Introduction to XAS Theory

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Abstract

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

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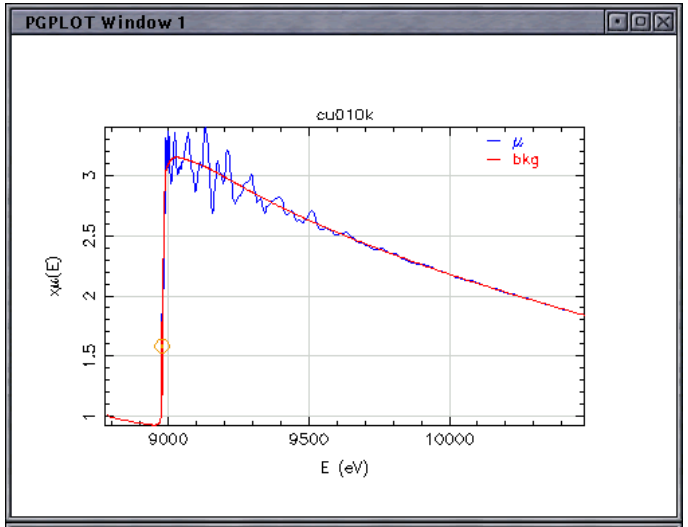
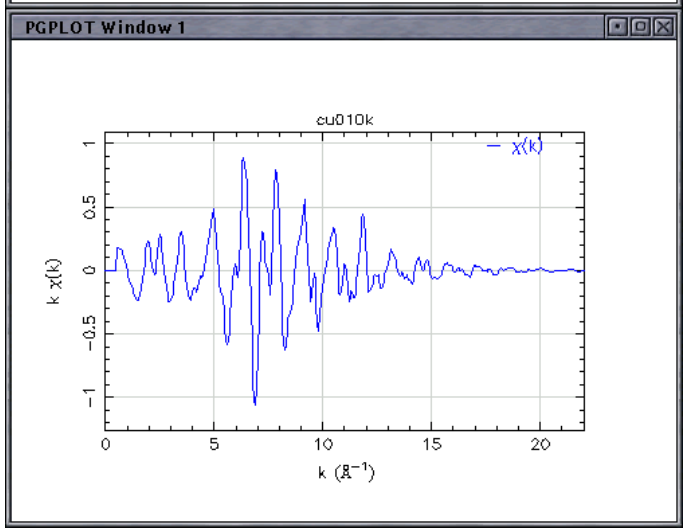
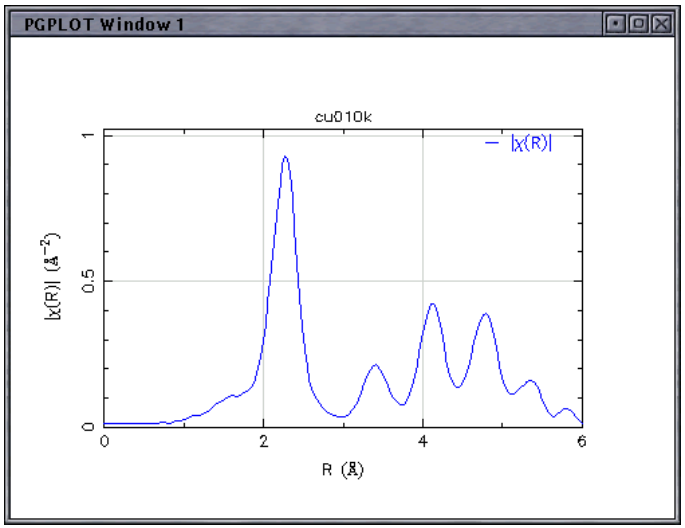
EXAFS data





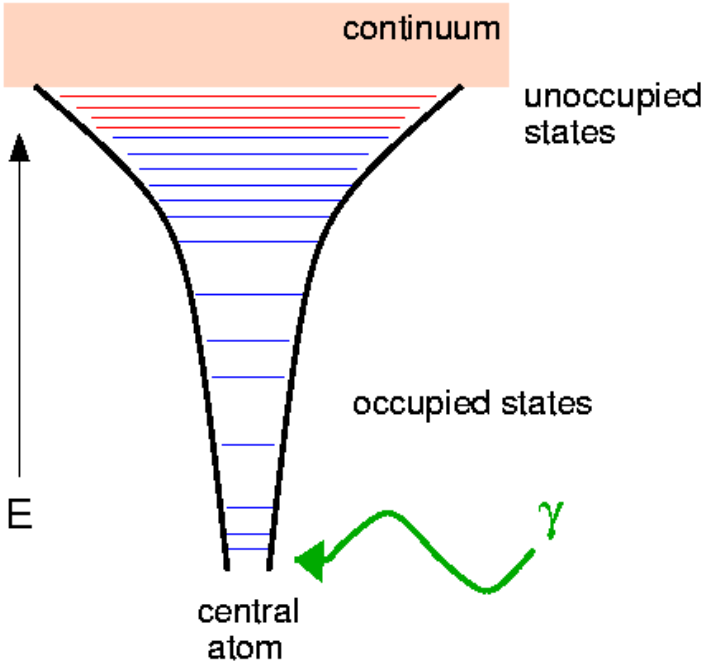
In EXAFS, we isolate the oscillatory structure, $\chi(k)$, from the absorption cross-section $\mu(E)$. Because the concepts behind the theory are more easily understood in real space, I also show the Fourier transform of $\chi(k)$, $\tilde{\chi}(R)$. We'll see the Fourier transform again in a few slides.

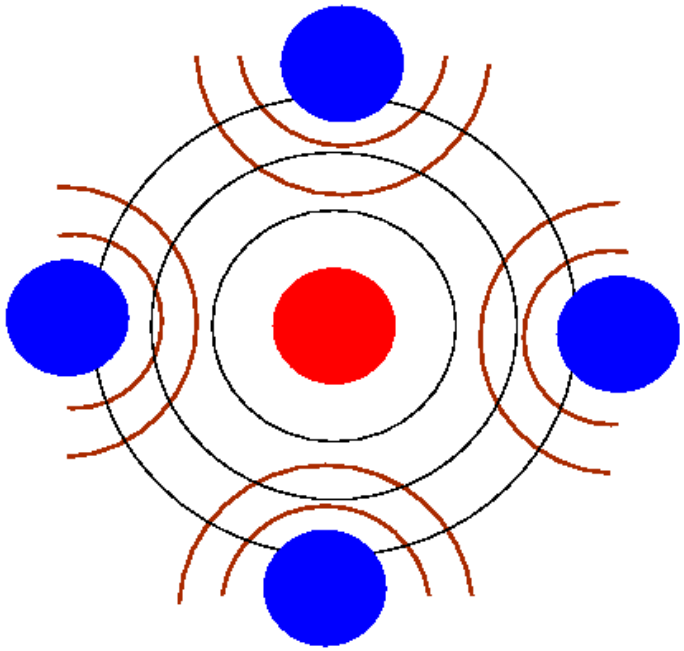
FT $\Longrightarrow$



A Heuristic Picture of EXAFS

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





The photoelectron propagates as a spherical wave and scatters off the surrounding atoms. This cartoon is overly simplistic, but serves to motivate an understanding of absorption.

Fermi's Golden Rule

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

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

There are two ways to solve this equation:

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

Motivating the multiple scattering expansion

In multiple scattering theory, we construct a Greens function from the Hamiltonian for a flat interstitial potential perturbed by an ensemble of atomic scattering sites (*which is just a fancy way of saying "a material"*).

