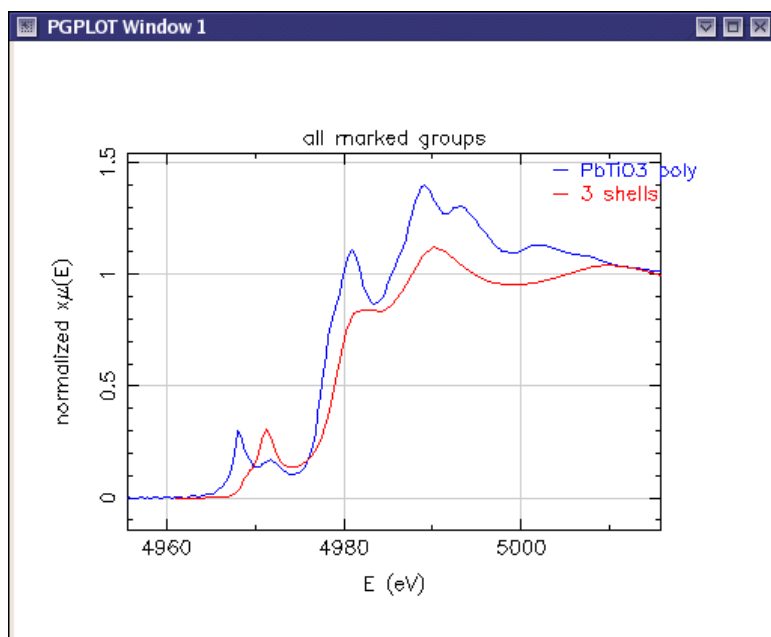
Note that the memory requirement of the calculation goes as the **square** of the matrix size and the time goes as its **cube**!

Second coordination shell of PbTiO_3 

shell	element	radius (Å)	number	matrix
1	O	2.40	7	33
2	Pb	3.60	15	161
3	Ti	4.20	21	215
4	O	5.00	45	311
5	Ti	5.71	57	419
6	O	6.30	86	535

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

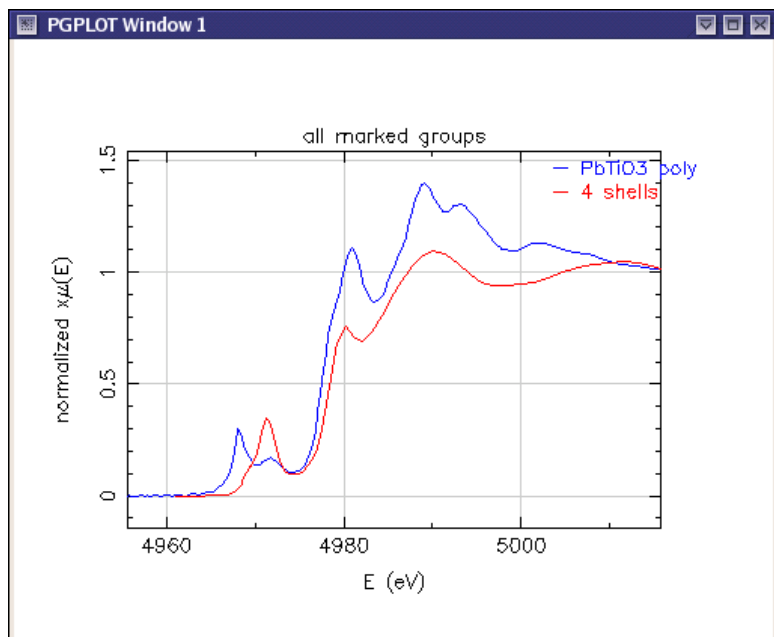
Third coordination shell of PbTiO₃



shell	element	radius (Å)	number	matrix
1	O	2.40	7	33
2	Pb	3.60	15	161
3	Ti	4.20	21	215
4	O	5.00	45	311
5	Ti	5.71	57	419
6	O	6.30	86	535

Very little changes by adding the 3rd shell Ti atoms!!

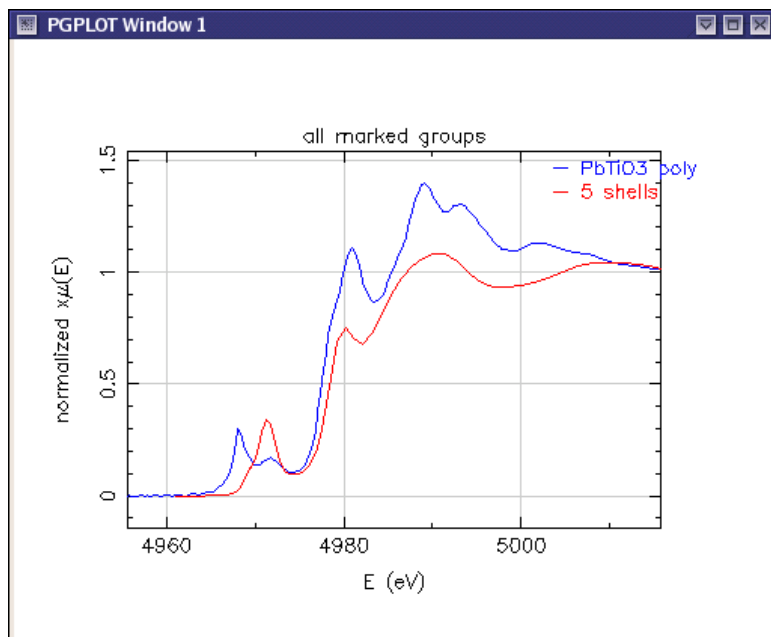
Fourth coordination shell of PbTiO₃



shell	element	radius (Å)	number	matrix
1	O	2.40	7	33
2	Pb	3.60	15	161
3	Ti	4.20	21	215
4	O	5.00	45	311
5	Ti	5.71	57	419
6	O	6.30	86	535

