A Practical Introduction to Multiple Scattering Theory

Bruce Ravel
Synchrotron Methods Group, Ceramics Division
Materials Science and Engineering Laboratory
National Institute of Standards and Technology
&
Local Contact, Beamline X23A2
National Synchrotron Light Source

2007 APS EXAFS Summer School
July 23-27, 2007
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Acknowledgements

Matt Newville, author of **IFEFFIT** and author of a presentation which covers similar material to this talk.

John Rehr and his group, authors of **FEFF**.

Ed Stern, for teaching us all so well and for getting all this XAS stuff started in the first place.

- The many users of my software: without years of feedback and encouragement, my codes would suck way more than they do
- The folks who make the great software I use to write my codes: **Perl**, **wxPerl**, **Emacs**, **The Emacs Code Browser**, **Git**, **GitHub**
- The folks who make the great software used to write this talk: **\LaTeX**, **Beamer**, **Avogadro**, **Inkscape**, **The Gimp**, **Gnuplot**
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.

- How RSMS is used to make XANES calculations.
- How RSMS is used in fitting EXAFS data.
We measure the **XAS data** and find the background function

\[ \mu(E) = \mu_0(E) \cdot (1 + \chi(E)) \]
XAS Data

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\[ \mu(E) = \mu_0(E) \cdot (1 + \chi(E)) \]

We subtract the background, \( \mu_0(E) \), to isolate the “fine structure” \( \chi(k) \).

(Remember, EXAFS \( \equiv \) Extended X-ray Absorption Fine Structure.)
XAS Data

We measure the XAS data and find the background function

$$\mu(E) = \mu_0(E) \cdot (1 + \chi(E))$$

We subtract the background, $\mu_0(E)$, to isolate the “fine structure” $\chi(k)$.
(Remember, EXAFS $\equiv$ Extended X-ray Absorption Fine Structure.)

We Fourier transform $\chi(k)$ and use multiple scattering theory to understand the local structure.
A simple picture of X-ray absorption

An incident x-ray of energy $E$ is absorbed, destroying a core electron of binding 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!**

When the incident x-ray energy is larger than the binding energy, 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 $\lambda$ 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 \(|f\rangle\):

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

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:

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

---

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 quantum mechanics
5. Hard work, lots of computation
6. \(\mathcal{G}\) 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.

\[ \mathcal{G} \text{ the function that describes all possible ways for a photoelectron to interact with the surrounding atoms} \]

\[ \mathcal{G}^0 \text{ the function that describes how an electron propagates between two points in space} \]

\[ \mathcal{t} \text{ the function that describes how a photo-electron scatters from a neighboring atom} \]

**Expanding the Green’s function**

\[ \mathcal{G} = (1 - \mathcal{G}^0 \mathcal{t})^{-1} \mathcal{G}^0 \]

\[ = \mathcal{G}^0 + \mathcal{G}^0 \mathcal{t} \mathcal{G}^0 + \mathcal{G}^0 \mathcal{t} \mathcal{G}^0 \mathcal{t} \mathcal{G}^0 + \mathcal{G}^0 \mathcal{t} \mathcal{G}^0 \mathcal{t} \mathcal{G}^0 \mathcal{t} \mathcal{G}^0 + \ldots \]

\[(\text{XANES})\]

\[(\text{EXAFS})\]
Scattering Paths

Full multiple scattering (XANES): Solving \( G = (1 - G^0 t)^{-1} G^0 \) considers **ALL** paths within some cluster of atoms:

- **Single scattering path**
  - (2 legs)

- **Double scattering path**
  - (3 legs)

- **Triple scattering path**
  - (4 legs)

**EXAFS path expansion**

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: 1\textsuperscript{st} path, 1 shell

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.

‘feff0001.dat’
Iron metal: 2\textsuperscript{nd} path, 2 shells

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: 3\textsuperscript{rd} path, 1 shell

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.

'feff0003.dat'

XANES
Iron metal: 4\textsuperscript{th} path, 2 shells

- This path contributes little to $|\tilde{\chi}(R)|$. Degeneracy = 48

- The contribution from this path and all higher order paths scattering among these the first two shells is in the second shell XANES calculation.