This allows us to rewrite Fermi's Golden rule as

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

From there, a bunch of matrix algebra leads us to a series expansion for the Green's function

$$\mathbb{G} = \mathsf{G}_c + \sum_{i\neq 0} \mathsf{G}_c \mathsf{t}_i \mathsf{G}_c + \sum_{\substack{i,j\neq 0\\ i\neq j}} \mathsf{G}_c \mathsf{t}_i \mathsf{G}^0_{i,j} \mathsf{t}_j \mathsf{G}_c + \sum_{\substack{i,k\neq 0\\ i\neq j\\ j\neq k}} \mathsf{G}_c \mathsf{t}_i \mathsf{G}^0_{i,j} \mathsf{t}_j \mathsf{G}^0_{j,k} \mathsf{t}_k \mathsf{G}_c + \cdots \equiv \sum_{\substack{\text{all possible}\\ \text{paths}}} \mathsf{G}^\Gamma$$

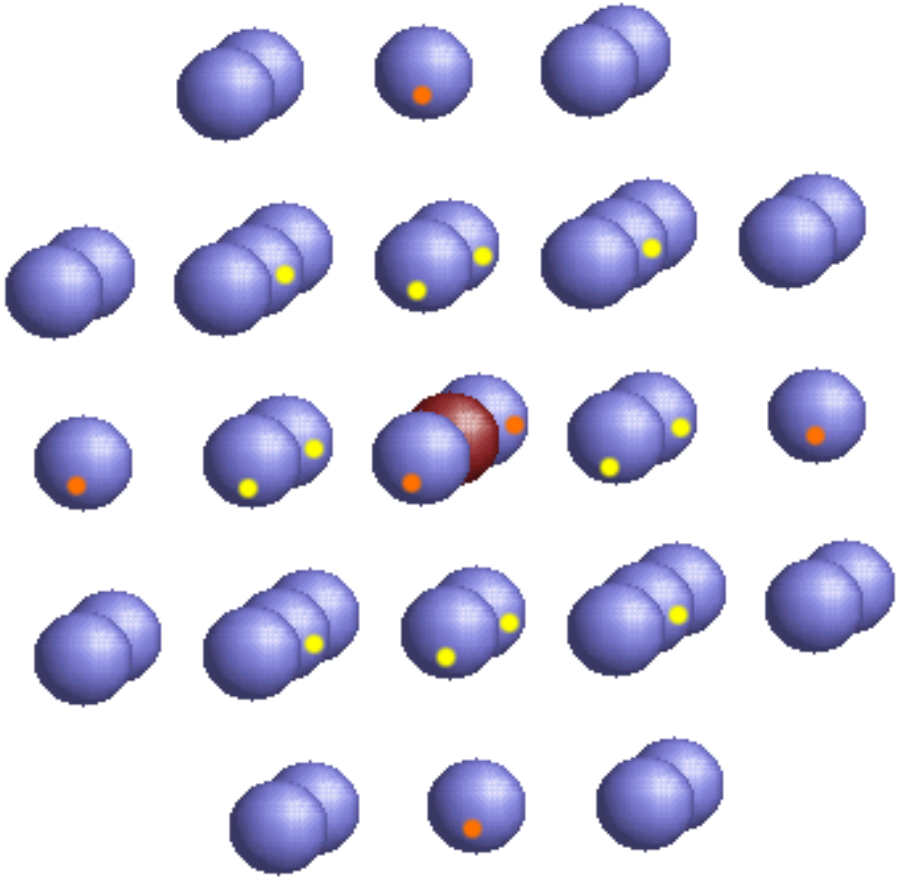
This equation tells us that we can compute the EXAFS by computing the contributions from each individual scattering path and then summing up the paths.

See Phys. Rev. **B58**, pp. 7565–7576 or my doctoral thesis for all the gory details.

Paths and clusters: FCC copper

So, what's a path?

A path is any geometry by which a photoelectron can propagate from the absorber, scatter off of one or more of the surrounding atoms, and return to the absorber.

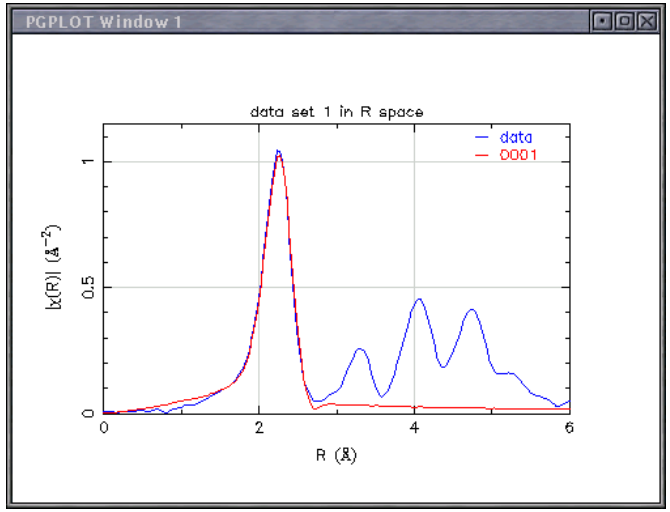


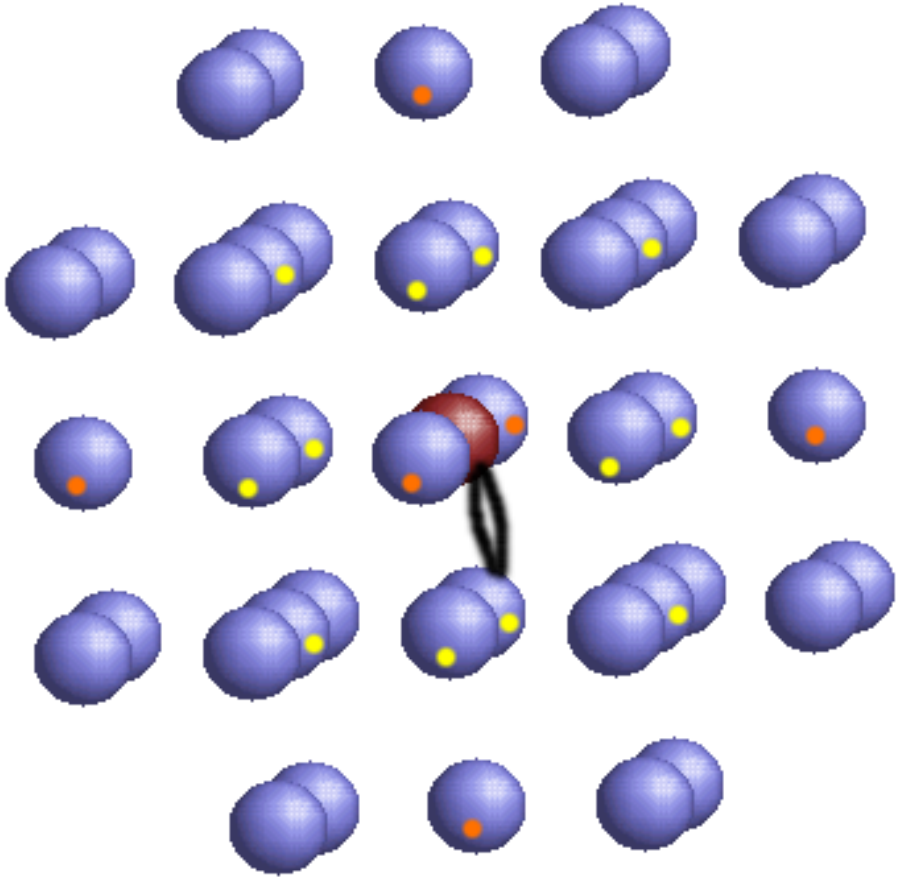
Here is ball-n-stick figure of a cluster of copper atoms containing the absorber and the first three coordination shells.

- 12 first shell atoms
- 6 second shell atoms
- 24 third shell atoms

The first path in FCC copper

The shortest path is a single scattering path between the absorber and one of its nearest neighbors. Since we organize the paths by increasing path length, this is path #1.

