Path aggregation techniques for EXAFS visualization and analysis

Bruce Ravel
National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
E-mail: bravel@bnl.gov

Abstract. The path expansion model used by FEFF considers the EXAFS spectrum as the sum of contributions from scattering geometries of two or more atoms in a cluster surrounding the absorbing atom. This model and its representation as a collection of files is the basis for a number of popular EXAFS analysis programs, including one co-developed by me. Here I present several tools which build upon the scattering path model to articulate analysis and visualization capabilities not normally included in FEFF-based analysis software. These include the generation of arbitrary single-scattering paths not represented in FEFFs input structure, consideration of non-Gaussian and non-cumulant distribution functions, easy visualization of arbitrary path summations, and others. Each of these tools is tightly integrated into the ARTEMIS EXAFS analysis program, making these analysis and visualization tools easily and widely available.

The widely used FEFF program provides a real-space, multiple-scattering approach to the calculation [1] of the X-ray absorption spectrum. As applied to the quantitative analysis of the extended XAFS region, FEFF provides a solution based on path enumeration. The input to the calculation includes a list of Cartesian coordinates of atoms in a cluster with one atom selected as the absorber. First, atomic potentials are computed using a muffin tin approximation and the list of Cartesian coordinates. Later versions of FEFF offer improvements to the potential and energy loss models, however the details of the potential calculation are not important to the context of this paper. FEFF then enumerates all scattering geometries [2] within the cluster up to some order of scattering. This enumeration is exhaustive (no scattering geometries are missed) and recognizes degeneracy (geometries contributing identically to the spectrum are flagged). FEFF also uses a simple algorithm to exclude geometries that contribute scant spectral weight. Finally, FEFF computes the spectral contribution from each scattering geometry.

This path expansion is the basis of the EXAFS data analysis program IFEFFIT [3], as well as several other popular analysis packages. This path-based representation of the EXAFS analysis problem has proven to be powerful and flexible. IFEFFIT and other analysis program using this representation have been applied successfully to complex analysis problems from all of the many scientific disciplines which use absorption spectroscopy.

The reason that the path expansion works so well is that it maps naturally onto the problem of EXAFS data analysis. In the simple case of a single-shell analysis, the first-shell single-scattering path is readily understood as the theoretical representation of the single shell data. Core complex analyses – multiple coordination shells, shells with more than one scattering species, multiple scattering contributions – the value of the path expansion is even more evident. In general, in a fit, there is value to parametrizing things such as \( \Delta R \) and \( \sigma^2 \) separately for different shells.
and different scattering species. A path-by-path parametrization of these terms in the EXAFS equation is inherent to IFEFFIT.

As valuable as the path expansion has proven to be in the nearly two decades that FEFF has been available in its current form (since the release of FEFF6 in 1995), it has its limitations, mostly related to its input structure. In normal use, FEFF’s output is strictly related to the input data. Contributions from scattering geometries not represented in the input cluster cannot be computed. While small changes to inter-atomic spacings can be accommodated by the parametrization of $\Delta R$, this approach is unreliable for large changes. This is because the effect of $\Delta R$ in IFEFFIT is only to change terms in the EXAFS equation which depend explicitly on $R$. The scattering amplitude and phase shift also have an $R$ dependence which is not considered by IFEFFIT, resulting in large inaccuracies when a $\Delta R$ parameter becomes large.

In this paper, I present several features newly available in the Artemis [4] EXAFS data analysis program. Each of these uses FEFF in a creative way to enable a data visualization or analysis capability not readily available when used in its conventional manner.

1. Virtual path
A virtual path is a grouping of two or more normal paths for the sake of visualization. Each path in the group is kept up to date with respect to its own parametrization of the EXAFS equation. The group is added together and the sum is Fourier transformed and plotted as a unit. While this serves no direct role in the evaluation of a fit, it is a powerful visualization tool.

Consider an EXAFS analysis on a mixed phase system, for instance a mixture of a metal oxide and a metal sulfide. FEFF calculations will be run on the structures of both phases. Paths will be selected from each calculation for use in the fitting model. One virtual path – called a VPath in Artemis – could be made using the paths from the oxide calculation. Another VPath could then be made using the paths from the sulfide calculation. Plotting VPaths along with the data, as in Fig. 1, makes it clear how each component of the sample contributes to the spectrum.

