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ATHENA, *ARTEMIS*, *HEPHAESTUS*: data analysis for X-ray absorption spectroscopy using *IFEFFIT*

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A software package for the analysis of X-ray absorption spectroscopy (XAS) data is presented. This package is based on the *IFEFFIT* library of numerical and XAS algorithms and is written in the Perl programming language using the *Perl/Tk* graphics toolkit. The programs described here are: (i) *ATHENA*, a program for XAS data processing, (ii) *ARTEMIS*, a program for EXAFS data analysis using theoretical standards from *FEFF* and (iii) *HEPHAESTUS*, a collection of beamline utilities based on tables of atomic absorption data. These programs enable high-quality data analysis that is accessible to novices while still powerful enough to meet the demands of an expert practitioner. The programs run on all major computer platforms and are freely available under the terms of a free software license.

Keywords: XAS; data analysis; *FEFF*; *IFEFFIT*.

1. Introduction

Users of X-ray absorption spectroscopy (XAS) beamlines and practitioners of XAS require software that meets a broad range of analytic, programmatic and social goals. To meet these goals we have developed a collection of programs providing a rich graphical interface to the extensive analytical and numerical capabilities of the popular *IFEFFIT* library (Newville, 2001). In this report we present the main features of the three programs: (i) *ATHENA*, a program for XAS data processing, (ii) *ARTEMIS*, a program for analysis of extended X-ray absorption fine structure (EXAFS) data using theoretical standards computed by the popular *FEFF* program (Zabinsky *et al.*, 1995; Ankudinov *et al.*, 1998) and (iii) *HEPHAESTUS*, a collection of beamline utilities based on tables of atomic absorption data. All three programs are written in the Perl programming language (Wall *et al.*, 1996), use the *Perl/Tk* graphical toolkit (Lidie & Walsh, 2002) for their user interface, and use the *PGPLOT* (Pearson, 1997) package for plotting data.

The development of this software project has been directed by a number of equally important motivations:

Versatile XAS and numerical algorithms. *ATHENA* and *ARTEMIS* use the programmers interface to *IFEFFIT*, as described by Newville (2001). Thus both programs have complete access to all the features of *IFEFFIT*, including all the capabilities of the programs *AUTOBK* (Newville *et al.*, 1993) and *FEFFIT* (Newville *et al.*, 1995). In this article, any analytic functionality ascribed to *ATHENA* or *ARTEMIS* is actually performed by *IFEFFIT via* its programming interface.

Graphical user interface. The *Perl/Tk* toolkit provides a full-featured forms-based environment for interacting with and processing data.

Simple for novices, powerful for experts. Those already familiar with analysis of XAS data will find *ATHENA* and *ARTEMIS* quite easy to begin using and will quickly familiarize themselves with the many features of those programs. Novices to absorption spectroscopy find that a usable graphical user interface combined with excellent analytic algorithms considerably lowers the barrier of entry into their new field of research. For the expert practitioner of the art of XAS data analysis, *ATHENA* and *ARTEMIS* provide sophisticated capabilities allowing the user to exploit deeply the information content of their measured data.

Useful at the beamline, useful at home. *ATHENA* and *HEPHAESTUS* compliment the data-acquisition software found at XAS beamlines. Since *ATHENA* can read most raw data formats, it provides flexible powerful data-processing capabilities right at the beamline. The utilities provided by *HEPHAESTUS* are useful while planning and executing XAS experiments.

Free of cost, free source code. *IFEFFIT*, *ATHENA*, *ARTEMIS* and *HEPHAESTUS* are available on the web. Because this software is free of cost, high-quality XAS analysis is available even to students and to scientists in developing countries. Because the code is licensed under very liberal terms, users are free to examine the code, understand its algorithms, modify the code to better suit their research needs, and share the codes with their colleagues.