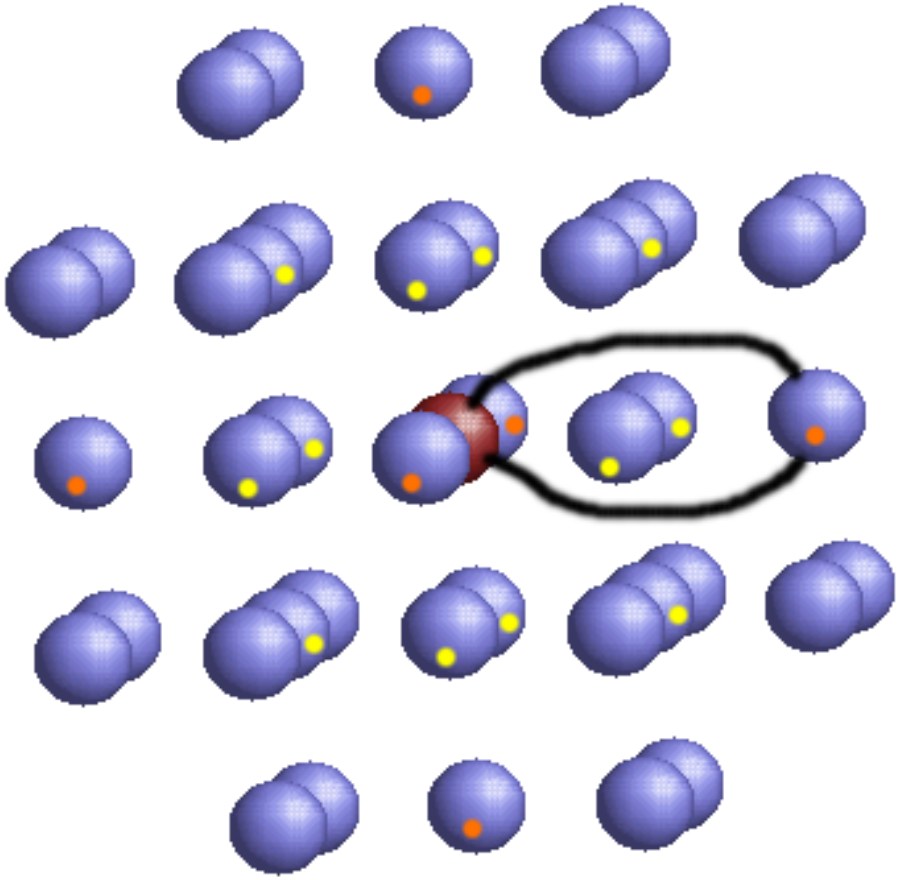


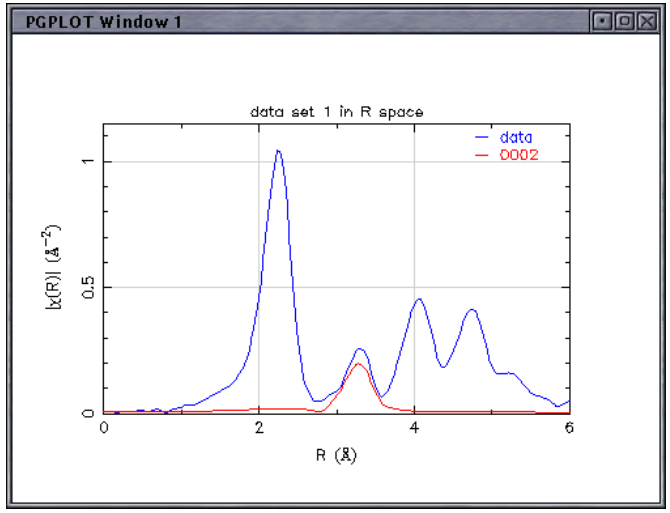


'feff0001.dat'

The second path in FCC copper

The next shortest path is between the absorber and an atom in the 2nd coordination shell. This is path #2.

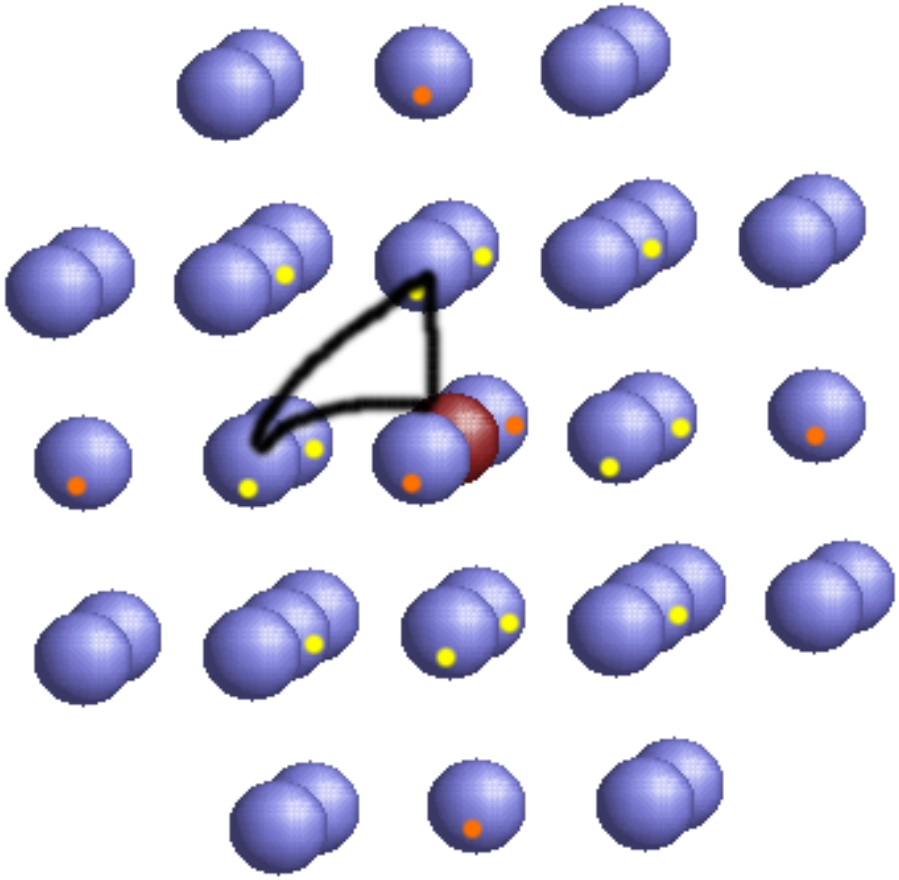


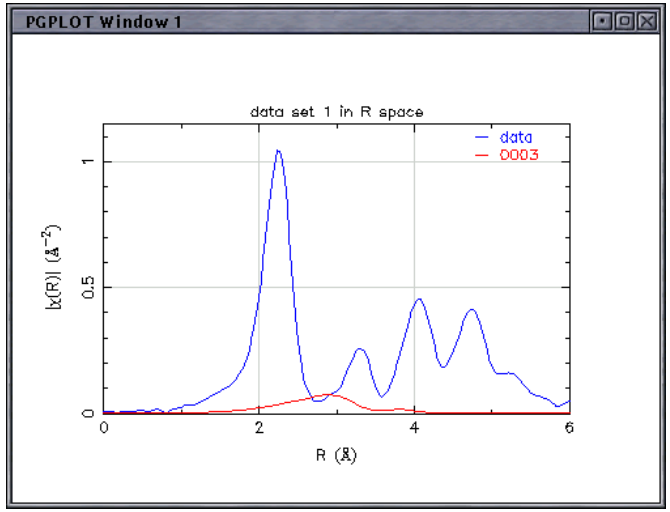


'feff0002.dat'

The third path in FCC copper

The next longer path is a double scattering path that bounces first off of one atom from the 1st coordination shell then off another before returning home. This is path #3.

