Lecture 2

How to avoid common errors in EXAFS and XANES analysis

Tutorials and other Training Material
Bruce Ravel's notes on using FEFFIT for data analysis
Daresbury Laboratory lectures on data analysis (EXCURV98)
Grant Bunker's XAFS tutorials
Frenkel et al on comparing PCA with other methods
Chantler (Uni. Melbourne) on the absolute determination of x-ray absorption

Programs
ESRF Software catalog
XFIT
EXAFSPAK
Athena and Artemis
    FEFFIT and IFEFFIT
DL EXCURV
WinXAS
Z ± 10
N ± 1
R ± 0.02 Å

\[ \chi(k) = \sum \frac{N_s A_s(k)}{k R_{as}^2} S_0^2 \exp(-2k^2 \sigma_{as}^2) \exp(-2R_{as} / \lambda) \cdot \sin(2kR_{as} + \phi_{as}(k)) \]

where

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

and

\[ \chi(k) = \frac{\mu(E) - \mu_a(E)}{\mu_a(E)} \approx \frac{\mu(E) - \mu_b(E)}{\mu_b(E)} \]

Radial structure only

Fourier transformation can be used to visualize frequencies contributing to EXAFS

\[ \chi(k) = \sum \frac{N_s A_s(k)}{k R_{as}^2} S_0^2 \exp(-2k^2 \sigma_{as}^2) \exp(-2R_{as} / \lambda) \cdot \sin(2kR_{as} + \phi_{as}(k)) \]

\[ \chi'(k) = \sum A(k) \sin(2kR + \phi) \]

\[ \phi = \phi_0 + R \phi_1 + R^2 \phi_2 + \ldots \]
Common errors in EXAFS analysis

- Least-squares minimization
- Fourier Filtering
- Resolution

- The job of a least-squares fitting program is to give you the best (smallest deviation) solution, *not* to give you the right solution.

- If you see something, it tells you something; if you see nothing, it tells you nothing.
Iterative refinements are especially susceptible to multiple minima

Minima give very different structures but nearly identical EXAFS

\[ N_{\text{free}} \text{ vs. } N_{\text{obs}} \]

\[ N_{\text{obs}} \sim 300 \]
\[ (\Delta k = 0.05 \text{ Å}; k_{\text{max}} = 15 \text{ Å}) \]
\[ N_{\text{free}} \sim (2 \Delta k \Delta R) / \pi \]
Further explorations of the difficulty of multiple minima

N and $\sigma^2$
R and $E_0$

Anatoly Frenkel
EXAFS Data Collection and Analysis Workshop, NSLS

How to model metal (Pt) foil data:

# Pt foil, T=200 K

guess S02 = 0.9
guess ss1 = 0
guess dr1 = 0
guess th1 = 0
guess e0 = 0

data = ptfoil-200avk.chi
out = ptfoil-200avk

rmin = 2.1 rmax = 3.3
kmin = 2 kmmax = 20 w = 2 dk=2

!% 1st path:
e0shift 1 e0
amp 1 S02
path 1 p1.dat
id 1 SS Pt-Pt(1), r=2.7719
delr 1 dr1
sigma2 1 abs(ss1)
third 1 th1

$$\chi(k) = \frac{NS^2_0}{kr^2} |f_{\text{eff}}(k)| e^{-2\sigma^2 k^2} \times \sin\left[2kr - \frac{4}{3} C_3 k^3 + \delta(k)\right]$$
Fit Results

This is not physically reasonable….

What caused S02 to be different at 200 K and 673 K?

- correlation with other fit variables:

\[
\chi(k) = \frac{NS_0^2}{kr^2} f^{\text{eff}}(k) e^{-2\sigma^2 k^2} \sin\left[2kr - \frac{4}{3} C_3 k^3 + \delta(k)\right]
\]

How to break the correlation?

One possible solution: a multiple-data-set (mds) fit.

What variables are not expected to change at different temperatures?

\[
\Delta E_0, N, \sigma_s^2, \Theta_E
\]

\[
\sigma^2 = \sigma_s^2 + \sigma_d^2
\]

\[
\sigma_d^2 = \frac{\hbar}{2\mu} \frac{1 + \exp(-\Theta_E/T)}{1 - \exp(-\Theta_E/T)}
\]
How to model XAFS data in nanoparticles?

A priori knowledge or a working hypothesis must exist (the “zero” approximation) otherwise: the transferability of amplitude/phase will not work!