\texttt{'feff0004.dat'}

XANES
**Iron metal: 5\textsuperscript{th} path, 3 shells**

1. This 3\textsuperscript{rd} 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.
Iron metal: 8\textsuperscript{th} path, 4 shells

1. The 4\textsuperscript{th} shell SS path contributes to the third peak in $|\tilde{\chi}(R)|$.
   \textbf{Degeneracy = 24}

2. Including this shell in the XANES calculation broadens the peak above the edge somewhat. It also introduces the second shoulder.

\textbf{XANES}

\texttt{feff0008.dat}
Iron metal: 10\textsuperscript{th} path + MS, 5 shells

There are several MS geometries with the same path length as the 5\textsuperscript{th} shell SS path. Some are bigger than the SS path!
Fermi’s Golden Rule revisited

The absorption is the dipole mediated transition from the initial state of the deep-core electron to its final state:

\[ \mu(E) \sim |\langle f | \mathcal{H} | i \rangle|^2 \]

The initial state \(|i\rangle\) This is the deep core, atomic state which is unaffected by the surroundings

The excitation \(\mathcal{H}\) The dipole operator, i.e. the incident photon

The final state \(|f\rangle\) This high-lying or continuum state is affected by the surroundings

Consider \(|f\rangle = |f_0 + \Delta f\rangle\)
- \(|f_0\rangle\) is the final state in the presence of the surrounding atoms but without any scattering of the photoelectron
- \(\Delta f\) is the perturbation to the final state caused by the scattering of the photoelectron from the surrounding atoms

The discussion on the following 8 pages is inspired by Matt Newville’s at http://xafs.org/Tutorials?action=AttachFile&do=view&target=Newville_Intro.pdf
The fine structure

With \( |f\rangle = |f_0 + \Delta f\rangle \)

\[
\mu(E) \sim \left| \langle f | \mathcal{H} | i \rangle \right|^2 \\
\sim \left| \langle f_0 | \mathcal{H} | i \rangle \right|^2 \left[ 1 + A(E) \left| \langle \Delta f | \mathcal{H} | i \rangle \right| + C.C. \right]
\]

Remember that

\[
\mu(E) = \mu_0(E) \cdot (1 + \chi(E))
\]

Therefore

\[
\chi(E) \sim \left( \left| \langle \Delta f | \mathcal{H} | i \rangle \right| + C.C. \right)
\]

Conclusion

The XAS fine structure, \( \chi(E) \), is caused by the scattering from the neighboring atoms.

\( A(E) \) contains a bunch of stuff having nothing to do with the scattering.

\[
A(E) = \langle i | \mathcal{H} | f_0 \rangle^* / \left| \langle f_0 | \mathcal{H} | i \rangle \right|^2
\]
Heuristic derivation of the EXAFS equation

The photoelectron:
- propagates as a spherical wave from absorber to scatterer
- scatters from the neighbor
- propagates as a spherical wave from scatterer to absorber

Energy and photoelectron wavenumber are related by

\[ k = \frac{\sqrt{2m_e(E - E_0)/\hbar^2}}{\hbar} \approx \frac{\sqrt{(E - E_0)}}{3.81} \]

So, in terms of \( k \)

\[ \chi(k) \sim \frac{e^{ikr}}{kr} \cdot 2kF(k)e^{\phi(k)} \cdot \frac{e^{ikr}}{kr} + C.C. \]
The EXAFS equation in its simplest form

We can now simplify the equation to

\[ \chi(k) \sim \frac{F(k)}{2kR^2} \sin (2kR + \phi(k)) \]

This describes the signal from a single atom at a distance \( R \).

If we consider the contribution from \( N \) atoms at distance \( R \) (i.e. a “shell” of atoms):

\[ \chi(k) \sim \frac{NF(k)}{2kR^2} \sin (2kR + \phi(k)) \]

On the following pages, we consider

1. the shapes of \( F(k) \) and \( \phi(k) \)
2. the amplitude reduction term \( S_0^2 \)
3. the mean free path term \( \lambda \)
4. disorder via the mean square displacement term \( \sigma^2 \)
The complex photoelectron scattering factor

The scattering function, \( F(k) \) and \( \phi(k) \) give EXAFS its sensitivity to atomic species.

\[
\chi(k) \sim \frac{NF(k)}{2kR^2} \sin (2kR + \phi(k))
\]