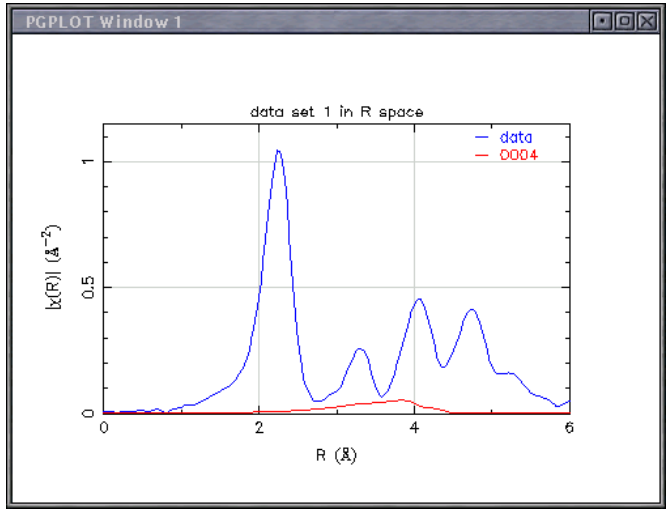


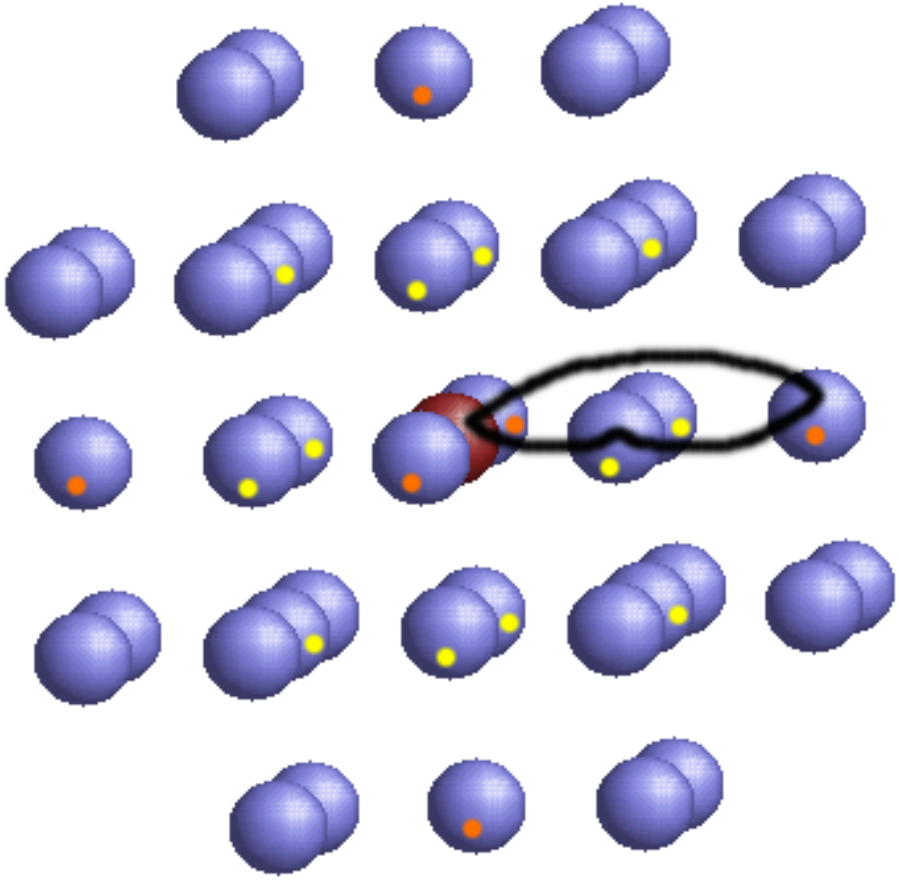


'feff0003.dat'

The fourth path FCC copper

Path #4 is also a double scattering path. It bounces first off of one atom from the 1st coordination shell then off one from the 2nd shell another before returning home.

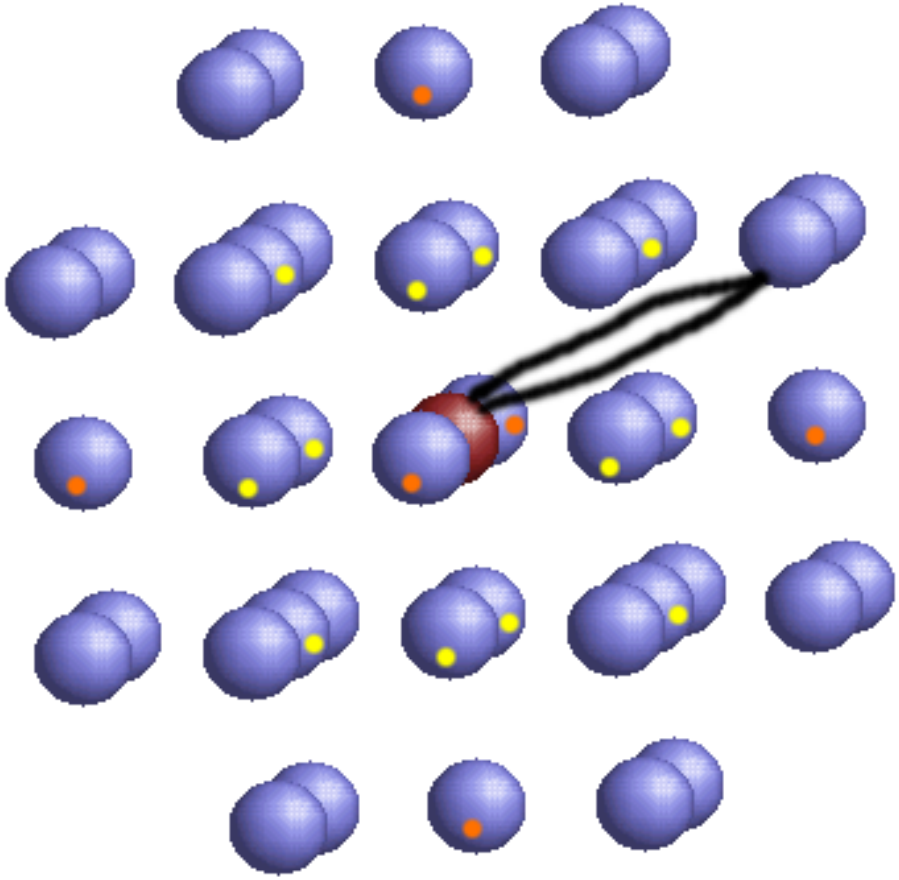


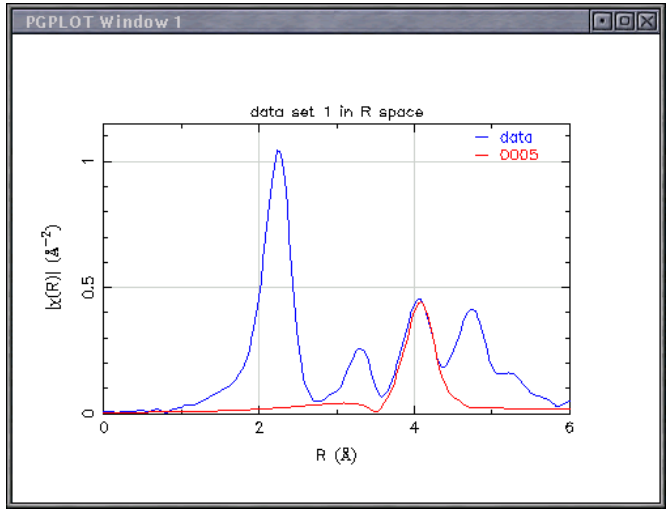


'feff0004.dat'

The fifth path in FCC copper

Path #5 is again a single scattering path, this time involving the 3rd co-ordination shell.





'feff0005.dat'

Selecting the important paths

Even in a limited cluster there are an infinate number of possible scattering paths. That's just way too many! Fortunately, there are two good ways of choosing the *important* paths for the fit.

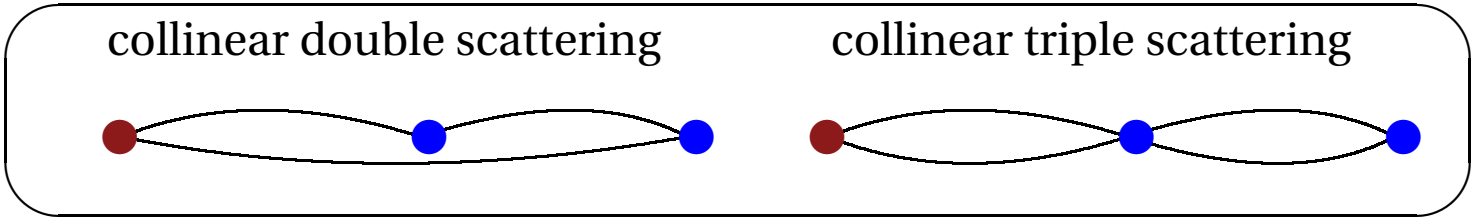
Filter by path length

Paths with *half path length* longer than some peak in $\tilde{\chi}(R)$ can probably be ignored.

Filter by path amplitude

Paths which are *small* can probably be ignored. Typically, only single scattering, short double scattering, and collinear multiple scattering paths need be considered in a fit.

Collinear multiple scattering paths are paths with atoms in a line or nearly in a line.



The information needed by FEFF

FEFF requires certain information to make its calculation.