Portability. *ATHENA*, *ARTEMIS* and *HEPHAESTUS* work on most common computer platforms including all versions of Microsoft Windows, Macintosh OSX, Linux, BSD, Solaris and other common unixes. This is possible because all of the tools upon which they rely, *IFEFFIT*, Perl, *Perl/Tk* and *PGPLOT*, themselves operate on all these platforms. Additionally *ATHENA* and *ARTEMIS* save data to project files which are easily transferable between users, even those working on different platforms. These project files capture the state of the program, all data and *FEFF* calculations, and all parameters associated with the data and *FEFF* calculations. Reimporting a project file thus restores the state of the data analysis project, even on a different computer.

At the time of this writing, *ATHENA*, *ARTEMIS* and *HEPHAESTUS* are employed by a community of several hundred users. A vigorous electronic mailing list is devoted to discussion of the use of these programs as well as to the science and practice of XAS.

2. Features of *ATHENA*

ATHENA is used for all the main steps in data processing including conversion of raw data to $\mu(E)$ spectra, background subtraction, Fourier transforming and plotting. As such it is useful for data visualization at the beamline as well as for processing of data in preparation for data analysis. The normal view of the *ATHENA* window is shown in Fig. 1.

Data conversion from its raw form is handled in a flexible manner, creating $\mu(E)$ spectra from transmission, fluorescence or electron yield experiments. The conversion utility allows for on-the-fly summation of data from a multi-element detector. Alternately, each column of multi-element data can be imported as individual data groups for later inspection and summation. *ATHENA* also supports powerful preprocessing of data as it is imported, including automated deglitching, truncation, alignment and constraint of analysis parameters.

Background subtraction is performed using the *AUTOBK* algorithm (Newville *et al.*, 1993) which determines an empirical background spline based on a distinction between data and background in terms of Fourier components. Edge-step normalization of the data is determined by a linear pre-edge subtraction and regression of a quadratic polynomial beyond the edge. The difference between these two polynomials extrapolated to the edge energy E_0 is used as the normalization constant in the definition of $\chi(E) = [\mu(E) - \mu_0(E)]/\mu_0(E_0)$. Normalized data are typically presented after subtracting the curvature of the regressed quadratic and the difference in slope between the post- and pre-edge polynomials after the edge. $\chi(k)$ are obtained by conversion of the abscissa of $\chi(E)$ by the formula $k = (2m_e/\hbar^2)(E - E_0)^{1/2}$. E_0 is determined automatically as the data is imported by finding the first large peak in the first derivative of the $\mu_0(E)$ spectrum, but can also be set interactively to the tabulated atomic value, to the position of half the edge step height or to any arbitrary value selected by the user.

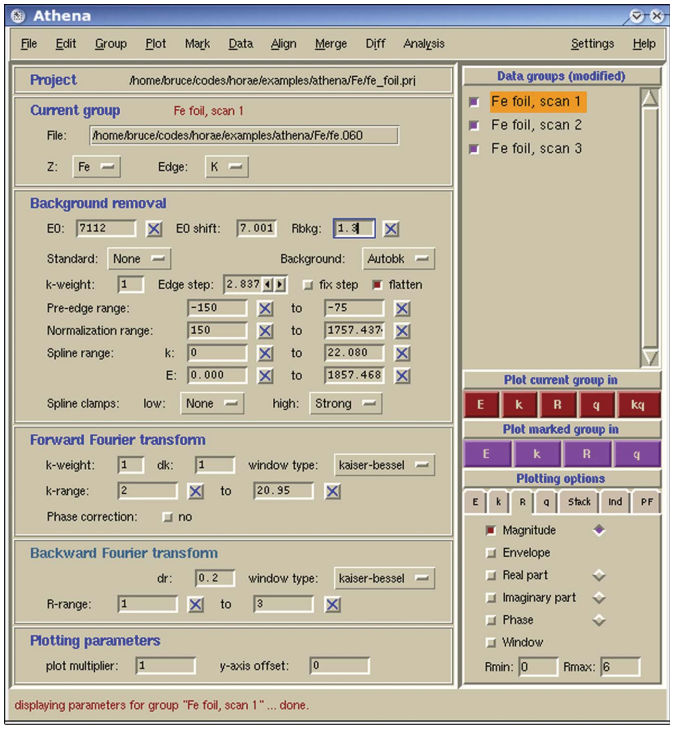

Figure 1
The main window of the *ATHENA* program. The data sets imported into *ATHENA* are listed on the right. The analysis parameters for the selected data set are displayed in the main panel on the left.