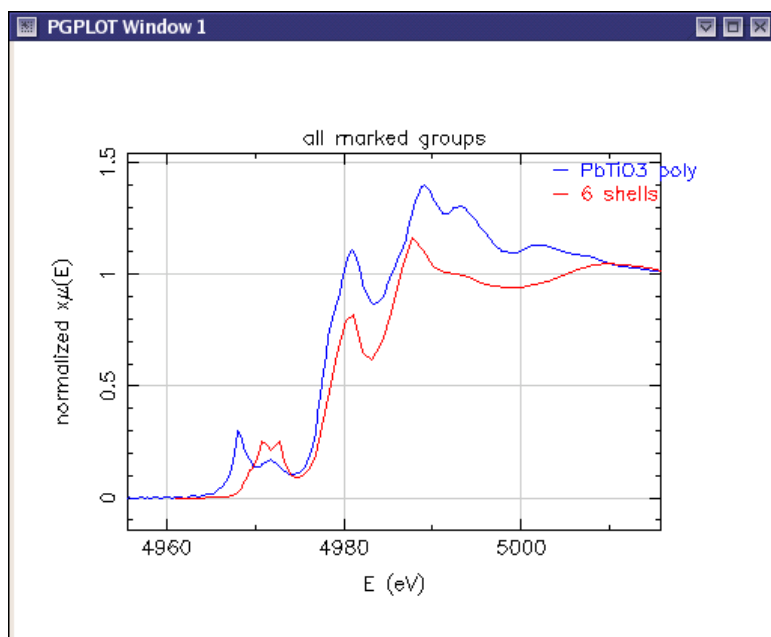
Adding an oxygen shell causes the features to become much more distinct. Low Z elements have strong scattering at low k . High Z elements have strong scattering at high k .

Fifth coordination shell of PbTiO₃



shell	element	radius (Å)	number	matrix
1	O	2.40	7	33
2	Pb	3.60	15	161
3	Ti	4.20	21	215
4	O	5.00	45	311
5	Ti	5.71	57	419
6	O	6.30	86	535

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

Sixth coordination shell of PbTiO_3 

shell	element	radius (Å)	number	matrix
1	O	2.40	7	33
2	Pb	3.60	15	161
3	Ti	4.20	21	215
4	O	5.00	45	311
5	Ti	5.71	57	419
6	O	6.30	86*	535

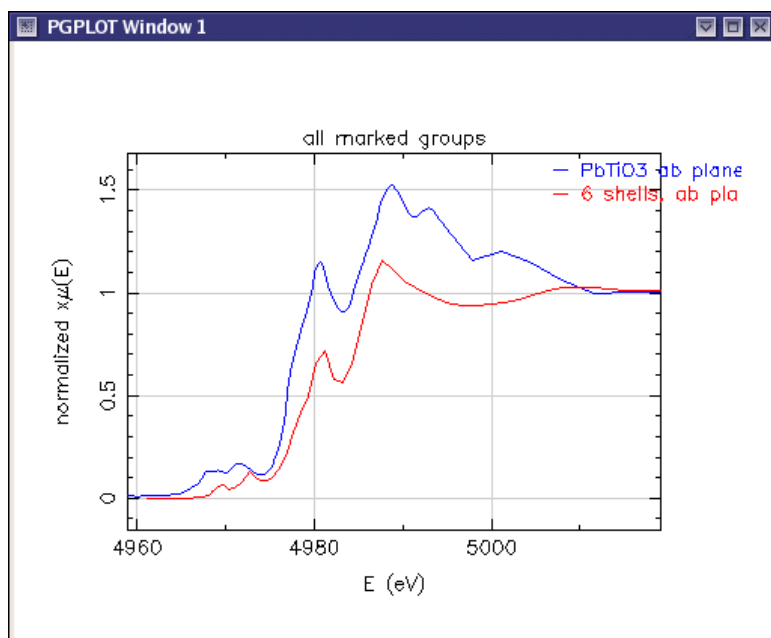
Once again, adding an oxygen shell causes the features to become much more distinct. Low Z elements have a strong effect on the XANES.

This is a fairly large cluster. Is the calculation converged? Probably not. Large clusters are required!

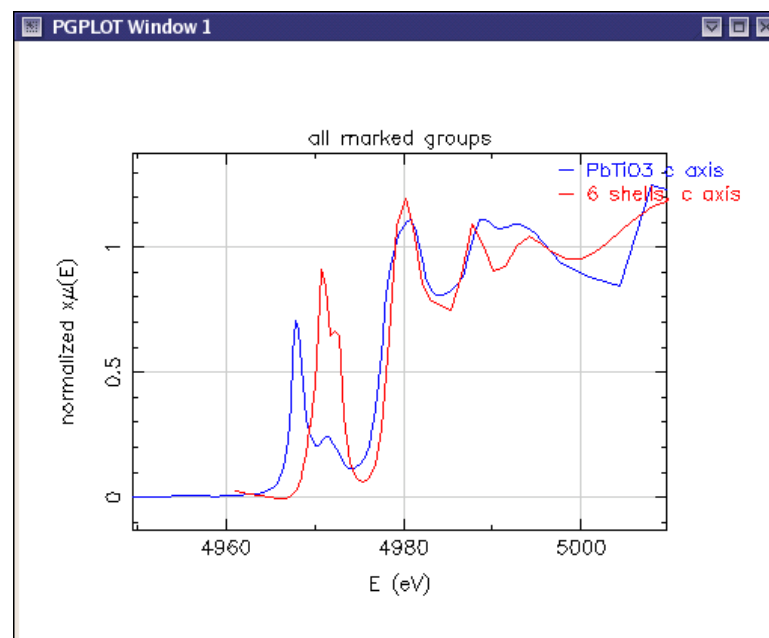
*Yes, 1 O atom was left out of the calculation.