Atomic coordinates

FEFF performs its calculation on a cluster of atoms and so requires a list of Cartesian coordinates. The absorber does **not** need to be at $(0, 0, 0)$.

Potential assignments

Each atom is assigned a potential index along with its coordinates. This is how FEFF knows what kind of atom is at each position. Typically each atomic species or each crystallographic position is assigned a potential.

Other parameters

FEFF also needs to know which edge is to be computed (i.e., K, L_{III}, and so on). Another common parameter is RMAX, which limits the radial extent of the calculation. XANES calculations using FEFF8 usually require a few additional parameters.

A FEFF input file

Here is an example of a FEFF input file:

```
* This feff input file was generated by TkAtoms 3.0beta7
* Atoms written by and copyright (c) Bruce Ravel, 1998-2001

* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
*   total mu =  1073.99 cm^-1,  delta_mu = 701.67 cm^-1
*   specific gravity =  4.852
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
*   Normalization correction:    0.00057 ang^2
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *


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 few more details about FEFF's input file

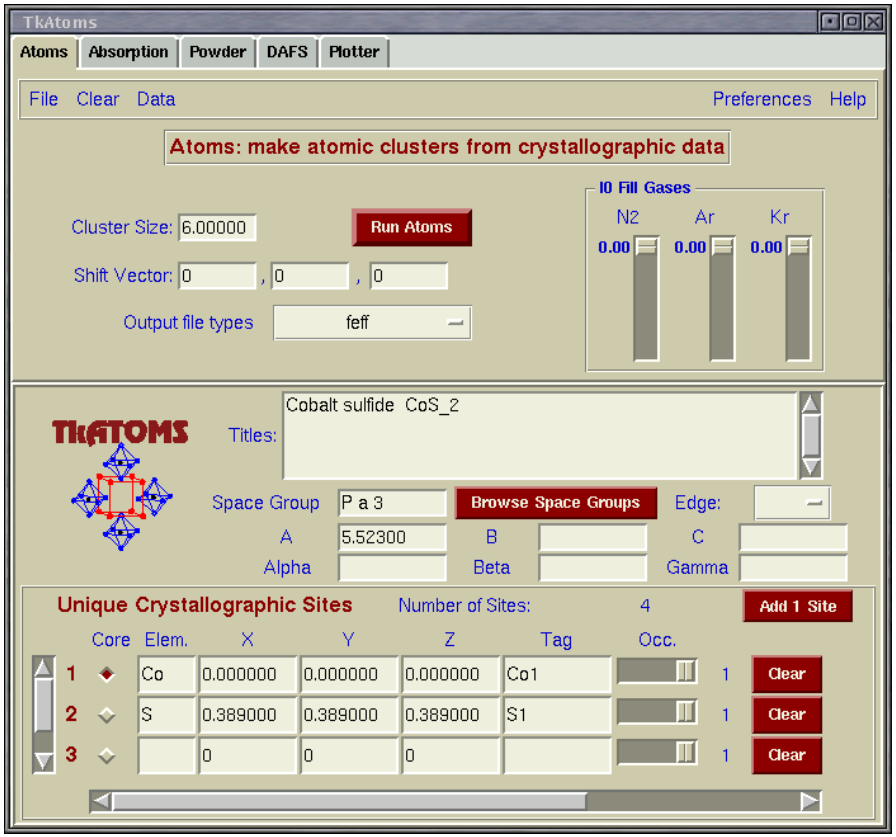
1. The input file **must** be called '`feff.inp`'.
2. All keywords **must** be uppercase. The asterisk $*$ marks text to be ignored by FEFF.
3. A full-featured graphical interface to FEFF does not yet (to my knowledge) exist. See *a later page*
4. For crystals, it is a good idea to give a long atoms list and limit the calculation using RMAX.
5. 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.
6. 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.
7. Making the list of atomic coordinates is the hard part of creating '`feff.inp`' files. Fortunately, there are some shortcuts....

Using Atoms to prepare the FEFF input file

If you are looking at a crystalline material (or something that resembles a crystal), the program TKATOMS is helpful.

It translates crystallographic data into atoms lists of arbitrary size.

Here is a picture of TKATOMS ready to generate the 'feff.inp' from a few pages back.



These data are typically taken from the crystallography literature.
Matt maintains a growing archive of ATOMS input files at
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. I found this on the web.

```
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
```

A little cutting and pasting, and voilá! A ‘`feff.inp`’ file is born.

```
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
```

Running FEFF

FEFF does not have a GUI and it's a bit ... stiff ... in its user interaction. Running FEFF is a bit clunkier than most 21st century programs.

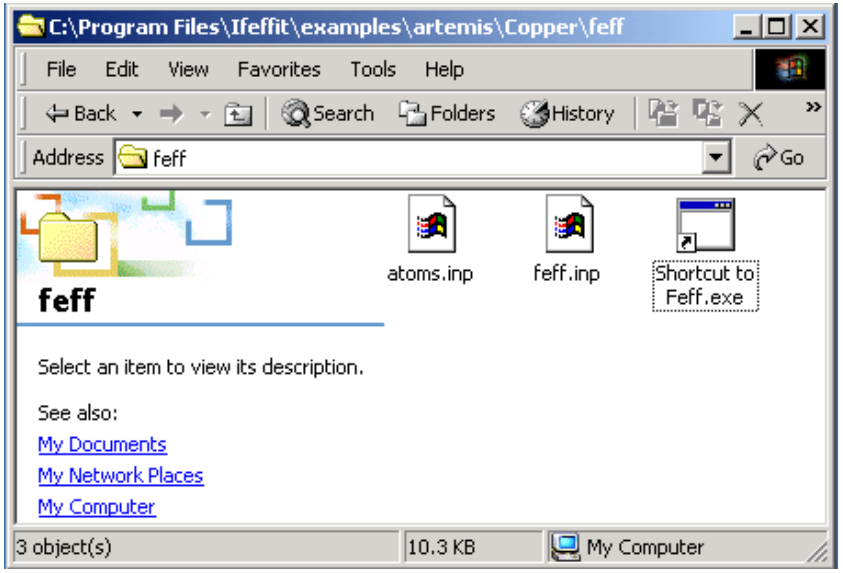
You can run FEFF from a command line in the directory containing the 'feff.inp' file.