ATHENA provides utilities for most common chores involved in the preparation of EXAFS data for analysis. There are tools for energy calibration of spectra, alignment of data, use of reference spectra, deglitching (*i.e.* the removal of spurious points from spectra) and merging of data by calculating the average and standard deviation at each point in a set of spectra. There is a utility for performing log-ratio/phase-difference analysis (Bunker, 1983) of back-transformed spectra. *ATHENA* also provides a tool for the energy calibration of dispersive XAS spectra (Hagelstein *et al.*, 1997).

ATHENA provides tools for the analysis of near-edge spectra. There are utilities for calculation of difference spectra, for fitting line shapes (arctangent, Gaussian, Lorentzian) to spectra, and for fitting linear combinations of standard spectra to unknown spectra. *ATHENA* can also import and display the results of *FEFF8* calculations (Ankudinov *et al.*, 1998) for comparison with measured data.

The most powerful feature of *ATHENA* is that processing and displaying many data sets simultaneously is as simple as for a single data set. In Fig. 1, the upper row of buttons labeled with the letters E, k, R, and q are for plotting single data sets in energy, k-space, R-space or back-transformed k-space, respectively. The lower row of buttons will plot multiple data sets. It is simple to mark any subset of imported data sets for plotting in this manner. *ATHENA* keeps track of all changes made to the parameters of any data set and will automatically perform background removal and Fourier transforms as needed. The parameters controlling background removal and Fourier transforms can be adjusted for each data set individually or constrained in a flexible manner between data sets.

ATHENA comes with extensive documentation accessible within the program and a number of examples demonstrating its many features. Features which are planned for implementation in *ATHENA* include principle component analysis, self-absorption corrections for fluorescence data, and dead-time corrections for data measured with solid-state detectors.

3. Features of *ARTEMIS*

ARTEMIS works within the framework of *FEFF*'s multiple-scattering path expansion (Zabinsky *et al.*, 1995; Rehr & Albers, 1990). This means that the data are described as a summation of one or more scattering paths as computed by *FEFF*. For each path, the XAFS equation must be evaluated. This means that values of the parametric terms in the EXAFS equation, N, S_0^2, E_0, ΔR and σ^2, must be specified for each path included in the fit. The path expansion and how it is parameterized and used in a fit is described elsewhere (Newville *et al.*, 1995; Ravel, 2000). As discussed in those references, EXAFS analysis can be quite subtle and complicated. By providing a graphical forms-based mechanism for handling the many bookkeeping chores required by *FEFF* and *IFEFFIT*, *ARTEMIS* makes basic analysis chores simple and sophisticated analysis problems tractable.

Shown in Fig. 2 is the *ARTEMIS* window in its data view. The data-processing parameters, including the range of the Fourier transform from k-space and the fitting range in R-space, are set in the main window. The far right panel is used to control how plots are displayed. The middle panel is a list of all data sets, *FEFF* calculations and paths used in the fit. This list is integral to the generation of plots and is used to determine which view is displayed in the main window. Other views (not shown) allow the user to set fitting parameters, to examine log files from previous fits, to manage *FEFF* calculations or to manage

