XAFS Tutorials for crystallographers and beginners: General introduction and analytical methods for crystallographers and beginners in the field of XAFS.

FEFF and Related Codes

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**FEFF:** John Rehr (U. Washington) and his group members

**IFEFFIT:** Matthew Newville (U. Chicago) and Bruce Ravel (NIST)

**AUTOBK:** Matthew Newville
(extension of the original UWXAFS package developed under the direction of Edward Stern)
Capabilities of EXAFS for studies of nanoparticle catalysts

- Size:

- Shape:

- Texture:

- Structure:

- Short range order:

- Core/shell or surface segregation

- Random nanoalloys


Theoretical EXAFS Equation

Single scattering path:

\[ \chi_\Gamma(k) = \frac{N S_0^2}{k R^2} \left| f_{\text{eff}}(k) \right| e^{-2 \sigma^2 k^2} e \frac{-2R}{\lambda} \sin \left[ 2kR - \frac{4}{3} C_3 k^3 + \delta(k) \right] \]

Multiple-scattering path:

\[ \chi_\Gamma(k) = \text{Im} N S_0^2 \frac{e^{i \left( k \sum_i R_{ii+} + 2 \delta(k) \right)}}{\prod_i k R_{ii+}} e^{-2 \sigma^2 k^2} e \frac{-2R}{\lambda} \text{Tr} MF^N \cdots F^2 F^1 \]

Path expansion:

\[ \chi(k) = \sum_\Gamma \chi_\Gamma(k) \]
Parameters in EXAFS Equation

\[ \chi_\Gamma(k) = \frac{NS_0^2}{kR^2} \left| f_{\text{eff}}(k) \right| e^{-2\sigma^2 k^2} e^{-\frac{2R}{\lambda}} \sin\left[ 2kR - \frac{4}{3} C_3 k^3 + \delta(k) \right] \]

Same parameterization for SS and MS paths.

\[ \chi(k) = \sum_{\Gamma} \chi_\Gamma(k) \]

IFEFFIT  
(GUI: Artemis)

• Easy and transparent parameterization of structural models for EXAFS data fitting
• FEFF theory
• Error analysis

\[ k = \sqrt{\frac{2m}{\hbar^2}} (E - E_0) \]
\[ E_0 = E_0^{\text{bkg}} + \Delta E_0 \]
\[ R = R_{\text{model}} + \Delta R \]
Main similarities and differences between EXAFS analysis packages

**Main purpose:**
- Construct structural model,
- Calculate theoretical EXAFS signal,
- Perform structural refinement,
- Carry out adequate error analysis,
- Pick the model that fits the data the best and **use the best fit results**
- Keep in mind that EXAFS is ensemble averaging method!

Use complementary techniques

**Difference between packages:**

- **Fitting Space:** k-space or r-space
- **Parameterization of a model**
- **Multiple data set fitting**
- **Theoretical method** (muffin tin or finite difference method)
FEFF

FEFF6,8, 9:
Spherically symmetric potentials (muffin tin approximation)
Input: (xyz) coordinates and atomic numbers
Mean free path
   Imaginary part of interstitial potential and life time broadening
Self Energy
   Metals – Hedin-Lundqvist
   Insulators – Hedin-Lundqvist or Dirac-Hara
   Molecules – Dirac-Hara or ground state
Multiple scattering expansion
   Each photoelectron path with its $f(k), \delta(k), \lambda(k)$ is saved as a file

Packages using FEFF:
IFEFFIT, EXAFSPAK, WINXAS, XDAP, XFIT, EDA, LASE, MAC
Fitting EXAFS Theory to the Data:

\[ f(R_i) = \tilde{\chi}(R_i) - \tilde{\chi}_M(R_i) \]

\[ \chi^2_v = \frac{1}{v} \sum_{i=1}^{N_{idp}} \left( \frac{f_i}{\epsilon_i} \right)^2 = \frac{N_{idp}}{Nv\epsilon^2} \sum_{i=1}^{N} \left[ \text{Re}(f_i)^2 + \text{Im}(f_i)^2 \right] \]

\( v = N_{idp} - P \) (Number of degrees of freedom)

\( N_{idp} = \frac{2\Delta k \Delta R}{\pi} \) (Number of relevant independent data points)
EXAFS data analysis and modeling

I. Processing and visual examination of the data
- Bkg removal
- Fourier Transform

II. Deciding on the model and refinement parameters
- Structural modeling (different for homogeneous and heterogeneous systems)
- Path expansion and FEFF modeling $\mathcal{A}(k)$, $\delta(k)$, $\lambda(k)$

III. Fitting theoretical EXAFS signal to the data
- Data
- Fit
Step by step data analysis tutorial

1. Analysis of bulk Pd foil

Directory: Foil fitting
Copy the Pdfoil.apj into Pdfoil-SingleShell.apj
Start Artemis application
Open Pdfoil-SingleShell.apj into Artemis
Discard existing theoretical signal (we will construct a new one from scratch) by
Right click on FEFF0, follow the link to theory → discard this FEFF calculation.
Click on Theory menu → New Atoms page → Blank page
Space group: f m 3 m (remember to put space between symbols)
A: 3.89
Element: Pd
Tag: Pd
X: 0
Y: 0
Z: 0
Click Define
Click Run Atoms
Click Run F eff
Pick “Just the first” option (the path1 will appear in the central panel).
Highlight the Path1 and you will see options in the left panel. Give names S02, enot, drpd, ss to
the variables amp, enot, delr, ss, respectively (or any other names)
Press Guess Def Set
Delete all values that are pre-set there
In the central panel, highlight the Path1 again
Right click on each variable and pick “make …. a guess and stay”
Go back to Guess Def Set to make sure all the variables appear there. In the S02 value change the
guess value from 0 to 1 and press enter
1. **Analysis of bulk Pd foil (Continued)**

Highlight the data and press R in the right panel
Adjust the r-range for the fit (make r-range from 1 to 3.06) to define the region of the first peak
Press the Fit button
Examine the fit quality in the graphic window. If it is good examine the results in the Palette.
Take a note of the best fit value for S02: 0.825

2. **Analysis of Pd nanoparticle data**

Open project file Pd-nw.....
Click on the Guess Def Set and replace the pre-set value of 0.815 by the value we obtained in the fit to the foil: 0.825
The theory now has the amplitude factor written in the form: the product of S02 (which we found from the fit to the foil) and the unknown coordination number Npd (which was fixed at 12 when we analyzed the foil). The rest of the fitting parameters are the same.
Press Fit and examine the fit quality and the results.
The coordination number is 9.31 +/- 0.35. That corresponds to a particle size of around 1.7 nm in diameter (assuming cuboctahedral geometry and particle on support).

**Questions:** contact anatoly.frenkel@yu.edu