Examining the magnitude explains why the signal from light elements does not extend much beyond 10 Å\(^{-1}\).
The amplitude reduction factor

When the core electron is ejected from its deep-core state, the remaining electrons relax:

\[ S_0^2 = |\langle \Phi_f^{N-1} | \Phi_i^{N-1} \rangle|^2 \]

where \( |\Phi^{N-1}\rangle \) is the state of all remaining electrons before (i) or after (f) the excitation.

\[ \chi(k) \sim \frac{NS_0^2 F(k)}{2kR^2} \sin (2kR + \phi(k)) \]

In practice, \( 0.7 \lesssim S_0^2 < 1.0 \), but note that \( N \) and \( S_0^2 \) are completely correlated!

DOI: 10.1103/PhysRevB.52.6332
The mean free path

The photoelectron may scatter \textit{inelastically} and fail to “return” to the absorber (loose coherence with the core-hole).

We consider this by replacing the photoelectron spherical wave with a damped spherical wave:

$$e^{ikr} \frac{e^{-r/\lambda(k)}}{kr}$$

Here is FEFF’s calculation of the mean free path in copper metal.

$$\chi(k) \sim \frac{NS_0^2F(k)}{2kR^2} \sin(2kR + \phi(k)) e^{-2R/\lambda(k)}$$

Note

$$\frac{e^{-2R/\lambda(k)}}{R^2}$$ is what makes EXAFS a local structure probe.
Even in a highly ordered crystal – like an FCC metal – the atoms are never actually on their lattice positions. Thermal motion (i.e. phonons) distribute atoms around their nominal positions such that

$$\sigma_{i,j}^2 = \langle r_{i,j} - \bar{r}_{i,j} \rangle^2 > 0$$

This behaves some like the crystallographic Debye-Waller factor:

The mean square displacement (disorder)

One can also consider higher moments of the distribution, $$\sigma^n = \langle r_{i,j} - \bar{r}_{i,j} \rangle^n$$. See

The magic of $F_{\text{EFF}}$ is that it expresses the effect of multiple scattering events entirely in $F(k)$ and $\phi(k)$:

$$
\chi(k) = \frac{NS_0^2 F_{\text{eff}}(k)}{2kR^2} \sin (2kR + \phi_{\text{eff}}(k)) e^{-2k^2\sigma^2} e^{-2r/\lambda(k)}
$$

That’s the same equation!

DOI: 10.1103/PhysRevB.52.2995
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)

CONTROL 1 1 1 1
PRINT 1 0 0 0
RMAX 6.0

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...
* etc...
END
```
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 stoil.
  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:

```plaintext
title Cobalt sulfide
space P a 3
rmax=6.0 a=5.523
core=Co
atoms
  ! At.type x y z tag
  Co 0.0000 0.0000 0.0000 Co
  S 0.3890 0.3890 0.3890 S
```

These data are typically taken from the crystallography literature, the *Inorganic Crystal Structure Database*, or from:

http://cars9.uchicago.edu/~newville/adb/search.html
Feff input files 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

Note that the absorber need not be at (0,0,0) and the list need not be in any particular order.
Multiple scattering and EXAFS: FeS$_2$
Multiple scattering and EXAFS: SS

The first sulfur SS path is from the octahedron surrounding the Fe atom. It provides most of the spectral weight under the first peak.

The next two S and one Fe SS paths overlap between 2.5 and 3.5 Å.
The relationship between the EXAFS spectrum and atomic structure can be quite complicated due to multiple scattering. S–S and S–Fe triangles contribute significantly between 2.5 and 3.5 Å. Collinear paths through the absorber involving 1\textsuperscript{st} shell S atoms contribute significantly around 3.9 Å.
Resources

- **Websites**
  - [http://xafs.org](http://xafs.org) offers tutorials, links to resources, information about upcoming workshops, and much more

- **Journal articles**

- **Other Software**
  - XANES calculations using Multiplets: [http://xafs.org/Software/TtMultiplet](http://xafs.org/Software/TtMultiplet)
  - XANES calculations by finite difference method: [http://xafs.org/Software/FDMNES](http://xafs.org/Software/FDMNES)
  - XANES fitting: [FitIt](http://xafs.org/Software/FitIt) and [MXAN](http://xafs.org/Software/MXAN) (PRB 65 (2002) 174205).