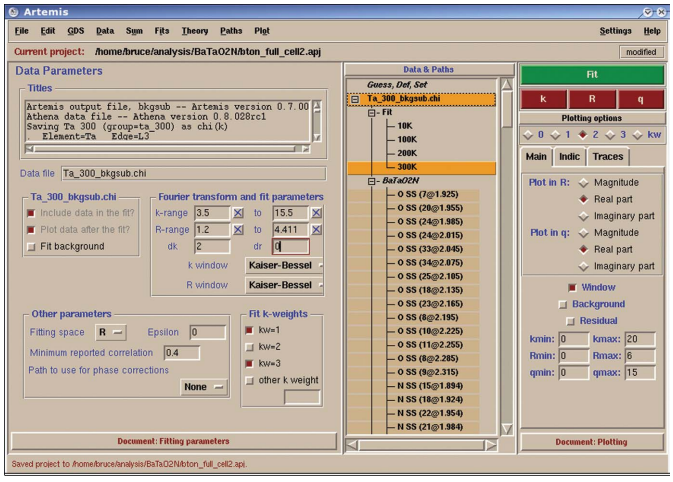

Figure 2
The main window of the *ARTEMIS* program. Shown in the main panel is the view for setting the Fourier transform and fit range parameters. The middle panel lists all data sets and *FEFF* paths used in the fit and provides a history of all fits performed within the project. The panel on the right contains plotting controls.

individual *FEFF* paths and the mathematical expressions used to evaluate the terms in the EXAFS equation.

ARTEMIS includes access to the functionality of the *ATOMS* (Ravel, 2001) program, which converts crystallographic data into a format suitable for *FEFF*. This interface can read crystallographic data either in the form of an *ATOMS* input file or a crystallographic information file (CIF) (Hall *et al.*, 1991). These data are then converted into a *FEFF* input file or can be converted into a form suitable for export to a molecule viewer. For materials that are not crystalline or do not have a crystalline analogue, *FEFF* input files prepared in some other way can be imported directly into *ARTEMIS*.

A simple interface to *FEFF* is included in *ARTEMIS*. This is little more than a simple text editor for altering the contents of the input file as needed and a button for launching an external instance of *FEFF*. Fortunately, this simple interface is quite adequate for the needs of EXAFS data analysis. After the *FEFF* run, *ARTEMIS* displays a page containing a concise interpretation of the paths computed by *FEFF* including the path distances, degeneracy, atomic species in the path, whether the path is single- or multiple-scattering, and estimated importance of the path. *ARTEMIS* has tools for organizing and plotting the results of the calculation, including plotting the individual contributions of each path in both *k*- and *R*-space.

ARTEMIS has several features which facilitate the creation and examination of fitting models. One such is the automated generation of parameters appropriate for a first-shell fit. When a *FEFF* calculation is made or imported, a set of fitting parameters are automatically generated. In many cases, a fit can be run immediately which will give a physically reasonable result. Because all fitting problems are unique, this fully automated fit is usually incomplete, but it provides a sensible starting point for almost any fitting problem from which the user can begin to refine the fitting model. *ARTEMIS* provides convenient plotting in *k*-, *R*- or back-transformed *k*-space of the data, the fit and any number of the individual paths used in the fit. Numerous tools are available to check the consistency and sensibility of the parameters used in the fit and to evaluate the results of the fit. For instance, if one of the parametric terms in the EXAFS equation for any path evaluates to a suspicious value (*e.g.* a negative σ^2, a very large energy correction E_0 or a very large change in path length), *ARTEMIS* will issue a warning message explaining the possible problem to the user. Warnings about large changes in path length or E_0 are particularly important as they might indicate that an inappropriate structural model was used in the *FEFF* calculation or that the fit has settled upon an unphysical solution (Michalowicz & Vlaic, 1998).

We acknowledge that there is a potential limitation of using *FEFF* calculations with an assumed distance in the analysis. That distance cannot be refined too far from its starting value (typically, less than 0.1 Å^{-1}). Outside that range the scattering amplitude and phase from the *FEFF* calculation should be recalculated with the new distance. In practice, we find that this is not a serious limitation, but can cause some slight errors especially at the beginning of an analysis. This is one of the reasons that *ARTEMIS* issues a warning about a distance that is too different from that used in the *FEFF* calculation. To overcome this limitation, the analysis package would have to recalculate the scattering contributions whenever the path distance changes too much. This is an area for future development.