Linear dichroism in PbTiO_3

\overline{ab} plane



\hat{c} axis

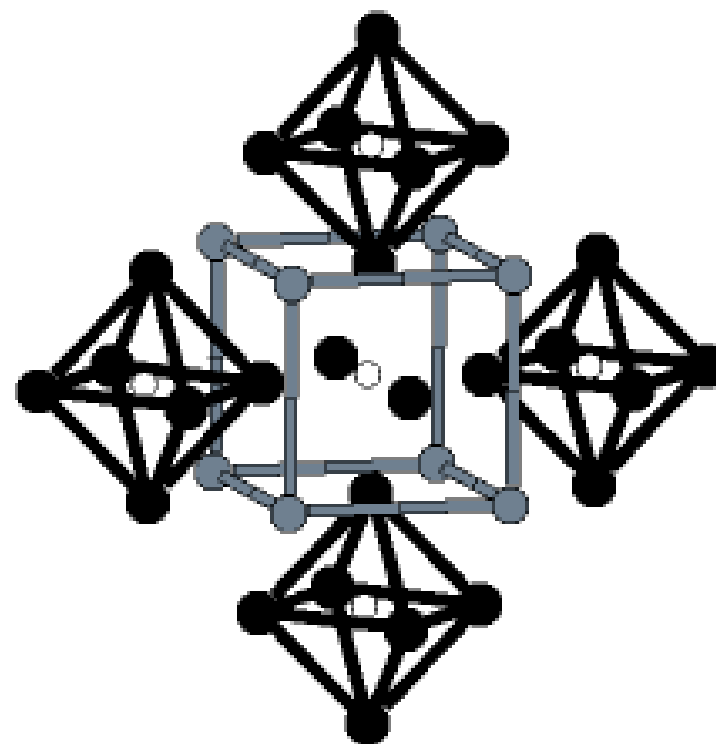
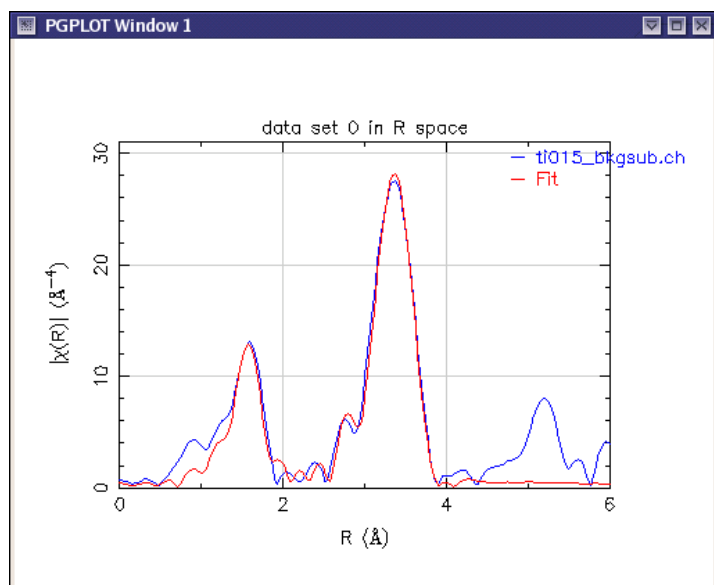


Polarization can be included directly in the XANES calculation and shows the correct behavior compared to the data.

Theoretical and empirical fitting standards

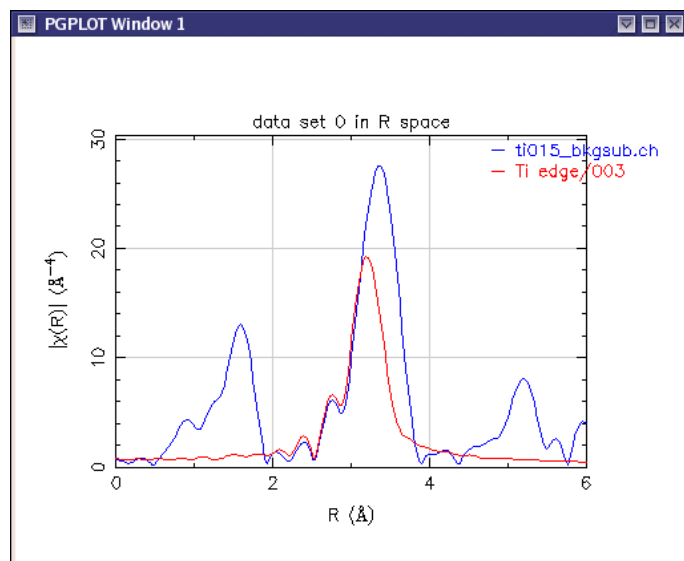
Empirical standards (and the software that use them) are fine, but there are many important limitations solved by theoretical standards.

- Unusual neighbor pairs
- Overlapping shells
- 3-body correlations
- Absolute parameter measurements
- Polarization dependence



EuTiO₃: a cubic perovskite
○ = Ti, ● = O, ● = Eu

Unusual neighbor pairs



The second shell of the EuTiO_3 Ti K edge is europium.

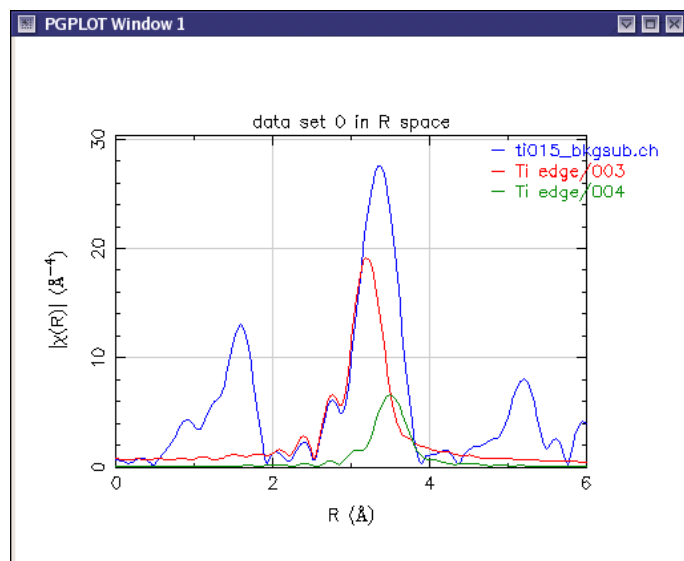
Shown to the right are the EuTiO_3 data and the contribution from the Eu shell.

No suitable empirical standard exists for an Eu–Ti pair but with theory we can create *any* pair.

Thinking up “unusual” neighbor pairs is not so hard...

1. Any material science problem with rare-earth and transition metal cations
2. The very short O path in an uranyl or plutanyl.
3. Organometallics, which may be poorly described by common, solid state standards.
4. Mixed shells, i.e. shells with more than one species.