```
examples/Cu/feff> ls
atoms.inp   feff.inp      feff0002.dat  feff0004.dat  files.dat   paths.dat
chi.dat     feff0001.dat  feff0003.dat  feff0005.dat  misc.dat
examples/Cu/feff> feff
```

On Windows you can use the

or you can make a shortcut from the FEFF executable to the folder containing the 'feff.inp' file.

Note: the "Start in" field of the shortcut's properties must be blank for this to work. (On Win2K: Right click ➜ Properties ➜ "Shortcut" tab ➜ "Start in" field.)



FEFF's output files

FEFF writes several output files:

'misc.dat'	General information about the potentials
'paths.dat'	Textual descriptions of all path geometries considered in the calculation
'files.dat'	A list of all path files written by FEFF
'phase.bin'	Binary file containing the data needed to compute the path files
'feffNNNN.dat'	The files containing the path data. The 1st path is in 'feff0001.dat', the 2nd in 'feff0002.dat' and so on.

FEFF8 writes several additional files containing partial electronic densities of state as well as other binary data and a file called 'feff.bin' containing all 'feffNNNN.dat' files.

The path files and the EXAFS equation

The '`feffNNNN.dat`' files contain the information needed to evaluate the EXAFS equation.

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

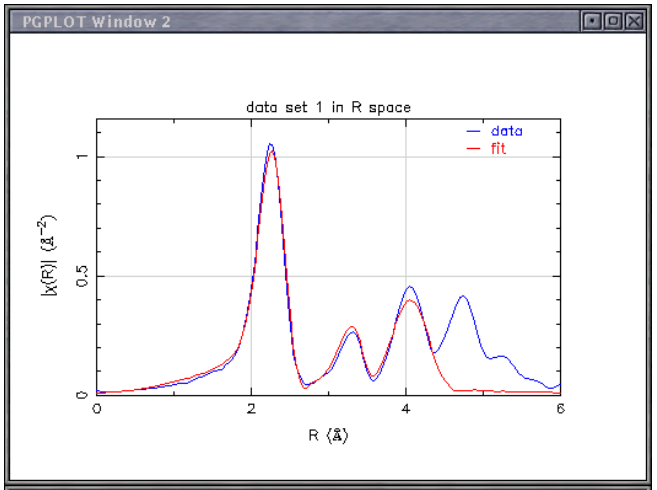
$$R_\Gamma = R_0 + \Delta R_\Gamma$$
$$k = \sqrt{2m(E - E_0)/\hbar^2}$$

From FEFF		Parameters	
$F_\Gamma(k)$	Scattering amplitude	N_Γ	Coordination (degeneracy)
$\Phi_\Gamma(k)$	Net phase shift	S_0^2	Amplitude reduction
$\lambda(k)$	Mean free path	ΔR_Γ	Change in path length
		σ_Γ	Mean square displacement
		E_0	Energy shift

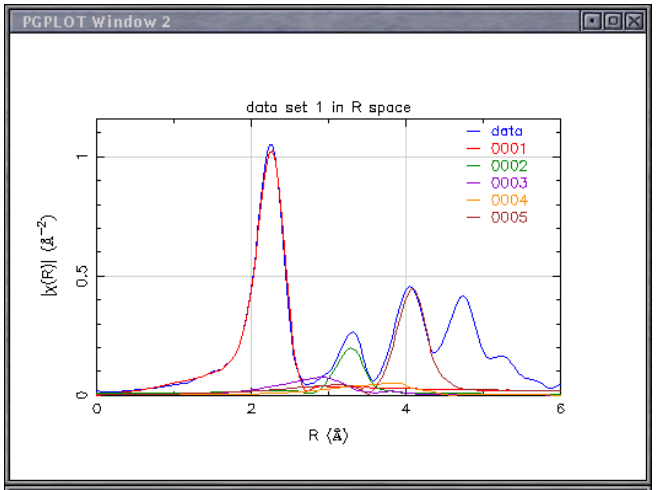
$$\chi(k) = \sum_\Gamma \chi(k,\Gamma)$$

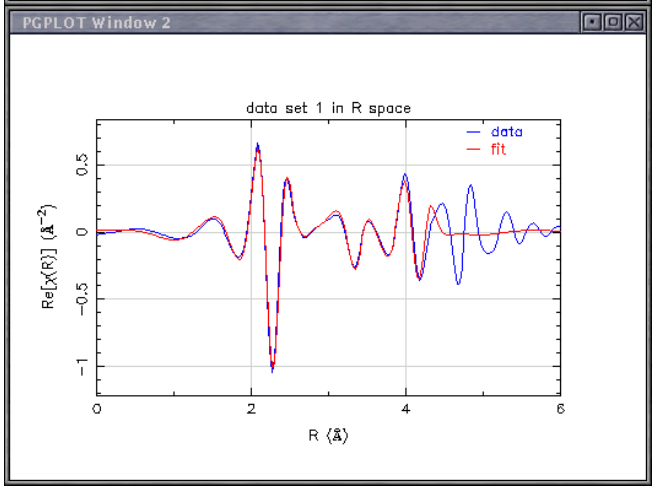
Fitting data as a sum of paths

Finally, the paths are summed to make a simulation of or a fit to the data.

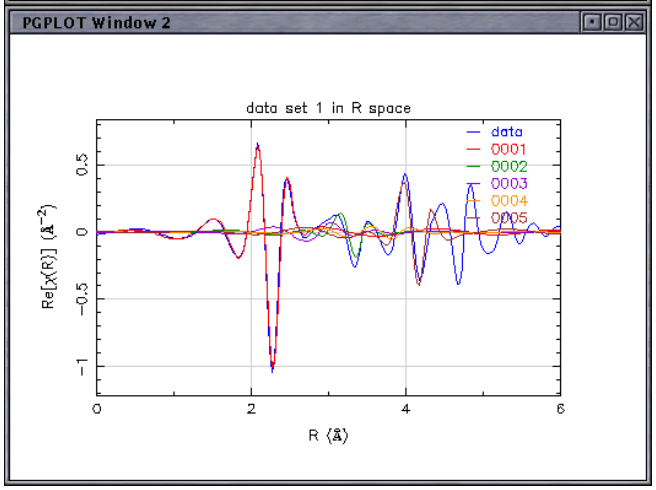


$|\tilde{\chi}(R)|$





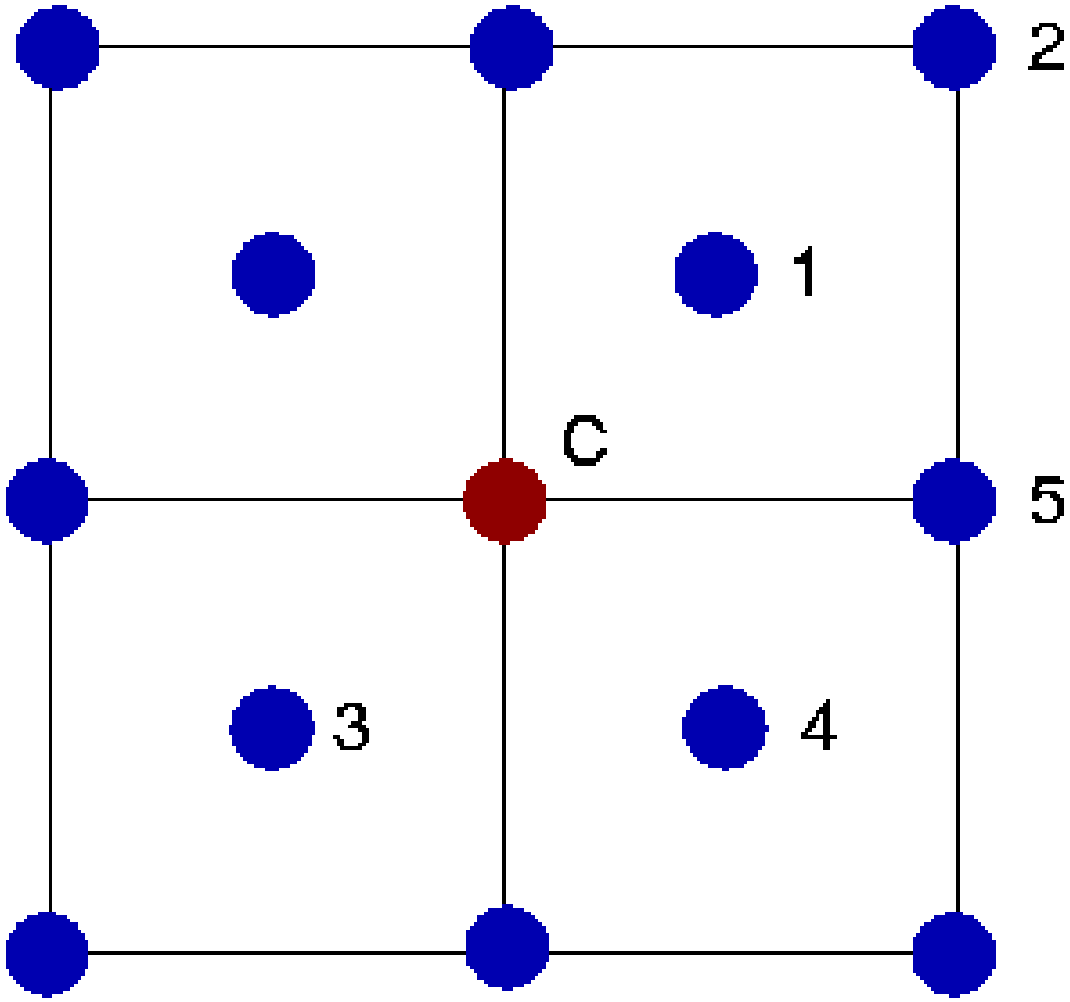
$\mathrm{Re}[\tilde{\chi}(R)]$



Paths at the fourth shell distance

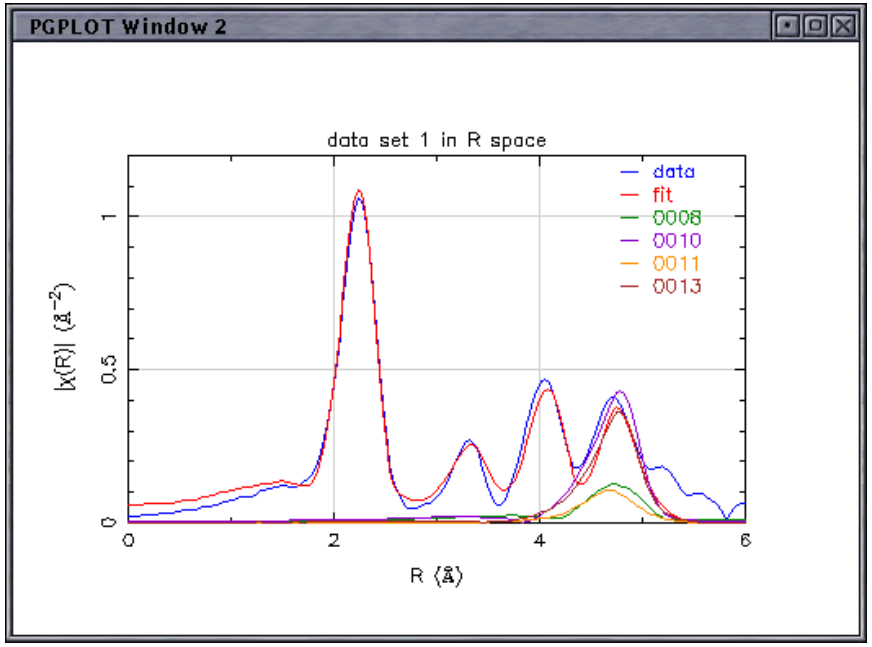
There are a variety of paths which contribute at the 4th shell distance. All 8 lie in a {100} plane.

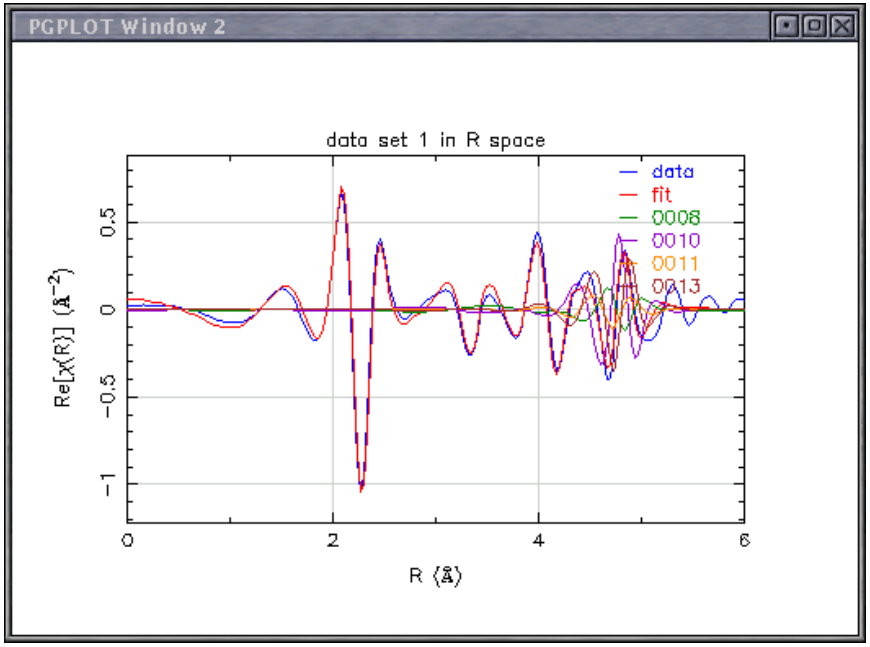
SS:	C→2→C	#8
DS:	C→1→3→C	#9
DS:	C→1→2→C	#10
TS:	C→1→C→3→C	#11
TS:	C→1→C→1→C	#12
TS:	C→1→2→1→C	#14
TS:	C→1→5→1→C	#15
TS:	C→1→C→4→C	



Fitting to the fourth shell distance

Extending the fit shown on earlier slides to the distance of the 4th shell, we see the effect of the four most important paths.