After a fit finishes, *ARTEMIS* displays a log file which includes a statistical analysis of the fit. The major fitting statistics, including the reduced χ^2 fitting metric and the $\mathcal{R}$-factor are displayed along with uncertainties in and correlations between all fitting parameters. Furthermore, the parameteric terms of the EXAFS equation are evaluated for each path used in the fit. This information along with easy graphical display of the paths can be used to evaluate the importance of each path to the fitting result.

While *ARTEMIS* is certainly well suited to simple first-shell analysis of single data sets, it is a very powerful tool applicable to the most challenging fitting models. Among its advanced features are:

(i) Simultaneous refinement of multiple data sets.

(ii) Refinement using multiple *k*-weightings for any data set.

(iii) Use of multiple *FEFF* calculations in a single fit.

(iv) Co-refinement of a background spline to reveal correlations between the spline and the fitting parameters.

(v) Arbitrary constraints between and restraints on parameters.

4. Features of *HEPHAESTUS*

HEPHAESTUS is a container application for several small utilities based on the periodic table of elements and on a database of absorption cross sections and other data for the elements. All calculations made by *HEPHAESTUS* use one of several published compilations of atomic cross sections. The default is that of Elam *et al.* (2002). The other sources of absorption data are by McMaster *et al.* (1969), Chantler (1995), Cromer & Liberman (1970) and Henke *et al.* (1993). It is easy to switch between the data resources to compare their results for common calculations.

Currently there are seven utilities in *HEPHAESTUS*. In the same order as the icons in the button bar on the left side of Fig. 3, they are:

(i) Display the absorption and fluorescence line energies of the elements using a periodic table interface.

(ii) Compute the absorption length and quantity of sample required for measurement given the chemical formula and density of a material.

(iii) Display chemical data such as melting point and electronegativity of the elements using a periodic table interface.

(iv) Compute the ideal gas mixture for ion chambers of various lengths and internal pressures.

(v) Display a chart showing the electronic transitions associated with the various absorption lines.

(vi) Find all absorption edges in the vicinity of a given energy or of the harmonics of that energy.

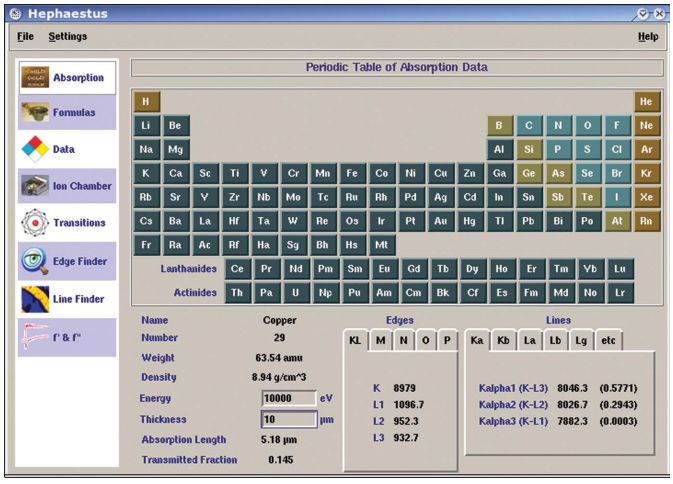

Figure 3
The *HEPHAESTUS* program, showing the absorption and fluorescence line energy utility. The various utilities provided by *HEPHAESTUS* are accessed by the button bar on the left.

(vii) Find all fluorescence lines in the vicinity of a given energy.

(viii) Plot the real and imaginary parts of the complex scattering factors of the elements using a periodic table interface.

HEPHAESTUS includes extensive built-in documentation and a tool for converting between energies and wavelengths.