Overlapping coordination shells

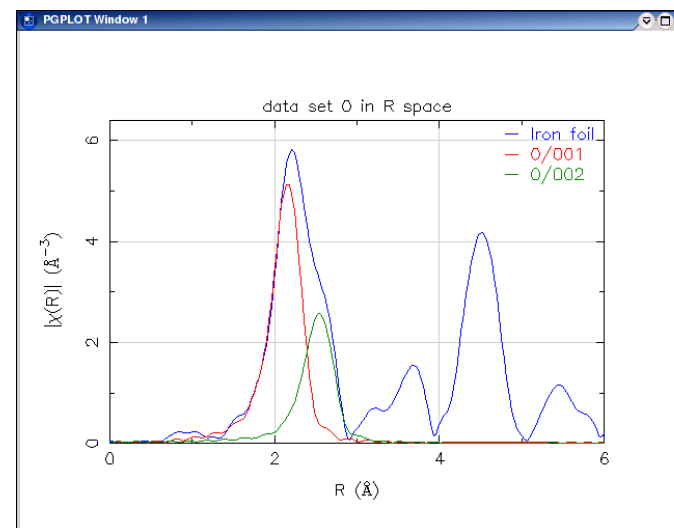


The second (Eu) and third (Ti) shells in EuTiO_3 are overlapped.

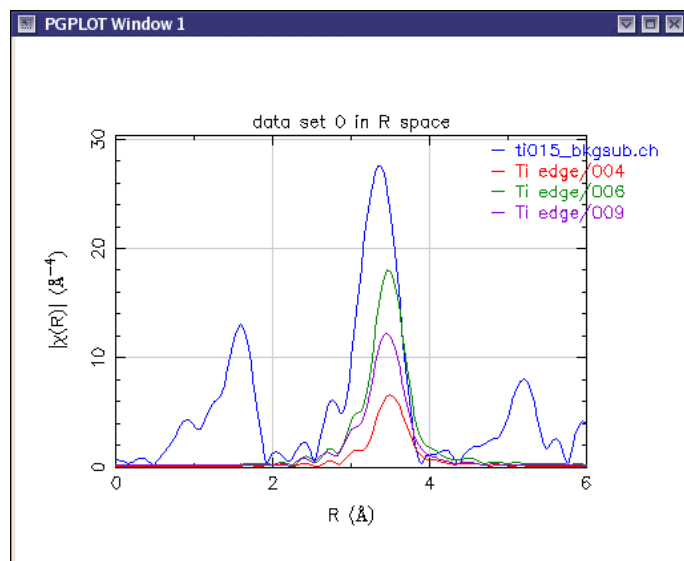
Shown to the left are the EuTiO_3 data and the contributions from those two SS paths.

Overlapping shells cannot be Fourier filtered as required by analysis programs using empirical fitting standards.

Even in a standard material like an iron foil, separation of peaks cannot be assumed. Here we see the 1st and 2nd SS paths.

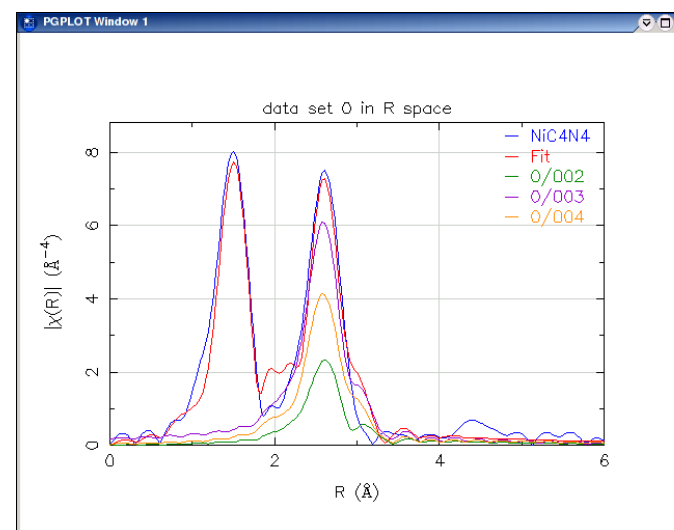


Three body correlations



Note the size of the paths which are MS among the 1st shell O and the 3rd shell Ti.

Three-body correlations are important in all kinds of materials. To the right is a fit to NiC₄N₄, a square planar solvated complex. The second peak is dominated by MS.



Measuring absolute parameters

Advantages of empirical standards

If the standard and unknown are prepared identically, are measured under identical experimental conditions, and the shells to be analyzed are well separated:

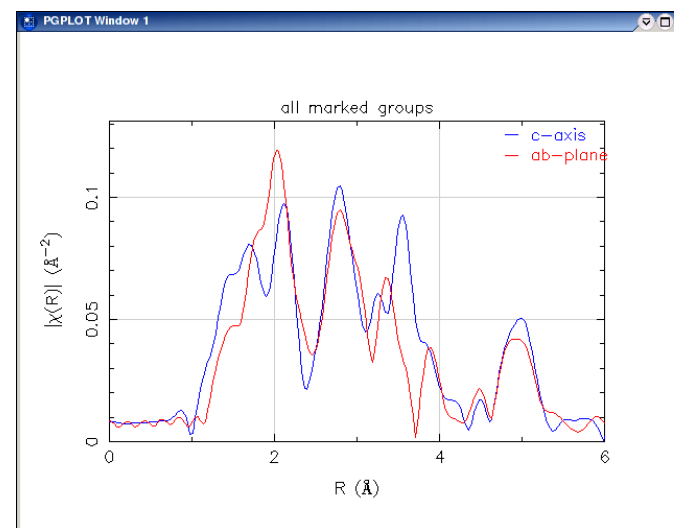
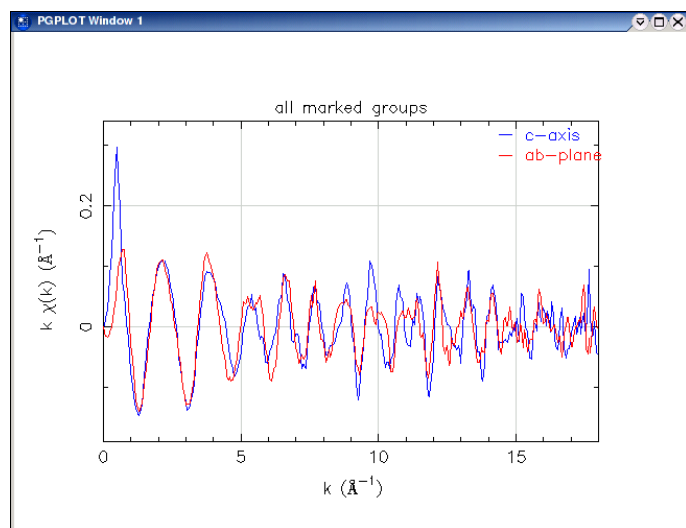
- Experimental effects (self-absorption, detector inefficiency, sample inhomogeneity) will largely cancel in many situations
- Changes in coordination may be measured more directly if other amplitude effects cancel