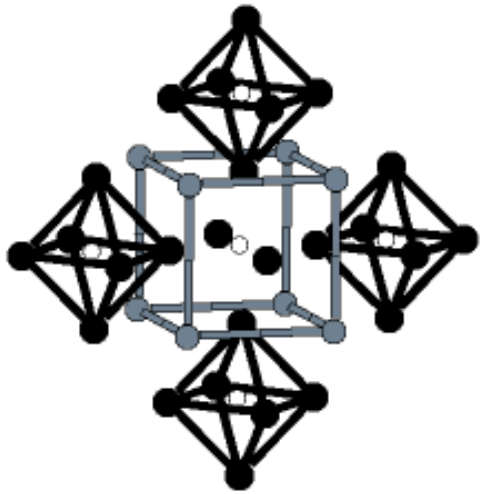


Paths of similar half path lengths thus have a subtle phase relationship

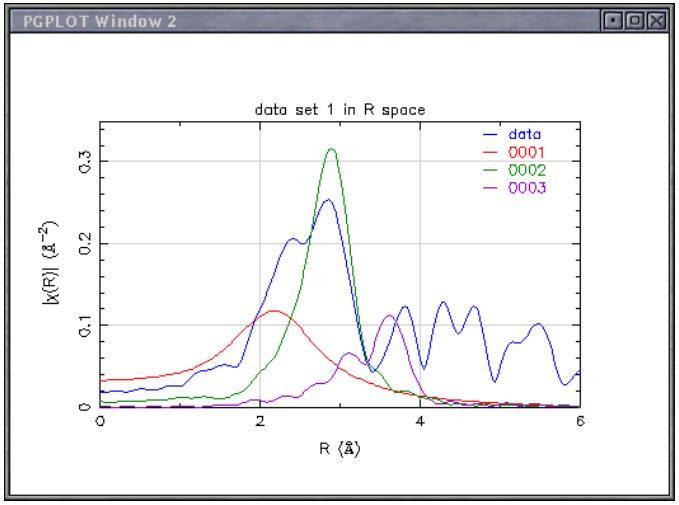
The need for theoretical standards: overlapping shells

The EXAFS literature is chock-full of data analysis performed using empirical fitting standards. There are various approaches, but all of them involve comparing an unknown data set to a well-known standard which is considered to be "sufficiently similar". There are times where such analysis may be appropriate, but there are many situations wherein analysis by empirical standards fails.

Overlapping Shells: $EuTiO_3$ is a simple perovskite. The first two shells overlap for the Eu L_{III} edge data.. This precludes analysis techniques requiring a reverse transform. Does an empirical standard for Eu–Ti exist? This problem is simple using FEFF.



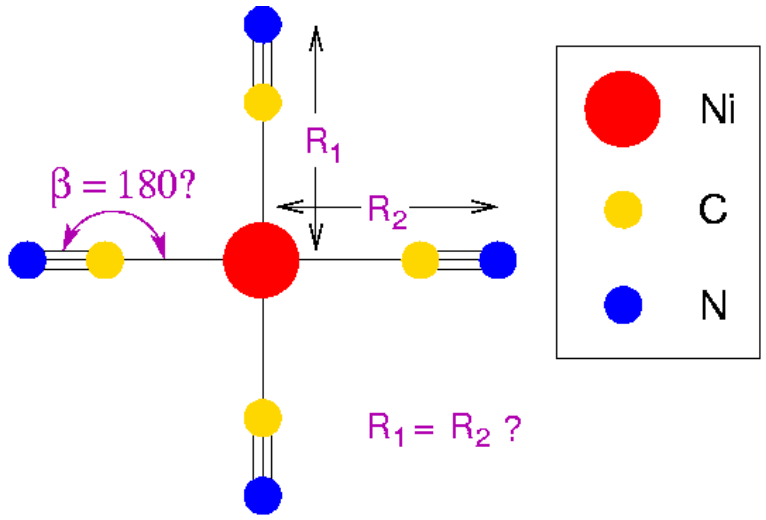
- ● 1st shell O 12
- ○ 3rd shell Ti 8
- ● 2nd shell Eu 6

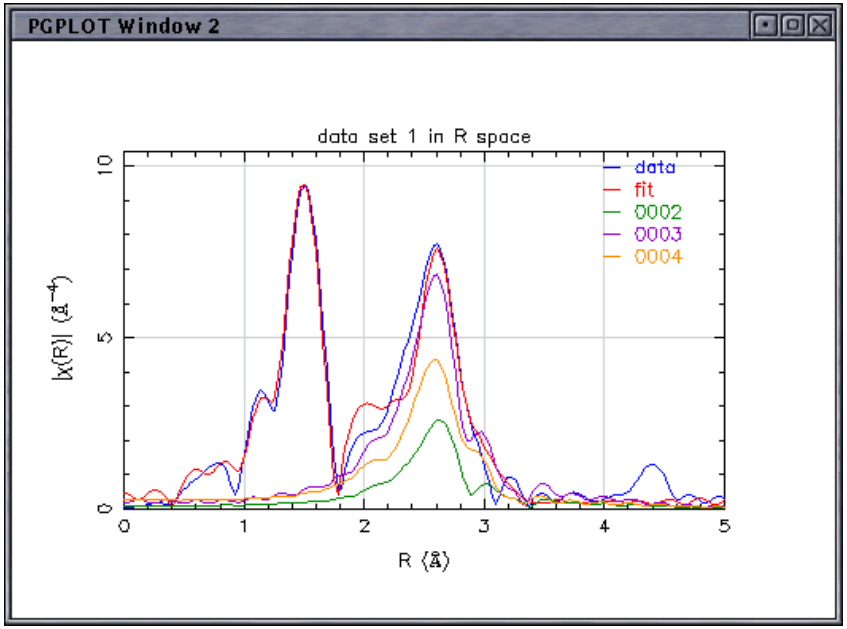


Three-body correlations

Three-body Correlations: Any analysis problem for which multiple scattering may be important is inaccessible by empirical standards yet tractable with FEFF. Already in Copper we saw that the effect of various MS paths out to the 4th shell distance.

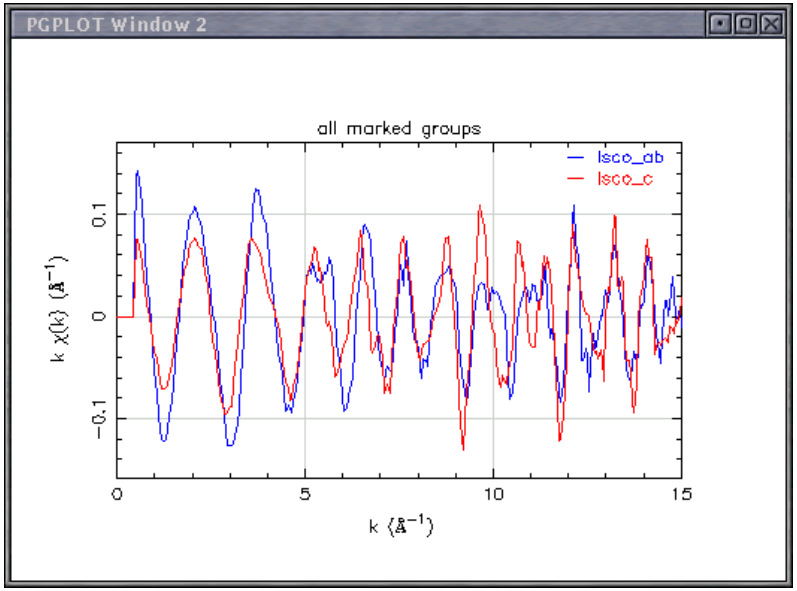
Here is the nickel cyanate, $Ni[(CN)_4]^{-2}$, compound. It is square planar with huge multiple scattering in the second peak which must be considered to answer any questions about arm lengths and angles.

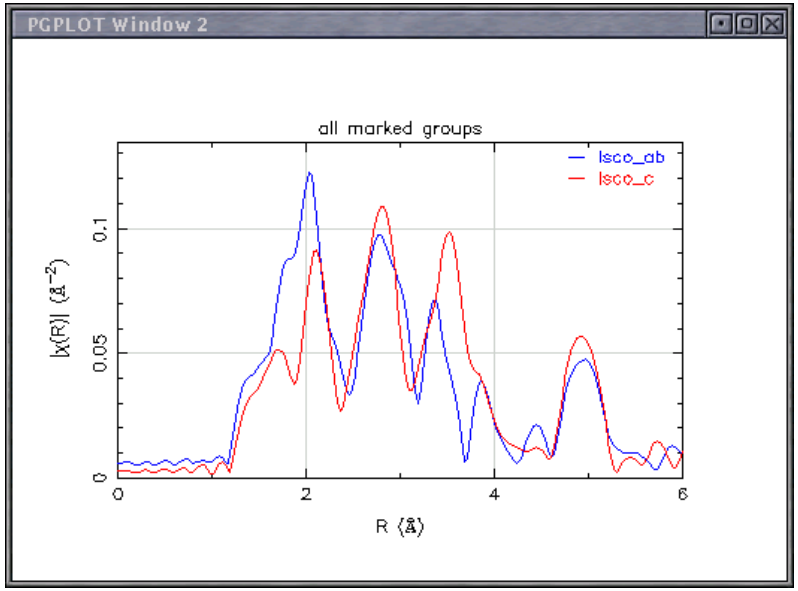




The effect of polarization

Polarized light and oriented samples: Synchrotron radiation is linearly polarized in the plane of orbit of the electron current. This can be exploited in an experiment on an oriented sample. The $La_{1-x}Sr_xCuO_4$ sample used in these data was highly textured in the $\hat{c}$ direction and shows a strong dependence on its orientation relative to the beam.





FEFF is capable of computing the effect of polarization directly. The polarized theory is easily used in analysis with polarized data.

Other examples

Uranium and transuranium compounds: U and Pu compounds in solid state or solution have highly complex f bonding for which adequate standards may not exist.

Rare earth compounds: The materials also have complex bonding. Additionally, any standards that may exist may be prohibitively expensive.