5. *ATHENA* and *ARTEMIS* as teaching tools

As discussed in §1, one of the motivations for these programs is to provide an entry into data analysis for students and non-experts in XAS. In our own teaching experience we have found these programs to be good pedagogical tools with relatively shallow learning curves. With plotting and data handling tightly integrated into a graphical user environment, users are freed from such minutiae as deciphering raw data formats, constructing $\mu(E)$ spectra or performing Fourier transforms. The user can arrive quickly at the point of considering the scientific content of her data.

Analysis of EXAFS data using theoretical standards from *FEFF* can be a daunting task. Along with processing the measured data, the user must run the *FEFF* program, organize its output and construct a fitting model using the contributions from the various scattering paths generated by *FEFF*. In some cases, tens or even hundreds of these paths might be required for adequate data analysis. *ARTEMIS* organizes all these tasks for the users. It integrates wrappers for *ATOMS* and *FEFF* and helps organize the paths from the *FEFF* calculation. The time for learning *FEFF*-based data analysis for new users is shortened and complex analysis is facilitated for experienced users. As an example, *ARTEMIS* makes it simple to plot the data along with the contributions from any number of scattering paths in *k*- or *R*-space, allowing the user to quickly evaluate which parts of the *FEFF* calculation are relevant to the data analysis. An extensive log file is presented upon completion of the fit, allowing the user to evaluate the quality of the fit, the reasonableness of the fitting parameters and the effects of the fitting parameters on the *FEFF* paths used in the fit.

6. Free software and the scientific method

Full disclosure of experimental procedures and results are integral aspects of the scientific method. Because scientific work should be independently reproducible, sufficient detail of sample preparation, experimental procedure, theoretical background and interpretation of the data are normally required for most scientific publications. For data such as XAS that are interpreted with the aid of complex computer programs such as those described here, we believe that the algorithms used in the analysis be also disclosed fully, both for the purposes of review and improvement. The source code for the programs described here are freely available and distributed under a free software license (The Open Source Initiative, 2004) allowing use, modification and re-distribution of the source code with very few restrictions. All users are allowed to study, modify and improve these programs to meet their own scientific needs and to disseminate these changes to others. Because of this license, we believe that these programs make a suitable basis for study and development of new EXAFS algorithms.

7. Resources

There are many examples in the XAS literature demonstrating the use of the software and analysis principles described in this paper. Some articles that demonstrate excellent analysis and good practices for reporting both the parameters used in the analysis and the results of the analysis include these references: Kelly *et al.* (2002) and Kolobov *et al.* (2004).

A project page for *IFEFFIT* exists at SourceForge.net, http://sourceforge.net/projects/ifeffit/. Information about *IFEFFIT* can be found at http://cars.uchicago.edu/ifeffit. A link to the *IFEFFIT* mailing list can also be found there. *ATHENA*, *ARTEMIS* and *HEPHAESTUS* have their own web pages, http://FEFF.phys.washington.edu/~ravel/software/exafs/. *ATHENA*, *ARTEMIS* and *HEPHAESTUS* as well as *IFEFFIT* are being actively developed.

The source codes for *ATHENA*, *ARTEMIS* and *HEPHAESTUS* are available at the web sites mentioned above. The codes are also packaged in ways that facilitate their installation on the various computer platforms. Automated installer packages are available for Windows, Macintosh OSX and Debian Linux. The source code packages include build scripts which make them easy to install on any other Unix-like platform.

We would like to thank S. Kelly and everyone on the *IFEFFIT* mailing list for their enthusiasm and support for this project. D. Barton contributed code for importing CIF files. Versions 0.8.038 of *ATHENA*, 0.8.0 of *ARTEMIS* and 0.08 of *HEPHAESTUS* are shown in this paper. Newer versions will, no doubt, be available by the time of publication. The screen shots in this article were made on a GNU/Linux computer with a KDE desktop. The programs may be different in appearance on other systems.

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