2. Quick first shell path
In the case of data requiring only a first shell analysis, the problem with FEFF is not that the input data limits the scope of the problem, but that input data must be provided at all for such a simple analysis problem. An common example of this situation is a measurement of a glassy material. With no long range order, the metal site in the glass has a well defined first shell, but little or no structure beyond that.

To expedite a simple first shell analysis, Artemis offers a quick first shell, or QFS, path. The user is prompted for the atomic species of the absorber and the scatterer, the edge symbol, and a nominal distance between the two atoms. From this, Artemis generates an input file for FEFF for a rock-salt structured crystal containing the two specified elements. This results in a sixfold coordinated structure about the absorber from which FEFF will compute muffin tin potentials for absorber and scatterer which are reasonable for the specified distance. After the calculation, only the first shell path is retained and the rest of the calculation is discarded. As a user option, Artemis can generate a set of fitting parameters to complete a simple, single-shell fitting model. This feature of Artemis was inspired by similar functionality in the SIXPACK [5] program.

3. Single scattering path
The limitation of the QFS path is that it is only applicable to single scattering paths in the first coordination shell. The user-supplied QFS distance parameter is the near neighbor distance. If that number is unphysically large, the muffin tin potentials for the absorber and scatterer will be inaccurate. Still, the concept of generating a single scattering path at an arbitrary distance is useful.
This fit to data collected on a solution of uranyl acetate demonstrates two virtual paths and a single scattering path. The inset shows the structure of the uranyl complex, which includes carbon atoms (gray) bound to the uranium (blue) by a bidentate bridge of equatorial oxygens (red). Two very short axial oxygens (red) extend out of the plane formed by the other atoms. The signal from the axial oxygens is shown by the first offset trace. This signal is a VPath composed of the single scattering from the axial oxygens and three significant multiple scattering paths. Note that the spectral weight from this VPath extends throughout the entire fitting range. The second offset trace is a normal path representing the equatorial oxygen atoms. The third offset trace is a VPath containing single scattering from the carbon and multiple scattering from carbon and the bridging oxygen. The final trace is an SSPath, discussed below.

In ARTEMIS, an SSPath uses the potentials from a successful FEFF calculation to compute a single scattering path for a scatterer at an arbitrary distance not represented in the input cluster. The user chooses the scatterer species from among those present in the FEFF calculation and the distance between the two atoms. ARTEMIS then instructs the GENFMT part of FEFF to use the previously computed potentials with the specified single scattering path.

Consider a mineral sample which contains an unknown secondary phase with the same elemental composition as the primary phase. An SSPath can be used to investigate the possibility of the second phase contributing a single scattering path at a distance not represented in the structure of the primary phase without requiring that further FEFF calculations be made on candidate structures.

Figure 1 shows a fit to uranyl acetate in solution. The structure used in the FEFF calculation was crystalline sodium uranyl triacetate. Paths for the surrounding oxygen and carbon atoms were included in the fit. An SSPath representing the hydration sphere was computed using the potential of the equatorial oxygen and a position of 3 Å. This provides a plausible explanation for part of the spectral weight around 3 Å in the data.

4. Histogram path
Another shortcoming of FEFF is that its input structure represents a static configuration of atoms. In a case where variation about that static configuration is well represented by Gaussian disorder – perhaps with small skewness and kurtosis represented by third and fourth cumulants
Figure 2. (Left) The distribution of first shell neighbors in a Pt nanoparticle as determined from a molecular dynamics calculation. (Right) $\chi(k)$ for the first shell in bulk Pt compared with the histogram. Note the differences in both amplitude and phase. Both are shown with $N = 1$, $S_0^2 = 1$ and $\sigma^2 = 0$.

– the conventional path expansion works very well. For more complex distributions, for example a multi-modal distribution, a cumulant expansion is a poor approximation.

For materials with substantial disorder, one approach to understanding the nature of that structure is to employ a molecular dynamics (MD) simulation. Typically an MD simulation is made on a cluster of some size and over some number of time steps. The distribution of atoms in a coordination shell can be found by extracting all absorber-scatterer pairs within some band of distances. This ensemble of pairs can be binned into a histogram. Shown on the left of Figure 2 is an example of the first shell histogram extracted [7] from an MD simulation on a small platinum nanoparticle. Contraction at the surface of the particle results in the peak at short distance.