Advantages of theoretical standards not yet mentioned

- σ^2 (and higher cumulants) is measured relative to 0 rather than to the standard, which itself may not be well known
- ΔR is measured relative to perfectly defined nominal distances

Analyzing polarized spectra

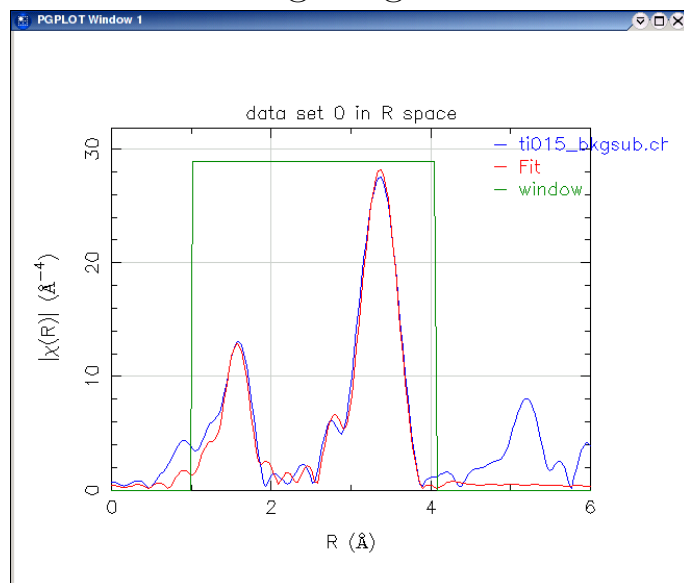
$\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}$, a cuprate superconductor, can be prepared highly textured along the \hat{c} -axis. This sample can be aligned parallel or perpendicular to the polarization of the incoming beam.



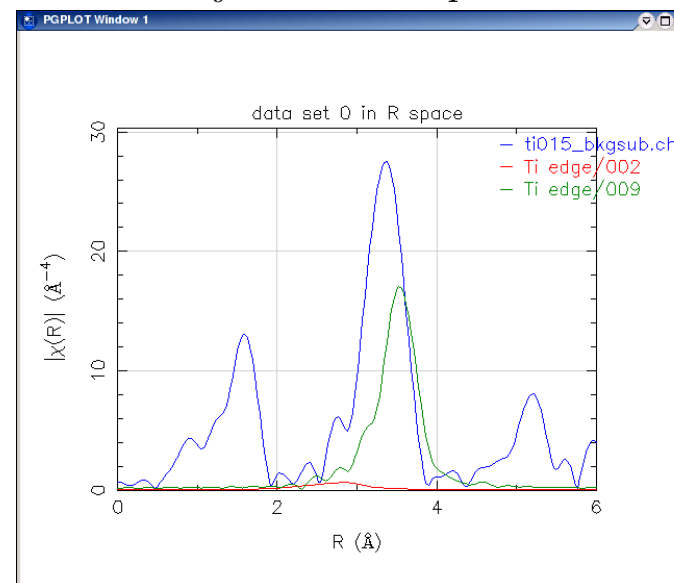
Shown here are the La K-edge spectra measured at 15 K for the two polarizations.

FEFF can compute the polarization directly both for XANES and for EXAFS to all orders of multiple scattering.

Filtering paths

Fitting range in R 

Reject “small” paths



Caveats

Watch out for leakage from higher shells!

Sometimes paths are small, but measurable, e.g.
short triangular paths

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), 2nd number is S0^2

*      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
      0.00000 -2.76150  2.76150  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
      0.00000 -2.76150 -2.76150  1  Co1_1    3.90535

*
* etc...
*
END
```

A FEFF8 input file

Here is the **FEFF8** input file for the same material. The only difference is in the header lines.

```
TITLE Cobalt sulfide CoS_2

EDGE K
SO2 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  stoich.
      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
0.00000 -2.76150 2.76150 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
0.00000 -2.76150 -2.76150 1 Co1_1    3.90535