1) Hemispherical
2) Crystal order
3) Size: about 20 Å

What information can be obtained from 1st shell EXAFS analysis?

1) Size of the particle (via N)
2) Distances, thermal vibration, expansion
3) Static disorder (icosahedral? surface tension?)
MDS fit (1shell) to the nanoparticles EXAFS
- Coordination number is now **guessed** (a variable)
- $S_0^2$ is **fixed** to be equal to that in Pt foil EXAFS
- E0 is **fixed** to be equal to that in Pt foil EXAFS

![Graphs showing EXAFS data at different temperatures](image)

**Summary**

- The more variables you control, the more likely you are to obtain a unique solution
- Multiple data sets (elements, temperature, concentration, time, etc.) almost always help
- Conclusions are only as good as your model
Fourier filtered data can be distorted

M-O at 2.0 and 2.2 Å give two apparently well resolved peaks in FT
Fitting each filtered peak gives the appearance of M-O and M-S EXAFS

Effect of limited resolution on EXAFS
EXAFS resolution is
~ π/2Δk = 0.13 Å

A case study in data under-determination

Zn EXAFS is remarkably insensitive to changes in ligation.

\[ Z \pm 10 \, \text{???} \]

XANES spectra are sensitive to ligation but show greater variation between different compounds than with changes in ligation.
Zn-S and Zn-N EXAFS signals are approximately out of phase

The observed EXAFS for mixed S/N sites is dominated by Zn-S scattering
One solution is to measure data over wide $k$ range (ZnS₂N₂ inorganic)

Note – $\Delta R \sim 0.25 \rightarrow \pi/2\Delta k = 0.25 \text{ Å} \rightarrow \Delta k_{\text{min}} \sim 6.3$

High resolution EXAFS is required to reliably distinguish Zn-S from Zn-N …
…and even with high resolution data, extremely high signal/noise ratios are required to detect Zn-N in the presence of Zn-S

![EXAFS spectrum](image)

It *is* possible to reliably distinguish between ZnS$_4$, ZnS$_3$N, and ZnS$_2$N$_2$ if variable parameters are carefully controlled.

Note that fit quality always improves for mixed ligation fits.

In addition to $P_i$, $\sigma^2$ depends on ligation.

Threshold energy changes apparent ligation.

5 eV is enough to change a sulfur into a nitrogen!
Distinction between S and N rests largely on phase, which depends on $E_0$.

Geometry determination

Multiple scattering in EXAFS
Outer shell scattering can provide ligand identification and geometric information

Multiple scattering makes EXAFS sensitive to angular arrangement of ligands
However, ability to reliably determine geometry is limited

\[ \Delta R \]

\[ \text{Information} \quad \rightarrow \quad \text{Parameters} \]

\[ \text{N = C = C = N} \]

\[ \text{N = C = N} \]

\[ \text{O - N - O} \]

\[ \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4 \]

\[ \theta \]

---

**XANES spectra contain useful information regarding structure**

- Quantitative comparisons (e.g., titration) requires accurate normalization.
- Correction for various artifacts (self-absorption) requires accurate normalization.
- Common normalization procedures were developed for extracting EXAFS and do not necessarily work well for XANES.
Normalization Schemes

Conventional

MBACK

Conventional normalization is sensitive to background shape

MBACK shows much weaker sensitivity
Conventional normalization is sensitive to range of data

MBACK shows only slight sensitivity for $E_{\text{max}} \geq 150$ eV above edge
Conventional normalization misses changes in XANES

MBACK reveals subtle changes when thiolate is added

4 possible difference spectra – should all be the same
With new normalization, difference signal is detectable

Dependence of XANES on Oxidation State
Edge “energy” is poorly defined

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**Linear Combination Fitting**

Fit experimental data to linear combination of known reference compounds.

TPR-XANES of in situ reduction of CeO$_2$/La$_2$O$_3$ oxide.

LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as a function of temperature.

Simon Bare, NSLS workshop
**Principal Component Analysis**

- PCA estimates number of distinct species in a series of spectra.
- Used as a first stage of analysis.
- Based on linear algebra - each spectrum represented as a vector.
- Goal is to find number of components that can reproduce the experimental spectra to within experimental (statistical) error.
- No *a priori* assumptions on number/type of components.


\[ X = U S V^T \]

\[ X^{(l)} = \sum_{k=1}^{l} u_k^s v_k^T \]

is the closest l-rank matrix to \( X \)