Organometallic compounds: These may be poorly described by commonly used empirical standards.

Absolute measurements of parameters: Parameters (σ^2, ΔR) are measured *relative* the values for the standard, which may not be well known. Parameters values determined using theoretical standards are *absolute*. (*Correct* is another issue and requires a discussion of statistics!)

XAFS theory links on the web

URLs for topics covered in this lecture

The FEFF *homepage*

http://feff.phys.washington.edu

The FEFF *Mailing Lists*

http://feff.phys.washington.edu/feff/Notes_comments/nc.html

The ATOMS *homepage*

http://feff.phys.washington.edu/~ravel/software/exafs/

General links and links to other theory codes

ESRF's XAFS Software links

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

GNXAS http://gnxas.unicam.it/

EXCURV/Cerius2

http://www.accelrys.com/cerius2/exafs.html

FEFF literature references

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  The fast, separable representation of the free-electron propagator
- Rehr, et al., J. Am. Chem. Soc. **113**:14 pp. 5135–5140 (1991)
  The FEFF4 reference – very useful background info!
- Zabinsky, et al., Phys. Rev. **B52**:2 pp. 2995–3009 (1995)
  The FEFF6 reference
- Ankudinov, et al., Phys. Rev. **B58**:12 pp. 7565–7576 (1998)
  The FEFF8 reference
- Rehr and Albers, Rev. Mod. Phys. **72**:3 pp. 621-654 (2000)
  A review article
- Ankudinov et al., Phys. Rev. **B65**:10 pp. 104107-104111 (2002)
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- Ravel, J. Synchrotron Radiat. **8**, 314-316 (2001)
  The ATOMS reference

This document was composed as a lecture for a three-day workshop on EXAFS Data Collection and Analysis at the National Synchrotron Light Source, September 23 – 25, 2002.

This document was composed using a variety of free software tools, including PDFLaTeX, the XEmacs text editor and the excellent editing mode AUCTeX, XFIG, and RASMOL. All of the screenshots were made using the GNOME Screen-Shooter Applet. The Adobe Acrobat Reader (which is free of cost, but is not really free software) was used to view the document as I was writing it.

All of the screenshots (except those on Page 3.1) are of the data analysis programs $\mathcal{TK}$ATOMS, ATHENA, or ARTEMIS. All 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. $\mathcal{TK}$ATOMS, ATHENA, and ARTEMIS all use IFEFFIT and were written by me. They were the programs used during the course at the NSLS.

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

Notes