*
* etc...
*
END
```

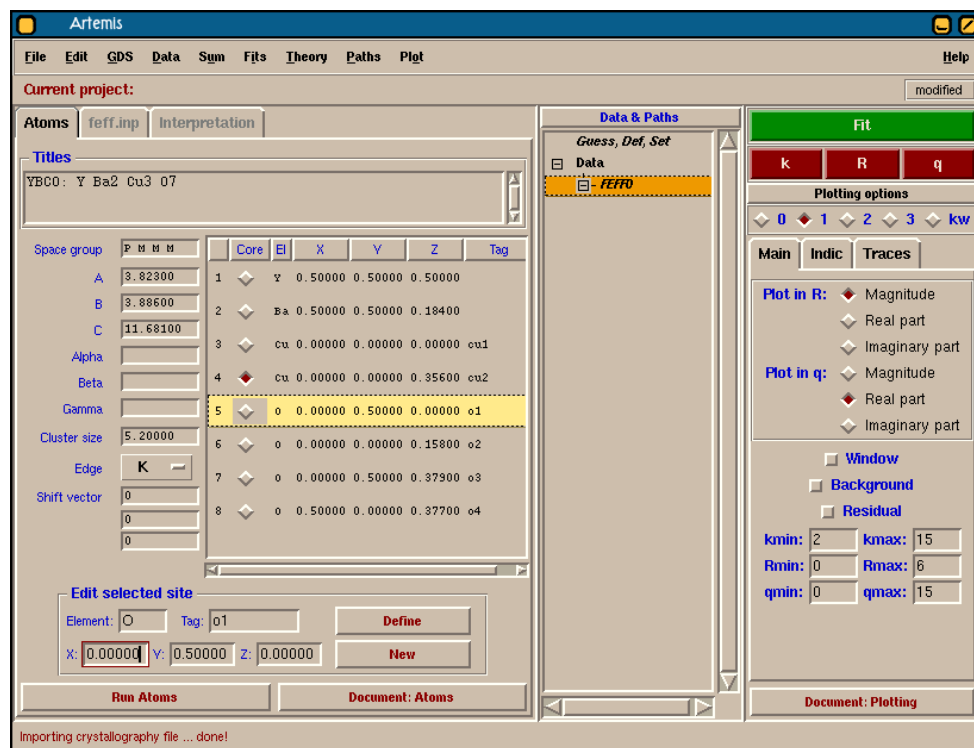
What goes into your FEFF input file

1. Each atom in the list is defined by Cartesian coordinates and a *potential index*.
2. The potentials are assigned in an integer list starting with 0 for the central atom. You may neither skip integers nor have an index larger than 7. Each index is associated with a Z number.
3. All keywords *must* be uppercase. The asterisk * marks text to be ignored by FEFF.
4. For crystals, it is a good idea to create a *long* atoms list and limit the calculation using RMAX.
5. For EXAFS it is better to set $S_0^2 = 1.0$ and not to compute any σ^2 values in the FEFF calculation. These are better handled in the fitting program.
6. FEFF always writes its output files to the **same** file names. Different calculations must be done in different folders or else the current calculation will overwrite the previous calculation.
7. Making the list of atomic coordinates is the hard part of creating 'feff.inp' files. Fortunately, there are some shortcuts....

FEFF6 or FEFF8 can be run inside ARTEMIS. Versions of FEFF6 exist for Windows and OSX which graphically prompt for an input file. Otherwise, FEFF *must* be run from a command line and its input file *must* be called 'feff.inp'.

Using ATOMS to prepare the FEFF input file

If you are looking at a crystalline material (or something that resembles a crystal), software exists to translates crystallographic data into 'feff.inp' files. The program **ATOMS** can be run from a command line or you can use **ARTEMIS**.



The input data can be a CIF file or this relatively simple format:

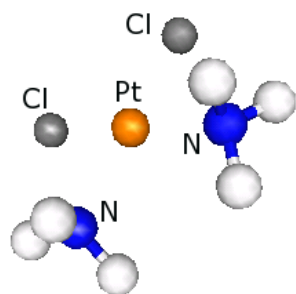
```

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
atom
! 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      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. Here, for example, is the *cisplatin* molecule in the form of a Protein Data Bank file, which I found by googling.



Cut, paste, and *voilà!* — you have a `'feff.inp'` file.

Note that the absorber need not be at (0,0,0) and the list need not be in any particular order.

```

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
    
```

```

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
    
```

Substitutions and vacancies

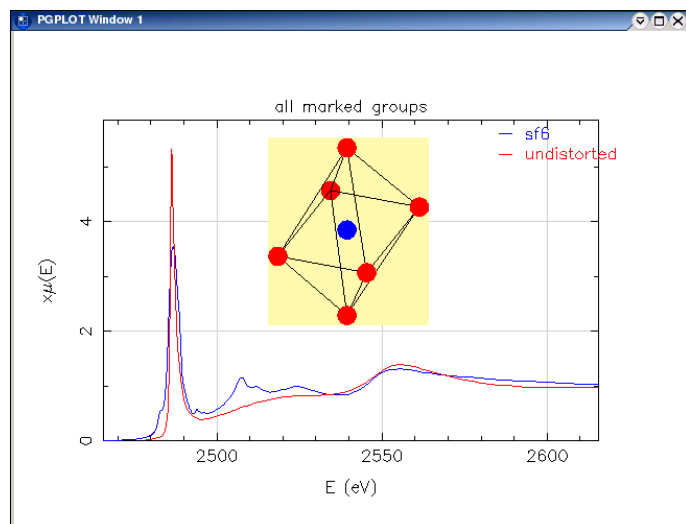
In **FEFF**, a point in space is occupied either by nothing or by an entire atom.

- Vacancy
- Substitution
- Partial Occupancy

These effects on a XANES spectrum cannot be calculated in a **single FEFF** calculation.

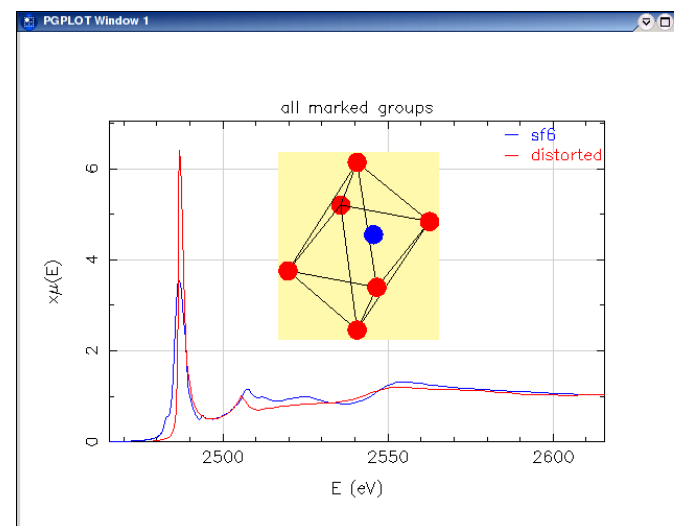
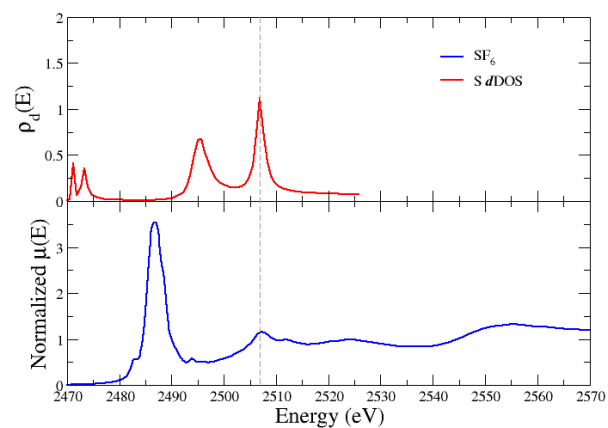
The most successful strategy is to make **multiple** calculations, randomly introducing substitutions or vacancies. Average these calculations until the average is converged.