Given a histogram representing a distance distribution, ARTEMIS computes an SSPath at the distance of each bin. Each such SSPath is weighted by the population of its bin. These SSPaths are added and normalized by the sum of the bin populations. The resulting object, then, is the contribution to the EXAFS from a single atom distributed over the histogram.

5. Empirical path
The final path-like object implemented in ARTEMIS is a small refinement of the concept of an empirical standard, which is useful for the rare situation when FEFF may not adequately compute a fitting standard. One such situation is the case of a near-neighbor atom with an intervening hydrogen atom. While the scattering from the hydrogen atom is typically quite weak and may contribute scant spectral weight to the EXAFS, its presence can alter the scattering potential of the non-hydrogen neighbor in ways that are poorly approximated by FEFF’s muffin tin model (particularly in FEFF6 or FEFF7).

The use of empirical standards [8] goes back to the early days of the EXAFS technique. The algorithm in ARTEMIS is much the same. Reference data are Fourier filtered to isolate the spectral contribution from the scatterer in question. In many implementations this Fourier filtered standards is fitted directly to the data, which are also filtered using identical transform parameters. The twist here is that the filtered reference data are exported in the format FEFF uses for the contribution from a scattering path. This export format saves the $\chi(k)$ function as a complex number, the imaginary part of which is extracted by IEFFFIT for use in a fit. Although FEFF exports this function on a rather sparse grid, because these amplitude and phase functions
are relatively slowly varying functions of $k$, empirical paths for scatterers at any distance can be reliably extracted from a reference material. The advantage of extracting the empirical standard to the format of a FEFF path is that it is incorporated into a fit with IFEFFIT and ARTEMIS like any other path.

6. Implementation
The recurring theme among all these path-like objects is that each is expressed in the form of a conventional FEFF path. In ARTEMIS, each data set included in a fitting model accumulates a list of paths as the theory used to describe that data. That list can contain any combination of conventional paths and the path-like objects described here. For each path or path-like object, the EXAFS equation must be parametrized and evaluated. Each type of path requires specification of the same set of parameters. These include an amplitude term (incorporating both degeneracy and $S_0^2$), an energy shift, a $\Delta R$, and a $\sigma^2$.

Each of these path-like objects is implemented in ARTEMIS and thus is available for any analysis problem. The histogram path requires a specific implementation based upon the source of the molecular dynamics output. To date, implementations for DL_POLY [9], LAMMPS [10], and VASP* [11] have been written and new sources for structural data can be included with limited effort.

The application of FEFF to EXAFS analysis has proven to be a great success over the past two decades. That FEFF is both robust and flexible is evident from its deployment as the theoretical back end to dozens of data analysis software packages. That said, there are still novel and creative ways that this solid framework can be used to solve interesting data analysis problems. This short paper documents some of these features of my own software package. The analysis tools discussed here are broadly useful and could easily be implemented by other FEFF-using analysis packages.

Acknowledgments
Without FEFF and IFEFFIT, my work would not be possible. John Rehr along with his many students and Matt Newville are responsible for those fine programs. The many users of my software have been a joy and an inspiration for me. A few deserve special mention for exceptional contributions over the years, including Shelly Kelly, Scott Calvin, Eric Breynaert, and Stephen Price.

References
[1] Rehr J J and Albers R C 2000 Rev. Mod. Phys. 72(3) 621–654
[2] Zabinsky S I, Rehr J J, Ankudinov A, Albers R C and Eller M J 1995 Phys. Rev. B 52(4) 2995–3009
[3] Newville M 2001 Journal of Synchrotron Radiation 8 322–324
[4] Ravel B and Newville M 2005 Journal of Synchrotron Radiation 12 537–541
[5] Webb S 2012 Sam’s Interface for XAS Package software website URL http://sixpack.sams-xrays.com/
[6] Lee P A and Pendry J B 1975 Phys. Rev. B 11(8) 2795–2811
[7] Price S W T, Zonias N, Skylaris C K, Hyde T I, Ravel B and Russell A E 2012 Phys. Rev. B 85(7) 075439
[8] Bunker G 1983 Nuclear Instruments and Methods in Physics Research 207 437 – 444 ISSN 0167-5087
[9] Smith W, Yong C and Rodger P 2002 Molecular Simulation 28 385–471
[10] Plimpton S 1995 Journal of Computational Physics 117 1 – 19 ISSN 0021-9991
[11] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 169

*Any mention of commercial products is for information only; it does not imply recommendation or endorsement by NIST.