Modeling structural distortions



SF_6 is an octahedral complex with nominal bond length of 1.54 Å. Introducing a **distortion** mixes d character into the final state. The peak near 2507 eV in the $dDOS$ then contributes to the corresponding peak in the spectrum.

1. Thermal — $\langle R_{S,F_x} - R_{S,F_{-x}} \rangle \neq 0$
2. Jahn-Teller



Fitting XANES spectra

If we consider XANES as a multivariate function of a (potential quite) large parameter space:

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

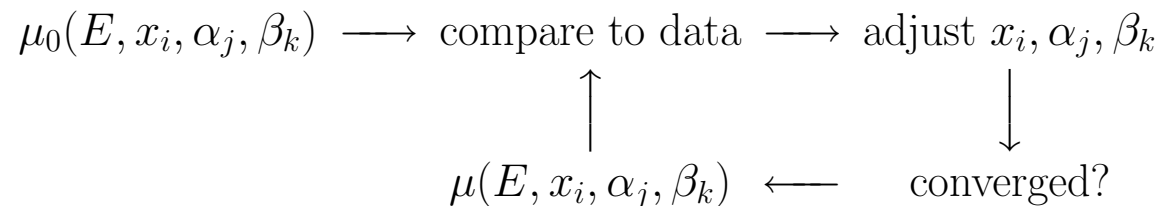
where

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)

Then we can fit:

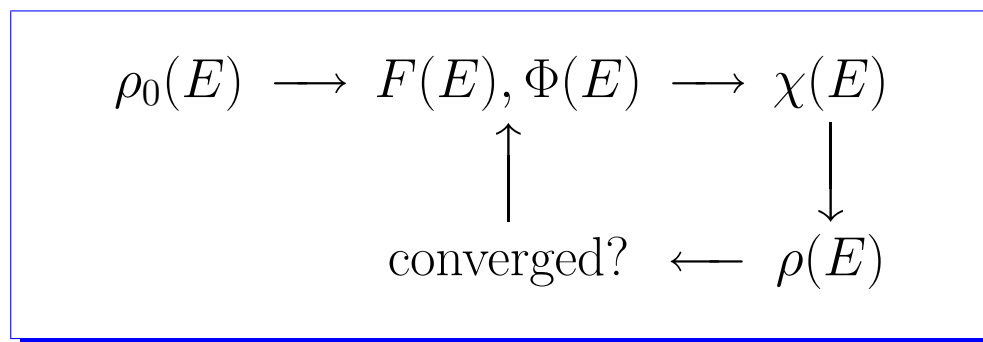


In the **FEFF** world, this is an open problem. But see, for example, Benfatto et al. Phys. Rev. **B65** (2002) 174205.

What is a self consistent potential?

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.

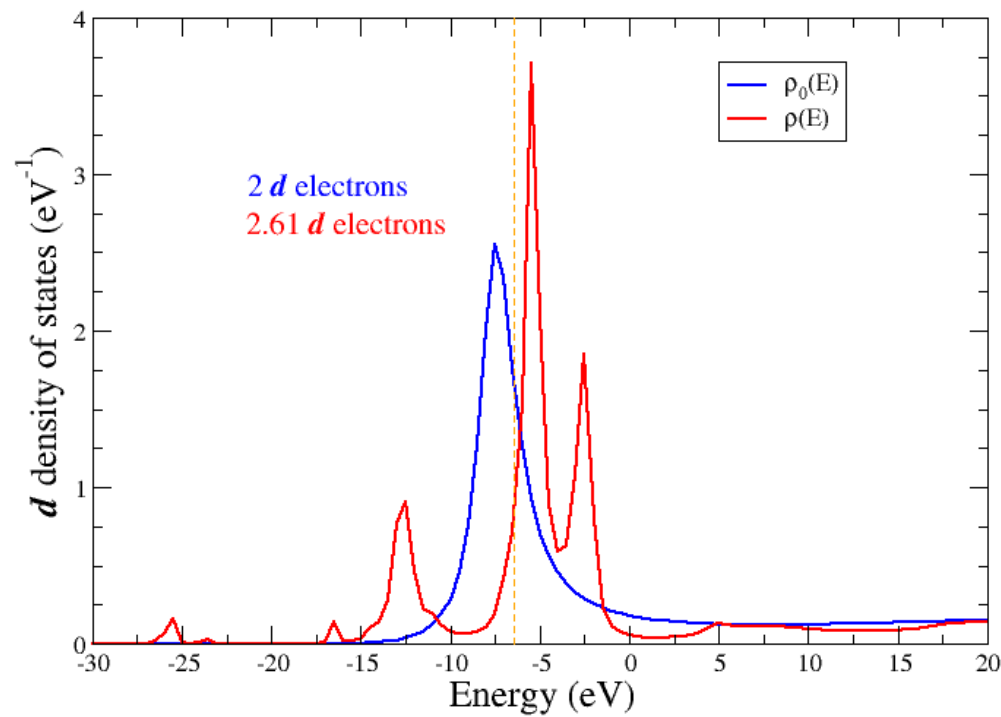
$$\rho_\ell(E) = \rho_{0,\ell}(E)(1 + \chi_\ell(E)) \quad \ell \in \{0, 1, 2, 3, \dots\}$$



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.

Self consistent density of states

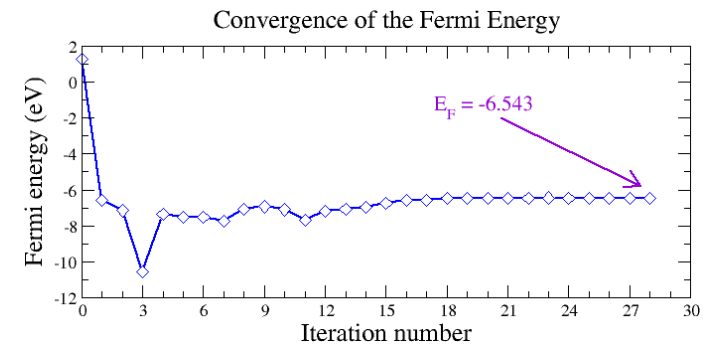
The d density of states for the Ti atom in PbTiO_3



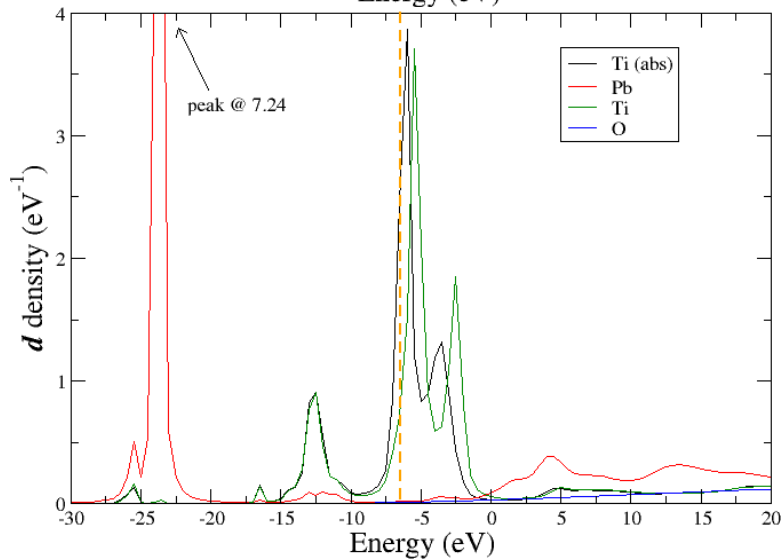
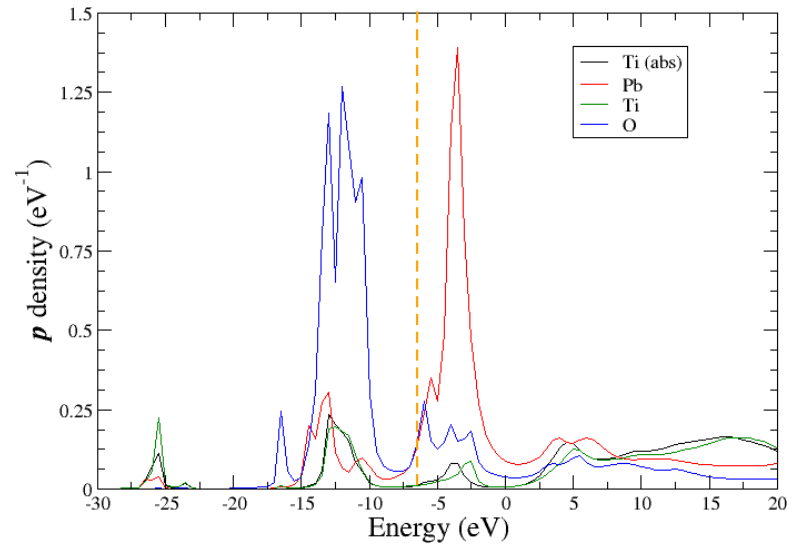
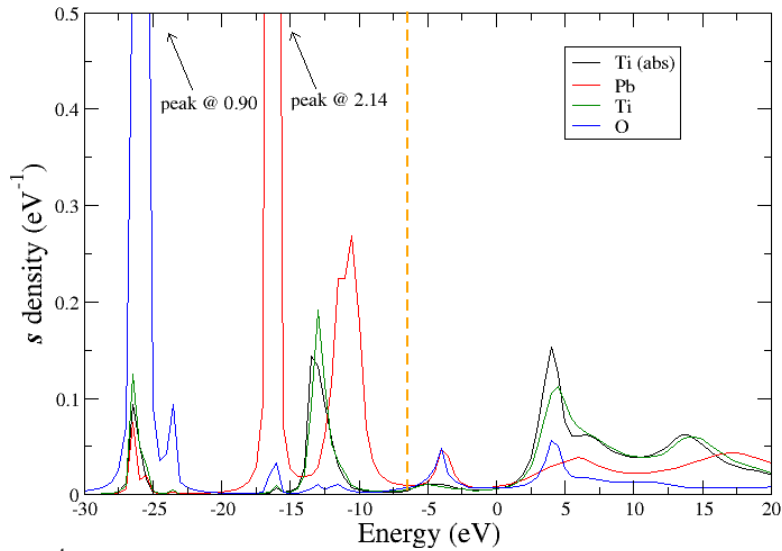
The self-consistency loop redistributes charge between atoms and among angular momentum states.

ℓ	free atom	in solid
s	2	0.427
p	6	6.660
d	2	2.610

Net transfer = $0.299 e^-$



All densities of states in PbTiO_3



Note the shift of the absorber relative to the normal Ti

atom	e^- transfered
abs	+0.170
Pb	+0.633
Ti	+0.299
O	-0.311

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/>
3. **ATOMS**, **ATHENA**, **ARTEMIS**: <http://feff.phys.washington.edu/~ravel/software/exafs/>

About this document

The first version of this document was composed for lectures given at

1. VII International School and Symposium on Synchrotron Radiation in Natural Science in Zakopane, Poland, 8-13 June, 2004
2. a four-day workshop on EXAFS Data Collection and Analysis at the National Synchrotron Light Source, June 22–25, 2004.

A paper on this material will be published in *Journal of Alloys and Compounds* in the second half of 2005.

This document was created using a variety of free software tools, including PDF \LaTeX , the XEmacs text editor and the really excellent AUCT \LaTeX mode, XMGRACE, XFIG, and RASMOL. 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*. Many of the 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. *IFEFFIT*, *ATHENA*, *ARTEMIS*, and *FEFF6* were all used during the course at the NSLS.

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.

Some slides were taken from the work of others. **Two pages** were adapted from Matt Newville's *Fundamentals of XAFS* lecture.

Notes
